Sol-gel chemistry to control morphology and porosity of actinide oxide feeds for electroreduction

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Introduction

In response to the increasing global energy demand, nuclear energy displays an important role to fulfill this demand while significantly reducing carbon emissions. However, the accumulation of highly radiotoxic spent nuclear fuel is the major obstacle to conquer. Reprocessing the spent fuel is therefore one of the key points in the development of future nuclear energy technology.

Pyroprocessing is a combination of electrochemical operations for the reprocessing of spent nuclear fuels in high temperature molten salt media. Two main sub-processes are electroreduction and electrorefining. In the electroreduction process, the spent oxide fuel is converted to its metallic form in a high temperature molten salt. This metallic fuel can be treated in the electrorefining process, where uranium will be recovered and separated from the other transuranium species.

These pyroprocessing steps can also be developed at lab scale or semi-industrial scale. In this project, the feasibility of pyroprocessing is investigated to valorize the LEU final oxide product that will be produced in the RECUMO project. It will be the first step in upscaling the electrochemical conversion of UO_2 towards U metal for reuse in radiation targets or MTR fuel, thus closing the loop for U recycling in medical isotope production.

Objectives

To develop a proof of concept metallization methodology for actinide oxides from irradiated medical isotope targets

Implementation and optimization of the electroreduction of uranium oxides in molten salt media.

- ⇨ Reducing reaction time
- ⇨ Improving faradaic efficiency
- ⇨ Maintaining feed purity

Exploring the possibility of applying electrorefining on untreated feed material for direct reuse of the purified actinide fraction as medical isotope targets or MTR fuel.

Electroreduction

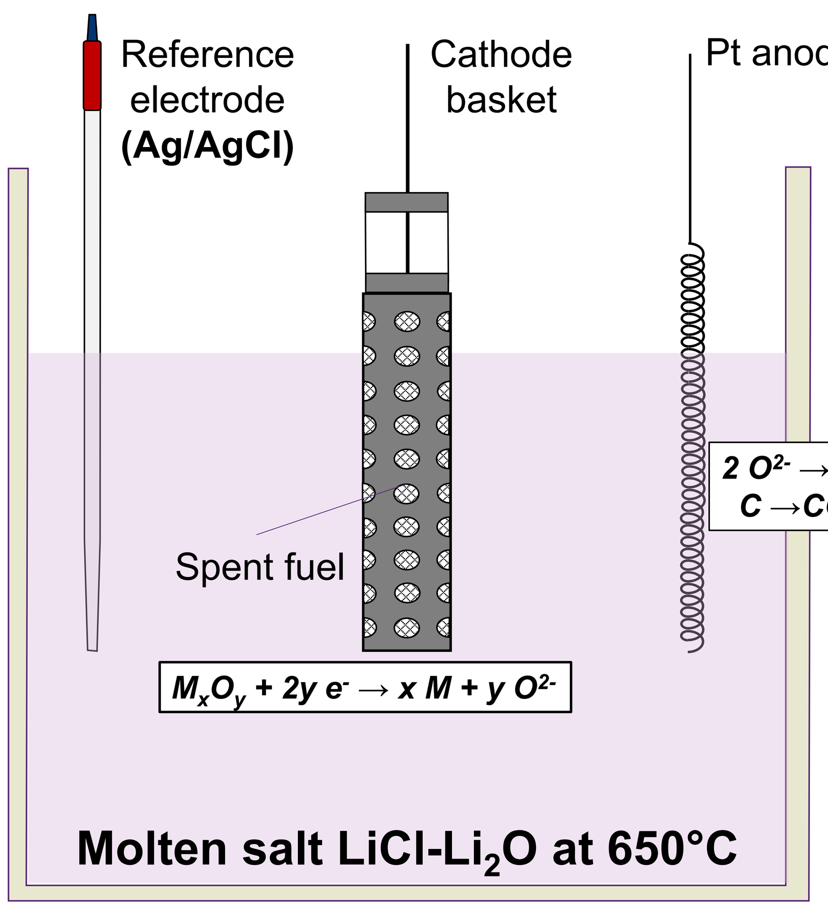


Fig. 1 Schematic representation of the electroreduction process.

