

Application to lithium battery electrolyte of lithium chelate compound with boron

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Abstract

The electrolytic conductivities and charge–discharge characteristics of lithium electrode are examined in propylene carbonate (PC)- and ethylene carbonate (EC) tetrahydrofurans, such as 2-methyltetrahydrofuran (2-MeTHF) and 2,5-dimethyltetrahydrofuran (2,5-DMeTHF), binary solvent electrolytes containing lithium bis[1,2-benzenediolato(2-)-*O,O'*]borate (LBBB), lithium bis[2,3-naphthalenediolato(2-)-*O,O'*]borate (LBNB), lithium bis[2,2'-biphenyldiolato(2-)-*O,O'*]borate (LBBPB) and lithium bis[salicylato(2-)]borate (LBSB). The order of specific conductivities in PC- and EC-based equimolar binary solutions containing these organoborates is LBBB \geq LBNB $>$ LBSB $>$ LBBPB. The conductivity in LBNB electrolyte with higher viscosity than that in LBSB electrolyte becomes high. The PC–2-MeTHF and PC–2,5-DMeTHF equimolar binary solutions containing LBSB and a mixed electrolyte (LBBPB + LiPF₆) show very high cycling efficiencies more than 90% at a higher range of cycle number. The EC–THF and EC–2-MeTHF equimolar binary solutions are moderate electrolytes with about 80% cycling efficiencies. It is found by using scanning electron microscope (SEM) that the films formed on the electrode in PC–2-MeTHF and PC–2,5-DMeTHF electrolytes with higher cycling efficiencies have a homogeneous surface with uniform grain size. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium battery; Electrolytic conductivity; Cycling efficiency; Lithium organoborates; Scanning electron microscope (SEM)

1. Introduction

The effort to develop improved electrolytes, which satisfy the requirement of a lithium rechargeable battery with high voltage and energy density as power sources for many portable instruments and electric vehicles because of protection against natural environment and resources, has been carried out by many works. Barthel et al. [1–5] reported new lithium organoborates as lithium salts for lithium battery electrolytes, such as lithium bis[1,2-benzenediolato(2-)-*O,O'*]borate (LBBB), lithium bis[2,3-naphthalenediolato(2-)-*O,O'*]borate (LBNB), lithium bis[2,2'-biphenyldiolato(2-)-*O,O'*]borate (LBBPB) and lithium bis[salicylato(2-)]borate (LBSB) in Fig. 1. In previous papers [6–8], we reported the thermal characteristics and the electrolytic behavior in propylene carbonate (PC)–1,2-dimethoxyethane (DME), ethylene carbonate (EC)–DME, PC–tetrahydrofuran (THF) and EC–THF binary solvent electrolytes containing LBBB, LBNB and LBBPB.

The purpose of the present paper is to elucidate the electrolytic behavior and charge–discharge characteristics of lithium electrode in PC- and EC-based tetrahydrofurans, such as 2-methyltetrahydrofuran (2-MeTHF) and 2,5-dimethyltetrahydrofuran (2,5-DMeTHF), binary solvent electrolytes, containing these lithium organoborates in comparison with those in PC- and EC-based DME and THF binary solvent electrolytes. In addition, the morphology of passivating films formed on the Ni (working) electrode after cycling is examined by using scanning electron microscope (SEM).

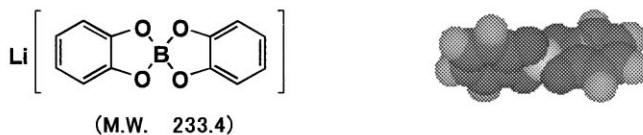
2. Experimental

2.1. Materials

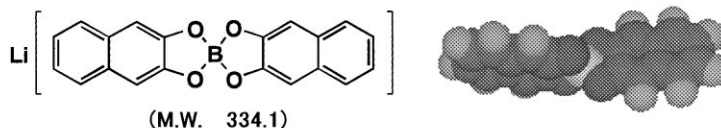
The preparation and purification of LBBB, LBNB and LBBPB have been described elsewhere [1,3,8]. The LBSB raw salt was easily obtained to give an 89% yield by using lithium carbonate as a starting material instead of lithium hydroxide monohydrate by Barthel et al. [4]. The raw salt was purified by recrystallization several times from

