

Functional nanolayers favor the stability of solid-electrolyte-interphase in rechargeable batteries

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Rechargeable batteries have brought us lots of convenience and changed the way we live. However, the demand for higher energy density, longer cycle life, and more fast charging ability urges researchers to develop advanced battery material and chemistry^[1, 2]. The solid-electrolyte-interphase (SEI) on the anodes strongly governs the rechargeable batteries' electrochemical properties, such as the coulombic efficiency, cycling stability, rate capability, and even safety. Conventionally, SEI forms as a result of the parasitic reactions between the electrolyte and anode materials during the first few battery cycles, and is further attached to the surface of anodes, separating the active materials and electrolyte^[3]. It mainly consists of inorganic and organic components, which differ in different battery systems and depend on many factors, including salt, solvent, additives, etc. An ideal SEI is stable and homogeneous in microstructure as well as components with a constant thickness, expecting to be electric insulation to prevent the persistently parasitic reactions and ionic conduction to facilitate Faradaic reactions of the electrode^[4, 5]. However, the continuous growth of SEI reduces electrolyte components, consumes cyclable ions, and increases the ion resistance, deteriorating the battery performance.

Different mechanisms have been developed to essentially explain the persisting growth of the SEI according to its electron leakage behavior, such as solvent diffusion, electron conduction, electron tunneling, and neutral radicals diffusion^[6]. Though tremendous difficulty existed to clarify the emergence and growth of SEI owing to its dynamic changes and the limited reliable characterization techniques, recent works using advanced operando techniques^[7–10], such as *in situ* atomic force microscopy (AFM), operando reflection interference microscopy, operando electron energy-loss spectroscopy in a scanning transmission electron microscope, three-dimensional (3D) focused ion beam scanning electron microscopy, as well as the combination of electrochemical AFM, 3D nano-rheology microscopy, and surface force-distance spectroscopy, have confirmed that the spontaneously formed SEI is heterogeneous in spatial and chemical resolution. Therefore, a desirable SEI with high qualities on anode materials should be well designed. Strategies such as electrolyte engineering on salts, solvents, additives and concentration changes have effective impacts on the formation and properties of SEI^[11–13]. Actually, most anode materials suffer

from large volume swelling during battery charge and discharge, especially Li/Na/K/Zn metals, alloy reaction anodes, and conversion reaction anodes^[14–16]. The unbearable volume expansion of the anode materials endangers the stability of the electrode and SEI, leading to SEI accumulation and electrochemical performance deterioration. Therefore, material design including active components selection, microstructure regulation, and surface modification are vital to the stability of SEI. Among them, constructing functional nanolayers on the surfaces of anode materials to favor the existence of stable SEI has proved to be an effective strategy to design high-performance batteries.

Functional nanolayers work as artificial SEI to improve battery performance. Graphite materials dominate the commercial lithium-ion batteries (LIBs) anode, however, the low capacity at a high rate precludes their further development on the fast-charging battery market. Fast charging is largely hindered by slow electrochemical reaction processes at the graphite surface, which involves the Li-ion desolvation and transportation activities in the SEI. A thin and stable SEI with high ion conductivity is needed. Zhou *et al.* reported an artificial SEI on natural graphite using ultrathin (~4 nm) amorphous polydopamine-derived carbon coating^[17]. This ultrathin artificial SEI effectively eliminates the severe graphite exfoliation and continuous SEI growth during long cycling, thus reducing the interface impedance and ensuring an improved rate capability of the modified graphite anode with a capacity retention of ~97.5% after 400 cycles at 1 C (here 1 C = 350 mA·h·g⁻¹). Very recently, Tu *et al.* demonstrated the phenomenal success of a compact Li₃P-based SEI on improving the fast charging ability of graphite anode^[18]. They intelligently turned common graphite into blue graphite (P–S-graphite) by coating a thickness of ~4.4 nm S-bridged P nanolayer uniformly on it (Fig. 1(a)), and then produced a continuously crystalline Li₃P-based SEI *in situ* during the initial battery cycling (Fig. 1(b)). Their molecular dynamics simulation and density functional theory calculation results reveal that Li₃P has a strong Li-ion affinity energy and that accelerates the Li-ion desolvation process, supporting fast Li ion desolvation and diffusion through the SEI. Meanwhile, the pristine graphite is covered by a regular SEI as usual (Fig. 1(c)), which is always thick and varies on the edge part and basal planes, causing sluggish Li ion desolvation and slow Li-ion transport within pristine graphite. Consequently, the as-fabricated blue P–S-graphite with a high areal capacity of ~2.3 mA·h·cm⁻² exhibits an excellent fast-charging performance and stable cycling at a 6 C charging rate

