Magnetron sputtering amorphous carbon coatings on metallic lithium: Towards promising anodes for lithium secondary batteries

Y.J. Zhang, X.Y. Liu, W.Q. Bai, H. Tang, S.J. Shi, X.L. Wang, C.D. Gu, J.P. Tu*

State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, and Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

HIGHLIGHTS

- Amorphous carbon coatings were deposited onto the surface of metallic lithium.
- The formation of dendritic can be prevented according to the SEM photograph.
- The electrochemical performance is promoted due to the existence of a-C coating.
- The thickness of a-C coating affects the electrode performance from two aspects.

ARTICLE INFO

ABSTRACT

All the Li metal anode-based batteries suffer from a high propensity to form Li dendrites. To prevent the formation of dendritic lithium on the electrodes, amorphous carbon coatings are deposited onto the surface of metallic lithium foil by magnetron sputtering technique. The electrochemical performances of the amorphous carbon-coated lithium (Li/C) electrodes are investigated by galvanostatic charge/discharge tests, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The compact carbon coatings on the surface of lithium foil can suppress the growth of dendritic lithium during charge−discharge process. The thickness of amorphous carbon coating affects the electrode from two aspects; the thick coating can prevent the formation of dendritic lithium much efficiently, but lead to a large impedance of Li^+ transfer.

1. Introduction

Rechargeable batteries with high energy density are essential for solving imminent energy and environmental issues [1,2]. In the past decades, a lot of research has been focused on finding new anode materials to improve the lithium storage capability of lithium secondary batteries [3–11]. Metallic Li has an extremely high theoretical specific capacity (3860 mAh g^{-1}), low density (0.59 g cm^{-3}) and the lowest negative electrochemical potential (−3.045 V *vs.* standard hydrogen electrode (SHE)), thus rechargeable Li metal batteries have been called the "Holy Grail" of energy storage systems and have been investigated extensively during the last 40 years. Recently, the lithium−sulfur and lithium−air batteries have attracted attention for their extremely high capacity [12–19]. So as to meet the ever-growing demand for lithium secondary batteries with higher power and energy densities, the improvement in electrochemical performance of Li metal anode is extremely urgent.

In order to achieve the commercialization of Li metal anode, there are two main problems to be solved [20–27]. One is that metallic Li is too active and it easily reacts with electrolyte, which results in a low cycling efficiency. The other one is the formation of dendritic lithium between the interface of Li anode and electrolyte. This kind of morphology may puncture the separator and lead to the safety problem. According to previous reports [28,29], the dendritic formation can be influenced by many kinds of factors, such as lithium surface tension and surface energy. Among them, it is mainly ascribed to the continuous deposition and dissolution of Li^+ during charge/discharge processes. As a result, the electrochemical performance is very poor due to the non-uniformity of solid electrolyte interface (SEI) layer.

Most approaches to dendrite prevention focus on improving the stability and uniformity of the SEI layer by adding some additives,

* Corresponding author. Tel.: +86 571 87952573; fax: +86 571 87952856.
  E-mail addresses: tujp@zju.edu.cn, tujplab@zju.edu.cn (J.P. Tu).

such as HF [30], AlI$_3$ [31] and carbonate [32,33]. But it is very difficult to achieve sufficient passivation between Li metal anode and the electrolyte, as indicated by Aurbach [23]. The approach to form protective films on the surface of metallic Li before electrochemical process has also been reported. Such protective films must conduct Li ions, and at the same time can prevent the contact between Li and electrolyte. Arie et al. reported that C$_{60}$ [28] and diamond like carbon [34] film deposited by vacuum techniques can play a role as a passive layer against the side reaction between Li surface and electrolyte. In Wu's work [35], a Li$_3$N film was fabricated on Li surface as a protective layer by the direct reaction between Li and N$_2$ gas at room temperature. Although the cycling performance of Li$_3$N modified Li electrode is better than the as-received Li, the preparation method is complicated. Amorphous carbon (a-C) films were usually used as protective coatings in mechanical applications due to their excellent physical and chemical properties [36–43]. In this present work, we fabricated a-C coatings on metallic Li foil by magnetron sputtering technique. The a-C coatings show positive effects on the electrochemical behaviors of Li in a conventional organic electrolyte. What's more, the magnetron sputtering technique is convenient and suitable for industrial production [44–49]. The effects of sputtering time on the electrochemical properties of Li/C anodes were then investigated.

2. Experimental

2.1. Fabrication of a-C coatings

The a-C coatings were deposited on metallic Li foil (200 μm in thickness) and Si (100) wafer substrates by a closed field unbalance magnetron sputtering system (TAJS-700, TENGAO). The coatings deposited on the silicon wafers were only used to characterize their morphology, as it is hard to observe the cross-section morphology of a-C coating on Li foil directly. The Si substrates were ultrasonically washed in acetone for 20 min, in ethanol for 10 min, and then blow-dried by nitrogen. Prior to deposition, the base pressure of the sputtering system was evacuated to 4×10^{-3} Pa, and then argon gas was introduced to keep the working pressure of 0.2 Pa. In order to remove the oxides and adsorptions, the substrates were etched by Ar$^+$ bombardment at a negative bias of 500 V for 30 min. During the deposition process, the current of graphite targets was kept at 1 A, and the sputtering bias was maintained at 50 V. The a-C coatings were deposited for 20 min, 40 min and 60 min, respectively.

