X-ray tomographic investigation and rational design of battery materials for rechargeable lithium-metal batteries and beyond

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an der Fakultät III – Prozesswissenschaften der Technischen Universität Berlin zur Erlangung des akademischen Grades

Doktor der Ingenieurwissenschaften
- Dr.-Ing. -

genehmigte Dissertation

Promotionsausschuss: Vorsitzender: Prof. Dr. Aleksander Gurlo Gutachter: Prof. Dr. John Banhart Gutachterin: Prof. Dr. Yan Lu

Tag der wissenschaftlichen Aussprache: 17. Dezember 2021

Berlin 2022

Abstract

Solid-state electrolytes (SSEs) are considered to inherently enhance the safety and improve the energy density of lithium-metal-batteries (LMBs) due to their nonflammability, good processability and high mechanical modulus facilitating the use of metallic lithium (Li) in allsolid-state batteries (ASSBs). Unfortunately, the practical application of ASSBs is severely hindered by the multifold challenges from the solid-solid interface to dendrites to deleterious chemo-mechanical degradation between Li-metal and the SSEs. Understanding these challenging problems at very basic level requires operando and multi-modal techniques for directly elucidating how solid-state interfaces evolve in real time. Non-destructive and highpenetration synchrotron X-ray tomography is an ideal technique to reliably investigate the buried interfacial evolution owing to it yields 3D reconstructions of materials with spatial resolution down to the sub-micron scale. Despite tremendous efforts have been made in developing ASSBs based on Li-metal anode, the high cost and limited resources of Li have caused some concerns of using LMBs in the large-scale energy storage applications. Potassium-ion batteries (KIBs) are promising supplements to LMBs considering the natural abundance and low redox potential of K. Nevertheless, the research progress of KIBs still faces great challenges due to the lack of suitable anode materials for the reversible depotassiation/potassiation of large size K⁺. In this dissertation, X-ray tomographic imaging technique was performed to study the underlying reactions of the operating ASSBs and K symmetrical batteries. On the other hand, by combining morphology, defect and structure engineering, three types of transition-metal-based nanomaterials were synthesized and evaluated as anodes for KIBs. Firstly, X-ray tomography visually discloses the formation of the (electro)chemically generated interphase, an unexpected mechanical deformation of the Li₁₀SnP₂S₁₂ SSE as well as an unanticipated creep behavior of Li-metal anode. Moreover, the (electro)chemically induced mechanical stress distribution and its effect on the electric/ion distribution have been also unveiled. Secondly, graphene-like V_5Se_8 (a) Carbon nanosheets hybrid were obtained in high-yield by a facile exfoliation strategy and subsequent solvothermal treatment, and investigated for the first time as an advanced anode for KIBs. Thirdly, we designed a facile synthetic avenue to fabricate multidimensional composite system, that is, 0D ultrasmall Co₉S₈ nanoparticles and 2D MoS₂ nanosheets incorporated into 3D hollow carbon framework with N, S codoping, for advanced K-ion battery. Fourthly, 1D peapod-like Fe₂VO₄ nanorods confined in nitrogen-doped carbon porous nanowires with internal void space have been successfully prepared by a facile approach without template assistance, and introduced as a novel promising anode for KIBs. Lastly, the interfacial stability between K-metal and different commercial separators was elaborately investigated in K symmetric cells via in-situ synchrotron X-ray tomography technique.

Kurzfassung

Festkörperelektrolyte (SSE) ermöglichen es, die Sicherheit und Energiedichte von Lithium-Metall-Batterien (LMB) signifikant zu erhöhen, da sie nicht entflammbar sind, sich gut verarbeiten lassen und aufgrund ihrer festen mechanischen Eigenschaften die Verwendung von metallischem Lithium (Li) in Festkörperbatterien (ASSB) erleichtern. Leider wird die praktische Anwendung von ASSBs durch vielfältige Probleme erschwert, die von der Festkörper-Festkörper-Grenzfläche über Dendritenbildung bis hin zur chemisch-mechanischen Degradation an der Grenzfläche zwischen Li-Metall und SSEs reichen. Um diese schwierigen Probleme auf einer sehr grundlegenden Ebene zu verstehen, sind multimodale Operando Messtechniken erforderlich, die direkt aufklären, wie sich Festkörper-Grenzflächen im Batterieinneren entwickeln. Die zerstörungsfreie Synchrotron-Röntgentomographie mit ihrer hohen Eindringtiefe ist eine ideale Technik, um die Entwicklung von inneren Grenzflächen zuverlässig zu untersuchen, da sie 3D-Rekonstruktionen von Materialien mit einer räumlichen Auflösung bis in den Submikrometerbereich liefert. Trotz enormer Anstrengungen bei der Entwicklung von ASSBs mit Li-Metall-Anoden haben die hohen Kosten und die begrenzten Ressourcen von Li einige Bedenken hinsichtlich der Verwendung von LMBs in groß angelegten Energiespeicheranwendungen hervorgerufen. Kalium-Ionen-Batterien (KIBs) sind vielversprechende Ergänzungen zu LMBs, wenn man das natürliche Vorkommen und das niedrige Redoxpotential von K bedenkt. Dennoch steht die Forschung an KIBs immer noch vor großen Herausforderungen, da es an geeigneten Anodenmaterialien für die reversible Speicherung von großen K⁺-Mengen fehlt. In dieser Dissertation wurde Röntgentomographie eingesetzt, um die zugrundeliegenden Reaktionen von ASSBs und symmetrischen K-Batterien zu untersuchen. Zum anderen wurden drei Arten von Nanomaterialien auf Übergangsmetallbasis mit unterschiedlichen Strukturen und Morphologien synthetisiert und auf ihre Eignung als Anoden für KIBs untersucht. Erstens zeigt die Röntgentomographie visuell die Bildung der (elektro)chemisch erzeugten Interphase, eine unerwartete mechanische Verformung der Li₁₀SnP₂S₁₂ SSE sowie ein nicht erwartetes Kriechverhalten der Li-Metall-Anode. Darüber hinaus wurden die (elektro)chemisch induzierte mechanische Spannungsverteilung und ihre Auswirkung auf die Elektro-/Ionen-Verteilung analysiert. Zweitens wurden graphenähnliche V₅Se₈@Carbon-Nanosheet-Hybride mit hoher Ausbeute durch eine einfache Exfoliationsstrategie und anschließende solvothermische Behandlung erhalten und erstmals als fortschrittliche Anode für KIBs untersucht. Drittens wurde eine einfache synthetische Methode entwickelt, um ein mehrdimensionales Verbundsystem herzustellen, im einzelnen 0D ultrakleine Co₉S₈-Nanopartikel und 2D-MoS₂-Nanosheets, die in ein hohles 3D-Kohlenstoffgerüst mit N- und S-Kodotierung integriert sind, um daraus eine fortschrittliche K-Ionen-Batterie herzustellen. Viertens wurden 1D peapod-ähnliche Fe₂VO₄-Nanostäbchen, die in stickstoffdotierten porösen Kohlenstoff-Nanodrähten mit internen Hohlräumen eingeschlossen sind, erfolgreich durch einen einfachen Ansatz ohne Templatunterstützung hergestellt und als neue vielversprechende Anode für KIBs vorgestellt. Schließlich wurde die Grenzflächenstabilität zwischen K-Metall und verschiedenen handelsüblichen Separatoren in Ksymmetrischen Zellen mittels In-situ-Synchrotron-Röntgentomographie eingehend untersucht.

Contents

1. Introduction 1 -	•
1.1. All-solid-state lithium-metal batteries (ASSLMBs) 2 -	-
1.1.1. Brief historic overview of ASSLMBs 2 -	-
1.1.2. Challenges and engineering strategies of ASSLMBs 3 -	-
1.1.3. Synchrotron X-ray microtomography for solid-solid interfacial evolution 5 -	-
1.2. Potassium-ion batteries (KIBs) 6 -	-
1.2.1 Cathode material for KIBs 7 -	-
1.2.2. Anode material for KIBs 10 -	-
1.2.3. Electrolyte for KIBs 12 -	-
1.2.4. Challenges and engineering strategies of KIBs 13 -	-
1.3. X-ray imaging setups 14 -	-
1.3.1. X-ray radiographic imaging setup 15 -	-
1.3.2. Synchrotron X-ray microtomographic imaging setup 16 -	-
1.4 Motivation of the thesis 17 -	-
1.5 References 18 -	-
2. Parts of doctoral work 20 -	-
2.1 Clarifying the electro-chemo-mechanical coupling in all-solid-state batteries 22 -	-
2.2 Ultrathin V_5Se_8 (acarbon nanosheet for stable and effective K-ion storage	-
2.3 Co ₉ S ₈ @MoS ₂ @carbon hollow nanoboxes for K-ion storage 90 -	-
2.4 Carbon-encapsulated Fe ₂ VO ₄ nanopeapods for K-ion batteries 120 -	-
2.5 Non-destructive characterization of K deposition in different separators 151 -	-
3. Summary and conclusions 170 -	-
4. Outlook 171 -	-
5. Acknowledgements 172 -	-

1. Introduction

The Nobel Prize in Chemistry 2019 was awarded to the research area of the "development of the lithium-ion batteries (LIBs)". There is no doubt that the LIB technology has revolutionized the power sources form portable electronics to electric vehicles and LIBs have become an indispensable part of human life.^[1] However, the use of flammable organic liquid electrolytes (OLEs) in LIBs severely limits corresponding energy density and overall safety, leading to the exploration and development of all-solid-state batteries (ASSBs) in recent years.^[2] The solid-state electrolytes (SSEs) with excellent thermal stability, wide electrochemical windows and high mechanical modulus are expected to replace the combustible OLEs for lithium-metal-batteries (LMBs) with good safety property and high energy density. Despite the development of SSEs with high ionic conductivity,^[3] both the understanding of and control over solid electrode/SSE interfaces are still facing several challenges in the development of ASSBs. These problems are interrelated and they arise from the solid-solid contact and chemo-mechanical transformations between lithium and the SSEs. As such, it is necessary to understand the fundamental science of how solid-state interfaces evolve in real time before the practical application of ASSBs can be realized. In this regard, high-penetration synchrotron X-ray tomography technique, which enables nondestructive, multiscale, and 3D reconstruction of the internal battery components before/during/after operation, becomes an ideal tool to reliably elucidate the electrode/SSE interfacial evolutions. X-ray tomography is of great help not only to improve the understanding of the solid-solid interfacial reaction mechanisms of ASSBs but also guide the design of high energy and performance-improved beyond-Li-based battery systems.

Despite considerable progress has been made in developing ASSBs based on metallic lithium anodes, the high-cost and scarcity of lithium resources have triggered everincreasing concerns of using lithium metal on a large-scale and cost-efficient stationary energy storage systems.^[4] With this background, potassium-ion batteries (KIBs) have been regarded as promising alternatives to Li-based batteries for such large-scale applications, owing to the earth-abundant K resources and low cost as well as the similar 'rocking-chair' K-storage mechanism to that of LIBs. However, the development of KIBs is seriously impeded by the inferior electrochemical performance resulting from the huge volume change and serious structure collapse of electrode materials during cycles due to the large size of K⁺. The study on KIBs is still in its infancy due to the lack of suitable anode materials, and the electrochemical reaction mechanism of most electrode materials during charge and discharge processes needs further make clear. Therefore, it is quite challenging to explore suitable anodes with superior K-storage performance and insight into their charge storage mechanism.

In this thesis, we used X-ray tomography to observe the structure changes at the lithium (lithium aluminum alloy) electrode and $Li_{10}SnP_2S_{12}$ solid electrolyte interface before and after charging. It is found that the (electro)chemically generated interphase is formed during Li electro-dissolution, an unexpected mechanical deformation occurs inside the $Li_{10}SnP_2S_{12}$ solid electrolyte as well as an unanticipated Li creep behavior appears in both Li anode and Li cathode. In addition, three types of transition-metal-based chalcogenides and oxides were prepared and firstly evaluated as anode materials for KIBs. The electrochemical reaction mechanisms of those transition-metal-based nanomaterials were also explored. In the last, we used the *in-situ* synchrotron X-ray tomography technique to study the interfacial stability between three types of separators (Celgard 2325, Celgard 2400 and glass fiber membranes) and the K electrodeposits in K|K symmetrical cells. It is demonstrated that the battery built with a Celgard 2400 separator can achieve a stable cycling performance as its high mechanical robustness and structural integrity along the thickness direction, thus alleviating the K dendrites growth and maintaining interfacial stability.

1.1. All-solid-state lithium-metal batteries (ASSLMBs)

1.1.1. Brief historic overview of ASSLMBs

Long before the coming out of lithium intercalation type electrode materials for lithiumion batteries (LIBs), solid-state battery technologies had been exploited since solid ionic conductors were discovered.^[5] As shown in Figure 1, the evolution of solid-state electrolytes (SSEs) is nearly synchronous to the development of the batteries. The SSEs in LIBs can generally be divided into three categories: inorganic, polymeric, and composite materials. The first report of inorganic electrolyte assembled batteries dates back to as early as the 1950s, when the first Li-ion conductor Li₃N with a high ionic conductivity of 10^{-3} S cm⁻¹ was demonstrated as a solid electrolyte in room temperature (RT) LIBs.^[6] Later, in 1973, the first concept of solid polymeric ionic conductor was begun when Fenton *et al.* found that polyethylene oxide (PEO)-based complexes were alkali-metal-ion conductive.^[6] In the 1970s, the new-type inorganic lithium superionic conductor (LISICON) and sodium superionic conductor were discovered, which opened the doors to applications of SSEs.^[7,8] Since then, various Li-ion conductors (*e.g.*, garnet-type Li₇La₃Zr₂O₁₂,^[9] argyrodite Li_6PS_5Cl ,^[10] $Li_{10}SnP_2S_{12}$,^[11] thio-LISICON $Li_{10}GeP_2S_{12}$,^[12] and $Li_7P_3S_{11}$,^[13]) have been increasingly exploited. Then in 2016 an exceptional superionic conductor of $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$,^[14] was also originally developed by Kanno and co-workers, showing the highest RT ionic conductivity of 2.5×10^{-2} S cm⁻¹ to date, which is comparable to or even higher than those of practical organic liquid electrolytes. Their work is an important step toward promoting the practical use of SSEs. Nowadays, many battery enterprises have begun to invest the layout on solid state Li-ion batteries.



Figure 1. A brief chronology of the development of typical solid-state electrolytes (SSEs) and the process of solid-state batteries (SSBs).^[15]

1.1.2. Challenges and engineering strategies of ASSLMBs

The solid-state electrolyte (SSE) is the core component in the solid-state lithium-metal batteries. To make a SSE actually work its way into commercially successful solid-state Limetal batteries, the SSEs are expected to satisfy the following requirements: 1) negligible electron conductivity; 2) high ionic conductivity ($>10^{-4}$ S cm⁻¹) at room temperature; 3) high thermal stability and robust mechanical property; 4) easy integration into batteries; 5)

excellent chemical compatibility against electrodes (such as Li-metal anodes and highvoltage cathode materials); 6) low interfacial resistance at the electrode-electrolyte solidsolid interfaces; 7) scalable manufacturing process at low cost and environmental friendliness. Unfortunately, so far, there has been no SSEs that can meet all of the above properties. Hence, it is crucial to explore new strategies to trade off all of this properties that enable commercial solid-state Li-ion batteries. In fact, there are two main tricky issues (*e.g.*, high electrode/electrolyte interfacial resistance and unfavorable mechanical stability) significantly limit the real-world application of SSEs in ASSLMBs and need to be solved urgently.



Figure 2. The overview of main existing problems and strategies for the solid-solid interface.^[6]

The interfacial resistances are mainly attributed to the poor chemical/electrochemical compatibility, inferior ion transport at solid-solid interface, interdiffusion, and mechanical instability caused by inhomogeneous stress distribution (Figure 2). In order to address the above challenges, several existing strategies are summarized as follows:

(1) Incorporation of an Li-conductive, electron-insulting and nanometer-thick buffer layer (*e.g.*, LiNbO₃) coating on electrode surface;

- (2) Introducing an artificial SEI layer between electrode and SSE;
- (3) Interfacial modification at the nanoscale (e.g., using atomic layer deposition technique);
- (4) Structural design (e.g., 3D structured electrode, hierarchical porous SSE framework).

1.1.3. Synchrotron X-ray microtomography for solid-solid interfacial evolution

Although some efforts have been made in solid-state battery engineering, the fundamental understanding of the chemo-mechanical transformations at solid-solid interfaces in real time still remains obscure. In fact, it is technically challenging to investigate the interfacial evolution during battery cycling because it is buried deeply underneath and inaccessible to most of the probing techniques. Fortunately, the non-destructive and high-penetration synchrotron X-ray tomography is an ideal method to characterize and analyze the mechanistic dynamics of solid-state interfacial reaction with high accuracy and reliability.



Figure 3. (a) Schematic of the custom X-ray tomography cell used to cycle Li/LSPS/Li cells during operando experiments. (b) Cross-section of the Li/LSPS interface before cycling at 1 mA cm^{-2} and after one full cycle at 1 mA cm^{-2} . Cross-sectional images of the Li/LSPS interface before (top) and after (bottom) reduction at 4 mA cm^{-2} (c) and 1 mA cm^{-2} (d), respectively. (e) 3D segmented renderings of the Li/LSPS interface at different times during stripping at 1 mA cm^{-2} . (f) The position of the Li/LSPS interface and the current collector tracked during stripping of the lithium. The arrows indicate the direction of motion of each interface: darker lines represent positions at earlier times during the stripping, with the transition to lighter lines as stripping proceeds.^[16]

In this respect, McDowell's group used the *operando* synchrotron X-ray tomography technique to investigate the interfacial evolution of Li-metal and $Li_{10}SnP_2S_{12}$ (LSPS) SSE during the operation of ASSLMBs.^[16] As shown in Figure 3a, a cylindrical solid-state cell was designed for X-ray 3D tomography. The authors found that the intermediate-contrast interphase and voids were formed at the interface when the battery after one cycle at 1 mA cm⁻² (Figure 3b-e). Importantly, the authors have successfully analyzed quantitatively the

volumetric changes and partial molar volume mismatch in Li/LSPS-SSE/Li symmetric cells during charging and discharging based on the tomography data (Figure 3f). At last, they successfully revealed how the complex interplay among void formation, interphase evolution and electrode volume changes at the Li/LSPS interface during cycling determine the overall cell performance. The above studies show that the formation of a uniform and stable interface between the lithium anode and SSE is beneficial to the long cycle lifetime of ASSLMBs.

1.2. Potassium-ion batteries (KIBs)

To meet the energy requirements of the rapid development of large-scale stationary applications, "Beyond Li-ion battery" systems are attracting more and more attention.^[17] Sodium-ion batteries (NIBs) and potassium-ion batteries (KIBs) as the promising substitutes to lithium-ion batteries (LIBs) have captured tremendous attention in recent years due to the natural abundance of their raw materials and the similar chemical properties to lithium.^[18] It is known that K/K⁺ couples have a lower redox potential (-2.93 V *vs.* standard hydrogen electrode, SHE) than that of Na/Na⁺ (-2.71 V *vs.* SHE), which endows KIBs with higher full-cell potential and larger energy density.^[19] In additional, KIBs have a better ionic mobility and conductivity in electrolyte than their sodium counterparts, and the usage of cheap and stable aluminum foil as current collectors. These merits make KIBs as one of the most attractive candidates for grid-scale stationary energy storage systems.

Similar to LIBs and NIBs, KIBs contain all the functional cell configurations including cathode, anode, and organic electrolyte. Figure 4 presents a cartoon of the working principle of KIBs, showing a typical "rocking chair" style similar to that of LIBs. Typically, during the charging process, K ions are extracted from the cathode, travel across the electrolyte, and finally intercalate into the anode. And upon discharge, the opposite process occurs, along with an equal charge of electrons transfer in the external circuit to offer electric energy. The energy density of KIBs is dependent on the capacity of the anode and cathode as well as the working potential. Therefore, the theoretical capacity of electrode materials can be calculated on the basis of the equation: $Q_{\text{theoretical}} = nF/3.6$ M, where n is the number of electron transfer per formula unit of the electrode material, F is the Faraday constant (96485), and M is the relative molecular mass of the electrode material. The corresponding unit of measurement is milliam-pere hours per gram (mAh g⁻¹). Based on this, small molar mass and multi-electron reaction can lead to high capacities, suggesting that favourable elements

for high-capacity electrode materials are mostly located in the first four rows of the periodic table.



Figure 4. Schematic illustration of a typical K-ion battery with P2-type layered oxides as cathode and graphite as anode materials, respectively.^[20]

1.2.1 Cathode material for KIBs

Until now, layered transition-metal oxides, polyanion compounds, prussian blue (PB), and its analogs (PBAs), along with organic compounds have been extensively investigated as cathode electrode materials for rechargeable KIBs. For layered transition-metal oxides (A_xMO_2 (A = alkali metal ion, M = one or more transition metal cations)), the layered framework can be classified into three groups (P2 type, P3 type, and O3 type) according to the stacking sequence of alkali ions between edge-shared MO₆ octahedral layers.^[20] The "P" and "O" represent the face-shared prismatic and edge-shared octahedral coordination environment for alkali ions in A_xMO_2 , respectively, while the "2" and "3" indicate the number of MO₆ layers in a repetitive stacking unit (Figure 5a-c). In this case, P2 and P3 phases are stacked in an ABBA and ABBCCA manner with the prismatic alkali metal ion, and the O3 phase is closely packed in the ABCABC pattern with the octahedral alkali metal ion. Particularly, compared with P2 or P3 phase, O3 phase usually undergo much more complicated multiple-phase transitions during the continuous charge/discharge process, owing to their smaller accommodation spacing for K ions, inevitably resulting in irreversible structural collapse of electrode materials, and fast capacity degradation.



Figure 5. Schematic of the layered K-containing oxides for (a) P2-type, (b) P3-type, and (c) O3-type stackings. (d) K^+ insertion and extraction along with phase transformation of $K_3V_2(PO_4)_2F_3$, in which VO_4F_2 octahedra and PO_4 tetrahedra are labelled in blue and purple, K atoms in cyan and white parts indicate vacancies. (e) A schematic of the crystal structure of $K_2MFe(CN)_6$, M=Fe, Co, Ni, and Cu. (f) Selected schematic for the proposed electrochemical reaction mechanism of PTCDA in KIBs.^[20]

Polyanionic compounds can be typically categorized into olivine-phosphates, NASICONphosphates, fluorophosphates, pyrophosphates, sulfates, and other polyanionic compounds based on the configuration of MO₆ (M = Fe, V, Ti, *etc.*) octahedral and XO₄ (X = P, S, Si, *etc.*) tetrahedral. Due to the strong inductive effect of electronegative anion group and the robust covalent framework, polyanionic compounds always possess high structural and thermodynamic stability, as well as adjustable operating voltages. To date, various polyanionic compounds including KFe(SO₄)₂,^[21] KTiPO₄F,^[22] K₃V₂(PO4)₃,^[23] KVPO₄F,^[24] KVOPO₄,^[25] K₃V₂(PO₄)₂F₃^[26] and KVP₂O₇^[27] are being reported as cathode materials for KIBs. For example, Zhang *et al.*^[26] synthesized a potassium-rich cathode material, K₃V₂(PO₄)₂F₃, in which during charging, two K ions are extracted from the structure, and an excellent electrochemical performance can be achieved (Figure 5d). In this regard, polyanionic compounds are recognized as promising cathodes for KIBs.

Prussian blue (PB) and its analogues (PBAs) have been explored as cathode materials for potential applications of KIBs because of their open framework, abundant electrochemically active sites, and robust lattice structure. The general chemical formula of PBAs is $A_xM[Fe(CN)_6]\cdot yH_2O$ (A represents alkali ions, M denotes transition metal ions, and 0 < x < 2),^[28] where Fe ions are octahedrally coordinated to carbon atoms of cyanide (CN)

ligands, M represents nitrogen-coordinated transition metal ions, constructing a 3D network with spacious interstitial sites and open ionic channels, as shown in Figure 5e. In this aspect, PBAs compounds have been investigated as a kind of suitable intercalation host for the large K^+ insertion/extraction from the electrode without serious structural deformation.

Organic compounds with the unique advantages of lightweight, flexible structures and large primary interlayer spacing have attracted numerous research attentions as cathode materials for KIBs. And up to now, various organic compounds have been extensively studied in rechargeable batteries, such as small organic molecules, conducting polymers, carbonyl compounds and functional polymers.^[29] In general, the performance for K-ion accommodation of the organic compounds is mainly determined by their electroactive functional groups, such as C=N, C=O, and N=N groups. For example, Chen *et al.*^[30] first investigated the electrochemical performance of 3,4,9,10-perylene-tetracarboxylic acid-dianhydride (PTCDA) for KIBs, which performed an outstanding accommodation ability for K⁺ with a value of two per molecular when discharged to 1.5 V *vs.* K/K⁺ (Figure 5f).

To comparatively study the electrochemical K^+ -storage properties of main cathode materials, average working potentials, reversible capacities, and energy density are summarized (Figure 6). Polyanion compounds generally have a high average redox potential of ~3.6 V, but with a small reversible capacity of ~100 mAh g⁻¹. Conversely, organic cathodes possess a relatively large reversible capacity of ~160 mAh g⁻¹, but the average redox potential is only ~2.4 V. The reversible capacities and average working voltages of PB and PBAs, along with the layered transition-metal oxides are between the values of organic materials and polyanion compounds. Currently, energy density based on the KIBs cathode material part is still less than 500 Wh Kg⁻¹.



Figure 6. Comparison of reversible capacities, average working voltage and energy density for reported cathode materials for KIBs.^[31]

1.2.2. Anode material for KIBs

Unlike the simple charge storage mechanism of intercalation/deintercalation in the cathode materials, the anodes in KIBs show various K⁺-storage mechanisms, such as the insertion/extraction reaction, conversion reaction, alloying reaction, and their synergetic reaction (insertion followed by conversion reaction, conversion reaction followed by alloying reaction, etc.). In addition, anode material is believed to play an important role in determining the charge storage property of KIBs. So far, the developed anode materials for KIBs mainly involve carbonaceous materials, organic materials, metal-based chalcogenides and oxides, and alloying materials. For carbonaceous anode material part, the major breakthrough was the realization that K-ion can insert into the layer of graphite to form KC₈ compound, and displayed a low potential plateaus with a theoretical reversible capacity of ~ 270 mAh g⁻¹ (Figure 7a). The intercalation process of K-ion into graphite was further described as $C \leftrightarrow KC_{60} \leftrightarrow KC_{48} \leftrightarrow KC_{36} \leftrightarrow KC_{24}/KC_{16} \leftrightarrow KC_8$.^[32] Aften then, the explorations of carbon materials as anodes for KIBs clearly show an increasing trend, including expanded graphite, soft/hard carbon, graphene, biomass derived carbon, MOFs derived carbon and heteroatom-doped carbon, and they can be mainly divided into graphitic carbon and non-graphitic carbon.



Figure 7. Schematic illustration of reversible K-ion insertion/extraction of graphite (a) and K_2TP (b). (c) Schematic illustration for K-ion storage mechanism of FeS₂ anode, disclosing its reversible insertion/extraction and conversion reaction during cycles. (d) Schematic potassiation/depotassiation reaction of Sn₄P₃/C anodes.^[33, 34]

Organic materials host many advantages, such as flexible molecule structure, facile synthesis, renewability and high theoretical gravimetric capacity, making them very attractive candidates for KIB anodes. The storage capability and working potential plateaus of organic materials show diversity according to the different aromatic environments and functional groups. For examples, dipotassium terephthalate (K₂TP) contains conjugated carboxylate groups that can electrochemically accept one K-ion for each group (Figure 7b), offering a theoretical capacity of 221 mAh g⁻¹.^[34]

Metal-based chalcogenides and oxides have attracted tremendous attention as anode materials for KIBs due to their high theoretical capacities arising from a combination of intercalation and conversion reaction. However, the huge volume variation of metal-based chalcogenides and oxides during K-ion intercalation/extraction is the Achilles' heel of these anode materials. Thus, they are generally coupled with carbon materials based on nanostructure design including yolk-shell, yolk-core, and 3D porous structures. Taking FeS₂ as an example, Guan and his co-workers^[35] reported a yolk-shell FeS₂@carbon structure on graphene matrix nanostructures as KIBs anode, which delivers high capacity, great rate capability and remarkable long-term stability (Figure 7c).

Alloying-based materials as an interesting anode candidate have been developed and investigated in KIBs owing to their unique alloying reaction mechanism corresponding to a relatively high specific capacity. Up to now, the alloying-based anodes regarding on Sn-K system (Figure 7d), Sb-K system, P-K system, and Bi system have aroused extensive interest.^[36] Although the alloying-based materials deliver high theoretical capacities, their dramatic volume fluctuations during repetitive cycles result in structural degradation and an inferior cycling stability. Therefore, improving the electrochemical performance of alloying-based materials should still be an important direction in future work.

As displayed in Figure 8, considerable progresses have been made in the discovery of anodes for KIBs. Different anodes have their respective advantages and shortcomings. Therefore, various rational engineering strategies combined with different electrode structural designs have been explored toward efficiently enhancing the electrochemical performance of KIBs anodes.



Figure 8. Comparison of reversible capacities and average working voltage for reported anode materials for KIBs.^[37]

1.2.3. Electrolyte for KIBs

The electrolyte is an essential component of the K-ion-battery systems, which directly affects the battery performance. In general, there are four major categories of electrolytes for KIBs, namely organic-liquid electrolytes, ionic-liquid electrolytes, solid-state electrolytes and aqueous electrolytes (Figure 9). Among these electrolyte systems, organic-liquid electrolytes are most widely used in KIBs mainly owing to their advantages in terms of high ionic conductivity, stable electrochemical performance, and good compatibility with various electrolyte materials. Potassium salts have been applied for organic-liquid electrolytes in the literature mainly including KPF₆, KBF₄, KClO₄, KCF₃SO₃, KFSI, and KTFSI.^[38]

Due to the advantages of high ionic conductivity, low vapor pressure, wide operation voltage window and superior electrochemical stability, ionic liquids (mainly comprising of KFSI- and KTFSI-based electrolytes) are a burgeoning class of safe electrolytes in KIBs. However, it should be pointed out that ionic-liquid electrolytes are usually too expensive, which may restrain their widespread commercial applications.

Solid-state electrolytes have gained great research attention owing to their intrinsic safety property, high electrochemical stability to guarantee long cycling capacity, and easy processing. Very recently, solid-state KIBs have also been studied with two categories of electrolytes, inorganic solid electrolyte and gel polymer electrolyte.



Figure 9. Categories and requirements of electrolytes in KIBs.^[39]

Aqueous KIBs are emerging as the promising candidates for large-scale energy storage mainly due to their nontoxicity, environmental friendly nature, low cost, innate superior safety characteristics, and fast ionic diffusion. Traditional aqueous KIB electrolytes usually use solutes of KNO₃, KCl, K₂SO₄, and KOH, and have realized exciting results on various electrodes. However, the electrochemical stability potential range is greatly limited by the narrow voltage window (<2 V), above this potential, the water gets splitted. Therefore, the demand of much higher energy density still renders non-aqueous KIBs be highly desirable. Suitable electrolyte design is expected not only to promote the full display of the electrochemical capacity of the electrode materials, but also to guarantee a safe and stable battery system.

1.2.4. Challenges and engineering strategies of KIBs

Despite great progress has been made in the development of KIBs, they still face the following challenges (Figure 10):

(1) Low K-ion diffusivity in electrodes/poor K⁺-reaction kinetics;

(2) Large volume expansion during potassiation/depotassiation;

(3) Severe side reaction, consumption of electrolyte and unstable solid-electrolyte-interface layer;

(4) K-dendrite growth;

(5) Limited energy/power density.



Figure 10. Summary of challenges and their correlations for KIBs.^[40]

Understanding the relationships between the five main challenges (Figure 10) is probably the most effective way to confront and address these issues. In order to overcome these bottlenecks for KIBs mentioned above, different strategies are summarized as follows:

(1) Nano-structural engineering for enhancing the K⁺-reaction kinetics;

(2) Buffering volume variation and improving electrical conductivity by using a carbon matrix;

(3) Enhancing the kinetics *via* manipulating the local coordination/electronic structure and increasing the defect/vacancy by heteroatom doping;

(4) Regulating salt chemistry and electrolyte additive to minimize side reaction and Kdendrite growth;

(5) Advanced post-potassium-ion batteries were designed to pursue high energy/power density and safe KIBs (including potassium-sulfur batteries, potassium-selenium batteries, all-solid-state potassium-ion batteries).

1.3. X-ray imaging setups

Currently, X-ray imaging based on either a traditional laboratory X-ray source or a synchrotron X-ray source has emerged as a powerful characterization tool to investigate the intrinsic link between the electrode microstructure and the overall battery electrochemical performance. The underlying working mechanism of X-ray imaging is based on the detection of the attenuation contrast or the phase shift of the beam transmitted through the

specimen. When an electro-magnetic X-ray flux passes through different materials, both the intensity and the phase-shift vary depending on the refractive index, n can be expressed as equation (1):^[41]

$$n = (1 - \delta) + i\beta \tag{1}$$

In this formula, the imaginary part β indicates the change of the attenuation and the real part δ refers to the extent of the phase change when X-ray propagating through the sample. The intensity change of the incident X-rays obeys the well-known Beer-Lambert's law (Equation (2)).^[41]

$$I = I_0 e^{-\mu d} \tag{2}$$

where I, I_0 , μ and d correspond to the detected intensity of the transmitted photon flux, the initial intensity of the incident beam, the linear attenuation coefficient of the specimen, and the path distance, respectively. The attenuated X-ray beam is finally collected by a detector and then converted into radiography images for further processing. In conventional X-ray radiography, one 2D image is obtained without sample rotation, while X-ray tomography refers to images are recorded at various angles during sample rotation that are then reconstructed to a 3D image.

1.3.1. X-ray radiographic imaging setup

The used X-ray radiographic imaging equipment contains a lab-based X-ray tube (Hamamatsu, L8121-03) and a flat-panel detector system (Hamamatsu, C7942SK-05). The micro-focus X-ray source generates a cone X-ray beam which varies for different ratios depending on the relationship between source-to-object and source-to-detector distances. In this manner, the field of view (FOV) and the spatial resolution are adjustable. The detailed experiment parameters for the X-ray radiographic imaging are: the voltage and current of the X-ray tube is set to 60 kV and 166 μ A, respectively; the exposure time is 2.1 s; the source-to-object distance (SOD) is 58 mm; the source-to-detector (SDD) is 500 mm. Considering the pixel size of the detector is 50 μ m, the resultant one pixel represents ~5.76 μ m (50/(500/58)) of the measured sample. The collected radiographic datasets are then normalized, filtered and reconstructed. More detailed experiment informations are available in section 2.1.



Figure 11. Photography of the employed X-ray radiographic imaging setup (located at the Helmholtz-Zentrum Berlin, Germany).

1.3.2. Synchrotron X-ray microtomographic imaging setup

Due to the multi-scale, high-penetration and non-destructive probing characters, synchrotron X-ray tomography is an excellent tool to investigate the complex chemomechanical phenomena that occur in rechargeable batteries at different microscopic scales. In general, the synchrotron beam produced from the storage ring is monochromatized by a double crystal monochromator or a double multilayer monochromator with a tunable energy range from 10 to 35 keV (Figure 11). Specifically, during the synchrotron X-ray imaging, the synchrotron X-rays are converted into visible light when passing the scintillator. The visible light will be optically magnified and imaged with a camera using charge-coupleddevice (CCD) or complementary metal-oxide-semiconductor (CMOS) detector. Moreover, the flat/dark field projections will also be recorded for further data analysis. To meet the technological needs, the widely used cells for 3D tomography imaging are cylindrical polymeric batteries (the inset of Figure 11, polymeric housing: low X-ray absorbing material). This geometry with a small cell diameter provides an unobstructed view of the electrode and sufficient X-ray transmission during the entire rotating process. The synchrotron X-ray imaging measurements were performed at the I13-2 beamline at DIAMOND (Oxfordshire, United Kingdom). The energy of the incident X-ray beam was monochromatized to 27 keV by a water-cooled Si <111> double crystal monochromator. The detector system comprised of a 26 µm thick GGG:Eu scintillator, an objective and optical systems relaying the optical image to a pco.edge 5.5 camera. The pco.edge detector has a 2560×2160 pixels format chip that was kept out of the direct beam by using a mirror. For the measurements conducted here, two different objective lens systems (Field of View

(mm): 4.2×3.5 and 2.1×1.8) were used during the synchrotron measurement and two different spatial resolutions (1.6 µm and 0.8 µm) were obtained. For the low-resolution (1.6 µm) measurements, 1200 projections within a 360° battery rotation were recorded with the exposure time of 0.2 s. For the high-resolution (0.8 µm) measurements, 3600 projections within a 360° battery rotation were recorded with the exposure time of 1 s.

In the present dissertation, synchrotron X-ray tomography technique is employed to characterize:

(1) The electro-chemo-mechanical coupling at the solid-solid electrode/electrolyte interface in all solid-state batteries (section 2.1);

(2) The interplay between three types of separators (Celgard 2325, Celgard 2400 and glass fiber membranes) and potassium dendrite growth in K|K symmetrical cells (section 2.5).



Figure 11. Schematic diagram of the beamline setup.^[1]

1.4 Motivation of the thesis

The main goals of this thesis are summarized as follows:

(1) High-energy synchrotron X-ray beams and ultra-high-speed imaging ability of synchrotron X-ray tomography technique can bridge the gap between the electrochemical performance of the batteries and the 3D morphologies of battery electrodes. Non-destructive and high-penetration synchrotron X-ray tomography technique is of great help not only to improve the understanding of the solid-solid interfacial reaction mechanisms of all-solid-state batteries, but also guide the design of high energy beyond-Li-based battery systems. We used X-ray tomography to observe the structure changes at the lithium and solid electrolyte interface before and after charging. We further used the X-ray tomography

technique to study the interfacial stability between potassium and different separators in Kion cells.

(2) The motivations triggering the study of potassium-ion batteries (KIBs) due to the abundant potassium resources. However, the current rate performance and cycling stability for KIBs are incomparable with the LIBs. In this regard, further exploration of suitable electrode for KIBs with high capacity as well as superior rate performance and excellent stability are urgently desirable but remain a great challenge. In our works, by rational design, three types of transition-metal-based nano-materials were prepared, which can realize high capacity, excellent rate performance and long cycle life for KIBs.

1.5 References

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2. Parts of doctoral work

2.1 Clarifying the electro-chemo-mechanical coupling in all-solid-state batteries

Fu Sun,* Chao Wang, Markus Osenberg, Kang Dong, Shu Zhang, <u>Chao Yang,*</u> Yantao Wang, André Hilger, Jianjun Zhang, Shanmu Dong, Henning Markötter, Ingo Manke and Guanglei Cui*. Clarifying the Electro-Chemo-Mechanical Coupling in Li₁₀SnP₂S₁₂ Based All-Solid-State Batteries. (It has been submitted to *Advanced Energy Materials*.)

Own contribution: Sample preparation and *in-situ* measurement; data analysis and results interpretation; manuscript composition.

2.2 Ultrathin V₅Se₈@carbon nanosheet for stable and effective K-ion storage

<u>Chao Yang</u>, Fan Lv, Kang Dong, Feili Lai, Kangning Zhao, Fu Sun*, Shuming Dou, Qian Wang, Jie Xu, Panpan Zhang*, Tobias Arlt, Xiaodong Chen, Yanan Chen*, Ingo Manke, Shaojun Guo. Carbon-Coated Ultrathin Metallic V₅Se₈ Nanosheet for High-Energy-Density and Robust Potassium Storage, *Energy Storage Materials*, 2021, 35, 1-11. (DOI: <u>https://doi.org/10.1016/j.ensm.2020.11.005</u>.) [Accepted Version]

Own contribution: Experimental design, materials preparation (bulk V_5Se_8 powders, $V_5Se_8@C$ nanosheets, assembled the cells), structural/physicochemical characterizations (SEM, XRD characterizations, *ex-situ* XRD measurement, X-ray photoelectron spectroscopy), electrochemical measurements (cyclic voltammetry, electrochemical impedance spectroscopy, galvanostatic charge/discharge tests and galvanostatic intermittent titration characterizations), data analysis and results interpretation, writing-original draft.

