

Full paper

Electro-plating and stripping behavior on lithium metal electrode with ordered three-dimensional structure

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ABSTRACT

The growth of lithium dendrite is one of the major problems that need to be solved before the application of metallic lithium anode to commercial rechargeable lithium batteries. The three-dimensional host framework with well-defined architecture acting as current collector has been proved to be able to regulate the lithium plating/stripping behavior and thus to suppress the dendrite growth. In this work, a surface-patterned lithium electrode (spLi) with hexagonal arrays of micro-sized holes has been successfully fabricated by micro-fabrication methods. By employing scanning electron microscope (SEM) and optical microscope, the lithium plating/stripping behavior on spLi was directly visualized. The electrochemical performances of the spLi electrode were evaluated in Li symmetric cell and Li|LiCoO₂ half-cell using carbonate ester and ether based electrolyte. It is found that the geometry of the hole has a strong influence on the lithium plating/stripping behavior, and the deposited lithium prefers to fill in the micro-sized holes due to the favorable kinetics. The hole structure preserves throughout battery cycling with no obvious dendrite growth and surface roughness after multiple plating/stripping cycles. These phenomena can well explain the excellent electrochemical performances of the surface-patterned lithium electrode (spLi) compared with bare lithium electrode. This research also demonstrates that lithium metal can serve as stable framework to host lithium plating/stripping, nevertheless, efforts are still needed to further optimize the architecture to achieve more evenly lithium plating/stripping.

1. Introduction

Lithium metal is an ideal anode material for rechargeable batteries due to the highest theoretical capacity (3860 mAh g⁻¹ and 2061 mAh cm⁻³) and lowest electrochemical potential (−3.040 V *versus* standard hydrogen electrode). Owing to the urgent need of high energy density batteries, the application of lithium metal anode to rechargeable batteries, such as rechargeable Li metal batteries [1,2], Li-S batteries [3] and Li-air [4] batteries, has attracted intense interest recently. However, lithium metal electrode suffers from two major problems which prevent its direct use in commercial rechargeable batteries. One is the low coulombic efficiency (CE) due to the high chemical reactivity between lithium metal and electrolyte, and the other is the growth of lithium dendrite due to non-uniform lithium plating/stripping. Generally, the former results in capacity fade of the assembled battery during prolonged cycling, while the latter leads to dramatic failure or even safety hazards [5]. Considerable research efforts have been devoted to overcome these problems in the past decades, and several

experimental methods and strategies have been proposed including: (1) using electrolyte additives [6–11] to improve the stability and uniformity of the solid electrolyte interface (SEI), and thus to prevent the continuous reaction between lithium metal and electrolyte; (2) using inorganic-compound-coated separator [12] or solid electrolyte [13–15] with sufficient mechanical strength to physically prevent the growth of lithium dendrite; (3) modifying the composition or architecture [16] of the lithium electrodes (*i.e.* lithium alloy electrodes [17] and lithium composite electrodes [18]) to suppress the growth of lithium dendrite; (4) applying specific charge-discharge protocols [19–21] to guide the uniform lithium plating/stripping, and *etc.* Meanwhile, a significant amount of work has been carried out to simulate, model [22] and observe the growth of lithium dendrite [23], in order to gain fundamental understanding about how to overcome such detrimental issues. In addition, operando observation of lithium dendrite growth, by using optical microscope [24], SEM [25] and TEM [26,27], has also been conducted by different research groups.

