

ETHYLENE CARBONATE/ETHER SOLVENTS FOR ELECTROLYTES IN LITHIUM SECONDARY BATTERIES

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Summary

An examination has been made of the effectiveness of ethylene carbonate(EC)/2-methyltetrahydrofuran(2-MeTHF) solvents incorporating LiAsF₆ as the solute as electrolytes in secondary lithium batteries. From -10 to 30 °C, the conductivities of EC/2-MeTHF are higher than those of 2-MeTHF and EC/propylene carbonate (PC). For lithium-on-lithium cycling in a half cell, the FOM (figure of merit) of lithium in EC/2-MeTHF has a value 2.2 to 2.7 times higher than that in 2-MeTHF and EC/PC. A coin cell of Li/amorphous V₂O₅-P₂O₅ with EC/2-MeTHF clearly exhibits higher capacity and longer cycle life than cells with 2-MeTHF or EC/PC. It is concluded that EC/2-MeTHF is a promising electrolyte system for secondary lithium battery applications.

Introduction

Efficient electroplating and stripping of lithium in non-aqueous media, as well as high electrolyte conductivity, are essential to the development of secondary lithium batteries. The most effective electrolyte for improving Li cycling efficiency is 2-methyltetrahydrofuran (2-MeTHF)//LiAsF₆ [1]. However, the conductivity of this electrolyte is low. It has been reported previously [2] that ethylene carbonate(EC)/ether solvent electrolytes are more effective with regard to conductivity and lithium cycling efficiency than other ester/ether solvents, such as propylene carbonate(PC), sulfolane, or γ -lactones plus ethers.

This work examines the efficacy of EC/2-MeTHF solvent electrolytes for use in secondary lithium batteries. It has been shown [2] that EC has a high dielectric constant of 95.3 at 25 °C and that 2-MeTHF has a low viscosity of 0.46 cP at 20 °C. Because the donor number of 2-MeTHF(18.0) is higher than that of EC(16.4), the former solvent has a higher solvation power with Li⁺ ions.

Experimental

The solvents were purified until the impurity content was less than 100 ppm. The solute, LiAsF₆ (US Steel Agri Chemicals), was used as received. The amorphous V₂O₅-P₂O₅ (a-V₂O₅, 95 mol% V₂O₅) and the coin cells (23 mm in diameter and 2 mm thickness, cathode active material ~0.1 g) were prepared as reported previously [3]. The cathode mixture was formed by mixing a-V₂O₅-P₂O₅ powder, acetylene black and PTFE powder in the respective weight ratio of 70:25:5. Lithium was electroplated and stripped on a lithium substrate (Li-on-Li cycling) in a half-cell, as described previously [2]. The excess lithium at the start of the experiment, the cycle capacity and the current density were 1.8 C cm⁻², 0.6 C cm⁻² and 0.5 mA cm⁻², respectively. The FOM (figure of merit [4]) is a value which reflects the cycling efficiency of lithium and is calculated from the relationship:

$$\text{FOM} = (\text{total accumulated discharge capacity}) / (\text{excess Li content}) \quad (1)$$

The ionic association constant (K_A) for LiAsF₆ was examined [2] by the Bjerrum equation:

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

where a , q and r are the distance of closest approach, the Bjerrum distance, and the distance between the ions, respectively N_A , z , e , T , ϵ and κ have their usual significance [2].

