

# Strategies to anode protection in lithium metal battery: A review

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## Abstract

Lithium metal batteries (LMBs) are considered the most promising energy storage devices for applications such as electrical vehicles owing to its tremendous theoretical capacity ( $3860 \text{ mAh g}^{-1}$ ). However, the serious safety issues and poor cycling performance caused by the dendritic crystal growth during deposition are concerned for any rechargeable batteries with a lithium metal anode. To make widespread adoption a possibility, considerable efforts have been devoted to suppressing lithium (Li) dendrite growth. In this review, the recent strategies to developing dendrite free Li anode, including constructing an artificial solid electrolyte interface, current collector modification, separator film improvement, and electrolyte additive, are summarized. The merits and shortcomings for different strategies are reviewed and a general summary and perspective on the next generation rechargeable batteries are presented.

## KEY WORDS

dendrite, Li metal batteries, solid electrolyte interface

## 1 | INTRODUCTION

Sustainable energy such as water and solar power<sup>1,2</sup> are drawing intensive attention because of the increasing energy demands of a global economy and the terrible

impacts of fossil fuels. Further, the distributed network of local power generating sources envisioned in the “Smart Grid” will be at least partially made up of “intermittent energy sources,” that is, wind or solar power. To fully utilize the intermittent energy sources, efficient and

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economical electrical energy storage (EES) systems are required. Rechargeable batteries are the most suitable option for EES, which enables the energy storage and release flexibly on demand to maintain daily activities.<sup>3–7</sup> Li-ion batteries (LIBs) have been widely investigated due to the light weight and high energy density<sup>8–10</sup> and successfully implemented in most portable electronic devices, such as mobile phones, electronic watches, and digital cameras with more than 11 billion dollar market in 2011.<sup>11</sup> Although the application of LIBs has expanded into larger domain, such as electrical vehicles (EVs), hybrid EVs, robots, and so on, the high energy storage densities (high gravimetric and volumetric energy density) for these applications remain a strong engineering challenge. To improve the performance of energy storage systems, researchers have been looking for new solutions beyond the conventional LIBs.<sup>12,13</sup>

Among varieties of alternatives, Li metal is recognized as a promising anode material due to its ultra-high theoretical specific capacity ( $\sim 3860 \text{ mAh g}^{-1}$ ) and most negative electrochemical potential ( $-3.04 \text{ V}$  vs. standard hydrogen electrode).<sup>14,15</sup> Differing from the intercalation-type interactions in layered graphite anode, the Li metal anode is simply converted between Li metal and Li ions. Typically, electrons are lost for Li metal and being oxidized into Li ion during the discharge process, while electrons are gained for Li ions and reduced into metallic Li where deposited on the Li metal anode when charging. In the perspective of energy density, the Li metal batteries with metallic Li anode, such as Li-air batteries ( $5210 \text{ Wh kg}^{-1}$ ), Li-sulfur (Li-S) batteries ( $2600 \text{ Wh kg}^{-1}$ ),<sup>16–18</sup> exhibits huge advantages compared to commercial LIBs ( $250 \text{ Wh kg}^{-1}$ ) with a graphite anode. To date, considerable efforts have been devoted to developing ultra-high energy density Li-S and Li-air batteries.<sup>19–22</sup> However, the safety issues caused by random growth of Li dendrites during Li deposition and low Coulombic efficiency (CE) induced by the formation of an unstable solid electrolyte interface (SEI) severely hinder its practical application.<sup>23,24</sup> However, the superior ultra-high energy density positions the Li metal-based batteries for wide-spread commercialization if dendritic growth challenges are overcome.

The uncontrollable growth of Li dendrites is induced by the inhomogeneity and vulnerability of SEI formed on the metallic Li anode during the plating process. The dendrite may keep growing and consequently penetrate the separator film which will lead to short circuit of the cell and even catastrophic fires.<sup>25–27</sup> Further, the growing Li dendrites may puncture the unstable SEI and then fresh Li metal is exposed, which would react with electrolyte, leading to continuous consumption of electrolyte and consequently deviling a high overpotential and low CE.<sup>28–31</sup> In response to these issues, a number of

approaches have been developed to restrain the formation of Li dendrites, including artificial SEI layer construction (inorganic or organic SEI layer),<sup>32–37</sup> separator modification,<sup>38–42</sup> current collector modification,<sup>43–48</sup> additives of electrolyte,<sup>49–53</sup> solid-state electrolyte, and so on.<sup>54–60</sup>

In this review, a variety of strategies aimed at suppressing the dendrite growth for metallic Li anode are reviewed. The first section focuses on the intrinsic Li metal dendrite-formation, growth mechanism, and SEI formation. In the following section, recently proposed protection strategies are systematically summarized from the perspective of components of a cell, such as electrode, electrolyte, current collector, and separator. Finally, a general summary and outlook are discussed for the future battery development.

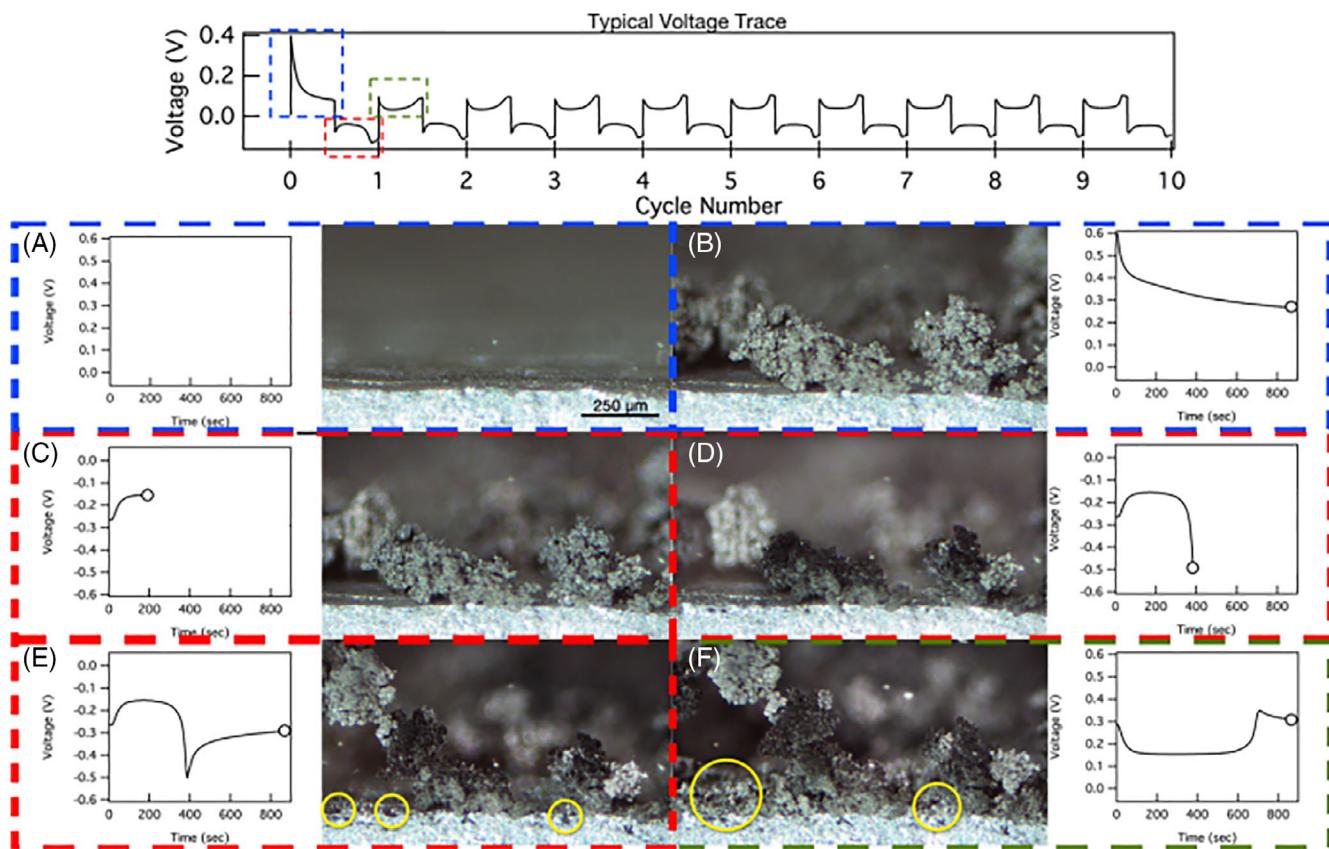
## 2 | UNDERSTANDING DENDRITIC LI GROWTH

The dendritic growth of Li metal has been known since the 1960s, but the underlying mechanism was not yet understood.<sup>61</sup> In recent years, the phenomenon has been comprehensively explained with the assistance of more advanced technologies, and its industrial application becomes more promising. Three main theories about why Li dendrites grow are proposed. First, the heterogeneous charge distribution on the uneven electrode surface leads to localized “hot spots” where Li preferentially nucleates.<sup>62</sup> The continuous deposition and growth of Li on the electrode results in subsurface disturbance, causing a localized fracture in the SEI and consequently consumes amount of Li. Second, because of the high activity of Li, the electrode surface forms insoluble SEI layer by newly deposited Li reacting with the electrode. The SEI layer is not mechanically steady enough, so it is easily cracked during the Li stripping/plating process.<sup>63</sup> The cracks in the SEI layer expose fresh Li metal and locally enhance the Li ion flux, which further aggravates the growth of uneven Li filaments and dendrites.<sup>64</sup> Finally, unregulated reactions at the Li surface create spatial variations in interfacial resistance, which prompt dendrite formation.<sup>65</sup> Figure 1 shows the typical dendritic Li plating and stripping at a current density of  $5 \text{ mA cm}^{-2}$  in a cell with cycling.<sup>66</sup>

## 3 | STRATEGIES

### 3.1 | Artificial SEI layer

SEI plays a crucial role in stabilizing the Li-electrolyte interface,<sup>61</sup> which would prevent Li dendrites from



**FIGURE 1** Morphology of electrodes at different stages. Li dendrites usually form dendritic structures through heterogeneous deposition of  $\text{Li}^+$  on the surface of the anode. (A) Before cycling. (B) After first half-cycle. (C) At cell polarization minimum. (D) At cell polarization maximum. (E) At end of half-cycle. (F) At end of third half-cycle.<sup>66</sup> Reproduced with permission: Copyright 2016, American Chemical Society

puncturing the separator leading to battery failure through short-circuit or even fire. The composition and structure of the in situ formed SEI film is multifarious and uncontrollable, therefore not effective in restricting dendritic growth in the metallic Li anode. To address this issue, researchers have focused on designing varieties artificial SEI layer with high mechanical strength and Li ionic conductivity that are stable and compatible with different electrolytes for a long life cycling.<sup>62,67</sup> Artificial SEI films are designed to possess the following properties: suppression of electrolyte decomposition and dendrite formation, ability to orient the changes in electrode volume, and promotion of uniform Li-ion transport throughout the whole electrode surface.<sup>68,69</sup> These films can be classified into two major categories: inorganic (e.g., nitride, sulfide, fluoride, oxide) and organic SEI.

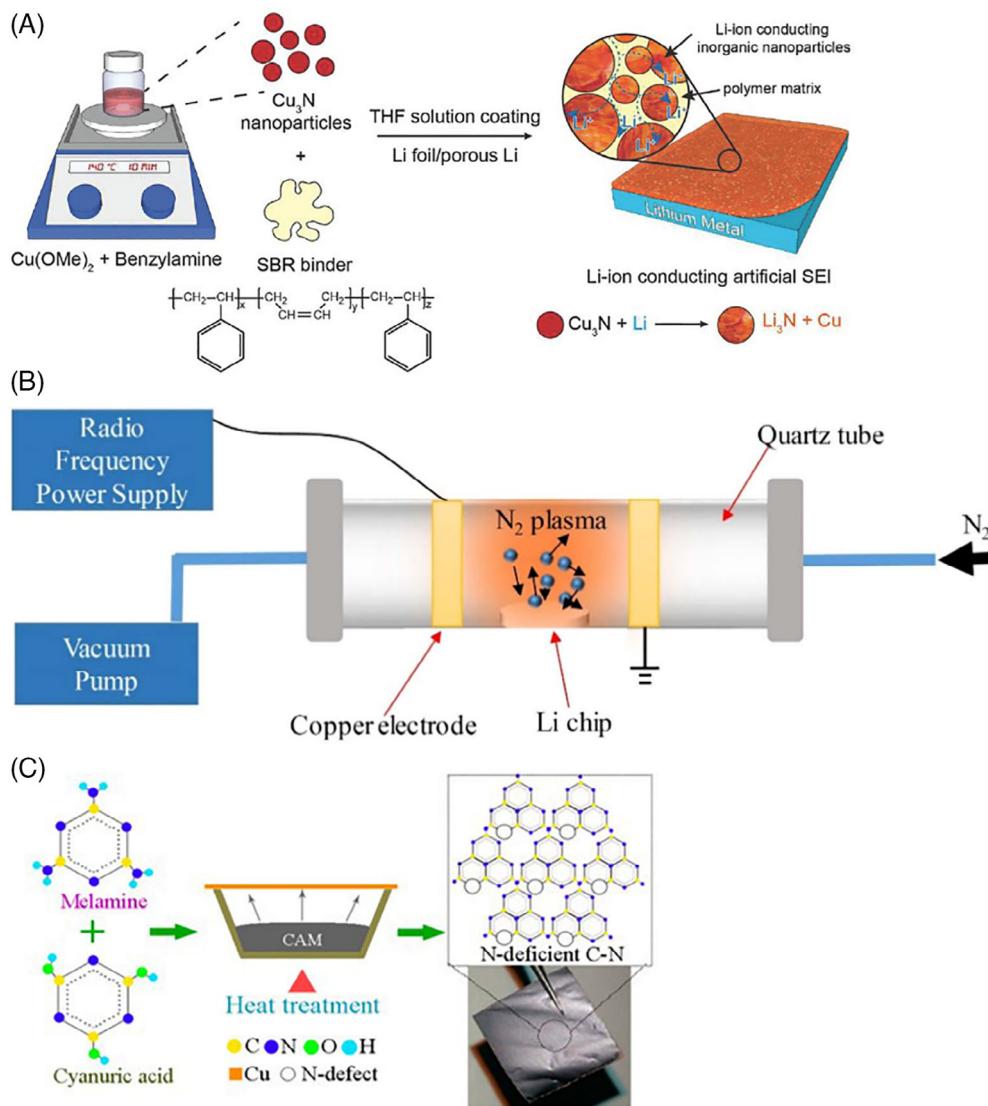
### 3.1.1 | Inorganic SEI layer

The synthesis of inorganic artificial SEI has been widely investigated due to its high mechanical strength and

conductivity. Up to now, different materials, such as oxides, nitrides, and so on, have been applied as artificial SEI layer.<sup>70</sup>

#### Nitride

Nitrated SEI has been used to improve the cycling performance of Li metal anode. Liu et al. proposed the design of an artificial SEI layer composed of  $\text{Cu}_3\text{N}$  nanoparticles bonded by styrene butadiene rubber (SBR) (Figure 2 (A)).<sup>71</sup> SBR synchronously possesses highly good flexibility, mechanical strength, and indispensably high Li-ion conductivity for an ideal SEI. The CE can achieve up to 97.4% at a current density of  $1 \text{ mA cm}^{-2}$  on copper (Cu) current collector and the coating promoted a 40% increase in cycle life when paired with Li Titanate (LTO). Chen et al. adopted a nitrogen plasma-based growth technique to form a  $\text{Li}_3\text{N}$  SEI on the Li metal chips-creating a protective layer after a few minutes treatment (Figure 2 (B)).<sup>72</sup> The obtained  $\text{Li}_3\text{N}$  SEI featured a pure [001] plane orientation possessing a high ionic conductivity and high Young's modulus. The cycling life of the cell was dramatically enhanced with such a stable  $\text{Li}_3\text{N}$  layer. The

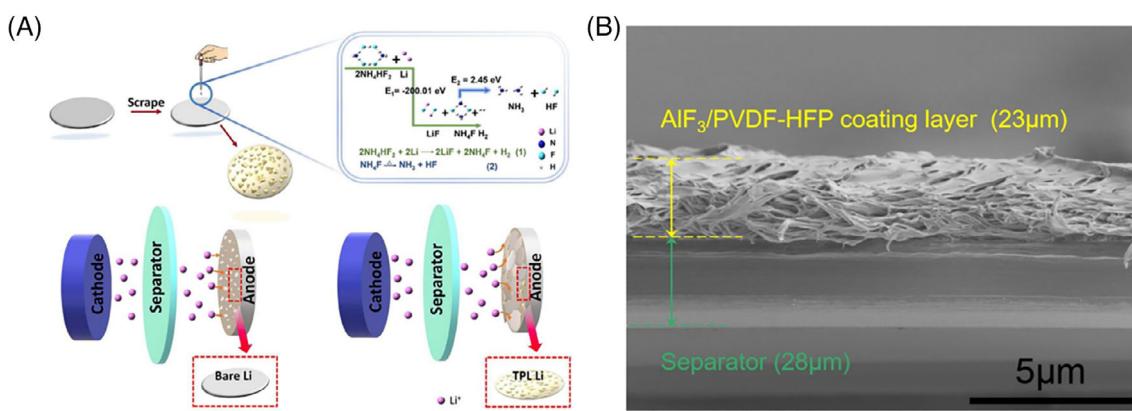


**FIGURE 2** (A) Schematic illustration of the fabrication of the  $\text{Cu}_3\text{N}$  + SBR composite artificial solid electrolyte interface (SEI).<sup>71</sup> Reproduced with permission: Copyright 2017, John Wiley and Sons. (B) Plasma treatment experimental setup.<sup>72</sup> Reproduced with permission: Copyright 2019, Elsevier. (C) Schematic illustration of the growth process of a N-deficient C—N thin film on copper foil.<sup>73</sup> Reproduced with permission: Copyright 2020, American Chemical Society

experiment demonstrates that  $\text{Li}||\text{LiCoO}_2$  cell with  $\text{Li}_3\text{N}$  film possesses a lower overpotential and superior rate capability compared to bare Li anode. Most astonishing is its excellent capacity retention during cycling—a performance increase of more than 96% after 100 cycles. Though a strict vacuum condition is required for plasma ignition, this approach is fast and efficient method to modify the Li anode battery. Yang et al. deposited a N-deficient C—N thin film on Cu foil by reactive thermal evaporation which enhanced the conductivity of Li anode (Figure 2(C)).<sup>73</sup> The film effectively inhibits severe dendrite extrusion and electric disconnect, gives  $\text{Li}||\text{Cu}$  cells an extended cycling reversibility over 400 cycles, and a highly stable CE of 99% at a current density of  $3 \text{ mA cm}^{-2}$ .

