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A strategy of selective and dendrite-free lithium deposition for lithium batteries

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ABSTRACT

Lithium (Li) dendrite alleviation via three-dimensional (3D) structured current collectors has been well studied for Li metal-based batteries. Here we demonstrate that a hollow carbon nanofiber with proper interior to exterior radius ratio can enable Li-ions to deposit on the inner surface of the channels selectively due to the drifting effect from the structural stresses. Based on this principle, a lotus-root like structure is further designed to realize a dendrite-free hybrid Li anode with a high Li loading capability. The lotus-root like carbon nanofiber (LCNF) anode, with being coated by a lithiated Nafion (LNafion) layer as artificial solid electrolyte interface (SEI), achieves a capacity of $> 3600 \text{ mA h g}_{\text{carbon}}^{-1}$ for Li deposition/stripping along with a greatly improved CE. The fundamental understanding of the relation between the Li deposition and the matrix geometry will provide new insight for the rational design of the hybrid Li anode in the Li metal-based battery system.

1. Introduction

The increasing fossil fuel shortage and environmental pollution have aroused an urgent demand for renewable energy technology and this boosts the rapid development of the rechargeable batteries across the world [1–4]. Among all the possible secondary battery systems, Li metal-based batteries have attracted increasing interest in recent decades due to the unapproachable theoretical specific capacity (3860 mA h g^{-1}) and low redox potential (-3.04 V vs. NHE) of Li [5]. Since the 1970s, countless efforts have been devoted to developing the secondary batteries with Li metal as anode, but all these attempts encounter a seemingly impassable obstacle: the inherent dendritic Li growth and low Coulombic efficiency (CE) during repeated Li stripping/plating process [6]. The Li dendrite growth may even result in “dead Li” and short circuiting of the battery that may lead to disastrous failures [7,8]. On the other hand, the reactions between Li metal and the solvent molecules form a layer of insoluble solid-electrolyte interphase (SEI) on the surface [9], which can passivate the Li anode from further corrosion. However, the SEI film in-situ formed on Li surface is not flexible enough to accommodate the large morphological variation caused by the volume change and the dendrite formation and it is likely cracked during the electrode process. The exposed Li surface will react

with the electrolyte, leading to not only low CE but also exhaustion of electrolyte [10].

For the past decades, many research works have been conducted to tackle the bottleneck. The basic strategies include modifying the surface SEI film via incorporation of elastic components by electrolyte optimization [11] or direct surface modification [12,13], adding CsPF_6 or RbPF_6 as electrolyte additive to improve the uniformity of Li-ion deposition [14,15], doping with elements like N, As, Al, Mg, Ca, etc. to decrease the reactivity of Li metal [16] or utilizing high-modulus polymer solid electrolytes or ceramic solid electrolyte to suppress the growth of Li dendrite by mechanical suppression [17–20]. All of these methods mentioned above indeed have some positive effects on dendrite inhibition and/or CE improvement. However, most of the electrolyte additives will continuously consume during cycles, so the effect of restraining the growth of Li dendrite will fade gradually [21]. For the solid state electrolyte, the Li metal is reported to be highly stable at elevated temperature in the PEO system, which has to work at an elevated temperature of $60 \text{ }^\circ\text{C}$, to obtain a decent conductivity ($10^{-3} \text{ S cm}^{-1}$) [22].

More recently, several 3D structured conductors were reported as current collectors for Li anode, including Si-coated carbon nanofibers [23], 3D-nickel foam host [24] and 3D carbonized wood [25] to

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suppress the dendrite growth. In general, the 3D current collectors facilitate the Li deposition in two ways: (1) To provide sufficient space to accommodate the volume change during Li deposition/stripping process, equivalent to constructing a host for Li deposition artificially; (2) to provide abundant active sites due to the large specific area to remarkably decrease the true current density of the anode [26,27]. For most previously reported 3D carbon nanofibers used as current collectors for Li anode, the capacity is severely limited because Li ions can only deposit on the outer surface of the carbon fibers, meanwhile, the side reactions between Li metal and the electrolyte can still happen since the deposited Li is exposed to the electrolyte directly [23–27].

2. Experimental section

2.1. Preparation of LCNF, LCNF@Nafion and Li-LCNF@LNafion

LCNF was prepared as reported [28]. Firstly, polystyrene (PS) (0.4, 1.0 and 1.6 g for different samples) and polyacrylonitrile (PAN) (2.0 g) were added to 20 ml N, N-dimethylformamide (NMP) under magnetic stirring for 12 h at 80 °C. Then the solution was sprayed at a speed of 0.8 ml h⁻¹ and a voltage of 15 kV with a distance between the syringe and the collecting tin foil fixed at 15 cm. The obtained precursor for LCNF was collected and dried at 80 °C overnight. The LCNF film was obtained by further heating the precursor in a tube furnace at 800 °C for 3 h with a heating rate of 3 °C min⁻¹ under argon atmosphere. The areal density of LCNF was ~2.2 mg cm⁻². As contrast sample, the solid carbon nanofibers (SCNF) were prepared via the same route as LCNF but without PS addition in the precursor solution. The LCNF film was cut into several squares (~0.5 cm²). These squares were completely dipped into the Nafion solution (5 wt% in a mixture of lower aliphatic alcohols and water) and held for 10 s. The ‘wet’ pieces were then placed under infrared baked lights till they became dry. The process of infiltration was repeated for three times to achieve Nafion coating with appropriate thickness. To obtain the lithiated Nafion-coated LCNF (LCNF@LNafion) [29], the LCNF@Nafion was carried out in aqueous 1 mol l⁻¹ LiOH solution at 80 °C for 12 h under vigorous stirring. The obtained film was then washed in deionized water at 80 °C for 1 h to remove the remaining salt. After vacuum drying at 80 °C for 12 h, the resulted LCNF@LNafion was used to assemble coin cells for electrochemical measurements.

