

The conductance behaviour of mixed organic electrolytes for a non-aqueous Li/MnO₂ battery*

Ding Yunchang**, Xia Guanguang and Chen Jianguo

Department of Chemistry, Henan Normal University, Xinxiang, Henan (China)

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Abstract

This paper reports a study of the electric performance of mixed organic solvents of propylene carbonate–1,2-dimethoxyethane–tetrahydrofuran and dimethyl sulphoxide–1,2-dimethoxyethane. The effects of the dielectric constants of the solvents, lithium perchlorate concentration, the viscosity of the solutions and the mixture ratio of the solvents upon ion electric conductivity are presented and discussed.

Introduction

The lithium battery has aroused great interest in recent years for a variety of power supply applications. The non-aqueous Li/MnO₂ battery was the first system to be studied and has already become commercialized. Much elementary research into the electrolytic solutions used in the non-aqueous Li/MnO₂ battery has been conducted [1–6]. At the present time the mixed organic electrolyte of propylene carbonate (PC) and 1,2-dimethoxyethane (DME), containing LiClO₄, is largely used [4]. Koch and Young used tetrahydrofuran (THF) in a study of the secondary electrode [7]. Matsuda and Satake, among others, have systematically studied the electric performance of mixed organic electrolytes of PC–DME and PC–THF [1], containing perchlorate. The electric performance of the systems PC–DME–THF and DMSO–DME, containing perchlorate, has not previously been reported. The electric performance of the above two kinds of mixed organic electrolytes is reported in this paper.

Experimental

Treatment of solute and solvents

Lithium perchlorate was dried for 2 h at 120 °C, then dried under reduced pressure for more than 5 h at 160 °C.

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**Author to whom correspondence should be addressed.

Propylene carbonate (PC) was left to stand over a 4A molecular sieve and after being separated from the molecular sieve was distilled under reduced pressure (2.5 mmHg, 78 °C) in the presence of Li slices.

1,2-Dimethoxyethane (DME) was left to stand over a 4A molecular sieve for 24 h and after being separated from the molecular sieve was refluxed for 5 or 6 h and distilled under constant pressure in the presence of Li slices.

Tetrahydrofuran (THF) was left to stand over ferrous sulphate and sodium hydroxide for 24 h, so as to remove peroxide, Li slices were then added and the THF was refluxed for 10 h and distilled under constant pressure at 65 °C.

Dimethyl sulphoxide (DMSO) was left to stand over a 4A molecular sieve for 24 h and distilled under reduced pressure in the presence of Li slices (21 mmHg, 94 °C).

Measurements

Specific conductance was directly measured with a DDS-11A type conductivity instrument. The electrode constant was calibrated with 0.01 M KCl. An experiment was conducted to measure absolute viscosity with a glass capillary tube viscosimeter. The viscosimeter constant was calibrated with pure water before the measurement.

Dielectric constants were measured using an instrument for determining capacity, with benzene as standard.

Results and discussion

Conductivity of the LiClO₄-PC-DMF-THF system

Effect of mixture ratio of solvents upon conductivity

According to the literature [1, 4, 6], the mixture ratio (vol.%) of solvents PC and DME can have a large effect upon conductivity in the system of a mixed electrolyte of PC and DME containing lithium perchlorate. Within the temperature range -60 to +60 °C, there appear maximum values of conductivity when the mixture ratio (vol.%) of PC and DME is 3:1, 1:3 and 1:1, respectively. Solvents of the above three ratios of solvents are base compositions, to which different amounts of THF were added. The conductivity of electrolytes containing 1 M LiClO₄ of different ratios of solvents was measured at 30 °C. The relation between the conductivity and the solvent ratio is shown in Fig. 1. Curves 1 and 2 are similar. As the amount of THF in the base solution increases so the conductivity gradually decreases. This is related to the decrease of dielectric constant in the mixed organic electrolyte (Fig. 2). As the concentration of THF increases so the dielectric constant decreases, enhancing coulombic forces between different charge-carrying particles, and making it difficult for the charge-carrying particles to migrate. Curve 3 in Fig. 1 is different from curves 1 and 2. The maximum in conductivity appears to be due to changes in the nature of the base system.

