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Size-dependent (≤ 50 nm) chemical and physical properties of electronic materials have been attributed to primarily either *intrinsic contributions*, such as changes in the lattice energy and discrete energy eigenstates, or *extrinsic contributions*, such as unsaturated bonding of the surface atoms. Surface factors can be interpreted as “surface relaxation,” which has been studied in ferroelectrics (BaTiO₃ and PbTiO₃) and CuO. In CeO₂ nanocrystals, the shift in lattice parameters with crystal size was assumed to be due to the formation of oxygen vacancies and the associated Ce³⁺. A model showed that the concentration of oxygen vacancies changed \approx two orders of magnitude when the crystal size increased from 4 nm to 60 nm. In this study, MnO_{2- δ} was chosen for the studies in this work since it exhibits a rich chemistry and crystalline phases. In addition, the use and modeling of nanometer scale MnO₂ in the fields of catalysis, supercapacitors, and battery electrodes prompted further exploration to understand anomalous observations of size-dependent behavior. In most of these applications, the redox reaction between Mn⁴⁺ and Mn³⁺ contributes to the unique property of MnO₂. Therefore, it is necessary to study nonstoichiometric chemistry and its role on the electronic conduction.

The MnO₂ nanowires were synthesized by oxidation of manganese sulfate with ammonium persulfate in a hydrothermal reactor. The precipitates were then filtered and washed for further characterization. The nonstoichiometry of the nanowires was studied by using a combined differential scanning calorimetry (DSC) / thermogravimetric analysis (TGA) at a ramp rate of 5°C/min. The baseline was acquired by conducting TGA in hydrogen, which resulted in formation of a thermodynamic stable phase, MnO. Electrical conductivity was measured in an alumina die with a pressure of 100 MPa via two-probe *dc* technique.

Manganese dioxide (MnO₂) is known with different allotropic polymorphs, denoted by α , β , γ , etc., which differ in the way of distribution of Mn ions in the octahedral sites of oxygen framework. Both x-ray diffraction and electron diffraction indicated that the as-synthesized MnO₂ phase is α -MnO₂. Figure 1 illustrates the calculated oxygen occupancy in MnO₂ nanowires. The presence of oxygen vacancies is consistent with our previous study showing a reduction of Néel temperature of MnO₂ nanowires due to changes of oxidation states of Mn ions. The changes of oxidation states in MnO₂ would thus result in variation of charge carrier density. Indeed, electrical conductivity measurements showed MnO₂ nanowires were electrically conducting (Figure 2). The activation energy for electronic conduction of the microparticles is ~ 0.095 eV (Figure 3), comparing to 0.22 eV for nanowires (Figure 2). The greater activation energy in MnO₂ nanowires is attributed to the enthalpy for oxygen vacancy formation. Defect chemistry modeling showed that the enthalpy for oxygen vacancy formation was ~ 0.38 eV in nanowires. Further results on high temperature phases and electrochemical properties will be reported.

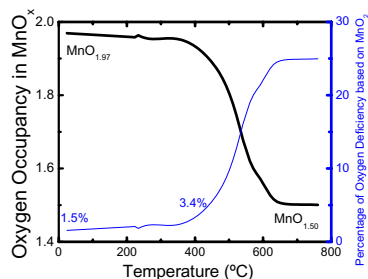


Figure 1: Oxygen occupancy of MnO_{2- δ} nanowires as a function of temperatures, measured in air.

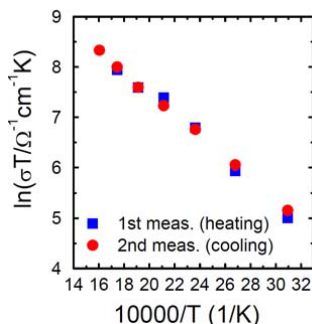


Figure 2: $\ln(\sigma T)$ as a function of temperature for MnO_{2- δ} nanowires.

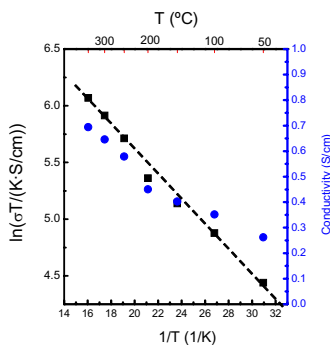


Figure 3: $\ln(\sigma T)$ and σ as a function of temperature for MnO₂ microparticles.

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