

Task 34

Solution-Based Synthesis of Nitride Fuels

T.A. Sullens and K.R. Czerwinski

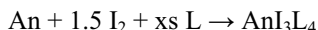
BACKGROUND

Nitride fuels have appropriate properties for advanced fuels, including high thermal conductivity, thermal stability, solid-state solubility of actinides, fissile metal density, and suitable neutronic properties. The presence of oxide and carbide impurities that occur during the current nitride fuel synthesis limits their utility in advanced fuel cycles. The presence of these impurities can lead to the formation of phases with different properties from the bulk material, including the formation of secondary phases. Even a small amount of oxygen in the nitride fuel can reduce thermal conductivity by 10%. This limits the ability to fully develop nitride fuels for advanced reactors. To avoid the entrainment of carbides and oxides in the final actinide nitride product, a non-aqueous, carbon free solution phase route is proposed and investigated in this project.

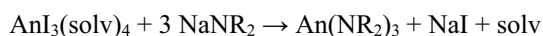
A drawback of nitride fuels involves their synthesis. For nitride fuels, the current synthetic route is carbothermic reduction from the oxide to the nitride, which is based on solid phase reactions involving a stepwise process from the metal oxide, to the carbide, and finally the nitride. This high temperature, solid-phase approach is plagued by impurities in the final nitride product and difficulties in the synthesis and fabrication steps. A direct solution-based synthesis would eliminate, or at least minimize, the impurities and other synthetic problems. The proposed solution route to nitride would also have the added benefit of providing several adjustable parameters that would allow control of the properties of the final solid product.

RESEARCH OBJECTIVES AND METHODS

The objective of this project is to develop solution phase synthetic routes for actinide nitrides for use in nuclear fuels. In the 1970s, a synthesis for actinide nitrides was proposed based on the reaction of plutonium triiodide (PuI_3) and uranium tetraiodide (UI_4) with sodium metal in liquid ammonia giving PuN and UN , respectively, as the reaction products. The synthetic chemistry of trivalent actinide complexes was advanced greatly with the discovery at Los Alamos National Laboratory (LANL) of efficient routes to soluble iodide starting materials of the type AnI_3L_4 , where An is uranium, neptunium, or plutonium, and L is tetrahydrofuran (thf), pyridine, dimethylsulfoxide, etc.

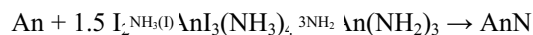


PuI_3 is soluble in ammonia, presumably as the ammonia adduct $\text{PuI}_3(\text{NH}_3)_4$. More recent efforts by ANL and LANL collaborators have investigated amido reactions with actinides to produce $\text{An}(\text{NR}_2)_3$ complexes, where An = U, Np, Pu:



These results suggest that the amido complexes could provide a

non-aqueous solution method for the synthesis of nitrides. The resulting sodium iodide is readily soluble in liquid ammonia, making separation of these products possible. From these results, a plausible route for the synthesis of nitride fuel AnN is:



where An is uranium, neptunium, plutonium or americium. To achieve the solution synthesis of actinide nitrides the fundamental chemical coordination and speciation involved in the above reaction will be examined. The non-aqueous synthetic route, based on amido chemistry, potentially provides property control over the nitride product. The resulting nitride product should be free of the impurities inherent in the carbothermic reduction technique.

The experiments are being performed by a joint research team from UNLV, LANL, and Argonne National Laboratory (ANL), with actinide experiments performed at each laboratory. This project maintains special emphasis on student participation in the project research with all team members collaborating in the educational efforts. The young researchers from UNLV have the opportunity to perform research at ANL and LANL, helping train the next generation of radiochemists and actinide scientists with experience in DOE laboratories. The synthesis of nitride fuels through this method is complementary to the ongoing carbothermic reduction syntheses being performed within the UNLV Radiochemistry program. The ANL and LANL participants are experts in synthetic actinide chemistry, including non-aqueous chemistry and materials science.

The experimental methods for the synthesis of the amido actinide species relies upon the use of inert atmosphere and elevated pressure. These conditions can be reached with the use of Schlenk



A depiction of the Schlenk line experimental set-up for the generation and storage of liquid ammonia, solvent transfer for the dissolution of iodine, and the cannula transfer of solution for reaction with uranium.

lines, pressure vessels, and glove boxes. A combination of these techniques is being utilized in the project. Characterization of the resulting amido species will primarily utilize X-ray diffraction, employing methods and equipment already developed by the UNLV, ANL, and LANL partnership.

