

Short Communication

Suppression of electrochemical decomposition of propylene carbonate at a graphite anode in lithium-ion cells

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Received 7 February 1996; accepted 13 March 1996

Abstract

The decomposition of propylene carbonate (PC) at a graphite anode in lithium-ion cells is suppressed remarkably by choosing a proper mixing ratio of PC with co-existing solvents. For example, the decomposition of PC is essentially inhibited using PC–diethyl carbonate (DEC), PC–methylene carbonate (MEC) or PC–dimethyl carbonate (DMC) with 1:4 (v/v) mixed solvent solution containing a volume % of PC of less than 25%. Conductivity measurements show that all PC molecules can be solvated to Li⁺ ions as Li(PC)₂ in these mixed solvents, where 1.0 M LiPF₆ and 25 vol. % of PC are used. This suggests that the solvated PC molecules are not decomposed at graphite anode.

Keywords: Graphite; Lithium-ion batteries; Intercalation; Propylene carbonate; Lithium organic electrolyte; Anodes

1. Introduction

Much research effort has been focused on the search for suitable carbon materials as an alternative negative active-material for rechargeable lithium batteries. The early studies were conducted primarily on graphite electrode [1–3]. More recently, other forms of carbon have been also investigated. Among these carbon materials, petroleum coke seems to be the most popular [4–6], although carbon fibre [7], pyrolytic carbon [8], and chemically modified carbon [9] are also promising compounds. Graphite has a nearly perfect layered structure and is able to intercalate lithium to a stoichiometry of LiC₆ [4] with a flat voltage curve near 0 V relative to lithium.

Ethylene carbonate (EC) is commonly used as the main solvent in a secondary lithium-ion batteries with a graphite negative electrode. This is because the electrochemical decomposition of propylene carbonate (PC) on graphite occurs during the initial lithium-ion intercalation process [1,2,4,10,11]. This decomposition is associated with the formation of a passivating layer on the surface of the graphite. This layer is thought to consist of lithium alkylcarbonates [11]. Using PC as a solvent would be desirable, because the low temperature performance of the battery is superior to that of a battery using EC.

In this paper, lithium intercalation into a graphite (MCMB6-28 (graphitized mesocarbon microbeads at 2800 °C)) electrode is carried out in various mixed solvents with PC to suppress the decomposition of the latter on the graphite electrode.

2. Experimental

The charge (de-intercalation of lithium ions from a graphite anode) and discharge (intercalation of lithium ions) characteristics of the graphite electrode were examined in a laboratory cell. The cell comprised a lithium metal electrode and a graphite electrode that were separated by a separator and glass fiber. The graphite electrode consisted of 20 mg of MCMB6-28 and 5 wt.% of ethylene/propylene/diene polymer (EPDM) as a binder. The graphite slurry (mixture of graphite and EPDM in cyclohexane) was spread evenly on the surface of a stainless-steel mesh substrate. The solvent was then evaporated and the electrodes compressed with pressures at about 2 ton/cm². The electrolyte solution was 1 M LiPF₆ in PC/DMC, PC/DEC or PC/MEC mixed solvents. Cells were cycled in the range 1.0–0.001 V. The typical charge/discharge current density was 0.4 mA/cm² except specified otherwise.

The donor number (DN) of the solvents were determined spectrophotocchemically [12] as follows. For the two maxi-

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mum absorption peaks (λ_1 and λ_2 in nm) of bis-(1,3-propanediolato)vanadium (IV) ($\text{VO}(\text{acac})_2$) in a desired solvent, the λ_1 is shifted markedly to the red with increase in DN of the solvent, while λ_2 is shifted a little to the blue. The difference in their frequency values ($D = 1.196 \times 10^5 (\lambda_2^{-1} - \lambda_1^{-1})$) increases with the DN of the aprotic solvent. The unknown DNs of the solvents used were determined using the linear relationship between the DNs [13] and D of various solvents for PC, EC, DMF, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile, benzonitrile, acetic anhydride and chloroform.

