


REVIEW ARTICLE

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Three-dimensional ordered porous electrode materials for electrochemical energy storage

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Abstract

The past decade has witnessed substantial advances in the synthesis of various electrode materials with three-dimensional (3D) ordered macroporous or mesoporous structures (the so-called “inverse opals”) for applications in electrochemical energy storage devices. This review summarizes recent advancements in 3D ordered porous (3DOP) electrode materials and their unusual electrochemical properties endowed by their intrinsic and geometric structures. The 3DOP electrode materials discussed here mainly include carbon materials, transition metal oxides (such as TiO_2 , SnO_2 , Co_3O_4 , NiO , Fe_2O_3 , V_2O_5 , Cu_2O , MnO_2 , and GeO_2), transition metal dichalcogenides (such as MoS_2 and WS_2), elementary substances (such as Si, Ge, and Au), intercalation compounds (such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiCoO_2 , LiMn_2O_4 , LiFePO_4), and conductive polymers (polypyrrole and polyaniline). Representative applications of these materials in Li ion batteries, aqueous rechargeable lithium batteries, Li-S batteries, Li- O_2 batteries, and supercapacitors are presented. Particular focus is placed on how ordered porous structures influence the electrochemical performance of electrode materials. Additionally, we discuss research opportunities as well as the current challenges to facilitate further contributions to this emerging research frontier.

Introduction

The continued exploration of green and sustainable energy storage devices is critical for addressing the worldwide problems of limited availability of fossil fuels and environmental pollution. Among various energy storage technologies, electrochemical energy storage devices are the most promising and common devices. Currently, research on electrochemical energy storage is mainly focused on supercapacitors and rechargeable batteries^{1–5}. Supercapacitors have high power densities and long cycling lives explained by surface charge storage mechanisms, while rechargeable batteries deliver high

energy densities due to the Faradaic charge storage mechanism^{2,6–8}. In the past three decades, Li ion batteries have served as the primary power supply for various portable electronic devices. However, intercalation-type electrode materials for Li ion batteries have reached their performance limit. Thus significant attention has been focused on high-capacity conversion reaction-type cathodes, such as sulfur (Li-S batteries) and oxygen (Li- O_2 batteries)^{9–12}. In addition, low-cost and safe aqueous rechargeable batteries are promising candidates for large-scale electrical energy storage systems. For any electrochemical energy storage device, electrode materials as the major constituent are key factors in achieving high energy and power densities. Over the past two decades, to develop high-performance electrode materials, researchers have designed and integrated one-dimensional (1D) (nanowires, nanoribbons, nanotubes), two-dimensional (2D) (nanosheets, nanoplates, nanomembranes), and

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three-dimensional (3D) architectures into electrode materials. Although 1D and 2D electrode materials with high stabilities and efficient charge-transport paths have been demonstrated^{13,14}, they still suffer from severe aggregation, which prevents the easy diffusion of electrolytes and fast kinetics of electrochemical reactions. To this end, engineering 3D structural configurations with interconnected porous channels is one of the most effective strategies to resolve the abovementioned problems. Moreover, in the practical fabrication of electrodes for use in commercial batteries and supercapacitors, the electrode materials will be squeezed, thus forming disordered 3D structures. These 3D structures in commercial bulk electrodes will be a benefit to electrolyte transportation and ion diffusion. For 3D materials, squeeze processing during industrial production will result in dual-3D structures in electrodes and favor superior electrolyte transportation and ion diffusion.

Among various 3D architectures, the 3D ordered porous (3DOP) structure is highly desirable for constructing high-performance electrode materials in electrochemical energy storage systems^{1,15–23}. Generally, 3DOP materials are prepared through colloidal crystal templating strategies^{20–23}. First, uniform monodispersed microspheres, such as polystyrene (PS), silica or poly(methyl methacrylate) spheres, are assembled into 3D ordered arrays via dense packing. Second, various precursors can infiltrate into the 3D ordered scaffold. Finally, solidification of the precursor and removal of the colloidal spheres are performed to obtain periodic 3D framework structures. To obtain the 3DOP nanocomposites, there are two typical methods. In the first method, in the second step, more desired active species can be directly introduced into the 3DOP templates by using the corresponding multicomponent solution as precursors. In the other method, the 3DOP material is utilized as a host structure for the further growth of active electrode materials by various growth mechanisms. Currently, it is well accepted that the spatial orientation/arrangement of 3DOP structures can not only shorten the diffusion path of ions within the thin walls of electrode materials but also improve the robust structural integrity of electrode materials during long-time cycles. Specifically, 3DOP electrode materials have better rate capabilities than nanocrystalline materials (in which the nanoparticles are loosely aggregated together) because the bicontinuous ordered 3D frameworks can ensure much higher metal ion flux across the electrode and serve as a pathway for efficient electron transport within the whole 3D scaffold. Furthermore, the free space within porous 3D electrodes can act as a buffer against volume variation of the entire electrode, thus reducing mechanical strain during the repeated charge–discharge processes.

To date, many reviews have summarized 3D porous materials and their applications in energy storage and conversion fields^{1,15,16,24–26}. For example, several early reviews from Rolison’s group focused on the design and fabrication of multifunctional 3D nanoarchitectures for microbatteries, supercapacitors, fuel cells, and photovoltaic cells^{27–29}. Recent progress in porous mixed metal oxides, including their synthesis, formation mechanism, and application in Li ion batteries, was discussed in 2015³⁰. In 2017, an overview of representative work on holey 2D nanomaterials—from general methodologies to their promising applications in various electrochemical energy storage devices—was provided¹⁵. However, with the rapid development of new materials and fabrication technologies, a systematic review regarding the progress of 3DOP electrode material for electrochemical energy storage systems, is still lacking. In this review, we summarize the recent progress of 3DOP electrode materials and their unusual electrochemical properties resulting from their intrinsic and geometric structures. Figure 1 summarizes representative 3DOP electrode materials and their applications in various electrochemical energy storage devices (metal ion batteries, aqueous batteries, Li-S batteries, Li-O₂ batteries, and supercapacitors). Emphasis is placed on the special 3DOP configuration and its corresponding effects on the enhancement of electrochemical properties. Research opportunities, as well as challenges, are also discussed to facilitate further research and development in this promising field.

3DOP electrode materials for use in Li ion batteries

Anode materials

Titanium dioxide (TiO_2) has been well studied as an anode for Li ion storage because it is chemically stable, abundant, inexpensive, and environmentally benign.

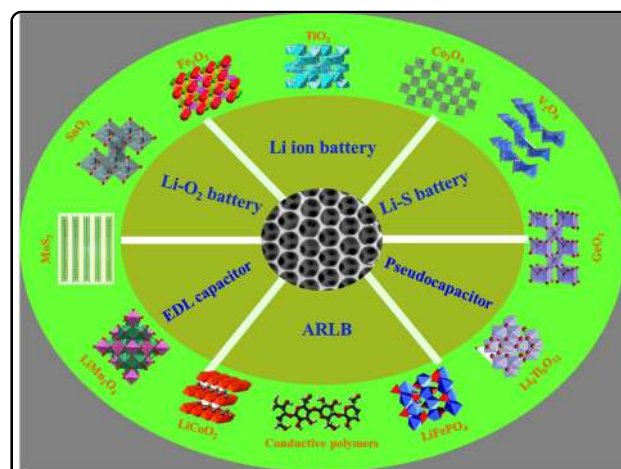


Fig. 1 An overview of three-dimensional ordered porous electrode materials for use in various electrochemical energy storage devices

Three types of TiO_2 have been well investigated, namely, $\text{TiO}_2(\text{B})$, anatase, and rutile. Among them, the rutile phase of TiO_2 is the most common natural form since it is the most thermodynamically stable phase under normal conditions. Li ion intercalation and deintercalation in TiO_2 involve much higher operating potentials (~ 1.5 V vs. Li^+/Li) than those in graphite (~ 0.2 V vs. Li^+/Li)^{31–33}. Although this operating potential cannot completely prevent the formation of a solid–electrolyte interphase (SEI) film, it eliminates the problem of lithium plating and dendrite formation. Early studies on 3DOP TiO_2 electrodes for Li ion batteries date back to 2007, when Professor Wu's group reported that as-synthesized TiO_2 with a 3DOP architecture exhibited a higher specific capacity and better cycling behavior than conventional TiO_2 ³⁴. Indeed, decreasing the particle size of TiO_2 to nanoscale dimensions can allow higher reversible capacity and faster charge–discharge rates due to the shortened pathlength for diffusion of Li ions. Specifically, the dense packing of nanoparticles due to aggregation reduces the overall surface area contact with the electrolyte (Fig. 2a). Thus deeper layers of active TiO_2 nanoparticles may not be completely accessible for lithiation. For the 3DOP TiO_2 electrode, the ordered porosity of the electrode ensures an even distribution of contact between the electrode and the electrolyte, as shown in Fig. 2b, which thus improves the mass transfer of electrolyte ions to the electrode surface and promotes complete lithiation³⁵. Moreover, thin pore walls in 3DOP materials enable short Li ion diffusion paths. Therefore, the 3DOP TiO_2 electrode shows a higher specific capacity and better rate capability than its nanoparticle counterpart.

Interestingly, another 3DOP rutile TiO_2 electrode presents an initial discharge capacity of up to 608 mAh g^{-1} , which is much higher than the theoretical capacity for TiO_2 (168 mAh g^{-1} for $\text{Li}_{0.5}\text{TiO}_2$ or 336 mAh g^{-1} for LiTiO_2)³⁶. Such high capacity mainly results from some formed defects that serve as additional charge-compensation sites. Moreover, an impressive cycling stability of up to 5000 cycles is achieved in this 3DOP rutile TiO_2 electrode in the absence of any binders or conductive additives. During the repeated insertion and removal of Li ions, the nanowalls in these 3DOP rutile TiO_2 electrodes are swollen but still maintain the 3DOP structure very well even after 1000 and 5000 cycles (Fig. 2c), demonstrating an extremely high level of structural integrity³⁶. Thus another advantage of the 3DOP electrode is that its periodic OP structure allows the interconnected walls to expand into the empty pores, preventing the walls from becoming pulverized.

Through a synergic dual template of the colloidal crystal and surfactant, the 3DOP TiO_2/C nanocomposite was prepared with a phenol–formaldehyde sol as an amorphous carbon source³⁷. Detailed synthetic conditions,

including the choice of chelating agents and temperatures, were investigated and optimized. Upon pyrolysis at 800°C using 2,4-pentadiene as a chelating agent, the obtained 3DOP TiO_2/C composites display the highest specific capacity. The TiO_2 content in the pyrolyzed TiO_2/C composite is approximately 70%³⁷. Upon decreasing the TiO_2 content and increasing the amorphous carbon content, a high capacity of 549 mAh g^{-1} is achieved in another 3DOP TiO_2/C nanocomposite with 55 wt% TiO_2 ³⁸. The ultrahigh specific capacity originates from the contribution of Li ion intercalation to the nongraphic carbon. Although 3DOP TiO_2 electrode materials deliver high capacity, even more than the theoretical value, the main contribution to capacity is within the potential range of 1.5–3.0 V (vs. Li^+/Li). Such high potentials allow the TiO_2 -based anode materials to appropriately couple only with cathode materials with high potentials.

Transition cobalt oxides are widely considered attractive anode materials for Li ion batteries because of their high theoretical capacities (890 mAh g^{-1} for Co_3O_4 and 716 mAh g^{-1} for CoO)^{39–41}. Currently, the practical application of cobalt oxides in Li ion batteries is seriously hindered by the poor capacity retention over long-time cycling due to relatively large volume changes. To alleviate this problem, 3DOP carbon inverse opals have been utilized to entrap CoO nanoparticles⁴². The 3DOP CoO/C electrode displays a high capacity of 674 mAh g^{-1} even after 1000 cycles, accounting for 94% of the theoretical capacity. The 3DOP carbon structure serves as not only the interpenetrating continuous conductive network but also a dimensional constraint to active nanoparticles.

