Advanced Electrochemical Separations of Actinide/Fission Products via the Control of Nucleation and Growth of Electrodeposits

Fuel Cycle Research and Development

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Advanced Electrochemical Separations of Actinide/Fission Products via the Control of Nucleation and Growth of Electrodeposits

Final Report

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Executive Summary

Objectives

It is well known that according to current knowledge the pyroprocessing of spent nuclear fuels invariably leads to the dendritic form of electrodeposits, which from technological point of view is undesirable for many reasons. The aim of this research was to study and preclude the formation of electrodeposits with dendritic morphology (of essential importance to FC-I Program).

This project is characterized with four novel study categories: (1) exploring electrodeposits morphology control by controlling the electrochemical deposition reaction rate, (2) the use of rotating disk electrode technique to distinguish the electrodeposition control modes (reaction rate vs. diffusion), (3) morphology studies of lanthanides (La) and actinides (U) in characteristic stages of nucleation and growth, (4) exploring the need for separation of electrochemical cell in compartments for cathodic and anodic reactions. All these study categories were applied on two distinct electrolyte systems (a) high temperature ionic liquids, i.e. molten LiCl-KCl salts, and (b) room temperature ionic liquids (compounds exclusively made of organic cations, and organic/inorganic anions).

Because the quality (dense and smooth) of electrodeposits is a direct function of the electrochemical reduction rate (slower the better), the major expectation was that addition of organic molecules would provide the desired slowing down of electroreduction effect, avoiding the undesired dependence on mass transfer.

The ultimate objective is training the students for research in the area of importance to U.S. Department of Energy. The training includes experimental planning, design and development of experimental apparatus, learning the electrochemistry principles, gathering and analysis of data, analysis and interpretation of research results.

What was learned

1. Electrodeposition is controlled by reaction rate (active region)

The PI decided to use the rotating disk electrode technique to study the electrodeposition in molten salts. Although this technique is regarded as one of the most informative toward the answers on reaction mechanisms it is almost absent from literature on electrochemistry from molten salt electrolytes.

What this research has found, by using the rotating disk electrode technique (RDE), that electrodeposition from molten salt is actually always in the electrochemical reaction rate control mode, not mass transfer controlled. If electrodeposition were a function of mass-transfer then electrodeposition would be a function of rotation speed. This is because faster rotation rates would produce smaller liquid film thickness at electrode, which would lead to higher concentration gradient, i.e. faster reaction rate. That is not what was found on the examples of electrodeposition of lanthanum and uranium. By running the effect of rotation speed on cyclic
voltammetry for particular scan rate it was found that the speed of rotation was effective only at very small scan rates, 5-20mV/s and lower. The independence from rotation speed above 20 mV/s scan rate tells that the mass transfer is not an important parameter because the electrodeposition itself is electrochemical reaction rate controlled. It is interesting to note that all published papers on the subject of electrochemistry of lanthanides and actinides in molten salts in unison conclude that electroreduction is reversible/quasi-reversible (mass transfer controlled) at scanning rates up to about 100mV/s. The contradictory conclusion is most likely caused by experimental conditions used by others, working electrode being of cylindrical geometry as the result of exclusive use of a wire for a working electrode.

2. Four stages of electrodeposition from molten salts

In contrast to stationary wire electrode used in almost all published literature, in this project with RDE technique, it was found that electrodeposition of lanthanides (La), and actinides (U) is characterized with four distinct stages. The first two stages are nucleation and growth of nuclei until thin, dense and uniform film is produced. These first two stages are independent of electrochemical potential scanning rate and the speed of electrode rotation. The independence from these two kinetic parameters can be explained by direct conversion of already adsorbed layer of LaCl$_3$ and UCl$_3$ to corresponding metallic state. In the first two stages, we have nucleation of new solid phase (La, or U) on the substrate of different metal (W) used as working electrode. Once the working electrode is covered with the film of metal being electroreduced then further metal electrodeposition happens on the substrate with matching crystalline lattice (La on La, U on U). These are third and fourth stages and they are strictly governed by surface area changes of the produced metal nuclei and nuclei aggregates. Cyclic voltammetry studies revealed that third and fourth stages are not a function of speed of electrode rotation for potential scanning rates 20mV/s and higher. Effect of speed of rotation is found only for slow scanning rates. This finding indicates that electrodeposition in molten salts is already controlled by electrochemical reaction rate (independent of speed of rotation) and that modulation of electroreduction rate by addition of organic additives is not necessary.

3. Very large electrodeposition currents at slow scanning rates

In cyclic voltammetry, if the rates were controlled by mass transfer then the slower scanning rates would respond with smaller currents, i.e. smaller rates, because of smaller concentration gradient in the vicinity of electrode surface. In this study, opposite was found that the smaller scanning rates produced very large electrodeposition currents. Furthermore, only at very slow scanning rates the speed of electrode rotation was effective, indicating the introduction of mass transfer rate as contributing factor in the overall rate of electrodeposition. The finding of dependence of electrodeposition on mass transfer at low scan rates contradicts the general knowledge in electrochemistry that at slow scanning rates the mass transfer is fast enough to
satisfy the rate of reaction demanded by the particular electrochemical potential. Obviously, some additional phenomena are influencing the electrodeposition (to be proposed below).

The current densities of 2.5-5.0A/cm² can readily be produced during electrodeposition of lanthanum at scanning rate of 5mV/s and electrode rotation rate of 800 rpm (rotation rate per minute). The high current densities present in electrodeposition of lanthanum (and uranium) surpass by far the typical current density of industrial aluminum production from molten salts, 1.0A/cm². While the high current density in aluminum production can be supported by high concentration of aluminum in molten salt (about 12 wt% of AlF₃) this is not the case in typical electrochemical studies with lanthanides and actinides, which are about ten times lower. Therefore, the exceptionally high current density observed during cyclic voltammetry of lanthanum at slow scan rate can be supported only by participation of additional electrochemical reduction reaction. In molten LiCl-KCl-AnCl₃ systems the supporting reaction can be only reduction of lithium chloride.

4. The influence of underpotential deposited lithium

Although the reduction of lithium requires potentials more cathodic than the reduction of lanthanum, lithium can still be deposited by so-called underpotential deposition mechanism. The co-reduction of lithium has received no attention in available literature sources and in PI’s opinion it must be addressed as perhaps this is the key reaction phenomenon that could guide the morphology of lanthanide and actinide deposits. Co-deposition of lithium during electrodeposition of lanthanum studies was confirmed by the stability of ceramic material that was used as shroud for working electrode. Thus, when rotating disk electrode was made by inserting tungsten rod in alumina tube (one end open and space between the electrode and alumina walls sealed) the alumina tube was not affected during the experimental runs in molten LiCl-KCl-LaCl₃. However, when mullite tubing was used as the replacement for alumina tubing, mullite was consistently attacked. The attack was not only at the transition from metal disk to ceramic surface (disk geometry) but also further away from the metal surface, even outside wall of ceramic tube constituting the rotating disk electrode assembly. That was readily confirmed by adding a drop of water on the surface of disk portion of electrode. Hydrogen gas bubbles were produced whenever rotating disk electrodes were made with mullite tube shroud. Lanthanum metal would not react with water (at least not as fast) while metallic lithium reacts instantaneously producing large number hydrogen gas bubbles all over the mullite surface. Also, solid metallic lanthanum would not be possible to leave the metallic disk area.

One more important notice on the reaction rate control and its effect on morphology of deposits. As stated above, the effect of electrode rotation speed was present only for slow scanning rates in cyclic voltammetry, but it is critical to state that even though the reaction rate increased with the increase of rotation speed the reaction never went into mass transfer (diffusion) controlled region. Mass-transfer controlled region is characterized by independence of reaction rate with increase of potential. That means that Stage 3a should have eventually produced a horizontal line on the current vs potential plot. That was never observed even at very fast speeds of rotation (3000rpm) and at very slow scanning rates. The effect of rotation speed was represented by Stage 3a never reached the limiting current status (horizontal line).
Experimentally, the current densities as high as 15A/cm$^2$ (very fast reaction rate) were produced but without limitation by mass transfer (diffusion control). These current densities were so high that the entire molten salt turned green due to excessive production of chlorine on the counter electrode.

Why are so high current densities experienced while working with rotating disk electrodes and are not as high when working with cylindrical geometry, universally used in published literature? The explanation must come again from the role of lithium. If lithium is produced during lanthanum deposition, buy underpotential deposition mechanisms, it stays trapped under electrode disk. Its accumulation under the disk leads to increase of reaction surface area, which in turn leads to faster reaction rate. It is in the form of droplets. In universally used wire-type electrodes lithium is still produced but vertical orientation of wire allows liquid lithium to readily float upward the electrode wall toward the surface of molten salt. This is not possible under horizontally oriented disk electrode.

5. Morphology of electrodeposits in each four stages of deposition

The PI is reporting scanning electron micrographs of metallic lanthanum and uranium not only as the final metal electrodeposit but is able to show the morphology of the nuclei and aggregates at each of the four cyclic voltammetry stages discussed above. To the PI’s knowledge, this type of information is not available in open literature, and it is appearing for the first time here in this final report. Just the ability to provide clear (salt free) morphological characteristics of La and U (see picture on the left) nuclei and aggregates produced in molten LiCl-KCl salt electrolytes on its own justifies the funding of this project.

6. Electrodeposition of La and Nd from room temperature ionic liquids

Electrodeposition of La was studied in 1-Ethyl-3-methylimidazolium dicyanamide (EMIM-DCA), while for Nd electrodeposition 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) was used.

The research with room temperature ionic liquids was fully successful. The reaction mechanisms were studied by using the rotating disk electrode technique (as with high temperature molten salts). The reaction mechanisms were determined for each studied system. What was found is that electrodeposition from of La and Nd from ionic liquids was irreversible and controlled by mixed kinetics (mass transfer and electrochemical reaction rates).

What was learned is that although the room temperature ionic liquids may find the practical application in various fields of chemical industry, but the PI is not convinced that they
would be feasible for electrowinning of metals on industrial scale. The main drawback from application on industrial scale is their poor solubility for metallic compounds (actinide and lanthanide chlorides, for example) and their high viscosity. High costs are another negative property. On the other hand, compared to electrodeposition from high temperature ionic liquids, such as molten LiCl-KCl salts, the room temperature ionic liquids, as the name suggests, offer low temperature operation temperatures. Also, they are not as sensitive to the presence of minor quantities of water (and oxygen) as molten LiCl-KCl do.

