

High Temperature Electrochemical Engineering and Clean Energy Systems

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Global power demand is projected to more than double by 2050 and meeting this increased power demand will require maintaining or increasing power output from all existing energy sources while adding a large amount of new capacity. The power sources that have the greatest opportunity to fulfill this demand gap over this time period are clean energy sources including solar and nuclear power. One of the areas of expertise that SRNL has been applying to help with a variety of clean energy technologies is in high temperature electrochemistry. Savannah River National Laboratory (SRNL) in collaboration with industrial and university partners has used high temperature electrochemical engineering to make improvements in solar power, nuclear fuel reprocessing, and fusion energy technologies. This article describes how high temperature electrochemistry has been applied at SRNL to mitigate corrosion in high temperature CSP systems, develop novel methods of nuclear fuel processing, and recover tritium in fusion energy technologies.

Due to population growth, global power demand is projected to more than double by 2050. Meeting this increased power demand will require maintaining or increasing power output from all existing energy sources while adding a large amount of new capacity. The power sources that have the greatest opportunity to fulfill this demand gap over this time period are clean energy sources including solar and nuclear power. The US Department of Energy (DOE) funds research programs to develop and mature these future power sources so that they will be ready to meet the power demands for tomorrow and Savannah River National Laboratory (SRNL) has programs that assist DOE in the development of these technologies. One of the areas of expertise that SRNL has been applying to help with a variety of clean energy technologies is in high temperature electrochemistry. SRNL in collaboration with industrial and university partners has used high temperature electrochemical engineering to make improvements in solar power, nuclear fuel reprocessing, and fusion energy technologies.

Many programs within the DOE that are focused on clean energy have integrated a strong focus on electrochemistry in recent years due to the high efficiency that can be achieved by electrochemical reactions. The high efficiency of electrochemical processes is due to the direct relationship between electrochemical energy and Gibbs energy from fundamental thermodynamics. Mechanical systems used in energy applications such as turbines are limited by Carnot efficiency, where electrochemical systems are only limited by the kinetics of the electrochemical reaction. DOE sponsored research on electrochemical systems for clean energy include batteries, fuel cells, photovoltaics, supercapacitors, and a variety of other technologies. Although they are less well known, electrochemical systems have been developed for reprocessing nuclear fuels to enable advanced fuel cycles for nuclear power. This research was pioneered at DOE national laboratories and is being researched and implemented globally by countries such as South Korea and Japan. Corrosion is also an electrochemical phenomenon that is important to understand and mitigate to prolong the lifetime for clean energy systems. All of these aspects make electrochemical engineering vital to further development of clean energy technologies.

One specific area of electrochemical engineering that has been increasing in importance is high temperature electrochemical engineering. There is a significant opportunity to increase the

efficiency of the power cycles used in concentrating solar power (CSP) and nuclear applications by moving to higher temperatures. However, achieving these higher efficiencies requires operating these systems at higher temperatures and requires heat transfer fluids such as molten salts that have good heat transfer properties at these conditions. Molten salt heat transfer fluids can cause corrosion in a large number of materials and the operating at temperatures above 700°C that DOE programs such as the SunShot Initiative have targeted limits material selection. Pyroprocessing to reprocess nuclear fuels is a combination of high temperature electrochemical processes that makes use of reactions that cannot be performed in aqueous solutions at low temperatures. Similarly, direct high temperature electrolysis of LiT in the molten lithium cooling blanket of fusion reactors has the potential to improve on current methods of tritium recovery that are needed to make these systems practical. All of these applications require pushing the frontiers of high temperature electrochemistry and this is one of the areas that SRNL has been actively working on with its partners.

High Temperature Molten Salt Corrosion Mitigation

The DOE SunShot program has the goal of reducing the cost of power from CSP systems to below \$0.06 / kWh by 2020. To achieve these cost reductions, it is projected that high efficiency power cycles such as the supercritical CO₂ cycle or super-heated Rankine cycle need to be used. These power cycles require a heat source between 700 and 750°C and a heat transfer system that can match these operating temperatures. Molten salts have excellent heat transfer properties, but can cause significant corrosion in Fe-Ni-Cr alloys such as stainless steels. Also, high-performance alloys, often known as superalloys, are needed for operation at elevated temperature because of the additional failure modes such as creep rupture that are occur under these conditions. Finding a combination of a molten salt with an alloy that can withstand corrosion and which has good strength at these conditions is very important for reaching the SunShot energy cost goals. To reach a 30-year system lifetime, the SunShot program estimate that corrosion rates below 15 microns / yr would be needed.

