

Lithium cycling efficiency and conductivity for γ -lactone-based electrolytes

SHIN-ICHI TOBISHIMA, TAKESHI OKADA

Ibaraki Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokai, 319-11 Japan

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Lithium cycling efficiency on a lithium substrate as well as conductivity were examined for γ -lactone-based electrolytes incorporating LiClO_4 for use in nonaqueous lithium secondary batteries. γ -butyrolactone (BL), γ -valerolactone and γ -octanoinclactone were used. Conductivity increased with a decrease in viscosity for lactone. Lithium cycling efficiency tended to increase with a decrease in reactivity between lithium and lactone, which would be expected from the oxidation potential for lactone. In order to decrease viscosity, tetrahydrofuran (THF) was mixed with lactone. Conductivity for lactone/THF was higher than those for systems using either lactone or THF alone. For example, 1 M LiClO_4 -BL/THF (mixing volume ratio = 1:1) showed conductivity of $13.0 \times 10^{-3} \text{ S cm}^{-1}$, approximately 20% higher than that for BL. Lithium cycling efficiency for BL/THF, which exceeded 90%, was also higher than that for BL. Morphology of the deposited lithium in BL/THF was smoother than that in BL and similar to that in THF, as observed with a scanning electron microscope. The reason for the enhancement of the lithium cycling efficiency for BL/THF seems to be the adsorption of THF or THF- Li^+ around the deposited Li, which has lower reactivity to Li and higher solvation power to Li^+ than BL.

1. Introduction

We have been studying the conductivity and lithium cycling efficiency for various solvent (s)-solute (s) systems for use in nonaqueous lithium secondary batteries [1-6]. In these studies, it was found that high dielectric ester/low viscous ether mixed solvent electrolytes, such as propylene carbonate (PC)/tetrahydrofuran (THF), were effective for the enhancement of lithium cycling efficiency as well as conductivity, while only ether systems showed low conductivity and only ester systems showed low lithium cycling efficiency.

γ -butyrolactone (BL) is known as a high dielectric ester and is sometimes used in primary lithium batteries [7-9]. However, available detailed data on conductivity for BL-based electrolytes are insufficient. Lithium cycling efficiency also has yet to be sufficiently studied.

Conductivity and lithium cycling efficiency for γ -lactone-based electrolytes are reported in this paper. The general chemical structure for γ -lactone

is shown in Formula I. In this study γ -butyrolactone (BL), γ -valerolactone (VL) and γ -octanoinclactone (OL) were used. Physical properties for BL, compared with those for the well-known high dielectric ester, PC, are shown in Table 1. Although the dielectric constant for BL is lower than that for PC, BL has lower viscosity and higher solvation power to Li^+ , which could be expected from the donor number (D_N) [11-13].

Table 1. Physical properties for the solvents [10]

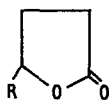
Solvent	Dielectric Constant (25° C)	Viscosity (cp. 20° C)	Donor† number	Molecular volume ($\times 10^{-3} \text{ nm}^3$)
BL	39*	1.7**	15.9	127.1
PC‡	64.4	2.5	15.1	140.5
THF	7.6	0.55	20.0	134.8

*20° C

**25° C

†Gutman [11]

‡Di Pietro [7]



R = H, BL; R = CH₃, VL; R = CH₃ (CH₂)₃, OL.

2. Experimental details

2.1. Electrolytes and measurements

γ -lactones were distilled at reduced pressure. Ethers were distilled with NaH at normal pressure [1]. Electrolytic solutions were prepared by mixing adequate amounts of solvent(s) and solute, LiClO₄, which was dried at 160°C *in vacuo* [1].

