Zeolite-Supported Metal Oxide Catalysts for Selective Methane Oxidation to Methanol

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ABSTRACT

The conversion of methane is known as the "Grail of the Catalysis."\textsuperscript{1} On the one hand, methane resources are abundant on earth, which is the main ingredient of natural gas, combustible ice and shale gas. However, the storage and transportation of methane are difficult, and it is also difficult to activate methane due to its stable chemical structure. On the other hand, methanol as one of the products of methane conversion is an important molecule in industry. However, the oxidation process of methane tends to generate CO or CO\textsubscript{2} that is more stable in thermodynamic.\textsuperscript{2} Thus, the reaction of methane to methanol is important and hard.

In this study, the activity of methane oxidation was examined for the zeolite supported metal oxide (M-ZEO), and we filtered out Cu-MOR as the suitable catalyst. In research of structure-activity relationship, two structures from Cu-MOR take effect on the selective oxidation of methane (SOM) reaction. One is the exchange site in inner zeolite framework, which can preferentially exchange its proton with copper cation and present more active than the site on outer surface. The other is Al\textsuperscript{3+} pair site. We quantified the aluminum distribution of mordenite samples and confirmed the relationship between the activity on the SOM reaction and Al\textsuperscript{3+} pair site.\textsuperscript{3} Meanwhile, the formation of the active sites on Cu-MOR detected by UV-vis spectra.

Our work proved some natural structures of zeolites can be an evaluation index to the metal supported zeolite on selective oxidation of methane to methanol, moreover, contribute to a rational design of more active catalysts.

REFERENCES
CoSx Anchored Nitrogen-doped Carbon as Efficient Bi-Functional Oxygen Catalysis for Ultra-Stable Zinc-Air Batteries

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ABSTRACT
Heteroatoms doped carbon is considered a promising electrocatalyst to overcome the sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) which are the core processes for many energy conversion devices. Here, highly dispersed CoSx nanocrystals anchored on N-doped mesoporous carbon (CoSx@NMC), derived from Fe/Co dual tuning nitrogen/sulfur-containing polymer as carbon precursor, manifests discrete dual-active-sites endowing excellent bifunctional catalytic activity toward both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).

The zinc-air battery system assembled with CoSx@NMC electrode exhibits an open circuit voltage of 1.44V (vs. Zn/Zn⁺) and a peak power density of 269.7 mW cm⁻². Notably, it exhibits a super stability in the galvanostatic discharge of 5 mA and 50 mA, and the voltage could be maintained stable at 1.25V over 90h galvanostatic discharge. The superior electrochemical catalytic properties for ORR/OER are attributed to the strongly coupled pyridine-N, graphitic-N and nanoscale CoSx, which can promote the simultaneous exposure of both OER and ORR active centers.

REFERENCES
Transition Metal Nitride Anode for Potassium-Ion Batteries

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ABSTRACT

Although Lithium-ion batteries (LIBs) have been regarded as fascinating energy storage device, the scarcity and high cost of lithium resources intrigue researchers’ interest in the next-generation batteries such as Potassium-ion batteries (KIBs) due to similar electrochemical characteristic of LIBs and abundant potassium resources. However, to date there are still significant problems about searching suitable anode materials for KIBs because of hazardous of potassium metals and unstable cycle performance of carbonaceous materials, metal oxide due to large ionic size of potassium. Herein, we report ordered mesoporous niobium nitride/N-doped carbon hybrids (m-NbN/NC) as anodes for KIBs with superior cyclability and rate capability. The electrode delivers reversible capacities of 145 mA h g⁻¹ at 0.01 A g⁻¹ and 50 mA h g⁻¹ at 1 A g⁻¹. Additionally, the capacity retention of 100% at 0.5 A g⁻¹ after 2000 cycles could be achieved. In situ XRD and ex situ SEM analysis demonstrates that m-NbN/NC electrode retains its structure during cycling and is accompanied by small strain, which is ascribed to high proportion of surface-controlled reaction. This work may suggest feasible new class of electrodes for superior cyclability of KIBs.
Intrinsic Activity of Oxygen Evolution Catalysts Probed at Single CoFe$_2$O$_4$ Nanoparticles

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ABSTRACT

Identifying the intrinsic activity of electrocatalytic nanoparticles (NPs) is challenging, since common evaluation methods are based on ensemble studies. There typically more than 10$^3$ NPs are involved and mixed with conductive additives and binders, prohibiting the identification of individual intrinsic particle activities. Herein, we use nano impact electrochemistry as an additive-free method to overcome this problem.$^{[1]}$ As shown in Scheme 1, here we use this approach to study the oxygen evolution reaction (OER) at 4 nm sized CoFe$_2$O$_4$ spinel NPs. Due to the efficient mass transport at individual NPs, high current densities of several kA·m$^{-2}$ are realized and it is shown that particles’ size and crystal structure of these used catalysts remain unaltered after OER. Moreover, the steady-state current scales with the particle size distribution and is limited by the diffusion of produced oxygen away from the particle. This versatile applicable method provides new insights into nanocatalyst activities, which is key to the efficient development of improved and precious metal-free catalysts for renewable energy technologies.$^{[2]}$

REFERENCES

Stable Li/Na-air battery in ambient air with in-situ formed gel electrolyte

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ABSTRACT

Li/Na-air batteries have been considered as promising power sources for electrical vehicles, consumer devices as well as power station. Greatly progresses have been achieved in highly efficient cathode, stable electrolyte as well as dendrite-free metal anode. However, most of the reported Li/Na-air batteries were cycled in pure O₂ condition which undoubtedly deteriorate the specific capacity. When operated in ambient air, some problems arise, such as Li anode passivation, poor cycle life as well as electrolyte volatilization.

