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Characterization of lithium tetrafluoroborate and N-methylacetamide complex as electric and ionic conductors

Byungsun Bang and Taewhan Yeu[†]

School of Chemical Engineering & Materials Science, Chung-Ang University,
221, Heulsuk-dong, Dongjak-gu, Seoul 06911, Korea

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Abstract−A complex of lithium tetrafluoroborate ($LiBF_4$) and N-methylacetamide was prepared and investigated. Both $LiBF_4$ and N-methylacetamide are solid at room temperature, but their mixture has liquid- or solid phase at room temperature, depending on the composition. When the complex is liquid, the complex has ionic conductivity. But if the complex is solid, it has electric conductivity. The room temperature ionic conductivities of some compositions in propylene carbonate of the complex exceed 6 mS/cm. Room temperature electric conductivity of the complex is 5.025×10^{-3} mS/cm^2. In addition, supercapacitors were constructed and tested using the above-mentioned complex electrolyte. The electrochemical properties of the complex and the supercapacitors were evaluated with cyclic voltammetry, ac impedance spectroscopy, etc. The supercapacitors with this complex show good electrochemical properties in specific capacitance, cycling performances.

Keywords: Ionic Complex, Amide Complex, Ionic Conductor, Electric Conductor, Supercapacitor

INTRODUCTION

Ionic liquids have attracted attention as safe electrolytes in energy storage devices characterized by stability of structure, limiting the flammability and volatility of organic electrolytes [1,2]. Ionic liquids containing cations such as quaternary ammonium, pyridinium, pyrrolidinium, phosphonium, or imidazolium, and anions, such as tetrafluoroborate, hexafluorophosphate, or bis(trifluoromethane sulfone)imide have been reported [1-10]. One of the properties of the ionic liquid is the good degree of dissociation. High soluble ionic liquids have gained much attention because of their high ionic conductivity.

Ion complex acts as an antistatic agent using electrical characteristics based on ionic bonding of molecular structure in contrast with the antistatic agent using a surfactant or a conductive polymer. The ion complex can be added directly to the coating solution in various films such as LCD. The ion complex is possible of suppressing the migration of the coating surface and improve the availability of the coating resin.

Supercapacitors have been a promising candidate for various applications because of their excellent reversibility and power density. Generally, supercapacitors can be defined as electric double layer capacitors and pseudocapacitors in accordance with energy storage mechanism [11,12]. Supercapacitor has been proposed for various electrochemical devices, such as green energy, solar cells, and electric vehicles [13,14]. Various studies of supercapacitors are underway for their high stability, good life performance, excellent energy density and power density [15-17]. The electrochemical properties of the electrolyte for wide electrochemical windows, safety and capacity have been studied, depending on viscosity of the solvent and size of the ion [18-21].

In this study, the ion complex having ionic conductivity or electric conductivity depending on the concentration was prepared with $LiBF_4$ and N-methylacetamide. The coupling structure and composition of the ionic complex were investigated by Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy (Raman). To measure the ionic conductivity and electric conductivity was confirmed the electrochemical properties of the ion complex.

Also, we applied the ion complex having ionic conductivity to electrolyte. Supercapacitors with complex electrolyte solutions were constructed and analyzed. Internal resistance, specific capacitance, specific energy density, and specific power density were measured and calculated by AC impedance analysis, cyclic voltammetry, and charge/discharge process.

EXPERIMENTAL

All materials were obtained from Aldrich and stored in a glove box under vacuum of 10 mbar prior to use unless specified otherwise.

The ion complex was prepared by mixing $LiBF_4$ and N-methylacetamide in an N_2-filled glove box (H_2O, 1 ppm). Homogeneous liquids with molar ratios of $LiBF_4$ and N-methylacetamide between 1 : 1 and 1 : 9 were obtained directly after stirring the mixtures at 80 °C. The water content of the complex was determined to be less than 50 ppm by Karl-Fischer titration method.

FT-IR spectra were obtained at 16 scans with a resolution of 0.1 cm on a Nicolet is 5 FT-IR spectrometer using ATR technique. All samples were kept in a glove box filled with nitrogen until everything was ready for the FT-IR measurements. Therefore, the influence of the moisture in air on the experimental results was negligible.