In addition to the 3DOP carbon, the 3DOP Ni scaffold has been uniformly utilized for the deposition of Co_3O_4 nanosheets^{43,44}. The thickness of the Co_3O_4 nanosheets can be easily controlled by adjusting the hydrothermal growth conditions. The initial discharge and charge capacities of the 3DOP $\text{Co}_3\text{O}_4/\text{Ni}/\text{Au}$ electrode are 1478 and 1224 mAh g^{-1} , respectively, which are much higher than the theoretical capacity of Co_3O_4 ⁴⁴. The additional capacity results from the contribution of Li ion alloying reactions with Au⁴⁵. The reversible redox reaction between Au and Li ions presents several sharp redox peaks below 0.5 V (vs. Li^+/Li). No redox peaks from the bare 3DOP Ni electrode were detected, indicating the stability of the 3D Ni as a scaffold.

Among the various transition metal oxides, iron oxides are another extensively studied anode because they offer several benefits, including high theoretical capacities (926 mAh g^{-1} for Fe_3O_4 and 1007 mAh g^{-1} for Fe_2O_3), high tap density ($5.1\text{--}5.3 \text{ g cm}^{-3}$), abundant resources, and environmentally friendly characteristics. A recent study demonstrates that 3DOP $\alpha\text{-Fe}_2\text{O}_3$ with a pore size of $\sim 250 \text{ nm}$ exhibits initial discharge and charge capacities of 1883 and 1139 mAh g^{-1} , respectively⁴⁶, which are

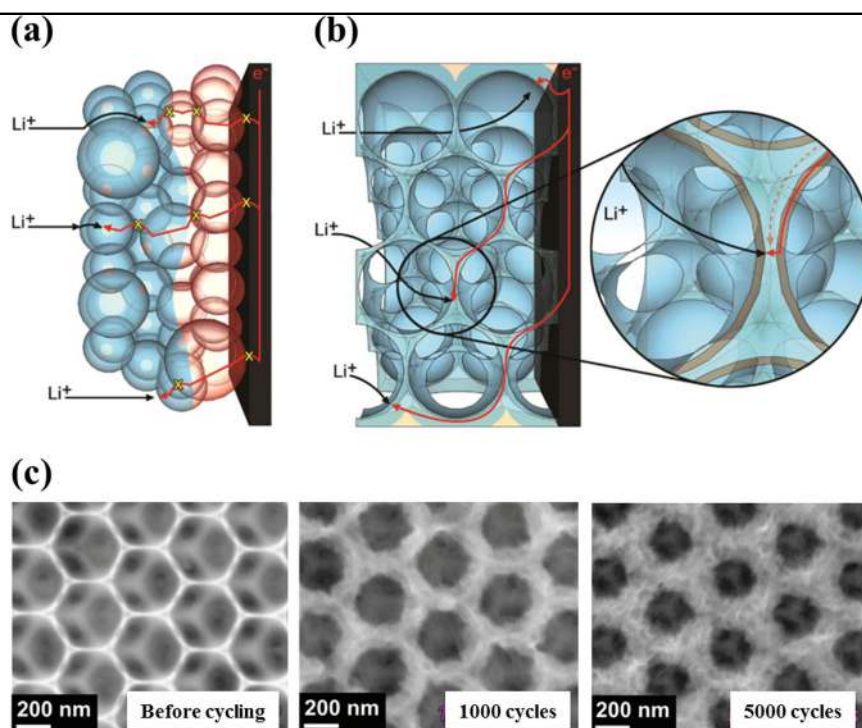


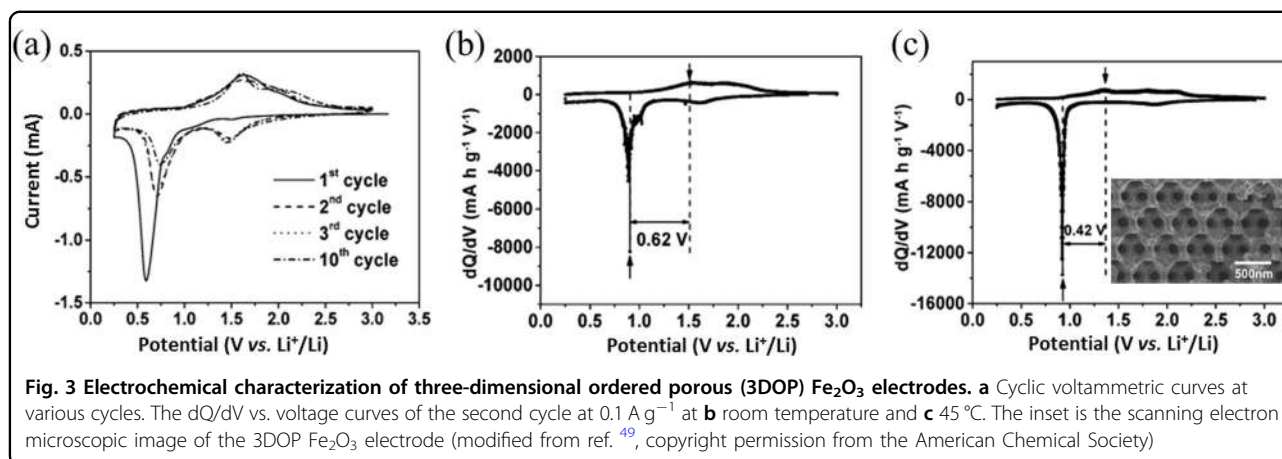
Fig. 2 The 3DOP structure in TiO_2 anode for fast ion and electron transport as well as the accommodation of volume change during cycling.

Schematic illustration of the lithiation pathways for **a** nanoparticle and **b** three-dimensional ordered porous (3DOP) electrodes. The active material (TiO_2) is blue, and potentially inaccessible lithiation sites are highlighted in brown (modified from ref. ³⁵, copyright permission from Elsevier). **c** Scanning electron microscopic images of the 3DOP TiO_2 electrode before and after cycles (modified from ref. ³⁶, copyright permission from Elsevier)

much higher than those of $\alpha\text{-Fe}_2\text{O}_3$ with a 1D nanorod structure or a 2D nanoflake structure^{47,48}. In another work, the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were deposited on 3DOP Ni by pulsed voltage electrodeposition at room temperature⁴⁹. To avoid formation of a thick Fe_2O_3 layer at the top of the electrode, the process of pulsed voltage electrodeposition must include a repeated sequence of “on” and “off” voltages. Notably, with an increase in the Fe_2O_3 loading, the sizes of pores in the 3DOP Ni would decrease, which may limit the accessibility of the electrolyte to all of the active materials. The optimized loading of $\gamma\text{-Fe}_2\text{O}_3$ on the 3DOP Ni current collector is 0.4 mg cm^{-2} . In the cyclic voltammetric (CV) curves, a large reduction peak at approximately 1.5 V (vs. Li^+/Li) is absent in the first cycle but appears at the beginning of the second cycle (Fig. 3a). This phenomenon may be caused by the “electrochemical grinding effect.” Smaller Fe_2O_3 particles are produced at the end of the first cycle. Then Li^+ ions can intercalate into the small Fe_2O_3 particles that were produced before complete conversion to Fe and Li_2O because of the short diffusion length and high surface area provided by the small domains. Thus this intercalation process leads to a large reduction peak at approximately 1.5 V (vs. Li^+/Li). At room temperature, the voltage hysteresis of the 3DOP $\gamma\text{-Fe}_2\text{O}_3/\text{Ni}$ electrode is only 0.62 V, as calculated from the separation between the conversion reaction redox

peaks (Fig. 3b), which is much smaller than those of other reported Fe_2O_3 anodes⁵⁰. When the temperature increases to 45 °C, the voltage hysteresis decreases, with a value of only 0.42 V (Fig. 3c), which suggests that the voltage hysteresis in the 3DOP $\gamma\text{-Fe}_2\text{O}_3/\text{Ni}$ electrode could result from a thermal activation process⁴⁹.

The addition of inactive 3DOP current collectors and the loading of low-activity materials on the 3DOP current collectors would lead to low gravimetric and volumetric capacities. In this regard, a scaffold-free 3DOP $\text{Fe}_3\text{O}_4/\text{C}$ composite without any current collectors or bonding additives has recently been demonstrated⁵¹. Toward commercial potential applications, the $\text{Fe}_3\text{O}_4/\text{C}$ anode with a thickness of 100 μm is achieved, presenting a specific capacity of 710 mAh g^{-1} based on the total mass of the whole electrode. The change in the overall dimensions of the electrode is almost unnoticeable because the volume expansion–contraction is buffered by the 3D nanocomposite matrix. In fact, the construction of 3DOP structures and the formation of nanocomposites are unable to completely solve the large intrinsic volume change and pulverization of Fe_2O_3 anodes. To avoid intrinsic pulverization of the Fe_2O_3 anode, an internally established magnetic field from the additional magnetic component (CoPt) was introduced into the 3DOP $\text{Fe}_2\text{O}_3/\text{TiO}_2$ electrode⁵². After being magnetized by an external



magnetic field as a result of the ferromagnetic nature of CoPt, the constant magnetic field inside of the anode can enable the active material to be tightly bonded to the framework of the electrode even after pulverization occurs.

Tin dioxide (SnO_2) is also a well-studied anode used in Li ion batteries, and its charge storage mechanism is based on an irreversible conversion reaction ($\text{SnO}_2/\text{Sn} + \text{Li}_2\text{O}$) combined with a reversible alloying reaction ($\text{Sn}/\text{Li}_{4.4}\text{Sn}$)^{53–55}. As early as 2004, the electrochemical study of SnO_2 anodes with an inverse opal structure was reported, in which the 3DOP geometry leads to reduced polarization in the alloying region of the CV curves⁵⁶. Upon initial formation of $\text{Li}_{4.4}\text{Sn}$ from Sn, there should be a theoretical volume expansion of 137%. However, after cycling four times at 0.1 C, the wall thickness of the 3DOP SnO_2 film is visibly swollen by 650%. This is because the continuous structural degradation of the electrode during cycling results in the separation of additional Li_xSn particles, resulting in a continuous expansion of the entire solid structure. Moreover, the expansion of the agglomerated Li_xSn alloy region gradually ruptures, resulting in an increase in the fraction of electronically isolated and swollen particles. When cycling at a high rate of 10 C, no morphological change was observed in this 3DOP SnO_2 film electrode. Another 3DOP SnO_2 electrode delivers a higher reversible specific capacity (653 mAh g^{-1}) than SnO_2 nanoparticles (327 mAh g^{-1})⁵⁷. The continuous void space of the 3DOP structure can be readily filled with the electrolyte solution, resulting in improved ionic and electronic conductivity of the whole electrode. Thus perhaps one can conclude that 3DOP structures for anodes that combine irreversible conversion reactions and reversible alloying reactions are more favorable for enhancing the rate capabilities instead of the cycling stabilities.