Conductivity for the electrolytic solution was measured at 1 kHz. Lithium charge-discharge tests on a lithium substrate (Li-on-Li cycling) [11] were galvanostatically carried out with a Teflon cell, which is similar to that reported by Rauh[14]. This cell with approximately 2 cm³ solution was constructed with a lithium counter electrode (20 mm diameter \times 0.5 mm thickness), lithium reference electrode and platinum working electrode (20 mm diameter \times 0.5 mm thickness) [5]. This experiment involved making a pre-plate of 2.4C cm⁻² of lithium on the platinum substrate followed by stripping and then re-plating of 0.6 C cm⁻² (0.5 mA cm⁻²) on the pre-plated lithium. The average efficiency per cycle, E_a , was calculated from Equation 1.

$$E_a = \frac{Q_{ps} - Q_{ex}/n}{Q_{ps}} 100(\%) \quad (1)$$

where n is the number of apparent '100%' cycles, Q_{ps} is the charge stripped (0.6C cm⁻²) and Q_{ex} is the charge in the excess Li(1.8 C cm⁻²) at the start of the experiment.

The oxidation potential for the solvent was measured by a potential linear sweep (1-10V sweep, 20 mV s⁻¹), using a Teflon cell with a platinum working electrode (0.32 cm²), lithium reference electrode and lithium counter electrode (1 cm²) solution volume is approximately 2 cm³. The oxidation potentials reported are those at which the current reached 1 mA on the working electrode [2]. The transference number for Li⁺ was obtained from the electromotive force of a concentration cell [15]. Stokes' radius for Li⁺, the practical ion radius with solvated solvent molecules,

was calculated by Stokes' law [16]. This value was calibrated by the method using a series of tetraalkylammonium ions [16]. The viscosity of the solvent (s) was measured with an Übbelohde-type viscometer at 25°C. Electrolyte preparations and all the tests were carried out in an argon filled dry-box at 25 \pm 1°C.

Scanning electron microscope (SEM) observations of deposited lithium were carried out as follows: Lithium was deposited on the aluminium holder for SEM observation (deposited surface area was approximately 0.13 cm²) and the deposited lithium was rinsed with dehydrated THF in the Ar-filled drybox. The sample in a glass case was transported to another drybox, which was connected to the pre-vacuum sample chamber of the JSM-T JEOL scanning electron microscope.

3.2. Evaluation of association constant

The ionic association constant (K_A) for LiClO₄ was defined by Equation 2. Various evaluation methods for K_A have been proposed. In this work, K_A values for LiClO₄ in various solvents were examined by two methods; the Bjerrum equation (Equation 3) [16] and the Fuoss-Onsager equation modified by Chen. (Equation 4) [17].

$$K_A = (1 - \alpha)/\alpha^2 c \gamma_{\pm}^2 \quad (2)$$

$$K_A = 4\pi N_A \int_a^q \exp(z^2 e^2 / \epsilon \kappa T r) r^2 dr \quad (3)$$

$$\Lambda = \Lambda_0 - S(\alpha c)^{1/2} + E \alpha c \log(\alpha c) + J \alpha c - K_A \alpha c \gamma_{\pm}^2 \Lambda \quad (4)$$

where α , γ_{\pm} , q and a are the degree of dissociation, the mean molar active coefficient, Bjerrum distance [16] and the distance of closet approach, respectively, Λ_0 and Λ are the molar equivalent conductivity at infinite dilution and at concentration, respectively. The necessary equations for the calculation of S , E and J have been summarized elsewhere [17]. N_A , z , e , T , ϵ and κ have their usual significance [18]. In these equations, the sum of the ion radii for Li⁺ (0.06 nm [1]) and ClO₄⁻ (0.283 nm [2]) was used as the a . The dielectric constant for the mixed solvents was obtained from the volumatic average values of those for each solvent [19, 20]. The density of the mixed solvents was assumed to have a linear

relationship to the molar mixing ratio for the densities of each solvent [21]. Equation 3 was solved by a pit-mapping method [18], in which Λ_0 and K_A are varied until a minimum was located for the standard error of estimate, σ , which is defined by Equation 5. In this simulation, γ_{\pm} was assumed to be unity,

$$\sigma = [\Sigma(\Lambda_{\text{obs}} - \Lambda_{\text{calc}})^2/N]^{1/2} \quad (5)$$

where N is the number of data.

