Ionic Conductivity of Nonflammable Ternary Electrolyte Consisting of Ionic Liquid and Fluorinated Alkylphosphate for Advanced Electrochemical Capacitors

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ABSTRACT
A novel ternary electrolyte system that consists of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (EMITFSA), LiTFSA, and tris(trifluoroethyl)phosphate (TFEP) has been developed as a nonflammable electrolyte for advanced electrochemical capacitors. The ionic conductivity of the system depended much on the electrolyte composition. Higher contents of EMITFSA gave higher conductivity in both binary EMITFSA-TFEP and ternary EMITFSA-LiTFSA-TFEP systems, whereas higher molar ratio of LiTFSA decreased the conductivity of the ternary system due to increased viscosity. In the systems keeping constant molar ratios of EMITFSA and LiTFSA, the conductivity showed maxima at ca. 70 mol% of TFEP, where the concentration of the charge carriers (ions) and the mobility of the species are balanced. Brief tests of a symmetric cell composed of activated carbon electrodes revealed that the present ternary component system work as a nonflammable electrolyte in carbon-based electrochemical capacitors.

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1. Introduction
Much attention has been focused on the technology of Lithium-Ion Capacitor (LIC), a kind of Electrochemical Hybrid Capacitors (HECs), which consists of faradaic process of lithium-ion insertion/desertion and non-faradaic ion adsorption/desorption process.1-3 A proper combination of such asymmetric electrode processes enables higher capacitance and operation voltage than those of conventional electric double-layer capacitors (EDLCs) and higher rate-capability than lithium-ion batteries (LIBs).3,4 Up to the present, almost the same composition as the electrolyte of common LIBs has been utilized as the electrolyte of LIC. That is, a mixed alkylcarbonate solution dissolving lithium salt, like LiPF6/EC+DMC (EC: ethylene carbonate, DMC: dimethyl carbonate), is used, but its composition has not yet been optimized for LICs.

In LIC consisting of graphite negative and activated carbon positive electrodes, both ions, Li+ cation and the counter anion, of the electrolyte also work as “active materials” at the both electrodes.3-5 Thus, higher concentration of electrolytic salt is desirable to achieve higher storage capacity for LIC. However, the maximum solubility of lithium salt is generally limited to around 1.5 mol dm−3 at ambient temperature in mixed alkyl carbonate solvents. On the other hand, alkylcarbonate-based solutions are highly flammable, which make the LIC system in hazard on thermal runaway of lithiated (charged) graphite electrode, especially for large-scale utilities.6

From the above viewpoint, safer and more reliable electrolyte systems with higher cell performances should be developed for LICs. We have so far proposed the utilization of ionic liquid (IL) and/or alkylphosphates as nonflammable or fire-retardant solvents and additives for LIBs.2-11 In the present work, we have adopted a high ion-concentration system based on an ionic liquid (IL) dissolving lithium salt for LIC. Generally IL-based high ion-concentration system causes extremely high viscosity of the electrolyte. Therefore, in a practical system, low-viscosity component is needed to meet high capacitor performances. A family of fluorinated alkylphosphates shows not only high flame-retardant property but also good compatibility with high voltage operation in LIB.12 Thus, we consider that the fluorinated alkylphosphate is suitable for the use as co-solvent in non-flammable electrolytes for high-energy density capacitor devices. In the present work, a ternary system consisting of IL, lithium salt and a flame-retardant organic solvent has been examined as the electrolyte of LICs. In this communication, ionic conductance behavior is reported as a function of the electrolyte composition for a ternary system, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (EMITFSA) as IL, LiTFSA as the lithium-ion source, and tris(trifluoroethyl)phosphate (TFEP) as the fire-retardant co-solvent (viscosity, η = 4.6 mPa s at 25°C). As a typical IL that has both low viscosity and wide potential window, and so far been well-examined, EMITFSA has been chosen in the present work.

2. Experimental
Each electrolyte component, EMITFSA (Kanto Chemical), LiTFSA (Kanto Chemical), and TFEP (TOSOH F-TECH), was used as received without further purification. As LiTFSA is rather hygroscopic, it was dried in a vacuum at 120°C for overnight before use. The electrolyte solutions were prepared by mixing each component with various molar ratios under a dry Ar atmosphere. Propylene carbonate (PC) was also used as a low-viscosity co-solvent for comparison (η = 2.5 mPa s at 25°C). The ionic conductivity of the electrolyte was measured by an AC method in a temperature range from −20 to 60°C.

A simple flammability test was conducted for the present ternary electrolyte system. A glass filter sheet impregnated with the electrolyte solution was placed over gas-burner flame of 7 cm length with 3 cm distance. The ignition and extinguish times were
used as a measure of the flammability. A capacitor performance was briefly examined using a conventional two-electrode cell, in which a symmetric combination of activated carbon (specific surface area: ca. 1500 m² g⁻¹) electrodes and the ternary electrolytes were employed, under voltage-scan cycling at 25°C.

