Use of Tetraethylammonium Bis(oxalato)borate as Electrolyte for Electrical Double-layer Capacitors

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The development of halogen-free electrolyte salts for electrochemical devices is desirable from the viewpoint of safety and cost. We have investigated the performance of electrical double-layer capacitors (EDLCs) composed of activated carbon electrodes as a positive and a negative electrode, tetraethylammonium bis(oxalato)borate (TEABOB) as an electrolyte salt, and propylene carbonate (PC) as a solvent. In spite of the larger anion size and lower ionic conductivity of the TEABOB, rate capability of a 2025-type coin cell utilizing a PC solution containing 1 mol dm^{-3} TEABOB is more excellent than that obtained for tetraethylammonium tetrafluoroborate (TEABF$_4$).

An electrical double-layer capacitor (EDLC) is an electrical energy device that accumulates electric charges in an interphase between an electrode and an electrolyte.[1] The EDLC is regarded as one of the most promising electrochemical devices for hybrid electric vehicles. Tetraethylammonium tetrafluoroborate (TEABF$_4$) is commonly used as an electrolyte salt for the EDLC. However, the BF$_4{}^-$ can be hydrolysed to generate hydrogen fluoride (HF) in the presence of moisture. The development of fluorine-free electrolyte salts is desirable from the viewpoint of safety and cost. A potential replacement of LiPF$_6$, which is more susceptible to the hydrolysis, by lithium bis(oxalate)borate (LiBOB) has been investigated for lithium-ion batteries.[2] Very little is known about the use of quaternary ammonium bis(oxalato)borates as electrolyte salts for the EDLCs, though the conductivities and the electrochemical stability are investigated.[3] In this paper we report the application of tetraethylammonium bis(oxalato)borate (TEABOB) to the EDLCs.

The synthesis of the TEABOB was as follows. Boric acid 6.18 g (0.1 mol) was dissolved in methanol (100 mL) boiling in a beaker under an inert atmosphere and then 35 wt % tetraethylammonium hydroxide solution 42.1 g (0.1 mol) was carefully added to the solution with stirring. Oxalic acid 18.0 g (0.2 mol) was gradually added to the solution. After the solution became clear, the solution was allowed to evaporate under reduced pressure, leaving a white crude product behind. The product was filtered off, purified three times by recrystallization from methanol, and dried in vacuo at 100 °C for 24 h. The total yield of the product was ca. 70%. The elemental analyses including inductively coupled plasma (ICP) emission spectroscopy were in good agreement with the calculated values.[4] The TEABOB was also identified by means of ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy.[5]

Specific conductivities of electrolyte solutions were measured by use of a conductometer (Toa Electronics, Model CM-60S) equipped with a cell (Model CGT-511B). Cyclic voltammetry (CV) was performed on a computer-controlled electrochemical system (Hokuto Denko, HZ-3000). A pair of activated carbon disks, 13 mm in diameter, was used as the working and the auxiliary electrode. Each activated carbon electrode was fixed with a glass filter and a Pt board. An Ag|Ag$^+$ (0.01 mol dm^{-3} AgClO$_4$ + 0.09 mol dm^{-3} (C$_4$H$_9$)$_4$NClO$_4$ in propylene carbonate (PC)) was employed as the reference electrode.

The activated carbon electrode contained 82 wt % activated charcoal (average surface area 866 m^2 g^{-1}), 9 wt % acetylene black as a conductor, and 9 wt % poly(tetrafluoroethylene) as a binder. The performance of 2025-type coin cells (can size: 20 mm in diameter and 2.5 mm in thickness) was investigated with a charge/discharge unit (Hokuto Denko, Model HJ-201B). A separator (Celgard Inc., #3501) was sandwiched between two identical activated carbon electrodes in the coin cell. The cell was charged in a CC–CV (constant current (1 mA cm^{-2})–constant voltage (2.5 V)) regime for 1 h. Afterward, it was discharged at various constant currents (1, 2, 3, 5, and 10 mA cm^{-2}). The PC and the TEABF$_4$ were used as received (battery grade). The preparation of PC solutions and the fabrication of the EDLCs were carried out in an argon-filled dry box.