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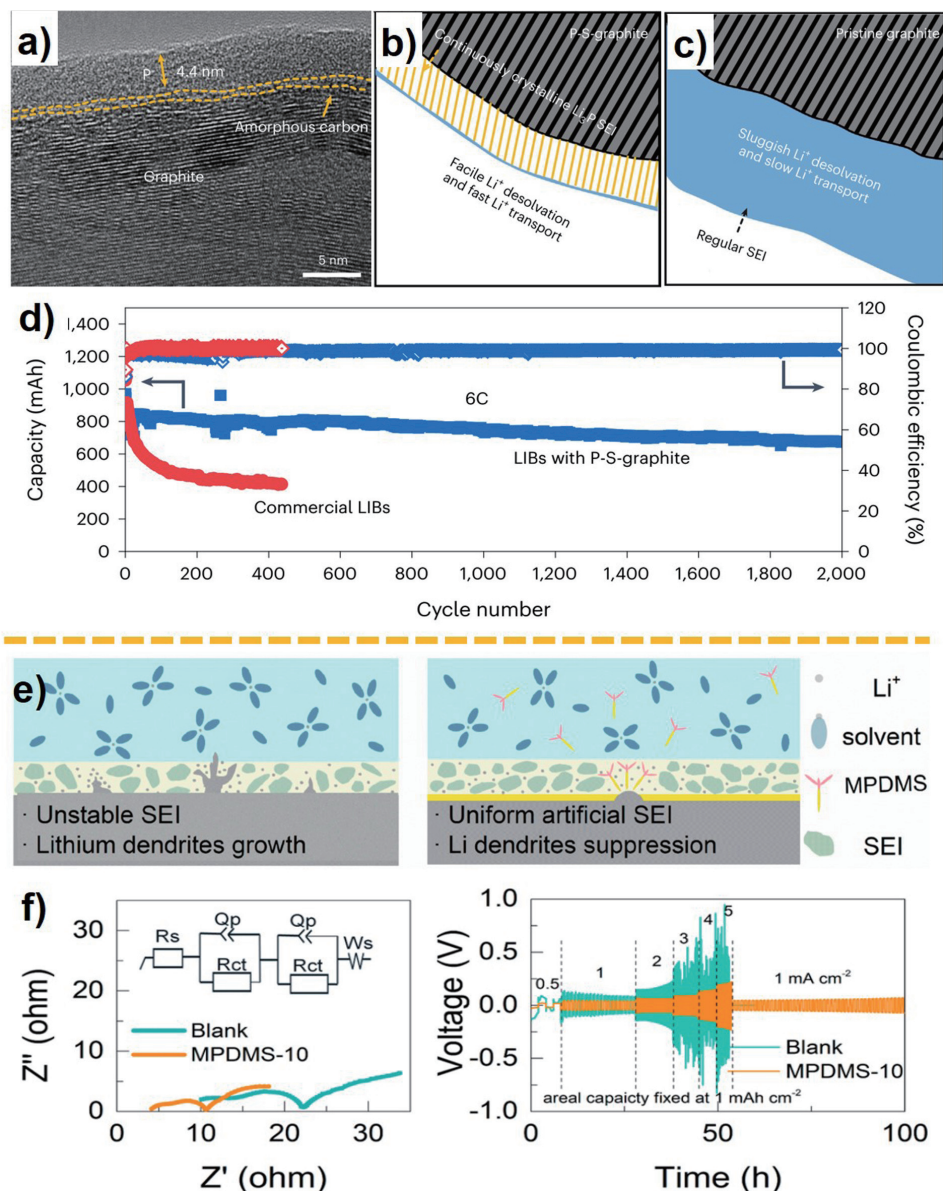


Fig. 1. (Color online) (a) HR-TEM image of P-S-graphite with ultrathin P nanolayer, and the schematics of (b) P-S-graphite and (c) pristine graphite anodes, (d) cycling performance of the pouch cells. Reproduced with permission^[18], Copyright 2023, Springer Nature. (e) Schematic illustration of the cycled blank Li metal (left) and MPDMS-coated Li metal (right) anodes, and (f) their EIS and rate performances. Reproduced with permission^[24]. Copyright 2023, American Chemical Society.

