



Short communication

2-Phenylimidazole as an additive to prevent the co-intercalation of propylene carbonate in organic electrolyte for lithium-ion batteries

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ABSTRACT

2-Phenylimidazole (PID), which is structurally different from previously reported compounds, has been studied as a film-forming additive for graphite anode in PC-based electrolyte for lithium-ion batteries. A 1.0 mol l⁻¹ LiPF₆/PC: DMC (1:1, v/v) electrolyte containing 3 wt.% 2-phenylimidazole was capable of suppressing the co-intercalation of PC and inhibiting the decomposition of electrolytes during the first lithium intercalation. The cyclic voltammogram shows that the reduction potential of PID is about 1.65 V vs. Li/Li⁺, forming a favorable solid electrolyte interface (SEI) on the graphite electrode. The morphologies and the chemical composition of the graphite electrode surface were characterized by SEM and XPS. The results show that a stable SEI film was formed on the surface of graphite by the addition of PID, which accounts for the excellent cycleability of the graphite electrode in PC-based electrolyte.

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1. Introduction

Organic solvents, especially ethylene carbonate (EC) and propylene carbonate (PC), have been studied for use in lithium-ion batteries [1,2]. Due to the formation of a stable solid electrolyte interface (SEI) with favorable characteristics, EC-based electrolytes have been used extensively in commercial lithium-ion batteries. However, EC-based electrolyte cannot be used at low temperatures owing to its high melting point (39 °C). Compared to EC, PC seems much more attractive due to its much lower melting point (−49.2 °C), higher ionic conductivity and low price. However, the decomposition of PC and the following co-intercalation of PC molecules into graphite give rise to exfoliation of the graphene layers [3–6]. In the past, many attempts have been made to improve the compatibility of PC-based electrolyte with graphite anodes, such as coating [7–9] and addition of additives such as allyl ethyl carbonate [5], acrylonitrile [6], tetrachloroethylene [10], ethylene sulfites [11], vinylene carbonate (VC) [12], propylene sulfite [13], chloroethylene carbonate [14], silanes [15,16], and triethyl orthoformate [17]. However, there is no report on the possible action of imidazole derivatives.

In this report, we show that 2-phenylimidazole (PID) is a novel electrolyte additive that is effective in suppressing exfoliation of graphite. After adding 3% (w/w) PID to the PC-based electrolyte, the graphitic anode performs very well.

2. Experimental

2-Phenylimidazole (PID, Aldrich, 98%) was used as received without further purification. The electrolyte was 1 mol l⁻¹ LiPF₆ dissolved in a 1:1 (v/v) mixture of propylene carbonate (PC) and dimethyl carbonate (DMC). CMS (artificial graphite, average diameter 15 μm) was obtained from Shan-shan Co. Ltd. (Shanghai, China). The electrolyte was mixed in a glove box under a dry argon atmosphere. The anode was prepared by mixing the CMS, polyvinylidene fluoride (PVDF) and carbon black in a ratio of 85:10:5 (w/w/w). The mixture was coated on a copper foil, and then heated 12 h in a vacuum oven at 120 °C. Electrochemical performance of the electrodes was tested with coin-type model cells with lithium foil as the counter and reference electrode, and Celgard 2400 as the separator. Scanning electron microscopy (SEM, Philips XL300) was used to observe the surface morphology of the CMS electrode. The chemical components of the CMS electrode surface were measured using XPS (PerkinElmer PHI-5000C). The discharge and charge test was galvanostatically measured by a Land CT2001A tester in the voltage range of 0–2.0 V at a current density of 0.8 mA cm⁻². Cyclic voltammograms were measured by a CHI604C electrochemical workstation between 2 and 0 V at a scan rate of 0.05 mV s⁻¹.