Figure 1 shows cyclic voltammograms obtained for PC solutions containing 1 mol dm^{-3} TEABOB or TEABF$_4$ with an activated carbon electrode at a scan rate of 5 mV s^{-1}. The potential sweep was started at the rest potential in the positive direction and was repeated three times between 0.55 and 1.95 V, where no significant decomposition of cation and anion was proceeded. The cyclic voltammograms recorded at the third cycle are depicted in the figure. The values of the gravimetric capacitance were determined to be 12.0 and 17.4 F g^{-1} for the TEABOB and the TEABF$_4$, respectively. They were calculated from the

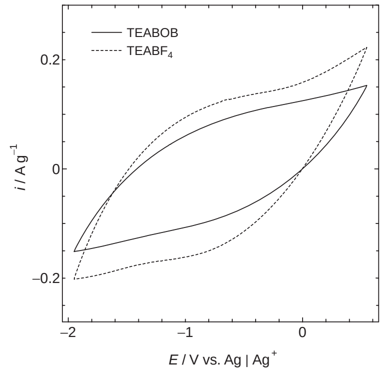

Figure 1. Cyclic voltammograms obtained for PC solutions containing 1 mol dm^{-3} TEABOB or TEABF$_4$ with an activated carbon electrode at a scan rate of 5 mV s^{-1} at 25 °C.

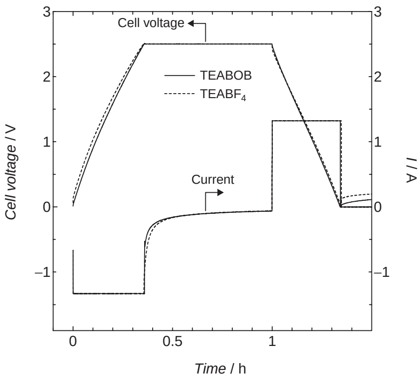

Figure 2. The first charge and discharge curves of 2025-type coin cells utilizing PC solutions containing 1 mol dm^{-3} TEABOB or TEABF$_4$. The coin cells were charged in a CC (1 mA cm^{-2})–CV (2.5 V) regime for 1 h at 25 °C. Afterward, they were discharged at 1 mA cm^{-2}. Current-time diagrams are also depicted in the figure.

half areas of the cyclic voltammograms and the width of the potential sweep (2.5 V). Ion sizes, viscosity coefficient, wettability, and specific conductivity are dominant factors governing the magnitude of the capacitance. The size and mass of the BOB$^-$ are larger than those of the BF$_4{}^-$ and the TEA$^+$, and accordingly the use of the TEABOB as an electrolyte salt produced more dense and viscous solutions. The specific conductivity of a PC solution containing 1 mol dm^{-3} TEABOB (6.79 mS cm^{-1} at 25 °C) was lower than that for 1 mol dm^{-3} TEABF$_4$ (13.14 mS cm^{-1} at 25 °C).

In spite of the larger anion size and lower ionic conductivity of the TEABOB, the CC–CV charging of 2025-type coin cells resulted in gravimetric capacitance comparable to that for the TEABF$_4$. Figure 2 shows the first charge and discharge curves of 2025-type coin cells utilizing PC solutions containing 1 mol dm^{-3} TEABOB or TEABF$_4$. The coin cells were discharged at 1 mA cm^{-2} at 25 °C.