3. Results and discussion

3.1. Conductivity for γ -lactone-based electrolytes

The conductivity (κ) dependence on LiClO_4 concentration for γ -lactones is shown in Fig. 1. The conductivity showed a maximum value in the range $0.5\text{--}1.25 \text{ mol l}^{-1}$ LiClO_4 . The decrease in conductivity with higher LiClO_4 concentration is due to the decrease in the number of free ions caused by ionic association [1]. The maximum conductivities are in the order $\text{BL}(11.0 \times 10^{-3} \text{ S cm}^{-1}) > \text{VL}(7.0 \times 10^{-3} \text{ S cm}^{-1}) > \text{OL}(1.1 \times 10^{-3} \text{ S cm}^{-1})$. This order agrees with that for the solvent viscosity, resulting from the decrease in the carbon number for lactones. It has been reported [5, 22] that enhancements of the ion migration rate based on a decrease in viscosity are effective for the conductivity of high dielectric esters incorporating lithium salts with large anions, such as LiClO_4 , because of a sufficient degree of ionic

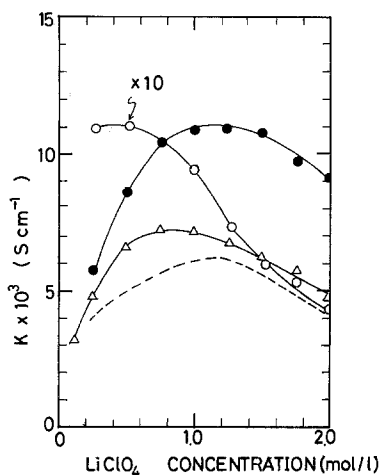


Fig. 1. Conductivity (κ) dependence on LiClO_4 concentration for γ -lactones, \bullet : BL, Δ : VL, \circ : OL, - - - : PC.

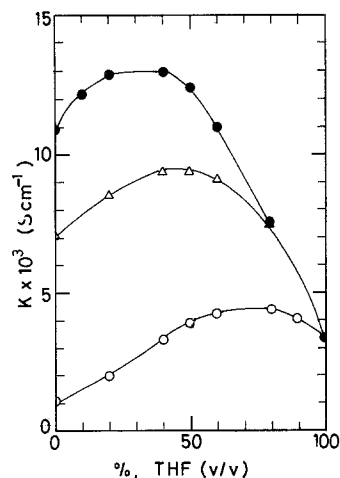


Fig. 2. Conductivity (κ) dependence on THF content for 1 M LiClO_4 - γ -lactone/THF, \bullet : BL/THF, Δ : VL/THF, \circ : OL/THF.

dissociation. In additional experiments, the conductivities for BL and VL were higher than that for PC, while the conductivity for OL was lower than for PC. This conductivity order also agrees with that for the decrease in solvent viscosity; i.e., $\text{BL}(1.7 \text{ cP}) < \text{VL}(2.4 \text{ cP}) < \text{PC}(2.5 \text{ cP}) < \text{OL}(4.3 \text{ cP})$. Tetrahydrofuran (THF), a low-viscosity ether, was mixed with lactones to improve their conductivity by decreasing the viscosity. Conductivity dependence on a THF content for 1 M LiClO_4 -THF/lactone is shown in Fig. 2. The conductivity dependence on LiClO_4 concentration for THF/lactone is shown in Fig. 3. Conductivities for the mixed solvent electrolyte were higher than those for systems using either lactone or THF alone. The conductivities showed maxima at different levels of THF content. The THF content level for maximum conductivity becomes higher with an increase in the carbon number; i.e. viscosity.

To examine the data on conductivity enhancement for BL/THF in more detail, an ionic association constant (K_A) and electrolytic parameters, such as transference number, were measured in an infinite dilution condition so that the anion effects could be disregarded [1]. The results are summarized in Table 2. In this study, the selective solvation of THF to Li^+ was applied for a BL/THF mixed system. The higher solvation tendency of THF to Li^+ as compared with BL was easily pre-

