Supporting Information

A Microfluidic Electrochemical Cell for Studying the Corrosion of Uranium Dioxide (UO_2)

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Experimental Details

Chemicals and Materials

 UO_2 particles were ground from a single crystal of UO_2 . To prepare the working electrode (WE) using micron-sized UO_2 particles, 1µL of UO_2 mixture slurry was deposited on Si₃N₄ membrane to form a 1.5-2 mm diameter working electrode (see Fig. S1). The UO_2 mixture slurry consisted of UO_2 particles, polyvinylidene fluoride (PVDF, Alfa Aesar), carbon black (TIMCAL, Graphite & Carbon Ltd), and was dissolved in N-methyl-2-pyrrolidone (NMP solvent, Sigma-Aldrich). PVDF binder is the most successful and widely used binder for lithium batteries¹ and has recently been used for electrode fabrication.²

The detailed electrode slurry preparation is described here. Firstly, the powder form of PVDF (1mg) was dissolved in 1mL NMP solvent at 40 °C with constant stirring for 10 minutes or until the white PVDF powder is entirely dissolved. Secondly, 1mg of carbon black (CB) was added into the solution with dissolved PVDF and stirred constantly at room temperature. Thirdly, 8mg of UO₂ powder was mixed with PVDF/CB and NMP solvent to form the slurry. Before each drop casting, the slurry was well stirred to ensure the homogenization of the particles in the slurry. The droplet containing UO₂ particles was deposited on the back of the Si₃N₄ membrane window to form the electrode and dried in the glass vacuum bell jar to evaporate the NMP solvent.

All chemicals were reagent grade or better. 0.1 M NaClO₄ (pH 9.5) electrolyte was used to compare the results from bulk analysis reported by Shoesmith's group.^{3, 4} A 0.1 M NaClO₄ (Sigma Aldrich) solution was adjusted by an aqueous NaOH solution (Sigma-Aldrich) pH 9.5 and purged with N₂ at least 30 minutes prior to be loaded into the microfluidic electrochemical cell. To determine the potential shifts owing to the use of different reference electrodes, a standard electrolyte solution containing 2 mM K₄Fe(CN)₆ (Sigma-Aldrich, 99%) and 2 mM K₃Fe(CN)₆ (Sigma-Aldrich, 99%) in 0.1 M aqueous KCl were used for determining the shift in potentials upon changing from a SCE to a Pt RE . The electrochemical experiments were conducted at room temperature. All solutions were prepared with the deionized water (18.1 MΩ.cm).

XPS Analysis and Fitting Method

X-ray Photoelectron Spectra (XPS) were collected on a Kratos AXIS Ultra DLD instrument equipped with a hemispherical analyzer. The instrument was using an Al-Ka x-ray source operated at a power of 150 W with the chamber pressure maintained below 2 x 10⁻⁹ Torr. The microfluidic devices were disassembled in an argon filled inert box connected to the load lock of the XPS instrument to prevent aerial oxidation of the sample. Prior to measurement, the

binding energy scale of the instrument was calibrated using sputter-cleaned copper and gold foils to yield 932.6 eV for Cu 2p3/2 and 84.0 eV for the Au 4f7/2 features. Data analysis was performed on an area of 700 mm x 300 mm at a normal emission angle, and any surface charging during analysis was minimized using a low-energy electron flood gun operating at 1.8 A and 3.6 V. The survey spectra were acquired at a pass energy (PE) of 160 eV, a step size of 1 eV, while the high-resolution U 4f scans were acquired at a PE of 40 eV, a step size of 0.1 eV. For reference, a sputter-cleaned Au foil produced a full width at half maximum, FWHM, of 0.84 eV for the Au 4f7/2 feature at a PE of 40 eV.

Data processing was performed using CasaXPS software, and the binding energy scale was charge referenced to C 1s (C-C/C-H component) at 285 eV. A background was applied on the entire U 4f region encompassing all satellite peaks, i.e., up to 25 eV above the main peak. An iterated Shirley was used as the background for the 'as-received' and PAMEC 02 samples, while a linear background was applied to the U 4f region of the PAMEC 01 working electrode due to low signal-to-noise in the spectra. Spectral fitting was performed using gaussian-lorenztian type curves, and the U 4f7/2 and U 4f5/2 primary peaks were fit using spin-orbit split components at a separation of 10.8 eV. The U 4f7/2 region comprised of three primary components corresponding to three different oxidation states of uranium. The FWHM of the satellite peaks were constrained relative to the corresponding primary component. Further detailed peak fitting protocols have been described earlier in Ilton, et al.⁵

Supporting Figures



Fig. S1 (a) BSE images of entire UO_2 WE area, (b) an example of WE area magnified to perform the particle analysis by converting the BSE image to a binary image (c) and estimate the particle size distribution (d) for entire WE area after all 19 sections in (a) were magnified and converted to binary images.

