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Research Highlights in 2020 (Jan-Sep)

Abstract: Rechargeable sodium-sulfur (Na-S) batteries are regarded as a promising energy storage technology due to their high energy density and low cost. High-temperature sodium-sulfur (HT Na-S) batteries with molten sodium and sulfur as cathode materials were proposed in 1966, and later successfully commercialised for utility-scale stationary energy storage. However, their high working temperature (300~350 °C) causes some detrimental problems such as high operating costs, difficulties of maintenance (corrosion), and severe safety issues. In particular, HT Na-S batteries with Na polysulfides as the final discharge product only deliver about a third of the sulfur’s theoretical capacity. These drawbacks greatly limited the broader applications of HT Na-S batteries. In recent years, extensive efforts have been devoted to developing next-generation intermediate-temperature sodium-sulfur batteries (IMT Na-S, operating at 120~300 °C) and room-temperature sodium-sulfur batteries (RT Na-S) with higher capacity, lower maintenance cost and enhanced safety. Herein, we provide a comprehensive review of the latest progress on IMT Na-S and RT Na-S batteries. We elucidate the working principles, opportunities and challenges of these non-high-temperature Na-S battery systems, and summarise the advances in the battery components including cathodes, anodes, electrolytes, and other battery constituents. In particular, the applications of solid-state electrolytes in IMT Na-S and RT Na-S chemistry are emphasised. The remaining challenges and clear perspectives are outlined for the future development of novel high-performance Na-S batteries.

https://doi.org/10.1039/D0EE02203A
Abstract: The practical applications of lithium metal anodes in high-energy-density lithium metal batteries have been hindered by their formation and growth of lithium dendrites. Herein, we discover that certain protein could efficiently prevent and eliminate the growth of wispy lithium dendrites, leading to long cycle life and high Coulombic efficiency of lithium metal anodes. We contend that the protein molecules function as a “self-defense” agent, mitigating the formation of lithium embryos, thus mimicking natural, pathological immunization mechanisms. When added into the electrolyte, protein molecules are automatically adsorbed on the surface of lithium metal anodes, particularly on the tips of lithium buds, through spatial conformation and secondary structure transformation from α-helix to β-sheets. This effectively changes the electric field distribution around the tips of lithium buds and results in homogeneous plating and stripping of lithium metal anodes. Furthermore, we develop a slow sustained-release strategy to overcome the limited dispersibility of protein in the ether-based electrolyte and achieve a remarkably enhanced cycling performance of more than 2000 cycles for lithium metal batteries.
Abstract: Selenium cathodes have attracted considerable attention due to high electronic conductivity and volumetric capacity comparable to sulphur cathodes. However, practical development of lithium-selenium batteries has been hindered by the low selenium reaction activity with lithium, high volume changes and rapid capacity fading caused by the shuttle effect of polyselenides. Recently, single atom catalysts have attracted extensive interests in electrochemical energy conversion and storage because of unique electronic and structural properties, maximum atom-utilization efficiency, and outstanding catalytic performances. In this work, we developed a facile route to synthesize cobalt single atoms/nitrogen-doped hollow porous carbon (CoSA-HC). The cobalt single atoms can activate selenium reactivity and immobilize selenium and polyselenides. The as-prepared selenium-carbon (Se@CoSA-HC) cathodes deliver a high discharge capacity, a superior rate capability, and excellent cycling stability with a Coulombic efficiency of ~100%. This work could open an avenue for achieving long cycle life and high-power lithium-selenium batteries.