In addition to SnO_2 , a 3DOP Sn scaffold containing a hollow sphere of Sn coated with carbon was recently

demonstrated⁵⁸. The 3DOP Sn/C anode with an electrode thickness of $100 \mu\text{m}$ can retain a volumetric capacity $>650 \text{ mAh cm}^{-3}$ after 100 cycles. The 3DOP structure allows volume expansion and extraction of the active material without changing the overall electrode dimensions during cycling. Thus no obvious volume expansion of the 3DOP Sn/C composite occurred after the various lithiation states (the dotted yellow line in Fig. 4) when in contact with the $\text{Li}/\text{Li}_2\text{O}$ flake from the in situ transmission electron microscope (TEM) study. For the real-time lithiation of the 3DOP Sn/C nanocomposite, a nanoscale battery device was designed and composed of a Sn/C nanocomposite as the working electrode and a Li metal flake covered by a natural thin Li_2O solid electrolyte layer as a counter electrode. Notably, the abovementioned device that employs a solid Li_2O on the Li anode surface as the electrolyte is the most commonly used model of nanobattery for the real-time TEM test. However, such a solid-state set-up cannot accurately represent a standard battery environment using organic liquid electrolytes. In this regard, in situ liquid TEM experiments are highly desired by sealing the liquid electrolytes with two thin membrane windows⁵⁹. However, the thin membrane windows may drastically decrease the spatial resolution of the microscope. Therefore, there is still a long way to achieve in situ TEM electrochemistry of 3DOP electrode materials.

Comparative research on Si anodes has demonstrated the highest specific capacity among all anode materials, but its largest shortcoming is the large volume expansion (400%) during alloying/dealloying with Li ions, greatly restricting their practical application^{60–63}. To solve the pulverization problem, several Si anode-coated 3DOP Ni electrodes (Si/Ni) were fabricated by electrodeposition^{64–67}. Based on the electrochemical impedance spectroscopic measurements, the Li ion diffusion coefficient of the 3DOP Si/Ni electrode is larger than that of the Si-nanowire-based electrode because of the different configurations⁶⁵. In

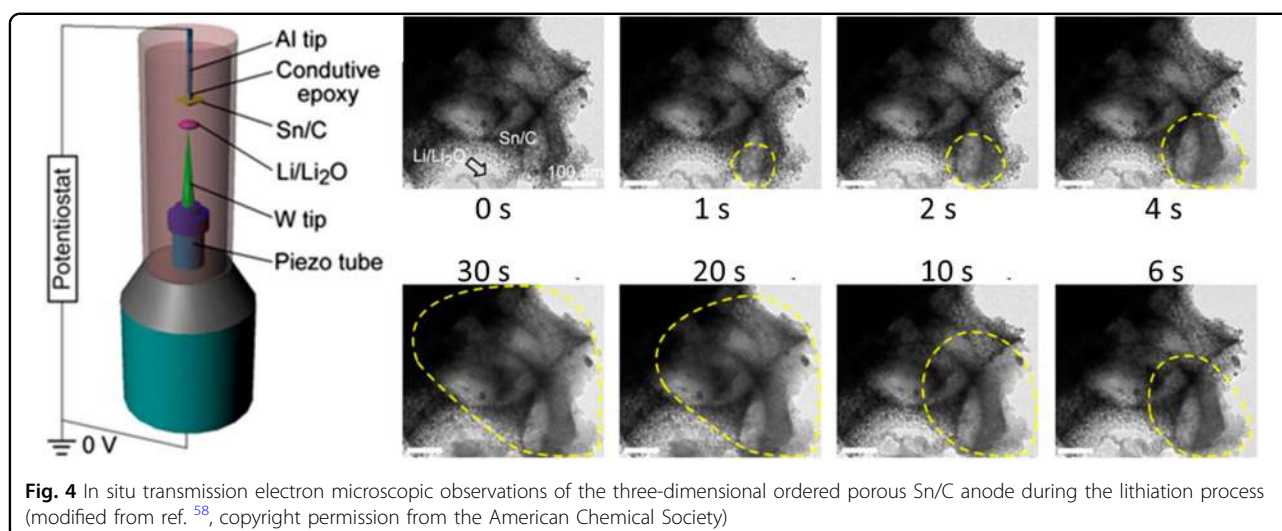
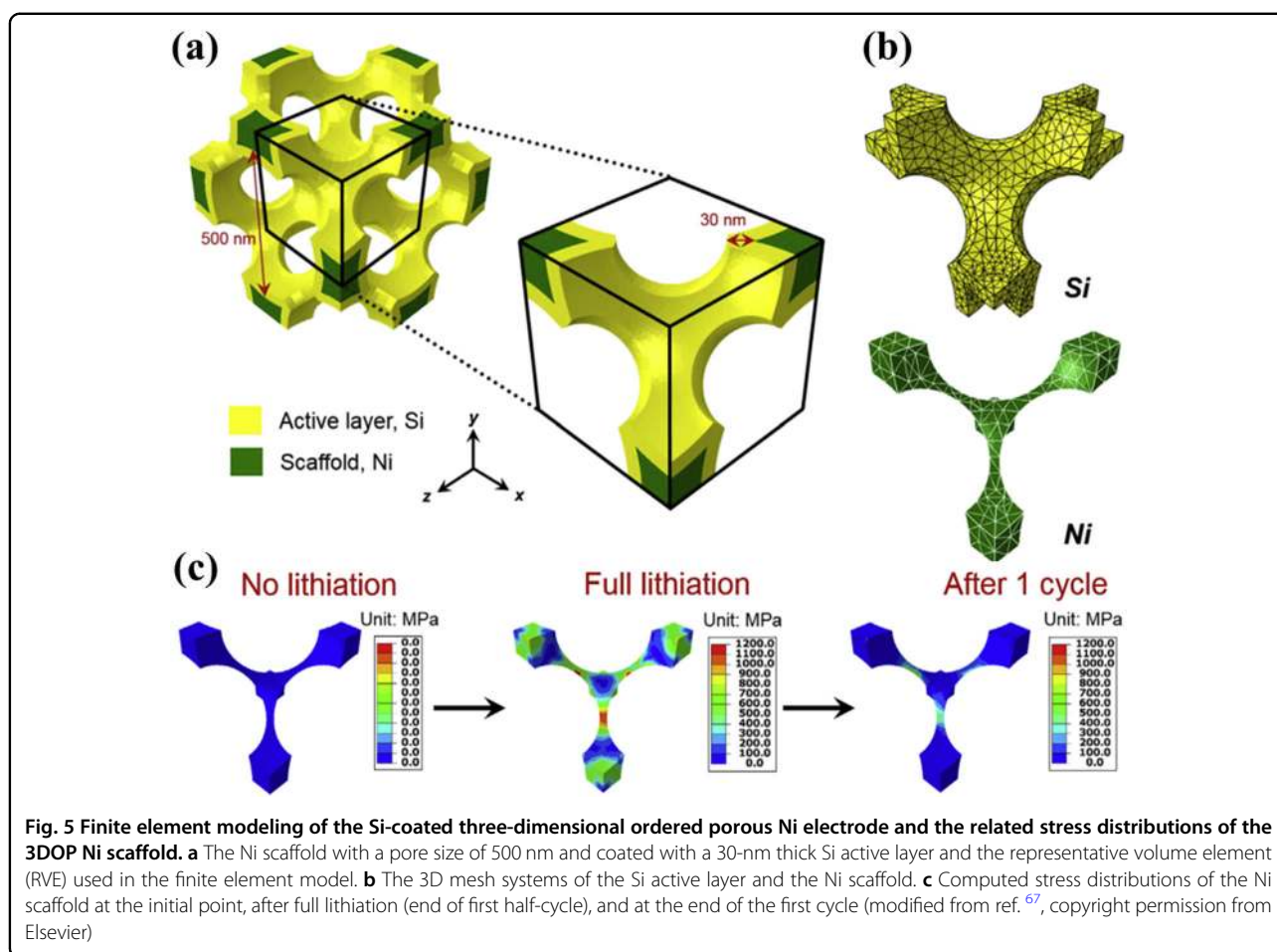


Fig. 4 In situ transmission electron microscopic observations of the three-dimensional ordered porous Sn/C anode during the lithiation process (modified from ref. ⁵⁸, copyright permission from the American Chemical Society)

addition, the Si anode has relatively low electronic conductivity. The Ni scaffold inside the structure can increase the electronic conductivity of the whole electrode⁶⁶. In the case of these 3DOP Si/Ni anodes, the capacity decrease is still obvious even though it was claimed that the 3DOP Ni inverse opal structure effectively accommodated volume changes of Si. Finite element (FE) analysis coupled with the experimental results was applied to investigate the Li ion diffusion-induced volume change and the corresponding mechanical damage of Si-coated Ni inverse opal structures⁶⁷. After comparing the numerical results for strains with prior in operando X-ray diffraction (XRD)-based strain experimental data⁶⁸, the FE approach verifies the feasibility of predicting the mechanical behavior of the 3D Si/Ni anode. Specifically, FE modeling is based on the 3D Ni scaffold with a pore size of 500 nm and coated with a 30-nm-thick Si active layer (Fig. 5a). Then this model is reduced to an one eighth subshell as the representative volume element of the Si-coated Ni inverse opal electrode. Finally, the Si and Ni structures are divided into 9063 and 696 tetrahedral elements, respectively, for computing mechanical deformation and diffusion during (de)lithiation (Fig. 5b). The Li concentration changes linearly during the (de)lithiation process, and the Li ion diffuses into/out of the Si according to the different Li concentration gradients. Through simulation, there is remaining Li concentration, with 1.22 mol Li per mole of Si after the first lithiation–delithiation cycle, which causes 95% volume expansion compared to the original electrode. This high volume change then leads to strains between the Si and Ni. Specifically, the Si active layer expands toward the pores and the scaffold during lithiation, and the expansion of Si toward the scaffold is constrained by the Ni scaffold, which puts the Ni scaffold under compression. By predicting plastic deformation in

the Ni scaffold during lithiation, as shown in Fig. 5c, a stress gradient between the nodes and struts is demonstrated because the stress developed in the struts is higher than that in the nodes during (de)lithiation⁶⁷, which thus causes mechanical degradation of the electrode after numerous lithiation cycles.

Other electrochemically active anode materials, such as graphene⁶⁹, TiNb_2O_7 ⁷⁰, MoS_2 ⁷¹, Ge ^{72,73}, and GeO_2 ⁷⁴, were also designed to be 3DOP electrodes for Li ion storage. Few-layer graphene nanosheets tend to aggregate or restack owing to the strong van der Waals interactions, leading to large interface resistance and impeding high-rate electronic conductivity⁷⁵. A synergistic effect of structure and doping in the 3DOP graphene anode was demonstrated for ultrafast Li ion storage with long-term cycling⁶⁹. 3DOP graphene with nitrogen (N) and sulfur (S) codoping was obtained through pyrolysis of the assembled graphene oxides and sulfonated polystyrene (S-PS) into a 3D continuous structure with the assistance of the surfactant of polyvinylpyrrolidone (PVP)⁶⁹. N atoms from PVP and S atoms from S-PS were successfully doped in situ into the graphene nanosheets. This 3DOP N/S codoping graphene electrode exhibits a high specific capacity of 860 mAh g^{-1} at 0.5 A g^{-1} . The reversible capacities still can reach a high value of 220 mAh g^{-1} even at an ultrahigh current density of 80 A g^{-1} , corresponding to a charge time of 10 s. The N and S doping effects result in extrinsic defects in the basal plane of graphene. Li ions may diffuse into the interlayer space of graphene sheets through these extrinsic defects⁶⁹. The special 3DOP structure combined with the heteroatom doping effect enables the as-prepared graphene electrodes with supercapacitor-like fast rate capabilities while maintaining battery-like high capacities. Certainly, the achieved ultrafast charge ability from the laboratory-scale half-cell



tests is not directly equivalent to the high-rate capability of the actual industrial batteries.