2.3 Co₉S₈@MoS₂@carbon hollow nanoboxes for K-ion storage

<u>Chao Yang</u>, Jianrui Feng, Yelong Zhang, Qifeng Yang, Peihao Li, Tobias Arlt, Feili Lai, Junjie Wang, Chaochuang Yin, Wei Wang, Guoyu Qian, Lifeng Cui,* Wenjuan Yang,* Yanan Chen* and Ingo Manke. Multidimensional Integrated Chalcogenides Nanoarchitecture Achieve Highly Stable and Ultrafast Potassium-Ion Storage, *Small*, 2019, 15, 1903720.

(DOI: <u>https://doi.org/10.1002/sml1.201903720</u>.) [Accepted Version]

Own contribution: Experimental design, materials preparation (ZIF-67 powder, $Co_9S_8/NSC@MoS_2@NSC$, Co_9S_8/NSC , and pure MoS_2, assembled the cells), structural/physicochemical characterizations (SEM, *ex-situ* SEM, TEM, XRD, *ex-situ* XRD, Raman, thermogravimetric analysis, X-ray photoelectron spectroscopy), electrochemical measurements (cyclic voltammetry, electrochemical impedance spectroscopy, galvanostatic charge/discharge tests and galvanostatic intermittent titration measurements), data analysis and results interpretation, writing-original draft.

2.4 Carbon-encapsulated Fe₂VO₄ nanopeapods for K-ion batteries

<u>**Chao Yang**</u>,[#] Fan Lv,[#] Yelong Zhang, Jie Wen, Kang Dong, Hai Su, Feili Lai, Guoyu Qian, Wei Wang, André Hilger, Yunhua Xu,* Yizhou Zhu,* Yida Deng, Wenbin Hu, Ingo Manke, and Yanan Chen*. Confined Fe₂VO₄⊂Nitrogen-Doped Carbon Nanowires with Internal Void Space for High-Rate and Ultrastable Potassium-Ion Storage, *Advanced Energy Materials*, 2019, 9, 1902674.

([#]equal contribution, DOI: <u>https://doi.org/10.1002/aenm.201902674</u>.) [Accepted Version]

Own contribution: Experimental design, materials preparation (peapod-like $Fe_2VO_4 \subset$ nitrogen-doped carbon nanowires, Fe_2VO_4 dense microparticles, assembled the cells), structural/physicochemical characterizations (SEM, *ex-situ* SEM, XRD, *ex-situ* XRD, Raman, X-ray photoelectron spectroscopy), electrochemical measurements (cyclic voltammetry, electrochemical impedance spectroscopy, galvanostatic charge/discharge tests and galvanostatic intermittent titration characterizations), data analysis and results interpretation, writing-original draft.

2.5 Non-destructive characterization of K deposition in different separators

Ling Ni, Markus Osenberg, Haijun Liu, André Hilger, Libao Chen, Dong Zhou, Kang Dong, Tobias Arlt, Xiayin Yao, Xiaogang Wang*, Yanan Chen, Yutao Li, Kangning Zhao, <u>Chao</u> <u>Yang*</u>, Ingo Manke, Fu Sun*, and Renjie Chen. In Situ Visualizing the Interplay Between the Separator and Potassium Dendrite Growth by Synchrotron X-ray Tomography, *Nano Energy*, 2021, 83, 105841.

(DOI: https://doi.org/10.1016/j.nanoen.2021.105841.) [Accepted Version]

Own contribution: Sample preparation and in-situ measurement; assembled, tested and measured the cells; data analysis and results interpretation; manuscript composition.

2.1 Clarifying the electro-chemo-mechanical coupling in all-solid-state batteries

Clarifying the electro-chemo-mechanical coupling in Li₁₀SnP₂S₁₂ based all-solid-state batteries

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Abstract

A fundamental clarification of the electro-chemo-mechanical coupling at the solid-solid electrode/electrolyte interface in all-solid-state batteries (ASSBs) is of crucial significance but has proven a huge challenge. Herein, non-destructive (synchrotron) X-ray tomography, electrochemical impedance spectroscopy, time-of-flight secondary-ion mass spectrometry and finite element analysis modeling are jointly used to decouple the interfacial chemistry, electrochemistry and mechanicality interactions at the interface of lithium (lithium aluminum alloy) electrode and $Li_{10}SnP_2S_{12}$ solid electrolyte. Non-destructive (synchrotron) X-ray tomography results visually disclose unexpected mechanical deformation of the solid electrolyte and electrode as well as an unanticipated evolving behavior of the (electro)chemically generated interphase. The impedance characterization and elementary probing results provide additional information that link the interphase/electrode properties to the overall battery performance. The modeling results complete the picture by providing the detailed distribution of the mechanical stress/strain and the potential/ionic flux within the electrolyte. Collectively, these results suggest that 1) the interfacial volume changes induced by the (electro)chemical reactions can trigger the mechanical deformation of the solid electrode and electrolyte; 2) the overall electrochemical process can accelerate the interfacial chemical reactions; 3) the reconfigured interfaces in turn influence the electric potential distribution as well as the charge transportations within the solid electrolyte. These fundamental discoveries that remain unreported until now bring about several nontrivial characteristics of ASSBs that need further in-depth investigations e.g., the ionic/electronic transportation pathways and the detailed disintegration process of the electrolyte. It is expected that the current work will significantly improve our understanding of the complicated electro-chemo-mechanical couplings in ASSBs as well as provide enlightening insights guiding their future development.

Keywords: all-solid-state battery; solid electrolyte; lithium metal battery; sulfide solid electrolyte; synchrotron X-ray tomography

1. Introduction

The development of all-solid-state batteries (ASSBs), which have been generally acknowledged as one of the most important next-generation battery technologies, critically depend on the fundamental understanding of the electrochemical reaction mechanisms and the synchronously occurred degradation causes.^[1,2] In this respect, considerable efforts using various probing techniques, such as optical microscopy,^[3] scanning electron microscopy (SEM),^[4-7] transmission electron microscopy (TEM),^[8,9] time-of-flight secondary-ion mass spectrometry (TOF-SIMS),^[10] X-ray photoelectron spectroscopy (XPS),^[11] magnetic resonance imaging (MRI),^[12,13] neutron depth profiling (NDP)^[14] and (synchrotron) X-ray computed tomography (CT)^[15,16] have been devoted to characterizing the physical, chemical and mechanical transformation at the solid-solid interfaces where both the electrochemical and degradation reactions occur. These dedicated endeavors have to some extent revealed how the compositional, structural and mechanical change evolve at the solid-solid interfaces.^[17-19] With that being said, the precise coupling mechanism by which these factors interact with each other remains elusive due to the incomplete understanding of the deeply-buried and dynamically-evolving solid-solid interface.^[20,21] A potential pathway toward addressing the aforementioned challenge is to combine noninvasive probing tools and theoretical modeling. Nevertheless, accurate experimental characterization and advanced modeling that can fundamentally clarify the underlying electro-chemo-mechanical coupling at the solid-solid interfaces in ASSBs are still missing.

Herein, synchrotron X-ray computed tomography (SX-CT), TOF-SIMS, electrochemical impedance spectroscopy (EIS) and finite element analysis (FEA) were jointly employed to deconvolve the underlying electro-chemo-mechanical coupling at the interface of the lithium (Li) electrode and the sulfide superionic conductor $Li_{10}SnP_2S_{12}$ (LSPS) solid electrolyte (SE).^[22] Synchrotron X-ray tomography visually discloses the formation of an

(electro)chemically generated interphase, an unexpected mechanical deformation of the LSPS SE as well as an unanticipated creep behavior of Li anode. EIS characterizations provide consistent results of the gradually increased inner resistance during both electrochemical cycling and the standing process. TOF-SIMS measurements supply an ultrasensitive spatial distribution of the elements of interest within the (electro)chemically generated interphase. The finite element analysis (FEA) elaborately illustrates the evolving strain/stress that accompanies the interfacial mechanical deformation, which is caused by the enormous volume variation at the electrode|SE interface. Moreover, FEA also simulates the influence of the morphological change of SE on the distribution of electric potential field and ion flux. These fundamental discoveries that remain unreported until now are expected to dramatically deepen our understanding of the complicated electro-chemo-mechanical couplings at the solid-solid interfaces as well as provide enlightening insights designing more robust and reliable interfaces to accelerate the further development of ASSBs.

2. Results

Both the tomography cell (tomo-cell) design and Swagelok cell (swag-cell) design^[23] were employed to study the electro-chemo-mechanical coupling in Li symmetrical ASSBs built with LSPS, due to its superior ionic conductivity that is comparable to that of liquid electrolyte.^[22] For the CT measurements, two types of symmetrical cells built with the tomocell design (Figure 1a), Li|LSPS|Li and Li-LiAl|LSPS|LiAl-Li symmetrical cells, whose schematic illustrations are shown in Figure 1b, were studied (LiAl denotes the lithium aluminum alloy containing 94 at% Li and 6 at% Al. The current study implies that using the LiAl shows similar results to that of Li due to the small amount of Al, see below). The swag-cells were assembled for the impedance measurements. Totally 10 different cells were studied and their assembly procedures, cycling conditions as well as measurement parameters are concisely listed in Table S1 in Supporting Information. Note that both CT tools (laboratory CT and SX-CT) reveal consistent results and hence only the SX-CT results are show in the main text (the laboratory CT results are shown in Supporting Information). During the SX-CT measurements, two different objective lens systems (Field of View (mm): 4.2×3.5 and 2.1×1.8) were used (Figure 1c) and hence two different spatial resolutions (1.6 µm and 0.8 µm) were obtained. The detailed CT, EIS, TOF-SIMS measurements and FEA analysis are shown in Supporting Information.



Figure 1. Schematic illustration of the customized tomography cell and the beamline set-up. a) The photograph of the customized tomo-cell. b) The corresponding illustration of the as-studied cells, the Li|LSPS|Li cell and the Li-LiAl|LSPS|LiAl|Li cell. c) The schematic illustration of the used beamline setup.

2.1. Mechanical Deformation of the Electrode and SE after First Discharge

The internal morphological view of the uncycled cell No.1 is shown in Figure S1 in Supporting Information, from which one can clearly recognize the electrode |SE| electrode sandwich structure. After cell No.2 was discharged for 17 hours at 0.2 mA/cm² until short-circuited (red arrow in Figure S2, Supporting Information), it was measured by SX-CT without cell disassembly and unexpected scenarios shown in Figure 2 are obtained. The 3D volume rendering of the LSPS SE as shown in Figure 2a clearly depicts that it deforms into a bowl-like shape with obvious surface cracks (white isolines). A sectional plane (green rectangle in Figure 2a) is selected to showcase the changes within the LSPS, as shown in Figure 2b. And the corresponding zoomed-in view is shown in Figure 2c, from which several distinguishable features are noteworthy: (1) The LSPS layer seems to slump downwards to the bottom electrode layer (the blue dash lines), forming the bowl-like shape shown in Figure 2a; (2) Several low X-ray absorption interphase regions are generated at the LiAl|SE interface (regions (12)(3)), giving rise to the surface cracks shown in Figure 2a; (3) The boundary lines between the Li metal and LiAl alloy seem to deform towards the LSPS

layer (yellow solid lines *vs.* yellow dot lines); (4) Crack/fissure structures are formed within the crooked area of the LSPS SE (dark grey regions). The horizontal view of the mechanically deformed Li|LiAl boundaries and the formed cracks are also shown in Figure S3, Supporting Information. The laboratory CT results of cells No.3 and No.4, which show similar mechanical deformation to that of cell No.2, are shown in Figure S4-S5 in Supporting Information.



Figure 2. SX-CT characterization results of cell No.2. a) The 3D volume rendering of the LSPS SE. b) The selected cross-section shown in a) (green rectangle). The in-set white dot rectangle marks the region shown in c). c) The zoomed-in view of the selected cross-section of the LSPS SE. The yellow dot and solid lines denote the original and current Li|LiAl interface. The blue dash lines depict the LiAl|LSPS interface. The green regions marked with (12)(3) indicate the (electro)chemically generated interphase. The red diamonds indicate the crack tips. The irregular dark grey regions indicate the as-formed cracks. The orange arrow lines denote the Li creep direction. Both the solid and dotted black and white arrow lines suggest the potential transportation pathways of Li ions and electrons during electrochemical cycling. Nevertheless, compared with the dotted lines, it is more likely that the Li ions and electrons transport along the solid lines. See more the Discussion part.

The unexpected scenarios shown in Figure 2, S3-S5 (Supporting Information) are caused by the complicated electrochemo-mechanical coupling. During the galvanostatic discharge, Li would be electrochemically extracted from the LiAl solid-solution alloy^[24] anode and then electrochemically deposited onto the LiAl alloy cathode, as shown in Reactions 1-2. However, previous investigations confirmed that the LSPS is thermodynamically unstable with Li and Reactions 3-4 would occur under physical contact and/or electrochemical cycling conditions:^[25]

$LiAl \rightarrow Li^+ + e^- + Al$	Reaction 1
$Li^+ + e^- + Al \rightarrow LiAl$	Reaction 2
$Li_{10}SnP_2S_{12} + 20Li \text{ (or } 20Li^+ + 20e-) \rightarrow 12Li_2S + 2Li_3P + Sn$	Reaction 3
$5Sn + 22Li \rightarrow Li_{22}Sn_5$	Reaction 4

The generated products are mostly low X-ray absorbent, low Li ion conductive and medium electronic conductive materials, and they form the so-called mixed conducting interphase (MCI), *i.e.*, the formed interphase (regions (12)(3) in Figure 2c).^[26] Considering that the formation of lithiated alloy has not been experimentally verified, it is assumed here the further lithiation of Sn would not occur.^[27] Looking at the newly formed MCI interphase regions (green regions in Figure 2c), it is interesting to note that the interphase region formed during Li electrodissolution are more abundant than that formed during Li electrodeposition. Additionally, Figure 2c visually showcase the consequence of Li dissolution at LiAl anode and the subsequent deposition of Li at LiAl cathode, *i.e.*, the concave deformation of the LSPS SE layer. This concave deformation behavior has been frequently observed in discharged Li symmetrical cells employing liquid electrolyte.^[28-32] However, unlike the previously reported morphological evolution of Li anode during electrochemical discharging,^[33] significant volume "expansion" of Li at the cathode side can be unambiguously noted (the upper vellow solid line), in addition to the volume "expansion" of Li at the anode side (the bottom yellow solid line). Elucidating the simultaneous volume expansion of Li electrodes necessitates re-exploring Reaction 3 and Li metal from a mechanical point of view. Janek's group have elaborately studied the chemo-mechanical expansion/contraction of electrode materials in ASSBs and they instructively suggested using the partial molar volume (\bar{V}_m) to calculate the reaction volume change ($\Delta_r V$) after electrochemical cycling.^[18] Adopting this notion, the reaction volume change of Reaction 3 is -130.55 cm³, indicating a reduced volume of 23.7%. Moreover, considering that the power-law creep deformation (ϵ_{true} (%)) of Li metal under room temperature can reach > 25 under 0.36 MPa after 15 hours, it is anticipated that Li metal that was located at both anode and cathode sides would experience significant creep deformation (orange arrows) during the galvanostatic discharge process (~0.3 MPa stress during 18 hours).^[34] The Reaction 3 induced volume shrunk and the stress-induced creep deformation of Li collectively lead to the observed volume "expansion" of Li at both electrodes. Another cross-section showing the similar results is shown in Figure S6, Supporting Information.



Figure 3. Illustrations of the mechanical stress/strain distribution within cell No.2 by finite element analysis. a) Schematic illustrations explaining crack initiation/openings under two different cases, the volume expansion of the electrodeposited Li (I) and volume contraction of the formed interphase (II) inside SE. b) The Von Mises plane stress analysis of cell No. 2. c) The zoomed-in view of the two selected regions in b). d) The plane strain analysis of cell No. 2. The black dot lines point to the potential strain direction caused by the volume contraction.

Along with the unexpected mechanical deformation of LSPS SE, two different types of LSPS fracture behaviors are noticeable in Figure 2c, namely, the irregular shapes of cracks within the SE (dark gray shadows) and the wedge-like crack openings (red diamonds) along the interface of LSPS and interphase. On the basis of the Griffith fracture theory, cracks will propagate when the available energy to extend the unit area of crack is equal to or greater than the energy required.^[35] The formation of the irregular shapes of the cracks within the LSPS can be explained by the increased strain energy built up during the enormous

mechanical deformation process (forming the bowl-shape in Figure 2a). This implies that the mechanical stress generated during the deformation process has reached a critical value σ_{crit} that can fracture the LSPS. On the other hand, the wedge-like crack openings (red diamonds in Figure 2c) along the interface of LSPS and the interphase have to be explained from an electrochemo-mechanical coupling perspective. If we only consider the mechanical property of a ceramic SE, its fracture stress σ_f can be calculated using the following equation:^[36]

$$\sigma_f = K_{IC} (\pi a_c)^{-1/2}$$
 Equation 5

where K_{IC} is the fracture toughness of the SE and a_c is the critical flaw size. Plugging the value of $K_{IC}\approx0.23$ MPa m^{1/2} for the sulfide SE into equation 5 and assume a flaw size of 1 or 5 µm in the SE, the fracture stress $\sigma_f = 130$ or 58 MPa can be obtained.^[36] Meanwhile, by taking the electrochemical process into consideration, Porz *et al.* introduced equation 6 to relate the electrochemical work (right side of Equation 6) to the mechanical work (left side of Equation 6) done by the electrodeposited Li dendrite to crack SE during Li electrodeposition:^[37]

 $\sigma V_M = F \bigtriangleup \Phi$

Equation 6

where, σ is the mechanical stress induced by the Li electrodeposition in a SE under an overpotential $\triangle \Phi$, F is the Faraday's constant (F = 9.65 ×104 C/mol) and V_m is the molar volume of Li ($V_{\rm m} = 13 {\rm cm}^3/{\rm mol}$). An overpotential of $\Delta \Phi = 100 {\rm mV}$ corresponds to a mechanical stress $\sigma = 750$ MPa, which is large enough to initiate cracks and their propagation in SE.^[37] The above electrochemical-mechanical coupling has been proposed to elucidate the crack propagation within the (electro)chemically stable SE during Li electrodeposition and it is schematically shown in scenario I in Figure 3a (the plane stress analysis). However, considering the extra chemical Reaction 3 occurred herein, a different crack initiation mechanism has to be proposed for the (electro)chemically unstable SE. Compared with the opening or tensile crack mode where it is the tensile loading stress that is perpendicular to the crack surfaces causes the crack to propagate (scenario I in Figure 3a), the volume shrunk caused by Reaction 3 induces a pressed loading stress on the crack surfaces that initiates the openings, as schematically shown in scenario II in Figure 3a. Figure 3b-d further show the FEA plane stress/strain analysis of cell No.2. The FEA results of the Von Mises stress (Figure 3b) clearly demonstrate that most of the stress are distributed around the reacted interphase region, and the zoomed-in view in Figure 3c clearly shows the maximum stress is localized at the crack tips (see also Figure S7, Supporting Information). In addition, Figure 3d clearly shows that the overall strain of LSPS

is positive while that of the reacted interphase region is negative. The potential strain direction that is caused by the significant volume shrink of Reaction 3, is also schematically shown in Figure 3d (black dot arrow lines).



2.2. Mechanical Deformation of the SE after Extended Cycles

Figure 4. Characterization results of cell No.5. a-b) The electrochemical cycling curve and the 3D volume rendering of the SE of cell No.5. c-d) Cross sections showing the LSPS after cycling. e) The FEA simulation of the localized current density distribution based on the uncycled cell No.1. f) A horizontal slice showing different types of cracks. g-h) Cross sections showing the LSPS after cycling. h) is the enlarged view of the region marked in red rectangle in g). In h), the half-highlighted green regions indicate the (electro)chemically generated interphase. The red diamonds indicate the crack tips. The yellow dash rectangle covers the tiled slit-like crack. Both the solid and dotted black and white arrow lines suggest the potential transportation pathways of Li ions and electrons. Nevertheless, compared with the dotted lines, it is more likely that the Li ions and electrons transport along the solid lines. i) The illustration of the generated interphase between the LSPS and the electrode (see below the TOF-SIMS results).

To further study the morphological changes inside the ASSBs during long-term electrochemical cycling, cell No.5, which underwent galvanostatic cycling as shown in Figure 4a, was investigated. From Figure 4a, one can clearly observe a gradual increase of

the overpotential, which is attributed to the continuous rising of the internal resistance (see below the EIS results).^[25] Additionally, a sudden voltage drop (red arrow in Figure 4a) indicating a short-circuit can be also noted.^[4] The SX-CT results of cell No.5 are shown in Figure 4b-h. From its 3D rendering as shown in Figure 4b, one can obviously note the existence of a variety of shallow gully-like and deep gorge-like cracks. Two sectional planes (green and blue rectangles) and one horizontal plane (purple rectangle) are selected to showcase the morphological changes from the cross-sectional and horizontal views, as shown in Figure 4c, 4g and 4f. Figure 4c shows that some part of the LSPS possess relatively smooth edges after cycling and a crack "slitting" through the LSPS can be also perceived (orange rectangle). Figure 4d is the enlarged view of the penetrating crack (white arrows). Figure 4g clearly demonstrates that some edges of LSPS after electrochemical cycling become meanderingly "bent" (red rectangle). A closer inspection of the zoomed-in view shown in Figure 4h shows an unexpected phenomenon of a tortuous and heterogeneous reaction interphase region (green region). In addition, some tilted slit cracks penetrating the LSPS (black arrows in Figure 4h), which are probably generated during battery assembly process, are also observable (yellow dash rectangle). Figure 4f depicts the gorge-like and slit-like cracks from a horizontal view. Although the uncycled state of this cell (cell No.5) was not measured, the original LSPS|LiAl interface is very likely to be the yellow dot lines shown in Figure 4c and 4g (similar to the results of cell No.2-4). This means that a great deal of LSPS have decomposed into the interphase that occupies the LSPS's surroundings during the long-term electrochemical cycling (green regions in Figure 4h). Figure 4i schematically illustrates the formed interphase between the LSPS and the electrode (see the TOF-SIMS results below). The laboratory CT results of cell No.6, which shows similar morphological changes to that of cell No.5 after cycling, are shown in Figure S8 in Supporting Information.

Although the short-circuit phenomena of ASSBs have been frequently detected electrochemically, yet directly probing its underlying mechanism is technologically challenging due to its deep-buried nature. Previous study from Manthiram's group have visualized the Na dendrite penetrating a Na symmetrical ASSB by TOF-SIMS.^[10] The currently observed scenario shown in Figure 4d provides direct and irrefutable evidence that the short-circuit phenomenon in ASSB can be caused by the direct connecting of the two electrodes via the electrochemically generated interphase, which is electronically conductive. This "piercing" interphase may be formed as a result of the local field amplification phenomenon observed recently by Chiang's group.^[38] To elucidate this process, the

uncycled state of cell No.1 as shown in Figure S1 in Supporting Information is employed to model the electric filed potential and current distribution and the results are shown in Figure 3e and Figure S9, Supporting Information. From these results, it can be clearly observed that the local electric field distribution is enhanced at the protrusion part of the electronically conductive LiAl electrode (the red five-pointed star in Figure 4e) due to the accumulated charges. This non-uniform electric field distribution would lead to the enhanced reaction of the LSPS neighboring the protrusion part. Meanwhile, the formed interphase would in turn promote the local field amplification at the already generated interphase regions due to their relatively higher degree of electron conductivity, again accelerating the reaction extent of the LSPS surrounding them. Through this process, a "piercing" interphase may be materialized after extended electrochemical cycling. Apart from this local field amplification effect, bewildering and random reaction patterns can be also found in the cycled cell, as shown in Figure 4g-h. The existence of these reaction "hot-spots" has been explained by grain boundaries, foreign impurities, and so on.^[39] A recent study from Yang's group clearly demonstrate that these SE defects exhibit faster Li deposition kinetics and high nucleation tendency.^[40] Nevertheless, given the scale and extent of the currently discovered reaction hot-spots (Figure 4h) it is suggested that further dedicated studies on ionic conduction path,^[41] electron conduction^[14] and/or electric field distribution^[38] in ASSBs are desirable.^[42]

2.3. Morphology, Impedance and Composition Evolution at the Li|SE Interface

To complete the understanding of the abovementioned Li|LSPS interfacial changes after electrochemical cycling, *in operando* laboratory CT measurement of cell No.7 experiencing non-electrochemical cycling was conducted and the results are shown in Figure 5a-5d (The cell was measured *in operando* after 6 days (d), 12 d, 35 d and 136 d after cell assembly). Figure 5a depicts its inner state, from which, two regions (marked as b and c in blue and red rectangles) are selected for further analysis. A series of snapshots shown in Figure 5b and Figure 5b1-b4 depict the decrease of the distance between the LSPS protrusion and the stainless steel (SS) current collector (yellow double-headed arrows) from 360 µm to 316 µm and 306 µm. The movement of the LSPS towards the SS under external pressure is resulted from the volume shrunk accompanying the Reaction 3, which agrees well with the previous report.^[43] In addition, a series of snapshots shown in Figure 5c and Figure 5c1-c4 depict the gradual formation of a transition layer between the LSPS|Li interface (white arrows). This newly generated transition layer is the formed "interphase" region, which becomes hardly discernable due to the used low-energy white X-rays. Aiming to further study the evolution
of the chemically formed interphase region, X-ray absorption changes along the green arrow line (600 µm long, middle point is the LSPS|Li interface) shown in Figure 5a was analyzed and the results are shown in Figure 5d. Figure 5d clearly shows an expansion of the thickness of the interphase as a function of contact time (black dash line). To sum up, the obtained interfacial changes via the *in operando* laboratory CT measurement distinguish themselves from the SX-CT results in the following two aspects. First, the chemically generated interphase is relatively uniform and the reason may result from the homogeneous chemical reactions between the LSPS and Li. Second, the chemically driven interphase formation may be governed by the diffusion-controlled Reaction 3 since its growth rate decreases as a function of reaction time.^[44] This may be fundamentally different from the electrochemically driven growth mode during electrochemical cycling.



Figure 5. The *in operando* laboratory CT measurement results of cell No.7. a) The cross-sectional view of the cell showing its main components (from top to bottom): stainless steel (SS) current collector, Li electrode, LSPS, Li electrode and SS. Two interesting regions (blue and red rectangles) marked with b and c are chosen for further studies. In b, the yellow double-headed arrow marks the distance from the LSPS protrusion to the SS. The solid green arrow line (600 µm long, middle point is the LSPS|Li interface) indicates the region where X-ray absorption changes are analyzed in figure d). b1-b4) and c1-c4) The morphological changes occurred in region b and region c after 6 days (d), 12 d, 35 d and 136 d

after cell assembly. d) The X-ray absorption along the solid green arrow line in Figure 5a. The Li region is marked by the black double-headed arrow line. The interphase regions are marked by the dotted and colored double-headed arrow lines. The colored triangles denote the beginning of the LSPS bulk. e) The TOF-SIMS depth profile of several interesting ion fragments within the interphase region. The in-set photo shows the as-studied sample and the in-set figures shows the reconstructed 3D spatial fragment distributions of the selected species.

To further correlate the generated interphase observed by CT measurements to the overall battery performance in a fundamental way, time resolved electrochemical impedance spectroscopy (EIS) and TOF-SIMS depth profiling experiments were performed. Figure S10 in Supporting Information shows the collected rime-resolved impedance spectra of different Li|LSPS|Li symmetrical cells during cycling (cell No.8), first discharging (cell No.9) and standing process (cell No.10). The EIS results of all these three cells (cell No.8-10) share a similar impedance evolution trend, i.e., a gradual increase of the inner resistance under both electrochemical cycling and chemical contact conditions, which is in good agreement with previous report.^[45] The EIS spectra were further fitted with an equivalent circuit^[45] and the analysis as shown in Figure S10 in Supporting Information suggest that the resistance that is assigned to the interphase is continuously growing, while the LSPS bulk resistance does not vary significantly with time. This continuously increasing resistance can be explained by the constantly growing reacted interphase between the electrode|LSPS, which has been straightforwardly detected by the CT measurements (Figure 2c, Figure 4h and Figure 5c1c4). Figure 5e shows the TOF-SIMS measurement results of the LSPS that was sputtered with ~100 nm thickness of Li, which mimics the scenario at the Li|LSPS interface (the in-set photo in Figure 5e).^[46] Figure 5e clearly shows the depth profiles of several secondary ion fragments of interest in the negative mode (Li⁻, P₂OH⁻, SO₂⁻, CH⁻, P⁻) and positive mode (Sn^+, Li_2F^+, Li_3O^+) as a function of sputtering depth. The fragment Li_3O^+ may be originated from the reaction of pure Li with trace H_20 impurities and the Sn^+ , P_2OH^- , SO_2^- may be correlated with the reacted interphase and LSPS. Considering that the sputtering depth is ~ 10 nm/60 sec, one can calculate that the formed interphase is ~ 90 nm thick due to the fact that the intensity of all these ion fragments plateau after around 500 sec (black dash line in Figure 5e). The slight decrease of the thickness of the detected interphase compared with the sputtered Li may be again caused by the Reaction 3. In addition, it is interesting to note that the intensity of the S- and P- containing ion fragments (except SO₂) is lower in the interphase region than that in the LSPS region, suggesting the "diluting" effect of the

reaction-participating Li (lower X-ray absorption). The reconstructed 3D spatial fragment distributions of selected species are shown in in-set figures in Figure 5e, which agree well with the depth profiling.





Figure 6. FEA analysis of the electric potential and ion flux density inside the as-studied cells. a-b) The electric potential field and the ion flux density within cell No. 5. c-d) The electric potential field and the ion flux density within cell No. 5. In b) and d), both the solid and dotted gray and white arrow lines suggest the potential transportation pathways of Li ions and electrons. Nevertheless, compared with the dotted lines, it is more likely that the Li ions and electrons transport along the solid lines.

To get an in-depth understanding of the complicated electro-chemo-mechanical coupling in Li|LSPS|Li symmetrical cells as shown in Figure 2 and Figure 4, FEA was employed to study the corresponding electric potential field and ion flux density within cells No.2 and No.5. It is worthy to note that the models (Figure S11, Supporting Information) employed herein were developed from the SX-CT results instead of hypothetical assumptions.^[47] The electrical potential, ion concentration and ion flux density during battery discharge were calculated^[48,49] and the FEA simulations with/without considering the interphase are shown in Figure 7 and Figure S12 in Supporting Information. The FEA results considering the interphase region clearly show that the maximum potential drop and the maximum ion flux density occur simultaneously at the interphase|LSPS interface, as shown respectively in Figure 7a, 7c and Figure 7b, 7d. In addition, the FEA results also show that there is a sudden change of the ion concentrations across the interphase|LSPS interface, as shown in Figure S12a-b in Supporting Information. To fundamentally explain these simulation results, one may reconsider the different electronic conductivities and Li⁺ electrochemical potentials among the electrode, the formed interphase and the LSPS.

Due to the 4 orders of magnitude of increase in electronic conductivity of the formed interphase compared with the LSPS, it is reasonable to conjecture that the maximum potential drop would be concentrated at the interphase|LSPS interface during electrochemical cycling.^[50] Meanwhile, considering that this potential drop $(e\Delta\phi)$ also equals the difference of the Li⁺ electrochemical potential ($\Delta \eta_{Li^+}$) at the interphase|LSPS and that the transfer of Li^+ is driven by the Li^+ electrochemical potential difference,^[51] one may reasonably confer that the Li⁺ flux density would be maximized mostly at the interphase|LSPS interface where the maximum difference of the Li⁺ electrochemical potential locates. The aforementioned scenario could also lead to a consequence that a sudden change of the Li⁺ concentration across the interphase|LSPS interface would develop. However, different FEA results of the potential distribution and ion flux density were obtained if no interphase region was taken into account during simulation. Figure S12c, S12e in Supporting Information clearly show that the electric field is distorted significantly and the distribution of the electric potential isolines (black lines) relies mostly on the unreacted LSPS. Figure S12d, S12f in Supporting Information also demonstrate that the ion flux (white solid lines) concentrates mostly on the junctional region. These results indicate that the (electro)chemical and electrical properties of the formed interphase play an essential role in distributing the electric potential and ion flux in the deformed solid-state electrolyte.

3. Discussion

On the basis of the results shown above, the current study suggests several nontrivial characteristics of ASSBs that need further in-depth investigations.

1) Carefully interpreting the electrochemically obtained ASSB performance. Electrochemical characterization is one of the most frequently used technique to evaluate the performance of battery materials as well as to understand the relevant electrode-reaction mechanisms of charge transfer, mass transport, electron transport, *etc.* The considerable advantage of the electroanalytical method is that an electrochemical instrument can appropriately transform the chemical/physical signal (within the studied battery) into a handling electric signal for further facile processing, whereby no detectors of any form other than electrodes are required.^[52] In this regard, it has to be noted that these electroanalytical methods almost consider all types of reactions occurring within the battery. Therefore, the acquired instrumental signal does not necessarily represent the reaction/process of

interest.^[53,54] For example, the galvanostatic charge-discharge is employed to investigate the electrochemical deposition/dissolution of Li (Reaction 1 & 2) in symmetrical ASSBs. However, in the current case, besides Reactions 1 & 2, the existence of Reaction 3 interferes significantly with the interesting reactions, contributing unavoidably to the signals captured by the electroanalytical instrument. For this reason, trustworthy and rigorous interpretation of the electrochemical data involved with the electrochemically unstable SE turns out to be extremely challenging. Furthermore, derivations on the electrochemical Li deposition/dissolution inferred solely from the electrochemical characterization thus becomes questionable as well when the studied SE is thermodynamically unstable with Li. It is suggested herein that caution and care should be taken when interpreting the electrochemical performance from ASSBs built with unstable SEs.

2) The unresolved ionic/electronic conduction path within the reaction matrix. The interfacial decomposition products, which form the interphase between the SE and electrode, influence predominantly the ASSB electrochemical performance built with unstable SEs. First-principles calculations suggest that the thermodynamically stable reaction products can mitigate the extreme chemical potential from the electrodes and protect the SE from further decomposition. However, the protection mechanism would not be effective if the decomposition interphase layer is electronically conductive. This applies to the currently studied Li|LSPS interface, wherein electronic conductive Sn could be generated. Nevertheless, it has been pointed out by Bron et al.^[55] that the percolating electronic pathways across the interphase do not form due to the limited volume fraction of these conductive compounds (10%, see also the Sn⁺ TOF-SIMS result in Figure 5e). With that being said, the currently observed short-circuit and the piercing-through reacted interphase suggest that a unique electronic conduction pathway may exist. And this unresolved electronic pathway (artificially represented by the white solid and dot arrow lines in Figure 2c and Figure 4h) may be mostly responsible for the Li electrodeposits in the SEs, as suggested recently by Wang et al.^[14] and Liu et al.^[56] From the Li⁺ conduction point of view, the low ionic conductive interphase would accumulate at the interface and inevitably inhibit Li^+ conduction pathways to some extent (the impedance results). Nevertheless, the Li^+ flux seems to continuously flow through the decomposition product rather than choose another way when considering the continuously growing hot-spots or the interphase (cf. the green regions in Figure 4h after continuous electrochemical cycling). The underlying mechanism remains elusive but its outcome may directly lead to the interphase penetrating the SE (cf. Figure 4d). Taken together, it seems that resolving the electronic and ionic conduction

pathway within the formed reaction matrix (or the interphase) is essential for a full mechanistic understanding of the continuously evolving reaction front and the electrochemically characterized voltage polarization.

3) Future dedicated researches to further clarify the underling electro-chemo-mechanical coupling. The currently disclosed scenarios have not only fundamentally advanced our understanding of the electro-chemo-mechanical couplings in ASSBs but also brought up several basic questions that have not been answered before. On the one hand, the correlation between the electrochemical and chemical reactions is open to debate. In this regard, McDowell et al. demonstrated that the electrochemical process can accelerate the chemical reaction at the interphase of NASICON-type SE and Li,^[8] which agrees well with the recent study of the SEI formation in liquid batteries.^[57] The current study also suggests that the electrochemical cycling can trigger relatively more chemical reactions under pure chemical contact condition (Figure 4 vs. Figure 5). Nevertheless, the extent to which and the mechanism by which the electrochemical cycling enhances the chemical reactions have not been tackled. For example, it is currently not clear why the Li|LSPS interfacial reaction extent during the Li electrodissolution process is higher than that during Li electrodeposition process (regions 12 vs. region 3 in Figure 2c). To make it more complicated, it is still not clear whether the electrochemical and the chemical reactions occur simultaneously or successively, that is to say, the sequence of the Reactions 1-3 is unclear. The *in operando* XPS study by Teeter et al. suggests that the Li₂S-P₂S₅ SE can be decomposed before Li⁺ being reduced to Li metal.^[58] Nevertheless, Dasgupta et al. have demonstrated that the Li plating process could occur before Li10GeP2S12 decomposition at high current density and they suggest a kinetic competition mechanism between these two different reaction pathways.^[5] The complexity of the link between electrochemical and chemical reactions has reached a new level by Wagemaker et al., who argued that the favorable decomposition pathway is via (de)lithiated states of the SE into the thermodynamically stable decomposition products.^[59] The underlying mechanisms remain undetermined and further in-depth explorations are desirable. On the other hand, the correlation between the mechanical effects and (electro)chemical reactions in ASSBs needs also further clarification. In traditional liquid electrolyte batteries, the volume expansion/contraction of the battery materials can be largely accommodated by the presence of soft polymer binders. In contrast, the volume change induced stresses in constrained ASSBs during cycling can reach values on the order of GPa.^[60] These stresses can significantly alter the open-circuit potential of the battery^[48] as well as the SE's ionic conductivity and/or decomposition reaction rate.^[61] The currently observed wedge-like reaction fronts following the crack openings (red diamonds in Figure 2c and Figure 4h) seems to indicate that the mechanical stress also play an import role in guiding the decomposition pathway. Yet, the correlations among the unexpectedly revealed heterogeneous reaction interphase, the complicated mechanical stress/strain evolutions and the unresolved electronic/ionic transportations has not been explicitly established. In a word, dedicated studies aimed to address these fundamental yet ambiguous questions are highly desirable.

4. Conclusion

A wealth of unanticipated insights on the fundamental electro-chemo-mechanical coupling mechanisms in Li symmetrical ASSBs have been revealed by (synchrotron) X-ray tomography, EIS, TOF-SIMS and finite element analysis. The unexpected morphological changes of the SE as well as the newly formed interphase regions buried within the SE matrix are disclosed for the first time. In addition, the electrochemically characterized voltage-rise and short circuit phenomena are directly interpreted via the accumulation and penetration of the generated interphases. Moreover, it is proposed that an externally applied electrochemical cycling. Furthermore, the (electro)chemically induced mechanical stress distribution and its effect on the electric/ion distribution have been also unveiled. In the last, the current study brings about several nontrivial characteristics of ASSBs that need further in-depth investigations. These novel insights from the current work have fundamentally improved our understanding of the complicated electro-chemo-mechanical couplings in ASSBs and may shed new insights guiding their future development.

5. Experimental Section

The Materials, Assembly and Electrochemical Cycling of the All-Solid-State-Batteries, Synchrotron X-ray and Laboratory X-ray CT Measurements, X-ray CT Data Reconstruction and Analysis, The EIS and TOF-SIMS Measurements and The Finite Element Analysis are elaborately detailed in the Supporting Information.

Acknowledgements

F. Sun and C. Wang contributed equally to this work. We thank Diamond Light Source Ltd., UK for providing the beamtime under experiment number MT18936-1 in the Diamond Manchester Imaging Branchline (I13-2). This work is sponsored by the National Natural Science Foundation of China (U1904216), QIBEBT I201922, Dalian National Laboratory For Clean Energy (DNL) CAS and the German Research Foundation DFG (MA 5039/4-1).

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Supporting information

Clarifying the electro-chemo-mechanical coupling in Li₁₀SnP₂S₁₂ based all-solid-state batteries

Cell No.	Cell Info	Cycling Info	Measure Info	Figures Info
1	LiAl SE LiAl	none	SX-CT, 1.6 μm	S1
2	Li-LiAl SE LiAl-Li	discharged to	SX-CT, 1.6 μm	2a, 2b, S3a
		short circuit	SX-CT, 0.8 μm	2c, S3b-d, S6
3	Li LSPS Li	discharged	Lab-CT, 5.7µm	S4
4	Li LSPS Li	discharged to	Lab-CT, 5.7µm	S5
		short circuit		
5	LiAl SE LiAl	cycled to short	SX-CT, 1.6 μm	4b, 4c, 4g
		circuit	SX-CT, 0.8 μm	4d, 4f, 4h
6	Li LSPS Li	cycled	Lab-CT, 5.7µm	S8
7	Li LSPS Li	none	Lab-CT, 3.6µm	5a-5d
8	Li LSPS Li	cycled	EIS	S10a-c
9	Li LSPS Li	discharged	EIS	S10d-f
10	Li LSPS Li	none	EIS	S10g-h

Table S1. Cell composition, electrochemical and measurement information of the studied cells in the current study. Details can be found in the experimental section.

