Short communication

Capacitance of porous carbon electrode in mixed salt non-aqueous electrolytes

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ABSTRACT

Capacitances of a porous carbon electrode in non-aqueous electrolytes containing tetraethylamonium tetrafluoroborate ($TEABF_4$) and a lithium salt with various compositions have been investigated for the potential use in electric double layer capacitor. In the electrolyte prepared by dissolving $TEABF_4$ and $LiBF_4$ into the mixed solvent of ethylene carbonate (EC) with diethyl carbonate (DMC), an activated carbon fiber (ACF) electrode exhibits a larger capacitance than in $TEABF_4$ single salt electrolyte on cyclic voltammograms. The symmetrical capacitor cell containing the $LiBF_4$–$TEABF_4$ mixed salt electrolyte also exhibits larger capacitance on a constant-current test compared with that containing the $TEABF_4$ single salt electrolyte, while the capacitance degradation is observable for this cell at a significant extent, while the test under controlled potential of the ACF electrode to -0.2 to 1.0 V vs. Ag provides somewhat stable capacitance over 30 cycles.

1. Introduction

Electrochemical capacitors, including electric double layer capacitors, have been recognized as novel rechargeable power sources, particularly for high-power applications. For electrochemical capacitors based on electric double layer phenomena, electrolyte plays dominant roles in determining its capacitance value as well as in determining its working voltage. For extending the working voltage of a capacitor cell, it is effective to use electrolyte consisting of electrochemically stable salt and solvent. On the other hand, electric double layer capacitance is in relation to the packing of relevant ions on the surface of a polarized electrode. From these requirements, electrolyte salts having sufficient electrochemical stability and consisting of small ions are selected for non-aqueous capacitor electrolytes. Early works summarize the properties of various single salt electrolytes [1–5]. Quaternary ammonium tetrafluoroborates, such as tetraethylammonium tetrafluoroborate ($TEABF_4$) and triethylmethylammonium tetrafluoroborate ($TEMABF_4$) appear to meet perfectly these requirements. Therefore the proposal of candidates as new salts has been rather minor, while such new candidates as ionic liquids and spiro-ammonium salts are attractive [6–9].

On the other hand, novel capacitor systems have been proposed to the energy density of capacitor. In particular, asymmetric capacitor system containing lithium intercalation that is utilized on either electrode process has been attracted [10–16]. Generally, non-aqueous electrolytes containing lithium salts provide rather poor properties for electric double layer capacitor usage compared with the ones containing tetraalkylammonium salts. The control of the properties of electrolyte based on lithium salt may be beneficial for the development of lithium ion type hybrid capacitor. From such a viewpoint, the influence of the coexistence of lithium and tetraalkylammonium salts in non-aqueous electrolyte for electric double layer properties is also attractive. There are only some special studies in which non-aqueous electrolytes containing lithium ion has been proposed [17–20].

In the present study, basic properties of mixed salt non-aqueous electrolytes containing various lithium salts and $TEABF_4$ for electric double layer capacitor have been evaluated. In some cases, these mixed salt electrolytes show properties unexpected from those of both $TEABF_4$ and lithium salt electrolytes. A preliminary investigation for the application in electric double layer capacitor has also been carried out by using a simply assembled capacitor cell.

2. Experimental

In the present study, $TEABF_4$ (Tomiyama Pure Chemical Co., Japan) was used as a standard salt, and $LiBF_4$ (Kishida Chemical Co., Japan), $LiPF_6$ (Tomiyama Pure Chemical Co.), and lithium bis(trifluoromethane)sulfoneimide (LiTFSI; Fluka) were applied as coexisting lithium salts. For electrolyte solvent, ethylene carbonate (EC; Kishida Chemical Co.) and dimethyl carbonate (DMC; Kishida Chemical Co.) was mixed at the volumetric ratio 1:1. The prescribed amounts of $TEABF_4$ and a lithium salt were dissolved into mixed solvent independently, but the total concentration of two salts was set at 1 mol dm^{-3}. All these chemicals are battery-grade, and the preparation procedure was carried out in a glove box filled with argon. The conductivity of the prepared electrolytes

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was measured by alternative current method under controlled temperature.