After the lengthy development, it is well recognized that composite

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lithium metal electrode or lithium metal electrode with three-dimensional (3D) host structure [28] has practical values for future applications. The composite and 3D lithium metal electrode have remarkable advantages comparing with the pure flat metallic lithium electrode. Firstly, the 3D host structure can provide void space for lithium plating, which can well reduce the side effect from huge volume change normally occurred during battery cycling. Secondly, the effective area for lithium plating/stripping increases dramatically, and therefore the effective areal current density decreases and the dendrite growth can be suppressed. Additionally, the architecture of host framework can be well designed to guide the uniform lithium plating/stripping. Various kinds of composite [29] and 3D electrodes [30], with different materials and different architectures, have been reported recently. For example, carbonaceous materials, including graphene family [31–33], carbon nanotubes (CNTs) [34], graphitized carbon fibers [35–37] and hollow carbon sphere [38], have been employed as host framework to accommodate lithium storage. Volume change associated with lithium plating/stripping as well as dendrite growth have been largely suppressed and the cycle performances of the electrodes have been greatly enhanced. Because lithium ion can be intercalated into carbon materials, the composite or 3D lithium electrodes using carbon materials as host framework can accommodate additional lithium other than that being stored in the void space. Host materials, those inert to metallic lithium, have also been reported to greatly improve the cycle performances of composite lithium electrodes, such as 3D Cu current collector [39–42], foam Ni [43,44], organic [45] and composite materials [46]. In order to improve the wetting properties between metallic lithium and host materials, surface-modified host materials have also been developed [30,47], showing superior electrochemical performances during lithium plating/stripping. Recently, numerous research groups have reported their studies on lithium storage behavior in host material with highly ordered 3D structure [48]. Due to the uniformity in large scale, fluctuation and heterogeneous reaction can be eliminated, leading to smooth lithium plating/stripping across the lithium electrode. The ordered structure can also be an ideal model to simulate or predict the lithium plating/stripping behavior. For examples, Cui and coworkers reported the use of well-arranged hollow carbon nanospheres on Cu substrate [38] and confined polyimide nanoscale channels [49] to accommodate the lithium plating, as well as to stabilize the SEI layer and homogenize lithium ion flux. Guo et al. [48] reported the regulated lithium plating/stripping behavior in 3D Cu current collector with ordered vertically-aligned microchannels. Park et al. investigated the lithium plating/stripping mechanism in spLi electrode by combining *ex situ* SEM measurement and finite element simulation [50].

In this work, we report the micro-fabrication of pure lithium electrode with modified surface constructed with hexagonal arrays of micro-sized holes. The employ of ordered hole as 3D host framework can improve the overall energy density of the lithium electrode, due to the use of low density lithium as host material. The lithium plating/stripping behavior was investigated by *ex situ* SEM and *in situ* optical microscope measurement. The electrochemical performances of surface-modified and unmodified lithium metal electrode were compared in symmetric Li|Li cell and Li|LiCoO₂ half-cell using carbonate and ether based electrolyte respectively.

2. Materials & methods

2.1. Fabrication of surface-patterned lithium metal anode

Micro-fabrication techniques including ultraviolet (UV) exposure (MA6, Karl Süss), inductively coupled plasma-reactive ion etching (ICP-RIE, PlasmaPro100Cobra, Oxford) and nano imprint (Eitre-3, Obducat) were mainly used. Firstly, a target pattern was obtained by UV exposure apparatus with the designed optical reticle. Positive photoresist (S1813) was spin-coated (4000r/min) on a cleaned Si wafer before UV exposure

process. After development and fixing, the Si wafer with the patterned photoresist was etched at $-110\text{ }^{\circ}\text{C}$ in ICP-RIE chamber. The etching gas was a mixture of oxygen and sulfur hexafluoride. Different etching rate and thus the different 3D structure can be achieved by changing the gas flow ratio, gas pressure and etching power. Then the hole structure on Si wafer was transferred to soft intermediate polymer (Intermediate Polymer Stamp, IPS, not react with lithium) by nano imprint. Finally, a lithium foil (200 μm , China Energy Lithium Co., Ltd.) with size fitted with IPS were seal-packed in aluminum plastic film and pressed by nano imprint. After mold unloading, lithium metal with ordered holes was fabricated successfully.

2.2. Cell assembly

The CR2032 coin cells were used to assemble the Li|Li symmetric cell and LiCoO₂|Li half-cell. LiCoO₂ cathode electrode was prepared by coating the slurry on Al foil with a thickness adjustable scraper. Strict mass stoichiometric ratio of the slurry is LiCoO₂: Super P: polyvinylidene fluoride (PVDF) = 8:1:1. The area capacity of LiCoO₂ cathode (0.234 mAh cm⁻², 1.67 mg cm⁻²) is matched with the capacity of lithium to fill in the holes in the spLi metal anode. Carbonate ester electrolyte composed of 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) and ether based electrolyte composed of 1 M LiTFSI in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume) were used as electrolyte respectively. The cells were assembled in a glove-box filled with argon gas (H₂O and O₂ < 0.1 ppm). A double-side Al₂O₃ coated polypropylene (PP) separator (25 μm) was purchased from Best New Energy Technology CO., LTD.

2.3. Electrochemical characterizations

Cells were tested at room temperature by Land BA2100A Battery Test System (Wuhan, China). LiCoO₂|Li cells were cycled in the voltage range of 3–4.2 V. The Li|Li symmetric cells were cycled by limiting capacity which was determined by the theoretical capacity of the holes (0.234 mAh cm⁻²). Electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical workstation (ZENNIUM, ZAHNER) in the frequency range from 4 MHz to 100 mHz with a perturbation voltage of 5 mV. The samples for the cross-section microscopic observations were prepared by using cross-section polisher (IB-19510CP, JEOL) to cut samples at about 0 $^{\circ}\text{C}$ with liquid nitrogen cooling. The morphology of lithium surface and cross section were recorded by scanning electron microscope (SEM, HITACHI S4800). All samples were transferred with a self-designed transfer box filled with high purity argon gas.