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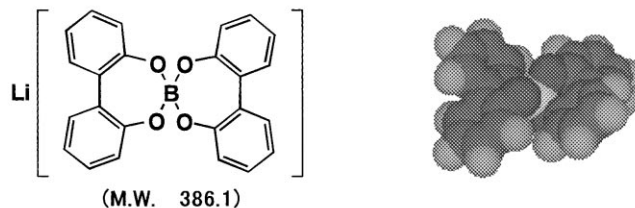
Lithium bis[1,2-benzenediolato(2-)-O,O']borate (LBBB)



Lithium bis[2,3-naphthalenediolato(2-)-O,O']borate (LBNB)



Lithium bis[2,2'-biphenyldiolato(2-)-O,O']borate (LBBPB)



Lithium bis[salicylato(2-)]borate (LBSB)

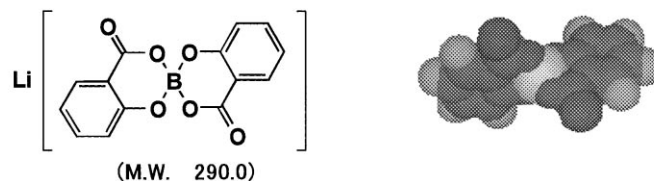


Fig. 1. Structures of LBBB, LBNB, LBBPB and LBSB.

acetonitrile and dried in vacuo at 120°C for 24 h. The yield was about 40%. The purity and structure of LBSB were confirmed by elemental and ICP analyses for B and Li (found: C, 57.6; H, 3.2; O, 33.3; B, 3.5; Li, 2.4 wt.%; calculated for $\text{LiBC}_{14}\text{H}_8\text{O}_6$: C, 58.0; H, 2.8; O, 33.1; B, 3.7; Li, 2.4 wt.%) and C–H COSY NMR. Commercial reagent grade 2-MeTHF and 2,5-DMeTHF were dehydrated using purified molecular sieves (4 Å) before preparation of the solutions. Commercial reagent grade $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ were dried in vacuo for 24 h at 150°C. In addition, LiPF_6 was used as received (battery grade).

2.2. Apparatus and measurements

The measurements of the conductivity and cycling efficiency of lithium electrode have been described elsewhere

[8]. Direct observation on the Ni electrode after cycling was carried out with a JEOL JMS-5310 SEM.

3. Results and discussion

3.1. Conductivity

The specific conductivities in PC- and EC-based equimolar binary solutions containing 0.3 and 0.5 M lithium organoborates in comparison with those of LiPF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ are shown in Table 1. The low solubility of these organoborates compared with that of LiPF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ is usually an unfortunate fact of life with the salts of larger anions. The order of specific conductivities in these binary solutions is

Table 1
Specific conductivities in PC- and EC-based equimolar binary solutions containing 0.3 and 0.5 mol dm⁻³ lithium organoborates at 25°C

Mixed solvent (mol ratio 1:1)	mol dm ⁻³	Specific conductivity (mS cm ⁻¹)						
		LBBB	LBNB	LBBPB	LBSB	LiPF ₆	LiN(CF ₃ SO ₂) ₂	LiN(C ₂ F ₅ SO ₂) ₂
PC-DME	0.3	4.21	4.25	1.09	2.45	9.23	8.05	7.55
	0.5	4.40	4.74	–	2.49	10.89	10.65	9.72
EC-DME	0.3	4.69	4.76	–	2.81	10.56	8.60	7.87
	0.5	5.04	5.25	–	2.97	12.45	11.38	10.52
PC-THF	0.3	3.77	3.75	–	1.57	8.23	7.41	6.62
	0.5	3.89	3.94	–	1.56	10.64	9.61	8.56
EC-THF	0.3	4.39	4.30	–	2.12	9.15	7.71	7.04
	0.5	4.96	4.50	–	2.11	11.84	10.25	9.11
PC-2-MeTHF	0.3	3.07	2.97	0.92	1.28	6.57	5.97	5.48
	0.5	3.22	–	1.03	1.12	8.63	7.62	6.77
EC-2-MeTHF	0.3	3.53	3.30	1.24	1.54	7.22	6.54	6.08
	0.5	3.76	3.47	1.37	1.38	9.38	8.25	7.41
PC-2,5-DMeTHF	0.3	2.27	–	0.60	0.87	5.13	4.84	4.60
	0.5	1.31	–	0.72	0.82	6.24	5.83	5.31

