Electrolytic Properties of Ethyl Fluoroethyl Carbonate and Its Application to Lithium Battery

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Monofluorination of solvents exerts the strong polar effect on various properties. We have investigated the electrolytic properties of ethyl fluoroethyl carbonate (EFEC) and its application to a lithium battery. Conductivities of EFEC solutions are higher than those of diethyl carbonate (DEC) counterparts above 25 °C or below 1 mol dm^{-3} of $LiPF_6$. The anodic stability of EFEC is also higher than that of DEC. The use of EFEC as a cosolvent improves the performance of a $Li/LiCoO_2$ coin cell.

Monofluorination of solvents exerts the strong polar effect on the physical and electrochemical properties such as permittivity, viscosity, and conductivity. Diethyl carbonate (DEC) is classified as a chain carbonate. DEC is commonly used as a low-viscosity solvent for electrochemical energy-storage devices such as lithium-ion batteries.[1] The boiling point of DEC (126.8 °C) is higher than those of dimethyl carbonate (DMC: 90.3 °C) and ethyl methyl carbonate (EMC: 108 °C), and DEC is suitable for practical applications. Smart et al. have reported several trifluorinated and hexafluorinated chain carbonates such as ethyl 2,2,2-trifluoroethyl carbonate and showed that the use of them as cosolvents improves the performance of lithium-ion cells.[2] However, very little is known about the electrolytic properties of monofluorinated DECs and their application to lithium batteries. We have investigated the physical and electrochemical properties of partially fluorinated DMCs[3] and EMC.[4]

In the present paper, we report the electrolytic properties of ethyl fluoroethyl carbonate (EFEC) as a novel solvent and its application to a lithium battery. Conductivities are shown as functions of the temperature and the molar concentration of $LiPF_6$. The cycling efficiency of a $Li/LiCoO_2$ coin cell is investigated by using an ethylene carbonate (EC)–EFEC binary solution. The characteristics are compared with those of DEC single or EC–DEC binary solutions.

We synthesized EFEC from 2-fluoroethanol and chloroethyl carbonate in the presence of pyridine. 2-Fluoroethanol was prepared by reaction of EC with potassium hydrogendifluoride (KHF_2) in 1-methyl-2-pyrrolidinone (NMP). After removal of pyridine by a dilute HCl solution, EFEC was purified under reduced pressure first by simple distillation and then by fractional distillation. The purity of EFEC was determined to be 99.98% by means of gas chromatography (Shimadzu Corp., GC-1700). EFEC was identified by use of GC-MS analysis (Shimadzu Corp., GCMS-QP2010) and ^{1}H and ^{13}C NMR spectroscopy (JEOL Ltd., JNM-LA500).[5] The distilled EFEC was dehydrated by purified molecular sieves (4A) before use. DEC, EC, and $LiPF_6$ were used as received (DEC and EC: Kishida Chemical Co., Ltd., LBG grade; $LiPF_6$: Stella Chemifa Corp.). The apparatus and techniques for measurements are essentially the same as those previously reported.[3,4,6] Linear potential sweep voltammetry (LSV) was performed with a Pt electrode, 1.6 mm in diameter, at a scan rate of 5 mV s^{-1} at 25 °C. Lithium foil and a platinum wire were used as the reference and the auxiliary electrode, respectively. 2025-Type coin cells (can size: 20 mm in diameter and 2.5 mm in thickness, stainless steel body) was assembled with a $LiCoO_2$ sheet cathode (16 mm in diameter), a lithium-metal sheet anode (16 mm in diameter), a separator (Celgard Inc., # 3501), and a test solution. We prepared the $LiCoO_2$ cathode by mixing $LiCoO_2$ (Nippon Chemical Industrial Co., Ltd., Cellseed C5) with acetylene black and poly(tetrafluoroethylene). The coin cells were charged in a constant current (0.5 C)–constant voltage (4.2 V) regime at 25 °C until total charge time reached 5 h. Afterward, they were discharged to 3.0 V at the constant current (0.5 C). The preparation of electrolytic solutions and the fabrication of three-electrode and coin cells were carried out in an argon-filled glove box system made by VAC.

