Use of Fluoroethylene Carbonate as Solvent for Electric Double-Layer Capacitors

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The use of partially fluorinated compounds as alternative solvents can improve the performance of electric double layer capacitors (EDLCs). Electrolytic conductivity of fluoroethylene carbonate (FEC) is slightly lower than that of propylene carbonate (PC), which is commonly used as a solvent for EDLCs. However, the capacitance of a coin cell is higher than that obtained for PC.

Key Words: Electric Double-Layer Capacitor, Partially Fluorinated Solvent, Capacitance, Substituent Effect

1 Introduction

In the past decade, there has been a growing interest in the utilization of electric double-layer capacitors (EDLCs) for electric and hybrid electric vehicles as well as back up power sources in many electronic systems. The EDLC is an energy storage device that accumulates electric charges in an interphase between an activated carbon electrode and an electrolyte.1

Propylene carbonate (PC, 4-methyl-1,3-dioxolane-2-one) is commonly used as a solvent for electric double layer capacitors (EDLCs), while mixtures of ethylene carbonate and chain carbonate are typical solvents for lithium-ion secondary batteries. Fluoroethylene carbonate (FEC, 4-fluoro-1,3-dioxolane-2-one) is expected as an excellent additive or solvent for the lithium-ion secondary batteries.2,3 FEC suppress the decomposition of the electrolytic solution and increases the efficiency of the charge and discharge of lithium-ion cells. Partial fluorination of organic solvents often increases their polarity, and the use of the fluorinated solvents improves the performance of lithium secondary batteries.4-11

The introduction of a substituent group into the 1,3- dioxolane-2-one (EC, ethylene carbonate) moiety lowers the symmetry and changes the polarity. The freezing point of EC is as high as 36.37°C,12 whereas those of PC and FEC are −54.53°C12 and 17.3°C,4 respectively. It is therefore of interest to investigate the substituent effect of the EC moiety on the bulk properties of the electrolytic solution and the characteristics of EDLCs.

In this paper, we describe the substituent effect of the EC moiety on the electrolytic properties and the charge and discharge characteristics of coin cells. The use of FEC as an alternative solvent can improve the performance of EDLC.

2 Experimental

2.1 Materials

The synthesis of FEC by direct fluorination is described in the literature.6 FEC was dehydrated with purified molecular sieves 4A before use. PC as a reference standard for a solvent and tetraethylammonium tetrafluoroborate (TEABF4) as an electrolyte were used as received (Kishida, battery grade). The preparation of FEC and PC solutions and the fabrication of EDLCs were carried out in an argon-filled glove box system made by VAC.

2.2 Apparatus and measurements

The apparatus and techniques for measurements are essentially the same as those previously reported.13-15 Electric conductivities of electrolytic solutions were measured by use of a conductometer (Toa Electronics, Model CM-60S) equipped with a cell (Model CGT-511B) over the temperature range of 10 or 15 to 70°C.

The activated carbon electrode contained 82 mass% activated charcoal (average surface area 866 m^2 g^-1, average pore size: 2.975 nm), 9 mass% acetylene black as the conductor, and 9 mass% poly(tetrafluoroethylene) as the binder. The performance of 2025-type coin cells (can size: 20 mm in diameter and 2.5 mm in thickness, stainless steel body) was investigated with a charge/discharge unit (ASKA, Model ACD-M01-05N). A separator (Celgard Inc., #3501) was sandwiched between two identical-size activated carbon electrodes in the coin cells. The coin cells were charged in a CC–CV (constant current (−1 mA cm^-2 (−1.33 mA) or −5 mA cm^-2 (−6.65 mA))–constant voltage (2.0 V)) regime for 60 min. Afterward, they were discharged at 1 or 5 mA cm^-2.

3 Results and Discussion

3.1 Electrolytic conductivity

Electrolytic conductivity is of practical importance,
because it determines the internal resistance, capacitance, and rate performance of the EDLC. Figure 1 compares electric conductivities (κ) of FEC and PC single solutions containing TEABF$_4$ as a function of Celsius temperature (θ). The solubility limit of TEABF$_4$ in PC is near 1 mol dm$^{-3}$, where the maximal electrolytic conductivity is observed.$^{10}$ Therefore, the molar concentration of TEABF$_4$ in FEC was also adjusted to 1 mol dm$^{-3}$. The electrolytic conductivities of both FEC and PC increased with an increase in the temperature. It should be noted that the electrolytic conductivity of FEC was slightly lower than that of PC and that the difference decreased with increasing the temperature.

