High-potential Cathode Properties of NASICON-type Cr(III)-based Phosphate

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Lithium-ion batteries have dominated the portable electronics market and nowadays its application is extending to larger-scale energy storage systems. As the market expands, sodium-ion batteries (SIBs) can be a possible alternative due to the abundance of sodium in the earth crust and the sea. However, inherently higher redox potential of Na/Na$^{+}$ than Li/Li$^{+}$ by ca. 0.35 V brings about lower operating voltages of a cell. To overcome this disadvantage, high-potential cathode materials for SIBs are required.

Based on the theoretical prediction,[1] we explored Cr$^{4+}$/Cr$^{3+}$ redox couple in polyanion framework to generate extremely high-potential in sodium cell. As an initiating example, NASICON-type Na$_3$Cr$_2$(PO$_4$)$_3$ showed reversible electrochemical activity at ca. 4.5 V vs. Na/Na$^+$ as shown in below Figure. The origin of capacity drop from 98 to 79 mAh g$^{-1}$ is a time-dependent degradation of the material itself. In addition to the well known high-potential with Ni$^{3+}$/Ni$^{2+}$ and Co$^{3+}$/Co$^{2+}$ redox couples, Cr$^{4+}$/Cr$^{3+}$ redox couple in several polyanion framework systems are now warrant exploration toward new high-voltage cathode materials.

In the poster, structural and valence state changes of NCP during the electrochemical reaction will be discussed with ex-situ X-ray diffraction/X-ray absorption spectroscopy together with possible degradation mechanisms.

![Figure](image.png)

**Figure** A galvanostatic charge/discharge curve during 1st cycle at constant rates of 58.5 mA g$^{-1}$ for charging and 117 mA g$^{-1}$ for discharging in Na half-cell with 1 M NaPF$_6$ EC:DEC (1:1 vol.)

References: