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Three-Dimensional Nanoporous Fe$_2$O$_3$/Fe$_3$C-Graphene Heterogeneous Thin Films for Lithium-Ion Batteries

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ABSTRACT Three-dimensional self-organized nanoporous thin films integrated into a heterogeneous Fe$_2$O$_3$/Fe$_3$C-graphene structure were fabricated using chemical vapor deposition. Few-layer graphene coated on the nanoporous thin film was used as a conductive passivation layer, and Fe$_3$C was introduced to improve capacity retention and stability of the nanoporous layer. A possible interfacial lithium storage effect was anticipated to provide additional charge storage in the electrode. These nanoporous layers, when used as an anode in lithium-ion batteries, deliver greatly enhanced cyclability and rate capacity compared with pristine Fe$_2$O$_3$: a specific capacity of 356 μAh cm$^{-2}$ μm$^{-1}$ (3560 mAh cm$^{-2}$ or ~1118 mAh g$^{-1}$) obtained at a discharge current density of 50 μA cm$^{-2}$ (~0.17 C) with 88% retention after 100 cycles and 165 μAh cm$^{-2}$ μm$^{-1}$ (1650 mAh cm$^{-2}$ or ~518 mAh g$^{-1}$) obtained at a discharge current density of 1000 μA cm$^{-2}$ (~6.6 C) for 1000 cycles were achieved. Meanwhile an energy density of 294 μWh cm$^{-2}$ μm$^{-1}$ (2.94 Wh cm$^{-2}$ or ~924 Wh kg$^{-1}$) and power density of 584 μW cm$^{-2}$ μm$^{-1}$ (5.84 W cm$^{-2}$ or ~1834 W kg$^{-1}$) were also obtained, which may make these thin film anodes promising as a power supply for micro- or even nanosized portable electronic devices.

KEYWORDS: heterogeneous structure · nanoporous · lithium-ion battery · thin film · anode

To meet the growing demand for portable electronic devices, the development of advanced electrodes for micro- or even nanosized Li-ion batteries (LIBs) with high power and energy density, long-term cyclability, and minimized size,1–3 such as thin film electrodes, is under consideration.4–6 In principle, a self-organized metal oxide nanoporous layer (NPL) would be more useful than its three-dimensional (3-D) counterparts as thin film electrodes since they have higher surface areas.7–10 Furthermore, the 3-D open frameworks in the porous structure have the ability to facilitate ion and mass transport and release mechanical stress during Li-ion insertion/extraction cycling, and their superior thermal stability and increased heat transfer ability are factors favoring their use over commercial LIBs.11–14

Apart from optimizing LIB performance by structural modification, designing new materials to replace those used commercially is an area of intense research.15–18 Metal oxides, especially Fe$_2$O$_3$, have been extensively regarded as an attractive anode material due their low toxicity and cost coupled with their high theoretical capacity of 1005 mAh g$^{-1}$ based on a maximum uptake of 6Li/Fe$_2$O$_3$.19 However, one of the commonly encountered challenges in using metal oxides, including Fe$_2$O$_3$ for LIBs, is the severe volume change during Li-ion insertion/extraction cycling along with the detachment of active materials from the current collector. That generally leads to a large initial capacity loss (ICL), low rate capacity, and poor cyclability.20 Simply decreasing the crystallite size to the nanoscale is not enough to overcome these problems because the larger surface area exposed to the electrolyte and higher surface energy of the nanoscale material make it easier to decompose the electrolyte during the initial discharge/charge cycles.21 Recently, approaches to form passivation coatings such as core–shell structures and carbon...
coatings or reduce the charge transfer resistance have been designed to improve the cyclability and rate capacity.\textsuperscript{22,23} Furthermore, the use of heterogeneous composites of electrochemically active metal oxides with inactive metal nitrides achieved a synergistic improvement in the LIB performance.\textsuperscript{24} The electrochemically inactive components have high hardness to provide structural integrity to the active material, thereby improving capacity retention.\textsuperscript{25} However, the improvement of LIB performance by forming Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}C heterogeneous structures, especially integrated in self-organized 3-D nanostructures covered by few-layer graphene, has not yet been reported. In the present work, a Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}C-graphene heterogeneous structure was fabricated into a 3-D nanoporous thin film; the following advantages are expected from this advanced anode material for LIBs: (1) the 3-D nanoporous structure provides open channels for lithium-ion transport and storage; (2) conductive graphene layers introduced into the heterogeneous structure should enhance the electrical conductivity of the electrode; (3) the electrochemically inactive Fe\textsubscript{3}C phase improves the capacity retention owing to its high hardness; (4) the electrochemically active Fe\textsubscript{2}O\textsubscript{3} phase with a high theoretical capacity should form a heterogeneous interface with Fe\textsubscript{3}C that provides the ability to store additional charge.\textsuperscript{26} Therefore, the Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}C-graphene heterogeneous thin film with a 3-D nanoporous structure could reduce the ICL, improve the rate capacity and the cycling stability of Fe\textsubscript{2}O\textsubscript{3}.

