Recent Progress of Porous Materials in Lithium-Metal Batteries

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Lithium-metal batteries (LMBs) are regarded as one of the best choices for next-generation energy storage devices. However, the low Coulombic efficiency, lithium dendrite growth, and volume expansion of lithium-metal anodes are dragging LMBs out of successful commercialization. Herein, the application of various porous materials in LMBs is focused on. First, several representative works are summarized to highlight the recent key progress of porous materials in LMBs, categorized into current collectors, thin 3D “hosts,” protection layers, and separators. Then, the existing challenges are discussed and future research needs to present more thorough characterizations of porous materials are advocated for, such as their porosity, electric conductivity, specific surface area, and mass density, to elaborate on their positive influence on electrochemical performance. Finally, future strategies with porous materials to build long-cycle-life, high-energy-density lithium-metal full cells toward realistic performance targets are envisioned.

1. Introduction

Lithium-ion batteries (LIBs) are ubiquitous in our daily life, from portable electronic devices to electric vehicles or plug-in hybrid electric vehicles.[11–6] Although the energy density of LIBs has steadily increased during the past decades, the practical energy density is close to its theoretical value and has hardly been further improved.[7–10] To break through the bottleneck of energy density, one of the effective strategies that are used is the lithium (Li)-metal anode, which delivers an ultrahigh theoretical specific capacity of 3860 mAh g⁻¹ and an extremely low operation potential of −3.040 V versus the standard hydrogen electrode. Replacing the graphite anode with Li metal coupling with intercalation cathodes would bring about a 35% increase of specific capacity and an ≈50% increase in energy density at the cell level.[11–18] Furthermore, the development of a Li-metal anode would facilitate other next-generation high-energy batteries, including Li–sulfur batteries and rechargeable Li–air batteries.[19–23]

Unfortunately, rechargeable Li-metal batteries (LMBs) have not been commercialized yet because the Li-metal anode still encounters great challenges.[26–29] High electrochemical performance of LMBs requires high-Coulombic-efficiency (CE), dendrite-free, and low-volume-expansion Li-metal anodes. To meet these critical requirements, tremendous approaches have been pursued in the past several years, mainly including, but not limited to, adjusting the architecture of current collectors,[30–38] optimizing the composition of electrolytes,[39–46] establishing an artificial solid electrolyte interface (SEI),[47–50] modifying the spectators,[51,52] and using solid-state or polymeric electrolytes.[53–55] The introduction of different strategies effectively mitigated the Li dendrite growth and significantly improved the CE, making the electrochemical performance of current LMBs obtain enormous progress.

Among all these different strategies, porous materials as Li-metal “hosts” have been widely applied to solve the problems of the Li-metal anode.[56–59] According to the International Union of Pure and Applied Chemistry (IUPAC) definition, the porous materials have been divided into three categories of microporous (<2 nm), mesoporous (2–50 nm), and macroporous (>50 nm) materials based on their pore size.[60] Due to the unique properties in terms of adjustable surface areas and abundant porosity, porous materials have been widely applied in different fields, such as rechargeable batteries,[61] catalysis[62] and biological[63] and environmental[64] fields. Porous materials also have attracted wide attention in LMBs in recent years. The positive influences of porous materials in LMBs are summarized as follows (Figure 1).

1. Porous materials with a large specific surface area can successfully decrease the local current density, which could inhibit Li dendrite growth. 2. Porous materials with abundant functional groups can provide the active site for Li nucleation and growth and induce homogeneous Li stripping/plating behavior. 3. A high pore volume can provide enough space for the accommodation of Li metal, emerging in a homogeneous surface and a stabilization electrode. 4. Porous materials usually show continuous and interconnecting architecture, which could diminish the polarization overpotential and prolong the cycle lifespan because of the high electronic conductivity. 5. Porous materials used as current collectors or 3D host could

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According to Chazalviel et al., the ionic concentration goes to zero at the negative electrode at a time called “Sand’s time” (τ), which is proportional to \( J^{-2} \) (current density), whereby a high value of \( τ \) means that a longer time is needed for Li deposition, which may reflect a less serious instability occurring at the electrode/electrolyte interface and creates a less dendritic, mossy, fibrous morphology of Li metal during the deposition process. The influence factors of \( τ \) are described in Equation (1)

\[
τ = \pi D \left( \frac{εC_0}{2J_t} \right)^2
\]  

where \( D \) represents the ambipolar diffusion coefficient, \( ε \) is the electronic charge, \( C_0 \) is the lithium-ion concentration in a liquid electrolyte, and \( J_t \) is the anionic transference number. According to the equation, the \( τ \) is proportional to \( J^{-2} \), which indicates that the high current density greatly accelerates the Li dendrite growth.