(~1 A·h, 2000 cycles and capacity retention rate of 82.9%, Fig. 1(d)). This work proves the vital role of the SEI component and structure in fast-charging LIBs and sheds light on the design of stable SEI with high ionic conductivity for advanced batteries.

Si, a promising high-capacity semiconductor anode for next-generation LIBs, suffers from low coulombic efficiency and capacity loss owing to the repetitive growth of SEI. He *et al.* revealed that the permeation of electrolyte into the inward voids produced by the volume swelling and that leads to the growth of SEI, which resulting in the disruption of electron transfer way and the formation of dead Si, causing capacity fading^[19]. Wang *et al.* constructed an artificial SEI on the ferrosilicon/carbon (FeSi/C) surface by a nucleophilic reaction of polysulfides with carbonate electrolyte^[20]. The well-designed artificial SEI is dense to prevent the electrolyte infiltration effectively and ionic conductive to let Li ions diffuse, thus stabilizing the FeSi/C anode interface and favoring

it to achieve a greatly elevated coulombic efficiency of 99.8% over 650 cycles. Pan *et al.* reported an *in situ* formed layered conductive polyaniline-integrated hybrid SEI skin on Si anode^[21]. The organic and inorganic components in this unique hybrid SEI skin distribute uniformly, guaranteeing the homogenous Li ion flux to assist the lithiation/delithiation kinetics and flexibility to tolerate local stress concentration. In this way, the Si particles are well protected from the electrolyte and the structure is reserved, eliminating the continuous electrolyte decomposition and SEI accumulation and improving the Li-ion storage performance as a consequence.

Metal anodes are widely considered the “ultimate” anode for high energy density rechargeable batteries, especially the “holy grail” Li metal anode. The main challenge for Li metal anode used in batteries is the dendrite formation because of the uncontrolled Li plating/stripping^[22, 23]. Li *et al.* coated Li metal with 3-mercaptopropylmethyltrimethoxysilane (MPDMS) protective monolayers as an artificial SEI by a

dip-coating method^[24]. As illustrated in Fig. 1(e), the blank Li anode (left) with unstable SEI proceeds Li dendrites growth, while the Li metal with MPDMS layer on the surface possesses uniform artificial SEI and the partially dissolved MPDMS molecules in the electrolyte can dynamically passivate possible dendrites, facilitating uniform Li plating/stripping and suppressing Li dendrite growth. The smaller R_{ct} value, superior cycling stability, and lower voltage polarization of the Li metal anode with MPDMS layer than those of the blank Li metal anode confirms the positive effect of the MPDMS protective nanolayer (Fig. 1(f)), which improves the charge transfer at the interphase, reduces impedance, and leads to optimal electrochemical performance of the modified Li metal anode. Ding *et al.* developed a metal electrode skin (MES) to protect the K metal anode^[25]. The artificial MES is made of fluorinated graphene oxide and works as the first protection on K metal and further induces a robust SEI as the second protect layer, effectively inhibiting the growth of K dendrites and favoring the full cell of K@MES|| Prussian blue achieving a ultralong cycle life (over 5000 cycles). These works highlight the promising strategy of using artificial SEI to design practical metal batteries.