**Abstract:** Beyond-lithium-ion batteries are promising candidates for high-energy-density, low-cost and large-scale energy storage applications. However, the main challenge lies in the development of suitable electrode materials. Here, we demonstrate a new type of zero-strain cathodes for reversible intercalation of beyond-Li⁺ ions (Na⁺, K⁺, Zn²⁺, Al³⁺) through interface strain engineering of a 2D multilayered VOPO₄-graphene heterostructure. In-situ characterization and theoretical calculations reveal a reversible intercalation mechanism of cations in the 2D multilayered heterostructure with a negligible volume change. When applied as cathodes in K⁺-ion batteries, we achieve a high specific capacity of 160 mA h g⁻¹ and a large energy density of ~570 W h kg⁻¹, presenting the best reported performance to date. Moreover, the as-prepared 2D multilayered heterostructure can also be extended as cathodes for high-performance Na⁺, Zn²⁺, and Al³⁺-ion batteries. This work heralds a promising strategy to utilize strain engineering of 2D materials for advanced energy storage applications.

https://www.nature.com/articles/s41467-020-17014-w
Abstract: Catalysts with single atom is one of the most efficient approaches to tuning the activity, stability, and reactivity for heterogeneous catalysts. Therefore, an atomistic understanding of the pertinent mechanism is essential to simultaneously boost the intrinsic activity, site density, electron transport, and stability. Herein, we report atomically dispersed nickel (Ni) in zincblende cadmium–zinc sulphide quantum dots (ZCS QDs) deliver an efficient and durable photocatalytic performance for water splitting under sunlight. The finely-tuned Ni atoms dispersed ZCS QDs exhibit an ultrahigh photocatalytic H\textsubscript{2} production activity of 18.87 mmol h\textsuperscript{-1} g\textsuperscript{-1}. It could be ascribed to the favorable surface engineering to achieve highly active sites of monovalent Ni(I), and the surface heterojunctions to reinforce the carrier separation owing to the suitable energy band structures, built-in electric field (BIEF), and optimized surface H\textsubscript{2} adsorption thermodynamics. This work demonstrates a synergistic regulation of the physicochemical properties of QDs for high-efficiency photocatalytic H\textsubscript{2} production.

https://advances.sciencemag.org/content/6/33/eaaz8447

Abstract: Rechargeable sodium battery is a promising technology for low–cost energy storage. However, the undesirable drawbacks originating from the glass fiber membrane separators have been long overlooked. Herein, we report a versatile “grafting–filtrating” strategy to controllably tune commercial polyolefin separators for sodium batteries. The as–developed Janus separators contain a single sodium–ion conducting polymer grafted side and a functional low–dimensional material coated side. When employed in room–temperature sodium–sulfur batteries as an example, a poly(1–[3–(methacryloyloxy) propylsulfonyl]–1–(trifluoromethanesulfonyl)–imide sodium) grafted side effectively enhances the electrolyte wettability, and inhibits the polysulfide diffusion and sodium dendrite growth. Moreover, a titanium–deficient nitrogen–containing MXene coated side electrocatalytically improve the polysulfide conversion kinetics. The as–developed batteries show high capacity, extended cycling life with lean electrolyte loading.


**Abstract:** Solid-electrolyte-based molten-metal batteries have attracted considerable attention for grid-scale energy storage. Although ZEBRA batteries are considered one of the promising candidates, they still have the potential concern of metal particle growth and ion exchange with the $\beta''$-$Al_2O_3$ electrolyte. Herein, a Li$_{6.4}$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$ solid-electrolyte-based molten lithium–molybdenum–iron(II) chloride battery (denoted as Li–Mo–FeCl$_2$) operated at temperature of 250 °C, comprising a mixture of Fe and LiCl cathode materials, a Li anode, a garnet-type Li-ion ceramic electrolyte, and Mo additive, is designed to overcome these obstacles. Different from conventional battery reaction mechanisms, this battery revolutionarily synchronizes the reversible Fe–Mo alloying–dealloying reactions with the delithiation–lithiation processes, meaning that the porous Mo framework derived from Fe–Mo alloy simultaneously suppresses the growth of pure Fe particles. By adopting a Li anode and a Li-ion ceramic electrolyte, the corrosion problem between the cathode and the solid electrolyte is overcome. With similar battery cost ($12 \text{kWh}^{-1}$), the theoretical energy density of Li–Mo–FeCl$_2$ battery surpasses that of a Na–FeCl$_2$ ZEBRA battery over 25%, to 576 Wh kg$^{-1}$ and 2216 Wh L$^{-1}$, respectively. Experimental results further prove this cell has excellent cycling performance (472 mAh g$_{\text{LiCl}}^{-1}$ after 300 cycles, 50 mg active material) and strong tolerance against the overcharge–overdischarge (3–1.6 V) and freezing–thawing (25–250 °C) incidents.