We herein present a method for preparation of gel electrolyte for Li/Na-air batteries, which the gel is formed in situ through a cross-linking reaction between the liquid tetraethylene glycol dimethyl ether and the lithium ethylenediamine grown on the surface of Li/Na anode. We demonstrate that the gel can efficiently alleviate the corrosion of the Li/Na anodes, and thus the Li-air batteries shows a cycle performance over 1175 hours while the Na-air battery shows over 2000 hours. There results are much superior to previous reports. The experimental details and the corresponding mechanism analysis will be introduced in the poster.

REFERENCES

High Performance Supercapacitor Derived by Carbonized Zeolitic Imidazolate Framework Incorporated with Molybdenum Disulfide

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ABSTRACT

Owing to their high-power density and superior cycle stability relative to batteries, supercapacitors have risen as an important electrical energy storage device\cite{1}. Since the high capacitance contingent on large surface area and high electrochemical response, metal organic framework (MOF) is a new class of materials whose eminent surface area and high porosity potentially allows them to challenge the dominance of supercapacitors\cite{2,3}. Herein, we have prepared standing nanosheets of highly conductive carbonized ZIF-67 (CZ) composite with MoS\textsubscript{2} having high electrical conductivity and large surface area. The CZ@MoS\textsubscript{2} owns multiple pores and thin nanosheets for fast ion diffusion and rich interfacial active sites that can speed up faradaic reactions resulting in high capacitance and greater capacity retention. Notably, compared to control sample ZIF-67, the CZ@MoS\textsubscript{2} electrode yields impressive and excellent cycling stability (<90% capacitance retention after 3000 charge–discharge cycles), mainly due to its robust porous architecture and good electronic conductivity. This carbonized MOF-driven strategy demonstrates that the well-designed CZ@MoS\textsubscript{2} is promising electrode materials for high-performance supercapacitors.

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\end{enumerate}
High-performance M–Nb–O Anode Materials for Lithium-Ion Batteries

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ABSTRACT

The great success that lithium-ion batteries (LIBs) have experienced in portable electronic devices is now being extended to electric vehicles (EVs), which require high power density, energy density, safety and cyclic stability. Despite of the large theoretical capacity of 372 mAh g$^{-1}$, the commonly used graphite anode material suffers from its poor rate capability and safety. Among the recently developed anode materials, Li$_4$Ti$_5$O$_{12}$ has probably received the most attention. Although Li$_4$Ti$_5$O$_{12}$ can be modified to be a superior anode material with high rate capability, safety and cyclic stability, its main problem of the intrinsically small theoretical capacity (175 mAh g$^{-1}$) cannot be solved. Very recently, we have explored a series of intercalating M–Nb–O anode materials,[1–8] which exhibit large theoretical capacities (374–403 mAh g$^{-1}$), high safety, open crystal structures, significant pseudocapacitive behavior, large density and good cyclability, perfectly fulfilling the above four key requirements.

REFERENCES

Flexible three-dimensional hierarchical lavender-like CC/TiO$_2$@ZnO hollow nano-arrays for high-performance lithium-ion battery anodes

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ABSTRACT

With growing demand for low-emission sources of energy, rechargeable lithium-ion batteries have received widespread attention in the past decades$^{[1]}$. The graphite anodes commonly used in commercial lithium-ion batteries have failed to meet escalating demands for smaller electronics and to extend the driving range of electric vehicles because of their poor ability to cycle and low theoretical capacity$^{[2]}$. The pursuit of high-performance anode materials with low weight, volume, and cost is a popular research topic.

Using an easy two-process, seed-free solvothermal method, the 3D flexible ranked CC/TiO$_2$@ZnO hollow nano-flower arrays were synthesized. To ensure rapid electron transport, TiO$_2$ hollow nanofiber arrays were cultivated directly on the conductive CC substrates, and then the 2D ultrathin ZnO nanosheets were combined in an upright fashion on the TiO$_2$ hollow nanofiber array surface to form a lavender-like shell through a chemical bath deposition. The lavender-like shells were composed of 2D ultrathin ZnO nanosheets and endowed the final hollow nano-flower arrays with a significant specific surface area. The mesoporous hollow architecture, as well as direct contact with the CC current collector, provided an efficient electronic pathway for the 3D flexible ranked CC/TiO$_2$@ZnO hollow nano-flower arrays. The 3D flexible hierarchical CC/TiO$_2$@ZnO hollow nano-flower arrays showed remarkable electrochemical properties thanks to their unique hierarchical structure. After 200 cycles at a current density of 200 mAg$^{-1}$, the capacity retention of the 3D flexible ranked CC/TiO$_2$@ZnO hollow nano-flower arrays remained stable and reached 846 mA hg$^{-1}$.

Figure 1- (a) Schematic illustration of the synthesized procedures of the final products. (b)SEM images of the final products. (c) Cycling performances of specimens.

REFERENCES

Organic molecule electrode with high capacitive performance based on the phenanthraquinone and holey graphene hydrogel

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ABSTRACT

The present work reports a holey graphene hydrogel-base organic molecule electrode (OME) with the phenanthraquinone (PQ) as non-covalently modified molecule, and \( \text{H}_2\text{O}_2 \) as activator (named as HGH–PQ). In such electrode system, the holey graphene sheets assemble into the 3D graphene hydrogel during the hydrothermal process which is benefit for exposing more active sites accessible to electrolyte and enhancing supercapacitive behaviors of the OME. The HGH–PQ electrode delivers a specific capacitance of 382.9 F g\(^{-1}\) at current density of 1 A g\(^{-1}\), and after 8000 cycles charge–discharge still retains 92.2% relative to the initial value. To match with the positive material, the graphene hydrogel–anthraquinone (GH–AQ) is used as negative electrode to assemble an asymmetric capacitor (ASC). The energy density of GH–AQ//HGH–PQ ASC is 21.05 Wh kg\(^{-1}\) along with the power density of 0.90 kW kg\(^{-1}\).
Synthesis and Regulation of Self-standing Non-Noble Metal Based Catalysts for Electrocatalytic Water Splitting