### Fluoride

Fluorides have gained enormous attention because of their excellent electrochemical stability over a wide potential window and tunability of the surface tension. Yuan et al. prepared a thin, porous layer (TPL) rich in LiF via an in-situ reaction between a small amount of ammonium hydrogen difluoride and Li metal (Figure 3 (A)).<sup>74</sup> A flat and well-proportioned Li metal anode surface is obtained after deposited a LiF layer. Symmetrical cells consisting of a TPL Li anode show remarkably stable cycling performance for over 100 cycles at a high current density of  $6 \text{ mA cm}^{-2}$ . The TPL  $\text{Li}||\text{LiFePO}_4$  cells maintain a capacity retention rate of more than 99% after 100 cycles at a high rate of 2 C. Wang et al. also used a composite layer consisting of a PVDF-HFP polymer and



**FIGURE 3** (A) Schematic of the fabrication procedure of TPL Li.<sup>74</sup> Reproduced with permission: Copyright 2019, Elsevier. (B) SEM image revealing the thickness of the AlF<sub>3</sub>/PVDF-HFP coating and blank separator.<sup>75</sup> Reproduced with permission: Copyright 2020, Royal Society of Chemistry

AlF<sub>3</sub> particles as a coating on separator to regulate even Li deposition.<sup>75</sup> Figure 3(B) shows the cross-sectional view of the AlF<sub>3</sub>/PVDF-HFP layer. This LiF-rich SEI layer effectively suppresses dendritic Li growth with a reduced interfacial impedance. A symmetric battery with modified electrodes show lower overpotentials and much longer cycling life (600 h) in comparison with pure Li||Li battery (45 h), while the Li||LiFePO<sub>4</sub> battery with composite separator has a high capacity retention of 78.3% after 300 cycles at a high rate of 3 C. Xu et al. constructed an artificial LiF-rich SEI layer at molecular-level using one-step photopolymerization of hexafluorobutyl acrylate-based solution.<sup>76</sup> The layer not only suppresses the dendritic growth but also blocks side reactions between the electrolyte and Li metal. With the LiF stabilized anode and NCM622 cathode, the fabricated full cell presents superior stable cycling performance at 1 mA cm<sup>-2</sup> for over 500 h without failure.

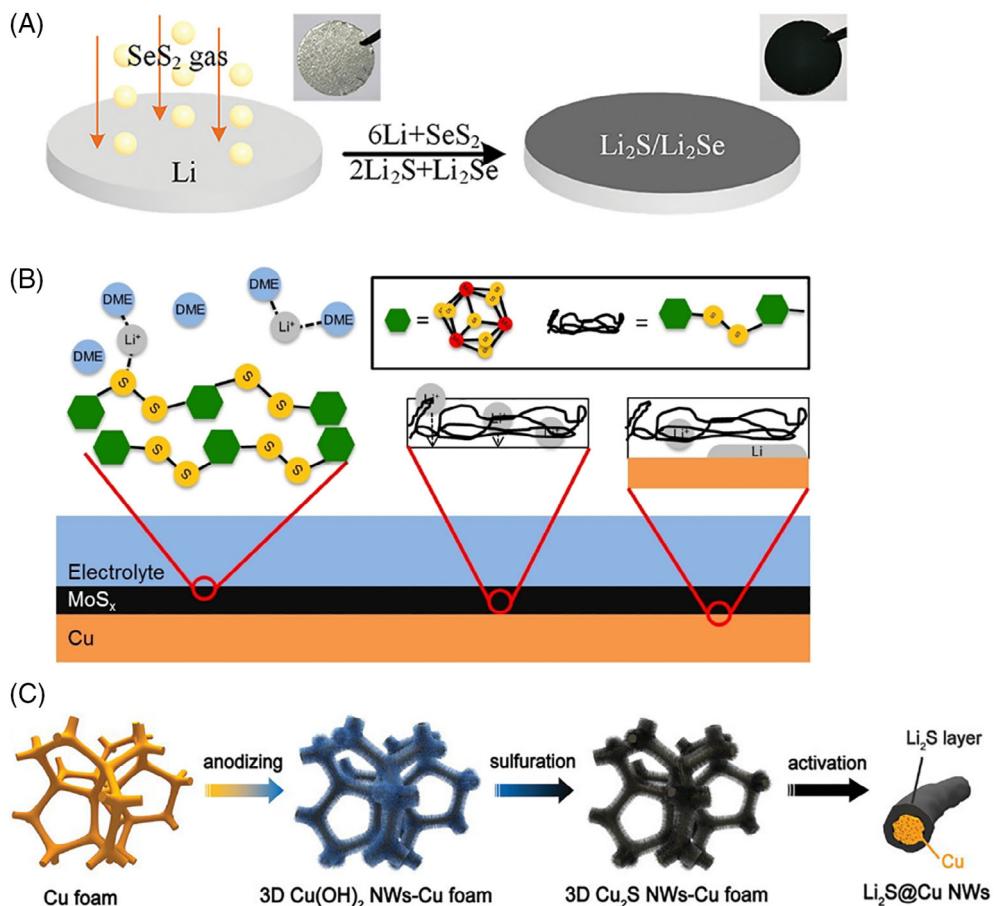
### Sulfide

Sulfurizing treatment for metal Li anode to form a sulfide SEI has been widely investigated due to the high ionic conductivity. Liu et al. constructed a Li-ion conductive Li<sub>2</sub>S/Li<sub>2</sub>Se (LSSe) protection layer by a facile and inexpensive gas-solid reaction (Figure 4(A)).<sup>77</sup> The artificial SEI can prevent nonuniform ion flux and Li deposition structures. The LSSe@Li||LiFePO<sub>4</sub> full cell displays a better cycle performance and stable CE compared with the bare Li metal anode based full cell, delivering a high-capacity retention rate of 91.5% at the current density of 160 mA g<sup>-1</sup> at the rate of 1 C after 450 cycles. Moreover, the LSSe artificial SEI can also significantly alleviate the suffering polysulfide reduction with metallic Li for Li-S battery. Meyerson et al. developed a sulfur-rich molybdenum sulfide film coated on the anode, which enables a long cycle life and high CE of Li metal battery (Figure 4

(B)).<sup>78</sup> The MoS<sub>x</sub> layer results in less exposed Li and dead Li compared to Li deposited on bare Cu. It is worth noting that the average CE for the first 100 cycles of MoS<sub>x</sub>||Cu cells reaches up to 98.3% at a current density of 0.5 mA cm<sup>-2</sup> with a life cycle of 500 cycles. Zhai et al. proposed a facile method to preparing a high-performance current collector by in-situ construction of an electric passivation Li sulfide (Li<sub>2</sub>S) layer with high ionic conductivity on 3D porous Cu foam (Figure 4(C)).<sup>79</sup> The Li<sub>2</sub>S protective layer can effectively restrain dendritic Li growth and, as a result, the modified current collector exhibits long-term cycling of 500 cycles at 1 mA cm<sup>-2</sup> and stable electrodeposition capabilities of 4 mAh cm<sup>-2</sup> at an ultrahigh current density of 4 mA cm<sup>-2</sup>. Besides, full cells with LiFePO<sub>4</sub> cathode paired with this designed 3D anode only require ~200% extra Li versus ~3000% extra Li for pure Li foil-based cells, which shows superior stability and rate performance.

### Oxide

Oxides are widely used as protection layers owing to their high chemical stability resistant to corrosion from the electrolyte. Wu et al. coated m-SiO<sub>2</sub>/PVDF film (10 wt% SiO<sub>2</sub>) on Li foil by a simple doctor-blading method.<sup>80</sup> Figure 5(A) illustrates the working mechanism of a hybrid artificial SEI layer composed of a PVDF polymer and mesoporous SiO<sub>2</sub>. The inorganic SiO<sub>2</sub> filler effectively adjusts ionic movement and enhances mechanical stiffness for symmetrical cells. The artificial SEI maintains a stable cycling performance for 1000 h at a high capacity of 5 mAh cm<sup>-2</sup>, which remarkably enhances the life span under specified conditions in combination with different commercial cathodes. Zhang et al. exploited a Li-free electrode with ultrathin Al<sub>2</sub>O<sub>3</sub> coated on reduced graphene oxide (rGO) membrane which covers a Cu foil current collector.<sup>81</sup> Figure 5(B) shows the principle of Li



**FIGURE 4** (A) Schematic illustration of fabrication process of LSSe@Li anode.<sup>77</sup> Reproduced with permission: Copyright 2020, John Wiley and Sons. (B) Schematic of Li<sup>+</sup> desolvation and transport through the MoS<sub>x</sub> film.<sup>78</sup> Reproduced with permission: Copyright 2020, John Wiley and Sons. (C) Schematic of the 3D Cu<sub>2</sub>S NWs-Cu foam fabrication process.<sup>79</sup> Reproduced with permission: Copyright 2020, John Wiley and Sons

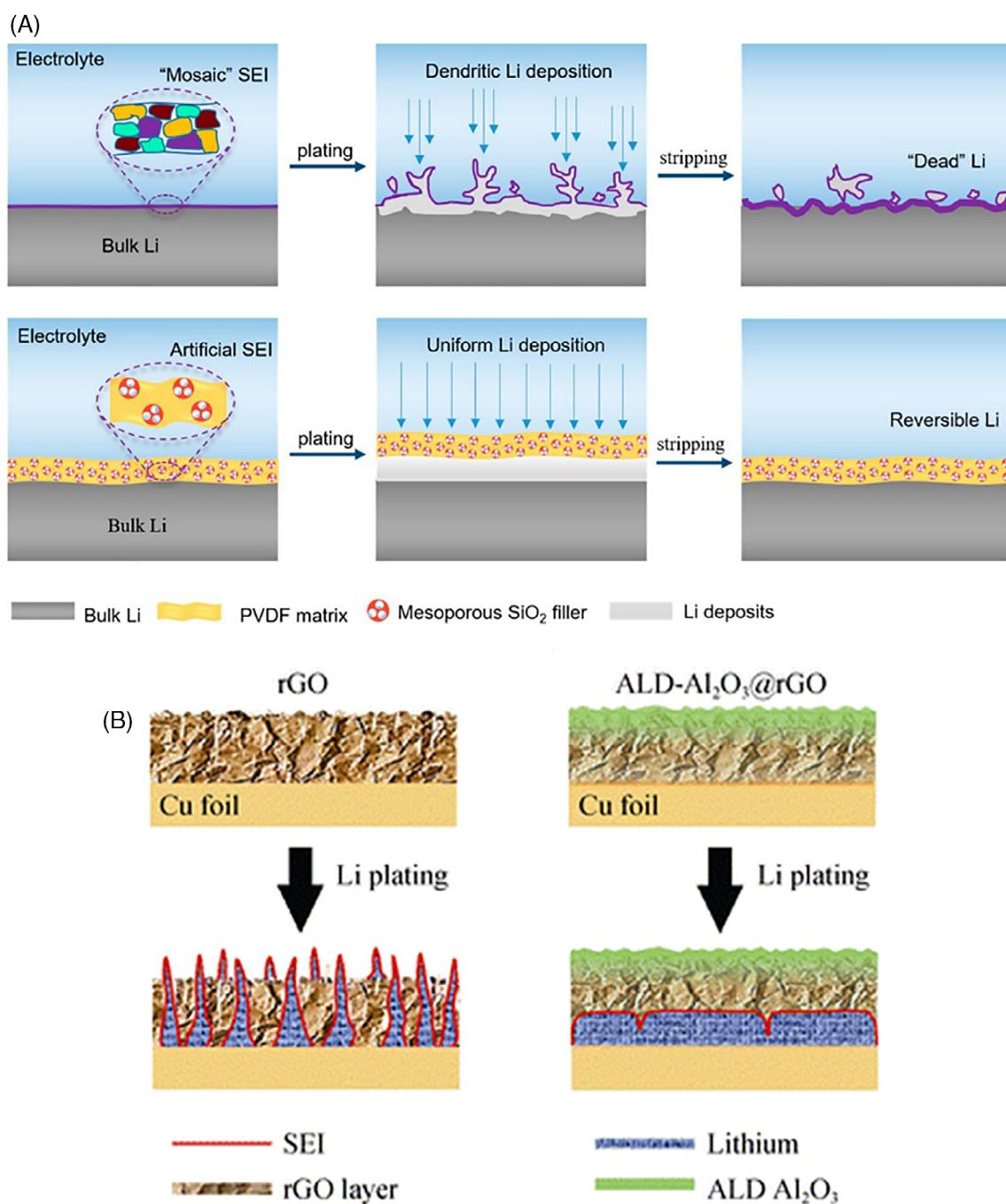
plating behavior on rGO-coated Cu and ALD-Al<sub>2</sub>O<sub>3</sub>@rGO-coated Cu current collector. The composite electrode possesses excellent interfacial protection that can inhibit the penetration of Li dendrite. The electrochemical results indicate >90% CE over 100 cycles at the current density of 0.5 and 1.0 mA cm<sup>-2</sup> with a deposition capacity of 1 mAh cm<sup>-2</sup>. Further, this superior electrochemical performance is sustained even at a high deposition capacity of 2 mAh cm<sup>-2</sup>.

### 3.1.2 | Organic SEI layer

The application of artificial organic SEI layer for Li anode has attracted extensive attention on account of its high strength, outstanding adhesion to the Li anode, and tolerance to dilatation and contraction stresses.

