

Sidorenkite ( $\text{Na}_3\text{MnPO}_4\text{CO}_3$ ), a new intercalation cathode material for Na-ion batteries.

Hailong Chen<sup>1</sup>, Qing Hao<sup>1</sup>, Olivera Zivkovic<sup>2</sup>, Geoffroy Hautier<sup>1</sup>, Lin-Shu Du<sup>2</sup>, Yuanzhi Tang<sup>3</sup>, Yan-Yan Hu<sup>2,4</sup>, Xiaohua Ma<sup>1</sup>, Clare P. Grey<sup>2,4</sup>, Gerbrand Ceder<sup>1</sup>

1. Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave, Cambridge, MA 02139, USA
2. Department of Chemistry, Stony Brook University, 100 Nichols Road, Stony Brook, NY, 11794-3400, USA
3. School of Earth and Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Dr, Atlanta GA 30332-0340
4. Department of Chemistry, University of Cambridge, Lensfield Rd, CB2 1EW, Cambridge, UK

Recently Na-ion battery has attracted lots of attention and research efforts as a promising electrochemical energy storage technology. Many layered transition metal oxides, such as  $\text{NaMnO}_2$ , and polyanion compounds, such as  $\text{NaFePO}_4$ , have been studied as cathode materials for Na-ion batteries. Here we report a new polyanion cathode material, sidorenkite, on its synthesis, electrochemical performances and the Na ion intercalation mechanism.

Sidorenkite, formula being  $\text{Na}_3\text{MnPO}_4\text{CO}_3$ , belongs to a rarely studied chemical group, the carbonophosphates<sup>3</sup>. It was synthesized in our lab by hydrothermal method. The crystal structure was examined by high resolution synchrotron X-ray powder diffraction and Rietveld refinement. In the electrochemical tests, sidorenkite shows high discharge capacity of ~125 mAh/g, which corresponds to 1.3 Na intercalation per formula unit. As shown in Figure 1, two voltage plateaus are observed at ~3.1 and 4.0 V, which agrees with the computationally predicted voltage for  $\text{Mn}^{2+}/\text{Mn}^{3+}$  and  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox couples.

<sup>23</sup>Na solid state NMR, XANES, and in situ synchrotron X-ray diffraction were used to investigate the Na ion deintercalation and intercalation processes in sidorenkite. <sup>23</sup>Na NMR reveals that Na ion is first extracted from the 6-coordinated site at lower voltage and then from the 7-coordinated site at higher voltage. From the in situ XRD experiments a solid solution like phase evolution was observed in the electrochemical cycling of sidorenkite. The NMR, XNAES and electrochemical testing results together demonstrate that sidorenkite undergoes a very rarely seen 2-electron intercalation reaction in which both  $\text{Mn}^{2+}/\text{Mn}^{3+}$  and  $\text{Mn}^{3+}/\text{Mn}^{4+}$  redox couples are electrochemically active.

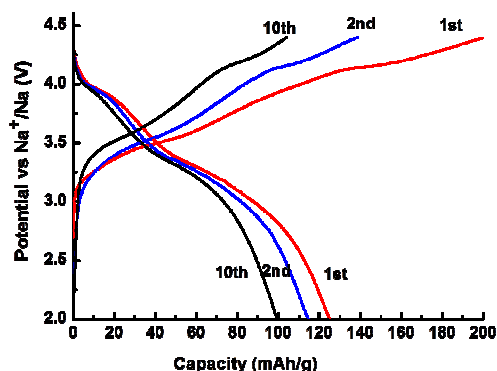


Figure 1. Electrochemical cycling curve of sidorenkite

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