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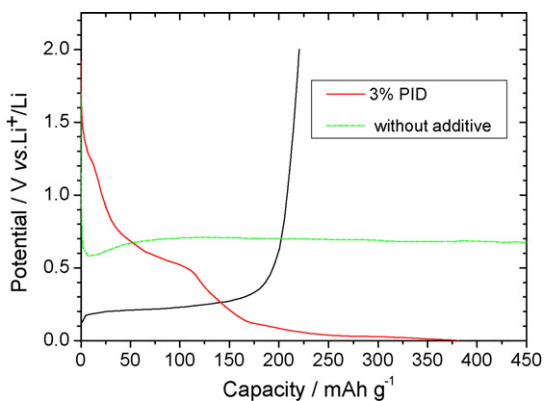


Fig. 1. First discharge-charge curves of the CMS electrode in 1 M LiPF₆/PC: DMC (1:1, v/v) without additive (dash line) and with 3 wt.% PID (solid line).

3. Results and discussion

The discharge-charge voltage curves of the Li||CMS cell in 1 mol l⁻¹ LiPF₆ solution of PC/DMC (1:1, v/v) with and without PID during the first cycle are shown in Fig. 1. For the cell without PID, there is a long plateau at about 0.7 V vs. Li/Li⁺ in the first discharge curve, which indicates that decomposition of PC and the co-intercalation of the PC-solvated lithium ion into the graphene layer occur [5–7]. Apparently, the lithium ion intercalation into the graphene layer is very rare. However, for the cell containing 3 wt.% PID, the discharge curve in the potential range of 1.6–1.2 V vs. Li/Li⁺ decreases slowly, which corresponds to the reduction of PID on the graphite surface, resulting in the formation of a passivating film. Furthermore, the formation of the SEI is effective enough to enable reversible lithium ion intercalation and deintercalation. The discharge curve below 0.2 V is ascribed to the intercalation of lithium ion into graphite, which reveals that the co-intercalation of PC has been suppressed by PID.

The cyclic voltammograms of CMS electrode in 1 mol l⁻¹ LiPF₆/PC: DMC (1:1, v/v) with and without 3% (w/w) PID are shown in Fig. 2. Propylene carbonate-based electrolytes without the addition of PID are incompatible with the CMS electrode, due to the decomposition and the co-intercalation of PC molecules into the graphene layers, eventually giving rise to the exfoliation of the graphite. After three cycles of cyclic voltammetry, there is no current response of lithium ion intercalation and deintercalation into and from the CMS electrode. This is consistent with earlier reports [3–17]. In contrast, the results are totally different for the electrolyte containing 3 wt.% PID. During the first three CV cycles the

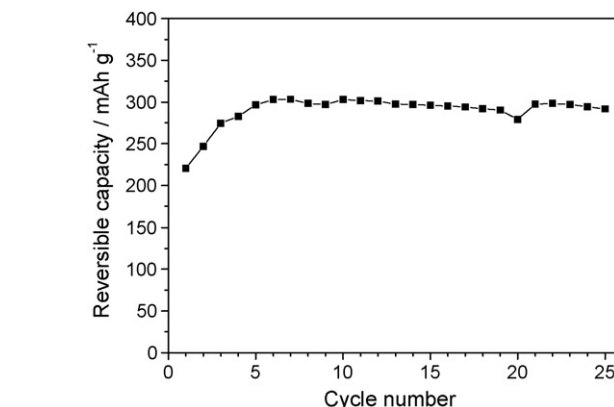
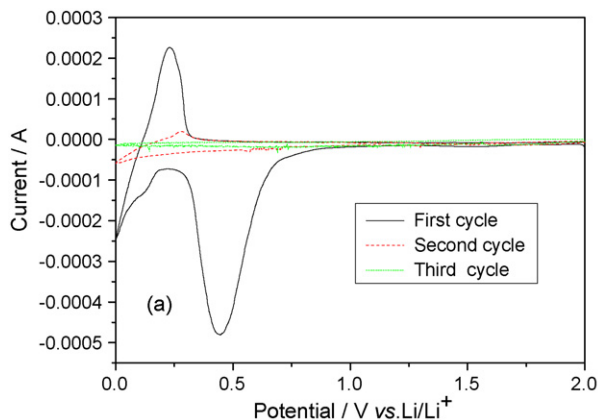