Activated carbon fiber cloth (ACF; Kureha Chemical Co., Japan) having ca. 2000 m² g⁻¹ of specific surface area was used as a capacitor electrode. The ACF cloth was cut into a disk with 10 mm in diameter, and fixed on platinum plate with conductive adhesive. A 3-electrode sealed Teflon cell was assembled by two ACF clothes as working and counter electrodes, and a silver wire as quasi-reference electrode. The electrodes were separated by dried filter paper (Toyo Roshi Co., Japan, No. 2). Cyclic voltammetry was measured by using an electrochemical measurement system (HZ-3000, Hokuto Denko Co., Japan) under the potential region between −1.0 and 1.0 V at the scan rate of 2 mV s⁻¹. Constant-current charge–discharge tests for a 2-electrode cell of ACF cloth electrodes were conducted by using a cycler (BTS2004, Nagano Co., Japan) under 0.5 mA cm⁻² of the current density, and 0 V of cut-off voltages at discharging process. The cut-off voltage at charging process was varied from 1.5 to 3.0 V. The cycle tests for the symmetric capacitor cells were performed at the cut-off voltage of 2.5 V. Similar constant-current charge–discharge tests for the 3-electrode cell under controlled potential of an ACF electrode were carried out using a potentio-galvanostat (Solartron 1287) between the cut-off potentials of 1.0 V vs. Ag and −0.2 V vs. Ag.

3. Results and discussion

The conductivities of the prepared electrolytes at 25 °C are plotted against the content of lithium salt, the ratio Li/(Li + TEA), in Fig. 1. It is known that the conductivity of non-aqueous electrolyte containing a lithium salt is generally lower than the case containing a quaternary ammonium salt when the same solvent and the same salt concentration are employed [21]. Also in the present result, 1 mol dm⁻³ lithium salt/EC–DMC electrolytes exhibit lower conductivities than 1 mol dm⁻³ TEABF₄/EC–DMC. The conductivity of mixed salt electrolytes exhibits the lower part than the line combined between both single salt electrolytes. In particular, the electrolyte containing 0.8 mol dm⁻³ LiBF₄ and 0.2 mol dm⁻³ TEABF₄ exhibits lower conductivity than that of 1 mol dm⁻³ LiBF₄/EC–DMC electrolyte. In this electrolyte system, EC molecules may be mainly solvated with lithium ion, and TEABF₄ may tend to form contact ion pair rather than LiBF₄ in 1 mol dm⁻³ LiBF₄ electrolyte. Such contact ion pairs decrease the conductivity of electrolyte solution compared with LiBF₄ single salt electrolyte. Therefore, the increase of conductivities for mixed salt solutions is
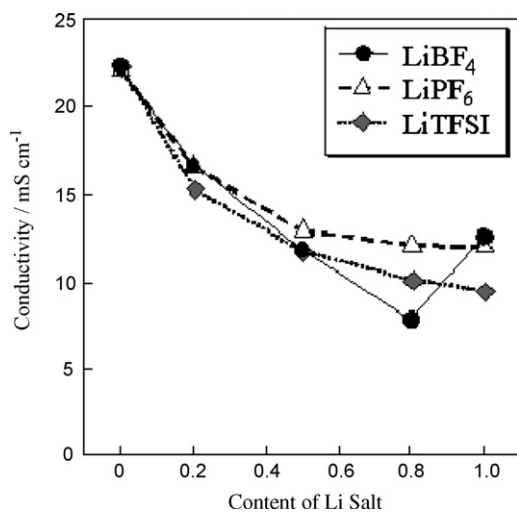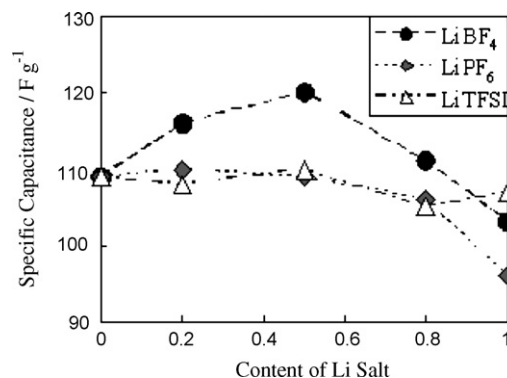

Fig. 2. The specific capacitance of ACF electrode in various electrolytes toward the concentration of lithium salt.

expected to be achieved by the optimization of solvent composition.

