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Physical and electrolytic properties of difluorinated dimethyl carbonate

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Abstract

The physical and electrolytic properties of difluorinated dimethyl carbonate (DFDMC) synthesized using F_2 gas (direct fluorination) were examined. The dielectric constant and viscosity of DFDMC are higher than those of monofluorinated dimethyl carbonate (MFDMC) and dimethyl carbonate (DMC). The oxidative decomposition voltage of DFDMC is higher than those of DMC and MFDMC. The specific conductivity in DFDMC solution is considerably lower than those in MFDMC and DMC solutions. The ethylene carbonate (EC)-DFDMC equimolar binary solution containing 1 mol dm⁻³ LiPF₆ shows a moderate conductivity of 6.91 mS cm⁻¹ at 25 °C. The lithium electrode cycling efficiency (charge–discharge coulombic cycling efficiency of lithium electrode) in EC-DFDMC equimolar binary solution containing 1 mol dm⁻³ LiPF₆ is higher than 80%. The EC-DFDMC solution is a good electrolyte for rechargeable lithium batteries. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

There has been increasing interest in development of new solvents on rechargeable lithium batteries with high energy density, oxidation durability, high liquidus range and nonflammability as power sources of mobile equipments and electric vehicles. One of the appropriate methods to find a solvent with good cell performance is the introduction of fluorine atoms into the solvent molecules. Among the important solvents for practical lithium batteries, fluorination using F₂ gas (direct fluorination) has already been applied to 1,2-dimethoxyethane (DME) [1], propylene carbonate (PC) [2] and ethylene carbonate (EC) [2]. In recent years, we reported the formation of three monofluorinated γ -butyrolactones [3]. It is possible for direct fluorination to synthesize various fluorinated organic solvents because of high reactivity of F₂. In addition, physical and electrolytic properties, and application to lithium batteries of monofluorinated dimethyl carbonate (MFDMC) obtained by direct fluorination of dimethyl carbonate (DMC) were first examined by us [4].

The purpose of the present paper is to elucidate the physical and electrolytic properties, and the charge–discharge characteristics of difluorinated dimethyl carbonate (DFDMC) in Fig. 1 newly synthesized by direct fluorination, compared with those of DMC and MFDMC.

2. Results and discussion

Fig. 2 shows GC-MS analysis of the fluorinated DMC derivatives after fluorination for 24 h [4]. RT means the retention time. It is found that four fluorinated DMC derivatives are formed by direct fluorination of DMC, which are monofluorinated dimethyl carbonate (MFDMC), two difluorinated dimethyl carbonates (DFDMC and gem-DFDMC), and trifluorinated dimethyl carbonate (TFDMC) as shown in Fig. 2. In Fig. 2, the boiling point of DFDMC is very different from that of gem-DFDMC, which has two fluorine atoms similar to DFDMC. This means that physical properties of the fluorinated DMC with same molecular weight such as DFDMC and gem-DFDMC are highly dependent on the positions of fluorine atoms introduced to DMC molecule. Variation in yields with time of the fluorinated DMC derivatives is shown in Fig. 3 [4]. In the present study, pure DFDMC was obtained by distillation of DMC sample after fluorination for more than 20 h.

Fig. 4 shows *i–E* curves in DFDMC, MFDMC and DMC solutions containing 1.0 mol dm⁻³ LiPF₆. In Fig. 4, oxidative decomposition voltage for these three solvents decreases in the order, DFDMC > FDMC > DMC, as expected from

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Fig. 1. Structure of difluorinated dimethyl carbonate (DFDMC).

HOMO energies calculated by B3LYP [4]. In other words, oxidation durability of the fluorinated DMC derivatives becomes higher with increasing the number of fluorine atom in the fluorinated DMC.

