Tetramethylammonium Difluoro(oxalato)borate as Novel Electrolyte for Electric Double-Layer Capacitors

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The use of an asymmetric borate anion, difluoro(oxalato)borate (DFOB⁻), improves the solubility of the tetramethylammonium salt in propylene carbonate (PC) and the capacitances of electric double-layer capacitors (EDLCs). Electric conductivity of the PC solution containing tetramethylammonium difluoro(oxalato)borate (TMADFOB) was slightly lower than that obtained for tetraethylammonium tetrafluoroborate (TEABF₄), but higher than those obtained for tetramethylammonium bis(oxalato)borate (TMABOB) and tetraethylammonium bis(oxalato)borate (TEABOB). The gravimetric capacitances of measurement cells increased with decreasing the ion sizes of the electrolytes. The PC solution containing TMADFOB afforded the highest gravimetric capacitance.

Key Words : Electric Double-Layer Capacitor, Electrolyte, Tetramethylammonium Cation, Asymmetric Anion

1 Introduction

Increasing attention has recently paid to the utilization of electric double-layer capacitors (EDLCs) for hybrid electric vehicles. Tetraethylammonium tetrafluoroborate (TEABF₄) is commonly used as an electrolyte for the EDLC. The use of the smallest quaternary ammonium ion, tetramethylammonium ion (TMA⁺), can increase the number of ions accumulated in pores of an activated carbon electrode and bring about high capacitance. Regretably, the solubility of tetramethylammonium tetrafluoroborate (TMABF₄) in propylene carbonate (PC) is as low as 0.1 mol dm⁻³ at 25 °C.¹⁾ The combination of TMA⁺ and a larger anion, bis(oxalato)borate (BOB⁻), improves the solubility in the PC (0.9 mol dm⁻³).^{2,3)} The use of a small asymmetric ion as a counter anion should further decrease the crystal lattice energy of the electrolyte and hence can increase the degree of ionic dissociation. Electric conductivity of the electrolyte solution is expected to become higher than that of the solution containing the corresponding symmetric chelatoborate, tetramethylammonium bis(oxalato)borate (TMABOB).

Tetramethylammonium difluoro(oxalato)borate (TMADFOB)

Tetramethylammonium bis(oxalato)borate (TMABOB)

Tetraethylammonium bis(oxalato)borate (TEABOB)

In this paper we report the use of tetramethylammonium difluoro(oxalato)borate (TMADFOB) as a novel electrolyte for EDLCs. TMADFOB has the potential of improving both the solubility in PC and the capacitance of EDLCs.

2 Experimental

The synthesis of TMABOB and TEABOB was previously reported.²⁻⁴⁾ TMADFOB was synthesized on the basis of the literature describing the production of lithium difluoro(oxalato)borate.⁵⁾ Tetramethylammonium tetrafluoroborate (TMABF₄) was allowed to react with oxalic acid ((COOH)₂) in the presence of silicon chloride (SiCl₄). A mixture of oxalic acid (26.5 g, 0.29 mol), TMABF₄ (67.69 g, 0.42 mol), and acetonitrile (AN, 500 ml) was stirred in a 1 dm³ reactor. SiCl₄ (25 g, 0.15 mol) was added dropwise to the AN solution. An Ar gas was passed through the reactor cooled in an ice bath. After stirred overnight, the AN solution was allowed to evaporate under reduced pressure. The crude product was purified by fractional recrystallization from a mixture of AN and ethyl acetate, and the purified TMADFOB was dried in vacuo at 70 °C for 48 h. TMADFOB was obtained in a yield of 45%. The results of the elemental analysis were in good agreement with the calculated values: calcd. for TMADFOB: C, 34.16; H, 5.73; N, 6.64, found for TMADFOB: C, 34.28; H, 6.21; N, 6.99. The TMADFOB was also identified by means of ¹H, ¹³C, ¹⁹F, and ¹¹B NMR spectroscopy (JEOL, JNM-LA500). The results are as follows: ¹H NMR (TMS/DMSO, 500.00 MHz): δ 3.16 (s, 3H). ¹³C NMR (TMS/DMSO, 125.65 MHz): δ 54.36, 159.23. ¹⁹F NMR (CF₃COOD/D₂O, 470.40 MHz): δ -148.86. ¹¹B NMR (NaBH₄/D₂O, 160.35 MHz): δ -15.67.

PC as a solvent and TEABF₄ as a reference standard for an electrolyte were used as received (Kishida, bat-

tery grade). The preparation of electrolytic solutions and the fabrication of three-electrode electrolysis and measurement cells were carried out in an argon-filled glove box system made by VAC. Activated carbon electrodes contained 82 mass% activated charcoal (average surface area $866 \text{ m}^2 \text{ g}^{-1}$, average pore size: 2.975 nm), 9 mass% acetylene black as the conductor, and 9 mass% poly(tetrafluoroethylene) as the binder.