The specific capacitances of the ACF electrode in single salt and mixed salt electrolytes determined from cyclic voltammograms are plotted in Fig. 2 toward the content of lithium salts. Electrolytes based on lithium salt provide lower specific capacitances than the one containing TEABF₄ except for the case of the one containing LiTFSI. The capacitance in a lithium salt electrolyte is normally smaller than that in tetraethylammonium salt electrolyte. When a lithium salt is coexisted with TEABF₄ in electrolyte, the capacitance of ACF is varied as the kind of lithium salt. The capacitances of ACF in the LiTFSI–TEABF₄ electrolytes are similar to those in TEABF₄ or LiTFSI single salt electrolyte. In contrast, the LiPF₆–TEABF₄ electrolytes provide the similar capacitances of ACF to the TEABF₄ electrolyte regardless the content of LiPF₆. Furthermore, in the binary salt system of LiBF₄–TEABF₄, the specific capacitance of ACF exhibits a maximum toward the content of LiBF₄. In the present result the content of LiBF₄ in the electrolyte for the maximum capacitance of ACF was 0.5 mol dm⁻³. This behavior is not expectable from a simple figure of electric double layer between ACF electrode and non-aqueous electrolyte. Therefore, some surface status of ACF electrode in the mixed salt electrolyte may differ from the single salt one by the change of surface adatom on ACF electrode. The cyclic voltammograms of ACF electrode in 1 mol dm⁻³ TEABF₄/EC–DMC, 1 mol dm⁻³ LiBF₄/EC–DMC, and 0.5 mol dm⁻³ TEABF₄–0.5 mol dm⁻³ LiBF₄/EC–DMC electrolytes are compared in Fig. 3. All voltammograms exhibit a similar butterfly-like shape which has been proposed to be observed frequently for a capacitive behavior of a porous electrode [22–24]. The mini-
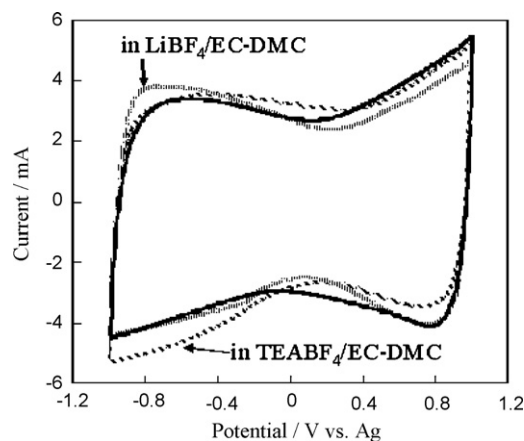

Fig. 1. The conductivities of the mixed salt electrolytes at 25 °C toward the concentration of lithium salt.

Fig. 3. Cyclic voltammograms of ACF electrode in LiBF₄–TEABF₄ (5:5) mixed salt electrolyte (solid line) compared with those in single salt electrolytes. Scan rate: 2 mV s⁻¹.
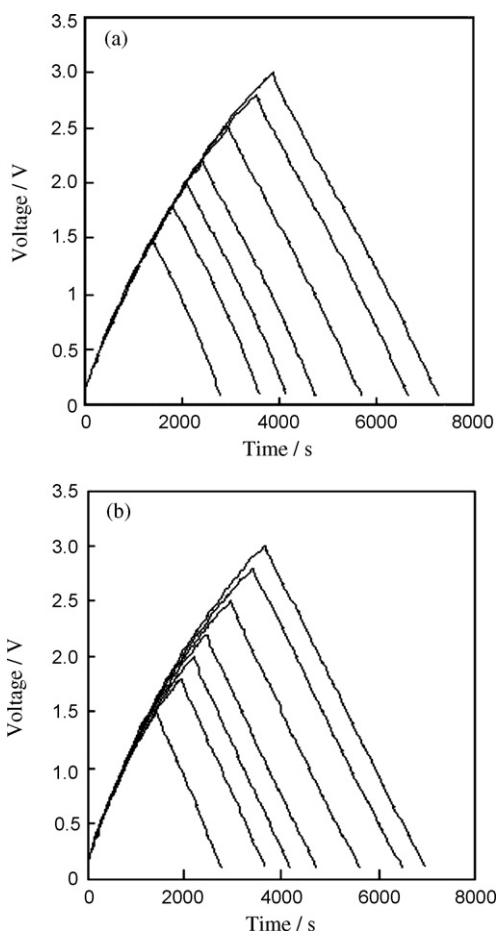
Fig. 4. Constant-current charge–discharge profiles of symmetric cells with ACF electrodes containing (a) TEABF$_4$ single salt electrolyte and (b) LiBF$_4$–TEABF$_4$ (5:5) mixed salt electrolyte. Current density: 0.5 mA cm^{-2}.

Fig. 5. Cycle behavior of the capacitance of ACF symmetric cells in various electrolytes.

the one obtained by CV measurements regardless of electrolyte. The cell containing LiBF$_4$–TEABF$_4$ mixed salt electrolyte exhibits capacitance fluctuation during initial several cycles, and the slight capacitance degradation at consequent cycles.