Permittivity and viscosity of the medium are dominant factors governing the electrolytic conductivity, though the contribution may depend on the concentration and type of the electrolyte used. As a general rule, the electrolytic conductivity can be affected by the ionic mobility, the charge numbers of ions, the concentration of the electrolyte, and the degree of ionic dissociation of the salt. The ionic mobility relates to viscosity of the electrolytic solution, while the degree of ionic dissociation of the electrolyte depends on the permittivity of the medium. Partial fluorination of organic solvents often increases their polarity. We have reported that monofluorination of γ-butyl lactone$^{51}$ and such chain carbonates as dimethyl carbonate (DMC)$^{6,11}$ and ethyl methyl carbonate (EMC)$^6$ increases relative permittivity, dynamic and kinematic viscosities, and mass density. The dynamic viscosity of FEC (4.1 mPa s at 40 °C)$^6$ is higher than that of EC (1.930 mPa s at 40 °C)$^{12}$ and PC (2.530 mPa s at 25 °C).$^{12}$ Strange to say, the relative permittivity of FEC (78.4 at 40 °C)$^6$ is lower than that of EC (89.78 at 40 °C).$^{12}$ The relative permittivity of PC is 64.92 at 25 °C.$^{12}$

Viscosity rather than permittivity can be a key factor determining the decrease in the electrolytic conductivity of a fluorinated solvent at high concentrations of electrolyte ions.$^{17}$ On the other hand, the electrolytic conductivity of the fluorinated solvent becomes higher than that of the corresponding nonfluorinated solvent at low concentrations of electrolyte ions.$^{17}$ The threshold concentration depends on the types of the solvents and electrolyte used. The permittivity can contribute to the increase of the conductivity at very low concentrations of the electrolyte, because the degree of ionic dissociation of the electrolyte may be high. However, the concentrations lower than 0.5 mol dm$^{-3}$ are not suitable for the use for electrochemical energy storage devices.

The viscosities of a solvent and its electrolytic solution often decrease rapidly with increasing the temperature, because the higher translational kinetic energy allows intermolecular attractions to be overcome more easily. The decrease in the viscosities of FEC and its electrolytic solution can result in the increase of the electrolytic conductivity at high temperatures.

3.2 Charge and discharge characteristics of 2025-type coin cells

We have investigated the performance of EDLCs using FEC as an alternative solvent by charge-discharge tests of 2025-type coin cells and compared the results with those obtained for PC.

3.2.1 Change of cut-off voltage The electrochemical stability of an electrolytic solution can be measured by the change of cut-off voltage of the coin cell. The cut-off voltage during a constant-current (CC) charge or the cell voltage during a constant-voltage (CV) charge was changed from 2.0 to 3.0 V at intervals of 0.1 V. Figure 2 compares charge and discharge curves of the coin cells using (a) FEC and (b) PC solutions containing 1 mol dm$^{-3}$ TEABF$_4$ at 25 °C. The coin cells were charged from 0 V to a cut-off voltage in a constant-current (−1 mA cm$^{-2}$, −1.33 mA) mode and further charged to keep the constant voltage (CV). Total charging time was set to 60 min. The coin cells were then discharged to 0 V at 1 mA cm$^{-2}$. Discharge curves observed for the FEC and the PC solution were roughly convex downward and upward, respectively. As the cut-off voltage increased, the convex region increased for the FEC solution. A time constant for a porous electrode influences the ease of progress of relaxation during the charge and the discharge. On the basis of a transmission-line network of finite thickness, the time constant can be expressed as the product of the resistance and capacitance in a pore.$^{13}$ The resistance as well as the capacitance in the pore may be higher for the FEC solution. The high resistance can result from the increased viscosity. The increase in the time constant leads to a noticeable rise and a drop in the cell voltage upon the charge and the discharge, respectively. Consequently, the plot of the cell voltage against time can show upward or downward curvature.