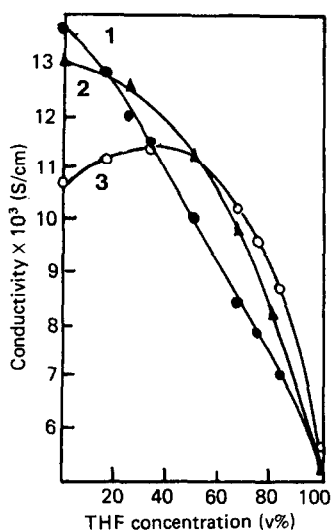


Fig. 1. Effect of the ratio of solvents on conductivity at 30 °C: curve 1 (●), PC:DME = 1:3; curve 2 (▲), PC:DME = 1:1; curve 3 (○), PC:DME = 3:1.

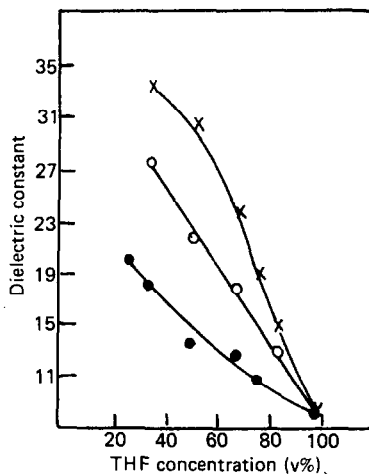


Fig. 2. Correlations between ratio of solvents and the dielectric constant at 25 °C: ○, PC:DME = 3:1; ●, PC:DME = 1:3; ×, PC:DME = 1:1.

On the left side of the peak, the proportion of PC is greatest. The dielectric constant of PC is large and so is its viscosity while the dielectric constant and viscosity of THF are small [8]. THF is added to the base solution of PC:DME = 3:1, so as to decrease the dielectric constant and viscosity of the system. On the left side of the peak, the viscosity tends to decrease. Therefore it is easy for the charge-carrying particles in the solvent to migrate and to increase the conductivity. On the right side of the peak of curve 3, the dielectric constant of the mixed organic electrolyte decreases markedly with the increase in proportion of THF so that it is more difficult for charge-carrying particles to migrate and there is a marked decrease of conductivity.

Effect of solute concentration and temperature upon conductivity

The solvent ratio PC:DME = 1:1 was chosen as base solution, to which THF was added. The THF made up 15% of the total amount. Under the conditions of the fixed composition of the mixed solvents of PC, DME and THF, the conductivity of the solution, containing lithium perchlorate, was measured at different concentrations and temperatures. According to the data obtained from the measurement, two figures were drawn to show the relationship between temperature and conductivity, and the relationship between solute concentration and conductivity (Figs. 3 and 4). These indicate that the conductivity of the solution of different concentrations increases with the increase of temperature. The curves in Fig. 3 show that in the low concentration range the conductivity increases with increase of LiClO_4 concentration and the slope of change of conductivity with the concentration

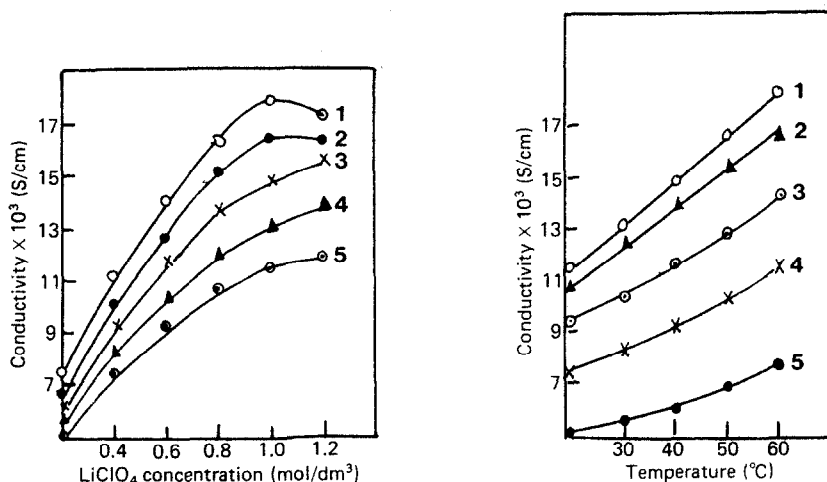


Fig. 3. Effect of LiClO_4 concentration on the conductivity in the mixed solvent PC–DME–THF containing lithium perchlorate at 20–60 °C: ○, 60; ●, 50; ×, 40; ▲, 30; ○, 20 °C.