Conductivity of a solution is of practical importance, because it determines the internal resistance and rate performance of a battery. Viscosity is regarded as an internal friction based on intermolecular forces and affects the conductivity. Figure 1a compares the temperature (θ) dependence of conductivities (κ) of EFEC and DEC single solutions containing 1 mol dm^{-3} $LiPF_6$. Dynamic viscosities (η) of EFEC and DEC single solvents are also depicted in Figure 1a. κ of both EFEC and DEC solutions increased with an increase in θ. κ of the EFEC solution was higher than that of the DEC counterpart above 25 °C. This is because η of EFEC decreases rapidly at high θ. The threshold temperature (25 °C), above which monofluorination evoked the increase in κ, was considerably lower than in the case of 2-fluoroethyl methyl carbonate (FEMC) (ca. 45 °C). The intersection of the plots of κ against θ was not observed for fluoromethyl methyl carbonate (FMMC) and DMC. High translational kinetic energy allows intermolecular attractions to be overcome more easily, and the internal friction is reduced at high θ.

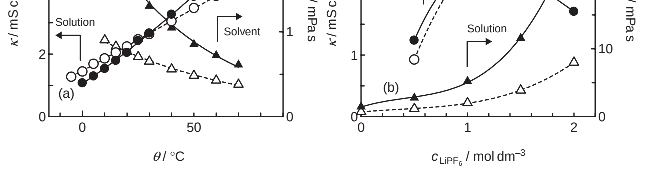

Figure 1. Conductivities (κ) of EFEC and DEC single solutions as functions of (a) temperature (θ) and (b) the molar concentration of $LiPF_6$ (c_{LiPF_6}). (a) c_{LiPF_6} was set at 1 mol dm^{-3}, and (b) θ was set at 25 °C. This figure also depicts dynamic viscosities (η) of (a) EFEC and DEC single solvents and (b) their single-solvent electrolytes.

Figure 1b compares the variations of κ and η of EFEC and DEC single solutions with respect to the molar concentration of $LiPF_6$ (c_{LiPF_6}) at 25 °C. κ increases to some extent with increasing the concentration, because the number of charge carrier per unit volume increases. The η and mass density of the electrolytic solution increase rapidly with increasing the concentration. Therefore, κ adversely decreases in high-concentration ranges. κ of the EFEC solution was about the same as that of the DEC counterpart even at ca. $1\,mol\,dm^{-3}$ of $LiPF_6$. The finding indicates that high permittivity rather than high viscosity is a dominant factor governing κ of the EFEC solution below $1\,mol\,dm^{-3}$ of $LiPF_6$ and that the high viscosity plays a major role in determining κ at higher concentrations. The threshold concentration ($1\,mol\,dm^{-3}$), below which monofluorination also caused the increase in κ, was higher than those observed for FMMC/DMC (ca. $0.3\,mol\,dm^{-3}$) and FEMC/EMC (ca. $0.7\,mol\,dm^{-3}$). Thus, κ of the EFEC solutions is higher than that of the DEC counterparts over wide temperature and concentration ranges.

The introduction of a fluorine atom into a DEC molecule increases the electric dipole moment but may decrease the electron-pair donicity of oxygen atoms in the –OCOO– moiety. The low electron-pair donicity results in the decreased solvation to Li^+ and, consequently, in the decreased degree of ionic dissociation. Accordingly, both the κ of the EFEC solutions at high concentrations and the solubility of the electrolyte become lower than in the cases of DEC. It is known that lithium salts form ion-pair dimers and quadrupoles in DEC and DMC.[1a] Such noncharged species may also be formed in EFEC.