Chemical vapor deposition (CVD) is generally considered an appropriate method to fabricate microdevices, thin films, and high-quality two-dimensional layers such as graphene, MoS\textsubscript{2}, and BN.\textsuperscript{27,28} Even though some aspects such as high cost and low yield rate need to improve before using this technique industrially, CVD is a fundamentally excellent method to fabricate thin film electrodes, especially when high-quality graphene layers are needed.\textsuperscript{29} It is known that metallic iron is a common catalyst in growing graphene layers or carbon nanotubes due to the high carbon solubility under CVD conditions.\textsuperscript{30–32} However, it is still a challenge to form few-layer graphene (FLG) by CVD on the surface of a self-organized Fe\textsubscript{2}O\textsubscript{3} NPL without the destruction of their well-defined nanostructures, and there has been no report on the CVD growth and energy storage applications of an FLG-coated heterogeneous Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}C NPL. Here, we report the growth of FLG on an Fe\textsubscript{2}O\textsubscript{3} NPL, simultaneously forming a heterogeneous Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}C structure, by low-temperature CVD (for the fabrication process, see the Experimental Section and Figure S1).

RESULTS AND DISCUSSION

An FLG-coated Fe\textsubscript{2}O\textsubscript{3} NPL (C–Fe\textsubscript{2}O\textsubscript{3} NPL) was fabricated by CVD from an anodically self-organized Fe\textsubscript{2}O\textsubscript{3} NPL (average diameter of the channels \(\sim40\) nm and length \(\sim1.2\) \(\mu\)m; see Figure 1a and Figure S2). The temperature used for CVD growth of FLG here (550 \(^\circ\)C) is much lower than conventionally used (\(\sim850\) \(^\circ\)C with iron particles as catalyst) due to the nanoporous layers that enable faster diffusion and better dissolution of carbon through their ordered channels (Figure S2).\textsuperscript{31} Proper postannealing of the C–Fe\textsubscript{2}O\textsubscript{3} NPL (reoxidized sample, ReO C–Fe\textsubscript{2}O\textsubscript{3} NPL) in air at 300 \(^\circ\)C for 1 h was performed to partially convert inactive Fe\textsubscript{3}C to electrochemically active Fe\textsubscript{2}O\textsubscript{3}. The obtained ReO C–Fe\textsubscript{2}O\textsubscript{3} NPL maintained its self-organized nanoporous structure (Figure 1b) with slightly increased wall thickness due to the grain growth and new phase formation, whereas attempts to elevate the temperature used...

