Title
The quest for safer nuclear fuels

Journal
Nature Reviews Chemistry, 8(5)

ISSN
2397-3358

Authors
Gunther, S Olivia
Schacherl, Bianca

Publication Date
2024-05-01

DOI
10.1038/s41570-024-00596-0

HEAVY ELEMENT CHEMISTRY

The quest for safer nuclear fuels

To increase the safety and performance of nuclear reactors, researchers are working on developing ‘accident tolerant’ fuels. Ideally, these fuel pellets will be less susceptible to swelling and be more resistant to extreme heat. This led chemists to develop uranium dioxide (UO_2) doped with divalent elements, E^{2+}. These dopants can introduce vacancies into the lattice that lead to larger grain sizes, which create longer pathways for fission gasses to migrate out of the grains. In undoped fuel, fission gas build-up at grain boundaries causes the fuel pellet to swell. Therefore, having larger grains that slow fission gas migration into grain boundaries is highly desired.

Divalent Cr^{2+} ions are a commonly explored dopant for UO_2 fuels. These materials have larger grain sizes while maintaining the dissolution kinetics of undoped UO_2, making their long-term storage and disposal paths similarly safe. Atomistic models have suggested that Mn^{2+} is a conceivable alternative doping material, with the potential to increase the sizes of grains even more than Cr^{2+} dopants. As such, experimental studies are required to understand the physical chemistry and reactivity of these potential fuels.

Now, Smith and colleagues from the University of Sheffield report an approach to generate and characterize Mn^{2+}-doped-UO_2 fuel candidates. The materials were made by co-precipitating Mn and U from solution to form a homogenous solid precursor. These were transformed into oxides through calcination or calcination followed by sintering. The optimal calcination conditions for Mn^{2+}-doped-UO_2 were found using differential gravimetric analysis (DGA) to be at 750 °C. X-ray diffraction (XRD) ensured that the starting materials had converted to the test fuel. In all, they synthesized a range of calcinated materials containing between 300 and 2,400 ppm Mn. Parts of the calcinated materials were then further sintered by pressing them into pellets with 2.5 tonnes of pressure and heating to 1,700 °C. Unfortunately, at these temperatures, the Mn in the lattice is somewhat volatile so the sintered materials only retained doping levels of about 500 ppm.

Both the calcinated and sintered materials were analysed using Mn K-edge extended X-ray absorption fine structure (EXAFS) analysis and a distorted cubic environment of the Mn was found in both materials. Mn K-edge X-ray absorption near edge spectroscopy (XANES) showed that all of the Mn was divalent (Mn^{2+}) akin to Cr^{2+}-doped-UO_2.

The formal swap of a U^{4+} for a Mn^{2+} requires a rebalancing of charge. This could be achieved by oxidizing some of the U, which may impact long-term storage options of the fuel, since oxidized U^{5+} and U^{6+} species are known to be more soluble and mobile in the environment than relatively insoluble UO_2 (U^{4+}). Smith and colleagues used U M_4-edge high-resolution (HR-) XANES to identify the oxidation state of uranium in the materials. The calcinated materials contained a fraction of U^{5+}, but the sintered materials contained no detectible U^{5+}. The presence of oxidized U^{5+} doesn’t take this material out of the running for commercialization; Cr^{2+}-doped-UO_2 contains some U^{6+}, but dissolves at similar rates to undoped UO_2. An alternative charge rebalancing can occur by removing some oxygens (O^{2-}), resulting in oxygen vacancies (O_v) in the lattice. The researchers identified such defect sites in the calcinated materials using Raman spectroscopy.

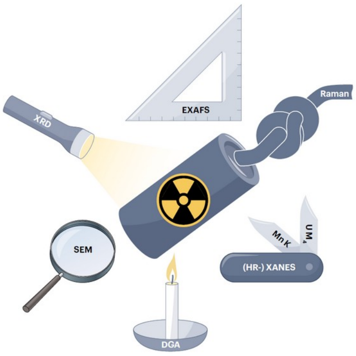
The hypothesized increase in grain growth from Mn^{2+} dopants could not be verified by scanning electron microscopy (SEM). Further kinetic studies on the dissolution rates of these Mn^{2+}-doped-UO_2 fuels will be necessary to determine their viability. For final waste disposal, the dissolution kinetics of a doped UO_2 fuel needs to be on par with or slower than UO_2 alone. Access to advanced spectroscopy is key to further the understanding of the actinides. Synthesis optimization to access sintered materials with higher levels of Mn would be a valuable next step, to determine whether they will be stable during normal reactor operation or in an accident scenario.

https://doi.org/10.1038/s41570-024-00596-0

S. Olivia Gunther and Bianca Schacherl

Lawrence Berkeley National Lab, Chemical Sciences Division, Berkeley, CA, USA. e-mail: sog@lbl.gov; bianca.schacherl@lbl.gov

ORIGINAL ARTICLE Smith, H.; Townsend, L. T.; Mohun, R.; Mosselmans, J. F. W.; Kvashnina, K.; Hyatt, N. C.; Corkhill, C. L. Fabrication, defect chemistry and microsctructure of Mn-doped UO2. *Scientific Reports* https://doi.org/10.1038/s41598-023-



Credit: Carl Conway/Springer Nature Limited

ACKNOWLEDGEMENTS We would like to acknowledge the support of DOE, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, Heavy Element Chemistry Program at the Lawrence Berkeley National Laboratory (LBNL) under contract DE-AC02-05CH11231.