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Objectives

To develop a safe and compact metallization process to convert purified actinide oxides and study the influence of feed morphology

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

⇒ Reducing reaction time

⇒ Study influence of feed morphology

⇒ Improving faradaic efficiency

⇒ Characterize product structure and composition

Introduction

In response to the increasing global energy demand, nuclear energy displays an important role which can not only fulfill this demand but reduce the CO₂ emission into the environment. However, The accumulation of highly radiotoxic spent nuclear fuel is one of the major obstacles to conquer. The reprocessing of the spent fuel is, therefore, a key point in the development of nuclear energy technology.

Pyroprocessing is a combination of electrochemical operations for the reprocessing of spent nuclear fuels in high temperature molten salt media, comprising of several sub-processes: head-end treatment, electroreduction, and electrorefining. In the electroreduction process, the spent oxide fuel is converted to its metallic form in the high temperature molten salt, such as LiCl-Li₂O. Then the metallic fuel can be fed to the electrorefining process, during this process, uranium will be recovered and separated from the other transuranium species in the spent fuel.

Electroreduction

Actinide oxides are electrochemically reduced into their metallic form. The oxide feed is contained in a cathode basket, and then the cathode basket is loaded in a high temperature molten salt, such as LiCl-KCl eutectic or LiCl-Li₂O. The oxide feed will be reduced electrochemically into its metallic form by applying current between the cathode and an inert anode (Pt or C). The oxygen ions produced on the cathode will diffuse to the anode to undergo an oxidation reaction: $2O^{2-} \rightarrow O_2 + 4e^-$.^[1]