Single crystal X-ray diffraction will be used for examination of final and intermediate products at the atomic level for the determination of molecular structure, atomic interaction and spacing, crystal structure, speciation, and elemental oxidation state. X-ray Powder Diffraction, high resolution Transmission Electron Microscopy in combination with Energy Dispersive X-ray Analysis, Parallel-collection Electron Energy-Loss Spectroscopy, Electron-beam Microprobe Analysis and Scanning Electron Microscopy are currently in use at UNLV and will also be used to evaluate the actinide nitrides. For complete product characterization, X-ray Absorption Fine-structure Spectroscopy will also be used for analysis. Thermal analyses (Thermogravimetric Analyzer, Differential Thermal Analyzer, and Differential Scanning Calorimetry) of the final products will also be performed at UNLV.

RESEARCH ACCOMPLISHMENTS

The preliminary studies into the synthesis of actinide nitride fuels through a low temperature, liquid ammonia based synthesis route have been conducted on the uranium containing system, and there is good indication for the success of synthesizing uranium(III) nitride. The dissolution of iodine in ammonia is a rapid process, resulting in a pale green solution, which does not result in any observable oxidation of iodine. The cannula transfer of dissolved iodine into the reaction vessel containing U metal has been conducted with little to no residual iodine remaining in the original flask. The metal being used for these reactions has a noticeable brown/black oxide coating that prevents the formation of $UI_3(NH_3)_x$.

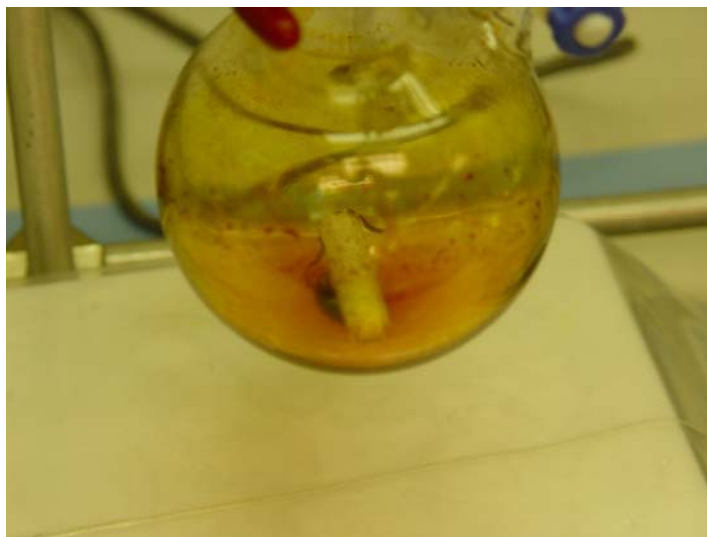
Stirring of U metal fragments with dissolved iodine in ammonia for 24 hours revealed a thickening of the oxide coating, which presumably is a result of O_2 or H_2O contamination in the solvent. Procedures for cleaning the metal prior to the reaction are under development. Two measures are being taken in order to use the most purified solvent possible; the highest grade ammonia available is being obtained and several procedures are being developed to dry and deoxygenate the solvent. These actions should allow the reaction to proceed without formation of the boundary oxide layer between the two reactants.

ACADEMIC YEAR HIGHLIGHTS

- ◆ T. Sullens and K. Czerwinski attended the 2006 Nuclear Energy Research Initiative (NERI) Fuels Review Meeting at Idaho National Laboratory, Idaho Falls, ID, August 7-8, 2006.
- ◆ This project was included in the Nuclear Energy Research Initiative 2006 Annual Report as a NERI recipient (awarded in FY06).

FUTURE WORK

There are a number of alternate synthetic routes for producing the $UI_3(solvent)_x$ precursor to $U(III)N$, which are available for successful project completion should this method be ineffective. Any number of these precursors can be adapted for inclusion into the reaction process, yet these precursors will increase the likelihood of carbon inclusion and contamination into the final product. However, it is believed that the proposed procedure would be most beneficial for the desired outcome and for the introduction of a novel, viable synthetic route for accessing $U(III)$. Once the synthetic process is understood for the uranium species, only minor modifications are anticipated for the transuranic species.



A depiction of dissolved iodine reacting with uranium metal after the liquid ammonia solvent has evaporated.

Research Staff

Tyler Sullens, Principal Investigator, Assistant Research Professor, Harry Reid Center for Environmental Studies
Ken R. Czerwinski, Co- PI, Associate Professor, Department of Chemistry

Students

Edward Mausolf, Undergraduate Student, Department of Chemistry

Collaborators

Al Sattelberger, Argonne National Laboratory
Dave Clark, Los Alamos National Laboratory
Gordon Jarvinen, Los Alamos National Laboratory