3. Results and discussion

The conductivities show a large increase when PC is added to lithium-ion containing solvents with lower DNs than that of PC, such as DMC, diethyl carbonate (DEC) or methyl carbonate (MEC). The conductivity of a constant concentration of LiPF_6 (0.1 M) in DEC is increased by the addition of PC and shows inflection points at a molar ratio of $\text{PC}:\text{Li} = 2$, as shown in Fig. 1. If there is no interaction between PC and lithium ions, then the conductivities should decrease with the addition of PC because of the high viscosity of PC. It is considered that specific solvation (preferential solvation) of PC to lithium ions occurs in the PC-DEC mixed solvent system [14] and that this increases the conductivity because its DN is higher than that of PC.

The data in Fig. 1 show that one molecule of lithium ions will be solvated by the two molecules of PC. Generally speaking, preferential solvation towards lithium ions by the sol-

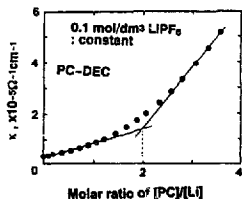


Fig. 1. Conductometric titration of PC-DEC solution of LiPF_6 under constant LiPF_6 concentration (0.1 M).

Table 1
Physical properties of various solvents

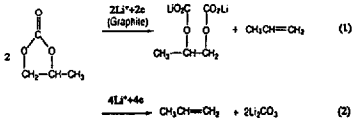
Solvents	DN	m.s. °C	b.p. °C	η , cP	t
Ethylene carbonate (EC)	16.4	38	248	1.90	90
Propylene carbonate (PC)	15.1	-49	242	2.50	65
Dimethyl carbonate (DMC)	8.7	4	90	0.59	3.1
Methyl ethyl carbonate (MEC)	6.5	-10	73	0.65	2.0
Diethyl carbonate (DEC)	8.0	-43	126	0.75	2.8

Note: $\rho = 40^\circ\text{C}$

vents with higher DNs occurs in the mixed solvent system. The DNs of several ester carbonate solvents are shown in Table 1.

Because solvents such as DMC, DEC or MEC has a much smaller DNs than PC, the PC molecule will solvate lithium ion preferentially in the mixed solvents with DEC, DMC or MEC.

Charge/discharge curves of a graphite electrode in PC-DEC mixed solvent systems of 1:1 and 1:4 (v/v) are shown in Fig. 2. For the (1:1 mixed solvent system) PC molecules were decomposed at a 0.7–0.8 V (versus lithium) plateau voltage on a graphite anode, see Fig. 2(b).



The current used for the decomposition of PC was calculated to be 830 mAh per g of graphite from Fig. 2(b). Initially, 1.64 mmol of PC solvent was used. After the first discharge, the remaining PC was 1.03 mmol. If the decomposition reaction of PC is based on one-electron reaction (Eq. (1)), as reported by Ohusid et al. [11] or two-electron reaction (Eq. (2)) by Aurbach et al. [10], the decomposed PC would correspond to 820 or 1640 mAh/g, respectively.

The results show that PC will be decomposed by the one-electron reaction at the graphite electrode.

As there is no plateau at 0.7–0.8 V in charge/discharge curve for the 1:4 electrolyte, see in Fig. 2(a), the decomposition of PC is negligibly small. In the electrolyte, the concentration of PC and lithium ions are 2.2 and 1.0 M, respectively. Thus, all the PC molecules are present as solvated molecules. It can be concluded that the solvated PC molecules towards lithium ions cannot be decomposed electrochemically on a graphite electrode.

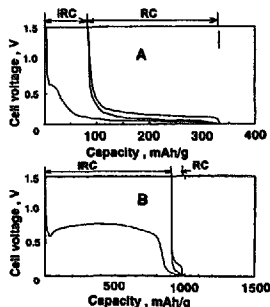


Fig. 2. Charge/discharge curves of graphite electrode (MCMB6-28) at 0.4 mA/cm^2 in 1 M $\text{LiPF}_6/\text{PC-DEC}$: (A) 1/4, and (B) 1/1 (v/v). RC: reversible capacity, and IRC: irreversible capacity.

