X-ray PDF to quantify defects in disordered 2-D MnO_2 nanosheet assemblies

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X-ray total scattering was teamed with X-ray spectroscopy and related tools to probe both the mesostructure and the atomic defects of MnO_2 nanosheet assemblies, revealing a direct link between surface Mn defects and capacitance. Beginning with high-perfection microcrystalline K_xMnO_2 powders, it is possible to exfoliate defect-free MnO_2 nanosheets and subsequently reassemble them into 3-D porous structures. Controlled reduction of some of the tetravalent Mn leads to tripling of the electrochemical charge storage capacity.

For the case of exfoliated and re-assembled nanosheets the nano and meso-scale order and disorder are reflected in the PDF measurement. The sheets re-stack to a limited degree, and the nanosheets themselves may be curved and bonded edge-to-face with neighboring sheets. In order to extract meaningful quantitative values of the numbers and geometries of Mn defects in this system, we present an approximate method of analysis for nanosheet assemblies with arbitrary stacking disordered that reduces the requisite parameter space by making use of the self-similarity of the composite nanosheets. A refineable stacking model provides a mechanism to propagate the 2D sheet motif along the disordered direction. The critical feature of this approach is the ability to refine a relatively small number of physically meaningful parameters for a massively defective atomic ensemble. The successfully-refined defect content includes the Mn-vacancy/surface-Mn defect pair, chemisorbed water sites, and free water sites. Refinement of 25 Å of real space highlights the success of this approach, where the refined mesostructure information may provide clues towards the intercalation kinetics of alkali species relevant to environmental remediation, biochemistry, and electrochemical electrodes.