https://doi.org/10.1002/adma.202000960
Abstract: It is highly desirable to design hollow structures with multi-scale functions by mimicking cells for the construction of micro/nanoreactors. Herein, we report the construction of hollow-structured submicrometer-photoreactors with bimetallic catalysts loaded within mesoporous silicas. The synthesis parameters are optimized to study the evolution of hollow structure through hydrothermal treatment and an “adhesive-contraction” formation mechanism is proposed. AuPt@HMZS catalysts exhibited broader absorbance region under visible light and the adsorption edge displayed a red-shift, indicating the strong metal-metal interactions at the alloy interface. It can tune the reaction performance of the coupled Au-Pt catalysts to achieve excellent catalytic activity in cinnamyl alcohol oxidation to cinnamic acid for 3.1 mmol/g with 99% selectivity. The proposed strategy to build hollow structures as multifunctional micro/nanoreactors is promising for the design of high-performance and sustainable catalysts for chemical synthesis.

**Abstract:** Potassium-ion batteries (PIBs) present great potential for large-scale energy storage applications owing to their high energy density and the abundance of potassium reserve. However, the large radius of $\text{K}^+$ and super-reactive metallic nature of potassium make it difficult to realize electrochemically reversible storage with most conventional electrode materials. Currently, it remains a great challenge to develop appropriate anode materials with high specific capacities, long cycle life and low cost for PIBs. Antimony-based materials are recognized as a promising anode candidate because of their high theoretical capacities, appropriate potassiation potential, and relatively low cost. Herein, we review the recent progress of antimony-based anode materials for PIBs, including metallic antimony, antimony-based alloys, antimony chalcogenides, and composite combinations. Meanwhile, this review also focuses on the electrochemical reaction mechanisms, strategies for design and synthesis of electrode materials, and the advances of electrolyte modulation and electrode formulation. Finally, we present the critical challenges to be addressed and perspectives for ways forward to promote the development of potassium-ion batteries.

Abstract: Potassium-ion batteries based on conversion/alloying reactions have high potential applications in new-generation large-scale energy storage. However, their applications are hindered by inherent large-volume variations and sluggish kinetics of the conversion/alloying-type electrode materials during the repeated insertion and extraction of bulky K$^+$ ions. Although some efforts have been focused on this issue, the reported potassium-ion batteries still suffer from poor cycling lifespans. Here, a superior stable antimony selenide (Sb$_2$Se$_3$) anode is reported for high-performance potassium-ion batteries through a combined strategy of conductive encapsulation and 2D confinement. The Sb$_2$Se$_3$ nanorods are uniformly coated with a conductive N-doped carbon layer and then confined between graphene nanosheets. The synergistic effects between conductive coating and confinement effectively buffer the large volumetric variation of the conversion/alloying anodes, which can maintain structural stability for superior cyclability. The as-prepared anodes exhibit a high reversible specific capacity of $\approx$590 mA h g$^{-1}$ and outstanding cycling stability over 350 cycles. In situ and ex situ characterizations reveal a high structural integration of the large-volume-change Sb$_2$Se$_3$ anodes during a reversible K storage mechanism of two-step conversion and multistep alloying processes. This work can open up a new possibility for the design of stable conversion/alloying-based anodes for high-performance potassium-ion batteries.

Abstract: Recently, flexible lithium metal batteries (LMBs) are considered as a promising power source for next-generation flexible and wearable electronic devices due to their high energy densities. However, the usage of metallic Li anodes inevitably causes safety risk due to the growth of Li dendrites. In this review, we summarized the recent research progresses on flexible LMBs, with specific emphasis on the design of composite Li metal anodes and solid-state electrolytes with high flexibility and safety. We begin with a brief introduction of flexible LMBs and the associated anodes and electrolytes. Then, the preparation of flexible composite Li metal anodes has been described in detail, with the evolution from the conventional electrodeposition method to thermal infusion and mechanical rolling methods. For solid-state electrolytes, the advanced progress on shapeable ceramic, polymer, and hybrid electrolytes have been introduced. We also presented comprehensive summaries on high-energy-density flexible LMBs, including flexible lithium-sulfur batteries and lithium-oxygen batteries. Finally, we proposed the future trends, challenges, and prospects toward the practical applications of advanced flexible LMBs.