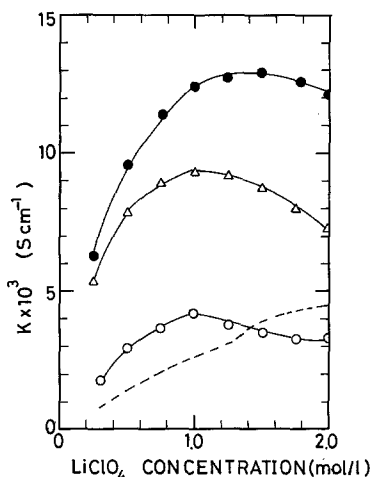


Fig. 3. Conductivity (κ) dependence on LiClO_4 concentration for γ -lactone/THF, \bullet : BL/THF (1:1), Δ : VL/THF (1:1) \circ : OL/THF (2:3), - - -: THF.

dicted from the donor-acceptor concept for the interactions between solvent and ions [11, 12]. Donor numbers of THF and BL are 20.0 and 15.9, respectively [11]. By mixing THF with BL, K_A increases because the dielectric constant decreases [22], as in the case of PC/THF [23]. The Stokes' radius for Li^+ (r_{so}^+) in BL/THF is slightly larger than that in BL, which may be attributed to the difference in solvent molecular volume between BL and THF, as shown in Table 1. On the other hand, the transference number for Li^+ (t_0^+) and the limiting Li^+ ionic conductivity (Λ_0^+) in BL/THF are higher than those in BL, which is advantageous for lithium battery application. These results indicate that the decrease in viscosity is effective for the conductivity of LiClO_4 -lactone-based electrolytes.

3.2. Lithium cycling characteristics for γ -lactone-based electrolytes

The dependence of lithium cycling efficiency (E_a)

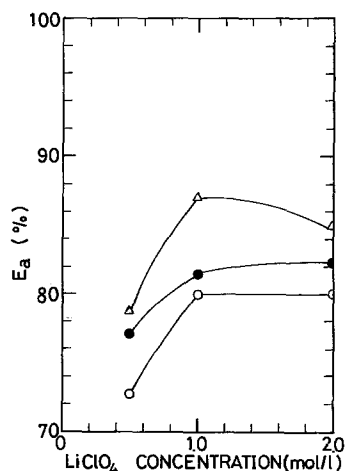


Fig. 4. Lithium cycling efficiency (E_a) dependence on LiClO_4 concentration for γ -lactones, $Q_{ex} = 1.8 \text{ C cm}^{-2}$, $Q_{ps} = 0.6 \text{ C cm}^{-2}$, 0.5 mA cm^{-2} , \bullet : BL, Δ : VL, \circ : OL.

on LiClO_4 concentration for lactones is shown in Fig. 4. The E_a values on the lithium substrate were obtained at $Q_{ex} = 1.8 \text{ C cm}^{-2}$, $Q_{ps} = 0.6 \text{ C cm}^{-2}$ and at 0.5 mA cm^{-2} . In the range of 1.0–2.0 M LiClO_4 , high E_a values were obtained for each lactone. The E_a values were in the order of VL (86.9%) > BL (81.3%) > OL (80.1%). This E_a order is different from that for the electrolyte conductivity (BL > VL > OL).

The relationship between the E_a and the oxidation potential (E_{ox}) for the solvent is shown in Fig. 5. E_a tended to increase with a decrease in E_{ox} . It has been reported [24, 25] that a decrease in lithium cycling efficiency is due mainly to the reduction of the solvent by lithium. It has been also reported [26] that solvents with kinetic stability against the reduction by lithium are easy to oxidize; i.e., the reactivity between lithium and the solvent can be evaluated from E_{ox} . The reason for the lower E_{ox} of VL as compared to BL may be explained as follows: In the reduction of the

Table 2. Electrolytic parameters for LiClO_4 -BL/THF (1:1), at 25°C

Solvents	K_A^*	K_A^{**} (δ)	t_0^+	Λ_0^+ ($\text{S cm}^2 \text{ mol}^{-1}$)	η_0 (cP)	r_{so}^+ (nm)
BL	13.5	8.5 (3.28)	0.36	15.3	1.7	0.42
BL/THF (1:1)	151.8	69.0 (4.38)	0.50	30.5	0.79	0.43

*by Bjerrum equation [16]

**by modified Fousee-Onsager equation [17]

K_A : Ionic association constants, t_0^+ : Transference number for Li^+ , Λ_0^+ : Limiting Li^+ ionic conductivity, η_0 : viscosity for the solvent (s), r_{so}^+ : Stokes' radius for Li^+ .