Porous current collectors with a high surface area could significantly reduce the local current density, thus effectively mitigating the Li dendrite growth. In addition, the porous structure with high pore volume can supply enough space to minimize the “swelling and shrinking” of Li metal during cycling. Copper (Cu) foil is the common negative current collector in LIBs and it also has been intensively investigated in LMBs. Guo and co-workers reported a porous Cu as the current collector to decrease the local current density and implemented to accommodate the Li metal during the plating processes.\(^\text{[71]}\) A schematic of the procedure to prepare a porous Cu from a planar Cu foil is shown in Figure 2a, which is divided into two steps, first using a chemical etching process to get the Cu(OH)\(_2\) and then a dehydration and reduction process to obtain porous Cu. Compared to the planar Cu current collector, the simulation of the distribution of electrons (Figure 2b) demonstrated that the porous structure provided numerous protuberant tips and reduced the local current density. Owing to the porous structure, the scanning electron microscope (SEM) and atomic force microscope (AFM) images shown in Figure 2c show the homogeneous morphology of the deposited Li. As a result, the Li metal/porous Cu cell can run up to 600 h with an average CE of \( \approx 98.5\% \). Later, similar research was published about establishing a porous Cu current collector in LMBs.\(^\text{[72–88]}\)

The Li nucleation and growth behaviors are not only dependent on the porous structure, but also connected to the surface properties of the current collectors. In principle, the Cu is regarded as a substrate with high surface energy that performs the “lithiophobic” property. It behaves as an incompatibility of Li, bringing about inhomogeneous Li nucleation and hardly forming a stable SEI. Zhao and co-workers coated a thin nitrogen-doped graphene layer on the surface of porous Cu via the chemical vapor deposition method (Figure 3a) to change the surface property.\(^\text{[89]}\) An optical photograph and SEM images are shown in Figure 3b–e, which indicate that the average pore size is \( \approx 2 \) \( \mu \)m. The transmission electron microscope (TEM) images (Figure 3f–g) prove that few-layer graphene is wrapped on the surface of the porous Cu scaffold. As a result, the carbon-coated porous Cu in Li||Cu half-cells exhibit a high deposition capacity of 4 mAh cm\(^{-2}\) with an average CE of 98%, as well as an ultralow overpotential of 19 mV.

2. Porous Current Collectors

Lithium ions obtain electrons on current collectors or electronic conductor substrates and then are reduced to Li metal during the plating process. Conversely, lithium atoms lose the electrons and are oxidized into lithium ions, which dissolve in the electrolyte during the stripping process. During the repeat plating and stripping processes, dendrite growth and low CE are common phenomena and depend on many factors.\(^\text{[65–69]}\) Based on previous literature, some models have been put up to simulate and predict the behavior of Li dendrite growth. The “Sand’s time” (\( τ \)) model proposed by Chazalviel et al. is regarded as one of the most acceptable ones for simulating and predicting Li deposition.\(^\text{[70]}\) According to Chazalviel’s model, the ionic concentration goes dramatically heighten the gravimetric energy density for its low tap density.

In this review, we first summarize the state of the art regarding porous materials in LMBs, including the four aspects of current collectors, thin 3D hosts, protection layers, and separators. We introduce some representative works to highlight the progress of porous materials in LMBs. We find that impressive results have been achieved; nonetheless, they are still far from practical applications. Then we suggest future research needs to present a more thorough characterization of porous materials, such as their porosity, electric conductivity, specific surface area, mass density, and functional groups. We also discuss the different relevant parameters, including electrolytes, current density, Li metal thickness, and testing, that affect the electrochemical performance. Ultimately, we provide pivotal factors for porous materials at full-cell level, such as mass loading, specific capacity, electrolyte amount, and Li metal amount, to satisfy the potential of reaching Li-metal full-cell configurations toward realistic performance targets.