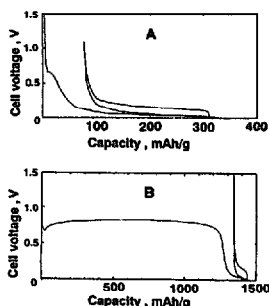


Fig. 3. Charge/discharge curves of graphite electrode (MCMB6-28) at 0.4 mA/cm^2 in $1 \text{ M LiPF}_6/\text{PC-MEC}$: (A) 1/4, and (B) 1/1 (v/v).

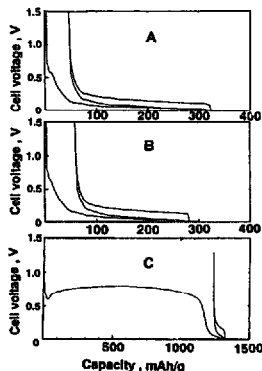


Fig. 4. Charge/discharge curves of graphite electrode (MCMB6-28) at 0.4 mA/cm^2 in $1 \text{ M LiPF}_6/\text{PC-DMC}$: (A) 1/5, (B) 1/4, and (C) 1/1 (v/v).

The charge/discharge curves of graphite electrode in $1 \text{ M LiPF}_6/\text{PC-MEC}$ and $\text{LiPF}_6/\text{PC-DMC}$ mixtures are shown in Figs. 3 and 4, respectively. In the 1:1 mixed solvent system, the PC molecules were always decomposed at $0.7\text{--}0.8 \text{ V}$ (versus lithium) on a graphite electrode as shown Figs. 3(b) and 4(c). In the 1:4 and 1:5 mixed solvent systems, the decomposition of PC molecules was negligibly small. A high reversible capacity (RC: lithium ions can be reversibly intercalated and de-intercalated) of 280 mAh/g and low irreversible capacity (IRC: decomposition of PC and/or formation of passivation layer) of 46 mAh/g were obtained from a 1:5 system when the molar ratio of PC/Li is 1.9.

The relationships between RC, IRC and molar ratio of PC:Li are shown in Fig. 5. The decomposition of PC is suppressed in the PC/DEC mixed solvent system, as shown from the data in Fig. 5(a), in which the capacity of IRC is roughly constant up to a PC:Li = 4 (mole ratio). While the value of IRC increases rapidly at a PC:Li molar ratio higher than 2 in the PC/DMC or PC/MEC mixed solvent system, recharge-

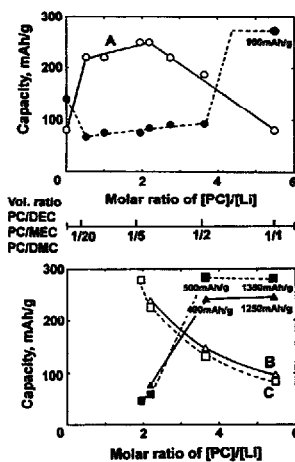


Fig. 5. Effect of molar ratio of $[\text{PC}]/[\text{Li}]$ on reversible capacity (RC) and irreversible capacity (IRC). (A) PC-DEC (O) RC and (●) IRC; (B) PC-MEC (Δ) RC and (\blacktriangle) IRC; (C) PC-DMC (□) RC and (■) IRC.

able intercalation into a graphite is obtained from the PC-DMC or PC-MEC mixed solvent system at the PC:Li molar ratio lower than 2.

4. Conclusions

Electrochemical intercalation of lithium ions into graphite in $1 \text{ M LiPF}_6/\text{PC-DEC}$ (1:1), PC-DMC (1:1) and PC-MEC (1:1) electrolytes gives rise to PC decomposition reactions at $0.7\text{--}0.8 \text{ V}$ (versus lithium) during the first discharge according to a one-electron reaction. The decomposition of PC molecules on a graphite anode is suppressed considerably by using $1 \text{ M LiPF}_6/\text{PC-DEC}$ (1:4), PC-MEC (1:4) and PC-DMC (1:4), in which free PC molecules do not exist and all PC molecules are solvated to lithium ions as $\text{Li}(\text{PC})^{2+}$ ions.

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