Functional nanolayers work as a matrix to reserve stable SEI to enhance battery performance. Wang *et al.* synthesized a P-S co-doped flexible carbon fiber film using Chinese art paper as the precursor through one-step calcination^[26]. The obtained carbon fiber film is covered by SiO₂ and MgO nanoparticles homogeneously, which benefits the formation of ultrathin SEI with a thickness of 2–4 nm. Meanwhile the thickness of the SEI on pure carbon anode without SiO₂ and MgO nanoparticles attached increases to ca. 29 nm, leading to a degraded K-ion storage performance. Obviously, the ultrathin SEI induced by the SiO₂ and MgO nanoparticles on the surface of carbon fiber film inhibits the electrolyte from constant decomposition and facilitates the rapid K-ion diffusion, benefiting the carbon electrode achieving a capacity of 177.3 mA·h·g⁻¹ at a high rate (2500 mA·g⁻¹) after 500 cycles. Zhou *et al.* demonstrated that MXene enables stable SEI on Si anode with improved cycling stability^[27]. They coated Si nanoparticles with homogeneous Ti₃C₂T_x MXene by electrostatic self-assembly with the aid of the natural negative charge of MXene and positive charge of Si nanoparticles. The MXene coating protects the Si nanoparticles from directly immersed in the electrolyte and thus favors the stable SEI formation on the hybrid nanoparticles. To hold the massive expansion of Si during cycling, a functional double-layer structured Si@void C@TiO₂ with multi-components was developed for LIBs by Hou *et al.* combining chemical vapor deposition and sol-gel method^[28]. The unique structure is featured with a double shell consisting of a carbon layer and crystalline TiO₂ outside and an appropriate void left inside. The void offers room for the expansion volume of the Si core, holding the stability and integrity of the electrode structure. Meanwhile, the double shell contributes to the enhanced electric conductivity and the isolation of electrolyte from directly contacting Si cores, favoring the achievement of high coulombic efficiency as a result of the stable SEI formation.

Transition metal sulfides and selenides with the merits of high specific capacity and conversion reaction reversibility have been considered as promising anode materials for alkaline ion batteries^[29–32]. However, they face challenges such as

limited electronic conductivity, large volume changes, and SEI instability, leading to low coulombic efficiency and inferior cycling stability. Yang *et al.* adopted N-doped carbon to suppress the volume expansion of CoSe₂ and insulate it from the electrolyte, improving the cycle stability of the CoSe₂ anode^[33]. Our group proposed a strategy that induces the rapid formation of continuous SEI layers using confinement effect to resolve the aforementioned challenges^[34]. We scattered typical transition metal sulfides including CuS, CoS₂, and NiS₂ nanoparticles in the inner carbon nanofibers and those were covered by Nb₂O₅ in the outer carbon nanofiber via coaxial electrospinning combining carbonization and sulfuration, constructing core-shell structure hybrids, such as CuS–C@Nb₂O₅–C nanofibers. As suggested by Fig. 2(a), the CuS–C nanofiber electrode without a Nb₂O₅–C confining layer exhibits a rapid capacity fading during the initial 20 cycles with the coulombic efficiency below 97.5%, and then the coulombic efficiency increases to 99.0% up to 30 cycles slowly with the reversible capacity stabilized. When the CuS anode is covered by the Nb₂O₅–C confining layer, the coulombic efficiency of the as-fabricated CuS–C@Nb₂O₅–C NFs electrode increases quickly to 99.0% only after 5 cycles, and that keeps above 99.5% from 10 cycles on with a large capacity retention. Obviously, the Nb₂O₅–C confining layer favors the improvement of coulombic efficiency and capacity retention. We further investigated how the confining layer influences the electrochemical performance of electrodes. As illustrated in Fig. 2(b), the exposed CuS in CuS–C nanofiber electrode proceeds structure reorganization owing to the conversion reaction mechanism and then aggregates during the initial cycles, which accompanies with the volume expansion and the slow formation of SEI on the changeable surfaces of bared CuS until a thick SEI formed. When the volume expansion is retained by the Nb₂O₅–C layer, a stable surface is established and that contributes to the rapid formation of continuous SEI. This work offers a reliable method to improve the electrochemical performance of active materials with volume expansion using the confinement effect of functional layers.

Atomic layer deposition (ALD) is a powerful tool to construct a functional layer with the thickness of atomic level (Å-level control) being precisely tailored. It has been widely applied on the surface-modification of active materials and thus promotes the formation of stable SEI. Han *et al.* deposited few-nanometer thick (~4.4 nm) Al₂O₃ film on FeS/MoS₂ yolk-shell sphere powder (ALD-40-P) and the electrode (ALD-40-E) by ALD^[35], just as illustrated in Fig. 2(c). They found that the ALD-40-P electrode exhibited lower reversible capacity and rate capability than the electrode without Al₂O₃ when used as Na-ion battery anodes, while the ALD-40-E electrode delivered the best electrochemical performance among them with the highest initial coulombic efficiency. Their study reveals that an Al₂O₃ nanolayer coated on the electrode surface could retain the conductive network among the active materials in the electrode and has an effective influence on suppressing the side reactions with electrolyte and inhibiting SEI overgrowth, thus increasing the coulombic efficiency and cycling stability. This work provides meaningful thoughts for designing advanced materials for batteries using functional nanolayers.

