



Short communication

Electrochemical behaviour of a graphite electrode in propylene carbonate and 1,3-benzodioxol-2-one based electrolyte system

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Abstract

The electrochemical behaviour of a graphite electrode in a 1 M LiPF₆-propylene carbonate (PC)/diethyl carbonate (DEC) (1:1 in volume) electrolyte system and in the same electrolyte system with the addition of 1,3-benzodioxol-2-one (C₆H₄CO₃) is investigated. The decomposition of PC molecules on the graphite during the first lithium intercalation is significantly reduced by the addition of 1,3-benzodioxol-2-one. A mechanism is proposed for the suppression of PC decomposition. The 1,3-benzodioxol-2-one is stable against a LiCoO₂ electrode up to 4.3 V (vs. Li⁺/Li). © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The development of the so-called ‘rocking-chair’ lithium battery is an exciting area in the battery field because of its high specific energy. Many efforts have focused on developing and/or improving high-voltage cathode materials, low-voltage and high-capacity anode materials, and the electrolyte systems suitable for such types of lithium-ion batteries. As an anode material, graphite has a nearly perfect layered structure and a high capacity of 372 mA h g⁻¹ with a flat voltage curve near zero volts relative to lithium. The high capacity makes graphite a most desirable anode material. Nevertheless, graphite has a major disadvantage in that it is unstable during lithium intercalation in PC-based electrolytes: co-intercalation with solvent molecules leads to exfoliation of the graphite. Indeed, the electrolyte solution commercially used for lithium-ion batteries with graphite electrodes is commonly limited to ethylene carbonate (EC)-based electrolytes. These batteries display poor low-temperature performance, however, due to their low conductivity (EC has a melting point of 37°C). By contrast, propylene carbonate (PC) has a higher melting

point (49°C). The problem that prevents the widespread use of PC is that it electrochemically decomposes at the graphite electrode during the initial lithium-ion intercalation process [1,2]. Thus, it would be suitable to use PC as the organic solvent for lithium-ion batteries if the decomposition reaction could be suppressed on the graphite electrode. In previous work [3], the electrochemical decomposition of PC was suppressed by choosing a proper mixing ratio of PC with co-existing solvents. In the present study, we report the electrochemical performance of a graphite electrode MCMB 6-28 (graphitised mesophasecarbon microbeads heated at 2800°C) in a 1 M LiPF₆-PC/DEC electrolyte system containing a small amount of 1,3-benzodioxol-2-one. In this system, the decomposition of PC is suppressed.

2. Experimental

The charge and discharge characteristics of the graphite electrode were examined in a laboratory cell which comprised a lithium metal electrode and a graphite electrode separated by a separator and glass fibre. The graphite electrode consisted of 20 mg MCMB 6-28 and 5 wt.% of ethylene/propylene/dien polymer (EPDM) as a binder. The graphite slurry (mixture of graphite and EPDM in

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cyclohexane) was spread evenly over the surface of a stainless-steel mesh substrate. The solvent was then evaporated and the electrode compressed at about 2 ton cm^{-2} . The electrolyte solution was 1 M LiPF_6 -PC/DEC (1:1) alone or with the addition of 0.1 to about 20 wt.% 1,3-benzodioxol-2-one. The water content of the electrolyte was less than 30 ppm. Cells were cycled at a constant current of 0.4 mA cm^{-2} between 1 mV and 1.5 V (or 1.0 V) using battery cyclers (ToyoSystem 3100 Japan).

In a lithium-ion cell, the anode was 20 mg MCMB 6-28 and the cathode was 30 mg LiCoO_2 . The cathode capacity was in excess. The cathode was prepared by mixing 30 mg LiCoO_2 and 18 mg conductive binder (CB), and compressing at about 2 ton cm^{-2} . The cells were cycled at a constant current of 0.4 mA cm^{-2} between 2.75 and 4.1 V.

The electrochemical stability of the electrolyte system against cathode material (i.e., LiCoO_2) was characterised by cyclic voltammetry (CV). The experiments were carried out in a three-electrode glass cell. Metallic lithium was used for both the counter and the reference electrodes. The working electrode consisted of 10 mg of LiCoO_2 and 6 mg of CB. CV measurements were performed using a Solartron Model 1287 electrochemical interface controlled by a COMPAQ PC. The scan rate was 0.15 mV s^{-1} .

