Local and Bulk Probe of Vanadium-Substituted alpha-Manganese Oxide (α-KxVγMn8-γO16) Lithium Electrochemistry

Diana M. Lutz1,1,1, Mikaela R. Dunkin1,2, Killian R. Tallman1,2, Lei Wang2,4, Lisa M. House2,4, Shizhe Yang5, Bingjie Zhang1, Ping Liu6, David C. Bock2,4, Yimei Zhu5,5, Amy C. Marschilok1,2,3,4, Kenneth J. Takeuchi1,2,3,4

1. Department of Chemistry, Stony Brook University, Stony Brook, NY 11794
2. Institute for Electrochemistry, UC Berkeley, Berkeley, CA 94720
3. Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY 11794
4. Interdisciplinary Science Department, Brookhaven National Laboratory, Upton, NY 11793

Introduction

Motivation:
α-MnO2 is an environmentally benign material with high ionic conductivity and theoretical capacity that has been investigated for Li-ion batteries. Even so, Jahn-Teller distortion of Mn causes material degradation that leads to increased capacity fade over extended electrochemical cycling.1

Goal:
By substituting tunnel wall Mn atoms for V atoms that do not suffer from Jahn-Teller effects, this distortion will be altered, and structural stability may be improved. This projects aims to fundamentally understand the multifaceted impact of V-substitution on α-MnO2 battery systems.

Material Characterization

• No impurities noted by XRD or Raman
• Rod-like morphology shortens & surface area increases as V-substitution increases

Electrochemistry and X-ray Absorption Spectroscopy

Ex situ XAS measurements were collected at the Mn and V K-edges at the Quick X-ray absorbing spectroscopy (QAS, 7-BM) and the Beamline for Materials Measurement (BM, 6-BM) lines at the National Synchrotron Light Source II (NSLS-II) of Brookhaven National Laboratory. Data workup was completed with the Athena software package.2

Characterization of Uncycled Materials

Mn K-edge X-ray Absorption Near-Edge Structure (XANES)

(A) XANES fingerprinting confirms formation of α-MnO2 polymorph for all materials
(B) Average Mn oxidation state decreases with increasing V substitution, likely the result of V3+ preferentially replacing Mn4+
and resulting in a higher Mn3+/Mn4+ ratio.

V K-edge X-ray Absorption Near-Edge Structure (XANES)

• (A) V XANES is distinct, suggesting V has substituted into MnO2 framework.
• (B) Analysis of the V pre-edge peak indicates V has substituted into a distorted octahedral environment with an oxidation state of 4 or 5

Characterization of Lithiated 10% V-substituted Material

Mn K-edge Extended X-ray Absorption Fine Structure (EXAFS)

• Mn-Mn corner-sharing relationship around 3 Å decreases in coordination after 1 ee and exhibits complete splitting by 4 ee.
• Movement of the Mn-Mn<sub>avg</sub> relationships are consistent with expansion of the tunnel due to lithium insertion