Abstract: Dual-ion sodium metal||graphite batteries are a viable technology for largescale stationary energy storage because of their high working voltages (above 4.4 V versus Na/Na⁺) and the low cost of electrode materials. However, traditional liquid electrolytes generally suffer from severe decomposition at such a high voltage, which results in poor cycle life. Herein, we report a stable dualion sodium metal battery employing a multifunctional gel polymer electrolyte, which was facilely prepared by in situ polymerizing an ethoxylated pentaerythritol tetraacrylate monomer in an optimized liquid electrolyte with fluoroethylene carbonate as co-solvent and 1,3-propanesultone as additive. This quasi-solid-state electrolyte not only exhibits high oxidative resistance and constructs stable protective layers on the electrode surfaces but also effectively facilitates homogeneous anion and cation fluxes and suppresses the sodium dendrite growth. The as-developed quasi-solid-state dual-ion batteries delivered a high capacity with long cycle life, which could be applied for low-cost energy storage.

https://doi.org/10.1016/j.chempr.2020.01.008

**Abstract:** Exploitation of cost-efficient active electrocatalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) plays a significant role for scalable electricity-to-hydrogen energy conversion. Crystalline transition metal oxides as the promising non-noble catalysts, however, are often suffering from the large excess overpotential and unsatisfactory performance. To boost their intrinsic catalytic property, we report here an incorporation of electronegative sulfur into crystalline cobalt oxide (S-CoO$_x$) to create structural disorder via a facile room-temperature ion exchange strategy. Compared with its crystalline form, the disorder in S-CoO$_x$ catalyst enables the increased low oxygen coordination and rich defect sites, which endows S-CoO$_x$ a superior catalytic activity for both OER and HER in alkali. Intriguingly, a water electrolyser adopting S-CoO$_x$ as both OER and HER electrode catalysts requires mere 1.63 V to reach a current density of 10 mA cm$^{-2}$ in 1 M KOH. This work highlights the effectiveness of designing high-performing electrocatalysts for water electrolysers based on disordered structural materials.

https://doi.org/10.1016/j.nanoen.2020.104652

Abstract: The deployment of high-energy-density lithium (Li) metal batteries has been greatly impeded by the Li dendrite growth and the safety concerns originating from flammable liquid electrolytes. Herein, we report a stable quasi-solid-state Li metal battery employing a deep eutectic solvent (DES)-based self-healing polymer (DSP) electrolyte. This electrolyte was facilely fabricated via in situ copolymerizing 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate (UPyMA) and pentaerythritol tetraacrylate (PETEA) monomers in a DES-based electrolyte containing fluoroethylene carbonate (FEC) additive. The well-designed DSP electrolyte simultaneously possesses non-flammability, high ionic conductivity and electrochemical stability, and dendrite-free Li plating. When applied in Li metal batteries with LiMn$_2$O$_4$ cathode, the DSP electrolyte effectively suppresses manganese dissolution from the cathode, and enables high capacity and long lifespan at room and elevated temperatures.
Layered lithium-rich cathode materials have attracted extensive interests owing to their high theoretical specific capacity (320 - 350 mA h g$^{-1}$). However, poor cycling stability and sluggish reaction kinetics inhibit their practical applications. After many years of quiescence, it is expected to revive the development of layered lithium-rich cathode materials to resolve our increasing dependence on high-energy-density lithium-ion batteries. Herein, we reviewed recent research progresses and in-depth understandings of structure characterizations and reaction mechanisms of layered lithium-rich manganese-based cathode materials. In particular, we comprehensively summarized the proposed reaction mechanisms on both the cationic redox reaction of transition-metal ions and the anionic redox reaction of oxygen species. Finally, we discussed opportunities and challenges facing the future development of lithium-rich cathode materials for next-generation lithium-ion batteries.

