Geo2-Coated MCMB Composite as Anode Material for Lithium Ion Battery in PC-Based Electrolyte

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Abstract. GeO2-coated MCMB was prepared by chemical reduction method. The structure and morphology of the material were characterized by X ray diffraction (XRD) and scanning electron microscopy (SEM). Cyclic Voltammetry and galvanostatic charge/discharge tests were carried out to measure electrochemical performance. The composites exhibited a stability in a PC-based electrolyte which can suppress the decomposition of propylene carbonate and the exfoliation of graphite layer, compared with bare MCMB electrode. GeO2-coated MCMB electrode is expected to have good performance at low temperature.

1. Introduction
Lithium-ion batteries have been widely used in aerospace, polar science, electric vehicles, military and other fields since the 21st century because of their high operating voltage, high energy density, long cycle life and environmental friendliness [1-3]. With the gradual expansion and deepening of the application field, lithium-ion batteries with poor low-temperature performance of the short slab gradually exposed. Today, it is required to achieve good performance at -40℃ or even lower temperature [4, 5].

Lithium-ion batteries have many problems at low temperature, such as poor cycle rate performance, low specific capacity and poor recovery. It is a current trend to use electrolyte with low melting point to improve low temperature performance. Propylene carbonate (PC) melting point (-49℃) is much lower than EC and has excellent low temperature performance. But the co-implantation of PC molecules and lithium ions leads to the continuous decomposition and peeling of graphite layers when the volumetric PC content is up to 25% [6]. There are two ways to prevent PC from decomposing on graphite surface. One is to add additives to the PC-based electrolytes and the other is to coat graphite with other materials. The main purpose of adding additives is to form SEI films before PC decomposition. Effective additives include fluoroethylene carbonate (FEC) and vinylene carbonate (VC) [7, 8]. Covering these active points with a layer of other materials on the surface of graphite, which can avoid the true contact of these active points with PC, thus can avoid the decomposition of PC. MoO3, Cu, TiO2 and Li4Ti5O12 have been found to be effective [9-12].

Ge has good low temperature properties and good compatibility with electrolyte [13], as far as we know, there is few study about GeO2 modified graphite. Here we coated MCMB surface with a layer of GeO2 particles to inhibit the decomposition of PC. The preliminary results show that the composite materials have fairly stable electrochemical properties in PC-based electrolytes.
2. Experiment

2.1. Preparation of GeO$_2$-coated MCMB composite materials

0.8 g GeO$_2$ powders and 0.02 g PVP (K-30) were dissolved completely in 40 mL 0.5 M NaOH solution under stirring to form a transparent and clear solution. Then the pH of the solution was adjusted to 7 by 0.5 M HCl solution. And then 0.833 g MCMB powders were added into the solution under magnetic stirring for 30 min. After that 80 mL 3 M NaBH$_4$ solution was quickly added into above solution and the beaker was transferred to a water bath at 60°C for 3 h. Then the precipitates were washed and filtered with deionized water several times, and dried in a vacuum at 60°C for 12 h.

2.2. Material characterization

The crystal structure of the composite was characterized by powder X-ray powder diffraction (XRD, D8 Advance) with Cu K-alpha radiation. The morphology of the composite was observed by field emission scanning electron microscope (SEM, HitachiS-4800).

2.3. Electrochemical measurements

Electrochemical performance of GeO$_2$-coated MCMB and bare MCMB anodes were investigated by using CR2016 coin cells, which were assembled in an argon filled glove box and consisted of a working electrode, a microporous film (Celgard 2400), a counter electrode (metallic lithium) and 1M LiPF$_6$(PC+DMC) (3:7, v/v) electrolyte. The working electrode were fabricated by mixing 70 wt.% active material, 20wt.% carbon black, and 10 wt.% Aqueous binder (sodium carboxymethyl cellulose (CMC)/styrene butadiene rubber (SBR) system). The slurry was coated on the copper foil and dried at 100°C for 12 h under vacuum. Cyclic voltammetry measurements were performed by an electrochemical workstation (CHI660C) at a scan rate of 0.1 mVs$^{-1}$ between 0.001 V and 1.5 V. The charge and discharge tests were performed using a battery testing system (CT2001A) at 0.5 C rate in 0.01 V and 1.5 V.

3. Results and discussion

Fig.1 shows the X ray diffraction pattern of GeO$_2$-coated MCMB composite material. In addition to the diffraction peak of the MCMB, there are five peaks contributed to crystalline hexagonal GeO$_2$ (JCPDS 36-1463). The results indicate the formation of GeO$_2$ in composite material.

![XRD pattern](image_url)  
**Figure 1.** XRD patterns of GeO$_2$-coated MCMB composite
The morphology of the bare MCMB and GeO₂-coated MCMB composite material was characterized by SEM observation. The bare MCMB was shown in Fig. 2(a), MCMB are spherical particles with the diameter about 10 μm. The surface of the bare MCMB is apparently very smooth. After GeO₂-coating, the surface of the GeO₂-coated MCMB is become rough, both XRD result and SEM images indicate that GeO₂ particles have been coated on the MCMB surface by liquid phase reduction method.

![Figure 2. SEM image of (a) bare MCMB (b) GeO₂-coated MCMB composite](image)

The CV curves of the GeO₂-coated MCMB and bare MCMB electrodes were shown in Fig. 3. In the case of bare MCMB, there is a large irreversible peak around 0.45 V, which can be attributed to PC decomposition and graphite spalling. For GeO₂-coated MCMB, the irreversible feature of 0.25 V can be attributed to transformation GeO₂ into germanium. The wide peaks observed in the 0.2 V and 0.01 V voltage ranges are attributed to the Li-Ge alloy formation and MCMB lithium ion implantation processes of MCMB. After the first cycle, the Li⁺ can intercalate/deintercalated into/from the GeO₂-coated MCMB composite reversibly and steadily.

![Figure 3. Cyclic voltammograms of the bare MCMB and GeO₂-coated MCMB](image)

The first discharge–charge profiles of the bare MCMB and GeO₂-coated MCMB electrodes are shown in Fig. 4(a). During the first discharge of graphite, there is a long platform of about 0.7 V. And MCMB has little charging capacity. It is well known that the phenomenon corresponds to the continuous PC decomposition and exfoliation of graphene sheets. The PC electrolyte decomposition platform was not observed at 0.7 V in the GeO₂-coated MCMB. It can be inferred that the GeO₂
coating inhibits the stripping of the graphite layer and retains the graphite structure, so that the lithium ions can intercalate/deintercalate on the MCMB. In the following cycle, discharge/charging curves of the 1th, 2th and 5th cycles are mostly overlapped, indicating that the GeO\textsubscript{2}-coated MCMB composite can exist stably in PC electrolyte. For Fig. 4(b). The cyclic stability of the GeO\textsubscript{2}-coated MCMB composite in PC-based electrolytes is as good as that in commercial EC-based electrolytes. Which still has 658.7 mAh g\textsuperscript{-1} reversible specific capacity after 10 cycles.

![Figure 4. (a) The discharge/charge tests; (b) Cycling performance of the bare MCMB and the GeO\textsubscript{2}-coated MCMB](image)

4. Conclusion
The GeO\textsubscript{2}-coated MCMB were prepared by chemical reduction, which were used as anode electrode materials in PC-based electrolyte respectively. CV and discharge/charge curves confirmed that GeO\textsubscript{2} coating inhibited the decomposition of PC-based electrolyte, as well as the co-insertion of solvents and the stripping of graphite layers. The composite material is expected to improve its electrochemical properties at low temperatures.

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