To sum up, functional nanolayers on anodes work as stable artificial SEI directly or matrix to induce the SEI formation

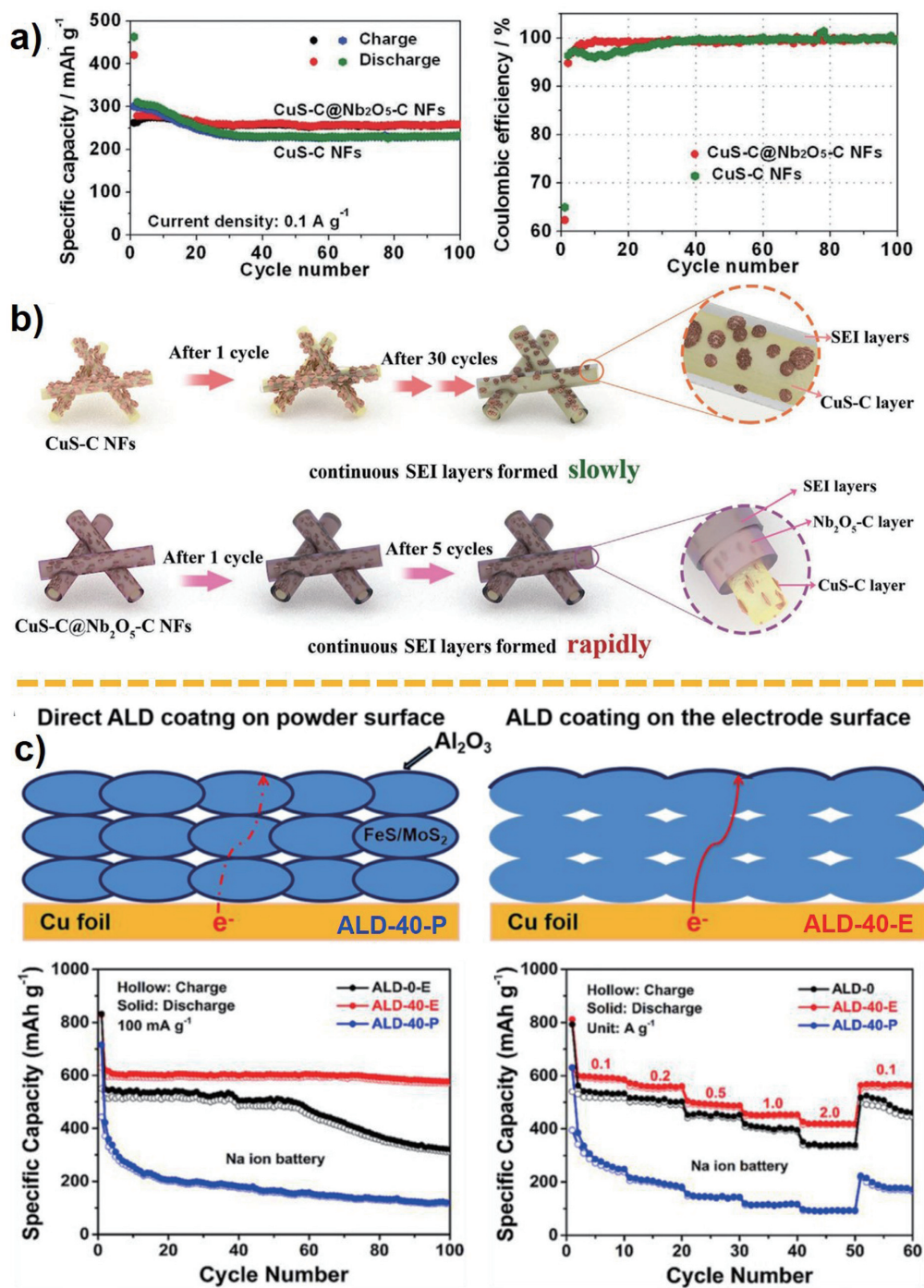


Fig. 2. (Color online) (a) Cycling performance and the corresponding coulombic efficiencies of CuS-C and CuS-C@Nb₂O₅-C NFs electrodes, (b) the schematic illustration of their SEI layers changes. Reproduced with permission^[34], Copyright 2020, Wiley-VCH. (c) Schematic illustration of ALD production of Al₂O₃ coating on (left) individual FeS/MoS₂ powders (ALD-40-P) and (right) on the surface of the electrode (ALD-40-E), as well as their electrochemical performance as Na-ion battery anodes. Reproduced with permission^[35], Copyright 2021, Elsevier.

and further maintain its high stability have outstanding advantages in improving the battery performances. The cycling stability, rapid charging capability, and coulombic efficiency could be enhanced remarkably by the design and regulation of the microstructure and components of the functional nanolayers, providing a reliable strategy for the construction of battery anode materials with high performance.

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References

- [1] Liu Y Y, Shi H D, Wu Z S. Recent status, key strategies and challenging perspectives of fast-charging graphite anodes for lithium-ion batteries. *Energy Environ Sci*, 2023, 16, 4834
- [2] Chao X, Yan C Z, Zhao H P, et al. Micro-nano structural electrode