7. Electrodeposition of uranium in the presence of additives to molten salts

Addition of organic molecules, in the form of charged ionic liquids, and neutral lubricants and greases, unfortunately did not work. This is because the proposed ionic liquids and ultra-high temperature greases showed no chemical stability when added to molten LiCl-KCl. The chemical instability was expressed in the form of produced smoke, and in case of molten salt containing UCl₃, immediate change of color from purple to gray. When high temperature grease was used, all uranium separated from molten salt and floated to the top of molten salt as a solid, black, crust (salt itself became colorless). This performance from ionic liquids and greases as additives to the molten salt electrolytes was not expected so the research had to refocus on the use of room temperature ionic liquids as the electrolytes to study the electrodeposition. The objective (justification) was to compare the electrodeposition from high temperature ionic liquids (molten LiCl-KCl electrolyte) with the one from room temperature ionic liquids. It should be recognized that in both systems the electrolytes are composed of fully ionized cations and anions. In high temperature electrolytes, the cations and anions are inorganic salts, while in the room temperature ionic liquids, the cations are organic molecules, while the anions can be organic or inorganic species. Lanthanum and neodymium were selected as the representatives to study the electrodeposition from room temperature electrolytes.

Future work

The future research should focus on the underpotential deposition of lithium and its effect on the morphology of lanthanides and actinides electrodeposits in molten LiCl-KCl electrolytes. This area of research is of importance for understanding the conditions for prevention of dendritic electrodeposits.
Project Summary

This is the final report to the NEUP regarding the “Advanced Electrochemical Separations of Actinide/Fission products via the Control of Nucleation and Growth of Electrodeposits” project. This report describes the project activities conducted during the period October 01, 2016 through September 30, 2019. The report includes a brief statement of the project objectives and approach, followed by the details of the performed research activities and suggestion for the future work.

Administrative

From the administrative aspects, the following are the key dated events.

- Official contract between DOE and University of Idaho was signed on 09/22/2016. This was done after several contract modifications. The total funds obligated were $350,000.

- The originally proposed two-year project was planned to terminate on September 30, 2018. However, the PI has asked NEUP for no cost extension, which was granted with the new termination date of September 30, 2019. The objective for no cost extension was to run some additional electrochemistry tests. The major reason for extension was the reproducibility of data when using the rotating disk technique.

- This contract had no collaborators.

- All reporting formalities have been fulfilled, including milestones, deliverables, quad charts, etc.

Research

The research project is characterized with five milestones, including the Final Report, Table 1.

Table 1: The project components in the form of milestones.

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<th>Milestone Code</th>
<th>Description</th>
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<td>M2NU-16-ID-UI__-020202-022</td>
<td>Search for ultra-high temperature ionic liquids, oils and lubricants</td>
</tr>
<tr>
<td>M2NU-16-ID-UI__-020202-023</td>
<td>Design of a two-compartment cell</td>
</tr>
<tr>
<td>M2NU-16-ID-UI__-020202-024</td>
<td>Morphology studies during La electrodeposition in a two-compartment cell</td>
</tr>
<tr>
<td>M2NU-16-ID-UI__-020202-025</td>
<td>Electrodeposition of uranium in the presence of additives to molten salts</td>
</tr>
<tr>
<td>M2NU-16-ID-UI__-020202-021</td>
<td>Final Report</td>
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</table>
Products Developed

A) Students trained/graduated

Trained and graduated two students with Master of Science degrees in Materials Science and Engineering:

Jacob Kline - Electrodeposition of Neodymium in the Room Temperature Ionic Liquid 1-Butyl-1-Methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide and the Effects of Water and Ethanol: A Rotating Disk Electrode Study, MS Thesis in Materials Science and Engineering, University of Idaho (2018).


B) Paper presentations

Batric Pesic and Ian C. Ehrsam – Electrodeposition of lanthanum in room temperature ionic liquid electrolyte, Metallurgical & Materials Engineering Congress of South-East Europe, June 5-7th, Belgrade, Serbia.

C) Manuscripts submitted for review

Jacob Kline - Electrodeposition of Neodymium in the Room Temperature Ionic Liquid 1-Butyl-1-Methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide and the Effects of Water and Ethanol: A Rotating Disk Electrode Study. Prepared for submission to Electrochimica Acta.


D) Final report, this project

Advanced Electrochemical Separations of Actinide/Fission Products via the Control of Nucleation and Growth of Electrodeposits
Project Background

Project Scope Description and Objectives

Electrochemical techniques are of vital importance for development of pyrochemical fuel treatment processes for separation of actinides from the fission products contained in spent nuclear fuel. Using pyroprocessing technology, actinides can be recovered from the spent fuel and prepared for recycle, as fuel, while the fission products can be encapsulated in durable leach resistant waste forms destined for storage. Extensive research has been, and continues to be performed in this area under the US Department of Energy’s Fuel Cycle Research and Development program with the ultimate goal of developing efficient, sustainable and environmentally responsible nuclear energy systems.

The development of pyrochemical fuel cycle technologies needs to accommodate both oxide and metallic fuels. The successful development of needed technologies requires deep fundamental knowledge of pertinent electrochemical reaction systems that utilize molten salt electrolytes.

Furthermore, when developing a method for pyrochemical reprocessing of spent nuclear fuels, the following criteria must be considered:

1. Recovered fuel materials must be compatible with current or next generation nuclear reactors
2. The process must be amenable to safeguarding nuclear materials
3. The number and complexity of processing steps should be minimal
4. Final nuclear waste should be amenable to characterization, minimal in volume, and have its final storage mode clearly identified.

Despite the large volume of research information available, produced by academia, industry and national labs in the USA, Japan, Korea, India, etc., on electrochemical methods/processes for separation of actinides in molten salts, still much more work is needed to obtain the necessary fundamental/technical information of the reaction mechanisms (kinetics) of involving materials and reactant species.

It is well known that according to current knowledge the pyroprocessing of spent nuclear fuels invariably leads to the dendritic form of electrodeposits, which from technological point of view is undesirable, for many reasons. The aim of this research is to find ways to preclude the formation of electrodeposits with dendritic morphology (of essential importance to FC-1 Program). This goal is very ambitious considering the fundamental challenges described below.

Objectives - The objectives of the proposed research are to:

- Search for technically acceptable and chemically functional additives to the LiCl-KCl molten salts that will place the electrodeposition of actinides and fission products in active region.
- For the first time, study the morphology (nucleation and growth) of electrodeposits as a function of electrolyte additives, such as ionic liquids.
- Redesign the electrochemical molten salt cell for use of distinct cathodic and anodic compartments, and reexamine the fundamental results obtained in one-compartment cell.
**Logical Path to Accomplish Scope** electrodeposition from molten salts due to the reactions being in the diffusion control region, caused by high temperatures. This fundamental obstacle is best described by the presentation of Figure 1. To obtain compact electrodeposits, it is mandatory that the electrodeposition is in the active region of electrochemical reaction. Whenever the electrodeposition is in mass transfer (diffusion) region, the electrodeposit will either be of dendritic, or powder form. The active region is readily achievable at low temperatures, as found in electrodeposition from aqueous solutions. However, at high temperatures, as in molten salts, it takes only 2-5 mV of overpotential to place the reaction outside of active region. Obviously, now, the potential control is out of consideration as the method to achieve the desired compact electrodeposit. The second approach, the modulation of electrolyte composition is left as the only solution to reach the set goal.

*How to modulate the nucleation and growth of electrodeposits in molten salts?* The nucleation and growth of electrodeposits is controlled by two approaches. One approach is based on the control of electrodeposition potential, and the other utilizes the electrolyte additives to adjust the interfacial phenomena at the electrode. However, the easier first approach, unfortunately, is not applicable for

![Diagram](image)

Fig. 1 Morphology of electrodeposits as a function overpotential (adapted according to K.I. Popov, S.S. Djokic and B. N. Grgur).  

Overall the project is comprised of four tasks:

2. Task-B: Design of a two compartment electrochemical cell.
3. Task-C: Morphology studies during La electrodeposition in a two-compartment cell.
4. Task-D: Electrodeposition of uranium in the presence of additives to molten salts.
Description of Proposed Individual Tasks

Task-A: Search for thermally stable ionic liquids, oils and lubricants

As described in Fig. 1, the electrodeposition must be in active region in order to obtain a compact electrodeposit. To control electrodeposition within the active region, the properties of solid electrode-molten salt interface must be controlled, which can be achieved by changing the composition of electrolyte. It is expected that by adding particular organic additives the same will adhere to the solid electrode controlling the kinetic parameters of importance to electrodeposition: availability of sites for discharge of metal ions, rate of discharge, nucleation of ad atoms, clustering of ad atoms, and surface diffusion. In order to make this principle applicable, the additives must be thermally stable, applicable for use at typical temperature of molten LiCl-KCl salts, which is 450-550°C range.

Ionic Liquids (IL). Ionic liquids are ionic salts comprising organic cations and organic/inorganic anions, Fig. 2. It is the combination of their components (cations and anions) that determine the physicochemical properties, and consequently the applications of ILs. Due to large differences in ionic size they are not packed, resulting in low lattice energy, i.e. they can exist liquid at room temperature. The number of known ILs is extremely large, about $10^6$, which requires some kind of name systematization, through coding. The key property that will decide on their selection will be the thermal stability. Thermal stability of ILs is defined by the type of cation and anion, Table 1. The most stable cations (its stability varies with type of anion) typically are imidazolium (with Tf2N) and tetra-alkyl ammonium (with BF4) cations. PF6, BF4, and Tf2N are the most stable anions (if cation is imidazolium). Chain length has no effect on thermal stability of imidazolium cations. On the other hand, the alkyl group on tetraalkyl ammonium cation significantly influences the thermal stability. Electrochemical stability is another important property, where typically stability of a cationic component is determined by the value of cathodic potential, and vice versa for anionic component, although not always true. Cathodic stability is generally higher for aliphatic than aromatic type of ILs. Reactivity of cations with metallic lithium that could be produced during electroreduction from molten LiCl-KCl is another important issue. The calculations show that aliphatic P13 ILs (N,N-propylmethylypyrrolidinium) would be stable against metallic Li. Cathodic and anodic stabilities, as well as the reactivity of ILs will be carefully considered.