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ABSTRACT

Electrochemical water splitting is one of effective technologies for clean hydrogen production, which has the advantages of simple technology, production of high purity hydrogen. However, the high overpotentials involving in hydrogen and oxygen evolution reactions limit and affect the energy conversion efficiency of the electrolysis process and the development of this technology. Therefore, reducing the overpotentials involved in the reactions at cathode and anode is important for reducing the operating voltage and improving the energy conversion efficiency. In this study, we use carbon materials with high conductivity and corrosion resistance to acid and alkali as substrates and develop a catalyst with high catalytic activity, excellent stability for both HER and OER. The catalytic activities of the catalyst were improved by optimizing the active sites exposure, conductivity, structure and synthetic process of the catalyst. Ni$_2$P with different Fe doping content can be controllably synthesized by low temperature phosphating of layered double hydroxide with different Fe/Ni molar ratios. The effect of Fe doping content on structure and catalytic activities of Ni$_2$P is studied. The experimental results show that the introduction of Fe can significantly improve the catalytic activity of Ni$_2$P for both hydrogen and oxygen evolution reaction. When the Fe/Ni molar ratio is 1:3, the as-prepared Fe$_{0.5}$Ni$_{1.5}$P exhibits the best electrocatalytic activity for both oxygen and hydrogen evolution reaction. The self-standing electrode Fe$_{0.5}$Ni$_{1.5}$P/CF prepared with this Fe/Ni molar ratio exhibits extremely high activity for oxygen evolution reaction and achieves 100 mA cm$^{-2}$ at an overpotential of 293 mV. The Fe$_{0.5}$Ni$_{1.5}$P/CF can deliver 10 mA cm$^{-2}$ at an applied potential 1.589 V together with an excellent stability for overall water splitting.
Structure and Reaction Mechanism of Pyrolyzed Sulfur and Polyacrylonitrile Nanocomposites for Metal-sulfur Batteries

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ABSTRACT

Pyrolyzed sulfur and polyacrylonitrile nanocomposites (SPAN) have been regarded as promising positive electrode materials for metal-sulfur batteries, since it allows the metal-sulfur battery operated in carbonate electrolyte [1]. However, the structure of SPAN, and its reaction mechanism during redox reaction are still under discussion.

In this contribution, SPAN is used as the positive electrode materials for lithium and potassium based batteries. In a K-S battery, it delivers a high capacity of 270 mAh g⁻¹ [2]. In addition, by using a gel polymer electrolyte, and SPAN as positive electrode material, the Li-S batteries can be operated at high temperature (60 °C) with excellent electrochemical performance. The structure of SPAN and the reaction mechanism are discussed as well [3].

REFERENCES
Controlled Synthesis of COFs Materials and Their Energy Storage Applications

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ABSTRACT

Through the design of topological structure and the choice of polymerization environment, we introduce energy storage components in COFs materials and achieve the control of microtopography. Here we incorporate redox-active 2,6diaminoanthraquinone (DAAQ) moieties into a 2D COF linked by \( \beta \)-ketoenamines, which confer outstanding hydrolytic stability. Compared to the DAAQ-TFP COF with spherulite morphology reported in the previous literature \cite{1}, COF_{DAAQ-TFP} (CS) has a uniform size and orderly distribution. Without altering the underlying topology, we added a prepolymerization step to change the nucleation environment and finally synthesized the COF_{DAAQ-TFP} (PS) adopts a unique rod cluster morphology. Based on the apparent differences in morphology, we describe the energy storage application for these two samples, respectively. They all exhibit rapid and completely reversible Faraday process which attribute to its networks with uniform micropores as well as introduced energy storage components.

REFERENCES

An Unconventional Iron Nickel Catalyst for the Oxygen Evolution Reaction

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ABSTRACT

The oxygen evolution reaction (OER) is a key process that enables the storage of renewable energies in the form of chemical fuels.\textsuperscript{[1-3]} Here, we describe a catalyst that exhibits turnover frequencies higher than state-of-the-art catalysts that operate in alkaline solutions, including the benchmark nickel iron oxide.\textsuperscript{[4]} This new catalyst is easily prepared from readily available and industrially relevant nickel foam, and it is stable for many hours. Operando X-ray absorption spectroscopic data reveal that the catalyst is made of nanoclusters of γ-FeOOH covalently linked to a γ-NiOOH support. According to density functional theory (DFT) computations, this structure may allow a reaction path involving iron as the oxygen evolving center and a nearby terrace O site on the γ-NiOOH support oxide as a hydrogen acceptor. It suggests that this structure may open up a bifunctional reaction pathway facilitating the O–O bond formation.

![Fig. 1](image-url) (a) TOFs and structures of NiFeOOH and γ-FeOOH/γ-NiOOH, (b) Volcano plots assuming mononuclear (black) and bifunctional OER mechanisms (green).

REFERENCES

Ionic Conductive, Mechanically Strong Hyperbranched PEO-Based Hyperstar Solid Polymer Electrolytes for Lithium Metal Batteries

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ABSTRACT

Poly(ethylene oxide) (PEO)-based solid polymer electrolytes (SPEs) with shape flexibility, nonflammability and high SPE–Li interfacial stability are poised to be an enabler for all-solid-state Li batteries,\textsuperscript{[1]} but their application is restricted by low room-temperature ionic conductivity and poor mechanical strength at elevated temperatures.