In terms of the supercapacitor-like ultrafast rate capability, electrode materials with intercalation capacitances should be the best choice for charge–discharge processes on the order of minutes or even seconds^{76–78}. 3DOP TiNb₂O₇ composed of interconnected single-crystalline nanoparticles exhibits the characteristics of Li ion pseudocapacitive storage⁷⁰. The proportion of surface-capacitance-controlled capacity is determined to be 51% and 79% at 0.05–1 mV s^{−1} (Fig. 6a, b), respectively. The diffusion-controlled charge is mainly generated near the peak voltage. The unique 3DOP architecture composed of interconnected nanocrystals provides enhanced capacitive charge storage, thus leading to good rate capability. As a typical layered transition-metal sulfide, MoS₂ has a structure analogous to that of graphite, in which hexagonal layers of Mo are sandwiched between the two S layers. S–Mo–S layers are held together by van der Waals forces, and the larger interlayer spacing (0.62 nm) provides ideal channels for the diffusion of Li ions as well as the transportation of electrons^{79,80}. 3DOP MoS₂/C was assembled in situ on carbon cloth (CC), in which the

surface of each carbon fiber was composed of 3D interconnected ordered macroporous few-layered MoS₂/C nanosheets⁷¹. The content of MoS₂ nanosheets in the MoS₂/C/CC hybrids was measured to be approximately 55%. It delivers a high discharge areal capacity of 3.802 mAh cm^{−2} (1130 mAh g^{−1}) at 0.1 mA cm^{−2}. Quantum density functional theory calculations reveal that the Li ion binding energy on the (100) facet of MoS₂ is stronger than those on the other facets. This suggests that exposing more (100) surfaces should be more beneficial for enhancing the specific capacity and rate capability of the MoS₂ anode. Moreover, the edge-enriched ultrasmall few-layer MoS₂ nanosheets with a lateral dimension of 5–10 nm are homogeneously incorporated into the 3DOP carbon wall, avoiding the restacking of MoS₂ and exposing more active (100) facets⁷¹.

Germanium can reversibly react with Li ions, forming the Li_{4.4}Ge alloy with a high theoretical capacity of 1638 mAh g^{−1}. Moreover, at room temperature, the Ge anode presents faster Li ion diffusivity (with diffusion coefficients of 4.55 × 10^{−5} cm² s^{−1} for Ge and 7.61 × 10^{−6} cm² s^{−1} for Si) and is comparatively closer to the conductor than the Si anode (with band gaps of 0.66 eV for Ge and

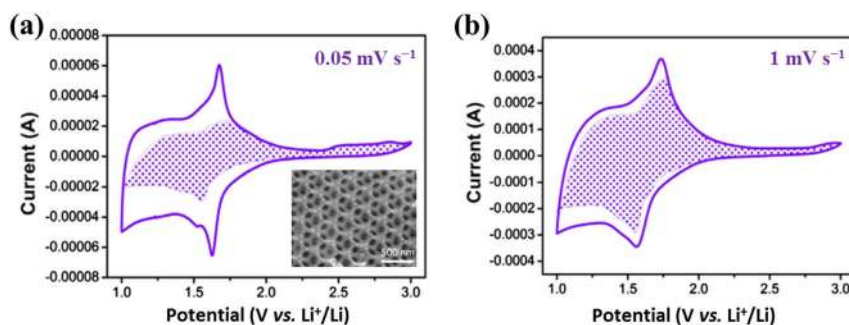


Fig. 6 The three-dimensional ordered porous (3DOP) structure enhances the intercalation capacitance in a TiNb_2O_7 electrode for Li ion storage. Cyclic voltammetric curves with separation between the total current (solid line) and capacitive currents (shaded regions) at **a** 0.05 mV s^{-1} and **b** 1 mV s^{-1} . The inset is the scanning electron microscopic image of the 3DOP TiNb_2O_7 electrode (modified from ref. ⁷⁰, copyright permission from Elsevier)

1.11 eV for Si)⁸¹. However, similar to the Si anode, the Ge electrode undergoes a drastic volume change during the alloying–dealloying process, leading to rapid capacity fading. 3DOP Ge electrodes were prepared via ionic liquid (IL) electrodeposition directly onto ITO and copper substrates followed by the PS template etching process⁷². The 3DOP Ge electrode displays a much lower charge-transfer resistance than the dense Ge electrode. The initial discharge- and charge-specific capacities of 3DOP Ge are 1748 and 1024 mAh g^{-1} , respectively. After 50 cycles, this material still retains a very high reversible capacity of 844 mAh g^{-1} . The whole 3DOP structure is swollen with a rough surface, but no evident crack formation is observed⁷³. Even with high Li ion storage capacity and satisfactory cycling stability, the scarcity and high cost of Ge compared to the other metal alloy anodes may still hinder its further large-scale application.

Cathode materials

Research on commercial cathode materials in Li ion batteries is mainly focused on LiCoO_2 and LiFePO_4 . LiCoO_2 is the first commercialized cathode material with a redox potential of approximately 4.0 V (vs. Li^+/Li) and a practical specific capacity of 140 mAh g^{-1} , with the amount of lithium, x , in $\text{Li}_{1-x}\text{CoO}_2$ usually below 0.5⁸². Overdelithiation would lead to a hexagonal phase transition from a monoclinic phase, leading to an abrupt shrinkage along the c axis direction and cation disorder^{83,84}. The olivine-structured LiFePO_4 is considered the most likely promising alternative for LiCoO_2 because of its large theoretical capacity (172 mAh g^{-1}), low cost, and environmental benignancy^{85,86}. Its main disadvantage is its poor conductivity and rate capability⁸⁷. To overcome the low electronic conductivity, the LiFePO_4 electrode is usually coated with conductive agents.

Early studies on the 3DOP LiCoO_2 cathode revealed that the 3DOP structure may improve its specific discharge capacities at higher current rates but cause poor

cyclability because the contraction/swelling of the small particles in the 3DOP walls during cycling leads to particle disconnections⁸⁸. The poor cycling stability is more serious for the 3DOP LiCoO_2 cathode synthesized at lower calcining temperatures⁸⁹. The 3DOP LiCoO_2 calcined at 700 °C presents a better crystal framework with a typical inverse opal structure. It displays a specific discharge capacity of 151 mAh g^{-1} at a current density of 1 C, which is higher than that of commercial LiCoO_2 . Moreover, 92% of the specific discharge capacity is retained after 50 cycles. Hierarchical 3DOP LiFePO_4 /carbon composites with macroporosity/mesoporosity/microporosity were synthesized via a multiconstituent and dual-templating method⁹⁰. These composites exhibit a specific capacity of 150 mAh g^{-1} . When the current density increases to 16 C, there is still a capacity of approximately 65 mAh g^{-1} . Using colloidal crystal spheres with different diameters of 100, 140, and 270 nm, three types of 3DOP LiFePO_4 samples were produced⁹¹. The 3DOP LiFePO_4 with a 270-nm colloidal crystal template displays both high surface area and improved electrolyte access and hence has the highest discharge capacity. In addition, the smaller colloidal crystal template (100 nm) produces an excess amount of residual carbon in the obtained LiFePO_4 sample. Although the addition of carbon to the LiFePO_4 electrode can improve the conductivity and overall electrochemical performance, excess carbon in the LiFePO_4 electrode would prevent the electrolyte from fully infiltrating into the pores at the center of the LiFePO_4 particles.

LiMnO_2 has attracted extensive interest owing to its high theoretical capacity of 285 mAh g^{-1} and realistic capacity of up to 200 mAh g^{-1} ⁹². The LiMnO_2 crystal possesses a layered monoclinic structure and orthorhombic structure with a zigzag arrangement of Li and Mn. Current studies on LiMnO_2 mainly focus on the orthorhombic phase because the monoclinic phase is very difficult to synthesize^{93,94}. To obtain 3DOP LiMnO_2 , MnO_2

was electrodeposited into the 3DOP Ni framework and subsequently lithiated in a molten salt⁹⁵. The 3DOP LiMnO₂ electrode with a thickness of 30 nm exhibits a high specific capacity of 198 mAh g⁻¹. Even when discharged at 185 C, it still retains a specific capacity of 75 mAh g⁻¹, approximately 38% of its initial capacity (Fig. 7a). The 3DOP LiMnO₂/Ni electrode provides both fast ion and electron transport in the electrolyte, electrode, and current collector. Recently, the fast-growing popularity of microelectronics has required the continuous development of miniaturized power sources. In this background, Li ion microbatteries based on 3DOP interdigitated LiMnO₂ microelectrodes are reported using an electrodeposition method on the interdigitated gold current collector (Fig. 7b). The interdigitated electrodes have a width of 30 nm and a spacing of 10 nm (Fig. 7c). This Li ion microbattery displays an energy density of 2.5 μWh cm⁻² μm⁻¹ at 0.5 C. It still retains 28% of its original energy even at 1000 C⁹⁶. The high-power delivery is the largest advantage of the Li ion microbattery based on 3DOP electrode materials. Another Li ion microbattery with 3DOP LiMnO₂ as a cathode and 3DOP Ni-Sn alloy as an anode was fabricated by 3D holographic lithography and conventional photolithography, followed by template-assisted electrodeposition⁹⁷. The resultant microbattery exhibits a volumetric energy density of 4.5 and 0.6 μWh cm⁻² μm⁻¹ at 1 and 1000 C, respectively. For practical applications, a conventional light-emitting diode is driven with a 500-μA peak current (600 C discharge) from the abovementioned microbattery with a thickness of 10 μm. After 200 cycles, this microbattery still presents an output current of 440 μA with only 12% capacity fade (Fig. 7d). The volumetric energy and power of the microbattery show a strong correlation with the structural parameters of the interdigitated electrodes, such as porosity, shape, digit width, and porosity. Certainly, for miniaturized electronics, the volumetric energy and power densities are less important than areal ones⁹⁸. However, the abovementioned Li ion microbattery still has relatively low areal energy densities owing to the limited electrode thicknesses.

As alternatives of phosphates (i.e., LiFePO₄), silicates (i.e., Li₂FeSiO₄) have attracted significant interest for next-generation Li ion batteries in recent years. The lower electronegativity of Si (2.03) than of P (2.39) would reduce the electronic band gap and increase the electronic transport. Importantly, Li₂FeSiO₄ can supply a high theoretical capacity of up to 331 mAh g⁻¹ through a potential two-electron transfer reaction. In addition, the earth-abundant elements Fe and Si are cost-effective and scalable resources^{99–101}. Recently, a 3DOP Li₂FeSiO₄/C composite was prepared via a “hard-soft” templating method^{102,103}. The 3DOP Li₂FeSiO₄/C cathode exhibits a high reversible capacity of 239 mAh g⁻¹ and superior

long-term cycling stability with a capacity retention of nearly 100% over 400 cycles¹⁰². The calculated Li⁺ ion diffusion coefficients in the 3DOP Li₂FeSiO₄/CF (carbon nanofiber) and bulk Li₂FeSiO₄/CF were 7.62×10^{-13} and 4.54×10^{-13} cm² s⁻¹, respectively¹⁰³. The ordered macropores create a short Li ion diffusion pathway and accommodate volumetric changes, while the carbon matrix serves as a conductive network to improve the electron transport of Li₂FeSiO₄.

Li₃V₂(PO₄)₃ possesses a high redox potential (3.8 V vs. Li⁺/Li) and a relatively high theoretical specific capacity (197 mAh g⁻¹)¹⁰⁴. Furthermore, monoclinic Li₃V₂(PO₄)₃ with a sodium superionic conductor (NASICON) structure provides a very high ion diffusion coefficient (from 10⁻⁹ to 10⁻¹⁰ cm² s⁻¹). However, it suffers from a low electronic conductivity (2.3×10^{-8} S cm⁻¹), which limits its practical application¹⁰⁵. Carbon-coated 3DOP Li₃V₂(PO₄)₃ was successfully synthesized by a simple one-pot procedure¹⁰⁶. This 3DOP Li₃V₂(PO₄)₃/C cathode displays a significantly improved rate capability relative to that of the corresponding bulk nanocomposite. After 60 cycles, a high reversible capacity of 148 mAh g⁻¹ is retained at 2 C with a capacity loss of only 0.08% per cycle. To further improve the electronic conductivity of Li₃V₂(PO₄)₃, a series of Ce³⁺-doped 3DOP Li₃V_{2-x}Ce_x(PO₄)₃/C materials ($x = 0, 0.01, 0.03, 0.05$) were obtained and evaluated as cathodes for Li ion batteries¹⁰⁷. Doping of the Ce element does not affect the formation of a 3D ordered macroporous structure. The 3DOP Li₃V_{1.97}Ce_{0.03}(PO₄)₃/C electrode has the best electrochemical behavior among the four samples. The radius of the Ce³⁺ ion is much larger than that of the V³⁺ ion. The unit cell volume of the Li₃V₂(PO₄)₃/C increases after an appropriate amount of Ce³⁺ doping. Such expansion in the crystal lattice may enhance the diffusion rate of Li⁺ ions into the Li₃V₂(PO₄)₃ lattice.