2.4. In situ optical measurements

A self-designed *in situ* cell was used for the *in situ* optical measurement. The *in situ* cell was constructed with spLi electrode as working electrode, lithium belt as counter electrode and Cu as current collector, and sealed with two pieces of glass slides with O ring in between. Optical microscope (DFC50, Leica Microsystems Ltd.), placed in the glove-box, was used to conduct the *in situ* optical measurement. The total magnification is 500 with an eye lens of a magnification of 10 multiple an objective lens of a magnification of 50. A long-focus objective lens was chosen, which enables enough operating distance.

3. Results and discussion

The surface patterned lithium electrode (spLi) was prepared by micro-fabrication and nano-imprint methods. The schematic illustration of the fabrication process is shown in Fig. 1a and the experimental details are described in the experimental section. A silicon template with ordered cylinder-shaped holes (inset of Fig. 1b) was prepared by a

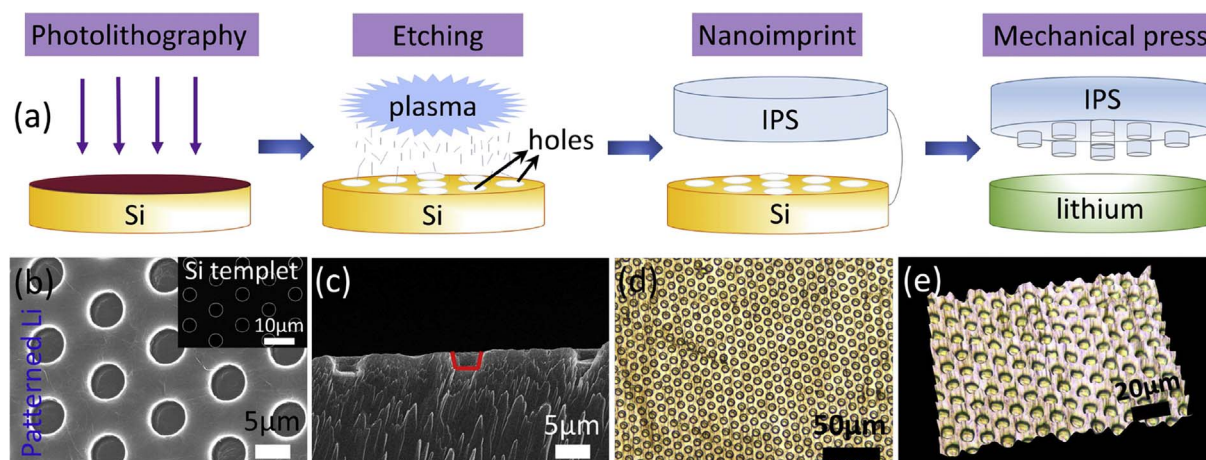


Fig. 1. Preparation of surface-patterned lithium (spLi) metal electrodes and their morphologies. (a) Schematic illustration of the main steps for fabrication of spLi metal electrode. SEM images of spLi electrodes: (b) top view and (c) cross-section view. (d) Optical image of spLi metal electrode with large field of view and (e) enlarged view in three dimension.

micro-fabrication method, and then was used to transfer the pattern to the lithium electrode. However, the template can not be used directly to transfer the pattern to lithium electrode because of the reactivity between silicon template and lithium metal, and therefore a soft intermediate polymer material (Intermediate Polymer Stamp, IPS) was introduced as an intermediate template. By using nano-imprint method, the pattern on silicon template was firstly transferred to IPS, forming a regular array of rods. Then, by pressing the IPS on flat lithium electrode, the spLi electrode with micro-sized hexagonal-packed holes was successfully prepared. Fig. 1b exhibits the top-view scanning electron microscope (SEM) image of the spLi electrode, where highly-ordered hexagonal-packed hole pattern can be observed. The depth of the hole is about 5 μm , as shown in the cross-section SEM image as shown in Fig. 1c. Such micro-fabrication and nano-imprint method can achieve large-scale fabrication of spLi electrode with high uniformity, as confirmed by the optical images with large field of view (Fig. 1d and e). The spLi electrodes with different pore size and depth were also fabricated (Fig. S1), however, they will not be discussed in detail in the main text due to the limited space of the paper.