Fig. 5 shows dielectric constants of DFDMC, MFDMC and DMC with temperature. The dielectric constant of DFDMC is very high compared with those of MFDMC and DMC at whole temperature range. It seems that the high dielectric constant of DFDMC is dependent on the high polarity of DFDMC due to the introduction of two fluorine atoms with high electron withdrawing into DMC molecule. In addition, the dielectric constant of DFDMC decreases linearly with increasing temperature, in a similar manner to MFDMC. This may mean that the orientation of the dipoles in DFDMC and MFDMC reduces with the rise of temperature. On the other hand, dielectric constant of DMC with low one is almost constant at whole temperature range, as shown in Fig. 5. Variation of viscosities (η) with temperature for DFDMC, MFDMC and DMC is shown in Fig. 6. The viscosities of these three solvents decrease in the order, DFDMC > MFDMC > DMC, similarly to those of the dielectric constants. Fig. 7 shows plot of $\log \eta$ versus 1/T



Fig. 3. Variation in yields with time of the fluorinated DMC derivatives.

for DFDMC, MFDMC and DMC. Activation energies of viscous flow estimated from the straight lines in Fig. 7 are 16.1, 12.9 and 10.3 kJ mol^{-1} for DFDMC, MFDMC and DMC, respectively. The activation energy of DFDMC with the highest viscosity shows a maximum value.

Table 1 shows specific conductivities with various concentrations of LiPF₆ in DFDMC, MFDMC and DMC at 25 °C. In Table 1, it was difficult to measure the conductivities for DFDMC solutions of more than 1.50 mol dm⁻³ because of low solubility of LiPF₆. Specific conductivities in DFDMC solutions (except 0.25 mol dm⁻³) with higher dielectric constant in Fig. 5 are considerably lower than those in MFDMC and DMC solutions. Accordingly, the



Fig. 2. GC-MS analysis of the fluorinated DMC derivatives after fluorination for 24 h.



Fig. 4. $i\!-\!\!E$ curves in 1.0 mol dm $^{-3}$ LiPF_6 solutions using a Pt electrode at a scan rate of 5.0 mV s $^{-1}$ at 25 $^\circ C.$



Fig. 5. Temperature dependence on dielectric constants of DFDMC, MFDMC and DMC measured with 1 MHz.

conductivities seem to be affected much by the viscosities of these three solvents as shown in Fig. 6. The conductivities with various LiPF₆ concentrations in EC-DFDMC, EC-MFDMC and EC-DMC equimolar binary solutions at 25 °C is shown in Fig. 8. Each conductivity in EC-DFDMC, EC-MFDMC and EC-DMC solutions shows the maximum values at 1 mol dm⁻³ LiPF₆. For example, the conductivity in EC-DFDMC solution is 6.91 mS cm⁻¹, which means a moderate conductivity for lithium batteries.



Fig. 6. Temperature dependence on viscosity (η) of DFDMC, MFDMC and DMC.



Fig. 7. Plot of log (η/c_P) vs. 1/T for DFDMC, MFDMC and DMC.

Table 1 Specific conductivities with various LiPF₆ concentrations in DFDMC, MFDMC and DMC at 25 $^\circ \rm C$

| Concentration (mol dm ⁻³) | Specific conductivities (mS cm ⁻¹) | | |
|---------------------------------------|--|-------|------|
| | DFDMC | MFDMC | DMC |
| 0.25 | 0.70 | 0.76 | 0.57 |
| 0.50 | 1.36 | 2.00 | 2.33 |
| 1.00 | 2.39 | 4.21 | 5.99 |
| 1.25 | 2.80 | 4.93 | 7.33 |
| 1.50 | 3.10 | 5.30 | 7.90 |
| 1.75 | _ | 5.24 | 8.15 |
| 2.00 | - | 4.99 | 7.71 |

Fig. 9 shows lithium electrode cycling efficiencies in DFDMC, MFDMC, EC-DFDMC, EC-MFDMC and EC-DMC equimolar binary solutions containing 1 mol dm⁻³ LiPF₆ at 25 °C. It is found that DFDMC and EC-DFDMC solutions show higher efficiencies than those of another solutions. In particular, EC-DFDMC solution shows the highest efficiency of more than 80% in a higher range of cycle number. This is a good electrolyte for rechargeable lithium batteries. In addition, it is very useful for fluorination of DMC to obtain a high lithium electrode cycling efficiency. It seems that the high cycling efficiency is



Fig. 8. Variation of specific conductivities (κ) with various LiPF₆ concentrations in EC-DFDMC, EC-MFDMC and EC-DMC equimolar binary solutions at 25 °C.