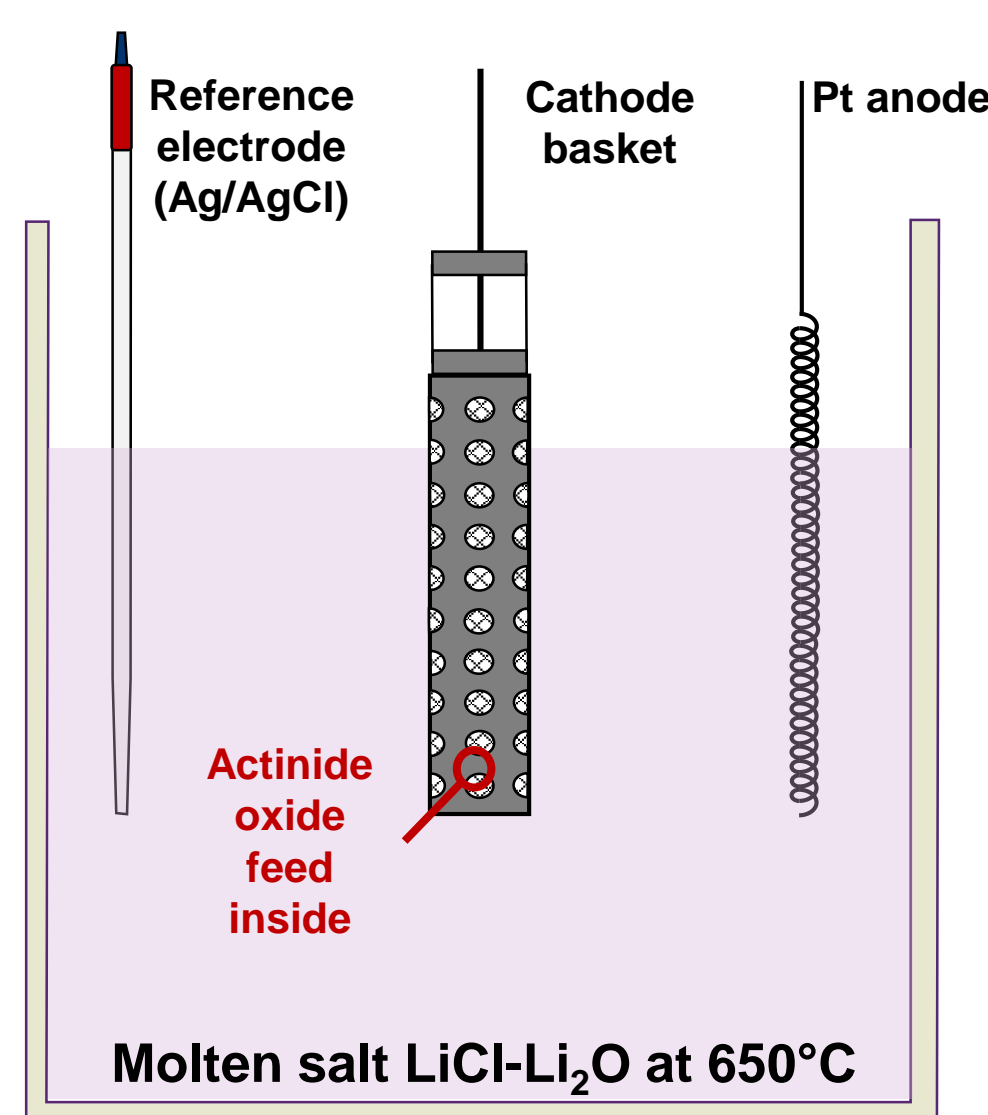


Figure 1. Schematic diagram of the electroreduction process.

Two different reduction mechanisms of UO₂ (Seo et al.^[3]):

- direct electrochemical reduction
- reduction via Li/Li⁺ couple

⇒ electroreduction process with higher reduction rate and higher stability can be performed.

In the LiCl-Li₂O system, the addition of Li₂O is used to speed up the reduction rate and to prevent the anodic dissolution of the platinum anode. The standard reduction potential (E⁰) of Li₂O decomposition is 2.47 V, which is comparable to the 2.40 V of uranium oxide reduction^[3]. Therefore, the decomposition of Li₂O results in Li formation on the cathode, and the O²⁻ oxidation reaction on the anode. Both reactions are beneficial to the electroreduction process from different perspectives:



