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# Graphite@MoO$_3$ composite as anode material for lithium ion battery in propylene carbonate-based electrolyte

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ABSTRACT

Graphite@MoO$_3$ composite was prepared by coating MoO$_3$ on graphite in order to improve the performance of graphite as an anode for lithium ion battery in propylene carbonate (PC)-based electrolyte. The coated MoO$_3$ layer acts as a protective layer which separates graphite from PC-based electrolyte solution. Cyclic voltammograms and discharge–charge measurement suggest that the cointercalation of PC is suppressed and lithium ions can reversibly intercalate into and deintercalate from the graphite@MoO$_3$ composite.

## 1. Introduction

Ethylene carbonate (EC)-based electrolytes have been widely applied for lithium ion batteries using graphitic carbons as anode materials. In such electrolytes, a film called solid electrolyte interface (SEI) can be formed on the surface of the graphite particles through the reductive decomposition of the solvent at 0.5–1.0 V vs. Li$^+$/Li during the first discharge process [1,2]. It has been generally accepted that the SEI plays an important role of preventing co-intercalation of solvated Li$^+$ ions, thus allows the reversible intercalation/deintercalation of unsolvated Li$^+$ ions into/from the graphite electrode in the subsequent cycles [3]. As the technology develops, lithium ion batteries are needed in broader fields where extreme conditions like ultra low temperature may be encountered. However, EC-based electrolyte cannot be used at very low temperature due to its high melting point (39 °C). In such situation, PC-base electrolytes become attractive because of its much lower melting point (−49.2 °C) than that of EC as well as superior ionic conductivity and low price [4]. However, lithium ions cannot reversibly intercalate into and deintercalate from graphite in PC-based electrolyte. Only poor SEI film is formed on the graphite electrode because PC molecules together with lithium ions co-intercalate into graphite followed by continuous decomposition of PC, leading to graphene sheet exfoliation [5–9]. To overcome these difficulties, many efforts have been paid, e.g., adding additives into PC solutions such as vinyl tris-2-methoxyethoxy silane [10], polyether-functionalized disiloxanes [11], propane sultone [12], maleimide (MI)-based compounds [13]. These additives produce stable SEI layers on the graphite, which significantly suppress the co-intercalation and decomposition of the PC molecules, allowing the desolvated Li$^+$ ions to intercalate. However, these additives will at same time affect the cathode because they are directly added into the electrolytes [3,14]. Another attempt is to coat graphite with other materials which play the role of SEI film to prevent direct contact between electrolyte and graphite, thus allow reversible intercalation/deintercalation of unsolvated Li$^+$ ions into/from the graphite electrode [15–18].

MoO$_3$, as one of the most intriguing transition-metal oxides, is widely used in various fields, such as photochromic and electrochromic devices, gas sensors, catalysts and lubricants [19–24]. It was recently reported that MoO$_3$ exhibits high capacities either as cathode [25–28] or anode [29,30] for lithium ion batteries. In this paper, we for the first time used molybdenum trioxide (MoO$_3$) as a coating material on an artificial graphite to get a graphite@MoO$_3$ composite. It was found that this method was effective in suppressing the decomposition of PC molecules and the exfoliation of graphite during cycling in PC-based electrolyte.

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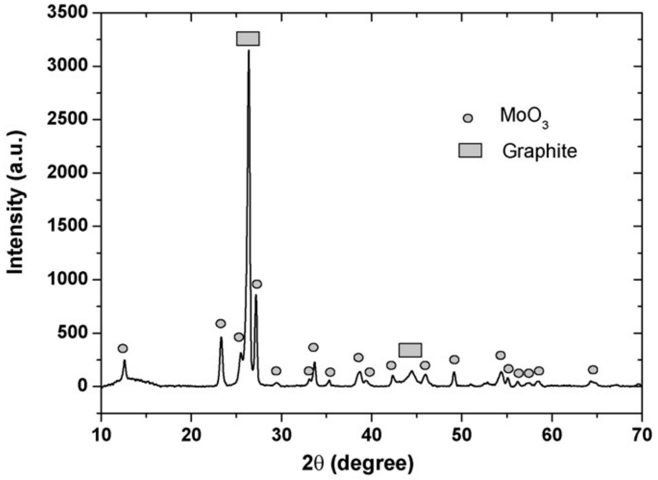