Since the lithium plating/stripping behavior greatly affects the electrochemical performances of the lithium electrodes, how the surface structure regulates the lithium plating/stripping on patterned lithium electrode has to be studied at first. On the basis of the Fick's law and Poisson equation, the lithium diffusion is influenced by the concentration gradient of Li^+ and the distribution of the electric field. The distribution of the electric field is related to the curvature of conductor surface in the electrostatic equilibrium condition. The larger curvature of the conductor surface is, the stronger the electric field becomes. In principle, metallic electro-deposition behavior is controlled by both electric field $\mathbf{E}$ and divergence of $\mathbf{E}$ [22]: $\Delta V = -\nabla \cdot \mathbf{E} = -\rho/\epsilon\epsilon_0 = -e(z_c C_c - z_a C_a)/\epsilon\epsilon_0$, $\frac{\partial C_c}{\partial t} = D_c \Delta C_c - \mu_c \mathbf{E} \cdot \nabla C_c - \mu_c C_c \nabla \cdot \mathbf{E}$. For the current instance of spLi electrode with cylinder-shaped holes, no matter upon discharging or charging, the electric field shows stronger gradient distribution along edge of the holes (schematically shown in Fig. 2a), where lithium plating/stripping is expected to take place at first. This effect can also be explained by the famous “lightning rod theory”: the density of charge significantly increases at the point of surface with large curvature, namely electrical charge tends to accumulate at sharp convexity and vanish at sharp concavity on the surface of an isolated conductor [51]. Therefore, the lithium ion may not deposit uniformly on the spLi metal anode over the discharge process.

Ex situ SEM measurements were performed to observe the lithium plating/stripping behavior on spLi electrode. Fig. 2 shows the SEM images of spLi electrodes after lithium deposition (0.117 mA cm^{-2} , fully discharged in spLi-Li cell). The theoretical capacity of the spLi electrode is calculated based on the amount of lithium that could be

stored in total void space (volume of the hole) of the spLi electrode ($0.234 \text{ mAh cm}^{-2}$). It can be seen from Fig. 2c that the surface of the electrode remains smooth after lithium plating and no lithium dendrite can be observed on top of the flat surface. The white spots on the SEM images can be ascribed to Al_2O_3 particles which are detached from the Al_2O_3 coated polypropylene (PP) separator, as confirmed by energy dispersive spectroscopy (EDS) measurement (Fig. S2). The cross-section SEM image focusing on a single hole is presented in Fig. 2d. It can be seen that the top part of the hole is mostly filled while the bottom part of the hole remains empty. This phenomenon agrees well with the prediction as schematically shown in Fig. 2b. In addition, the total amount of lithium deposited into the holes increases with the depth of discharge (Fig. S3). It is found that the holes can be filled in completely when increasing the specific surface capacity to some extent. It can be inferred that the lithium ions prefer to deposit on the top edge of the hole at the beginning of the plating process and then the deposited lithium will be “pushed” into inner part of the hole upon further lithium plating (discharging). The freshly deposited lithium on the top edge of the holes reacts with the electrolyte, forming solid electrolyte interface (SEI) film rich in fluoride as detected by EDS (Fig. 2g and h). The hole is not fully filled and semi-quantitative analysis (Fig. 2e and f) indicates that the hole area (on surface) is reduced by 57.06% of the original size after fully lithium plating. Such surface pore filling ratio reduces to an even smaller value of 47.35% for spLi electrode with larger hole size of $50 \mu\text{m}$ under the same discharge condition (0.117 mA cm^{-2}), and the growth of lithium dendrites on the surface of the pores can be clearly seen (Fig. S1 and S4). Overall, the hole size and shape has a great influence on the lithium deposition behavior, and rational design of the host framework architecture could regulate the uniform lithium plating/stripping process. It is worth noting that the lithium can not fully fill in the holes at fully discharged state for spLi electrodes with all kinds of hole sizes, indicating that portion of the lithium is deposited on top of the flat surface of the electrodes. Moreover, it is found that less lithium can be filled in the pores when applying a higher current density (Fig. S5). The counter electrode was also examined by SEM (lithium stripping at first during discharge). Lithium stripping, initiated from the top edge of the holes, (Fig. S5) can also be observed as expected.

