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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|$LiCoO_2$ 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 perfers 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 columbic 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 channles [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|$LiCoO_2$ 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 °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 $LiCoO_2$|Li half-cell. $LiCoO_2$ cathode electrode was prepared by coating the slurry on Al foil with a thickness adjustable scraper. Strict mass stoichiometric ratio of the slurry is $LiCoO_2$: Super P: polyvinylidene fluoride (PVDF) = 8:1:1. The area capacity of $LiCoO_2$ 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 $LiPF_6$ 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 (H_2O and O_2 < 0.1 ppm). A double-side Al_2O_3 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). $LiCoO_2$|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 °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