In-situ XRD and XAS Study of Electrochemical Strain and Charge Storage Mechanisms of 2D δ-MnO_2

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Defect chemistry in 2-D oxides and the role defects play in electrochemical charge storage remain largely unexplored. δ-MnO_2 nanosheets demonstrate an interesting response to reduction of Mn^{4+} to Mn^{3+}, where Jahn-Teller distorted Mn^{3+} ions are displaced out of the plane of the nanosheet forming a "surface Frenkel" defect. δ-MnO_2 is also unique in that it exhibits psuedocapacitance, a phenomenon that occurs when a material stores charge through Faradic redox reactions while retaining a capacitive CV signature.

High energy X-ray scattering was teamed with X-ray absorption spectroscopy, Raman spectroscopy, and related tools to probe the local atomic structure during electrochemical cycling. Bond distances obtained from Pair Distribution Functions strongly correlate to the degree of disorder in δ-MnO_2, and results from previous studies show this disorder correlates to capacitance. A reversible expansion of the Mn-O and Mn-Mn bond distances upon charging leads to an also reversible expansion of the lattice in the a and b direction while the c lattice parameter remains constant. Changes to the lattice during electrochemical cycling are morphology dependent. Nanosheets with a higher degree of restacking experience greater changes to the a and b axes during charge and discharge. Restacked nanosheets also show similar changes in the a- and b-axes, but contract in the c direction on charging due to electrostatic changes to the interlayer. XANES study of the Mn ion confirms Faradic redox reactions where charging of the electrode leads to a greater fraction of Mn^{3+}.