Fig. 3. Cycling performance of CMS at 0.8 mA cm⁻² in 1 mol l⁻¹ LiPF₆/PC: DMC (1:1, v/v) with 3 wt.% PID addition.

current response representative of lithium ion intercalation and deintercalation into and from the CMS electrode does not decrease significantly. The CV in the first cycle also shows that the reduction peak at 0.7 V ascribed to the co-intercalation of PC into graphite is greatly reduced and a new peak appears at 1.65 V ascribed to the decomposition of PID on the CMS electrode. In the second and third cycle, the peaks at 1.65 and 0.7 V are not visible anymore, indicating that the film-forming process is by and large finished in the first cycle and the co-intercalation of PC into graphite is effectively suppressed. Compared with other additives, since PID does not have an unsaturated vinylene group, during the first cycle it does not form solely as the SEI film. As a result, the CV peak at around 0.5 V corresponding to decomposition or reduction of PC still appears in the first scan, which contributes to the partially effective composition of SEI films. This is also consistent with the data from Fig. 1. In the case of other additives such VC, the action of PC is completely prevented in the first CV scan.

To observe the effect of the addition of PID on the CMS electrode in PC-based electrolyte, the cycle performance of the Li||CMS cell in 1 M LiPF₆ solution of PC/DMC (1:1, v/v) with PID addition was carried out in the voltage range of 2.0–0 V at 0.8 mA cm⁻² (see Fig. 3). The reversible capacity in the first cycle is about 220 mAh g⁻¹, lower than the discharge capacity, which may be due to the irreversible decomposition of PC on the CMS surface. After four cycles, the reversible capacity of the CMS electrode arrives at a steady value of about 300 mAh g⁻¹, suggesting that the SEI film on the surface of CMS has become stable and compact. This phenomenon is in agree-

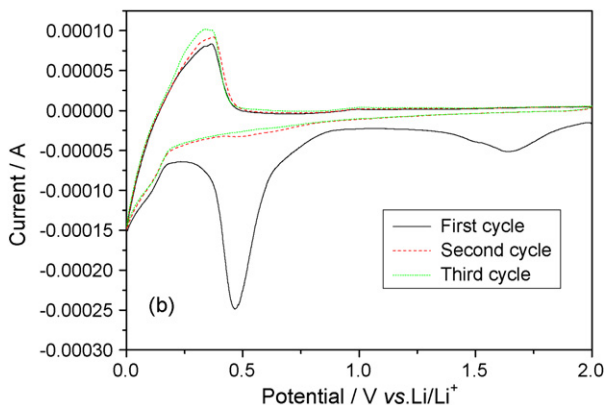


Fig. 2. Cyclic voltammograms of the CMS electrode in 1 mol l⁻¹ LiPF₆/PC: DMC (1:1, v/v) electrolyte: (a) without additive and (b) with 3 wt.% PID.

