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Solution-Based Synthesis of Nitride Fuels

Kenneth Czerwinski  
*University of Nevada, Las Vegas, czerwin2@unlv.nevada.edu*

Tyler A. Sullens  
*University of Nevada, Las Vegas*

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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 (PuI₃) and uranium tetraiodide (UI₄) 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 AnI₃L₄, where An is uranium, neptunium, or plutonium, and L is tetrahydofuran (thf), pyridine, dimethylsulfoxide, etc.

\[
\text{PuI}_3 + 1.5 \text{I}_2 + \text{xS} \rightarrow \text{PuI}_3(\text{NH}_3)_3
\]

PuI₃ is soluble in ammonia, presumably as the ammonia adduct PuI₃(NH₃)₃. More recent efforts by ANL and LANL collaborators have investigated amido reactions with actinides to produce An(NR₂)₃ complexes, where An = U, Np, Pu:

\[
\text{AnI}_3(\text{solv})_4 + 3 \text{NaNR}_2 \rightarrow \text{An}(\text{NR}_2)_3 + \text{NaI} + \text{solv}
\]

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 fuels is:

\[
\text{An} + 1.5 \text{I}_2 \rightarrow \text{AnI}_3(\text{NH}_3)_3 \rightarrow \text{An}(\text{NH}_2)_3 \rightarrow \text{AnN}
\]

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 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**

One of the original synthetic routes devised for the synthesis of U (III)N involved the entire reaction taking place in liquid ammonia. Several experimental reactions were conducted in an attempt to synthesize the UI$_3$(THF)$_4$ and U(NH$_2$)$_3$(NH$_3$)$_x$ precursors of U(III)N. Each attempt involved cleaning of the uranium metal to remove the oxide coating of the metal reagent with 3 washes of concentrated nitric acid, each followed by a rinse with liquid ammonia. Success of this cleaning procedure was varied, with a majority of cleaned metal oxidizing rapidly once in contact with the liquid ammonia, despite the precautions taken to eliminate oxygen contamination in the reaction flasks. Due to the continual presence of oxide coating of the uranium metal, it was decided to alter the proposed synthetic route to utilize the synthesis of the UI$_3$THF$_4$ precursor, as described in *Inorganic Chemistry*. This involves the purification of THF through distillation, cleaning of the metal uranium, and slow reaction of U and I$_2$. Equipment to perform this synthesis was not available for immediate use, but all necessary glassware was purchased.

It was discovered that the uranium metal turnings being used for the synthesis had a possibility of containing niobium as well. Waste solutions were analyzed by ICP-AES, and no niobium was identified. Other reaction waste solutions were also analyzed in order to determine the reactivity of uranium in the liquid ammonia solution. These analyses determined that only a minimal amount of uranium became dissolved, indicating that either there was little reactivity in the liquid ammonia or the reaction was only taking place on the surface of the metal. Neither of these possibilities is desirable, therefore the synthetic route involving THF was selected to avoid these outcomes.

Single crystal and powder diffractometers are necessary instruments for the determination of the intermediate and final products.

**ACADEMIC YEAR HIGHLIGHTS**


**Other progress**

- Reaction of UCl$_4$ + 4 NaNH$_3$ in liquid ammonia was performed. UI$_3$(THF)$_4$ + 3 NaNH$_2$ in liquid ammonia was performed. The samples were treated and processed.
- Samples were prepared for EA Modeling reactions and crystals were obtained. Modeling reactions were extended to scorpionates. This represents a new synthetic route actinide nitride. Initial characterization indicated other products are present.
- UN was obtained from UI$_3$ and Li$_3$N direct reaction and was characterized.
- Metallocenes were synthesized from starting materials. Reaction and monitoring of these metallocenes with amide salts was conducted.
- Liquid ammonia reaction between uranium (III) iodide and sodium amide yielded a new product with indications of being a UN pre-cursor. The product was characterized by XAFS.