



Three-dimensional pie-like current collectors for dendrite-free lithium metal anodes



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ABSTRACT

Lithium (Li) metal possesses very high specific capacity and low electrochemical potential, which shows great advantages to be used in next generation rechargeable Li metal batteries (LMBs). However, poor cyclability of Li metal anodes caused by inhomogeneous and uncontrolled Li deposition hinders the practical applications of rechargeable LMBs. Here, in order to effectively suppress Li dendrite growth without degrading the specific capacity, a three-dimensional (3D) pie-like porous current collector was prepared based on copper nanowires (CuNWs) and graphene (GE). The inter-spaces inside the CuNWs framework efficiently accommodate Li deposition. Meanwhile, the GE layer wrapped outside CuNWs functions as flexible interfacial protective layer that could protect extra Li deposition. Furthermore, the GE shell can also decelerate the oxidation of CuNWs in ambient atmosphere. The CuNWs@GE current collectors demonstrated several merits to achieve better Li metal anodes with significantly improved Coulombic efficiency and cyclability for rechargeable LMBs.

1. Introduction

Lithium metal has an extremely high theoretical capacity (3860 mA h g⁻¹), a low gravimetric density (0.534 g cm⁻³) and the lowest electrochemical potential (−3.04 V vs. the standard hydrogen electrode) among all other candidates [1,2]. Thus, Li metal is the ultimate choice as anodes for LMBs. However, poor cycling efficiency and safety issues caused by Li dendrite formation prevent the use Li metal anodes in commercial lithium batteries [3,4]. Although lithium-ion (Li-ion) batteries have been commercialized successfully in the last few decades since Sony and Asahi Kasei replaced Li metal with graphite as the anode to avoid Li dendrite formation, the inherent limited theoretical energy density of Li-ion batteries cannot meet the growing demand for long-range electric vehicles (EVs) [1,5,6]. Therefore, it is now widely accepted that developing alternative energy storage systems beyond the horizon of Li-ion batteries is urgently needed to satisfy the requirement of these emerging markets [4,7,8]. Recently, growing research efforts have been devoted to improving the understanding on Li metal chemistry toward better Li metal anodes [9–21]. Meanwhile, lithium-air (Li-air) batteries and lithium-sulfur (Li-S) batteries demonstrate great potentials to significantly increase the energy densities of rechargeable LMBs, both of which are being intensively studied for next-generation energy-storage applications

and Li metal anode is indispensable for these two battery systems [13,22–29].

The major challenges for the development of high-performance Li-metal batteries are the serious safety concerns and poor cyclability, which are mainly caused by the formation of Li dendrites on the surface of Li metal anodes [4]. During the Li deposition process (charging process), the Li ions (Li⁺) receive electrons and deposit solid Li metal on the surface of the Li metal anode. Protrusions and impurities on the anode surface can create an inhomogeneous surface environment, which leads to non-uniform current density and uneven Li deposition rates. This finally results in Li to be deposited in dendritic form, which is well known to be the main reason of short-circuit hazards that caused explosive accidents [30,31]. During the Li stripping process (discharging process), the root of the Li dendrite is apt to receive electrons and dissolve earlier. These dendrites easily break off and become isolated from the Li anode, forming so-called ‘dead Li’, which aggravates the loss of available Li metal [13]. Furthermore, the reactions between Li metal and electrolytes is known to form a natural SEI as a passivation layer on the Li anode surface [32,33]. However, the infinite volumetric change of the Li anodes during Li stripping/plating induces significant mechanical instability in the relatively fragile SEI, leading to the formation of cracks. The recurring breakdown/repairment of SEI during charge/discharge processes upon cycling leads to the contin-

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uous consumption of Li metal and electrolytes, which severely decreases Coulombic efficiency [34,35].

A series of approaches have been proposed to suppress Li dendrite growth since 1960s [36]. Previous studies have demonstrated that the current density of the electrodes during Li deposition is a crucial factor to regulate Li dendrite formation. A lower local current density can delay initial dendrite growth and reduce the growth rate as well. In order to reduce the electrode current density, some conductive and non-conductive 3D microstructures have been proven to be useful for suppressing the growth of Li dendrites and enhancing the cyclabilities [13,23,37–39]. Recently, the re-design of 3D current collectors, such as 3D copper structures with submicron skeletons, free-standing copper nanowire networks and porous copper foils have exhibited high Coulombic efficiencies and good cyclabilities [13,23,37,40]. In addition to its excellent conductivity, copper material deserves more attentions because of its wide availability [41].

Another effective method to tune the growth behavior of Li dendrites is to generate a stable SEI on the Li metal surface as a passivation layer. Although SEI can form spontaneously during cycling, its mechanical instability can hardly protect Li metal due to the infinite volume change during Li plating/stripping [32,33]. Therefore, the high quality of the SEI layer is essential to stabilize the operation of Li metal anodes with high efficiency [21]. The ideal SEI layer needs to be chemically stable in a highly reducing environment, mechanically strong and flexible to accommodate the volumetric change during Li plating/stripping. Comparing with intrinsic SEI layer, interfacial layers such as graphene layers, hexagonal boron nitride (h-BN) layers, interconnected hollow carbon nanosphere layers, and graphite/graphene layers, show better mechanical strength in protecting Li metal anodes [15,42,43].