![Figure 1. Applications of porous materials in LMBs and their advantages.](image-url)
Except for the aforementioned methods, other works with similar strategies for improving the binding affinity or wettability of Li and current collectors have been reported. But the modification of the surface of copper current collectors with functional groups is usually difficult. In addition, the high density of Cu lessens the energy density at the pouch-cell level. Other current collectors have been considered as alternatives to Cu current collectors. In particular, Huo and co-workers reported lithiated NiCo2O4 nanorods anchored on 3D Ni foam as the current collector. Not only could the pore architecture with a large surface area dramatically decrease the local current density, but also the in situ formed Li2O composition is a “lithiophilic” product and ionic conductive, which provides Li nucleation active sites and reduces the overpotential during the plating/stripping process. Consequently, the lithiated NiCo2O4 nanorods anchored on porous nickel foam/Li cell exhibit an overpotential of 16 mV with a high CE of 98.7% and long cycle life. Liu and co-workers utilized lithiophilic ZnO coated on porous Ni foam to guide the homogenous plating/stripping of Li metal. In this case, the Zn metal–organic framework (MOF) in situ grew on the surface of the Ni foam and could be in situ transformed into a ZnO layer. During the initial discharging process, the ZnO could be transformed into Li2O and LiZn alloy, which improved the Li wettability between the electrode and electrolyte interface. In a half-cell, the ZnO-coated Ni foam performed with a CE of 98.5% and for more than 150 cycles.

The aforementioned pore current collectors, e.g., Cu and nickel (Ni), belonging to metallic substrates with high tensile strength and electronic conductivity, are intensively realized, but the high density of metals decreases the gravimetric energy density of the full cells. Carbon materials with the advantages of low density and high electronic conductivity were thought of as ideal alternatives to the metallic current collectors. Moreover, carbon is well known for its amenability to microscopic heteroatom doping and macroscopic material hybridization. This structural and morphological designability collectively renders carbon...
materials as a versatile platform to regulate Li plating. Guo and co-workers exploited graphitized carbon fibers to build LMBs.\cite{97}

The discharge curves and illustration of the lithium-ion intercalation and deposition process are shown in Figure 4a. The electrochemical processes can be observed in the SEM images (Figure 4b–g). They found that the graphitized carbon fiber electrode provides not only large intercalation and deposition capacity but also porous frameworks, which decrease the local current density and accommodate the large volume expansion. The large pore volume of graphitized carbon fibers delivers a specific areal capacity up to 8 mAh cm$^{-2}$, as well as high cycle stability. Following, there was a lot of research focusing on using different structures, graphitization degrees, morphologies, and functional groups of porous carbons as Li-metal hosts.\cite{98–119}

The melt infusion method with advantages in terms of spatial control and a smooth surface to prepare Li/carbon composite electrodes was regarded as another potential strategy, which was first put forward by Cui and co-workers in 2016.\cite{120}

Inspired by water that could be absorbed into a hydrophilic porous structure, they designed a silicon-coated carbon matrix composite as the current collector. The silicon as a lithiophilic material makes melting Li flow into the fiber layer region and occupy the empty spaces among every single fiber. Silicon-coated carbon fiber shows excellent wettability as molten Li quickly flows into the framework structure. A Li/carbon composite electrode prepared with Li metal encapsulated in a porous carbon scaffold can deliver the gravimetric specific capacity of 2000 mAh g$^{-1}$ and volumetric specific capacity of 1900 mAh cm$^{-3}$. Thereafter, much effort has been invested in surface functionalization of carbons to facilitate wetting and binding with Li. The experiments include doping heteroatoms or groups (nitrogen, phosphorus, sulfur, –NH$_2$, –COOH, –OH), loading with different metallic nanoparticles (silver, zinc, Cu, gold (Au)), have been widely investigated to improve the wetting between carbon substrates and Li metal.\cite{121–131}

The Li/carbon composite electrode manufactured by the melt infusion process not only performs with both high gravimetric specific capacity and volumetric specific capacity but also presents a simply controllable Li and carbon ratio, as well as mass production.

### 3. Porous Materials as Li Hosts

In this section, we selected some representative works about porous materials as Li-metal “host” to solve the problems of the Li-metal anode. Different from porous current collectors, the porous materials coated on the surface of planar metallic...
collectors via a chemical process or the doctor blading method are regarded as Li “hosts” to protect the Li-metal anode. The porous host is dominated by carbon-based materials because of its chemical stability when in contact with Li metal. As we mentioned before, the electronic conductivity and surface properties of carbons can be easily adjusted. The chemical process or doctor blading method ensures the porous carbon layer moves up and down during the Li plating/stripping process because the porous carbon layer is weakly bonded with a metallic collector, which provides enough space to accommodate the Li metal and stabilize the SEI. As a result, Li dendrite growth can be inhibited. A stable and conformal SEI is formed to isolate the Li metal and electrolyte solvents, avoiding deleterious side reactions.\textsuperscript{[132–140]}

