Nanostructured Frontiers: Enabling Next-Generation All-Solid-State Lithium-Ion Batteries

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Abstract. There is a growing need for energy storage solutions with high energy density and high safety due to the quick growth of smart grids and electric cars. Although traditional liquid lithium-ion batteries have been commercialized, their energy density is close to the theoretical limit, and there are safety hazards such as electrolyte leakage and flammability. In contrast, all-solid-state lithium-ion-batteries (ASSLIBs) with non-combustible solid electrolytes can completely eliminate the risk of thermal runaway, making them the core direction of the next-generation energy storage technology. However, issues including the development of lithium dendrites and the high interfacial impedance between the solid electrolyte and the electrode have made it difficult to commercialize. This paper systematically reviews the key roles and design strategies of nanomaterials in the positive electrode, negative electrode and electrolyte of ASSLIBs. Through size effect, high specific surface area and controllable interface characteristics, nanomaterials provide innovative solutions for optimizing ion transport, suppressing volume expansion and enhancing interface stability. Research shows that nanotechnology significantly enhances the energy density, cycle life and fast charging performance of ASSLIBs through material nanoscale, composite structure design and interface optimization. In the future, through the integration of multi-disciplinary technologies and innovation in preparation processes, nanomaterials are expected to promote the commercial application of ASSLIBs in fields such as electric vehicles, and become the core technology of high-safety, high-energy-density energy storage technologies of the future.

Keywords: All-solid-state lithium-ion-batteries; nanomaterial; nanotechnology.

1. Introduction

Since the 21st century, the global energy structure has been accelerating its transformation towards cleanliness and electrification. The popularization of electric vehicles and the large-scale deployment of smart grids have put forward unprecedented demands for the energy density, safety and cycle life of energy storage technologies. At the moment, lithium-ion-batteries are the most used energy storage technology, and have been widely applied in consumer electronics, new energy vehicles and energy storage power stations and other fields due to their high energy conversion efficiency and mature industrial chain [1]. However, there are a number of issues facing conventional lithium-ion batteries that use organic liquid electrolytes as their core. On the one hand, its energy density has approached the theoretical limit and is difficult to meet the long-range requirements of electric vehicles. On the other hand, the inherent flammability and leakage of liquid electrolytes make batteries prone to thermal runaway and even explosion when overcharged, short-circuited or mechanically damaged [2]. For instance, investigations into multiple self-ignition accidents of electric vehicles in recent years have shown that the combustion of liquid electrolytes is the main cause of the expansion of the accidents. Furthermore, the theoretical capacity of graphite anodes and the intense volume expansion of silicon-based materials further restrict the development of high-energy-density batteries.

Against this backdrop, all-solid-state lithium-ion-batteries (ASSLIBs) have become the focus of next-generation energy storage technologies due to their disruptive advantages [3]. Compared with liquid batteries, ASSLIBs use non-flammable solid electrolytes, completely eliminating the risk of thermal runaway. Meanwhile, high-capacity lithium metal anodes and high-voltage cathode materials can be used with the solid-state system [4]. Theoretically, electric vehicles could have a driving range of more than 1,000 kilometers if their energy density exceeded 500 Wh/kg. Furthermore, the strong

mechanical strength of solid electrolytes can successfully prevent lithium dendrite formation, prolonging the battery's cycle life [5].

Research on ASSLIBs began in the 1960s. In the early days, oxide solid-state electrolytes were mainly used, but their room-temperature ionic conductivity was extremely low and the interface impedance was high, making it difficult to put them into practical use. In the 1990s, the discovery of sulfide solid electrolytes became a turning point. Their ionic conductivity exceeded 10^{-2} S/cm in 2011, approaching the level of liquid electrolytes for the first time. In 2011, Toyota was the first to introduce a prototype of a sulfide all-solid-state battery. It started a trial production line in 2020 and plans to commercialize it in 2025. Meanwhile, because of their processing simplicity and flexibility, polymer solid electrolytes have demonstrated promise in the field of flexible electronics [6]. However, the large-scale application of ASSLIBs still faces three major bottlenecks: high impedance brought on by inadequate solid-solid interface contact; Interface peeling brought on by the cycling process's alteration in electrode volume; The difficulty of producing expensive solid electrolytes on a big scale [7].

