

Probing Uranyl Peroxide Materials U_{60} and Studtite Using *in situ* Electrochemical XAS Methods

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Introduction

The electrochemical nature of the uranium-60 nanocluster (U_{60}), a fullerene cluster of uranyl polyhedra, has yet to be fully characterized since its first synthesis in 2005 [1]. While our initial studies on U_{60} and its naturally-occurring analogue, studtite, focus on monitoring the redox behavior in differing solutions and concentrations in order to characterize redox switching in both compounds (U^{6+} to U^{5+} and U^{4+}), we have recently studied local structural changes as a function of redox state using x-ray absorption spectroscopy (XAS, *i.e.*, XANES and EXAFS) [2].

Purpose

Our hypothesis is that we can measure and calculate the thermodynamics and redox potential of the redox switching of the U oxidation state, including its kinetics and reversibility (*i.e.*, switching within the cluster without destroying it) in U_{60} clusters and studtite as a function of pH, solution chemistry, and pe/Eh. In addition, changes in the kinetics of growth, structural, and electronic changes are monitored by a combination of electrochemical XAS and computational treatment of activated complexes. Synchrotron XANES/EXAFS allows us to determine the oxidation state of U as a function of the applied potentials and elucidate the structure and changes on U_{60} clusters found on the electrode.

Results

Electrochemical results describe the proton-coupled nature and similarity of U_{60} and studtite U^{6+}/U^{5+} and U^{5+}/U^{4+} redox behavior (peaks within 0.1 V of each other) in addition to the alteration of $(UO_2)^{2+}$ in the presence of uranyl peroxides. *In situ* electrochemical XAS results support our reversible peak characterizations, purity of our synthetic samples throughout cycling, and the design of our *in situ* cell.

Ex situ experiments were performed in tandem to obtain oxidation state, electronic configuration, vacant orbitals, coordination environment, nature of scattering atoms, interatomic distances, and the Debye-Waller factor.

Such information is essential to any experiment concerning sorption, precipitation, diffusion, surface complexation, and solid solution formation.

[1] Sigmon *et al.* (2009) *JACS* **131**, 16648-49. [2] Gebarski & Becker (in submission) *GCA*.