Experimental Section

Materials

The housing of the customized cell, the polyamide-imide (Torlon), was purchased from Drake plastics Europe and Bang Der plastics China. The Li metal and the LiAl alloy (contains 94 at% Li and 6 at% Al) were purchased from China Energy Lithium Co,.LTD. The 3 mm diameter polyimid tube was purchased from DETAKTA GmbH, Germany. The $Li_{10}SnP_2S_{12}$ (LSPS) solid electrolyte was purchased from NEI Corporation and/or self-prepared by the solid-state reaction method. During self-preparation of LSPS, stoichiometric amounts of Li_2S (Alfa Aesar, 99.9%), P_2S_5 (Macklin, \geq 99%), and SnS_2 (Macklin, \geq 99%) were mixed by ball milling at 400 rpm for 24h. The synthesized powders were then pressed into pellets, sealed in a tube (Ar-filled) and heated at 550 °C for 8 h.

Assembly and Electrochemical Cycling of the All-Solid-State-Batteries

All ASSBs studied herein were assembled in an Ar-filled glove box. Two different types of the battery designs were employed in the current work, the tomography cell design and the Swagelok cell design^[1] (manufactured by Hefei Kejing Material Technology Co., Ltd). During the assembly of the ASSBs using the tomography cell design (cells No.1-No.7 in the current work), punctured lithium (lithium aluminum alloy) disc of 3 mm diameter was firstly placed in a polyimide tube (diameter of 3 mm). Then, the LSPS (~6 mg) and another lithium (lithium aluminum alloy) disc of 3 mm diameter were successively placed on top of each other. Afterwards, a pressure of ~370 MPa was applied to them to form a pellet. After releasing the pressure, the obtained pellet was sandwiched by two stainless-steel screws during cell assembly. The cell was properly sealed off before taking out of the glovebox. Before the electrochemical measurements (except cells No.1 and No.7), the cells were placed in an oven at 50 °C for 5 h. Cells No.2 and No.4 were discharged at 0.2 mA/cm² until short circuited. Cell No.3 was discharged at 0.2 mA/cm² for 25 hours. Cell No.5 was cycled (1 hour discharge and 1 hour charge) at 0.2 mA/cm² for 108 hours. These cells were cycled at 50 °C by Neware battery cycler (CT-4008).

During the assembly of the ASSBs using the Swagelock cell (manufactured by Hefei Kejing Material Technology Co., Ltd, cells No.8-No.10 in the current work), SE discs (10 mm diameter) were prepared by cold pressing the LSPS powder (100 mg) at 500MPa into a solid state battery mold. Then two-electrode symmetrical cells were constructed by sandwiching the SE disc between two pieces of Li metal (9 mm diameter). The obtained structure was sandwiched by two stainless-steel columns during cell assembly. The battery was fixed by an iron frame.

Synchrotron X-ray and Laboratory X-ray CT Measurements

The SX-CT measurements were conducted at the I13-2 beamline at DIAMOND (Oxfordshire, United Kingdom). The energy of the incident X-ray beam was monochromatized to 27 keV by a water-cooled Si <111> double crystal monochromator. The detector system comprised of a 26 μ m thick GGG:Eu scintillator, an objective and optical systems relaying the optical image to a pco.edge 5.5 camera. The pco.edge detector has a 2560×2160 pixels format chip that was kept out of the direct beam by using a mirror. For the measurements conducted here, two different objective lens systems (Field of View (mm): 4.2 × 3.5 and 2.1 × 1.8) were used during the synchrotron measurement and two different spatial resolutions (1.6 μ m and 0.8 μ m) were obtained. For the low-resolution (1.6 μ m) measurements, 1200 projections within a 360° battery rotation were recorded with the exposure time of 0.2 s. For the high-resolution (0.8 μ m) measurements, 3600 projections within a 360° battery rotation were recorded with the exposure time of 1 s.

Two laboratory X-ray CT instruments were used in the current work. The first one is located at Helmholtz-Zentrum Berlin, Germany.^[2] The cells (No.3, No.4 and No.6) were measured by this instrument and the parameters were: the voltage and current of the X-ray tube were set to be 60 kV and 166 μ A, respectively; the exposure time was 2.1 s; the source-to-object distance (SOD) was 58 mm; the source-to-detector (SDD) was 500 mm. Considering the pixel size of the detector is 50 μ m, the resultant one pixel represents ~5.76 μ m (50/(500/58)) of the measured sample. The second laboratory X-ray CT instrument (Rigaku CT lab HX) is located at QIBEBT, China. The cell No.7 was measured by this instrument under an automatic mode. The scan mode was High Resolution and the scan time was 68 min. During the measurement, the X-ray tube voltage was 70 kV and the tube current was 116 μ A. The geometry between the sample and the detector was Long and the used field of view (FOV) was 10. The distance between Focus and Object was 3.6 μ m.

X-ray CT Data Reconstruction and Analysis

The raw tomography data from I13-2 beam line were processed using in-house reconstruction software programmed in IDL 8.2. The data was first normalized, de-noised and in some cases, filtered and underwent phase retrieval. Then the filtered back projection was used for final reconstruction. The 3D volume renderings shown in Figure 2a and Figure 3b were generated by Avizo software. The reconstruction software Octopus (Tomoshop) was used to reconstruct the obtained dataset from the laboratory X-ray CT instrument in Germany (China).

The EIS and TOF-SIMS Measurements

The impedance measurements were conducted by using the electrochemical work station (VMP300) with a frequency range of 7 MHz to 0.1 Hz at an amplitude of 10 mV. *In situ* impedance data were collected during electrochemical charge-discharge (1h charge and 1h discharge) at 0.15 mAcm⁻² by using the Swagelok cell (designed by Hefei Kejing Material Technology Co., Ltd). The EIS data were collected at every half an hour in all EIS tests. For cell No.8, the EIS data were collected during the cycle. For cell No.9, the EIS data were collected during the first discharge. For cell No.10, the EIS data were collected during the standing process. In a typical Nyquist plot, the high frequency region is attributed to the LSPS bulk resistance, the low frequency region indicates the interfacial resistance of Li|interphase and the interfacial resistance between the interphase and LSPS is included in the intermediate frequency region). Accordingly, the EIS spectra can be fitted with an equivalent circuit consisting of three parallel electric elements in series as shown in the in-set figure in Figure S10c.^[3]

PHI nanoTOF II Time-of-Flight SIMS was employed to study the compositional elements of the interphase. The interphase sample was prepared via sputtering ~ 100 nm thickness of Li onto the LSPS pellet, as shown in the in-set figure in Figure 6c. The sample were investigated by using a 30 keV Bi₃⁺⁺ analysis beam at 2 nA. Ar ions (Energy/current = 3KV/100nA) were used for sputtering/cleaning. During the measurements, both positive and negative modes were used.

The Finite Element Analysis

The finite element analysis of the distribution of the mechanical, electric and ionic flux within the LSPS was computed using the COMSOL Multiphysics finite element software. The SX-CT results of cell No.1, No.2 and No.5, which were approximated and represented by the models shown in Figure S11, were used as the simulation models. During the mechanical stress/strain calculation, the structural

mechanics and heat transfer modules were used. During the electrochemical calculation, the electrostatics and the mass transport modules were used. The coordinates of x and y are defined as the horizontal and vertical axis in the models as shown in Figure S11. The parameters and their corresponding descriptions and values are shown in Table S2.

Variables	Description	Value [unit]
$C_{Li^+,LSPS}$	Concentration of active Li-ion in LSPS	$2.8 \times 10^{-2} [\text{mol/cm}^3]^{[4]}$
$C_{Li^+,interphase}$	Concentration of active Li-ion in interphase	$2.8 \times 10^{-8} [\text{mol/cm}^3]^{[5]}$
$D_{Li^+,LSPS}$	Diffusion coefficient of Li-ion in LSPS	10^{-9} cm ² /s] ^[6]
$D_{Li^+,interphase}$	Diffusion coefficient of Li-ion in interphase	$2x10^{-11} [cm^2/s]^{[7]}$
$\sigma_{Li^+,LSPS}$	Li-ion conductivity of LSPS	$4 [{\rm mS/cm}]^{[8]}$
$\sigma_{Li^+,interphase}$	Li-ion conductivity of interphase	$5 \times 10^{-3} [\text{mS/cm}]^{[7]}$
$\sigma_{e^{-,LSPS}}$	Electron conductivity of LSPS	$10 \times 10^{-9} [\text{S/cm}]^{[7]}$
$\sigma_{e^{-},interphase}$	Electron conductivity of interphase	$10^{-5} [\text{mS/cm}]^{[7]}$
$t_{Li^+,LSPS}$	Li-ion transference number in LSPS	1 ^[6]
t _{Li⁺,interphase}	Li-ion transference number in interphase	1 ^[9]
E _{LSPS}	Young's modulus of LSPS	37.2 [GPa] ^[10]
ν_{LSPS}	Poisson's ratio of LSPS	$0.3^{[10]}$
ρ_{LSPS}	Density of LSPS	$2.183 \ [g/cm^3]^{[8]}$
E interphase	Young's modulus of interphase	$40 [\text{GPa}]^{[11]}$
ν _{interphase}	Poisson's ratio of interphase	0.1[11]
$ ho_{interphase}$	Density of interphase	$1.8 [g/cm^3]^{[11]}$
E _{LiAl}	Young's modulus of LiAl alloy	7.9 [GPa] ^[12]
ν_{LiAl}	Poisson's ratio of LiAl alloy	0.38 ^[13]
ρ_{LiAl}	Density of LiAl alloy	$0.6 [g/cm^3]^{[14]}$

Table S2 the variables, descriptions and values used in the FEA simulation

During the mechanical stress/strain calculation, it was assumed that the Young's modulus of the LiAl (E_{LiAl}) , LSPS (E_{LSPS}) and the generated interphase $(E_{interphase})$ are isotropic. In addition, the thermal expansion coefficient in the heat transfer module was used to represent the volume expansion/contraction coefficient of the Reaction 3 in the main text, which is -23.7%. The vertical boundaries were fixed during the simulation. The elastic strain of the material follows the Hook's law:

$$\varepsilon_{ij} = \frac{1}{E} \left[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\sigma\delta_{ij} \right]$$

where ε is the strain, *E* is the Young's modulus, ν is the Poisson's ratio, σ is the stress. If the bulky stress of the materials is neglected, the stress neutrality of the system has to be satisfied:

$$\sigma_{ji,j} = 0$$

In addition, the strain and the displacement μ should meet the following equation during small mechanical deformation:

$$\varepsilon_{ij} = \frac{1}{2}(\mu_{i,j} + \mu_{j,i})$$

The electrochemical FEA results shown in the current work are the transient states during the simulation. The vertical boundaries in the models shown in Figure S11 were insulated boundaries. The requirements of mass conservation and charge neutrality were taken into account during the simulation. The potential and ion distribution were calculated by the following equations:

$$\vec{E} = -\nabla\phi$$

$$J_i = -D_i \nabla C_i - z_i u_i F C_i \nabla\phi$$

$$\frac{\partial C_i}{\partial t} + \nabla J_i = 0$$

where \vec{E} is the electrical field vector, ϕ is the electrical potential, J_i is the flux, D_i is the diffusivity, C_i is the concentration, z_i is the charge number, u_i is the mobility, F is the Faraday constant. In addition, the charge neutrality requires:

$$\sum_i z_i C_i = 0$$

The local charge flux density was calculated by:

$$i_{l} = -\sigma_{l} \nabla \phi_{l} + \frac{2\sigma_{l} RT}{F} (1 + \frac{\partial lnf}{\partial lnc_{l}})(1 - t_{+}) \nabla lnc_{l}$$

where σ is the conductivity, t_+ is the transference number, $\frac{\partial lnf}{\partial lnc_l}$ is activity dependent.

During the simulation, 0.2 mA/cm^2 current was applied to the model and other parameters can be found in Table S2.



Figure S1. The selected cross-section of the uncycled cell No.1. The sandwich structure of LiAl|LSPS|LiAl is obviously displayed. The red five-pointed stars indicate the localized electrical potential (see the FEA analysis below). The region marked by the black rectangle was used for FEA analysis and the result is shown in the main text in Figure 4e.



Figure S2. The electrochemical curve of cell No.2



Figure S3. The horizontal view of the Li|LiAl boundary and cracks of cell No.2. a) An overall view of the reconstructed SX-CT dataset. The orange, red and blue rectangles indicate the position where figures b-d are selected. b) The horizontal view showing the deformed Li|LiAl boundary. c-d) The horizontal views showing the cracks formed on the selected planes in the main text in Figure 2a (the red and blue rectangles).



Figure S4. The electrochemical curve and laboratory CT results of cell No.3. a) The electrochemical curve. b) A horizontal view of the LSPS. In b), the green line implies the location where c) is selected. c) A cross-sectional view of the cell. The red line implies the location where b) is selected.



Figure S5. The electrochemical curve and laboratory CT results of cell No.4. a) The electrochemical curve. b) A horizontal view of the LSPS. In b), the green line implies the location where c) is selected. c) A cross-sectional view of the cell. The red line implies the location where b) is selected.

Li	Li creep	
LiAl	boundary	*
LSPS		
LiAl		
Li	Li creep	50 μm

Figure S6. Another cross-section taken from the SX-CT result of cell No.2. The solid yellow lines indicate the Li|LiAl interface. The orange arrow lines indicate the Li creep direction.



Figure S7. The FEA simulation results of the stress distribution in a) y direction and b) xy direction of cell No.2.



Figure S8. The electrochemical curve and laboratory CT results of cell No.6. a) The electrochemical curve. b) A horizontal view of the LSPS. The green and blue lines imply the locations where c) and d) are selected. c)-d) The selected cross-sections of the cell. The red line implies the location where b) is selected.



Figure S9. The FEA results of the potential and current distribution of cell No.1. During the simulation, 0.015 mA current was applied from the upper LiAl electrode (grey part) to the bottom LiAl electrode (grey part). a) The potential distribution. The black iso-lines denote the iso-potential. Due to the protrusion of the LiAl electrode, the electrical charges will be concentrated on the protrusion part, which is highlighted by the red five-pointed start in the black rectangle. b) The corresponding current distribution.



Figure S10. The electrochemical and EIS results of cells No.8-No.10. a-c) The electrochemical cycling curve, the temporal evolution of the impedance spectra and the calculated resistance contributions of cell No.8. d-f) The electrochemical cycling curve, the temporal evolution of the impedance spectra and the calculated resistance contributions of cell No.9. g-h) The temporal evolution of the impedance spectra and the calculated inner resistances in cell No.10.



Figure S11. The FEA models that were developed from the SX-CT results for the mechanical and electrochemical simulations. a-c) The models that were developed from cell No.1, No.2 and No.5.



Figure S12. The FEA analysis results. a-b) The ionic concentration inside cell No.2 and No.5 calculated with the interphase considered. c-d) The electric potential field and ion flux density in cell No.2 without considering the interphase region. e-f) The electric potential field and ion flux density inside cell No.5 without considering the interphase region.

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2.2 Ultrathin V_5Se_8 (a) carbon nanosheet for stable and effective K-ion storage

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Carbon-Coated Ultrathin Metallic V₅Se₈ Nanosheet for High-Energy-Density and Robust Potassium Storage

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Abstract

Earth-abundant potassium is a promising alternative to lithium in energy-storage systems, but a pivotal limitation of potassium-ion batteries (KIBs) is their relatively low capacity and inferior cycle stability. Here we report the first synthesis of ultrathin metallic V₅Se₈ nanosheets embedded in porous carbon (graphene-like V₅Se₈@C) as a superior anode for KIBs, which achieves a high reversible depotassiation capacity along with unprecedented rate performance and outstanding cycling stability (a reversible depotassiation capacity of 145 mAh g^{-1} after 800 cycles at 4 A g^{-1} with 82.9% capacity retention). The impressive performances achieved are attributed to the synergistic contributions of the NiAs-type superstructure, ultrathin nanosheet architecture, sufficient accessible active sites, multidimensional electronic/ionic transport pathways and significant pseudocapacitive behaviors. Combined experimental analysis and first-principles calculations reveal fast reaction kinetics, high ionic/electronic conductivity and low diffusion barriers of K-ion in graphene-like $V_5Se_8@C$ hybrid. *Ex-situ* characterizations confirm that $V_5Se_8@C$ electrode undergo a reversible phase-evolution by the sequential intercalation and conversion reactions with synergistic K^+ -storage mechanisms. Furthermore, by coupling with pre-treated $K_{0.5}MnO_2$ cathode, the full-cell is demonstrated to exhibit large energy density of 160.2 Wh kg⁻¹ with average discharge voltage of 2.2 V and capacity retention of 86% over 200 cycles. These

desirable findings demonstrate graphene-like $V_5Se_8@C$ nanosheets hold great practical application in future grid-scale energy storage.

Keywords: V₅Se₈; ultrathin nanosheet; high energy and power; superior cycling stability; potassium-ion battery

Introduction

Electrical energy storage (EES) technologies are critically important for integrating the intermittent renewable energy resources into large-scale smart grids, which are beneficial to restrict the depletion of traditional fossil fuels and avoid severe environmental pollution [1-5]. Among the EES systems, state-of-the-art lithium-ion batteries (LIBs) are dominating the energy storage markets by virtue of their high reliability and energy density [6-8]. Unfortunately, the scarcity of lithium reserves in the Earth's crust (only 0.0017% in weight) and the increasing cost of lithium resources seriously impede the further popularization of LIBs in large-scale energy storage systems [5]. Sodium-ion batteries (NIBs) and potassiumion batteries (KIBs) as the potential alternatives have recently captured tremendous attention on account of the high-abundance and low-cost of their raw materials. So far, much efforts have been devoted to NIBs and some progress has been achieved [9-12]. On the contrary, the developments of KIBs are still at an early stage, mainly due to the larger size of K^+ (1.38 Å) than that of Na⁺ (1.02 Å). However, KIBs possess several advantages relative to NIBs, including the relatively lower redox potential of K⁺/K couples (-2.92 V vs. standard hydrogen electrode, compared with -2.71 V for Na⁺/Na) and fast ionic mobility of K⁺ in liquid electrolyte, implying that KIBs are predicted to achieve a higher operation potential and good rate performance [13-18]. Nevertheless, it is a bottleneck to look for suitable anode materials, which can host the large radius of K⁺ and at the same time accommodate the huge volume variations during repetitive cycling. Until now, a veriety of anode materials have been studied for KIBs, such as carbonaceous materials [19-25], alloy-type materials [15,26-28], transition metal compounds [16,29-35], and organic material [36]. In general, two tricky issues, inferior rate capability and problematic cycle behaviors stemming from insufficient K⁺-uptake, sluggish reaction kinetics and structure degradation of these electrodes during continuous potassiation and depotassiation processes, significantly hinder their practical applications in futuristic KIBs. In fact, there is another crucial issue limits the application of KIBs and need to be solved urgently: a low initial Coulombic efficiency (CE) is often observed in KIBs, which is mainly triggered by the nonreversible decomposition of electrolyte and subsequent formation of unstable electrode/electrolyte interface. Although various methods were applied to overcome the intrinsically deficient properties of the

electrode materials [37-43], the current rate performance and cycling stability for KIBs are incomparable with the high performance of LIBs [7]. Therefore, further exploration of feasible anode candidates for KIBs with high reversible capacity as well as superior rate capability and excellent structural stability are urgently desirable but remain a great challenge.

Two-dimensional (2D) layered transition metal dichalcogenides (TMDs), which emerges as new inorganic graphene analogues, have been recently extensively investigated for KIBs due to their intriguing physical and chemical properties, as well as their unique structural features [44-47]. The interlayer gallery of layerd TMDs with weak van der Waals interaction facilitate the intercalation of K^+ without significant structural resistance, thus enabling an enhanced cycle capacity and reversibility during the cycling process. Nevertheless, practically, they usually have very limited electronic/ionic conductivity between two neighboring layers along the c-axis affect the electrochemical reaction kinetics to some extent, thus leading to relatively low utilization efficiency of the active materials. Furthermore, due to the high surface energy of these 2D nanostructure materials, fewlayered TMDs nanosheets tend to restack and aggregate, giving direct rise to rapid capacity degeneration at a high current density. In the face of this challenges, one can expect that the carbon-coated quasi-2D metallic V₅Se₈ nanosheet (V₅Se₈@C) is able to become a very attractive anode material for KIBs with the following merits. First, the metallic V₅Se₈, typically in the form of V_{0.25}VSe₂, possesses a distorted NiAs-type superstructure with periodically-aligned interstitial V-atoms linking the two adjacent VSe₂ monolayer building blocks (see crystal structure in Figure 1a), which would provides multiple diffusion pathways for electronic/ionic charge carriers, and thus improve the electronic/ionic conductivity along the c-axis direction (perpendicular to the VSe₂ monolayers). Meanwhile, such intriguing crystal structure could also further enhances the structural stability of the whole electrode during the potassiation/depotassiation processes. Second, the 2D nanoarchitecture construction combined with porous carbon coating can effectively prevent the aggregation and restacking concerns, enhance the active material/electrolyte interface reaction, provide much more electrochemically active sites, reduce ions/electrons diffusion paths and further enhance charge transport kinetics, trigger significant pseudocapacitive behavior, promote the growth of a stable solid-electrolyte interface (SEI) film, accommodate volume variation and help to maintain overall structural integrity of electrodes during the repeated cycles. Unfortunately, to the best of our knowledge, investigations on the charge storage mechanisms of the $V_5Se_8@C$ hybrids together with its application as KIBs anode have not yet been reported.

Herein, we report the first example of designing ultrathin metallic V_5Se_8 nanosheets embedded in porous carbon layer ($V_5Se_8@C$) hybrids as an anode for KIBs by integrating all of the above-mentioned advantages into such a composite. By using this $V_5Se_8@C$ hybrids, the half-cell delivers a high reversible specific depotassiation capacity (327 mAh g⁻¹ at 0.1 A g⁻¹ after 50 cycles) and superior rate performance (201 and 162 mAh g⁻¹ at 2 and 4 A g⁻¹) as well as an improved long-term cyclability (145 mAh g⁻¹ after 800 cycles at 4 A g⁻¹ with a capacity retention of 82.9%). Moreover, the underlying K⁺-storage mechanism and possible phase transition of the $V_5Se_8@C$ hybrid electrode during the discharge/charge process were extensively explored through electrochemical tests, *ex-situ* X-ray diffraction (XRD), *ex-situ* transmission electron microscopy (TEM), and first-principles calculations. In the last, by coupling with pre-treated $K_{0.5}MnO_2$ cathode, the full-cell assembled with the currently reported graphene-like $V_5Se_8@C$ nanosheets hybrid electrode also exhibits a satisfactory electrochemical performance, demonstrating its great potential practical application in energy storage system.

Materials and methods

Materials preparation: First, the bulk V₅Se₈ was synthesized by a conventional solidstate selenylation method. In a typical synthesis procedure, vanadyl acetylacetonate (VO(acac)₂, 99%, Aladdin) and Se powder (Aladdin, 99.5%) with a stoichiometric ratio of 1:5 were mixed and ball-milled under an argon atmosphere for 2 h. Subsequently, the VO(acac)₂/Se precursor and Se powder were placed in a different upstream part of the tubular furnace and calcined at 800 °C for 2 h with a 1 °C min⁻¹ ramp rate in a mixed H₂/Ar (5% H₂) atmosphere. After cooling to room temperature, black bulk V₅Se₈ powders were obtained. In the next step, the exfoliated V₅Se₈ nanosheets were prepared by a facile ion intercalation-assisted liquid exfoliation method [48]. Typically, 600 mg bulk V₅Se₈ powders and 3.5 mg NaOH were put into a 20 mL flask, and then a 15 mL of N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich) was added as the dispersion solvent. The flask was sealed and the mixture was sonicated for 5 h in ice-bath system to prevent overheating during ultrasonication. After centrifuging at 6000 rpm for 15 min, the sediments containing the unexfoliated V₅Se₈ or some thick flakes were removed. Finally, the top 2/3 portion of the suspension were centrifugated, washed by deionized (DI) water and then freeze-dried to obtain the exfoliated V₅Se₈ nanosheets. The yield was calculated by measuring the weight of the exfoliated V₅Se₈ nanosheets in the final dispersion via the drying method and

subsequently dividing it by the initial weight of the bulk V₅Se₈ powders precursor. The yield of suspended V₅Se₈ nanosheets was calculated to be 35–39 wt.%. For the control test, the V₅Se₈ dispersion was prepared by sonication without NaOH under the same conditions. For the preparation of V₅Se₈@C nanosheets, 80.0 mg of exfoliated V₅Se₈ nanosheets were dispersed in 30.0 mL of glucose solution (0.1 M). After strong stirring for 30 min, the obtained mixture was transferred to a Teflon-lined stainless steel autoclave and maintained at 200 °C for 24 h. After the reaction, the black precipitate was rinsed with DI water and freeze-dried. Last, the as-obtained powders were annealed at 800 °C for 2 h in N₂ atmosphere to obtain V₅Se₈@C nanosheets.

Materials characterization: Morphology and micro-structure of as-prepared samples were investigated by field-emission scanning electron microscopy (FESEM, FEI Nova-450) and transmission electron microscope (TEM, JEM-2100). X-ray diffraction patterns were collected using a high power microarea X-ray diffractometer (XRD, Bruker D8 Advance) using Cu K α radiation. Raman spectra were collected with a Horiba JY Evolution spectrometer using a 633 nm laser source. The specific surface area and pore structure of the composite were analyzed by the N₂ adsorption isotherm at 77 K using the Micromeritics ASAP 2020 analyzer, and the samples were outgassed at 150 °C for 8 h before analysis. X-ray photoelectron spectroscopy (XPS) (ESCALAB 250) were performed to analyze the chemical properties of the products to explore electrochemical reaction mechanism. Atomic force microscopy (AFM) analysis was conducted on a Veeco MultiModeV atomic force microscope. Electronic conductivity of V₅Se₈@C nanosheets was carried out using the MET-007 four-point probe configure.

Electrochemical measurements: To perform the electrochemical measurements for KIBs, coin-type half cells (CR2032) were assembled in an Ar-filled glovebox using K metal foil as a counter electrode, glass microfiber filters (whatman, Grade GF/F) as the separator and 1 M potassium bis(fluorosulfonyl)imide (KFSI) dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) in a 1:1 volume ratio with 5 wt.% fluoroethylene carbonate (FEC) was used as the electrolyte. The working electrodes were fabricated by mixing 80 wt.% active material, 15 wt.% acetylene black and 5 wt.% polyvinylidene fluoride (PVDF) in NMP solvent, then pasted uniformly on a Cu foil. The resultant electrodes were dried in vacuum at 80 °C for 12 h followed by compressed at 15 Mpa and the mass loading of the active material was ~1.2 mg cm⁻² for electrochemical test and ~5 mg cm⁻² for ex-situ XRD measurements. The cells were aged for 10 h before measurements. Cyclic voltammetry (CV)

and electrochemical impedance spectroscopy (EIS) analysis were both operated using a CHI660B electrochemical workstation (Chenhua, Shanghai, China). The CV scanning rates were 0.1, 0.2, 0.4, 0.8 and 1.2 mV s⁻¹. EIS were tested with an amplitude of 5 mV and a frequency range of 100 kHz to 10 mHz. Galvanostatic charge/discharge tests and galvanostatic intermittent titration technique (GITT) measurements of the half cells were performed in a voltage range of 0.01–2.6 V (K⁺/K) at different current densities on a LAND CT2001A multichannel battery testing system. The GITT was measured with a pulse current of 0.1 A g⁻¹ for 20 min at 2 h rest intervals to reach an equilibrium potential. All the electrochemical tests were performed at room temperature. For the *ex-situ* SEM, TEM, XPS and XRD characterizations, the working electrodes, obtained from the disassembled coin cells at various states, were washed with DEC and dried in a vacuum to remove excess solvents.

Computational methods: The calculations are conducted by the Vienna Ab-Initio Simulation Package (VASP) [49,50]. The projected augmented wave method is applied to deal with the ion-electron interaction and the electron exchange-correlation energy is described by the generalized gradient approximation [51]. In the simulations, the kinetic cutoff energy is 380 eV. Based on optimized V₅Se₈ and graphene (Gr), V₅Se₈/Gr supercell is established by putting a (3×3) Gr on a (1×1) V_5Se_8 (002) surface, with an 18 Å vacuum layer applying along the z direction to remove the interaction between the neighbouring atom layers. The interface structure contains 32 Se atoms, 18 V atoms and 36 C atoms. The lattice mismatch is 5% and the lattice parameters are 12.465 and 7.214 Å, as seen in Figure S1. The interlayer distance between Gr and V₅Se₈ is 3.45 Å. To find the structure with global energy minimum, we firstly move the Gr monolayer along the z, y, and x direction relative to the bottom V_5Se_8 surface. Then, the obtained structure is further relaxed by applying the conjugate gradient optimization method. The $5 \times 5 \times 4$ and $2 \times 3 \times 1$ k-points are applied for the bulk and interface calculations, respectively. The convergence criterion for residual forces is 0.03 eV/Å. The DFT-D2 method of Grimme is selected to describe the van der Waals interaction at the interface and spin-polarized calculations are considered in the simulations [52]. The climbing image nudged elastic band method (CI-NEB) has been used to determine the diffusion energy barriers and paths of a K-ion [53]. The charge distribution is described by using grid-based Bader analysis algorithm [54].

Results and discussion

The ultrathin V₅Se₈ nanosheets were prepared in high-yield by direct exfoliation of bulk V₅Se₈ powder *via* ultrasonication in NaOH-assisted N-methyl pyrrolidone (NMP) solution,

as schematically illustrated in **Figure 1a**. In order to improve the exfoliation efficiency of bulk V_5Se_8 powder, the NMP was used as solvent originating from its surface energy is close to that of TMDs, and NaOH as an intercalator into the interlayer space in bulk V_5Se_8 . During the vigorous ultrasonication procedure, tremendous energy can be generated and it could effectively break the interlayer bonding force to form the ultrathin V_5Se_8 nanosheets.

The powder XRD measurements were used to identify the crystalline structure of the bulk V_5Se_8 , the exfoliated V_5Se_8 nanosheets, and the V_5Se_8 (QC hybrids (Figure 1b). All characteristic diffraction peaks can be perfectly indexed to the standard monoclinic V₅Se₈ (JCPDS card No. 18-1455) without any impurities. Nevertheless, they show notable differences in their diffraction peak densities. To be specific, the (002) diffraction peaks of the exfoliated V_5Se_8 and the V_5Se_8 (a)C hybrids became weaker and broader compared to that of the bulk counterpart, implying successful formation of the ultrathin V₅Se₈ nanosheets. Interestingly, no any typical signals for carbon are observed in the $V_5Se_8(a)C$ hybrid, which may be due to the trace amount of the carbon. However, the presence of carbon in the hybrid can be convincingly verified by the Raman analysis (Figure S2). Raman spectra of the exfoliated V_5Se_8 and the V_5Se_8 (a)C hybrids are almost identical except for the weak peaks located at 1350 and 1581 cm⁻¹ (Figure S2), which correspond to the defect induced D-band and in-plane vibrational G-band of carbon, respectively. In addition, the I_D/I_G intensity ratio for $V_5Se_8(a)C$ hybrid is calculated to be 0.95, corroborating a moderate degree of graphitization of the coating carbon. This is in favor of the improvement of the electrical conductivity. The characteristic bands at 280.4 and 406.1 cm^{-1} are similar to those observed in VSe_2 and thus they can be assigned to the in-plane E_{2g} and A_{1g} vibration modes of VSe₂, respectively, which confirms the layered arrangement of VSe₂ frame in the V_5Se_8 crystals [55]. The crystal structure of V_5Se_8 is illustrated in **Figure 1b**, which can be regarded as a superstructure consisting of well-ordered interstitial VSe₆ octahedra within the van der Waals gaps in the VSe₂ structure according to previous reports [56,57]. Since the periodically-aligned VSe₆ octahedra bridging the two neighbor VSe₂ monolayer building blocks can provide multi-dimensional transportation paths for electronic and ionic charge carriers, increased electronic and ionic conductivities in V₅Se₈ crystals can be obtained.

The detailed morphology and microstructure of the as-prepared products were then examined *via* SEM and TEM measurements. As shown in **Figure 1c**, SEM images of the exfoliated V_5Se_8 display the morphology of crumpled-film-like nanosheets with a lateral dimension ranging from 600 nm up to micrometer. These wrinkles were formed in the freeze-drying process and they can effectively prevent the agglomeration and restacking

of the nanosheets, leading to a fast ion flux transport on the electrode-electrolyte interface. At higher magnification (the *inset* of Figure 1c), it can be observed that the surfaces of these nanosheets are smooth without any individual particles on it. Further, these crimped nanosheets are nearly transparent under the SEM electron-beam, indicative of their ultrathin nature. In contrast, the bulk V₅Se₈ is consisted of tabular particles with sizes of up to several micrometers, each consisting of tightly stacked layers (Figure S3). Figure S4 shows SEM image of the exfoliation of bulk V₅Se₈ powder in NMP without the addition of NaOH and it is surprisingly to find that the sheets are interweaved to form a bundle of agglomerated microflowers and that a large amount of unexfoliated particles are still present. Hence, one can conclude that the improved exfoliation efficiency of the bulk V₅Se₈ results from the assisting role of NaOH in NMP. In addition, the TEM image (Figure 1d) further confirms that the ultrathin character of the exfoliated V₅Se₈ nanosheets by the light contrast. From the high-resolution TEM image (HRTEM, Figure 1e) of the edge of the folded nanosheet in Figure 1d, the thickness of the exfoliated V₅Se₈ nanosheets was ~ 2.98 nm with approximately 5 atomic layers, while V₅Se₈ crystallinity was verified by the lattice spacings of 0.59 and 0.27 nm can be assigned to the (002) and (222) crystalline planes of the monoclinic V₅Se₈, respectively. Atomic force microscopy (AFM) characterizations provide further information on the thickness of the exfoliated V₅Se₈ nanosheets (Figure 1f&S5a). The corresponding AFM height profiles (Figure 1f) reveal that the average topographic height is ~ 3.1 nm, which is close to the evaluated value in Figure 1e and corroborated the ultrathin character.

To further improve the electrochemical performance of the exfoliated V₅Se₈ nanosheets, a strategy of carbon-coating by a facile solvothermal reaction followed by a post-annealing process is adopted (**Figure 1a**). After carbon coating, the overall morphology of the exfoliated V₅Se₈ nanosheets was well retained but their surface became coarser (**Figure 1g&S6**). Nevertheless, a thin layer of carbon evenly coated on the surface of V₅Se₈ nanosheets was also confirmed by the lesser transparency TEM image shown in **Figure 1h** *vs*. **Figure 1d**. The energy-dispersive X-ray spectrometry mappings of the v₅Se₈@C further substantiate the coexistence of V, Se, and C elements, which are uniformly distributed in the selected area (**Figure S7**). The interplanar spacing of 0.18 nm is corresponding well with the (620) crystallographic plane of the monoclinic V₅Se₈ phase (**Figure 1i**). The corresponding selected area electron diffraction (SAED) pattern of V₅Se₈@C nanosheet (the *inset* of **Figure 1i**) gives the monoclinic structure, where the diffraction spot can be indexed to the (002) plane of the V₅Se₈ structure.

The result is in good agreement with the XRD results in Figure 1b. Moreover, a carbon layer with an average thickness of ~ 2 nm on the surface of the exfoliated V₅Se₈ nanosheet is clearly visible (Figure 1i&S5b) verifying the successful formation of the as-predicted V₅Se₈@C hybrid composite. The mass content of the carbon in the hybrid was estimated as ~9.8 wt.% with the thermogravimetric analysis (Figure S8). The HRTEM image unambiguously reveals that the coating carbon is consisted of fingerprint-like twisted wrinkles which possess numerous micro-pores at subnanometer scale. These micropores are not only beneficial for electrolyte infiltration but also could prevent the V₅Se₈ ultrathin nanosheets from self-aggregation. There isn't obvious interfacial stress/strain on the V_5Se_8 (a)C hybrid due to the carbon grown on V₅Se₈ is amorphous, which is different from the reported vertically stacked 2D heterostructure [58]. Thus, the interfacial stress/strain is not discussed in this manuscript. Such thin conductive carbon film would be favorable to accelerate the electron transport and at the same time help to sustain structural integrity. The greatly enhanced conductivity together with the short K-ion diffusion length within nanosheets is expected to enable the V₅Se₈@C nanosheets electrode with fast reaction kinetics, thus yielding higher rate capability.

X-ray photoelectron spectroscopy (XPS) was performed to further investigate the surface chemical composition of the resulted V₅Se₈@C nanosheets. The wide full survey scan spectrum (Figure S9a) shows the co-existence of V, Se, C and O elements in the hybrid sample. As demonstrated in the high-resolution XPS spectrum of C 1s (Figure S9b), besides the C=C covalent bond, the trace O element is attributed to the C=O functional groups attached on the carbon surface. The high resolution Se 3d spectra in Figure S9c show two well-defined peaks at 54.8 and 55.8 eV, separately assigned to Se $3d_{5/2}$ and Se $3d_{3/2}$, which suggests that Se is in the form of Se²⁻ in the final V₅Se₈@C nanosheets [44,59]. In addition, another two weak peaks at 58.8 and 59.7 eV can be observed and they can be assigned to the Se-C bond. The peaks at 524.2 eV (V $2p_{1/2}$) and 516.3 eV (V $2p_{3/2}$) are assigned to the typical characteristics of V^{4+} , while those centered at 523.1 eV in V $2p_{1/2}$ and 515.7 eV in V $2p_{3/2}$ are indexed to V³⁺ state (Figure 1j). These results further verified the formation of the as-predicted $V_5Se_8@C$ nanosheets. The specific surface area and its diverse porosity of the V₅Se₈@C nanosheets were investigated by N₂ adsorption-desorption analysis. As depicted in Figure S10, the obvious hysteresis characteristic in the isotherm curve displays the existence of a multi-scale pore structure in the $V_5Se_8@C$ nanosheets, and its specific surface area is calculated to be 176.3 m² g⁻¹. To be more specific, the V₅Se₈@C nanosheets have a bimodal pore size distribution with big mesopore (>20 nm) generated from the abundant buffering space between the nanosheets and small pores from the coating carbon shell. The graphene-like multimodal pore nanoarchitecture can effectively increase the electroactive sites, facilitate the electron/K-ion flux transport, give rise to significant surface pseudocapacitive effect and effectively alleviate the volumetric expansion during repeated cycling. Moreover, the existence of Se–C bond can stabilize the discharging product and prevent Se from dissolving, thus greatly enhancing the cyclic stability of the electrode. Therefore, satisfactory electrochemical behaviors and superior K⁺storage efficiency of the V₅Se₈@C nanosheets can be anticipated.



Figure 1. (a) Schematic illustration of the preparation process of the graphene-like V_5Se_8 @C nanosheets. (b) XRD patterns of bulk V_5Se_8 , exfoliated V_5Se_8 nanosheets, and V_5Se_8 @C hybrids. Inset is the sideview of atoms arrangements in V_5Se_8 . The purple (big) and yellow (small) balls represent V and Se atoms, respectively. SEM (c) and TEM (d, e) images of the exfoliated V_5Se_8 nanosheets. The *inset* of (c) is highmagnification SEM, and the *inset* of (e) is the HRTEM images of the exfoliated V_5Se_8 nanosheets. (f)

Representative AFM image of the exfoliated V_5Se_8 nanosheets and the corresponding linear scan analysis. (g) SEM image, (h) TEM image, (i) HRTEM image of the graphene-like $V_5Se_8@C$ nanosheets. The HRTEM image viewed from the [001] direction. The *inset* of (i) is the corresponding SAED pattern. (j) XPS high-resolution V 2p spectra of the $V_5Se_8@C$ nanosheets.