Hyperstar polymers (\textit{hb}PPEGMA-\textit{s}-PS) are synthesized with hyperbranched PEO serving as the star core and linear polystyrene (PS) serving as the arms.\textsuperscript{[2]} The hyperbranched topological structure suppresses crystallization and facilitates PEO segmental motion (higher ionic conductivity than linear PS-\textit{b}-PEO-\textit{b}-PS and brush gPS-\textit{b}-gPEO-\textit{b}-gPS). The rigid PS arms entangle during phase separation and form mechanically strong physical cross-links (higher mechanical strength than \textit{hb}PS-\textit{s}-PPEGMA).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Illustration of the correlation between topological structures and phase separation of PEO-PS copolymers blending with LiTFSI: (a) PS-\textit{b}-PEO-\textit{b}-PS triblock copolymer, (b) gPS-\textit{b}-gPEO-\textit{b}-gPS brush polymer, (c) \textit{hb}PS-\textit{s}-PPEGMA star polymer, and (d) \textit{hb}PPEGMA\textsubscript{m-n}-s-PS\textsubscript{n} hyperstar polymer.}
\end{figure}

REFERENCES

ABSTRACT

Lithium metal batteries (LMBs) are promising next-generation batteries for EV applications because of their high energy density. Ether electrolytes with high reductive stability against Li metal are troubled by their poor stability under high voltage (>4 V), thus being excluded from high voltage batteries. Therefore, improving the oxidation stability of ether electrolytes and developing practical ether electrolytes suitable for high voltage lithium metal batteries have significant importance.

Figure 1. (a) Cathode-electrolyte interphase in different electrolytes, (b) the solvation structures in HCE and LHCE, (c) the cycling stability of NMC811 in different electrolytes, (d) the cycling performance under practical conditions in ether electrolytes.

We have designed and developed a series of high concentration (HCE) and local high concentration ether electrolytes (LHCE), which have significantly improved their high voltage stability. The novelty of this work lies in revealing the mechanism of corrosion induced by catalytic decomposition of ether electrolyte on the surface of high voltage active cathode, and the construction of a stable and efficient protective CEI, which significantly inhibit the decomposition of ether electrolytes and improve the stability of cathode. The LHCE solves the problems of high viscosity, high cost and low ionic conductivity of conventional HCE, and greatly improves the battery stability under strict practical conditions.

REFERENCES
High-Performance Fiber-Shaped Aqueous Rechargeable Zinc-Ion Batteries

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ABSTRACT

Increasing efforts have been devoted to developing high-performance flexible Zn-ion batteries for wearable electronics due to acceptable security, high eco-efficiency, and abundant resources. Nevertheless, the practical applications of Zn-ion batteries are still limited by their relative low energy and power density as well as poor rate capability. Herein, we developed high-performance fiber-shaped aqueous rechargeable zinc-ion batteries (FARZIBs) by the design of nanostructure electrode materials and device structures. In the electrode materials, we constructed a finely crafted nanocomposite with a hierarchical core-shell structure on a carbon nanotube fiber (CNTF), in which three-dimensional (3D) porous N-doped carbon nanowall arrays and thin V$_2$O$_5$ nanosheets serve as the core and shell (NC@V$_2$O$_5$), respectively. Besides, we reported a novel self-sacrificed route to construct 3D vanadium-based MOFs (V-MOFs, MIL-47) nanowire-bundle arrays on CNTFs as advanced binder-free cathodes. The unique constructions of 3D electrode materials not only greatly increase the active reaction sites of electrode materials for higher volumetric capacities, but also enhances the electron transfer and ion diffusion of the electrodes for better rate performance. In the device structures, we demonstrated the first prototype of high-voltage FARZIBs with coaxial structure, which delivered small contact resistance and excellent mechanical flexibility. Thus, our works pave novel ways to construct high-performance fiber-shaped Zn-ion batteries for next-generation wearable electronics.

Figure (a, c) Schematic of the formation mechanism of NC@V$_2$O$_5$ core-shell hierarchical structure and V-MOF nanowire-bundle arrays on CNTFs. (b, d) SEM images of NC@V$_2$O$_5$ and V-MOF. (e) Schematic illustrations showing the fabrication process of the coaxial-fiber ARZIB.

REFERENCES

In-situ Electrochemical Production of Ultrathin Nickel Nanosheets for Efficient Hydrogen Evolution Electrocatalysis

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ABSTRACT
Hydrogen has been emerging as the next-generation energy carrier for both economic and environmental considerations. Combined with electricity generation from renewable energy sources, alkaline water electrolysis is considered to be a clean and sustainable way to produce hydrogen. Herein, we first demonstrated a facile method to prepare 2D Ni-thiolate nanosheets exhibiting excellent HER performance under alkaline conditions.\textsuperscript{4, 5} The Ni-thiolate nanosheets were prepared using Ni(OH)\textsubscript{2} as template and 1,4-benzenedithiol (BDT) as ligand, and made of a coordination polymer (Ni-BDT) with interconnected square-planar Ni(SR)\textsubscript{4} motifs. Surprisingly, the electrochemical in-situ X-ray absorption spectroscopy studies demonstrated that under the alkaline HER condition, Ni-BDT were entirely converted into ultrathin metallic Ni nanosheets with trace sulfide adsorbed on their surface. The electrochemical activated catalyst showed superior activity towards HER with the overpotentials of 80 mV and 150 mV to reach the current densities of 10 and 100 mA cm\textsuperscript{-2}, respectively. Using the in-situ generated ultrathin Ni nanosheets as the HER electrocatalyst, we further demonstrated how the presence of Ni\textsuperscript{0}-S\textsubscript{ad}\textsuperscript{δ} interface promote the HER by enhancing the water dissociation.

REFERENCES
A Versatile Single-Ion Electrolyte with a Grotthuss-like Li Conduction Mechanism for Dendrite-Free Li Metal Batteries

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ABSTRACT

Given the limitations inherent in current battery technologies, much of the research on next generation energy storage technologies has been focused on potential successors to lithium ion batteries such as Li–S batteries or Li–O2 batteries. However, the use of alkali metal anodes is needed to realize the potential of batteries, but these anodes are likely to suffer from dendrite formation, which results in excessive electrolyte decomposition. Herein, we present a versatile single-ion electrolyte, which is achieved by coordinating the anions in the electrolyte on the open metal sites of a metal organic framework. Further investigations of the activation energy and theoretical quantum mechanical calculations suggest that Li ion transport inside the pores of Cu-MOF-74 is via a Grotthuss-like mechanism where the charge is transported by coordinated hopping of Li ions between the perchlorate groups. This single-ion electrolyte is versatile and has wide applications. When the single-ion electrolyte is used for Li||Li symmetric cells and Li||LiFePO4 full cells, Li dendrites are suppressed. As a result, an ultralong cycle life is achieved for both cells. In addition, when the single-ion electrolyte is assembled into Li||LiMn2O4 batteries, the dissolution of Mn2+ into the electrolyte is suppressed even at elevated temperatures, and a long cycle life with improved capacity retention is achieved for Li||LiMn2O4 batteries. Finally, when the single-ion electrolyte is applied to Li–O2 batteries, an improved cycle life with reduced overpotential is also achieved.