Fig. S1a shows the BSE image of UO₂ WE, divided into 19 sections for acquiring magnified BSE images as an example shown in Fig. S1b. Fig. S1c depicts the example of converting the BSE image to the binary image processed by ImageJ software. The lognormal distribution of particles size was analyzed in MATLAB, showing the average size of the UO₂ particles counted from the entire WE area (all 19 sections) is 1.6 μ m (Fig. S1d). The accumulated top area of the UO₂ WE is 0.069 cm² based on all the binary image results, assuming the particle is a sphere and surface roughness factor is 3. The actual surface area of UO₂ exposed to the electrolyte may be much larger. Most of the UO₂ particles are embedded in the PVDF-carbon black network, which may not be all captured in the BSE images. Compared to the disc UO₂ electrode (~1.4 cm in diameter) used in the bulk analysis reported elsewhere,^{3, 6} UO₂ WE studied in this work is much smaller in mass (~8 µg) but provides the comparable active surface area due to the micronsized UO₂ particles.



Fig. S2 (a) Cyclic voltammograms of K_4 Fe(CN)₆, K_3 Fe(CN)₆ and KCl scanned at 5mV/s to 100mV/s and (b) relationship of currents and the square root of the various scan rates.

For ease of PAMEC cell fabrication, Pt wire was selected for making the reference electrode (RE); while bulk analysis from Shoesmith's group used saturated calomel electrode (SCE) as an RE. It is necessary to determine the potential shift due to the use of different REs to compare the UO₂ redox potential results. Thus, a standard electrolyte ferrocyanide-ferricyanide redox couple were tested for determining the potential differences between using Pt and SCE REs. Wang et al. reported that the midpoint potential of the ferrocyanide-ferricyanide redox couple is 0.19 V vs. SCE⁷. The midpoint potential obtained from PAMEC control E-cell (only PVDF/carbon composite, PAMEC-6) is -0.01 V vs. Pt scanned at 10 mV/s (Fig. S2a). Thus, the potential obtained from Pt has a negative shift of ~0.2 V vs SCE. This explains the cathodic peak observed in our PAMEC cell attached with UO₂ WE is -0.81 V vs. Pt, which has the negative shift of potential comparing to what Sunder and Shoesmith's group reported using SCE RE³. Fig. S2b shows that the anodic peak currents (I_{pa}) and cathodic peak currents (I_{pc}) are proportional to the square root of the scan rate (5, 10, 20, 50, 100 mV/s), indicating that the redox couple is under the diffusion controlled condition, which is consistent with the bulk analysis results.⁸



Fig. S3 (a) Cyclic voltammograms comparison among E-cells w/ (red and blue contours) and w/o UO_2 (black contour) WE at 20 mV/s scan rate from -1.0V-0.5V vs SCE, and (b) the cyclic voltammogram acquired at wider potential range (-1.3V-0.7V vs SCE).

Fig. S3a overlays the cyclic voltammograms obtained from UO₂-attached PAMEC(-1 and -2) and the control PAMEC-5 scanned at 20 mV/s in 0.1M NaClO₄ (pH 9.5) solution. The WE in control Ecell only contains the PVDF/CB. By comparison, the reduction peak around -0.5V- -0.8V vs SCE was not observed in the control E-cell -4. The reduction peaks observed in two UO₂-WE E-cells (PAMEC-1 and -2) were relatively consistent, i.e., -0.65V and -0.70V, respectively. Considering the potential shift (-0.2V) (Fig. S2), the reduction peaks are in good agreement with the observation in the bulk analysis (-0.67V-0.75V).³ In addition, the results show an excellent combination of good electrode with small background current and reproducible response. Fig. 3b presents the cyclic voltammogram acquired at wider scan range (-1.3V-0.7V vs SCE), showing the current in process (ii) continues to increase after 0.4V vs SCE.



Fig. S4 (a) BSE images of entire detection window w/o electrolyte loaded and (b) in situ SEM providing BSE image of the window with electrolyte loaded.

Fig. S4 shows the entire detection window of the PAMEC-1 with UO_2 WE attached beneath the Si_3N_4 window and concentrated on the left of the window. Fig. 4a is the BSE image of the detection window when the E-cell was not loaded with electrolyte solution; Fig. 4b was obtained via in situ SEM when the UO_2 WE was immersed in the electrolyte. The selected region of interest (ROI, red circle) was magnified to obtain a detailed micrograph of the UO_2 particles in Fig. 6.



Fig. S5 (a) SE image of UO_2 particle selected from PAMEC-3 after anodic corrosion for STEM imaging, and (b) SE image shows the preparation of lamella using focused ion beam.

Fig. S5 depicts the preparation of lamella for STEM imaging. The UO_2 particle was selected from PAMEC-3 after 4 hours of anodic corrosion (Fig. S5a). The device was dissembled after the corrosion and UO_2 electrode was sent for SEM imaging and FIB lift-out. Before the focused ion milling, the surface of the oxidized UO_2 was protected and deposited by platinum and carbon (Fig. S5b).

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