The potassium storage behaviors of the as-prepared samples were evaluated by cyclic voltammetry (CV) and galvanostatic discharge/charge. CV tests of V₅Se₈@C nanosheets electrode for the first four cycles from 0.01 to 2.6 V (vs. K⁺/K) at a scan rate of 0.1 mV s⁻¹ are shown in Figure 2a, the initial reduction peak at 0.95 V corresponds to the intercalation of K^+ into V_5Se_8 lattice to form $K_rV_5Se_8$, and the broad peak centered at 0.64 V is related to the formation of irreversible SEI layer on the electrode surface [55,60]. The other broad cathodic peak observed at the range of 0.20–0.50 V can be attributed to the conversion of $K_xV_5Se_8$ into metallic V and K_2Se . A pronounced oxidation wave range from at around 1.5 and 2.1 V has also been detected in the following scan can be ascribed to the conversion reaction between K₂Se and V, further depotassiation and generation of V₅Se₈. Note that except the first scan, the V₅Se₈@C nanosheets always show decreased polarization in the subsequent CV curves, indicative of the increased reaction kinetics and the effective utilization of active material due to the increasing wetting of the electrode by the electrolyte after the first cycle. From the second cycle onward, the CV curves show good reproducibility, demonstrating a good electrochemical reversibility of K^+ -storage reaction in the V₅Se₈@C nanosheets electrode.

Figure 2b shows the representative discharge/charge profiles of the $V_5Se_8@C$ nanosheets electrode in the 0.01–2.6 V window at 0.1 A g⁻¹. The voltage plateaus of discharge/charge curves are well consistent with the CV results mentioned above, further corroborating the multi-step electrochemical potassiation/depotassiation processes of the $V_5Se_8@C$ nanosheets electrode. The high potassiation plateau can play a pivotal role in relieving the risk of dendrite formation on electrode surface over cycling [16,61]. The $V_5Se_8@C$ electrode delivered discharge and charge capacities of 602 and 353 mAh g⁻¹ in the first cycle, giving a low CE of 58.6%. The initial capacity fading and low CE value can be mainly attributed to the formation of SEI layer and the irreversible decomposition of electrolyte during potassiation/depotassiation reaction. Nevertheless, the subsequent CE values quickly reach over 78.5% from the second cycle and exceed 94.2% from the 10th cycle, resulted from the formation of a stable SEI film on the electrode

surface. In the following cycles, all the charge-discharge curves have no significant capacity loss, reflecting a good reversibility character of the $V_5Se_8@C$ nanosheets in K⁺-storage. Of especial note, in order to boost the initial CE of KIBs, a facile yet effective prepotassiation strategy has been conducted and a high initial CE of 80.7% for $V_5Se_8@C$ nanosheets electrode can be achieved (**Figure S11**).

The rate capabilities of the bulk V_5Se_8 , the exfoliated V_5Se_8 nanosheets, and the V₅Se₈@C hybrids electrodes were systematically evaluated at different rates from 0.1 to 4 A g^{-1} (Figure 2c). For V₅Se₈@C nanosheets, upon successive cycling under varying current densities, the corresponding reversible charge capacities dropped only slightly on doubling the rates. When cycled at the current densities of 0.1, 0.2, 0.5, 1 and 2 A g^{-1} , V₅Se₈@C nanosheets anode can deliver reversible depotassiation capacities of 328, 316, 293, 257, and 201 mAh g^{-1} after each 20 cycles, respectively, which are higher than those of bulk V_5Se_8 and exfoliated V₅Se₈ nanosheets under the same condition, revealing the excellent electrochemical reaction kinetics of V₅Se₈@C hybrid. Even at a large current density of 4 A g^{-1} , the reversible depotassiation capacity still remained at 162 mAh g^{-1} , highlighting the high-power application of the V₅Se₈@C nanosheets in KIBs. When the current density switched back to 0.1 A g^{-1} after 120 cycles, the depotassiation capacity can restore to above 319 mAh g⁻¹ with a CE of >98%, suggesting the exceptional reversibility of $V_5Se_8@C$ anode towards KIBs. For comparison, the rate capabilities of the V₅Se₈@C nanosheets prepared with different ultrasonication times were also examined (Figure S12a). Interestingly, it seems that there is no significant difference in the rate capability of the products obtained at 7 and 10 h sonication. The results suggest that ultrasonication time is not the major determining factor for the whole K⁺ storage reaction.

Figure 2d displays the cycling stability and the corresponding CE of the $V_5Se_8@C$ nanosheets electrode at the current density of 0.2 A g⁻¹. The depotassiation capacities increase gradually from 309 to 387 mAh g⁻¹ at the end of 300 cycles, which can be attributed to the enhancing wetting of the electrode by the electrolyte at a low current density [55,62]. Meanwhile, the corresponding CE quickly approaches 96% within 20 cycles and stays the high value in the ensuing cycles. Further tests of cycling behaviors for the $V_5Se_8@C$ nanosheets electrode over 300 cycles at various current densities of 0.5 and 1 A g⁻¹ also reveal its excellent structural rigidness and reversibility in K⁺-storage (**Figure S12b**). Besides, the excellent structural integrity of the $V_5Se_8@C$ electrode is also further verified by the *ex-situ* SEM and TEM images characterized after 300 cycles at a current density of 1 A g⁻¹ (**Figure S13**). It is clear that the sheet-like morphology of the $V_5Se_8@C$ is well

retained, with a thick K⁺-permeable SEI layer is stable constructed on the surface of the electrode after the repetitive cycling. By contrast, the bulk V₅Se₈ electrode displays inferior cycling performance with substantial capacity attenuation (Figure S14), derived from the big volumetric expansion during the repeated charge/discharge processes. Furthermore, the long-term cycling performances of the exfoliated V₅Se₈ nanosheets and the V₅Se₈@C hybrid electrodes are further evaluated, as depicted in Figure 2e&S15. When galvanostatistically cycled at a high current density of 4 A g^{-1} , a stable reversible depotassiation capacity of 145 mAh g⁻¹ was achieved over 800 consecutive cycles with impressive capacity retention of 82.9%. The corresponding CE quickly reaches to near unity after the initial several cycles and remains the high value afterwards, indicating a high reversible potassiationdepotassiation process. In comparison, the exfoliated V₅Se₈ nanosheets electrode delivers a depotassiation capacity of only 81 mAh g⁻¹ at 2 A g⁻¹ after 800 cycles with a capacity loss of 47.5% (Figure S15), highlighting the contribution of coating carbon shell acts as a skeleton to sustain the cycling stability. To the best of our knowledge, the electrochemical performances of the graphene-like $V_5Se_8(a)C$ nanosheets are better than that of some previously reported state-of-the-art results for KIBs (Table S1), showing attractive characters for future large-scale energy storage systems.

To explore the origin of high-rate capabilities in the V₅Se₈@C nanosheets, we performed CV tests under different sweeping rates of 0.2-1.2 mV s⁻¹ to evaluate its electrochemical reaction kinetics (Figure 3a). All CV curves show analogous shapes with distinct redox peak and limited overpotential can be observed along with the increasing scan rates, indicating a high reversibility and fast kinetics for K⁺-storage. The relationship between peak current (i) and scanning rate (v) follows the formula: $i = av^{b}$ [44,63,64], in which both a and b are constants, and b-value is determined by the slope of the log(i) vs. log(v) plots (Figure 3b). The b-value of 0.5 denotes extreme diffusion-controlled process, while 1.0 represents the ideal pseudo-capacitive behavior. The b-values of the three redox peaks are 0.75, 0.94 and 0.73, respectively, manifesting that K^+ -storage mechanism of V₅Se₈@C nanosheets involves both diffusion-controlled process and pseudo-capacitive effect. The standard error for cathodic fitting (peak 1) is 0.01434 (intercept) and 0.03523 (slope), while the Adj. R-Square value is 0.99334. For reduction peak 2 fitting, the standard error is 0.00814 (intercept) and 0.02001 (slope), while the value of Adj. R-Square is 0.99863. For anodic fitting (peak 3), the standard error is 0.01128 (intercept) and 0.02773 (slope) while the Adj. R-Square value is 0.99563. In addition, the contribution of capacitive can be quantitatively deduced from the equation i (V) = $k_1v + k_2v^{0.5}$, where k_1v represents the capacitive fraction while $k_2 v^{0.5}$ belongs to the diffusion-controlled process [65]. The pseudocapacitive contribution ratio of $V_5Se_8@C$ nanosheets anode gradually intensifies with the increase of the scanning rate, and a very high value of 90.1% can be achieved at 1.2 mV s⁻¹ as illustrated by the shaded area (Figure S16a). In a control experiment, using the same analysis discussed for $V_5Se_8@C$ nanosheets, the pseudocapacitive behaviors of bulk V_5Se_8 were studied by the CV curves obtained at different sweep rates ranging from 0.2–1.2 mV s⁻¹

¹ (Figure S16b&S16c). Figure 3c summarizes the pseudo-capacitive contribution ratios of $V_5Se_8@C$ nanosheets and bulk V_5Se_8 electrodes at the various sweep rates. Apparently, the pseudo-capacitive contribution increases with increasing sweeping rate while the contribution of diffusion-controlled process decreases in both electrodes. Moreover, the pseudo-capacitive contributions in $V_5Se_8@C$ nanosheets electrode seem to be always higher than the corresponding values of bulk V_5Se_8 electrode regardless of the sweeping rate. The superior pseudocapacitive behavior of $V_5Se_8@C$ nanosheets electrode can be ascribed to the graphene-like nanoarchitecture increases the interface reaction with electrolyte, provides more electrochemically active sites and further enhance reaction kinetics, which are helpful to boost its electrochemical performance for K⁺-storage.



Figure 2. (a) CV curves for the graphene-like $V_5Se_8@C$ nanosheets electrode in the first four cycles at a scan rate of 0.1 mV s⁻¹. (b) Galvanostatic discharging/charging profiles for the $V_5Se_8@C$ nanosheets at

different cycles at 0.1 A g^{-1} . (c) Rate capabilities of the bulk V_5Se_8 , exfoliated V_5Se_8 nanosheets, and $V_5Se_8@C$ hybrid electrodes at various current densities from 0.1 to 4 A g^{-1} . (d) Cycling stability and corresponding CE of the $V_5Se_8@C$ nanosheets electrode at 0.2 A g^{-1} . (e) The cycling performance and CE of the $V_5Se_8@C$ nanosheets electrode for 800 cycles at 4 A g^{-1} . (Note that all the specific capacity values of half cell were calculated based on the total mass of the anode material).

Electrochemical impedance spectroscopy (EIS) test of the V₅Se₈@C nanosheets electrode was performed to investigate the reaction kinetics variation at different cycles, and the corresponding Nyquist plots are displayed in Figure 3d. All plots consist of a highfrequency depressed semicircle and a low-frequency sloping line, in which the former represents the resistance of charge transfer (R_{ct}) [44], and the latter is correlated to K-ion diffusion and phase transformation within V₅Se₈@C nanosheets. The corresponding equivalent circuit model is displayed in the inset of Figure 3d, and the fitted results are listed in **Table S2**. Apparently, the R_{ct} -value of $V_5Se_8@C$ nanosheets electrode gradually decrease and remains stable in the following cycles, which are explained by the improved electrochemical kinetics and effective utilization of the active material derived from microstructure change and stable SEI film formation. The K⁺ chemical diffusion coefficients of V_5Se_8 (a)C electrode are calculated to be 0.87×10^{-9} cm² s⁻¹ before cycle, 1.39×10^{-9} cm² s⁻¹ ¹ after the 50th cycle, and 3.40×10^{-9} cm² s⁻¹ after the 100th cycle (Figure S17a&Table S2), implying the stable and fast diffusion kinetics of K⁺ in V₅Se₈@C nanosheets during repetitive cycling. To further investigate the largely different electrochemical performance between the V₅Se₈@C nanosheets and bulk V₅Se₈ electrodes in KIBs, the EIS tests after the first cycle were also performed. As shown in Figure S17b, all the spectra contained a compressed semicircle in the high-frequency range and an inclined line in the lower frequency regime. The V₅Se₈@C nanosheets electrode shows a smaller semicircle after the first cycle, implying a better conductive property than the bulk V₅Se₈ counterpart. What's more, the closer inclined line toward 90° indicates an improved K^+ diffusion can be obtained in the V₅Se₈@C nanosheets electrode, thus enabling excellent high-rate pseudo-capacitive performance in the whole K^+ storage process. The electronic conductivity of V₅Se₈@C is determined to be 639 S cm⁻¹ at room temperature (25 °C), further corroborating its relatively high conductivity (Figure S18). These desirable results are mainly attributed to the 3D monoclinic structure of the V₅Se₈ that can provide multi-dimensional pathways for convenient electronic/ionic transport and the graphene-like hybrid nanoarchitecture that can shorten the electron/ K^+ shuttling paths, thus enabling superior rate ability.



Figure 3. (a) CV profiles at different scan rates and (b) the plots of log(i) vs. log(v) at each redox-peak pair (peak current: *i*, scan rate: v) of the V₅Se₈@C nanosheets electrode. (c) The percentages of K-ion diffusion controlled and pseudocapacitive contributions at different scanning rates of V₅Se₈@C nanosheets and bulk V₅Se₈ electrodes. (d) Nyquist plots of V₅Se₈@C nanosheets electrodes after different cycles (inset: selected equivalent circuit). (e) Reaction resistance during potassiation/depotassiation processes of V₅Se₈@C nanosheets electrode in KIBs. (f) *Ex-situ* XRD patterns of V₅Se₈@C nanosheets electrodes at the different state (D: state of discharge, C: state of charge). (g) Schematic illustration of reversible potassiation/depotassiation process in the graphene-like V₅Se₈@C nanosheets electrode. The purple, yellow, and blue spheres represent V, Se and K atoms, respectively.

To further understand the thermodynamics and kinetics of the K⁺-storage, galvanostatic intermittent titration (GITT) test was conducted after the initial cycle by applying a galvanostatic pulse of 0.1 A g⁻¹ for 20 min between 2h-relaxation intervals to experimentally evaluate the reaction resistance of K⁺ in V₅Se₈@C nanosheets electrode. The open-circuit-potential at the end of the relaxation interval is considered to be quasithermodynamically equilibrium voltage [16,55]. Multiple quasi-equilibrium potential platforms are detected in **Figure S19**, further verifying the multistep electrochemical discharge and charge processes of V₅Se₈@C nanosheets. An obvious quasi-thermodynamic voltage hysteresis between K⁺ intercalation and deintercalation is observed owing to the large strain/stress during the potassiation-depotassiation processes. The corresponding reaction resistance at different K^+ intercalation/deintercalation stages can be determined by dividing the overpotentials with the applied pulsed current density in GITT measurement (**Figure 3e**). During the discharge process, the reaction resistance progressively decreasing with more K^+ insertion, which can be attributed to the enhanced conductivity of the electrode caused by the metallic phase formation upon potassiation. There is an opposite tendency in the depotassiation process, which can be assigned to the decreasing ionic/electronic conductivity and worsening contact derived from the volume contraction and extraction of K^+ . The reaction resistances of $V_5Se_8@C$ nanosheets are consistently smaller than those of previously reported anodes for KIBs [16,27,66], which again confirms a better electrochemical kinetic behaviour of $V_5Se_8@C$ nanosheets, thus delivering outstanding rate capability.

To further reveal the detailed working mechanisms of the V_5Se_8 (a)C nanosheets electrode, ex-situ XRD was carried out at selected potassiation/depotassiation states in the second cycle of the half-cell to trace the fundamental phase transformation process (Figure 3f). When the voltage was decreased to 0.75 V, the overall intensity of the XRD peaks decreased and the (002) and (004) reflections for V_5Se_8 slightly shift to the left. This left-shift phenomenon is associated with the formation of non-stoichiometric K⁺-intercalated compounds, corroborating the expansion and distortion of the V₅Se₈ crystal lattice during $K^{\scriptscriptstyle +}$ insertion. Further discharged deeply to 0.01 V, the reflection peaks of the V_5Se_8 were totally disappeared, and a series of new characteristic peaks were emerged: the ones observed at 20.0°, 32.9°, and 38.8° were, respectively, assigned to the (111), (220), and (311) crystallographic planes of K_2Se , while the diffraction peaks located at 41.2° and 48.0° were related to the metallic V phase (JCPDS card No. 88-2322), demonstrating the occurrence of conversion reaction. Finally, when charged to 2.6 V, all the diffraction peaks of V₅Se₈ can be recovered to their original position, revealing a good reversibility of the potassiation-depotassiation process for the V5Se8@C nanosheets electrode. These results were further confirmed by ex-situ HRTEM tests. After discharged to 0.01 V, a visible interlayer spacing of 0.27 nm belonging to (220) plane of K₂Se, while the interplanar distances of 0.19 and 0.22 nm were indexed to the (200) and (111) planes of the metallic V, respectively (Figure S20a-b). When the electrode was fully charged to 2.6 V, the regular interplanar spacings of 0.28 nm and 0.19 nm are observed, which can be ascribed to the (222) and (620) planes of the monoclinic V_5Se_8 , respectively (Figure S20c-d). Moreover, the electrochemical reaction is further verified by tracking the variations of V 2p signals at fully potassiation/depotassiation states (**Figure S21**). Based on the above-mentioned characterizations and discussions, the underlying reaction mechanism of K⁺-storage within $V_5Se_8@C$ nanosheets anode proceeds initially with the K⁺ insertion into the V_5Se_8 layer to form $K_xV_5Se_8$, followed by the reversible conversion reaction to metallic V and K_2Se , which is schematically presented in **Figure 3g**.

To better understand the essence of the superior K-ion storage capability, we performed density theory functional (DFT) calculations to investigate the reaction mechanism, ionic and electronic transport properties of bulk V₅Se₈ and V₅Se₈/graphene (V₅Se₈/Gr). Charge density difference shows that charge transfer occurs at interface between Gr and V₅Se₈. As shown in Figure 4a, C and V atoms lose electrons while there is charge accumulation at top of Se atoms in the interface region. Bader charges results show that there is an increased charge transfer from V to Se atoms at V₅Se₈/Gr interface (1.26 electrons/atom) than that in bulk V_5Se_8 (1.21 electrons/atom), indicating that the formation of V_5Se_8 /Gr hybrid slightly enhances the Se-V ionic bonding. Besides, weak Se-C ionic bonding is also revealed at interface with charge transfer of 0.009 e/atom. Compared with the electronic structure of the bulk V₅Se₈ (Figure S22), the obvious characteristics of the density of states of V₅Se₈/Gr hybrid are the strong peak strength and sharp peaks, which reveals the strong chemical bonding in the interface system (Figure 4b). In addition, the larger value at Fermi level (E_F) unveils a strong metallic bonding, which suggests the improved electronic conductivity of the composite. This is contributed by V 3d states at $E_{\rm F}$. Besides, strong covalent hybridization among V 3d, Se 4p and C 2p states in the energy range from -6 to 4 eV can be determined, reflecting the strong covalent bonding in the V₅Se₈/Gr composites. Therefore, there is a mix of metallic, ionic and covalent bonding in the V₅Se₈/Gr hybrid. The strong chemical bonding can result in improved structural integrity. Based on the above theoretical analysis, the formation of heterostructure can increase the electronic conductivity and structural stability, which will contribute to the rate performance and cycling stability of electrode materials during the charging and discharging processes. Furthermore, the adsorption energy (E_{ads}) of an isolated K⁺ on various sites of V₅Se₈/Gr hybrid was calculated to reveal the K⁺ intercalation behaviour (Figure 4c-d&S23). As seen in Table S3, the results show that it is energetically favourable to adsorb a K^+ on all these positions. Specially, it is more stable for K^+ to adsorb on V_5Se_8 surface (-3.30 eV) than at interface (-3.07 eV), in the interior of V_5Se_8 (-1.43 eV) and on Gr surface (-1.64 eV) in the V_5Se_8/Gr hybrid.


Figure 4. (a) The charge density difference of V_5Se_8/Gr interface, where blue represents charge depletion and yellow indicates charge accumulation. (b) The total density of states and projected density of states of V_5Se_8/Gr interface. Stable structures of K adsorption (c) at the interface sites of V_5Se_8/Gr and (d) on the surface of V_5Se_8 in V_5Se_8/Gr interface. The K diffusion path (e) and diffusion energy barrier (g) in bulk V_5Se_8 . K diffusion on V_5Se_8 surface in V_5Se_8/Gr interface system: (f) diffusion path and (h) energy barrier.

In order to evaluate the thermodynamic properties of K^+ adsorption on various sites, the formation energy is also considered. As depicted in **Table S4**, the V₅Se₈/Gr composite could enhance the thermodynamic stability of K^+ adsorption on V₅Se₈ surface. Additionally, the effect of heterogeneous structures on K^+ diffusion kinetics in the bulk V₅Se₈ and V₅Se₈/Gr composites have also been investigated (**Figure 4e-h&S24**). The K^+ diffusion path in the bulk V₅Se₈ and interface system are given in **Figure 4e-f&S25**, respectively. As seen in **Figure 4g-h**, K^+ diffusion in the V₅Se₈ (0.64 eV). Due to the different coordinate environment, for bulk V₅Se₈, a K^+ adsorb on the site near the top of V has a lower energy than that adsorbed on the region near the top of Se atom. In comparison, the adsorption of K^+ in V₅Se₈/Gr interface system shows an opposite trend where the site near the top of V is the

saddle point. The low energy barrier will contribute to a fast K^+ diffusion in the interface system. Apart from that, K^+ diffusion coefficient in the interface system $(1.08 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1})$ is much larger than that in the bulk $(8.40 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1})$. Thus, the heterogeneous structure can noticeably improve the rate performance of $V_5Se_8@C$ hybrid by effectively decreasing K^+ diffusion energy barrier and increasing electronic conductivity, which is in good agreement with the enhanced rate performance of $V_5Se_8@C$ composites in experiment.

Encouraged by the excellent performance of V₅Se₈@C nanosheets anode in half-cells, Kion full cells were further matched with pre-treated $K_{0.5}MnO_2$ (Figure S26) as the cathode with the same separator and electrolyte as the half cell. The working mechanism of the full cell is schematically illustrated in Figure 5a, where K ions are extracted from the pre-treated K_{0.5}MnO₂ and inserted into the V₅Se₈@C anode during the potassiation process, and a reverse process occurs during depotassiation. As depicted in Figure 5b, the full-cell provides a considerable discharge capacity of 93 mAh g^{-1} for the second cycle at 0.05 A g^{-1} (based on the cathode mass) in a voltage window of 1.50-3.60 V with an average discharge voltage of 2.2 V, corresponding to an energy density of 160.2 Wh kg⁻¹ (based on the total mass of both cathode and anode materials, and the mass ratio of $K_{0.5}MnO_2$: V_5Se_8 (a)C is 3.6:1 in the full-cell), which apparently superior to most of the recently reported K-ion full battery (Table S5). Furthermore, there is no significant capacity attenuation in the discharge capacity between the 10th and 30th cycles at the low current density, suggesting a good reaction reversibility and an outstanding electrochemical stability. Figure 5c presents the rate capability of the full cell, which delivers reversible discharge capacities of 99, 87, 80, 72 and 60 mAh g^{-1} at a current rate from 0.02 to 0.4 A g^{-1} . When the current density recovered to 0.05 A g⁻¹, the discharge capacity returned back to 75 mAh g⁻¹, implying a reasonable rate performance of V₅Se₈@C nanosheets in the full cell. Moreover, the roundtrip efficiency of present full-cell is 81.3% (Figure 5d), which is almost equivalent with the reported value for NIBs [67]. It is worth mentioning that the as-prepared full battery after a long-term cycling could easily make the commercial LED lights shine (Figure 5e). Besides, the as-fabricated K_{0.5}MnO₂//V₅Se₈@C full cell also exhibits a prominent durability at various current densities from 0.2 to 0.3 A g^{-1} , as shown in Figure S27. Figure 5f displays the cycling stability test of the full-cell at a current density of 0.4 A g^{-1} . After 200 cycles, the full cell retains 86% of its initial capacity with an average CE ~95.3%, manifesting the considerable cycling stability of our full battery. Such exceptional K⁺-storage performance suggests promising practical applications of the graphene-like V₅Se₈@C nanosheets in full KIBs for energy storage.



Figure 5. (a) Schematic illustration of the $K_{0.5}MnO_2//V_5Se_8@C$ nanosheets K-ion full battery. (b) Charge/discharge curves the as-fabricated full cell at 0.05 A g⁻¹ in the voltage range of 1.50–3.60 V (*vs.* K⁺/K). (c) Variation in rate performances and the corresponding CE of the full cell under different current densities. (d) Energy density and round-trip efficiency of the $K_{0.5}MnO_2//V_5Se_8@C$ full-cell at different current densities. (e) Digital photo of two LED lights powered by one full cell after a long-term cycling. (f) Cyclic performance and the corresponding CE at 0.4 A g⁻¹.

Conclusion

In summary, graphene-like $V_5Se_8@C$ nanosheets hybrid were obtained in high-yield by a facile exfoliation strategy and subsequent solvothermal treatment, and investigated for the first time as an advanced anode for KIBs. On the one hand, the metallic V_5Se_8 exhibits a NiAs-type superstructure with ordered interstitial V atoms linked the two neighbor VSe_2 monolayer building blocks, which would not only provide multi-dimensional pathways for convenient electronic and ionic transportation, but also improve their structure durability. On the other hand, graphene-like nanostructure combined with porous carbon coating layer can effectively prevent the aggregation of the active material, increase the

electrode/electrolyte interface area, provide abundant electrochemically active sites for K⁺storage, facilitate fast transportation of K-ion/electron, give rise to significant pseudocapacitive-like electrochemical behavior, accommodate volume expansion and help to sustain overall structural integrity of electrode during repetitive cycling. Owing to the multiple collaborative effects of the aforementioned advantages, the V₅Se₈@C nanosheets electrode shows an impressive reversible depotassiation capacity (327 mAh g⁻¹ at 0.1 A g⁻¹ after 50 cycles), splendid rate capability (201 and 162 mAh g⁻¹ at 2 and 4 A g⁻¹), and prominent long-term cycling stability (82.9% capacity retention over 800 cycles at 4 A g⁻¹). Systematical experimental characterizations and first-principles calculations bring insights into the intrinsic correlations between the electrochemical reaction kinetics and the K⁺storage mechanisms of the V₅Se₈@C electrode. Particularly noteworthy, pairing this V₅Se₈@C nanosheets anode with a pre-treated K_{0.5}MnO₂ cathode yields a potassium-ion full cell with a large energy density of 160.2 Wh kg⁻¹, impressive rate performance and negligible capacity decay within 200 cycles, revealing the great application potential of V₅Se₈@C nanosheets in future grid-scale energy storage.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 91963113, 51671003, 51802007 and U1904216), the Helmholtz Association, the China Scholarship Council (CSC) and was partially funded by the German Research Foundation (DFG, Project No. MA 5039/4-1). The simulation was supported by resources provided by the Pawsey Supercomputing Centre with funding from the Australian Government and the Government of Western Australia.

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Supporting information

Carbon-Coated Ultrathin Metallic V₅Se₈ Nanosheet for High-Energy-Density and Robust Potassium Storage

Experimental section

Full cells were assembled by using pre-treated $K_{0.5}MnO_2$ (synthesized as previously reported) [S1] as the cathode and pre-treated $V_5Se_8@C$ as the anode with the same separator and electrolyte as the half cells. The electrode slurry was prepared by mixing 80 wt.% of active material ($K_{0.5}MnO_2$ and $V_5Se_8@C$), 15 wt.% of acetylene black, 5 wt.% of PVDF. Then working electrodes were fabricated by casting the slurry onto the Al foil. Specifically, the cathode electrodes ($K_{0.5}MnO_2$) were charged/discharged for 3 cycles at 0.05 A g⁻¹ in the voltage window of 2.0–4.2 V, and finally discharged to 2.0 V at the same rate to increase the amount of extractable K-ion. The anode electrodes ($V_5Se_8@C$) were charged/discharged for 3 cycles between 0.01-2.6 V at a current density of 0.05 A g⁻¹ and finally charged to 2.6 V at the same rate to eliminate the irreversible capacity. An optimized mass ratio of cathode to anode was set to be 3.6:1 based on the charge balance of the two electrodes. Galvanostatic charge/discharge tests of the full cell were performed by using a LAND CT2001A battery testing system within 1.50–3.60 V at different current densities. The energy density of the full cells is estimated by integration of voltage with the specific capacity which is automatically done by the LAND CT2001A multichannel battery testing system. The average discharge voltage was obtained by dividing the energy density by the specific capacity. The binding energy (E_{bin}) is defined as

$$E_{\rm bin} = (E_{\rm Gr} + E_{\rm V5Se8} - E_{\rm total})/A \qquad (S1)$$

where E_{Gr} , E_{V5Se8} are the energies of Gr monolayer, V_5Se_8 substrate, respectively. A is the area of the interface [S2]. To evaluate the stability of the established interface system, the E_{bin} of V_5Se_8 /Gr interface is calculated to be 22 meV Å⁻², which is similar to the value of van der Waals force (~20 meV Å⁻²) [S3]. Thus, the interfacial interaction is mainly van der Waals interaction. To have a deep understanding of the interface structure, we further compare the chemical bonding and electric properties of bulk V_5Se_8 and V_5Se_8 /Gr. Bader charges results show that in V_5Se_8 /Gr interface, Se atoms obtain 22.85 electrons (e), while V and C atoms respectively lose 22.53 (1.25 e/atom) and 0.32 e (0.009 e/atom), indicating the formation of Se–V and Se–C ionic bonds. From the charge transfer from C to Se atom, the ionic bonding is weak, which is consistent with the calculated binding energy (**Equation S1**).

The adsorption energy and formation energy of isolated K atoms on V_5Se_8/Gr are calculated by the following equations:

$$E_{ads} = E_{total} - E_{sub} - E_{isolated K}$$
(S2)
$$\triangle H_{f} = E_{total} - E_{sub} - E_{metal K}$$
(S3)

where E_{total} , E_{sub} and $E_{\text{isolated K}}$ are total energies of V₅Se₈/Gr interface system with and without a K atom and isolated K atom, respectively. $E_{\text{metal K}}$ is the energy of a K atom in metal K [S4].

The diffusion coefficient is calculated by

$$D = d^2 v_0 \exp\left(-\frac{E_a}{k_{\rm B}T}\right) \tag{S4}$$

where d, E_a , k_B , T and v_0 are the K hopping distance, the energy barrier, the Boltzmann constant, the temperature and the attempt frequency (10¹³ Hz), respectively [S5].



Figure S1. (a) Structure of V₅Se₈ (b) Side and top views of the crystal structure of V₅Se₈/Gr interface.



Figure S2. Raman spectra of the exfoliated V_5Se_8 and V_5Se_8 @C hybrids.



Figure S3. SEM image of the bulk V₅Se₈.



Figure S4. SEM image of the exfoliation of bulk V_5Se_8 powder in N-methyl pyrrolidone without the addition of NaOH.



Figure S5. Representative AFM images of (a) the exfoliated V_5Se_8 nanosheets and (b) the $V_5Se_8@C$ nanosheets. The individual nanosheets were obtained *via* the high-energy ultra-sonication. As shown in Figure S5b, the thickness of individual $V_5Se_8@C$ nanosheets is found to be around 5 nm.



Figure S6. SEM image of the V₅Se₈@C hybrid.



Figure S7. The energy-dispersive X-ray spectroscopy analysis of the V₅Se₈@C hybrid.



Figure S8. Thermogravimetric analysis curves of $V_5Se_8@C$ and V_5Se_8 , which were carried out from 50 °C to 600 °C in Ar atmosphere.



Figure S9. Full survey XPS (a), high-resolution C 1s (b) and high-resolution Se 3d (c) regions of $V_5Se_8@C$ nanosheets.



Figure S10. N_2 adsorption-desorption isotherm curve of $V_5Se_8@C$ nanosheets. Inset is the corresponding pore size distribution.



Figure S11. Charging/discharging profiles for the $V_5Se_8@C$ nanosheets electrode in the first cycle at 0.1 A g^{-1} after a pre-potassiation strategy.



Figure S12. (a) The rate capabilities of the $V_5Se_8@C$ nanosheets with different ultrasonication times. (b) The cycling performance of the $V_5Se_8@C$ nanosheets electrode measured under different current densities of 0.5 and 1 A g⁻¹. The $V_5Se_8@C$ nanosheets electrode still retains reversible depotassiation capacities of 284 and 247 mAh g⁻¹ over 300 cycles at current densities of 0.5 and 1 A g⁻¹, respectively.



Figure S13. *Ex-situ* SEM (a) and TEM (b) images of the $V_5Se_8@C$ nanosheets electrode after 300 cycles at 1 A g⁻¹.



Figure S14. The cycling performance of the bulk V_5Se_8 electrode measured at 0.5 A g⁻¹.



Figure S15. Cycling stability of exfoliated V_5Se_8 nanosheets for 800 cycles at 2 A g^{-1} .



Figure S16. (a) Blue region shows the CV curve with the pseudocapacitive contribution at 1.2 mV s⁻¹ of $V_5Se_8@C$ nanosheets electrode. (b) CV profiles at different scan rates and (c) the plots of log(i) vs. log(v) at each redox-peak pair (peak current: *i*, scan rate: v) of the bulk V_5Se_8 electrode.



Figure S17. (a) Relationship between real impedance with low frequency for the $V_5Se_8@C$ nanosheets electrodes. (b) Nyquist plots of $V_5Se_8@C$ nanosheets and bulk V_5Se_8 electrodes after the first cycle. The K-ion diffusion coefficients of various $V_5Se_8@C$ nanosheets electrodes with different cycles can be calculated according to the following equations:

$$Z = R_s + R_{ct} + \sigma \omega^{-1/2}$$
(S5)
$$D = R^2 T^2 / (2A^2 n^4 F^4 C^2 \sigma^2)$$
(S6)

where Z, ω , R, T, A, n, F, and C correspond to the real part of the impedance, the angular frequency in the low-frequency region, the gas constant, the absolute temperature, the surface area of the electrode, the number of electrons transferred electrochemical reaction, the Faraday's constant, and the insertion/extraction K⁺ concentration in the anode material, respectively, and σ refers to the Warburg coefficient, which is relative to Z'- $\omega^{-1/2}$ (Equation **S5**) and can be acquired by fitting the low frequency region of the Nyquist profiles (**Figure 3d**).



Figure S18. Temperature-dependent electronic conductivities of $V_5Se_8@C$ nanosheets and VSe_2 nanosheets measured using the four-probe method. The $V_5Se_8@C$ nanosheets show a relatively high conductivity value at room temperature (25 °C), exhibiting a better conductive property than VSe_2 nanosheet.



Figure S19. Quasi-thermodynamically equilibrium potential profiles of the $V_5Se_8@C$ nanosheets electrode during the potassiation/depotassiation processes.



Figure S20. HRTEM images of the V₅Se₈@C nanosheets electrodes at the (a, b) fully discharged (0.01 V vs. K^+/K) and (c, d) fully charged (2.6 V vs. K^+/K) state.



Figure S21. *Ex-situ* XPS spectra of V 2*p* for the V₅Se₈@C nanosheets electrode: (a) discharged to 0.01 V (*vs.* K^+/K); (b) charged to 2.6 V (*vs.* K^+/K).

For the fully discharged electrode, the V 2p spectrum can be well fitted by metallic V. After full charge to 2.6 V, the peaks of the V 2p signal shift back to the positions corresponding to the typical characteristics of V³⁺ and V⁴⁺, respectively.



Figure S22. The total density of states and projected density of states of bulk V_5Se_8 . The finite value at Fermi level (E_F) indicate metallic bonds in V_5Se_8 , which is mainly contributed by V 3*d* states. The covalent mixing between V 3*d* and Se 4*p* states at about $-6\sim4$ eV suggests the existence of covalent bonds.



Figure S23. Stable structures of K adsorption on the (a) surface of Gr and (b) in the interior of V_5Se_8 in V_5Se_8/Gr interface. (c) Three adsorption sites of isolated K atom on the surface of V_5Se_8 in V_5Se_8/Gr interface.

The top, hollow, and bridge sites of C atoms are considered for the adsorption of K atom on the surface of Gr. To find the most stable adsorption site on V_5Se_8 surface and interface site, we test isolated K adsorption on various sites, including the top of V and Se atoms and the bridge of V–Se bonds, as shown in **Figure S23c**. The adsorption energy on various sites of V_5Se_8 surface are all larger than those of other positions. The region near the top of Se is the most stable adsorption site (–2.39 eV), its E_{ads} is lower than those of the top of V atom (–2.30 eV) and bridge site (–2.28). And the adsorptions of K on the bridge site and the top of V atom are prone to move to the region near the top of V (**Figure S23c**).



Figure S24. The bulk V_5Se_8 (2×2) supercell with three tunnels (T). As seen in **Figure S24**, there are three main tunnels (T1, T2 and T3) in the bulk V_5Se_8 . When putting a K ion in positions of these tunnels, K ions in T2 and T3 tend to move to the positions in T1. Thus, the sites in T1 is energetically the stable adsorption sites. Therefore, we only simulate K diffusion along T1. For the interface system, K diffusion is simulated by moving K from the region near the top of one Se atom (which is found to be the most stable adsorption site) to another. This path goes through the region on the top of V atom (**Figure S24**).



Figure S25. The K diffusion path in bulk V₅Se₈.



Figure S26. (a) The powder XRD pattern and (b) SEM image of the as-synthesized $K_{0.5}MnO_2$, showing irregular granule morphology with micrometers in particle size. (c) Galvanostatic charge and discharge voltage profiles of $K_{0.5}MnO_2$ cathode (half cell) at 0.05 A g⁻¹. It shows reversible discharge capacity of 98 mAh g⁻¹ (based on the cathode mass).



Figure S27. The cycling performance of the as-fabricated full cell measured under different current densities of 0.2 and 0.3 A g^{-1} . The full cell is capable to deliver reversible discharge specific capacities of 65 and 59 mAh g^{-1} after 150 cycles at current densities of 0.2 and 0.3 A g^{-1} , respectively. The specific capacity is calculated on the mass of K_{0.5}MnO₂.

Table S1. Comparison of electrochemical properties of the $V_5Se_8@C$ nanosheets electrode with previously reported electrode materials (has similar composition or similar types of V_5Se_8) for potassiumion batteries. Electrode compositions are listed using mass ratios of active material : conductive carbon : binder.

Material	Electrode	Loading	Rate capability	Cycling performance	Reference	
	composition	density				
		$(mg \ cm^{-2})$				
	00.15.5	1.2	200, 216, 202	00.00/ 0.000 1		
V ₅ Se ₈ (<i>a</i>)C	80:15:5	1.2	328, 316, 293,	82.9% after 800 cycles	This work	
Nanosheets			257, 201 and 162 mAh g ⁻¹ at	at 4 A g		
			$0.1, 0.2, 0.5, 1, 2 \text{ and } 4 \text{ A g}^{-1}$			
			after each 20 cycles,			
			respectively			
Hierarchical	60: 20: 20	1.0	$100 \text{ mAh g}^{-1} \text{ at } 2 \text{ A g}^{-1}$	105% after 100 cycles at	Adv. Mater. 2017, 29,	
VS ₂ Nanosheet				$1 \mathrm{Ag}^{-1}$	1702061.	
MoS ₂	No data	2	65 mAh g^{-1} at 0.02 A g^{-1}	90% after 200 cycles at	Nano Res. 2017. 10,	
				$0.02 \mathrm{~A~g}^{-1}$	1313.	
V ₃ S ₄ @C	70: 20: 10	1.0-1.5	$250 \text{ mAh g}^{-1} \text{ at } 1 \text{ A g}^{-1}$	83% after 1000 cycles at	Angew. Chem. Int.	
				$1 \mathrm{Ag}^{-1}$	Ed. 2020, 59, 2473-	
					2482.	
MoS ₂ /N-	70: 20: 10	1.0	200 mAh g^{-1} at 1 A g^{-1}	80% after 200 cycles at	Adv. Funct. Mater.	
Doped-C				$0.1 \mathrm{A g}^{-1}$	2018, 28, 1803409.	
MoS ₂ -	60: 20: 20	1.0	270 mAh g^{-1} at 0.5 A g^{-1}	78% after 250 cycles at	J. Mater. Chem. A	
Monolayer/Car				$0.5 \mathrm{A g}^{-1}$	2018,6, 11147-11153.	
bon						
MoSe ₂ /N-	80: 10: 10	1.0 ± 0.2	180 mAh g^{-1} at 2 A g $^{-1}$	88% after 300 cycles at	Adv. Energy Mater.	
Doped Carbon				$0.1 \mathrm{~A~g}^{-1}$	2018, 8, 1801477.	
MoS _{1.5} Se _{0.5}	80: 10: 10	No data	270 mAh g^{-1} at 5 A g^{-1}	83% after 600 cycles at	Adv. Energy Mater.	
				$0.2 \mathrm{~A~g}^{-1}$	2020, 10, 1904162.	
V ₅ S ₈	80: 10: 10	1 ± 0.2	153 mAh g^{-1} at 10 A g^{-1}	77% after 100 cycles at	ACS Nano 2019, 13,	

				$0.05 \mathrm{~A~g}^{-1}$	7939–7948.
MoS ₂ /MXene	80: 10: 10	No data	145.5 mAh g^{-1} after 50 cycles at $0.2 \ A \ g^{-1}$	75.9% after 100 cycles at 0.05 A $\rm g^{-1}$	J. Power Sources 2020, 449, 227481.
SnS2@NC	70: 20: 10	No data	206.7 mAh g^{-1} at 1 A g^{-1}	262.5 mAh g^{-1} after 100 cycles at 0.05 A g^{-1}	ChemElectroChem, 2019, 6, 2254–2263.
rGO@ReS2@N -C	70: 20: 10	0.7–1.0	231 mAh g^{-1} at 10 A g^{-1}	192 mAh g^{-1} at 2 A g^{-1} after 4000 cycles	Adv. Energy Mater. 2019, 9, 1901146.
MoSe2/MXene @C	80: 10: 10	1.0	183 mAh g^{-1} at 10 A g^{-1}	355 mAh g^{-1} at 0.2 A g^{-1} after 100 cycles	ACS Nano 2019, 13, 3448–3456.
PDDA- NPCN/Ti ₃ C ₂	80: 10: 10	1.0–1.2	358.4 mAh g^{-1} after 300 cycles at 0.1 A g^{-1}	60% after 2000 cycles at 1 A $\rm g^{-1}$	Energy Environ. Sci., 2020, 13, 246–257.
Vacancy-Rich MoSSe	70: 15: 15	No data	263.1 mAh g^{-1} at 5 A g^{-1}	219.6 mAh g^{-1} after 1000 cycles at 2 A g^{-1}	ACS Nano 2019, 13, 11843–11852.
Alkalized Ti ₃ C ₂ MXene Nanoribbons	70: 20: 10	No data	78 mAh g^{-1} at 0.2 A g^{-1}	42 mAh g^{-1} at 0.2 A g^{-1} after 500 cycles	Nano Energy, 2017, 40, 1–8.