- architecture for high power energy storage. *J Semicond*, 2023, 44, 050201
- [3] Wang H W, Zhai D Y, Kang F Y. Solid electrolyte interphase (SEI) in potassium ion batteries. *Energy Environ Sci*, 2020, 13, 4583
- [4] Xu Y B, Jia H, Gao P Y, et al. Direct *in situ* measurements of electrical properties of solid–electrolyte interphase on lithium metal anodes. *Nat Energy*, 2023, 8, 1345
- [5] Hou M J, Zhou Y J, Liang F, et al. Research progress of solid electrolyte interphase for sodium metal anodes. *Chem Eng J*, 2023, 475, 146227
- [6] Single F, Latz A, Horstmann B. Identifying the mechanism of continued growth of the solid-electrolyte interphase. *ChemSusChem*, 2018, 11, 1950
- [7] Feng G X, Jia H, Shi Y P, et al. Imaging solid-electrolyte interphase dynamics using operando reflection interference microscopy. *Nat Nanotechnol*, 2023, 18, 780
- [8] Lodico J J, Mecklenburg M, Chan H L, et al. Operando spectral imaging of the lithium ion battery's solid-electrolyte interphase. *Sci Adv*, 2023, 9, eadg5135
- [9] Qian G Y, Li Y W, Chen H B, et al. Revealing the aging process of solid electrolyte interphase on SiO_x anode. *Nat Commun*, 2023, 14, 6048
- [10] Chen Y, Wu W K, Gonzalez-Munoz S, et al. Nanoarchitecture factors of solid electrolyte interphase formation via 3D nano-rheology microscopy and surface force-distance spectroscopy. *Nat Commun*, 2023, 14, 1321
- [11] Cao C C, Zhong Y J, Shao Z P. Electrolyte engineering for safer lithium-ion batteries: A review. *Chin J Chem*, 2023, 41, 1119
- [12] Zheng J, Hu C, Nie L J, et al. Recent advances in potassium-ion batteries: From material design to electrolyte engineering. *Adv Mater Technol*, 2023, 8, 2201591
- [13] Yang Y, Yang W H, Yang H J, et al. Electrolyte design principles for low-temperature lithium-ion batteries. *eScience*, 2023, 3, 100170
- [14] Liu H Q, He Y N, Cao K Z, et al. Activating commercial Al pellets by replacing the passivation layer for high-performance half/full Li-ion batteries. *Chem Eng J*, 2022, 433, 133572
- [15] Liu H Q, He Y N, Zhang H, et al. Lowering the voltage-hysteresis of CuS anode for Li-ion batteries via constructing heterostructure. *Chem Eng J*, 2021, 425, 130548
- [16] Ye M H, Zhao W G, Li J H, et al. Integration of localized electric-field redistribution and interfacial tin nanocoating of lithium microparticles toward long-life lithium metal batteries. *ACS Appl Mater Interfaces*, 2021, 13, 650
- [17] Zhou J H, Ma K N, Lian X Y, et al. Eliminating graphite exfoliation with an artificial solid electrolyte interphase for stable lithium-ion batteries. *Small*, 2022, 18, e2107460
- [18] Tu S B, Zhang B, Zhang Y, et al. Fast-charging capability of graphite-based lithium-ion batteries enabled by Li₃P-based crystalline solid–electrolyte interphase. *Nat Energy*, 2023, 8, 1365
- [19] He Y, Jiang L, Chen T W, et al. Progressive growth of the solid-electrolyte interphase towards the Si anode interior causes capacity fading. *Nat Nanotechnol*, 2021, 16, 1113