Zhong et al. fabricated a Li alginate-based artificial SEI (ASEI) layer, which is chemically steady and allows smooth Li ion transport on the surface of Li metal anode

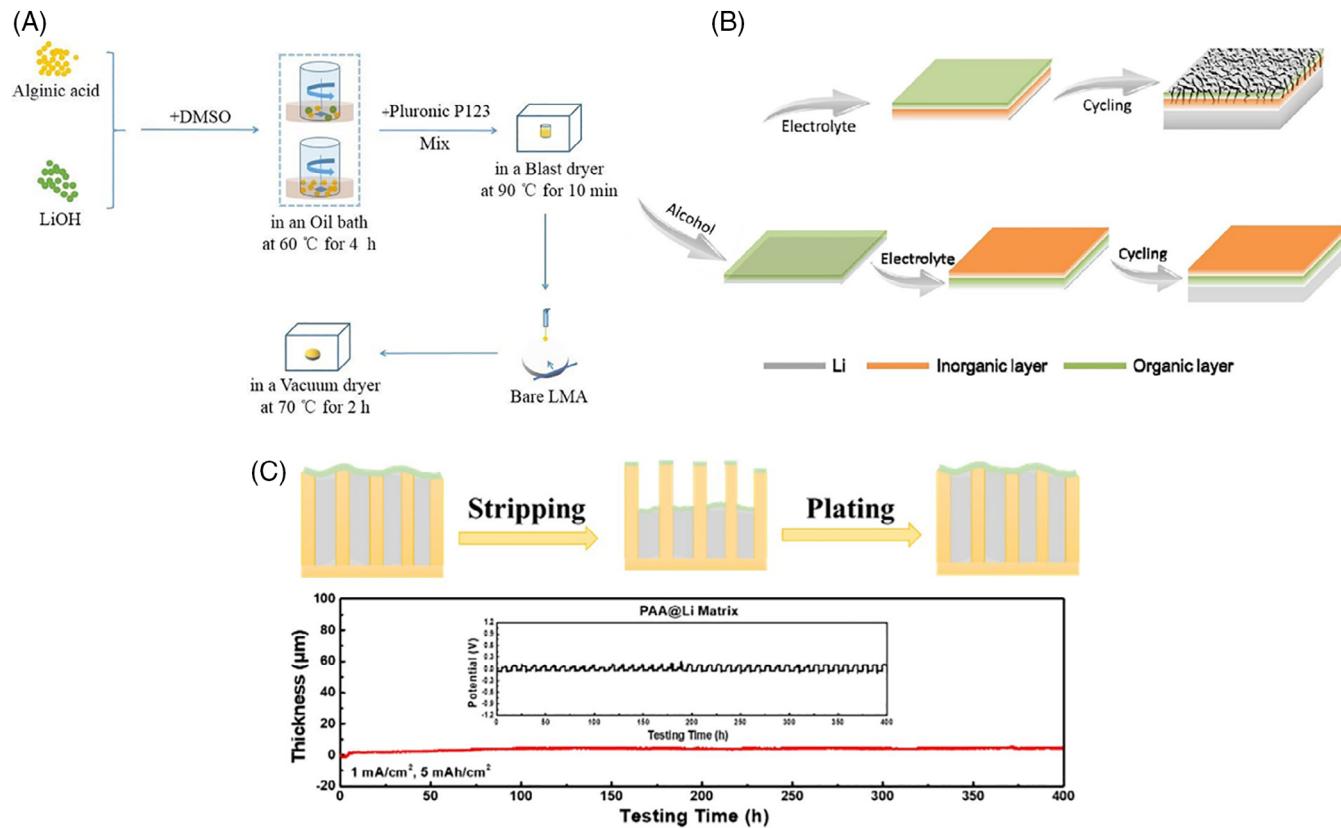
(Figure 6(A)).<sup>82</sup> The Li anode with ASEI layer shows more effective suppression of dendrite growth and stable Li insertion/removal behavior compared with the bare LMAs. The symmetric Li||Li cells with the ASEI layer can steadily cycle for 850 and 350 h at current densities of 0.5 and 1 mA cm<sup>-2</sup>, respectively. In the full cell with LiFePO<sub>4</sub> cathode and ASEI layer-modified metallic Li anode, an ultrahigh capacity retention of ~94.0% and a CE of 99.6% after 1000 cycles at the rate of 4 C are reported. Kang et al. exploited a Li alkoxides protection layer for Li anode by using a spin coating method.<sup>35</sup> Figure 6(B) shows the evolution of morphology of SEI formed in different ways. With the assistance of organic alkoxide layer, the reaction between the electrolyte and Li is effectively suppressed, and both the interfacial resistance and Li deposition overpotential are significantly reduced. More importantly, Li anode layer modified with organic alkoxide demonstrates a more stable cycling performance with less volume expansion, 10%, compared to that of bare Li anodes (30%). Feng et al. constructed a



**FIGURE 5** (A) Schematic illustrations of the working mechanism of a hybrid artificial solid electrolyte interface (SEI) layer composed of a PVDF polymer and mesoporous SiO<sub>2</sub>.<sup>80</sup> Reproduced with permission: Copyright 2020, American Chemical Society. (B) Schematics of Li plating behavior on rGO-coated Cu and ALD-Al<sub>2</sub>O<sub>3</sub>@rGO-coated Cu current collector (rGO-coated Cu leads to growth of dendritic Li, while ALD-Al<sub>2</sub>O<sub>3</sub>@rGO coating leads to a uniform plating of Li).<sup>81</sup> Reproduced with permission: Copyright 2018, Springer

stable artificial SEI layer by directly coating PAA layer on the surface of a 3D Li framework (Figure 6(C)).<sup>83</sup> The in situ formed high-ion conductive LiPAA effectively restrains Li dendrites by facilitating Li<sup>+</sup> transmission rather than deposition. As a result, PAA@Li matrix exhibits near-zero volume change upon the cycling and intensive battery performance with excellent cycling

stability for 350 h at both high areal capacity (5 mAh cm<sup>-2</sup>) and high current density (5 mA cm<sup>-2</sup>). Additionally, the LiCoO<sub>2</sub>||PAA@Li matrix full cell demonstrates outstanding long-term stability of 81% retention after 1000 cycles. The novel capped 3D framework may open up a new horizon to achieve highly stable Li anode with zero volume change.



**FIGURE 6** (A) Scheme of fabrication procedure for the ASEI layer-protected LMA.<sup>82</sup> Reproduced with permission: Copyright 2019, American Chemical Society. (B) The morphology evolution of natural-formed solid electrolyte interface (SEI) and rearranged SEI with alcohol pretreating process.<sup>35</sup> Reproduced with permission: Copyright 2020, Elsevier. (C) Schematic illustration of the fabrication process of PAA-capped Li matrix.<sup>83</sup> Reproduced with permission: Copyright 2020, Elsevier

The severe dendritic growth problem of Li metal significantly impacts its performance as a rechargeable battery. Coating of artificial SEI layers on Li metal is remarkable in its ability to suppress dendritic growth and improve the electrochemical performance of the battery. However, research into artificial SEI layers is still at the preliminary stage so there is much of underlying mechanisms, which remains unknown. Additional research needed to understand SEI layers include: (i) develop advanced in situ characterization technology to provide deep understanding about the regularity and mechanism of artificial SEI formation, (ii) develop cheaper and simpler methods of preparation, and (iii) combine the artificial SEI layer approach with other methods to further improve the performance of Li metal batteries to bring unexpected effects.

### 3.2 | 3D current collector

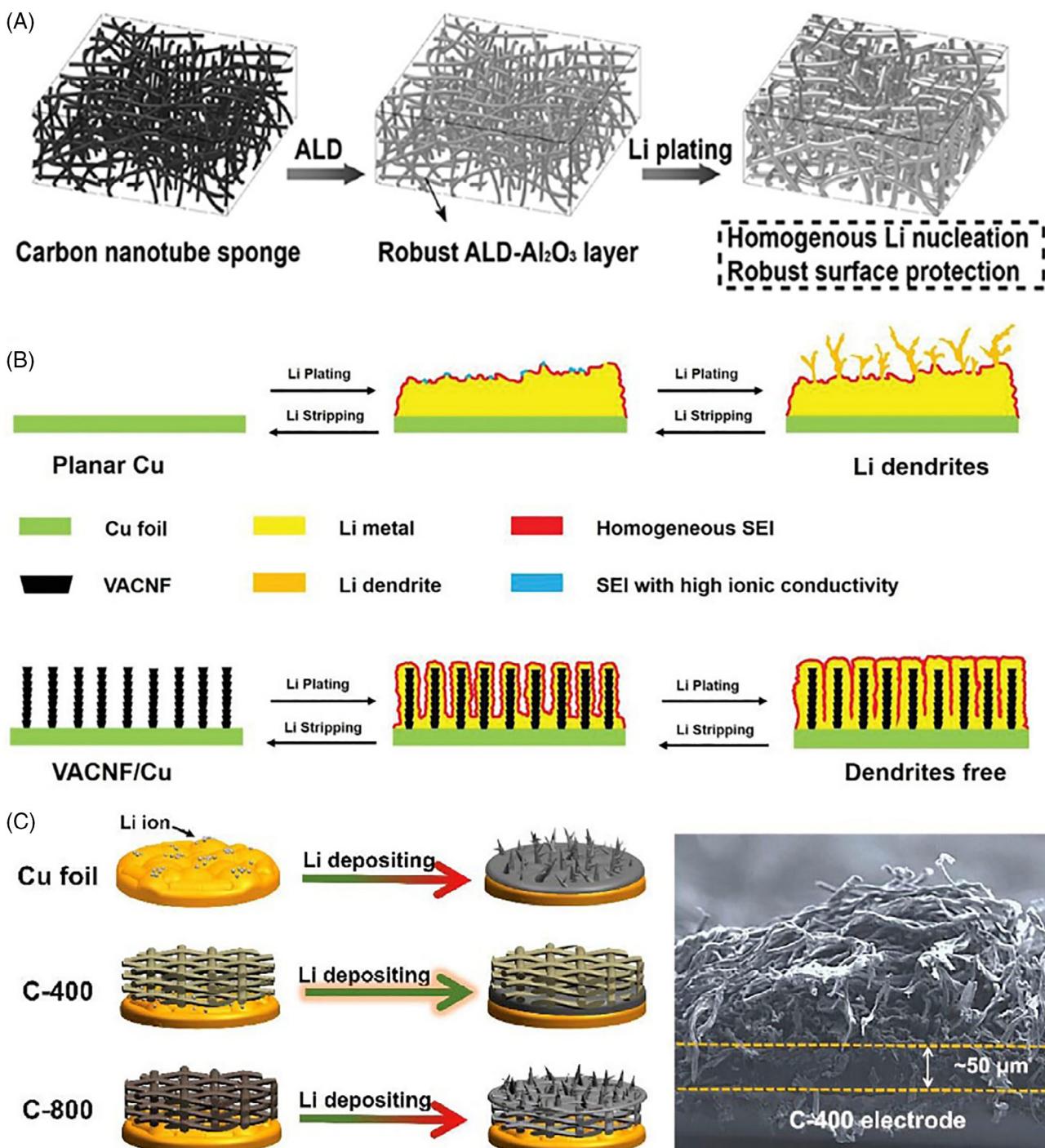
To be an ideal current collector for the anode in Li metal battery, excellent chemical stability, high electrical

conductivity, and excellent mechanical stability are required to avoid any reaction with electrolyte. In this regard, carbon, metal, and lithophilic current collector are emerging and being investigated. Novel 3D porous current collector scaffolds for Li-based battery technology in particular are receiving considerable attention due to its low impact on battery performance and matching requirements to other battery components. The skeleton of a 3D current collector inhibits the dendritic Li growth in two main ways: (i) large surface-to-volume ratio increases interaction time of Li ions with collector thereby consuming Li ions which may form dendrites and (ii) normalizes Li ion flux through the collector thereby improving uniformity of Li plating or stripping on lithophilic sites.<sup>15,84-86</sup> In addition, the 3D porous current collector is acts as a stable Li host material. Its excellent mechanical strength ensures the high structural stability of Li anode during fast and repeated Li plating and stripping. As a result, the 3D Current collector can effectively avoid issues such as the uneven Li deposition, severe volume change, and safety risks of Li metal battery.<sup>85</sup>

### 3.2.1 | Carbon-based 3D current collector

A carbon-based 3D current collector is easy to manufacture and modify. The intrinsic properties of high conductivity, flexibility, and light weight for carbon greatly strengthen performance when incorporated into an Li anode.<sup>87</sup>

Zhang et al. proposed a  $\text{Al}_2\text{O}_3$ -coated 3D carbon nanotube sponge (CNTS) as a Li deposition host by using atomic layer deposition (ALD) technology (Figure 7(A)).<sup>88</sup> The high specific surface area of the CNTS enables homogenous charge distribution for Li nucleation and minimizes the effective current density to overcome dendrite growth.



**FIGURE 7** (A) Schematic illustration of the Li deposition process on 3D ALD-CNTS substrates.<sup>88</sup> Reproduced with permission: Copyright 2017, Springer. (B) Schematic processes of Li plating and stripping in the planar Cu electrode and the electrically conductive 3D VACNF/Cu host.<sup>89</sup> Reproduced with permission: Copyright 2019, John Wiley and Sons. (C) Schematic diagrams of Li deposition on the bare Cu foil, C-400 electrode and C-800 electrode.<sup>90</sup> Reproduced with permission: Copyright 2020, Elsevier

Through this restriction, Li@ALD-CNTS electrodes have exhibited stable voltage profiles with a small overpotential ranging from 16 to 30 mV over 100 h of cycling at  $1.0 \text{ mA cm}^{-2}$  is exhibited. Moreover, the electrode presents an excellent electrochemical stability with a CE of 92.4% over 80 cycles at  $1.0 \text{ mA cm}^{-2}$ . These results provide guidance on how to design a current collector with stable Li metal anodes. Chen et al. employed a vertically aligned carbon nanofiber (VACNF) array with unique conically stacked graphitic structure directly grown on a planar Cu current collector (VACNF/Cu) as a high-porosity 3D host to suppress dendrite growth from the Li anode.<sup>89</sup> Figure 7(B) shows the process of Li plating and stripping in the planar Cu electrode and the electrically conductive 3D VACNF/Cu host. The excellent electrical conductivity and highly active lithiophilic graphitic edge sites facilitate homogenous coaxial Li plating/stripping around each VACNF and result in a uniform solid electrolyte interphase. The high specific surface area and open nanoscale vertical 3D structure lower the local current density and accommodate volume change, leading to the suppression of dendrite growth. Consequently, the Li-S battery using a Li plated VACNF/Cu anode presents outstanding rate performance at a high capacity of  $2 \text{ mAh cm}^{-2}$  and supernal cycling stability with no fade in capacity over 600 cycles-better performance than that of bare Cu current collector. Meng et al. also prepared light weight 3D carbon cloth (C-400) via a simple pyrolysis of cotton, a process which results in a large amount of polar functional groups.<sup>90</sup> Figure 7(C) shows Li deposition on the bare Cu foil (a), C-400 electrode (b), and C-800 electrode. The polar functional groups play crucial roles in normalizing Li plating/stripping behavior and increasing the lithiophilicity of carbon cloth. As a result, the C-400 electrode can achieve a lofty areal capacity over  $10 \text{ mAh cm}^{-2}$  without the formation of Li dendrites. Additionally, the C-400@Li||LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> full cell displays better voltage polarization, rate performance than that of bare Li anode. Benefiting from the environmentally friendly and abundant resource of the precursor of electrode, this method gives a broad prospect for high energy density Li batteries.

### 3.2.2 | Metal-based 3D current collectors

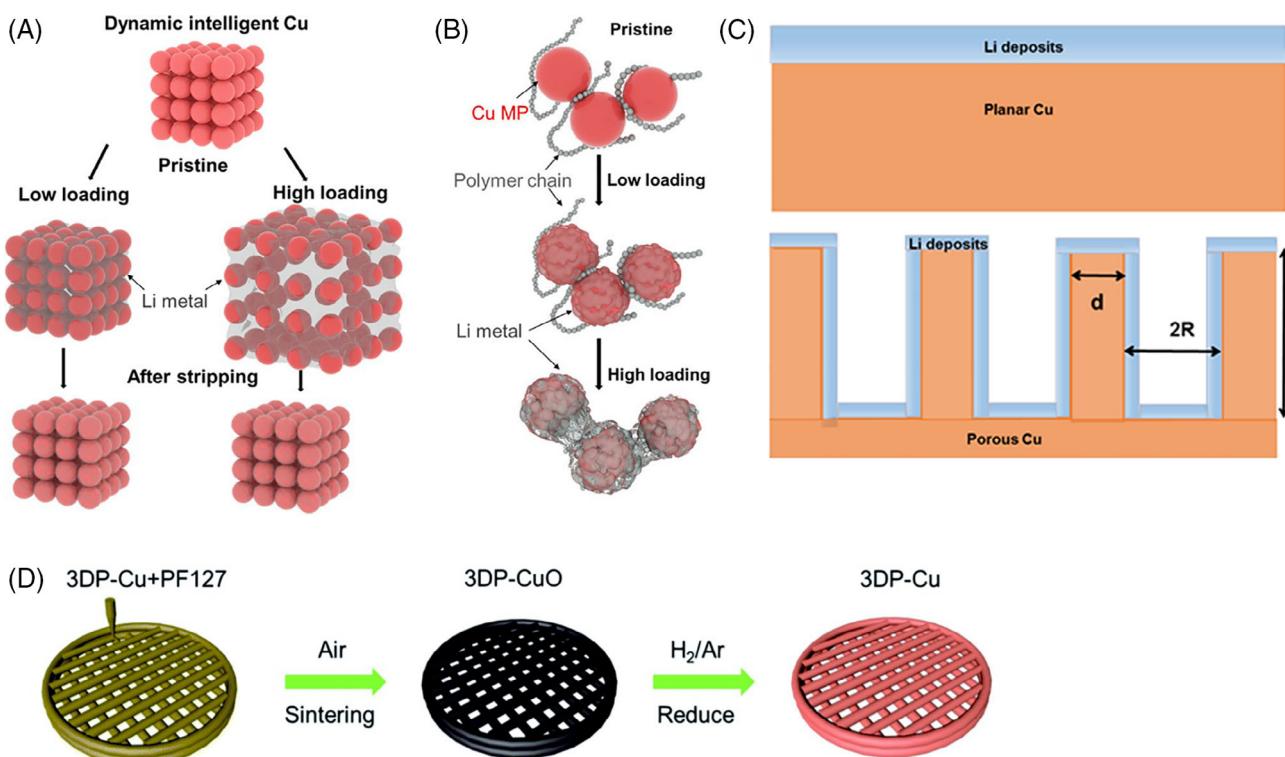
The metal-based 3D current collector has better electron transfer and mechanical properties compared to carbon-based or 3D framework alone due to its unique physical properties (Figure 8(A,B)).<sup>15</sup> Chen et al. fabricated a dynamic intelligent Cu (DICu) current collector with a granular piling structure via solution casting of commercial Cu microparticles onto Cu foils demonstrating excellent performance.<sup>91</sup> Collection and interaction among the

Cu MPs before and after Li plating are illustrated in Figure 8(B). The fabricated current collector can adapt to volume change through alteration of the packing density of assembled particles. As a consequence, the Li/DICu electrode achieves a CE above 99.6% even after 800 cycles and the symmetrical cell retains excellent cycling stability over a high current density of  $10 \text{ mA cm}^{-2}$ . Wang et al. fabricated a vertically aligned Cu micro-channel using a laser micro-processing system.<sup>92</sup> Figure 8(C) shows distinct differences of Li deposition between planar Cu and porous Cu. These micro-channel structures visibly suppressed the formation of dendritic Li through a combination of Cu pore size, shape, and surface-to-volume ratio. The proper combination was found to effectively control the current density distribution, thereby controlling dendrite formation. This resulted in an average CE of 98.5% within 200 cycles, additionally, the LiFePO<sub>4</sub>||Li full battery shows excellent rate capability and stable cycling performance. This method provides simple and reliable conceptual framework to formulate a new generation of Li-ion batteries. Lim et al. developed a low-cost, simple method to construct a firm Cu porous framework by extrusion 3D-printing (Figure 8(D)).<sup>93</sup> The 3D-printed Cu framework (3DP-Cu) can hold constructed micro-channels between filaments even over supernal compressive pressure of 1.4 MPa, which would effectively restrain Li dendrite growth and alleviate volume changes. The cell with 3DP-Cu based Li anode reaches an exceptional areal capacity of  $20 \text{ mA h cm}^{-2}$  with over  $1 \text{ mA cm}^{-2}$ , and steady Li plating/stripping behavior even at a high current density of  $10 \text{ mA cm}^{-2}$ . The work provides a novel and promising approach for fabricating copper-based electrodes or materials using 3D-printing for advanced battery applications and beyond.

