Journal of Power Sources 386 (2018) 77–84

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Dendrite-free Li metal anode enabled by a 3D free-standing lithiophilic nitrogen-enriched carbon sponge

Guangmei Hou[a], Xiaohua Ren[a], Xiaoxin Ma[a], Le Zhang[a], Wei Zhai[a], Qing Ai[a], Xiaoyan Xu[a], Lin Zhang[a], Pengchao Si[a], Jinkui Feng[a], Fei Ding[b], Lijie Ci[a,*]

[a] *SDU & Rice Joint Center for Carbon Nanomaterials, Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan 250061, PR China*
[b] *National Key Lab of Power Sources, Tianjin Institute of Power Sources, Tianjin 300384, PR China*

HIGHLIGHTS

- Nitrogen-rich carbon sponge is proposed as lithiophilic matrix for Li deposition.
- Uniform lithium nucleation and growth without dendrites is achieved.
- The optimized Li anode can deliver an ultra-high specific capacity.
- The optimized Li anode exhibits a long-term stable cycling.

ARTICLE INFO

Keywords:
Battery
Li dendrites
Free-standing
Lithiophilic matrix
Li metal anode

ABSTRACT

Lithium metal is considered as the ultimate anode material for high-energy Li battery systems. However, the commercial application of lithium anode is impeded by issues with safety and low coulombic efficiency induced by Li dendrite growth. Herein, a free-standing three-dimensional nitrogen-enriched graphitic carbon sponge with a high nitrogen content is proposed as a multifunctional current collect for Lithium accommodation. The abundant lithiophilic N-containing functional groups are served as preferred nucleation sites to guide a uniform Li deposition. In addition, the nitrogen-enriched graphitic carbon sponge with a high specific surface area can effectively reduce the local current density. As a result of the synergistic effect, the nitrogen-enriched graphitic carbon sponge electrode realizes a long-term stable cycling without dendrites formation. Notably, the as-obtained composite electrode can deliver an ultra-high specific capacity of ~3175 mA h g^{-1}. The nitrogen-enriched graphitic carbon sponge might provide innovative insights to design a superior matrix for dendrite-free Li anode.

1. Introduction

High-energy-density batteries are urgently demanded with the booming advances in high-end portable electronics and electric vehicles. Lithium metal, with the highest specific capacity (3860 mA h g^{-1}) and the lowest potential (-3.04 V *vs* the standard hydrogen electrode), has long been considered as the ultimate anode material for high-energy Li battery systems [1]. In particular, Li metal batteries, which are represented by lithium sulfur and lithium-air batteries at the present stage, are promising candidates for next-generation energy storage systems with greatly increased theoretical energy density relative to the current Lithium-ion batteries (LIBs) [2]. Despite all these advantages, issues induced by the formation of Li dendrites during repeated Li stripping/plating are one of the major hurdles to the practical application of Li-metal-based energy-storage systems [3–5]. Undesired dendrites may pierce the separator and induce internal short circuit, causing serious safety issues (e.g., fire, burning, and explosion) [6,7]. Moreover, due to the infinite relative volumetric variation of Li anode owing to its hostless nature, the growth of dendrites will lead to the breakage of the protective solid electrolyte interface (SEI) layer. As a serious consequence, repeated breakage/repair of the SEI film during Li plating/stripping leads to a low coulombic efficiency (CE) and a shorted cycle life due to the continuous consumption of Li metal and electrolyte [8].

To address the above issues, extensive strategies have been developed to suppress Li dendrite growth. Modifying the electrolyte by the

---

[*] Corresponding author.
E-mail address: lci@sdu.edu.cn (L. Ci).

https://doi.org/10.1016/j.jpowsour.2018.03.049
Received 10 October 2017; Received in revised form 8 March 2018; Accepted 19 March 2018

introduction of additives, or the utilization of high concentrated electrolytes, nanostructured electrolytes, and ionic liquid electrolytes in an attempt to reinforce the SEI film have been proved to be effective to inhibit Li dendrite growth [9–12]. In addition to the *in-situ* formed SEI films, a stable and compact *ex-situ* artificial SEI on Li anode can prevent fresh Li from exposure to electrolyte and homogenize Li^+ surface flux, and thus a smooth Li deposition morphology will be realized [13]. Guo's group designed a stable and uniform Li_3PO_4 film on Li metal, which demonstrated an improved cycling performance and inhibition of Li dendrite growth [14]. Other preformed interfacial layers with chemical stability and mechanically flexibility, which can inhibit Li dendrites growth and reduce side reactions, such as BN/amorphous carbon, Al_2O_3 layers, can also play roles to be excellent Li surface protective coatings [15–17]. In addition, solid state electrolytes with a high modulus can efficiently suppress Li dendrites growth [18–20]. These strategies have partially solved the problems, and the achievements provided us novel insight and systematic understandings into lithium electrochemical kinetics and helped us manipulate the Li deposition better. Yet, there is still a long way to go for implementation of Li metal anode.

