The role of metal-oxo clusters in energy and advanced materials

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Why might you care about metal-oxo clusters? My goals of this seminar are to 1) introduce you to metal-oxo cluster chemistry, 2) introduce you to X-ray scattering as a powerful technique for studying all forms of soluble materials, 3) describe several studies in which metal-oxo clusters are applied in energy and advanced materials applications.

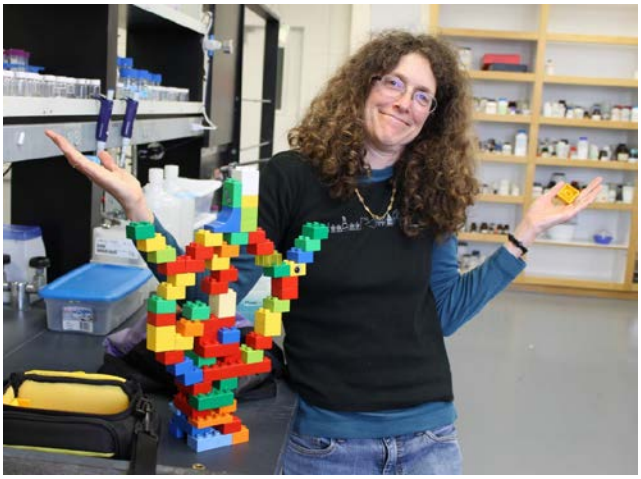
The first project[1] I will describe is exploitation of uranium-oxo clusters for separations in the nuclear cycle. Nuclear energy is a viable carbon-free alternative to fossil fuels. A closed nuclear fuel cycle is optimal for safety and stewardship of the environment and societal acceptance of nuclear energy. Mining, reprocessing fuel, and waste disposal all require numerous chemical separation steps. We are developing a solvent extraction technique for recovery of uranium from spent fuel, where the uranium is extracted in a cluster form. Since each cluster contains 20-60 uranium atoms, the extraction process is 'atom efficient', meaning fewer extraction molecules are required per uranium atom extracted. X-ray scattering and corroborative techniques provide atomic level details of the phase transfer process.

Nanolithography is used in the microelectronics industry to create very small microcircuits. As higher density memory devices demand smaller features, 'engineering' these features becomes less feasible without control of the atomic level chemistry. Researchers at OSU have developed the highest resolution lithography process that takes advantage of small metal-oxo clusters as the building blocks for the deposited and patterned material. The contribution of my research group to cluster-based lithography is studying the cluster evolution throughout all steps of the process including precursor solution preparation, film deposition, thermal annealing and patterning, and dissolution (developing) of film material to ultimately create patterns. I will describe the solution chemistry of three metal oxide deposition chemistries that all feature clusters: 1) Hf-sulfate (HfSOx),[2] 2) Ta and Nb oxide,[3] and 3) tin oxide. Electrospray ionization mass spectrometry, X-ray scattering and other techniques show the evolution of the clusters throughout film deposition and pattering. The influence of clusters on film quality and lithographic features will be presented.

[1] Harrison Neal, Jennifer Szymanowski, Jeremy Fein, Peter Burns, and May Nyman. **(2016)** Benchmarking uranyl peroxide capsule chemistry in organic media. *European Journal of Inorganic Chemistry*. Publication date: November 4, 2016. **DOI:** 10.1002/ejic.201601219

[2] Sara Goberna Ferron, Deok-Hie Park, Jenn M. Amador, Douglas A. Keszler, May Nyman. (**2016**) Ampotheric Aqueous Hafnium Cluster Chemistry. *Angewandte Chemie International Edition.* 55: 6221-6224. **DOI:** 10.1002/anie.201601134; Ruther, R. E., Baker, B. M., Son, J.-H., Casey, W. H., & Nyman, M. (**2014**). Hafnium Sulfate Prenucleation Clusters and the Hf18 Polyoxometalate Red Herring. *Inorganic Chemistry*, *53*(8), 4234–4242. doi:10.1021/ic500375v

[3] Fullmer, L. B.; Mansergh, R. H.; Zakharov, L. N.; Keszler, D. A.; Nyman, M. (**2015**). Nb_2O_5 and Ta_2O_5 thin films from polyoxometalate precursors: A single proton makes a difference. *Crystal Growth and Design.* 15(8): 3885-3892. **DOI:** 10.1021/acs.cgd.5b00508



May NYMAN is a Professor in the Department of Chemistry at Oregon State University. Prior to joining the OSU faculty in 2012, she was a staff scientist at Sandia National Laboratories in Albuquerque, NM. May started her scientific career developing materials for nuclear waste treatment and disposal, and characterizing nuclear wastes. Her interests and expertise have largely have evolved to the fundamentals of cluster chemistry, ion-pairing in water, metal oxide growth mechanisms, X-ray scattering of solutions, and aqueous metal oxide chemistry; leading to materials development in energy and environmental applications. You can learn more about May and her research group at her website.