**Fig. 1.** XRD pattern of the as-prepared graphite@$MoO_3$ composite.

## 2. Experimental

The preparation of graphite@$MoO_3$ composite is as follows. 0.15 g phosphomolybdic acid $H_3PMo_{12}O_{40}\cdot 6H_2O$ (PMA) was dissolved in 5 ml ethanol, and then 3 g graphite (CMS, an artificial graphite from heat-treatment at 2800 °C, Shanshan Co. Ltd., Shanghai, China, average diameter 15 μm) was added into the solution. After sonicated for 5 min, the suspension was stirred until the ethanol was evaporated away. The as-prepared mixture was then calcined under 500 °C in a tube furnace under Ar atmosphere, through which PMA was decomposed into $MoO_3$ and a graphite@$MoO_3$ composite ($MoO_3$ 14.4 wt%, CMS 85.6 wt %) was obtained.

The crystalline structure of the product was characterized by X-ray powder diffraction (XRD) using Rigaku D/MAX-IIA diffractometer equipped with CuKα radiation (λ = 1.54056 Å). The scanning electron microscopic (SEM) images were obtained on a Philips XL 30 scanning electron microscope.

Coin-type half-cells were assembled for evaluating the electrochemical performance of the as-prepared product. The as-synthesized active material, carbon black and poly(vinylidene difluoride) (PVDF) at a ratio of 8:1:1 (w/w/w) were mixed and then suspended in *N*-methylpyrrolidone to make a slurry that was spread uniformly on a copper foil as current collector. The coated copper foil was cut into round pieces with a diameter of 1 cm, which were dried under ambient condition and then at 120 °C in a vacuum overnight. Finally, model cells were assembled in a glove box with the round pieces as working electrode, lithium foil as the counter and reference electrode, Celgard 2400 as the separator, and 1 M $LiClO_4$ solution of PC/DMC (dimethyl carbonate) (1:1, v/v) as the electrolyte. Cyclic voltammetry was measured using a CHI 600C electrochemical work station (Shanghai CH instruments). Galvanostatic cycling was performed using LANDct3.3 battery tester.

## 3. Results and discussion

XRD pattern of the as-prepared product is shown in Fig. 1. The diffraction peaks can be assigned to graphite and $MoO_3$ as denoted in the figure, which indicates that PMA was completely decomposed to $MoO_3$ and there is no by-product in the reaction.

SEM images of original graphite and the graphite@$MoO_3$ composite are shown in Fig. 2. It can be seen that the surface of the graphite is rough while that of the graphite@$MoO_3$ composite is smooth. Apparently, the graphite@$MoO_3$ composite is covered by a layer of $MoO_3$ according to the XRD characterization.

The CV curves shown in Fig. 3 were measured at a scan rate of 0.1 mV/s in 1 M $LiClO_4$ solution of PC/DMC (1:1, v/v). In the first cycle, a cathodic peak located at about 0.4 V vs. $Li/Li^+$ was observed, which is ascribed to the PC decomposition [26]. However, unlike the previously reported results [17,18], in the following anodic polarization there is also a prominent anodic peak located at around 0.2 V which corresponds to the deintercalation of lithium ions. In the subsequent cycles, the cathodic peak at 0.4 V vanishes while the anodic peak at 0.2 V is retained, and the curves for these cycles mostly overlap, implying PC decomposition stops after the first cycle and lithium ions can intercalate/deintercalate into/from graphite@$MoO_3$ composite reversibly and stably.

