Structural Isomerism Effect on Physical and Electrochemical Properties of Monofluorinated Linear Carbonates

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ABSTRACT

Methyl propyl carbonate (MPC) shows a liquid temperature range that is wider than that of diethyl carbonate (DEC). Monofluorinated organic solvents exert the strong polar effect on the physical and the electrochemical properties. 2-Fluoropropyl methyl carbonate (2FPMC) and ethyl 2-fluoroethyl carbonate (E2FEC) are isomeric with each other. The relative permittivity and viscosity of 2FPMC were higher than those of E2FEC, MPC, and DEC. The ion conductivity of 1 mol dm−3 LiPF6 solution in 2FPMC was lower than those in E2FEC, MPC, and DEC. The use of 2FPMC as a co-solvent greatly improved cycling efficiency of a lithium anode.

Keywords: Monofluorinated Solvent, Polar Effect, Structural Isomerism, Metamerism

1. Introduction

Methyl propyl carbonate (MPC) and diethyl carbonate (DEC) are isomeric with each other: structural isomerism, which is especially called metamerism. MPC and DEC are asymmetric and symmetric linear carbonates, respectively. DEC is commonly used as a low-viscosity solvent for electrochemical energy-storage devices such as lithium-ion batteries. 1 The boiling point of MPC (131°C)2 is slightly higher than that of DEC (126.8°C). 3 The melting point of MPC (−49°C)4 is lower than that of DEC (~43.0°C).5 The lower melting point of MPC may result from the asymmetry. Although the electrolytic characteristics of asymmetric linear carbonates are reported,6 the effect of structural isomerism is not fully discussed.

Partially fluorinated organic solvents exert the strong polar effect on the physical and the electrochemical properties such as permittivity, viscosity, ionic conductivity, and electrochemical stability.4–10 Smart et al. reported several trifluorinated and hexafluorinated linear carbonates such as ethyl 2,2,2-trifluoroethyl carbonate and bis(2,2,2-trifluoroethyl) carbonate.11 They showed that the use of them as co-solvents improved the performance of lithium-ion cells.

In the present paper, we describe the effect of structural isomerism on the physical and electrochemical properties of monofluorinated linear carbonates: 2-fluoropropyl methyl carbonate (2FPMC) and ethyl 2-fluoroethyl carbonate (E2FEC). 2FPMC and E2FEC are also isomeric with each other. Relative permittivity, viscosity, and ionic conductivity are shown as a function of temperature. We have investigated cycling efficiency of a lithium anode by using 1 mol dm−3 LiPF6 solution in ethylene carbonate (EC)-2FPMC and EC-E2FEC equimolar binary mixtures. These characteristics are compared with those of the corresponding MPC-based systems and DEC-based systems. Figure 1 shows the structures of 2FPMC, E2FEC, MPC, and DEC.

2. Experimental

We synthesized 2FPMC and MPC from methyl chlorocarbonate (Kanto Chemical Co., Inc.) and 2-fluoro-1-propanol or 1-propanol in the presence of pyridine catalyst in yields of about 60%. 2-Fluoro-1-propanol was prepared by reaction of propylene carbonate (PC) with potassium hydrogendifluoride (KHF2). After removal of pyridine by a dilute HCl solution, 2FPMC was purified under reduced pressure first by simple distillation and then by fractional distillation. The purity of 2FPMC was determined to be more than 99.9% by the use of gas chromatograph equipped with a FID detector (Shimadzu Corp., GC-1700). The distilled 2FPMC was dehydrated by purified molecular sieves (4A) before use. EC, DEC, and LiPF6 were used as received (Kishida Chemical Co., Ltd., LBG grade for EC and DEC; Stella Chemifa Corp. for LiPF6).