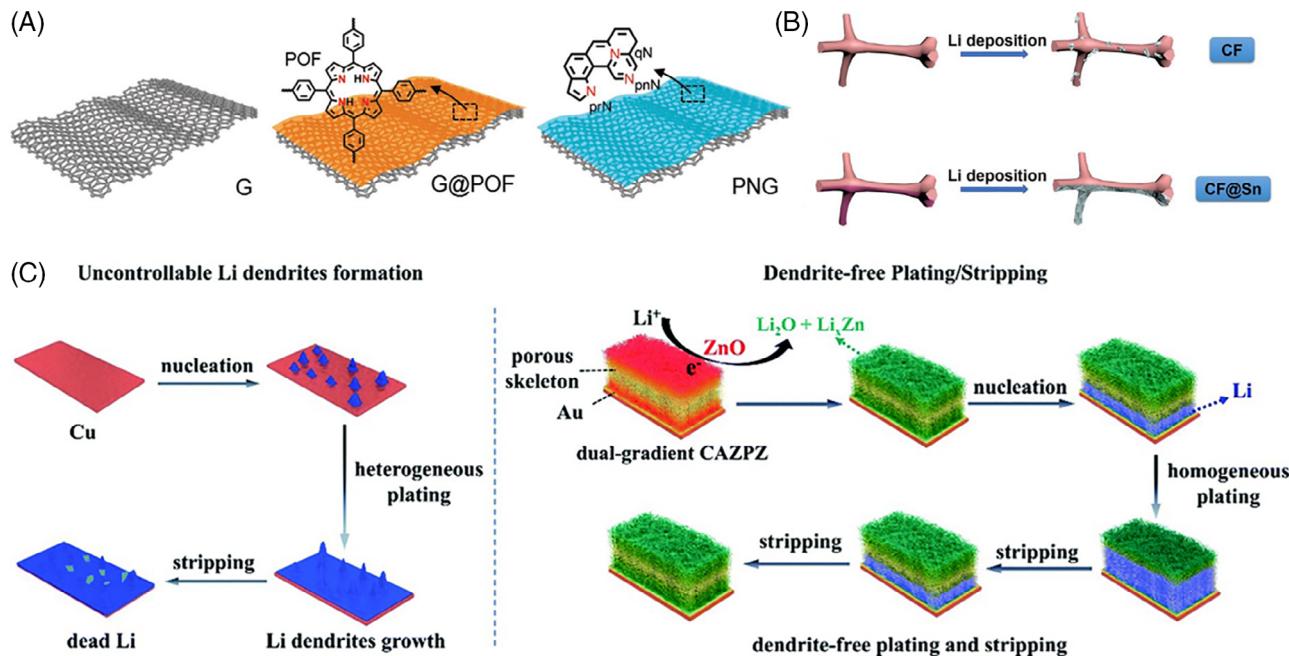
### 3.2.3 | Lithiophilic 3D current collector

The concept of “lithiophilicity,” proposed by Cui et al., is based on previous studies related to the wetting behavior of Li between the molten Li and network surface.<sup>86</sup> From this concept, lithiophilic 3D current collector are expected to effectively regulate the concentration of Li ions in the electrolyte and electrolyte/Li interface, sequentially restrain the Li dendrites, and ultimately achieve superb cycling stability.

A typical method to achieve lithiophilicity is to decorate the current collector with uniform lithiophilic functional groups. Kong et al. exploited porphyrin-derived graphene-based nanosheets (PNG) by pyrolyzing a conformal and thin layer of 2D porphyrin organic framework on graphene (Figure 9(A)).<sup>94</sup> The structure possesses ample lithiophilic functional groups, such as pyridinic,



**FIGURE 8** (A) Illustration of the Li plating and stripping process on the DICu current collector.<sup>91</sup> Reproduced with permission: Copyright 2020, American Chemical Society. (B) Schematic of the interaction among the Cu MPs varied before and after Li plating.<sup>91</sup> Reproduced with permission: Copyright 2020, American Chemical Society. (C) Li deposition of planar Cu and porous Cu.<sup>92</sup> Reproduced with permission: Copyright 2017, John Wiley and Sons. (D) Schematic illustration of the fabrication process of 3DP-Cu.<sup>93</sup> Reproduced with permission: Copyright 2020, Royal Society of Chemistry



**FIGURE 9** (A) fabrication process of PNG.<sup>94</sup> Reproduced with permission: Copyright 2018, John Wiley and Sons. (B) Schematic illustration of the Li deposition process on bare CF and composite CF@Sn current collector.<sup>95</sup> Reproduced with permission: Copyright 2020, John Wiley and Sons. (C) Li plating/stripping behavior on Cu and Cu–Au–ZnO–PAN–ZnO current collectors.<sup>96</sup> Reproduced with permission: Copyright 2020, Royal Society of Chemistry

pyrrolic, and quaternary nitrogen atoms. These functional groups have a strong affinity for Li ions, as a result, the Li anode with PNG current collector presents an excellent electrochemical stability with Coulombic efficiency of 98% after 200 cycles at  $1.0 \text{ mA cm}^{-2}$ . Lithiophilicity can be achieved via other methods, such as letting Li react with metal, metal oxide, or other substances to form a lithophilic compound. Liu et al. constructed a 3D copper foam by depositing a thin lithophilic tin (Sn) layer on the copper foam (CF) surface, which was accomplished using physical vapor deposition (PVD).<sup>95</sup> Figure 9(B) shows the Li deposition process on bare CF and composite CF@Sn current collector. In the modified current collector, the Li ions tend to deposit on the Sn layer to form the Li-Sn alloy, which can restrain Li dendritic growth. Ultimately, the composite matrix leads to a high CE (98.5%) over 400 cycles for the symmetric cell at  $1 \text{ mA cm}^{-2}$ . For the full cell with CF@Sn@Li and LiFePO<sub>4</sub> cathode, excellent rate performance and discharging capacity of  $140 \text{ mAh g}^{-1}$  with high capacity retention of 95.2% after 300 cycles at 0.5 C are presented. By reasonably utilizing the lithophilic/lithiophobic materials, it is also possible to accommodate even Li deposition.<sup>15</sup> Zheng et al. used combined electrostatic spinning and magnetron sputtering to produce a 3D porous dual-gradient (philiphobic-philic) Cu-Au-ZnO-PAN-ZnO (CAZPZ) current collector. Figure 9(C) shows the Li plating/stripping process on Cu and Cu-Au-ZnO-PAN-ZnO current collectors. The Li metal battery can effectively decrease nucleation overpotential and even accommodate Li deposition by combining lithophilic Au and dual-gradient ZnO. Consequently, the symmetric cell shows a long cycle capacity for 1200 h at  $0.5 \text{ mA cm}^{-2}$ . Additionally, the CAZPZ current collector greatly enhance the electrochemical performance of full cell systems matched with LTO, LFP and MNC-411 cathode materials.

Although good results have been obtained in the laboratory, 3D current collectors are still far from actual production. Further research is needed in order to realize full utilization and commercial adoption of the 3D current collector, including: (i) development of carbon nanostructures structures to change surface-to-volume ratios and consequently boost the CE of battery, (ii) increase specific energy while decreasing mass density of the metal collector, (iii) address the problem of mass gain in the anode due to the presence of increased voids in 3D scaffolds.

### 3.3 | Separator film modification

The separator plays an important role in improving electrochemical performance of the battery by avoiding direct

interaction between positive and negative electrodes and granting the ions transportation. Nowadays, researchers focus on the modification of Li metal anode and designing artificial SEI to inhibit the dendritic Li growth to enhance Li battery performance. However, separators also play an important role in terms of prohibiting the direct interaction between positive and negative electrodes and granting ion transport. Therefore, it is necessary to discuss the role of separators in order to comprehensively ameliorate the performance of Li metal batteries.<sup>38,97</sup> Recently, some researchers have tried to exploit novel separators by upgrading the ion conductivity and wettability.<sup>98</sup> Hasanpoor et al. studied the dependence of the electrochemical performance on the property of separators.<sup>99</sup> The results demonstrate that a high-quality separator can facilitate the formation of relatively stable SEI, which inhibits the emergence and accumulation of inactive substances and reduces the continuous electrolyte consumption, subsequently, improving the cycling stability of Li metal batteries. Thus, it is of great significance for the development of separators for Li metal batteries.

The most widely used commercially available separator in Li secondary batteries is the microporous polyolefin. Due to their performance<sup>97,100</sup> such as good chemical stability, uniform pore structure and distribution, and low cost,<sup>101,102</sup> polyethylene (PE), polypropylene (PP) and their hybrids are becoming the most representative separator materials in this field. However, there are plenty of factors that limit their extensive development—their poor wettability and absorbability in liquid electrolytes, causing low conductivity and high impedance of Li ions in liquid electrolyte. In addition, the polyolefin separator has poor thermal stability, which will cause short circuiting and even explosion of the battery, a significant safety hazard.<sup>103-105</sup> In order to overcome the deficiencies of traditional polyolefin multiple approaches have been suggested including novel membrane design, the introduction of a multilayer functional membrane, or modification of the microporous polyolefin membrane.

#### 3.3.1 | Modify the microporous polyolefin membrane

Polyolefin separators have been commercially used in batteries; however, the mechanical stability, ion conductivity, and wettability of the electrolyte are relatively poor. In order to improve its properties, nanostructured materials, such as porous carbon or silicon nanowires are used to coat on the surface of the films.

Han et al. were first in researching activated carbon nanofibers (ACNF) coated on a traditional commercial

PP septum. Their results show the flexible and robust ACNF filter-coated separator with adjustable micropores can effectively improve cycle stability of Li-based battery.<sup>106</sup> Kannan et al. modified a conventional PE membrane by coating nitrogen and sulfur on graphene (NSG), which effectively inhibit the growth of Li dendrites (Figure 11(A))<sup>107</sup> by enhancing the interfacial interactions between the NSG-coated separator and the Li electrode. These designs not only effectively improve the ion conductivity of the separator but also greatly increase the thermal stability and safe operation of the separator.

The addition of silicon nanomaterials also enhances the properties of polymer membranes. For example, Li et al. were first to report silicon nanowires (SNFs) grown on the surface of the PE membrane (Celgard 2400) leading to the fabrication of superlephilic/superhydroobic separators (Figure 11(B)).<sup>100</sup> In such a design, the wettability, Li ion conductivity and thermal stability of the membrane are significantly improved due to the addition of the SNFs. Therefore, it provides an advanced idea for the further development of Li metal batteries.

In addition to the exploration of membrane coating materials, researchers have also been exploring different coating methods to achieve effective results. Ma et al. developed a simple, binder less coating method called Langmuir–Blodgett Scoping (LBS).<sup>108</sup> This simple coating method can rapidly prepare polyaniline (PANI), multiwalled carbon nanotube (MWCNT) and other multifunctional materials onto the porous and non-porous solid scaffolds by using self-assembly of air/water interface and Marangoni stress.

### 3.3.2 | Design novel separators

Modification of the traditional polyolefin membrane has been well developed and studied; however, these modifications can come at a cost. According to Yang et al., there are defects can arise due to the modification of the polyolefin membrane, such as; blocking the ion transport channels and increasing thickness, and reducing  $\text{Li}^+$  conductivity shown to increase the impedance of the batteries.<sup>100,109,110</sup> As can be clearly shown in Figure 10, modifying the surface of polyolefin membrane, leads to thickening of the membrane. Meanwhile, a dense coating layer would partially block the structure of porous polyolefin membrane, making the ion transport path longer in the solid phase and thus reducing the rate performance of the battery. Further, the modified layer is weak, so it is likely to become dislodged or break during charge and discharge process. To date, no methods have been shown to effectively solve the poor mechanical properties and high-temperature resistance of polyolefin films.

Attention has therefore turned to polymer separator, due to their unparalleled electrolyte absorption, ion transfer performance and high-temperature resistance. These polymer membranes are generally electrospun polymer nanofiber materials, commonly including poly-vinylidene fluoride (PVDF), poly-acrylonitrile (PAN), and others. They exhibit high specific surface area and porosity, making them ideal materials to improve channels or pathways for Li ion transportation and the electrolyte uptake.<sup>98</sup>

#### *Poly-vinylidene fluoride*

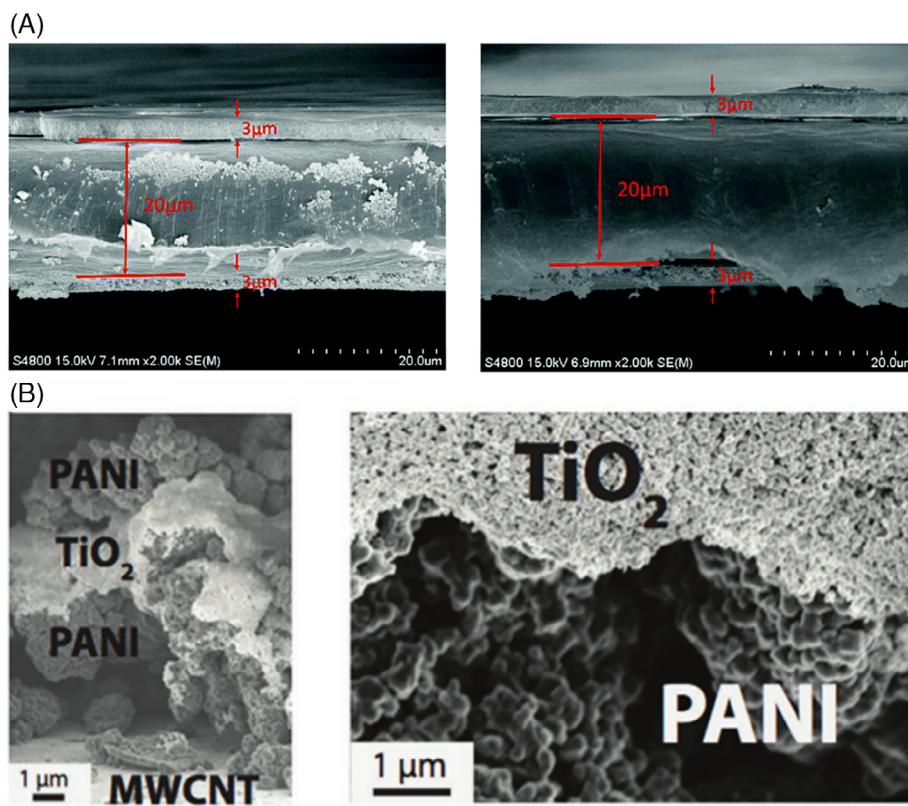
Yang et al. developed a novel nano Li ion transport channel interlayer for Li battery applications (Figure 11 (C)).<sup>112</sup> This kind of intermediate layer is formed by swelling the dense PVDF membrane electrolyte and isolating the polysulfide component through a size repulsion effect. In this way, the polysulfide component cannot transport to the surface of Li anode, reducing the consumption rate of the Li anode during operation. This strategy provides insight toward developing high-performance membranes for Li batteries.

