Li^+ Insertion/Extraction Reaction into/from Carbon Electrode in Room Temperature Molten Salt using Asymmetric Quaternary Ammonium Cation

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Room Temperature Molten Salt (RTMS) recently has attracted many researchers as a new solvent for electrochemical process. Due to the extremely low vapor pressure and flame resistant properties, RTMS could be a candidate electrolyte for the lithium batteries with improved safety in the next generation.

Chemical and physical properties of the RTMS basically depends on the combination of cation and anion species. One of the authors, Matsumoto, discovered the useful series with asymmetric quaternary ammonium cations, which enabled the reversible plating/stripping of lithium metal[1]. Then authors have investigated the electrochemical reaction of several electrode material in practical use in the half-cell using the ammonium RTMS as an electrolyte. We have already found that a few kind of the ammonium RTMS showed the excellent properties in Li/$LiCoO_2$ cell [2]. Our main purpose is to demonstrate the properties of the “whole cell” system using the RTMS. In this paper, Li insertion/extraction reaction into/from carbon electrode was studied.

N-methyl-N-proopylpiperidinium bis(trifluoro methanesulfonyl)imide (PP13-TFSI, Fig.1) were used for the electrolyte base for the experimental cell. After the vacuum-drying of PP13-TFSI, supporting electrolyte LiTFSI which was dried separately in advance was added to PP13-TFSI. Concentration of the Li^+ was adjusted to be $[Li^+]/([Li^+]+[PP13])=0.12$. This corresponds to the mole concentration of 0.4 M. Conventional two-electrode cell was used for the electrochemical measurement. Working electrode was prepared by coating the anode mixture (carbon active material + PVdF binder with a N-methyl-pyrrodinone as a dilluent) onto the copper current collector. Li metal and glass filter were used as a counter electrode and separator, respectively. Galvanostatic charge and discharge was conducted to examine the Li^+ insertion/extraction behavior of the electrode.

Fig.2a shows the charge-discharge curves for the acetylene black (AB, from Denka, Co. Ltd) at the C/10 current rate assuming that AB would have the theoretical capacity of 372 mAh/g. For the first cycle, large irreversible capacity was observed and the Coulombic efficiency was c.a. 33%. First discharge capacity was 148mAh/g, which was a little bit smaller than the discharge capacity of AB (more than 200mAh/g) in the liquid electrolyte (1.0M $LiPF_6$/EC-DEC(1:1), Fig.2b). Lithium insertion/extraction into/from AB seems to be quite reversible, and it is implied that the lower-crystallized carbon could be a good candidate for anode material of RTMS battery. In the case of Galvanostatic charge-discharge test of carbon material with high crystallinity, for example graphitized MCMB, showed extremely small capacity of c.a. 30mAh/g in the electrolyte with PP13-TFSI base. When the charge method was changed to the CCCV (constant-current and constant-voltage) mode, discharge capacity increased (Fig.2c). This result indicates that the charge transfer resistance of the lithium intercalation into the carbon at the edge plane would be rather high in PP13-TFSI. Anyway, the results in this study could mark the beginning of the possibility of PP13-TFSI as an electrolyte for lithium-ion type battery because this could be the first example of the observation of lithium insertion/extraction into/from the carbon anode in the neat RTMS.

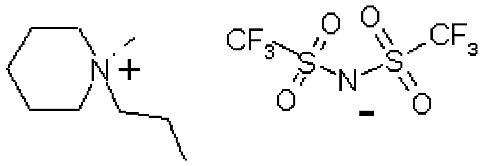

Fig.1 PP13-TFSI structure.

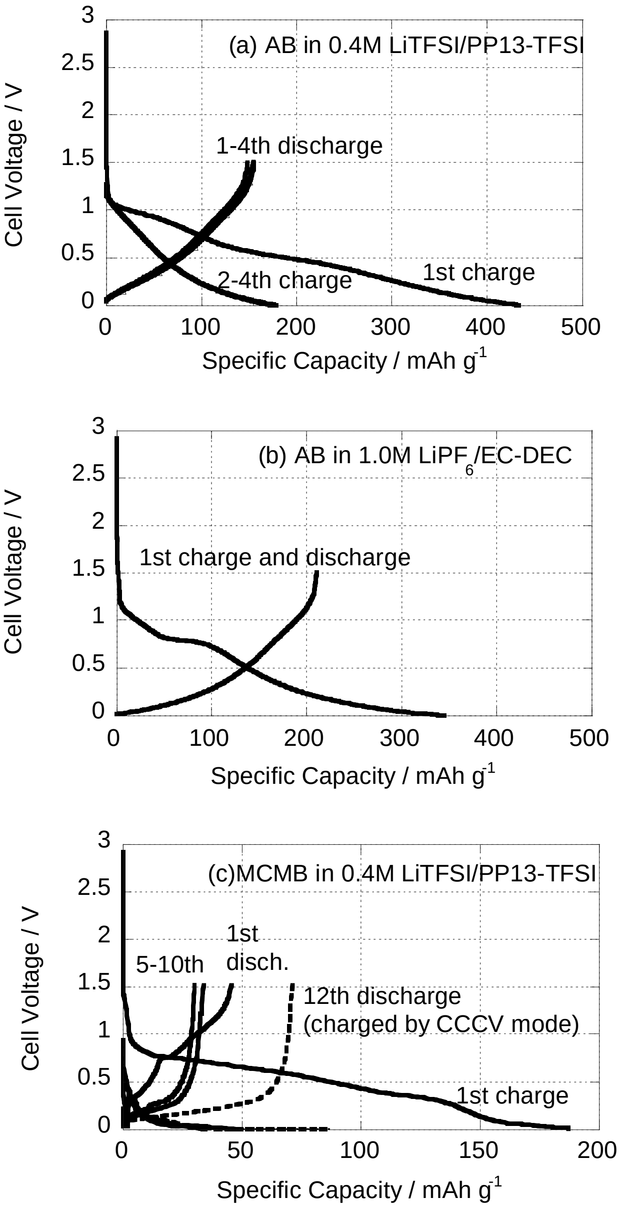

Fig.2 Charge-discharge curves for the initial few cycles of (a) acetylene black in 0.4M LiTFSI/PP13-TFSI, (b) acetylene black in 1.0M $LiPF_6$/EC-DEC, and (c) MCMB in 0.4M LiTFSI/PP13-TFSI at the C/10 current rate in the voltage region of 0-1.5V.

REFERENCES

1. H. Matsumoto, et al., Molten Salts XII, edited by P.C.Trulove et al., ECS, Pennington, NJ, 2000, p.186
2. H. Sakaebe, et al., Proc. of the Japanese Battery Symposium, Yokohama, 2B04, (2001).