3. Results and discussion

3.1. Charge/discharge profile of Li/graphite cell

The charge and discharge profiles of a graphite electrode in 1 M LiPF_6 -PC/DEC (1:1 in volume) electrolyte,

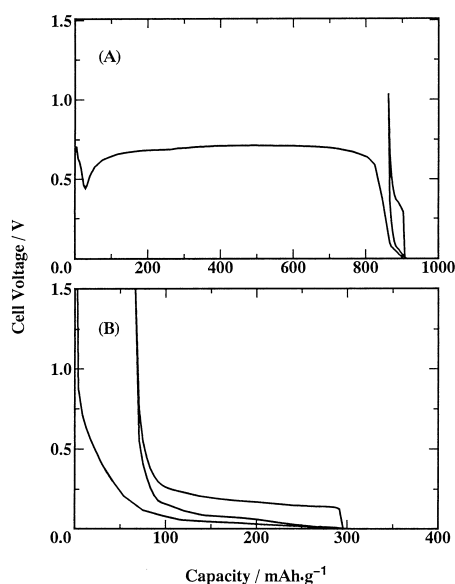


Fig. 1. Charge–discharge curves of graphite electrode (MCMB 6-28) at 0.4 mA cm^{-2} in (A) 1 M LiPF_6 /PC–DEC (1:1 in volume) electrolyte system and (B) the same electrolyte system with 2 wt.% 1,3-benzodioxol-2-one.

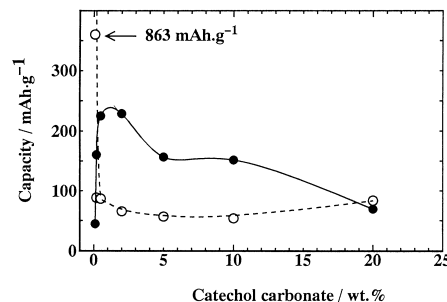


Fig. 2. Effect of 1,3-benzodioxol-2-one content in 1 M LiPF_6 /PC–DEC(1:1) on (●) reversible capacity and (○) irreversible capacity of MCMB 6-28.

undoped or doped with 2 wt.% 1,3-benzodioxol-2-one, are compared in Fig. 1. For the cell containing 1 M LiPF_6 -PC/DEC electrolyte (Fig. 1A), a long discharge potential plateau at $\sim 0.7 \text{ V}$ (versus Li^+/Li) is observed on the first discharge curve (in a Li/graphite cell, the counter electrode is metallic lithium and the discharge process is the intercalation of lithium ions into graphite; charging reverses the process). The decomposition of PC molecules takes place and the capacities were about 836 mA h g^{-1} [1,2]. In the case of the electrolyte with the addition of 2 wt.% 1,3-benzodioxol-2-one (Fig. 1B), the plateau at 0.7 V in the first discharge curve is absent. The total capacity during the first discharge is 295 mA h g^{-1} . When the cell is charged to 1.5 V, only lithium de-intercalation occurs, corresponding a capacity of 230 mA h g^{-1} . Therefore, the irreversible capacity for the first cycle is 65 mA h g^{-1} , which is much smaller than the value of the additive-free electrolyte system (see Fig. 2, later). A part of this irreversible capacity would be due to the formation of a passivation film. This reveals apparently that the decomposition of the electrolyte is suppressed significantly in the presence of 1,3-benzodioxol-2-one.

3.2. Effect of concentration 1,3-benzodioxol-2-one

The effects of 1,3-benzodioxol-2-one on the electrolyte decomposition on a graphite anode was examined by varying the weight percent of 1,3-benzodioxol-2-one. The