In situ observation of lithium plating/stripping was further conducted by using optical microscope. Optical microscopy is a useful tool to observe the Li dendrite and it has been widely used as an *in situ* method to observe and record the lithium plating/stripping processes in real time under working conditions. Although the resolution of optical microscope is not high as SEM, still it could easily and instantaneously distinguish the surface morphological change and dendrite formation. A self-designed transparent cell was used for the *in situ* experiment. The

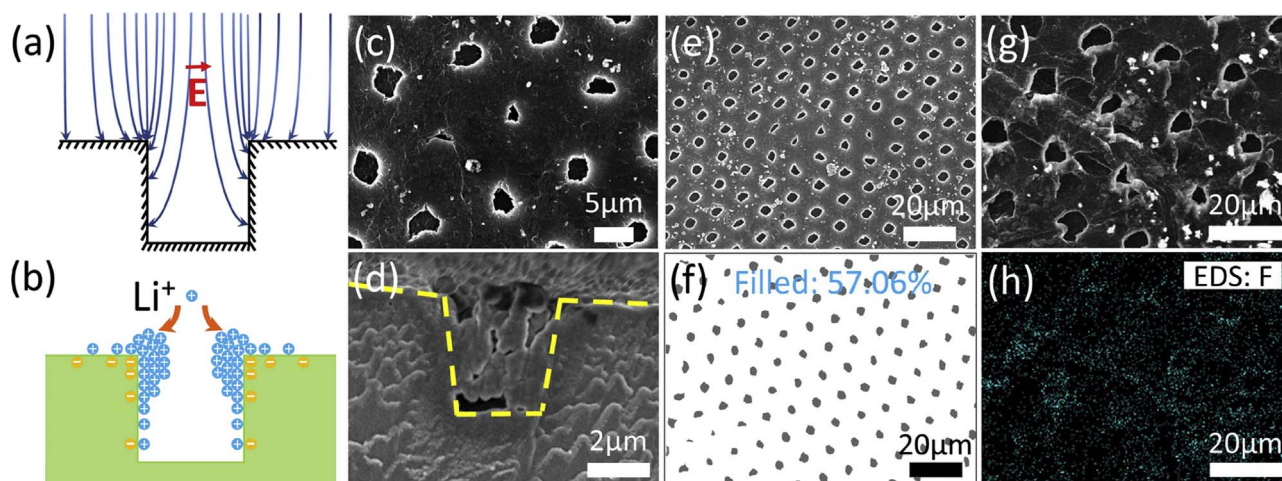


Fig. 2. Schematic illustrations of (a) electric field distribution and (b) Li^+ flow on conductor surface under electrostatic equilibrium condition. (c) Top and (d) cross-section view of spLi metal electrode after initial lithium plating (Li-spLi symmetric cell). (e) and (f) Semi-quantitative statistic analysis of lithium filling ratio in hole structure after lithium plating. (g) and (h) EDS analysis of spLi metal electrode harvested from spLi-spLi symmetric cell after lithium plating. Fluorine is found to be rich at the edge of the hole.