The apparatus and techniques for measurements are essentially the same as those previously reported.^{2,4)}

3 Results and Discussion

3.1 Electrolytic properties

Conductivity and viscosity of an electrolytic solution are of practical importance, because they determine the internal resistance, capacitance, and rate performance of the EDLC. Figure 1 shows (a) electric conductivities (κ) and (b) dynamic viscosities (η) of solutions containing quaternary ammonium salt (QA) as a function of the molar concentration (c_{QA}) at 25 °C. The solubility of TMADFOB in PC was 2 mol dm^{-3} or more. The solubility of TMABF₄ and TEABF₄ is about 0.1 and 1 mol dm^{-3} , respectively,¹⁾ and these values are much lower than the solubility of TEABOB.^{2,4)} The solubility of TMABOB is 0.9 mol dm^{-3} .^{3,4)} The use of an asymmetric anion, DFOB⁻, exerted its effect. The crystal lattice energy of based on the asymmetric anion may be lower, and the solubility of the salt can greatly increase.

The electric conductivities increased to some extent with increasing the concentration of quaternary ammonium salt, because the number of charge carrier per unit volume increased. It should be noted that the molar concentration of the maximal conductivity of TMADFOB was as high as 1.6 mol dm^{-3} . The molar concentrations of the maximal conductivity were about 0.9, 1, and 1 mol dm^{-3} for TMABOB, TEABOB, and TEABF₄, respectively. The electric conductivities of TMADFOB-based solutions were slightly lower than TEABF₄-based counterparts throughout concentration measured. The electrolytic conductivities decreased in approximately the following descending order: TEABF₄ > TMADFOB >> TEABOB > TMABOB, which was the inverse order of the dynamic viscosity.

As a general rule, the electric conductivity can be

Fig. 1 (a) Electric conductivities (κ) and (b) dynamic viscosities (η) of PC single solutions containing TMADFOB, TMABOB, TEABOB, or TEABF₄ as a function of the molar concentration (c_{QA}) at 25 °C.

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. The dynamic viscosities of the electrolytic solutions increased with increasing the concentration of the quaternary ammonium salt, because the internal friction can increase. Therefore, the electric conductivity can adversely decrease in high concentration ranges.

3.2 Cyclic voltammetry

Integral single-electrode capacitance per unit mass of activated carbon ($C_{\text{g}}^{\text{int}}$) can be calculated from cyclic voltammograms. Figure 2 shows cyclic voltammograms obtained for quaternary ammonium salt with activated carbon electrodes at a scan rate of 5 mV s^{-1} . The molar concentrations of TMABOB, TMADFOB, TEABOB, and TEABF₄ were adjusted to 0.9, 1, 1, and 1 mol dm^{-3} , respectively. The maximal conductivity was observed around these concentrations except for TMADFOB, as described above. The electrode potential was changed from the rest potential in the positive direction, and the potential sweep was repeated three times between +0.55 V and -1.95 V, where no significant decomposition of electrolyte cations, anions, and PC was proceeded. The cyclic voltammograms recorded at the third cycle are depicted in this figure. The values of the integral single-electrode capacitance were determined to be 27.9, 27.6, 11.1, and 9.9 F g^{-1} for TMADFOB, TEABF₄, TEABOB, and TMABOB, respectively (Table 1). They were calculated according to $C_{\text{g}}^{\text{int}} = Q / (E \cdot m)$, where Q is the quantity of electricity corresponding to the half area of the cyclic voltammogram, E is the width of the potential sweep (2.5 V), and m is the dry mass of activated carbon. The gravimetric capacitance observed for TMADFOB

Fig. 2 Cyclic voltammograms recorded at the third cycle for TMADFOB, TMABOB, TEABOB, or TEABF₄ with activated carbon electrodes at a scan rate of 5 mV s^{-1} at 25 °C. The molar concentrations of TMABOB, TMADFOB, TEABOB, and TEABF₄ were adjusted to 0.9, 1, 1, and 1 mol dm^{-3} , respectively. The electrode potential was swept between +0.55 and -1.95 V vs. Ag | Ag⁺, and the width was set to 2.5 V.

was not only considerably higher than those for TMABOB and TEABOB, but also comparable to that for TEABF₄. The highest gravimetric capacitance can be accounted for by the small size of TMA⁺ and the planar structure of the oxalate moiety in DFOB⁻. The gravimetric capacitance obtained for quaternary ammonium salts based on symmetric anions decreased in the order of TEABF₄ > TEABOB > TMABOB. The finding indicates that bulk properties of the solution such as conductivity and viscosity are also dominant factors governing the capacitance.^{2,4)} Mobility of moderately small ions is high in the bulk of the solution, and the ionic mobility may decrease in approximately the following descending order: BF₄⁻ > DFOB⁻ > TEA⁺, TMA⁺ > BOB⁻.

3.3 Charge and discharge characteristics of three-electrode measurement cells

Furthermore, we evaluated integral single-electrode and integral full-cell capacitances per unit mass of activated carbon from the discharge curves of three-electrode measurement cells. The potentials of the positive and negative electrodes in the measurement cells were monitored separately with an Ag|Ag⁺ reference electrode. Figure 3(a) shows the charge and discharge curves of the three-electrode measurement cells using quaternary ammonium salt as an electrolyte at 25 °C. The molar concentrations of the quaternary ammonium salts are the same as in Fig. 2. Table 1 summarizes the gravimetric capacitances and *IR* potential drops observed. The *IR* potential drop is observed at the beginning of the CC discharge. The individual capacitances of the positive and the negative electrode were estimated from the reciprocals of the slopes of the discharge curves. Currents greatly decayed to low values during CV charge, as shown in Fig. 3(b). The results also suggest that no significant decomposition of electrolyte cations, anions, and PC is proceeded.