![Fig. 2 Design of ionic liquids for special purposes (reproduced from Park J. et al.).](image-url)
Table 1 Structure and examples of thermally most stable cationic and anionic components of ionic liquids.

<table>
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<th>Cations:</th>
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<td>pyridinium; tetraalkylammonium; imidazolium</td>
<td>hexafluorophosphate; tetrafluoroborate; bis(trifluoromethylsulfonyl)imide (Tf2N)</td>
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Mechanistically, it is expected that the negative potential of cathode will attract the cationic component of IL, “affixing” it to the electrode, with the net effect as if chemisorbed, Fig. 3. The structure and the properties of the interface, defined by IL dominantly present within, will determine if the metal cation discharge (electrodeposition) will be governed by the electrochemical reaction rate (active region- precondition for dendrite free growth.)

The project will start with the following cationic liquids: 1-ethyl-3-methyl-imidazolium [EMIM], 1-ethyl-3-methyl-imidazolium [BMIM, also called P13], 1,2,3-trimethyl-imidazolium [MMMIM] and tetraalkylammonium [R4N]. The anions to be combined with the listed cations will be Tf2N, PF6 and BF4. Therefore the ionic liquids to use as additives will be: [EMIM][Tf2N], [EMIM][PF6], [EMIM][BF4]; [BMIM][Tf2N], [BMIM][PF6], [BMIM][BF4]; [MMMIM][Tf2N], [MMMIM][PF6], [MMMIM][BF4]; [R4N][BF4].

**Lubricants and Greases.** This class of compounds is interesting because it can provide the neutral molecules that may have the propensity to adhere to the solid surface and modulate the properties of the electrode interface. Unfortunately, here, when the temperature is around 400 C and higher the choices of lubricants is quite limited. The following is the list of class of chemicals, with thermal decomposition temperatures given in parenthesis: polyphenol ethers (440-485 C), phosphate esters (triaryl phosphates) (420 C), silicates (345-450 C). The commercial perfluoropolyethers are known under the trade names such as Krytox (DuPont, USA), Fomblin (Ausimont/Montedison, Italy) and Demnum (Daikih, Japan). The typical chemical formula, as for Krytox, is: \( CF_3-(CF_2)_{2}-O-(CF(CF_3)-CF_2-O)s-(mixture\ of\ CF_2CF_3\ and\ CF(CF_3)_2) \). In addition of being thermally stable, these oils are also refractory to oxidation by oxygen.

(A side note on this topic is that ionic liquids because of their thermal stability are beginning to find the application as lubricants, as well.)
This Task is very challenging and by itself could have been a standalone proposal. The research concept of adding ionic liquids to the molten LiCl-KCl salts to modulate the electroreduction mechanisms is absolutely unknown. As the consequence, there are no research leads that one can benefit from by using prior publications. However, the PI is optimistic that it is possible to find (or develop) a functional molten salt additive that would place the electrodeposition of lanthanides and actinides in the mandatory active region, as illustrated in Fig. 1.

**Task-B: Design of a two-compartment electrochemical cell**

This is a mandatory approach when one seeks to study the fundamentals of electrodeposition from molten salts. In the open literature, all experiments relevant to the NEUP type of projects with molten salt electrolytes are done in one-compartment cell. The main characteristics of one-compartment cell are excessive migration (turbulence) of molten salts thus enabling the reaction products formed on the counter electrode to readily arrive at the working electrode, where they interfere with the main reactions being studied. Under these conditions it is impossible to obtain reliable thermodynamic and kinetic results. For example, if the reaction mechanisms (reaction reversibility) were to be determined by using cyclic voltammetry technique then for the electrolyte (molten salt) being quiescent is a mandatory precondition, and the counter electrode reaction products should never be allowed to arrive at the working electrode. Therefore, any electrolyte turbulence, such as the one caused by the thermal migration effects, or by the gas bubbles as the reaction products released at the counter electrode, must be avoided. The counter electrode should be placed as far away from the working electrode as practically possible. These conditions are not possible to achieve in one-compartment cell as can be clearly seen in Fig. 4b, where the objective was to study the reduction of lithium from Li$_2$O dissolved in LiCl-KCl molten salt. The expected electrochemical reactions are straightforward, lithium production on the working electrode, and generation of oxygen by oxidation of O$_2^-$ at the counter electrode. This is exactly what was happening, except that the glowing lithium also confirmed that this electroreduction product was simultaneously being consumed by the oxidation with oxygen produced on the counter electrode.

For this project, the crucibles for two-compartment cell, Fig. 4a, will be made of alumina, or aluminum nitride, as the materials of sufficient refractoriness to metallic lithium. A private company has been identified that can custom make the specifically designed crucibles. The volume of each compartment will be 20ml.
**Task-C: Morphology studies during La electrodeposition in a two-compartment cell.**

The PI has developed unique capabilities to study the morphology of electrodeposits from molten salts in the early stages of nucleation and growth. This has been verified by a series of recent publications on nucleation and growth of six lanthanide metals. No other lab, thus far, has been able to match this highly valuable capability. It will be important to reevaluate and compare the morphologies of electrodeposits produced in two type of electrochemical cells, one-compartment vs. two-compartment cell. Lanthanum will be used as a representative metal. Eutectic molten LiCl-KCl will be the electrolyte. The main reasons for selecting lanthanum as a representative for lanthanides are: (a) well defined dendritic morphology of electrodeposits during nucleation and growth stages, (b) prior experimental experience, particularly during frozen salt separation and SEM characterization, and (c) being a surrogate for depleted uranium. Among these, the well-defined dendritic morphology property is the most important because the most inviting objective of the project is to study the mechanisms how to preclude the dendrites from development and growth. Because the composition modulation of molten LiCl-KCl salts (Task 4, below) by specific additives is the proposed method for prevention of dendritic morphology, lanthanum electrodeposition characteristics during the nucleation and growth of nuclei stages will readily provide the information on the effectiveness and the mechanistic role of additives. Additional reason for using lanthanum is the lab safety. Although depleted uranium is considered as safe for use in a regular laboratory it is still radioactive, thus requiring particular precautions and handling. A lot of information, in various stages of the project (evaluation of selected additives), can be obtained with lanthanum as surrogate.
**Task-D: Nucleation and growth of U during electrodeposition from molten salts.**

Thus far, there is no publication that demonstrates the morphology of U in early stages of nucleation and growth. The PI has the capability to fill that gap by performing the proposed study, in both, one-compartment and two-compartment cells. The nucleation and growth mechanisms will be studied under two different electrochemical approaches: (a) electrowinning of uranium and (b) electrorefining of uranium. For electrowinning, uranium will be electrodeposited onto a working electrode from dissolved UCl₃ in LiCl-KCl eutectic salt. The working electrode will be either stainless steel, tungsten or molybdenum disks. The counter electrode will be a tungsten rod. For electrorefining, a rod of depleted uranium, serving as the counter electrode, will provide the uranium for electrodeposition on the working electrode. The working electrode will be the same (SS, Mo, W) as in electrowinning experiments. The difference between electrowinning and electrorefining is in the counter electrodes. Electrowinning is using inert (insoluble), while electrorefining is using active (soluble) electrodes.

For the reaction mechanism studies, the experimental techniques to employ are: cyclic voltammetry, square wave voltammetry, chronoamperometry, and chronopotentiometry. For the nucleation and growth studies, chronoamperometry will be the main electrochemical technique. The nucleation and growth will be examined for at least three reduction potentials: the onset of electroreduction, the mid stage of electroreduction, and at the potential providing the maximum rate of electroreduction (peak current). The values of these potentials will be determined from the prior cyclic voltammetry studies.

The nuclei morphology of U-electrodeposits will be studied in Task-D by using the methods developed by PI.
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RESULTS AND DISCUSSION

Task-A: Search for ultra-high temperature ionic liquids, oils and lubricants

The following cationic ionic liquids were acquired as proposed in the project background 1-ethyl-3-methyl-imidazolium [EMIM], 1-ethyl-3-methyl-imidazolium [BMIM, 1,2,3-trimethyl-imidazolium [MMMIM] and tetraalkylammonium [R4N], in combination with Tf2N, BF4 and DCA anions. The ionic liquids were purchased from IOLITEC, Ionic Liquids Technologies GmbH, Salzstrasse 184, D-74076 Heilbronn, Germany.

The rotating disk studies of neodymium electrochemistry were done in 1-Butyl-1-methylpyrroolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI), while electrochemistry of lanthanum was performed in 1-Ethyl-3-methylimidazolium dicyanamide (EMIM-DCA).

The details from these studies is given below.

The results from addition of ionic liquids to molten LiCl-KCl salts at 450-500C will not be presented because the proposed idea did not work as expected. There will be some comments from the addition of ionic liquids, and ultra-high temperature greases, in the section describing Task D.
Task-B: Design of a two-compartment cell

As already stated above, this is an important component of the experimental setup. The main feature of the electrochemical cell is its division into a catholyte and anolyte compartments. The PI has used the simplest solution to achieve the given objective. The solution is to use a porous tube for the compartment separation, Fig. 5. The porous alumina tube is placed into a crucible under free standing condition or held secured by a rigid Mo-wire twisted in such a way for an easy grip onto the crucible wall.

Fig. 5 The approach to having a compartmentalized electrochemical cell. Porous alumina tube is used for separation of catholyte and anolyte compartments. The tube is affixed onto crucible with a rigid Mo-wire. This design allows easy withdrawal from the crucible, molten salt pouring out of crucible and individual transfer to cleaning by dissolution in water and 1:1 HCl, drying and baking at 600 C.

The porous alumina tubes were custom made by Seneca Ceramics (www.senecaceramics.com). The diameter of alumina tubes is ½”, with the porosity of 10, 20, and 50 microns, Fig. 6. Although 100-micron porosity was also ordered Seneca’s response was to abandon this request due to difficulties of manufacturing.

Fig. 6 Porous alumina tubes made by Seneca Ceramics. The tubes are used to host either a counter electrode or working electrode in order to prevent its reaction products reaching the working electrode.
**Experimental Setup**

For morphological studies it was decided to use the rotating disk technique. The main reason for this decision is the ability to polish the surface of electrode to mirror polish grade that would enable distinguishing morphological features created during the electrodeposition. This is not possible with the wire type of working electrode.