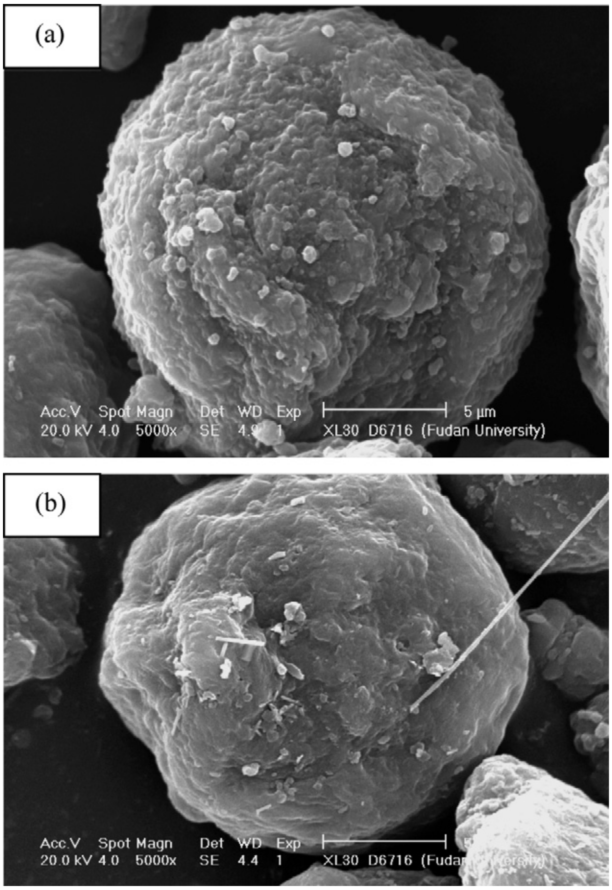

**Fig. 2.** SEM images of (a) the virginal graphite and (b) the graphite@$MoO_3$ composite.

The discharge–charge profiles of the graphite@$MoO_3$ composite and the virginal graphite tested under a current density of 60 mA/g in 1 M $LiClO_4$ solution of PC/DMC (1:1, v/v) are shown in Fig. 4. During the discharge process of the virginal graphite in the first cycle, there is an extended plateau at around 0.8 V and in the following charge process the voltage rises steeply. It is well known that the plateau corresponds to the insertion of PC-solvated lithium ions which causes heavy exfoliation of graphene sheets, thus no lithium ion intercalates reversibly and no charge capacity

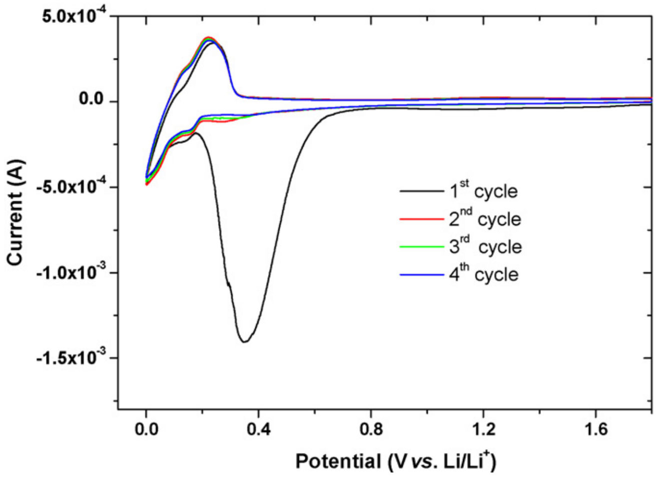

**Fig. 3.** Cyclic voltammograms of the graphite@$MoO_3$ composite measured in 1 M $LiClO_4$ solution of PC/DMC (1:1, v/v) at a scan rate of 0.1 mV/s during the initial consecutive 4 cycles.