3. Results and Discussion

Figure 1 shows variations in the ionic conductivity of binary EMITFSA-TFEP and ternary EMITFSA-LiTFSA-TFEP systems measured at 25°C, as a function of EMITFSA content (mol%) for ternary EMITFSA-LiTFSA-TFEP (EMITFSA:TFEP = 1:1 by mol) systems. The ionic conductivity increases monotonously with EMITFSA content. The increase in charge carrier (ionic species) concentration would be a main reason for the increase in conductivity with IL content in the system. In Fig. 2, a variation in the ionic conductivity with LiTFSA content is shown for the ternary system where the molar ratio of EMITFSA and LiTFSA is 1:1 or 2:1. For both cases, maximum conductivity was observed at ca. 70 mol% LiTFSA being 1:1 molar ratio. The temperature dependence reveals positive deviation from a linear relation in the log $\sigma$ vs. $1/T$ plot, which is generally observed for ionic conductors containing concentrated charge carriers in viscous media. The ionic conductivity once increases with the increase in TFEP content, especially in lower temperature region [Fig. 3(A)]. This trend is probably caused by the decrease in viscosity of EMITFSA dissolving LiTFSA with the increase in TFEP content, as a low viscosity component in the system. However, further addition of TFEP leads to a decrease in the conductivity because the lowering in the ionic species concentration becomes to influence dominantly [Fig. 3(B)]. This dilution effect appears significantly in higher temperature region. That is, the effects of viscosity lowering and charge-concentration decreasing by TFEP addition are respectively reflected in the lower and higher temperature regions. In Fig. 4, variations in the conductivity at 25°C are plotted as a function of TFEP content for the ternary systems, in which the molar ratio of EMITFSA and LiTFSA was 1:1 or 2:1. For both cases, maximum conductivity was observed at ca. 70 mol% of TFEP. With respect to the molar ratio of EMITFSA and LiTFSA, higher conductivity was obtained in a system containing lower molar ratio of the Li salt. A ternary system containing PC instead of TFEP as the co-solvent shows higher conductivity (5.6 mS cm⁻¹) than that of TFEP-containing system. As the solution viscosity was almost the same (22 mPa s for the TFEP-containing system, 23 mPa s for the PC-containing system), this significant difference in the conductivity would be attributed to some difference in the ionic structure including the degree of ion-association in these two ternary systems. The same tendency was also observed over a wide composition range in the ternary system.

The ionic conductivity of the present ternary system, EMITFSA-LiTFSA-TFEP, is summarized in Fig. 5, where the figure at each
composition point indicates the value in mS cm\(^{-1}\) unit at 25°C. In the EMITFSA-TFEP binary system, the conductivity increased with EMITFSA content. The ionic conductivity also increased with IL content in the ternary system consisting of LiTFSI-TFEP = 1:1. These are attributable to the increase in concentration of charge carriers (ionic species) in the system. With respect to the conductivity in a ternary system composed of EMITFSA:LiTFSI = 1:1, a maximum value of 1.93 mS cm\(^{-1}\) was obtained for the composition of ca. 70 mol% TFEP (EMITFSA:LiTFSI:TFEP = 1:1:5 in mol). Both the viscosity and charge carrier concentration decreasing with TFEP concentration are responsible for the conduction behavior in this ternary system.

The combustion tests of the present electrolyte system confirmed that the composition of EMITFSA:LiTFSI:TFEP = 1:1:5 was completely non-flammable. On the other hand, the electrolyte containing PC as a co-solvent instead of TFEP (EMITFSA:LiTFSI:PC = 1:1:5 in molar ratio) showed considerable flammability. As the present ternary system contains no flammable components, the nonflammability of the electrolyte will be guaranteed for other mixing ratios, although combustion tests have not yet been done over whole composition ranges.

Figure 6 shows a current-voltage profile of a symmetric capacitor using high-surface area activated carbon electrodes and the ternary electrolyte containing ca. 70 mol% TFEP (EMITFSA:LiTFSI:TFEP = 1:1:5 in mol), with a voltage scan rate of 2 mV s\(^{-1}\). The current-voltage profile of the cell using a ternary electrolyte containing flammable PC (EMITFSA:LiTFSI:PC = 1:1:5 in mol) is also shown for comparison. A similar polarization profile was obtained in the system containing TFEP as that in PC, while the apparent capacitance was slightly low, especially in the high-voltage region. The integration of charging current gave about 30 F g\(^{-1}\) of specific capacitance for the cell using the nonflammable ternary electrolyte system. This value for apparent specific capacitance is almost ideal one generally observed for the carbon sample examined in non-aqueous electrolyte systems. As a reference, the system containing the same mole fraction of PC showed 33 F g\(^{-1}\). That is, the present ternary electrolyte system can deliver maximum capacitance for activated carbon materials. The capacitor performances of asymmetric systems using Li\(^+\)-insertion electrode are now being investigated, whose results will be published in a next paper.

4. Conclusions

A novel ternary electrolyte system consisting of EMITFSA, LiTFSI, and TFEP has been developed as a nonflammable electrolyte for electrochemical capacitors. Ionic conductivity was measured as a function of the electrolyte composition. Higher contents of EMITFSA tend to give higher conductivity in both binary EMITFSA-TFEP and ternary EMITFSA-LiTFSI-TFEP systems. Higher molar ratio of LiTFSI decreases the conductivity due to increased viscosity. The addition of TFEP to EMITFSA:LiTFSI being 1:1 or 2:1 once increases the conductivity giving maximum values at ca. 70 mol%, and then decreases the conductivity due to diluted ionic species in the higher TFEP concentration regions. The ternary component system was found to work as nonflammable electrolyte in a symmetric carbon/carbon electrochemical capacitor.

References