As we know, spatial heterogeneity of electron/ion distribution, which will directly affect the initial nucleation behavior of Li metal, is the root of the generation Li dendrites. Recently, a novel strategy of using an interconnected 3D matrix for metallic Li has proven great promise in inhibiting Li dendrite growth by mediating the Li deposition behavior. Several kinds of materials, including copper nanowires, carbon nanofiber, unstacked graphene “drum”, porous Cu and Mxene have been reported as promising candidates for such 3D porous matrix [21–25]. The matrix with an increased specific surface area (SSA) can reduce the local current density for Li plating, and thus afford the feasibility to effectively delay the Li dendrite initiation and slow its growth rate. More importantly, not only the SSA which can enable a better current distribution but also the surface chemistry of Li plating matrix have been verified to play an important role in affecting the plating behavior of Li metal especially in the initial period, which is actually decisive for the final morphology of plated Li [26]. A lithiophilic matrix with a higher binding energy presents a feasibility to guide a smooth Li^+ distribution and achieve a uniform dendrite-free morphology. Glass fiber cloths, oxidized polyacrylonitrile (PAN) nanofiber, and polyacrylonitrile submicron array have been proved to guide the lithium ions distribution to form uniform lithium metal deposits [27–29]. Nevertheless, these kinds of matrix characterized by abundant polar surface functional groups always suffer from poor electrical conductivity. Therefore, extra Cu foil as the current collector is indispensable, which will greatly add weight to the electrode and against the realization of high specific energy. Although coating a lithiophilic layer (such as Si and ZnO) onto a conductive matrix will solve the problem, an intricate materials processing impedes these materials to be scaled up [30]. Therefore, developing a proper matrix with favorable lithiophility, a high surface area, abundant active sites, superior conductivity and cost-effectiveness is highly desirable to enable a high performance Li metal anode.

In this context, we propose a free-standing N-enriched graphitic carbon sponge (NGCS) featured by a combination of abundant uniformly distributed lithiophilic functional groups and a high SSA as multifunctional current collector for Li deposition. As illustrated in Fig. 1, the NGCS electrode can address the problems associated with metallic lithium anode by effective control of evenly distributed Li nucleation and growth due to the following attributes: (*i*) a high N-doping level up to 9.87 at%, enables densely and uniformly distributed lithiophilic N-containing functional groups (i.e. abundant preferred nucleation sites), availing spatially homogeneous Li nucleation; (*ii*) the graphitic N-enriched 3D network has improved electrical conductivity, which favors the charge transfer kinetics and reduces the interfacial resistance; (*iii*) Compared to Cu foil, the free-standing 3D NGCS has ultra low gravimetric density, which is beneficial to achieve a high-energy density of the NGCS/Li composite anode. Totally, a ultrahigh specific capacity of $3175\,mA\,h\,g^{-1}$ based on NGCS mass can be obtained; (iv) a high specific surface area (SSA) and spaces introduced by the porous structure for Li metal accommodation, resulting in locally lowered current density and thus Li dendrite suppression and alleviated volume change of Li metal during cycling. As expected, the 3D NGCS/Li-metal composite anode has a promoted uniform lithium deposition and improved cycling stability with a high areal capacity. More promisingly, the 3D NGCS is obtained by single-step carbonization of porous melamine foam, a kind of cost-effective commercially available polymer materials. The facile strategy is easy to realize industrial production, which is beneficial to promote the development and commercialization of high-energy Li-metal based batteries.

2. Experimental

2.1. Material and electrode preparation

The commercially available melamine foam (MF) was washed successively in acetone, deionized water and alcohol. Then the vacuum dried MF was directly used as precursor for preparing 3D macroporous nitrogen-enriched carbon sponge (NGCS) at 900 °C for 1 h and heating rate of $3\,°C\,min^{-1}$ under highly pure N_2 atmosphere. It's worth noting that the heat treatment was carried out in a crucible with a cover to prevent sublimation of melamine. The as-prepared material was punched into circular disks and directly employed as electrode.

2.2. Characterization

SEM images were acquired using a JSM-7610F (JEOL Ltd.). X-ray diffraction (XRD) pattern was recorded on an X-ray diffractometer (MiniFlex 600, Rigaku, Japan) using Cu Kα radiation ($\lambda = 0.154\,nm$) at a power of 40 kV. Raman spectra were collected using a Renishaw InVia Reflex system equipped with 532 nm laser source. TG experiment was carried out by using a METTLER TOLEDO TGA 1 thermogravimetric analyzer. The BET surface areas and porosity properties were calculated based on the Nitrogen adsorption/desorption isotherms obtained using a Micromeritics ASAP 2020 adsorption apparatus. The chemical compositions of the materials were identified by using an X-ray photoelectron spectrometer (PH1-5700 ESCA system, USA) equipped with a hemispherical analyzer and an aluminum anode (monochromatic Al Kα 1486.6 eV) as source (at 12–14 kV and 10–20 mA).

2.3. Electrochemical performance test

For coulombic efficiency test, CR2032-type coin cells were assembled with NGCS or Cu electrodes as work electrode and bare Li foil as counter electrode in an Ar-filled glove box with O_2 and H_2O content below 0.01 ppm. All the batteries were first cycled between 0.01 V and 1 V at the current density of $0.5\,mA\,cm^{-2}$ to remove surface contamination and form a stable SEI on the electrode surface. In each galvanostatic cycle, a fixed amount of Li was plated on 3D NGCS or bare Cu and then stripped away controlled by a cut-off voltage up to 0.5 V.

For symmetric batteries, 4 mA h of Li was first plated on NGCS or Cu foil to form a NGCS@Li and Cu@Li anode respectively. Then the anodes were harvested from the preprocessed batteries and two NGCS@Li electrodes (or Li foil, Cu@Li) were reassembled into symmetric batteries. $0.5\,mA\,h\,cm^{-2}$ of Li was plated and then stripped at the current density of $0.5\,mA\,cm^{-2}$ for each cycle to evaluate the electrochemical properties of lithium plating/stripping and the cycling stability.

1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in cosolvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (volume ratio: 1:1) with 1.0 wt% $LiNO_3$ was used as electrolyte in this work and a fixed amount (100 μL) of electrolyte was used in each cell to standardize the measurement. The coin cells were monitored in galvanostatic mode on a multi-channel battery tester (Land 2001A Battery