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Electrochemical Manipulation and Radiolytic Evaluation of Organic Phase Neptunium

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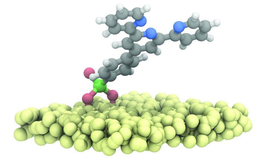

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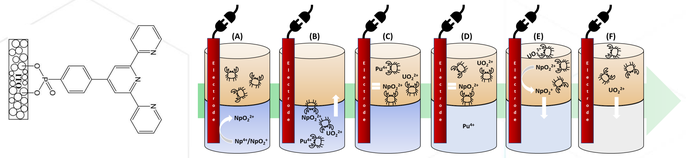
Background

- Under envisioned used nuclear fuel reprocessing conditions, neptunium (Np) is present in a mixture of extractable Np(IV)/Np(VI) and inextractable Np(V) species, the distribution of which is dependent on several factors that lead to the unintentional partitioning of Np into various phases and product streams, reducing process and cost efficiency.
- With this in mind, we tested an innovative approach to precisely control the oxidation state distribution of Np using novel, high surface area, optically transparent, ligand modified tin-doped indium oxide electrodes (LMEs).



- These proof-of-concept experiments employed a variety of radiation and electrochemistry (echem) techniques to determine: electrode radiation stability; aqueous echem behavior of Np at nITO|P3 electrode surfaces; radiation-induced Np-extractant reaction kinetics; and non-aqueous echem of Np in diethylhexyl butyramide (DEHBA) solutions.

Irradiation Studies

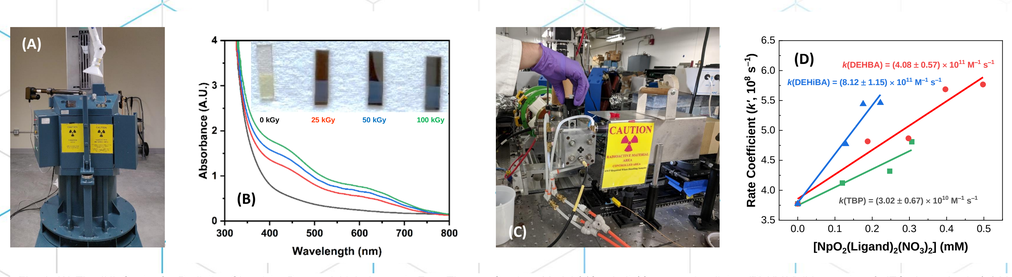


Fig. 1. (A) The *INL Center for Radiation Chemistry Research* high dose rate Foss Therapy Services Model 812 cobalt-60 gamma irradiator; **(B)** UV-Visible spectra of nITO electrodes in 0.1 M HNO_3 solution after exposure to 0 (**black**), 25 (**red**), 50 (**blue**), and 100 (**green**) kGy of gamma radiation; **(C)** the Brookhaven National Laboratory (BNL) Laser Electron Accelerator Facility (LEAF) actinide pulse radiolysis setup; and **(D)** the second-order determination of the rate coefficients (k) for the reaction of the dodecane radical cation ($RH^{\bullet+}$) with Np(VI) complexed tributyl phosphate (TBP), diethylhexyl butyramide (DEHBA), and diethylhexyl isobutyramide (DEHiBA) in 0.5 M dichloromethane/dodecane solution at 800 nm.

Electrochemical Manipulations

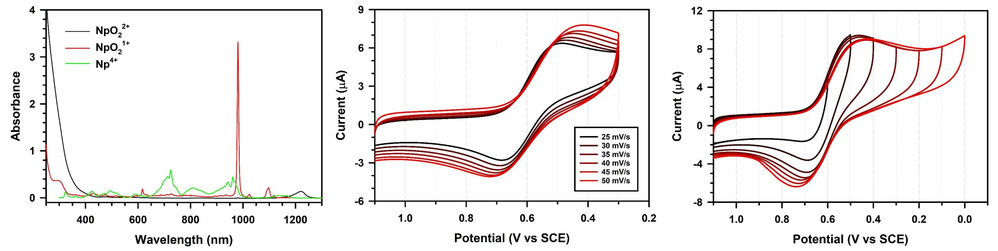


Fig. 3. (A) UV-Visible spectra of an aqueous 1.0 M HNO_3 solution containing ~10 mM: Np(VI) after bulk electrolysis at 1.6 V *vs.* SCE (**Black**); Np(V) after bulk electrolysis at 0.4 V *vs.* SCE (**Red**); and Np(IV) after bulk electrolysis at -0.3 V *vs.* SCE (**Green**) at a nITO|Tripolyphosphate electrode. **(B)** Cyclic voltammograms at GCE of the Np(VI/V) couple in DEHBA with an $E_{1/2}$ = ~0.55 V *vs.* SCE. The linear trend through the plot's origin confirms the Np(VI/V) couple is diffusion limited, with $D_0Np(VI) = 1.24 \times 10^{-8}$ cm^2 s^{-1}. **(C)** Cyclic voltammograms at GCE of the Np(VI/V) couple in DEHBA at various cathodic limits. As the cathodic limit is extended, the wave corresponding the reoxidation of Np(V) to Np(VI) shifts, possibly due to a change in coordination environment or some other chemical phenomena.

Research Outputs

Peer-Reviewed Publications

1. McLachlan, Jones, Hou, Horne, and Dares, The Interaction of Solvent Radiolysis Products with a Transparent Conductive Oxide. *ChemPhysChem* (Impact Factor = 3.520), **2023**, Submitted.
2. Culbertson, Celis-Barros, Pilgrim, McLachlan, Cook, Mezyk, and Horne, Elucidating the Impact of Neptunium and Plutonium Complexation on TBP, DEHBA, and DEHiBA Radiation-Induced Reaction Kinetics. *Inorganic Chemistry* (Impact Factor = 5.436), **2023**, In Preparation.
3. McLachlan, Wineinger, Sperling, Albrecht-Schönzart, Dares, and Horne, The Electrochemical Behavior of Neptunium at Phosphate Modified Metal Oxide Electrodes. *ChemComm* (Impact Factor = 4.9), **2024**, In Preparation.
4. McLachlan, Wineinger, Sperling, Albrecht-Schönzart, Dares, and Horne, The Electrochemical Behavior of Neptunium in DEHBA and DEHiBA Solvent Systems. *Dalton Transactions* (Impact Factor = 4.569), **2024**, In Preparation.

Conference Poster Presentation

- *3rd International Conference on Ionizing Processes, Idaho Falls, ID, U.S.,* July **2022**.

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