Herein, we developed a porous current collector with 3D pie-like structure of copper nanowires wrapped by GE, in which Li deposition can be accommodated inside the porous framework and be protected by a GE-based interfacial layer. The GE shell was chosen as the protective layer because of its excellent mechanical feature to suppress Li dendrite as well as its high electrical conductivity that can effectively reduce the interfacial resistance. Meanwhile, the GE nanosheets prepared via a hydrogen reduction process have defects that allows Li^+ diffusion through the GE protective layer. This work provided an alternative solution to control Li dendrite growth without degrading the specific capacity of Li metal anodes through combining a copper nanowire porous microstructure with a graphene-based interfacial protective layer.

2. Experimental section

2.1. Synthesis of copper nanowires

Copper nanowires were synthesized through a facile aqueous reduction route at low temperatures in an oil bath [44]. In particular, NaOH (200 mL, 15 M) solution was first prepared and kept in oil bath at 60 °C for 20 min. Then, $\text{Cu}(\text{NO}_3)_2$ (10 mL, 0.1 M), ethylenediamine (EDA) (1.6 mL, 99 wt%) and hydrazine (500 μL , 35 wt%) aqueous solutions were successively added into the NaOH solution. The mixed solution was kept stirring to form a homogenous solution and heated at 60 °C for 2 h. Gradually, the yielded CuNWs floated onto the surface of the solution. The CuNWs were collected and washed with deionized water and ethanol 3 times through centrifugation (4500 rpm for 5 min). The CuNWs were stored in 25 ml of ethanol solution with 5 ml added hydrazine (3 wt%) aqueous solution at room temperature to minimize the oxidation.

2.2. Fabrication of 3D pie-like CuNWs@GE current collector

CuNWs current collector were first prepared. In detail, 2 mL of graphene oxide (GO) solution (2 mg mL^{-1}) was filtered under vacuum

to form a thin film on a filter membrane (Millipore) within a filter funnel. Then, 25 mL CuNWs dispersed suspension (containing about 120 mg CuNWs) was first sonicated for 5 min and gently poured into the filter funnel. After standing for 6 h, the supernatant was decanted away. A CuNWs paper (~ 35 mm in diameter) was formed after the solvent evaporated totally. The CuNWs paper was peeled off from the GO film and punched into disks (12 mm in diameter). The obtained CuNWs current collector were first annealed under 5% H_2 in Ar atmosphere at 300 °C for 2 h to enhance the mechanical strength. The areal weight of CuNWs membrane is about 8.14 mg cm^{-2} .

The 3D pie-like CuNWs@GE current collector was synthesized using as-prepared CuNWs current collector and graphene oxide (GO) solution. Typically, 60 μL GO solution (0.2 mg mL^{-1}) was dropped on the annealed CuNWs current collector and dried at 60 °C for 2 h. The other side of the CuNWs current collector was also covered by GO through the same process. Finally, the CuNWs@GE current collector was obtained after annealing under 5% H_2 in Ar atmosphere at 600 °C for 1 h.

2.3. Characterization

A field emission scanning electron microscope (FESEM, Zeiss Supra 55 VP) was employed to observe morphology changes of different current collectors before and after Li deposition. Transmission electron microscopy (TEM, Field-emission CM200, Fei) was used to identify the structure changes of the GE from the CuNWs@GE current collectors after long-term cycling. X-Ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB250Xi (Thermo Scientific, UK) equipped with mono-chromated Al K alpha (energy: 1486.68 eV). Raman spectra were performed on an inVia Renishaw Raman spectrometer system (HR Micro Raman spectrometer, Horiba JOBIN YVON US/HR800 UV) using a 632.8 nm wavelength laser.

2.4. Electrochemical characterization

All the electrochemical measurements were carried out using CR2023 coin cells assembled in an argon-filled glovebox (MBRAUN) with water and oxygen levels of less than 0.1 ppm. The electrolyte is 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 in volume) with 1% LiNO_3 as additive. For the Coulombic efficiency tests, bare Cu foil, CuNWs and CuNWs@GE current collectors were used as the working electrodes and Li metal was used as the counter and reference electrode. The Li deposition/stripping process was conducted at the current density of 1 mA cm^{-2} , with fixed deposition capacity of 2.0 mA h cm^{-2} in the voltage range of $-0.5/+0.5$ V. The Coulombic efficiency was calculated based on the ratio of Li stripping and plating. In order to remove the surface contaminations and stabilizing the SEI, all batteries were first cycled at 0 – 1 V (versus Li^+/Li) at 50 μA for five cycles. Electrochemical impedance spectra (EIS) measurement was performed using a Biologic VMP3 electrochemical workstation in the frequency range of 100 kHz to 0.1 Hz.

3. Results and discussion

The CuNWs current collector was synthesized from the as-prepared Cu nanowires. The morphology of the CuNW current collector was first observed by SEM as shown in Fig. 1a-c. The length and diameter of CuNWs measured from the SEM image are about 45 μm and 400 nm, respectively, which is similar to the previous report [44]. CuNWs current collectors can be obtained after punching out an appropriately-sized disk from CuNWs paper (the inset in Fig. 1a). After annealing in a reducing atmosphere at 600 °C, the mechanical strength of the CuNWs current collector can be further enhanced owing to the fusion of adjacent Cu nanowires. The CuNWs electrodes exhibits good flexibility and robustness and can be rebound even after being folded back (Fig.

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