#### *Poly-acrylonitrile*

PAN is considered as a suitable polymer for battery separator application, due to its remarkable oxidation resistance, easy processing characteristics, and excellent thermal stability.<sup>104</sup> Hu et al. designed an ammoniated polyacrylonitrile nanofiber separator (APANF) to effectively inhibit the formation of Li dendrites and the shuttle effect of polysulfide. PAN was further decorated by using PEI to functionalize the surface.<sup>98</sup> The cross-linked nanofiber structure and high density of polar groups attached to the surface produce uniformly distributed Li ions, leading to a spherical Li deposition pattern. As a result, APANF enables Li-S batteries to achieve better cycle stability and longer life span.

#### *Others*

Researchers have explored other types of separators materials, which greatly contribute to expansion of this field. For example, Yanilmaz et al. designed a glass fiber (GF) membrane as a separator for Li-S batteries.<sup>114</sup> GF membranes, with high porosity structure, good thermal stability, and high liquid electrolyte absorption, effectively suppress side reactions between polysulfides and the Li metal. This increases the current density by 42% (after 100 cycles at 0.2 C) over Li-S batteries using a conventional commercial PP membrane. Therefore, GF membrane can be considered a promising high performance separator material for Li batteries. Gong et al. designed a reduced graphene oxide fibers attached to aramid separator.<sup>113</sup> Figure 11(D) shows that in the



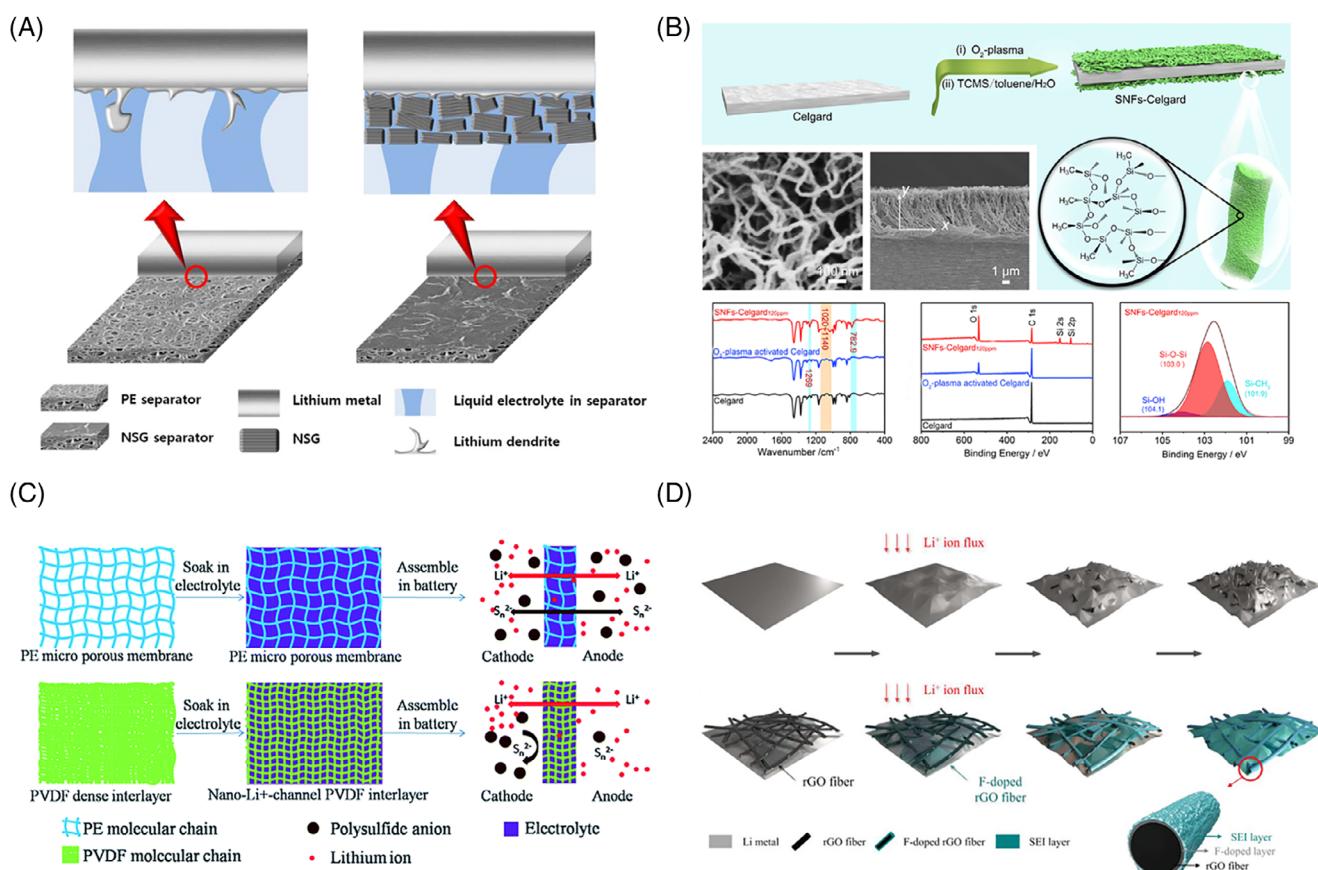
**FIGURE 10** (A) SEM images of the surface and cross-section of the PE-SiO<sub>2</sub> separator(left) and the PE-SiO<sub>2</sub>@PDA separator(right).<sup>111</sup> Reproduced with permission: Copyright 2016, The Royal Society of Chemistry. (B) SEM images of the surface and cross-section of coatings of multiwalled carbon nanotube (MWCNT), polyaniline (PANI), titania nanoparticles (titania NPs) on Celgard polypropylene separators.<sup>108</sup> Reproduced with permission: Copyright 2016, John Wiley and Sons

electrolyte, F<sup>-</sup> chemically reacts with C=C on rGOF surface to form C—F bond or semi-ionic C—F bond—equivalent to F doping. When the F-doped rGOF surface encounters Li<sup>+</sup> ions, it forms a stable SEI layer during the Li<sup>+</sup> ion plating process. Therefore, the rGOF-A functional separator ensures cyclic stability of the Li metal anode with high current density and high areal capacity, and as such the Li metal anode operates stably at high current of 20 mA cm<sup>-2</sup> and high capacity of 20 mAh cm<sup>-2</sup>. Finally, Park et al., following a membrane design originally intended for skin care, successfully demonstrated the suppression of dendritic Li growth.<sup>115</sup>

### 3.3.3 | Introduce multilayer functional membrane

The most used separators for Li metal batteries are comprised of a single monolayer. Although they have a microporous structure allowing the rapid transmission of Li ions, there also contain many defects. For example, in Li-S batteries, polysulfide can easily pass through the microporous structure, resulting in a shuttlecock effect

for ion transport, which will cause a severe side effect to the metallic anode. Therefore, in order to further solve the problem for both positive and negative electrodes, some researchers have adopted the multilayer film, which can effectively inhibit the growth of Li dendrites and improve the electrochemical properties of the positive electrode. He et al. designed and prepared a double-layered MOF-PAN/rGO-PAN nanofiber membrane for Li-S battery to replace the traditional commercial polyolefin membrane (Figure 12(A)).<sup>103</sup> The PAN-based membrane has excellent properties, such as thermal stability, superior resistance to oxidative degradation, and high electrolyte uptake.<sup>104,118</sup> The MOF particles (closely attached to the surfaces of nanofibers) absorb the polysulfides during operation leading to a reduction of polysulfide interaction with the anode surface. Using this multilayer separator, Li-S batteries show a high initial capacity and perfect cycle stability, with a capacity decay rate of only 0.03% per cycle over 600 cycles at a high rate of 5 C. In another example, Rao et al. fabricated a double functional separator for Li-S batteries (Figure 12(B)).<sup>104</sup> One layer, based on the 0-D CeO<sub>2</sub> nanocrystals surrounded by carbon nanofiber, acts as an electrocatalyst to



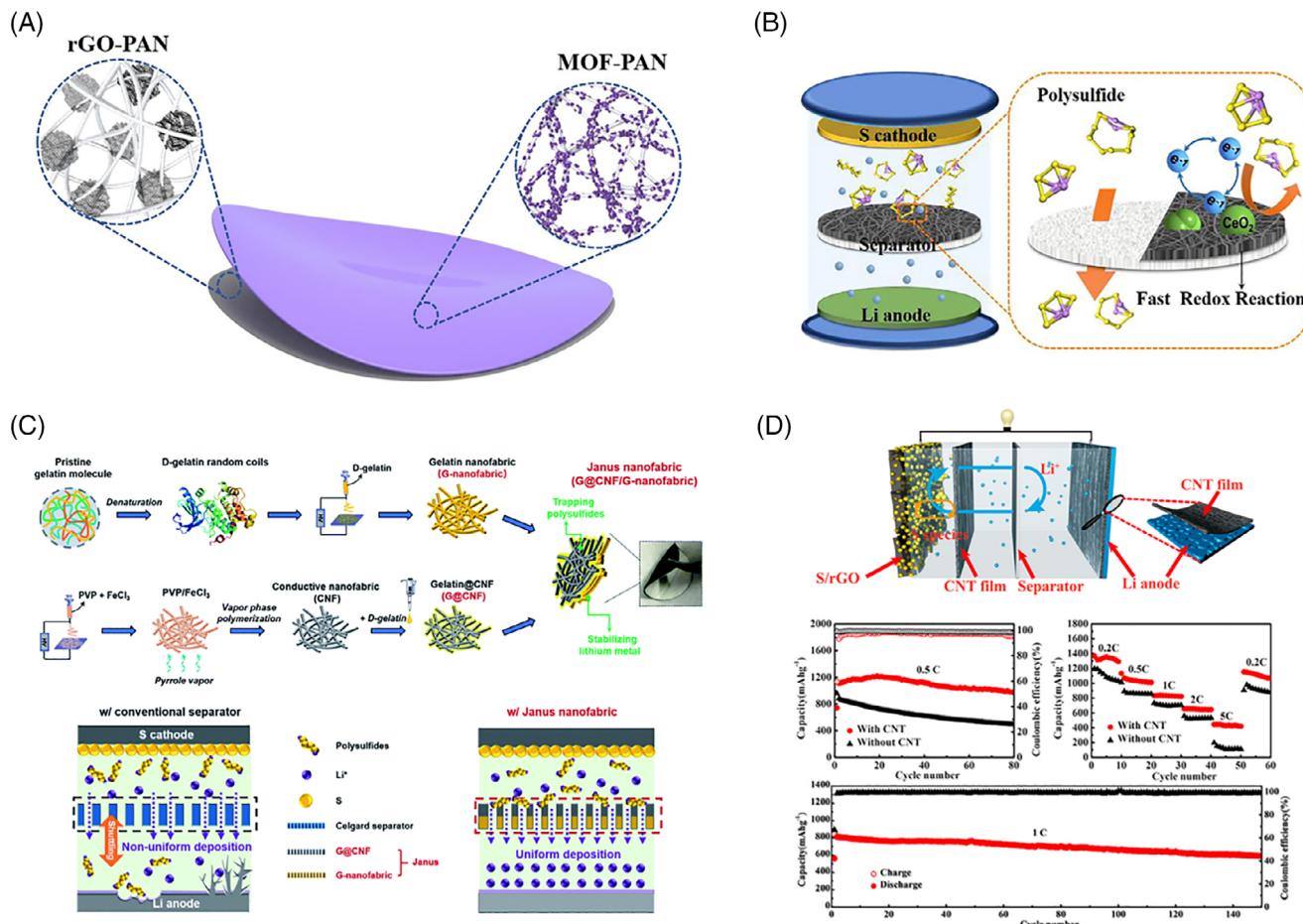
**FIGURE 11** (A) Dendrite growth on Li metal anode using PE membrane (left) and NSG-coated PE separator (right).<sup>107</sup> Reproduced with permission: Copyright 2016, American Chemical Society.(B) Preparation process and performance of SNFs.<sup>100</sup> Reproduced with permission: Copyright 2019, Cell Press. (C) Comparison of nano Li ion channels between PVDF membrane and microporous PE membrane.<sup>112</sup> Reproduced with permission: Copyright 2015, Royal Society of Chemistry. (D) Schematic diagram of Li metal anode mechanism of different separator.<sup>113</sup> Reproduced with permission: Copyright 2020, John Wiley and Sons

accelerate polysulfide reduction reaction. Another layer as a support layer, maintaining the integrity of the separator and ensuring the safety of Li-based batteries. Consequently, such bilayer separator cells present good initial specific capacity, high-rate capability, and excellent cycle stability with a capacity decay rate of 0.04% per cycle at 0.5 C over 300 cycles. Other researchers have explored the use of biomass as a multilayer separator material, which can more effectively inhibit the Li dendritic growth problem and improve performance of the battery. For example, Chen et al. designed and fabricated a dual functional separator by combining two kinds of functional nanofabrication cloth.<sup>116</sup> One is gelatin nanofabric (Figure 12(C)) is used to inhibit the growth of Li dendrites. It has excellent wettability and a high Li ion transference value. The other is a gelatin-coated conductive nanofabric used to absorb polysulfide. From the two functional layers of the Janus nanofabric, the resulting Li metal batteries show remarkable capacity, rate performance and cycling stability. This design shows

exceptional initial discharge capacity of  $890 \text{ mA g}^{-1}$  with a decay rate of 0.117% up to 300 cycles at  $0.5 \text{ A g}^{-1}$ .

In the above examples, the electrochemical performance of the battery was improved by using the design scheme of double-layer separator. However, in general, they focused more on the role of catalytic polysulfide in the charge discharge cycle of Li-S battery and ignored the problems existing in the Li anode. Addressing the problems of the Li anode, Yuan et al. proposed a new battery structure in which CNT films were inserted on both sides of the Li battery separator (Figure 12(D)).<sup>117</sup> This schema proposed the CNT film on the cathode side will inhibit the “shuttlecock effect” while the CNT film on the anode side shields from the growth of Li dendrites.

From the initial motivation to suppress dendritic growth of Li using a separator, research led to many additional benefits. Modification of the traditional polyolefin membrane, addition of new types of separator materials, and design of multilayer film structure has led to improvement of the mechanical properties of the Li



**FIGURE 12** (A) Schematic diagram and characterization of multifunctional MOF PAN/RGO PAN separator for Li-S battery.<sup>103</sup>

Reproduced with permission: Copyright 2020, Elsevier. (B) Schematic diagram of PAN/CNF-CeO<sub>2</sub> separator for Li-S battery and comparison of cycle performance of PP and PAN/CNF-CeO<sub>2</sub> separator Li-S battery with current density of 0.5 C.<sup>104</sup> Reproduced with permission: Copyright 2020, Elsevier. (C) Janus nano fabric production process diagram.<sup>116</sup> Reproduced with permission: Copyright 2020, Royal Society of Chemistry. (D) Structure and electrochemical performance of a novel Li-S battery.<sup>117</sup> Reproduced with permission: Copyright 2017, American Chemical Society

metal battery, its ion transport performance, interface stability and conductivity of the membrane. However, from this work, it is clear it is not enough to improve the thermal and mechanical properties of the separator to achieve practical application. Therefore, new material systems should be sought to fully suppress dendritic growth of the metal anode during operation.

Further, other negative side effects need to be dealt with such as cost, environmental impact form material choice or operation, design simplification, and more. These problems cannot be ignored if Li metal batteries are to be adopted by the industry. In the long run, more efficient processes are also needed for separator fabrication, keeping in mind a Li metal battery and ionic liquid electrolyte need to operate with high safety and stability. From polymer separator to gel electrolyte, to all solid-state electrolyte, this is a clear trend, with great challenges to overcome. But it is worth affirming that the

development of battery separator system will a tremendous benefit to the field.

### 3.4 | Additives for liquid electrolytes

It is well known that the growth of Li dendrites on the surface of Li metal during charging and discharging is closely related to the chemical composition of the electrolyte in Li metal batteries. Li metal readily interacts with the electrolyte at low voltage. Side reactions lead to the formation of unevenly distributed surface and electric field, which cause the growth of Li dendrites and the reduction of CE. Therefore, additives in electrolyte designed to guide Li deposition and react with Li anode to give birth to a stable and dense interphase layer will improve the electrochemical performance of Li metal batteries.

So far, the inorganic and organic additives such as halogenated salt, trace-amount of  $H_2O$ , tris (2, 2, 2-trifluoroethyl) borate,  $Cs^+$ , polymers, fluoroethylene carbonate (FEC), pyrrole, and so on have been studied and present obvious effects on improving the stability and uniformity of the SEI layer.<sup>119,120</sup>

### 3.4.1 | Inorganic additives

The inorganic additives are extensively studied due to their regulation effect on the components of SEI membrane. They are conducive, strengthen, and stabilize the SEI film. These functional additives contribute to the rapid transport of Li ions in the SEI films and improve the mechanical strength to effectively withstand the internal stress caused by the volume change during the cycle.