Fig. 4. Correlation between temperature and conductivity in the three-component solvent containing 0.2–1.0 M LiClO_4 : ○, 1.0; ▲, 0.8; ○, 0.6; ×, 0.4; ●, 0.2 M.

is greatest. With progressive increase of concentration, the slope becomes small and at the highest concentration becomes negative. In the early part (low LiClO_4 concentration) of the curve, the increase of conductivity is due to the increase of number of ions. At higher concentrations the change in slope may be due to an increase of ion density leading to association between ions.

Relation between Λ and $C^{1/2}$

The conductivity data for different concentrations at 30 °C are converted into molar conductivity Λ and the relation between Λ and $C^{1/2}$ is shown in Fig. 5. The data follow two straight lines of different slope. Apparently, the change in slope is related to a change in solution structure which results from the change of the relaxation force and electrophoretic force hindering the movement of ions.

Conductivity of the LiClO_4 –DMSO–DME system

Dielectric constant and viscosity of the LiClO_4 –DMSO–DME system

Figure 6 shows the relation between the dielectric constant and composition of the system at 30 °C. With increasing DMSO content, the dielectric constant rises sharply. Figure 7 shows that viscosity increases with the increase of DMSO content in the system DMSO–DME.

Effect of solvent composition upon conductivity

Figure 8 shows that a peak appears with the increase of DME in the mixed organic electrolyte containing 1 M LiClO_4 in DMSO–DME. When the

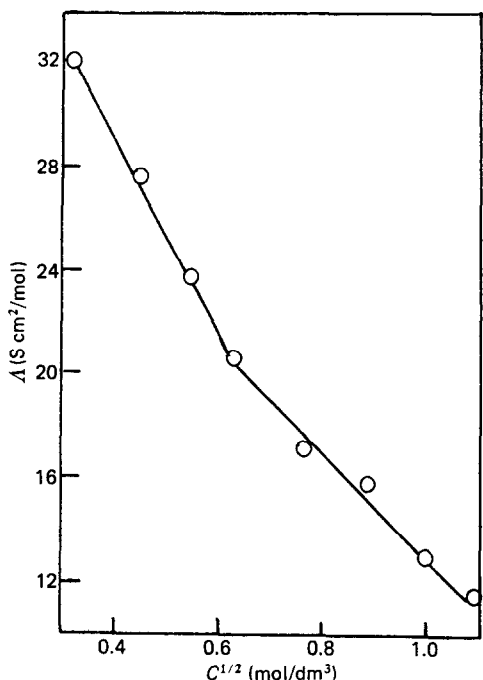


Fig. 5. Molar conductivity of mixed organic electrolytes plotted against the square root of the concentration at 30 °C.

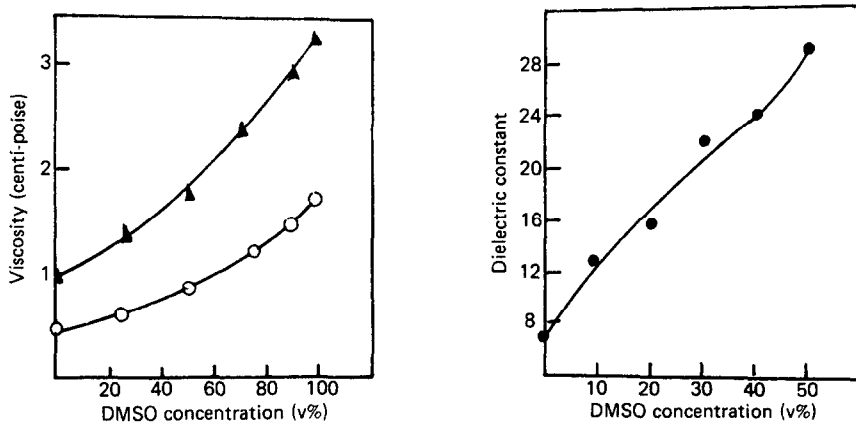


Fig. 6. Plot of dielectric constant vs. composition of DMSO–DME system at 25 °C.

Fig. 7. Correlation between the composition of DMSO–DME system and the viscosity at 30 °C: ▲, solution containing 1 M LiClO₄; ○, solvent only.

DMSO content (vol.%) in DMSO–DME is about 50%, there appears a maximum value of conductance. This behaviour is similar to that of the mixed solvent PC–DMF [1]. Evidently, the changing trend in conductivity can be explained in terms of changes in viscosity and dielectric constant.