In recent years, the innovative application of nanomaterials has provided breakthrough solutions to the above-mentioned problems [8]. By carefully controlling the size, shape, and interface properties of materials, nanotechnology greatly improves the core performance of ASSLIBs [9, 10]. This paper starts from the three major components of positive electrode, negative electrode and electrolyte, systematically reviews the design strategies and action mechanisms of nanomaterials in ASSLIBs, and analyzes the challenges and prospects of their large-scale application. This review aims to offer a technical reference and theoretical foundation for the creation of energy storage systems with safety and high energy density.

2. The Application of Nanomaterials in ASSLIBs

2.1. Cathode Nanomaterials

Composite nanomaterials are of great significance to the improvement of solid-state batteries cathodes. For example, a graphene and carbon nanotube composite material for a battery's cathode was studied by Chen et al. [11]. The improved Hummers method was adopted to obtain graphene oxide (GO) through the chemical oxidation of graphite. Following the dispersion of GO and acidified carbon nanotubes (CNTs) in varying mass ratios in the aqueous solution, microwave radiation was applied to the combination. Microwave selective heating of polar solvents rapidly reduces GO to RGO, while achieving a tight combination of CNTs and RGO. RGO-CNT composite material has an excellent three-dimensional conductive network. CNTs act as "wires" connecting RGO layers, forming continuous electron transport channels and suppressing the agglomeration of RGO (Fig. 1). CNTs filled the interlayer gaps of RGO, forming open nanopores, which promoted electrolyte penetration and lithium-ion diffusion. Experiments have proved that the increase of CNTs content significantly enhances the electrode conductivity (Fig. 2). The resistance of GC-10 is the lowest (421.3 Ω). The initial reversible capacity of GC-1 reached 682 mAh/g. This material has a relatively high specific capacity and is superior to pure RGO (223 mAh/g) and pure CNTs (143 mAh/g). CNTs inhibit the re-stacking of RGO sheets, retain the characteristics of a few layers of graphene, slow down capacity attenuation, and increase the cycle life of the material. After 50 cycles, GC-2 still maintained 298 mAh/g.

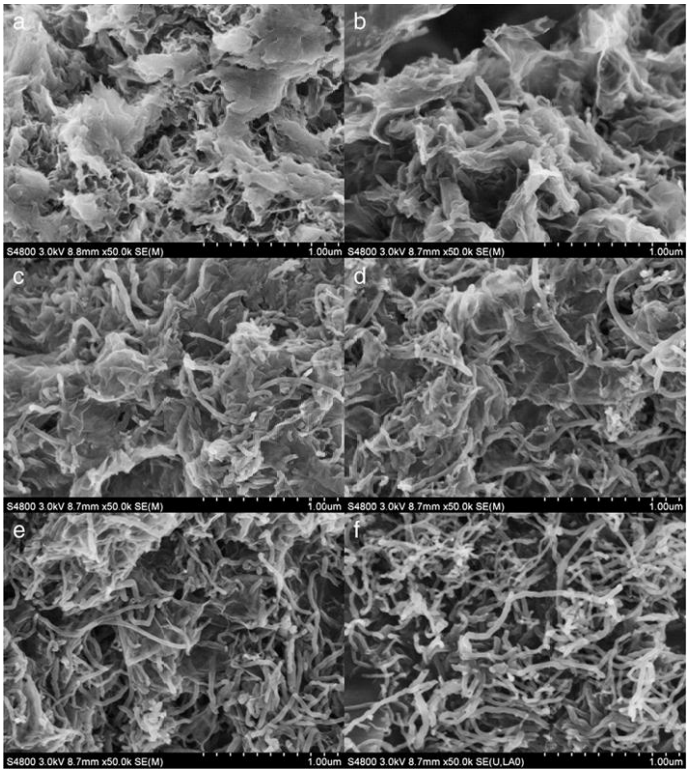

Fig. 1 The FESEM images of RGO-CNT composites of different proportions [11]