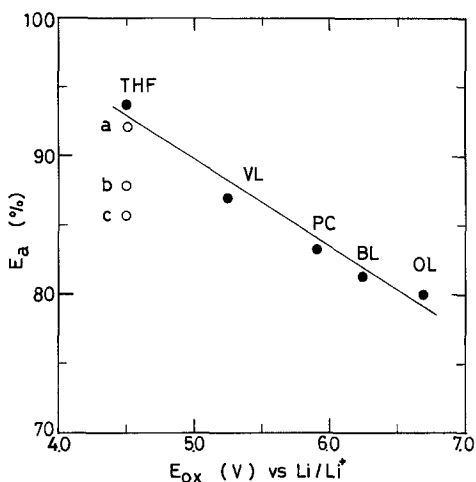


Fig. 5. Relation between lithium cycling efficiency (E_a) and oxidation potential (E_{ox}) for the solvent in 1M LiClO_4 - γ -lactone-based electrolytes, $Q_{ex} = 1.8 \text{ C cm}^{-2}$, $Q_{ps} = 0.6 \text{ C cm}^{-2}$, 0.5 mA cm^{-2} , (a) BL/THF (1:1), (b) VL/THF (1:1), (c) OL/THF (2:3).

solvent by lithium, lithium attacks oxygen atoms [24]. If the electron density of the oxygen atoms increase, reduction becomes difficult. Alkyl groups have a tendency to donate electrons through the single bond with an increase in the number of CH_3 groups (+ inductive effect [27]). Therefore, VL with CH_3 seems to have a lower reactivity than BL with hydrogen. This explanation is similar to that for the structure-reactivity relation with lithium between THF and 2-methylated-THF [25]. In the case of OL, this effect can not be expected due to the two methylene groups between carbon atoms in the cyclopenta-ring and the CH_3 end group.

The E_a values for lactone/THF mixed systems are also shown in Fig. 5. For BL/THF and OL/THF the E_a values were rather higher than those for systems using either BL or OL alone. Although the E_a value for BL/THF was slightly lower than that for THF, the E_a value for VL/THF was slightly higher than that for VL. The reason for the enhancement of the E_a value in ester/ether mixed systems has been explained previously, as in the case of PC/THF [1, 6]. In many cases, the ether has a stronger solvation power to Li^+ than the ester. The depositing Li^+ is selectively solvated by the ether even in ester/ether mixed systems. This phenomenon may lead to adsorption around the deposited lithium of the ether which is less reactive with lithium than the ester, as expected from the

oxidation potential. According to this explanation, it is considered that VL has the same or higher solvation power to Li^+ than THF ($D_N = 20.0$), because the electron density on the oxygen atom in VL is higher than in BL ($D_N = 15.9$). Therefore, it is considered that VL or a mixture of VL and THF exists in the VL/THF around the deposited lithium, while THF mainly exists in the BL/THF around it. Thus, the E_a value for VL/THF is approximately the same as that for VL.

SEM photographs of the deposited lithium in BL (a), BL/THF (b) and THF (c) are shown in Fig. 6. For deposited lithium in BL alone, cracks were observed in many places. On the other hand, for the BL/THF mixed system, the number of cracks decreased and the morphology of the deposited lithium in BL/THF was found to be similar to that in THF alone. Therefore, the E_a enhancement for BL/THF is well explained by adsorption around the deposited lithium, of THF or THF-Li^+ , which is less reactive with lithium than BL. The E_a dependence on THF content for LiClO_4 -BL/THF is shown in Fig. 7. The E_a value increased with an increase in THF content, and approached the E_a value for THF. The E_a dependence on LiClO_4 concentration for BL/THF (1:1) is shown in Fig. 8. In the range of 1.0–2.0 M LiClO_4 , high E_a values were obtained.