REFERENCE

Preparation of low platinum alloy and study on oxygen reduction properties

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ABSTRACT

In proton exchange membrane fuel cells, the oxygen reduction reaction on the air electrode has a slow kinetic process, which is the main consumption reaction of noble metal Pt catalyst. However, the limited reserves, high cost and poor stability of Pt seriously restrict the large-scale commercial application of PEMFC. In recent years, although some progress has been made in the research of carbon-based non-noble metals with certain oxygen reduction catalytic activities, there is still a considerable gap between the practical application of these catalysts. Nanoparticles (platinum nanoparticles supported by carbon materials) are currently the only commercially available fuel cell catalyst and one of the most active catalysts among all metals. Platinum, as a basic element in catalytic oxygen reduction reaction, plays an important role in reducing cost and improving catalytic efficiency.

In this paper, the traditional methods were improved and innovated in the process of preparing the alloy. After physical characterization and electrochemical activity test, we found that the obtained samples showed better morphology and structural characteristics. In figure 1(a), the XRD surface is synthesized as ordered PtFe. In figure 1(c), SEM shows that the particle size of the synthesized nanocrystals is 2-3 nm. The resulting material was coated on the GC electrode and the Pt load was 2 micrograms during the test.

Fig 1. (a) TEM and (b) XRD images of PtFe; (c) LSV curves of PtFe in O\textsubscript{2} -saturated 0.1 M HClO\textsubscript{4} at a scan rate of 10 mV s\textsuperscript{-1} and a rotation rate of 1600 rpm.

REFERENCES

Li/Garnet Interface Modification Through Alloy Interlayer

ABSTRACT

Various artificial interlayers like metal/metallic oxides have been introduced to improve Li wettability through alloy reaction for the Li/Garnet interface. However, huge volume change during continuous alloying/de-alloying process is detrimental to the rigid solid-to-solid contact of Li/Garnet, and subsequently lead to the instability of polarization voltage. Herein, we demonstrate an improved artificial interlayer of Cu₆Sn₅ to simultaneously restrict the volume change and ensure the intimate contact of Li/Garnet interface. It is proved that Cu atom in Cu₆Sn₅ can not only mitigate the volume change but also restrain the diffusion of Sn. Intimate solid contact of Li with Garnet can still be realized after Li stripping due to the uphold of Li₂ₓ+SnCu₁₋ₓ framework. Moreover, Li/Garnet/Li symmetric cell with Cu₆Sn₅ modification displays smaller voltage polarization and impedance change than the pure Sn modified counterpart.
Dual Oxidation by Hybrid Electrode: Efficiency Enhancement of Direct Hypophosphite Fuel Cell

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ABSTRACT

Sodium hypophosphite is newly reported as fuel for direct liquid fuel cell, hoping to replace methanol and borohydride for its power performance, safety and low-cost. However, the hydrogen evolution problem during discharge has seriously restricted the widespread use of direct hypophosphite fuel cell. We reported\textsuperscript{[1]} a new design of anode electrode assembly, bringing in an additional layer for hydrogen oxidation above the original catalyst layer, which eventually increases the Faradaic efficiency and energy efficiency in different discharge conditions. The analyzing methods by \textsuperscript{31}P-Nuclear Magnetic Resonance (\textsuperscript{31}P-NMR) are also established and carefully discussed. The new designed membrane electrode assembly (MEA) reaches 90\% Faradaic efficiency when the fuel is discharged to 0 V and the energy efficiency of our best cases (20-34\%) is among the top rank of reported energy efficiencies for different direct liquid fuel cells. This dual oxidation strategy may bring new solution for other biproduct-generating fuels in direct liquid fuel cells.

\textbf{Scheme}  a) Graphical description on how dual oxidation works with laminated structure and how it is different from single oxidation. b) Illustration of the laminated structure of dual oxidation MEA.

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Metal organic framework derived Cu-embedded graphite carbon host for dendrite-free lithium metal anodes with long cycle life

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ABSTRACT

The development of high energy rechargeable battery technology is crucial to meet the ever growing demand for energy storage applications.[1, 2] Lithium metal has been considered as a promising anode material for a long time because of its inherent high capacity and low potential. However, dendrite formation on cycling hinders its application.[3-5] Herein, a metal-organic framework derived Cu nanoparticle-embedded graphite carbon (Cu@GC) is developed and applied as a host for Li deposition. It is found that the nano-Cu particles are unfirmly embedded in the bulk and surface of the carbon, integrating the high conductivity and high surface area. DFT calculations and experiment data indicate that the CuCx formed at interface can serve as the lithiophilic sites for Li nucleation and growth. Accordingly, such host material exhibits a dendrite-free Li plating/stripping. Li-half cell (Li//Cu@GC) displays a stable coulombic efficiency for 400 cycles at a current density of 1.0 mA cm-2, with an average value of about 99.1% for 400 cycles, and the Li@Cu@GC based symmetric cell can cycle stably for over 2000 h at 1.0 mA cm-2. Furthermore, the lithium metal batteries coupled with Li@Cu@GC anode (i.e., Cu@GC pre-plated Li) and two different cathodes (LiFePO4 and sulfur cathodes) show good cycling performance, as evidenced by 94.7% retention after 1000 cycles in LiFePO4//Li@Cu@GC, and 63.4% retention after 250 cycles in S//Li@Cu@GC.