Recently, the electrochemical performance of a 3DOP V₂O₅ cathode was reported for Li ion storage¹⁰⁸. The 3DOP V₂O₅ electrode presents a series of discrete redox peaks. The subsequent CV curve cycles for the 3DOP V₂O₅ electrode are much smoother than the initial cycles because of the formation of an irreversible ω-Li_{2+x}V₂O₅ phase confirmed by ex situ Raman spectral studies¹⁰⁸. Notably, the walls of the 3DOP V₂O₅ structure became thicker after 100 cycles due to volume changes associated with lithiation. Additionally, some regions of the 3DOP V₂O₅ appeared pulverized. Thus the 3DOP V₂O₅ electrode on the stainless steel current collector displays a significant fading from an initial capacity of 151–51 mAh g⁻¹ after 100 cycles. When using FTO-coated glass as a current collector, it exhibits improved cyclability with a specific capacity of ~191 mAh g⁻¹ after 75 cycles¹⁰⁸. Then graphene-wrapped 3DOP V₂O₅ was demonstrated to further improve the cycling stability¹⁰⁹. The electrically

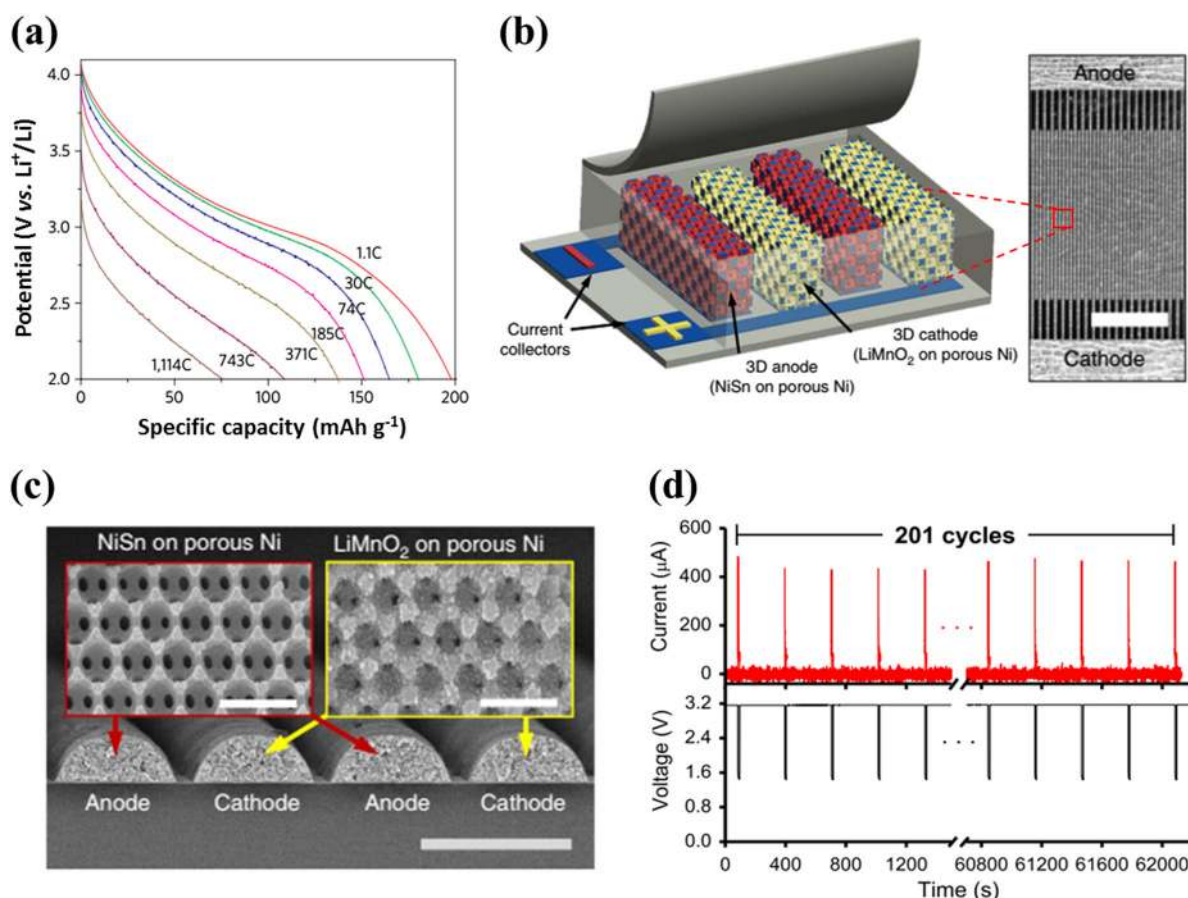


Fig. 7 The Li ion microbattery based on three-dimensional ordered porous (3DOP) electrodes. **a** The ultrafast discharge of the 3DOP LiMnO₂ cathode. **b** Schematic illustration of the Li ion microbattery containing a 3DOM LiMnO₂ cathode and a 3DOP NiSn alloy anode with the top-down scanning electron microscopic (SEM) image of the interdigitated electrodes. Scale bar, 500 nm. **c** SEM cross-section of the interdigitated electrodes. Scale bars, 50 and 1 μm in the insets. **d** Current and voltage profiles of the microbattery that is controlled by a single-pole-double-throw (SPDT) relay to periodically power a red light-emitting diode for 10 s and is charged with two AA batteries for 5 min (modified from ref. ⁹⁶, Copyright permission from Nature Publishing Group)

conductive graphene nanosheets with thicknesses of 4–10 layers are embedded into two thick layers of V₂O₅. The resultant 3DOP V₂O₅/graphene/V₂O₅ electrode exhibits a capacity of approximately 198 mAh g⁻¹ over 1000 cycles. In addition, the 3DOP graphene embedded inside the V₂O₅ cathode enables good electronic conductivity for fast electron transportation. This is essential for high-performance V₂O₅ electrodes because of their poor electronic conductivity. Interestingly, a symmetric microbattery based on the V₂O₅ film was confined within 3DOP anodic aluminum oxide (AAO) microchannels¹¹⁰. By using the atomic layer deposition, a 7.5-nm-thick Ru layer as the current collector and a 23-nm-thick V₂O₅ film as the active material were conformably coated on AAO nanotube arrays. V₂O₅ on one side was prelithiated to serve as the anode, and the pristine V₂O₅ film on the other side was used as the cathode. In 3DOP

microchannel templates, the V₂O₅ electrodes tended to expand upon lithiation and form uniform structures within the microchannels over repeated cycles. This may prevent thin-film active materials from falling off from the electrodes during the cycles, thus achieving a long-term cycle lifespan of up to 1000 cycles. In addition to the improved cycling stability, the enhanced kinetics of the Li ion insertion reaction is demonstrated in the interconnected 3DOP V₂O₅ electrodes¹¹¹, which are associated with the enhancement in Faradaic reaction utilization of both the surface-dominant and the bulk diffusion-dominant reactions. Moreover, the symmetric V₂O₅ microbattery with a low voltage can be easily extended to a V₂O₅-SnO₂ asymmetric microbattery with a high voltage¹¹².

Iron trifluoride (FeF₃) is considered another promising cathode material due to its high theoretical capacity of

237 mAh g⁻¹ (1-e transfer) and 712 mAh g⁻¹ (3-e transfer)¹¹³. Poly(3,4-ethylene dioxithiophene) (PEDOT) was coated on the 3DOP FeF₃ electrode by an in situ polymerization method¹¹⁴. The 3DOP FeF₃ electrode without a conducting PEDOT coating shows a specific capacity of 148 mAh g⁻¹, which is much lower than that of 3DOP FeF₃-PEDOT (210 mAh g⁻¹). The homogeneous coating of conductive polymer greatly improves the conductivity of the 3DOP FeF₃ electrode. However, the commercial nonporous FeF₃ electrode coated by conducting PEDOT displays only a capacity of 105 mAh g⁻¹. This result suggests that the conductivity is not the only key factor and that the 3DOP structure also plays a key role in improving the electrochemical performance of the FeF₃ cathode.

3DOP electrode materials for use in aqueous rechargeable lithium batteries (ARLBs)

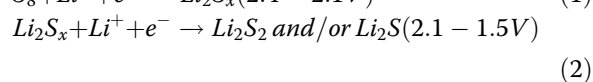
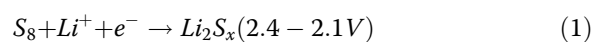
ARLBs are one of the most promising alternatives for large-scale applications due to their advantages of safety, low cost, superfast charge ability, and environmental friendliness. As the most commonly used cathode in ARLBs, spinel-type LiMn₂O₄ has attracted increasing interest for both fundamental and practical applications. In a neutral aqueous electrolyte, the 3DOP LiMn₂O₄ electrode exhibits a capacity retention of 93% after 10,000 cycles (Fig. 8a)¹¹⁵. The capacity of the bulk LiMn₂O₄ electrode rapidly decreases over 2000 cycles. The ordered macroporous structure can accommodate some strain/stress during the charge and discharge process, which is demonstrated via the changes of the XRD patterns of the 3DOP and bulk LiMn₂O₄ electrodes prior to cycling and after 10,000 cycles¹¹⁵.

3DOP LiFePO₄ coated with carbon and interwoven with multiwall carbon nanotubes (CNTs) also exhibits a superfast capability in 0.5 M Li₂SO₄ aqueous electrolyte¹¹⁶. Even at charging rates of 120 C (30 s), 300 C (12 s), and 600 C (6 s), specific discharge capacities still remain at 97, 84, and 62 mAh g⁻¹, respectively (Fig. 8b). The charging/discharging rate of 3DOP LiFePO₄ in an aqueous electrolyte is much higher than that in nonaqueous electrolytes by nearly five times. Ab initio calculations indicate that a special solid/liquid interface forms at the LiFePO₄ surface, which lowers the energy barriers of the Li⁺-desolvation process and enables fast Li ion transport across the solid/liquid interfaces. To further improve the operating voltage and energy density of ARLBs, a new generation of aqueous rechargeable batteries is built using a coated Li metal as an anode and 3DOP LiFePO₄ as a cathode, whose average discharge voltage can reach 3.30 V¹¹⁷. The lithium metal used was first coated with a gel polymer electrolyte (GPE) with an ionic conductivity on the order of 10⁻⁴ S cm⁻¹. Then a LISICON film (solid fast Li ion conductor) was further placed on the surface of GPE. The LISICON film allows only the Li ions to pass

through for the charge balance. The GPE acts as a buffer to endure the volume change of Li metal and prevent the reaction between lithium metal and the LISICON film. More importantly, the formation of lithium dendrites will be suppressed because the GPE has higher viscosity than the organic liquid electrolytes. Since both the coated Li anode and the 3DOP LiFePO₄ are stable in the aqueous electrolyte for reversible redox reactions, the fabricated ARLB exhibits an excellent cycling life with a Coulombic efficiency of nearly 100%¹¹⁷.