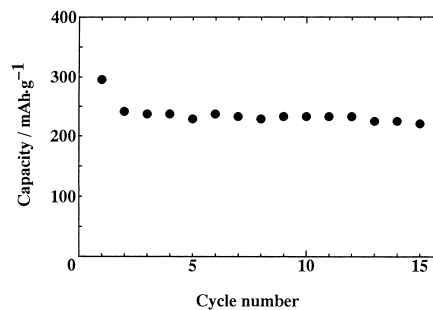
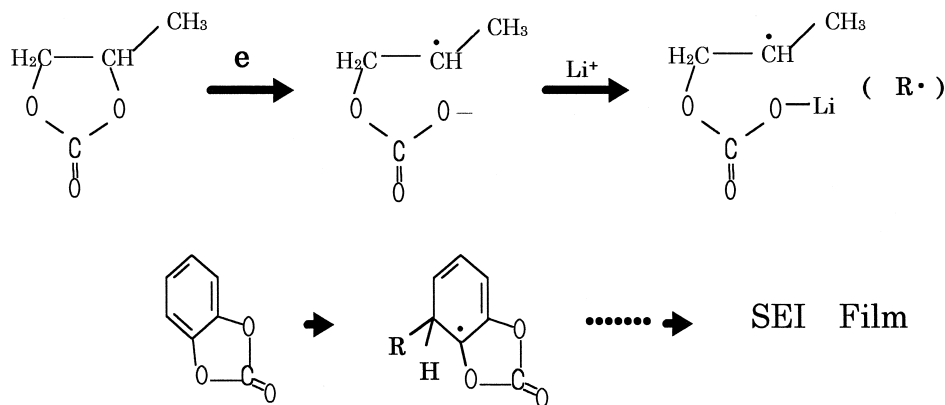


Fig. 3. Capacity vs. cycle number of graphite electrode (MCMB 6-28) cycled in 1 M LiPF_6 /PC–DEC (1:1 in volume) containing 2 wt.% 1,3-benzodioxol-2-one at 0.4 mA cm^{-2} .



Scheme 1. Proposed mechanism of the suppression of PC decomposition on the graphite anode in a PC and 1,3-benzodioxol-2-one electrolyte system.

reversible and irreversible capacity is plotted in Fig. 2 as a function of the weight fraction of 1,3-benzodioxol-2-one. The results clearly show that the irreversible capacity decreases rapidly with the addition of 1,3-benzodioxol-2-one. When 0.5 wt.% of 1,3-benzodioxol-2-one was added, the irreversible capacity is suppressed to 87 mA h g^{-1} and the capacity for de-intercalation of lithium ions reaches to 225 mA h g^{-1} . Further increase in the amount of 1,3-benzodioxol-2-one to 2 wt.% has little effect on the irreversible capacity, while the reversible capacity increases slightly, then decreases. The data suggests that the optimum concentration of 1,3-benzodioxol-2-one should lie in the range of 0.5 to ~ 2 wt.%. A cycle-life plot of a Li/graphite cell containing 1 M LiPF_6 -PC/DEC with the addition of 2 wt.% of 1,3-benzodioxol-2-one is presented in Fig. 3. The graphite electrode displays good rechargeability with a reversible capacity of 230 mA h g^{-1} . It is of interest to note that the amount of the additive is very small. It has been reported [4–6] that the decomposition of PC on the graphite could also be suppressed by addition of some co-solvents, e.g., ethylene carbonate, crown ether, and choroethylene carbonate. The volume or molar fraction of the co-solvent was usually large in these electrolyte systems. It was suggested [4] that these co-solvents change the solvation cloud about the Li ion to a sufficient degree

that co-intercalation is almost entirely suppressed. In the present case, however, it is difficult to envisage that the same mechanism holds because the amount of added 1,3-benzodioxol-2-one is very small. We suggest that the additive, 1,3-benzodioxol-2-one, may act as a scavenger for PC radicals.

Shu et al. [5] have proposed a mechanism for the decomposition of PC on graphite electrodes. The suggested process involves formation of lithium/carbonate complexes followed by one-electron reduction to a radical anion. The radical anions undergo further one-electron reduction yielding gaseous products or radical termination to form a solid electrolyte interface (SEI) film. Chusid et al. [7] have suggested a similar mechanism, i.e., PC is directly reduced by a one electron process to form PC radical anions, then radical termination occurs to form lithium alkylcarbonate and propylene gas. If this is indeed the case, we propose the mechanism shown as Scheme 1: 1,3-benzodioxol-2-one reacts predominantly with PC radicals as a scavenger prior to PC radical termination and forms a stable film to limit further decomposition of PC on the graphite electrode. Unfortunately, at this stage, we do not have sufficient direct evidence to support this argument. We are pursuing further work in this area.