The rotating disk electrode systems is made of a rotator with a rotation speed controller, Fig. 7. The rotator consists of a DC motor and the working electrode chuck assembly. The purpose of a DC motor is to rotate the working electrode at predetermined speed of rotation. When designing a rotating electrode disk apparatus, the main issues to pay attention to are the prevention of electrode wobble during rotation, and to ensure very good electrical contacts between the working electrode chuck, the rotator shaft and the working electrode lead wire. No compromise is possible with respect to these two requirements.

The DC motor controller is mounted on the outside wall of the glove box, not shown here. The DC motor controller is connected to a laptop computer for issuing rotating speed commands.

![Rotating disk assembly for work in molten salts. The DC motor controller is placed outside the glove box.](image)

The PI has built another rotating disk experimental system for work with ionic liquids. Because the project proposal calls for the use of ionic liquids as the high temperature modulators of the molten salt electrolytes it was decided to perform detailed electrochemical studies with these compounds. Electrochemical deposition of lanthanum and neodymium were selected for
that purpose. Because ionic liquids are very expensive it became obvious that the electrochemical cell had to be of small volume, and still to allow the accommodation of all three required electrodes: rotating disk electrode, counter electrode and reference electrode. The electrochemical cell was designed to permanently hold the counter electrode at the bottom, while the working and reference electrodes were insertable from the top. The typical electrolyte (ionic liquid) volume that can be readily used is 5ml. The entire experimental setup is built in such a way that it can be readily dismantled and assembled for an easy transfer to and from the glove box, in case the controlled atmosphere is required.

The components of the setup for studies with ionic liquids are shown in Fig. 8. The electrochemical setup is very similar to the setup for research with molten salts. The difference is in the use of crucible to hold the electrolyte and the need for the furnace to keep eutectic LiCl-KCl salt electrolytes in molten form.

The experimental setup for research in ionic liquids outside and inside the glove box is given in Fig. 9.

![Components of the electrochemical setup for research on electrodeposition of lanthanides from ionic liquid electrolytes.](image)

Fig. 8 Components of the electrochemical setup for research on electrodeposition of lanthanides from ionic liquid electrolytes.
Fig. 9 Electrochemical setup for research with ionic liquids outside (left) and inside (right) the glove box.
Task-C: Morphology studies during La electrodeposition in a two-compartment cell

Summary

The motivation for exploration of this research task, the use of a two-compartment electrochemical cell, was the PI’s visible observation of high convective mass transfer in molten salt electrolytes. For example, in LiCl-KCl eutectic molten salts, gaseous chlorine produced on the counter electrode is readily transferred to the working electrode interfering with the study of reactions of interest. The effect of chlorine transfer from the counter electrode to the working electrode is particularly present in the reactions with high cathodic currents on the working electrode. That is readily demonstrated below in the set of lanthanum cyclic voltammetry experiments at slow scan rates under rotating electrode conditions. The amount of chlorine produced on the counter electrode was so high that the entire molten salt turned green. The molten salt clears readily of chlorine by degassing at high experimental temperature. When the currents at working electrode are small the amount of chlorine released on the counter electrode is also small. Nevertheless, the chlorine produced still dissolves into the molten salt and finds its way to the working electrode. The geometry of the working electrode now becomes the key parameter that determines if the presence of chlorine will be effective. The geometries in question are (a) horizontal disk and (b) vertical cylinder (rod) electrode. In literature, the electrochemistry in molten salts is exclusively done with vertical cylinder (rod) electrode, mainly because of simplicity of application. With this electrode type any species, liquid, solid and gaseous, readily detach from the electrode floating away toward the molten salt surface, minimizing their effect.

Rotating disk electrode is mounted vertically into the electrolyte (molten salt) only several millimeters deep, but the disk faces the molten salt horizontally. Because the electrode is made by sealing a metal/metal alloy rod in a cylindrical ceramic tube, the overall diameter that will face the molten salt is enlarged. The resulting physical characteristic, large diameter disk facing molten salt horizontally, serves as a very effective trap for all the species that would have otherwise floated toward the top of molten salt, as found with vertical cylinder electrode. Trapping the species under the rotating disk creates major reproducibility of data problems, particularly in molten salts.

Next experimental challenge that has been experienced (for almost a year) is construction of rotating disk electrode. The main problem is in finding an efficient sealant for the space between the metal rod and insulating shroud, which can be a glass tube, or ceramic tube. Sealing tungsten rod in glass is well documented but only for wires much smaller than 1mm in diameter. Larger diameter wires (rods) lead to inevitable glass cracking. Because glass sealing technique had to be abandoned, it was decided to seal the space between metal rod and ceramic tube with a refractory cement. However, finding a refractory cement that can be chemically stable against liquid lithium proved to be almost non-resolvable task. Because all refractory cements are oxide-based they immediately become a target for chemical reduction with liquid lithium produced during the electrochemical studies. The PI has spent about a year of time searching (almost every DOE Report from past studies on the subject has been consulted) for refractory sealants that can close the space between tungsten rod and mullite, or alumina, tube used as the
insulators in rotating disk electrode. Completely satisfactory solution was not found, but what was found to work reasonably well is to crash and grind Corning 7720 Nonex, or Corning 7052 Kovar glass, and use the powder to fill the space between the tungsten rod and ceramic tube, before high temperature treatment to melt the powder and achieve the sealing. The electrodes prepared by this method are not fully refractory to liquid lithium but are usable sufficiently long for the needed experimentation. Developing ceramic materials that are refractory to lithium is a big challenge and a project in itself. Thus far, even the most stable oxides, Y$_2$O$_3$ and CaO have shown reactivity with lithium$^9$.

On this project, almost all of the work was done with the rotating disk electrode (RDE). The wire (cylindrical) electrode under stationary conditions was intentionally avoided because this type of work in eutectic LiCl-KCl has been done so extensively that it has almost become a repetitive characteristic. The main reasons for selecting RDE are the well-defined experimental parameters, such as the electrode area, and the thickness of liquid boundary film. The mass transfer through the liquid boundary film is mathematically described by Levich$^{10}$. The main project goal was to arrive at the information under which conditions the electrodeposition from molten salts is reversible and to determine the morphology of deposit as a function of the reaction mechanisms. Only a fraction of the work will be presented here. More detailed information will be provided in the forthcoming publications.

The most significant findings from this research project are:

1. Electrochemical studies in molten salts should be done in an electrochemical cell with separated anolyte/catholyte compartment.

2. Electrodeposition of lanthanum (and uranium) happens in minimum two stages. In the first stage, the electroreduction happens so fast (instantaneously) that entire electrode (tungsten) area is covered with a very thin dense film of La. In the second stage, lanthanum nucleates as a new solid phase on lanthanum substrate produced in the first stage of electroreduction. Thus, in the first stage we have lanthanum formation on the tungsten substrate (La-W, lattice mismatch mechanism), while in the second stage we have lanthanum nucleation and growth on lanthanum substrate (La-La, lattice matching mechanisms).

In cyclic voltammetry studies, it was found that two more stages could be present depending on the vertex of scanning reversal potential. One of them is the further growth of cathodic current even though the scanning direction is reversed in anodic direction. The current growth in this case is caused by nuclei area growth until the overlap of diffusion boundaries is achieved. The final stage is regular deposition until the reversed scan crosses over into the anodic region.

These stages are verified by SEM examination of the electrode surface at a particular potential position on a cyclovoltammetry scan.

3. With respect to scanning rate and rate of electrode rotation it was found that cathodic current of lanthanum deposition is increasing with the increase of rotation rate but only
until 200 mV/s scanning rate. If the scan rate is higher, 500 mV/s and 1000 mV/s, then there is no effect of rotation rate on cyclic voltammetry, the results are identical.

On the other hand, when the scanning rates are slow then the rotation rate increase produces the opposite effect from the one described above. Thus, at 5mV/s scan rate, the lowest currents are produced at the highest rotation speed (e.g. 2000 RPM). At slow speed of rotation, such as 200 RPM, the cathodic current was so high that induced high matching anodic current on the counter electrode, where so much chlorine was produced that entire molten salt turned green.

C1. Experimental Procedures

The schematics of electrochemical cell for experiments with rotating disk electrode in compartmentalized (or non-compartmentalized cell) is given in Fig. 10. The actual picture of the experimental setup is present in Fig. 7. The electrochemical cell consists of a 20ml alumina crucible that hosts a working (WE), counter (CE), and reference (RE) electrodes. The cell is compartmentalized by using a porous (50 microns porosity) alumina tube. The porous alumina tube can host either counter electrode, or working electrode, depending on the objective of experimentation. Its purpose is to prevent (or minimize) the transport of reaction products produced on counter electrode reach the working electrode. Working electrode is mounted in a rotator that is powered by a small DC-motor above. The DC motor itself is encoded for computerized control of rotation speed.

The home-made furnace uses Kanthal wire wrapped around alumina tube into which a graphite crucible is inserted. The purpose of graphite crucible is to accommodate 20ml alumina crucible for holding molten salt, and for insertion of thermocouple tube for temperature control. The furnace together with motorized working electrode assembly is placed in a glove box (VAC-Atm) filled with ultra-pure argon. Typical composition of glove box atmosphere was less than 1ppm of oxygen and 0.5 ppm of moisture.

The potentiostat (Bio-Logic, VSP), temperature controller (Automation Direct, SOLO 4824), and rotation rate controller are all mounted outside the glove box and connected to the electrochemical setup and furnace inside the glove box by using glove box feedthroughs.

When needed, the working electrode is taken out for analysis by scanning electrochemical microscope (Tescan, Vega II).
C2. Results and Discussion

Cyclic voltammetry technique was used to study lanthanum electrochemistry in molten LiCl-KCl-LaCl3. Two types of electrode were used, rotating disk (RDE) and rotating cylinder (RCE). The electrodes were 99.5% W rods, 1/16” diameter, inserted in 1/16” diameter alumina sleeve and sealed. The sealing method was a very difficult problem to solve, and it is not fully resolved. The major problem is to find the materials that would be resistant to liquid lithium that is produced during the electrochemical experimentation. Final solution was to use powder of glass (Corning, 7720-Nonex, or Corning 7052-Kovar) to fill the alumina sleeve and to insert tungsten rod under pressure while simultaneously melting the glass powder. Heating for this step was achieved by using a gas torch with a mixture of MAP-oxygen gas. Rotating cylinder were also tungsten rods but with alumina sleeve positioned 5mm away from the tip of the electrode. For positioning alumina sleeve a high temperature cement was used (Cotronics, Durapot 809).

