

Effect of Cu_2O coating on graphite as anode material of lithium ion battery in PC-based electrolyte

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Received 23 March 2007; received in revised form 22 May 2007; accepted 26 May 2007

Available online 6 June 2007

Abstract

Cuprous oxide-coated graphite was synthesized by a polyol reduction process and analyzed by scanning electron microscopy, charge–discharge measurements and cyclic voltammetry. Cu_2O exists at the surface of graphite in the form of nanoparticles and nanorods. The coated cuprous oxide layer acts as a protective layer separating graphite from the propylene carbonate (PC)-based electrolyte solution, and greatly suppresses PC decomposition and graphite exfoliation in PC-based electrolyte systems.

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Keywords: Lithium ion battery; Cuprous oxide; PC-based electrolyte; Graphite exfoliation; Cuprous oxide; Coatings

1. Introduction

With the development of lithium ion batteries various classes of anode materials have been studied [1], however, graphite is still the most common anode material in practical batteries for its high energy density, low cost, and low toxicity. Therefore, many researchers concentrate on improving the electrochemical performance of graphite such as rate capability [2] and cycling behavior [3]. A recent direction is to broaden the application of graphite electrode at low temperature in propylene carbonate (PC)-based electrolyte systems. PC-based electrolyte systems show higher ionic conductivity at low temperature compared to EC-based electrolyte systems, because of their different melting points (39 °C for EC and –49 °C for PC) [4]. However, the decomposition of PC electrolyte and sequent intercalation of PC-solvated lithium ions give rise to continuous exfoliation of graphite, which may limit its further utilization as an anode material for lithium ion batteries. It was found that the main irreversible reaction is caused by the active sites on the surface

of graphite, thus the main thrust is focused on surface modification of graphite, including addition of some additives into PC electrolyte, for example, vinylene carbonate [5], silver hexafluorophosphate [6], tetrachloroethylene [7], triethyl orthoformate [8], and vinyl tris-2-methoxyethoxy silane [9], to form an effective SEI film at potentials over 1 V versus Li/Li^+ , and coating with other materials (carbon, metals, etc.) on the surface of graphite to prevent the direct contact between electrolyte and graphite [10,11].

Cuprous oxide is a substance attracting high research attention for its promising application in hydrogen production, solar energy, catalysis [12,13] and as anode material for lithium ion batteries [14,15]. Recently, carbon nanotube-supported cuprous oxide was synthesized by adopting a polyol process for better photocatalyst activity [16]. Here, we report that cuprous oxide could be coated on the surface of graphite with a polyol reduction process and is effective in suppressing decomposition of PC electrolyte and exfoliation of graphite during cycling in PC-based electrolyte.

2. Experimental

The preparation of cuprous oxide-coated graphite is as follows. Before coating by the polyol reduction process, the

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artificial graphite (CMS, from heat-treatment at 2800 °C, Shan-shan Co. Ltd, Shanghai, China, average diameter 15 μm) was pre-treated with saturated (NH₄)₂S₂O₈ solution for 8 h under stirring at 60 °C to get oxygenated functionalities on the surface, such as hydroxyl groups, carboxyl groups [17,18]. The treated graphite was then washed with water until neutral and dried for further treatment. The treated CMS was sonicated together with the precursor Cu(NO₃)₂·3H₂O in alcoholic solvent for 4 h. After that, the suspension was dried at 40 °C to remove the solvent. The obtained mixture was then reacted with ethylene glycol (EG) at 160 °C for 3 h to get the cuprous oxide-coated graphite. Magnetic stirring was continuously applied throughout the entire process. Finally, the Cu₂O-coated graphite was separated from solution by filtration and washed with deionized water and alcohol. Scanning electron microscopy SEM (Philips XL 300) was used to measure the surface morphology of Cu₂O-coated graphitic and original graphite.

Electrochemical performance of electrodes was evaluated by assembling model coin-type cells using lithium foil as the counter and reference electrode, Celgard 2400 as the separator, and a 1 M LiClO₄ solution of PC-DMC (1:1, v/v) as the electrolyte. The anode was prepared by mixing anode material, poly(vinylidene fluoride) (PVDF) and carbon black at a ratio of 85:10:5 (w/w). The mixture was coated on a copper foil. After drying, the coated foils were cut into pellets. Prior to assembling into coin-type model cells under argon atmosphere in a glove box, all electrode pellets were dried overnight under vacuum. These pellets were used as working electrodes for the model cells. The capacity measurements for Cu₂O-coated graphite and virginal graphite were carried out in the voltage range 0–1.5 V with constant current of 0.1 mA/cm².

Cyclic voltammetry (CV) behavior was measured at room temperature using the model cells. CV was carried out in the voltage range 0–3 V at a scanning rate of 0.1 mV s⁻¹.