Table S2. Impedance parameters and K-ion diffusion coefficients of the various V5Se8@C nanosheets samples with different cycles.

Sample (V5Se8@C nanosheets)	$R_{\rm s}\left(\Omega ight)$	$R_{ct}(\Omega)$	$\sigma \left(\Omega \text{ s}^{-0.5} ight)$	$D (\rm cm^2 s^{-1})$
Prestine	6.47	1193	8.65	0.87×10^{-9}
After the 50 cycles	8.53	745	7.14	1.39×10 ⁻⁹
After the 100 cycles	9.72	719	3.52	3.40×10 ⁻⁹

Table S3. E_{ads} and $riangle H_{f}$ of the adsorption isolated K atom on the surface and interior of $V_{5}Se_{8}$, the interface sites and the top of Gr in V_5Se_8/Gr interface, as well as those on the V_5Se_8 (002) surface.

Gr/V ₅ Se ₈ interface					
	Adsorption sites	E _{ads} (eV)	$\Delta H_{\rm f}$ (eV)		
	Top V	-3.31	-2.30		
V ₅ Se ₈ surface	Top Se	-3.40	-2.39		
	Bri V–Se	-3.29	-2.28		
V ₅ Se ₈ interior	Top V	-1.43	-1.46		
Interface site	Top V	-3.05	-2.04		
Interface Site	Top Se	-3.07	-2.06		

	Top C	-1.56	-0.55
Top Gr	Bri C	-1.58	-0.57
	Hollow C	-1.64	-0.63
	Top V	-3.24	-2.23
V ₅ Se ₈ (002) surface	Top Se	-3.25	-2.24
	Bri V–Se	-3.24	-2.23

As shown in **Table S3**, the negative formation energy ($\triangle H_f$) show that the adsorptions of isolated K atom on all considered sites are thermodynamically favourable. The V₅Se₈ surface of V₅Se₈/Gr interface system are thermodynamically stable adsorption site. Its $\triangle H_f$ of the three sites are lower than those of other positions and the top of Se is most stable adsorption site, with a lowest $\triangle H_f$ of -2.39 eV. To deepen the understanding of the influence of interface on the K adsorption behaviour on V₅Se₈, the adsorptions of K on V₅Se₈ surface are also calculated (**Table S3**), which illustrates a lowest E_{ads} of -2.24 eV, which is a higher than that of V₅Se₈ surface (-2.39 eV) in V₅Se₈/Gr interface. Therefore, the formation of V₅Se₈/Gr interface decrease the K adsorption energy on V₅Se₈ surface.

Table S4. The thermodynamic properties and simulations of V₅S₈ and V₅Se₈.

$$\gamma_{\rm s} = \frac{1}{2A_{\rm s}} (E^{\rm unrelax} - NE_{\rm b}) + \frac{1}{A_{\rm s}} (E^{\rm relax} - E^{\rm unrelax})$$

where E^{relax} and E^{unrelax} are the energies of relaxed and unrelaxed surfaces, respectively, A_s is the surface area, N is the number of formula units, and E_b is the energy of one formula unit of bulk V₅Se₈.

	Simulations of V ₅ S ₈ and V ₅ Se ₈						
	Terminal	E ^{unrelax}	$2E_{\rm b}$	E ^{relax}	As	$Y_{\rm s}~({\rm ev}/{\rm A}^2)$	$Y_{\rm s}({\rm J/m^2})$
	S2	-175.068	-180.115	-176.438	37.951	0.030394	0.486919
	S3	-167.461	-180.115	-169.307	37.951	0.118073	1.891534
V ₅ S ₈	V1	-171.735	-180.115	-172.963	37.951	0.078048	1.250329
	V2	-169.938	-180.115	-171.232	37.951	0.099984	1.601747
	V3	-169.937	-180.115	-173.008	37.951	0.053174	0.851845
	V4	-167.462	-180.115	-172.539	37.951	0.032924	0.527443
V ₅ Se ₈	Sel	-161.009	-164.336	-161.94	42.551	0.017215	0.275778
	Se3	-152.565	-164.336	-157.425	42.551	0.0241	0.38609
	Se4	-149.78	-164.336	-153.202	42.551	0.090621	1.451743
	V2	-153.189	-164.336	-153.201	42.551	0.130702	2.093846
	V3	-154.335	-164.336	-155.35	42.551	0.093664	1.500498

Material:	The mass ratio	Average	Discharge	Energy	Reference
Positive//negative	of cathode	discharge	capacity	density	
	material:anode	voltage	(mAh g ⁻¹)	(Wh kg ⁻¹)	
	material	(V)			
K _{0.5} MnO ₂ //V ₅ Se ₈ @C	3.6:1	2.2	72.8	160.2	This work
K _{0.3} MnO ₂ //Hard Carbon	1.35:1	2.05	51.7	106	J. Electrochem. Soc. 2016, 163, A1295–A1299.
K _{0.8} CrO ₂ //Graphite	1:1.4	2.2	33	72.6	J. Power Sources 2019, 430, 137– 144.
K _{0.77} MnO2•0.23H2O/ /Hard Soft Composite Carbon	1.8:1	1.8	77	138.6	Adv. Mater. 2019, 31, 1900060.
K _{0.65} Fe _{0.5} Mn _{0.5} O ₂ //H ard Carbon	2.1:1	2	51.4	102.8	Adv. Funct. Mater. 2018, 28, 1800219.
K _{0.6} CoO ₂ //Graphite	2:1	2.5	35.3	88.3	Adv. Energy Mater. 2017, 7, 1700098.
KCrO ₂ //Graphite	3:1	1.9	67.5	128.3	Chem. Mater. 2018, 30, 6532–6539.
K _{0.6} CoO ₂ //Hard Carbon	3:1	1.9	54	102.6	Nano Lett. 2018, 18, 1522–1529.
K _{0.7} Fe _{0.5} Mn _{0.5} O ₂ //Sof t Carbon	2.1:1	1.6	55.5	88.8	Nano Lett. 2017, 17, 544–550.
Prussian Blue//V3S4@C	3.8:1	2.2	49	108	Angew. Chem. Int. Ed. 2020, 59, 2473–2482.
K _{0.72} Fe[Fe(CN) ₆]//Bi	6:1	2.8	41.8	108.1	Angew. Chem. Int. Ed. 2018, 57, 4687-4691.
K _{0.5} MnO ₂ //Graphite	2:1	2.64	73.7	194.6	ACS Energy Lett. 2020, 5, 1916– 1922.
PTCDA//Bi _{0.5} 1Sb _{0.49} OCl/rGO	3:1	1.8	62.5	112.5	Adv. Energy Mater. 2020, 10, 2000884.
PTCDA//V ₅ S ₈ @C	5.3:1	1.38	57.2	78.9	ACS Nano 2019, 13, 7939–7948.

Table S5. Comparison of the electrochemical performances of some reported K-ion full battery. Discharge capacity and energy density is calculated based on the total mass of the cathode and anode materials in the full-cell.

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2.3 Co₉S₈@MoS₂@carbon hollow nanoboxes for K-ion storage

This is the peer reviewed version of the following article: Multidimensional integrated chalcogenides nanoarchitecture achieves highly stable and ultrafast potassium-ion storage, which has been published in final form at https://doi.org/10.1002/smll.201903720. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

Multidimensional Integrated Chalcogenides Nanoarchitecture Achieve Highly Stable and Ultrafast Potassium-Ion Storage

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Abstract

Potassium-ion batteries (KIBs) have come into the spotlight in large-scale energy storage systems because of cost-effective and abundant potassium resources. However, poor rate performance and problematic cycle life of existing electrode materials are the main bottlenecks to future potential applications. Here we report the first example of preparing 3D

hierarchical nanoboxes multidimensionally assembled from interlayer-expanded nano-2D $MoS_2@dot-like Co_9S_8$ embedded into nitrogen and sulfur co-doped porous carbon matrix (Co_9S_8/NSC@MoS_2@NSC) for greatly boosting the electrochemical properties of KIBs in terms of reversible capacity, rate capability and cycling lifespan. Benefiting from the synergistic effects, Co_9S_8/NSC@MoS_2@NSC manifest a very high reversible capacity of 403 mAh g⁻¹ at 100 mA g⁻¹ after 100 cycles, an unprecedented rate capability of 141 mAh g⁻¹ at 3000 mA g⁻¹ over 800 cycles and a negligible capacity decay of 0.02% *per* cycle, boosting promising applications in high-performance KIBs. Density functional theory calculations demonstrate that Co_9S_8/NSC@MoS_2@NSC nanoboxes have large adsorption energy and low diffusion barriers during K ion storage reaction, implying the fast K ion diffusion capability. This work may enlighten the design and construction of advanced electrode materials combined with strong chemical bonding and integrated functional advantages for future large-scale stationary energy storage.

Keywords: metal sulfides; anode materials; high capacity; electrochemical property; potassium-ion battery

Introduction

At present, the demand for cost-effective, high capacity, long cycle life and high rate capability energy storage technology is drastically increasing due to the rapid development of portable electronics, electric vehicles and large-scale smart grids.^[1-5] However, the widely used and most advanced lithium-ion batteries (LIBs) is severely limited by the scarcity, uneven global distribution and the rising cost of lithium resources as well as the safety issues caused by lithium dendrites.^[6,7] Hence, development of alternative energy storage devices with natural abundance, low cost, high energy density and high safety, such as sodium-ion batteries (NIBs), have been paid great efforts and achieved encouraging progresses in recent vears.^[8-10] Besides NIBs, potassium-ion batteries (KIBs) are attracting tremendous interests recently due to the unique advantages that K^+/K shows much closer redox potential (-2.93 V) to Li⁺/Li (-3.04 V) than Na⁺/Na (-2.71 V) implying wider voltage window and higher energy density in full cell; much higher potassiation potential (0.2 V vs. K^+/K) compared with that of 0.05 V vs. Na⁺/Na and 0.1 V vs. Li^+/Li , guaranteeing the higher safety than LIBs and NIBs; smaller solvated ions and lower desolvation energy of K than that of Li or Na, favoring the fast diffusion kinetics.^[11-15] Therefore, KIBs show great potential in low-cost, large-scale energy storage devices with high energy density and high safety. However, the research on KIBs is still in an early stage where only a few materials have been investigated as anode (such as carbonaceous materials, Bi, phosphorus-based alloys, and transition metal

compound) and cathode (such as prussian blue and its analogues) for KIBs and the electrochemical performances are far away from practical applications.^[16-24] KIBs employing an aqueous electrolyte represent one of the best solutions owing to their long cycle life and innate superior safety characteristics.^[6] However, the demand of much higher energy density still renders non-aqueous KIBs be highly desirable. In this regard, it is significant to explore suitable electrode materials for non-aqueous KIBs with high capacity and energy density.

Recently, transition metal sulfides (TMSs) shows promising electrochemical performance and are attracting great attentions due to its high theoretical capacity, high electrical conductivity and enhanced safety.^[25] For example, Guo et al. prepared pistachio-shuck-like MoSe₂/C core-shell nanostructure by a simple one-pot colloidal technique, which showed a high reversible K ion storage capacity of 322 mAh g^{-1} at 200 mA g^{-1} over 100 cycles.^[26] Wang et al. investigated that CoSe2 threaded by carbon nanotubes framework electrodes had a K ion capacity of 253 mAh g⁻¹ at 200 mA g⁻¹ over 100 cycles and ~82% capacity retention after 600 cycles at 2000 mA g^{-1} .^[27] Among these TMSs, Co₉S₈, MoS₂ exhibits the surprising performance benefits from the high electrical conductivity of Co₉S₈ and high ionic conductivity of MoS₂. For example, Wei et al. recently synthesized vertical MoS₂ "Nano-Rose" on reduced graphene oxide sheets as host materials for potassium ion intercalation, and the material gave a reversible capacity of 178 mAh g⁻¹ at 500 mA g⁻¹.^[28] Zhang et al. reported a sandwich-like MoS₂@SnO₂@C composite as KIB anode, which can maintain a discharge capacity of 312 mA h g⁻¹ after 25 cycles at 0.05 A g⁻¹.^[29] Jia et al. fabricated a mesoporous MoS2-monolayer/carbon composite for K ion intercalation and demonstrated a high specific capacity of 323 mA h g⁻¹ at 100 mA g^{-1.[30]} Wang et al. reported a bamboo-like MoS₂/N-doped-C hollow tubes as an anode material for KIBs, which also exhibited a good rate performance and cycling stability.^[31] Li and co-workers prepared the interlayer expanded MoS_2-N/O doped carbon composite as an anode for K⁺ storage, delivering a high capacity of 220 mA h g⁻¹ after 300 cycles at a current density of 250 mA g^{-1} , and it still remains at 176 mA h g^{-1} after 500 cycles even at 1000 mA g^{-1} .^[32] Another nano-rose-like MoS₂ anchored on reduced graphene oxide composite was able to retain a high capacity of 416.7 mA h g^{-1} over 200 cycles at 100 mA g^{-1} as KIB anode.^[33] Guo and co-workers prepared cobalt sulfide quantum dot nanoclusters anchored on graphene nanosheets as high capacity electrode materials for KIBs.^[34] Although reasonable capacity has been achieved, the cycling stability is still not satisfied suffering from the large volume expansion as well as the resulted structure collapse during the long-time kinetics of largesized K ions with active materials, and the rate capability is limited by the sluggish ion/charge transfer. Hybridizing with the flexible carbon matrix, creating void spaces between active materials and enlarging the interlayer distance for 2D layered structure materials, are demonstrated as effective approaches to buffer the large volume variation, maintain the structural integrity and improve the electrochemical stability.^[35] In addition, the carbon matrix contributes to the enhancement of charge transfer velocity. Although progresses have been made,^[36,37] the further improvement of the electrochemical performance of Co_9S_8 and MoS_2 is still limited by the low ionic conductivity and low electrical conductivity, respectively. In fact, in such related hybrid structures, the MoS_2 directly exposed at the outer layer could be attributed to the absence of the confinement effect of carbon frame, resulting in unstable structure that is easy to accelerate their pulverization and aggregation during the repeated cycling. Therefore, it is significant and full of great challenge to design and fabricate TMSs with unique structure and morphology towards high reversible capacity and excellent cycling stability as well as superior rate performance.

Here, we design a facile synthetic avenue to fabricate multi-dimensional composite system, that is zero dimensional (0D) ultrasmall Co₉S₈ nanoparticles and two dimensional (2D) MoS₂ nanosheets incorporated into three dimensional (3D) hollow carbon framework with N, S co-doping, for advanced K ion battery. This combination of various dimensionalities on the nanoscale enables characteristic synergistic effects, in which each individual component exerts its own merits and overcomes the deficiencies of the other units. The interactions of MoS₂ with Co₉S₈ and carbon improve the electrical conductivity and charge transfer capability of MoS_2 . The expanded interlayer space (1.02 nm) between MoS_2 nanosheets future promote the dynamic diffusion of K ions and greatly release the stress and strain during the intercalation/deintercalation of K ions, effectively favoring the structural integrity. The ultrasmall-sized Co₉S₈ nanopartiles connected to the "sponge layer" of MoS₂ transmission channels filling with the high concentrated K ions, exceptionally facilitate the ionic conductivity of Co₉S₈. Moreover, the N, S co-doped carbon matrix prevents the agglomeration of nanosized Co₉S₈ and MoS₂ and could anchor and confine the intermediates of Co₉S₈ and MoS₂, and the void spaces induced by the hollow framework could buffer volume variation during the long-time charge and discharge process, which further enhance the overall conductivity and structural stability, boosting the capacity, cycling life and rate capability of this complex composite as anode for KIBs. The Co₉S₈/NSC@MoS₂@NSC hybrid with multidimensional nanosized subunits rationally integrates several merits

including enlarging the electrode/electrolyte interface area, shortening the diffusion path of electrons/K ions, enhancing electric conductivity, arousing outstanding pseudo-capacitive behaviors, inhibiting particle self-aggregation, and accommodating volume variation of the electrode materials. As a result, the as-synthesized multi-dimensional composite nanoarchitecture exhibits a long cycle life and high reversible capacity of 403 mAh g^{-1} at 100 mA g^{-1} after 100 cycles and 273 mAh g^{-1} at 1000 mA g^{-1} after 300 cycles; and even at 3000 mA g^{-1} after 800 cycles is still up to 141 mAh g^{-1} , which is comparable with the best electrodes reported for KIBs.

Results and discussion

The detailed synthetic procedure of hierarchical Co₉S₈/NSC@MoS₂@NSC nanoboxes is schematically illustrated in Figure 1a. First, the monodisperse well-defined ZIF-67 polyhedrons were synthesized through a simple room-temperature precipitation method, producing ZIF-67 nanocubes with an average size of 500 nm, as shown in Figure S1a. The surface of ZIF-67 nanocubes is smooth without any individual particles on it. The powder X-ray diffraction (XRD) pattern (Figure S1b) exhibited typical characteristic peaks for (011), (002), (112), and (222) crystallographic planes, demonstrating the successful formation of pure ZIF-67 products. These ZIF-67 nanocubes were converted to Co/NC hybrids through a subsequent annealing treatment in H_2/Ar atmosphere at 600 °C for 2 h. After the calcination process, the average size of the resultant ZIF-67 nanocubes was reduced to ~430 nm, and their smooth surfaces became a little coarser (Figure S2a), arising from the pyrolysis of organic ligand (2-methylimidazole) and the crystallization of Co/NC (Figure S2b). These structure characters make it good as a self-sacrificial host and reactor Finally, for the inoculation of $Co_9S_8(a)MoS_2$ hybrids. the hierarchical Co₉S₈/NSC@MoS₂@NSC nanoboxes were synthesized by a typical solvothermal synthesis using thiourea and glucose as catalyst and carbon sources, and then thermal treatment of these precursor nanoboxes at 800 °C to improve the crystallinity of products. Notably, thiourea was decomposed in this hydrothermal reaction to release NH₃ and H₂S, which simultaneously acted as the N and S doping resources and the S source to in-situ form MoS₂ and Co₉S₈ precursors.



Figure 1. (a) Schematic illustration of the preparation process of the $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes. (b) Schematic process of transport of electrons and K ions in the $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes electrode and structural models of the $Co_9S_8/NSC@MoS_2@NSC$ with expanded interlayer spacing and strong chemical bonding.

The field-emission scanning electron microscopy (FESEM) of image Co₉S₈/NSC@MoS₂@NSC show morphology of highly uniform nanoboxes completely wrapped by numerous crumpled MoS₂@C nanosheets, and the average diameter of the overall nanoboxes reaches ~625 nm (Figure 2a). Observation of broken particle unambiguously exhibits interior void space and nanoarchitecture-assembled shell (Figure S3), revealing their hollow nature. The well-defined hollow structure of the Co₉S₈/NSC@MoS₂@NSC nanoboxes was further identified by transmission electron microscope (TEM) technique. The TEM image in Figure 2b clearly displays that the monodisperse Co₉S₈/NSC@MoS₂@NSC nanoboxes have a shell thickness of ~175 nm and an inner cavity size of \sim 275 nm. The formation mechanism of this inner cavities can be attributed to the heterogeneous diffusion effect during the heat treatment process. Further high-resolution transmission electron microscope (HRTEM) images of $Co_9S_8/NSC@MoS_2@NSC$ (Figure 2c&2d) indicate that the crystalline nanoparticles of Co₉S₈ were embedded in the continuous MoS₂ and carbon matrixs, while Co₉S₈ crystallinity was verified by the interfringe distances of 0.22 and 0.29 nm can be assigned to the (331) and (311) crystallographic planes of the cubic Co₉S₈ phase, respectively. These tiny Co₉S₈/MoS₂ hybrids were integrated into the carbon matrix rather than exposed on the outer surface, which can well accommodate the volume changes during repetitive cycling, anchor the reaction products and prevent they from self-aggregation, reduce

the electron/ion diffusion distance in the solid phase, induce the synergistic effect of the binary sulfides and eventually enhance the electrochemical performance and charge storage efficiency. In addition, a visible interlayer spacing of 0.27 nm belongs to (100) plane of MoS₂ (Figure 2c). Interestingly, HRTEM measurements shown in Figure 2d&S4 suggest that $Co_9S_8/NSC@MoS_2@NSC$ possess 5-8 layers stacked MoS_2 nanosheets with an expanded interlayer spacing of 1.02 nm, which is much larger than the standard interlayer spacing (0.63 nm) of bulk MoS₂ (Figure S5). This dramatically increase can be ascribed to the intercalation of carbon layer between two adjacent MoS2 monolayers (Figure S4). The few-atomic-layer thick with enlarged interlayer structure is more advantageous to the interface storage and facilitates ion and electron fast transport in the electrode material (Figure 1b), thus yielding higher rate capability. The welldefined crystallinities of two sulfide phases in the Co₉S₈/NSC@MoS₂@NSC nanoboxes were further confirmed by the corresponding selected-area electron diffraction (SAED) pattern was shown in Figure 2e. The line-scan energy-dispersive X-ray spectroscopy (EDS) spectra of the Co₉S₈/NSC@MoS₂@NSC nanoboxes also strongly demonstrates that the shell is MoS₂@C hybrids (Figure 2f&2g), agreeing well with the results from above HRTEM observation. The corresponding EDS mapping images (Figure 2g) show the homogeneous Co, Mo, S, C and N element distributions, further confirming the role of N, S-codoped-C acts as a protective shell to keep the structural robustness and form a continuous conductive network.



Figure 2. (a) SEM image, (b) TEM image, (c, d) HRTEM images, and (e) SAED pattern of the Co₉S₈/NSC@MoS₂@NSC nanoboxes. The cross-sectional compositional line-scan profiles (f) and EDS mapping images (g) of the Co₉S₈/NSC@MoS₂@NSC nanobox.

Figure 3a depicts the powder XRD patterns of the as-synthesized samples. The Co₉S₈/NSC@MoS₂@NSC hybrid displays two broaden diffraction peaks at ~33.7° and ~56.3° can be respectively assigned to the (100 Ψ) and (110 Ψ) planes of hexagonally structured MoS₂ (2H-MoS₂, JCPDS card No. 37-1492). The prominent diffraction peaks located at ~15.1°, ~29.8°, ~31.7°, and ~52.2° can be matched well with the (111*), (311*), (222*), and (440*) planes of face centered cubic Co₉S₈ phase (JCPDS card No. 86-2273), respectively. Besides, the broad peak appeared at $\sim 24.5^{\circ}$ can be related to the typical graphitic carbon (002) plane, indicating partial graphitization of the carbon. While, two obvious diffraction peaks at ~8.7° and ~17.5° correspond to the (002 \checkmark) and (004 \checkmark) planes of 2H-MoS₂ have also been observed in the hybrid, compared with pure MoS₂,^[38] the $Co_9S_8/NSC@MoS_2@NSC$ with a lower 2 θ degree of (002) reflection, indicating that the significantly expanded interlayer spaces along c-axis. According to Bragg's formula $(2d\sin\theta = n\lambda),$ the (002)interlayer spacing calculation of MoS_2 in $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes was determined to be ~1.02 nm, which agrees well with the HRTEM results in Figure 2d&S4. These results further corroborating the enlarged interlayer distance between two adjacent MoS₂ layers arising from the intercalation of N,S-codoped carbon layers (Figure 1b). The steep climb of diffraction intensity at low scattering angle below $\sim 7.6^{\circ}$ indicates the disturbed order of MoS₂ along caxis at a certain extent due to carbon species.^[39] The Raman spectra of Co₉S₈/NSC@MoS₂@NSC, Co₉S₈/NSC and pure MoS₂ are shown in Figure 3b. In the Raman spectra of the Co₉S₈/NSC@MoS₂@NSC and Co₉S₈/NSC, two dominant peaks are observed at 1338 cm⁻¹ (D-band) and 1579 cm⁻¹ (G-band), which correspond to the defects in the hexagonal graphitic layers and vibration of sp²-hybridized carbon atoms in a lattice, respectively.^[40] The relative intensity ratio of the D to the G band (I_D/I_G) for the Co₉S₈/NSC@MoS₂@NSC was calculated to be 1.19, indicating a high ratio of defective sites in the carbon lattices induced by the doping of S and N elements. Moreover, compared with the Raman absorption peak of 470 cm⁻¹ for Co_9S_8 , and vibration modes of in-plane E^{1}_{2g} at 374 cm⁻¹ and out-of-plane A¹_{1g} at 409 cm⁻¹ for pure MoS₂ (Figure S6a), slight deviations occur in the spectrum of the Co₉S₈/NSC@MoS₂@NSC hybrid, which were derived from the formation of electronic coupling at the junction of the two sulfide phases (Figure 1b) and the expansion of interdistance between basic MoS₂ layers. The specific surface area and porosity of the Co₉S₈/NSC@MoS₂@NSC and Co₉S₈/NSC were analyzed by measuring the N₂ adsorption-desorption isotherms. As shown in Figure S6b-d, the typical hysteresis loops

in the isotherm curves indicate the existence of mesopores structures in the $Co_9S_8/NSC@MoS_2@NSC$ and Co_9S_8/NSC , and their Brunauer–Emmett–Teller (BET) specific surface area are calculated to be 169.1 (Figure S6b) and 96.4 m² g⁻¹ (Figure S6c), respectively. The pore diameter distribution based on the Barrett–Joyner–Halenda (BJH) method exhibits hierarchical mesopore sizes centered in the range of 2–5 nm in $Co_9S_8/NSC@MoS_2@NSC$ (Figure S6d). This highly porous structure with large specific surface area can provide sufficient space for the infiltration of electrolyte, short diffusion distance for electron/K ion flux, give rise to significant pseudocapacitive behaviors, and abundant buffering space to accommodate volume change during repetitive cycling.

The carbon content in Co₉S₈/NSC@MoS₂@NSC hybrid is estimated to be approximately 17.7 wt% based on the thermogravimetric analysis (Figure S7). X-ray photoelectron spectroscopy (XPS) was used to further evaluate the chemical compositions and elemental valence states of Co₉S₈/NSC@MoS₂@NSC and Co₉S₈/NSC. XPS full survey profile of Co₉S₈/NSC@MoS₂@NSC (Figure S8a) reveals the coexistence of Mo, Co, N, C and S elements. In the case of the C 1s spectra shown in Figure S8b, four characteristic peaks at ~284.7, ~284.9, ~285.6, and ~288.1 eV for Co₉S₈/NSC@MoS₂@NSC can be observed ascribed to the C=C-C, C-S, C-N/O, and C=O coordination bonds, respectively, further verifying successful incorporation of N and S atoms into the lattice of carbon structure. In the high-resolution S 2p spectra (Figure 3c), the peaks located at 161.8 and 163.1 eV are attributed to the S 2p_{3/2} and S 2p_{1/2} of the Co₉S₈, respectively. While the peaks at 162.4 and 164.5 eV are assigned to the S $2p_{3/2}$ and S $2p_{1/2}$ orbitals of divalent sulfide ions in MoS₂, and the peak at 168.3 eV is indexed to the SO4²⁻ species.^[37] The N 1s core level XPS spectrum in Co₉S₈/NSC@MoS₂@NSC can be deconvoluted into three components centered at around 398.5, 400.6, and 402.1 eV, corresponding to pyridinic N (N-6), pyrrolic N (N-5), and graphitic N (N-Q), respectively (Figure 3d).^[41] Among these N functional groups, the percentage of pyridinic N was calculated to be 40.6%, being higher than those of graphitic N (33.7%) and pyrrolic N (25.7%), consistent with the I_D/I_G ratio of Raman spectra. Schematic illustration of the three types of N-containing functional group was presented in the *inset* of **Figure 3d**. The pyridinic N atoms are generally locating on the edge of the honeycomb-like lattice, which are of high chemical active to obtain electrons from the adjacent K atoms.^[42] The high content of pyridinic N and graphitic N can induce a large amount of defects, improve conductivity properties by enhancing the kinetics of K ion/electron diffusion, and create more electrochemically active sites to enhance the potassium storage performance. In addition, the N, S-codoped-C continuous conductive matrix can absorb the intermediate

products generated during conversion reaction to prohibit them aggregated and dissolved in the electrolyte. The XPS high-resolution spectra of Co 2p (Figure 3e) can be deconvoluted into two pairs of spin-orbit doublets and two shakeup satellites. The binding energies observed at 780.6 eV (Co 2p_{3/2}) and 795.1 eV (Co 2p_{1/2}) originate from the spin-orbit characteristics of Co^{3+} , while those centered at 782.3 eV in Co $2p_{3/2}$ and 797.8 eV in Co $2p_{1/2}$ could be associated with Co²⁺. Compared to Co₉S₈/NSC, the Co 2p peaks of Co₉S₈/NSC@MoS₂@NSC slightly shift toward the lower binding energies, suggesting that a strong coupling interaction between the Co₉S₈ and the surrounding MoS₂/NSC shell by their nano-interface. In the Mo 3d spectrum (Figure 3f), two distinct peaks located at 228.9 and 232.1 eV are indexed to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$, demonstrating the existence of Mo⁴⁺ in the Co₉S₈/NSC@MoS₂@NSC hybrid. The nearby S 2s peaks can be deconvoluted into two peaks centered at 225.7 and 224.2 eV, which are assigned to the Co-S and Mo-S binding structures, respectively. The Mo 3d peaks also show shifts compared to the pure MoS₂ nanoplates,^[43] providing further evidence of the strong coupling interfaces between the two phases (Co_9S_8) The interfacial interaction in and MoS_2). strong the Co₉S₈/NSC@MoS₂@NSC hybrid via chemical bonding significantly enhances the charge transfer, which is expected to greatly improve the rate capability and cycling stability of the electrode during repetitive potassiation/depotassiation process.



Figure 3. (a) XRD patterns of the $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes. Insets are the unit cells of MoS_2 and Co_9S_8 nanocrystals. The peaks of Co_9S_8 are marked by *, and the peaks of MoS_2 are marked by \checkmark . (b)

Raman spectra of the $Co_9S_8/NSC@MoS_2@NSC$ hybrid, Co_9S_8/NSC and MoS_2 . XPS high-resolution spectra of the S 2p (c) and N 1s (d) for the $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes. The *inset* of (d) is schematic illustration of the three types of nitrogen defects in carbon matrix: pyridinic N (N-6), pyrrolic N (N-5), and graphitic N (N-Q). (e) Co 2p spectra of the $Co_9S_8/NSC@MoS_2@NSC$ and Co_9S_8/NSC . (f) Mo 3d spectra of the $Co_9S_8/NSC@MoS_2@NSC$ hybrid.

We then investigated the K ion storage behaviors of Co₉S₈/NSC@MoS₂@NSC electrodes with Co₉S₈/NSC as a comparison (The microstructure characterizations of Co₉S₈/NSC are presented in Figure S9. Notably, a number of dot-like of Co₉S₈ tiny nanoparticles (dark dots) are uniformly encapsulated within the N, S-codoped carbon matrices.). Figure 4a shows the cyclic voltammetry (CV) profiles of Co₉S₈/NSC@MoS₂@NSC electrode for the initial three cycles within the voltage window of 0.01 to 2.6 V (vs. K/K^+) at a sweeping speed of 0.1 mV s^{-1} . In the first cycle, four reduction peaks centered at 1.20, 0.81, 0.63, and 0.36 V can be clearly observed. The intensive peaks located at 0.81 and 0.36 V can be ascribed to the multistep phase transformation of MoS₂ derived from K ions intercalation into MoS₂ interlayer and further reduction of $K_x MoS_2$ into metallic Mo, respectively, while the peak at 1.20 V can be related to the reduction of Co₂S₈ to metallic Co and K₂S matrix. The reduction waves range from at around 1.05 and 0.60 V have also been detected in the first curve for the Co₉S₈/NSC electrode as shown in Figure S10, indicating the electrochemical conversion reaction of Co₉S₈ with K. A broad cathodic peak is found at 0.63 V, and disappears in the following cycles, resulted from the decomposition of electrolyte and the formation of a stable solid-electrolyte interphase (SEI) film on the surface of the Co₉S₈/NSC@MoS₂@NSC during the initial discharge process.^[44] During the anodic scan, two strong peaks at 1.52 and 1.85 V can be assigned to the oxidization of metallic Mo and Co, respectively. From the second cycle onwards, the CV curves almost completely overlapping, indicative of high reversibility and cycling stability of K storage in the Co₉S₈/NSC@MoS₂@NSC electrode.

Figure 4b displays the galvanostatic charge/discharge profiles of $Co_9S_8/NSC@MoS_2@NSC$ electrode in the 0.01–2.6 V window at 100 mA g⁻¹. The slopes are well consistent with the CV results, further evidencing the multistep electrochemical potassiation/depotassiation processes of the $Co_9S_8/NSC@MoS_2@NSC$ electrode. The high potassiation potential can play a critical role in relieving the danger of dendrite formation on $Co_9S_8/NSC@MoS_2@NSC$ electrode surface during cycling. The initial discharge and charge capacities are 663 and 437 mAh g⁻¹, respectively, with a Coulombic efficiency (CE) of 65.9%. The low initial CE can be assigned to the irreversible SEI film formation on the

electrode surface, agreeing well with the results of the CV profiles (**Figure 4a**). Except for the remarkable capacity loss between the initial and fifth cycles, the potassiation/depotassiation curves at the 100^{th} cycle almost overlap with those at the 50^{th} cycle, reflecting the high stability and superior reversibility characters of Co₉S₈/NSC@MoS₂@NSC in K ion storage.

The cycling performance of the Co₉S₈/NSC@MoS₂@NSC electrode at a current density of 200 mA g^{-1} is described in Figure 4c. A high reversible specific capacity of 367 mAh g^{-1} is achieved after 300 cycles without apparent capacity fading. During the entire course of cycling test, the CE is close to 99.8% except for the initial several cycles, indicating the stabilization of SEI on the Co₉S₈/NSC@MoS₂@NSC electrode surface. Further studies of cycling characteristic for the Co₉S₈/NSC@MoS₂@NSC electrode over 300 cycles under different current densities also demonstrate their remarkable structural stability and reversibility (Figure S11), which can be ascribed to the designed significant structure and the effective synergistic interactions between the binary sulfides components. In contrast, the Co₉S₈/NSC electrode indicates poor cycling performance with substantial capacity loss (Figure S12). The rate capabilities of the Co₉S₈/NSC@MoS₂@NSC, Co₉S₈/NSC and pure MoS₂ electrodes are evaluated at various current densities as shown in Figure 4d. When the current densities gradually increase from 100, 200, 500, 1000, to 2000 mA g^{-1} , corresponding reversible specific capacities can be kept at 414, 390, 359, 292 and 221 mAh g^{-1} for Co₉S₈/NSC@MoS₂@NSC after each 20 cycles, respectively. Even at the ultrahigh current density of 3000 mA g⁻¹, the Co₉S₈/NSC@MoS₂@NSC can still maintain a high reversible capacity of 163 mAh g⁻¹ after 120 cycles, delivering 71.5% of its original capacity at 2000 mA g^{-1} . Then the capacity is able to return to 372 mA g^{-1} , when the current density is switched back to 200 mA g^{-1} . For comparison, the specific capacity of Co₉S₈/NSC and pure MoS₂ electrodes quickly drop to 68 and 89 mAh g^{-1} with the increase in current density, respectively, highlighting the contribution of MoS₂/NSC shell with expanded layers to excellent electrochemical performance. The most appealing characteristic of Co₉S₈/NSC@MoS₂@NSC hierarchical nanoboxes is its ultrastable cyclic performance at ultralarge current density of 3000 mA g^{-1} (Figure 4e). When galvanostatistically cycled at 3000 mA g^{-1} , a stable reversible capacity of 141 mAh g $^{-1}$ was obtained even after 800 cycles with a capacity retention of 84.4%. The corresponding CE maintains beyond 99.4% after the first 20 cycles and remain the high value in the ensuing cycles, which is indicative of extraordinary cycling stability at high charge/discharge rates. In addition, the excellent structural integrity of Co₉S₈/NSC@MoS₂@NSC is also further confirmed by the unchanged

ex-situ SEM image after 800 cycles at 3000 mA g^{-1} (Figure S13). The electrochemical performances of Co₉S₈/NSC@MoS₂@NSC anode are better than for most other reported KIBs anode materials (Table S1), demonstrating attractive properties for future large-scale energy storage system.

To elucidate why the $Co_9S_8/NSC@MoS_2@NSC$ electrode has the superior rate performance, the CV tests at various sweep rates ranging from 0.1 to 1.1 mV s⁻¹ were performed to evaluate the reaction kinetics and the redox pseudocapacitance-like contribution (Figure 5a). The CV profiles are not substantially changed especially the anodic and cathodic peaks can still be recognized with increasing sweeping rates, implying a high reversibility for potassium storage. The relationship of peak current (i) and the scan rate (v) match with the equation log(i) = blog(v) + log(a), where both a and b are adjustable parameters, and b determines the potassiation and depotassiation types.^[45] Figure 5b exhibits the plots of log(i) vs. log(v) and the corresponding b-value at different voltage states. It is worth noting that the values of b approaching 0.5 and 1.0 represent the diffusioncontrolled behavior and the ideal pseudocapacitive effect, respectively. The b-values of the five redox-peak are 0.74, 0.76, 0.78, 0.73 and 0.69, respectively, which suggested that the redox processes of Co₉S₈/NSC@MoS₂@NSC are dominated mainly by both the diffusion- and pseudocapacitive-controlled mixed mechanisms. In the CV plots (Figure **5c**), the quantitative storage contributions in $Co_9S_8/NSC@MoS_2@NSC$ can be calculated by separating the current response (i) at a fixed voltage based on the equation i (V) = $k_1 v^{0.5}$ + k_2v , in which the $k_1v^{0.5}$ indicates diffusion-controlled and the k_2v represents pseudocapacitive effect.^[22,46] The detail-fitting capacitive contribution ratio for Co₉S₈/NSC@MoS₂@NSC electrode is ~86.9% at a relatively high sweeping rate of 1.1 mV s⁻¹. In addition, the proportions of pseudocapacitive contribution at four different scanning rates between 0.1 and 1.1 mV s⁻¹ is summarized in Figure 5d. The outstanding pseudocapacitive behaviors of Co₉S₈/NSC@MoS₂@NSC can be ascribed to the synergistic effect of the unique box-like multidimensional integrated nanoarchitecture, which contribute to fast reaction kinetics to achieve high-rate performance.

