P2- and P3-type $Na_xCr_xTi_{1-x}O_2$ 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 $NaCrO_2$[1, 2] is known to show excellent cycle performance and thermal stability[3]. 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 $Na_xCr_xTi_{1-x}O_2$ ($0.5 \leq x \leq 1$) 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.[4] 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 $Na_{2/3}Cr_{2/3}Ti_{1/3}O_2$ as the positive electrode and P3 $Na_{0.58}Cr_{0.58}Ti_{0.42}O_2$ as the negative electrode shows 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.

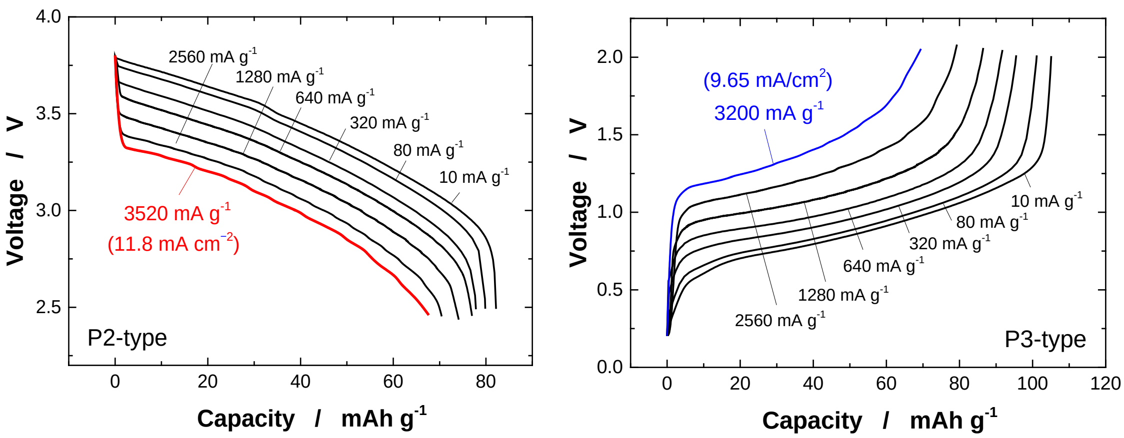

Figure 1. Rate capability of (left) P2 $Na_{2/3}Cr_{2/3}Ti_{1/3}O_2$ and (right) P3 $Na_{0.58}Cr_{0.58}Ti_{0.42}O_2$ in Na cells.

References

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