LBBB ≥ LBNB > LBSB > LBBPB, which is inversely proportional to that of the viscosities of the solutions (LBBPB > LBNB > LBSB > LBBB) due to the molecular weight of the electrolyte. However, the conductivity of LBNB electrolyte with higher viscosity than that of LBSB

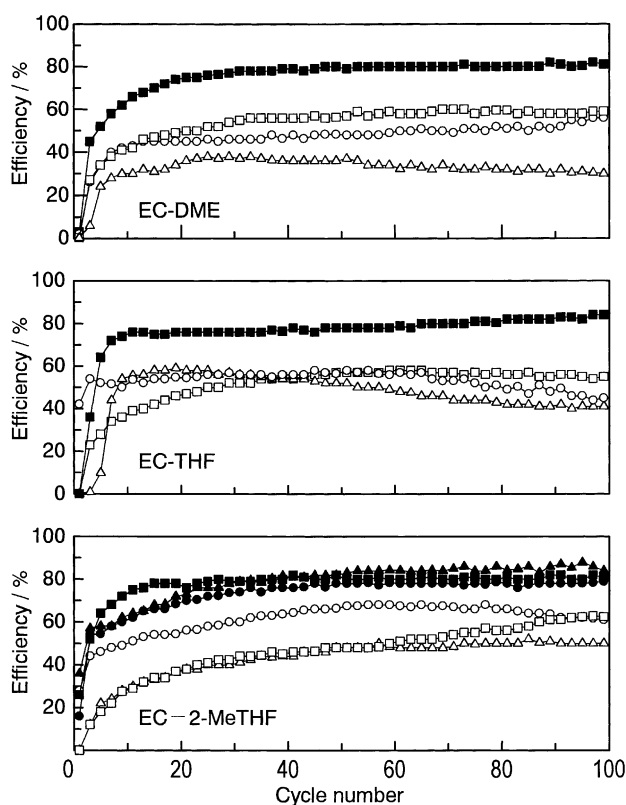


Fig. 2. Cycling efficiencies of lithium electrode in EC-based equimolar binary solutions containing LiPF₆, lithium organoborates and a mixed electrolyte, $i_p = i_s = 0.1 \text{ mA dm}^{-2}$, $Q_p = 0.01 \text{ C cm}^{-2}$. (○) 0.3 M LiPF₆; (△) 0.3 M LBBB; (□) 0.3 M LBNB; (●) 0.3 M LBBPB; (▲) mixed electrolyte (0.15 M LBBPB + 0.15 M LiPF₆); (■) 0.3 M LBSB.