In 2014, Zheng et al. designed a flexible, crosslinking, porous, hollow carbon sphere to induce homogenous Li deposition.\textsuperscript{[141]} The hollow carbon nanospheres were coated on the Cu substrate by the chemical process. The top-view and cross-sectional SEM images of the electrode shown in Figure 5b indicate that the hemispherical carbon nanospheres are interconnected to form a thin film, which loosely adheres to the surface of the Cu current collector. The schematic of Li deposition on Cu and hollow carbon-coated Cu is shown in Figure 5a. For the low electronic conductivity of the porous amorphous carbon, the Li would preferentially nucleate and grow between the hollow carbon nanosphere layer and Cu substrate, which is confirmed by the cross-sectional SEM images (Figure 5c). In addition, the porous hollow spheres could accommodate volume expansion during the Li metal plating/stripping process and the SEI layer was kept stable. As a result, the CE of Li plating/stripping was as high as 99% for more than 150 cycles. Since then, several similar works have been reported on the modification of a thin, porous, hollow carbon layer to improve the electrochemical performance of the Li plating and stripping process, dominantly focusing on the following aspects: 1) introducing various metal nanoparticles into porous hollow carbons to induce Li nucleation and growth and decrease the nucleation barriers and 2) decorating the surface of porous carbons with heteroatoms or groups to change surface properties, which could successfully govern the Li nucleation and growth process. Those strategies exhibit enhanced electrochemical performance in LMBs in contrast to undecorated porous carbons.

Yan et al. systemically investigated the nucleation pattern of Li metal on various metal substrates. They surprisingly found that the metals exhibit a definite solubility in Li metal with no nucleation barriers. Au exhibits the lowest overpotential among different metals (Figure 6a). Based on their theoretical analysis, they designed hollow carbon spheres with Au nanoparticles inside, which were used in LMBs. Through in situ TEM analysis (Figure 6b), they found that the Li metal preferentially nucleates and grows inside the hollow carbon spheres.\textsuperscript{[142]} The CE and cycle life were improved compared to pure hollow carbon spheres. The introduction of Au nanoparticles or other metallic nanoparticles could successfully regulate the Li nucleation and growth but sacrificed the energy density and dramatically increased the costs simultaneously. Wang and co-workers designed hollow porous carbon spheres with different surface properties of the outer and inner carbon shell for the Li deposition process (Figure 6c).\textsuperscript{[143]} The porous carbon shell could facilitate the easy migration of Li ions through the outer space. The nitrogen-doped dense layer in the inner surface ensured
the Li nucleated and grew preferentially inside the hollow carbon spheres, as demonstrated by in situ TEM images (Figure 6d). The obtained electrochemical performance was similar to the introduction of metallic nanoparticles inside hollow carbon spheres, but the energy density can be greatly improved without the unnecessary introduction of metallic nanoparticles.

4. Porous Protection Layer

A Li metal anode with high active property can react with the electrolyte solvents to form an SEI. The high surface areas of deposited Li are more reactive, which leads to continuous decomposition and depletion of electrolytes and the formation of “dead Li” that completely loses electronic contact with the anode.[28] In this section, we focus on the introduction of a porous protection layer in LMBs. Different from the mechanism of the aforementioned 3D Li host, the protection layer is like an artificial SEI to prevent Li metal from contacting the liquid electrolyte, which would reduce the deleterious side reaction of Li metal and electrolyte solvents.[144–160] Universally, the protection layer should meet the requirements of high Li-ion diffusion conductivity with electronic insulation property, suitable porosity, high mechanical and chemical stability, and compatibility with the electrolytes.
majorly including inorganic films, polymeric films, and organic and inorganic hybrid films.

Zhu and co-workers prepared a poly(dimethylsiloxane) (PDMS) organic thin film as a stable interfacial layer to protect the Li metal anode.\[161\] Figure 7a shows schematic diagrams of Li deposition on bare Cu and PDMS thin film decorated Cu. The advantages of a PDMS film with high chemical stability not only can prevent side reactions from occurring, but the flexibility can also accommodate the volumetric expansion during Li swelling and shrinking. Figure 7b,c shows cross-sectional SEM images of the PDMS film and top view of the PDMS film after hydrofluoric acid treatment. During the charging and discharging process, the Li metal would deposit under the PDMS organic thin film, which is confirmed by a cross-sectional view of the

Figure 6. a) Schematic of Li deposition in porous hollow carbon spheres with Au nanoparticles inside. b) In situ TEM images of Li deposition process inside carbon shells during the Li-metal plating process. Reproduced with permission.\[142\] Copyright 2016, Nature Publishing Group. c) Schematic of Li deposition in porous hollow carbon spheres with a N-doped dense layer existing in the inner surface. d) In situ TEM images of Li deposition process. Reproduced with permission.\[143\] Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA.
SEM image (Figure 7d). In addition, the surface electrode was kept homogenous after Li deposition (Figure 7e). Consequently, the Li-metal electrode with PDMS thin film exhibited an impressive high CE (up to 94.5%), long cycle life (over 200 cycles), and was dendrite free. Furthermore, the important role of the pore characteristics of the PDMS film should be emphasized because the PDMS film is either an electronic insulator or an ionic insulator. Chemical etching process by hydrofluoric acid was used to create a porous structure. The pore size could be easily controlled by etching time. After optimizing the process, 40–100 nm pore sizes were created, which showed the best electrochemical performance.

