



# Electron-rich functional doping carbon host as dendrite-free lithium metal anode

Qingyuan Dong<sup>a</sup>, Bo Hong<sup>b,\*</sup>, Hailin Fan<sup>a</sup>, Chunhui Gao<sup>a</sup>, Shu Hong<sup>b</sup>, Yanqing Lai<sup>a</sup>

<sup>a</sup> School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China

<sup>b</sup> School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, China



## ARTICLE INFO

### Article history:

Received 14 May 2018

Received in revised form

22 July 2018

Accepted 22 July 2018

Available online 29 July 2018

### Keywords:

Carbon material  
Lithium dendrite  
Lithium metal anode  
Electron-rich group  
Nitrogen doping

## ABSTRACT

The Li metal anode has been regarded as the ultimate anode because of high theoretical capacity and low potential. Unfortunately, dendrite growth and safety issues impede its practical applications. Herein, we report a series of electron-rich functional groups, such as nitrogen, oxygen and phosphorus, doped Ketjen Black (ECP) as a lithium deposition/dissolution host. The electron-rich functional groups can effectively improve the wettability and lithiophilicity of the carbon host, which is benefit to induce homogeneous lithium deposition in the Ketjen Black (ECP), rendering significant inhibition of dendrite growth and effective improvement of electrochemical stability. Under the roles of these factors, the nitrogen doped Ketjen Black (ECP) electrode achieves a high Coulombic efficiency of 97.8% over 300 cycles at 1.0 mA cm<sup>-2</sup>, while the pristine ECP electrode only maintains 110 cycles. What's more the O-doped ECP and P-ECP electrode also keeps longer cycles than the pristine ECP electrode.

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## 1. Introduction

Nowadays, high energy density lithium battery systems, such as Li–S and Li–O<sub>2</sub> batteries, have drawn extensive attention due to their broad application prospects [1–3]. Lithium metal with the unrivaled theoretical specific capacity (3860 mAh g<sup>-1</sup>) and lowest potential (–3.04 V versus standard hydrogen electrode) is regarded as the ideal anode material for above systems [4–6]. However, low Coulombic efficiency, short cycle life and safety issues induced by lithium dendrite growth hinder its commercial application [7–9]. Thus, great efforts have been devoted to solve the dendrite problem for the lithium metal batteries. All strategies employed can be divided into these sorts: optimizing electrolytes [10–13], introducing novel solid electrolytes [14–16], using modified separators [17–19], fabricating artificial protection layers [20–24], and employing 3D current collectors [25–28]. Among these approaches, the 3D current collectors with high specific surface area, which can effectively reduce the current density during the process of lithium deposition/dissolution, seems to be an availability method for the inhibition of lithium dendrites [25–28]. Therefore, porous copper [29,30], porous foam [31,32], artificial graphite [33],

graphene [34,35], carbon nanotubes [36], and carbon fiber [37] are widely used as 3D host materials for lithium deposition.

In previous lithium ion battery designs, carbon-based materials have made a great success as electrode materials and conductive agents because of their favorable electrons conductivity and stable electrochemical properties under the redox environment [38–40]. On the basis of these advantages, three-dimensional (3D) porous carbon-based materials are the ideal host for constructing lithium metal anode. However, if the normal porous carbon is selected as the host for Li deposition, Li will preferentially plate on the out layer of carbon host because of the poor wettability in electrolyte and poor lithiophilicity [41,42]. Then the deposition of lithium in host would be heterogeneous in spatially and even result in undesirable growth of Li dendrites. To overcome this spatially heterogeneous deposition of lithium in carbon materials, lithophilic nanoparticles [41–45] and functional groups [26,46–48] have been proposed. For instance, Cui et al. [41] adopted Au nanoparticles modified hollow carbon spheres for Li deposition, resulting in an enhanced cycle life of 300 cycles at 0.5 mA cm<sup>-2</sup>. Hu et al. [43] used ultrafine Ag nanoparticles as nanoseeds to direct the deposition of Li within the 3D carbon nanofibers, achieving a stable and reversible cycle for 50 cycles at 0.5 mA/cm<sup>2</sup>. Zhang et al. [46] employed nitrogen (N) doped graphene as the Li deposition matrix, rendering nearly 200 cycles at 1.0 mA cm<sup>-2</sup>.

