STABLE ELECTROLYTES FOR LITHIUM BATTERIES

Y. MATSUDA

Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi 755 (Japan)

Summary

The physical and chemical properties of organic electrolytes for lithium batteries, and the factors affecting their conductivity, are discussed. In particular, attention is focussed on the modification of the solvent structure, organic electrolytes based on sulfolane or dimethyl sulfoxide, the addition effect of special organic compounds into the electrolyte, and some characteristics of miscellaneous electrolytes.

Introduction

Lithium battery technology has progressed remarkably since the early 1970s. For example, Li/CF_n, Li/MnO_2 and $Li/SOCl_2$ batteries [1 - 3] have now appeared in the commercial market. In addition, other prototype, rechargeable lithium batteries [4 - 9] have been investigated.

In 1967, the author and coworkers started research on lithium batteries with pyridine–hydrobromide–perbromide, pyridine–hydroiodide–periodide and poly(4-vinylpyridine)–bromine complex cathodes [10, 11]. There followed studies [12] on an electrolyte solution consisting of a mixed propylene carbonate (PC)–1,2-dimethoxyethane (DME) solvent containing $LiClO_4$ [12]. This electrolyte system [13, 14], as well as γ-butyrolactone (BL) containing $LiBF_4$, is used in present commercial lithium batteries. However, it is still necessary to develop new, stable and conductive electrolytes in order to obtain batteries with high output power and good rechargeability. Fundamental aspects and problems concerned with the development of such batteries are discussed in this paper.
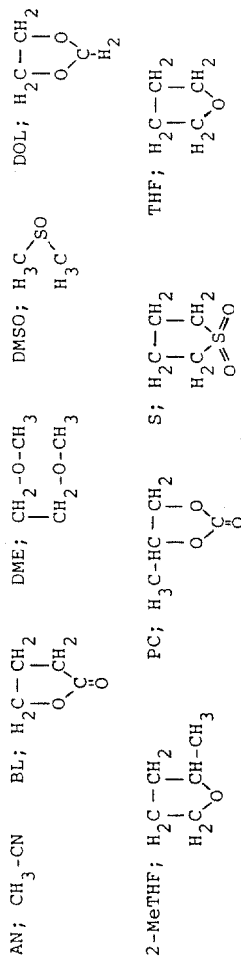
Physical and chemical properties of organic electrolytes

Many kinds of organic solvents have been examined as electrolytes for lithium batteries; the physical properties of some candidates are given in Table 1 [15 - 17]. Molecular weight is a fundamental property that is associated with the concentration of the molecule, and connects vapor pressure

TABLE 1

Physical properties of organic solvents (25 °C)

Solvent	Molecular weight	m.p. (°C, 1 atm)	b.p. (°C, 1 atm)	Density (g cm⁻³, 25 °C)	Relative dielectric constant	Viscosity (cP)	Dipole moment (Debye)	D.N.	A.N.
Acetonitrile (AN)	41.1	−45.72	81.77	0.783	38	0.345	3.94	14.1	18.9
γ-Butyrolactone (BL)	86.1	−42	206	1.125	39.1	1.751	4.12	—	—
1,2-Dimethoxyethane (DME)	90.1	−58	84.7	0.86	7.20	0.455	1.07	20	—
Dimethylsulfoxide (DMSO)	78.1	18.42	189	1.0955	46.45	1.991	3.96	29.8	19.3
Dioxolane (DOL)	74.1	−95	78	1.0600 (20 °C)	6.79 (30 °C)	0.58	—	—	—
2-Methyltetrahydrofuran (2-MeTHF)	86.1		78 - 80	0.848	6.24	0.457	—	—	—
Propylene carbonate (PC)	102.1	−49.2	241.7	1.198	64.4	2.530	5.21	15.1	18.3
Sulfolane (S)	120.2	28.86	287.3	1.2619 (30 °C)	42.5 (30 °C)	9.87 (30 °C)	4.7	14.8	19.3
Tetrahydrofuran (THF)	72.1	−108.5	66	0.888	7.25 (30 °C)	0.46 (30 °C)	1.71	20.0	8.0