The moderate small ion size can account for the low *IR* potential drop and the high gravimetric capacitance. While the measurement cell is charged, the surface excess concentrations of anions and cations increase at the positive and the negative electrode, respectively. The

IR potential drop at the positive electrode was lower than that at the negative electrode. The gravimetric capacitance of the positive electrode ($C_{+,g}^{\text{int}}$) was higher than that of the negative electrode ($C_{-,g}^{\text{int}}$). The gravimetric capacitance of the positive electrode decreased in approximately the following descending order: BF₄⁻ > DFOB⁻ > BOB⁻. The gravimetric capacitance of the negative electrode observed for TMA⁺ was higher than that for TEA⁺.

The integral total capacitance of the positive and negative electrodes connected in series ($C_{\text{total},g}^{\text{int}}$) can be readily calculated according to $1 / (2C_{\text{total},g}^{\text{int}}) = 1 / C_{+,g}^{\text{int}} + 1 / C_{-,g}^{\text{int}}$. Therefore, the total gravimetric capacitance becomes considerably lower than the half of the decreased gravimetric capacitance of the negative electrode ($C_{-,g} / 2$). The finding indicates that the ease with which quaternary ammonium ions move in and out of

Fig. 3 (a) Charge and discharge curves of three-electrode measurement cells using TMADFOB, TMABOB, TEABOB, or TEABF₄ as an electrolyte at 25 °C. The molar concentrations of the quaternary ammonium salts are the same as in Fig. 2. The measurement cells were charged from 0 to 2.5 V in a constant-current (CC) (−1 mA cm^{−2}, −1.33 mA) mode and further charged to keep constant voltage (CV) (2.5 V). Total charging time was set to 60 min. The measurement cells were then discharged to 0 V at 1 mA cm^{−2}. We have used a redox couple of Ag|Ag⁺ as the reference electrode for monitoring potentials of the positive and negative electrodes separately. (b) Current-time diagrams are also depicted.

Table 1 Comparison of integral single-electrode and integral total capacitances of activated carbon electrodes and *IR* potential drops obtained for three-electrode measurement cells at 25 °C (Figs. 2 and 3). Electrolytic solutions: PC solutions containing TMADFOB, TMABOB, TEABOB, or TEABF₄. The molar concentration of TMABOB was 0.9 mol dm^{−3}, and those of the other quaternary ammonium salts were adjusted to 1 mol dm^{−3}.

Electrolyte	Gravimetric capacitance / F g ^{−1}				IR potential drop / mV		
	Cyclic voltammetry (5 mV s ^{−1})	CC (−1 mA cm ^{−2}) – CV (2.5 V) charge followed by CC (1 mA cm ^{−2}) discharge					
	W. E.	Positive	Negative	Total	Positive	Negative	Total
TMADFOB	27.9	76.1	62.4	17.1	31.9	53.8	85.7
TMABOB	9.9	70.8	62.7	16.6	33.1	49.5	82.6
TEABOB	11.1	72.5	52.8	15.3	18.6	101.3	119.9
TEABF ₄	27.6	78.8	57.1	16.6	21.2	88.3	109.5

pores of the activated carbon negative electrode can be a key factor determining the total gravimetric capacitance. This is the reason why the total gravimetric capacitances obtained for TMADFOB is slightly higher than that for TEABF₄. It should be noted that the charge and discharge characteristics of TMADFOB are in accord with the results of the cyclic voltammetry, but the same relation does not hold for both TMABOB and TEABOB. The gravimetric capacitance evaluated by cyclic voltammetry for TMADFOB was comparable to that obtained for TEABF₄, while the gravimetric capacitances for TMABOB and TEABOB were considerably lower than for TEABF₄. However, the total gravimetric capacitances determined by the discharge in a CC regime for the three quaternary ammonium salts were comparable to that for TEABF₄. A very small distance between activated carbon electrodes in the measurement cell may compensate for lower ionic mobility of TMABOB and TEABOB in the PC solutions.^{2,4)}

Potential-time curves of the positive and the negative electrode obtained for TMADFOB and TMABOB were slightly shifted in the positive directions. The observation supports idea that the use of TMA⁺ as a counter cation increases the capacitance of the negative elec-

trode, and accordingly the total capacitances are higher than that obtained for TEABOB.

4 Conclusion

TMADFOB is a novel tetramethylammonium salt based on an asymmetric chelate anion. TMADFOB has the potential of improving both the solubility in PC and the capacitance of EDLCs. It is very intriguing to investigate the performance of EDLCs at the higher concentration ($\sim 1.6 \text{ mol dm}^{-3}$) of the maximal electric conductivity.

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