[†] To whom correspondence should be addressed.
E-mail: twyeu@cau.ac.kr

Each spectrum was scanned 32 times.

Raman measurements were carried out on a Jobin Yvon T64000 spectrometer. The laser power on the samples was 5.0 W with a beam diameter of 1.4 mm. The wavelength of the laser was 1,064 nm. The samples were sealed in disposable optical glass test tubes. All of the samples were assembled and prepared in the glove box.

The electric conductivities of the ion complex were measured by a 4-probe conductivity meter. For electric conductivity measurements, the ion complex was coated on a slide glass. The ionic conductivities of ion complex dissolved in PC were measured in the temperature ranges of 20-90 °C and concentration ranges of 0.0-1.6 M by the Radiometer RA2010 conductivity meter.

Electrochemically active materials used in this study were activated carbon (Kuraray, RP20) and lithium manganese oxide ($LiMn_2O_4$). Both positive and negative electrodes were prepared by coating slurries on the 20 μm thick aluminum foil. The slurry was prepared by ball mill mixing of 20 wt% solid powder and 80wt% N-Methyl-2-pyrrolidone solvent for 24 hrs to secure a proper viscosity for doctor blade coating. Solid powders were an active material, a conductor, and a binder at weight ratio of 75 : 15 : 10, respectively. The active material of a composite positive electrode was a mixture of a lithium metal oxide and an activated carbon, whereas the active material of negative electrode was activated carbon. Carbon black (MMM, super P) and polyvinylidene fluoride were used as a conductor and a binder.

After coated electrodes were dried at 120 °C and 24 hrs under vacuum of 10 mbar, the electrodes were hot pressed at pressure of 0.8 ton/cm^2. The coating thickness of the composite positive electrode was 70 μm, whereas the coating thickness of negative electrode was 140 μm.

Cylindrical supercapacitor (Ø10, h30 mm) was assembled with lithium manganese oxide/C positive electrode, C negative electrodes, electrolyte solution, and a membrane (NKK, CB4035).

The AC impedance analysis of the supercapacitor was conducted at frequency ranges of 0.1-100,000 Hz with voltage amplitude of ±5 mV by ZAHNER IM6ex frequency impedance analyzer. The cyclic voltammetry was performed at voltage ranges of 1.0-2.3 V with scan rate of 5 mV/s by potentiostat/galvanostat (EG&G, 273A). The charge and discharge performance at 10 C-rate were conducted up to 1,000 cycles by the cycler (Wonatech, WBCS 3000).

RESULTS AND DISCUSSION

The ion complex showed either electric conductivity or ionic conductivity, depending on the mole ratio. The $LiBF_4$/N-methylacetamide complex at a molar ratio of 1 : 1 became solid at room temperature. On the other hand, the $LiBF_4$/N-methylacetamide complex with a molar ratio of N-methylacetamide more than 50% was made a liquid at room temperature. In the ion complex, when the molar ratio of N-methylacetamide was 50% or under, the complex had electric conductivity. The ion complex with the molar ratios of N-methylacetamide of 50% had the highest electric conductivity. On the other hand, when the molar ratio of N-methylacetamide was more than 50%, the complex had ionic conductivity.

If the mole ratio of the N-methylacetamide is less than 50%, it is not possible to complete the reaction with the lithium salt not completely dissolved in the N-methylacetamide.

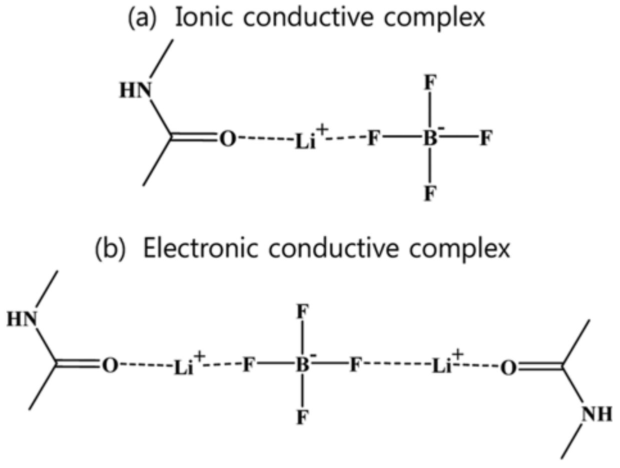

Fig. 1. Proposed Structure of the Li/N-methylacetamide complex.