Electrochemical characterizations combined with thermodynamic modeling helped to validate that the selective oxidation of Cr that occurs preferentially at the grain boundaries

of Fe-Ni-Cr alloys is the principle corrosion mechanism. This selective oxidation of Cr had been proposed in literature, but the reaction mechanism was not known along with the rate limiting step for the corrosion. It was also unclear why the corrosion rate was affected by the choice of the crucible material used to contain the alloy coupons during corrosion measurements. Electrochemical experiments using techniques such as corrosion potential monitoring, cyclic potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) helped to show that the corrosion rate in molten chloride systems had fast kinetics and was limited by mass transfer. Figure 1 shows EIS data for one of the samples. The EIS data show that the phase angle never goes above 45°, which is indicative of mass transfer limitations that have elements of both resistive and capacitive behavior. This also led to the realization that one of the reasons that Cr selective oxidation was observed along grain boundaries is that the diffusion coefficients for mass transfer are orders of magnitude higher in this region than they are in the bulk of the sample.

The fact that the corrosion has fast kinetics led to a decision investigate methods to inhibit corrosion thermodynamically and prevent corrosion reactions from being able to occur in the first place. One method of inhibiting corrosion thermodynamically is to include a species in the system that has an electrochemical reduction potential below the components of the system that are being selectively oxidized. For the MgCl₂-KCl molten salt system, metallic Mg was identified as a potential corrosion inhibitor. Figure 2 shows the electrochemical equilibrium potential for Mg going to MgCl₂ and compares that to the potentials for other alloy components going to their molten chlorides. This shows that the equilibrium potential is well below the equilibrium potentials of the Cr that is selectively oxidized.

The results of corrosion inhibition experiments showed that the corrosion rate of samples in MgCl₂-KCl containing 1.15 mol% Mg showed 35 times lower corrosion than baseline tests with no corrosion inhibitor and met the DOE SunShot targets. Additional experiments to aggravate corrosion by adding convective flow using a thermosiphon were conducted with and without the Mg corrosion inhibitor. The corrosion rate in baseline tests with convective flow and no Mg corrosion inhibitor increased by a factor of 3. However, thermosiphon tests with the 1.15 mol% Mg corrosion inhibitor reduced corrosion below the DOE targets. Figure 3 summarizes data from tests with the corrosion inhibitor and demonstrates how metallic corrosion inhibitors such as Mg can help to effectively eliminate corrosion in molten salt heat transfer systems.

It has also been demonstrated that since addition of Mg lowers the corrosion potential of alloys that electrochemical monitoring of alloy corrosion potential using a reference electrode can be used as a corrosion mitigation method. This would enable the use of Mg to be monitored in real time so that the systems susceptibility to corrosion could be monitored and develop the use of metallic corrosion inhibitor into an effective corrosion mitigation method that could be implemented in CSP plants to ensure that plant lifetime goals will be achieved.

Electrochemical Reprocessing of Nuclear Materials

The electrochemical processing of nuclear materials has the potential to separate the high value components of nuclear fuel for reuse, while preventing individual separation of metals such as Pu that could be used in nuclear weapons. This potentially makes it a very attractive technology to enable large reductions in the amount of nuclear waste generated from nuclear fuels.

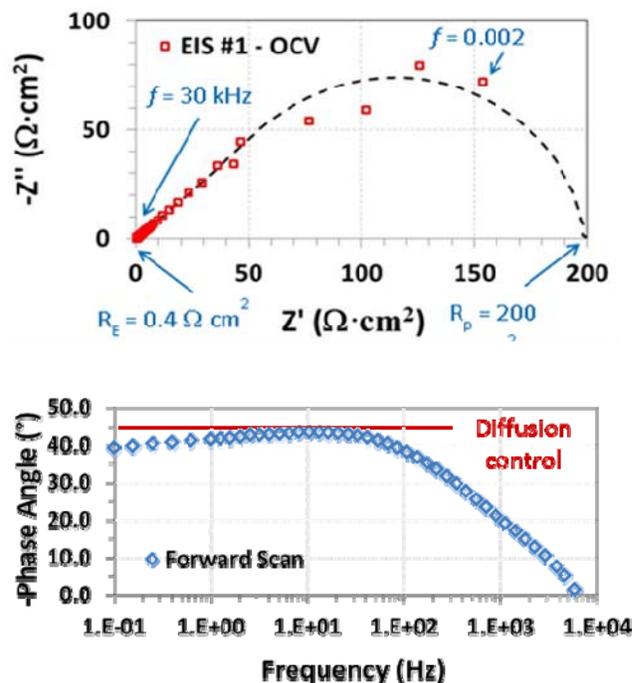


Figure 1. Electrochemical impedance spectroscopy testing of Haynes 230 at 850°C in KCl-MgCl₂