#### *Halogenated salt additives*

The introduction of Li iodide (LiI) can form uniform and stable SEI layer in-situ on the surface of Li metal anode. This inhibits the accumulation of dead Li and reduces side reactions by reducing the direct contact of Li and electrolyte. In addition, LiI can also improve the ion conductivity of SEI layer, effectively promoting the migration of Li ions and inhibiting the formation of Li dendrites. For example, Xiong et al. designed a simple and effective method using LiI as an additive to a traditional ester electrolyte-inducing the polymerization of organic solution into flexible oligomers, which forms the ion-conducting SEI layer inhibiting the growth of Li dendrites.<sup>121</sup> The results demonstrate that LiI can effectively improve the cycling stability of Li metal batteries.

#### *Trace-amount of $H_2O$ additives*

Water is traditionally believed harmful in Li-based battery systems due to its reactivity with  $LiPF_6$  salt and other battery modules during charging and discharging. Recently, Togasaki et al. systematically studied the effects of water in Li metal battery.<sup>122</sup> Interestingly, a trace amount of water in electrolyte was shown to enhance the cycle performance of Li metal anode. Compared with the original electrolyte, the cycle performance of the water-added electrolyte improved by 34.5%. Xu et al. studied the effect of trace amounts of water as well,<sup>123</sup> finding that controlling trace amounts of water can lead to Li-free dendritic growth. They explained that a small amount of HF produced by the decomposition reaction of  $LiPF_6$  with  $H_2O$  electrochemically reduced to form a homogeneous and dense LiF rich SEI layer on the surface of Li metal. This LiF rich SEI can further enhance the

electrochemical performance of the battery. By controlling trace amount of  $H_2O$  (25–50 ppm) as an effective electrolyte additive, dendrite free Li metal deposition was realized in  $LiPF_6$  based electrolyte without harmful effect. Simultaneously, due to the consumption of HF during the formation of LiF, the adverse effects of HF on other battery components are also reduced.

#### *Nitrate and polysulfide additives*

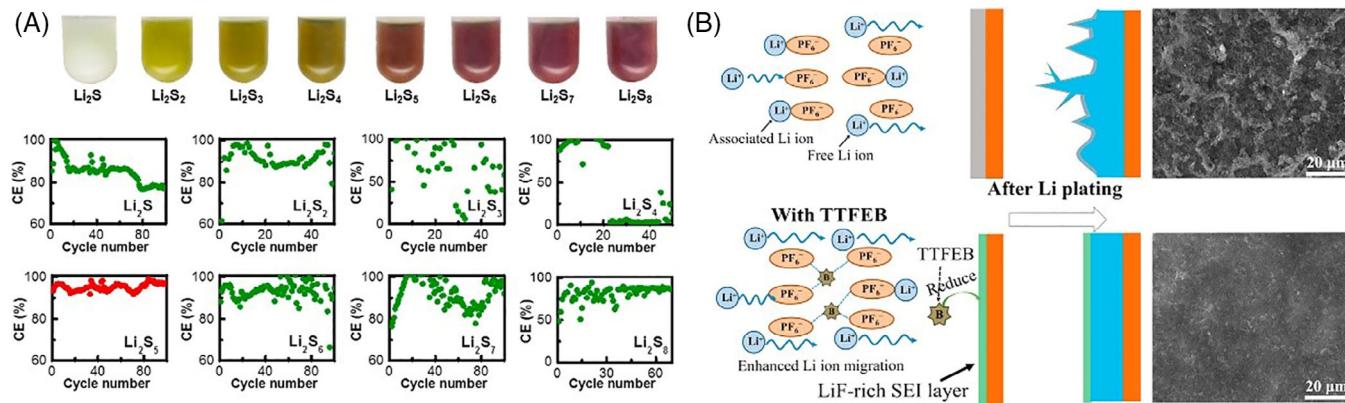
In 2008, Mikhaylik first proposed Li nitrate ( $LiNO_3$ ) can be used as an effective electrolyte for Li metal batteries. Since then, it has been widely studied for improving the performance of novel battery systems.<sup>124</sup> At present, it is generally understood that the reaction of  $LiNO_3$  with metal Li forms insoluble  $Li_xNO_y$  products. The solid surface layer on the Li anode can protect the Li anode from reactions with chemicals in the electrolyte. However, the intrinsic mechanism of the addition of  $LiNO_3$  for both the anode and cathode is still not fully understood. Therefore, researchers are still working on this field and trying to enhance the overall performance of Li metal batteries. Li et al. comprehensively studied the effect of  $LiNO_3$  additive by using Li-S batteries.<sup>125</sup> The results demonstrate that the additive cannot only form a stable passivation layer on the Li metal, but it can also inhibit the continuous shuttle effects between  $LiNO_3$  and other substances. In addition, as long as Li nitrate is still in the electrolyte, these reactions will improve CE. It is believed that the mechanism of Li nitrate in electrolyte will be well explained in the near future.

Further studies show that a stable and dense SEI layer may be obtained by the synergistic reaction of polysulfide and  $LiNO_3$ . Zhang et al. demonstrated that  $LiNO_3$  and polysulfide are equally important to form a SEI film, which is effective in suppressing the shuttle effects.<sup>126</sup> They further proved that a small amount of  $Li_2S_5$  can help to construct  $Li_2S_5$ - $LiNO_3$ -LiTFSI ternary salt electrolyte, effectively inhibiting dendrite growth of the Li metal anode. Thus, the batteries present excellent cycle performance and high efficiency (Figure 13(A)).

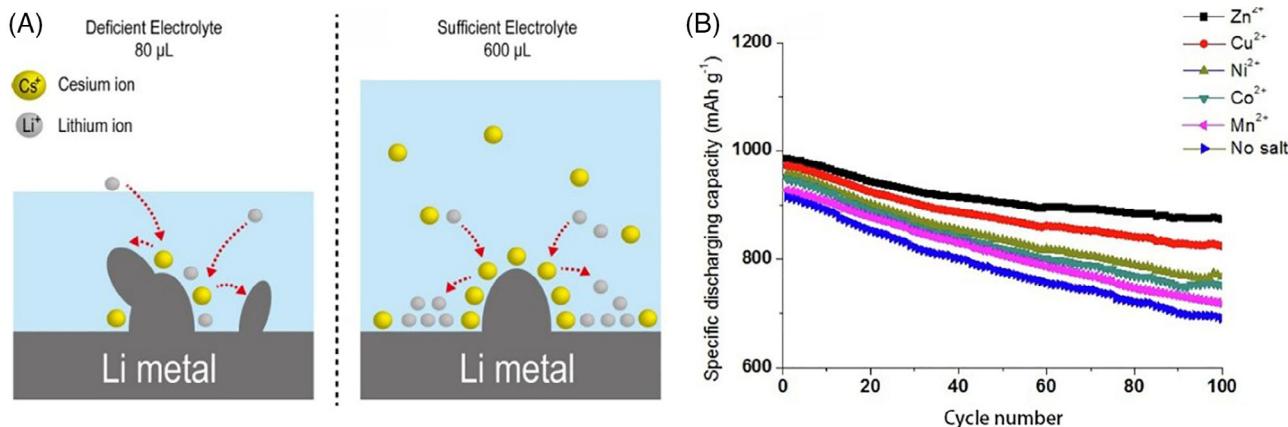
Some researchers have been exploring other new multifunctional additives. For example, Ma et al. used tris-(2,2,2-trifluoroethyl) borate (TTFEB) as a bi-functional electrolyte additive to improve the performance of Li metal anode (Figure 13(B)),<sup>127</sup> which is conducive to the surface chemistry of anode and the performance of electrolyte.

#### *Transition metal cation additives*

Generally speaking, transition metal cation additives can enhance the stability of SEI membrane, inhibit the growth of Li dendrites, and become an effective barrier to prevent the interaction between Li metal and electrolyte.



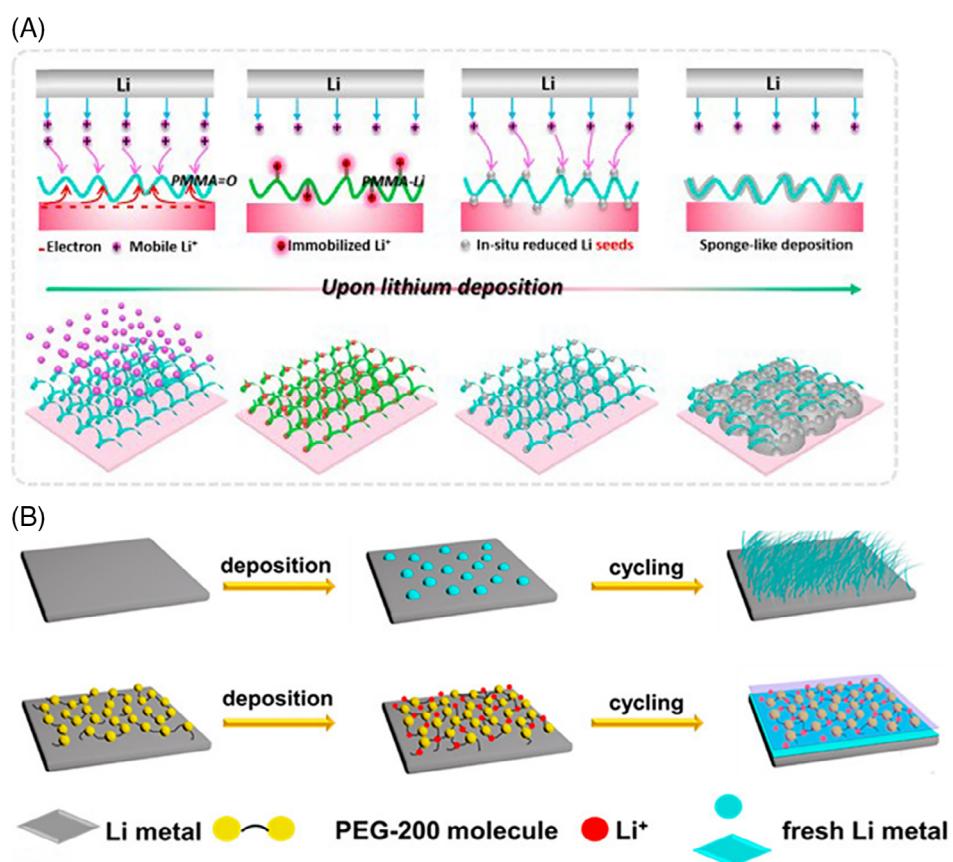
**FIGURE 13** (A) Pictures of different ternary salt electrolytes and the CE and current density of ternary salt electrolyte batteries with different LiPSs are  $0.5 \text{ mA cm}^{-2}$ .<sup>126</sup> Reproduced with permission: Copyright 2016, Elsevier. (B) Comparison of structural changes of Li metal anodes in electrolyte containing tris-(2,2,2-trifluoroethyl) borate (TTFEB) and without TTFEB.<sup>127</sup> Reproduced with permission: Copyright 2018, Elsevier



**FIGURE 14** (A) In 80  $\mu\text{L}$  and 600  $\mu\text{L}$  electrolyte, the amount of Cs<sup>+</sup> ions required to stabilize Li metal surface was compared with that required by she mechanism.<sup>128</sup> Reproduced with permission: Copyright 2019, American Chemical Society. (B) Cycle performance of transition metal cation and no salt batteries at 0.2 C.<sup>107</sup> Reproduced with permission: Copyright 2016, American Chemical Society

Particularly, in Li-S batteries, the protective layer formed with the assistance of transition metal sulfide also hinders the diffusion of polysulfide to Li metal, thus further alleviating the shuttle reaction of polysulfides, and preventing the loss of active substances and self-discharge. Yoon et al. used cesium hexafluorophosphate (CsPF<sub>6</sub>) as an electrolyte additive to modify the surface of Li metal anode (Figure 14(A)),<sup>128</sup> which can efficiently improve the electrochemical performance such as cycle number and rate capability of the battery. These enhancements are due to the self-healing electrostatic shielding mechanism of Cs<sup>+</sup> ions, which depends on the concentration of Cs<sup>+</sup>. Meanwhile, Manthiram introduced a simple method by adding copper acetate to the electrolyte as a surface stabilizer for Li metal in a polysulfide-rich environment of Li-S battery.<sup>129</sup> This additive effectively inhibits the formation of Li dendrites and improves

the electrochemical performance by controlling Li deposition and improving the surface chemical activity. The primary mechanism is the strong intermolecular interaction between copper and Li sulfide, which destroys the growth sequence of Li sulfide crystals. This attracts Li ions deposition associated with the deposition of copper sulfide. From this study, Zeng et al. used a facile method to explore the protective effect of different transition metal cation additives to forming an *in situ* passivation film for Li metals (Figure 14(B)).<sup>130</sup> The overall result shows that, by adding the above transition metal cations, the batteries present a higher stability, higher rate capability, and better redox kinetics over cycles. Therefore, it can be concluded that the low-cost application of transition metal cation as electrolyte additives is one of the promising strategies for the development of Li metal batteries.



**FIGURE 15** (A) Schematic diagram of mechanism of spongy Li deposition.<sup>131</sup> Reproduced with permission: Copyright 2019, Elsevier. (B) Comparison of Li deposition process with or without PEG additive.<sup>132</sup> Reproduced with permission: Copyright 2019, American Chemical Society

### 3.4.2 | Organic additives

Compared with inorganic additives, organic additives have some unique properties, such as more flexible Li surface and higher interface stability.

#### Polymers additives

Polymer additives are widely studied because they are more efficient in protecting Li metal anodes than inorganic ions. Among them, Guo et al. successfully prepared a three-dimensional continuous, sponge-like Li structure by adding electrochemical active polymethyl methacrylate (PMMA) into the electrolyte,<sup>131</sup> which can inhibit the growth of Li dendrites (Figure 15(A)). During the discharge process, Li ions react with PMMA and are immobilized. These trapped Li ions are in situ reduced to the initial Li, and the surrounding Li ions are further deposited to form a three-dimensional PMMA molecular chain model. This morphology not only provides a fast electron transport path to eliminate the formation of dead Li, but also reduces the current density on the surface of Li metal, which is a good protection for Li metal. Moreover, Wang et al. introduced polyethylene glycol

(PEG) as an additive in traditional liquid electrolyte (Figure 15(B)).<sup>132</sup> PEG molecules dispersed on the surface of Li metal were found to interact effectively with Li ions, fundamentally inhibiting the growth of Li dendrites, thus improving the cycling stability of the Li metal battery.

#### Organic molecule additives

Although the additives in the electrolyte have achieved good results, it is difficult to achieve the desired passivation effect at the interface of Li metal anode and electrolyte over a long cycle. Therefore, researchers have developed more effective electrolyte additives to solve the problems encountered in practical application. For example, Fu et al. reported that a stable SEI could be formed in situ on the surface of a Li metal anode by adding appropriate amounts of sulfonyl chloride to a conventional ester electrolyte solution.<sup>133</sup> The SEI layer rich in Li chloride can inhibit the growth of Li dendrites and accelerate the migration of Li ions, thus improving the performance of Li metal batteries. Chu et al. have designed a series of metal–organic framework particles as a new type of solid additive.<sup>134</sup> These additives have porosity, multifunctional groups, and flexibility, which

play an important role in achieving smooth Li plating behavior.

In summary, in order to make the electrolyte of Li metal battery respond to modern demands of efficiency, environmental friendliness, and more, a feasible approach is to optimize the performance of electrolyte by using additives. Researchers are actively exploring and developing functional additives to obtain uniform and stable SEI films and improve battery life. Based on the above description, it is generally believed that strong SEI films with good combination of soft and hard ingredients can be developed by optimizing the content of reagents, additives, and Li salts. It is known that SEI films need good ionic conductivity to reduce the diffusion resistance of Li ions through the SEI layer. Therefore, the utilization of functional additives and electrolyte components needs further efforts to achieve success in LMBs. Finally, multifunctional additives not only play a good role in Li metal anode but also optimize the electrolyte itself and even the surface of separator and cathode. Given the strong research push in this direction, novel effective electrolyte additives are expected to be realized soon.