The electric conductivity of the $LiBF_4$/N-methylacetamide complex at a molar ratio of 1 : 1 reaches 5.025×10^{-3} mS/cm^2. The $LiBF_4$/N-methylacetamide complex at a molar ratio of 1 : 1 was present in solid at room temperature. This result can be described as that of the coupling structure of the complex [22]. Increasing the concentration of N-methylacetamide, the structure is coupled one $LiBF_4$ and one N-methylacetamide are increased in the complex. Decreasing the concentration of N-methylacetamide, the structure is coupled N-methylacetamide-Li-BF_4-Li-N-methylacetamide are increased in the complex. We considered such a structure the reason for creating the electrical conductivity of the complex.

Fig. 2 shows the FT-IR spectra of the $LiBF_4$/N-methylacetamide complex with various molar ratios between 1,700 and 1,600 cm^{-1}. The band at 1,647 cm^{-1} is assigned to the C=O stretching mode of N-methylacetamide [23]. The C=O stretching band changes significantly and splits into two components located at 1,625 and 1,662 cm^{-1} upon introducing $LiBF_4$ into the N-methylacetamide. Considering the resonance structure of N-methylacetamide, the Li^+ ions have a tendency to coordinate with the O atoms in the C=O group

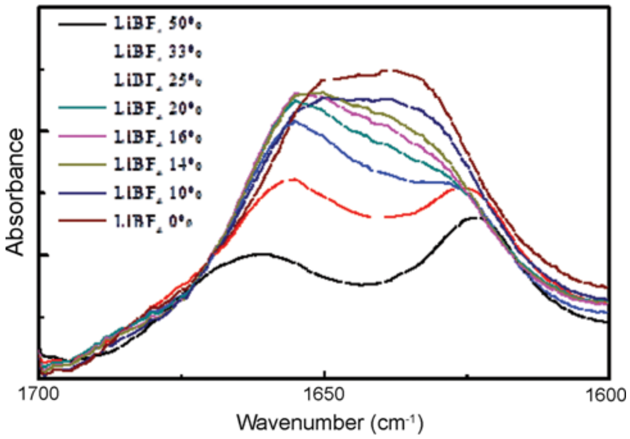

Fig. 2. Evolution of FT-IR spectra of the C=O stretching mode in the $LiBF_4$/N-methylacetamide complex with different molar ratios.

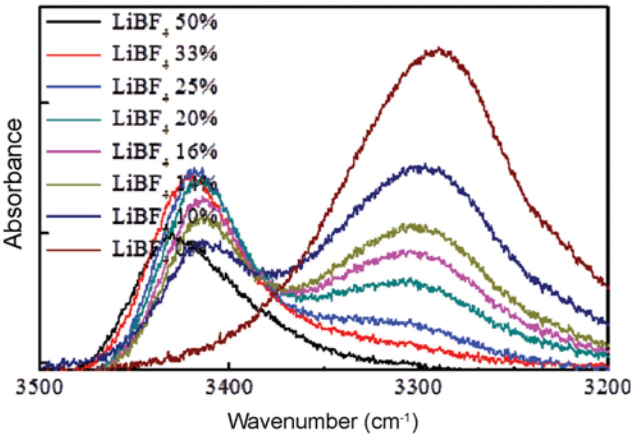

Fig. 3. FT-IR spectra of the $LiBF_4$/N-methylacetamide complex with different molar ratios in the N-H stretching mode region.

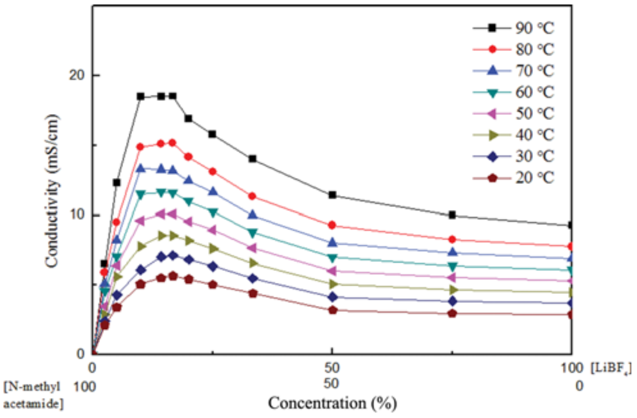

Fig. 5. Ionic conductivity of the $LiBF_4$/N-methylacetamide complex as a function of molar ratio of [$LiBF_4$]/[N-methylacetamide].