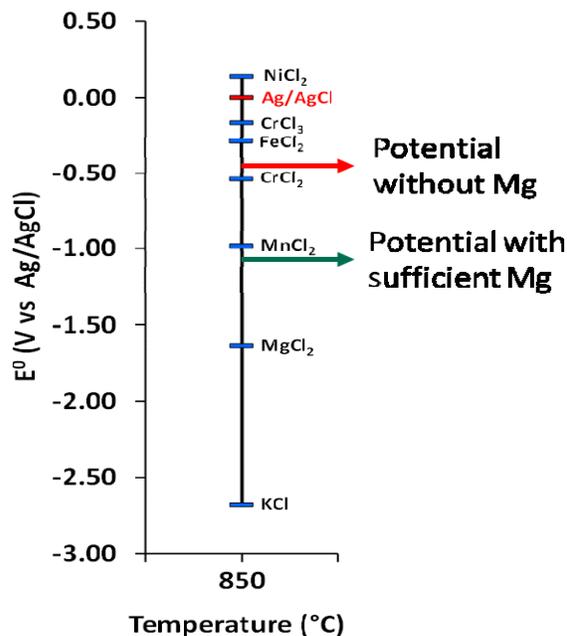


Figure 2. Electrochemical potential for alloy components and Mg corrosion inhibitor

SRNL has developed multiple technologies in this area based on high temperature electrochemical techniques including electrochemical fluorination and the reduction of metal oxides using solid oxide electrodes.

Electrochemical fluorination is a process that has been proposed that has the potential to combine aspects of the two main literature methods to reprocess nuclear fuels: 1) molten chloride pyroprocessing, and 2) fluoride volatility. Molten

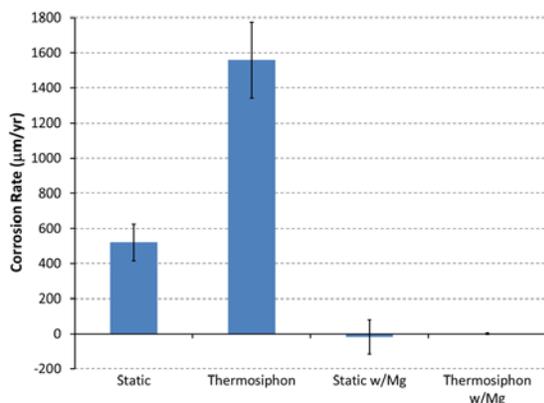


Figure 3. Corrosion rate for Haynes 230 alloy in MgCl₂ for cases with and without Mg corrosion inhibitor

chloride pyroprocessing uses electrorefining to separate most of the uranium from metallic nuclear materials using electrorefining and captures the rest of the uranium along with transuranic elements such as Pu in a liquid Cd cathode to make U/TRU fuel that can be used in a sodium cooled fast reactor. The electrorefining of the uranium is time consuming and energy intensive in this process. Fluoride volatility uses a fluorinating agent to convert uranium oxide in nuclear fuel to UF₆ and separate it in the gas phase. The main problem with the fluoride volatility method is that other fission products are also converted to their gaseous form and need to be separated from UF₆, which can only be done with some difficulty due to similarities in physical properties for some of the gaseous fission products.

The electrochemical fluorination process uses a galvanic electrochemical reaction between a fluorinating agent and metallic nuclear fuel to create UF₆ and fission product fluorides that are maintained in the salt. These fission product fluorides could be reacted to form a U/TRU product for reuse as well as generating UF₆ that could immediately go into gaseous separation processes to re-enrich it for use in commercial light water reactors. A diagram of the electrochemical fluorination process is shown in Figure 4. This electrochemical fluorination system would combine the advantages of molten chloride pyroprocessing and fluoride volatility to improve nuclear fuel separation. Proof-of-concept testing at SRNL has demonstrated the viability of the electrochemical reaction and additional testing is planned to improve the electrode structure and kinetics. This high temperature electrochemical method along with other enabling technologies has the potential to create alternative cycles for nuclear fuels that will lower the amount of waste from nuclear power that needs to go for long term storage.