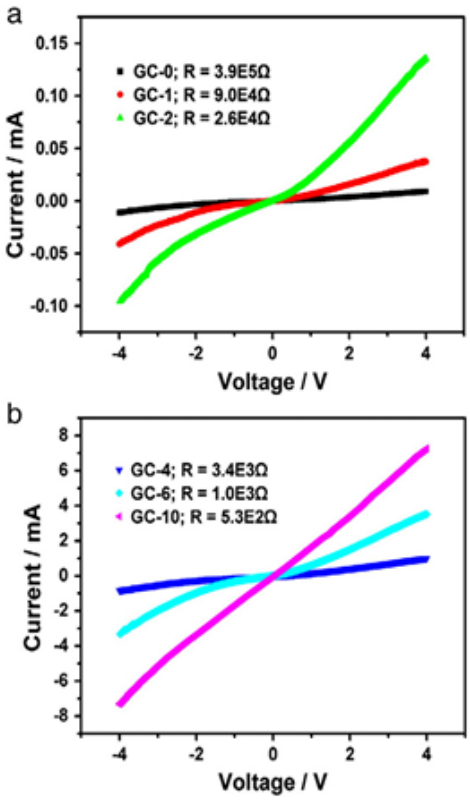

Fig. 2 I-V curves and the calculated resistance of RGO-CNT composites of different proportions [11]

Another example is Fe_3S_4@$Li_7P_3S_{11}$ nanocomposite. The raw material Fe_3S_4 is cheap and abundant in resources. Combined with the low-cost characteristics of sulfide electrolytes, it can also reduce the manufacturing cost of ASSLIBs. Coupled with having a long cycle life and a high specific capacity, in the future, it might encourage the use of ASSLIBs which have high-energy-density.

To enhance battery performance, Zhang et al. synthesized a Fe_3S_4@$Li_7P_3S_{11}$ nanocomposite for use as the cathode of ASSLIBs [12]. A nano-flower-like structure composed of Fe_3S_4 nanosheets was obtained through a polyvinyl alcohol (PVA) assisted precipitation method. A nanocomposite with a uniformly coated surface of $Li_7P_3S_{11}$ was formed by mixing the Fe_3S_4 nanosheets with Li_2S and P_2S_5 in acetonitrile using the in-situ coating method. This composite material can effectively improve the efficiency of the battery. The Fe_3S_4 nanosheet is only 15 nm thick and has an ultra-thin two-dimensional structure, which shortens the lithium-ion diffusion path. Following an in-situ liquid phase deposition process, the Fe_3S_4@$Li_7P_3S_{11}$ nanocomposite maintains its nanosheet architecture, as illustrated in Fig. 3. Obviously, after in-situ coating with the $Li_7P_3S_{11}$ solid electrolyte, the Fe_3S_4 nanosheets became thicker and rougher. The uniform coating of $Li_7P_3S_{11}$ provides a tight electrode - electrolyte interface contact. With an 842.6 mAh g^{-1} initial discharge capacity, the battery that uses this cathode has a high specific capacity. After 200 cycles, it still maintains 1001 mAh g^{-1} and can still deliver 676 mAh g^{-1} at 2.0 A g^{-1}. The $Li_7P_3S_{11}$ coating can also significantly reduce low interfacial resistance, suppress element diffusion and the space charge layer effect. Fe_3S_4@$Li_7P_3S_{11}$ composites address poor interfacial contact between the electrode and the electrolyte, reduce charge transfer resistance, minimize interfacial side effects during cycling, and improve structural stability.

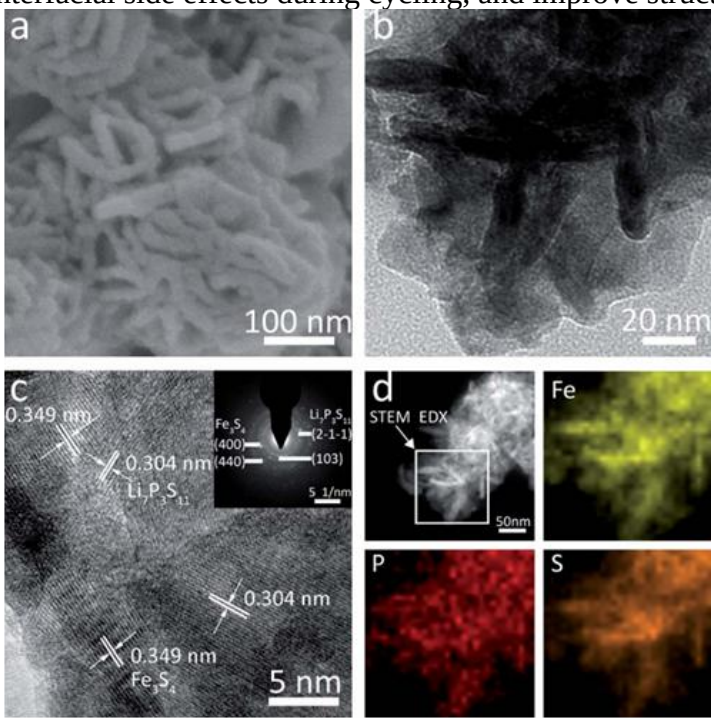

Fig. 3 (a) SEM, (b) TEM, (c) HRTEM and (d) STEM-EDS images of Fe_3S_4@$Li_7P_3S_{11}$ nanocomposites [12]