The reaction kinetics analysis of $Co_9S_8/NSC@MoS_2@NSC$ through the electrochemical impedance spectroscopy (EIS) measurements was explored to understand the in-depth reason of the outstanding K ion storage performance. The Nyquist plots at different cycles are similar in profile (**Figure 5e**), composed of a depressed semi-circle in high-frequency accompanied by a sloping straight line in low frequency region. The high-frequency depressed semi-circle signifies the interfacial

charge-transfer resistance (R_{ct}), while the low-frequency inclined line is associated with K ion diffusion Warburg impedance and phase transformation within bulk crystals. The corresponding EIS spectrum was simulated with equivalent circuit as shown in the *inset* of **Figure 5e**. The fitting results are tabulated in **Table S2**. Apparently, the R_{ct} -value of the Co₉S₈/NSC@MoS₂@NSC electrode slightly increase with continuous cycling, probably ascribed to formation of a stable electrode–electrolyte interface and a phase transformation during conversion reaction. The K ion diffusion coefficients of Co₉S₈/NSC@MoS₂@NSC electrode are calculated to be 3.64×10^{-10} cm² s⁻¹ before cycle, 3.34×10^{-9} cm² s⁻¹ after the 50 cycles, and 2.58×10^{-9} cm² s⁻¹ after the 100 cycles (**Figure S14&Table S2**), revealing the stable and fast K ion shuttling reaction kinetics inside the electrode during repetitive cycling. The high ionic diffusivity of Co₉S₈/NSC@MoS₂@NSC was attributed to the expanded interlayer distance filling with the high concentrated K ions and shorted electrons/K ions diffusion paths by synergistic design of the multidimensionally assembled nanoarchitecture.



Figure 4. (a) CV curves for the Co₉S₈/NSC@MoS₂@NSC nanobox electrode in the first three cycles at a scan rate of 0.1 mV s⁻¹. (b) Charging/discharging profiles for the Co₉S₈/NSC@MoS₂@NSC nanoboxes at different cycles at 100 mA g⁻¹. (c) Cycling stability and Coulombic efficiency (CE) of the Co₉S₈/NSC@MoS₂@NSC nanobox electrode at 200 mA g⁻¹. (d) Rate capabilities of the Co₉S₈/NSC@MoS₂@NSC, Co₉S₈/NSC and pure MoS₂ electrodes at various current densities from 100 to 3000 mA g⁻¹. (e) The cycling performance and CE of the Co₉S₈/NSC@MoS₂@NSC nanobox electrode

for 800 cycles at 3000 mA g^{-1} . (Note that all the specific capacity values were calculated based on the total mass of Co₉S₈/NSC@MoS₂@NSC nanoboxes).

The electrochemical kinetics of the K ions storage in the Co₉S₈/NSC@MoS₂@NSC anode was further investigated using galvanostatic intermittent titration technique (GITT) technique. A sequential current pulse of 100 mA g^{-1} was applied for 20 min, which was then followed by a relaxation interval of 2 h. The open-circuit voltage at the end of the long-time rest is considered to be thermodynamic quasi-equilibrium potential. Multiple quasiequilibrium voltage plateaus for the first cycle are observed in Figure S15, further corroborating the multistep electrochemical reactions occur. The reaction resistance at different potassiation/depotassiation stages was calculated by dividing the overpotential by the pulse current density, as presented in Figure 5f. During the potassiation process, the reaction resistance gradually decreases with K ion uptake, which could be assigned to the increased conductivity caused by the metallic phase formation upon discharge. There is an opposite tendency during the depotassiation period, which can be explained by the decreasing electric conductivity. The reaction resistance of Co₉S₈/NSC@MoS₂@NSC is consistently smaller than some other reported anode materials for KIBs,^[47-50] which is in favour of the fast and highly reversible uptake/extraction of K ion, thus yielding excellent electrochemical performance.



Figure 5. (a) CV profiles at different scan rates and (b) the plots of log(i) *vs.* log(v) at each redox-peak pair (peak current: *i*, scan rate: *v*) of the Co₉S₈/NSC@MoS₂@NSC nanoboxes. (c) Blue region shows the
CV curve with the pseudocapacitive contribution at 1.1 mV s⁻¹. (d) Bar chart shows the percentages of pseudocapacitive contributions at different sweep rates. (e) Nyquist plots of the $Co_9S_8/NSC@MoS_2@NSC$ nanobox electrodes after different cycles (inset: selected equivalent circuit). (f) Reaction resistance during potassiation/depotassiation processes of the $Co_9S_8/NSC@MoS_2@NSC$ nanobox electrode in KIBs.

In order to better understand the superior K ion storage and energy conversion behaviors of Co₉S₈/NSC@MoS₂@NSC, density functional theory (DFT) based firstprinciples calculations were performed to theoretically investigate the conductivity of electrons and ions. Charge density difference (Figure S16) indicate that charge transfer occurs in the interface between C and Co₉S₈. Moreover, the charge transfer is more significant between MoS_2 and Co_9S_8 (Figure S17), which implies the good ability of electronic transfer in Co₉S₈/NSC@MoS₂@NSC. The metallic character of Co₉S₈/NSC can be also verified by projected density of states (PDOS), where the states at Fermi level are occupied by C element (Figure 6a). As for Co₉S₈/NSC@MoS₂@NSC, there are higher peaks derived from Co, Mo, S and C elements (Figure 6b) at Fermi level, disclosing their much better electric conductivity than Co₉S₈/NSC. To perform the computations of ionic conductivity, we carefully studied the possible ionic diffusion path. The K ion is assumed to migrate from a stable site to another stable site and there is a transition states in the path, which is visualized in Figure 6c&d for Co₉S₈/NSC and Figure 6e&f for Co₉S₈/NSC@MoS₂@NSC, respectively. Diffusion barriers were determined to be 0.33 eV and 0.11 eV for the path in Co₉S₈/NSC (Figure 6g) and Co₉S₈/NSC@MoS₂@NSC (Figure 6h). It can be concluded that the fast kinetics of K ions storage process in Co₉S₈/NSC@MoS₂@NSC at room temperature are enabled by sufficiently low migration barrier. Even though the further conversion reaction is too complicated to DFT simulate by our calculations. the calculation results with Co₉S₈/NSC@MoS₂@NSC bulk model can provide rationalization for the remarkable high-rate performance observed experimentally.



Figure 6. Energy diagram of K ion migration path in Co_9S_8/NSC model (a) and $Co_9S_8/NSC@MoS_2@NSC$ model (b). The top view (c, e) and side view (d, f) of K ion migration path in Co_9S_8/NSC model (c, d) and $Co_9S_8/NSC@MoS_2@NSC$ model (e, f). (yellow for S, blue for Co, pink for Mo, brown for C and purple for K). Projected density of states of in Co_9S_8/NSC model (g) and $Co_9S_8/NSC@MoS_2@NSC$ model (h).

To make a thorough investigation on the structural evolution mechanisms of Co₉S₈/NSC@MoS₂@NSC electrode, the ex-situ XRD was performed to identify the possible phase transition among the depotassiation/potassiation process. Figure S18 shows the corresponding ex-situ XRD results of the Co₉S₈/NSC@MoS₂@NSC electrode at various depotassiation/potassiation states. There are two strong diffraction peaks in the patterns, which result from the current collector (Cu foil). When discharged to 0.4 V, the (002) and (004) peaks for MoS₂ shift to lower angles can be attributed to the formation of nonstoichiometric K⁺-intercalated compounds, demonstrating the expansion of the MoS₂ lattice spacing with the insertion of K ions. Similarly, the graphitic carbon (002) peak shifts to 23.8°, further confirming the potassiation reaction. The characteristic peaks are observed at 34.2° , 42.2° , and 49.5° are respectively indexed to the (220), (222), and (400) crystallographic planes of K₂S, meanwhile a new diffraction peak located at 44.2° is derived from the metallic Co. After the electrode is further full discharged to 0.01 V, the characteristic peaks of MoS₂ are missing. While, a new peak appears at 40.5°, which belongs to the metallic Mo. Finally, when fully charged to 2.6 V, all the peaks can be returned to their original state, implying a highly reversible structure evolution behaviors in $Co_9S_8/NSC@MoS_2@NSC$ electrode.

Conclusion

In summary, we describe a multidimensionally assembled 3D hierarchical nanoboxes composed of interlayer-expanded nano-2D MoS₂@dot-like Co₂S₈ nanoarchitecture and further embedded into N/S codoped porous carbon matrix. The unique box-like multidimensional integrated nanoarchitecture effectively can promote the electrode/electrolyte interface contact area, provide abundant accessible active sites, facilitate rapid electron/K ion transportation, give rise to significant pseudocapacitive behavior, prevent particle self-aggregation, and help to maintain structural durability during the depotassiation and potassiation processes. We initially applied Co₉S₈/NSC@MoS₂@NSC anode material for KIBs, and the as-prepared as Co₉S₈/NSC@MoS₂@NSC electrode demonstrates superior electrochemical performances in term of ultrahigh reversible capacity (up to 403 mAh g^{-1} at 100 mA g^{-1} after 100 cycles), outstanding rate capability (273 mA h g^{-1} at 1000 mA g^{-1} after 300 cycles and 141 mA h g^{-1} at 3000 mA g⁻¹ after 800 cycles), as well as excellent cycling durability (only 15.6% capacity loss after 800 cycles at 3000 mA g^{-1}), making it a very attractive anode for KIBs. The first-principles calculations suggest that the Co₉S₈/NSC@MoS₂@NSC hybrid has large adsorption energy and low diffusion barriers, further confirming the excellent electrochemical reaction kinetics of the electrode. The multidimensionally assembled 3D architecture with integrated functional advantages is the future research spotlight toward the next-generation energy-storage systems, and opening a path of a great potential in the design of high-performance electrodes.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51671136), International Technological Collaboration Project of Shanghai (Grant No. 17520710300), the Helmholtz Association, the China Scholarship Council (CSC) and was partially funded by the German Research Foundation, DFG (Project No. MA 5039/4-1).

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Supporting information

Multidimensional Integrated Chalcogenides Nanoarchitecture Achieve Highly Stable and Ultrafast Potassium-Ion Storage

Experimental details

Materials synthesis. In the first step, cobalt-nitrate hexahydrate (2.0 mmol) and 2-methylimidazole (110.0 mmol) were respectively dispersed in 20.0 mL of deionized (DI) water containing 10.0 mg of hexadecyl trimethylammonium bromide (CTAB) and 140.0 mL of DI water to form clear solutions, and then the two solutions were mixed and stirred for 30 min at room temperature. Finally, purple solid powder (ZIF-67) can be collected by centrifugation and washed with ethanol several times, and dried at 70 °C for overnight. The Co/NC hybrid was obtained through a thermal decomposition of ZIF-67 at 500 °C in N₂ atmosphere for 2 h. In the next step, 80.0 mg of Na₂MoO₄·2H₂O and 160.0 mg of CH₄N₂S were dissolved in 30.0 mL of glucose solution (0.08 M) under strong stirring. Then 30.0 mg of the above Co/CN precursor was added into the mixture and sonicated for 20 min to form a uniform solution. The obtained homogeneous solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 200 °C for 20 h. After the reaction, the black precipitate was rinsed with DI water and dried. Finally, the as-obtained powders were annealed at 600 °C for 2 h in N₂ atmosphere to obtain Co₉S₈/NSC@MoS₂@NSC nanoboxes. For comparison, the Co₉S₈/NSC have been prepared *via* the similar procedures except for the absence of Na₂MoO₄·2H₂O and glucose.

Materials characterization. The morphology and microstructure were characterized by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA), transmission electron microscope (TEM; JEM-2011F) and high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20 S-TWIN, USA). Elements distribution was collected *via* energy dispersive spectroscopy (EDS) mapping attached to the TEM instrument. X-ray diffraction (XRD) was carried out on Rigaku UltimaIV-185 with Cu K alpha radiation operating at 40 mA and 40 kV to determine the crystallographic structure of the samples. Thermogravimetric analysis (TGA) and Raman measurement were performed at Mettler-Toledo TGA/DSC1 and a laser Raman spectrometer (Jobin Yvon, T6400, 532 nm incident wavelength), respectively. Nitrogen adsorption–desorption isotherms were measured by using a surface area&porosity analyzer (Quantachrome NOVA 2200e, USA) at 77 K. The specific surface areas and the pore size distributions were calculated based on the Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) models, respectively. X-ray photoelectron spectroscopy (XPS) spectra of samples were recorded using an HP5950A ESCA spectrometer with monochromatic Al K alpha radiation to detect the chemical states of the products.

Electrochemical measurements. Electrochemical properties of the as-prepared samples were investigated by using CR2032-type coin cell assembled in an Ar-filled glovebox with K metal foil as a counter electrode. The working electrodes were fabricated by mixing the active material, carbon black and polyvinylidene fluoride (PVDF) in NMP solvent with a weight ratio of 80:15:5, then coated

uniformly on a Cu foil with a mass loading of ~1.3 mg. The resultant electrodes were dried at 80 °C under vacuum for more than 12 h. Glass microfiber membrane (Whatman, Grade GF/B) was employed as the separator, and 0.8 M KPF₆ dissolved in an ethylene carbonate (EC)/diethyl carbonate (DEC) solution (1:1 by volume) was utilized as the electrolyte. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) analysis were operated at CHI 660E electrochemical workstation with a voltage range of 0.01-2.6 V and in the frequency range from 100 kHz to 0.01 Hz, respectively. Galvanostatic charge-discharge measurements and galvanostatic intermittent titration technique (GITT) measurements were performed on a NEWARE battery testing system in the potential window of 0.01–2.6 V. During the GITT test, the assembled Co₉S₈/NSC@MoS₂@NSC half-cell was first discharged and charged by applying a series of pulse current of 100 mA g^{-1} for 20 min followed by an open-circuit relaxation interval of 2 h for each pulse to reach an equilibrium potential. To test the cycled electrodes, all the anodes for *ex-situ* SEM and XRD measurements were rinsed with dimethyl carbonate several times after disassembling from the cells and dried in the glovebox for further analyses.

Computational Methods. All the simulations were performed using density functional theory (DFT). The Vienna ab initio simulation package (VASP) was implemented to optimize the structures and investigate their properties. The ion-electron interactions were described by projector augmented waves (PAW) when the function of Perdew,^[S1] Burke and Ernzerhof (PBE) based on the generalized gradient approximation (GGA) was used to describe the exchange and correlation potential.^[S2] $7 \times 7 \times 1$ and $3 \times 3 \times 1$ Monkhorst-Pack sampled k points were chosen for DOS (density of states) and NEB (Nudged Elastic Band) calculation,^[S3,S4] when a cut-off energy of 400 eV was adopted. The threshold of convergence was set to 1×10^{-5} eV and 0.01 eV/Å for the self-consistent field (SCF) and ion steps, respectively.^[S4] The adsorption energy of K is referred to the energy of bcc K bulk.



Figure S1. (a) SEM image and (b) XRD pattern of the ZIF-67 nanocubes.



Figure S2. (a) SEM image and (b) XRD pattern of the Co/NC hybrids.



Figure S3. SEM image of Co₉S₈/NSC@MoS₂@NSC nanoboxes.



Figure S4. HR-TEM image of Co₉S₈/NSC@MoS₂@NSC nanoboxes.



Figure S5. HR-TEM image of MoS₂.



Figure S6. (a) Raman spectra of the $Co_9S_8/NSC@MoS_2@NSC$ hybrid, Co_9S_8/NSC and MoS_2 . Nitrogen adsorption-desorption isotherms of (b) $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes and (c) Co_9S_8/NSC . (d) The BJH pore-size distribution curve of $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes.



Figure S7. TGA curve of the synthesized $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes under air flow with a temperature ramp of 10 °C min⁻¹. The content of carbon in $Co_9S_8/NSC@MoS_2@NSC$ was determined by following equations: 30-151 °C: H_2O (ads) $\rightarrow H_2O$ (g) (1) 151-570 °C: $Co_9S_8/NSC@MoS_2@NSC + O_2$ (g) $\rightarrow MoO_3 + CoSO_4 + CO_2$ (g) (2) 570-801 °C: $CoSO_4 + O_2$ (g) $\rightarrow Co_3O_4 + SO_3$ (g) (3)



Figure S8. (a) XPS full survey profile and (b) C 1s spectra of the Co₉S₈/NSC@MoS₂@NSC nanoboxes.



Figure S9. (a) SEM image, (b) element mapping images and (c) TEM image of the Co_9S_8/NSC nanoboxes.



Figure S10. CV curves for the Co_9S_8/NSC nanoboxes electrode in the first cycle at a scan rate of 0.1 mV s⁻¹.



Figure S11. The cycling performance of the $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes electrode measured under different current densities from 500 to 1000 mA g⁻¹.

The $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes electrode still retains reversible capacities of 336 and 273 mAh g^{-1} after 300 cycles, respectively.



Figure S12. The cycling performance of the Co_9S_8/NSC nanoboxes electrode measured at 500 mA g⁻¹.







Figure S14. Relationship between real impedance with low frequency for the $Co_9S_8/NSC@MoS_2@NSC$ nanobox electrodes.



Figure S15. Quasi-thermodynamically equilibrium potential profiles of the $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes electrode during the potassiation/depotassiation processes.



Figure S16. Charge density difference of Co₉S₈/NSC model. (yellow for S, blue for Co and brown for C).



Figure S17. Charge density difference of $Co_9S_8/NSC@MoS_2@NSC$ model. (yellow for S, blue for Co, pink for Mo and brown for C).



Figure S18. *Ex-situ* XRD patterns of the Co₉S₈/NSC@MoS₂@NSC nanoboxes nanosheet electrodes at the different state (D: state of discharge, C: state of charge)

Table S1. Comparison of electrochemical properties of $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes electrode with previously reported electrode materials for potassium-ion batteries. Electrode compositions are listed using mass ratios of active material : conductive carbon : binder.

Material	Electrode compositi on	Loading density (mg cm ⁻²)	Rate capability	Cycling performance	Reference
Co ₉ S ₈ /NSC@Mo S ₂ @NSC nanoboxes	80: 15: 5	1.3	414, 390, 359, 292, 221 and 163 mAh g ⁻¹ at 0.1, 0.2, 0.5, 1, 2 and 3 A g ⁻¹ after each 20 cycles, respectively	92.4% after 100 cycles at 0.1 A g ⁻¹ 93.3% after 300 cycles at 0.5 A g ⁻¹ 92.0% after 300 cycles at 1 A g ⁻¹ 84.4% after 800 cycles at 3 A g ⁻¹	This work
TiNb ₂ O ₆ @MoS ₂ /C	70: 20: 10	1.0	450, 420, 373 and 309 mAh g^{-1} at 0.05, 0.1, 0.2 and 0.5 A g^{-1} , respectively	79.3% after 300 cycles at 1 $$\rm A~g^{-1}$$	J. Mater. Chem. A 2019, 7, 5760.
Sandwich-like MoS2@SnO2@C	70: 15: 15	0.8–1.0	597, 345, 276,153 and 86 mAh g^{-1} at 0.05, 0.1, 0.2, 0.5 and 0.8 A	78% after 450 cycles at 1 A g^{-1}	Small 2018 , 14, 1703818.

Interlayer expanded MoS ₂ – N/O doped	80: 10: 10	1.0–1.3	g^{-1} , respectively. 455, 362, 345, 315 and 247 mAh g^{-1} at 0.05, 0.1, 0.25, 0.5 and 1 A g^{-1} , respectively	55% after 500 cycles at 1 A g^{-1}	J. Mater. Chem. A 2019 , 7, 9305.
carbon composite Nano-rose-like MoS ₂ anchored on reduced	80: 10: 10	1.0	364.8, 302.9, 253.0 and 196.8 mAh g^{-1} at 0.2, 0.5, 1 and 2 A g^{-1} respectively	90% after 200 cycles at 0.1 A g^{-1}	Nano Energy 2019 , 63, 103868.
Mesoporous MoS ₂ - monolayer/carbo	60: 20: 20	1.0	397, 323, 256, 183 and 164 mAh g^{-1} at 0.05, 0.1, 0.5, 1 and 2 A g^{-1} , respectively	89% after 500 cycles at 1 A g^{-1}	J. Mater. Chem. A 2018, 6, 11147.
MoS ₂ /N-Doped- C	70: 20: 10	1.0	258, 238, 204, 171 and 131 mAh g^{-1} at 0.1, 0.2, 0.5, 1 and 2 A g^{-1} , respectively	73% after 1000 cycles at 0.5 $$\rm A~g^{-1}$$	<i>Adv. Funct. Mater.</i> 2018 , 1803409.
Alkalized Ti ₃ C ₂ MXene nanoribbons	70: 20: 10	Not provided	78 mAh g^{-1} at 0.2 A g^{-1} 136 mAh g^{-1} at 0.02 A g^{-1}	55% after 500 cycles at 0.2 $$\rm A~g^{-1}$$	Nano Energy 2017 , 40, 1.
Hierarchical VS ₂ nanosheet	60: 20: 20	1.0	100 mAh g^{-1} at 2 A g^{-1}	105% after 100 cycles at 1 A g^{-1}	Adv. Mater. 2017 , 29, 1702061.
Hard/soft composite Carbon	80: 10: 10	2.0	261 mAh g^{-1} at 0.028 A g^{-1}	89% after 440 cycles at 0.05 $$\rm A~g^{-1}$$	Adv. Funct. Mater. 2017, 27, 1700324.
Few-layer F- doped graphene foam	80: 10: 10	1.0–1.2	300 mAh g^{-1} at 0.05 A g^{-1} 200 mAh g^{-1} at 0.5 A g^{-1}	60% after 200 cycles at 0.5 $\mathrm{A}~\mathrm{g}^{-1}$	ACS Appl. Mater. Interfaces 2016 , 8, 20682.
MoS_2	Not provided	2.0	65 mAh g^{-1} at 0.02 A g^{-1}	90% after 200 cycles at 0.02 A g^{-1}	Nano Res. 2017 . 10, 1313.
Sn/C	70: 20: 10	1.2	$150~{\rm mAh~g}^{-1}$ at 0.025 A ${\rm g}^{-1}$	75% after 30 cycles at 0.025 A g^{-1}	Chem. Commun. 2016, 52, 9279.
Ultra high pyridinic N- doped porous carbon	70: 20: 10	1.0	487, 388, 319, 286, 253, 225, and 199 mAh g^{-1} at 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2 A g^{-1} , respectively	72% after 3000 cycles at 1 $$\rm A~g^{-1}$$	Adv. Mater. 2017 , 29, 1702268.
Carbon	70: 20: 10	Not provided	263, 234, 172, and 80 mAh g^{-1} are obtained at 0.028, 0.06, 0.15, and 0.28 A g^{-1} , respectively	52% after 50 cycles at 0.05 $$\rm A~g^{-1}$$	J. Am. Chem. Soc. 2015, 137, 11566.
Porous carbon nanofiber paper Amorphous ordered mesoporous	Not provided Not provided	Not provided Not provided	270 mAh g^{-1} at 0.2 A g^{-1} 307 mAh g^{-1} at 0.05 A g^{-1}	87% after 1200 cycles at 0.2 A g^{-1} 70% after 1200 cycles at 1 A g^{-1}	J. Mater. Chem. A 2017, 5, 19237. Adv. Energy Mater. 2017, 1701648.
carbon Hard carbon microspheres Na ₂ Ti ₃ O ₇	80: 10: 10 70: 20: 10	2.0 1.0	250 mAh g^{-1} at 0.028 A g^{-1} 130 mAh g^{-1} at 1.04 A g^{-1} 107.8 mAh g^{-1} at 0.1 A g^{-1} after 20 cycles	83% after 100 cycles at 0.028 A g^{-1} 90.9% and 82.5% after 200 and 1555 cycles at 0.1 A g^{-1}	Adv. Energy Mater. 2016 , 6, 1501874. ACS Appl. Mater. Interfaces 2018 , 10,
N-doping few- layered graphene	70: 20: 10	1.1–1.4	300 mAh g^{-1} at 0.1 A g^{-1}	73% after 100 cycles at 0.1 A g^{-1}	37974. ACS Nano 2016 , 10, 9738.

Table S2.Impedance parameters and K ion diffusion coefficients of the various $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes electrodes at the different state.

Sample (Co ₉ S ₈ /NSC@MoS ₂ @NSC nanoboxes)	$R_{\rm s}\left(\Omega ight)$	$R_{ct}\left(\Omega ight)$	$\sigma \left(\Omega \ { m s}^{-0.5} ight)$	$D (\mathrm{cm}^2 \mathrm{s}^{-1})$
Before cycle	4.36	580	3.78	3.64×10 ⁻¹⁰
After the 50 cycles	6.79	642	1.64	3.34×10 ⁻⁹
After the 100 cycles	8.05	694	1.96	2.58×10 ⁻⁹

The calculation of K ion diffusion coefficient. The K ion diffusion coefficients of various $Co_9S_8/NSC@MoS_2@NSC$ nanoboxes electrodes at the different state can be calculated by the following classical equations:

$$Z = R_s + R_{\rm ct} + \sigma \omega^{-1/2} \tag{1}$$

$$D = R^2 T^2 / (2A^2 n^4 F^4 C^2 \sigma^2)$$
⁽²⁾

where Z, ω , R, T, A, n, F, and C are the real part of the impedance, the angular frequency in the lowfrequency region, the gas constant, the absolute temperature, the real surface area of Co₉S₈/NSC@MoS₂@NSC, the number of charge transfer, the Faraday constant, and the bulk concentration, respectively, and σ refers to the Warburg coefficient, which is relative to Z'- $\omega^{-1/2}$ (eq 1) and can be determined from the low frequency region of the Nyquist plots (Figure S14).

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2.4 Carbon-encapsulated Fe₂VO₄ nanopeapods for K-ion batteries

This is the peer reviewed version of the following article: Confined $Fe_2VO_4 \subset$ nitrogen-doped carbon nanowires with internal void space for high-rate and ultrastable potassium-ion storage, which has been published in final form at <u>https://doi.org/10.1002/aenm.201902674</u>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

Confined Fe₂VO₄⊂Nitrogen-Doped Carbon Nanowires with Internal Void Space for High-Rate and Ultrastable Potassium-Ion Storage

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Abstract

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Developing low-cost, high capacity, high rate and robust earth-abundant electrode materials for energy storage is critical for the practical and scalable application of advanced battery technologies. Herein, we report the first example of synthesizing one-dimentinal peapod-like bimetallic Fe₂VO₄ nanorods confined in N-doped carbon porous nanowires with internal void space (Fe₂VO₄ \subset NC nanopeapods) as a high-capacity and stable anode material for potassium ion batteries (KIBs). The peapod-like Fe₂VO₄ \subset NC nanopeapods heterostructures with interior void space and external carbon shell efficiently prevent the aggregation of the active materials, facilitate fast transportation of electrons and ions and

accommodate volume variation during the cycling process, which substantially boost the rate and cycling performance of Fe₂VO₄. The Fe₂VO₄ \subset NC electrode exhibits high reversible specific depotassiation capacity of 380 mAh g⁻¹ at 100 mA g⁻¹ after 60 cycles, and remarkable rate capability as well as long cycling stability with a high capacity of 196 mA h g⁻¹ at 4 A g⁻¹ after 2300 cycles. The first-principles calculations reveal that Fe₂VO₄ \subset NC nanopeapods have high ionic/electronic conductivity characteristics and low diffusion barriers for K⁺-intercalation. This study opens up new way for investigating high capacity metal oxide as high rate and robust electrode materials for KIBs.

Keywords: Fe₂VO₄ nanowire; anode materials; heterostructure; electrochemical property; potassium-ion battery

Introduction

The demand for low-cost, green energy storage system with high energy density, high rate capability and superior stability is highly urgent with the rapid consumption of fossil fuels and the increasing requirement for advanced electronic products and smart public facilities.^[1-6] The well-developed lithium-ion battery (LIB) technology now confronts the rising crises of the limited lithium resources and the unaffordable price. Alternatively, novel energy storage techniques, including sodium-ion batteries (NIBs), potassium-ion batteries (KIBs), magnesium-ion batteries (MIBs) and aluminum-ion batteries (AIBs), are getting numerous attentions due to the natural abundance and low cost of the metal resources and great progresses have been achieved in recent years.^[7-21] Among the various battery technologies, KIBs is considered as one of the most promising battery technologies towards large scale energy storage systems, benefiting from its similarity of electrochemical reaction with mature LIBs, higher safety than LIBs and NIBs, lower reduction potential and faster ion transport kinetics than NIBs and higher energy density compared to MIBs and AIBs.^{[8,19-} ^{25]} However, it is still a challenge to investigate suitable electrode materials for KIBs with satisfactory performance. Although a few materials have been successfully explored as electrode materials, for instance, carbonaceous materials, Bi and alloys as anode and prussian blue, 3,4,9,10-perylene-tetracarboxylicacid-dianhydride (PTCDA) as cathode for KIBs, they still have great potentials to improve the electrochemical performance to achieve practical applications.^[26-43] Among them, the carbon-based anode materials with the capacities in the range from 190 to 340 mAh g⁻¹ have been widely studied.^[31-37] However, the graphitic carbon in KIBs have poor cycling stability and unsatisfying rate capability, which are derived from the dramatic volume variation and lower crystallinity of graphite during repetitive cycling. Besides the rapid capacity fading, there is another critical issue hampered the application of KIBs and need to be enhanced urgently: a low initial Coulombic efficiency (CE, 20%-50%) is often observed in KIBs for carbon-based anodes, which is mainly triggered by the irreversible decomposition of electrolyte and subsequent formation of unstable solid-electrolyte interface (SEI) layer on the electrode surface. Hence, it is significant to prosper feasible electrode materials for KIBs with unique buffered structure toward high energy density and excellent cycling stability as well as superior rate capability.

Transition metal compounds have been widely used as promising electrode materials for LIBs and NIBs which exhibit outstanding electrochemical capacity.^[44-48] Among the transition metal compounds, transition metal vanadate, such as $Fe_x VO_y$, is attracting tremendous interests recently due to the natural abundance of raw materials, higher electrochemical activity than single metal oxide, high theoretical capacity benefiting from the multivalent vanadium and the multielectron transfer process, and the relatively robust structural maintenance during the cycling process resulting from strong V-O bonds.^[49-51] Yang et al. first presented the surprisingly good electrochemical performance of Fe₂VO₄ for LIBs which synthesized by a solid-state method.^[49] Luo et al. showed that the prepared Fe₂VO₄ porous microparticles exhibited high electrochemical performance delivering a high capacity of 799 mAh g^{-1} at 0.5 A g^{-1} for LIBs and a high capacity of 382 mAh g^{-1} at 1 A g^{-1} for NIBs.^[50] Nevertheless, to the best of our knowledge, the investigation of bimetallic element oxides as electrode for KIBs is rarely reported. When we prepare the manuscript, Niu et al. report their results that applying amorphous FeVO₄ as anode for KIBs. Although the amorphous FeVO₄ shows fast rate ability of ~180 mAh g^{-1} at 2 A g^{-1} and relatively stable cycling, the amorphous micro-particles synthesized by the ball-milling method still inevitably face the challenges of the severe aggregation, the low ionic and electric conductivity as well as the large volume expansion and pulverization/inactivation during long-time cycling.^[52] To resolve these issues, it would be an effective strategy to develop stable nanostructured transition metal vanadate based hybrid nanostructure to furthur boost its electrochemical performance for KIBs.

In this work, we report a facile process to synthesize one-dimentinal (1D) peapod-like Fe_2VO_4 nanorods confined in N-doped carbon porous nanowires with internal void space ($Fe_2VO_4 \subset NC$ nanopeapods) for advanced KIBs. The unique Fe_2VO_4 based hybrid nanostructure provides substantial active site for electrochemical reactions and remarkably shortens the ions and electrons diffusion paths. The external carbon shell and the internal void space of $Fe_2VO_4 \subset NC$ nanopeapods can prevent the aggregation of the active materials,

release mechanical stress-strain and accommodate volume variation during the cycling process, while enhance the whole conductivity and stablize the solid electrolyte interface (SEI) membrane formation. As a consequence, the as-synthesized Fe₂VO₄ \subset NC nanopeapods exhibited a high reversible specific depotassiation capacity of 380 mAh g⁻¹ at 100 mA g⁻¹ after 60 cycles, and exceptional cycling stability as well as superior rate capability (as high as 196 mA h g⁻¹ at 4000 mA g⁻¹ after 2300 cycles). By combining experimental characterizations and theoratical calculation, we reveal that Fe₂VO₄ \subset NC nanopeapods go through an interclation reaction followed by conversion reactions. Fe₂VO₄ \subset NC nanopeapods and its K-intercalated phase both have good electronic and ionic transportation properties, making it promising potassium anode material.

Results and Discussion

The $Fe_2VO_4 \subset NC$ nanopeapods were prepared as illustrated schematically in Figure 1a (see Experimental Section in the Supporting Information for details). In brief, the uniform one-dimensional FeVO₄·1.1H₂O nanowires with tiny diameter (~180 nm) and smooth surface were first fabricated as precursor through a facile one-pot hydrothermal method by using $FeCl_3 \cdot 6H_2O$ and NH_4VO_3 as the starting materials (Figure S1a&S1b). The X-ray diffraction (XRD) pattern of the sample (Figure S1c) can be well indexed to FeVO₄·1.1H₂O, and the sample shows a low crystalline degree. The as-prepared FeVO₄·1.1H₂O nanowires mixed with different mass ratios of FeVO₄·1.1H₂O to dopamine were dispersed in aqueous solution under stirring so that dopamine could automatically coat on the surface of FeVO₄·1.1H₂O nanowires and could undergo pH-induced self-polymerization under weak alkaline condition to form a polydopamine-shell on the surface of FeVO₄·1.1H₂O nanowires (Figure S2). Figure 2a&2b&S3 show field-emission scanning electron microscopy (FESEM) images of the Fe₂VO₄⊂NC nanowires at different mass ratios of FeVO₄·1.1H₂O and dopamine during the carbonization process in an inert gas. We were amazed to find that the FeVO₄·1.1H₂O precursor nanowires were broken into small Fe₂VO₄ nanocrystals with increasing the mass ratio of FeVO₄·1.1H₂O and polydopamine to 5:4 (Figure 2a&2b), and the peapod-like N-doped carbon-encapsulated Fe₂VO₄ heterostructures with large internal void space were formed during the calcination process.

The detailed morphologies and microstructures of the as-obtained $Fe_2VO_4 \subset NC$ nanopeapods were investigated using FESEM, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) techniques. As shown in **Figure 2a&2b**, the obtained $Fe_2VO_4 \subset NC$ nanopeapods are highly uniform with relatively rough surface and

diameter of around 210 nm. These peapod-like nanowires are intertwined in 3D conductive network, providing fast transportation path of electrons. Compared with pure Fe₂VO₄ dense microparticles (Fe₂VO₄-DMP, Figure 1a&S4), the carbon shell in Fe₂VO₄⊂NC nanopeapods suppresse the undesired particle growth and self-aggregation during the thermal treatment, resulting in small grain size.^[53] The TEM image in Figure 2c indicates that a large amount of smaller Fe₂VO₄ nanoparticles are well-confined in porous N-doped carbon nanotubes. The individual view of $Fe_2VO_4 \subset NC$ nanowires (Figure 2d) clearly displays the unique peapod-like heterostructure with large internal void space, which is thermally stable without structural collapse. The thickness of the carbon shell is determined to be ~15 nm. High-resolution transmission electron microscope (HRTEM) images of $Fe_2VO_4 \subset NC$ nanopeapods (Figure 2e&2f) indicate that the crystalline nanoparticles of Fe₂VO₄ were encapsulated into the carbon shell rather than exposed on the outer surface, while Fe₂VO₄ crystallinity was verified by the lattice spacing of 0.30 nm which was matched well with the (220) crystallographic plane of the cubic Fe₂VO₄. In addition, the HRTEM image (Figure 2f) also reveals that N-doped carbon consists of locallyordered nano-crystallites and fingerprint-like twisted wrinkles, which could produce plenty micropores at sub-nanometer scale and provide massive surface defects, facilitating the electrochemical insertion/extraction of K ions and consequently improving its rate capability.^[54] The single crystal character of the Fe₂VO₄ nanocrystallite was also identified by the sharp selected-area electron diffraction (SAED) spots (Figure 2g). The line-scan EDX spectra of the $Fe_2VO_4 \subset NC$ nanopeapods also strongly demonstrates that the shell is N-doped carbon (Figure 2h&2i), in accordance with the results from above HRTEM observation. The corresponding EDX mapping images (Figure 2j) show the homogeneous Fe, V, O, C and N element distributions in the nanowire, which further verify the role of N-doped-carbon acts as a protective shell to keep the structural stability and form a continuous conductive network. These results further indicate the formation of $Fe_2VO_4 \subset NC$ nanopeapods.



Figure 1. (a) Schematic illustration of the preparation process of the $Fe_2VO_4 \subset NC$ nanopeapods and the Fe_2VO_4 dense microparticles (Fe_2VO_4 -DMP). (b) Schematic illustrations for the potassiation behaviors of $Fe_2VO_4 \subset NC$ nanopeapods and Fe_2VO_4 -DMP as anode materials for KIBs. Pure Fe_2VO_4 -DMP suffer from great volume expansion and pulverization upon repeated cycling, leading to fast capacity fading. The heterostructured $Fe_2VO_4 \subset NC$ nanopeapods can provide enough interior void space to fully accommodate the volume variation of Fe_2VO_4 during cycles without cracking of carbon coating, ensuring the structural integrity.

To get further insight into the microstructure of the as-prepared Fe₂VO₄ \subset NC nanopeapods, XRD and Raman spectroscopy measurements were performed. As shown in **Figure 3a**, the diffraction peaks of Fe₂VO₄ \subset NC nanopeapods are much broader than that of pure Fe₂VO₄-DMP, which could be related to the presence of carbon shell that inhibits the growth of Fe₂VO₄ crystalline. The peak broadness is indicative of the significantly small grains in final Fe₂VO₄ \subset NC nanopeapods. The broad diffraction peak appeared at ~24.2° can be indexed to the graphitic carbon (002) plane. An interesting point for the (002) plane of graphitic carbon is that an expanded interlayer spacing of 0.38 nm is observed (**Figure 2f**), which is larger than that of graphite (0.34 nm) and could provide a robust scaffold to buffer the volume fluctuation during the fast potassiation and depotassiation processes of K ions.^[55] The expanded carbon layers can be ascribed to

the insertion of nitrogen doping groups in the carbon matrix by regulating the electronic structure. According to the Bragg equation, the (002) interlayer spacing can be calculated to be ~ 0.377 nm, which is in accordance with the result of HRTEM (Figure 2f). Besides, the prominent diffraction peaks located at ~30.1°, ~35.5°, ~43.1°, ~57.2°, and ~62.7° can be assigned to the (220), (311), (400), (511), and (440) planes of pure cubic Fe₂VO₄ phase, respectively (JCPDS card No. 01-075-1519).^[50] However, it is noteworthy that pure $Fe_2VO_4 \subset NC$ cannot be achieved when calcined at higher temperature (*e.g.*, 800 °C, Figure S5). In the Raman spectrum of the Fe₂VO₄⊂NC nanopeapods, two strong peaks centered at around 1343 cm⁻¹ and 1585 cm⁻¹, corresponding to the disorder/defectinduced D-band and in-plane vibrational G-band, respectively (Figure 3b).^[5] The intensity ratio of the D to G band (I_D/I_G) for the Fe₂VO₄ \subset NC nanopeapods is calculated to be 1.16, indicating a high defect concentration induced by nitrogen doping, which is derived from the intrinsic nitrogen in dopamine and beneficial for the potassium storage. The specific surface area and porous structure of the Fe₂VO₄⊂NC nanopeapods were characterized by measuring the nitrogen adsorption-desorption isotherms. As exhibited in Figure 3c, the typical hysteresis loop in the isotherm curve indicates the existence of a multimodal pore structure in the Fe₂VO₄⊂NC nanopeapods, and its Brunauer-Emmett-Teller (BET) specific surface is measured to be 192.6 m² g⁻¹, which is 6.9 times larger than that of Fe₂VO₄-DMP (28.0 m²) g^{-1} , Figure S6). The detailed pore-size distribution was analyzed based on the Barrett-Joyner–Halenda (BJH) method in the inset in Figure 3c. The heterostructured Fe₂VO₄⊂NC nanopeapods have a multimodal mesopore size distribution of big cavity (>10 nm) from the inner void-space between adjacent Fe₂VO₄ nanoparticles and small-pore (<4 nm) from the carbon shell. The unique peapod-like highly porous N-doped carbon-encapsulated Fe₂VO₄ nanoarchitecture can effectively increase the electrode/electrolyte interface contact area, facilitate the electron/K-ion flux transport, provide sufficient reaction active sites, improve the electronic conductivity, giving rise to significant pseudocapacitive effects during the electrochemical reaction and abundant internal buffering space to accommodate the severe volume variation during repetitive cycling. Therefore, satisfactory electrochemical performance and superior K-ion storage efficiency of the Fe₂VO₄⊂NC nanopeapods can be anticipated.



