

Cs-exchange in birnessite: Reaction mechanisms inferred from time-resolved X-ray diffraction and transmission electron microscopy

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ABSTRACT

We have explored the exchange of Cs for interlayer Na in birnessite using several techniques, including transmission electron microscopy (TEM) and time-resolved synchrotron X-ray diffraction (XRD). Our goal was to test which of two possible exchange mechanisms is operative during the reaction: (1) diffusion of cations in and out of the interlayer or (2) dissolution of Na-birnessite and reprecipitation of Cs-birnessite. The appearance of distinct XRD peaks for Na- and Cs-rich phases in partially exchanged samples offered support for a simple diffusion model, but it was inconsistent with the compositional and crystallographic homogeneity of (Na,Cs)-birnessite platelets from core to rim as ascertained by TEM. Time-resolved XRD revealed systematic changes in the structure of the emergent Cs-rich birnessite phase during exchange, in conflict with a dissolution and reprecipitation model. Instead, we propose that exchange occurred by sequential delamination of Mn oxide octahedral sheets. Exfoliation of a given interlayer region allowed for wholesale replacement of Na by Cs and was rapidly followed by reassembly. This model accounts for the rapidity of metal exchange in birnessite, the co-existence of distinct Na- and Cs-birnessite phases during the process of exchange, and the uniformly mixed Na- and Cs-compositions ascertained from point analyses by selected area electron diffraction and energy dispersive spectroscopy of partially exchanged grains.

Keywords: Cation exchange, cesium, birnessite, synchrotron, X-ray diffraction, transmission electron microscopy