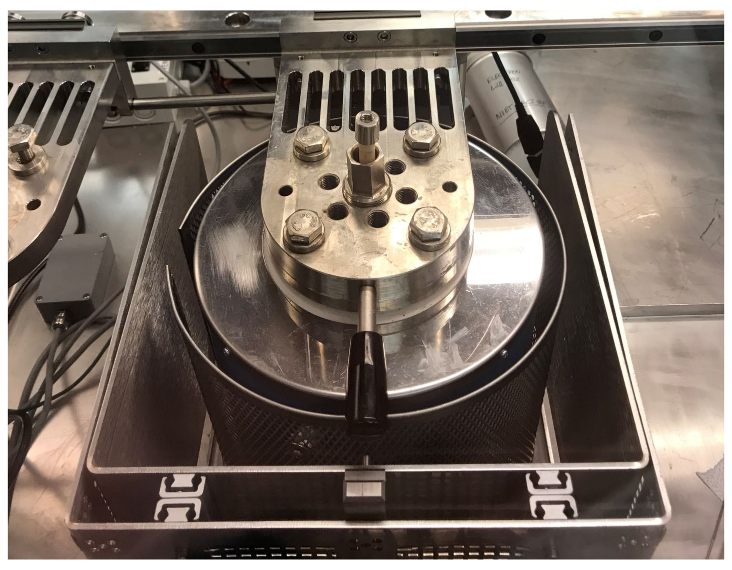


Fig. 2 Custom made High Temperature Electrochemical Cell (HTEC) for electroreduction.

Standard Decomposition Potential

$LiCl \rightarrow Li + 0.5\,Cl_2$	$E^o = 3.46$ V
$Li_2O \rightarrow 2Li + 0.5\,O_2$	$E^o = 2.47$ V
$UO_2 \rightarrow U + O_2$	$E^o = 3.40$ V

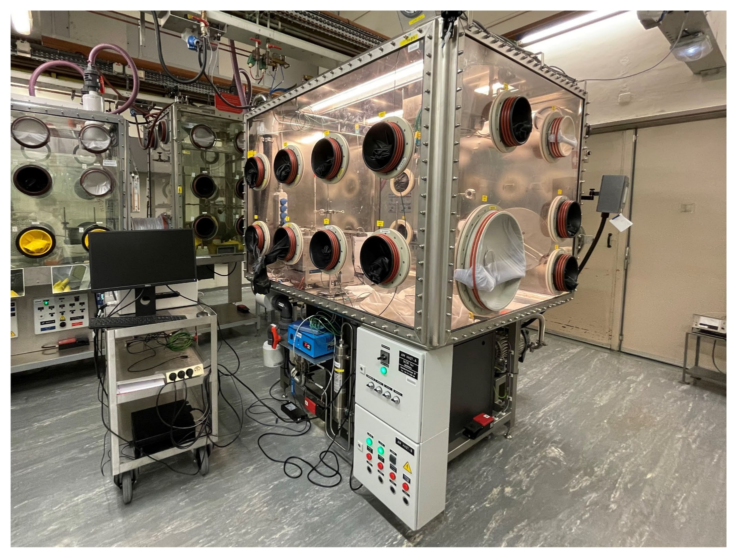


Fig. 3 Glovebox of ELECTRON.

Two pathways of Reduction:

$UO_2 + 4e^- \rightarrow U + 2O^{2-}$	*Direct electrochemical reduction*
$Li^+ + e^- \rightarrow Li$ $UO_2 + 4Li \rightarrow U + 2Li_2O$	*Chemical reduction via Li/Li⁺ couple*

Result and Discussion

To simulate and optimize the electrochemical cell and the electrolysis procedure for uranium oxide reduction process, the TiO_2 reduction experiments were performed.

