P2- and P3-type Na$_x$Cr$_x$Ti$_{1-x}$O$_2$ Layered Oxides for Rechargeable Sodium Batteries

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Rechargeable Na batteries are promising to realize sustainable energy development in the future because of the material abundance, and many electrode materials have been actively researched in the world. O3-type NaCrO$_2$ is known to show excellent cycle performance and thermal stability. Additionally, O3 NaCrO$_2$ shows second highest operating voltage among O3-type layered oxides, next to O3 NaFeO$_2$. In this study, to increase of the operating voltage of Cr$^{3+}$/Cr$^{4+}$ redox by inductive effect, Ti$^{4+}$ is substituted for Cr$^{3+}$, according to the formula of Na$_x$Cr$_x$Ti$_{1-x}$O$_2$ ($0.5 \leq x \leq 1$) and crystal structures and electrode performance are systematically examined as positive and negative electrode materials for rechargeable Na batteries.

After the survey on the Na-Cr-Ti-O ternary oxide system, three different phases were isolated in the range of $0.5 \leq x < 1$. For the sample of $x = 0.80$ at 950 °C, Na-deficient O3 phase, Na$_{0.8}$Cr$_{0.8}$Ti$_{0.2}$O$_2$, is found. For the sample of $x = 0.67$ at 1000 °C, P2-type phase, Na$_{2/3}$Cr$_{2/3}$Ti$_{1/3}$O$_2$, is observed. Similar to our work, P2 Na$_{0.6}$Cr$_{0.6}$Ti$_{0.4}$O$_2$ is also found in the literature. Additionally, for the sample of $x = 0.58$ at 800 °C, Bragg diffraction lines of the sample, Na$_{0.58}$Cr$_{0.58}$Ti$_{0.42}$O$_2$, were assigned into P3-type layered structure. These samples with different layered stacking manners are used as both positive and negative electrodes. Especially, P2 Na$_{2/3}$Cr$_{2/3}$Ti$_{1/3}$O$_2$ and P3 Na$_{0.58}$Cr$_{0.58}$Ti$_{0.42}$O$_2$ show excellent cyclability, and operating voltage of the P2 phase is much higher than that of O3 NaCrO$_2$. In addition, both samples show excellent rate capability as shown in Figure 1c, d. Large reversible capacities are observed for both samples even at $>3,000$ mA g$^{-1}$.

From these results, we will further discuss the impact of Ti$^{4+}$-substitution for Cr$^{3+}$ on electrode performance and reaction mechanisms in Na cells for more details.

Figure 1. Rate capability of (left) P2 Na$_{2/3}$Cr$_{2/3}$Ti$_{1/3}$O$_2$ and (right) P3 Na$_{0.58}$Cr$_{0.58}$Ti$_{0.42}$O$_2$ in Na cells.

References