

Multiple-scattering EXAFS analysis of tetraalkylammonium  
manganese oxide colloids

Ressler T, Brock SL, Wong J, Suib SL

Addresses:

Ressler T, Univ Calif Lawrence Livermore Natl Lab, POB 808, Livermore, CA 94551 USA

Univ Calif Lawrence Livermore Natl Lab, Livermore, CA 94551 USA

Univ Connecticut, Dept Chem, Storrs, CT 06269 USA

Univ Connecticut, Dept Chem Engr, Storrs, CT 06269 USA

Univ Connecticut, Inst Sci Mat, Storrs, CT 06269 USA

Abstract:

X-ray absorption spectroscopy at the Mn K edge was employed to elucidate the structure of colloidal tetraalkylammonium (TAA) manganese oxides in sols and gels obtained by different preparation and heat treatment procedures. Two series of colloidal TAA MnO<sub>x</sub> prepared with tetrapropylammonium (TPA) and tetraethylammonium (TEA) cations were studied. Several manganese oxides, birnessite, and feitknechtite were also measured and served as model compounds for structural refinements. Near edge structure (XANES) analysis revealed different average valences of the colloidal systems. As synthesized and heat-treated, TAA colloids exhibited an average valence of 3.6-3.7, whereas gelled TAA colloids showed a lower average valence of similar to 3.5. Extended absorption fine structure (EXAFS) analysis was carried out to distances of -6.0 Angstrom around the central Mn atom using theoretical backscattering phases and amplitudes calculated from the ab initio FEFF code. All multiple-scattering (MS) paths with a weight of 2% and more with respect to the main Fourier transform peak were included in the refinement. It is found that, except for gelled TAA samples, no significant amount of corner-shared MnO<sub>6</sub> units was detected in the colloidal systems. Theoretical EXAFS phases and amplitudes were derived for a monoclinic birnessite MnO<sub>x</sub> layer structure consisting of edge-shared MnO<sub>6</sub> octahedra. EXAFS refinements utilizing these phases and amplitudes resulted in good agreement with experimental data. Differences in the refined scattering shell distances between the TPA and TEA series suggest a structure influencing effect of the two ammonium ions. Bond angles between neighboring MnO<sub>6</sub> octahedra were determined from the amplitude dependence of a collinear Mn-Mn-Mn MS path on deviations from 180 degrees ("focusing effect"). On the basis of the bond angles, and with use of the average valence to define the distribution of tri- and tetravalent manganese in the MnO<sub>x</sub> layers, three distinct 2D structures are proposed: one for birnessite, one for TAA sols, and one for TAA gels.



MAX-PLANCK-GESELLSCHAFT

JOURNAL OF PHYSICAL CHEMISTRY B

103 (31): 6407-6420 AUG 5 1999



**Publisher:**

AMER CHEMICAL SOC, 1155 16TH ST, NW, WASHINGTON, DC  
20036 USA