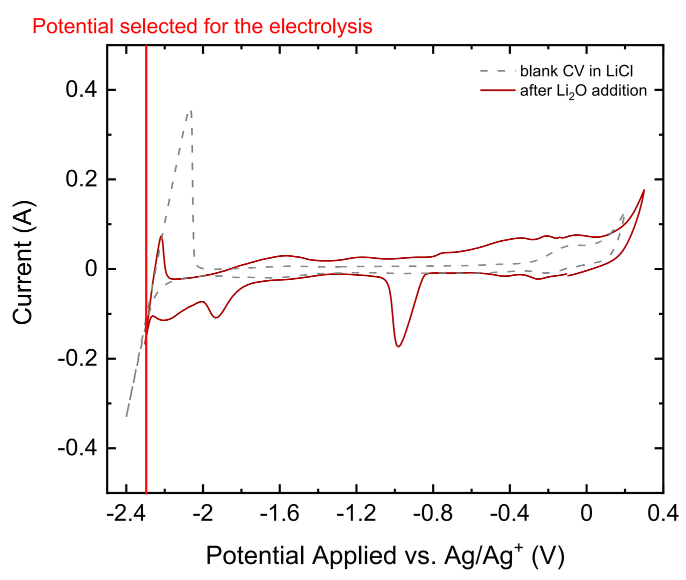
Reduction Pathway of TiO_2

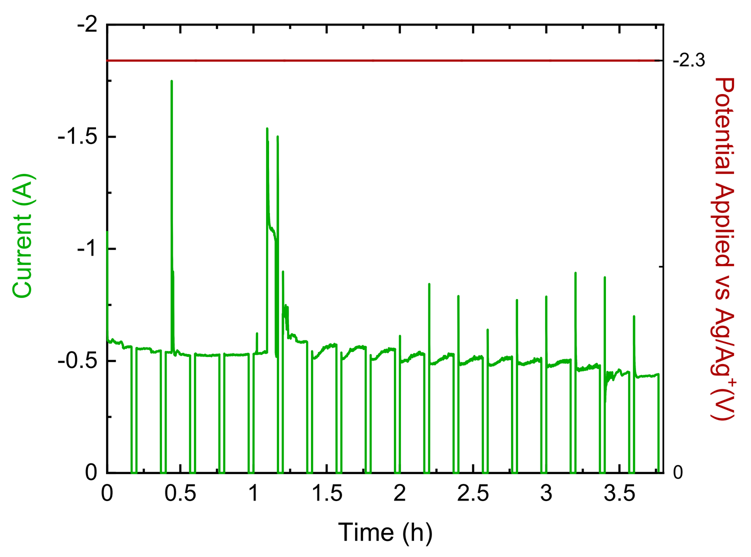
$Li^+ + TiO_2 + e^- \rightarrow LiTiO_2$

$LiTiO_2 + e^- \rightarrow Li^+ + TiO + O^{2-}$

$TiO + e^- \rightarrow 0.5\,Ti_2O + 0.5\,O^{2-}$

$0.5Ti_2O + e^- \rightarrow Ti + 0.5\,O^{2-}$





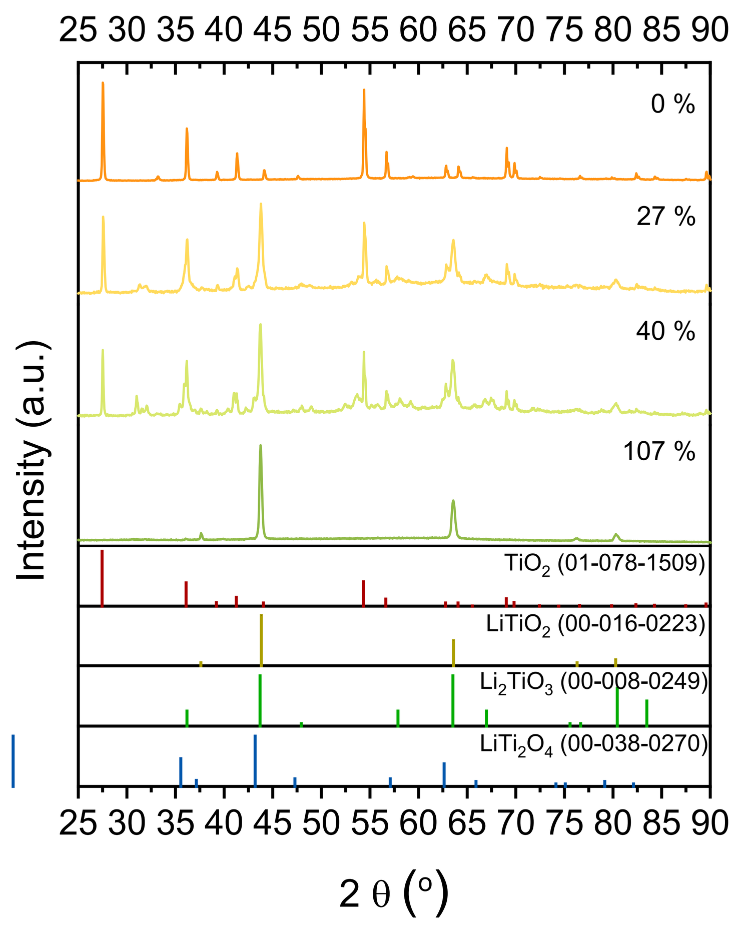


Fig. 4 XRD patterns of the oxide feeds after electrolysis (corresponding to the following percentage of the theoretical charge 0%, 27%, 40 %, and 107%.)