Summarizing the results regarding conductivity and lithium cycling efficiency for γ -lactone-based electrolytes, conductivity is in the order BL/THF > BL > VL/THF > VL > OL/THF > THF > OL, and the E_a values are in the order BL/THF \approx THF > VL/THF \approx VL > OL/THF > BL > OL. Therefore, among the electrolytes examined in this study, BL/THF was found to be preferable for use in nonaqueous lithium secondary batteries.

3.3. Conductivity and lithium cycling efficiency for BL/ether mixed systems

Conductivity and lithium cycling efficiency for BL/THF were compared with those for other ether/BL mixed systems. For the other ethers, 1, 2-dimethoxyethane (DME), 1, 2-diethoxyethane (DEE) and 1, 3-dioxolane (DOL) were used. Conductivities for 1M LiClO_4 -BL/ether are shown in Table 3. In all the mixed systems, conductivities for BL/ether were higher than those for systems using either BL or ether alone. The conductivities

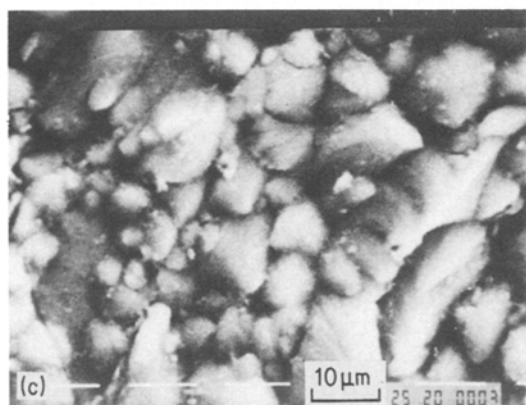
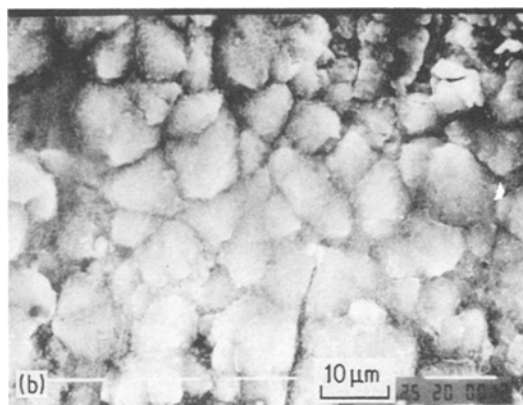
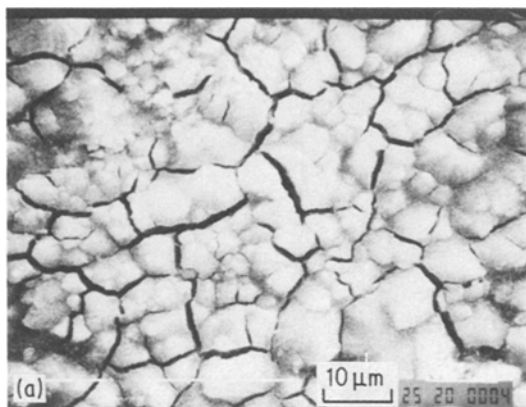


Fig. 6. SEM photographs for the deposited lithium, 1 mA cm^{-2} , 3.6 C cm^{-2} , on the aluminium substrate, 1 M LiClO_4 ($\times 1500$), (a) BL, (b) BL/THF (1:1), (c) THF.

for BL/DME and BL/DOL were slightly (approximately 6%) higher than that for BL/THF. The relation between the E_a and the E_{ox} of the ether in BL/ether mixed systems is shown in Fig. 9. The

E_a values increased with a decrease in E_{ox} for the ether. Although the E_a value for BL/DOL was the highest among the BL/ether mixed systems except for BL/THF, the E_a value for BL/DOL was

