

Studying the UO₂ Electrochemistry In Situ Using SEM

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Repositories for the disposal of radioactive waste depend on a multi-barrier system to segregate the waste from the biosphere. The multi-barrier system generally consists of the natural (geological) barrier by the repository host rock and its surroundings and an engineered barrier system (EBS). *In situ* and laboratory testing and modelling constitute an important aspect of research to ensure that an EBS will perform to its desired functions to contain spent uranium oxide (UO₂) fuel [1]. Of specific interest in the dissolution and oxidation of UO₂ is the determination of its corrosion potential. Although such processes are described in the Mixed Potential Model (MPM) and Fuel Matrix Dissolution Model (FMDM), microscopic understanding of the electrochemical and diffusion processes is needed to validate advanced models such as MPM.

We use *in situ* liquid cell and microanalysis in scanning electron microscopy (SEM) to study UO₂ chemistry following recent successes [2, 3]. We invented a vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI) to study liquids using vacuum surface tools including SEM [4, 5]. The electrochemical version of the E-cell [6] was redesigned to investigate the oxidation of UO₂ in this work. This paper shows initial results of *in operando* study of spent fuel relevant systems using the SALVI E-cell. The radiological material was analyzed in the Quanta 250 FEG SEM housed in the Radiological Processing Laboratory (RPL) at the Pacific Northwest National Laboratory (PNNL). Non-radiological materials were analyzed to optimize imaging conditions. Optimized *in situ* SEM procedures were described earlier [7, 8]. Prior to performing microanalysis of UO₂ in the microfluidic E-cell, the cyclic voltammogram of uranyl (VI) nitrate was acquired (Figure 1). The electrochemistry of U(VI) was run using a three-component electrochemical cell, with Pt-disc working electrode, Pt wire auxiliary electrode, and Ag/AgCl as reference electrode.

Next, we performed electrochemistry experiments using a uranium containing electrolyte in the SALVI E-cell. An EHI 660 E (CH Instruments, Inc., Austin, TX) electrochemical workstation was used. The E-cell was mounted on the sample stage of the SEM and was tested. The three electrodes were connected to the electrochemical workstation via corresponding wires as shown in Figure 2. The electrochemistry of U(VI) was conducted using a three-electrode SALVI E-cell, with gold film (~1mm²) as working electrode, Pt wires as counter electrode and reference electrode, respectively. A series of *in operando* SEM experiments of UO₂ will be performed to simulate the spent fuel conditions. New *in situ* SEM imaging results in studying nuclear materials will be presented [9].