Considering the cost and industrial manufacture problem, we

\* Corresponding author.

E-mail address: [bop\\_hong@163.com](mailto:bop_hong@163.com) (B. Hong).

propose an electron-rich functional group Ketjen Black (ECP) coated electrode as a lithium deposition host. It is found out that the evenly distributed electron-rich functional group can improve the wettability and lithiophilicity of ECP host. It is beneficial to induce the uniform deposition of lithium metal in treated ECP, thereby the electrochemical stability of lithium deposition is obviously improved.

## 2. Experimental

### 2.1. Preparation of ECP and doped ECP electrode

Ketjen Black (Carbon, ECP600JD) was purchased from Triquo Chemical Technology Co., Ltd. N-doped Ketjen Black (N-ECP) was prepared at 900 °C in NH<sub>3</sub> flowing (150 mL min<sup>-1</sup>) for 9 h in a quartz tube. For O-ECP, ECP was acidized by sulphuric acid and nitric acid (3:1 vol%) for 12 h, and then filtered, dried and grinded. As for P-ECP, ECP and triphenyl phosphine (2:1 wt%) dispersed in acetone solution uniformly, then treated at 900 °C in Ar flowing (150 mL min<sup>-1</sup>) for 9 h in a quartz tube. ECP and doping ECP electrodes were mixed with the PVDF binder (4:1 by weight separately) into N-methyl-2-pyrrolione (Aladdin), then coated on a cleaned Cu foil, respectively, followed by the evaporation in a vacuumed oven at 60 °C overnight. The mass loading of ECP or doping ECP is about 0.39 mg cm<sup>-2</sup>, the thickness of the ECP or doping ECP is about 22 μm (Fig. S3).

### 2.2. Characterization

Scanning electron microscopy (SEM, Philips, FEI Quanta 200 FEG) operated at 30 kV was employed to characterize the morphology of ECP, N-ECP as well as their electrodes before and after Li deposition. The microscopic morphology and element distribution in ECP and N-ECP were characterized by transmission electron microscopy (TEM, JEM-2100F) and energy dispersive X-ray spectroscopy (EDX, attached to TEM). An XPS (ESCALAB 250Xi, Thermo Fisher Scientific Inc. USA) was employed to analyze the chemical composition of ECP and doped ECP. The contact angle was test by the Contact Angle System (FTÅ200, HARVEY, MAIN&CO.LTD).

### 2.3. Electrochemical test

2032-type coin cells were assembled in an argon-filled glove box, which were adopted ECP or doped ECP electrode (13.0 mm in diameter) as the working electrode, Li foil with a diameter of 16.0 mm and thickness of 0.5 mm as the counter electrode. The electrolyte was 1.0 M LiTFSI in DME/DOL (1:1 vol%) with 1.0 wt% LiNO<sub>3</sub>. The cells were first initialized by cycling at 0 – 1.0 V (versus Li<sup>+</sup>/Li) at 0.1 mA cm<sup>-2</sup> for five cycles to remove surface contaminations and stabilize the interface. Afterwards, Li deposition was tested at different current densities with different areal capacities, and then stripping to 1.0 V at the same current density. Electrochemical impedance spectroscopy (EIS) measurements were tested at frequency range of 10 mHz–100 KHz on a Solartron 1470E system.

## 3. Results and discussion

TEM images of ECP and N-ECP are shown in Fig. 1 (a) and Fig. 1 (b), respectively. It notes that the pristine ECP is a nanoparticle structure with an average diameter of ~30 nm, and the morphology of ECP particles do not change after nitrogen doped process. Similar results can be seen from the SEM images (Fig. S1). Owing to nano sizes of ECP particles, it exhibits a high specific surface area of

146.43 m<sup>2</sup> g<sup>-1</sup> (Fig. S2). The full range XPS analysis of N-ECP clearly shows the presence of nitrogen (N) with an atomic percentage of 3.43% (Fig. 1(c)). While there is almost no nitrogen observed in the pristine ECP. The fitting result of the N1s doped in ECP exhibits three peaks, including pyridinic nitrogen (398.5 eV), pyrrolic nitrogen (400.2 eV), and quaternary nitrogen (401.5 eV) [26,45]. The pyridinic and pyrrolic nitrogen are the main components among the N-doped functional groups in ECP, as shown in Fig. S5. The EDX elemental mappings indicates that N atoms are even uniform distributed in the N-ECP (Fig. 1(d–f)) [26,46].

