Fabrication of All-Solid-State Sodium Polymer Battery

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All-solid-state lithium polymer batteries have been extensively studied to realize safe batteries with high energy density [1]. As solid polymer electrolyte (SPE) consists of a lithium salt and a polar polymer matrix, the lithium salt can be replaced with a sodium salt to be applied to all-solid-state sodium polymer batteries which is free from minor metals like lithium. We expect Al foil can be used as bipolar current collector because of no alloy formation between Al and Na [2]. Although ionic conductivity and electrochemical stability window of Na SPE have been widely studied, reactivity of the SPE are still unclear against electrode materials and metals. In this study, we examine not only ionic conductivity of Na SPE but also electrochemical properties of different electrode materials in the all-solid-state sodium polymer batteries.

Na SPE was prepared by dissolving sodium bis(trifluoromethanesulfonyl)amide (NaTFSA) and polyethylene oxide (PEO) at a $[Na^+]/[EO]$ ratio of 1/20 in deionized water and drying. Positive electrodes were prepared by mixing active materials such as P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ (P2-NiMn), AB, and PVdF with *N*-methylpyrrolidone and casting on Al foil current collector followed by drying the electrodes at 80 ºC under vacuum for overnight. Na metal and negative electrode materials such as hard carbon were used as negative electrode materials. Electrochemical properties of assembled all-solid-state sodium polymer cells were evaluated at 45 °C.

Fig. 1 shows charge/discharge curves of Na//P2-NiMn cells with electrolyte of PEO20:NaTFSA and 1 mol dm^{-3} $NaPF_6$/propylene carbonate (PC) in the voltage range of 2.5 – 4.5 V at 45 and 25 °C, respectively. The SPE cell shows stepwise initial charge curve similar to that for the PC cell. In contrast, discharge curve of the SPE cell is gently sloping and less stepwise without any plateau above 4.0 V compared to that for the PC cell, which is probably due to decomposition of SPE and/or increase of electrode resistance caused by large volume shrinkage of P2/O2-NiMn transition on charge above 4.1 V [2]. Figure 2 shows that lowering the upper cut-off voltage to 3.8 V enhances reversibility of Na extraction/insertion from/into P2-NiMn in the Na SPE cell at 45 °C. We will discuss detailed data of solidified Na-ion batteries with the SPE.

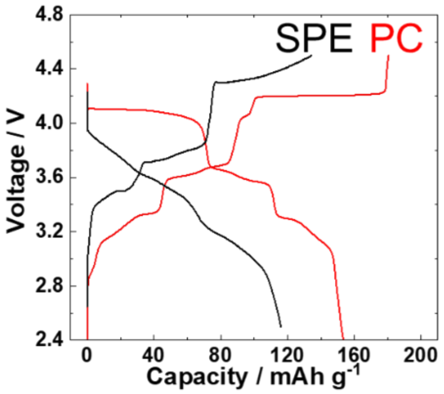

Figure 1 Charge/discharge curves of Na//P2-NiMn cells with electrolyte of PEO20:NaTFSA and 1 M $NaPF_6$/PC at 45 and 25 °C, respectively.

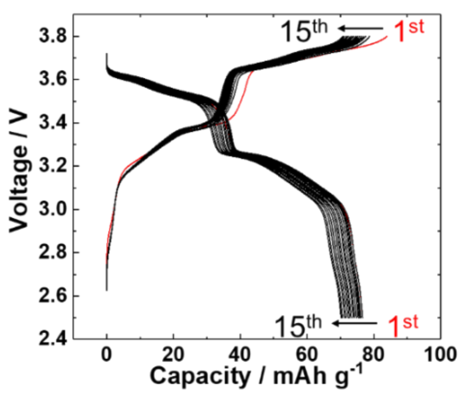

Figure 2 Charge/discharge curves of Na/PEO20:NaTFSA/P2-NiMn cell cycled at 45 °C.

References:

[1] R. C. Agrawal, and G. P. Pandey, *J. Phys. D: Appl. Phys.*, **41**, 223001 (2008).
[2] K. Kubota, S. Komaba *et al., Chem. Rect.* in press (2018).