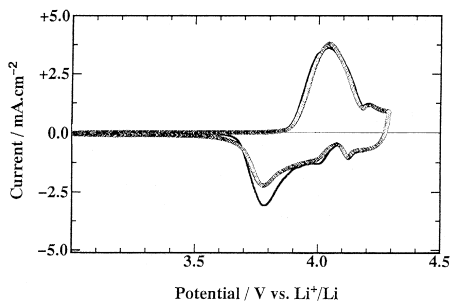


Fig. 4. Cyclic voltammograms of LiCoO_2 in (●) 1 M LiPF_6 /PC-DEC (1:1 in volume) electrolyte system and (◇) same electrolyte system with 2 wt.% 1,3-benzodioxol-2-one at a scan rate of 15 mV s^{-1} .

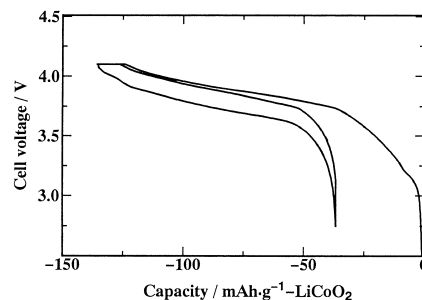


Fig. 5. Charge-discharge curves of lithium-ion batteries: MCMB 6-28/1 M LiPF_6 /PC-DEC (1:1 in volume)+2 wt.% 1,3-benzodioxol-2-one/ LiCoO_2 . Cell cycled between 2.75 and 4.1 V at a current rate of 0.4 mA cm^{-2} .

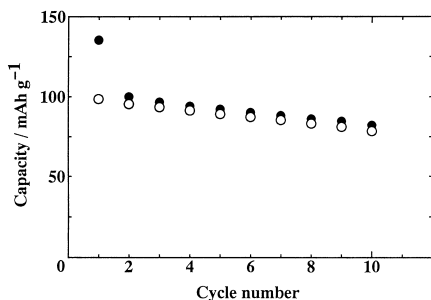


Fig. 6. Capacity vs. cycle number of lithium-ion batteries: MAMBA 6-28/1 M LiPF₆/PC-DEC (1:1 in volume) + 2 wt.% 1,3-benzodioxol-2-one/LiCoO₂. Cell was cycled between 2.75 and 4.1 V at a current rate of 0.4 mA cm⁻².

3.3. Electrochemical stability against cathode

As demonstrated above, the decomposition of PC on the graphite electrode can be critically suppressed by the addition of 1,3-benzodioxol-2-one, and the graphite electrode can cycle reversibly. If the electrolyte system being used in practical lithium-ion batteries, however, the electrochemical stability against the cathode material must be considered. This was accomplished by measuring the cyclic voltammetry of LiCoO₂ electrodes in 1 M LiPF₆-PC/DEC electrolyte system alone or with the addition of 2 wt.% 1,3-benzodioxol-2-one. The results are presented in Fig. 4. Negligible differences were observed between the two systems. In particular, both electrolyte systems are stable against LiCoO₂ in the electrochemical window between 3.0 and 4.3 V (vs. Li⁺/Li). This suggests that 1,3-benzodioxol-2-one does not decompose on the LiCoO₂ electrode.

3.4. Graphite / LiCoO₂ lithium-ion cell

The charge and discharge profiles of lithium-ion cells based on 1 M LiPF₆-PC/DEC with the addition of 2 wt.% 1,3-benzodioxol-2-one was further investigated; the anode was MCMB 6-28 graphite and the cathode was LiCoO₂. Cells were cycled between 2.75 and 4.1 V. The initial charge and discharge curves of such a cell are shown in Fig. 5. The cell has a reversible capacity of 90 mA h with per g of LiCoO₂. The cycle life is shown in Fig. 6. The preliminary results indicate that the cell has a good cycleability.

4. Conclusions

The decomposition of propylene carbonate at the graphite electrode in a PC/DEC-based electrolyte system is appreciably suppressed by the addition of a small amount of 1,3-benzodioxol-2-one. This electrolyte system can also be used in graphite/LiCoO₂ lithium-ion batteries.

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