Figure 3 compares the rate capabilities of the 2025-type coin cells at various discharge rates of 1, 2, 3, 5, and 10 mA cm^{-2} at 25 °C. The charge rate was fixed at 1 mA cm^{-2}. The gravimetric capacitance obtained is summarized in Table 1. Although the reciprocal of the slope of the discharge curve represents the capacitance, it can be calculated from the cell voltage and the area of a current-time diagram with accuracy. Additionally, the retention of the gravimetric capacitance, which is defined as the ratio of the gravimetric capacitance at 1 mA cm^{-2} to that at a given discharge rate, is listed. As the discharge rate increased, the slope of the curve of the TEABF$_4$ became remarkably steep. The use of the TEABOB suppressed the fading of the gravimetric capacitance at high discharge rates, and the retention of the gravimetric capacitance for the TEABOB was more excellent than that for the TEABF$_4$.

Table 1. Gravimetric capacitance (C_g) of activated carbon electrodes and its retention obtained for PC solutions containing 1 mol dm^{-3} TEABOB or TEABF$_4$ at various discharge rates at 25 °C

i/mA cm^{-2}	C_g/F g^{-1}		Retention/%	
	TEABOB	TEABF$_4$	TEABOB	TEABF$_4$
1	11.9	12.9	100	100
2	11.6	12.4	97.5	96.1
3	11.3	12.0	95.0	93.0
5	11.0	11.4	92.4	88.4
10	10.3	10.2	86.6	79.1

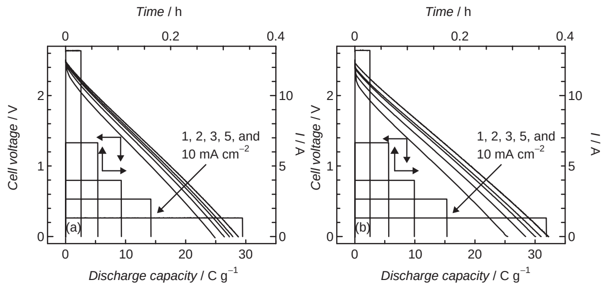

Figure 3. Comparison of rate capabilities of 2025-type coin cells utilizing PC solutions containing 1 mol dm^{-3} (a) TEABOB or (b) TEABF$_4$ at various discharge rates of 1, 2, 3, 5, and 10 mA cm^{-2} at 25 °C. The charge rate was fixed at 1 mA cm^{-2}. Current-time diagrams are also depicted in the figure.

A very small distance between activated carbon electrodes in a coin cell may compensate for low ionic mobility of the BOB$^-$, and accordingly the gravimetric capacitance for the TEABOB is comparable to that for the TEABF$_4$. The gravimetric capacitance of a single electrode in an electrolytic cell was evaluated by cyclic voltammetry while the total gravimetric capacitance of two electrodes connected in series in a coin cell was determined by the discharge in a CC regime. However, the former gravimetric capacitance was considerably lower than the four times latter gravimetric capacitance, though the measurements by the two methods are not essentially identical to each other. The finding indicates that ions are not sufficiently accumulated in pores of the working electrode in the electrolytic cell.

In conclusion, in spite of the larger anion size and lower ionic conductivity of TEABOB, the CC–CV charging of a 2025-type coin cell resulted in the gravimetric capacitance higher than that for TEABF$_4$ at the highest discharge rate (10 mA cm^{-2}). The use of the BOB$^-$ should allow us to find the optimum minimum size of a quaternary ammonium ion for the counter cation, and hence the capacitance can increase.

References and Notes

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4 Calcd for TEABOB: C, 45.5; H, 6.36; N, 4.42; B, 3.41%. Found for TEABOB: C, 45.1; H, 6.06; N, 4.52; B, 3.38%.

5 ^{1}H NMR (1% TMS/(CD$_3$)$_2$CO, 500.00 MHz): δ 1.39 (s, 3H), 3.49 (s, 2H). ^{13}C NMR (1% TMS/(CD$_3$)$_2$CO, 125.65 MHz) δ 10.64, 54.95, 163.54. ^{11}B NMR (0.1 mol dm^{-3} NaBH$_4$/D$_2$O, 160.35 MHz): δ −11.3.

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