LSV was carried out to investigate electrochemical voltage windows of chain carbonate solutions. Figure 2a shows linear potential sweep voltammograms obtained with a Pt electrode for EFEC and DEC single solutions at a scan rate of $5\,mV\,s^{-1}$ at 25 °C. These solutions contain $1\,mol\,dm^{-3}$ $LiPF_6$. The anodic stability of EFEC was higher than that of DEC, while the reductive-decomposition potentials were uncertain. A shoulder peak observed at ca. 5.8 V can be ascribed to trace amounts of degradation products of $LiPF_6$.

An alkaline metal ion (Lewis acid) such as Li^+ has an influence on the reduction of organic compounds in aprotic solvents.[7] The metal ion forms ion-pairs with reduced organic compounds, and the formation shifts peaks to positive potentials to greater or lesser extents. This influence is known to be pronounced in protophobic solvents such as propylene carbonate and acetonitrile. The reduction of chain carbonates can also involve the formation of the ion-pairs and their decomposition on a lithium anode.

We assembled 2025-type coin cells to evaluate the performance by a charge–discharge test. Figure 2b shows the evolution of cycling efficiency with respect to the cycle number at 25 °C. The cycling efficiency stands for the capacity ratio of discharge to charge. The cycling efficiencies observed were 98% and 95–96% for EC–EFEC and EC–DEC equimolar binary solutions, respectively, after the 2nd cycle. The cycling efficiency at the first charge/discharge cycle was somewhat lower than that above the 2nd cycle, and the irreversible capacity was observed at the first cycle. This is because the electric charge is consumed for forming the solid electrolyte interphase (SEI). The irreversible capacity in the EC–EFEC system was lower than that in the EC–DEC system.

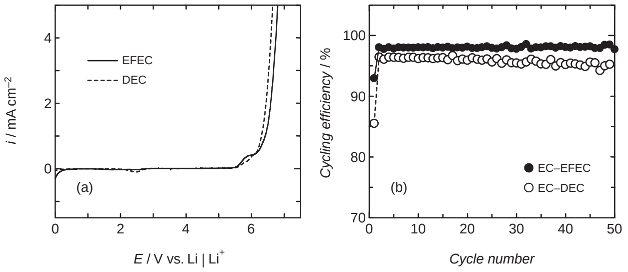

Figure 2. (a) Linear potential sweep voltammograms obtained with a Pt electrode for EFEC and DEC single solutions at a scan rate of $5\,mV\,s^{-1}$ at 25 °C. These electrolytic solutions contain $1\,mol\,dm^{-3}$ $LiPF_6$. (b) Evolution of cycling efficiency of Li/$LiCoO_2$ coin cells at 25 °C with respect to the cycle number. Electrolytic solutions: EC–EFEC and EC–DEC equimolar binary solutions containing $1\,mol\,dm^{-3}$ $LiPF_6$. The coin cells were charged in a constant current (0.5 C) mode and further charged to keep constant voltage (4.2 V). Total charging time was set to 5 h. The coin cells were then discharged to 3.0 V at the constant current (0.5 C).

The use of the EC–EFEC binary solution improved the cycling efficiency over the range of high cycle numbers. Degradation products of the EC–EFEC binary solution by reduction on a lithium anode can form a passive film containing fluorine compounds. Although the components have not been identified, they would show low electron-pair donicity. Therefore, Li^+ ion may readily be permeable into the surface film. The use of EFEC can decrease the interfacial resistance between the electrode and the electrolytic solution.

In conclusion, EFEC is a candidate for prominent cosolvents for lithium batteries.

References and Notes

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5 GC-MS (EI) (m/z): 45 $CH_3CH_2O^+$ (60), 47 $CH_2FCH_2^+$ (69), 63 $CH_2FCH_2O^+$ (23), 91 $CH_2FCH_2OCO^+$ (11). ^1H NMR ($CDCl_3$, 500.00 MHz): δ 1.60 (t, 3H), 4.51 (q, 2H), 4.66 (m, 2H), 4.93 (m, 2H). ^{13}C NMR ($CDCl_3$, 125.65 MHz): δ 13.69 (s), 64.10 (s), 66.72 (s), 81.63 (d, $^1J_{CF} = 167\,Hz$), 155.23 (s).

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