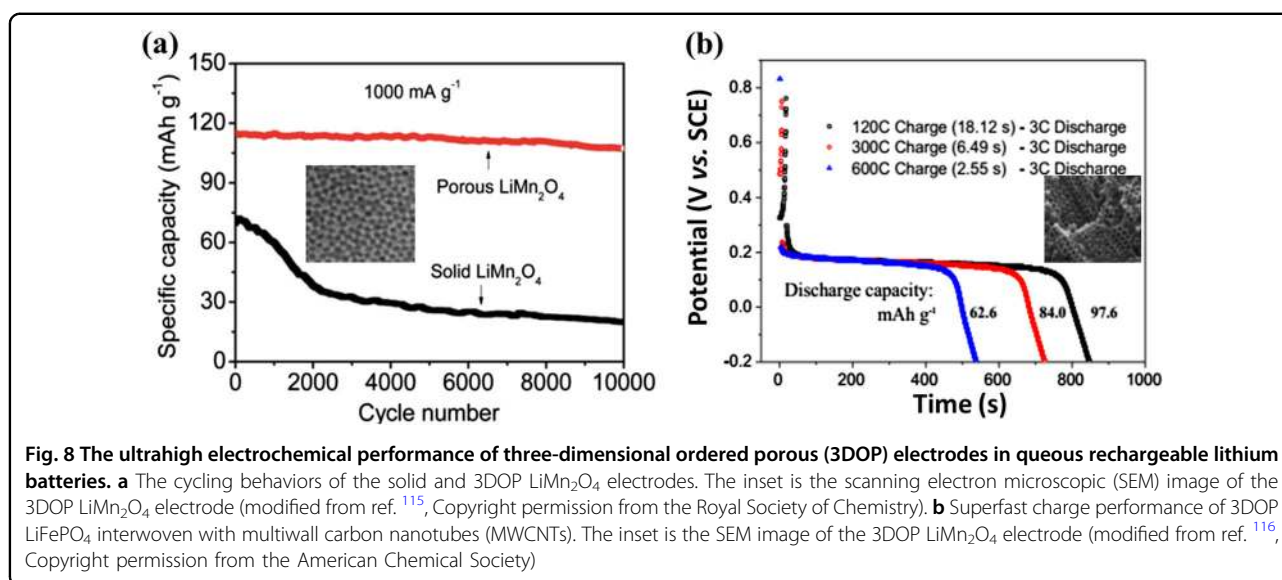
3DOP electrode materials for use in Li-S batteries

Li-S batteries should be one of the most promising next-generation electrochemical energy storage devices because they have a high specific capacity of 1672 mAh g⁻¹ and an energy density of 2600 Wh kg⁻¹ (including the mass of the Li anode), which are three to five times higher than those of state-of-the-art Li-ion batteries^{118–120}. A Li-S battery is a highly complex system with two typical electrochemical reactions between lithium metal and elemental sulfur:



Many significant issues resulting from both the sulfur cathode and the lithium metal anode hinder their practical application, including the poor electrical conductivities of sulfur and Li₂S, the large volume expansion over the reversible transformation between sulfur and Li₂S, the dissolution of lithium polysulfides (such as Li₂S₈, Li₂S₆, Li₂S₄), and the instability and dendrite growth of Li metal anodes. Intensive efforts have been devoted to the rational design of the electrode structure to address the abovementioned issues¹²¹. To alleviate the problem of extremely low conductivity and large volume expansion of the sulfur cathodes upon cycling, an effective method is the utilization of a 3DOP carbon as the substrate (or host) for the insulating sulfur electrode¹²². For example, a 3DOP carbon coupled with mesopores (3–6 nm) can act as a framework to encapsulate the intermediate products and restrain the shuttle effect of lithium polysulfide¹²³.

N-doped 3DOP carbon is used as a host for sulfur cathodes in Li-S batteries^{124,125}. The 3DOP N-doped C/S composite achieves an ultralong cycle life up to 500 cycles with a capacity decay as low as 0.057% per cycle¹²⁴. Interestingly, N doping and 3DOP carbon work synergistically to further entrap the dissolvable polysulfides, hence enabling the immobilization of sulfur. To maximize the areal sulfur loading, the formation of a thick 3DOP N-doped C/S composite was achieved with close-packed interconnected nanosphere clusters and high sulfur loading of up to 5 mg cm⁻²¹²⁵. Such high areal sulfur loading is of commercial interest to replace current Li ion



batteries. Nevertheless, the long-term lifespan is still unsatisfactory considering the low affinity of carbon materials for polysulfide species.

To increase the affinity of carbon hosts for polysulfide species, metals or metal oxides are introduced into the heteroatom-functionalized 3DOP carbon materials, which can further reduce the polysulfide shuttle issue and benefit the kinetics of polysulfide redox reactions^{126–128}. Specifically, the novel two-in-one cobalt (Co)-embedded N-doped mesoporous carbon nanosheets were fabricated as stable hosts for both sulfur cathodes and a metallic lithium anode. On the one hand, owing to the high electronic conductivity and excellent structural polarity for the polysulfide containment, the Co nanoparticles can work synergistically with N heteroatoms to promote the redox reaction kinetics and alleviate the polysulfide solubility, thus endowing the sulfur cathodes with an excellent rate capability and long lifetime of 400 cycles with a capacity decay of <0.036% per cycle. On the other hand, the high surface area of the mesoporous structure and the N heteroatoms can regulate metallic lithium plating/stripping and hinder dendrite overgrowth, yielding lithium metal anodes with an excellent Coulombic efficiency of nearly 100% over 100 cycles¹²⁶. Interestingly, through the delicate incorporation of ZrO_2 in holey CNTs/S electrodes, permselective gateways for Li ion transportation were realized at sufficient mesopore openings, which are impenetrable to lithium polysulfides¹²⁷. In addition to the metal and metal oxides, B-, N-, or O-doped holey graphene also exhibits a distinguished ability to trap the polysulfides due to the strong polar-to-polar interaction¹²⁸.

3DOP carbon as a substrate for sulfur cathodes is then utilized to couple with room-temperature IL

electrolytes to further improve the immobilization of lithium polysulfides^{129,130}. The dissolution of Li_2S_x was efficiently suppressed in the electrolyte comprising *N*-butyl-*N*-methyl-piperidinium bis(trifluoromethanesulfonyl) amide¹²⁹. The weakly acidic/basic nature of the lithium bis(trifluoromethanesulfonyl)amide-tetraglyme complex electrolyte, may cause low coordination ability toward Li_2S_x . In terms of some solvate ILs, polysulfides are insoluble and tend to form an inhomogeneous layer that covers the 3DOP carbon surface. In this case, the more suitable structure should be the 3DOP carbon with both large macropores and a large volume instead of the widely accepted mesopores and/or micropores that work well for conventional polysulfide-soluble electrolytes¹³⁰. Unfortunately, the cost of the IL electrolyte may render them impractical and uneconomical for applications. In contrast, for traditional organic electrolytes, the bimodal micropores/mesopores of the 3DOP carbon materials are now the most popular materials for enhancing the confinement of dissoluble intermediate lithium polysulfides because of the combination of sulfur loading sites in micropores and the electrolyte reservoir (or channels) in mesopores to enhance the transportation of ions throughout the architecture¹³¹.

3DOP electrode materials for use in Li-O_2 batteries

Oxygen (O_2) as a cathode has received significant interest in the past decade since it provides a high thermodynamic voltage of 2.96 V (vs. Li^+/Li) and a theoretical capacity of 1675 mAh g^{-1} with Li_2O_2 as the discharge product. When considering the total mass of Li (with a theoretical capacity of 3860 mAh g^{-1}) and O_2 , the theoretical capacity of a Li-O_2 battery is 1168 mAh g^{-1} , with a corresponding theoretical specific energy density of 3460 Wh kg^{-1} . In a Li-O_2 battery, the cathode functions as an

oxygen reduction reaction (ORR) catalyst during discharge with the reduction of O_2 as $2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$ and hopefully works as an oxygen evolution reaction (OER) catalyst during charge with the electrochemical decomposition reaction of Li_2O_2 as $Li_2O_2 \rightarrow 2Li^+ + O_2 + 2e^-$. Currently, the development of Li- O_2 batteries is encumbered with vast scientific and technological challenges, involving high charge/discharge overpotentials directly related to low energy efficiency, deposition of insulating Li_2O_2 product, poor stability of cathodes and electrolytes, and safety hazards associated with Li metal anodes. Most of these challenges are associated with the oxygen reactions occurring in the cathode. To realize the high energy density of Li- O_2 batteries, many research efforts have been devoted to designing suitable and effective cathode catalysts^{132–134}. In fact, the performance of Li- O_2 batteries (such as discharge/charge overpotential, energy efficiency, cycle life) is closely related to the catalyst materials and the architecture of the catalyst electrodes¹³⁵. Generally, an ideal catalyst electrode requires a highly conductive and porous structure to facilitate both electron and oxygen transport and provide sufficient space for the formed Li_2O_2 ¹³⁶.

Porous network models were recently developed to simulate the electrochemical behaviors of Li- O_2 cathode mesostructures, which clearly demonstrate that 3DOP structures with rich interconnectivity and the microscopic arrangement of pores may lead to variations in electrochemical behaviors¹³⁷. A composite based on a rock salt-structured $(Mn_{1/3}Co_{2/3})O$ catalyst and CNT microspheres was designed as an efficient cathode material for Li- O_2 batteries. The wetting of the electrolyte and the diffusion of oxygen are greatly facilitated within the macroporous structure of CNTs, which also provides enough space to accommodate Li_2O_2 species. Thus the 3DOP macroporous $(Mn_{1/3}Co_{2/3})O$ -CNT composite microspheres serve as a highly efficient bifunctional catalysts with excellent ORR and OER activities¹³⁸.

The 3D ordered macroporous/mesoporous carbon was synthesized using a dual-template method and then used as a catalyst for Li- O_2 batteries^{139,140}. The O_2 catalytic cathode was obtained by coating a homogeneous mixture of the ordered macroporous/mesoporous carbon, carbon black, and a polyvinylidene fluoride binder (PVDF, 20 wt%) onto carbon paper disks. Increasing the content of ordered macroporous/mesoporous carbon leads to higher capacities and operating voltages. A high discharge capacity (7000 mAh g^{-1} based on the catalyst) and operating voltage (2.75 V) are realized when the content of the ordered macroporous/mesoporous carbon is 50 wt%. However, the overly high weight ratio of the ordered macroporous/mesoporous carbon may decrease the mechanical strength of the catalytic cathode¹³⁹. When the 3D ordered macroporous/mesoporous carbon is further

functionalized by low-crystalline Ru nanoclusters, the cycle life of the related Li- O_2 battery is greatly improved owing to the reduced side products and the undecomposed discharge products¹⁴⁰. Generally, the ordered macroporous channels enable an effective space for O_2 diffusion and O_2/Li_2O_2 conversion, while the ordered mesoporous channels in the electrode can effectively facilitate Li ion diffusion and electron transfer. Although 3DOP carbon materials are commonly utilized in Li- O_2 batteries, one disappointing issue is that carbon-based electrocatalysts are prone to decomposition under the attack of oxygen radicals during the charging process, which may promote the degradation of electrolytes and produce the insulator Li_2CO_3 ¹⁴¹. The excess byproducts would block further access of Li_2O_2 to the 3DOP carbon cathode, ultimately leading to premature battery death.