Several hundreds of cyclic voltammetry experiments were run with the goals to search for proper sealing technique, and control of the reproducibility of results. Problems experienced in each of these two goals were very difficult to solve. In this report, only partial and most important results will be presented, those that lead to better understanding of reaction mechanism including morphology of deposits.

C2.1 Morphology in Various Stages of Cyclic Voltammetry

It was found that there are four stages of cathodic reduction of lanthanum on rotating disk electrode (same is true for rotating cylinder electrode), Fig. 11. The first stage includes the time from the onset of La(III) electroreduction till the limiting current is reached, Stage-2. Once the onset potential is reached the electroreduction of La(III) is very fast, almost instantaneous. It does not depend on rotation rate of electrode, as it will be shown below. In SEM studies below, it was found that in Stage-1 very thin film of lanthanum produced quickly covers the entire surface of electrode and for that reason the current stays constant, limiting current, while the scan progresses toward the vertex cathodic potential. The limiting current range represents the Stage-2. This stage serves as the ground for nucleation of lanthanum on just prepared film of lanthanum substrate. Rapid rate of nucleation, characterized with fast cathodic current increase, represents the Stage-3 of lanthanum reduction. The Stage-3 can be divided into two sections, Stage-3a, until the vertex potential is reached, and Stage-3b, further cathodic current increase even though the scanning potential was reversed in anodic direction. Stage-3a is easy to explain. The cathodic current increase is caused by the nucleation of lanthanum nuclei (on lanthanum film substrate) and by increase of their surface area caused by nuclei growth. The area growth continues even after the reversal of scanning direction at the vertex potential. The cathodic current increase lasts until the diffusional zones of individual nuclei begin to overlap, the
Fig. 11  Cyclic voltammogram of La in LiCl-KCl-0.1M LaCl3. Four stages of lanthanum electrodeposition can be observed.

Fig. 12  SEM of the electrode surface at the completion of Stage-1 (very small currents). The individual nuclei of La, all of the same size could be seen. They will cover the entire surface as a thin layer of lanthanum. If the termination potential is moved toward more cathodic potential another nucleation (lanthanum on lanthanum) will ensue followed by nuclei growth. Although not seen clearly here, this nucleation mechanism is more readily evidenced during electrodeposition of uranium.

Fig. 12a  Termination point at which cyclic voltammetry was stopped and working electrode taken out for analysis by SEM.
Fig. 13 SEM of electrode surface at Stage-3a.

Fig. 13a Termination point at which cyclic voltammetry was stopped and working electrode taken out for analysis by SEM.

Fig. 14 SEM of electrode surface at the end of Stage-3b (peak of cathodic current). Crystal clear nuclei of La, all of the same size, can be seen.

Fig. 14a Termination point at which cyclic voltammetry was stopped and working electrode taken out for analysis by SEM.
phenomenon caused by growth (of surface area), resulting in the cathodic peak current. Beyond the peak-current, further scanning in anodic direction leads to Stage-4 of electroreduction until the potential is reached to set anodic dissolution of lanthanum. Anodic dissolution of lanthanum is very rapid and complete.

C2.2 Cyclic Voltammetry Studies

These studies were done with objective to determine if compartmentalization (separation) of anolyte and catholyte compartments is needed. Compartmentalization of the electrochemical cell was done by placing the counter (or working) electrode in a porous alumina cylinder. Two types of electrodes were used, rotating disk electrode (RDE) and rotating cylinder electrode (RCE), each made of 1/16” tungsten rod. The role of compartmentalization was done by studying the cyclic voltammetry as a function of speed of rotation and speed of voltage scanning.

C2.2a Effect of RPM on CV of La in a Divided Cell by Using Rotating Cylinder Electrode

The effect of rotation on cyclic voltammetry of lanthanum was examined at five different scanning rates: 20 mV/s, 50 mV/s, 100 mV/s, 200 mV/s and 500 mV/s. Working electrode, a rotating cylinder, was tungsten rod 1/16” diameter with 5mm length of immersion into the molten salt. The length of immersion was fixed by cementing ½ inch alumina sleeve 5mm away from the tip of tungsten rod. W-RCE was polished by using fine grit metallographic paper. The counter electrode was also a tungsten rod, of the same diameter as the working electrode. It was placed in a porous alumina cylinder of 50 microns porosity. Its purpose was to prevent the reaction products generated at the counter electrode reaching the working electrode. The main reaction product of concern in molten chloride systems is the generation of chlorine. The working electrode rotation rates were: 200, 400, 800, 1200 and 2000 rpm, rotations per minute. The results are given in Fig. 15a-e.
Fig. 15a Effect of RPM on cyclic voltammetry of La at 20mV/s scanning rate by using the rotating cylinder electrode. Counter electrode, a tungsten rod, is placed in porous alumina cylinder.

Fig. 15b Effect of RPM on cyclic voltammetry of La at 50mV/s scanning rate by using the rotating cylinder electrode
Fig. 15c  Effect of RPM on cyclic voltammetry of La at 100mV/s scanning rate by using the rotating cylinder electrode.

Fig. 15d  Effect of RPM on cyclic voltammetry of La at 200mV/s scanning rate by using the rotating cylinder electrode.
From the results in Fig. 15a-e it can be seen that the rotation rate had very little effect on the deposition current in the Stage-1 of reaction. Some effect was present in the scanning rate range 20-100mV/s, which was lowered at 200mV/s scanning rate, and fully eliminated at 500mV/s scanning rate. At the fastest scanning rate the reaction of lanthanum deposition is fully controlled by electron transfer rate, i.e. it independent on mass transfer (rotation rate). Only for 500mV/s scanning rate the reverse scan crosses over the forward scan indicating nucleation and growth of new phase. It should be pointed out, although not shown here, that if vertex potential was set just another 100 mV more negative than the current -2.2V, all four stages of lanthanum nucleation would have been exposed, just as with rotating disk electrode.

Next, if the currents produced on working electrode are small then there would be no difference between cyclic voltammograms if counter electrode was placed inside or outside the alumina cylinder. The SEM studies showed numerous circular features on the working electrode whenever the counter electrode was not in the anolyte separator (porous alumina cylinder).

### C2.2b Effect of Speed of Rotating Disk Electrode Rotation on CV of La at Fixed Scanning Rate

Effect of RPM on the cyclic voltammetry of lanthanum on rotating disk electrode was studied for five different scanning rates: 50mV/s, 100mV/s, 200mV/s, 500mV/s and 1000mV/s. The results are given in Fig. 16a-e.
Fig. 16a  Effect of RPM on cyclic voltammetry of La at 50mV/s scanning rate by using the rotating disk electrode. Porous alumina cylinder was not used because lanthanum rod was used as the counter electrode, thus avoiding all issues with impurities generation.

Fig. 16b  Effect of RPM on cyclic voltammetry of La at 100mV/s scanning rate by using the rotating disk electrode.
Fig. 16c  Effect of RPM on cyclic voltammetry of La at 200mV/s scanning rate by using the rotating disk electrode.

Fig. 16d  Effect of RPM on cyclic voltammetry of La at 500mV/s scanning rate by using the rotating disk electrode.
Effect of RPM on CV of La at 1000mV/s Scan Rate

Fig. 16e Effect of RPM on cyclic voltammetry of La at 1000mV/s scanning rate by using the rotating disk electrode.

C2.2c Effect of Scanning Rate on CV of La at Fixed Speed of Working Electrode Rotation

Effect of scanning rate on cyclic voltammetry of lanthanum at three different rates of electrode rotation is presented in Fig. 17a-c.
Fig. 17a Effect of scanning rate on cyclic voltammetry of lanthanum at 200 RPM.

Fig. 17b Effect of scanning rate on cyclic voltammetry of lanthanum at 800 RPM.
Notice that the effect of scan rate at low rotation rate, such 200 RPM, follows the customary increase of maximum current with increase of scan rate, Fig. 17a. This dependence on scanning rate is identical to the electrochemical behavior of a stationary electrode. However, when the rate of rotation is higher, 800 and 2000 RPM, the decrease of diffusion layer thickness places the overall reduction rate in electron transfer rate control regime. In that case, the smaller scan rates provide longer time for electrodeposition, i.e. producing larger electroreduction currents.

**C3.1 Linear sweep voltammetry studies**

Because the cyclic voltammograms at scan rates 100mV and higher were not showing the effect of speed of electrode rotation, it was decided to examine the effect of rotation in the low range, 1-20mV/s, scanning speed. Although at low scanning speeds the currents were dependent on the speed of rotation and very large currents were produced still the limiting currents were absent. The only faintly visible limiting currents were present for the Stage-1 and State-2 of lanthanum deposition. For that reason it was decided to examine linear sweep voltammetry at low scanning speeds. The results for 5mV/s, 10mV/s, 20mV/s, 50mV/s and 100mV/s are presented in Fig. 17a-e. Notice that for 100mV/s, Fig. 10e, the Stage-1 is fully independent of the speed of electrode rotation, with reproducible limiting currents at about 5mA. After the production of a peak the Stage-2 entered the diffusion zone whose currents decreased but the decrease was orderly expressed with the increase of speed of electrode rotation.
Fig. 17a Effect of speed of rotating disk electrode rotation on the La LSV for 5mV/s scanning rate.

Fig. 17b Effect of rotating disk electrode rotation on the La LSV for 10mV/s scanning rate.
Fig. 17c Effect of rotating disk electrode rotation on the La LSV for 20mV/s scanning rate.

Fig. 17d Effect of rotating disk electrode rotation on the La LSV for 50mV/s scanning rate.
Fig. 17e Effect of rotating disk electrode rotation on the La LS for 100mV/s scanning rate.
3.1.1 Application of Levich and Levich-Koutecky equations on the Stage-2 La\(^{3+}\) reduction

It was decided to select the data in Fig. 10a, the effect of speed of electrode rotation, to examine if the selection of the currents at the end of Stage-2 and the onset of Stage-3 can be utilized to evaluate if these currents would follow the well-known equation for mass transfer control, i.e. the Levich eqn. (1).

The Fig. 17a is replotted and given in Fig. 18. The limiting current were identified at the intersection of tangents for Stage-2 and Stage-1 of lanthanum deposition. The limiting currents were then used in Levich equation to plot limiting current versus square root of rotating disc electrode rotation. The results are presented in Fig. 19. Because the data did fall on a straight line passing through the origin it can be stated that the transition stage from Stage-2 to Stage-3 is controlled by mass transfer rate mechanisms. If this is so, then the Levich-Koutecky plot, equation (2), the inverse of limiting current vs. inverse of speed of electrode rotation, should also follow the straight line and pass through the origin. That is exactly what was found, Fig. 20.