Figure 2. (a, b) SEM images, (c, d) TEM images, (e, f) HRTEM images, and (g) SAED pattern of the $Fe_2VO_4 \subset NC$ nanopeapods. The cross-sectional compositional line-scan profiles (h, i) and EDS mapping images (j) of the $Fe_2VO_4 \subset NC$ nanopeapods.

The content of carbon in Fe₂VO₄ \subset NC nanopeapods is determined to be ~17.3 wt% based on the thermogravimetric analysis (TGA, **Figure S7**). The inductively coupled high frequency plasma (ICP) result reveals that the ratio of molarity of Fe and V is about 1.96:1 in Fe₂VO₄ \subset NC nanopeapods, well consistent with the expected value of Fe₂VO₄ (2:1). The X-ray photoelectron spectra (XPS) was used to evaluate the chemical compositions and elemental valence states of Fe₂VO₄ \subset NC nanopeapods. XPS full survey profile of Fe₂VO₄ \subset NC nanopeapods (**Figure S8a**) reveals the coexistence of Fe, V, O, C and N elements. In the high-resolution C 1s spectra (**Figure S8b**), three characteristic peaks centered at 284.5 eV, 285.4 eV and 288.0 eV can be attributed to C=C, C=N and C=O coordination bonds, respectively, which further demonstrate that N is successfully doped into the lattice of carbon structure.^[56] The N 1s core level XPS spectrum in Fe₂VO₄ \subset NC nanopeapods can be fitted with three peaks centered at around 398.3, 400.6, and 401.6 eV, assigned to pyridinic-N, pyrrolic-N, and graphitic-N, respectively (**Figure 3d**).^[57] Among these N pieces, the content percentage of pyrrolic-N is determined to be 39.9%, being higher than those of pyridinic-N (32.2%) and graphitic-N (27.9%), which agree well with the I_D/I_G ratio of Raman spectra (**Figure 3b**). The high content percentages of pyridinic-N and graphitic-N can bring a large amount of defects, improve the electronic conductivity, facilitate K ion and electron diffusion, and create additional electrochemically active sites to enhance the rate performance. As illustrated in **Figure 3e**, two peaks located at 515.6 and 523.1 eV are indexed to the spin-orbit splitting of the V $2p_{3/2}$ and V $2p_{1/2}$, respectively, demonstrating the existence of V³⁺ in the Fe₂VO₄⊂NC nanopeapods. In the case of the Fe 2p spectra shown in **Figure 3f**, two peaks with the binding energies of 711.5 eV (Fe $2p_{3/2}$) and 724.3 eV (Fe $2p_{1/2}$) correspond to the typical characteristics of Fe³⁺, while those observed at 709.8 eV in Fe $2p_{3/2}$ and 722.9 eV in Fe $2p_{1/2}$ could be associated with Fe²⁺ state.



Figure 3. (a) XRD patterns of the $Fe_2VO_4 \subset NC$ nanopeapods and the pure Fe_2VO_4 -DMP. (b) Raman spectrum of the $Fe_2VO_4 \subset NC$ nanopeapods. (c) N_2 adsorption-desorption isotherms of the heterostructured $Fe_2VO_4 \subset NC$ nanopeapods. The *inset* of (c) shows the corresponding pore-size distribution curve. XPS high-resolution spectra of the (d) N 1s, (e) V 2p and (f) Fe 2p of the heterostructured $Fe_2VO_4 \subset NC$ nanopeapods.

The potassium storage performances of Fe₂VO₄⊂NC nanopeapods and Fe₂VO₄-DMP were evaluated in half-cells with metallic K as both counter and reference electrodes. As depicted in Figure 4a&S9, the corresponding cyclic voltammograms (CV) profiles of $Fe_2VO_4 \subset NC$ and Fe_2VO_4 -DMP electrodes were characterized in the potential range of 0.01 and 2.6 V (vs. K/K⁺) at a sweeping speed of 0.1 mV s⁻¹. Both specimens exhibit similar redox peaks in the second cycle. However, Fe₂VO₄⊂NC nanopeapods electrode demonstrates larger area, sharper current peaks, and less polarization at the same scan rate, all of which suggest that the K-ion storage kinetics is more facile in Fe₂VO₄⊂NC nanopeapods electrode. In the first cathodic sweep, three reduction peaks located at 1.36, 0.70, and 0.37 V can be clearly observed (Figure 4a). The two well-defined peaks centered at 1.36 and 0.70 V can be attributed to the formation of nonstoichiometric K⁺-intercalated compounds and further conversion formation of VO and FeO, respectively, while the broad reduction peak located at ~0.01–0.55 V can be well associated with the reduction of Fe^{2+} to metallic Fe and the formation of a stable SEI layer on the electrode surface.^[58] During the following anodic scan, a series of anodic peaks are observed between 1.53 and 2.13 V which can be ascribed to the reversible extraction of K ions in the product. The subsequent CV profiles of Fe₂VO₄⊂NC are slightly different from the initial one, which is attributed to the enhanced electrochemical reaction kinetics and the effective utilization of active materials stemming from the microstructure change during the first cycle. Note that except the first scan, the subsequent CV curves almost overlap, indicative of high reversibility of electrochemical reaction of $Fe_2VO_4 \subset NC$ nanopeapods.

Figure 4b shows the galvanostatic discharge/charge profiles of Fe₂VO₄ \subset NC electrode at a current density of 100 mA g⁻¹ in a potential window of 0.01 and 2.6 V (*vs.* K/K⁺). The pronounced platforms during the discharge process are well matched with the results of the CV profiles, further corroborating the multistep electrochemical potassiation/depotassiation processes of the electrode. The Fe₂VO₄ \subset NC electrode delivers a high initial potassiation and depotassiation capacities of 648 and 394 mAh g⁻¹, respectively, with a CE of 60.8%. The irreversible capacity loss in the first-cycle can be assigned to the occurrence of side reactions on the electrode surfaces due to SEI layer formation, a common phenomenon amongst transition metal-based anode materials.^[59-61] Actually, to boost the initial CE of KIBs, prepotassiation is an effective strategy, besides, it is of importance to select appropriate electrolyte system as it facilitates the stabilization of electrode/electrolyte interface by constructing a favorable SEI layer on the electrode surface.^[36,37] The highly stable SEI layer formed on the electrode facilitated the improvement of electrochemical reversibility to achieve ultrahigh coulombic efficiencies. Except for the initial few cycles, the potassiation and depotassiation curves for the 5th, 60th and 100th cycles almost coincide with each other, indicating a high reversibility character of Fe₂VO₄ \subset NC in K-ion storage. For reference, the discharge and charge capacities of Fe₂VO₄-DMP electrode at 100 mA g⁻¹ after 20 cycles are 336 and 252 mAh g⁻¹ (**Figure S10**), respectively, corresponding to a low CE of 75.1%, which is due to the sluggish reaction kinetics and poor reversibility towards K-ion storage.



Figure 4. (a) CV curves for the Fe₂VO₄ \subset NC nanopeapods electrode in the first three cycles at a scan rate of 0.1 mV s⁻¹. (b) Charging/discharging profiles for the Fe₂VO₄ \subset NC nanopeapods at different cycles at 100 mA g⁻¹. (c) Rate capabilities of the Fe₂VO₄ \subset NC nanopeapods and the pure Fe₂VO₄-DMP electrodes at various current densities from 100 to 4000 mA g⁻¹. (d) Cycling stability and Coulombic efficiency (CE) of the Fe₂VO₄ \subset NC nanopeapods electrode at 200 mA g⁻¹. (e) The cycling performance and CE of the Fe₂VO₄ \subset NC nanopeapods electrode for 2300 cycles at 4000 mA g⁻¹. (Note that all the specific capacity values were calculated based on the total mass of the Fe₂VO₄ \subset NC nanopeapods).

Figure 4c compares the rate capability between the $Fe_2VO_4 \subset NC$ electrode and Fe_2VO_4 -DMP electrode at varying current densities ranging from 100 to 4000 mA g⁻¹. For $Fe_2VO_4 \subset NC$ electrode, upon continuous cycling under variable current densities, the corresponding reversible depotassiation capacities dropped only marginally on doubling the rates. As the current density increases from 100, 200, 500, 1000 to 2000 mA g⁻¹, the Fe₂VO₄ \subset NC electrode is capable to deliver reversible specific depotassiation capacities of 389, 368, 323, 284, and 228 mAh g⁻¹ after each 20 cycles, respectively, which is much higher than for the Fe₂VO₄-DMP, revealing the excellent kinetics of the Fe₂VO₄ \subset NC. Even when measured at a ultralarge current densities of 4000 mA g⁻¹, significantly high depotassiation capacity of 159 mAh g⁻¹ (71.3% of its original capacity at 2000 mA g⁻¹) are delivered after 120 cycles, manifesting that the Fe₂VO₄ \subset NC nanopeapods electrode shows not only an impressive specific capacity but also an excellent power capability. Moreover, when the current density is switched back to 200 mA g⁻¹, the depotassiation capacity quickly increases to 326 mAh g⁻¹, indicating the exceptional reversibility.

The cycle performance and corresponding CE of the Fe₂VO₄⊂NC nanopeapods electrode under a low current density of 200 mA g^{-1} are shown in Figure 4d. The specific depotassiation capacities increase gradually from 365 to 414 mAh g⁻¹ at the end of 233 cycles, ascribed to the electrochemical activation process of the electrode.^[59] After that, the Fe₂VO₄⊂NC nanopeapods electrode shows negligible capacity fading over 400 cycles and the corresponding CE stays close to unity during the entire course of measurement after the first few cycles. Further tests of cycling characteristic for the Fe₂VO₄⊂NC electrode over 500 cycles under varied current densities also indicate its remarkable structural stability and reversibility (Figure S11), derived from the well-designed structure and the stable SEI film constructed on the electrode surface. As comparison, the Fe₂VO₄-DMP electrode demonstrates poor cycling performance with substantial capacity attenuation (Figure S12), highlighting the contribution of N-doped-carbon acts as a skeleton to maintain the electrode structural stability (Figure 1b). To further evaluate the cycling stability of the heterostructured Fe₂VO₄⊂NC nanopeapods electrode, a long-term cycling test was performed. As indicated in Figure 4e, cycling $Fe_2VO_4 \subset NC$ electrode at 4000 mA g⁻¹ gradually enhances the specific depotassiation capacity of Fe₂VO₄⊂NC initially from 174 to 196 mAh g^{-1} at the end of 2300 cycles, probably due to the increasing wetting of the electrode film by the electrolyte.^[59,62] The corresponding CE of Fe₂VO₄⊂NC quickly reaches to near 100% after the first several cycles and keeps the high value afterwards, suggesting a superior reversibility during potassiation/depotassiation process. Furthermore, the excellent structural integrity of Fe₂VO₄⊂NC electrode is also further confirmed by the unchanged ex-situ SEM and TEM images even after 500 cycles at an ultrahigh current density of 2000 mA g⁻¹ (Figure S13). As listed in Table S1, the electrochemical performances of Fe₂VO₄ \subset NC nanopeapods electrode are better than of many other state-of-the-art anodes for KIBs, demonstrating attractive properties for an energy system. The outstanding electrochemical performance of Fe₂VO₄ \subset NC electrode could be largely attributed to the unique structural design (Figure 1b). The peapod-like heterostructure with large internal void space offers abundant room to effectively buffer the severe volume expansion for Fe₂VO₄ nanoparticles based on the conversion reaction during repetitive cycling, thus alleviating the pulverization issue. In addition, the interconnected porous N-doped carbon shells not only prevent the aggregation of embedded active Fe₂VO₄ nanoparticles, but also provide highly efficient diffusion pathways for electrons and ions, enabling remarkable rate capability and excellent cycling performance.

To fully clarify the electrochemical reaction kinetics of the as-prepared Fe₂VO₄⊂NC nanopeapods electrode, a series of measurements were carried out. Typically, CV curves at stepped scan rates from 0.1 to 1.1 mV s^{-1} can be used to evaluate the redox pseudocapacitance-like contribution. As shown in Figure S14a, the CV profiles of the Fe₂VO₄⊂NC electrode exhibit similar shapes with distinct redox peaks and small overpotential under the increasing scan rate, demonstrating the high reversibility and fast reaction kinetics for potassium storage. The relationship of the peak current (i) and the scan rate (v) obeys a power law: $i = av^{b}$, where a and b are the adjustable parameters, and bvalue can be extracted by the slope of the log(i) vs. log(v) plot (Figure S14b). The b-value of 0.5 represents a solid-state diffusion-controlled behavior, while 1.0 denotes the ideal pseudocapacitive effect. As illustrated in Figure S14b, the b-value of the four redox-peak are 0.68, 0.82, 0.76 and 0.75, respectively, manifesting that the K-ion storage kinetics of Fe₂VO₄⊂NC is a combination of diffusion- and pseudocapacitive-controlled mechanism. The contributions to the capacity can be further quantified by the equation i (V) = $k_1 v^{0.5}$ + k_2v , in which the $k_1v^{0.5}$ and k_2v correspond to diffusion-controlled process and pseudocapacitive behavior, respectively.^[59,63] With the increase of the scan rates, the pseudocapacitive contribution ratio gradually improves and the value reaches 90.2 % at a relatively high scan rate of 1.1 mV s⁻¹ (Figure S14c). Additionally, the results of pseudocapacitive contribution at different scanning rates are summarized in Figure 5a. The outstanding pseudocapacitive behaviors of Fe₂VO₄⊂NC nanopeapods electrode should be attributed to the unique nanoarchitecture increases the contact area with electrolyte and

provides more K-ion adsorption sites, which are favorable for the fast K storage kinetics and outstanding rate capability.



Figure 5. (a) Bar chart shows the percentages of pseudocapacitive contributions at different sweep rates. (b) Nyquist plots of the Fe₂VO₄ \subset NC nanopeapods electrodes after different cycles (inset: selected equivalent circuit). (c) Reaction resistance during potassiation/depotassiation processes of the Fe₂VO₄ \subset NC nanopeapods electrode in KIBs. (d) Ex situ XRD patterns of the Fe₂VO₄ \subset NC nanopeapods electrodes at the different state (D: state of discharge, C: state of charge). HRTEM images of the Fe₂VO₄ \subset NC nanopeapods electrodes at the (e) fully discharged (0.01 V vs. K⁺/K) and (f) fully charged (2.6 V vs. K⁺/K) state.

Electrochemical impedance spectroscopies (EIS) of the Fe₂VO₄ \subset NC nanopeapods electrode in different cycles are measured to investigate the in-depth reason of the superior electrochemical performances, and the corresponding Nyquist plots are shown in **Figure 5b**. The resultant EIS spectra are similar in profile, composed of a medium-to-high frequency depressed semi-circle and a low frequency linear tail, in which the former is related to interfacial charge-transfer resistance (R_{ct}), and the latter is ascribed to the process of semi-infinite Warburg diffusion.^[59] The inset of **Figure 5b** discloses the corresponding equivalent circuit model of the EIS spectrum. The fitting results are

provided in **Table S2**. It can be found that the R_{ct} -value of the Fe₂VO₄ \subset NC nanopeapods electrode gradually decrease and keeps a low value with continuous cycling, which can be explained by the enhanced reaction kinetics and effective utilization of active materials originating from the microstructure change, and formation of a stable SEI film after the first cycle. The K-ion diffusion coefficients of Fe₂VO₄ \subset NC nanopeapods electrode are maintained to be 2.16×10^{-10} cm² s⁻¹ before cycle, 3.07×10^{-10} cm² s⁻¹ after the 50 cycles, and 1.09×10^{-9} cm² s⁻¹ after the 100 cycles (Figure S15&Table S2), reflecting the stable and fast K ions electrochemical reaction kinetics within bulk crystals through continuous cycling. This is probably due to the expanded carbon-shell interlayer distance filling with the high concentrated K ions, leading to high localized charge-transfer and the small size of Fe₂VO₄ can shorten the electrons/K ions shuttling paths, thus enabling remarkable rate performance.

To further understand the electrochemical kinetic features of the K-ion storage in the Fe₂VO₄⊂NC nanopeapods electrode, the galvanostatic intermittent titration technique (GITT) measurement was performed with a pulse current of 100 mA g^{-1} for 20 min between 2 h rest intervals to obtain the thermodynamic quasi-equilibrium potential. A series of quasiequilibrium potential plateaus in the first-cycle are observed in Figure S16, further evidencing a multistep potassiation/depotassiation process of Fe₂VO₄⊂NC nanopeapods. As shown in Figure S16, a large quasi-thermodynamic potential hysteresis between K deintercalation and intercalation was observed, which can be explained by the large strain/stress during K intercalation/deintercalation processes. The corresponding reaction resistance at varying potassiation/depotassiation levels was obtained by dividing the overpotentials by the pulse current applied in the GITT test, as shown in Figure 5c. During the potassiation process, the reaction resistance in Figure 5c shows a fluctuant curve that gradually decreases, then shows moderate growth, and finally descends to its lowest value during K-ion uptake process. The reduction in reaction resistance can be explained by the increased conductivity caused by the K ions insertion, while the value gets bigger can be assigned to metallic phase formation upon discharge. During the depotassiation processes, the curves are nearly opposite to those for the potassiation process, which can be attributed to the decreasing electric conductivity and worsening contact resulted from the volume contraction. The reaction resistances of Fe₂VO₄⊂NC nanopeapods are consistently smaller than some previously reported anodes for KIBs, ^[64,65] further verifying the attainment of the fast and highly reversible energy storage process.

To deeply understand the detailed working mechanisms of Fe₂VO₄⊂NC nanopeapods, the ex-situ XRD and HRTEM were conducted after 50 cycles to identify the possible phase transformations. Figure 5d indicates the corresponding ex-situ XRD patterns of the $Fe_2VO_4 \subset NC$ anode at selected depotassiation/potassiation states in the 51th cycle. The Cu peaks in each spectrum are origin from the current collector. After discharge to 1.0 V, the peak intensities of the Fe₂VO₄⊂NC phase decreased and the (220) and (311) reflections for Fe₂VO₄ \subset NC nanopeapods slightly shift to lower 2 θ angles are related to the formation of nonstoichiometric K⁺-intercalated compounds, indicating the expansion and distortion of lattice with the insertion of K ions. Similarly, the graphitic carbon (002) diffraction peak shifts to $2\theta \sim 23.9^\circ$, further verifying the potassiation reaction. When discharged to 0.50 V, the peaks of Fe₂VO₄⊂NC totally disappeared, and a series of new peaks appears: the ones located at 36.3° and 42.2° are respectively indexed to the (111) and (200) crystal planes of FeO, while reflections at 54.0° belongs to the peak of VO. However, taking into consideration the strong V-O bonding during the electrochemical process, obtaining metallic V will be difficult.^[35] Meanwhile, two additional diffraction peaks are observed at 25.4° and 29.4°, which can be derived from K₂O phase. Further discharging deeply to 0.01 V, the peaks of FeO are missing, and new diffraction peaks of the metallic Fe at 43.1° and 50.2° were found, indicating the occurrence of conversion reaction at the low voltage. When fully charged to 2.6 V, all the peaks of $Fe_2VO_4 \subset NC$ can be recovered, revealing a highly reversible structure evolution. The ex-situ HRTEM results also further confirm the reaction processes. When the electrode is discharged to 0.01 V, the lattice fringes with interlayer spacing of 0.21 nm is related to the (111) plane of the metallic Fe, while the interlayer distance of 0.35 nm correspond to the (111) plane of K₂O (Figure 5e). When fully charged to 2.6 V, the HRTEM image (Figure 5f) displays a clear lattice fringe of 0.48 nm, ascribed to the (111) plane of Fe₂VO₄, consistent with the *ex-situ* XRD results. It is worth noting that a thick K⁺-permeable stable SEI layer is formed on the edge of the electrode after the repetitive cycling, which can be related to the unique robust heterostructure performs dual functions on buffering additional volume changes of Fe₂VO₄ nanoparticles by inner voids and stabilizing SEI films using outer porous N-doped carbon shells (Figure 5f). In addition, the reaction mechanism is further confirmed by tracking the variations of the V element at fully discharged and charged states. For the fully discharged electrode, the V 2p spectrum can be well fitted by V^{2+} (Figure S17a). The absence of metallic V in above potassiation reaction, which proves our assumption. After full charge to 2.6 V, the peaks of the V 2p

signal shift back to the positions corresponding to V^{3+} (Figure S17b). Based on the above results, the reaction mechanism of Fe₂VO₄ is determined. Consequently, Fe₂VO₄ can achieve a six-electron reaction based on the equation of Fe₂VO₄ + 6K⁺ + 6e⁻ \leftrightarrow VO + 2Fe + 3K₂O.



Figure 6. (a) Schematic potassiation reaction mechanism of Fe_2VO_4 . The gold, red (big), purple, and red (small) spheres represent Fe, V, K, and O atoms, respectively. (b) Calculated voltage profile of Fe_2VO_4 . (c) The calculated K⁺ migration barrier in KFe₂VO₄ (d) Projected density of states of Fe_2VO_4 (upper) and KFe₂VO₄ (lower panel).

To get more insight into the essence of the superior K ions storage performance of $Fe_2VO_4 \subset NC$ nanopeapods, we performed density theory functional (DFT) calculations to investigate the reaction mechanism, ionic and electronic transport properties of Fe_2VO_4 . During the intercalation process, cations at 16d (octahedral) sites remain at their original positions, while half of Fe ions at 8a (tetrahedral) sites move to the nearby 16c interstitial (octahedral) sites. The other half of the 16c sites are occupied by the intercalated K. The formed intercalated phase has a rock-salt structure (**Figure S18**). Similar spinel to rock-salt transformation in intercalation process was also observed in the spinel Fe_3O_4 , which is an isostructure of Fe_2VO_4 , during lithium intercalation process. Based on our XRD results, the pristine Fe_2VO_4 structure is constructed based on a disordered-spinel structure (ICSD-31044). In this structure, half Fe occupies the tetrahedral 8*a* sites, while the other half Fe share the 16*d* octahedral sites with V. We ordered the arrangement of Fe and V at 16*d* sites and selected the one with lowest DFT energy as the ground state. Based on the estimated intercalation capacity, we also considered K-intercalated KFe₂VO₄ as an intermediate phase.

Here we used a rock-salt type host structure as a representative structure for the intercalated phase, as similar reaction path was found in other spinel prototype cathode material.^[66,67] The ground state structure of KFe₂VO₄ was determined using similar method as for Fe₂VO₄. For the conversion reaction products, FeO, VO, K₂O, and Fe were considered. We adopted the lowest energy structures of these four phases from Materials Projects database.^[68] The calculated reaction stages and voltage profile are shown in Figure 6a&6b. The first reaction is an intercalation reaction while the latter two are conversion reactions. The calculated reaction voltages are 0.56, 0.32 and 0.21 V (referenced to K/K⁺), respectively. Despite that the calculated reaction voltage are lower than our experimental results, the voltage profile qualitatively agrees with our electrochemical measurements. To study the ionic diffusion property K-intercalated Fe₂VO₄, we calculated the diffusion barrier in our representative structure KFe₂VO₄. Nudged Elastic Band (NEB) method were used and the diffusion pathway was constructed between two neighboring octahedral K sites. The diffusion barrier is about 0.8 eV (Figure 6c). Given that this is the diffusion barrier in bulk KFe₂VO₄, while our Fe₂VO₄ sample are nano-crystalline and are highly defected, we would expect our Fe₂VO₄ nanopeapods have a high ionic conductivity and can provide facile K ion transport. We further investigated the electronic transport properties of Fe₂VO₄ and KFe₂VO₄. Figure 6d shows the calculated density of states of Fe₂VO₄ (upper panel) and KFe₂VO₄ (lower panel). The calculated band gap of Fe₂VO₄ and KFe₂VO₄ are 0.9 and 1.5 eV, respectively. This shows that both materials are semi-conductors with good electronic conductivity. Based on the calculation results, we conclude that Fe₂VO₄ and its K-intercalated phase both have good electronic and ionic transportation properties, making it promising potassium anode material.

Conclusions

To summarize, one-dimentinal (1D) peapod-like Fe₂VO₄ nanorods confined in N-doped carbon porous nanowires with internal void space (Fe₂VO₄ \subset NC nanopeapods) have been successfully prepared by a facile approach without template assistance, and introduced as a novel promising anode material for KIBs. The unique peapod-like Fe₂VO₄ \subset NC nanopeapods heterostructures with interior void space can effectively increase the electrode/electrolyte contact area, offer sufficient accessible active sites, facilitate rapid transport of both electrons and K ions, give rise to significant pseudo-capacitive effects, inhibit particle self-aggregation during cycling, and help to retain the structural integrity during the repetitive depotassiation/potassiation processes. These important features make

Fe₂VO₄⊂NC electrode demonstrates remarkable electrochemical characteristics in term of high reversible specific depotassiation capacity (380 mAh g⁻¹ at 100 mA g⁻¹ after 60 cycles), excellent rate capability and splendid cycling stability (as high as 196 mA h g⁻¹ at 4000 mA g⁻¹ after 2300 cycles), making it a very attractive anode for high-performance KIBs. The first-principles calculations reveal that the Fe₂VO₄⊂NC nanopeapods electrode undergoes interclation and conversion reaction states. The material can provide facile ionic and electronic transport, which boosts its electrochemical performance. We expect that our strategy could be further extended to prepare other advanced electrodes with large volume variation for superior alkali-metal-ion storage performance for practical application in stationary energy storage systems.

Acknowledgements

C.Y. and F.L. contributed equally to this work. This work was financially supported by the National Natural Science Foundation of China (Grant No. 51571151, 51701139, 51671143 and U1601216), the Helmholtz Association, the China Scholarship Council (CSC) and was partially funded by the German Research Foundation, DFG (Project No. MA 5039/4-1).

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Supporting Information

Confined Fe₂VO₄⊂Nitrogen-Doped Carbon Nanowires with Internal Void Space for High-Rate and Ultrastable Potassium-Ion Storage

Experimental Section

Materials Preparation: First, the FeVO₄·1.1H₂O nanowires were prepared from FeCl₃·6H₂O and NH₄VO₃ through the solvothermal method. In a typical synthesis process, 0.2 mol of FeCl₃·6H₂O and 0.2 mol of NH₄VO₃ were dispersed in 60 mL deionized water with vigorous stirring. The resultant solution was then transferred into an autoclave, which was kept at 180 °C for 3 h. After the autoclave was cooled down to room temperature, the sample was obtained by centrifugal separation, wash with deionized water and ethanol, and then dried under vacuum at 50 °C for 10 h. For polydopamine coating, 50 mg of asobtained FeVO₄·1.1H₂O nanowires were dispersed in a 50 mL of 1×10^{-3} M Tris-buffer solution by ultrasonication for 0.5 h. Then, 40 mg of dopamine hydrochloride was added into the above solution, which was kept stirring for 12 h. The resultant product was collected by centrifugal separation, wash with deionized water for several times, and then dried in a vacuum oven at 80 °C overnight. Finally, peapod-like Fe₂VO₄⊂nitrogen-doped carbon nanowires were prepared through calcination treatment in N₂ atmosphere at 700 °C for 5 h with a heating rate of 2 °C min⁻¹. Fe₂VO₄⊂nitrogen-doped carbon nanowires were also synthesized under the same condiiton by changing different mass ratios of FeVO₄·1.1H₂O and dopamine to study the formation process of the peapod-like nanowire morphology.

Materials Characterization: The morphology and microstructure characterizations of the products were carried out through field-emission scanning electron microscopy (FESEM; JEOL, JSM-7500FA), transmission electron microscope (TEM; FEI, Tecnai G2 F20) and high-resolution transmission electron microscope (HRTEM, FEI, Tecnai G2 F20 S-TWIN, USA). Elements distribution was collected *via* the X-ray spectrometer attached to the TEM instrument. X-ray diffraction (XRD) was performed on Rigaku MiniFlexII with Cu Kα radiation ($\lambda = 1.5408$ Å) operating at 40 mA and 40 kV to determine the crystal structures of the samples. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Agilent 7500ce, USA) was used to determine the ratio of the metal ions. Thermogravimetric analysis (TGA, TA Instruments 2000) was conducted under air from 25 to 700 °C with a heating rate of 5 °C min⁻¹. Raman spectroscopy were performed using using LabRAM Aramis with an excitation laser wavelength of $\lambda = 532$ nm. The specific surface area and pore structure of the composite were analyzed by using a Brunauer–Emmett–Teller surface area analyzer (BET, Quantachrome NOVA 2200e, USA). X-ray photoelectron spectroscopy (XPS) spectra of samples were recorded using Thermo Escalab 250Xi with monochromatic Al Kα radiation to analyze the chemical states of the products to explore electrochemical reaction mechanism.

Electrochemical Measurements: Electrochemical measurements were evaluated by assembling CR2032-type coin cell assembled in an argon-filled glovebox with K metal foil as a counter electrode. The working electrodes were prepared by mixing the active material, carbon black and polyvinylidene fluoride (PVDF) in NMP solvent with a weight ratio of 80:15:5, then coated uniformly on a Cu foil with a mass loading of ~ 1.2 mg cm⁻². The resultant electrodes were dried at 80 °C under vacuum for overnight followed by compressed at 15 MPa. The whatman glass microfiber filters (Grade GF/F) were employed as the separator, and 0.8 M KPF₆ dissolved in an ethylene carbonate (EC) and diethyl carbonate (DEC) solution (EC: DEC = 1:1 by volume) was used as the electrolyte solution. The cells were aged for 6 h before measurements. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis were both operated using a CHI660B electrochemical workstation (Chenhua, Shanghai, China). The CV scanning rates were 0.1, 0.2, 0.4, 0.7 and 1.1 mV s⁻¹. EIS were tested with a frequency range from 100 kHz to 0.01 Hz and a potential amplitude of 5 mV. Galvanostatic charge/discharge tests and galvanostatic intermittent titration technique (GITT) measurements were performed on a LAND CT2001A multichannel battery testing system in the potential window of 0.01-2.6 V. During the GITT test, the assembled half-cell was first discharged and charged by applying a series of pulse current of 100 mA g⁻¹ for 20 min followed by an open-circuit relaxation interval of 2 h for each pulse to reach an equilibrium potential. To prepare the electrodes for the ex-situ SEM, TEM, HRTEM, XPS and XRD measurements, the working electrodes, obtained from the disassembled coin cells at various states, were washed with DEC more than 4 times to remove the residual electrolyte and then dried in a vacuum oven at 70 °C overnight to remove excess solvents.

Computational Methods. The density functional theory (DFT) calculations in this work were performed using the Vienna Ab initio Simulation Package (VASP)^[S1] within the projector augmented-wave approach,^[S2] and the Perdew–Burke–Ernzerhof (PBE) generalized gradient

approximation (GGA) functional was used.^[S3] We used a cutoff energy of 520 eV for the plane– wave basis set. The structure of Fe_2VO_4 used in DFT calculation is based on ICSD entry (collection ID: 31044), while the intercalated phase was constructed based on a rock-salt type host structure. Supercells with 4 formula units were constructed. Since the structures have disordered sites, we use the supercell program^[S4] to enumerate possible orderings and select the one with lowest DFT energy as the ground state structure. For all the calculated reaction energies and voltages neglected the contribution of the PV terms.



Figure S1. (a, b) SEM images and (c) XRD pattern of the FeVO₄·1.1H₂O nanowires.



Figure S2. SEM images of $FeVO_4 \cdot 1.1H_2O \subset$ dopamine precursors prepared with different mass ratios of $FeVO_4 \cdot 1.1H_2O$ and dopamine: (a) 5:1; (b) 5:2; (c) 5:4. (d) Photo of as-synthesized $FeVO_4 \cdot 1.1H_2O \subset$ dopamine precursor with the mass ratio of $FeVO_4 \cdot 1.1H_2O$ and polydopamine is 5:4.



Figure S3. SEM images of $Fe_2VO_4 \subset NC$ hybrids prepared with different mass of $FeVO_4 \cdot 1.1H_2O$ and dopamine: (a) 5:1; (b) 5:2. (c) Photo of as-synthesized $Fe_2VO_4 \subset NC$ nanopeapods annealed in an inert gas with the mass ratio of $FeVO_4 \cdot 1.1H_2O$ and polydopamine is 5:4.



Figure S4. SEM image of pure Fe₂VO₄ dense microparticles (Fe₂VO₄-DMP).



Figure S5. (a) XRD pattern, SEM(b) and TEM (c) images of the sample annealed at 800 °C.



Figure S6. Nitrogen adsorption-desorption isotherms of Fe₂VO₄-DMP.



Figure S7. TGA curve of the synthesized $Fe_2VO_4 \subset NC$ nanopeapods under air flow with a temperature ramp of 10 °C min⁻¹.

It can be seen that the mass losing of Fe₂VO₄ \subset NC nanopeapods mainly appears between 100-550 °C. The loss of weight is about 3.83% below 100°C, which corresponds to the loss of water or some substance absorbed on the surface of the material. Then the loss with 2.37% between 100-450 °C may be caused by some organic functional groups onto the carbon shell. Finally, the loss in weight with 17.5% is caused by reaction of the carbon in the samples and oxygen. Therefore, the content of carbon in the composite is about 17.5%.



Figure S8. (a) XPS full survey profile and (b) C 1s spectra of the $Fe_2VO_4 \subset NC$ nanopeapods.



Figure S9. CV curves for the Fe_2VO_4 -DMP electrode in the second cycle at a scan rate of 0.1 mV s⁻¹.



Figure S10. Charging/discharging profiles for the Fe_2VO_4 -DMP electrode at 100 mA g⁻¹ after 20 cycles.



Figure S11. The cycling performance of the $Fe_2VO_4 \subset NC$ nanopeapods electrode measured under different current densities from 1000 to 2000 mA g⁻¹.

The Fe₂VO₄ \subset NC nanopeapods electrode still retains reversible depotassiation capacities of 291 and 228 mAh g⁻¹ over 500 cycles at current densities of 1000 and 2000 mA g⁻¹, respectively.



Figure S12. The cycling performance of the Fe_2VO_4 -DMP electrode measured at 500 mA g⁻¹.



Figure S13. *Ex-situ* SEM (a) and TEM (b) images of the Fe₂VO₄ \subset NC nanopeapods electrode after 500 cycles at 2000 mA g⁻¹.



Figure S14. (a) CV profiles at different scan rates and (b) the plots of log(i) vs. log(v) at each redox-peak pair (peak current: *i*, scan rate: *v*) of the Fe₂VO₄⊂NC nanopeapods electrode. (c) Blue region shows the CV curve with the pseudocapacitive contribution at 1.1 mV s⁻¹.



Figure S15. Relationship between real impedance with low frequency for the $Fe_2VO_4 \subset NC$ nanopeapods electrodes.

The K-ion diffusion coefficients of various $Fe_2VO_4 \subset NC$ nanopeapods electrodes with different cycles can be determined by the following equations:

$$Z = R_s + R_{ct} + \sigma \omega^{-1/2}$$

$$D = R^2 T^2 / (2A^2 n^4 F^4 C^2 \sigma^2)$$
(S1)
(S2)

where Z, ω , R, T, A, n, F, and C refer to the real part of the impedance, the angular frequency in the lowfrequency region, the gas constant, the absolute temperature, the active surface area of the electrode/electrolyte interface, the number of electrons transferred electrochemical reaction, the Faraday constant, and the bulk concentration, respectively, and σ denotes the Warburg coefficient, which is relative to Z'- $\omega^{-1/2}$ (eq S1) and can be estimated from the low frequency region of the Nyquist plots (Figure 5b).



Figure S16. Quasi-thermodynamically equilibrium potential profiles of the $Fe_2VO_4 \subset NC$ nanopeapods electrode during the potassiation/depotassiation processes.



Figure S17. Ex situ XPS spectra of V 2p for the $Fe_2VO_4 \subset NC$ nanopeapods electrode: (a) discharged to 0.01 V (*vs.* K⁺/K); (b) charged to 2.6 V (*vs.* K⁺/K).



Figure S18. Spinel crystal structure of Fe_2VO_4 . The gold polyhedral represent (Fe/V)O₆ 16d octahedral sites. The gold spheres without polyhedral are Fe ions at 8a tetrahedral sites. The green spheres are vacant 16c interstitial sites. Our proposed intercalation mechanism is Fe ions at 8a sites are pushed to nearby 16c sites. And K ions also occupies 16c sites. The intercalated KFe₂VO₄ phase would have a 1:1 cation-anion ratio and adopts a rock-salt type structure.

Table S1. Comparison of electrochemical properties of $Fe_2VO_4 \subset NC$ nanopeapods electrode with previously reported electrode materials for potassium-ion batteries. Electrode compositions are listed using mass ratios of active material: conductive carbon: binder.

Material Electrode		Loading	Rate capability	Cycling performance	Reference	
	composition	density				
		(mg cm ⁻)				
Fe₂VO₄⊂NC	80:15:5	1.2	389, 368, 323,	105.4% after 400 cycles at	This work	
nanopeapods			284, 228 and 159 mAh g^{-1} at	$0.2 \mathrm{~A~g}^{-1}$		
			$0.1,0.2,0.5,1,2$ and 4 A g^{-1}	97.0% after 500 cycles at 1		
			after each 20 cycles,	$A g^{-1}$		
			respectively	104.6% after 500 cycles at 2		
				$A g^{-1}$		
				112.6% after 2300 cycles at		
				$4 \mathrm{A g}^{-1}$		
Ultra-High	70:20:10	1	487, 388, 319, 286, 253, 225,	72% after 3000 cycles at 1	Adv. Mater. 2017, 29,	
Pyridinic N-			and 199 mAh g^{-1} at 0.02,	$A g^{-1}$	1702268	
Doped Porous			0.05, 0.1, 0.2, 0.5, 1 and 2 A			
Carbon			g ⁻¹ , respectively			
Hard–Soft	80:10:10	2	261 mAh g^{-1} at 0.028 A g^{-1}	89% after 440 cycles at 0.05	Adv. Funct. Mater. 2017,	
Composite				$A g^{-1}$	27, 1700324	
Carbon						

Hard Carbon	80:10:10	2	$250 \ mAh \ g^{-1}$ at $0.028 \ A \ g^{-1}$	83% after 100 cycles at	Adv. Energy Mater.	
Microspheres			130 mAh g^{-1} at 1.04 A g^{-1}	$0.028 \mathrm{A g}^{-1}$	2016 , <i>6</i> , 1501874	
Hierarchical	60:20:20	1.0	100 mAh g^{-1} at 2 A g^{-1}	105% after 100 cycles at 1	Adv. Mater. 2017, 29,	
VS ₂ Nanosheet				$A g^{-1}$	1702061	
Few-Layer F-	80:10:10	1.0-1.2	300 mAh $\mathrm{g}^{^{-1}}$ at 0.05 A $\mathrm{g}^{^{-1}}$	60% after 200 cycles at 0.5	ACS Appl. Mater.	
Doped			200 mAh $\rm g^{-1}$ at 0.5 A $\rm g^{-1}$	$A g^{-1}$	Interfaces 2016, 8,	
Graphene					20682.	
Foam						
MoS_2	-	2	$65 \ \mathrm{mAh} \ \mathrm{g}^{-1}$ at 0.02 A g^{-1}	90% after 200 cycles at 0.02	Nano Res. 2017. 10,	
				$A g^{-1}$	1313.	
N-doping of	70:20:10	1.1–1.4	300 mAh g^{-1} at 0.1 A g^{-1}	73% after 100 cycles at 0.1	ACS Nano 2016, 10,	
few-				$A g^{-1}$	9738.	
layered						
graphene						
Sn-C	70:20:10	1.2	150 mAh g^{-1} at 0.025 A g^{-1}	75% after 30 cycles at 0.025	Chem. Commun. 2016,	
				$A g^{-1}$	52, 9279.	
Alkalized	70:20:10	-	78 mAh g^{-1} at 0.2 A g^{-1}	55% after 500 cycles at 0.2	Nano Energy 2017 , 40,	
Ti ₃ C ₂ MXene			136 mAh g^{-1} at 0.02 A g^{-1}	$A g^{-1}$	1	
nanoribbons				-		
Carbon	70:20:10	-	263, 234, 172, and 80 mAh	52% after 50 cycles at 0.05	J. Am. Chem. Soc. 2015,	
			g^{-1} are obtained at 0.028, 0.06,	$A g^{-1}$	137, 11566	
			0.15 , and 0.28 A g^{-1} ,			
			respectively			
Porous carbon	-	-	270 mAh $\rm g^{-1}$ at 0.2 A $\rm g^{-1}$	87% after 1200 cycles at 0.2	J. Mater. Chem. A,	
nanofiber				$A g^{-1}$	2017 , <i>5</i> , 19237	
paper						
Amorphous	-	-	307 mAh g^{-1} at 0.05 A g^{-1}	70% after 1200 cycles at 1	Adv. Energy Mater.	
ordered				$A g^{-1}$	2017 , 1701648	
mesoporous						
carbon						

Table S2. Impedance parameters and K-ion diffusion coefficients of the various $Fe_2VO_4 \subset NC$ nanopeapods samples with different cycles.