2.2. Characterization

The surface and cross-section morphologies of the a-C coatings were observed using scanning electron microscope (SEM, Hitachi S-4800 equipped with GENENIS 4000 EDAX detector). The bonding structure of coatings was characterized by an X-ray photoelectron spectroscopy (XPS) using an ESCAL 220i-XL electron spectrometer, operating with a monochromated Al-Kα X-ray radiation source in a base pressure of 10^{-7} Pa. To avoid air contamination, the Li electrode samples were transferred in the sealed box filled with argon gas and loaded into the SEM and XPS machine under pure argon atmosphere.

All the electrochemical measurements were performed with sealed CR2025 coin cells. The a-C coated Li foil pressed on copper sheet (0.05 mm in thickness) was used as the working electrode and a copper sheet with a diameter of 15 mm was used as the counter electrode. Before the tests, the copper sheet was cleaned with the diluted hydrochloric acid at first, then washed with alcohol and blow-dried in air. Celgard 2300 was used as the separator and a solution of 1 M LiPF$_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) was employed as the electrolyte. The cells were assembled in a glove box filled with high-purity argon. The charge–discharge measurements were carried out on LAND battery test system (Wuhan, China). Li of 0.9 C cm^{-2} was deposited at a cycling current density of 0.5 mA cm^{-2}. The cut-off potential was controlled at 1.0 V (vs. Li/Li$^+$) for the Li dissolution. The Li cycling efficiency (Eff) is calculated using Eq. (1):

$$\text{Eff} = \frac{Q_{\text{dissolution}}}{Q_{\text{deposition}}} \times 100\% \tag{1}$$

where $Q_{\text{depositon}}$ represents the charge quantity of Li deposition, and $Q_{\text{dissolution}}$ represents the dissolution quantity of deposited Li [35].

Cyclic voltammetry (CV) tests were carried out using the CHI660C electrochemical workstation in a potential range of −0.4 to 0.8 V (vs. Li/Li$^+$) at a scan rate of 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were performed on this apparatus over a frequency range of 100 kHz to 10 mHz under AC stimulus with 10 mV of amplitude. After the electrochemical tests, the cells were disassembled by the battery removal machine (Kejing, MSK-110D).

3. Results and discussion

Fig. 1 shows the surface and cross-section SEM morphologies of a-C coatings on Si substrate, while the sputtering time is 20 min (Fig. 1a and b), 40 min (Fig. 1c and d) and 60 min (Fig. 1e and f), respectively. It can be seen that the surface is quite compact and uniform without any grain boundaries or holes. From Fig. 1b, the thickness of the a-C coating deposited for 20 min is estimated to be about 50 nm. In the same way, the thickness of the a-C coating deposited for 40 min and 60 min is about 80 nm and 110 nm, respectively.

Fig. 2 shows the surface morphologies of pure Li and Li/C electrodes before and after 50 charge/discharge cycles. Fig. 2b to Fig. 2d show the SEM images of Li/C electrodes deposited for different time spans. The island structure of amorphous carbon can be observed on the metallic Li substrate. From Fig. 2a, the surface of pure Li is not as flat as Si wafer, which can lead to the rough morphology of Li/C electrodes. There have been many reports on the morphology of the metallic Li that is electrochemically deposited in various kinds of organic electrolyte. Yamaki et al. [29] reported that there are three kinds of morphology of dendritic lithium: dendritic, granular and mossy. Fig. 2e shows the surface micrograph of pure Li electrode after 50 cycles. A granular morphology can be clearly observed. The particle-like lithium deposits are rough and loose due to the non-uniformity of SEI layer. When the lithium ions transfer between the electrodes repeatedly, the formation of dendritic morphology will occur. By contrast, the surface morphologies of Li/C electrodes in Fig. 2f to Fig. 2h are relatively blunt, indicating that no matter how long the sputtering time is, the dendritic lithium always display a mossy-like morphology.

Fig. 3 shows the C 1s and Li 1s XPS spectra of the Li/C electrode deposited for 40 min before and after 50 cycles. According to the NIST X-ray Photoelectron Spectroscopy Database, the peaks at 284.1 eV and 284.8 eV in C 1s XPS spectra can be assigned to the diamond band (D-band, sp^3 bonding) and graphite band (G-band, sp^2 bonding), respectively. In addition, the C−O bonding, C=O bonding and C−F bonding are also found at binding energy of 286.5 eV, 288.8 eV and 289.7 eV, respectively (Fig. 3a). The existence of C−O bonding and C=O bonding can be ascribed to the oxidation by O$_2$, while the presence of C−F bonding may result from the electrolyte vapors in glove box. Under the effect of catalytic reduction of lithium, the carbon and oxygen can react with