The slope in Fig. 19 was used for calculation of diffusion coefficient of La\(^{3+}\) at the transition stage from Stage-2 to Stage-3. For the initial concentration of La\(^{3+}\) of 1.62x10\(^{-4}\) M/cm\(^3\), kinematic viscosity 0.0136 cm\(^2\)/s, electrode disc area 0.0197 cm\(^2\), number of electrons 3, from the found slope of 0.623 the diffusion coefficient of La\(^{3+}\) that was calculated is D= 1.22x10\(^{-5}\) cm\(^2\)/s.

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Fig. 18 Linear sweep voltammetry at 5mV/s scanning rate as a function of speed of rotating disc electrode rotation. Intersection of tangents for Stage-2 and Stage-3 were taken to represent the current for particular RPM.
Fig. 19  Levich plot for the currents at the end of Stage-2 and onset of Stage-3 of lanthanum electrodeposition.

Fig. 20  Levich-Koutecky plot for the currents at the end of Stage-2 and onset of Stage-3 of lanthanum electrodeposition.
Task-D: Electrodeposition of uranium in the presence of additives to molten salts

Summary

The key characteristics of this research are described in the milestone Task-C, morphology studies during La electrodeposition in a two-compartment cell, and will not be repeated here.

The expectations from using thermally stable additives was to slow down the electrodeposition rate of uranium, i.e. to take the reaction out of mass transfer control and place it into electron transfer control (reaction rate control), as the means of morphology control.

However, with the progress of experimentation in this project it became clear that the electrodeposition from molten salts was already near the electron transfer rate control, at least for the two metals studies, lanthanum and uranium. Electrochemistry of lanthanum is described in the stated milestone. Some electrochemistry results with respect to uranium will be given here.

As to the effect of additives on electrodeposition of uranium that concept did not prove beneficial. The originally proposed additives were selected per their chemical and physical properties. It was expected that by using organic ionic liquids in mixture with molten inorganic salts some electron transfer rate modulation at the interface would lead to conditions for deposition of smooth deposits. The ionic liquids were therefore selected per their thermal stability. However, it was discovered that thermal stability of ionic liquid as reported in literature from the differential scanning calorimetry (DSC) studies did not satisfy the chemical stability when placed in a chemical processing environment, such as molten salts. For example, when ionic liquid 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI), one of the most stable ionic liquids, was added to molten LiCl-KCl at 450 C,

![Fig 21a Solidified UCl$_3$-LiCl-KCl salt. Purple color is typical for UCl$_3$.](image1)

![Fig. 21b The purple color of UCl$_3$ disappeared and the salt gained gray color upon addition of BMP-TFSI. CV-s of this salt showed no reaction characteristic for uranium.](image2)
the ionic liquid either degraded in molten salt containing lanthanum, or reacted with uranium to produce a lasting frothing and smoking reaction products. The purple molten salt, characteristic for UC13, changed the color to gray, Fig. 21. Therefore, the use of ionic liquids in molten salts was abandoned and the research was shifted to electrochemistry of lanthanum and neodymium studies in BMP-TFSI and EMIM-DCA.

With respect to uranium study the major emphasis was on exploring the morphology of this metal in various stages of polarization potential. Some of the results will be presented here. It was found that uranium, just like lanthanum, electroreduction happens in four stages. In Stage-1, a very fast (instantaneous) coverage of electrode surface with uranium happens. The film is exceptionally thin and spreads over the entire electrode surface. Upon the completion of Stage-1, the Stage-2 is characterized with a limiting current range. Further polarization to more cathodic direction leads to development of uranium nuclei on the already developed uranium film. These newly formed nuclei grow very fast, their increase in surface area due to clustering leads to increase of reaction rate (cathodic current), which now corresponds to the Stage-3a. On the reversal of scanning in anodic direction, the cathodic current still keeps increasing and peaks out at the overlap of diffusional zones. This is Stage-3b, just as is in the case of reaction mechanisms of lanthanum. After passing the cathodic peak potential, further polarization in anodic direction eventually enters the anodic region where dissolution of uranium happens.

The cyclic voltammograms were studied as a function of rotation rate of working electrode. It was found that they depend not only on the scanning rate, but also on the vertex potential at which the scanning direction is reversed. Therefore, if the vertex potential is reversed in the vicinity of Stage-2 of electroreduction then the anodic currents are characterized with sharp peaks, leading to zero current upon full dissolution of deposited uranium. However, if the vertex potential is more cathodic, and involves Stage-3a and Stage-3b, then anodic currents appear in two stages. First stage is characterized with sharp peaks, and the second stage is very broad.

The electrode rotation rate showed that this parameter is effective only for the very slow scanning rates, such as 5mV/s. For this scan rate, the increase of rotation increases the deposition rate as high as 375 mA/cm2 at 1200 RPM. Anodic currents were minimal however, most likely due to the falling-off of the reaction product at the high rotation speeds.

D1. Experimental Procedures

The experimental procedure is same is in Task-C, Morphology studies during La electrodeposition in a two-compartment cell.

The source of UC13 were some unused samples from the research activities supported by Idaho National Laboratory about ten years ago. The samples were UC13 in LiCl-KCl salt, with the composition of 40%U. Just as a precaution, the samples were dried in a stream of dry HCl gas. The UC13 salt dehydration was done with incremental increase of temperature until 200C. Upon treatment, argon gas was introduced to expel the HCl gas. The vessel holding UC13-LiCl-
KCl salt, enclosed with argon gas, was subsequently transferred to a glove box for experimental use.

The LiCl and KCl salts used were ultra-dry and ultra-pure, provided by Thermo-Fisher. However, the PI has found that these salts, which come in granular form, must have some surfactants (from granulation process) because the salt invariably led to production of brownish film that caused a lot of problems in experimentation with rotating disk electrode. It was found that eutectic LiCl-KCl salt provided by Sigma-Aldrich produced crystal clear eutectic liquid and the salt from this vendor was used since that finding.

The electrode preparation and other experimental particularities are the same as in the work with lanthanum.

**D2. Results and Discussion**

**D2.1 Morphology of Uranium in Various Stages of Cyclic Voltammetry**

As stated above, there are four stages of cathodic reduction of uranium on rotating disk electrode (same is true for rotating cylinder electrode), Fig. 22. The first stage includes the time from the onset of U(III) electroreduction till the limiting current is reached, Stage-2. Once the onset potential is reached the electroreduction of U(III) is very fast, almost instantaneous. It does not depend on rotation rate of electrode, as it will be shown below. It was found that in Stage-1 very thin film of uranium produced quickly covers the entire surface of electrode and for that reason the current stays constant, limiting current, while the scan progresses toward the vertex cathodic potential. The limiting current range signifies the Stage-2 of electroreduction. This stage serves as the ground for nucleation of uranium on just prepared film of uranium substrate. Rapid rate of nucleation, characterized with fast cathodic current increase, represents the Stage-3 of uranium reduction. The Stage-3 can be divided into two sections, Stage-3a, until the vertex potential is reached, and Stage-3b, further cathodic current increase even though the scanning potential was reversed in anodic direction. Stage-3a is easy to explain. The
The cathodic current increase is caused by the nucleation of new uranium nuclei (on uranium film substrate) and by increase of their surface area caused by further nuclei growth and their clustering. The area growth continues even after the reversal of scanning direction at the vertex potential. The cathodic current increase lasts until the diffusional zones of individual nuclei/clusters begin to overlap, resulting in the cathodic peak current. Beyond the peak current, further scanning in anodic direction leads to Stage-4 of electroreduction until the polarization potential is reached to initiate anodic dissolution of uranium. Anodic dissolution of uranium is not fast and it takes time to complete. It is a function of the vertex potential at which the scanning direction reversed. For reversal in Stage-2 the anodic peak is sharp and dissolution of uranium happens fast. For reversal in Stage 3, or 4, the anodic peak becomes like the one in Fig. 22.

Fig. 23 SEM of the electrode surface at the Stage-1 to Stage-2 (very small currents). The individual nuclei of U, of the same size, could be seen. They will cover the entire surface as a thin dense layer of uranium. If the termination potential is moved toward more cathodic potential another nucleation (uranium on uranium) will ensue followed by nuclei growth. Notice the formation of clusters of uranium that will keep growing in size and numbers during Stage 3a-3b, all laying on top of dense film of uranium.

Fig. 23a Termination point at which cyclic voltammetry was stopped and working electrode taken out for analysis by SEM.
Fig. 24  SEM of electrode surface around Stage-3a. Notice that the uranium nuclei are clustered over a very dense (gray background) film of uranium.

Fig. 25  Circular area now serves as an aide to clearly see very dense film of uranium over which large clusters (10-20 microns) of pure uranium are present. Clustering of about 100nm individual nuclei is most likely produced by electrode rotation. The reaction is in Stage 4.

Fig. 24a  Termination point at which cyclic voltammetry was stopped and working electrode taken out for analysis by SEM.

Fig. 25a  Termination point at which cyclic voltammetry was stopped and working electrode taken out for analysis by SEM.
Fig. 26 EDS analysis of observed clusters showed the existence of pure uranium (no chlorides from UCl₃, or LiCl-KCl are present in the clusters.) Notice one more time the densely packed underlying film of uranium.
D2.2 Cyclic Voltammetry Studies

These studies were done with the objective to determine if compartmentalization (separation) of anolyte and catholyte compartments is needed. Compartmentalization of the electrochemical cell was done by placing the counter (or working) electrode in a porous alumina cylinder. Two types of electrodes were used, rotating disk electrode (RDE) and rotating cylinder electrode (RCE), each made of 1/16” tungsten rod. The role of compartmentalization was done by studying the cyclic voltammetry as a function of speed of rotation and speed of voltage scanning.

D2.2a Divided Cell - Effect of Speed of Rotating Disc Electrode Rotation on CV of U at Fixed Scanning Rate

The effect of rotation on cyclic voltammetry of uranium was examined at three different scanning rates: 20 mV/s, 50 mV/s and 100 mV/s, Fig. 27a-c.