3. Results and discussion

Scanning electron micrographs of original graphite and cuprous oxide-coated graphite (1:1, w/w) are shown in Fig. 1. Obviously the CMS is coated by a layer of Cu₂O nanoparti-

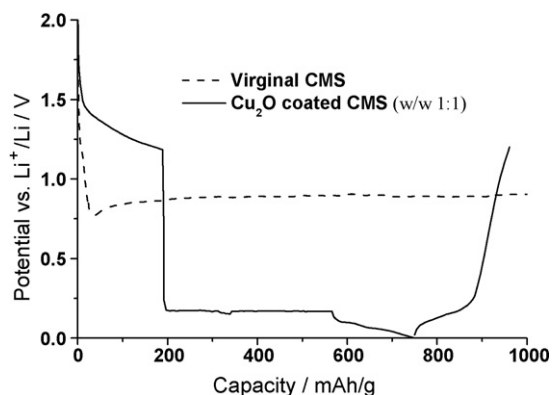


Fig. 2. Discharge–charge profiles of Cu₂O-coated graphite and the virginal graphite in 1 M LiClO₄ solution of PC/DMC (1:1, v/v) during the first cycle at 0.1 mA cm⁻².

cles and nanorods, which will function as a protective layer for graphite during cycling in PC-based electrolyte systems. In the case of Cu₂O, it has long been studied as negative electrode material in the primary lithium batteries, and its coating layer will not produce unfavorable effects on intercalation and de-intercalation of lithium ions [1].

The discharge–charge profiles of Cu₂O-coated graphite and the virginal graphite in 1 M LiClO₄ solution of PC/DMC (1:1, v/v) during the first cycle are shown in Fig. 2. For the virginal graphite, during the discharge process in the first cycle, there is a long plateau around 0.8 V versus Li/Li⁺, which indicates heavy exfoliation of graphite due to the insertion of PC-solvated lithium ions, and there is no intercalation of lithium ion into graphite. However, for Cu₂O-coated graphite, after lithium ion insertion into Cu₂O at the potential 1.5–1.2 V versus Li/Li⁺, there is no potential plateau around 0.8 V during the discharge process in the first cycle, following a steep potential decay to 0.2 V, revealing that the exfoliation has been greatly suppressed by the Cu₂O coating. Part of the plateau at 0.2 V can be ascribed to formation of a SEI-like film on the surface of Cu₂O [19], and a small part is due to the reversible intercalation of lithium into graphite. However, the reversible capacity of modified graphite is only 211 mAh g⁻¹, much smaller than the discharge capacity. This problem needs further investigation. Fig. 3 indicates that

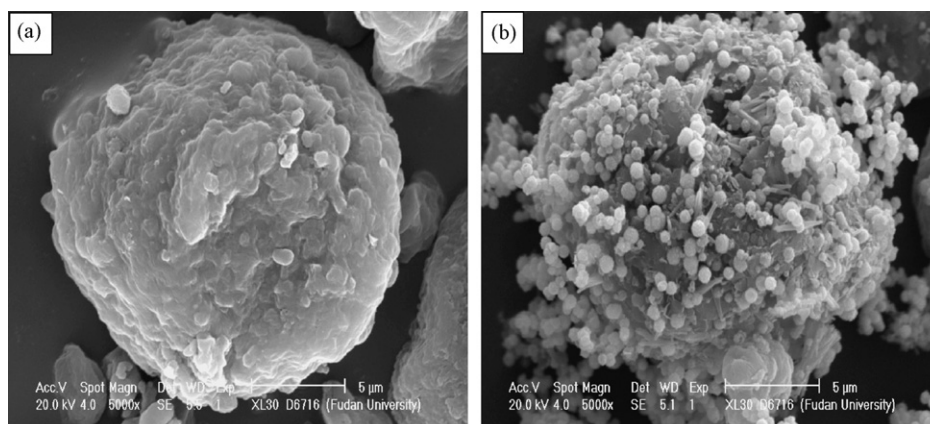


Fig. 1. Scanning electron micrographs of (a) virginal graphite and (b) Cu₂O-coated graphite (1:1, w/w).