Figure 1. Microstructure of the nanoporous layer (NPL). (a and b) SEM images of the NPL before and after forming the heterogeneous structure, respectively. (c) Top-view TEM image of the heterogeneous NPL with the ordered porous structure. (d) Cross-sectional TEM image of the heterogeneous NPL with channel-like morphology. (e) HRTEM image of the heterogeneous structure with FLG shell (highlighted by the arrow). The HRTEM image in (e) was rotated and taken from the circled region marked in (d). (f–l) Atomic-resolution STEM images of the junction of the Fe\textsubscript{2}O\textsubscript{3}/Fe\textsubscript{3}C interface boundary (highlighted by the arrow in (f) with the Fe\textsubscript{3}C in a [010] zone axis). (f and h) High angle annular dark field images; (g and i) bright field images. Fast Fourier transform (FFT) was performed on the regions marked by white dashed boxes with scale bars being 10 nm\textsuperscript{1}.
in CVD led to collapse of the ordered nanoporous structure (Figure S3). Samples annealed at lower temperatures show only more graphite-like structure instead of FLG (Figure S4), and more disordered defects were formed in dissolution/C0 precipitation processes (for the potential mechanism of formation of the heterogeneous structure, see Figure S5 and the Supporting Information). TEM observations of a ReO C–Fe2O3 NPL also clearly show that the ordered nanoporous structure from the top (Figure 1c) and channel-like morphology from the cross-section (Figure 1d) were well maintained. The three- to four-layer graphene shell coated on the surface of the NPL was identified from the typical 0.34 nm d-spacing that corresponds to the C(002) plane as indicated by the lattice fringes (Figure 1e and Figure S6a,b). Fe2O3 (110) lattice fringes with a d-spacing of ~0.25 nm and Fe2C (100) planes with lattice fringes of ~0.51 nm are also indentified from the NPL, which indicates the formation of the heterogeneous structure. To investigate the junction between Fe2C and Fe3C, atomic-resolution scanning TEM (STEM) observation was performed on the heterogeneous NPL (Figure 1f–i and Figure S6c,d). It is apparent that Fe2C is continuously grown with Fe3C under the coating of FLG, and it forms a distinct interface boundary. The formation of an Fe2O3/Fe3C heterogeneous NPL with well-bonded interfaces appears to occur without loss of the FLG coating (Figure 1i). To investigate the porous structure of the NPL thin film, Brunauer–Emmett–Teller (BET) analysis by adsorption/desorption of nitrogen gas was performed. The data were used to determine the Barrett–Joyner–Halender (BJH) pore size. Nanoscale pores were distributed mainly in a range from 2 to 40 nm (Figure S7).

From the Raman spectra of the samples (Figure 2a), typical bands for Fe2O3 at 219, 283, 398, 491, and 597 cm⁻¹, as well as graphene bands at 1580 and 2700 cm⁻¹, were indentified. From the intensity ratio of the G/2D bands (1.046), three- to four-layer graphene was formed, which is consistent with the HRTEM observations. However, a difference was apparent in the 1300 to 1400 cm⁻¹ range of the samples before and after annealing. The Raman band at ~1322 cm⁻¹ was from magnon scattering in Fe2O3, whereas the band at 1350 cm⁻¹ was assigned to the dissolved carbon (graphite) in the Fe3C phase. From the X-ray diffraction (XRD) patterns (Figure 2b) the diffraction peaks for Fe3C (PDF #00-035-0772) along with a carbon peak (PDF #04-014-0362) at ~26° are identified. After postannealing treatment on the sample in air, Fe2O3 (α-phase, PDF #00-033-0664) is also distinguished, indicating the formation of a polycrystalline Fe2O3/Fe3C heterogeneous structure. The observed Fe peaks in both samples were from the iron foils that were used as substrates to grow the thin films. A semiquantitative estimate from the XRD pattern indicates the heterogeneous thin film is composed of ~9 wt % carbon, ~24 wt % Fe2O3, and ~67 wt % Fe3C. X-ray photoelectron spectroscopy (XPS) shows clear changes in Fe 2p and O 1s spectra (Figure 2c,d and Figure S8), which indicates the conversion from Fe3C to Fe2O3 by postannealing.