Sample (Fe₂VO₄⊂NC nanopeapods)	$R_{\rm s}\left(\Omega ight)$	$R_{ct}\left(\Omega ight)$	$\sigma(\Omega~{\rm s}^{-0.5})$	$D (\mathrm{cm}^2 \mathrm{s}^{-1})$
Prestine	4.13	861	6.89	2.16×10^{-10}
After the 50 cycles	6.64	643	6.11	3.07×10^{-10}
After the 100 cycles	7.95	522	2.29	1.09×10^{-9}

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2.5 Non-destructive characterization of K deposition in different separators

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In Situ Visualizing the Interplay Between the Separator and Potassium Dendrite

Growth by Synchrotron X-ray Tomography

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Abstract

Rechargeable potassium (K) batteries are a promising next-generation technology for low-cost grid scale energy storage applications. Nevertheless, the undesirable interfacial instabilities originating from the interplay between the employed separators and electrodes largely compromise the battery's performance, and the underlying mechanism of which remains elusive. Herein, the interfacial stability between three types of commercial separators (Celgard 2325, Celgard 2400 and GF/D) and the K electrodeposits is investigated in K|K symmetric cells via *in-situ* Synchrotron X-ray tomography technique. It is demonstrated that the cell built with a Celgard 2400 separator can achieve a stable cycling performance due to its high mechanical strength and integrity along the thickness direction, thus alleviating the K dendrites growth. In contrast, a GF/D membrane of low mechanical cohesion and excessive porosity is found to be easily deformed and filled with deciduous potassium dendritic aggregates during battery cycling. Similarly, the tri-layer Celgard 2325 separators, which are weakly bonded by interlaminar forces, are found to be severely delaminated by the overgrowth of K dendrites. Furthermore, it is revealed that the delamination failure behaviors of Celgard 2325 is driven by the local stress induced by the

spatially and heterogeneously formed "dead" K dendrites. Our work provides direct visualization of morphological evolvement of the separators in presence of potassium dendrites in K|K symmetric cells and highlights the significance of mechanical cohesion, porosity distribution and mechanical integrity of separators in dictating the battery's performance under realistic battery operation conditions. As a result, these discoveries provide an in-depth understanding that is needed to design next-generation high performance separators to mitigate the formation of potassium dendrite in KMBs.

Keywords: Potassium metal anode, Synchrotron X-ray Tomography, High mechanical separator, Bulky potassium deposition

Introduction

With the soaring energy storage requirement for intermittent solar and wind energy, developing high energy-density lithium-ion batteries (LIBs) is a vital choice.¹ However, LIBs cannot meet the demand for low-cost and large-scale energy storage because of the lithium rarity (0.0017 wt%) and uneven distribution.² Potassium-based rechargeable batteries are gaining rapid scientific attention as promising alternative for the upcoming stationary and electrical grid applications, due to the abundant resources and low potential of K.^{3,4} In addition, K⁺ also possesses a higher transference number and ionic conductivity than that of Na⁺ and Li⁺ due to its low desolvation energy and weak Lewis acidity, which is beneficial to facilitate fast diffusion kinetics during battery operation. Among the anode candidates of potassium-based batteries, K metal has attracted special attention due to its lower potential (-2.93 V versus standard hydrogen electrode) and higher specific capacity (≈ 687 mAh g⁻¹) compared to other anode materials including alloying, carbonaceous, and intercalation compounds. Moreover, K metal anodes can enable the application of potassium-free cathodes for high-energy density battery systems, such as potassium metal batteries (KMBs), potassium superoxide (K-O₂) and potassium-sulfur batteries (K-S).^{5,6} Wu et al. demonstrated that the K-O₂ battery based on thermodynamically and kinetically stable KO₂ can offer a high theoretical specific energy density of 935 Wh kg⁻¹ under long-term cycling conditions.⁷ Chen et al. demonstrated that the theoretical capacity of the potassiumsulfur battery could reach 1023 Wh kg^{-1.8} The K metal batteries coupled with the conversion chemistry electrodes (sulfur or oxygen cathodes) could deliver much higher energy densities than that of LIBs, which is practically attractive for grid-scale energy storage applications.⁹

Although these studies have showcased the potential capabilities of KMBs, their further development has been greatly hindered by many challenges, especially the uncontrollable growth of K dendrites.¹⁰ Tremendous efforts have been proposed to tackle the uncontrolled

K dendrites by altering the solvents, designing artificial solid electrolyte interphases (SEIs), using solid-state electrolytes, adding electrolyte additives and constructing three dimensional (3D) host materials.¹¹⁻¹⁴ These endeavors have contributed to the development of KMBs by alleviating the formation of K dendrites to some extent during battery cycling. For example, it has been reported that the K immersion into the fluoroethylene carbonate (FEC) for two minutes is beneficial to stabilize the K metal anode with a uniform and compact solid electrolyte interphase film¹¹. In addition, puffed millet/NiO scaffolds and MXene/carbon nanotube scaffolds have been demonstrated to effectively reduce the local electron and ion densities to suppress K dendrites growth. It was found that the deposited K metal was well-confined in the scaffolds with a smooth morphology and minor thickness variation.^{13,15} Nevertheless, reports of KMBs possessing long-term cyclability under practical cycling conditions remain scarce. Aiming to further improve their performance, an in-depth understanding of the working/decaying mechanisms of KMBs are highly desirable.

From the battery's components point of view, separators play a pivotal role in determining the cell performances during battery operation. In KMBs, the porous separator together with its interaction with electrode materials and liquid electrolytes (LEs), significantly affect the ion transport process and electrodeposition behavior of K. The extensively used separators in rechargeable K batteries are the commercial polyolefin separators and/or glass fiber (GF) membranes.¹⁶ These separators have been widely used in LIBs and various strategies have been developed to further improve their performance, among which includes the mechanical and physical enhancement, together with the modification and functionality. These are the most practical and facile methods to improve the mechanical/thermal properties of the commercial separators.¹⁷⁻¹⁹ While the crucial role of separators in LIBs has been considerably studied, the failure mechanisms of separators in KMBs remain unknown. Additionally, different properties of battery components in KMBs, including the mechanical properties of K dendrites, the volume change behavior of K electrodes, the solubility of decomposition products and SEI layers may exert dissimilar influence on separators as that in LMBs.^{5,20,21} In fact, the interaction/interplay between K dendrites growth and separators under realistic electrochemical conditions have been insufficiently studied.

Herein, the exploration of the interaction between K electrodeposits and separators is elaborately investigated based on the *in-situ* synchrotron X-ray tomography technique (SX-CT) in K|K symmetric cells built with three commercial separators (Celgard 2325, 2400, and

GF/D). The high-resolution X-ray imaging could reveal the underlying correlation between the electrochemical performance of the battery and the battery components' change in a nondestructive way.²²⁻²⁵ The current work not only provides direct visualization of the K dendrites growth and propagation processes, but also correlates the electrochemical behavior of batteries to the penetration of K dendrites. In addition, 3D SX-CT data clearly reveal the accompanying break-down of the widely used commercial separators in presence of the generated K electrodeposits. Specifically, it has been found that the large pore size (micron scale) across the glass fiber separators can be easily filled with dendritic K electrodeposits. It is also revealed that the multilayered Celgard 2325 separators can be delaminated into three layers by deciduous K dendrites due to the mechanical stresses generated from the inhomogeneous formation of K deposition during K plating/striping, as confirmed by finite element method (FEM) analysis. Compared to Celgard 2325 and GF/D separators, Celgard 2400 separators, which feature strong mechanical properties and suitable thickness, are found to maintain high structural integrity and suppress the growth of K dendrites. This work affords the fundamental understanding of the interaction between K electrodeposits and the used separators and sheds new lights on developing rational strategies for highperformance separators for KMBs.

Results and Discussion

The composition and structure of the employed separators (Celgard 2325, 2400, and GF/D) are analyzed and the results are shown in Fig.1. The Scanning Electron Microscope (SEM) characterizations of the Celgard separators, as shown in Fig. 1a,b, obviously show the highly oriented "slit-like" pore structures parallel to the stretching direction (uniaxial stretching direction).²⁶ Notably, the pore size of Celgard 2400 separators are much larger than those of Celgard 2325 separators, as confirmed by Barrett–Joyner–Halenda (BJH) (Fig. 1c). Cross-sectional SEM images of both the membranes (Fig. 1d, e) clearly show that the Celgard 2325 separator is a membrane composed of tri-layers (polypropylene-polyethylene-polypropylene (PP|PE|PP)), while Celgard 2400 separator is assembled by bilayer PP membranes.^{27,28} The amplified images (insets of Fig. 1d, e) not only demonstrate the existence of an interlayer spacing among the composing layers but also confirm that the thickness of each layer of Celgard 2325 (~8 μ m) was less than that of Celgard 2400 (~12 μ m). The X-ray diffraction (XRD) measurement in Fig. S1 further corroborates the composition of these multilayer separators.²⁶ Fig.1f presents the SEM result of the GF/D

separator, which is formed by the typical nonwoven glass fibers under low mechanical cohesion state.²⁹

The evolution of the interphase between the separator and K electrodes as well as the morphological evolution of the electrodeposited K in symmetric K|K cells are visualized by in-situ Synchrotron X-ray computed tomography (SX-CT). A total number of 7 cells built with different electrolytes (1M KTFSI (EC/DEC (v/v) =1:1), 0.8 M KPF6 (EC/DEC (v/v) =1:1 and 1M KFSI (EC/DEC (v/v) =1:1)) and cycled under different conditions are studied. The detailed information of these studied cells is concisely shown in Table 1. Fig. S2 shows the schematic in-situ measurement setup and the corresponding measuring protocols, in which, the customized tomography cell (tomo-cell) is rotated 180° while 2400 projections of 25 milliseconds exposure time are collected. The spatial resolution of 1.2 µm is achieved by using the 10X objective system and a 2 by 2 binning process. The specific battery assembly procedures, SX-CT measurement parameters, and tomography data analysis could be found in the Methods Section in Supporting Information (SI). The 3D rendering of the uncycled cell No.1 is shown in Fig.1g, from which the Celgard 2325 separator (green) and the GF/D separator (black) are found to maintain their original compact structure. However, the pristine K foils soaking in the electrolytes after 4h show granularly rough surface with pits and heaves, demonstrating that the SEI on K metal surface is relatively unstable in carbonate ester solvents due to the intrinsic high chemical/electrochemical activity of K metal (Fig. S3). A SX-CT scan of cell No.2 after discharging for 67 h (Fig. S4) is conducted to investigate the change of Celgard 2325 and the results are shown in Fig. 1h. It vividly demonstrates that the originally integrated Celgard 2325 is delaminated into three layers and the pore spaces of GF/D is filled with a large amount of K dendrites (red dot line). The increase of voltage polarization of the No.2 cell (Fig. S4) is in accordance with the accumulated K electrodeposits in which insulating SEI layers would be continuously generated due to the formation of new surfaces during the electrodeposition process.³⁰

Cell No.	Electrolyte	Current density (mA cm ⁻²)	Duration time (h)	Separator	Measurement protocle	Cell structure
1	1 M KTFSI (EC/DEC (v/v) =1:1)		0	Celgard 2325+GF/D+ Celgard 2325	Standing	Tomo-cell
2	1 M KTFSI (EC/DEC (v/v) =1:1)	0.5	67	Celgard 2325+GF/D+ Celgard 2325	Discharge	Tomo-cell
3	$0.8 \text{ M KPF}_{6} (\text{EC/DEC} (v/v) = 1:1)$	0.5	46	Celgard 2325+GF/D+ Celgard 2325	Discharge	Tomo-cell
4	0.8 M KPF ₆ (EC/DEC (v/v) =1:1)	0.5	10	Celgard 2325+GF/D+ Celgard 2325	Discharge	coin cell
5	1 M KFSI (EC/DEC (v/v) =1:1)	0.5/1h	116	Celgard 2325+GF/D+ Celgard 2325	Cycle	Tomo-cell
6	1 M KFSI (EC/DEC (v/v) = 1:1)	2/0.5h	118	Celgard 2325+GF/D+ Celgard 2325	Cycle	Tomo-cell
7	1 M KFSI (EC/DEC (v/v) =1:1)	0.5/1h	160	Celgard 2400+GF/D+ Celgard 2400	Cycle	Tomo-cell

Table 1. The details of the studied cells in the current experiment.



Fig. 1. (a)-(e) The surface SEM images, BJH desorption pore-size distribution and cross-sections of Celgard 2325 and Celgard 2400 separators, respectively. The insets of (d), (e) are the enlarged interface spacing between composing layers. (f) The surface SEM image of GF/D separator. (g) 3D rendered volume of a pristine Celgard 2325 and GF/D immersed into electrolyte 1 M KTFSI within a K|K symmetric cell. (h) 3D rendered volume of the Celgard 2325 and GF/D within a K|K symmetric cell after discharging at 0.5 mA cm⁻².

Dendrite growth phenomena have been frequently observed during alkali metal anodes electrodeposition while their specific morphologies vary with electrolyte components, the depth of discharge, current densities, cycling conditions and separator.³¹ Using Celgard 2325 and GF/D separators, different types of electrolytes and varied depth of cycling conditions are studied in terms of their abilities to "stop" the growth of K dendrites towards the separators. Using 1 M KPF₆-EC/DEC electrolytes, the cell *No*.3 tested in Fig. 2a was short-circuited after 45 h. The short-circuited failure mechanism may result from the continuously accumulated K dendrites are found to approach toward the counter electrode (yellow solid line in Fig. 2e), which is consistent with the cell's electrochemical performance.

Moreover, one can observe that the Celgard 2325 contacting K cathode (defined as cathode because it experiences electrodeposition) is delaminated into three layers (between yellow dash lines) by K dendrites and the pores space of GF/D (between yellow dash line and solid line) are filled with deciduous K electrodeposit aggregates. These observations are in a stark contrast with that of the Celgard 2325 separator nearby K anode (solid yellow line). The segmented tomography data (Fig. 2c) of the spatial distribution of K dendrites, together with the corresponding integral 3D rendering (Fig. 2d), demonstrate that a large number of K electrodeposits have permeated through the Celgard 2325 separator and then accumulated inside the loose compartments of the GF/D separator. In addition, the finite element analysis (FEA) is undertaken to simulate the distribution of equivalent (Von-Mises) stress generated due to the dynamic volume expansion of K electrodeposits as well as the stress evolution exerted on the neighbouring Celgard 2325.³² From this simulation (Fig. 2f), it is hypothesized that the delamination of Celgard 2325 is driven by the locally inhomogeneous pressure generated from K electrodeposits, e.g., the K dendrites. This agrees well with the observation that K dendrites tend to penetrate through the pores and stratify the multilayer separators, followed by continuous propagation/migration towards the GF/D separator. To further understand the dynamic propagation/migration process of the K electrodeposits inside the Celgard 2325 separator, short-time discharge test (cell No.4) was conducted (Fig. 2b). Because cell No.4 was discharged for 5 h, one would expect that the amount of K electrodeposits is less and some electrodeposits may grow through the pores of the separator. This scenario is confirmed by SEM measurement and the results are vividly shown in Fig. 2g, h, and i, from which the penetration/trespass of K electrodeposits through the pores of the separator is unambiguously notable (Fig. 2g). A closer examination further suggests that the pores' size become smaller due to K dendrites blocking (Fig. 2h). In certain areas (blue dash box), it is found that some of the K dendrites are agglomerated on the surface of separators (Fig. 2i) after they have "grow" through them. To conclude, these results suggest that K electrodeposits can penetrate easily through the pores of Celgard 2325 separator and continue to grow through the glass fiber membrane.³³

The experiment and simulation shown above provide important insights into how the Celgard 2325 can be delaminated into three layers by the continuously growing K electrodeposits, *e.g.*, dendrites, whiskers and/or filaments, during discharge process. Practically speaking, understanding the interactions between the separator and the K electrodeposits under extended cycling condition is highly desirable. For this reason, two more cells (*No.* 5, and 6) are electrochemically cycled before the SX-CT measurement and

their voltage profiles are shown in Fig. 3a, b. The increased voltage overpotential of these two cells suggest that their failure is caused by a steady increase of cell impedance, which agrees well with their electrochemical impedance spectrum (EIS) results (Fig. S5a, b). ^{34,35} As shown in Fig. S5a,b, the charge-transfer resistance can be estimated from the diameter of the semicircle, which is inversely proportional to the surface area. The larger semicircle diameter of the Nyquist plot obtained from the cycled cells indicates significantly increased charge-transfer resistance, compared to that of the fresh cells. The increase is attributable to the formation of excessive SEI and the deposited porous K. The SX-CT results of these two cells are shown in Fig. 3c-k. As shown in the cross-sectional slice of cell No.5 (Fig. 3c), one can observe that a highly porous and loose K electrodeposits structure, with parts of them disconnected from the current collector and forming "dead" K (Fig. 3c), is generated after electrochemical cycling. The enlarged images (Fig. 3d, e) provide direct visual evidence of the penetration of K electrodeposits through the Celgard 2325 separator, as well as an inhomogeneous distribution of K electrodeposits during battery operation. In addition, one can clearly note that the Celgard 2325 separator is stratified into three layers within local regions (Fig. 3d, e, purple dash lines). Fig.3f shows an orthorhombic slice view of the internal state of cell No.6 and the corresponding slices (along x, y, and z-direction) are individually shown in Fig.3g, h, and i. It can be observed from Fig. 3g that the K electrode becomes porous after electrochemical cycling and some of the K-metal domains are electrically disconnected from the current collector, resulting in severe migration of "dead" K (purple area) and void space.³³ The delamination behavior of the Celgard 2325 separator is also obvious in cell No. 6 (Fig.3 g, h, yellow dot lines). The K dendrites migration/propagation becomes more severe with increased areal current density, as confirmed from the 3D renderings of cell No.5 and No.6 (Fig. 3j, k). The vigorous propagation/migration behavior of K electrodeposits may be related to their penetrability of different composing components, such as moss-like, tree-like and/or needle-like features.³⁶ These observations directly demonstrate that the physical deformation behavior of separators can be significantly influenced by the test mode, e.g., the current density and the electrodeposits morphologies.



Fig. 2. The electrochemical performance and morphological evolution of Celgard 2325 within K|K symmetric cells (using 0.8 M KPF₆ in EC/DEC (v/v) =1:1 electrolyte). (a), (b) The discharge curves of cell *No.* 3 and 4, respectively. (c) The volume fraction of K deposition in d) along the through-plane direction from cathode K to the anode K. (d) 3D reconstructed volumes of cell *No.* 3. (e) Cross-sectional view of slice from cell *No.* 3. (f) Simulation of compression stress of regions where K deposition contacted with the Celgard 2325.³² (h) The SEM image of Celgard 2325 separator harvested from cell *No.* 4. (g), (i) The enlargement of SEM images in green and blue dash box of Fig. h.

It is worthy to note that the delamination failure behavior of Celgard 2325 in KMBs is inherently different from the fracture and melting behavior in lithium metal battery (LMB).³⁷ One may attribute the difference to the high Young's modulus of Li whiskers, up to 130 MPa, that greatly exceeds the Young's modulus of the separator.^{38,39} In addition, the shear modulus of potassium metal (1.3 GPa) is also lower than that of lithium metal (4.1 GPa), which is potentially another explanation.^{5,40} The lamination of Celgard 2325 separator indicates that the weak interaction force among the PP/PE/PP layers could not sustain the dramatic volume change of K-nearly 4 times larger than that of Li-during potassium plating/stripping process. Nevertheless, it has to be noted that the mechanical integrity of the separators is mainly related to the manufacturing process using winding machines to

laminate the three independent layers into one single separator by mechanical compression.³⁷ Based on the previous knowledge, the growth of K dendritic structures may be more easily alleviated by employing separators of higher mechanical stability.⁴¹⁻⁴³

Compared with Celgard 2325 separators, Celgard 2400 separators, which are consisted of two thick-layers membrane of polypropylene (PP), possess relatively higher mechanical integrity.^{44,45} To probe the mechanical effect of Celgard 2400 on the electrochemical deposition/dissolution behavior of K, galvanostatic cycling of symmetric cell (No.7) built with Celgard 2400 at 0.5 mA cm^{-2} is conducted and the results are shown in Fig.4. As shown in Fig. 4a, the cell displays stable voltage hysteresis without obvious fluctuations over the course of a 160 h experiment. The smooth and flat voltage profile suggests that the Celgard 2400 separator can ensure a homogeneous K deposition/dissolution. The EIS (Fig. 4b) result reveals a much smaller interfacial resistance of the symmetrical K|K cell built using the Celgard 2400 separator compared with that using Celgard 2325 (Fig. S5). The average CE values (Fig. 4c) also demonstrate that cells built with different separators possess varying electrochemical performance. As shown in Fig. 4c, one can observe that the CE values of the cells built with the Celgard 2400 separator in all studied electrolyte are the highest compared with other cells. For example, the average CE of the cell built the Celgard 2400 separator and KPF₆ electrolyte is 73.9%, while the cells built with the Celgard 2325 and GF/D separators were short circuited during cycling. The SX-CT results shown in Fig.4d-k provide extra insights into the improved electrochemical performance of cell No.7, together with the experimental evidence that the morphology of K electrodeposits can be tuned by using separators of high mechanical property. As shown in Fig. 4d and e, it can be observed that the Celgard 2400 separator is slightly delaminated into two flat PP sheets by the insertion of a small amount of electrodeposited K (yellow dash lines 1 and 2). The location where electrodeposited K could insert into the two PP layers may be an engineered artifact of binding two thick PP layers during the manufacturing process,⁴⁶ which agrees well with the SEM image of Fig. 1e. The morphological changes of Celgard 2400 are further shown in area 2 of Fig. 4e and area 4 of Fig. 4g (in-plan image corresponding to the red dash line in Fig.4d), from which one could observe that the dense PP layer (region 3 of Fig. 4g) became loosened. The in-plane image of GF/D (Fig.4f, corresponding to the pink dash line in Fig.4d) nearby Celgard 2400 shows no K dendrites aggregating. This indicates that the Celgard 2400 separator is favorable to prevent the growth of dendritic K electrodeposits and penetration due to its thick nature and enhanced mechanical structure. In addition, as shown in Fig. 4g (area 5), cycled K metal displays a flat and bulky morphology with a small

amount of foam-like K (area 6 of Fig. 4g). Observed from the top view (Fig. 4h, i), the compacted aggregates of granular K of sizes in the range of a few microns further confirms the same finding, *i.e.*, a relatively flat and bulky K electrodeposits are generated. The denser K deposition would lead to less exposure to the electrolyte, thus reducing the detrimental decomposition reactions and improving battery cyclability. The foam-like structures show distinct boundaries that are different from the previously scattered dendrites. The currently observed foam-like structures may be formed due to repeated stripping and plating of granular potassium (Fig. 4j). The corresponding 3D rendering (Fig. 4k) provides a more direct and comprehensive picture of the distribution of the compacted K deposition (yellow regions in Fig. 4k). Furthermore, the GF/D membrane keeps its original state, and few "dead" K dendrites can be observed within. These results clearly indicate that the Celgard 2400 separator possessing higher mechanical integrity and strength could relatively suppress the growth of "dead" potassium dendrites and enable reversible K plating/stripping. The underlying cause may be explained by the knowledge obtained during the study of Li electrodeposition/electrodissolution.



Fig. 3. Electrochemical data and mechanical degradation of Celgard 2325 and GF/D in cell *No*.5 and cell *No*.6. (a), (b) Galvanostatic cycling curves of cell *No*.5 and *No*.6. (c) 2D SX-CT cross-sectional slice of

cell *No*.5. (d), (e) the enlarged images of the delaminated separator and blocked GF by the accumulated "dead" K in black and green boxes in (c). (f), (g), (h), and (i) represent orthogonal slices and the cross-sectional slices with xz, xy, yz face of the cell *No*.6. (j), (k) 3D reconstructed volumes of cell *No*.5 and *No*.6, respectively.

For Li metal anode, the discovery of the existence of an optimum pressure that facilitates the electrochemical kinetics and mass transport processes of lithium ions is previously reported.⁴⁷ Furthermore, previous studies also showed that stiff compacting nanocomposite separator of high Young's Modulus helped to alleviate Li dendrite formation and provide a stable interface for lithium electrodeposition/stripping.⁴⁸ Considering the much lower mechanical modulus of K deposition in the present study, the stiff Celgard 2400 separator may provide sufficient and uniform uniaxial stack pressure during battery operation. Thus, it can effectively improve K nucleation and growth process during electrochemical deposition. The formation of bulky-type K electrodeposit is desirable since it has been widely accepted that the morphology is one of the determinantal factors that influence the cycle life of alkalis metal batteries.⁴⁷⁻⁴⁸ The large bulky-type K electrodeposits with minimal tortuosity can ensure continuous electron conducting pathway during stripping process, and reduce the amount of isolated K and facilitate high CE.⁴⁹

The mechanism of the interaction between the K electrodeposits and the separators is proposed in Fig. 5. During K electrodeposition (Fig. 5b), uneven K depositions caused by nonuniform thickness and fragile tips can accelerate the K dendrite growth, which could immensely disturb the distribution of the generated pressure. In the meantime, the dendritic K electrodeposits with high activity would lead to continuous dissolution and regeneration of SEI. During the extended electrochemical cycling, these dendritic K electrodeposits could penetrate through the pores of the Celgard 2325, accumulate within the locations between the tri-layers, stratify the separator and finally propagate into the loose pores of GF/D membrane (Fig.5b), resulting in severe battery polarization or short-circuit. Therefore, separators with loose pore structure are more vulnerable to fail. In contrast, Celgard 2400 separators of high mechanical integrity and bulk Young's modulus are desirable to facilitate compact K deposition to some extent (Fig.5b). It is assumed that the dendrite-free potassium electrodeposits and self-adaptable pressure originated from separators could significantly improve the reversibility of K metal anodes. The self-adaptable pressure generated by high mechanical separators would surpass the generation of dendritic K electrodeposits and facilitate the formation of bulky-type K electrodeposition. These results suggest that the intricate interplay between K electrodeposits and the separator critically affect the cyclability and safety of KMBs.



Fig. 4. The electrochemical data and morphology of K electrodeposits in cell *No*.7. (a), (b) Galvanostatic cycling curve and electrochemical impedance spectrum of cell *No*.7 after discharge for 160 h. (c) Comparison of average CE values of K|Cu cells built using different separators in three electrolytes of 0.8 M KPF₆, 1 M KTFSI, and 1M KFSI in EC/DEC (v/v) =1. (d) 2D cross-sectional slice of cell *No*.7. (e) The enlarged image of the green dash box in Fig. 4c. (f), (g) Horizontal slices corresponding to the pink and red dash line in Fig. 4c. (h) Horizontal slice of deposited K close to the Celgard 2400 separator. (i), (j) The enlarged images of deposited K in the pink (7) and red (8) dash box of Fig. 4g. (k) 3D rendering of cell *No*.7, the yellow and brick-red regions represent bulky K depositions, and porous structure, respectively.



Fig. 5. Schematic illustration of the morphology evolution of the separator during electrodepositing, (a) A uniform K electrodeposition under a separator of ideal mechanical integrity. (b) An un-uniform K electrodeposition under separators of low/high mechanical integrity.

3. Conclusion

In summary, we have investigated the underlying interplay between the potassium electrodeposits and used separators by using customized tomography cells under various parameters, *i.e.*, electrolyte, depth of discharge, and cycling current density. Combining the *in-situ* visualizations of the customized tomography cells with the SEM analyses of the widely studied coin cells provides a reliable and comprehensive platform to assess the performance of the commercial separators. Our work highlights the importance of correlating electrochemical responses to the morphological changes of the electrode/separators. These results unambiguously demonstrate that the Celgard 2325 separator can be easily delaminated by the continuously growing and unevenly distributed K electrodeposits. In addition, the results also suggest that the loose space within the GF/D separator can function as a suitable "accommodation" for the accumulated K dendrites. In the last, the results imply that the Celgard 2400 separator which features relatively enhanced structural integrity and mechanical robustness can restrain the growth of K dendrites and maintain interfacial stability. Considering that the formation of dendrite-free and bulky-type K electrodeposits improves the reversibility of K anode, such unprecedented enhancement of battery electrochemical behavior by using mechanically improved separator represents a critical step towards new design rules of next-generation separators. Therefore, the selfcompacting nanocomposite separator, and solid electrolyte with high mechanical flexibility and self-healing ability may enable practical K metal batteries. To conclude, the direct visualization of the interplay of the interface chemistry and the K plating/stripping opens up new opportunities to understand the mechanism of the K deposition morphology. Combining such visualization technologies with other complementary techniques, such as *in-situ* TEM, cryo-EM, and FIB-SEM would be critical to further reveal the underlying mechanisms of nucleation and growth process of K electrodeposits.

Acknowledges

We acknowledge BESSY II for providing us valuable beam time. The work is supported by QIBEBT I201922, Dalian National Laboratory For Clean Energy (DNL) CAS, the China Scholarship Council (CSC), the National Natural Science Foundation of China (U1904216) and it is partially supported by the German Research Foundation, DFG (Project *No.* MA 5039/4-1).

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Supporting information

In Situ Visualizing the Interplay Between the Separator and Potassium Dendrite Growth by Synchrotron X-ray Tomography

Methods Section

Materials

Electrolyte used in this study are KFSI in EC:DEC solution (1:1 by volume), KFP₆ in EC:DEC solution (1:1 by volume) and KTFSI in EC:DEC solution (1:1 by volume). All materials were used under argon gas filled glove-box. K metal was purchased from Sigma Aldrich (bulks, under mineral oil, 99.9% trace metals basis). Celgard 2325, 2400 and GF/D were purchased from MIT Corporation.

Characterization

SEM images were taken by the Hitachi S-4800 Scanning Electron Microscope. Pore size distribution data were collected by Quantachrome 3Gz. XRD data was collected from a Bruker D8 Advance diffractometer with Cu K α source. The used separators and K foils contacting with electrolyte were sealed in a glove box under a high-purity Ar atmosphere and then transfer under protection for SEM testing. For the control experiments, fresh K foil was soaked into the electrolyte for 4 hours to study the morphological changes of K metal without electrochemical cycling.

Cell Fabrication

The specially fabricated beamline cell is made of polyamide-imide. In an Ar-filled glove box ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm), thin potassium metal foil was punched into 3 mm diameter disks, pressed onto the stainless steel and assembled into the tomography cells. 2032 type K|K symmetric cells were assembled in the argon filled glove box using either Celgard 2325 separator, Celgard 2400 separator and glass fiber as the separator with 10 mm diameter potassium discs.

Electrochemical testing

The constant current discharge and cycle experiments were carried out on a standard eight-channel Wuhan Land battery test system at room temperature. Electrochemical impedance spectra (EIS) measurements are conducted under open circuit voltage (OCV) conditions by Bio-Logic VMP3. 10 mV amplitude was used to obtain the measured impedance spectra of cells within range of 100 kHz to 0.1 Hz. The testing method for average K CE values within the K|Cu coin cells is briefly described below. First, a formation step in which a given amount of charge (Q_T) was transported to deposit K onto the Cu substrate as a K reservoir. This process is aimed to eliminate unwanted effects of substrate (Cu) conditions. After

the formation step, a small portion of this charge (Qc) was cycled between the working and the counter electrodes for n cycles. After cycling n times, a final thorough stripping of the remaining K reservoir to the cut-off voltage of 1.0 V was performed. The final stripping charge capacity (Q_s), corresponding to the quantity of remained K after cycling, is thus measured. Finally, the average CE after n cycles can be calculated from the ratio of $(nQc + Q_s)/(nQc + Q_T) \times 100\%$. In this work, the Q_T, the Qc, and the cycle number n are set as 3 mAh/cm², 0.6 mAh/cm², and 6, respectively.

Synchrotron X-ray measurements

We conducted the synchrotron X-ray tomography at P05 beamline at DESY, Hamburg, Germany. A CdWO4 single crystal scintillator of 100 µm thickness converts the X-ray to visible light. The detector system contains a serious of microscope optics and a KIT CMOS camera with 5120 × 3840 pixel. The field of view was $3.28 \times 2.46 \text{ mm}^2$ (length × height) was used and the corresponding resolution was 0.6 μ m. For tomography measurements, 2400 projections within a 180° battery rotation were recorded with the exposure time of 25 milliseconds. Additionally, a 2 by 2 binning was used and the resultant resolution was 1.2 µm. The illustration for the CT imaging at P05 beamline is shown in Fig S2. In the current manuscript, only the tomography data of cell No.3 underwent data segmentation and quantitative analysis, as shown in Fig. 2c-d. Other tomography datasets were not segmented due to 1) segmentation of the rest datasets may not be reliable since the K electrodeposits are tangled with the glass fibers and 2) segmentation of the K dendrites from the voids may also be not trivial since their X-ray absorption coefficient is nearly the same. Nevertheless, more accurate and reliable segmentation algorithms are under development and it is hoped that in the future all tomography datasets will be segmented. Note also that during the synchrotron X-ray tomography measurement, only the cycled K symmetrical cells were measured in situ without cell disassembly. The in operando synchrotron CT study of the K anodes during the electrochemical cycling was not conducted due to the limited allocated beamtime. However, it is planned that the *in operando* synchrotron CT study will be conducted once sufficient synchrotron X-ray beamtime is allocated.



Fig. S1. XRD of Celgard 2325 and Celgard 2400 separators.



Fig. S2. Schematic diagram of the SX-CT experimental set-up.



Fig. S3. SEM images of the K before the cycling test in K|K symmetric cell after 4h soaking in electrolytes of (a) 0.8 M KPF₆, (b) 1 M KTFSI, (c) 1 M KFSI in EC/DEC (v/v) =1:1.



Fig. S4. The discharge plot of symmetric K|K (cell No.2) at a current density of 0.5 mA/cm² in 1 M KTFSI (EC:DEC (v:v) =1:1) electrolyte.



Fig. S5. Electrochemical impedance spectrum of cell No.5 and No.6.

3. Summary and conclusions

In order to observe the evolution of lithium/solid-state electrolyte interfaces during battery cycling, the *in-situ* synchrotron X-ray tomography technique which is capable of monitoring the 3D microstructure and chemo-mechanical evolution of electrode materials is highly suitable. In Section 2.1, we used synchrotron X-ray tomography to investigate how the complex interplay among void formation, interphase growth and volumetric evolve at the Li/Li₁₀SnP₂S₁₂ interface during cycling. Synchrotron X-ray microtomography visually uncovers the formation of the (electro)chemically induced interphase, void formation at the Li/Li₁₀SnP₂S₁₂ interface, an unexpected mechanical deformation of the Li₁₀SnP₂S₁₂ solidstate electrolyte as well as an unanticipated creep behavior of lithium metal. From its 3D rendering figure, one can obviously note the existence of a variety of gorge-like and slit-like cracks at the interface due to the accumulated strain variation. Lastly, the (electro)chemically generated mechanical stress-distribution and its effect on the chargedistribution have been also studied. Owing to the natural abundance and low standard redox potential of potassium, potassium-ion batteries (KIBs) are regarded as one of the most promising candidates for the next-generation large-scale low-cost energy storage devices replacing lithium-based batteries. In Sections 2.2-2.4, three types of transition-metal-based chalcogenides and oxides compounds (V₅Se₈@carbon nanosheet, Co₉S₈@MoS₂@carbon hollow nano-box and carbon-encapsulated Fe₂VO₄ nano-peapod) were rational designed and then evaluated as anode material for KIBs. Moreover, theoretical calculations, kinetics analysis, and *ex-situ* characterizations have been applied to systematically investigate the origin of superior electrochemical performance for those transition-metal-based nanomaterials. This work is expected to provide meaningful guidance to develop transitionmetal-based chalcogenides and oxides as anode materials for high-performance KIBs.

Synchrotron X-ray tomography is also important in potassium metal batteries. We employed this technique to study the interfacial stability between the different commercial separators and potassium dendrite growth in K symmetrical cells (Section 2.5). It is demonstrated that the battery built with a Celgard-2400 separator can achieve a highly structural stability due to its robust mechanical strength along the thickness direction, thus alleviating the K-dendrite formation. By providing direct visualization of the deformation behaviors of the studied separators in presence of K electrodeposits, the present results highlight the significance of the mechanical cohesion, porosity distribution and mechanical integrity of the separators in dictating the electrodes' overall performance.

4. Outlook

Followings are the recommendations for future work:

(1) Despite progress in solid-state battery engineering, suitable solid-state electrolytes have not been identified and their development is quite challenging. In general, three tricky problems, the terrible interface compatibility, lower ionic conductivity and unfavorable mechanical stability still hinder the development of solid-state batteries. Therefore, to further explore a novel solid-state electrolyte with high electrode compatibility and ionic conductivity is greatly imperative. In addition, the working mechanism of the fabricated solid-state electrolyte will be studied by the operando synchrotron X-ray microtomography and in-situ X-ray photoelectron spectroscopy (XPS), comprehensive experimental analysis and theoretical calculations.

(2) The cathode is also important in determining the electrochemical performance of KIBs, particularly the energy density of a full cell system. The K-storage behavior and structureperformance relationship of different categories of cathodes will be investigated in future studies. In future work, we will focus on rational structural designing strategies to overcome main challenges of layered transition metal oxides, polyanionic insertion materials, prussian blue analogues and organic compounds. In order to improve the ionic-conductivity of electrolytes, it is essential to explore suitable potassium salts companies with electrochemical stable solvents to ensure the full expression of electrochemical properties of cathode materials.

(3) In order to satisfy the ever-increasing demands for large-scale energy-storage system, the further development of new K-based batteries, particularly post-KIBs (potassium-sulfur and potassium-selenium batteries), are urgently required to achieve desirable energy/power density, longer lifespan, and lower cost. Specifically, the sulfur or selenium cathodes with the rational structural designing strategy, which possess high gravimetric capacity, improved mechanical stability and lower cost, are designed to construct potassium-sulfur and potassium-selenium batteries with enhanced energy densities compared to those of traditional KIBs. Meanwhile, the electrochemistry mechanism for such post-KIBs will be investigated in future studies via advanced in-situ and high-resolution technologies.

5. Acknowledgements

Due to Coronavirus disease COVID-19, these two years have been very difficult years, especially for my Ph.D. student life. Fortunately, I finished my experiments and thesis and survive now. Hope VOVID-19 will end soon, and everything will get better.

Time flies and three years have quickly passed. I would like to thank my supervisor Prof. Dr. John Banhart and Dr. Ingo Manke for providing me the opportunity to pursue my Ph.D. at the Technische Universität Berlin and the Helmholtz Zentrum Berlin. I would like to take this opportunity to show my deepest gratitude to my supervisor, Dr. Ingo Manke, who has always supported my ideas and offered me selfless help.

My special thanks to Prof. Dr. John Banhart, Prof. Dr. Yan Lu and Prof. Dr. Aleksander Gurlo for being the evaluators of my thesis. I would like to thank my colleagues Dr. Fu Sun, Dr. Kang Dong and Dr. Nikolay Kardjilov for providing valuable help during my experiments. In addition, I would like to take this opportunity to thank Dr. Fan Lv from Prof. Shaojun Guo's group in Peking University for providing me material characterizations for my thesis. Also, I would like to take this opportunity to thank my colleagues Dr. Fu Sun, Dr. Kang Dong, Dr. Ling Ni, Dr. André Hilger, Dr. Tobias Arlt, Dr. Markus Osenberg, and Dr. Henning Markötter for their assistance on both scientific and other occasions.

I would like to thank China Scholarship Council for providing me financial support.

Last but not least, I would like to thank my parents and my elder brother for supporting me all the way. Without their persistent support, encouragement and love, it would have been impossible for me to go so far.