REFERENCES
Engineering a High Energy-density and Long Lifespan Aqueous Zinc Battery via Ammonium Vanadium Bronze

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ABSTRACT

Aqueous rechargeable zinc batteries (ARZBs) are desirable for energy storage devices owing to the low cost and abundance of Zn anode, but their further development is limited by a dearth of ideal cathode materials that can simultaneously possess the high capacity and stability[1-2]. Herein, we employ a layered structure of ammonium vanadium bronze (NH$_4$)$_{0.5}$V$_2$O$_5$ as the cathode material for ARZBs. The large interlayer distance supported by the NH$_4^+$ insertion not only facilitates the Zn$^{2+}$ ion intercalation/de-intercalation, but also improves electrochemical stability in ARZBs. As a result, the layered structural (NH$_4$)$_{0.5}$V$_2$O$_5$ cathode delivers a large capacity up to 418.4 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$. A reversible capacity of 248.8 mAh g$^{-1}$ is still remained after 2000 cycle and a capacity retention of 91.4 % was kept at 5 A g$^{-1}$(Fig.1). Furthermore, in comparison with previously reported Zn ion batteries, the results would enlighten and push the ammonium vanadium compounds to a brand new stage for the application of aqueous batteries.

REFERENCES
Electrospun ultrathin W$_4$Nb$_{26}$O$_{77}$ nanowires with enhanced lithium-storage properties

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ABSTRACT

Lithium-ion batteries (LIBs) have been widely used to meet the needs of current energy applications. At present, commercial LIBs based on graphite anodes inevitably possess some issues, such as low safety and energy density. In this work, ultrathin W$_4$Nb$_{26}$O$_{77}$ nanowires have been successfully prepared through a simple electrospinning method followed by a post-treatment process. The W$_4$Nb$_{26}$O$_{77}$ shows high capacity, excellent cycling stability and rate performance. The average working voltage plateau of W$_4$Nb$_{26}$O$_{77}$ nanowires is similar to those of Li$_4$Ti$_5$O$_{12}$ (about 1.55 V) and Nb$_2$O$_5$ (about 1.7 V). Moreover, W$_4$Nb$_{26}$O$_{77}$ shows a large theoretical capacity of 253 mAh g$^{-1}$. For example, when cycled at 100 mA g$^{-1}$, W$_4$Nb$_{26}$O$_{77}$ nanowires can still possess an initial reversible capacity of 230 mAh g$^{-1}$. Such excellent electrochemical performances of W$_4$Nb$_{26}$O$_{77}$ nanowires make it a suitable anode material for LIBs.

Fig.1 Galvanostatic discharge/charge curves of the W$_4$Nb$_{26}$O$_{77}$ nanowires and its cycling performance at 100 mA g$^{-1}$

REFERENCES

Patterned macroporous Fe$_3$C/C membrane induced high ionic conductivity for integrated Li–sulfur battery cathodes

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ABSTRACT
To realize an Al-free cathode and to push forward the Li–S battery technology for practical applications, a multifunctional three-layer-structured Fe$_3$C/C membrane was prepared at a large-scale via a facile phase-inversion method. The scalable yet flexible self-supporting Fe$_3$C/C membrane is an ideal Al foil-free cathode material for high-energy and long cycling Li–S batteries. The conductive dense layer of the Fe$_3$C/C membrane can replace the Al foil as a current collector and the finger-like macropores can host most of the sulfur active material (1.5–3.0 mg cm$^{-2}$), thus buffering the volume expansion of the sulfur species and facilitating the ion/electrolyte transport for fast reaction kinetics; meanwhile, the sponge-like pores in the top layer of the composite membrane enable further S slurry loading. Density functional theory simulation (DFT) and Li$_2$S$_6$ adsorption measurements reveal that the doped Fe$_3$C species in the composite membrane could effectively immobilize the S species and suppress the shuttle effect of the soluble polysulfides (LiPSs). The rationally designed Fe$_3$C/C membrane cathodes could deliver a capacity of ~601 mA h g$^{-1}$ at 1C after 200 cycles even at a high sulfur loading of 3.4 mg cm$^{-2}$, with a high areal capacity of 2.1 mA h cm$^{-2}$. The cell with the sulfur loading of 3.4 mg cm$^{-2}$ delivered a gravimetric energy density and volumetric energy density of 850 W h kg$^{-1}$ and 1223 W h L$^{-1}$, respectively. The self-supporting membrane cathode with simultaneous commercial S filling and S/C slurry coating provides an alternative sulfur loading approach for battery assembly, thus presenting a useful strategy for practical applications in high energy-density and long cycling Li–S batteries.
Triple-Layered Carbon-SiO$_2$ Composite Membrane for High Energy Density and Long Cycling Li–S Batteries

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ABSTRACT

Here we report a highly scalable yet flexible triple-layer structured porous C/SiO$_2$ membrane via a facile phase inversion method for advancing Li–sulfur battery technology. As a multifunctional current-collector-free cathode, the conductive dense layer of the C/SiO$_2$ membrane offers hierarchical macropores as an ideal sulfur host to alleviate the volume expansion of sulfur species and facilitate ion/electrolyte transport for fast kinetics, as well as sponge-like pores to enable high sulfur loading. The triple-layer structured membrane cathode enables the filling of most sulfur species in the macro pores and additional loading of a thin sulfur slurry on the membrane surface, which facilitates ion/electrolyte transport with faster kinetics than the conventional S/C slurry-based cathode. Furthermore, density functional theory simulations and visual adsorption measurements confirm the critical role of the doped SiO$_2$ nanoparticles (∼10 nm) in the asymmetric C membrane in suppressing the shuttle effect of polysulfides via chemisorption and electrocatalysis. The rationally designed C/SiO$_2$ membrane cathodes demonstrate long-term cycling stability of 300 cycles at a high sulfur loading of 2.8 mg cm$^{-2}$ with a sulfur content of ∼75%. This scalable yet flexible self-supporting cathode design presents a useful strategy for realizing practical applications of high-performance Li–S batteries.
Solid-state Battery with Heterogeneous Multilayer Structure Exhibits Improved Electrochemical Performances