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Abstract: The stacking of complementary 2D materials into hybrid architectures is desirable for batteries with enhanced capacity, fast charging and long lifetime. However, the 2D heterostructures for energy storage are still underdeveloped, and some associated problems like low Coulombic efficiencies need to be tackled. Herein, we reported a phosphorene/MXene hybrid anode with an in situ formed fluorinated interphase for stable and fast sodium storage. The combination of phosphorene nanosheets with Ti$_3$C$_2$Tx MXene not only facilitate the migration of both electrons and sodium cations but also alleviate structural expansion of phosphorene and thereby improve the cycling performance of the hybrid anode. XPS in-depth analysis reveals that the fluorine terminated MXene stabilize the solid electrolyte interphase by forming a fluorine-rich layer on the anode surface. DFT calculations confirm that the sodium affinities and diffusion kinetics are significantly enhanced in the phosphorene/MXene heterostructure, particularly in the phosphorene/Ti$_3$C$_2$F$_2$. As a result, the hybrid electrode achieved a high reversible capacity of 535 mAh g$^{-1}$ at 0.1 A g$^{-1}$ and superior cycling performance (343 mAh g$^{-1}$ after 1000 cycles at 1 A g$^{-1}$ with a capacity retention of 87%) in a fluorine-free carbonate electrolyte.

https://doi.org/10.1021/acsnano.0c00177
Abstract: Selenium (Se), due to its high electronic conductivity and high energy density, has recently attracted considerable interest as a cathode material for rechargeable Li/Na batteries. However, the poor cycling stability originating from the severe shuttle effect of polyselenides hinders their practical applications. Herein, highly stable Li/Na–Se batteries are developed using ultrathin (≈270 nm, loading of 0.09 mg cm\(^{-2}\)) cetrimonium bromide (CTAB)/carbon nanotube (CNT)/Ti\(_3\)C\(_2\)Tx MXene hybrid modified polypropylene (PP) (CCNT/MXene/PP) separators. The hybrid separator can immobilize the polyselenides via enhanced Lewis acid–base interactions between CTAB/MXene and polyselenides, which is demonstrated by theoretical calculations and X-ray photoelectron spectroscopy. The incorporation of CNT helps to improve the electrolyte infiltration and facilitate the ionic transport. In situ permeation experiments are conducted for the first time to visually study the behavior of polyselenides, revealing the prohibited shuttle effect and protected Li anode from corrosion with CCNT/MXene/PP separators. As a result, the Li–Se batteries with CCNT/MXene/PP separators deliver an outstanding cycling performance over 500 cycles at 1C with an extremely low capacity decay of 0.05% per cycle. Moreover, the hybrid separators also perform well in Na–Se batteries. This study develops a preferable separator–electrolyte interface and the concept can be applied in other conversion-type battery systems.

https://doi.org/10.1002/aenm.202000446
Abstract: Benefiting from higher volumetric capacity, environmental friendliness and metallic dendrite-free magnesium (Mg) anodes, rechargeable magnesium batteries (RMBs) are of great importance to the development of energy storage technology beyond lithium-ion batteries (LIBs). However, their practical applications are still limited by the absence of suitable electrode materials, the sluggish kinetics of Mg$^{2+}$ insertion/extraction and incompatibilities between electrodes and electrolytes. Herein, we present a systematic and insightful review of recent advances in RMBs, including intercalation-based cathode materials and conversion reaction-based compounds. The relationship between microstructures with their electrochemical performances has been comprehensively elucidated. In particular, we discussed anode materials beyond metallic Mg for RMBs. Furthermore, other Mg-based battery systems have also been summarized, including Mg-air batteries, Mg-sulfur batteries and Mg-iodine batteries. This review provides a comprehensive understanding of Mg-based energy storage technology and could offer new strategies for designing high-performance rechargeable magnesium batteries.
ABSTRACT: The formation of sodium (Na) dendrites during cycling has impeded the practical application of Na metal anodes. Herein, we developed a flexible graphene-based matrix, e.g., porous reduced graphene oxide (PRGO) film, to support dendrite-free Na nucleation and plating, contributing to high-performance Na metal batteries. The PRGO film possessed outstanding merits of sodiophilicity and flexibility. The sodiophilic PRGO film enabled uniform Na nucleation in the initial electroplating stage. Furthermore, the flexible PRGO film with a small Young’s modulus effectively alleviated the texture deformation of electrodeposited Na, leading to a compact and dendrite-free Na deposition layer. The well-maintained Na metal anodes on the PRGO film exhibited superior cyclability, high Coulombic efficiency, and improved energy density in both half-cell and full-cell testing. This work illustrates the great significance of mechanical properties of the supporting matrix for the Na electroplating, which provides a new strategy to develop high-performance dendrite-free Na metal batteries.