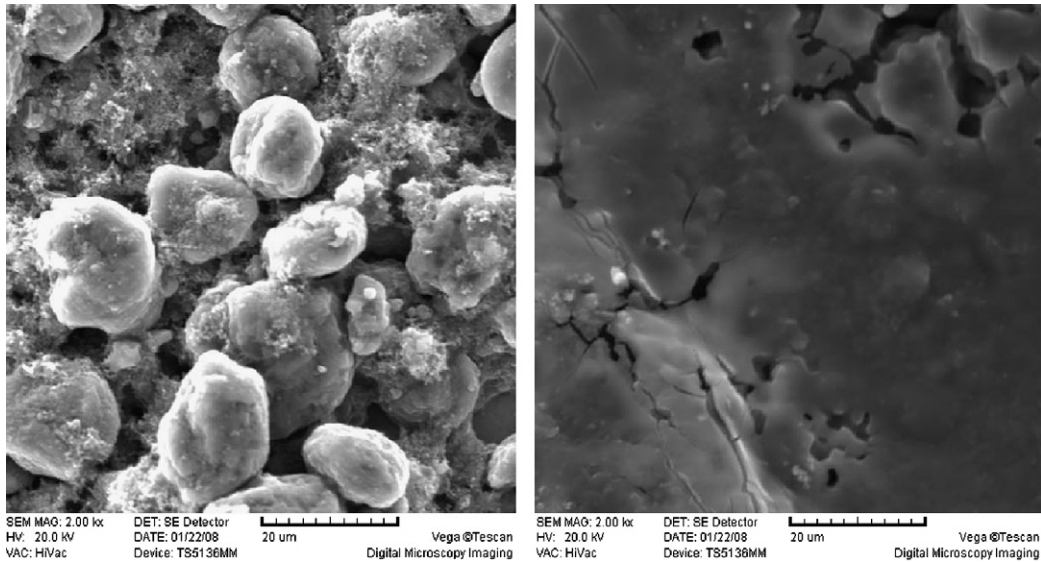


Fig. 4. SEM images of CMS electrode (a) before cycling and (b) after electrochemical cycles discharged to 0V in 1 mol l^{-1} $\text{LiPF}_6/\text{PC}:\text{DMC}$ (1:1, v/v) with 3 wt.% PID.

ment with the results of other researchers [1,5,18]. After 25 cycles, the loss of specific capacity is very small, which indicates that the addition of PID could prevent the decomposition of PC and suppress the intercalation of PC-solvated ion into the graphene layer of the CMS electrode, leading to the reversible insertion of lithium ion into graphite.

To gain some useful information on the morphology of the CMS surface, scanning electron micrographs of the CMS electrode are shown in Fig. 4. It can be seen clearly that the original CMS has a ball-

shaped structure. For the CMS electrode having cycled in 1 mol l^{-1} $\text{LiPF}_6/\text{PC}:\text{DMC}$ (1:1, v/v) electrolyte containing 3 wt.% PID, the surfaces of the CMS spheres are covered by a plate-like film, which agrees with the result of other researchers [7,19]. It is believed that PID has decomposed during the first insertion of lithium ion and formed a stable SEI film on the surface of the CMS electrode. Addition of 3 wt.% PID suppressed effectively the decomposition and co-intercalation of PC, and hence prevented the exfoliation of the graphene layer.

