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In Operando SEM Imaging of Electrochemical Oxidation of UO_2 in Liquid

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A Fuel Matrix Dissolution Model (FMDM) is being developed that is based on the electrochemical behavior of spent uranium oxide (UO_2) fuel as within an Engineered Barrier System (EBS) in a geologic repository [1]. The FMDM model requires experimental validation that accounts for the interaction of dissolved oxygen, hydrogen peroxide, and hydrogen with UO_2. *In situ* liquid cell and microanalysis using scanning electron microscopy (SEM) have been shown recently to be a viable approach to study the oxidation of UO_2 particles [2].

A vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI), was developed to study liquids using vacuum surface tools including SEM [3, 4]. Of particular interest to study the oxidation and reduction of UO_2, the electrochemical version or the E-cell [5] was used and adapted in this work. The feasibility of using SALVI for *in situ* characterization of particles in liquid was demonstrated in our previous work [6]. This paper shows initial results of *in operando* study of spent fuel relevant systems using the SALVI E-cell. Two FEI Quanta 3D FIB-SEM instruments were used. Both low and high vacuum modes SEM were employed. The radiological material was analyzed in the Quanta 250 FEG SEM housed in the Radiological Processing Laboratory (RPL) at the PNNL. Non-radiological materials were analyzed to optimize imaging conditions. The iron oxide (Fe_3O_4) in deionized water (DI) mixture was analyzed in the Quanta SEM located at the Environmental Molecular Sciences Laboratory (EMSL). A standard operation procedure of *in situ* liquid SEM was described previously [7].

Figure 1 depicts SEM secondary electron (SE) and backscattered electron (BSE) imaging results of Fe_3O_4 particles in the high vacuum mode in a microchannel. The SE and BSE images were collected at the same location. The SE and BSE images show the particle size and morphology in liquid. *In situ* energy-dispersive x-ray spectroscopy (EDS) spectrum (results not shown) collected at the same location verifies elemental composition. This result supports the follow-up study of spent fuel materials using the novel *in situ* liquid SEM to study particle evolution of relevance in EBS. The goal of this work is to conduct *in operando* SEM of UO_2 simulating the spent fuel conditions. Figure 2a depicts the experimental setup including an electrochemical station connected with a SALVI E-cell (see insert). Figure 2b shows a series of cyclic voltammograms obtained with this setup using a standard solution consisting of 2 mM $K_3Fe(CN)_6$ and 1 M KNO_3 in DI water. Reagents were acquired from Sigma-Aldrich. This initial result demonstrates the performance of the approach prior to using radiological materials. *In operando* results and the application of *in situ* SEM imaging in studying nuclear materials will be presented [8].

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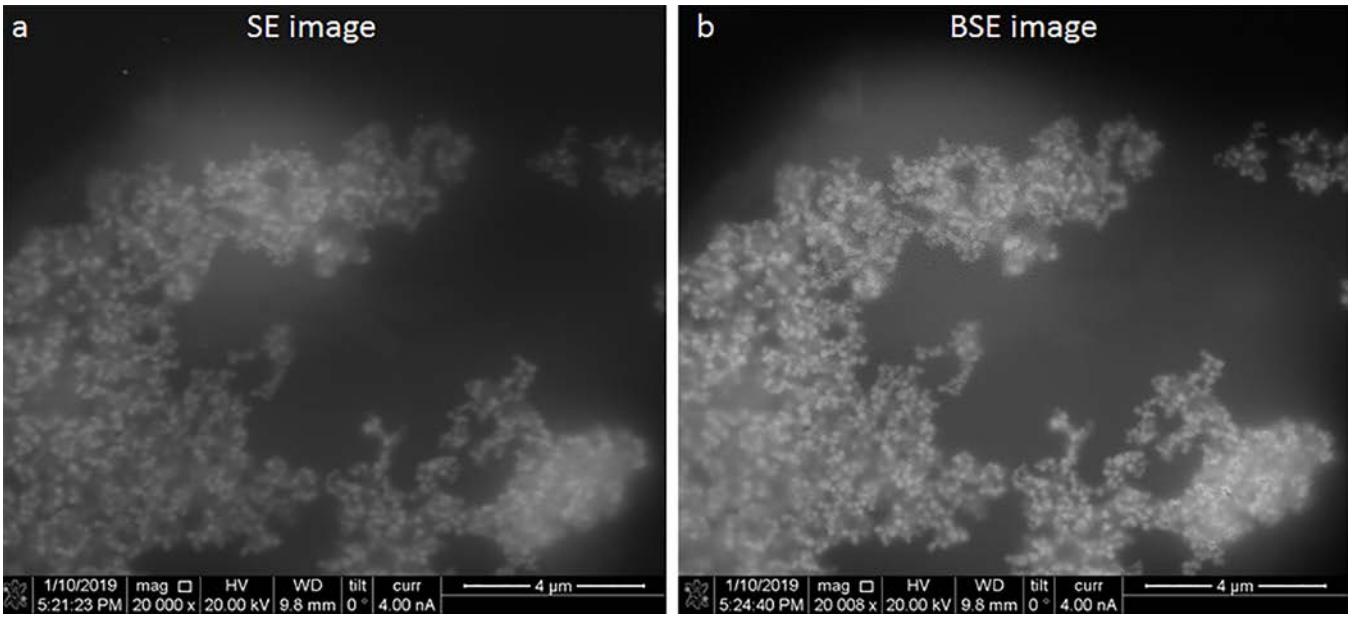