because these O atoms are negatively charged in the complex system. This interaction results in the shifting of the C=O stretching mode which shifts from 1,647 to 1,662 cm^{-1}. The intensity of the component at 1,625 cm^{-1} increases markedly with decreasing $LiBF_4$ concentration, indicating that there is a large amount of O atoms in N-methylacetamide interacting with the Li^+ ions and, therefore, a stronger interaction occurs when the N-methylacetamide concentration is high.

Fig. 3 shows the FT-IR spectra of the $LiBF_4$/N-methylacetamide complex with different molar ratios in the N-H stretching mode region. For all concentrations, the component at 3,295 cm^{-1} corresponds to the hydrogen-bonded N–H stretch, and the component at 3,420 cm^{-1} corresponds to the free N-H stretch [24]. It is understandable that when the Li^+ ions coordinate strongly with the C=O group of N-methylacetamide, part of the F atoms of BF_4^- anion are absent from coordination with the Li^+ ions and possess negative charges.

Fig. 4 shows the Raman spectra $LiBF_4$/N-methylacetamide complex with different molar ratios. It can be seen that this broad band shifts from 765 cm^{-1} at low salt concentration to 779 cm^{-1} at high lithium salt concentration. For the $LiBF_4$/N-methylacetamide complex, the peak of the F atom of BF_4 shifts to higher frequencies; we attribute the shifting to the interaction between the BF_4 group of lithium tetrafluoroborate and the N-H group of N-methylacetamide via hydrogen bonding as confirmed by the N-H stretching modes.

Fig. 5 shows the ionic conductivity of $LiBF_4$/N-methylacetamide complex in propylene carbonate. From 20 to 90 °C, the ionic conductivity of 1.0 M $LiBF_4$/N-methylacetamide complex solution linearly increased with temperature, as expected. For the $LiBF_4$/N-methylacetamide complex at a molar ratio between 1 : 1 and 1 : 5, the ionic conductivity increased with decreasing salt concentration over the entire temperature range studied.

Fig. 6 showd the ionic conductivity at different temperatures for concentration of ion complex dissolved in PC, when the molar ratio of the $LiBF_4$/N-methylacetamide complex is 1 : 1. At room temperature, the ionic conductivity of $LiBF_4$/N-methylacetamide complex solution increased linearly with concentration reaching 4.72 mS/cm at 0.8 M. After 0.8 M of concentration, the ionic conductivity did not vary significantly. This could be because $LiBF_4$/N-

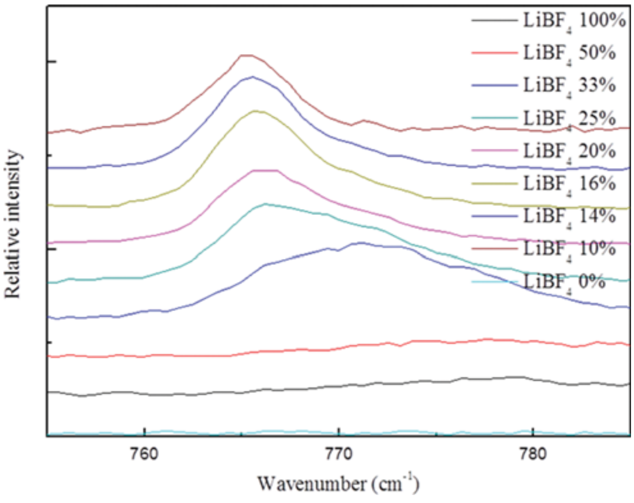

Fig. 4. Raman spectra of the $LiBF_4$/N-methylacetamide complex with different molar ratios.