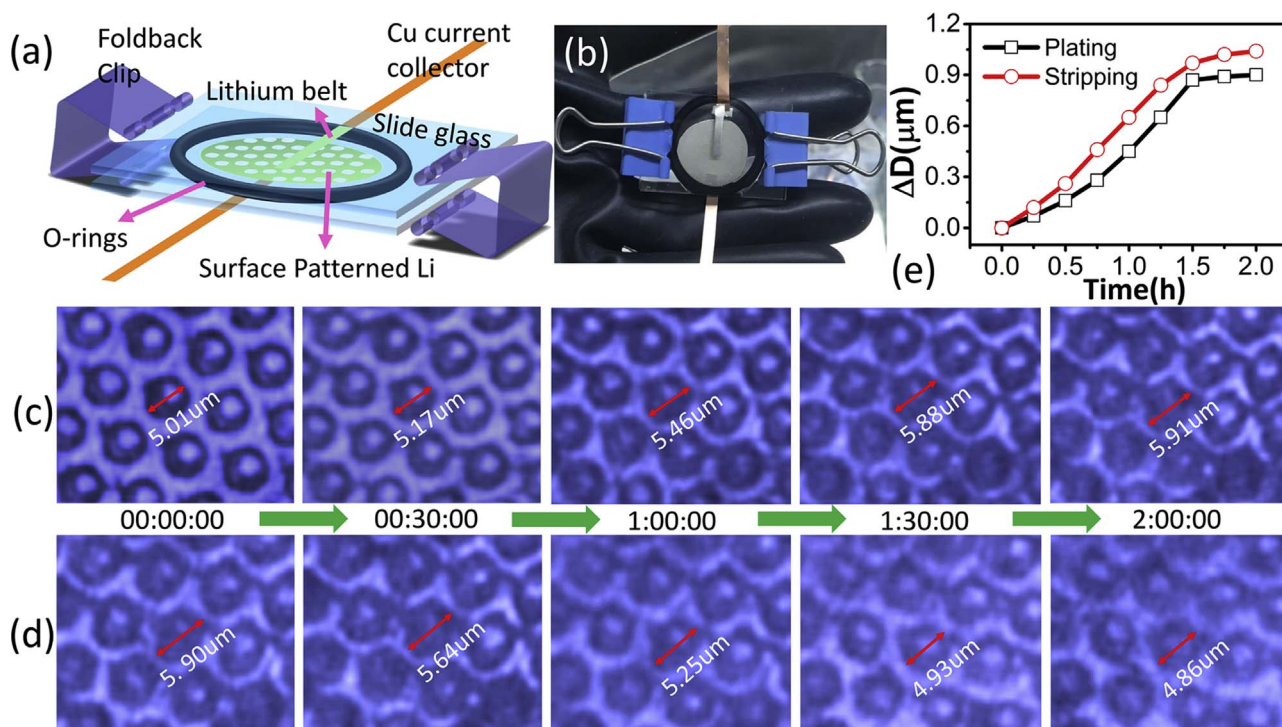


Fig. 3. *In situ* morphological observation of spLi electrode with optical microscope. (a) Scheme and (b) real optical image of *in situ* cell. Tracking the evolution of the size of the hole during (c) lithium plating and (d) lithium stripping. (e) Semi-quantitative analysis of the diameter change of the hole as a function of reaction time.

configuration of the cell is schematically presented in Fig. 3a and the photo of the real *in situ* cell is displayed in Fig. 3b. A transparent glass slide was used as cell holder which allowed the direct observation under optical microscope. A total magnification of 500 times can be achieved for the current optical setup by using a high resolution telephoto lens. The evolution of the surface morphology of the patterned lithium electrode was recorded, and the representative optical images captured at different discharge/charge states are shown in Fig. 3c and d. The change of the contrast in the hole area on the images (from bright to dark and blurred during discharge and vice versa during charge) indicates that the lithium plating/stripping mainly takes place at the inside of the holes. The outer peripheral diameter of the hole on surface also changes as a function of the reaction time. However, as indicated by the cross-section SEM image, the inner diameter of the hole doesn't show notable change. The dynamic change of the outer

peripheral diameter of the hole on surface (surface plating/stripping) can be ascribed to the continuous accumulation/consumption of lithium at the top edge of the hole during lithium plating/stripping processes. Semi-quantitative analysis of the diameter change (ΔD) as a function of reaction time was performed and the result is shown in Fig. 3e. Because the surface plating/stripping is affected by dynamics of lithium plating/stripping in holes, SEI formation/deposition and other unidentified factors, the surface stripping process does not proceed in a fully reversed manner as the surface plating process, therefore the “ ΔD versus Time” plots do not completely overlap for lithium plating and stripping. Overall, the lithium plating/stripping occurs at both inside of the hole and on the flat surface of the spLi electrode. The structure of the hole preserves after lithium plating and stripping process, and no obvious lithium dendrite growth and surface roughness change can be observed.

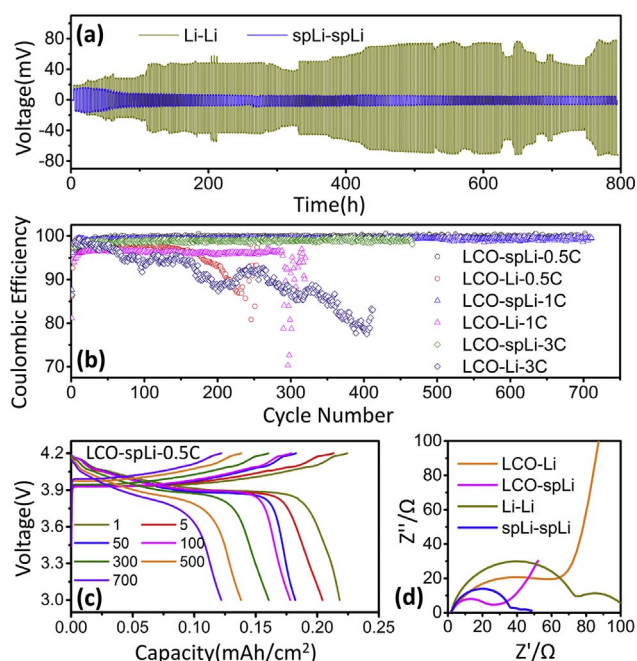


Fig. 4. Comparison of the electrochemical performances of spLi electrode with bare lithium metal electrode. (a) Polarization curves of spLi|spLi and Li|Li symmetric cells for the first 200 cycles. (b) Coulombic efficiency of LiCoO₂|spLi and LiCoO₂|Li half-cells cycled at 0.5 C, 1 C and 3 C rate. (c) Charge-discharge curves of LiCoO₂|spLi at different cycles at 0.5 C rate. (d) Electrochemical impedance spectra of LiCoO₂|spLi and LiCoO₂|Li half-cells, Li|Li and spLi|spLi symmetric cells. The spLi electrode shows much improved electrochemical performances in terms of improved coulombic efficiency and decreased polarization resistance.