To develop cheap and carbon-free electrocatalysts, 3DOP $FePO_4$ was synthesized and applied as a high-efficiency catalyst for Li- O_2 batteries¹⁴². Li- O_2 batteries with 3DOP $FePO_4$ electrocatalysts exhibit a cycling life of 300 cycles with discharge voltages above 2.2 V at a cut-off capacity of 1000 mAh g^{-1} . Because of the excellent electrochemical performance in solid oxide fuel cells, perovskite-based oxides have recently been employed as a promising electrocatalyst for Li- O_2 batteries¹⁴³. 3DOP $LaFeO_3$ was synthesized as an electrocatalyst in an ether-based electrolyte¹⁴⁴. The 3DOP- $LaFeO_3$ /carbon black electrode displays a higher ORR onset potential and ORR/OER peak current than carbon black and bulk- $LaFeO_3$ /carbon black electrocatalysts (Fig. 9a). Using 3DOP- $LaFeO_3$ /carbon black as the cathode, the obtained charge voltage is 0.15 and 0.25 V lower than that of a Li- O_2 battery with bulk- $LaFeO_3$ /carbon black and carbon black, respectively (Fig. 9b). Moreover, its discharge voltage is slightly higher than that of bulk- $LaFeO_3$ /carbon black and carbon black. The unique “honeycomb” porous structure unit in 3DOP- $LaFeO_3$ can provide uniform Li_2O_2 and Li ion distribution inside the electrode due to more abundant oxygen and electrolyte transport paths.

3DOP electrode materials for use in supercapacitors

In contrast to rechargeable batteries that store charge in the bulk of the electrode, supercapacitors store charge at the interface between an electrode and the electrolyte. Generally, there are two categories of supercapacitors: electric double layer capacitors (EDLCs) that store charge based on reversible electrostatic ion adsorption/desorption at the electrode/electrolyte interface and pseudocapacitors that store charge based on additional surface redox reactions as well as electrostatic absorption/desorption^{145–149}. 3DOP electrode materials have a continuous nanostructured skeleton with a large interfacial area, which ensures a large number of active sites for surface charge storage.

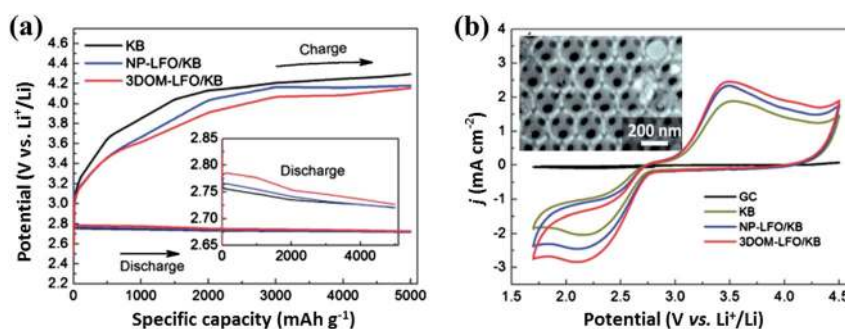


Fig. 9 The electrochemical behaviors of the Li-O₂ battery based on a three-dimensional ordered porous (3DOP) LaFeO₃/carbon black catalyst. **a** First charge/discharge curves of Li-O₂ battery with carbon black (black line), nanoporous LaFeO₃/carbon black (blue line), and 3DOP LaFeO₃/carbon black electrodes at a current density of 0.025 mA cm⁻². **b** Cyclic voltammeters of glassy carbon (black line), carbon black (yellow line), nanoporous LaFeO₃/carbon black (blue line), and 3DOP LaFeO₃/carbon black (red line) recorded in an O₂-saturated electrolyte at a sweep rate of 10 mV s⁻¹ and a rotation rate of 900 rpm. The inset is a scanning electron microscopic image of 3DOP LaFeO₃/carbon black (modified from ref. ¹⁴⁴, Copyright permission from the Royal Society of Chemistry)

Electric double layer capacitors

The electrodes for EDLCs mainly focus on carbon-based active materials with a high surface area^{2,15}. In the case of anodes for Li ion batteries, the rich mesoporous structures with very high specific surface areas usually lead to low initial Coulombic efficiency due to the increased side reactions. However, this is different from EDLCs because the capacitance is proportional to the specific surface area of carbon materials to a certain degree. Thus, although 3D ordered macroporous electrode materials enable certain advantages for Li ion batteries, as previously discussed, one limitation of 3D ordered macroporous electrode materials is the lower surface area accessible for application in EDLCs compared to ordered mesoporous materials. Thus 3D ordered macroporous/mesoporous carbon was synthesized for EDLCs by using the colloidal crystal template method with highly ordered templates, including monodisperse SiO₂ spheres, monodisperse PS latex, colloidal silica, and other opal materials^{150–153}. These bimodal porous carbons show high capacitances of up to 120 and 130 F g⁻¹ in organic¹⁵⁰ and aqueous alkaline electrolytes¹⁵¹, respectively. Mesopores have a significant positive effect on the rate capability of the carbon electrode, and the interconnection of macropores facilitates electrolyte transport to whole surfaces. Specifically, the large number of mesopores can contribute to the adsorption of ionic species at the electrode/electrolyte interface for electric double-layer formation without an ionic sieving effect. The existence of mesopores (ranging from 2 to 50 nm) greatly contributes to the total pore volume in the 3DOP carbon. Decreasing the diameter of the template spheres can greatly promote both high surface area and pore volume (Fig. 10a). The 3DOP carbon electrode with a pore size distribution of 50 nm shows the highest specific capacitance (Fig. 10b). The gravimetric capacitance of the

3DOP carbons increases linearly with the surface area (Fig. 10c). Although the activated carbon has a larger surface area of 1700 m² g⁻¹, its capacitance is still lower than that of the 3DOP carbon electrode with a pore size distribution of 50 nm. In fact, micropores in carbon electrodes <0.7 nm should be a disadvantage for double-layer formation, especially in organic electrolytes, because the diameters of the (C₂H₅)₄N⁺ and BF₄⁻ ions are 0.7 and 0.5 nm, respectively¹⁵².

The assembly of 2D graphene sheets into 3D structures is attractive for EDLCs. Free-standing foams composed of 3DOP graphene were obtained via chemical vapor deposition (CVD) grown on templated Ni scaffolds and etched method in concentrated HCl solution¹⁵³. The calculated highest specific capacitance was 2.7 F cm⁻³ for the 3DOP graphene electrode. Unfortunately, it is difficult to synthesize a sufficient quantity of materials when using the CVD method.

Pseudocapacitors

The electrode materials of pseudocapacitors mainly include transition metal oxides, transition metal sulfides, and conductive polymer materials. A large amount of 3DOP electrode materials were demonstrated for use as pseudocapacitors in the past several years, as summarized in Table 1.

Among various transition metal oxides, MnO₂ has attracted significant interest owing to its advantages of high specific capacitance, low cost, environmental friendliness, etc.^{154,155}. The electrochemical performances of 3DOP MnO₂ electrodes with different pore diameters (200–900 nm) were evaluated in an aqueous Na₂SO₄ electrolyte¹⁵⁶. It is established that the pseudocapacitive behaviors of the 3DOP MnO₂ electrodes greatly depend on the electrode pore sizes. For example, the 3DOP MnO₂ electrode with a pore diameter of

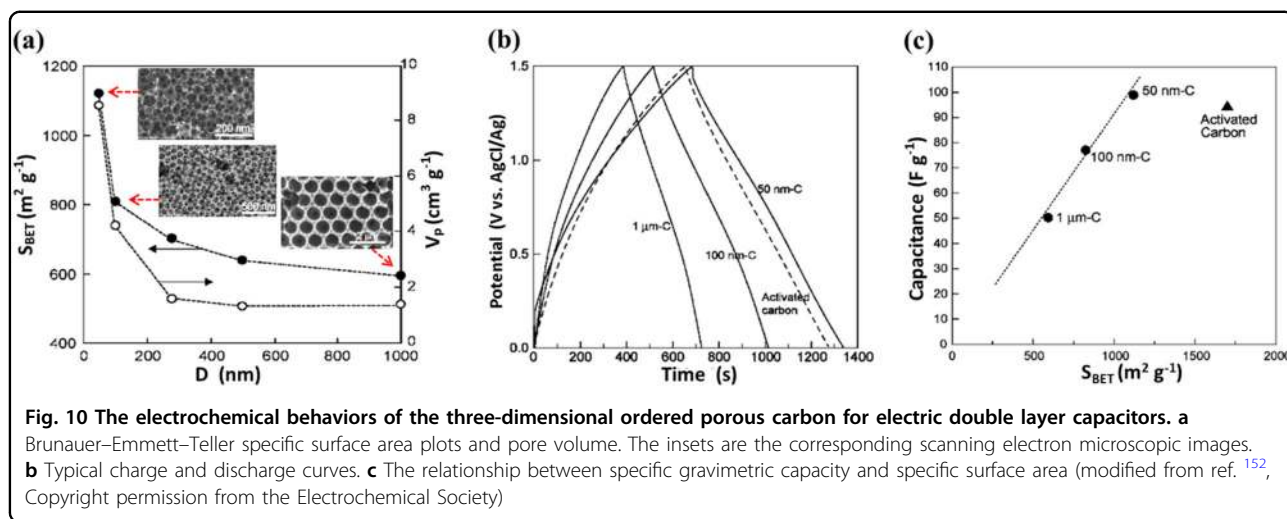


Table 1 The summary of the electrochemical performance based on the 3DOP-based electrodes for pseudocapacitors

Electrode	Ordered pores	Electrolyte	Working voltage	Specific capacitance	Cycle	Ref.
MnO ₂	200 nm	0.5 M Na ₂ SO ₄	0–1 V	765 F g ⁻¹	2000 (98%)	¹⁵⁶
MnO ₂ /V ₂ O ₃	360 nm	1 M Na ₂ SO ₄	–0.8–0.8 V	1301 F g ⁻¹	15000 (86%)	¹⁵⁷
MnO ₂ /Mn	450 nm	3 M KCl	0–0.9 V	1260 F g ⁻¹	2000 (96%)	¹⁵⁸
MnO ₂ /C	280 nm + 3.9 nm	1.0 M Na ₂ SO ₄	0–1 V	234 F g ⁻¹	1000 (95%)	¹⁵⁹
MnO ₂ /C	250 nm	0.1 M Na ₂ SO ₄	0–0.8 V	347 F g ⁻¹	5500 (92%)	¹⁶⁰
V ₂ O ₅	165 nm	1 M LiClO ₄ /PC	–1–1 V	355 F g ⁻¹	—	¹⁶⁴
V ₂ O ₅	210 nm	1 M LiClO ₄ /PC	–1–1 V	0.05 C cm ⁻²	—	¹⁶⁷
NiO	500 nm	0.5 M NaOH	–0.4–0.6 V	—	—	¹⁷¹
Co ₃ O ₄ /C	225 nm	6 M KOH	0–0.6 V	687 F g ⁻¹	5000 (96%)	¹⁷²
Cu ₂ O/Ni	300 nm	6 M KOH	–0.2–0.4 V	502 F g ⁻¹	500 (75%)	¹⁷⁴
In ₂ O ₃ /C	250 nm	6 M KOH	0–0.5 V	287 F g ⁻¹	5000 (86%)	¹⁷⁵
WS ₂	800 nm	1 M H ₂ SO ₄	–0.3–0.4 V	262 F g ⁻¹	3000 (95%)	¹⁷⁶
Functionalized PPy	120 nm	0.5 M LiClO ₄	–0.1–0.5 V	130 F cm ⁻³	10000 (90%)	¹⁷⁷
PPy/CNT	500 nm	1 M KCl	–0.4–0.2 V	427 F g ⁻¹	1000 (90%)	¹⁷⁸
PPy/C		1 M LiPF ₆ /EC-DEC	2–4 V	140 F g ⁻¹	—	¹⁷⁹
PANi		1 M LiPF ₆ /EC-DEC	2–4 V	200 F g ⁻¹	—	¹⁸⁰

C carbon, CNT carbon nanotube, EC ethylene carbonate, DEC diethyl carbonate, 3DOP three-dimensional ordered porous, PANi polyaniline, PC propylene carbonate, PPy polypyrrole

approximately 200 nm exhibits a specific capacitance of 390 F g⁻¹, which is much higher than those of the 3DOP electrodes with larger pores (400 and 900 nm). However, the low electronic conductivity (10⁻⁵–10⁻⁶ S cm⁻¹) of the MnO₂ electrode results in a practical capacitance that is far lower than its theoretical capacitance (1370 F g⁻¹). One promising strategy to solve this problem is the incorporation of nanostructured MnO₂ into a conductive metal or carbon matrix¹⁵⁷. Thus a core–shell Mn/MnO₂ film was designed to anodize a 3DOP Mn

film in a KCl aqueous solution, which displayed an ultrahigh specific capacitance of 1200 F g⁻¹ at a scan rate of 10 mV s⁻¹¹⁵⁸. The core of the Mn layer greatly enhances the electron transportation for charge transfer reactions due to its large electronic conductivity. In addition to the conductive metal, the 3DOP carbon framework is a promising substrate for the MnO₂ electrode^{159,160}, which can provide good mechanical stability and is favorable for electron transport within the well-interconnected wall structure.

