

## Phase transition behavior of NaCrO<sub>2</sub> during sodium extraction studied by synchrotron-based X-ray diffraction and absorption

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### Introduction

Recently, rechargeable batteries with high energy density and low cost are in great demand as energy sources for various applications. Lithium ion batteries are being widely used in portable electronics and considered as the promising power sources for future electric vehicles. However, the large scale commercialization of electric vehicles using lithium batteries might be hindered significantly due to the relatively high cost and limited resource of lithium. In contrast, the abundance of sodium (2.75%) is about three orders of magnitude more than that of lithium (0.002%). Sodium has the similar electronic structure as lithium. Rechargeable sodium-ion batteries are promising energy storage candidate for large-scale and cost sensitive applications.

Layered structured intercalation compounds are considered as promising cathode materials for sodium-ion batteries as enlightened by their use in lithium-ion batteries, including NaCoO<sub>2</sub>, NaMnO<sub>2</sub>, NaCrO<sub>2</sub>, NaNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub>, NaFeMnO<sub>2</sub>, NaNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> etc.. Among them, NaCrO<sub>2</sub> is the most promising one, since NaCrO<sub>2</sub> has desirable flat and smooth charge/discharge voltage plateau, which is similar as the widely commercialized LiCoO<sub>2</sub> cathode for lithium-ion batteries [1, 2]. In addition, NaCrO<sub>2</sub> has the highest thermal stability at the charged state comparing with LiCoO<sub>2</sub>, LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, even LiFePO<sub>4</sub>, making it a potentially safer cathode material [3]. Interestingly, LiCrO<sub>2</sub> with similar layered structure (space group: R-3m) is electrochemically inactive for lithium batteries. Previous study suggests that it is due to the so called “freeze effects” of Cr<sup>6+</sup> ions at tetrahedral sites after delithiation. In charging process, the oxidized Cr<sup>4+</sup> has a tendency to disproportionate into Cr<sup>3+</sup> and Cr<sup>6+</sup> with the stable electronic configuration of d3 and d0, respectively. The Cr<sup>6+</sup> cations prefer to migrate from the octahedral sites to the interstitial tetrahedral sites and to be “freeze” there in both location and electronic configuration, since the size of Cr<sup>6+</sup> matches the space of the interstitial tetrahedral site very well. As a result, LiCrO<sub>2</sub> lost its electrochemical activity after first charge. In contrast, NaCrO<sub>2</sub> with similar structure as LiCrO<sub>2</sub> shows a reversible capacity around 110 mAh g<sup>-1</sup> in sodium-ion batteries, which

means half of Na can be reversibly extracted and inserted back per NaCrO<sub>2</sub>. Previous study attributed the good performance of NaCrO<sub>2</sub> to the mismatch between Cr<sup>6+</sup> ion and the interstitial tetrahedral site of NaCrO<sub>2</sub> structure [2]. The structure change during Na de-intercalation was studied using ex-situ XRD [4], which suggested a phase transition from hexagonal O3 to monoclinic P3 structure, similar as the structure change during NaCrO<sub>2</sub> chemical de-intercalation. However, the detailed structure evolution, the valence change of Cr and ion coordination during electrochemical charging has not been thoroughly studied yet.

In this work, synchrotron-based in-situ X-ray diffraction was utilized to monitor the structure evolution of layered NaCrO<sub>2</sub> cathode material during electrochemical charge in a real time. Three solid-solution phases with two two-phase co-existence regions were observed. The local structural changes and the oxidation state changes of Cr were characterized by ex-situ X-ray absorption (XAS) technique. More details will be presented in the meeting.

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### References

- [1] J. J. Ding, Y. N. Zhou, Q. Sun, Z. W. Fu, *Electrochem. Commun.* 22 (2012) 85.
- [2] S. Komaba, C. Takei, T. Nakayama, A. Ogata, N. Yabuuchi, *Electrochem. Commun.* 12 (2010) 355.
- [3] X. Xia, J. R. Dahn, *Electrochem. Solid-State Lett.* 15 (2012) A1.
- [4] S. Komaba, T. Nakayama, A. Ogata, T. Shimizu, C. Takei, S. Takada, A. Hokura, I. Nakai, *ECS Trans.* 16 (2009) 43.