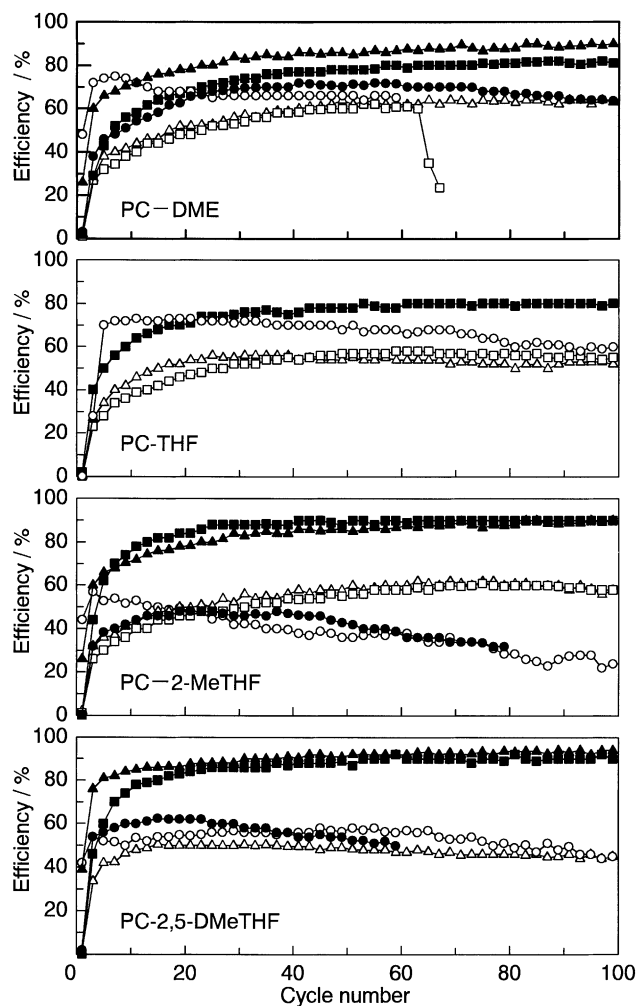


Fig. 3. Cycling efficiencies of lithium electrode in PC-based equimolar binary solutions containing LiPF₆, lithium organoborates and a mixed electrolyte, $i_p = i_s = 0.1 \text{ mA dm}^{-2}$, $Q_p = 0.01 \text{ C cm}^{-2}$. (○) 0.3 M LiPF₆; (△) 0.3 M LBBB; (□) 0.3 M LBNB; (●) 0.3 M LBBPB; (▲) mixed electrolyte (0.15 M LBBPB + 0.15 M LiPF₆); (■) 0.3 M LBSB.