Vanadium pentoxide (V_2O_5) is another potential electrode material for pseudocapacitors both in aqueous and organic electrolytes owing to its lamellar structure and different oxidation states^{161,162}. In the organic electrolyte, in contrast to MnO_2 , V_2O_5 is an extrinsic intercalation pseudocapacitive material. The intercalation pseudocapacitive behaviors of the V_2O_5 electrode become apparent only with rational engineering of its architectures at the nanoscale¹⁶³. Recently, the pseudocapacitive effect of 3DOP V_2O_5 films was studied in organic Li salt electrolytes¹⁶⁴. The capacitive contribution of a 3DOP V_2O_5 film with a pore diameter of 165 nm is approximately 68% at 10 mV s^{-1} , which is much higher than those of films with a pore diameter of 480 nm (40%) and the compact film (18%). The 3DOP V_2O_5 film with a wall thickness of 14 nm displays a capacitance-based high-rate capability and an intercalation-based high capacitance. V_2O_5 is also an excellent electrochromic oxide, which can be integrated into the electrochromic supercapacitor on the conductive transparent current collector^{165,166}. For example, the 3DOP V_2O_5 -based supercapacitor displays a higher optical contrast and faster switching response time (1.7 s for coloration and 3.2 s for bleaching)¹⁶⁷. Integrating electrochromism into a supercapacitor presents a significant opportunity in the development of smart supercapacitors with imaginative and humanization features.

Nickel- or cobalt-based oxides (NiO and Co_3O_4) show high-rate performance as electrode materials in alkaline batteries, involving typical diffusion-limited redox reactions^{168,169}. They are often matched with EDLC-type carbon materials to fabricate hybrid supercapacitors¹⁷⁰. 3DOP NiO and Co_3O_4 electrodes were shown to enhance the electrochemical performance^{171,172}. Color changes are observed during the redox process with darkening upon oxidation and bleaching upon reduction in the 3DOP NiO electrode¹⁷¹. The 3DOP $\text{Co}_3\text{O}_4/\text{C}$ nanocomposite shows a specific capacitance of 687.5 F g^{-1} at 20 mV s^{-1} , which is much higher than those of the 3DOP Co_3O_4 and Co_3O_4 -free 3DOP carbon counterparts. Moreover, the 3DOP structure of the $\text{Co}_3\text{O}_4/\text{C}$ nanocomposite is still well maintained after 5000 cycles¹⁷². One disadvantage of Ni- or Co-based oxides is that the related charge storage generally occurs within a very narrow potential range in alkaline electrolytes. Whether their redox kinetics belong to surface-controlled pseudocapacitive behavior or diffusion-controlled battery behavior remains controversial¹⁷³.

Other electrode materials with 3DOP structures, including Cu_2O ¹⁷⁴, In_2O_3 ¹⁷⁵, and WS_2 ¹⁷⁶, are also investigated for use in supercapacitors. The pseudocapacitance of the Cu_2O electrode in an alkaline electrolyte originates from transitions between the oxidation states Cu(I) oxide and Cu(II) oxide and vice versa¹⁶². The surface faradaic reactions of the In_2O_3 electrode materials can be

expressed as follows: the reversible transitions between the oxidation state ($\text{In}_2\text{O}_3 + 3\text{H}_2\text{O}$) and the reduction state ($\text{In} + 6\text{OH}^-$)¹⁶³. In contrast, the distinctive surface capacitive behavior of the 3DOP WS_2 electrode is associated with reversible and rapid proton insertion/deinsertion into/out of the in-plane W–S lattice¹⁶⁵.

Another good example of how 3DOP electrode materials facilitate good electronic and ionic conductivity can be identified in the case of organic electrodes for supercapacitors. The 3DOP organic hybrid electrode consisting of a catechol derivative and polypyrrole (PPy) was prepared by a simple one-step electrosynthesis method¹⁷⁷. A fast redox transition of the quinone/hydroquinone pair occurs in this hybrid electrode. At a small current density of 0.4 A cm^{-3} , this 3DOP hybrid electrode exhibits a capacitance of 130 F cm^{-3} (385 F g^{-1}), which is higher than those of the bulk hybrid electrode (117 F cm^{-3}) and the pure PPy electrode (95 F cm^{-3}). Another 3DOP PPy/CNT composite electrode shows a specific capacitance of 427 F g^{-1} , while the planar CNT/PPy composite film has a specific capacitance of only 128 F g^{-1} ¹⁷⁸. A mathematical model of mass transport to evaluate the ion diffusion capability reveals that ions can approach the inside wall of the pore and then transfer much deeper into the surface of the electrode with well-ordered 3D macropores (diameter of 300 nm) compared to those electrodes with a planar surface or nanosize pores (diameter of 30 nm)¹⁷⁸.

Both PPy and PANi are incorporated into the 3DOP carbon electrodes by electropolymerization of pyrrole and aniline, respectively, and the products are then examined as cathodes for supercapacitors in non-aqueous electrolytes^{179,180}. In addition to the current response due to the formation of an electric double layer, redox current responses were observed in the CV curves of these 3DOP composites due to doping/undoping of PF_6^- anions into/from PPy (or PANi). Through a combination of the redox capacity of the conductive polymers and the electric double-layer capacitance of the 3DOP carbon, large capacitances were observed for these 3DOP conducting polymer/carbon composites even at high current densities in organic electrolytes. Additionally, the incorporation of PANi and PPy into the macroporous carbon does not change the geometric volume of the carbon electrode at all, since the porosity of the 3DOP carbon is up to 70%. The incorporation of PPy and PANi into the macroporous carbon electrode is an effective method to increase the volumetric energy density of 3DOP electrodes.

Conclusions

This review highlights the recent progress in the development of 3DOP electrode materials for electrochemical energy storage. In the past decade, an increasing number of 3DOP electrode materials have been exploited for use in various electrochemical energy storage devices.

There is a strong relationship between 3DOP structures and electrochemical performance in various electrode materials. (1) Incorporating ordered porosity into anode and cathode materials for Li ion batteries is beneficial for fast ion and electron transport as well as robust integrity. For anode materials based on alloying and conversion reactions, volume expansion and poor electrical conductivity are serious problems that hinder the cycling stability and rate capability. On the one hand, the 3DOP structures can accommodate volume changes during lithiation and delithiation and alleviate the significant swelling and shrinkage, improving the structural stability of the electrodes. On the other hand, the high specific surface area and rich active sites of 3DOP structures very easily result in unwanted reductions and thick SEIs compared with those of their solid counterparts. (2) For electrode materials for ARLBs, the hierarchical 3D structures with well-defined pore dimensions and interconnected active sites are more effective for Li ion intercalation/deintercalation due to the shortened Li ion diffusion pathlength. Together with the high ionic conductivity of aqueous electrolytes, the ultrafast charge storage concept is demonstrated using OP cathodes in aqueous batteries. (3) In the cases of Li-O₂ and Li-S batteries, significant efforts have been devoted to hierarchical bimodal pore systems that contain ordered, tunable, and interconnected mesopores within the macroporous skeleton. Specifically, for the Li-S battery, the large volumetric expansion/shrinkage of sulfur during lithiation/delithiation can be almost eliminated owing to the extra free space to alleviate structural strain, thus achieving mechanical integrity and stability of the composite cathode. Of course, one key limitation of the low areal sulfur loading cannot be ignored, which may directly restrict the wide practical application of these materials. For the Li-O₂ battery, in addition to serving as catalysts to promote both the ORR and the OER, 3DOP cathodes will act as a substrate for the accommodation of discharge products and will facilitate the permeation of oxygen and Li ions with minimal diffusive resistance. There are still some other obstacles for Li-O₂ batteries, such as electrolytes; the unavoidable byproducts (such as LiOH and Li₂CO₃) from side reactions with the electrolyte may cover the 3DOP cathodes, thus blocking the pathways of the electrolytes and oxygen. Thus optimization of the properties and the reliability of each part of the Li-O₂ battery is necessary to improve the overall electrochemical performance. (4) Regarding supercapacitors, the power density is one of the most important parameters, and it determines how fast the energy can be discharged or charged. Its performance is highly dependent on the engineered pore structure. The ordered interconnected pore network of 3DOP allows easy electrolyte infiltration throughout the pores, resulting in the higher ionic

conductivity and high power density of EDLCs. For pseudocapacitors, the enlarged contact between the active 3DOP materials and the electrolyte will undoubtedly contribute to outstanding surface redox charge storage.

However, there are still several challenges in this booming field. (1) Although there are great academic achievements, 3DOP materials have not yet been utilized as commercial electrodes. Some problems could be associated with their low volumetric energy/capacity values and high-cost manufacturing methods. Currently, gravimetric specific energy and capacity are the most commonly used figure-of-merit in most reported 3DOP electrode materials. However, the related volumetric values are more important parameters for practical applications, as there is always limited space for electrochemical energy devices in portable electronic products. The design of 3DOP materials usually leads to a low tap density for electrodes and, consequently, a low volumetric capacity for the electrochemical energy storage device. An efficient way to compensate for the low volumetric capacity is to deposit high-performance active materials on a 3DOP substrate. (2) For 3DOP anode materials, the formation of the SEI layer on electrodes tends to consume more electrolytes because of the larger surface areas in 3DOP anode materials than in bulk materials. Control of the specific and stable SEI on the electrode/electrolyte surface area plays a critical role in achieving the high initial Coulombic efficiency and long cycle life of electrodes^{181,182}. (3) It is vital to further investigate new materials with OP structures, such as Mxene¹⁸³, 2D elemental materials¹⁸⁴, and metal-organic frameworks¹⁸⁵. It is also attractive to develop 3DOP materials with advantageous microstructures for other promising energy storage devices^{186–188}. (4) For fundamental understanding of the charge transport properties of 3DOP materials at the nanoscale, various in situ and ex situ characterization techniques are often required to better reveal microstructural evolutions during the charge–discharge process and to fully analyze the important structure–property relationships^{189–191}. For example, in situ stress and strain measurements of graphite-based electrodes during electrochemical cycling have been developed to calculate the electrochemical stiffness of the electrodes¹⁹¹. This new analytical tool and approach may offer new insights into 3DOP electrode materials. (5) The production of 3DOP electrode materials is largely demonstrated at the laboratory scale with high cost. Innovative synthesis methodologies with large-scale and low-cost production are always highly desirable¹⁹². Achieving industrial-scale production is a key next step. (6) The electrochemical behaviors of most reported 3DOP electrode materials mainly focus on the half-cell system. Obtaining high-performance full-cell devices for practical applications is still challenging because of the complex matching of the

cathode and anode materials in terms of rate capability and volumetric capacity.

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