To study the wettability of electrolyte with nitrogen doped ECP, contact angle is tested on the three electrodes (Cu foil, ECP and N-ECP) with the ether electrolyte (1.0 M LiTFSI in DME/DOL (1:1 vol%) with 1.0 wt% LiNO<sub>3</sub>), as shown in Fig. S4. It noted that N-ECP electrode has a contact angle of 4.24° (Fig. S4(c)), which is much less than that on the Cu foil electrode (33.62°, Fig. S4(a)) and ECP electrode (11.32°, Fig. S4(b)). It indicates that nitrogen-rich functional groups can improve the wettability of electrolyte on carbon surface, which may be beneficial to increase the lithium ion flux and decrease the Li ion concentration gradient at the surface of electrode. To directly prove the lithiophilicity of the molten lithium with N-ECP electrodes, we dropped the molten Li on the surface of Cu foil, ECP and N-ECP electrodes. The molten lithium can wet with N-ECP electrode and spread onto the surface of N-ECP with a smaller contact angle (Fig. 2 (a), (b), (c)).

The nucleation overpotential is usually used to evaluate the lithiophilicity degree of the current collector for Li deposition. Thus we investigated the overpotential of metallic Li plating on Cu foil, ECP and N-ECP electrodes, as shown in Fig. 2(d). At 1.0 mA cm<sup>-2</sup> with a capacity of 1.0 mAh cm<sup>-2</sup>, the voltage curve on the N-ECP electrode drops to minimum of –68 mV, indicating the beginning of Li nucleation. After nucleation, the voltage curve rises to a stable voltage platform at –37 mV, which is the mass-transfer-controlled overpotential [46]. And the difference between the minimum voltage and the later stable voltage platform is been defined as the nucleation overpotential, which is 31 mV for N-ECP electrode. Under the same current density, the Li nucleation overpotentials on the Cu foil and ECP electrode are 78 mV and 45 mV (Fig. 2(d)). From the previous study [46], the pyrrolic nitrogen owing one extra electron which N provides a pair of p-electrons to conjugated p bond, while there are large-pair electrons in the pyridinic nitrogen. The p orbitals has extra pair of p elections are expected as Lewis base sites to strongly adsorb Lewis acidic Li ions through acid-base interactions, promoting the ionization of the LiTFSI by the acid–base interactions [49,50]. These values indicate that the N-ECP electrode renders the best affinity with Li metal, which is almost consistent with Zhang's results [46]. Thus, the deposition barrier for lithium metal depositing on the N-ECP electrode is small, which is benefit to obtain a minimum of the overpotential, homogeneous deposition and even regular growth of lithium metal without dendrites.

To further prove the beneficial effect of N doping ECP electrode, we perform a deposition test with different time (5 h and 10 h) at the current density of 0.1 mA cm<sup>-2</sup>, as shown in Fig. 3. For Cu foil electrode, some uneven nubby lithium was clearly observed on the Cu foil surface with a deposition time of 5 h (Fig. 3(a)). When the deposition time increases to 10 h, an unconsolidated mossy Li layer covers the surface of Cu foil, and even the Li dendrites appear among the mossy Li layer (Fig. 3(d)). As for ECP electrode, there are some lithium dendrites appeared in ECP electrode surface when plating for 5 h (Fig. 3(b)), and the sharp dendrites of metallic Li grow up attained to the length more than one micrometer with a continuously deposition (Fig. 3(e)). It illustrates that Li preferentially plate on the out layer of ECP host, resulting in an undesirable growth of Li dendrites during the deposition [41,42]. However, the

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