

Thermal Stability of  $\text{NaCrO}_2$  for Rechargeable Sodium Batteries: Studies by Differential Scanning Calorimetry, and High-Temperature X-Ray Diffraction

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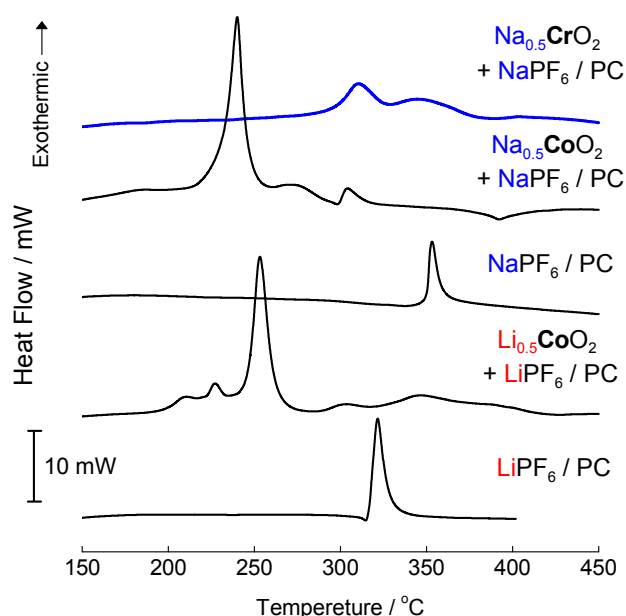
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The demand for large-scale batteries is rapidly increasing, which potentially provides sustainable energy development. In the past few years, research interest on rechargeable sodium batteries (Na-ion batteries) is completely renewed for the large-scale applications. Na-ion batteries, operable at room temperature, consist of two different sodium insertion materials as positive and negative electrodes with aprotic solvent as electrolyte. Safety is essential for battery systems, especially for the large scale applications. Nevertheless, only few studies are available in the literature.[1,2]

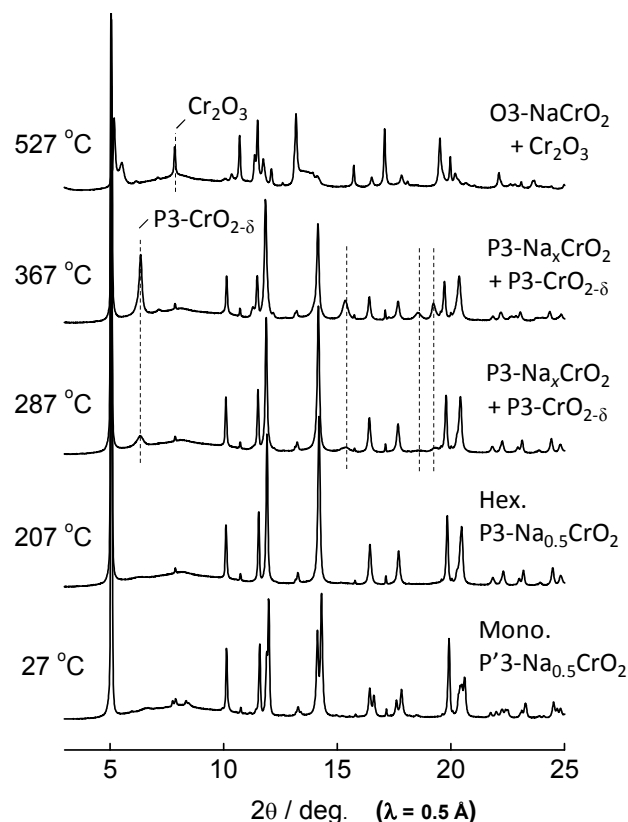
Our group reported that O3-type  $\text{NaCrO}_2$  was electrochemically active in a Na cell, whereas a lithium counterpart,  $\text{LiCrO}_2$ , was inactive in a Li cell.[3] Very recently, a study on thermal stability of  $\text{NaCrO}_2$  by accelerating rate calorimetry (ARC) revealed that  $\text{NaCrO}_2$  is a fundamentally safe positive electrode material even with the aprotic solvent.[1] In this study, the thermal stability of  $\text{Na}_x\text{CrO}_2$  is examined by differential scanning calorimetry (DSC), thermogravimetry (TG), and high-temperature X-ray diffraction (HT-XRD), and the results are compared with those of other layered oxides.

Figure 1 compares DSC curves with different electrode materials,  $\text{Na}_{0.5}\text{CrO}_2$ ,  $\text{Na}_{0.5}\text{CoO}_2$ , and  $\text{Li}_{0.5}\text{CoO}_2$  with the aprotic electrolyte ( $\text{NaPF}_6$  or  $\text{LiPF}_6$  in propylene carbonate, PC). As shown in Figure 1, broad exothermic peaks are observed for  $\text{Na}_{0.5}\text{CrO}_2$ . A mild exothermic reaction with electrolyte is noted in comparison to  $\text{Na}_{0.5}\text{CoO}_2$  and  $\text{Li}_{0.5}\text{CoO}_2$ . This observation is consistent with the results of ARC.[1] To further study structural changes at elevated temperatures, high-temperature X-ray diffraction was conducted in the temperature range of 27 – 527 °C (Figure 2). Diffraction lines from  $\text{Na}_{0.5}\text{CrO}_2$  at 27 °C can be assigned into a distorted layered structure with a monoclinic lattice (P'3-phase). As increase in temperature, monoclinic distortion is relaxed, and a single phase with a rhombohedral lattice (P3-phase) is found at 207 °C. Some of new diffraction lines appear by further heating >250 °C. These lines can be assigned into a P3-phase with anomalously short interlayer distance (4.51 Å). This phase is also found in the previous report, and is proposed as the crystallization of Na-deficient P3-phase ( $\text{P3-CrO}_{2-\delta}$ ).[1] Another diffraction line is found at 7.8 degrees in 2-theta by heating >400 °C. This peak originates from  $\text{Cr}_2\text{O}_3$  with a corundum-type structure.

In conclusion, the heating beyond 250 °C results in the segregation of Na-rich and Na-deficient P3-phases. The Na-deficient phase is thermally decomposed (approximately 400 °C) by which oxygen is released from  $\text{Na}_{0.5}\text{CrO}_2$ . The high decomposition temperature indicates superior thermal stability of  $\text{Na}_{0.5}\text{CrO}_2$ . From these results, we will further discuss thermal stability of sodium insertion layered oxides as electrode materials for rechargeable sodium batteries.



**Figure 1.** DSC curves of  $\text{Na}_{0.5}\text{CrO}_2$ ,  $\text{Na}_{0.5}\text{CoO}_2$ , and  $\text{Li}_{0.5}\text{CoO}_2$  (6.0 mg) with electrolyte (2.5 mg). Pressure resistive vessels (~10 MPa) were utilized for the measurement.



**Figure 2.** Synchrotron high-temperature X-ray diffraction patterns of  $\text{Na}_{0.5}\text{CrO}_2$  at elevated temperatures.

#### References

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