In order to clarify the dominating process of the capacitance degradation for the LiBF$_4$–TEABF$_4$ mixed salt electrolyte cell, the constant-current test with controlled potential of a working electrode using the 3-electrode cell has been conducted. When the working potential range was set between −0.2 and 1.0 V vs. Ag, where anion may mainly contribute to the formation of electric double layer on the ACF electrode, similar triangle response was observed. The specific capacitance at discharge state in each cycle is plotted toward cycle number in Fig. 6. Unlike from the capacitance of a 2-electrode cell, the ACF electrode in the LiBF$_4$–TEABF$_4$ electrolyte retains its specific capacitance as large as 140 F g^{-1} over 30 cycles. The capacitance value rather increase, probably because of the gradual penetration of the electrolyte into pores of the ACF electrode. Unfortunately the structure of the 3-electrode cell assembly did not allow the cell to continue the charge–discharge test above 30 cycles. However, the good cycle performance of ACF electrode under controlled potential condition suggests that negative electrode process is responsible for the capacitance degradation on the 2-electrode cell. While the rigorous potential of the negative electrode on the 2-electrode cell was not observed, it may reach the potential region where electrolyte containing lithium ion decomposes. The result in Fig. 6, even for only 30 cycles, also suggests that the capacitance of the LiBF$_4$–TEABF$_4$ mixed salt electrolyte has possibility for the usage to a practical system by using a porous electrode as positive electrode and controlling the potential of pos-

mum point of charging current is considered as an apparent zero charge point of an electrode. TEABF$_4$-based electrolyte and LiBF$_4$-based one provides different minimum point of charging current, indicating that they provide different apparent zero charge point of ACF electrode [22–24]. Perhaps the surface state of ACF electrode is influenced by the composition of electrolyte through the specific adsorption. The shape of voltammogram in LiBF$_4$–TEABF$_4$ mixed electrolyte near apparent zero charge point appears to be a combined feature of those in each single salt electrolyte. In this sequence the apparent zero charge capacitance in the LiBF$_4$–TEABF$_4$ mixed salt system appears to be larger than those in the LiBF$_4$ and TEABF$_4$ single salt electrolytes. This capacitance behavior in apparent zero charge point may contribute to the larger capacitance in the LiBF$_4$–TEABF$_4$ mixed salt system.

The constant-current charge–discharge profiles of ACF 2-electrode symmetric cells containing 1 mol dm^{-3} TEABF$_4$/EC–DMC and 0.5 mol dm^{-3} LiBF$_4$–0.5 mol dm^{-3} TEABF$_4$/EC–DMC electrolytes under various charging cut-off voltages are shown in Fig. 4a and b, respectively. In both cases, the profiles are triangular shape typically observed in electric double layer capacitor system even when the cut-off voltage is 3.0 V. This result indicates that the LiBF$_4$–TEABF$_4$ mixed salt electrolyte as well as the TEABF$_4$ single salt electrolyte is stable without any sign of the decomposition of electrolyte. The specific capacitances based on the mass of both ACF electrodes obtained from the profiles under the cut-off voltage of 2.5 V are plotted over cycles in Fig. 5. While the specific capacitance values estimated by a simple 2-electrode test cell are approximate, the obtained capacitances are at similar extent to
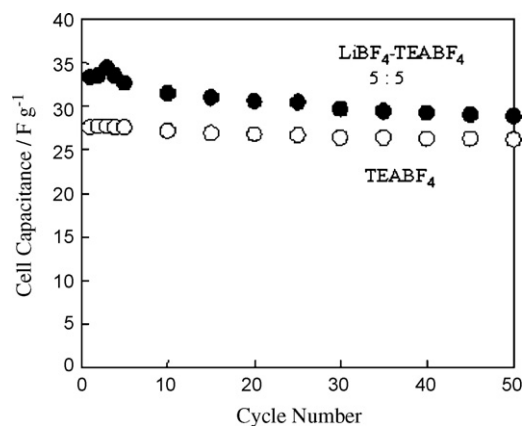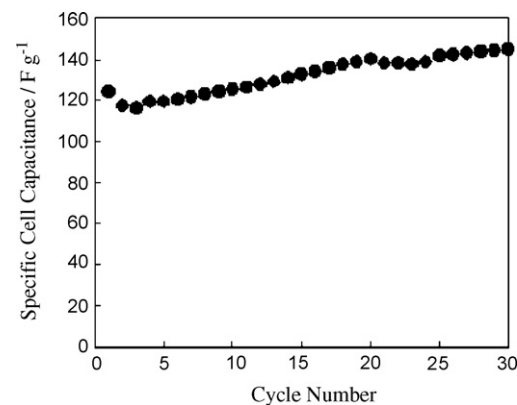

Fig. 6. Cycle behavior of the capacitance of ACF electrode in the 3-electrode cell containing LiBF$_4$–TEABF$_4$ (5:5)/EC–DMC electrolyte.

itive electrode, for example by applying to an asymmetric hybrid capacitor system.

In order to confirm the availability of the LiBF$_4$–TEABF$_4$ mixed salt electrolyte for practical capacitors, the more precise assessment and optimization of various properties, such as long-term cycle stability and rate capability, is inevitable. In addition, the mechanism of capacitance increase in the mixed salt system should also be revealed precisely. Throughout such efforts, more effective candidate of mixed salt electrolyte may be found. From the present trial, the authors intend to propose the concept of 'salt mixing' as a potential method to tune the performance of an advanced capacitor system.

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