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Improving electrochemical performance of graphitic carbon in PC-based electrolyte by nano-TiO_2 coating

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Abstract

Graphitic carbon was coated with nano-TiO_2 by a simple mechanical process. X-ray diffraction and scanning electron microscopy were used to measure the crystal structure and surface morphology of the coated composite. Tests of galvanostatic discharge and charge and cyclic voltammograms suggest that the decomposition of propylene carbonate and the exfoliation of graphite are greatly suppressed. Lithium ions can reversibly intercalate into and deintercalate from the TiO_2-coated graphite, and quite stable cycling behavior in propylene carbonate-based electrolyte is achieved.

Keywords: Lithium ion battery; Anode material; Graphitic carbon; Propylene carbonate; Nano-TiO_2 coating

1. Introduction

Desirable low-temperature performance is one of the important improving aspects for the application of lithium ion batteries. It is also one of the pivotal problems to be solved for power sources in military, aviation and aerospace fields. Most current commercial lithium ion batteries can work only at temperature above −20 °C because of higher melting point of exclusively used ethylene carbonate (EC)-based electrolytes. Propylene carbonate (PC)-based electrolytes are well known for their excellent low-temperature performance [1,2]. Compared with EC, PC has a very poor compatibility with graphitic carbon because PC molecule co-intercalates into graphite together with lithium ions followed by ceaseless decomposition of PC, leading to graphite exfoliation [3–6].

To overcome the inherent incompatibility of PC with graphite, some additives are often added to PC-based electrolytes. These additives form a protective solid–electrolyte interface (SEI) layer in advance at potentials higher than 1 V (vs. Li/Li^+) before PC begins to decompose [7]. Effective additives include vinylene carbonate [7–10], acrylonitrile [9], butyl methyl carbonate [11], silver hexafluorophosphate [12], copper trifluoromethanesulphonate [13], aromatic esters [14], tetrachloroethylene [15], triethyl orthoformate [16], vinyl tris-2-methoxyethoxy silane [17] and 2-cyanofuran [18].

It is well-known that the surface of graphite can be modified by other materials due to the existence of active sites at the surface of graphite [19]. The purpose of some modification is to prevent direct contact of active sites on graphite surface with PC [20,21]. For example, carbon coated natural graphite showed much better electrochemical performance in PC-based electrolyte than bare natural graphite [22,23]. Natural graphite encapsulated by pyrolytic carbon from polyurea can work stably in a PC-based electrolyte with the volumetric PC content up to 25% [24]. Palladium coating on graphite reduces the initial irreversible capacity of graphite in PC-based electrolyte [25]. Nano-Ag deposited on graphite boosts the formation of a stable SEI film in PC-based electrolyte [26]. Cu layer coated on graphite suppressed the decomposition of PC and exfoliation of graphite [27].

TiO_2 has been coated onto cathode materials to improve their electrochemical performance since it has high ionic

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conductivity [28,29]. In addition, TiO_2 has a good compatibility with PC-based electrolyte as anode material [30]. To our knowledge, there is no report on the modified graphite by TiO_2 as the anode material of lithium ion batteries. Here we coated graphite with a layer of nano-TiO_2 particles to suppress PC decomposition and primary results showed that the prepared composite had rather stable electrochemical performance in PC-based electrolyte.

2. Experimental

TiO_2-coated graphitic carbon was prepared by a modified simple mechano-thermal process, which was used for coating cathode materials [29,31]. This modified coating method is called mechanical coating. Before coating, 0.4 g lipophilic nano-TiO_2 (average particle size 5 nm, Haitai Company, China) was first dispersed in 30 ml ethanol by 1 h sonication followed by 10 h vigorous stirring. Then 3 g graphitic carbon powder (CMS, from heat-treatment at 2800 °C, Shanshan Co. Ltd., Shanghai, China, average particle size 15 μm) was added to this dispersion by 30 min sonication followed by 24 h vigorous stirring. After slow evaporation of the solvent at 50 °C, nano-TiO_2-coated CMS was obtained.

X-ray diffraction measurements were performed with Cu Kα target at a Bruker D8 Advanced Spectrometer instrument. Scanning electron microscope (SEM) (Philips XL 30) was used to measure the surface morphology of Cu-coated graphitic carbon.

