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***In Situ* Correlation of Volummetric Expansion with Charge Storage in Nanostructured MnO_2** TETYANA IGNATOVA, BRAD CORSO, DENG PAN, O. TOLGA GUL, PHILLIP G. COLLINS, Department of Physics and Astronomy, University of California at Irvine — Pseudocapacitors aim to meet developing energy storage needs by combining the high energy density of batteries with the power performance of capacitors. However, degradation remains a critical issue for pseudocapacitor electrodes. After many cycles, nanostructured metal oxides like MnO_2 lose their capacity through mechanisms that remain poorly understood. In this work, we studied the volummetric changes that accompany charge storage in nanoscale MnO_2 electrodes by combining in-liquid atomic force microscopy (AFM) with 3-terminal electrochemical cycling. Typical samples consisted of thin films (100 to 400 nm) of porous, amorphous MnO_2 deposited onto 2 μm^2 Pt electrodes and then cycled in aqueous $LiClO_4$ electrolyte. *In situ* measurements of film expansion during charge insertion observed 3.6% volummetric expansion for partial charging of 0.1 electron per Mn atom over a wide range of scan rates and voltage windows, even though these parameters change the balance between fast, double-layer capacitance and bulk, redox pseudocapacitance mechanisms. In fact, volume expansion is universally attributed to bulk charging, so the invariance highlights an unexpected role for surface processes in nanostructured electrode materials.

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