Results and discussion

The data of Fig. 1 show that the resistivities from -10 to 30 °C for EC/2-MeTHF have lower values than those for 2-MeTHF and EC/PC (PC was added to reduce the melting point of EC). The lower resistivity of EC/2-MeTHF is mainly due to the combined effects of the high dielectric constant of EC and the low viscosity of 2-MeTHF, *i.e.*, there is a significant degree of ionic dissociation and an easy ion migration [2]. At 25 °C, the resistivity exhibited a minimum value when the EC/2-MeTHF mixing volume ratio was 2:3 (Fig. 2). The 2-MeTHF content at minimum resistivity increased with decrease in temperature. This may be due to the influence of viscosity. Table 1 gives Li⁺ ionic conductivities (Λ_0^+) at infinite dilution [2], together with association constants (K_A) for EC/2-MeTHF and EC/PC, calculated using the Bjerrum equation [2]. The K_A value is larger in mixtures of EC/2-MeTHF than it is in EC/PC because the dielectric constant of EC/2-MeTHF decreases almostly linearly with an increase in 2-MeTHF content. However, Λ_0^+ is higher for EC/2-MeTHF than it is for EC/PC, which is advantageous for lithium battery applications. The reason for the higher value of Λ_0^+ in EC/2-MeTHF is as follows: an electrolyte with a large anion, such as AsF₆⁻,

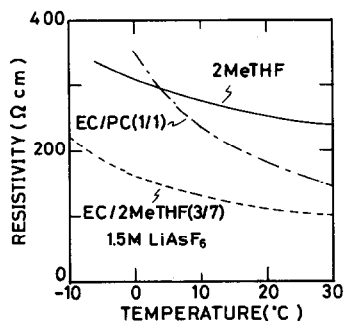


Fig. 1. Relation between resistivity and temperature.

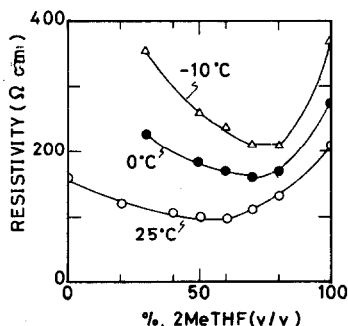
Fig. 2. Resistivity for 1.5 M LiAsF₆-EC/2-MeTHF.

TABLE 1

Electrolytic parameters for EC/2-MeTHF//LiAsF₆

Solvents	K_A	t_0^+	Λ_0^+ (S cm ² mol ⁻¹)	D_0 (cm ² s ⁻¹) × 10 ⁶
EC/2-MeTHF(1/1)	3.93	0.39	18.1	6.15
EC/PC(1/1)	~ 0	0.37	11.1	2.55

 K_A for 2-MeTHF is 4×10^4 . t_0^+ : transport number for Li⁺.

tends to have a high degree of dissociation because the coulombic force between the Li⁺ ion and the anion is low. Therefore, for LiAsF₆, the ion migration rate (controlled by viscosity) has a stronger effect on conductivity than has the ionic dissociation (controlled by dielectric constant). The diffusion constants (D_0) of ions in EC/2-MeTHF are higher than are those in EC/PC [5].

The specific discharge capacity for an Li/a-V₂O₅ cell at 25 °C is shown in Fig. 3. The discharge capacity was calculated with reference to the V₂O₅-P₂O₅ weight. The discharge capacity for the cell with EC/2-MeTHF was greater than that for the cell with 2-MeTHF. The highest capacity was obtained at an EC/2-MeTHF mixing volume ratio of 2:3. This 2-MeTHF content coincides with that for the minimum resistivity.

Table 2 shows FOM values from Li-on-Li cycling tests using either a half-cell or an Li/a-V₂O₅ cell. The FOM values for EC/2-MeTHF were higher than were those for 2-MeTHF and EC/PC. The relation between the discharge (stripping) voltage (E) of lithium (*versus* Li/Li⁺) at the stripping end point and the cycle number is given in Fig. 4. The increase in anodic overpotential with increase in cycle number for EC/2-MeTHF is lower than that for 2-MeTHF. The constant E values of ~3.4 V beyond the 50th cycle in 2-MeTHF and beyond the 140th cycle in EC/2-MeTHF correspond to the oxidation of 2-MeTHF after the apparent "100%" cycle ends in the Li-on-Li cycling test. The reason for the high lithium cycling efficiency in 2-MeTHF is