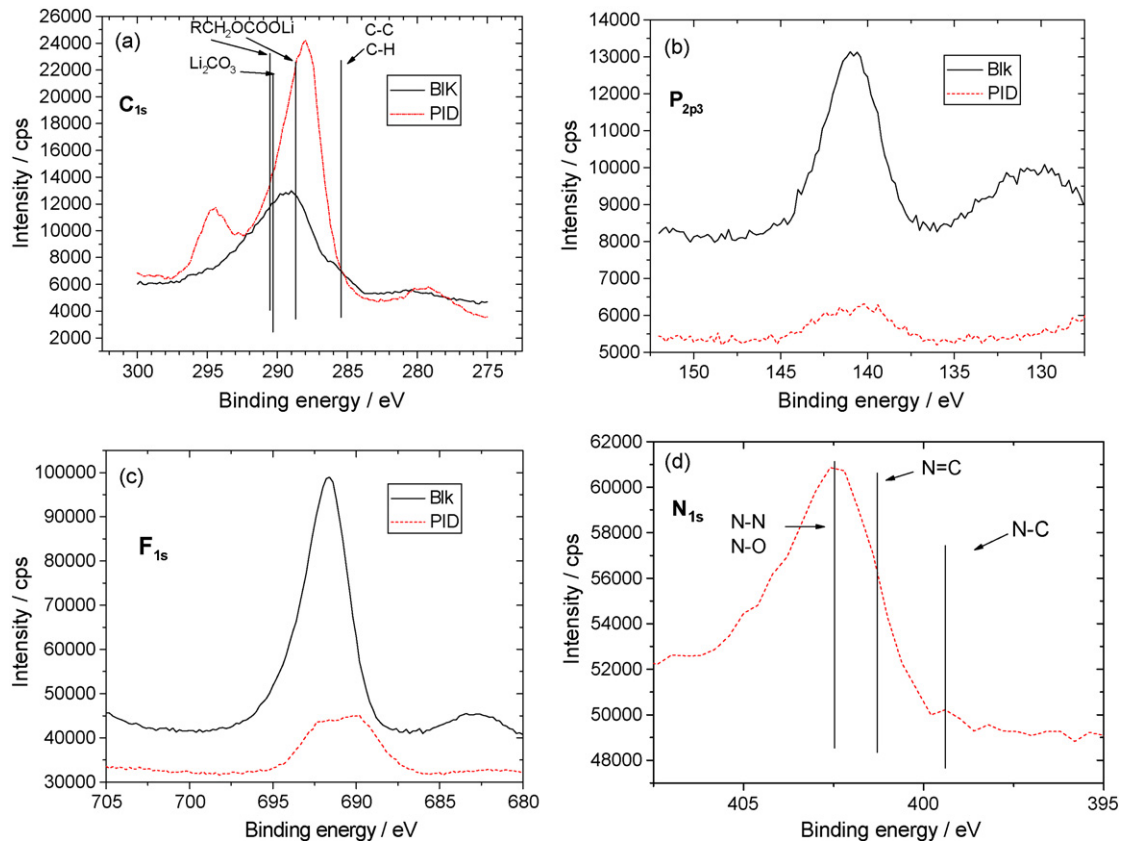


Fig. 5. XPS of CMS electrode after cycling in 1 mol l^{-1} $\text{LiPF}_6/\text{PC}:\text{DMC}$ (1:1, v/v) with and without 3 wt.% PID: (a) C_{1s} , (b) P_{2p_3} , (c) F_{1s} and (d) N_{1s} .

The XPS spectra of the CMS electrode after cycling in PC-based electrolyte with and without PID are shown in Fig. 5. Compared to the PC-based electrolyte without the additive, the surface film of the CMS electrode with PID contains much more ROCO_2Li and Li_2CO_3 , which are considered the main decomposition products of PC on the surface of graphite [2]. Meanwhile, in the XPS spectra of P_{2p3} and F_{1s} , we found that the components of the SEI film have less P and F, which shows that the decomposition of LiPF_6 was prevented by the addition of PID. Furthermore, we found that the amount of nitrogen is as high as 2.49% on the surface of the CMS after cycling in the electrolyte with the additive, which clearly indicates that the additive was reduced and became a part of the chemical components of the SEI film. As to the detailed mechanism, further study is needed. However, from the data in Fig. 5(d), the reduction or breaking of the C–N bond is one of the main reactions since the peak corresponding to N–N bonding is very strong.

These results obtained from XPS and SEM indicate that the addition of PID is helpful to form a stable and favorable SEI film, which accounts for the excellent cycleability of the graphite in PC-based electrolyte. The results are consistent with those of the cyclic voltammetry and constant current charge–discharge study.

4. Conclusions

A new film-forming additive (2-phenylimidazole, PID) was explored for lithium-ion batteries in PC-based electrolyte when the graphite electrodes are used as anode material. Both the discharge–charge measurements and cyclic voltammograms show that the PC decomposition and graphite exfoliation were greatly suppressed after the addition of PID. The reduction reaction of PID occurs at 1.65 V, much higher than the potential of PC co-intercalation, and forms a stable and favorable SEI film after the first cycling. Therefore, the CMS electrode shows good electrochemical

performance in $1 \text{ mol}^{-1} \text{ LiPF}_6/\text{PC}$: DMC (1:1, v/v) electrolyte with 3 wt.% PID.

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