An organic thin film with high elastic deformation can keep completeness during the repeated Li plating/stripping process, but the low shear modulus cannot effectively prevent Li dendrite from growing and the film is easily penetrated by Li dendrite, which shortens the lifespan of LMBs. Noked and co-workers developed an inorganic Al₂O₃ thin layer (about 14 nm) coated on the Li metal surface through atomic layer deposition to protect the Li metal anode. The results showed that a 14 nm thick Al₂O₃ layer can prevent Li metal from reacting with electrolyte solvents. Furthermore, Li dendrite growth can be inhibited due to the high shear modulus of the Al₂O₃ layer. Unfortunately, the elastic modulus of the Al₂O₃ layer is too low to suppress volume changes during operation, which restricts the cycle performance of LMBs. An ideal protection layer should have a high elastic modulus and shear modulus concurrently. Liu et al. proposed a rational design of a protection layer composed of inorganic Cu₃N nanoparticles and organic polymer styrene–butadiene rubber (Figure 8a). The hybrid thin-film simultaneously possesses high mechanical strength, good flexibility, and high Li-ion conductivity. During the initial discharge
process in a Li||Cu half-cell, the Cu₃N is transformed into Li₃N, which disperses uniformly in the polymer matrix. Consequently, the protection layer using the hybrid film with a high elastic modulus and shear modulus not only mechanically suppresses Li dendrite formation and isolates the Li metal and liquid electrolyte (Figure 8b), but also maintains the high stability of the integrity of the SEI during repeated cycles. This is confirmed by top-view SEM images and the corresponding digital photographs of the deposited Li (Figure 8c–f). Accordingly, the CE of the Li-metal anode is ≈98.5% for more than 300 cycles. Another point that should be emphasized is that the in situ formation of Li₃N can facilitate the transport of Li ions across the electrode and electrolyte interface.

5. Porous Separators

The separator is an important part of LMBs. In general, polymeric matrices with high electrochemical stability, such as polyethylene (PE) and polypropylene (PP), are widely utilized in current rechargeable Li batteries, but the properties of low mechanical strength and wide pore size distribution restrict the electrochemical performance in LMBs. Especially the wide pore size distribution of conventional separators brings about steep local concentration gradients at the electrode and electrolyte interface, which accelerates inhomogeneous Li deposition and the formation of fibrous, mossy, and dendritic Li metal. Recently, intensive investigations on separator modification have been realized and applied in Li-metal protection.[51,163–176] An advanced separator with high mechanical strength can prevent Li dendrites from penetrating it. In addition, the narrow pore size distribution and functionalities of modified separators can regulate homogenous Li-ion flux near the electrode surface and thus promote uniform Li nucleation and growth. In this section, we summarize the applications of advanced porous separators, as well as the application of solid-state electrolytes in LMBs.

Figure 8. a) Schematic illustration of the fabrication of a CuₓN and SBR composite artificial SEI. b) Schematic illustration of the Li plating/striping behavior of bare Li and artificial-SEI-protected Li. c–f) Top-view SEM images and the corresponding digital photographs of Li deposition on artificial-SEI-protected Cu foil and bare Cu foil. Reproduced with permission.[47] Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA.
Archer and co-workers designed a nanoporous separator with both high mechanical moduli and facile ion transport, which consists of a highly ordered nanoporous $\gamma$-Al$_2$O$_3$ sheet between microporous poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) polymer layers, showing a sandwich-type composite architecture (Figure 9a). Top-view and cross-sectional view images of the PVDF-HFP/Al$_2$O$_3$ separator are shown in Figure 9b,c, which indicate the uniform distribution of nanometer-sized pores. The physical properties in terms of elastic modulus and ionic conductivity were affected by the pore size, which plays an important role in electrochemical performance. The elastic modulus is close to 0.4 GPa for the PVDF-HFP/Al$_2$O$_3$ separator, with an Al$_2$O$_3$ pore dimension of 200 nm (Figure 9d). The ionic conductivity of the PVDF-HFP/Al$_2$O$_3$ separators was calculated to $1 \times 10^{-1}$ S cm$^{-1}$ with 100 and 200 nm pore sizes (Figure 9e). After optimization, the separators based on Al$_2$O$_3$ with 100 nm nanopores used in LMBs exhibited the best performance in terms of low internal resistance, high CE, and long cycle life.