2.2. Anode Nanomaterials

The nanoscale Si dispersion structure as the anode in ASSLIBs can increase the contact area with solid electrolytes, reduce the interface impedance, and improve the lithium-ion transport efficiency. For example, a SiNPs@Mxenes composite material was created by Hu et al. to serve as the anode of ASSLIBs [13]. As shown in Fig. 4, Ti_3AlC_2 powder was etched with LiF and HCl solutions. After centrifugal cleaning, it was ultrasonically exfoliated into a few layers of $Ti_3C_2T_x$ (MXenes). Then, to create silicon nanoparticles (SiNPs) coated with PVA on the surface, for ten hours, SiNPs and PVA were mechanically ball-milled at a mass ratio of 1:1. Then, SiNPs@PVA was mixed with the MXenes dispersion and vacuum filtered to form a layered stack structure. Annealed at 600 ℃ for 2 hours in an argon atmosphere, PVA transforms into disordered carbon, providing voids for the extension of SiNPs, while the MXenes cross-linked network forms conductive channels. Finally, the compound was mixed with conductive additives (carbon black, sodium carboxymethyl cellulose) and coated on copper foil to form the working electrode. The MXenes cross-linked network of this material wraps

around SiNPs and provides mechanical support, which can suppress particle breakage caused by volume expansion (300 %-400 %). There is a void design in the structure, so that the disordered carbon (DC) formed after pyrolysis reserves a buffer space for the expansion of SiNPs, thus maintaining the integrity of the electrode structure. The battery using this material has high specific capacity and high conductivity. After the first 5 cycles, its capacity reaches 734.95 mAh g^{-1}, and it still maintains 564.82 mAh g^{-1} after 50 cycles, which is significantly higher than that of commercial graphite (370 mAh g^{-1}).

Fig. 4 Schematic diagram of the preparation process of SiNPs@MXenes composite material [13]

In addition, a Si/TiC composite anode material was investigated by Patel et al. [14]. High-energy mechanical ball milling was used to evenly distribute the nano-scale Si particles in the TiC matrix after Si powder and TiC powder were combined at a ratio of 40 mol% Si. In order to create a slurry for electrode production, the Si/TiC composite powder was combined with carbon black (7.3 weight percent) and polyvinylidene fluoride (PVDF, 5.6 weight percent) in N-methylpyrrolidone. The size of Si particles in the composite material after ball milling is reduced to the nanometer level and can be uniformly dispersed in the TiC matrix. By preventing Si's volume from expanding while it charges and discharges (~300 %), the TiC matrix preserves the electrode's structural integrity. This material enables the battery to have a certain high capacity and cycle stability. Excellent cycle stability is demonstrated by the nanocomposite material's shape, which did not change much over the course of the cycling period (Fig. 5). In the first cycle, the capacity hits 340 mAh g^{-1} at a current density of 100 $\mu A/cm^2$, and it stays constant after 30 cycles.

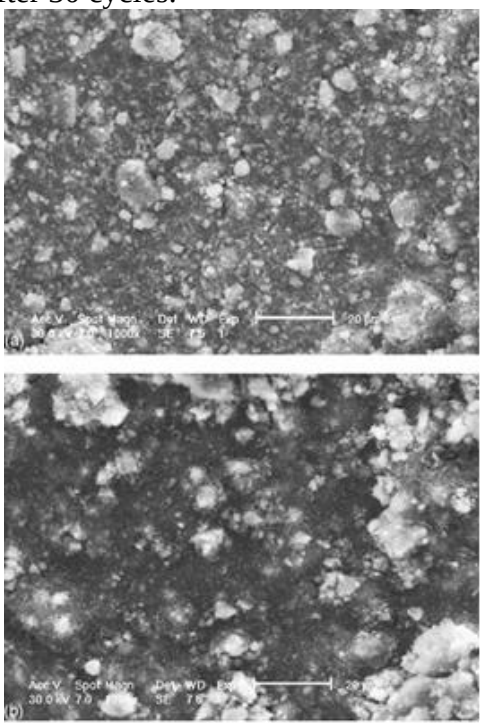

Fig. 5 Scanning electron microscope images of electrodes containing silicon after ball milling for 6 hours (a) before electrochemical testing and (b) after 30 cycles of electrochemical testing [14]