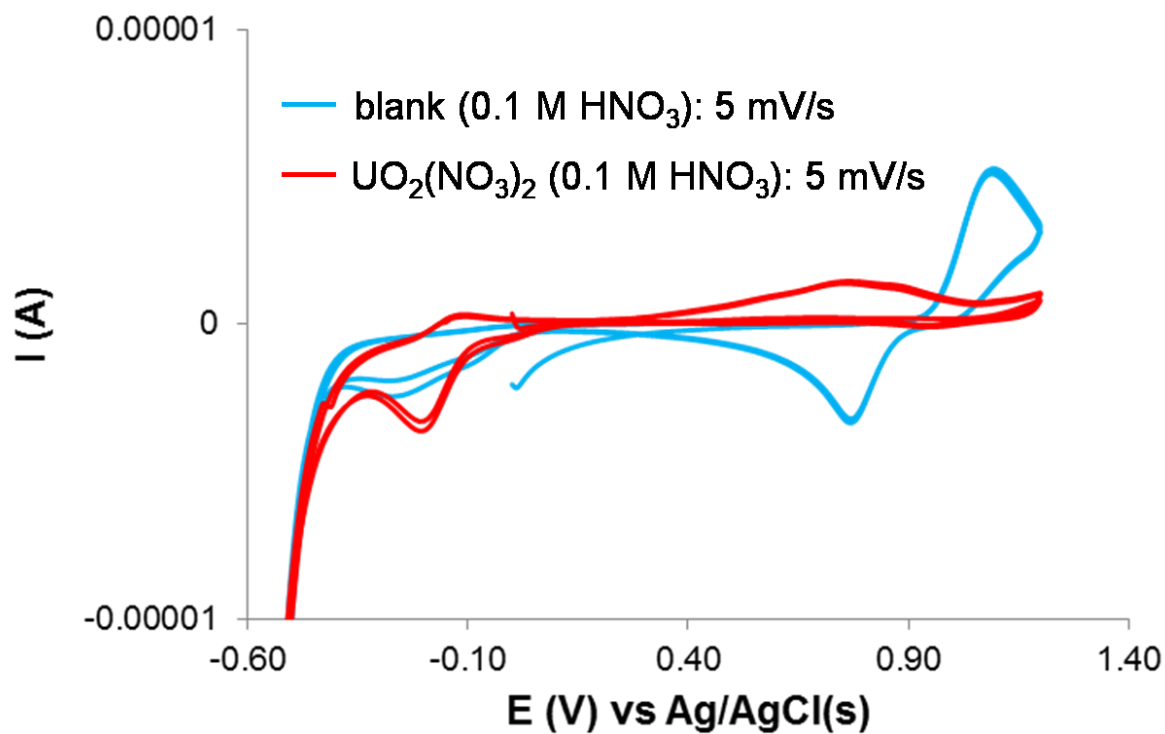


Figure 1. Cyclic voltammogram of 10 mM uranyl (VI) nitrate in 0.1 M HNO₃.

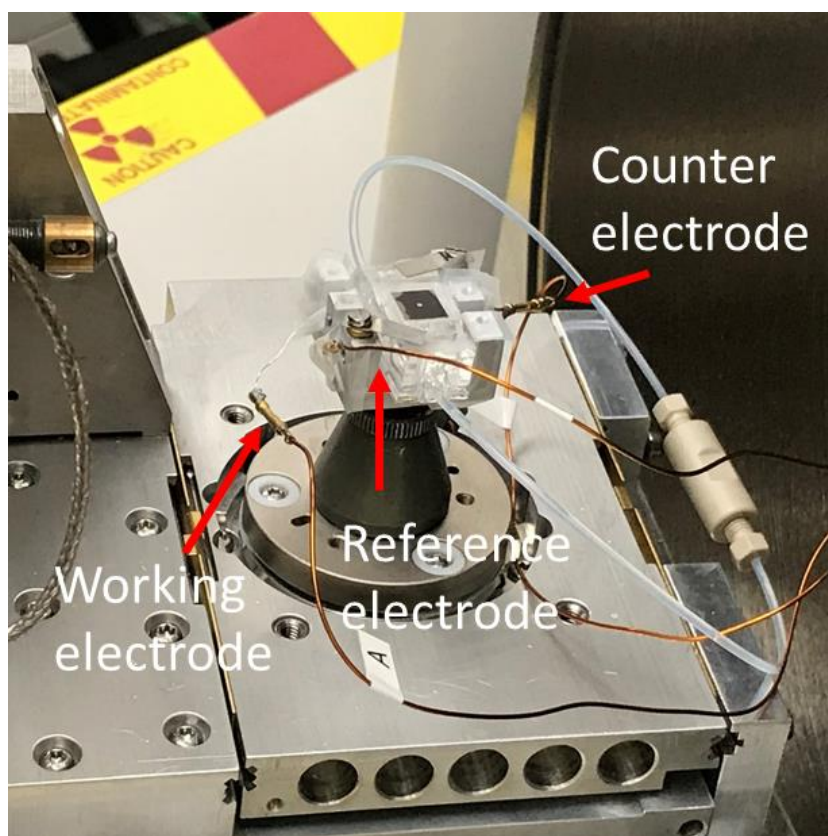


Figure 2. The SALVI E-cell with uranium containing electrolyte setup installed in the SEM stage.

References

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- [9] We acknowledge support from the U.S. Department of Energy (DOE) Nuclear Energy (NE) Spent Fuel and Waste Science and Technology (SFWST) program.