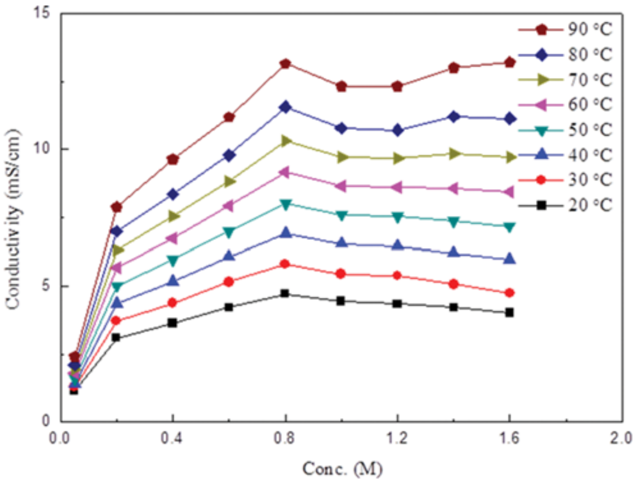

Fig. 6. Ionic conductivity of $LiBF_4$/N-methylacetamide complex at a molar ratio 1 : 1 in propylene carbonate.

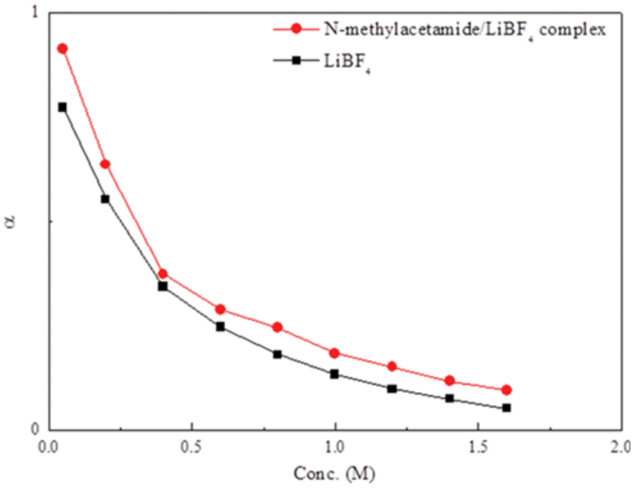

Fig. 7. Degree of dissociation $LiBF_4$/N-methylacetamide complex and $LiBF_4$ with concentration.

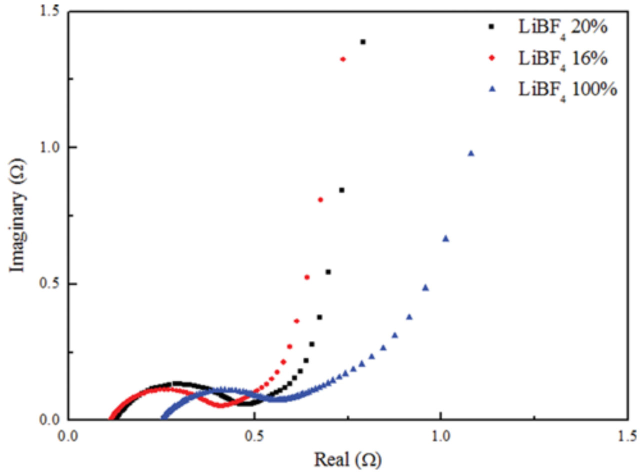

Fig. 8. Nyquist plots of supercapacitors by using $LiBF_4$/N-methylacetamide complex.

methylacetamide complex dissolved up to 1.6 M in PC, but $LiBF_4$/N-methylacetamide complex only dissociated at maximum of 0.8 M. When the temperature increased from 20 to 90 °C, the ionic conductivity of 1.0 M $LiBF_4$/N-methylacetamide complex solution linearly increased with temperature, as expected.

Fig. 7 shows the degree of dissociation of the 1 : 1 $LiBF_4$/N-methylacetamide complex and $LiBF_4$ calculated from Fig. 6. The degree of dissociation (α) was calculated as follows (ref):

$$\Lambda = \frac{k}{c}$$

$$\alpha = \frac{\Lambda}{\Lambda^0}$$

where k was specific conductivity (S/cm), c was concentration (M), Λ was the molar conductivity (S·cm/mol), and Λ^0 was molar conductance at infinite dilution (S·cm/mol).