The fabrication of electrochemical cells and galvanostatic discharge–charge measurements were carried out as follows: 90 wt.% CMS or TiO_2-coated CMS, the anode material for the Li-ion test cells, was mixed with 5 wt.% poly(vinylidene difluoride) (PVDF) binder and 5 wt.% acetylene black in a solvent of *N*-methyl-2-pyrrolidone to prepare slurry. The slurry was coated onto a copper foil and dried at 120 °C under vacuum. After drying, the electrode was cut into small pieces and assembled into coin-type model cells in a glove box filled with argon. The pieces were used as working electrodes. Lithium foil was used as the counter and reference electrode. Celgard 2400 separator was placed between working electrode and lithium metal foil. The discharge and charge was galvanostatically measured in 1 M $LiClO_4$ solution of PC–DMC (dimethyl carbonate) (1:1 by volume) by a Land CT2001A tester at about 0.25*C* at the voltage range of 0.0–2.0 V versus Li^+/Li.

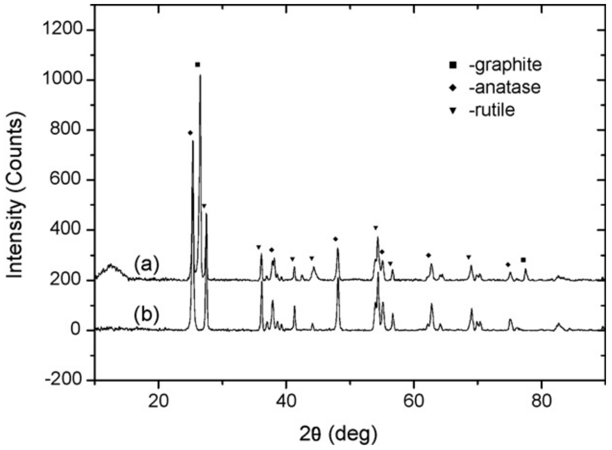

Fig. 1. X-ray diffraction pattern of (a) the TiO_2-coated CMS and (b) the original TiO_2.

Cyclic voltammograms (CV) were measured with the same cells by CHI604C electrochemical analyzer between 2.5 and 0 V at a scan rate of 0.1 mV/s.

3. Results and discussion

Fig. 1 depicts the X-ray diffraction pattern of TiO_2-coated CMS and the original TiO_2. Sharp diffraction peaks for graphite and TiO_2 are seen in the composite and no other impurities appear (Fig. 1a). Both anatase and rutile phases of TiO_2 are observed in the coated composite. From the comparison with the original nano-TiO_2 powders (Fig. 1b), it can be seen that there is no evident change of the crystal structure during coating process since the original TiO_2 is also composed of anatase and rutile phases. The coated composite was just endured at 50 °C without other heat-treatment, and such a low temperature cannot exert effect on the crystal structure of TiO_2.

Fig. 2 presents the scanning electron micrographs (SEM) of the original CMS and TiO_2-coated CMS. It can be observed that the surface of the original CMS is apparently very smooth. In contrast, the surface of TiO_2-coated CMS is uniformly covered by a layer of TiO_2 particles and the surface is rough. The main reason is that the surface of graphitic carbon is full of active sites [2,10,32], which can easily absorb the lipophilic nano-TiO_2 particles. These results together with X-ray diffraction pattern

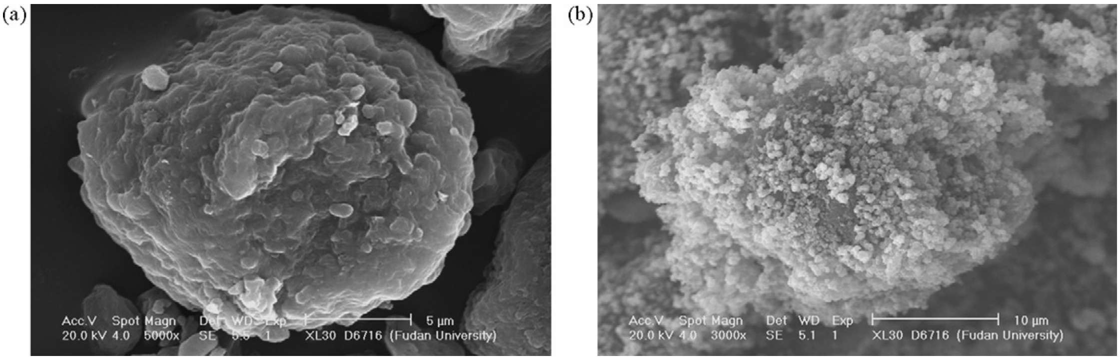

Fig. 2. Scanning electron micrographs of (a) the original and (b) the TiO_2-coated CMS.