2.3. Electrolyte Nanomaterials

MXene nanomaterials (such as $Ti_3C_2T_x$) as electrolyte materials have multiple advantages. For instance, its metallic surface is more conducive to electron transport, and the material has high electrical conductivity. The surface functional groups (-O, -OH, -F) can be adjusted through the regulation of synthetic conditions to optimize the ion transport path. The uniform electric field

distribution on the negatively charged surface of MXene guides the uniform deposition of metal ions (such as Li^+, Zn^{2+}), which can inhibit the dendrite growth of ASSLIBs. Compounding using polymers has significantly increased the solid electrolyte's compressive strength. Furthermore, the surface functional groups of materials encourage lithium salts to dissociate, enabling the material to have a high ionic conductivity. Liew et al. studied a variety of MXene electrolyte materials [15]. They respectively listed various preparation methods, such as using HF Etching, directly immersing the MAX phase (such as Ti_3AlC_2) into a high-concentration HF solution to selectively etch off the Al layer and generate multilayer MXene (such as $Ti_3C_2T_x$). As shown in Fig. 6, within 24 hours at room temperature, efficient aluminum layer exfoliation requires a HF concentration of 30-50 %. In addition, fluorine-free MXene can be synthesized by molten salt etching, electrochemical etching or ball-milling method. At high temperatures, the MAX phase is etched with molten salts (such as SnF_2, $CuCl_2$), avoiding the use of HF. Electrochemical etching allows for selective etching of Al layers by overvoltage control in the electrolyte. The ball-milling method combines chemical etching and mechanical exfoliation to synthesize porous MXene in one step, avoiding the use of HF.

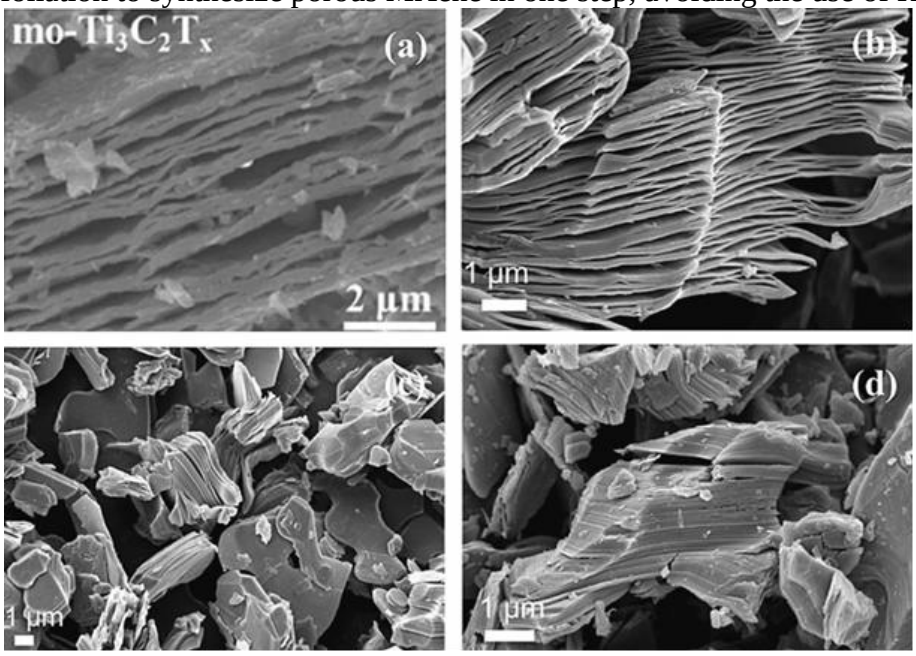

Fig. 6 The FESEM images of (a) 30%, (b) 50%, (c) 5%, and (d) 10% HF-etched MAX [15]

3. The Improvement Prospects of Nanotechnology for ASSLIBs

3.1. High Electrical Conductivity and Structural Stability

An interpenetrating network formed by the 1D structure of CNTs and the 2D sheets of RGO can ease the issue of poor solid-solid contact and lower the solid-state battery's interface impedance between the electrode and solid electrolyte. Moreover, the CNTs-filled pore structure offers a quick diffusion path for lithium ions by utilizing the nano-channel effect, perhaps making up for the solid electrolytes' low ionic conductivity flaw. That can significantly improve the electrode's electrical conductivity. In addition, the combination of nanoscale RGO and CNTs can improve mechanical stability via preventing the electrode materials' volume from expanding during charging and discharging.

