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 $Na_3Cr_2(PO_4)_3$ 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 witu *ex-situ* X-ray diffraction/X-ray absorption spectroscopy together with possible degradation mechanisms.

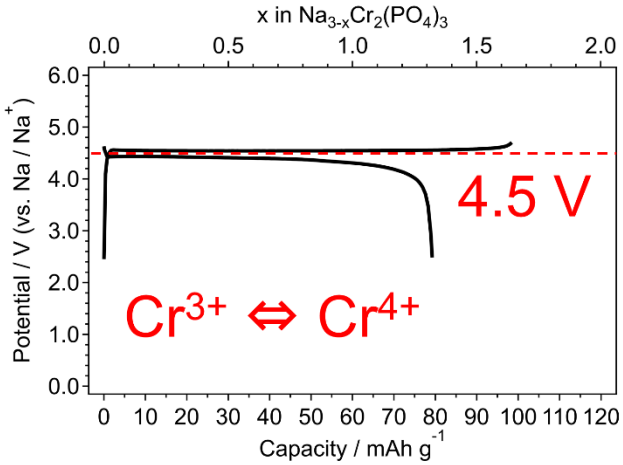

Figure A galvanostatic charge/discharge curve during 1st cycle at constant rates of 58.5 mA g^{-1} for charging and 117 mA g^{-1} for discharging in Na half-cell with 1 M $NaPF_6$ EC:DEC (1:1 vol.)

References:

[1] G. Hautier, A. Jain, S.P. Ong, B. Kang, C. Moore, R. Doe, G. Ceder, Cham. Mater. 23 (2011) 3495-3508.