- [20] Wang H, Miao M R, Li H, et al. *In situ*-formed artificial solid electrolyte interphase for boosting the cycle stability of Si-based anodes for Li-ion batteries. *ACS Appl Mater Interfaces*, 2021, 13, 22505
- [21] Pan S Y, Han J W, Wang Y Q, et al. Integrating SEI into layered conductive polymer coatings for ultrastable silicon anodes. *Adv Mater*, 2022, 34, e2203617
- [22] Yu Z A, Cui Y, Bao Z N. Design principles of artificial solid electrolyte interphases for lithium-metal anodes. *Cell Rep Phys Sci*, 2020, 1, 100119
- [23] Chen A L, Shang N, Ouyang Y, et al. Electroactive polymeric nanofibrous composite to drive *in situ* construction of lithiophilic SEI for stable lithium metal anodes. *eScience*, 2022, 2, 192
- [24] Li C, Liang Z Y, Li Z Z, et al. Self-assembly monolayer inspired stable artificial solid electrolyte interphase design for next-generation lithium metal batteries. *Nano Lett*, 2023, 23, 4014
- [25] Ding H B, Wang J, Zhou J, et al. Building electrode skins for ultrastable potassium metal batteries. *Nat Commun*, 2023, 14, 2305
- [26] Wang B, Yuan F, Li W, et al. Rational formation of solid electrolyte interface for high-rate potassium ion batteries. *Nano Energy*, 2020, 75, 104979
- [27] Zhou H, Cui C, Cheng R F, et al. MXene enables stable solid-electrolyte interphase for Si@MXene composite with enhanced cycling stability. *ChemElectroChem*, 2021, 8, 3089
- [28] Hou L, Cui R W, Xiong S S, et al. A multilayered sturdy shell protects silicon nanoparticle Si@void C@TiO₂ as an advanced lithium ion battery anode. *Phys Chem Chem Phys*, 2021, 23, 3934
- [29] Liu H Q, He Y N, Cao K Z, et al. Stimulating the reversibility of Sb₂S₃ anode for high-performance potassium-ion batteries. *Small*, 2021, 17, 2008133
- [30] Chen C, Hu Q L, Xue H Y, et al. Ultrafast and ultrastable FeSe₂ embedded in nitrogen-doped carbon nanofibers anode for sodium-ion half/full batteries. *Nanotechnology*, 2024, 35, 055404
- [31] Wei Z N, Wang L N, Chen P L, et al. Constructing layered vanadium disulfide nanosheets via wet-chemistry: A superior anode material for sodium ion batteries. *J Xinyang Norm Univ Nat Sci Ed*, 2020, 33, 612
- [32] Xu J, Dong Z, Li Y J, et al. Freestanding wide layer spacing MoS₂@WS₂@CC ternary structure with fast diffusion path for a highly activity zinc-ion batteries. *Appl Surf Sci*, 2023, 613, 156146
- [33] Yang G W, Yan C Z, Hu P, et al. Synthesis of CoSe₂ reinforced nitrogen-doped carbon composites as advanced anodes for potassium-ion batteries. *Inorg Chem Front*, 2022, 9, 3719
- [34] Cao K Z, Zheng R T, Wang S D, et al. Boosting coulombic efficiency of conversion-reaction anodes for potassium-ion batteries via confinement effect. *Adv Funct Mater*, 2020, 30, 2007712
- [35] Han B, Chen S Q, Guo C F, et al. Atomic layer deposition of alumina onto yolk-shell FeS/MoS₂ as universal anodes for Li/Na/K-ion batteries. *Electrochim Acta*, 2022, 402, 139471



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