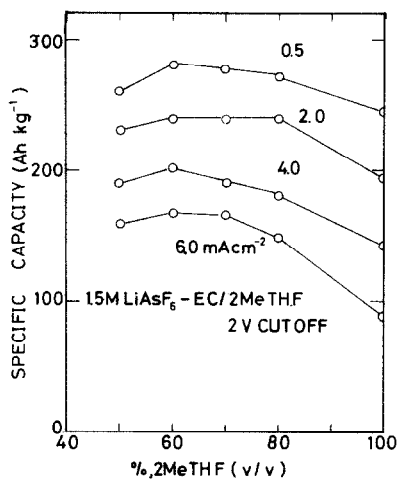


Fig. 3. Specific capacity for an Li/a-V₂O₅ cell with 1.5 M LiAsF₆-EC/2-MeTHF at 25 °C.

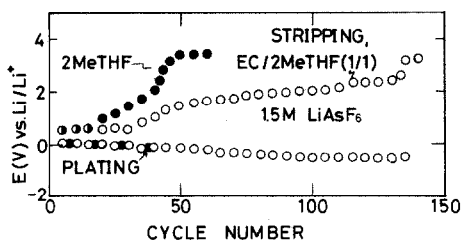


Fig. 4. Relation between discharge(stripping)-charge(plating) voltages and cycle number by Li-on-Li cycling test using a half-cell at 25 °C.

TABLE 2

FOM of lithium in 1.5 M LiAsF₆

Solvent	FOM	
	Half cell (Li-on-Li)	Li/a-V ₂ O ₅ cell*
2-MeTHF	13.2	9.4(270)
EC/2-MeTHF(1/1)	35.7	28.2(400)
EC/PC(1/1)	16.0	14.8(280)

*90 mA h Li; discharge current, 3 mA cm⁻²; charge current, 1 mA cm⁻²; voltage limit, 2 - 3.5 V.

Parentheses indicate cycle number.

attributed to the formation of a porous and/or electron conductive protection film of (As-O-As)_n on the lithium surface [1] resulting from the reactions of lithium with 2-MeTHF and with AsF₆⁻. It is reported [6] that the thickness of the surface film on lithium is reflected in the anodic overpotential value. In EC/2-MeTHF mixtures, depositing Li⁺ ions are selectively solvated with 2-MeTHF molecules because 2-MeTHF has a higher solvation power for Li⁺ ions than has EC. Therefore, a 2-MeTHF-rich atmosphere exists around the deposited lithium, even in EC/2-MeTHF mixed systems [3]. One possible reason for EC/2-MeTHF having a higher FOM value than 2-MeTHF is due to the difference between EC/2-MeTHF and 2-MeTHF in the formation rate of the protective film (suppression of 2-MeTHF-deposited lithium interaction), which may be due to EC-2-MeTHF interactions.

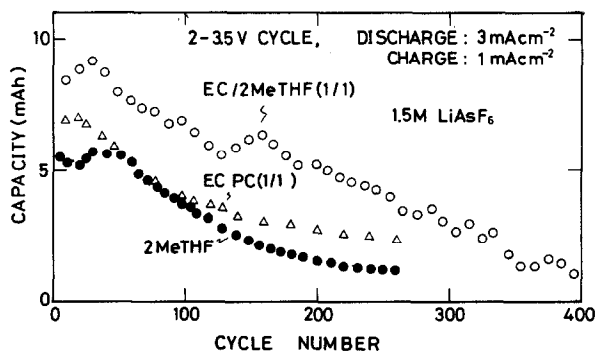


Fig. 5. Relation between capacity and cycle number for an Li/a-V₂O₅ cell at 25°C.

The relation between cell capacity and cycle number for an Li/a-V₂O₅ cell is presented in Fig. 5. The cell with EC/2-MeTHF exhibits a higher capacity and a longer cycle life than those with 2-MeTHF and EC/PC, respectively.

It is concluded that EC/2-METHF//LiAsF₆ is an excellent electrolyte for achieving high-rate and long cycle-life lithium batteries.

References

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