AN; CH_3-CN

BL; H_2C-CH_2 / CH_2 / $O\diagdown C=O$

PC; $H_3C-HC-CH_2$ / $O\diagup C=O$

DME; CH_2-O-CH_3 / CH_2-O-CH_3

DMSO; $H_3C\diagdown SO$ / $H_3C\diagup$

S; H_2C-CH_2 / $H_2C\diagdown S\diagup CH_2$ / $O=S=O$

DOL; H_2C-CH_2 / $O\diagdown C\diagup O$ / H_2

THF; H_2C-CH_2 / $H_2C\diagdown O\diagup CH_2$

2-MeTHF; H_2C-CH_2 / $H_2C\diagdown O\diagup CH-CH_3$

and viscosity. Usually, the battery electrolyte must have: a high relative dielectric constant (relative permittivity), a low viscosity, a high boiling point, and a low melting point. However, these properties are generally incompatible with each other. The solubility of the electrolytic salt is of special importance, and is closely related to the dipole moment of the solvent. The solvent must have a high relative dielectric constant in order to prevent ion-pair formation in the electrolyte. The viscosity should be low to decrease the viscous drag on the ion migration. The electrolyte solution must be chemically stable and have a wide range of operating potentials. In particular, the electrolyte should be stable in contact with the lithium electrode. Therefore, solvents with less noble reduction potentials should be chosen.

Solution conductivity

The important factors determining solution conductivity are the dielectric constant and the viscosity. A mixed solvent system has been frequently used: one component has a high dielectric constant and the other a low viscosity. Figure 1 shows the molar conductivity of $LiClO_4$ in PC–DME and PC–THF. It can be seen that mixing exerts significant effects on the conductivity.

According to Bjerrum's theory of the associated ion-pair, the critical distance for ion-pair formation, q, is given by:

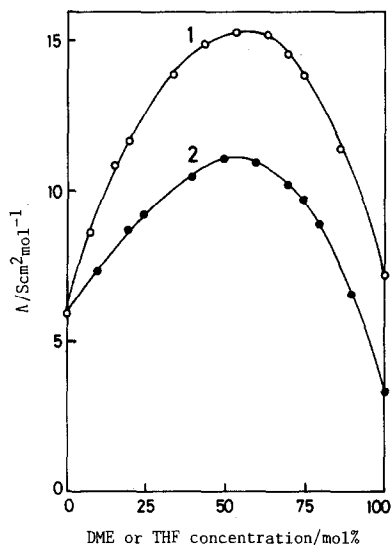$$q = |z_i z_j| e^2 / (8\pi\epsilon_0 \epsilon_r k T) \tag{1}$$

Fig. 1. Variation of Λ of 1 mol dm^{-3} $LiClO_4$ with solvent composition. 1: PC–DME; 2: PC–THF.

where ϵ_0 is the dielectric constant of a vacuum, ϵ_r is the relative dielectric constant of the medium, z is the charge number of each ion, e is the charge of an electron, and k is the Boltzman constant. Using this ion association concept, a relation between the degree of ion association and the distance of the closest approach for ions can be calculated. A typical relation for a PC–DME system is shown in Fig. 2 [18]. This suggests that the possibility of ion-pair formation is rather high in the high DME concentration range. Although Walden's law (*i.e.*, $\Lambda\eta$ = constant) is well recognized in solution chemistry, significant deivations from this law are observed when ion-pair formation takes place. The law holds approximately true in solutions where the dielectric constants of the solvents are high. Therefore, in such solutions, an inverse relationship between viscosity and conductivity is observed.
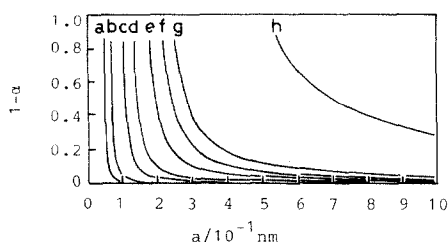

Fig. 2. Variation in degree of association of closest approach in mixed PC–DME system. a: DME, 0%; b: 25%; c: 50%; d: 60%; e: 70%; f: 75%; g: 80%; h: 90%.

Ion solvation also plays an important part in the conduction behaviour of the solution. Ions whose solvation radii are relatively large are unable to approach one another closely, and thus ion-pair formation would not be expected. Donicity (D.N.) and acceptor number (A.N.) of the solvent are responsible for the solvation of cation and anion, respectively. That is, these properties are closely related to the ion-pair formation [19].

In view of the above mentioned criteria, the properties required of the solvent for lithium batteries are: (i) low melting point, (ii) high boiling point, (iii) high solubility of the electrolytic salt, (iv) low viscosity, (v) high dielectric constant, (vi) high capability of solvation towards Li^+, and (vii) high chemical and electrochemical stability. Therefore, in order to design a stable and conductive electrolyte, attention should be directed towards the combination of the solvents and the electrolyte. In particular, solvent blending is one approach to developing suitable electrolytes.