In principle, the nonuniform deposition of Li metal depended on many factors, such as ionic conductivity, charge-transfer resistance, mechanical stress, and electrolyte component. One of the most important factors is the local concentration of Li ions on the anode surface. As we mentioned before, conventional polymer separators with a wide pore size distribution would accelerate the heterogeneity of the surface Li-ion concentration, resulting in the heterogeneous nucleation and deposition of Li metal. The other strategy was focused on decorating conventional polymeric separators to address these issues of the Li-metal anode. Zhang and co-workers proposed a concept of ion redistributors to regulate the migration of lithium ions near the anode side surface. A ceramic solid-state electrolyte (Al-doped Li$_{6.75}$La$_{0.25}$Zr$_{1.75}$Ta$_{0.25}$O$_{12}$ (LLZTO)) as an ion redistributor coated on PP separators was used in LMBs to increase the homogeneity.
of lithium-ion distribution for dendrite-free Li deposition (Figure 10a). Figure 10b shows SEM images of Li deposition using a routine PP separator and a decorated PP separator. The morphology of Li metal exhibits a dense, smooth surface under the decorated PP separator, whereas quantities of sharp Li dendrites were observed using the routine PP separator. The results validated that a decorated separator can effectively suppress Li dendrite formation. As a result, the CE of Li metal anodes in a Li||Cu half-cell was ≈98%, maintained over 450 cycles. Porous separators with different compositions, pore sizes, and different functional groups have significantly enhanced the electrochemical performance of Li metal anodes, but the foundation of the mechanism and the achievement of progress of these works are similar to those of LMBs.[180–186]

Recently, all-solid-state LMBs have been attracting wide attention for next-generation energy storage devices due to safety and high-energy-density characteristics.[187–191] Porous materials with rich pore structures have also been widely used in solid-state LMBs. Currently, the applications of porous materials could be divided into two aspects. One of these is solid-state electrolytes instead of liquid electrolytes, such as solid polymer electrolytes, ceramic/polymer hybrid electrolytes, and MOF-based single-ion-conducting solid-state electrolytes to regulate the migration of lithium ions near the anode side surface. Very recently, Zhou and co-workers developed a unique electrolyte by regulating the MOF pore size, which demonstrated largely expanded electrochemical stability windows and high compatibility with Li-metal anodes. Although the MOF-based electrolyte does not belong to all-solid-state electrolytes, the properties of the pore of the MOF change the status of solvents and solutes of a liquid electrolyte, which provides critical lessons on the directions for a new electrolyte for Li anodes in LMBs.[192] The other application is used as a host for a Li-metal anode, which can make Li metal grow smoothly in the pores of the solid-state electrolyte host without forming Li dendrites. In addition, the electrolyte with a Li-ion migration channel successfully decreases the overpotential during cycles. Hu and co-workers used a 3D garnet-type ion-conductive framework (Li7La2.75Ca0.25Zr1.75Nb0.25O12) as Li-metal host to make Li grow smoothly in the pores of the garnet without forming Li dendrites.[193] The results show the impressive electrochemical performance in terms of high cycle stability and low overpotential compared to several publications using oxide-based solid-state electrolytes.[194–196] The previous literature has proved that 3D porous solid-state electrolytes have been widely used to solve the problems of Li-metal anodes, but several challenges, such as the porosity, thickness, and stability of the Li and electrolyte interface, need breakthrough in the future.

Figure 10. a) Schematic illustration of the electrochemical deposition behaviors of Li-metal anodes using PP separator and PP with a LLZTO layer. b,c) SEM images of Li-metal deposits through routine PP separator and decorated separator. Reproduced with permission.[179] Copyright 2018, American Association for the Advancement of Science.
6. Conclusion

The Li-metal anode is important for the development of high-energy-density rechargeable lithium batteries. In this review, we have summarized the impressive results of porous materials that are thought of as a significant direction to solve the critical problems of the Li-metal anode. The representative works demonstrate that porous materials can effectively improve the electrochemical performance of LMBs in terms of mitigating Li dendrite growth, inhibiting volume expansion, increasing CE, and extending cycle life. Unfortunately, porous materials are still far from practical application in LMBs because of the existing challenges that need to be overcome.