The electrochemical performances of the spLi electrode were investigated with Li symmetric cells and LiCoO₂|Li half-cells. For comparison, Li symmetric cell and LiCoO₂|Li half-cell using bare lithium electrode were also investigated. Fig. 4a displays the potential-time profile of Li|spLi symmetric cell obtained during galvanostatic cycling with a constant current (0.117 mA cm^{-2}). The symmetric cell employing spLi electrode shows a lower polarization value compared to

that using bare lithium electrode, implying a lower Li⁺ and e⁻ transportation resistance in the spLi electrode during operation (Fig. 4d). The effect of surface-pattern on the electrochemical performances of Li half-cells was also investigated. The coulombic efficiencies of LiCoO₂|Li half-cells with spLi electrode and pure lithium electrode upon electrochemical cycling are compared (Fig. 4b). The LiCoO₂|spLi half-cells reveal high and stable coulombic efficiencies at all charge-discharge rates (0.5 C, 1 C and 3 C), indicating a uniform lithium plating/stripping process during the charge and discharge process. In contrast, the LiCoO₂|Li half-cells with bare lithium electrode present remarkable failure after hundreds of charge-discharge cycles, which is likely due to the surface roughening (*i.e.* dendrite formation) and thus the deterioration of the interfacial properties. Fig. 4c shows the capacity retention of LiCoO₂|spLi half-cell cycled at a rate of 0.5 C. It can retain 55% of the initial capacity after 700 cycles and the polarization does not increase remarkably until 500 cycles. The reduced polarization and improved cycle performances of the spLi electrode are well consistent with the small overall impedance of the cell using spLi electrode (Fig. 4d). Impedance of Li|spLi cell upon electrochemical cycling was also measured (Fig. S6a), and a lower impedance of the cell with ether based electrolyte was observed (Fig. S6b).

The electrochemical performances of the spLi electrode were also evaluated in Li|spLi symmetric cells with carbonate ester and ether based electrolytes. Polarization profiles were recorded and the morphology of the electrode after multiple lithium plating/stripping cycles were studied. Both Li|spLi cells show excellent cycle performances (Fig. S7), especially for the cell using ether based electrolyte. The representative polarization profiles at 2nd, 5th, 10th, 20th and 50th cycle are shown in Fig. 5. The Li|spLi cell using carbonate ester based electrolyte exhibits a slight increase in the polarization value, while Li|spLi cell using ether based electrolyte shows an increase and then decrease in the polarization value. After stabilization for 10 cycles, the Li|spLi cell with carbonate ester based electrolyte shows larger polarization compared to that with ether based electrolyte. This can be ascribed to the different SEI formed in ester carbonate and ether based electrolyte. The structure of the hole preserves very well for spLi electrode cycled within both ester carbonate and ether based electrolyte, implying that the host framework is stable for lithium plating/stripping. Slight difference in surface morphology can still be observed, which is the