$IR$ potential drops for the FEC solution were higher at various cut-off voltages. The $IR$ potential drop is observed at the beginnings of the CC discharge and the discharge rest. When the cut-off voltage was set at 2.6 V, the plot displayed great upward curvature for the FEC solution at the end of the CC charge. The fluorination of

![Electric conductivities (κ) of FEC and PC single solutions containing 1 mol dm$^{-3}$ TEABF$_4$ as a function of Celsius temperature (θ) from 10 or 15 to 70 °C.](image-url)
the EC moiety can increase the stability to the anodic decomposition and inversely decrease the stability to the cathodic decomposition, as compared to the introduction of the methyl group into the EC moiety. The charge of the coin cell at cut-off voltages higher than 2.6 V should involve the cathodic decomposition of FEC.

3. 2. 2 Rate capabilities Figure 3 compares rate capabilities of 2025-type coin cells using FEC and PC solutions containing 1 mol dm$^{-3}$ TEABF$_4$ at charge and discharge rates of (a) ±1 and (b) ±5 mA cm$^{-2}$ at 25°C. The cut-off voltage was set to 2.0 V. The technique of a CC (−i)−CV (2.5 V) charge followed by a CC (i) discharge is the same as in Fig. 2. The reciprocals of the slopes of the charge and discharge curves represent the integral full-cell capacitances ($C_{\text{full}, \text{i}}$). The slopes of the curves of the coin cell using PC became increasingly steep at ±5 mA cm$^{-2}$, and the capacitances decreased. The use of FEC slightly suppressed the fading of the integral full-cell capacitances. Table 1 summarizes the capacitances. The integral full-cell capacitances were calculated according to $C_{\text{full}, \text{i}} = Q / (E \cdot 2m)$, where $Q$ is the quantity of electricity obtained by the integration of the current transient during the CC discharge. $E$ is the width of the cell-voltage range (2.0 V), and 2$m$ is the dry mass of carbon contained in both electrodes. A very small distance between activated carbon electrodes in the coin cell may compensate for lower ionic mobility of TEABF$_4$ in the bulk of the FEC solution. The introduction of a fluorine atom into the EC moiety can decrease the donicity of lone pairs of electrons on the oxygen atoms as compared to PC. FEC may more weakly solvate TEA$^+$ than PC, so that the TEA$^+$ in the FEC solution easily migrates to pores of the activated carbon electrode for its naked-ion size.

4 Conclusion

We have investigated the substituent effect of the EC moiety on the bulk properties of the electrolytic solutions and the performance of EDLCs. The electric conductivity of a FEC solution containing 1 mol dm$^{-3}$ TEABF$_4$ was slightly lower than that of a PC solution. However, the use of FEC as a solvent improved the capacitance and rate performance of coin cells. It is very intriguing to investigate the charge and discharge characteristics of the cells at higher concentrations or by using other quaternary ammonium salts.

References


Table 1 Comparison of integral full-cell capacitances ($C_{\text{full}, \text{i}}$) of activated carbon electrodes obtained for 2025-type coin cells at 25°C (Fig. 3). Electrolytic solutions: FEC and PC solutions containing 1 mol dm$^{-3}$ TEABF$_4$. The coin cells were charged in a CC (−i)−CV (2.0 V) mode and then discharged in a CC (i) regime.

<table>
<thead>
<tr>
<th>$i / \text{mA cm}^{-2}$</th>
<th>$C_{\text{full}, \text{i}}$ / F g$^{-1}$</th>
<th>FEC</th>
<th>PC</th>
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<tr>
<td>1</td>
<td>17.5</td>
<td>14.1</td>
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<td>5</td>
<td>15.2</td>
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Fig. 2 Charge and discharge characteristics of 2025-type coin cells at various cut-off voltages of 2.0 to 30 V at 25°C. Electrolytic solutions: (a) FEC and (b) PC single solutions containing 1 mol dm$^{-3}$ TEABF$_4$. The coin cells were charged from 0 to a cut-off voltage in a constant-current (CC) (−1.33 mA, −1 mA cm$^{-2}$) mode and further charged to keep the constant voltage (CV). Total charging time was set to 60 min. The coin cells were then discharged to 0 V at 1 mA cm$^{-2}$. The cut-off voltage was varied stepwise to the positive direction at every 0.1 V interval.

Fig. 3 Rate capabilities of 2025-type coin cells at charge and discharge rates of (a) ±1 and (b) ±5 mA cm$^{-2}$ at 25°C. Electrolytic solutions: FEC and PC single solutions containing 1 mol dm$^{-3}$ TEABF$_4$. The technique of a CC (−i)−CV (2.0 V) charge followed by a CC (i) discharge is essentially the same as in Fig. 2.