![Graph](image)

Fig. 27a Effect of RPM on cyclic voltammetry of U at 5mV/s scanning rate by using the rotating disk electrode. Counter electrode, a tungsten rod, is placed in porous alumina cylinder.
Fig. 27b  Effect of RPM on cyclic voltammetry of U at 50mV/s scanning rate by using the rotating cylinder electrode.

Fig. 27c  Effect of RPM on cyclic voltammetry of U at 100mV/s scanning rate by using the rotating cylinder electrode.
D2.2b Undivided Cell - Effect of Speed of Rotating Disk Electrode Rotation on CV of U at Fixed Scanning Rate

Fig. 28a Effect of tungsten rotating disk electrode speed of rotation on cyclic voltammetry of U at 5mV/s scanning rate.

Fig. 28b Effect of tungsten rotating disk electrode speed of rotation on cyclic voltammetry of U at 50mV/s scanning rate.
As can be seen from Fig. 28a-c, the slower the scan rate the higher the cathodic currents are produced with increase of electrode rotation speed. When the scanning rate was higher, such as 100mV/s, the speed of electrode rotation was not effective (Fig. 28c).

**D2.2c Undivided Cell - Effect of Speed of Rotating Cylinder Rotation on CV of U at Fixed Scanning Rate**

Sharp cyclic voltammograms are obtained with rotating cylinder electrode. With the rotating disk electrode typically these types of voltammograms are obtained if the polarization is reversed within Stage-3 (before the clustering occurs as in Stage-3.)

After comparison of cyclic voltammetry scans for La with those with U it can be observed that the reaction mechanisms (four stages of nucleation) are the same. However, the difference between the two metals is in their rate of electron transfer during the electroreduction. This can be easily seen from the effect of RPM on cyclic voltammetry of lanthanum and uranium. The rotation rate did not have any effect on lanthanum electroreduction when the scanning speed was 500 and above, while for uranium the effect of rotation was minimal at as low as 100mV/s scanning rate (Fig. 27c).
Fig. 29a Effect of tungsten rotating cylinder electrode speed of rotation on cyclic voltammetry of U at 100mV/s scanning rate.

Fig. 29b Effect of tungsten rotating cylinder electrode speed of rotation on cyclic voltammetry of U at 50mV/s scanning rate.
Fig. 29c Effect of tungsten rotating cylinder electrode speed of rotation on cyclic voltammetry of U at 5 10mV/s scanning rate.

**D3.1 Chronoamperometry studies**

Because the cyclic voltammetry studies did not show the dependence of electroreduction of U$^{3+}$ on speed of rotation except at very slow scanning rates it was decided to explore the use of fixed step cathodic potential. That technique is called chronoamperometry (CA). The CA was studied with the same electrodes as in cyclic voltammetry studies, WE (tungsten rotating disc), CE (w-rod) and RE (PtIr-QRE). Three cathodic step potentials were selected, one near the onset of uranium reduction (-1.15V), one in between (-1.25V) and one most cathodic potential (-1.5V), Fig. 30-32.
Fig. 30 Effect of rotating disk speed of rotations on electrodeposition of U at fixed -1.5V potential (vs. PtIr QRE).

Fig. 31 Effect of rotating disk speed of rotations on electrodeposition of U at fixed -1.25V potential (vs. PtIr QRE).
Fig. 32 Effect of rotating disk speed of rotations on electrodeposition of U at fixed -1.15V potential (vs. PtIr QRE).

Because steady state currents (dI/dt=0) were present within 0.5-2.0 minutes it was decided to use these values in the Levich equation (1),

\[ I_{\text{max, c}} = 0.62nFAD^{2/3}v^{-1/6}\omega^{1/2}C \] (1)

Where, \( I_{\text{max, c}} \) is the steady state current (limiting current), \( n \) - number of electrons, \( F \) - Faraday constant (96500 Amp-sec), \( A \) - the electrode disc area, \( D \) - diffusion constant (cm\(^2\)/s), \( v^{-1/6} \) - kinematic viscosity (cm\(^2\)/s), \( \omega \) - speed of rotation in (rad/s), and \( C \) - concentration (M/cm\(^3\)).

According to equation (1), the plot of steady state currents vs. square root of rotation speed should produce a straight line, with zero value at origin, if the reaction is controlled by mass transfer. The results presented in Fig. 33 show two following characteristics. First, the straight lines do not pass through origin, and second, the slope of the lines depend on the step potential. These two characteristics indicate that the electoreduction of uranium is not purely mass transfer controlled, but it also depends on the electron transfer rate (reaction rate), in other words the reaction is under mixed kinetics control. For the mixed kinetics control, in rotating disc
electrode experiments, the Levich equation had to be modified. Its modified form is known as Levich-Koutecky equation (L-K) [2],

\[
\frac{1}{I_c} = \frac{1}{0.62nAD^{2/3} \beta^{-1/6} \omega^{1/2} C} + \frac{1}{nFk_h C}
\]

(2)

where \(k_h\) (cm/s) is reaction rate constant.

According to equation (2) a plot of reciprocal of limiting current vs. reciprocal of square root of rotation speed produces a straight line with an intercept. The slope of the straight line contains the information on the diffusion coefficient, while the intercept value can be utilized to calculate the standard reaction rate constant. In case of pure mass transfer control (no electron transfer rate contribution) the straight line should go through the origin on the X-Y plot.

The reason for the slope variation with cathodic step potentials in Fig. 33 is the dependence of reaction rate on potential, eqn. (3):

\[
k_h = k_0 e^{-\frac{-\alpha F \eta}{RT}}
\]

(3)

Where \(k_0\) is the standard reaction rate constant, and \(\eta\) is the step potential.

![Levich Plot from Steady State Chronoamperometry Currents at -1.15V, -1.25V and -1.5V](image)

Fig. 33 Levich plot for the effect of speed of rotation on electrodeposition of uranium at three different step potentials.
It is interesting to note that although the plot of Levich equation produced straight line dependence for the entire studied speed of rotation range (200-3000 rpm) the Levich-Koutecky plot showed a slope break in the lines, Fig. 34. In the L-K plot, the speed of rotation is increasing from right to left, and we can see that above 800 RPM the data points are linear going through the origin of the graph. That was so for the step potentials of -1.25V and -1.50V. For the step potential of -1.15V the reaction of uranium reduction is predominantly controlled by the electron transfer rate (reaction rate control).

![Levich-Koutecky plot for the data in Fig. 33. Note that for the high speed or rotation the (800-3000 rpm) the straight lines pass through the origin, for -1.25V and -1.5V step potentials, indicating mass transfer control.](image)

Because of the break of the lines in L-K plot in Fig. 34, it was decided to replot the Levich equation in the initial kinetics region going incrementally toward the steady state. Thus, in Fig. 30, for -1.5V step potential, the effect of rotating speed was observed at 0.1s, 0.2s, 0.3s, 0.4s and 0.5s. The plot of current vs square root of rotating speed, Levich plot, for corresponding selected time is presented in Fig. 35. All of the current data followed straight line dependence. As the time was approaching the steady state condition (0.5 seconds) the intercepts in Fig. 35 were getting closer to the origin, the known diagnostic for mass transfer control mechanism. In the next step, the L-K plot for the data in Fig. 35 is produced, Fig. 36. Again, just as in Fig. 34, there are slope breaks in the lines, but this time only for 0.2s, 0.3s, 0.4s and 0.5s. For 800 r.p.m. and higher linear data do go through the graph origin. The data for 0.05s and 0.1s do not have the slope break and the lines have the same value intercept. These lines
show that the mixed kinetics control is present from the very beginning of the uranium electrodeposition.

Fig. 35 Levich plot for the initial kinetics of uranium electrodeposition at -1.5V (vs. PtIr QRE). Currents corresponding to rotation rates at 0.1, 0.2, 0.3, 0.4 and 0.5 seconds (cross of vertical lines and RPM) are taken from Fig. 30.

Fig. 36 Levich-Koutecky plot for data in Fig. 34. Note that straight lines data for 0.05s and 0.1s originated at the intercept.
The line for step function of -1.5V in Fig. 34 is used for further analysis. It is broken in two segments according to the speed range of rotation. For the speed range 800-3000 r.p.m. only the slope of the line was evaluated. For the 200-400 r.p.m. range (unfortunately, only two data points are available), both the slope and the intercept of the line were evaluated. These data were used in Levich-Koutecky equation ( ) to calculate the diffusion coefficient for $\text{U}^{3+}$, and the electron transfer rate constant, $k_h$. The following values were used in equation (2), for given molten LiCl-KCl system: kinematic viscosity, $\nu=0.0136 \text{ cm}^2/\text{s}$, $C_{\text{U}^{3+}}=6.8\times10^{-5} \text{ M/cm}^3$, $A=0.0196 \text{ cm}^2$, $n=3$, and $F=96,500 \text{ Asec}$.

The calculated values for $D$ and $k_h$ are: $D = 3.6\times10^{-6} \text{ cm}^2/\text{s}$; $k_h = 5.32\times10^{-4} \text{ cm/s}$.
ADDENDUM

TASK A1 - Electrodeposition In Low Temperature Ionic Liquids

The objective of this task was to perform a comparative study between two ionic liquids, (1) high temperature ionic liquids represented by molten inorganic salts (LiCl-KCl), and (2) low temperature ionic liquids composed of organic cations and organic/inorganic anions. As stated in the scope of work the primary intention was to use thermally stable room temperature ionic liquids as additives to the high temperature ionic liquids (molten salts) as the moderators for electroreduction rate of actinides. The prevention of dendritic morphology was the concept to be tested in this approach. Although the available most thermally stable room temperature ionic liquids proved to be not chemically stable when introduced in molten LiCl-KCl salts it was decided to continue with electrodeposition studies in room temperature ionic liquids as the standalone electrolytes. Electrodeposition of neodymium and lanthanum, as the key fission products, were selected as the subject of these studies with room temperature ionic liquids. The individual reports given here are prepared by the graduate students researching the respective metals.
TASK A1.1  Electrodeposition of Neodymium in the Room Temperature Ionic Liquid 1-Butyl-1-Methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide and the Effects of Water and Ethanol: A Rotating Disk Electrode Study

by Jacob C. Kline
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Abstract

The goal of this study was to examine the electrochemistry and deposition morphology of neodymium in the RTIL 1-butyl-1-methyppyrrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI). BMP-TFSI is designed to be a hydrophobic RTIL for use in open atmosphere. This particular RTIL is stable in the cathodic direction up to -3 V vs Ag/AgCl which provided adequate stability to observe the deposition of neodymium metal. The rotating disk electrode technique was used to study the electrochemistry of neodymium, water, and ethanol in BMP-TFSI. Neodymium deposition was observed at -2.4 V and the morphology was characterized using scanning electron microscopy. The effects of water and ethanol additions to BMP-TFSI were also investigated to determine their effects on the stability of the RTIL. While BMP-TFSI is designed to be hydrophobic, moisture from the atmosphere can be absorbed in small amounts. Ethanol has been proposed as a viscosity modifier to ionic liquids to make them less viscous. The diffusion coefficients of water and ethanol in BMP-TFSI were calculated to be 7.6x10^{-7} cm^2/sec and 1.8x10^{-9} cm^2/sec respectively. The reduction of ethanol on platinum in BMP-TFSI exhibited sluggish kinetics and the rate constant was calculated to be 4.3x10^{-4} cm/sec. Both water and ethanol additions drastically reduced the stability window of the RTIL to approximately 2 V.