Each component of the mixed-solvent system should have at least one of the following properties:

(i) low viscosity;

(ii) high dielectric constant;

(iii) high donicity.

Furthermore, some additives may be included as:

(a) chemical and/or electrochemical stabilizing reagents;

(b) inhibitors to polymerization of the electrolyte; or

(c) depolarizers for negative and/or positive electrodes.

Electrolytic salts

The compounds $LiClO_4$ and $LiBF_4$ are widely employed as electrolytic salts in lithium batteries using PC–DME and BL solvents, respectively. However, $LiClO_4$ is not appropriate as an electrolyte for rechargeable batteries due to its tendency to explode in some ether solvents. In the USA and Canada, $LiAsF_6$ [4, 5, 20, 21] has been examined as an alternative electrolytic salt due to the resulting formation of a protective film on lithium electrodes. By contrast, $LiBF_4$ [6, 7, 22 - 24] and $LiPF_6$ [8, 9] have been mainly adopted in Japan. In these cases, lithium alloy electrodes have been employed because alloying depresses the reaction between lithium and the solvent. Some other salts, *e.g.*, $LiBMe_4$, $LiB\phi_2Me_2$, $LiB\phi_4$, $LiSeCl_4$, $LiCF_3SO_3$, etc., have been examined, but most of them have not been used in prototype rechargeable batteries because of their rather low solubility and other disadvantages.

Modification of solvent structure

The electrolyte in lithium batteries should be both chemically and electrochemically stable, but many solvents react to some degree with both the metal and the electrolytic salt [4, 15, 25]. In particular, tetrahydrofuran (THF) and 1,3-dioxolane (DOL) exhibit degradation or polymerization in the presence of $LiAsF_6$ or $LiPF_6$. In these cases, some modification of the solvents must be undertaken. Substitution of the methyl group to THF (MTHF) slows down the ring-opening reaction of THF [4]. Also, methyl-substituted DOL(4-methyl-1,3-DOL) has been adopted instead of DOL. The modification of other solvent molecules appears possible. The authors have attempted to use some alkoxyethanes, and found that ethoxymethoxyethane–PC/$LiClO_4$ [26] and DME–THF/$LiPF_6$ [27] are superior electrolyte systems.

Organic electrolytes based on sulfolane (S) or dimethyl sulfoxide (DMSO)

One approach to developing a stable electrolyte is to blend stable solvents. Sulfolane and DMSO are chemically and electrochemically stable, and the dielectric constants of these solvents are 40 or higher. Figure 3 shows the DME-concentration dependence of the conductivity for 1 M solutions of $LiBF_4$, $LiClO_4$, and $LiPF_6$ in S–DME [28]. These results show that S–DME containing 1 M $LiPF_6$ has the highest conductance and that the anions of the salts strongly affect the electrolytic conductivity.

The cycle efficiencies of lithium on a nickel substrate measured in S–DME solutions with different electrolytes are compared in Fig. 4 [28]. The average efficiency was highest in the $LiPF_6$ solution. The differences in cycle efficiency among the three electrolytes arise from differences in the
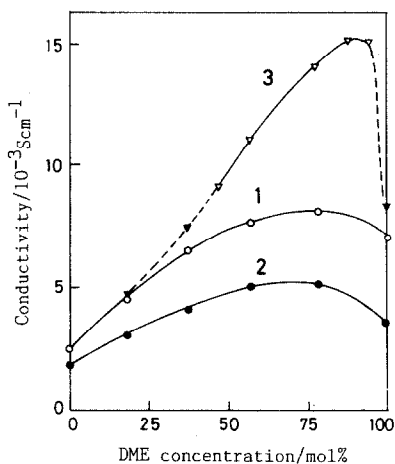
Fig. 3. Variation of conductivity with DME concentration for 1 mol dm^{-3} LiClO$_4$ (1); LiBF$_4$ (2); LiPF$_6$ (3) in S–DME.
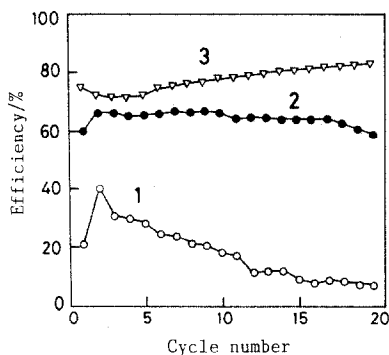
Fig. 4. Variation of Li cycling efficiency with cycle number in 1 mol dm^{-3} LiClO4 (1); LiBF$_4$ (2); LiPF$_6$ (3). Solvent: S–DME (1:1 by volume).

electrochemical stability of the solution. The latter depends on the magnitude of polarization during the charge/discharge process.