Results

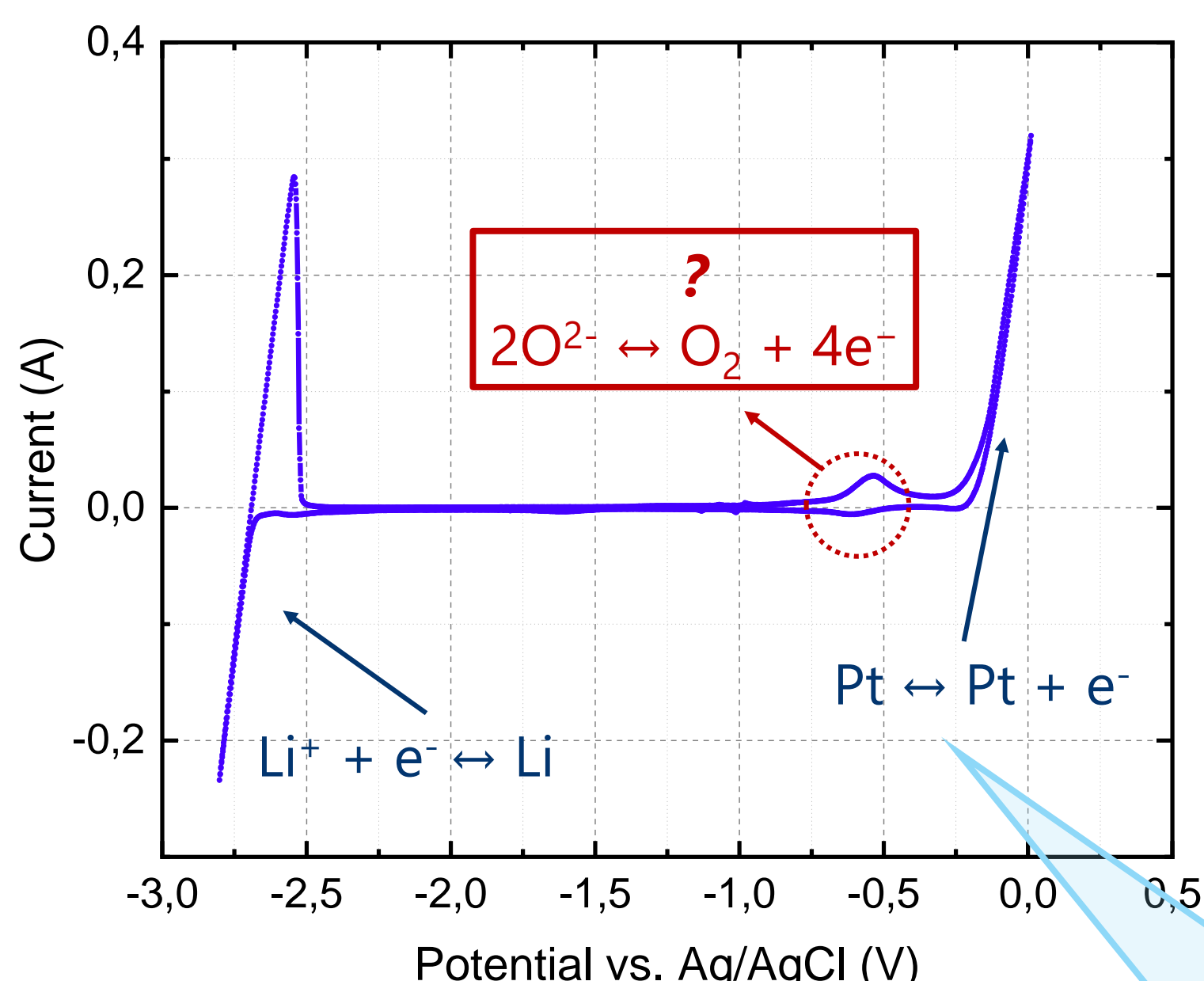


Figure 2. Cyclic voltammogram of LKE salt at 450°C, from 0,01 V vs Ag/AgCl to -2,8 V (Scan rate: 0,05 V/s)

- The unknown redox pair could be: $2O^{2-} \leftrightarrow O_2 + 4e^-$ or $2Li + Pt + 3O^{2-} \leftrightarrow Li_2PtO_3 + 4e^-$ ^[5]
- O²⁻ could possibly come from the residual moisture in LiCl.

However, from the SEM images:

1. No deposition shown on the surface of the Pt coil.
2. Anodic Pt dissolution presented, (undesirable in the electroreduction process).

→ The redox pair was less likely to be Li₂PtO₃ formation.

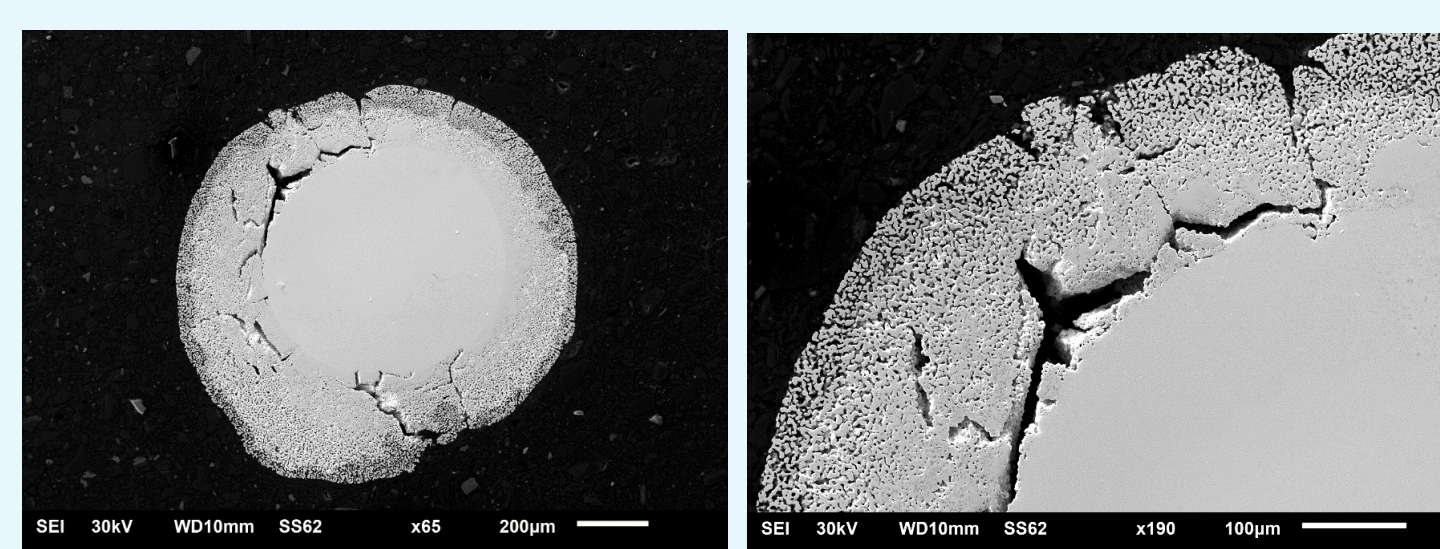


Figure 3 & 4. SEM images of the cross section of the used Pt wire. (*65 and *190, respectively)