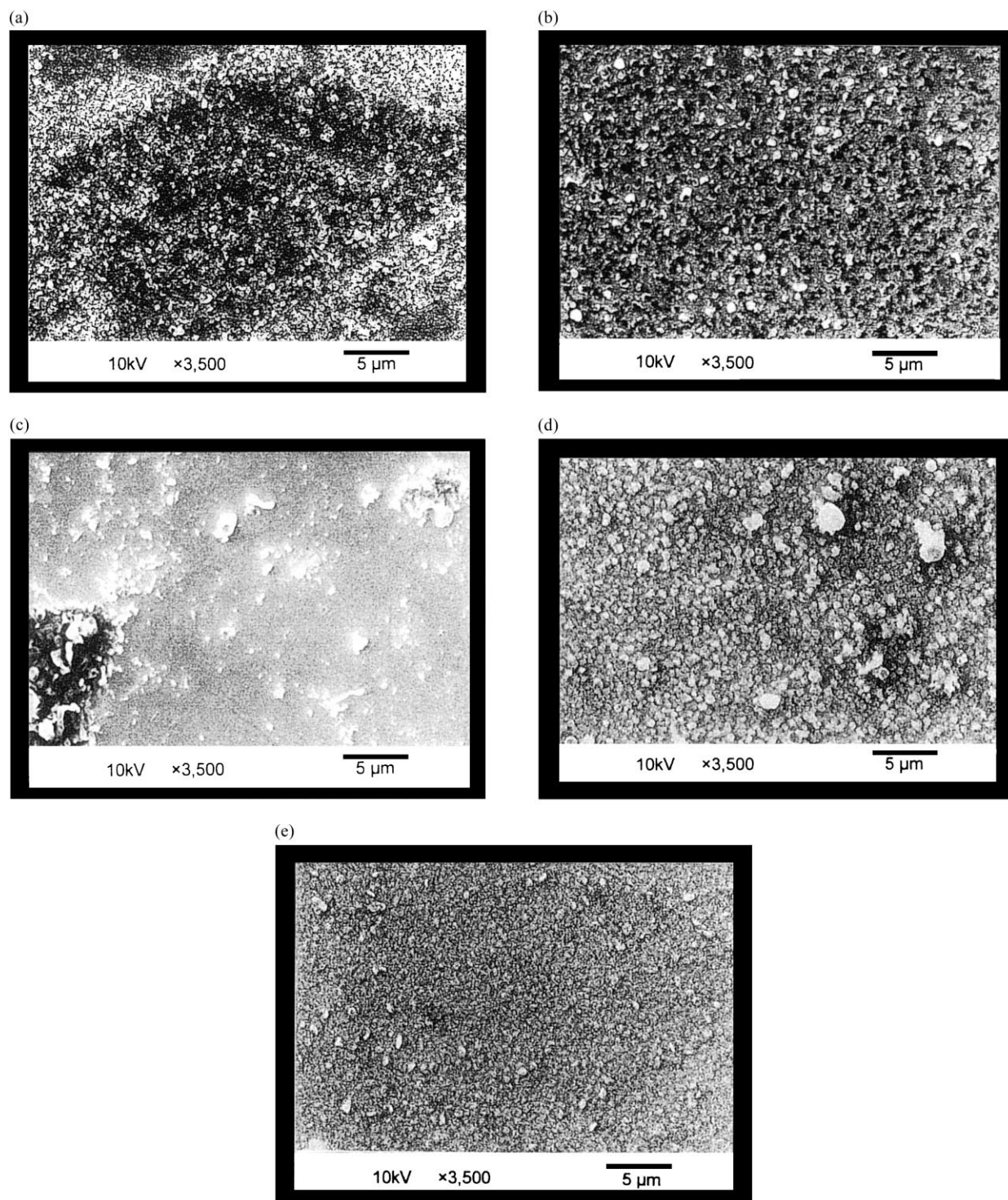


Fig. 4. SEM photographs on Ni electrode in PC–2,5-DMeTHF equimolar binary solutions containing 0.3 M electrolytes after 40th cycle by measurements of cycling efficiencies at 25°C. (a) 0.3 M LBBB; (b) 0.3 M LBSB; (c) 0.3 M LiPF₆; (d) 0.3 M LBBPB; (e) mixed electrolyte (0.15 M LBBPB + 0.15 M LiPF₆).

electrolyte becomes high. This means that the conductivity of LBNB electrolyte is affected by the increase in dissociation degree of LBNB due to the high charge delocalization by two naphthalene diols, rather than viscosity of the solution.

3.2. Cycling efficiency of lithium electrode

Fig. 2 shows the cycling efficiencies of the lithium electrode in EC-based equimolar binary solutions containing LiPF₆ and lithium organoborates. The efficiencies in

every EC-based solution containing LBSB show the highest values of about 80% at a higher range of cycle number in comparison with those of other lithium organoborates and LiPF_6 which is a typical lithium battery electrolyte. In addition, it is found that the efficiency in 0.5 M LBSB/EC–DME equimolar binary solution becomes more than 90%. The measurement of the efficiency in EC–2,5-DMeTHF system was impossible because it is difficult for EC to be miscible with 2,5-DMeTHF. The cycling efficiencies in PC-based equimolar binary solutions are shown in Fig. 3. The efficiencies in PC-based euimolar binary solutions are generally higher than those in EC-based solutions. Especially, the PC–2-MeTHF and PC–2,5-DMeTHF electrolytes containing LBSB and the mixed electrolyte ($\text{LBBPB} + \text{LiPF}_6$) show very high cycling efficiencies around 90% at a higher range of cycle number. This means that the charge–discharge processes in these electrolytes take place very smoothly due to the formation of the appropriate passivating films on the Ni electrode. Therefore, these solutions are interested in studying the electrolyte for rechargeable lithium batteries. Fig. 4 shows the SEM photographs on Ni electrode in PC–2,5-DMeTHF equimolar binary solutions containing 0.3 M LiPF_6 , LBBB, LBBPB, LBSB and the mixed electrolyte (0.15 M LBBPB + 0.15 M LiPF_6) after 40th cycle. The surface of the films formed on the electrode in PC–2-MeTHF and PC–2,5-DMeTHF electrolytes with higher cycling efficiencies in Fig. 3 is homogeneous, and consists of uniform grain size. In addition, the surface of the film in the mixed electrolyte seems to be relatively thin. On the contrary, the surface in LiPF_6 , LBBB and LBBPB electrolytes with lower cycling efficiency is coarse and heterogeneous, which has irregular grain size. Consequently, it was found that the charge–discharge characteristics are significantly dependent on the morphology on the electrode.

In conclusion, the PC–2-MeTHF and PC–2,5-DMeTHF solutions containing LBSB and the mixed electrolyte ($\text{LBBPB} + \text{LiPF}_6$) are good electrolytes for rechargeable lithium batteries with very high cycling efficiencies more than 90% at a higher range of cycle number. In addition, EC–THF and EC–2-MeTHF solutions containing LBSB and EC–2-MeTHF/($\text{LBBPB} + \text{LiPF}_6$) electrolyte show the moderate cycling efficiencies.

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