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Electrolytic Properties and Application to a Lithium Battery of Ternary Solvent Electrolytes with Ethylene Carbonate – Dimethyl Carbonate – 3-Methylsydnone and 3-Ethylsydnone

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The electrolytic conductivity and charge-discharge characteristics of the lithium electrode were examined in ternary solvent systems made up of an ethylene carbonate (EC)-dimethyl carbonate (DMC) equimolar binary mixture with 3-methylsydnone (3-MSD) and 3-ethylsydnone (3-ESD). The electrolytes used were LiClO_4 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$. The order of the decrease in conductivity of the ternary solvent electrolytes at a mol ratio 0.5 of 3-MSD and 3-ESD was $\text{LiPF}_6 > \text{LiClO}_4 > \text{LiN}(\text{CF}_3\text{SO}_2)_2 > \text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2 > \text{LiBF}_4 > \text{LiCF}_3\text{SO}_3$. The 1 mol dm^{-3} $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ electrolytes with large anions showed moderate conductivities of higher than $6\text{--}7 \text{ mS cm}^{-1}$ at a mol ratio 0.5 of 3-MSD and 3-ESD. Addition of 3-MSD and 3-ESD to the EC-DMC equimolar binary mixtures containing LiClO_4 , LiBF_4 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is effective for raising lithium electrode cycling efficiency. We found by using scanning electron microscope (SEM) that the cycling efficiency is dependent on the dendrite formation and the morphology of the film formed on the Ni (working) electrode.

Key Words : Lithium Batteries, Sydnone Compounds, Cycling Efficiency, Scanning Electron Microscope

1 Introduction

A sydnone compound is well known as a typical mesoionic compound, which can not be satisfactorily represented by any one canonical structure.^{1–3)} This unique structure leads to a large dipole moment^{4, 5)} and high dielectric constants^{6–9)} compared with those of other organic solvents. Especially, 3-methylsydnone (3-MSD) and 3-ethylsydnone (3-ESD) (Fig. 1) among the 3-alkylsydnones have high dielectric constants, 144.0 (40°C)^{6, 7)} and 102.3 (25°C),¹⁰⁾ respectively. However, it is preferable to use mixed solvents of these sydnones and a low viscosity solvent as the overall solvent for electrolytes because of the high viscosity of the sydnones. We have already reported that the mixed solvents of 3-propylsydnone with tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were favorable solvents for electrolytes.^{11, 12)} In previous papers,^{12–14)} the electrolytic

properties and application to lithium batteries of binary mixtures with some 3-alkylsydnones and low viscosity solvents have been examined based on the conductivity and the lithium electrode cycling efficiency.

The purpose of the present study is to elucidate the electrolytic behavior and charge-discharge characteristics of the lithium electrode in the ternary solvent systems of ethylene carbonate (EC)-dimethyl carbonate (DMC) equimolar binary solvent mixture, which is a typical mixed solvent for lithium batteries, with 3-MSD and 3-ESD.

2 Experimental

2.1 Apparatus and measurements

Conductivities of the electrolytes were measured using a conductometer (Toa Electronics, Model CM-60S) with a cell (Model CGT-511B). By use of a charge/discharge unit (Hokuto Denko, Model HJ-201B), the lithium electrode cycling efficiency was estimated by a galvanostatic plating-stripping method which was reported by Koch and Brummer.¹⁵⁾ The preparation of the electrolyte solutions and the cell assembly were carried out in an Ar-filled dry box. The morphology of the films formed on the Ni (working) electrode after cycling was examined by using a scanning electron microscope (SEM, JSM-5310).

2.2 Materials

The synthesis of 3-ethylsydnone (3-ESD), starting with ethyl bromoacetate and ethylamine, was carried out essentially using the literature procedure.^{6, 16, 17)} Commercial sarcosine (N-methylglycine), which is an intermediate

Fig. 1 Structure of 3-alkylsydnone. 3-MSD ($\text{R} = \text{CH}_3$), 3-ESD ($\text{R} = \text{C}_2\text{H}_5$).

product of 3-methylsydnone (3-MSD), was used as a starting material for the synthesis of 3-MSD. The purity and structure were confirmed by elemental analysis and C-H COSY NMR. Commercial reagent grade ethylene carbonate (EC), diethyl carbonate (DEC), and sydnone were dehydrated using purified molecular sieves (4 Å) before preparation of the solutions. Commercial reagent grade LiPF_6 , LiBF_4 , LiClO_4 , and LiCF_3SO_3 were dried in vacuo for 24 h at 70°C. 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.