### 3.4.3 | High-concentration electrolyte

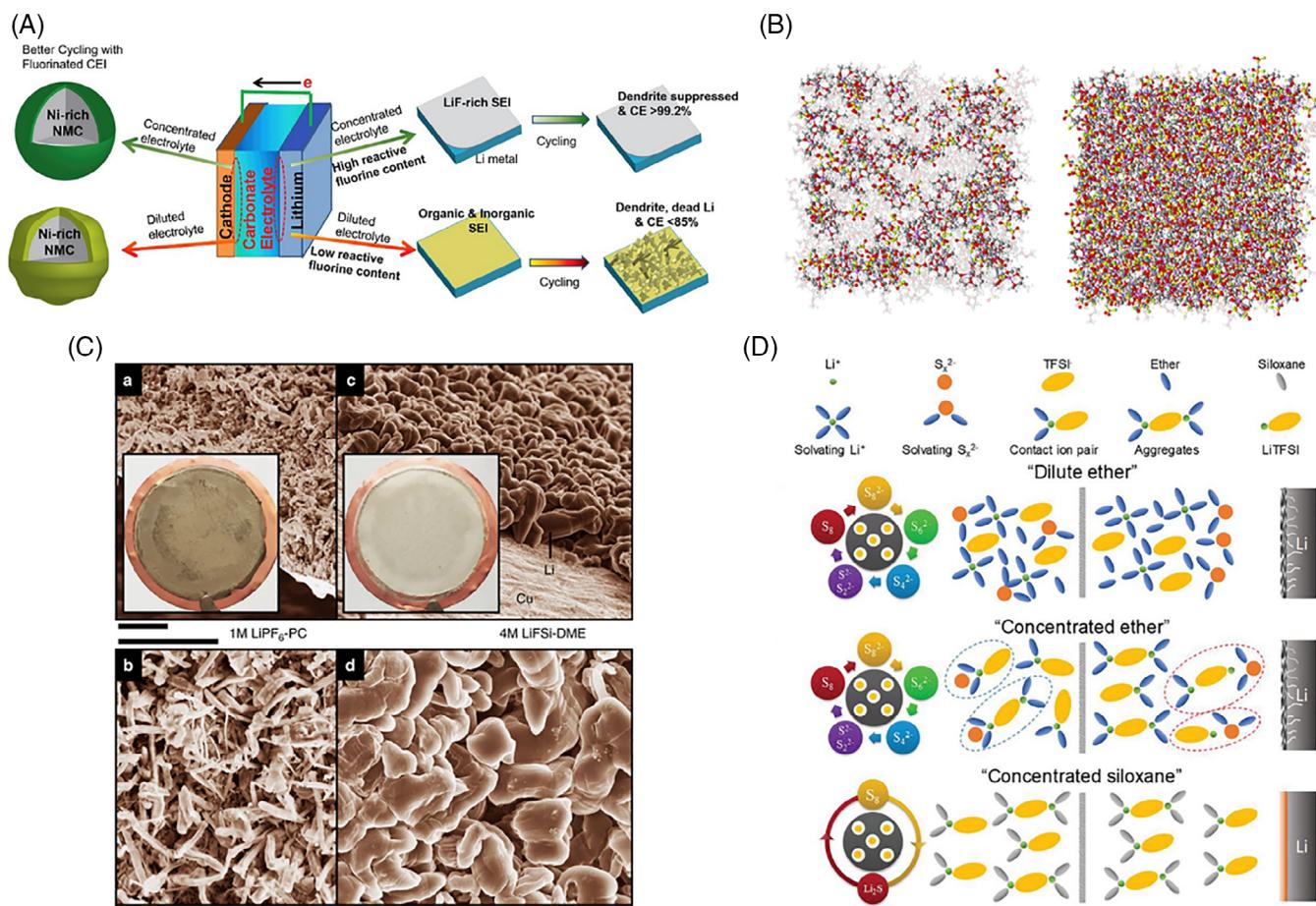
In general, ionic conductivity and viscosity will rise sharply with the increasing concentration of electrolyte, which is not conducive to the rate performance of the electrolyte and will lead to the performance decline of lithium metal battery.<sup>135</sup> However, an increase in electrolyte concentration greatly reduces the number of free solvent molecules and the probability of their interaction with lithium metal, and also significantly changes the chemical properties of lithium metal surface. This prompted the researchers to explore and study the high electrolyte concentration.<sup>136</sup>

Fan et al. verified that the lithium metal anode had good cycling performance in carbonate electrolyte after increasing Li bis (fluorosulfonimide) imide (LFSI) concentration to ~10 M.<sup>137</sup> The existence of  $\text{FSI}^-$  makes the interface of lithium metal anode and nickel-manganese-cobalt (NMC) cathode rich with F content (Figure 16(A)). The F-rich interface effectively inhibits the formation of Li dendrites. Under high charging voltage of 4.6 V and high load of  $2.5 \text{ mAh cm}^{-2}$ , the NMC622||Li battery still maintains 86% of its original capacity after 100 cycles. This electrolyte optimization method presents a unique conceptual framework for continued improvement of Li metal batteries. In addition, Qian et al. reported that a high concentration electrolyte composed of ether solvent and Li bis (fluorosulfonyl) imide salt can realize high-rate cycling of Li metal anode without dendrite growth.<sup>138</sup>

Due to the low reactivity of these electrolytes, the probability of side reactions decreases, thus showing high Coulomb efficiency. For the dilute electrolyte, the solvent reacts with the Li metal to a greater extent, thus reducing the CE of Li plating/stripping. Moreover, the SEI layer is highly dense, preventing further corrosion of Li metal anode and imparting strong electrode stability in high concentration LFSI-DME electrolyte (Figure 16(B,C)). The results show that in 4 M LFSI-DME electrolyte, the Cu||Li battery can cycle more than 1000 times at  $4 \text{ mA cm}^{-2}$ , and the CE is as high as 98.4%. With further optimization of the electrolyte, it is possible for this Li metal battery to move towards practical application. Amine et al. have demonstrated that a new type of concentrated siloxane electrolyte has excellent performance, especially for stabilizing sulfur cathode and Li metal anode and reducing flammability.<sup>139</sup> They point out siloxane solvents can effectively regulate the interaction of cations/anions (such as  $\text{Li}^+$ ,  $\text{TFSI}^-$  and  $\text{S}^{2-}$ ) with solvents in high concentration electrolyte (Figure 16(D)). Therefore, this battery design can realize reversible lithium plating/stripping and solid-solid electrolyte interphase chemical reaction. Moreover, they emphasize the solution ion exchange process in high concentration electrolyte is a key factor in understanding and designing electrolyte for other high-energy Li metal batteries.

### 3.4.4 | Localized high-concentration electrolyte

Although the high concentration electrolyte has achieved good results, there are still some critical shortcomings such as the increase in electrolyte concentration leading to the increase of viscosity, which leads to the decrease of ionic conductivity. As a result, the performance of the battery at low temperature is poor, the manufacturing process of the battery is difficult, the wettability to the diaphragm and electrode is poor, and the cost is increased.<sup>140-142</sup> Especially for sulfone-based electrolyte, because of its high viscosity and melting point, the above problems become more and more egregious with increasing the concentration. In recent years, some researchers have overcome these shortcomings by choosing the cosolvent of high-concentration electrolyte. For example, Doi et al. studied different kinds of fluoroalkyl ethers as diluents to reduce the high viscosity of high concentration  $\text{LiBF}_4/\text{PC}$  electrolyte solutions.<sup>143</sup> It was found 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropane ether (HFE) is the most suitable diluent, and the interaction between HFE,  $\text{Li}^+$  cation, and  $\text{BF}_4^-$  anion is very weak. It was also shown that the  $\text{LiBF}_4/\text{PC}$  system with high concentration can be diluted with HFE without losing high



**FIGURE 16** (A) Schematic diagram of influence of active fluorine content in concentrated electrolyte on battery poles.<sup>137</sup> Reproduced with permission: Copyright 2018, Elsevier. (B) Snapshots of the MD simulation boxes (1-M and 4-M  $\text{LiFSI-DME}$  electrolyte).<sup>138</sup> Reproduced with permission: Copyright 2015, Springer Nature. (C) SEM images of the morphologies of Li metal after plating on Cu substrates in different electrolytes.<sup>138</sup> Reproduced with permission: Copyright 2015, Springer Nature. (D) Schematic illustration of internal chemical reaction diagram of lithium sulfur battery in different electrolytes.<sup>139</sup> Reproduced with permission: Copyright 2020, John Wiley and Sons

antioxidant stability. Moon et al. analyzed the solvation structure of  $\text{Li}^+$  and the formation of ion pairs in an electrolyte composed of triglyme (G3) and a hydrofluoroether (HFE) containing 1 M Li [TFSAs] (TFSAs: bis(trifluoromethanesulfonyl) amine).<sup>144</sup> The results show when the molar ratio of G3 to Li [TFSAs] is close to 1, the activity of G3 in the electrolyte decreases significantly. This shows the oxidation stability of electrolyte is enhanced and the corrosion rate of positive aluminum collector decreases, improving the stability of Li metal battery. From this study, the activity of the solvent in the electrolyte of Li metal battery is the key factor to improve the electrochemical reaction of lithium metal battery.

### 3.5 | Other types of electrolyte

Due to the intrinsic problems, such as Li dendrite growth, depleting the electrolyte, safety hazards, and

more, widespread industrialization of liquid electrolytes has been hampered. Solid or gel electrolyte minimizing Li dendrite growth has been developed to tackle the drawbacks of liquid electrolytes. Yamada et al. designed a new type of all solid-state Li battery, which demonstrates a comprehensively high performance.<sup>145</sup> Its capacity is close to the theoretical value and the CE of the initial charge/discharge cycle is close to 99%. In addition, the activation energy of the charge transfer process is much smaller than that of the corresponding liquid electrolyte battery and its transference number of Li in solid electrolyte is close to 1. This makes the deposition of Li metal uniform and inhibits the formation of Li dendrites.<sup>146,147</sup> Moreover, it can improve the mechanical strength and service life of the battery. However, compared with traditional liquid electrolyte, solid state electrolytes (SSEs) possess very poor ionic conductivity. Therefore, researchers have focused on improving the ionic conductivity of SSEs.

### 3.5.1 | All-solid electrolyte

#### Inorganic-based SSEs

The inorganic solid electrolytes are structurally nonporous and high strength, which are necessary to prevent the penetration of Li dendrites and improve the reliability of Li metal batteries. Recently, sulfides, oxides, and phosphates have been extensively studied due to their unique properties as SSEs.<sup>85</sup>

#### Sulfide-based SSEs

Due to the high ionic conductivity, it is beneficial to design a high conductive SSE at room temperature using sulfides. Therefore, in recent years, sulfides have been widely investigated in solid Li batteries.<sup>148</sup> Yamada et al. developed and tested solid-state Li batteries by using  $\text{Li}_3\text{PS}_4$  as electrolyte.<sup>145</sup> The batteries show a good circulation retention capacity, which demonstrates that  $\text{Li}_3\text{PS}_4$  is effective on promoting the battery performance. However, the stability of sulfides is generally poor in ambient, because sulfides are hygroscopic and form toxic  $\text{H}_2\text{S}$  when exposed to moisture.<sup>149</sup>

#### Oxide-based SSEs

Compared with sulfides, oxides are highly chemical stable and easy treat. To the best of our knowledge, the most promising Li ion conducting oxide is garnet  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO). Murugan et al. found that LLZO demonstrate high conductivity and electrochemical stability.<sup>150</sup> Schmidt et al. used various experimental and computational methods to study the mechanical strength of high conductivity LLZO based on Al and Ta doping.<sup>151</sup> Data show the Al/Ta-doped LLZO maintains a high hardness during operation, which moves the needle on Li battery development. Novel oxides are also in development, for example, Zheng et al. prepared amorphous lanthanum titanate (LLTO) powder by sol-gel method, and studied the compatibility between the oxide and Li metal.<sup>152</sup> The results show that the amorphous LLTO maintains ionic conductivity after direct contact with Li, demonstrating compatibility between these two.

#### Polymer-based SSEs

The soft polymer electrolyte forms a stable interface with the electrode during charging and discharging, as well as good mechanical stability. Liu et al. designed a nonporous, polymer electrolyte, and the battery presented a good performance.<sup>153</sup> The polymer electrolyte not only inhibits the Li dendritic growth under high current density but also adapts to the volume change of Li metal by elastically deforming. However, low ionic conductivity at room temperature and instability at high-temperature limit its application.

In response to this deficiency, composite electrolytes of polymer and other materials are being studied LMBs. They are expected to meet modern demands placed on LMBs by combining the advantages of inorganic and polymer mixed electrolytes.<sup>154</sup> For example, Wu et al. have prepared a novel polyethylene oxide (PEO) composite polymer electrolyte using nickel phosphate (VSB-5) nanorods as fillers (Figure 17(A)).<sup>155</sup> At 30°C, the ionic conductivity of the solid polymer electrolyte is as high as  $4.83 \times 10^{-5} \text{ s cm}^{-1}$ , and the electrochemical stability is about 4.13 V. In addition, it has good compatibility with Li metal anode and exhibits effective suppression on of Li dendrite growth. Zagorski et al. designed a composite electrolyte using ion-conducting garnet LLZO micro-particles into a PEO polymer electrolyte (Figure 17 (B)),<sup>156</sup> which resulted in significantly improved interface stability with Li metals during the electrochemical cycle. This work provides a new strategy for suppressing Li dendrite formation in solid-state batteries. At the same time, it was also pointed out the elastic and shear moduli of the electrolyte do not play a key role in uniform Li electrodeposition. This role is determined by the interface composition and local  $\text{Li}^+$  dynamics. This work provides interesting clues towards optimum the design of other solid composite electrolyte system.

#### MOFs and COFs based-SSEs

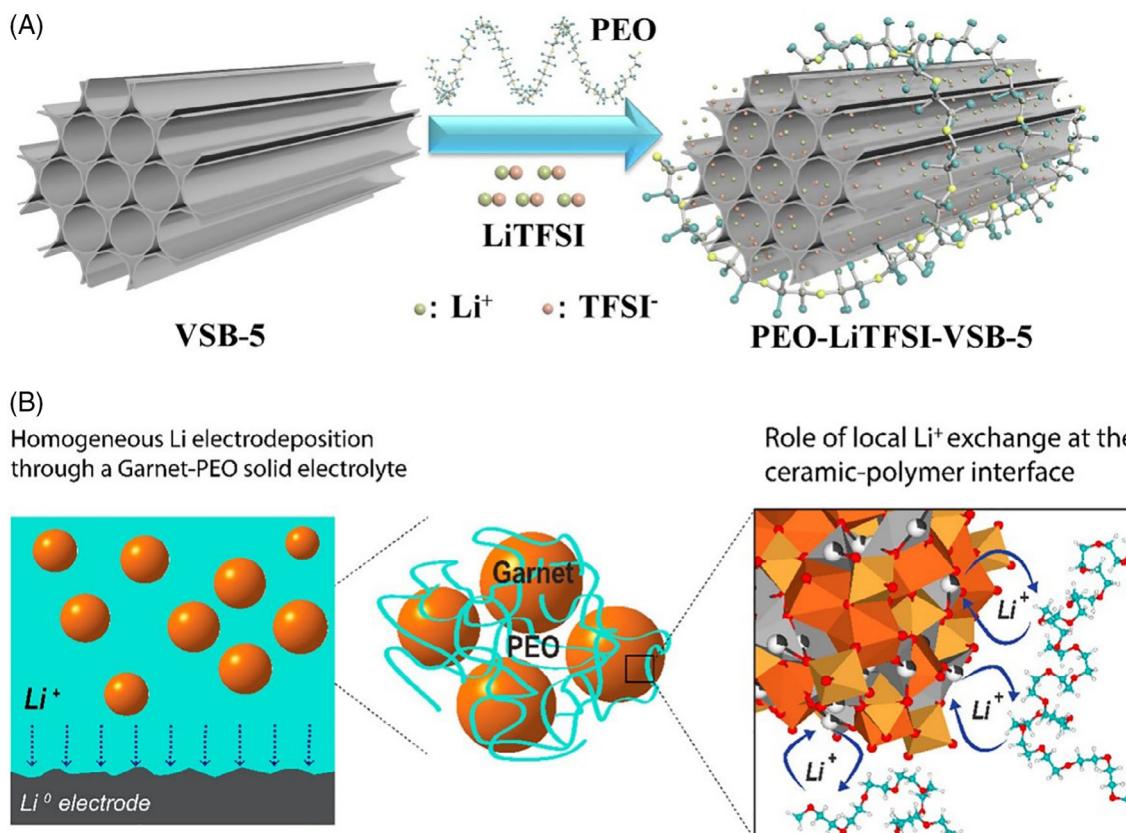
The solid electrolyte mentioned above has distinguishing performance in the suppression of Li dendrite for Li anode, but its ionic conductivity is low and the interface resistance between electrolyte and active electrode is high.<sup>157,158</sup> Therefore, there is an urgent need for solid electrolyte with excellent Li ion transport kinetics internally and at the interface. Crystalline porous materials, including MOFs and COFs, have attracted much attention in the field of batteries due to their ordered porous structure providing fast ion transport channels.<sup>159</sup> Due to its large number of narrow pores, large specific surface area and high stability, it is considered a promising candidate material for Li metal battery solid electrolyte. Long et al. reported was first to report MOF derived solid ion conductors consisting of  $\text{Mg}_2(\text{dobdc})$  ( $\text{dobdc}^{4-} = 1,4\text{-dioxido-2,5-benzenedicarboxylate}$ ) and Li-containing hybrids have high ionic conductivity (Figure 18(A)).<sup>157</sup> It was shown that when the anions in the hybrid react with  $\text{Mg}^{2+}$  cations, Li ions migrate in  $\text{Mg}_2(\text{dobdc})$ , and the ionic conductivity reaches  $0.31 \text{ mS cm}^{-1}$  at room temperature. These results provide a new method and reference for the preparation of solid lithium electrolyte materials. In 2019, Wu et al. designed a new nanostructured MOF-derived solid electrolyte.<sup>158</sup> Due to the abundant nano-porous structures in UIO-66, the nanostructured MOF of  $\text{UIO-66}[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6]$

( $BDC^{2-}$  = 1,4-benzoic acid radical) was used (Figure 18(B)). The  $Zr^{4+}$  metal ions of MOFs are difficult reduce, so side reactions can be avoided when contacting with metal Li. In addition, UIO/Li-IL SSE also demonstrated excellent electrochemical stability at high potential. At the same time, the nanostructure lowers the interface resistance between the electrode and electrolyte, so the solid-state lithium battery shows excellent performance.