Dimethyl sulfoxide is another promising component for the electrolyte of lithium batteries. Figure 5 shows the conductivities of 1 M LiClO$_4$, LiBF$_4$ and LiPF$_6$ in DMSO–DME. The conductance behaviour of LiPF$_6$ is somewhat different from that of LiClO$_4$ and LiBF$_4$ [29]. Lithium cycling efficiencies in DMSO–DME (vol. 1:1) containing 1 M LiClO$_4$, LiBF$_4$ and LiPF$_6$ are shown in Fig. 6 [29]. It can be seen that the cycling efficiency of Li in LiPF$_6$ is much higher than that in LiClO$_4$ or LiBF$_4$.

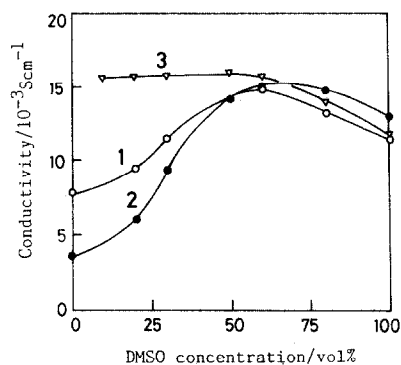Fig. 5. Conductivity of 1 mol dm^{-3} LiClO$_4$ (1); LiBF$_4$ (2); LiPF$_6$ (3) in the mixed DMSO–DME system.
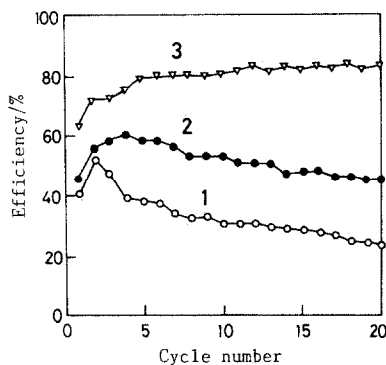
Fig. 6. Lithium cycling efficiency for 1 mol dm^{-3} LiClO$_4$ (1); LiBF$_4$ (2); LiPF$_6$ (3) in the mixed DMSO–DME system.

Addition of special organic compounds

The addition of some special organic compounds to the electrolyte of rechargeable lithium batteries can affect both the conductivity and the cycling efficiency. For example, the addition of crown ether, 12-crown-4 (12C4) or 15-crown-5 (15C5), into PC containing 1 M $LiClO_4$ increases the molar conductivity [30]; the highest conductivity occurs at a mol addition ratio of 1:1 (crown ether: Li^+). These phenomena are closely connected with the solvation of lithium with crown ether. Similarly, the addition of N,N,N',N'-tetramethylethylenediamine (EDA) to PC containing 1 M $LiClO_4$ also increased the charge/discharge efficiency of lithium [31].

As stated above, the addition of a small amount of organic additives can also improve Li cycling efficiency. In this area, the use of 2-methylfuran (MeF) [32, 33] and related additives, 2-methylthiophene [33], and quinone-imine [34] dyes have been reported. The action of these compounds is to modify the properties of the film which is formed by reaction of the additive with lithium or by adsorption of the additive on lithium.

Miscellaneous electrolytes

The electrolyte of the Li/SOCl$_2$ battery is usually $LiAlCl_4$. Lithium iodide (LiI) is the best known solid electrolyte, *e.g.*, commercial batteries use $Li/LiI/I_2$, P2VP [35].

On the other hand, solid polymer electrolytes such as $(PEO)_8 LiCF_3 SO_3$ have been reported [36, 37]. Lithium ion conductive glasses are also candidates for the electrolyte and can operate over a wide temperature range. These glasses are B_2S_3–Li_2S–LiI [38], B_2O_3–P_2O_5–Li_2O [39], Si_2–Li_2S–LiBr [40], LiF–LiH, LiF–LiOH, LiF–Li_2O, Li_2S–Li_2O, Li_2S–LiCl, Li_2S–LiBr [41], etc.

The development of new, stable, and high conductive electrolytes is expected to result in the development of lithium batteries with high power and good rechargeability for use in a wide variety of applications.