To evaluate the LIB performance of the nanoporous thin film anode without overestimation, the specific capacity, energy density, and power density were calculated by area capacity (divided by thin film geometrical area and thickness), volumetric capacity, and gravimetric capacity. Cyclic voltammograms (CVs) were
taken of the samples within a potential window between 0.01 and 3 V (vs Li/Li⁺) at a scan rate of 0.5 mV s⁻¹ to investigate the electrochemical reactions that occur during the initial two Li-ion insertion/extraction cycles (Figure 3a). By assigning the cathodic and anodic peaks to the redox reactions (see Supporting Information), Li-ion insertion/extraction reactions are identified: Fe₂O₃ + 6 Li⁺ + 6e⁻ → 2 Fe + 3 Li₂O (lithium-rich phase).¹⁹

Galvanostatic discharge/charge tests were performed within a potential window from 0.01 to 3 V (vs Li/Li⁺), a window conventionally used for Fe₂O₃ anodes,¹⁹,²⁰ at a current density of 50 μA cm⁻² for 10 cycles (Figure 3b) and other current densities up to 1000 μA cm⁻² (Figure 3c; the correspondence between applied current densities and C-rates is listed in Table S1). It was found that the capacity of the pristine Fe₂O₃ NPL showed a continuous decay throughout the tests and a rapid capacity drop at high current densities: 275 μAh cm⁻² μm⁻¹ (2750 mAh cm⁻³ or ~864 mA h g⁻¹) at 50 μA cm⁻² and 62 μAh cm⁻² μm⁻¹ (620 mAh cm⁻³ or ~195 mA h g⁻¹) at 1000 μA cm⁻², indicating a large ICL and poor rate performance. After coating with graphene, C/Fe₂O₃ NPLs deliver a capacity of 105 μAh cm⁻² μm⁻¹ (1050 mAh cm⁻³ or ~330 mA h g⁻¹) with 90% retention, whereas after postannealing ReO C/Fe₂O₃ NPLs have an enhanced capacity of 356 μAh cm⁻² μm⁻¹ (3560 mAh cm⁻³ or ~1118 mA h g⁻¹) with 88% retention after 10 discharge/charge cycles at 50 μA cm⁻². Greatly improved electrical conductivity was achieved by the passivation of Fe₂O₃ NPL through a conductive FLG protective shell. The C/Fe₂O₃ NPL shows an improved rate performance, with a capacity of 58 μAh cm⁻² μm⁻¹ (580 mAh cm⁻³ or ~182 mA h g⁻¹) at a current density of 1000 μA cm⁻², and it delivers an increased capacity of 109 μAh cm⁻² μm⁻¹ (1090 mAh cm⁻³ or ~343 mA h g⁻¹) when the current is reduced back to 50 μA cm⁻². After postannealing, ReO C–Fe₂O₃ NPL demonstrated a greatly improved rate performance with a capacity of
160 μAh cm⁻² μm⁻¹ (1600 mAh cm⁻³ or ~503 mAh g⁻¹) at 1000 μA cm⁻² as well as a recovered capacity of 315 μAh cm⁻² μm⁻¹ (3150 mAh cm⁻³ or ~990 mAh g⁻¹) when the current goes back to 50 μA cm⁻². The advantages of FLG coating can also be assessed by analysis of the changes in discharge profiles during cycling and the contribution from different lithium storage processes (Figure S9). The enhanced capacity of the ReO₃ contribution from di(29).

More interesting is that the nanoporous layers for most of the state-of-the-art 3-D thin capacities obtained in this work are larger than those advantages of FLG coating can also be assessed by analysis of the changes in discharge profiles during cycling and the contribution from different lithium storage processes (Figure S9). The enhanced capacity of the ReO₃ contribution from di(29).