The degree of dissociation of complex was higher than that of lithium salt over the entire concentration range. $LiBF_4$ is an ion conductor, N-methylacetamide is not an ion conductor. Nevertheless, when producing a complex with $LiBF_4$ and N-methylacetamide, it was confirmed that the ionic conductivity was higher than the ionic conductivity of $LiBF_4$.

The increase of ionic conductivity is in good agreement with the increase of the effective ions in the $LiBF_4$/N-methylacetamide complex. Thus, the ionic conductivities of the $LiBF_4$/N-methylacetamide complex with different molar ratios depend on the relative amount of effective ions in the complex. The number of charge carriers is proportional to the ionic conductivity. The number of charge carriers should be referred to the effective number of charge carriers. As N-methylacetamide concentration increases, the effective number of charge carriers also increases. As LiBF4 concentration increases, the number of charge carriers also increases; however, the effective number of charge carries decreases due to the strong ionic association.

Figs. 8-11 represent the electrochemical characteristics of supercapacitor with 70 μm thick $LiMn_2O_4$/C composite positive electrode, 140 μm thick C negative electrode, and 1 M $LiBF_4$/N-methylacetamide complex electrolyte solution. The Nyquist plots of AC impedance analysis of fresh supercapacitors in the frequency range of 0.01-100,000 Hz with voltage amplitude of ±5 mV are shown in Fig. 8.

Fig. 8 shows a typical Nyqist plot of fresh supercapacitors [25]. Semicircle was observed at the high frequency regions (100-100,000 Hz) and Warburg mass effect was observed at the low frequency ranges (0.01-100 Hz). In comparing the Nyquist plots, it is obvious that the solution resistance (Rsol) for the $LiBF_4$/N-methylacetamide complex was lower than that of the $LiBF_4$, corresponding to a decreasing Rsol value with increasing the concentration of N-methylacetamide, which was confirmed by ionic conductivity in Fig. 4. The charge transport resistance (Rct) was similar in the high-to-medium frequencies region. And, in the low-frequency range, the steep line indicated faster ion diffusion in the electrolyte and adsorption onto the electrode surface and closer behavior to ideal capacitors. A $LiBF_4$/N-methylacetamide complex containing 20% of $LiBF_4$ and 80% of N-methylacetamide showed the lowest solution resistance of 13 mΩ and charge transport resistance of 40 mΩ

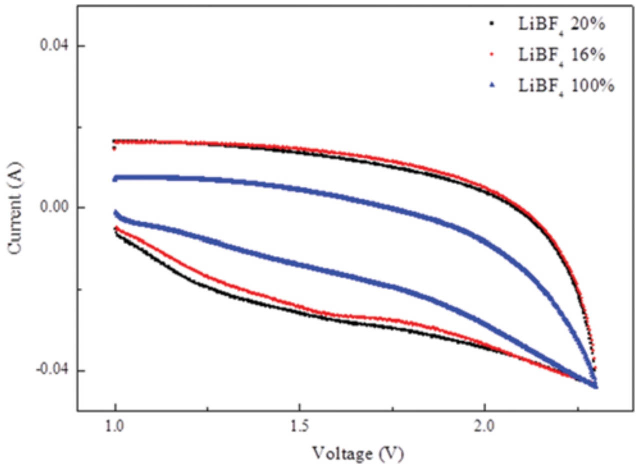

Fig. 9. Cyclic voltammograms of supercapacitors by using $LiBF_4$/N-methylacetamide complex at 5 mV/sec.

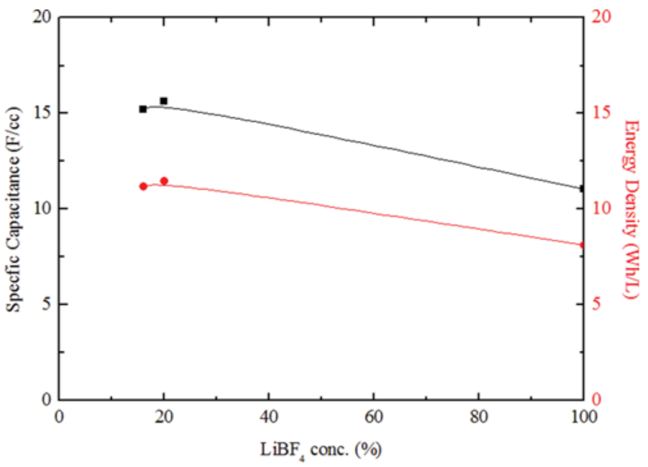

Fig. 10. Specific capacitances and energy densities of supercapacitors with various compositions of LiBF$_4$/N-methylacetamide complexes.