Abstract: With the ever-increasing growth in next-generation flexible and wearable electronics, fiber-shaped zinc-air batteries have attracted considerable attention due to their advantages of high energy density and low cost, though their development, however, has been seriously hampered by the unavailability of efficient electrocatalysts. In this work, we designed a trimetallic nitride electrocatalyst in an unusual molecular sheet form, which was stabilized by metallic titanium carbide sheets. Besides the expected elevation in catalytic activity toward the oxygen evolution reaction, the material simultaneously unlocked excellent catalytic activity for oxygen reduction reaction with the half-wave potential as small as 0.84 V. A flexible fiber-shaped zinc-air battery, employing the designed electrocatalyst as the air cathode and a gel as the electrolyte, demonstrated an enhanced and durable electrochemical performance, outputting a competitive energy density of 627 Wh kg\textsuperscript{-1}Zn\textsuperscript{-1}. This work opens new avenues for utilizing two-dimensional sheets in future wearable and portable device applications.

https://pubs.acs.org/doi/10.1021/acs.nanolett.0c00717

**Abstract**: Cost-effective material with a rational design is significant for both sodium-ion batteries (SIBs) and electromagnetic wave (EMW) absorption. Herein, we report an elaborate yolk–shell FeS$_2$@C nanocomposite as a promising material for application in both SIBs and EMW absorption. When applied as an anode material in SIBs, the yolk–shell structure not only facilitates a fast electron transport and shortens Na ion diffusion paths but also eases the huge volume change of FeS$_2$ during repeated discharge/charge processes. The as-developed FeS$_2$@C exhibits a high specific capacity of 616 mA h g$^{-1}$ after 100 cycles at 0.1 A g$^{-1}$ with excellent rate performance. Furthermore, owing to the significant cavity and interfacial effects enabled by yolk–shell structuring, the FeS$_2$@C nanocomposite delivers excellent EMW absorption properties with a strong reflection loss ($-45$ dB with 1.45 mm matching thickness) and a broad 15.4 GHz bandwidth. This work inspires the development of high-performance bifunctional materials.

https://pubs.acs.org/doi/abs/10.1021/acs.nanolett.0c00789
Abstract: The application of NASICON-type Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$P$_3$O$_{12}$ (LAGP) solid electrolyte in lithium (Li) metal batteries has been retarded by its instability toward metallic Li and the poor interfacial compatibility with cathodes. Here we report a durable LAGP-based Li metal battery by employing self-healing polymer electrolytes (SHEs) as Janus interfaces. The SHEs were constructed on both sides of LAGP pellets by in situ polymerizing a functional monomer and a cross-linker in ionic liquid-based (anodic side in contact with Li metal) or adiponitrile (AN)-based (cathodic side) electrolytes. The as-developed SHEs show flame-retardant, high ionic conductivity (>10$^{-3}$ S cm$^{-1}$ at 25 °C), excellent interfacial compatibility with electrodes, and effective inhibition of Li dendrite formation. The LAGP-based Li metal||LiMn$_2$O$_4$ batteries with the SHE interfaces deliver a high reversible capacity with a long cycle.
Editorial


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http://www.cailiaoniu.com/202623.html