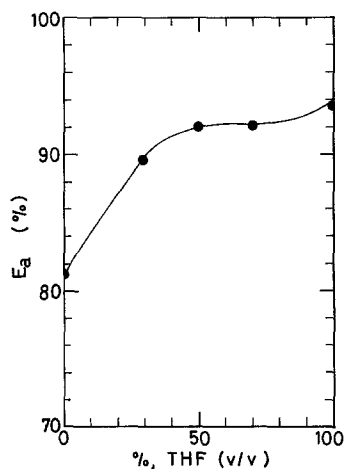


Fig. 7. Lithium cycling efficiency (E_a) dependence on THF content for 1 M LiClO_4 -BL/THF, $Q_{ex} = 1.8 \text{ C cm}^{-2}$, $Q_{ps} = 0.6 \text{ C cm}^{-2}$, 0.5 mA cm^{-2} .

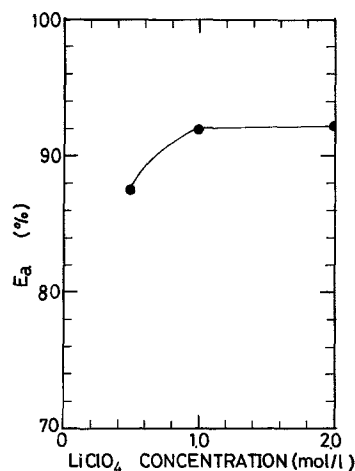


Fig. 8. Lithium cycling efficiency (E_a) dependence on LiClO_4 concentration for BL/THF (1:1), $Q_{ex} = 1.8 \text{ C cm}^{-2}$, $Q_{ps} = 0.6 \text{ C cm}^{-2}$, 0.5 mA cm^{-2} .

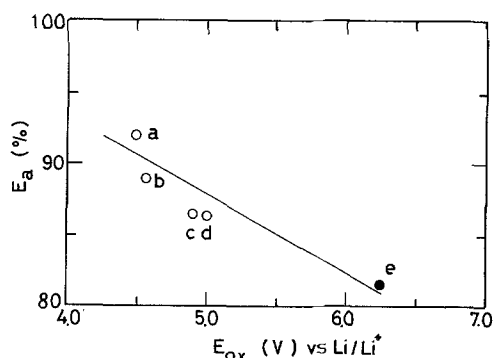


Fig. 9. Relation between lithium cycling efficiency (E_a) and oxidation potential (E_{ox}) for the ether in 1M LiClO_4 -BL/ether (1:1), $Q_{ex} = 1.8 \text{ C cm}^{-2}$, $Q_{ps} = 0.6 \text{ C cm}^{-2}$, 0.5 mA cm^{-2} , (a) BL/THF, (b) BL/DOL, (c) BL/DEE, (d) BL/DME, (e) BL.

approximately the same as that for VL/THF, whose value was, of course, rather lower than that for BL/THF.

4. Conclusion

Conductivity and lithium cycling efficiency on a lithium substrate were studied for γ -lactone-based electrolytes for use in nonaqueous lithium secondary batteries. Conductivities increased with a decrease in the solvent viscosity. Lithium cycling efficiency tended to increase with a decrease in the reactivity between lithium and the solvent, which was expected from the oxidation potential for the solvent. Conductivity for BL/THF was approximately 20% higher than that for BL, and 3.7 times higher than that for THF. Lithium cycling efficiency for BL/THF was also higher by approximately 10% than that for BL. The reason for the enhancement of the lithium cycling efficiency for BL/THF mixed system seems to be adsorption around the deposited lithium, of THF or THF-

Table 3. Conductivity for 1M LiClO_4 -BL/ether (1:1)

Solvents	Conductivity $\times 10^3$ (S cm^{-1})
BL/DME	13.8 (-)*
BL/DOL	13.8 (1.6)
BL/THF	12.4 (3.5)
BL/DEE	9.2 (3.2)
BL	10.9

Values in parentheses are conductivities for 1M LiClO_4 -ether.

*Solubility of LiClO_4 is less than 1M for DME.

Li^+ , which have lower reactivity to lithium, and higher solvation power to Li^+ than BL. From these results, the BL/THF mixed system was found to be the preferable among the γ -lactone-based electrolytes examined in this work for use in nonaqueous lithium secondary batteries.

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