Molecular Electrochemistry of Actinides: Redox and Reactivity of Uranium, Neptunium, and Plutonium Complexes

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Redox chemistry strongly influences the reactivity and speciation of the actinides. Particular oxidation states often display unique properties and, therefore, understanding these states and their interconversion can assist with development of new strategies to control their chemical properties. Consequently, electrochemical and electroanalytical methods have a great deal to offer in facilitating studies of actinide-containing systems—from detection of particular species to targeted generation of reactive intermediates of relevance to mechanistic studies. In this presentation, I will share recent examples from my group's ongoing efforts to apply electrochemical methods to actinide chemistry and develop new chemistries built upon control of redox transformations. In the first part, the nonaqueous redox chemistry of a family of uranium, neptunium, and plutonium complexes[1] will be described, highlighting opportunities to study redox processes in nonaqueous media that may not be accessible in conventional aqueous work.[2] Additionally, the use of electrochemical methods to generate and characterize a reactive uranium-containing intermediate will be described, highlighting the opportunity to use electrochemical methods to study the properties of otherwise difficult species.[3] In the second part, the redox chemistry of crown-ether-ligated uranyl complexes will be described, including ongoing work on spectroelectrochemical studies coupled to various spectroscopies.[4]

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[1] E. R. Mikeska, R. E. Wilson, A. Sen, J. Autschbach, and J. D. Blakemore, Preparation of Neptunyl and Plutonyl Acetates to Access Nonaqueous Transuranium Coordination Chemistry, *J. Am. Chem. Soc.* **2024**, *in press*, doi: 10.1021/jacs.4c04613

[2] E. R. Mikeska, T. D. Curry, R. E. Wilson, and J. D. Blakemore, *Available on ChemRxiv*, **2024**, doi: 10.26434/chemrxiv-2024-cpkqj

[3] R. R. Golwankar, M. Z. Makos, N. Cajiao, M. L. Neidig, A. G. Oliver, C. S. Day, V. W. Day, V.-A. Glezakou, and J. D. Blakemore, Electrochemical Activation and Functionalization of the Uranyl Ion, *Available on ChemRxiv*, **2023**, doi: 10.26434/chemrxiv-2024-kqthl-v2

[4] R. R. Golwankar,[#] A. C. Ervin,[#] M. Z. Makos, E. R. Mikeska, V.-A. Glezakou, and J. D. Blakemore, Synthesis, Isolation, and Study of Heterobimetallic Uranyl-Crown Ether Complexes, *J. Am. Chem. Soc.*, **2024**, *146*, 9597–9604, doi: 10.1021/jacs.3c12075