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Communication

A synergistic strategy for stable lithium metal anodes using 3D fluorine-doped graphene shuttle-implanted porous carbon networks

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ABSTRACT

It remains a challenging task to solve the imperative problems facing lithium metal anodes for next-generation rechargeable batteries. Herein, a synergistic strategy is developed to suppress lithium dendrite growth, facilitate solid electrolyte interphase stabilization, and consequently improve lithium metal anode performance, through using a self-supporting three-dimensional fluorine-doped graphene shuttle-implanted porous carbon network as the multifunctional host matrix for lithium. The methodology emphasizes structural and interfacial synergism in controlling the nucleation and growth of lithium deposits, which can enable lithium dendrite-free deposition and high-efficiency lithium plating/stripping. Such a structure and interface-engineered electrode matrix not only acts as a favorable lithium reservoir to enable the electrode-level stability, as a current density regulator to manage the initial nucleation and subsequent growth of lithium, but also as an interfacial modifier to stabilize solid electrolyte interphase layers. As a result, the developed anode exhibits excellent electrochemical performance, retaining an average Coulombic efficiency as high as 99% over 300 cycles. Combined with a simple and efficient fabrication process, the study presented here offers a viable option for fabricating dendrite-free lithium metal anodes for lithium metal battery systems and at the same time, sheds light on other high-performance metal battery construction.

1. Introduction

Electrochemical energy storage is an intrinsic driving force for improving the quality of modern life. Lithium-ion batteries (LIBs), an excellent example in electrochemical energy storage systems, have achieved remarkable success in commercial markets such as mobile electronics and more recent electric vehicles [1–4]. Yet, as the ever-increasing demand for high-energy and high-power batteries in many fields such as electric vehicle and aerospace applications, as well as renewable energy integration, the current LIB techniques based upon graphite anodes must be innovated to meet such application requirements. Metallic lithium (Li) is an attractive choice as the ultimate anode for LIBs and next-generation rechargeable batteries (e.g., based upon Li-S and Li-O_2 chemistries), because it possesses an extremely high theoretical specific capacity (3860 mAh g^{-1}), almost ten times higher than that of graphite anodes, as well as the lowest negative electrochemical potential (−3.040 V versus the standard hydrogen electrode). Unfortunately, rechargeable batteries based on Li metal anodes have not yet been commercialized because of the unsolved challenges, for example, lithium dendrite growth-involved structural and interfacial instability issues during repeated discharge/charge processes [5]. The uncontrollable formation of Li dendrites inevitably induces the cracks and collapses of solid electrolyte interphase (SEI), brings more surface area of Li metal exposing in electrolyte, and increases the possibility of side reactions with electrolyte, thereby resulting in a low Coulombic efficiency (CE) and poor cycling stability [6]. Such interfacial variations during cycling can in turn exacerbate the locally favorable lithium dendrite growth. The continuous growth of Li dendrites can penetrate the separator and reach the cathode, causing the electrical contact and short circuit of a working cell [7]. Consequently, solving these interactional structure and interface instability issues existed in lithium metal anodes is the key step to the commercialization of high-energy-density rechargeable lithium metal batteries (LMBs).

Massive efforts have recently been devoted to addressing the challenges of Li metal anodes. An important focus is the design and use of three-dimensional (3D) porous host matrices from the viewpoint of

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electrode structure. The effectiveness of such designated host matrices has been intensively proved by theoretical calculation [8] and experiments [9–24]; some representative host matrices include connected carbon nanotubes [9–12], 3D graphene and/or carbonaceous frameworks [13–18], and 3D metallic current collectors [19–24]. Upon the use of these host matrices, the local effective current density is regulated toward restraining the lithium nuclei size and thereby inhibiting lithium dendrite growth, and the dramatic volume variation upon Li striping/plating is accommodated toward stabilizing the dimension of the electrode. Although efficacious to a certain extent to suppress lithium dendrite growth and improve the structural and dimensional stability, these methodologies are usually incapable of fundamentally solving the interfacial instability issue of lithium metal anodes. The continuous growth and propagation of SEI during Li stripping/plating retard charge transfer, lower the Coulombic efficiency, cause capacity fading, and also make safety issues recur. As an alternative, the SEI engineering represents a direct and energetic way to regulate the lithium dendrite nucleation and growth from the electrode interface viewpoint [25–31]. In particular, creating lithium fluoride (LiF)-enriched artificial SEI layers has recently been demonstrated capable of enabling smooth Li deposition and dissolution at the given current density [29–31]. Notably, such a strategy can become inefficient and even ineffective during long-term cycling at higher current densities, especially when the space is limited to accommodate the volume change resulted from Li stripping/plating. Moreover, most processes for the creation of LiF-enriched SEI layers are tedious and the involved fluorine-containing reagents (e.g., hydrofluoric acid [32], fluoroethylene carbonate [27,29], Freon R134a [33], F_2 [34], and XeF_4 [35],) are not environmentally friendly, both of which would be a constraint to commercial manufacture [36]. Therefore, it remains a challenging task to construct stable lithium metal anodes, and new stabilization strategies and/or electrode construction principles are highly desirable.