Moreover, a possible interfacial lithium storage effect introduced by the formation of the Fe₂O₃/Fe₃C interface may also contribute to the higher capacity. One of the common causes of the ICL is from the side reaction of electrolyte decomposition at the electrochemically active surface of the materials. This becomes even more pronounced in nanoscale materials due to their high electrochemically active surface area. By partially converting the electrochemically active Fe₂O₃ phase to the Fe₃C phase, as well as by forming graphene on the surface as a passivation layer, the electrochemically active area exposed to the electrolyte is decreased. This reduces the ICL. Additionally, the hard Fe₃C in the heterogeneous structure maintains its structural integrity. This minimizes detachment between the active materials and the current collector, further reducing the ICL. Considering the thickness of the film used for the tests here (~1.2 μm), the capacities obtained in this work are larger than those for most of the state-of-the-art 3-D thin film batteries (Table S2). More interesting is that the nanoporous layers are located in the high power/energy region of the Ragone plot (Figure 3d), which indicates the superior power supply capability of these thin film electrodes. Especially, the ReO₃ – Fe₂O₃ NPL shows an energy density up to 294 μWh cm⁻² μm⁻¹ (2.94 Wh cm⁻³ or ~924 Wh kg⁻¹) and a power density of 584 μW cm⁻² μm⁻¹ (5.84 W cm⁻³ or ~1834 W kg⁻¹), which demonstrates more than an order of magnitude enhanced energy storage performance compared to most published values for 3-D thin film electrodes. Long-term cyclability tests (Figure 3e) show greatly improved capacity retention from 17% (Fe₂O₃ NPL) to 88% (ReO₃ – Fe₂O₃ NPL) at 50 μA cm⁻² for 100 cycles. Especially for the cycling tests at current density of 1000 μA cm⁻², the capacity retention is improved from 42% (Fe₂O₃ NPL) after 100 cycles to 90% (ReO₃ – Fe₂O₃ NPL) after 1000 cycles (Figure 3f).

The corresponding Coulombic efficiency plots for Figure 3e,f are provided in Figure S10a,b. It is evident that the initial Coulombic efficiency was enhanced due to the reduced ICL from forming heterogeneous structures. For the C – Fe₂O₃ NPL, the capacity even increases by 30% and 43%, at 50 and 1000 μA cm⁻², respectively.

The gradually increased capacity during discharge/charge cycling has also been found in other nanoscale or porous materials; however there is still no clear explanation. Considering the 3-D nanoporous structure of the Fe₂O₃/Fe₃C-graphene heterogeneous thin film, possible reasons for the gradually increased capacity are due to either the reduced nanoparticle size (by an electrochemical milling effect), which could expose more electrochemically active sites to the electrolyte, or gradual activation of the active materials in the porous structure during the cycling test. The stabilized capacities delivered over long-term cycling (normalized to the first discharge capacity) are better than other forms of Fe₂O₃ reported recently, such as graphene oxide/Fe₂O₃ composite (only 60% retention after 50 cycles at ~0.1 C) and Fe₂O₃ hollow spheres (less than 60% retention after 100 cycles at ~0.2 C). The greatly improved capacity retention, as we expected, is attributed to the hard Fe₃C in the heterogeneous structure that maintains the structural integrity and buffers the severe volume change during Li-ion insertion/extraction cycling.

Although there is no benefit in decreasing the potential hysteresis of the Fe₂O₃ NPL, intrinsic to conversion systems, a much decreased ICL greatly improved rate performance, and cycling stability are achieved by forming an Fe₂O₃/Fe₃C-graphene heterogeneous structure. Moreover, any attempts to convert more of the Fe₃C back to Fe₂O₃ by postannealing the C – Fe₂O₃ NPL at 300 °C for 6 h lowered the capacity retention and lowered the initial Coulombic efficiency (Figure S11).