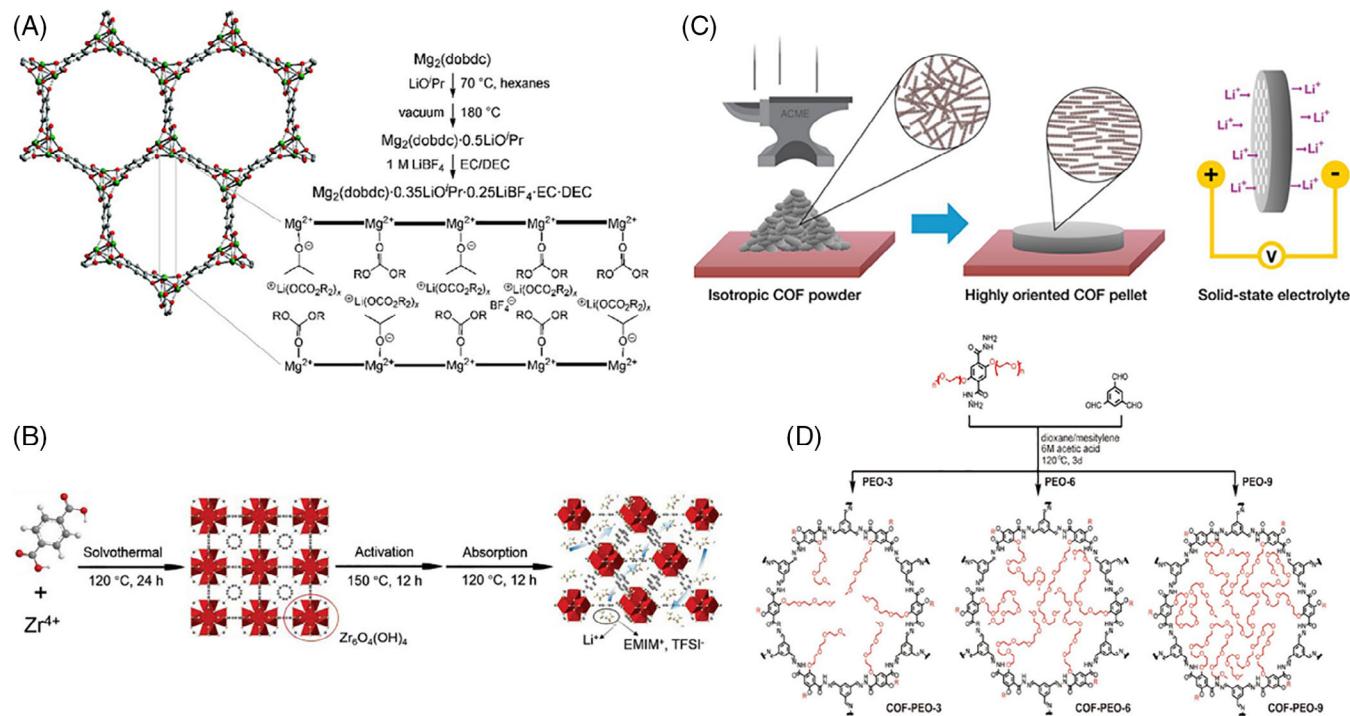
Applications of COFs in ionic conductive materials has been widely studied, showing great potential in SSEs fabrication. Vazquez-Molina et al. demonstrated that COF becomes highly oriented during mechanical pressing (Figure 18(C)), increasing ionic conductivity and enhancing the kinetic properties of COF.<sup>160</sup> In addition, the particles prepared by impregnating COF powder with  $LiClO_4$  show a high conductivity of  $0.26\text{ mS cm}^{-1}$  and excellent electrochemical stability at room temperature. These results indicate it is possible to use COFs as solid electrolyte in the Li metal battery. Meanwhile, Zhang et al. designed a flexible, bulky, glassy PEO partially covalently meshed to form a rigid two-dimensional COF structure (Figure 18(D)).<sup>161</sup> In this system,  $Li^+$  reaches  $1.33 \times 10^{-3}\text{ s cm}^{-1}$  at  $200^\circ\text{C}$ . Further, the robustness of

the structure enables long periods of high for a given temperature. The COF electrolyte was first used in all solid-state Li battery at  $100^\circ\text{C}$ . Therefore, these novel solid electrolytes as described show great potential in inhibiting the growth of Li dendrites in Li metal batteries.

Thus, all solid-state Li battery featuring with metrics of good safety and wide potential window, among others, are peerless in combination with liquid electrolyte. This combination inhibits the growth of Li dendrite and resolves operational problems such as the shuttle effect of Li sulfur battery.<sup>162</sup> As such, consensus places the solid-state Li metal battery as the most promising battery in the new generation of energy storage systems. However, compared with liquid electrolytes, solid electrolytes have low ionic conductivity, high interface resistance with electrode and, in some cases, show sensitivity to operation in air,<sup>147,162</sup> hindering its commercialization. In review, studies have demonstrated all solid electrolytes have undergone significant development, but their mechanism of operation and breakdown are not well explained yet. Therefore, there is still a long way to go for the development of all solid electrolyte.



**FIGURE 17** (A) Schematic diagram of  $Li^+$  migration in SPE reinforced by VSB-5.<sup>155</sup> Reproduced with permission: Copyright 2020, Elsevier. (B) The schematic diagram of  $Li^+$  exchange between LLZO particles and PEO (LiTFSI) interface.<sup>156</sup> Reproduced with permission: Copyright 2019, American Chemical Society



**FIGURE 18** (A) The structure of  $\text{Mg}_2(\text{dobdc})$  and the schematic diagram of its solid electrolyte formation.<sup>157</sup> Reproduced with permission: Copyright 2011, American Chemical Society. (B) Schematic of preparation of UIO/Li-IL SSE.<sup>158</sup> Reproduced with permission: Copyright 2019, John Wiley and Sons. (C) Preparation of highly oriented COF and its application in solid electrolyte of lithium battery.<sup>160</sup> Reproduced with permission: Copyright 2016, American Chemical Society. (D) Synthesis of COF-PEO-x ( $x = 3, 6, 9$ ).<sup>161</sup> Reproduced with permission: Copyright 2019, American Chemical Society

### 3.5.2 | Gel-polymer electrolyte

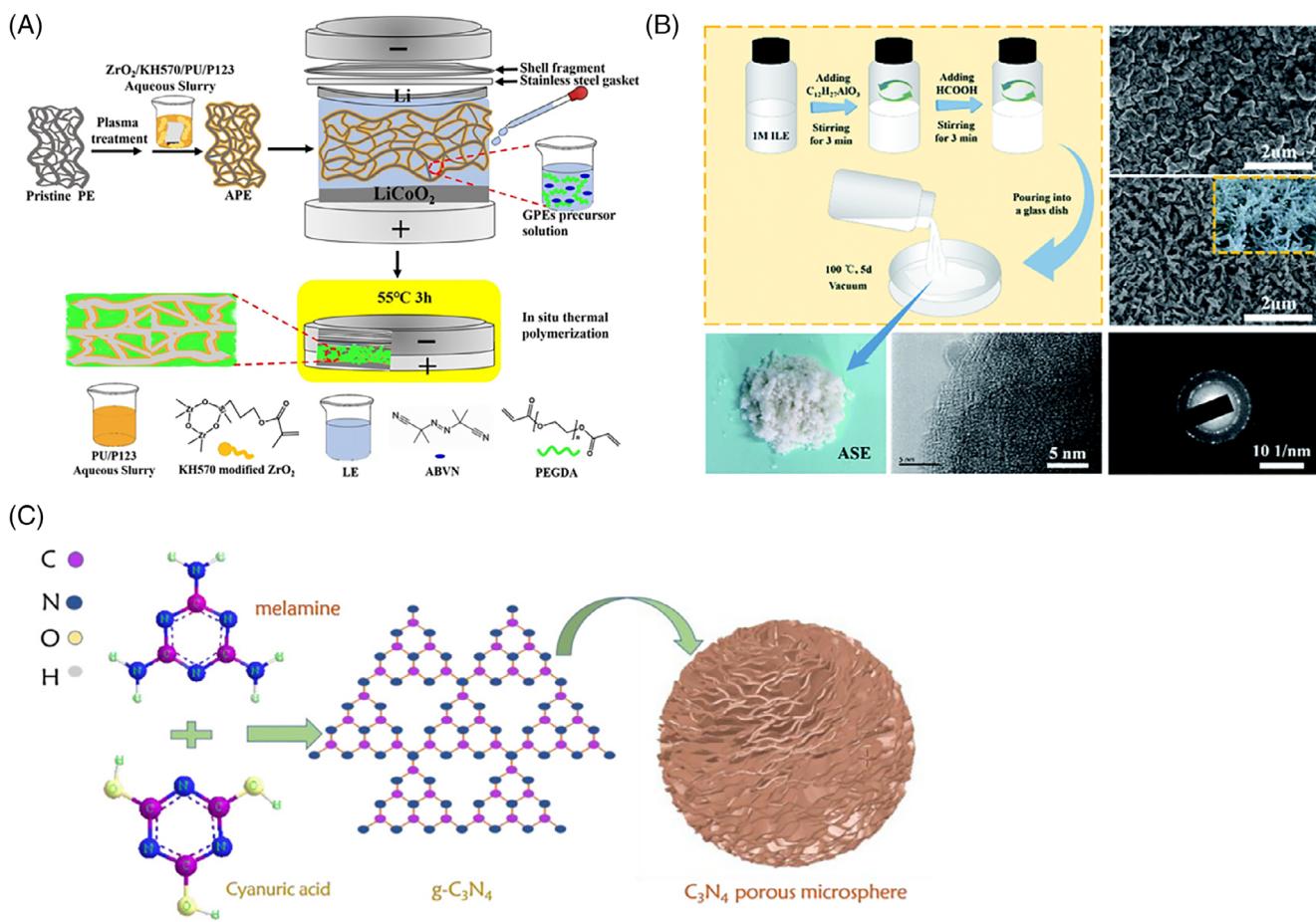
Although solid electrolyte effectively improves the safety performance of Li metal batteries, the high impedance and low ionic conductivity between the electrolyte and the electrode remain an issue. In response, solutions are being developed for the polymer gel electrolyte to improve its ionic conduction and contact adhesion with electrodes. This strategy might be a good choice for the development of LMBs.<sup>163–165</sup>

The mechanical properties of GPEs are poor because the polymer becomes very soft after expansion. Therefore, further modification of GPEs is critical. Fu et al. demonstrated that the use of  $\text{ZrO}_2/\text{KH570}/\text{PU}/\text{P123}$  layer coating on a PE separator can effectively counteract the negative effects of the PE-supported gel polymer electrolyte (Figure 19(A)).<sup>163</sup> The modified GPE electrolyte can simultaneously possess a considerable ion transport performance, the high stability of interface with Li metal and enhanced mechanical property.

In recent years, researchers have developed a number of other electrolytes with improved results. For example, Hu et al. were first to devise a slurry-like electrolyte using polymeric graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) as filler (Figure 19(C)).<sup>167</sup> Carbon nitride possesses both high

mechanical strength and multistage pore structure, which effectively suppresses the growth of Li dendrites and improves the electrochemical performance of Li metal batteries. In addition, to solve the problem of poor interface contact and Li dendrite growth, Wen et al. reported a new biomimetic quasi solid electrolyte, which is injected into the  $\text{Al}_2\text{O}_3$  framework by in situ sol-gel method (Figure 19(B)).<sup>166</sup> The results show this structure can effectively improve the poor interface contact and protect the Li metal anode. The above strategy to modifying the interface of solid-state Li metal via coated bionic foliar electrolyte with Li aluminum conductive layer offers a distinctive perspective to metallic Li anode protection and an alternative way for practical application of LMBs.

Despite of the rapid development of solid-state electrolyte, there are still obstacles to remove. The ceramic electrolytes are brittle and not easy to plate evenly on top of the electrode, leading to a high interfacial resistance and poor mechanical property. Polymer electrolytes are poor in conductivity. They cannot endure a high current density, making them incompatible with commercialization demands. Therefore, ameliorating the interface between ceramic electrolytes and the electrodes or modifying the ion conductivity of polymer electrolytes are of



**FIGURE 19** (A) Schematic diagram of preparation process of GPEs.<sup>163</sup> Reproduced with permission: Copyright 2019, Springer Nature. (B) The flow chart of ASE preparation was shown.<sup>166</sup> Reproduced with permission: Copyright 2020, Royal Society of Chemistry. (C) Schematic diagram of preparation of g-C<sub>3</sub>N<sub>4</sub> porous microspheres.<sup>167</sup> Reproduced with permission: Copyright 2017, American Chemical Society

great importance in promoting the industrialization of Li metal batteries.<sup>149</sup>

#### 4 | CONCLUSION AND PERSPECTIVE

Rechargeable Li metal batteries with high energy density are recognized as an emerging next generation of energy storage system. In order to realize Li metal anode adoption in commercial markets, researchers have made great efforts to overcome the shortcomings of Li dendrite growth, volume fluctuation, low mechanical strength, and high interface resistance between electrolyte and electrode. These efforts primarily manifest in artificial SEI layer construction, current collector modification, separator modification, electrolyte additive, and solid-state electrolyte development. This review gives a detailed overview of the strategies which used to overcome the existing problems. Since the research on Li

metal batteries is still in the initial stage, and there remains numerous pathways to optimize performance of these batteries, multiple approaches were proposed in this review according to the research results.

Coating an artificial SEI layer remarkably improves the performance of Li metal battery. It is likely these artificial SEI layer can effectively suppress Li dendritic growth dramatically improving electrochemical performance. This research is still at the primary stage, and fundamental mechanisms resulting in performance gains are poorly understood. Further efforts are envisioned to: (i) develop advanced *in situ* characterization technology to investigate the mechanism of artificial SEI formation, (ii) develop cheaper and simpler methods of preparation, and (iii) combine the artificial layer strategy with other methods to further improve the performance of Li metal batteries, different combinations may bring unexpected effects.

3D current collector can effectively suppress dendritic Li growth and is highly compatible with other battery

components. Although good results have been obtained in the laboratory, it is still far from actual production. Further effort towards developing a 3D current collector for commercial application must solve at least three major issues: (i) improve CE of battery using, for example, nanostructured carbon materials; (ii) solve the problem of low specific energy density caused by high mass density of metal collector; and (iii) address mass increase due to void filling of the 3D collector.

The actual separator plays an important role in improving the electrochemical performance of the battery by removing direct interaction between positive and negative electrodes and enabling the ion transport. Approaches to separator optimization, including modification of polyolefin membrane using nanoparticles, developing multi-layer films. Both approaches offer unique solutions to facilitating ion transport and increasing mechanical strength while suppressing Li dendrite growth and the shuttle effect from polysulfide interaction.

Additives in electrolyte are designed to guide Li deposition, react with Li anode to nucleate, and grow a stable dense interphase layer to improve the electrochemical performance of Li metal batteries. In laboratory, researchers actively explore and develop functional additives to obtain uniform and stable SEI film and improve battery life. Researchers surmise strong SEI films comprised of organic and inorganic components will lead to optimal Li metal battery function. Research is pursuing efforts to ascertain the appropriate combination of organic and inorganic SEI film components to optimize layer conductivity. These components include multifunctional additives to optimize the performance and properties of not only the electrolyte additives but also cathode and separator surfaces. Different electrolyte types have been found to convey advantages and disadvantages: solid or gel electrolyte minimize dendrite growth because they rarely react with Li metal electrodes-research is on-going to address their drawbacks. Ceramic electrolytes are normally brittle and are not easy to plate evenly on top of the electrode, leading to a high interfacial resistance and poor mechanical property. Polymer electrolytes are poor in conductivity and cannot endure a high current density but are highly desirable viable for commercial if this issue can be addressed. Ameliorating the interface between ceramic electrolytes and the electrodes or modifying the ion conductivity of polymer electrolytes are of great importance in promoting the industrialization of Li metal batteries. Concentrated effort in each of these areas of LMB research is expected to lead to make Li metal anode a commercial-viable reality.

The eventual commercial realization of LMBs is in the hands of the community. The potential of LMBs is to become a staple device in the storage of energy for a vast array of applications, including EVs, portable devices,

flexible electronics, and so on. Through continual focused scientific exploration of the remaining challenges such as, the mechanism of deposition and stripping of Lithium, the adoption of this technology can become a reality soon. LIMs with high power and energy density, long life span are expected in coming years with more advanced Li anode for their applications in practice.

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## CONFLICT OF INTEREST

The author declares that there is no conflict of interest.

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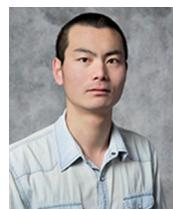
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