In this contribution, we propose and demonstrate a synergistic strategy for stable lithium metal anodes by using a self-supporting 3D fluorine-doped graphene shuttle-implanted porous carbon network (MGCN) as the multifunctional host matrix for Li (Fig. 1). The MGCN holds several notable advantages. First, the 3D hierarchical porosity allows for better accommodation of the volume change resulted from Li stripping/plating upon cycling, thus ensuring the stability at the electrode level during cycling. Second, the high surface area significantly reduces the local effective current density and consequently suppresses lithium dendrite growth at the initial nucleating stage. Third, the anchored graphene shuttles help enhance the electronic conductivity of such a hierarchically porous scaffold, thereby enabling the uniform distribution of current density and benefiting the uniform nucleation and growth of Li. Fourth, the F-doping plays a role in stabilizing SEI while the LiF-enriched interfacial layers form through initial electrochemical lithiation. Based on the structural and interfacial synergism, this self-supporting electrode exhibits outstanding electrochemical performance, revealing its superiority for a dendrite-free and efficient lithium metal battery.

2. Material and methods

2.1. Fabrication of MGCN

Typically, a desirable amount of polyvinylidene fluoride powder (PVDF, M_w = 534,000, Sigma Aldrich) was dissolved in 10 mL N-methyl-2-pyrrolidinone (NMP), and then infiltrated into the as-received Cu foam (Kunshan Jiayisheng Electronics, ~ 14 mm in diameter) by vacuum filtration. The resultant PVDF-infiltrated Cu foam (with ~ 15 mg of PVDF) was annealed at 600 °C for 2 h in a horizontal tube furnace under Ar, during which the infiltrated PVDF was carbonized. After being cooled to room temperature, the sample was put into 3 M $FeCl_3$ solution at around 80 °C for 3 h to completely dissolve the Cu foam template. Finally, the self-supporting MGCN was obtained by washing with deionized water and drying at 60 °C in vacuum.

2.2. Material characterizations

The scanning electron microscopy (SEM) micrographs were performed with a Hitachi S-8220 instrument at an acceleration voltage of 5 kV. The transmission electron microscopy (TEM) micrographs were performed with an FEI Tecnai F20 instrument operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was implemented on an ESCALAB250Xi apparatus at base pressure of 1×10^{-9} mbar, and X-ray source of Al Kα. Raman spectra were measured by a Renishawin Via Raman microscope in which laser wavelength is 515 nm. Nitrogen adsorption/desorption isotherms were measured at 77 K with an ASAP 2020 physisorption analyzer. The Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model were utilized to estimate the specific surface area and pore size distribution, respectively.

2.3. Electrochemical characterizations

For electrochemical measurements, two-electrode half-cells (CR2025) were assembled in an Ar-filled glovebox with oxygen and water contents below 1 ppm. The cells consisted of lithium foil as the counter electrode, self-supporting MGCN, Cu foam, or Cu foil as the working electrode, and a standard polypropylene membrane as the separator. A solution of 1 M lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (DOL/DME = 1:1) with lithium nitrate (2 wt%) was used as the electrolyte. Galvanostatic experiments were performed using the LAND CT2001 battery system; in each galvanostatic cycle, the charge time was fixed in the lithium plating process with desirable current densities, and the discharge time in the lithium stripping process was controlled by a cut-off voltage of 1 V. Electrochemical impedance spectroscopy

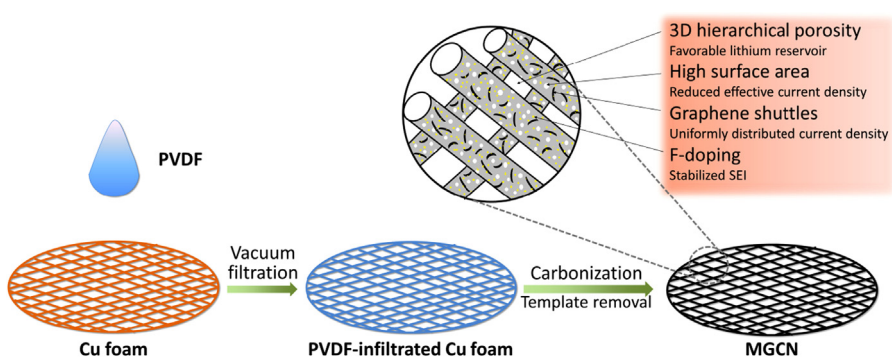

Fig. 1. Schematic of the fabrication of MGCN and its favorable advantages as the host matrix of Li originating from the structural and interfacial synergism.

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