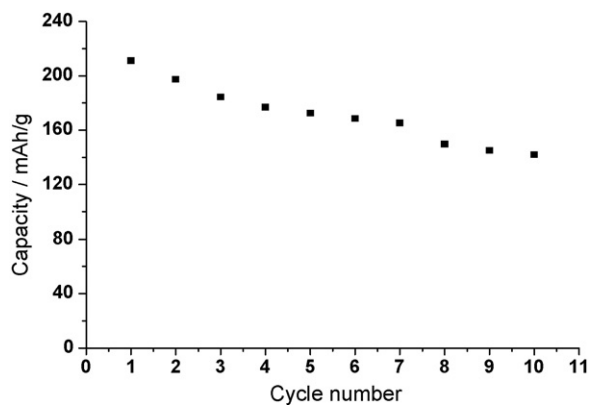


Fig. 3. Cycling performance of Cu₂O-coated graphitic at 0.1 mA cm⁻² in 1 M LiClO₄ solution of PC-DMC (1:1, v/v).

after 10 cycles, for the cuprous coated graphite, the reversible capacity retains 142.8 mAh g⁻¹, 67.7% of its reversible capacity in the first cycle. These results indicate that the coating layer functions as a protective layer on graphite keeping it from contact with PC electrolyte, and suppresses the insertion of PC-solvated lithium ion and graphite exfoliation, giving rise to reversible insertion of lithium ions into graphite.

Our results obtained from cyclic voltammetry are consistent with these phenomena. Fig. 4 shows the cyclic voltammograms of Cu₂O-coated graphite and virginal graphite in 1M LiClO₄ solution of PC/DMC (1:1, v/v) during the first cycle a scanning rate of 0.1 mV s⁻¹. With virginal graphite in the cathodic polarization process, there is a large irreversible peak around 0.5 V versus Li/Li⁺, which can definitely be ascribed to PC decomposition and graphite exfoliation [1]. In contrast, for the graphite coated with Cu₂O, it is obvious that the peak around 0.5 V versus Li/Li⁺ is much smaller, whereas the peaks around 1.0 V and ca. 0.2 V versus Li/Li⁺ are prominent, which are ascribed to the lithium ion insertion into Cu₂O and graphite, respectively. The results indicate that PC decomposition and graphite exfoliation are greatly suppressed by the coated cuprous oxide layer, which acts as a protective layer of the graphite from electrolyte, and giv-

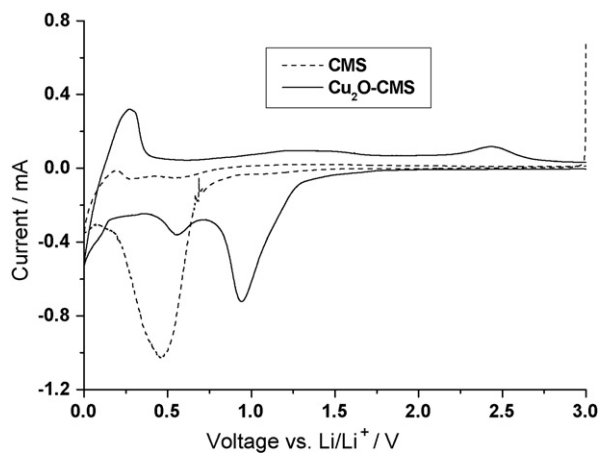


Fig. 4. Cyclic voltammograms of Cu₂O-coated graphite and the virginal graphite electrodes in 1 M LiClO₄ solution of PC-DMC (1:1, v/v) during the first cycle with scanning rate of 0.1 mV s⁻¹.

ing the promising results of reversible lithium ions intercalation into graphite in PC-based electrolyte.

However, it appears to us that the coulombic efficiency of the Cu₂O-coated graphite during the first cycle is very low, which is due to the irreversible reaction between Cu₂O and lithium to form Li₂O, and formation of a SEI-like film on the surface of Cu₂O [19]. In addition, its cycling is not satisfactory. Perhaps the Cu₂O coating is not very stable and separates from the graphitic base during cycling since the coating amount of Cu₂O based on the graphite is 1:1 (w/w). Another reason may be associated with the fact that the Cu₂O coating particles are perhaps too large so that PC can gradually penetrate into the coating layer via the empty space between the fine particles and get into contact with the graphite. Thus, other materials such as Cu and Ag have been adopted to coat graphite in our laboratory, and better electrochemical performance including cycling behavior has been achieved [20,21].

4. Conclusion

Cu₂O-coated graphite was synthesized with a polyol reduction process. The coated Cu₂O acts as a protective layer of graphite from electrolyte when Cu₂O-graphite composites are used as anode material in lithium ion batteries in PC-based electrolyte. Both the charge–discharge measurements and cyclic voltammetry show great suppression of PC decomposition and graphite exfoliation after coating Cu₂O, compared to the virginal graphite. However, the coulomb efficiency of Cu₂O-graphite during the first cycle is poor, which is due to the irreversible reaction of Cu₂O towards lithium to form Li₂O and formation of a SEI-like film on the surface of Cu₂O. The stability of the Cu₂O coating needs improvement since reversible capacity still fades.

Acknowledgments

Financial support from Natural Science Foundation Committee of China (50573012), Shanghai Committee of Science & Technology (0552 nm05025 & 04QMX1406) and Alexander von Humboldt Foundation are greatly appreciated.

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