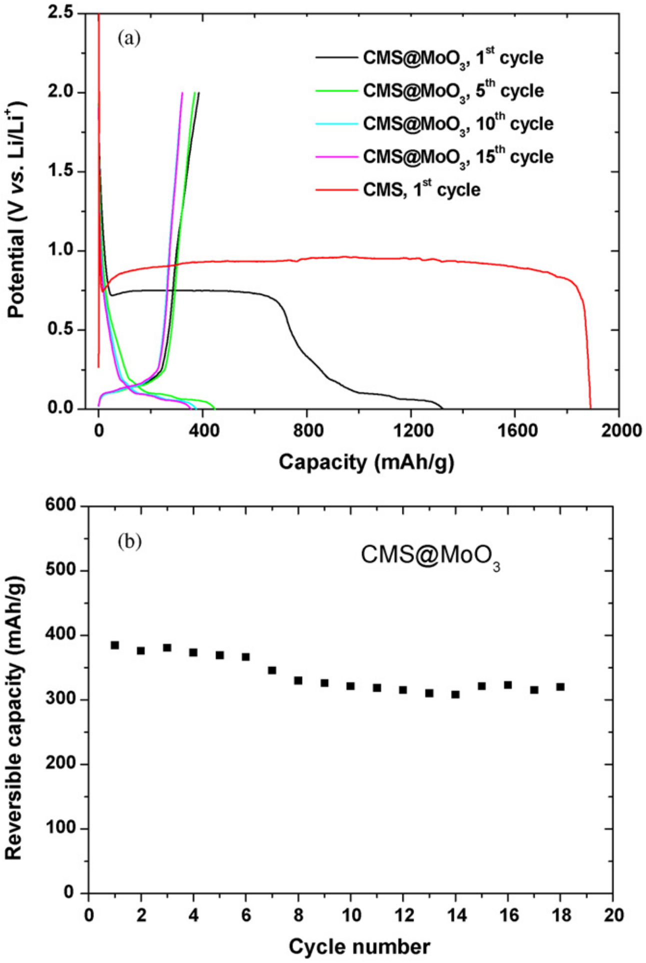

**Fig. 4.** (a) The discharge–charge profiles of the virginal graphite and the graphite@$MoO_3$ composite and (b) the cycling performance of the graphite@$MoO_3$ composite tested at a current density of 60 mA/g (about 1/6 C) in 1 M $LiClO_4$ solution of PC/DMC (1:1, v/v).

is obtained. However, for the graphite@$MoO_3$ composite in the discharge process of the first cycle, following a plateau around 0.75 V, the voltage slowly drops to another plateau at about 0.1 V which corresponds to the intercalation of lithium ions into graphite; and in the following charge curve, unlike the virginal graphite, there is a plateau at 0.2 V, corresponding to the deintercalation of lithium ions from the graphite. It can be deduced that the $MoO_3$ coating depresses the graphene sheets exfoliation, preserves the graphite structure, and therefore enables lithium ions to intercalate/deintercalate into/from the graphite reversibly. Although there is still some PC decomposition which makes the Colombic efficiency low in the first cycle, in the following cycles the PC decomposition stops and the discharge/charge curves of the 5th, 10th and 15th cycles mostly overlap, suggesting good reversibility of lithium ion storage in the graphite@$MoO_3$ composite. The graphite@$MoO_3$ composite exhibits a reversible capacity of 385 mAh/g in the first cycle, which is larger than the theoretical capacity of graphite because $MoO_3$ as an anode exhibits a much higher reversible capacity (>600 mA/g) in the initial cycle [29,30]. The cycling performance of graphite@$MoO_3$ composite shown in Fig. 4 is quite desirable. The reversible capacity of the graphite@$MoO_3$ composite preserves 320 mAh/g after 18 cycles, which is comparative with the reversible capacity of graphite in EC-based electrolyte [3]. From these results together with the cyclic voltammograms, it can be speculated that the coating layer of $MoO_3$ plays an important role of SEI film to keep the surface of graphite from direct contact with PC. Due to some possible cracks or unevenness of the film, the PC decomposition is not completely avoided in the first cycle. However, it does not affect the intercalation of lithium ions into the graphite during the following cycles.

## 4. Conclusions

Graphite@$MoO_3$ composite was synthesized and studied as anode material of lithium ion battery in PC-based electrolyte. The cyclic voltammograms and discharge–charge curves show clearly that the coating $MoO_3$ layer effectively suppresses the decomposition of PC and the exfoliation of graphite and enables lithium ions to intercalate/deintercalate into/from graphite reversibly in PC-based electrolyte. The graphite@$MoO_3$ composite is stable and its cycling performance in PC-based electrolyte is good as in the commercial EC-based electrolyte, which proves that $MoO_3$ coating is a good way to improve the electrochemical performance of graphite carbon as anode in PC-based electrolyte and will be promising for the application of lithium ion batteries at low temperature.

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