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ABSTRACT

Solid-state batteries with organic-inorganic composite solid electrolyte (CSE) membranes were hot scientific issues to be illustrated in developing high safety lithium-ion battery systems. In view of the advantages of high ionic conductivity and excellent mechanical strength, the poly(vinylidene fluoride) (PVDF)-based composite solid electrolyte exhibits excellent performance.[1] Unfortunately, the higher hardness of the PVDF and the slow redox reaction with the Li metal usually rendering a poor structure at the electrode/electrolyte interfaces, limiting its further application.[2]

Based on the afore-mentioned problems, an interfacial transport layer precursor was prepared by dissolving poly(ethylene oxide) and a film-forming additive in volatile solvent. A uniform interfacial transport layer can be seen on the electrode surfaces after volatilizing the added solvent (Fig.1a). To verify the function of the transport layer, the Li/LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$ (NCM523) solid-state batteries were assembled using PVDF-based CSE membranes as the electrolyte. With the transport layer, the internal impedance of this battery was significantly reduced according to the observation of Fig.1b. Shown in Fig.1c, the initial discharge capacity was 153.4 mAh·g$^{-1}$ and the capacity retention rate was in 92% after 100 cycles when adding the transport layer, together higher than just applying a single PVDF-based CSE. The results presented in this work opened up methods to tap the potentials of PVDF-based CSEs.

Figure 1 (a) SEM image of interfacial transport layer on the cathode. (b)EIS spectra and (c) cycling performances at 0.1 C and 25°C of the Li/NCM523 batteries with and without the interfacial transport layer.

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MnCo$_2$S$_4$ Nanoparticles Anchored N and S Dual-Doped 3D Graphene as a Prominent Electrode for Asymmetric Supercapacitors

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ABSTRACT

Binary composites MnCo$_2$S$_4$ nanoparticles are potential and attractive materials for supercapacitors. Here, we synthesized the MnCo$_2$S$_4$ nanoparticles anchored on both N and S co-doped 3D graphene composites via a facile two-step controlled sulfurization route. Thiourea contents shows strong effect on the nanostructures and electrochemical properties of the 3D composites. When adjusting the molar ratio of thiourea to Mn$^{2+}$ as 48:1, the optimal composite electrode achieved a largest specific capacitance of 1324.3 F g$^{-1}$ at 1 A g$^{-1}$, with high conductivity, excellent rate performance and outstanding cyclic stability due to its unique structural advantages. The two-step fabrication process of MnCo$_2$S$_4$ nanoparticles in situ anchored on N, S dual-doped graphene was illustrated as below:

Moreover, we fabricated an asymmetric supercapacitor with an operating voltage of 1.5 V using the composite and N, S co-doped graphene nanosheets as both electrodes. It delivered a high energy density of 62.9 Wh kg$^{-1}$ at a power density of 0.74 kW kg$^{-1}$, and 28.0 Wh kg$^{-1}$ at a power density of 1.80 kW kg$^{-1}$, which were higher than those of reported similar devices. These results proved that the design and optimization of MnCo$_2$S$_4$ and graphene composites was a method to achieve high performance.
supercapacitors.\textsuperscript{[1]}

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Ni\textsuperscript{3+}-Induced Hole States Enhance the Oxygen Evolution Reaction Activity of Ni\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4} Electro catalysts

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ABSTRACT

Electrochemical water splitting to produce hydrogen and renewable energy in the form of chemical fuels.\textsuperscript{[1−3]} In this work, we report a systematical study on the relationship of electronic structure to oxygen evolution reaction (OER) activity of Ni\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4} (x = 0–1) mixed oxides.\textsuperscript{[4]} The specific OER activity is substantially increased by 16 times from 0.02 mA cm\textsuperscript{-2} BET for pure Co\textsubscript{3}O\textsubscript{4} to 0.32 mA cm\textsuperscript{-2} BET for x = 1 at an overpotential of 0.4 V and exhibits a strong correlation with the amount of Ni ions in the +3 oxidation state. X-ray spectroscopic study reveals that inclusion of Ni\textsuperscript{3+} ions upshifts the occupied valence band maximum (VBM) by 0.27 eV toward the Fermi level (E\textsubscript{F}) and creates a new hole (unoccupied) state located ∼1 eV above the E\textsubscript{F}. Such electronic features favor the adsorption of OH surface intermediates on Ni\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4}, resulting in enhanced OER. Furthermore, the emerging hole state effectively reduces the energy barrier for electron transfer from 1.19 to 0.39 eV, and thereby improves the kinetics for OER. The electronic structure features that lead to a higher OER in Ni\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4} can be extended to other transition metal oxides for rational design of highly active catalysts.
REFERENCES
Experiments and simulations on two-step ionic aggregation induced by divalent cation additive in anion exchange membranes

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Anion exchange membranes (AEMs) have been widely applied in flow redox battery, fuel cells and electrodialysis. Microstructured morphologies have a great effect on the properties of AEMs. In this work, a novel two-step ionic aggregation method, induced by electrostatic regulation of cation additive (Zn$^{2+}$), has been proposed to effectively promote micro-phase separation in imidazolium-functionalized polysulfone AEMs (PSF-ImOH). Reorientational process of imidazolium (Im$^+$) groups is analyzed at the molecular level by a combined experimental data and molecular dynamics simulation to cast new light on the fabrication of high-performance AEMs. In the first step, Zn$^{2+}$ ions and Im$^+$ groups are found to be aggregated together to form Zn$^{2+}$ clusters via the bridging anions in the Zn(CH$_3$COO)$_2$ incorporated PSF-ImCl AEMs (PSF-ImCl/Zn-x). The further step of removing Zn$^{2+}$ ions by ion exchange promotes the rearrangement of the adjacent Im$^+$ groups to form Im$^+$ clusters in the OH-type AEMs (PSF-ImOH-x). With the increase of Zn$^{2+}$ content (x), more Zn$^{2+}$ ions and Im$^+$ groups are assembled in Zn$^{2+}$ clusters to develop an interconnected Zn$^{2+}$ ionic network, which provides the possibility to induce a better Im$^+$ aggregate after the removal of Zn$^{2+}$ ions. With 2.9 Zn$^{2+}$ wt%, the induced PSF-ImOH-x has the biggest Im$^+$ clusters and consequently achieves the highest hydroxide conductivity, which is ~1.5 folds as high as that of the non-induced AEMs.