The first challenge is that porous materials usually perform at a low tap density with high surface area, delivering low volumetric density in cells. As shown in Table 1, the thickness of porous current collectors is in the range 44 μm to 1 mm, much higher than the thickness of conventional graphite anode electrodes. Research is expected to be continued in the pursuit of high areal capacity (>3 mAh cm⁻²). Most researchers have favored evaluating performance through areal capacity, but practically the volumetric capacity of the fabricated electrodes is dramatically decreased, which is usually neglected by researchers. Second, when using a porous material as Li host or for the protection layer, a porous material with high surface area and abundant functional groups would accelerate side reactions of Li metal and electrolyte solvents, which are detrimental to the cycle life. But the flooded electrolytes used during cell assembling would usually hide the deleterious side reaction. Third, the massive production of porous materials and capital costs should also be taken more into consideration. Overall, utilizing porous materials in LMBs could improve the gravimetric energy density for the low tap density, ultrahigh specific capacity, and low operation potential, but that does not mean high volumetric energy density.

In our opinion, the mass production and low-cost of carbon hosts should be developed in the future. It is also imperative to carefully design the micro- or nanostructures of carbon hosts and optimize the architecture of electrodes to balance the gravimetric density and volumetric density. In addition, chemical modification with nitrogen or oxygen groups, doping with heteroatoms, and coating or loading of metallic nanoparticles could facilitate wetting and binding with Li metal, which can heighten the electrochemical performance of rechargeable LMBs. Furthermore, dense Li deposition in porous materials Li hosts would be quite significant for decreasing the contact of the Li metal/electrolyte and inhibiting the "swelling/shrinking" of Li metal during cycles. Recently, several research results have confirmed that dense Li deposition can be successfully achieved through controlling the uniaxial stack pressure, which might be a potential strategy to obtain dense Li deposition and is expected to be applied in the future.⁴¹,¹⁹⁷,¹⁹⁸

Another point should be emphasized that the electrochemical performance of a Li-metal anode is determined by many factors, including, but not limited to, the electrolytes, current density, deposition capacity, and testing conditions of pressure and temperature, and instruments. We summarized the electrochemical performance of LMBs with different porous materials (Table 1), which indicated the Li-metal-anode electrodes with a long cycle life, but an excess amount of Li metal and flooded electrolytes are generally used, leading to deceptively "good" cycling results. Furthermore, the electrochemical performance in a lot of the literature lacked comparability in terms of gravimetric or volumetric capacity, CE, and cycle life. In addition, the performance is usually overestimated based on the areal capacity when being critically evaluated at a realistic full-cell level. The volumetric capacities and volumetric energy density of full cells have been rarely discussed in most of the previous literature, but they are dramatically important parameters, especially for applications of porous materials in LMBs because a porous material with a high specific surface area would diminish the volumetric energy density of cells. We strongly advocate the future research needs to present more detailed relevant parameters to evaluate the electrochemical performance more comprehensively and fairly, such as providing the gravimetric and volumetric capacity when using

Table 1. Comparison of electrochemical performance for different porous materials in terms of thickness, areal capacity, CE, cycle life, and electrolytes.

| Porous materials⁴¹ | Thickness | Areal capacity [mAh cm⁻²] | CE  | Cycle [hour] | Electrolyte | Ref. |
|-------------------|-----------|--------------------------|-----|--------------|-------------|-----|
| Porous Cu         | 44 μm     | 1                        | 98.5% | 600 h        | 1 M LiTFSI DOL/DME with 1 wt% LiNO₃ and 0.005 M Li₂S₂  | [71] |
| N-doped graphene modified 3D porous Cu | 70 μm | 4 | 98% | 150 cycles | 1 M LiTFSI DOL/DME (1:1) with 1 wt% LiNO₃ | [89] |
| Graphitized carbon fibers | 1 mm | 8 | 98% | 300 h | 1 M LiTFSI DOL/DME (1:1) with 1% LiNO₃ | [97] |
| Hollow carbon nanospheres | 500 nm | 1 | ≈99% | 150 cycles | 1 M LiTFSI in DOL/DME with 1 wt% LiNO₃ and 100 mm Li₂S₂ | [141] |
| Ag hollow carbon nanospheres | 10 μm | 1 | 98% | 300 cycles | 1 M LiPF₆ in EC/DEC with 1% VC and 10% FEC | [142] |
| N-doped hollow porous carbon spheres | 18 μm | 1 | 98.5% | 270 cycles | 1 M LiTFSI DOL/DME (v/v 1:1) with 2 wt% LiNO₃ | [143] |
| Poly(dimethylsiloxane) thin film | 0.5 μm | 1 | 93.2% | 100 cycles | 1 M LiPF₆ in EC/DEC (1:1 v/v) with 2 wt% VC | [161] |
| Cu₃N + SBR composite thin film | 1 μm | 1 | 97.4% | 150 cycles | 1 M LiPF₆ in EC/DEC (1:1 v/v) with 10 wt% FEC | [47] |
| PVDF-HFP/Al₂O₃ separator | 0.8 mm | N/A | ≈100% | 1000 cycles | 1 M LiTFSI in PC | [177] |
| Al-doped LLZTO coated PP separators | 30 μm | 1 | 98% | 450 cycles | 1 M LiTFSI in DOL/DME (v/v = 1:1) with 5 wt% LiNO₃ | [179] |
| 3D ion-conductive framework | 47 μm | N/A | 300 h | Li₅La₂,₇₅Ca₁₀Zr₁₀Ta₂₅O₆₂ | [193] |