Figure 1. In situ liquid SEM imaging of Fe_3O_4 particles in high vacuum (a) SE imaging and (b) BSE imaging using SALVI and a FEI Quanta 3D FIB-SEM.

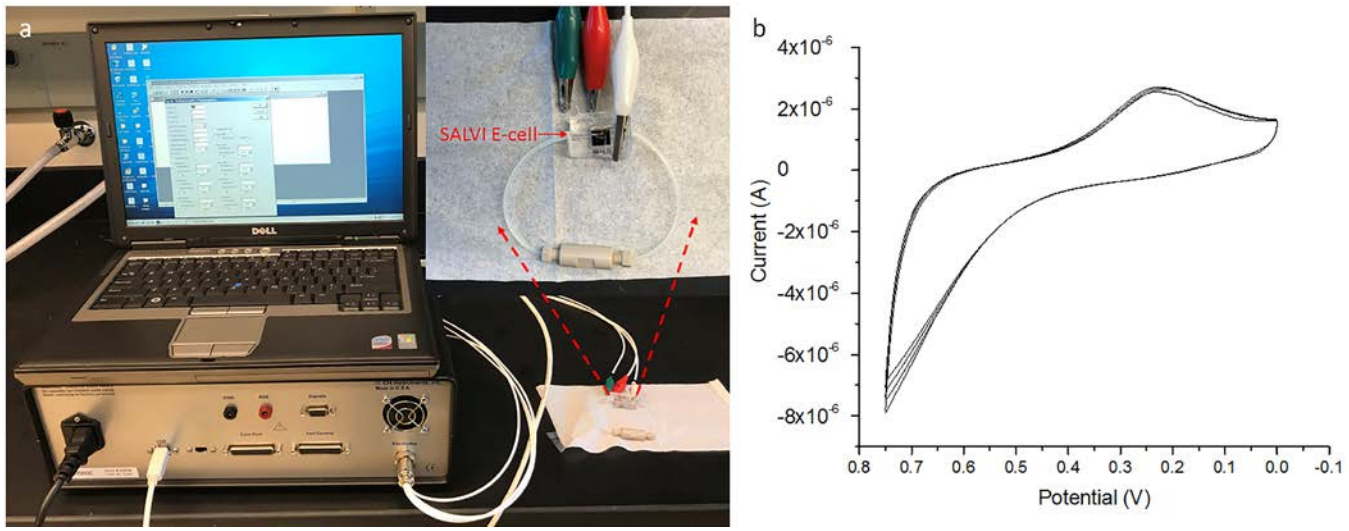

Figure 2. (a) *In operando* SEM setup showing the SALVI E-cell (insert) connected with an electrochemical station; and (b) cyclic voltammograms acquired using this setup.

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