References

1 M. Fukuda and T. Iijima, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, Ch. 9.
2 H. Ikeda, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, Ch. 8.
3 C. R. Schlaikjer, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, Ch. 13.
4 K. M. Abraham and S. B. Brummer, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, Ch. 14.
5 J. A. R. Stiles, *New Mater. New Process.*, 3 (1985) 89.
6 Y. Toyoguchi, S. Nankai, J. Yamaura, T. Matsui and T. Iijima, *Preprint, 24th Battery Symp., Japan, 1983*, p. 205.

7 N. Koshiba, H. Hayakawa and K. Momose, *Preprint, 26th Battery Symp., Japan, 1985*, p. 145.
8 K. Kajita, Y. Yoshimitsu, N. Koyama and S. Kitagawa, *Preprint, 25th Battery Symp., Japan, 1984*, p. 296.
9 K. Yoshimitsu, S. Kitagawa, K. Kajita and T. Tanabe, *Preprint, 26th Battery Symp., Japan, 1985*, p. 49.
10 Y. Matsuda, T. Inoue, H. Yoneyama and H. Tamura, *Kogyo Kagaku Zasshi, 74* (1971) 2205.
11 T. Saito, H. Ikeda, Y. Matsuda and H. Tamura, *J. Appl. Electrochem., 3* (1973) 99.
12 T. Saito, H. Ikeda, Y. Matsuda and H. Tamura, *J. Appl. Electrochem., 6* (1976) 85.
13 Y. Matsuda and H. Satake, *J. Electrochem. Soc., 127* (1980) 877.
14 Y. Matsuda, H. Nakashima, M. Morita and Y. Takasu, *J. Electrochem. Soc., 128* (1981) 2553.
15 G. E. Blomgren, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, London, 1983, Ch. 2.
16 Y. Matsuda, *Denki Kagaku, 48* (1980) 665.
17 *Kagaku Binran*, Chem. Soc. Jpn., Maruzen, 3rd Edn., 1984.
18 Y. Matsuda, M. Morita and H. Kosaka, *J. Electrochem. Soc., 130* (1983) 101.
19 Y. Matsuda, M. Morita and F. Tachihara, *Bull. Chem. Soc. Jpn., 59* (1986) 1967.
20 E. J. Plichta and M. Salomon, *J. Power Sources, 13* (1984) 319.
21 V. R. Koch, J. L. Goldman, C. J. Mattos and M. Mulvaney, *J. Electrochem. Soc., 129* (1984) 1.
22 Y. Matsuda, M. Morita and K. Takata, *J. Electrochem. Soc., 131* (1984) 1991.
23 Y. Matsuda, M. Morita and T. Yamashita, *J. Electrochem. Soc., 131* (1984) 2821.
24 K. Takata, M. Morita, Y. Matsuda and K. Matsui, *J. Electrochem. Soc., 132* (1985) 126.
25 V. R. Koch, *J. Power Sources, 9* (1983) 247.
26 Y. Matsuda, M. Morita and S. Kanameda, *Denki Kagaku, 52* (1984) 702.
27 M. Morita, H. Miyazaki and Y. Matsuda, *Electrochim. Acta, 31* (1986) 573.
28 Y. Matsuda, M. Morita, K. Yamada and K. Hirai, *J. Electrochem. Soc., 132* (1985) 2538.
29 Y. Matsuda, M. Morita and F. Tachihara, *Preprint, 26th Battery Symp. Japan, 1985*, p. 13.
30 Y. Matsuda, H. Hayashida and M. Morita, *Denki Kagaku, 53* (1985) 628.
31 S. Tobishima and A. Yamaji, *J. Power Sources, 12* (1984) 53.
32 S. Tobishima and T. Okada, *Denki Kagaku, 53* (1985) 742.
33 K. M. Abraham, *J. Power Sources, 14* (1985) 179.
34 S. Tobishima and T. Okada, *J. Appl. Electrochem., 15* (1985) 901.
35 A. A. Schneider, D. E. Harney and M. J. Harney, *J. Power Sources, 5* (1980) 15.
36 W. C. Maskell and J. R. Owen, *J. Electrochem. Soc., 132* (1985) 1602.
37 R. D. Armstrong and M. D. Clarke, *Electrochim. Acta, 29* (1984) 1443.
38 M. Monetrier, A. Levasseur and P. Hagenmuller, *J. Electrochem. Soc., 131* (1984) 1971.
39 A. Magistris, G. Chiodell and M. Villa, *J. Power Sources, 14* (1985) 87.
40 S. Sahami, S. W. Shea and J. H. Kennedy, *J. Electrochem. Soc., 132* (1985) 985.
41 W. Weppner, *J. Power Sources, 14* (1985) 105.