The mechanical flexibility and metal-like conductivity of MXenes give SiNPs conductive channels and buffer area for volume expansion. The mechanical flexibility of MXenes can also effectively alleviate the volumetric stress during charging and discharging processes and reduce capacity attenuation.

The volume expansion issue of the Si anode in solid-state batteries can be resolved in practical applications by the high mechanical strength of the TiC matrix, which lowers the possibility of

electrode cracks and SEI film rupture. The nanoscale Si dispersion structure can increase the contact area with solid electrolytes, enhance the efficiency of lithium-ion transport by lowering the interface impedance. The metal-like conductivity of this TiC and the carbon black additive jointly construct an efficient electronic conduction network, which is suitable for the low-conductivity electrolyte system of solid-state batteries.

3.2. High Energy Density

Because of their enormous specific surface area, nanostructures offer a lot of active sites and facilitate ion transport and adsorption. Nanocomposite electrodes, through high specific capacity active materials and efficient interface design, have an energy density far exceeding that of traditional graphite.

The lightweight design of the thin-layer structure of two-dimensional nanomaterials reduces the weight of the electrode and can increase the energy density per unit mass.

3.3. Long Cycle Life

The mechanical stability of nanostructures (such as stratified, porous) and matrix materials (such as TiC, MXenes) can suppress electrode degradation. Additionally, the hierarchical design or nano-porous structure can evenly distribute the mechanical stress, reducing the occurrence of fractures during the lithiation/delithiation process. In real-world applications, the strong mechanical strength and electrical conductivity of MXenes can enhance the solid electrolyte-electrode interface contact in ASSLIBs, reducing the interface impedance. By reducing adverse reactions between the electrode and the solid electrolyte, its cross-linked network structure may increase the stability of the interface. The conserved gap design significantly reduces electrode fracture brought on by stress accumulation and is appropriate for the volume expansion of silicon-based materials in solid-state batteries.

3.4. Fast Charging and Discharging Capability

Nanoscale ion/electron transport paths (such as MXenes conductive networks) reduce polarization and enhance rate performance. MXenes (intrinsic high conductivity) and DC jointly construct a fast electron transport channel, reducing the charge transfer resistance [16].

Nanoscale active materials shorten the diffusion distance of lithium ions and enhance the reaction kinetics. Conductive additives such as MXenes and carbon nanotubes can construct continuous electron channels, thereby supporting high-rate charging and discharging.

4. Conclusion

Through material nanometization, composite structure design, and interface optimization, nanotechnology gives solid-state batteries fundamental benefits like high energy density, extended life, and quick charging and discharging. Carbon nanotubes and nanoscale reduced graphene oxide work in concert to improve mechanical stability and lessen electrode material volume expansion. Utilizing the nano-channel effect helps to compensate for solid electrolytes limited ionic conductivity. Insufficient contact between the electrode and the electrolyte on the surface is addressed by Fe_3S_4@$Li_7P_3S_{11}$ composites, reducing charge transfer resistance, minimizing interfacial side effects during cycling, and improving structural stability. The raw material Fe_3S_4 is cheap and abundant in resources. Combined with the low-cost characteristics of sulfide electrolytes, it can also reduce the manufacturing cost of ASSLIBs. When combined with a long cycle life and high specific capacity, it could encourage the future use of high-energy-density solid-state batteries. In addition, the strong mechanical strength and electrical conductivity of MXenes can lower interfacial impedance and enhance the interfacial contact between electrodes and solid electrolytes. Its cross-linked network structure can suppress side reactions and improve interface stability. After the combination of MXenes and MOFs, porous ion transport channels are provided, the interfacial resistance is reduced and the interfacial stability is improved.

However, there are still some problems to be solved in nanotechnology, such as the need to suppress interfacial side reactions like chemical degradation during long-term cycling through surface passivation or modification with solid electrolytes, and the large-scale production of nanomaterials is rather difficult. Nanomaterials are anticipated to support the commercialization of ASSLIBs in industries like electric vehicles and smart devices in the future when preparation technology advances and various disciplines are integrated. They will probably also have a big impact on the creation of the next energy storage technologies.

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