Fig. 9 shows the cyclic voltammograms of fresh supercapacitors. The capacitance of supercapacitor used by complexes was higher than the capacitance of supercapacitor with LiBF$_4$ 100%. The specific capacitances and energy densities of fresh supercapacitors calculated from cyclic voltammograms are shown in Fig. 10 [25]. The specific capacitances and energy densities decreased as the ratio of LiBF$_4$ increased. The maximum specific capacity and energy density of 15.62 F/cc and 11.47 Wh/L were observed for the LiBF$_4$/N-methylacetamide complex containing 20% of LiBF$_4$. The values were much higher than 11.2 F/cc and 8.2 Wh/L of the LiBF$_4$ electrolyte. These could be explained by the degree of dissociation of the LiBF$_4$/N-methylacetamide complex.

Fig. 11 shows the total pseudocapacitor capacity during charge/discharge cycles at 10 C-rate between 1.0 and 2.3 V. Most of the capacity decreases were observed within initial 20 cycles regardless of the concentration of LiBF$_4$/N-methylacetamide complex. Decreasing of the capacities of the supercapacitors in charge-discharge curve, which is determined in the initial. The reduction of the capacities confirmed the similar over the entire concentration of the N-methylacetamide range.

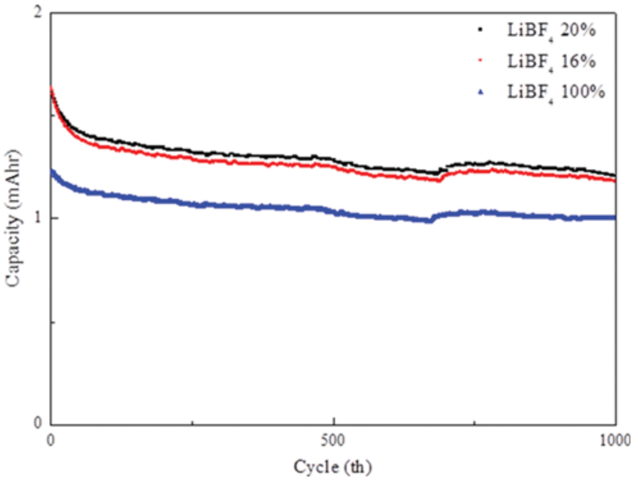

Fig. 11. Cycle performance of supercapacitors by using LiBF$_4$/N-methylacetamide complex.

CONCLUSION

We prepared an ion complex having ion conductivity or electric conductivity depending on the concentration by using lithium tetrafluoroborate and N-methylacetamide. Lithium tetrafluoroborate and N-methylacetamide complexes were prepared in various compositions. In the ion complex, when the molar ratio of N-methylacetamide was 50% or under, the complex had electric conductivity. On the other hand, when the molar ratio of N-methylacetamide was more than 50%, the complex had ionic conductivity. The room temperature ionic conductivities of some compositions in propylene carbonate of the complex exceed 6 mS/cm. And room temperature electric conductivity of the complex is 5.025×10^{-3} mS/cm^2.

To get the optimum composition of Lithium tetrafluoroborate and N-methylacetamide complex for supercapacitor, electrolytes were prepared by using Lithium tetrafluoroborate and N-methylacetamide complex of various compositions and solvent of propylene carbonate. A supercapacitor with the operating voltage of 2.3 V, the specific capacitance of 15.62 F/cc and the energy density of 11.47 Wh/L could be obtained in case of adopting lithium tetrafluoroborate and N-methylacetamide complex through the analyses such as cyclic voltammetry, electrochemical impedance analysis, life characteristics, etc. These are explained by degree of dissociation of lithium tetrafluoroborate and N-methylacetamide complex. In addition, capacitance of supercapacitor with LiBF$_4$/N-methylacetamide (1 : 4) complex after 1000 cycles at 10C-Rate was 21% higher than that of supercapacitor with LiBF$_4$.

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