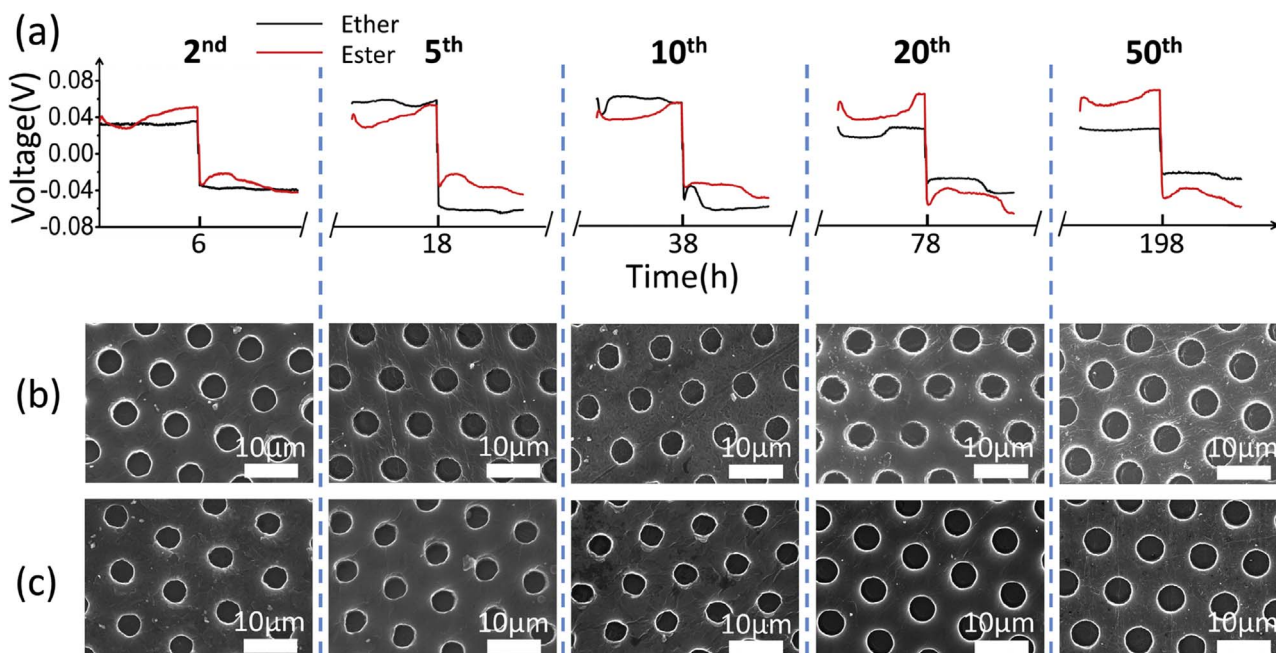


Fig. 5. Morphology of spLi metal electrode after different charge-discharge cycles. (a) Representative charge-discharge voltage profiles. The spLi metal electrodes were cycled in (b) carbonate ester and (c) ether based electrolyte respectively, and harvested after lithium stripping.

electrode cycled in ether based electrolyte has a neater and denser surface.

Overall, the geometry or shape of the host framework can regulate the lithium plating and stripping behavior. For the current instance of the spLi electrode, although the host framework (hole) can be well preserved after multiple cycles, it cannot be completely filled with lithium to achieve the full utilization for each lithium plating process. Therefore, further optimization of the patterned structure (density and geometry of the hole) will be necessary to maximum the lithium storage capacity as well as to obtain stable cycle performances. As it is revealed that the electrolytes also play an important role in determining the electrochemical performances of the surface modified patterned electrode, the reactivity of the freshly deposited and stripped lithium with organic liquid electrolyte should not be overlooked. Comprehensive strategies have to be considered for the implementation of the patterned lithium metal electrode in future.

4. Conclusion

A surface-patterned lithium electrode with hexagonal arrays of cylinder-shaped holes to host lithium plating/stripping was successfully fabricated by micro-fabrication and nano-imprint method. The lithium plating/stripping behavior was investigated by *in situ* morphological observations with optical microscope, in conjunction with *ex situ* SEM measurements. The deposited lithium is found to mainly fill in the inside of the hole and the geometry of hole has a great influence on the plating/stripping behavior. The structure of the spLi electrode is well preserved after multiple charge-discharge cycles, and thus the spLi electrode shows significantly reduced polarization as well as greatly improved cycle performances in Li|Li symmetric and Li|LiCoO₂ half-cell with both carbonate ester and ether based electrolyte. From a practical point of view, the spLi electrode, with the host framework composing of pure lithium, has remarkable advantage in energy density over the lithium electrode with host framework composing of heavier elements. The fabrication approach introduced in this work also promises a low-cost and highly reproducible large-scale manufacturing of spLi electrode, as the templet can be utilized repeatedly. The preferred deposition of the lithium into the hole structure revealed in this work also inspires us the design of lithium and lithium composite electrodes with micropores. Further efforts are being made to optimize the host framework (configuration of the pattern) and hole structure (geometry) to achieve higher specific capacity of lithium storage with stable cycle performances.

Acknowledgement

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2018.01.019>.

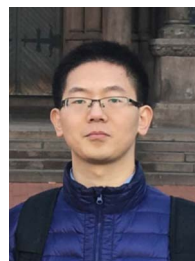
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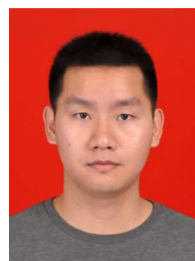
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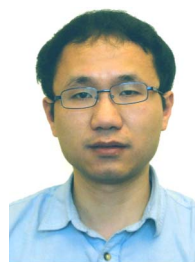
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