Experimental Setup

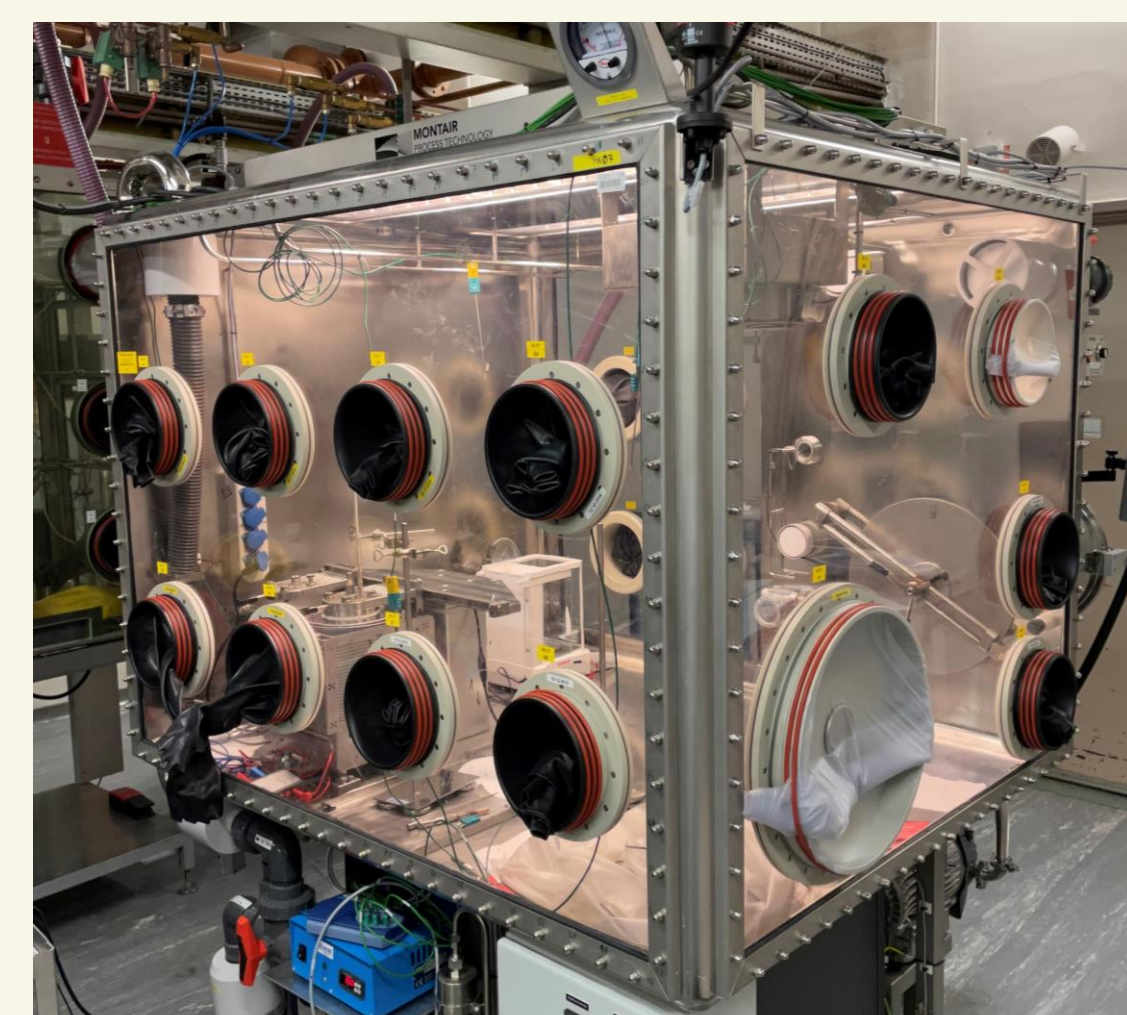


Figure 5. The Glovebox (Montair HK-07) with Argon atmosphere which is applied in the electroreduction process.