Fig. 1. Illustration of microstructures of Zn$^{2+}$ clusters in PSF-ImCl/Zn-x membranes and Im$^+$ clusters in PSF-ImOH-x membranes with the increase of Zn$^{2+}$ wt.% All anions for stabilizing ionic aggregation are neglected for clarity

REFERENCES


A novel polyanionic compound Li$_2$VSiO$_5$ as anode material for lithium ion batteries

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ABSTRACT

Herein, a new type polyanionic vanadium-based anode material Li$_2$VSiO$_5$ has been studied for the first time as an anode material for lithium ion batteries, which delivers a reversible specific capacity of 618 mA h g$^{-1}$ under a current density of 25 mA g$^{-1}$ and a high initial coulombic efficiency of 82.7%. Moreover, it maintains a capacity retention of 87% after 200 cycles at 200 mA g$^{-1}$. The GITT-determined Li$^+$ diffusion coefficient ranges from 10$^{-9}$ to 10$^{-11}$ cm$^2$ s$^{-1}$ along with the voltage at 3.0–0.01 V vs. Li$^+$/Li. In-situ synchrotron XRD testing during the first cycle reflects the solid solution-conversion-solid solution reaction of Li$_2$VSiO$_5$. The lithium-storage mechanism of this material is conducive to improving initial coulombic efficiency and cyclic stability comparable to that of most other conversion-type anode materials. This study will benefit the discovery of novel anode materials for lithium-ion batteries.

REFERENCES
Turning waste into treasure: the recycle of CFx primary battery

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ABSTRACT

Lithium/graphite fluoride battery holds the highest specific energy. Accompanying with stable voltage platform, wide operating temperature range and small self-discharge\textsuperscript{[1]} that could meet the requirements of aerospace, military and other harsh environments.\textsuperscript{[2]} Based on the carbon generated after battery used could not be utilized, resulting in great waste, this paper designs an easily method for recycling used CFx batteries.

The waste CFx batteries were recovered in a simple way and carbon was used to be electrode active materials to assemble button half-cells. Its charge-discharge curves are similar to that of hard carbon\textsuperscript{[3]} (Fig.1(a)). Interestingly, in the process of 70 charge and discharge cycles, the coulomb efficiency of each cycle is higher than 100% (Fig.1(b)), there is no low initial effect which likes the hard carbon. This reason should be that CFx loses the F element after discharge and converts it to hard carbon.

Figure 1. (a) charge and discharge curves for the 1st and 70th of the recovered material; (b) cycle performance and coulombic efficiency of the recovered material.

In conclusion, a simple and efficient method was used to recover the waste CFx batteries. The charge-discharge curves shows that the recycled material has excellent coulombic efficiency and cycle performance. This method opens up a new way of thinking about the green recycling of used batteries.

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Graphene Boron Nitride Hybrid Supported Single Mo Atom Electro catalysts for Efficient Nitrogen Reduction Reaction

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ABSTRACT

Converting nitrogen into ammonia at ambient conditions is of great significance but remains as a great challenge. Interfacing graphene and hexagonal boron-nitride (h-BN) to form a hybrid sheet, namely as BCN, offers stable and conductive supports for efficient single atom catalyst (SAC). Using first principles calculations, we designed a single Mo atom anchored on a defective BCN monolayer (Mo@BCN) as durable, highly stable, and efficient SAC for nitrogen reduction reaction (NRR). Different from the semiconducting Mo-anchored h-BN, the Mo@BCN exhibits metallic property which favors charge deliverer to active sites to drive NRR. Importantly, this hybrid catalyst promotes the dominant NRR while suppressing the competitive hydrogen evolution reaction (HER). Examinations of detail mechanisms for N2 reduction to NH3 including distal, alternating, and pathways, revealed outstanding catalytic performance with a quite low overpotential of 0.42 V via the enzymatic pathway, independent of carbon concentrations. These would lead to a new strategy for developing efficient and stable SACs with BN-based materials as substrate.
ABSTRACT

Energy and environment is currently the most关注的问题，新型清洁能源的开发和利用是解决当前能源危机和环境污染的重要途径。而储能技术是新能源发展的重要瓶颈之一。锂离子电池等储能设备的研究和开发日益受到人们的关注，其应用性能主要取决于电极材料。过渡金属氧化物 (TMO) 基复合材料由于其理论比电容/比容量高、电化学可逆性好、使用寿命长和环境友好等特点，而被广泛应用到电化学领域。为获得高容量、稳定循环性能和高能量密度的 TMO 基复合材料，我们构筑了不同形状的 TMO 基复合材料，如花状 TiO₂/MoS₂、核-壳结构 Ni–CeO₂@PANI[1]、核-壳结构 Fe₃O₄@C@MnO₂、双壳层结构 CeO₂@C[2]、大米状 TiO₂/RGO[3] 等；进一步地，以 Ni–CeO₂@PANI 为超级电容器电极材料，在循环 10000 圈后，电容保持率仍高达 85.6%，预示着其具有极大的应用前景。以花状 TiO₂/MoS₂ 为锂离子电池负极材料，表现出优异的循环、倍率性能。这些工作展示了用结构稳定材料来提升材料综合性能方面的优势，丰富了复合电极材料的类型，推动了过渡金属氧化物复合材料的研究与进展。

图 1. TMO 基复合电极材料

关键词： 过渡金属氧化物；复合材料；电化学

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