Fig. 9. Variation of lithium electrode cycling efficiencies in DFDMC, MFDMC, EC-DFDMC, EC-MFDMC and EC-DMC equimolar binary solutions containing $1.0 \text{ mol dm}^{-3} \text{ LiPF}_6$ at 25 °C.

dependent on the morphology of the films formed on the electrode [4].

3. Conclusions

The dielectric constant and viscosity of DFDMC are higher than those of MFDMC and DMC. The oxidative decomposition voltage of DFDMC is higher than those of DMC and MFDMC. The specific conductivity in DFDMC solution is considerably lower than those in MFDMC and DMC solutions because of high viscosity of DFDMC. The lithium electrode cycling efficiency in EC-DFDMC equimolar binary solution containing 1 mol dm⁻³ LiPF₆ is higher than 80%. The EC-DFDMC solution is a good electrolyte for rechargeable lithium batteries.

4. Experimental

F2 gas was generated by the electrolysis of KF·2HF (Fluorodec ^{TM₃₀}, Toyo Tanso Co., Ltd.) at 80–90 °C. Fluorination of DMC was carried out using 15% F2 gas diluted by N₂ gas. The diluted gas was poured onto the DMC sample surface at 22.4 ml min⁻¹ with stirring in PFA vessel at 25 °C. The fluorinated DMC derivatives were confirmed by gas chromatograph and mass spectrometer (GC-MS) (JMS-SX102A) [5]. The purification of DFDMC was carried out by fractional distillation of the fluorinated DMC sample. The formation and structure of DFDMC were confirmed by GC-MS and ¹H (Fig. 10), ¹³C NMR (Fig. 11) (JEOL, JNM-LA500) [6]. The purity of DFDMC was measured as 99.5% by using GC (SHIMAZU, GC-1700). DMC, EC and LiPF₆ were used as received (battery grade). DFDMC was dehydrated using purified molecular sieves (4A) before preparation of the solution. The preparation of the solution and the assembly of the cell were carried out in an argon-filled dry box. The apparatus and techniques for measurements of specific conductivity [7–9], dielectric constant [10], density [10] and viscosity [10] were reported previously. The lithium electrode cycling efficiency (charge-discharge coulombic cycling efficiency of lithium electrode) was measured with a charge/discharge unit (Hokuto Denko, HJ-201B) and estimated by a galvanostatic plating-stripping method reported by Koch and Brummer [11]. The decomposition voltage in electrolyte using a three-electrode system



Fig. 10. ¹H NMR spectra of DFDMC, MFDMC and DMC.



Fig. 11. ¹³C NMR spectra of DFDMC, MFDMC and DMC.

(Pt working, Li counter and reference electrodes) were measured at a scan rate of 5 mV s^{-1} by means of an ELECTROCHEMICAL INTERFACE (Solartron Analytical, Model SI-1287).

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- [5] DFDMC, CIMS: 127 [M + H]⁺, EIMS: 77 [M–OCH₂F]⁺ (15.74), 33
 [M–OCOOCH₂F]⁺ (100), MFDMC, CIMS: 109 [M + H]⁺, EIMS: 77
 [M–OCH₃]⁺ (4.33), 59 [M–OCH₂F]⁺ (84.25), 33 [M–OCOOCH₃]⁺

(100), gem-DFDMC, CIMS: 127 $[M + H]^+$, EIMS: 95 $[M-OCH_3]^+$ (2.38), 59 $[M-OCHF_2]^+$ (30), 51 $[M-OCOOCH_3]^+$ (100), 31 $[M-COOCHF_2]^+$ (30.95), TFDMC, GCCI: 145 $[M + H]^+$, GCEI: 33 $[M-OCOOCHF_2]^+$ (46.27), 51 $[M-OCOOCH_2F]^+$ (100), 77 $[M-OCHF_2]^+$ (7.05), 95 $[M-OCH_2F]^+$ (3.52).

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