3 Results and Discussion

The variation of specific conductivities in ternary solvent electrolyte solutions by the addition of 3-MSD to the EC-DMC equimolar binary mixture containing 1.0 mol dm^{-3} electrolytes at 25°C is shown in Fig. 2. The conductivities in LiPF_6 , LiClO_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ electrolytes gradually decrease with increasing 3-MSD concentration with higher viscosity. For LiBF_4 and LiCF_3SO_3 electrolytes, the addition of 3-MSD affects scarcely the conductivities. The conductivities of these electrolytes seem to be more significantly influenced by the viscosity rather than the dielectric constant of the solution due to the addition of 3-MSD.⁶⁾ The order of the decrease in conductivities of the electrolytes at mol ratio 0.5 of 3-MSD is $\text{LiPF}_6 > \text{LiClO}_4 > \text{LiN}(\text{CF}_3\text{SO}_2)_2 > \text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2 > \text{LiBF}_4 > \text{LiCF}_3\text{SO}_3$. The moderate conductivities of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ with a large anion as well as LiClO_4 are dependent on the resonance structure¹⁸⁾ of the $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ and $\text{N}(\text{C}_2\text{F}_5\text{SO}_2)_2^-$ ions. This means that the resonance structure contributes to stabilization of the $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ and $\text{N}(\text{C}_2\text{F}_5\text{SO}_2)_2^-$ ions. This electrolytic behavior is similar to that in the 3-ESD system.

Figure 3 shows the lithium electrode cycling efficiencies (charge-discharge characteristics of lithium electrode) in ternary solvent electrolytes by the addition of 3-MSD to the EC-DMC equimolar binary mixture contain-

Fig. 2 Specific conductivities in ternary solvent electrolyte solutions by the addition of 3-MSD to the EC-DMC equimolar binary mixture containing 1.0 mol dm^{-3} electrolyte at 25°C. X_s means the mol ratio of 3-MSD given in EC-DMC-3-MSD (1 : 1 : X_s mol ratio). (○): LiPF_6 , (●): LiClO_4 , (□): LiBF_4 , (■): LiCF_3SO_3 , (△): $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, (▲): $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$.

Fig. 3 Lithium electrode cycling efficiencies in ternary solvent electrolytes by the addition of 3-MSD to the EC-DMC equimolar binary mixture containing 1.0 mol dm^{-3} LiClO_4 at 25°C. (○): EC-DMC (mol ratio 1 : 1), (▲): EC-DMC-3-MSD (mol ratio 1 : 1 : 0.1), (■): EC-DMC-3-MSD (mol ratio 1 : 1 : 0.3), (▼): EC-DMC-3-MSD (mol ratio 1 : 1 : 0.5).

Fig. 4 Lithium electrode cycling efficiencies in ternary solvent electrolyte solutions containing 1.0 mol dm^{-3} electrolyte at 25°C. (○): EC-DMC (mol ratio 1 : 1), (□): EC-DMC-3-MSD (mol ratio 1 : 1 : 0.1), (△): EC-DMC-3-ESD (mol ratio 1 : 1 : 0.1).

ing 1.0 mol dm^{-3} LiClO_4 . It is found that the cycling efficiencies in these solutions become higher at mol ratio 0.1 of 3-MSD and 3-ESD. The cycling efficiencies in ternary solvent electrolytes at mol ratio 0.1 of 3-MSD and 3-ESD containing 1.0 mol dm^{-3} each lithium salt are shown in Fig. 4. In Fig. 4, an addition of 3-MSD and 3-ESD to the EC-DMC equimolar binary mixtures containing LiClO_4 , LiBF_4 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is effective for raising the cycling efficiency. On the other hand, the addition effect to the LiPF_6 electrolyte is minor. However, the cycling efficiency in $\text{LiPF}_6/\text{EC-DMC-3-MSD}$ is