The apparatus and techniques for measurements are essentially the same as those previously reported.5,9

3. Results and Discussion

3.1 Physical properties

Figure 2 shows the temperature (θ or T) dependence of (a) relative permittivity (εr) and (b) viscosity (η) of 2FPMC, E2FEC, MPC, and DEC. The relative permittivity reflects the ease of dielectric polarization. The relative permittivity has a significant effect on the strength of the interactions between ions in electrolytic solutions. The viscosity is regarded as internal friction based on
intermolecular forces and affects ionic conductivity. The relative permittivities of 2FPMC and E2FEC decreased linearly with an increase in temperature. Despite the increase in temperature, the relative permittivities of MPC and DEC were approximately constant. This finding suggests that molecular association, which cancels out dipole moments, takes place in MPC and DEC especially at low temperatures. Monofluorination of MPC and DEC results in the larger net electric dipole moment and, consequently, in the increase in both the relative permittivity and the viscosity. In particular, the relative permittivity and viscosity of 2FPMC were higher than those of E2FEC. The net dipole moment of the 2FPMC molecule may be larger than that of the E2FEC molecule. The attraction of 2FPMC and E2FEC molecules can be based on nonconventional weak intermolecular hydrogen bonding (CF-H–O=C or C-H–F-C)\(^{12}\) as well as conventional dipole-dipole interactions. The weak hydrogen-bonding system does not exchange its proton and therefore it is no more a genuine hydrogen bond; it is an electrostatic attraction of a positive charge on the acidic hydrogen and a negative charge on the organic fluorine or the organic oxygen.\(^{12}\)

Viscosities of 2FPMC, E2FEC, MPC, and DEC decreased exponentially with an increase in temperature, and plots of log\(_10(\eta/\text{mPa s})\) vs. \(T^{-1}\) gave straight lines. The high translational kinetic energy allows intermolecular attraction to be overcome more easily, and the internal friction is reduced at high temperatures. The viscosity of a solvent may be written as

\[
\eta = A_\eta \exp(E_a_\eta/RT)
\]

where the quantity \(E_{a_\eta}\) is the apparent activation energy for viscosity.\(^{13}\) This energy barrier must be overcome before the self-diffusive flow process in the solvent can occur. The \(E_{a_\eta}\) is determined to be 16.72, 16.59, 11.76, and 10.62 kJ mol\(^{-1}\) for E2FEC, 2FPMC, DEC, and MPC, respectively. Although the viscosity of E2FEC was lower than that of 2FPMC, the \(E_{a_\eta}\) of E2FEC was comparable to that of 2FPMC.

3.2 Ionic conductivity

Conductivity of a solution is a key factor determining the internal resistance and rate performance of lithium batteries. Figure 3(a) compares the temperature (\(\theta\)) dependence of ionic conductivities (\(\kappa\)) of 1 mol dm\(^{-3}\) LiPF\(_6\) solution in 2FPMC, E2FEC, MPC, and DEC. The conductivities increased with an increase in temperature. The viscosities of 2FPMC and E2FEC decreased rapidly with an increase in temperature and approached those of MPC and DEC at high temperatures, as shown in Fig. 2(b). The conductivity of the 2FPMC solution was lower than that of the MPC counterpart. However, as the temperature increased, the conductivity of the 2FPMC solution approached that of the MPC counterpart. The relative permittivity and viscosity of 2FPMC were higher than those of MPC, as described in the previous section. The high relative permittivity of 2FPMC would not so much influence the conductivity especially at low temperatures. The conductivity is affected by the ionic mobility, the charge numbers of the ions, the concentration of the electrolyte, the degree of ionic dissociation, etc. The ionic mobility relates to viscosity of the electrolytic solution. The degree of ionic dissociation of lithium salts is set by the balance between the permittivity and Lewis basicity of the medium, depending on the concentrations of the lithium salts.\(^{8}\) The intersection of the plots of conductivity against temperature is not also observed for fluoro- methyl methyl carbonate (FMMC) and DMC solutions,\(^{5}\) and fluoropropylene carbonate (FPC: 4-fluoromethyl-1,3-dioxolan-2-one) and propylene carbonate (PC: 4-methyl-1,3-dioxolan-2-one) solutions.\(^{5}\) On the other hand, there existed a threshold temperature for the E2FEC and the DEC solutions. The threshold temperature was about 25°C, above which monofluorination led to the increase in ionic conductivity. The threshold temperature is considerably lower than that in 2-fluoroethyl methyl carbonate (2FEMC) and EMC systems (about 45°C).\(^{4}\)

Figure 3(b) shows the temperature dependence of the product of ionic conductivity and viscosity (\(\kappa\eta\)). These plots are different from the so-called Walden products. The \(\kappa\eta\) was slightly decreasing at high temperatures. The decrease in the \(\kappa\eta\) and the presence of the threshold temperature indicate that the conductivity does not merely depend on the viscosity especially at elevated temperatures.