Direct LiT Electrolysis for Fusion Energy

The separation of lithium tritide (LiT) from molten lithium cooling blankets is an essential enabling technology for fusion energy systems to allow the capture and reuse of tritium. The current leading method for separating the tritium is known as the Maroni process where the LiT is extracted from the molten lithium using a molten salt that is then separated in a centrifuge and then the molten salt undergoes electrolysis to decompose the LiT. The use of a molten salt for this process can be problematic because it can cause corrosion and salt components can become irradiated if they get entrained with the molten lithium and are sent inside the fusion reactor. SRNL has proposed direct LiT electrolysis in the molten lithium blanket based on advanced

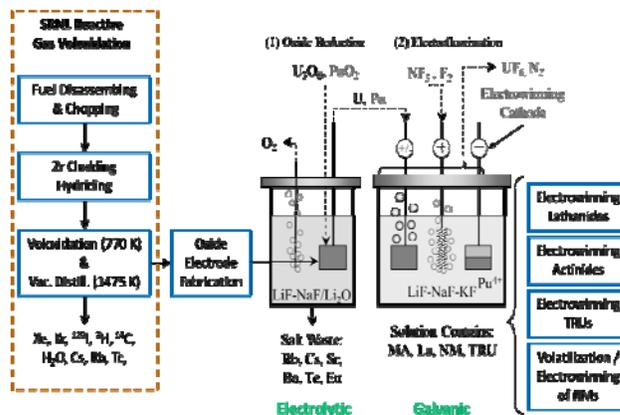


Figure 4. Electrochemical fluorination process for nuclear fuel reprocessing

lithium ion conductors. The direct LiT electrolysis method would eliminate the need for a molten salt to extract the LiT and would perform the electrolysis reaction directly in the buffer tank used to store the molten lithium for the cooling blanket. This modification would simplify the process and could lead to reduced cost and complexity for tritium recovery. Figure 5 shows flow diagrams comparing the Maroni process and direct LiT electrolysis method.

SRNL has been able to demonstrate the electrolysis of LiD (as an LiT surrogate) from molten lithium by using a residual gas analyzer to detect deuterium gas that is a product of the reaction. The evolution of the deuterium gas started and ended when the electrolysis voltage was applied and removed. These results provide support for the solid state LiT electrolysis process and make an advancement toward improving the feasibility of fusion energy systems.

Summary

High temperature electrochemistry has a large variety of application in the area of clean energy and the unique features of high temperature electrolytes to process materials in non-aqueous environments provides many unique opportunities. Applications have been described in solar energy technologies, nuclear fuel reprocessing, and fusion energy, but there are a large number of potential areas that could benefit from high temperature electrochemistry including energy storage, light metals production, and others. Through collaboration with university partners at the University of South Carolina and Clemson University as well as partnering with industry, SRNL is using areas of expertise like high temperature electrochemistry to find solutions to the energy challenges that we will face globally in the future.

Acknowledgements

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Notes

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Maroni Process

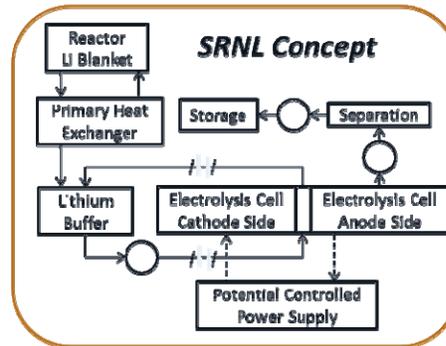
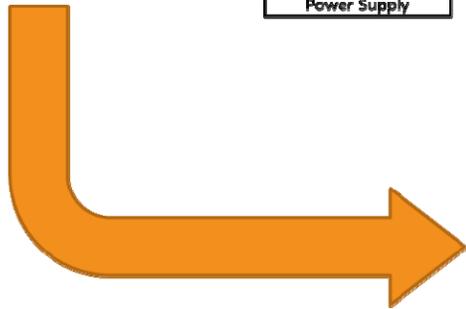
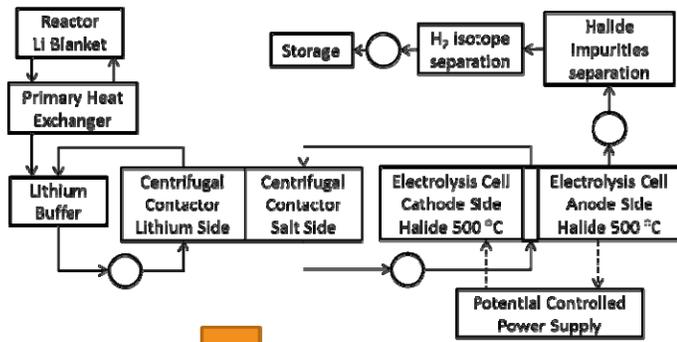


Figure 5. Comparison of the direct LiT electrolysis method with the Maroni process