Fig. 5 SEM photographs of the Ni electrode (working) in EC-DMC, EC-DMC-3-MSD, and EC-DMC-3-ESD systems containing 1.0 mol dm^{-3} LiClO_4 and $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ after the 40th cycle.

lower than that in $\text{LiClO}_4/\text{EC-DMC-3-MSD}$ at the 40th cycle. Figure 5 shows the scanning electron microscope (SEM) photographs of the Ni working electrode in EC-DMC and EC-DMC-3-MSD systems containing 1.0 mol dm^{-3} (a) LiClO_4 and (b) $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ after the 40th cycle. The formation of the lithium dendrite is appreciably observed in the $\text{LiClO}_4/\text{EC-DMC}$ electrolyte. On the contrary, the dendrite formation in $\text{LiClO}_4/\text{EC-DMC-3-MSD}$ and $\text{LiClO}_4/\text{EC-DMC-3-ESD}$ electrolytes is scarcely observed. In addition, the film on the electrode surface in $\text{LiClO}_4/\text{EC-DMC-3-MSD}$ electrolyte is significantly homogeneous and consists of an uniform grain size. However, the formation of lithium dendrite is not observed in EC-DMC, EC-DMC-3-MSD, and EC-DMC-3-ESD electrolytes containing $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ as shown (b) in Fig 5. Further-

more, the film in the $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2/\text{EC-DMC-3-MSD}$ electrolyte is considerably heterogeneous compared with that in the $\text{LiClO}_4/\text{EC-DMC-3-MSD}$ electrolyte. Accordingly, it is thought that the lithium electrode cycling efficiency is dependent on the dendrite formation and the morphology of the film formed on the electrode.

In conclusion, addition of 3-MSD and 3-ESD to the EC-DMC equimolar binary mixtures containing LiClO_4 , LiBF_4 , LiCF_3SO_3 , and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ is effective for raising cycling efficiency. Especially, the addition of 3-MSD for mol ratio 0.1 to EC-DMC equimolar binary mixture containing LiClO_4 is useful for obtaining higher efficiency at a higher cycle number range.

References

- 1) W. Baher, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, **1949**, 307.
- 2) W. Baher and W. D. Ollis, *Quant. Rev. (London)*, **11**, 15 (1957).
- 3) F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964).
- 4) R. A. W. Hill and L. E. Sutton, *J. Chem. Soc.*, **1949**, 746.
- 5) G. H. Schmid, *J. Mol. Struct.*, **5**, 236 (1970).
- 6) R. J. Lemire and P. G. Sears, *J. Chem. Eng. Data*, **22**, 376 (1977).
- 7) R. J. Lemire and P. G. Sears, *J. Solution Chem.*, **9**, 553 (1980).
- 8) Y. Sasaki and Y. Ishibashi, *Bull. Chem. Soc. Jpn.*, **63**, 1422 (1990).
- 9) Y. Sasaki, I. Komiya, and M. Handa, *Bull. Chem. Soc. Jpn.*, **67**, 2571 (1994).
- 10) M. Handa, T. Suzuki, H. Fukuda, and Y. Sasaki, *Chem. Lett.*, **1998**, 457.
- 11) Y. Sasaki, K. Miyagawa, N. Wataru, and H. Kaido, *Bull. Chem. Soc. Jpn.*, **66**, 1608 (1993).
- 12) Y. Sasaki, M. Ohashi, S. Okahata, H. Kaido, T. Mori, and M. Handa, *Nippon Kagaku Kaishi*, **1993**, 1217.
- 13) Y. Sasaki, K. Sekine, and M. Handa, *Prog. Batteries & Battery Materials*, **17**, 239 (1998).
- 14) S. Iinou, M. Handa, and Y. Sasaki, *Electrochemistry*, **67**, 22 (1999).
- 15) V. R. Koch and S. B. Brummer, *Electrochim. Acta*, **23**, 55 (1978).
- 16) L. B. Kier and D. Dhawan, *J. Pharm. Sci.*, **51**, 1058 (1962).
- 17) V. F. Vasil'eva and V. G. Yashunskii, *J. Gen. Chem. USSR (Engl. Transl.)*, **32**, 2845 (1962).
- 18) A. Webber, *J. Electrochem. Soc.*, **138**, 2586 (1991).