2.2. Preparation of hollow carbon nanofibers with interior (R₀) to exterior (R₁) radius ratios of 5:10, 8:10

The hollow carbon nanofibers were prepared as reported [30]. Typically, 1 g polyacrylonitrile (PAN) was added to 10 ml N, N-dimethylformamide (NMP) under magnetic stirring for 12 h at 80 °C as the outer fluid and the inner fluid was mineral oil. The sprayed speed for the outer (PAN) and inner solution (mineral oil) were set at 0.6 and 0.2 ml h⁻¹ (R₀: R₁ = 5:10) or at 0.6 and 0.4 ml h⁻¹ (R₀:R₁ = 8:10). A high voltage of 18 kV was supplied and the distance between the syringe and the collecting tin foil was fixed at 15 cm. The collected electropun nanofibers were soaked in n-octane overnight to remove the inner mineral oil. Then the collected nanofibers were calcined at 800 °C for 3 h with a heating rate of 3 °C min⁻¹ under argon atmosphere in a tube furnace to obtain the hollow carbon nanofibers with different radius ratios.

2.3. Preparation of “1 mA h LiFePO₄/1.8 mA h Li-Cu” cells

The “1 mA h LiFePO₄/1.8 mA h Li-Cu” cell was assembled via prelithiation treatment. In a typical process, CR2023 coin cell was assembled with Cu foil as working electrode and Li foil as counter electrode in argon-filled glove box. The electrolyte was 1 mol l⁻¹ LiTFSI in DOL/DME (1:1 by volume). Then the coin cell was discharged on a LAND electrochemical testing system at current density of 1 mA cm⁻²

for 1.8 h. After that, the Cu foil with 1.8 mA h cm⁻² Li deposited was taken out and was used as the anode in “1 mA h LiFePO₄/1.8 mA h Li-Cu” cell. The cathode was prepared with 80 wt% commercial LiFePO₄ powder, 10 wt% carbon black, 10 wt% polyvinylidene fluoride (PVDF). For battery cycling with a limited amount of Li, LiFePO₄ electrodes with areal capacities of ~1 mA h cm⁻² were used. Celgard 2325 (25 μm PP/PE/PP) was used as the separator in this system.

2.4. Characterizations

The morphology and microstructure of the samples were studied with a field-emission scanning electron microscope (FSEM, SIRION200) and a field-emission transmission electron microscopy (FTEM, FEI Tecnai G2 F30). The element distribution was measured on the energy dispersive X-ray spectroscopy (EDX) attached to the FEI Tecnai G2 F30. The material phase information was analyzed using an X-ray diffractometer (PANalytical X'pert PRO-DY2198, Holland) with Cu Kα radiation.

2.5. Electrochemical measurements

CR 2023 coin cells were assembled with LCNF@LNafion composite as working electrode and Li foil as counter electrode in an argon-filled glove box with water and oxygen contents less than 0.1 ppm. The electrolyte was 1 mol l⁻¹ LiTFSI in DOL/DME (1:1 by volume, 50 μl). The galvanostatic deposition/stripping behavior of the Li-LCNF anode was measured on a LAND electrochemical testing system at room temperature at various current densities. The deposition/stripping tests were performed at two conditions: (1) to test the CE, 5 mA h cm⁻² of Li metal was deposited on the LCNF substrate at various current densities and then stripped till the potential reached 0.5 V vs. Li/Li⁺; (2) to test the stability of the anode, the same amount Li was deposited on and stripped from the anode by controlling charge-discharge time. Li/Li symmetric cells were assembled with Li metal used as both working and counter electrodes.

3. Results and discussion

Herein, we propose a new strategy to realize selective and dendrite-free Li deposition via the hollow structured current collector matrix. So far, two mechanisms are proposed to explain Li deposition: charge transfer and Li solid diffusion [31]. Firstly, Li plating occurs as soon as applied potential reaches plating potential (so-called ‘charge transfer limitation’) and metallic Li forms on carbon surfaces [32]. Plated Li may either dissolve into the electrolyte or intercalate into carbon wires under certain conditions [33]. If the Li concentration of the electrolyte is sufficiently large, the former process will hardly occur and the Li diffusion inside carbon becomes a critical point that determine whether or not plated Li will remain (so-called ‘solid diffusion limitation’). Based on this understanding, we carried out a series of chemo-mechanical simulation with different particle geometry and current density. The details of the model can be found in the supplementary. As indicated by the simulation (Fig. 1A), the drifting effect from the stresses to the diffusion process drives the Li atom away from the compression region, so Li diffusion inside the particle is thus slowed down. Correspondingly, the Li atoms tend to deposit on the interior surface. So we can control Li deposition via matrix geometry design. Fig. 1B-D exhibit the deposition behavior of Li in hollow carbon nanofibers with different interior to exterior radius ratios (R₀:R₁), which verifies the simulation conclusion: The Li deposition preferentially occurs on the interior surface with the decrease of the R₀:R₁ (Fig. 1B-D). When R₀:R₁ is ~8:10, Li deposits on the outer and inner surface simultaneously (Fig. 1B); When R₀:R₁ decreases, for instance, R₀:R₁~5:10, the plated Li on the outer surface decreases, and that on the inner surface should increase since the total amount of the plated Li stays the same (Fig. 1C); When the ratio of R₀:R₁ further reduces to ~1:10, we can see that almost all the Li

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