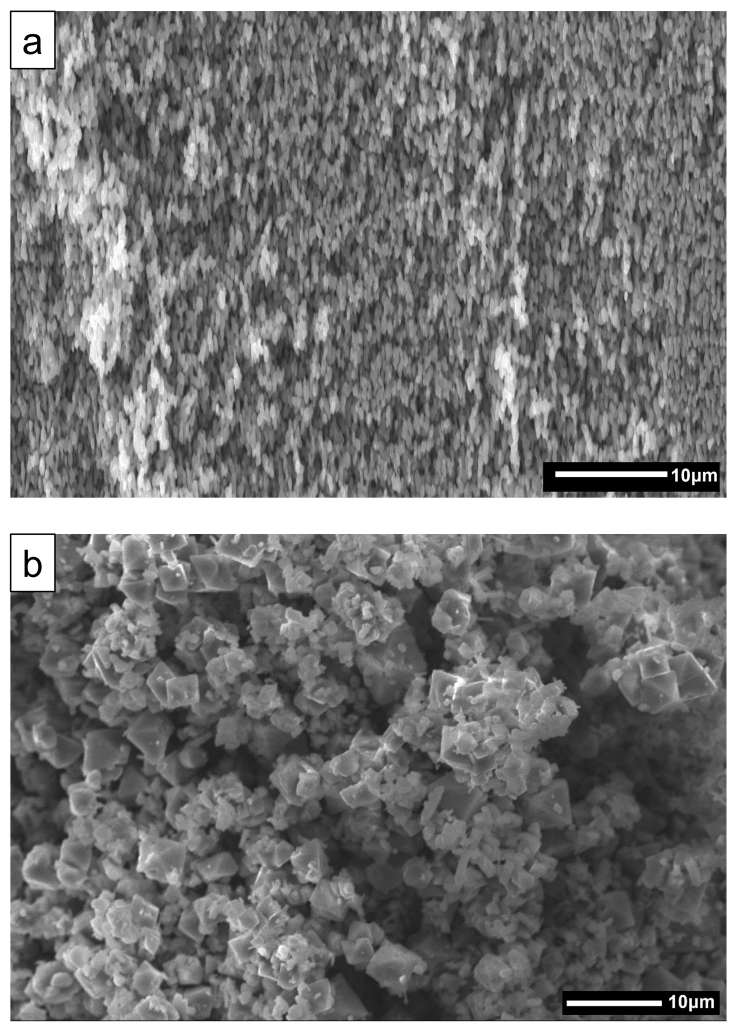


Fig. 5 SEM images before (a) and after (b) electrolysis.

Outlook

- Better understanding on Li formation during the electrolysis, and its influence on the system.
- Study the effect of the morphology of the oxide feed on the electrolysis.
- Optimization of the electrolysis procedure, via multi-step electroreduction at selected potentials

[1] Nuclear Energy Agency, "State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry," 2018.
[2] Choi, E. Y., & Jeong, S. M. (2015). Electrochemical processing of spent nuclear fuels: An overview of oxide reduction in pyroprocessing technology. *Progress in Natural Science: Materials International*, *25*(6), 572–582.
[3] Seo, C. S., Park, S. Bin, Park, B. H., Jung, K. J., Park, S. W., & Kim, S. H. (2006). Electrochemical study on the reduction mechanism of uranium oxide in a LiCl-Li2O molten salt. Journal of Nuclear Science and Technology, 43(5), 587–595.
[4] Herrmann, S. D., Li, S. X., & Simpson, M. F. (2005). Electrolytic Reduction of Spent Oxide Fuel – Bench-Scale Test Results. American Nuclear Society - Global 2005, 1–7.
[5] Shin, H. S., Hur, J. M., Jeong, S. M., & Jung, K. Y. (2012). Direct electrochemical reduction of titanium dioxide in molten lithium chloride. Journal of Industrial and Engineering Chemistry, 18(1), 438–442. https://doi.org/10.1016/j.jiec.2011.11.111