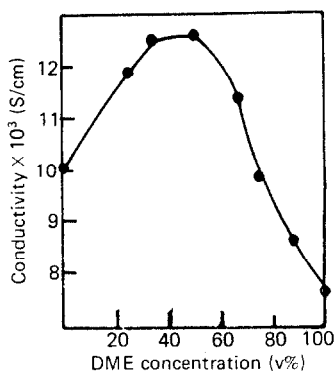


Fig. 8. Correlation between composition of DMSO–DME mixture containing LiClO_4 (1 M) and conductivity at 30 °C.

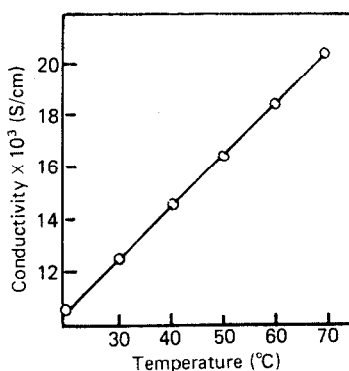


Fig. 9. Temperature dependence of conductivity in mixed solvent of DMSO–DME (1:1).

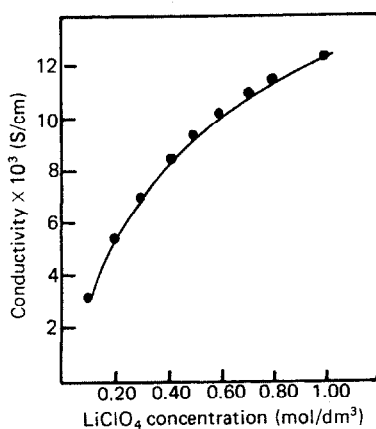


Fig. 10. Correlation between LiClO_4 concentration in mixed solvent DMSO–DME (1:1) and conductivity at 30 °C.

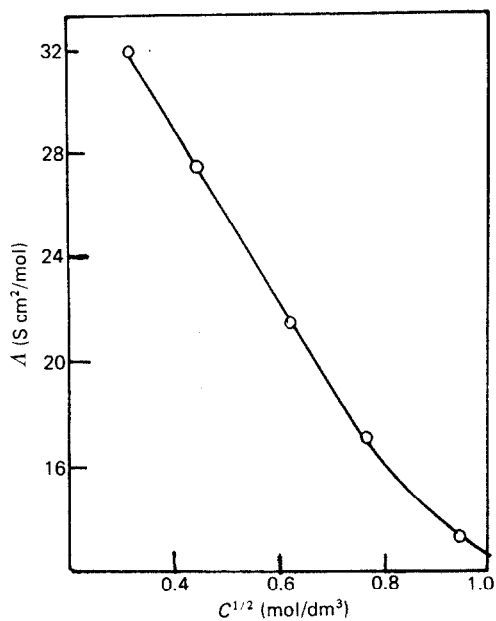


Fig. 11. Correlation between concentration of LiClO_4 and the molar conductivity in DMSO–DME.

Effect of temperature upon conductivity

Figure 9 shows the effect of temperature upon conductivity. The Figure shows that conductivity increases with the increase of temperature.

Effect of solute concentration upon conductivity

Figure 10 shows that the conductivity of the solution increases with increase in LiClO_4 concentration. If the concentration increases beyond some

critical value, the attractive forces between ions will rise, and the conductivity will decrease; if the mixed organic solvent DMSO–DME is chosen as the electrolyte for the non-aqueous Li/MnO₂ battery, 1 M of solute is perhaps an optimum concentration. This is similar to the composition of PC–DME in the manufacture of the Li/MnO₂ battery.

Relation between Λ and $C^{1/2}$

Figure 11 shows that the relation between Λ and $C^{1/2}$ is approximately a linear one in the mixed solvent of DMSO:DME = 1:1.

Conclusions

1. When THF was added to the mixed organic solvent PC–DME, the dielectric constant and the viscosity fell. Generally speaking, the more THF was added, the lower they became. The addition of THF also affects the conductivity of the base solution of PC–DME containing 1 M LiClO₄. The magnitude of the effect depends on the relative proportions of PC and DME in the base solution. For example, if the content of PC in the base solution is high enough the addition of THF can improve the conductive performance of electrolyte.

2. The effect of composition of the mixed solvent DMSO–DME upon the conduction of ions is similar to that of the mixed solvent PC–DME. The experimental results show that the electrolyte, containing 1 M LiClO₄ in mixed solvent (DMSO:DME = 1:1), is perhaps practical for the Li/MnO₂ battery.

Acknowledgement

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