Nyquist plots (Figure 4a) for the samples measured at the open-circuit potential illustrate a depressed semicircle from high to medium frequency followed by a straight sloping line at the low-frequency end. The correspondence between frequency-dependent impedance and equivalent circuit elements in this work can be logically distinguished after fitting to the equivalent circuit (Figure S12). It is evident that charge transfer resistance (Rct) is reduced from 275.9 ± 7.8 Ω (Fe₂O₃ NPL) to 135.4 ± 4.8 Ω (C – Fe₂O₃ NPL) and 117.3 ± 6.9 Ω (ReO₃ – Fe₂O₃ NPL) after coating the graphene layers. To demonstrate the electrode kinetics of the samples during Li-ion insertion/extraction reactions, impedance spectra were also measured during discharge/charge cycling (Figure S13). The variations of Rct and Zw (Warburg impedance) at different electrode potentials are illustrated in Figure 4b,c. Rct of the heterogeneous nanoporous anodes at the same electrode potentials in the discharge and charge process show similar values, an indication of reversible reactions occurring on the electrodes, whereas the significant deviation observed in the pristine Fe₂O₃ NPL represents irreversible reactions that are taking place. Moreover, both Rct and Zw of the heterogeneous anodes are substantially reduced when compared to the Fe₂O₃ NPL throughout the discharge/charge cycling. The reduced Rct and Zw indicate that by forming a heterogeneous structure charge-transfer and
Li-ion diffusion kinetics are improved in the NPL. By measuring the cathodic/anodic peak current changes vs the scan rates in CVs, the rate-controlling step of electrode reactions can be identified through calculating the $b$-values (Figure S14), which were 0.5 for the diffusion-controlled process and 1 for the surface-controlled process. As shown in Figure 4d, the cathodic and anodic $b$-values of the pristine Fe$_2$O$_3$ NPL are 0.54 and 0.51, respectively, which are close to diffusion-controlled rates. Hence, lithium insertion and diffusion are difficult in the pristine Fe$_2$O$_3$ NPL, whereas after FLG coating and formation of the heterogeneous structure, the $b$-values are more capacitive: 0.68 (cathodic) and 0.71 (anodic) for the C–Fe$_2$O$_3$ NPL; 0.74 (cathodic) and 0.79 (anodic) for the ReO C–Fe$_2$O$_3$ NPL. After forming the heterogeneous structure, the graphene coating in the NPL plays an important role in enhancing the electrical conductivity, which reduces the electrode polarization during discharge/charge at high current densities and makes the nanoporous electrode show more capacitive than diffusion-controlled behavior. A possible interfacial lithium storage effect in the oxide/carbide heterogeneous structure is likely responsible for the improved performance of the nanoporous thin film anode (see Figure 4e and Supporting Information).

**CONCLUSION**

In summary, a self-organized Fe$_2$O$_3$/Fe$_3$C-graphene heterogeneous thin film anode was successfully fabricated by CVD growth. The electrode kinetics during
Li-ion insertion/extraction cycling was greatly improved by forming a graphene protective shell and heterogeneous structure in the thin film. Fe3C was introduced to maintain the structural integrity and improve capacity retention during cycling. Possible interfacial lithium storage at the heterogeneous interface by charge separation in space charge layers may also contribute to the enhanced capacity. By this approach a new 3-D heterogeneous nanoporous thin film anode with prominent energy storage capability, i.e., capacity of 356 μAh cm⁻² μm⁻¹ (3560 mAh cm⁻² or ~1118 mAh g⁻¹) at 50 μA cm⁻² (0.17 C), 160 μAh cm⁻² μm⁻¹ (1600 mAh cm⁻² or ~503 mAh g⁻¹) at 1000 μA cm⁻² (6.6 C), energy density of 294 μWh cm⁻² μm⁻¹ (2.94 Wh cm⁻³ or ~924 Wh kg⁻¹), and power density of 584 μW cm⁻² μm⁻¹ (5.84 W cm⁻³ or ~1834 W kg⁻¹), is achieved. Cycling tests show that the advanced nanoporous thin film anodes maintain their good performance at different current densities. Taken together, these properties are a harbinger of important advances in thin-film rechargeable batteries.

