Electrochemical performance of micro-sized Sn for Na-ion Battery

Mika Fukunishi\textsuperscript{a}, Kei Kubota\textsuperscript{a,b}, Mouad Dahbi\textsuperscript{a,b}, Satoshi Yasuno\textsuperscript{c}, and Shinichi Komaba\textsuperscript{a,b}
\textsuperscript{a}Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601
\textsuperscript{b}Unit of Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto, 615-8520
\textsuperscript{c}JASRI, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198
m.fukunishi@rs.tus.ac.jp

Electrode materials for Na-ion battery have been extensively studied to realize low-cost and high-energy battery. Hard carbon, which delivers 300 mAh g\(^{-1}\), is one of the promising candidates as the negative electrode.\cite{1} However, its reversible capacity (actually energy density) is not high enough compared to LIB. Therefore, materials with higher capacity are still required to high energy density Na-ion battery. We reported that nano-sized Sn electrode delivers a reversible capacity of ca. 600 mAh g\(^{-1}\) with a good capacity retention in a voltage range of 0.0 – 0.65 V, which corresponds to 70\% of the theoretical capacity of 847 mAh g\(^{-1}\) for Sn / Na\(_2\)Sn\(_4\) sodiation.\cite{2} In this research, the impact of the Sn particle size of electrochemical properties was examined for practical Na-ion battery and the current density on the electrode surface is discussed based on the results of surface analyses; secondary ion mass spectroscopy and soft and hard photoelectron spectroscopy.

To prepare the working electrode, 80 wt\% Sn powder (<150 nm or 10 μm, Sigma-Aldrich Co., Ltd), 10 wt\% sodium polyacrylate (PANa) and 10 wt\% graphite were mixed with 10 vol\% methanol aqueous solution, and the resultant slurry was pasted onto an Al foil. Na metal was used as the counter electrode and 1 mol dm\(^{-3}\) NaPF\(_6\)/EC:DEC:FEC (49:49:2 vol\%) was used as the electrolyte. The charge/discharge measurements were carried out using coin-type cell with a sodiation/desodiation current density of 50/50 or 50/750 mA g\(^{-1}\).

Nano-sized Sn delivers reversible capacity of ca. 600 mAh g\(^{-1}\) over 100 cycles at 50 mA g\(^{-1}\) (Fig. 1(a)). On the other hand, micro-sized Sn delivers reversible capacity of ca. 700 mAh g\(^{-1}\) for 10 cycles but it declines rapidly after 20 cycles as seen in Fig. 1(b). However, Figure 1(c) reveals that micro-sized Sn does demonstrate better capacity retention at a higher desodiation rate of 750 mA g\(^{-1}\), which means it delivers ca. 600 mAh g\(^{-1}\) over 60 cycles. By comparing Figures 1(b) and 1(c), the desodiation plateau at 0.18 V disappears and that at 0.55 V shifts to 0.6 V. This means that the phase transition during desodiation depends on the current density, resulting in the different capacity retention. We will discuss the details of the difference between nano- and micro-sized Sn particles from surface analysis data.

![Fig. 1 Charge/discharge curves of Sn particle size of (a) φ150 nm at a desodiation current density of 50 mA g\(^{-1}\), (b) φ10 μm at 50 mA g\(^{-1}\), and (c) φ10 μm at 750 mA g\(^{-1}\) in Na cells.](image)

\[2\] M. Fukunishi, S. Komaba \textit{et al}., 2014 ECS / SMEQ Joint Meeting, Mexico, Abs. #94 (2014).