⁴¹N/A: not available; LiTFSI: lithium bis(trifluoromethanesulfonyl)imide; PC: propylene carbonate; EC/DEC: ethylene carbonate and diethyl carbonate; DOL/DME: 1,3-dioxolane and 1,2-dimethoxyethane; VC: vinyl carbonate; FEC: fluoroethylene carbonate; LLZTO: Li₆.75La₃Zr₁.75Ta₀.25O₁₂; PP: polypropylene; PVDF-HFP: poly(vinylidene fluoride-co-hexafluoropropylene); SBR: styrene-butadiene rubber.

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porous current collectors, use the protocol method to test the lithium CE, and control the composition and number of electrolytes. Finally, significant factors such as cathode mass loading, the porosity of electrodes, the amount of electrolyte, and the N/P ratio or E/C ratio (N/P represents negative/positive electrode area ratio and E/C represents electrolyte volume/capacity) and tabbing should be taken into account with porous materials to build long-cycle-life, high-energy-density Li-metal full cells toward realistic performance targets.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

current collectors, lithium-metal anodes, lithium-metal batteries, porous materials, protection layer

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[1] Z. P. Cano, D. Banham, S. Y. Ye, A. Hintennach, J. Lu, M. Fowler, Z. W. Chen, Nat. Energy 2018, 3, 279.
[2] R. Schmuch, R. Wagner, G. Horpel, T. Placke, M. Winter, Nat. Energy 2018, 3, 267.
[3] B. Dunn, H. Kamath, J. M. Tarascon, Science 2011, 334, 928.
[4] M. Armand, J. M. Tarascon, Nature 2008, 451, 652.
[5] J. B. Goodenough, K. S. Park, J. Am. Chem. Soc. 2013, 135, 1167.
[6] J. B. Goodenough, ACS Catal. 2017, 7, 1132.
[7] M. Li, J. Lu, Z. W. Chen, K. Amine, Adv. Mater. 2018, 30, 1800561.
[8] Y. Ding, Z. P. Cano, A. Yu, J. Lu, Z. Chen, Electrochem. Energy Rev. 2019, 2, 1.
[9] J. Lu, Z. Chen, F. Pan, Y. Cui, K. Amine, Electrochem. Energy Rev. 2018, 1, 35.
[10] H. Li, Z. Wang, L. Chen, X. Huang, Adv. Mater. 2009, 21, 4593.
[11] P. Albertus, S. Babinec, S. Litzelman, A. Newman, Nat. Energy 2018, 3, 16.
[12] J. Liu, Z. Bao, Y. Cui, E. J. Dufek, J. B. Goodenough, P. Khalifah, Q. Li, B. Y. Liaw, P. Liu, A. Manthiram, Y. S. Meng, V. R. Subramanian, M. F. Toney, V. V. Viswanathan, M. S. Whittingham, J. Xiao, W. Xu, J. Yang, X.-Q. Yang, J.-G. Zhang, Nat. Energy 2019, 4, 180.
[13] M. Winter, B. Barnett, K. Xu, Chem. 2018, 178, 11433.
[14] H. Wang, Y. Liu, Y. Li, Y. Cui, Electrochem. Energy Rev. 2019, 2, 509.
[15] Y. Zhang, T.-T. Zuo, J. Popovic, K. Lim, Y.-X. Yin, J. Maier, Y.-G. Guo, Mater. Today 2020, 33, 56.
[16] X. Zhang, Y. Yang, Z. Zhou, Chem. Soc. Rev. 2020, 49, 3040.
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