3.3 Electrochemical stability and cycling efficiency of lithium anode

Linear potential sweep voltammetry (LSV) was carried out to compare electrochemical stabilities of 2FPMC, E2FEC, MPC, and DEC. Figure 4(a) shows linear potential sweep voltammograms obtained for 1 mol dm\(^{-3}\) LiPF\(_6\) solutions in 2FPMC, E2FEC, MPC, and DEC with a Pt electrode at a scan rate of 5 mV s\(^{-1}\) at 25°C. The anodic stability of 2FPMC was higher than that of MPC, as easily predicted by the highest electronegativity of fluorine. The anodic stability of 2FPMC was nearly the same as that of E2FEC.

Cycling efficiency of a lithium anode indicates coulometric efficiency achieved with the repetitiveness of the deposition and dissolution of lithium on a nickel electrode. Figure 4(b) shows the variation of the cycling efficiency with respect to the cycle number at 25°C. We have used 1 mol dm\(^{-3}\) LiPF\(_6\) solutions in EC-2FPMC,
nonformed on electrode surfaces by cathodic decomposition of alkylcarbonates (ROCOOLi) and lithium alkoxides (ROLi) are mono
binary compounds are readily pass through the surface.

Carbonate-based solutions on lithium anodes can form passive layers containing adequate amounts of fluorine compounds. Although the fluorine compounds have not been identified, lithium ions may readily pass through the surface film. The possible organo fluorinated linear carbonates. The cathodic decomposition of monofluorinated lithium alkylcarbonates and monofluorinated lithium alkoxides. It is well-known that lithium fluorine chemistry.

EC-E2FEC, EC-MPC, and EC-DEC equimolar binary mixtures as the electrolytic solutions. The cycling efficiency was only 13 and 8% at the 20th cycle in the EC-DEC and EC-MPC systems, respectively.


4. Conclusion

We have investigated the effect of metamerism on the physical and electrochemical properties of monofluorinated linear carbonates: 2FPMC and E2FEC. The relative permittivity and viscosity of 2FPMC were higher than those of E2FEC, MPC, and DEC. The ionic conductivity of 1 mol dm\(^{-3}\) LiPF\(_6\)/2FPMC was lower than that of 1 mol dm\(^{-3}\) LiPF\(_6\)/E2FEC. The anodic stability of 2FPMC was almost the same as that of E2FEC. The use of an EC-2FPMC equimolar binary mixture suppressed the cycling efficiency fading.

References


Figure 3. (a) Ionic conductivities (\(\kappa\)) of 1 mol dm\(^{-3}\) LiPF\(_6\) solutions in 2FPMC, E2FEC, MPC, and DEC as a function of temperature (\(\theta\)) from \(-5\) or \(0^\circ\)C to 70°C. (b) The product of ionic conductivity and viscosity (\(\kappa n\)) as a function of temperature from 10 to 70°C.

Figure 4. (Color online) (a) Linear potential sweep voltammograms obtained with a platinum electrode for 1 mol dm\(^{-3}\) LiPF\(_6\) solutions in 2FPMC, E2FEC, MPC, and DEC at a scan rate of 5 mV s\(^{-1}\) at 25°C. Electrolytic solutions: 1 mol dm\(^{-3}\) LiPF\(_6\) solutions in EC-2FPMC, EC-E2FEC, EC-MPC, and EC-DEC equimolar binary mixtures. The plating and the stripping current densities were measured at fixed 20th cycle in the EC-DEC and EC-MPC systems, respectively. The monofluorination of MPC and DEC greatly improved the cycling efficiency. In particular, the cycling efficiency in the EC-2FPMC system was higher than that in the EC-E2FEC system. The cathodic decomposition of monofluorinated linear carbonate-based solutions on lithium anodes can form passive films containing adequate amounts of fluorine compounds. Although the fluorine compounds have not been identified, lithium ions may readily pass through the surface film. The possible organo-fluorinated compounds are monofluorinated lithium alkylcarbonates and monofluorinated lithium alkoxides. It is well-known that lithium alkylcarbonates (ROCOOLi) and lithium alkoxides (ROLi) are formed on electrode surfaces by cathodic decomposition of nonfluorinated linear carbonates.