Experiments are performed in an inert atmosphere glovebox (Figure 5), as LiCl is extremely hydrophilic. Both oxygen and water can have an impact on the electroreduction process.

A custom High Temperature Electrochemical Cell (HTEC) is designed and constructed for this project (Figure 6).

A melting furnace (Borel KP1100) is used to heat the molten salt electrolyte to 650 °C. The furnace is covered by a lid with shielded electrode throughputs, including the working electrode (stainless steel cathode basket), counter electrode (Pt coil), the reference electrode (Ag/AgCl) and throughputs for thermocouples, allowing temperature tracking during the process.

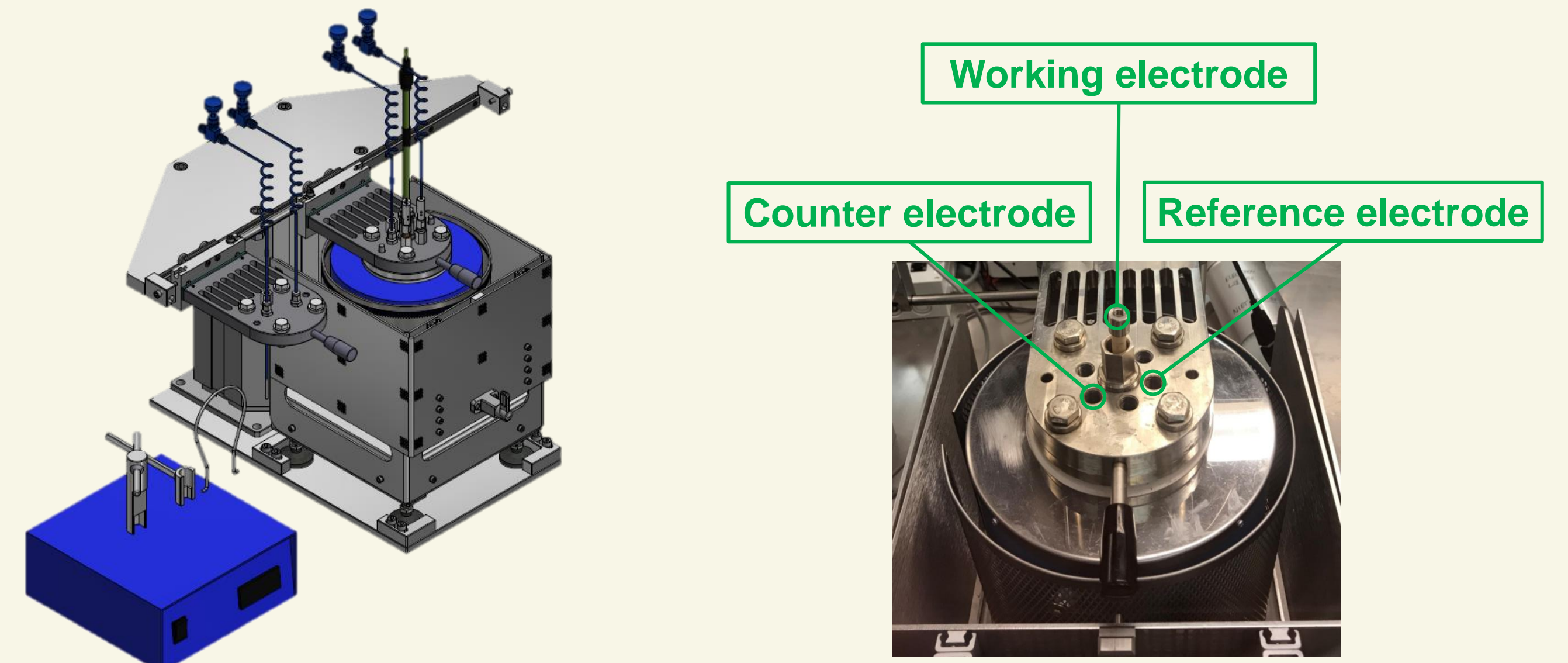


Figure 6. High Temperature Electrochemical Cell which is applied in the electrochemical process.

Future Work

- Simulant electroreduction tests on TiO₂ will be performed, followed by reduction of UO₂ and U₃O₈.
- Investigation of the uranium oxide feeds prepared via Sol-gel synthesis to study the kinetics and efficiency of the electroreduction process.
- Development of a salt distillation setup to eliminate residual salts from the actinide products

References

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