**EXPERIMENTAL SECTION**

**Fabrication.** Iron foils (0.05 mm, 99.5%, Advent Materials, UK) were used as substrates and were cleaned and degreased by sonication in 2-propanol (≥99.7%, Sigma-Aldrich, USA) and acetone (≥99.9%, Sigma-Aldrich, USA) before use. Electrochemical anodic treatment was carried out at room temperature in a solution of 0.1 M NH4F (≥98%, Sigma-Aldrich, USA) with 1 M deionized water in ethylene glycol (Fisher Scientific, USA) to grow iron oxide nanoporous layers on the iron substrates. Anodization was conducted at 40 V for 20 min in a two-electrode setup with platinum foil as a counter electrode. To grow thicker layers, extended growth duration is suggested. After that, the samples were immersed in ethanol overnight to remove the residual organic electrolyte in the nanoporous layer followed by annealing at 300 °C for 3 h in air. To form the heterogeneous structure, a CVD apparatus was used. The samples were partially reduced at 300 °C for 30 min in a reducing atmosphere composed of H2 (200 standard cubic centimeters per minute, sccm)/Ar (200 sccm) at 6.4 Torr followed by CVD growth at 550 °C for 15 min in H2 (200 sccm)/C2H2 (2 sccm) at 6.4 Torr. During the CVD growth process, H2/O was supplied by bubbling H2 throughout degassed water at 200 sccm to remove the amorphous carbon. After that, the nanoporous layers were postannealed at 300 °C for 1 h in air.

**Characterization.** A JEOL 6500F scanning electron microscope (SEM) was used to investigate the morphology of the samples. A JEOL 2010 high-resolution transmission electron microscope (HRTEM) was used to observe the morphologies and lattice fringes of the samples. Atomic-resolution scanning TEM images were recorded by a probe Cs-corrected JEOL JEM-ARM 200F operated at 80 kV. All STEM images were acquired with an exposure time of 31 μs dwell time and a convergence angle of 50 mrad and outer collection angle of 22 pA. High-angle annular dark field images were acquired with an inner collection angle of 50 mrad with an exposure time of 31 μs dwell time and a convergence angle of 50 mrad and outer collection angle of 22 pA. Bright field STEM images were acquired with a collection angle of 11 mrad. The Raman spectra were recorded with a Renishaw Raman Re6001 scope (Renishaw Inc., USA) using a 514 nm excitation argon laser. Pore distribution of the NPL was investigated by the BET technique (Quantachrome Autosorb-3B, USA) by nitrogen adsorption and desorption at 77 K. The specific surface area and the total pore volume were calculated by the Brunauer-Emmett-Teller (BET) model.

**Electrochemical Measurement.** The nanoporous layers on iron foil were used directly as working electrodes without adding additives such as binder, current collector, or conducting carbon. The geometrical area of the electrode was 1 cm in diameter (~0.785 cm²), and the mass of the electrode was found to be ~0.3 mg (measured based on the entire films) for each piece. Coin cells (CR2032, MITS Corporation, USA) were assembled in argon-filled glovebox (Vac NEXUS, USA) with both moisture and oxygen content <1.5 ppm, using Li-metal foil (0.38 mm thick; 99.9%, Sigma-Aldrich, USA) as both the counter and reference electrodes, 1 M LiPF6 in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1 vol %, MITS Corporation, USA) as the electrolyte, and polypropylene foil (Celgard, USA) as the separator. After assembling, the cells were aged for 12 h before the electrochemical measurements. The discharge/charge cycling tests were performed on a multi-channel battery analyzer (Land, CT2001A). The CVs and EIS measurements were carried out with an electrochemical analyzer (CH 608D, CH Instruments, USA). The CVs were measured at a scan rate of 0.5 mV s⁻¹ in a potential window from 0.01 to 3 V (vs Li/Li⁺). The EIS were carried out on fresh cells at open-circuit potentials with a frequency range from 10⁶ to 10⁻² Hz with an ac signal amplitude of 5 mV. To investigate the electrode kinetics of the samples, the EIS were also carried out at different potentials (0.01, 0.1, 1.5, 2.5, and 3 V) during discharge/charge cycling. The impedance data were simulated by Z-view software (version 2.2, Scribner Associates, USA) to obtain the fitted Nyquist plots and simulated values for each equivalent circuit element.

**Conflict of Interest:** The authors declare no competing financial interest.

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**Supporting Information Available:** Experimental details and more discussions. This material is available free of charge via the Internet at http://pubs.acs.org.

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