1 Introduction

Neodymium metal is widely used throughout the electronics industry with its unique magnetic and optoelectronic properties. Due to the volatile supply of neodymium and other rare earth metals, alternative sources of neodymium have to be examined. Room temperature ionic liquids have been proposed as a medium for electrodeposition of rare earth metals to circumvent the use of high temperature inorganic molten salt processing. Matsumiya et al. [11] studied the
recovery of Nd, Pr, and Dy from an aqueous solution using a phosphonium based ionic liquid. Once the rare earths were extracted from aqueous solutions, the researchers showed electrodeposition of Nd at -2.4V vs Fc/Fc+ via reduction of Nd$^{3+}$ directly to metallic Nd. In a separate publication $^{[12]}$ Matsumiya et al. examined the electrodeposition of Nd in a DEME-TFSA ionic liquid again reporting a single, 3 electron transfer reduction step corresponding to Nd$^{3+}$ reduction at -3.3 V vs Ag/Ag+. Chronoamperograms showed an instantaneous nucleation mechanism and semi-integral analysis of a cyclic voltammogram yielded a diffusion coefficient of $1.45 \times 10^{-13}$ m$^2$s$^{-1}$. Chou and Hussey $^{[13]}$ studied the complexation of Nd (III) and Pr(III) in BMP-TFSI and found an initial single electron transfer step at around -1.5V vs Ag/Ag+. The researchers reported that no further reduction peaks attributable to neodymium reduction were seen in the stability range of their ionic liquid.

Literature is scarce concerning the use of the rotating disk electrode technique to examine the electrochemistry of metals in ionic liquids, especially lanthanide elements. Pan and Hussey $^{[14]}$ studied the electrochemical and spectroscopic behavior of the trivalent lanthanides Sm, Eu, and Yb in BMP-TFSI. Using rotating disk voltammetry, they determined the diffusion coefficients for Ln$^{2+}$/Ln$^{3+}$ and found them to be on the order of $1 \times 10^{-10}$ cm$^2$s$^{-1}$ for Eu and $1 \times 10^{-7}$ cm$^2$s$^{-1}$ for Sm and Yb. C. J. Rao et al.$^{[15]}$ studied Eu (III) in a BMP-TFSI system and reported the diffusion coefficient of Eu to be $3.1 \times 10^{-8}$ cm$^2$s$^{-1}$. Yang et al.$^{[16]}$ studied the electrochemistry of Eu, Sm, Dy, and Nd in an imidazolium ionic liquid and found reduction peaks at approximately -0.6 V vs Ag/AgCl that they assigned to the first reduction step of the trivalent species to a divalent one. They reported diffusion coefficients on the order of $10^{-8}$ cm$^2$/s for Eu(III) and on the order of $10^{-10}$ cm$^2$/s for Sm, Dy, and Nd.

The objective of this research was to examine the electrochemistry of neodymium in the RTIL BMP-TFSI. Published literature provides conflicting information on the electrochemical processes involved in the electrochemical reduction of neodymium in ionic liquids. It was also desired to understand the effects of water and ethanol impurities on the electrochemical stability and properties of BMP-TFSI. As the end goal of research in ionic liquids is to provide a low temperature, open atmosphere process for deposition of electronegative metals in ionic liquids, the role of water on BMP-TFSI should be understood. This is due to the fact that atmospheric moisture can be absorbed by RTIL’s in spite of the hydrophobic design. Ethanol is a commonly
used organic solvent and has been used in literature as a dissolution agent for hard to dissolve salts in RTIL’s. Ethanol has also been proposed as a viscosity modifier to decrease the relatively high viscosity of RTIL’s.

2 Experimental

2.1 Electrochemical Cell and electrodes

A standard three electrode electrochemical cell was used throughout this work consisting of a platinum, molybdenum, or glassy carbon working electrode, a graphite counter electrode, and a Ag/AgCl reference electrode. The general structures of the working electrodes used throughout this work are presented below in Figures 3.2a and 3.2b.

![General structure of working electrodes](image)

**Figure 1**: General structure of working electrodes utilized in electrochemical experiments (a) top down view of working electrode surface (b) side view of electrode.

Figure 3.5 presents the Ag/AgCl reference electrode used throughout this work. The electrode consisted of a silver wire that was anodized in a 3M KCl solution to generate an AgCl
layer on the silver wire. That wire was then placed into the plastic tube which was filled with 3M KCl. The end of the plastic tube was sealed with a conductive plug, which provides electrical contact with the solution, but prevents leakage of the electrolyte and contamination of the experimental solution.

![Diagram](image.png)

**Figure 2:** Ag/AgCl reference electrode utilized in electrochemical experiments.

A CHI Instruments (Austin, TX, USA) model 760B potentiostat as seen in Figure 3.6 was used for all electrochemical experiments. The potentiostat was controlled by CHI Version 5.0.7 software.

### 2.2 Electrolytes and chemicals

BMP-TFSI >99% purity was procured from IoLiTec (Ionic Liquids Technologies, Tuscaloosa, AL, USA). Unless otherwise noted, all ionic liquid preparation was carried in the glove box under inert argon atmosphere. The ionic liquid was dried overnight at 80° C prior to use.

HTFSI >99% purity was procured from Tokyo Chemical Industry (Portland, OR, USA). All handling of HTFSI was performed in the glove box. HTFSI was dried at 80° C prior to use. NdCl₃ >99.99% (Arcos Organics) was dried under vacuum with heating prior to use.
2.3 Scanning Electron Microscopy and X-Ray Diffraction Characterization

A Tescan Vega II (Czech Republic) scanning electron microscope was used for all SEM characterization reported in this work. A Siemens D5000 Diffraktometer XRD machine was used for XRD characterization.

3 Electrochemical Results and Discussion

3.1 Validation of reference electrodes in BMP-TFSI

A stable and reproducible reference electrode potential is critical in electrochemistry. In ionic liquids in particular, the reference electrode is a particular challenge. Potentials in ionic liquids are commonly reported with respect to a quasi reference which can be difficult to reproduce between different solutions, and additives to the ionic liquids can significantly affect their stability. In our work, a specialized reference electrode was used following validation with respect to the redox reactions of hydrogen as shown below in Figure 3.

In order to establish the validity of the Ag/AgCl reference electrode in the RTIL BMP-TFSI, 421mg of HTFSI was added to 5g of BMP-TFSI to provide the free hydrogen ion. These free hydrogen ions should be easily oxidized and reduced on a platinum surface. Figure 3 presents cyclic voltammograms in BMP-TFSI with HTFSI added to the ionic liquid. Notice the pronounced peaks centered around roughly + 8 mV versus our reference electrode for the scan performed at 5 mV/s. Increasing the scan rate as shown in Figure 3 leads to consistently increasing separation of the peak potentials indicating the redox reaction for hydrogen are quasi-irreversible. The redox reactions for hydrogen are presented below in Equation 1.

\[
H_2 \leftrightarrow 2H^+ + 2e\\ \text{Eqn. 1}
\]
**Figure 3:** Cyclic voltammetry to determine the location of the hydrogen redox potentials in BMP-TFSI with respect to the Ag/AgCl reference electrode.

This observation of quasi-reversibility agrees well with those made by Bentley et al. \[17\] who studied the redox reactions of hydrogen in an imidazolium-TFSI ionic liquid, as well as Meng et al. \[18\] who studied the reactions of hydrogen on several metallic electrodes in an imidazolium RTIL. It should also be noted that multiple stability and reproducibility studies were performed which showed our Ag/AgCl reference electrode to be reproducible and stable in the room temperature ionic liquid BMP-TFSI.

### 3.2 Baseline CV scan of pure BMP-TFSI

The electrochemical window of BMP-TFSI is of critical importance, especially in the cathodic direction. The ionic liquid should demonstrate good stability without electrochemical degradation. To determine the electrochemical window of BMP-TFSI, CV was used to locate the potentials at which BMP-TFSI begins to break down on the platinum electrode and the results are shown below in Figure 4.
Figure 4: Baseline CV scan of pure BMP-TFSI.

Figure 4 demonstrates that BMP-TFSI has excellent stability in the cathodic region as the potential can be scanned to approximately -3.5 V vs Ag/AgCl before large currents are seen due to the electrochemical breakdown of the BMP cation.

3.3 Effect of water addition to BMP-TFSI

In order to understand the effects water additions on the electrochemical behavior of BMP-TFSI, incremental amounts of water were added to a 5 gram sample of BMP-TFSI. Because water has a far smaller electrochemical window than BMP-TFSI, cyclic voltammetry was used to examine the stability range of the ionic liquid as water was added. The CV’s demonstrating the effects of water addition are presented in Figure 5a. Figure 5b provides a simplified graph, demonstrating the extreme decrease in electrochemical stability of BMP-TFSI with a large amount of water present. Figure 5c presents LSV experiments to examine the effect of RPM on the reduction of water in BMP-TFSI on a platinum working electrode. Figure 5d presents a Levich plot generated from Figure 5c.
Figure 5: Electrochemistry of water in BMP-TFSI on a Pt working electrode (a) CV demonstrating effect of incremental addition of water to BMP-TFSI (b) CV to display effect of addition of 0.5 mL water to 5g BMP-TFSI (c) LSV in the cathodic region to examine effect of RPM effect on water reduction (d) Levich plot of limiting/peak cathodic currents as a function of rotation speed.
It is expected that addition of water to BMP-TFSI should decrease the electrochemical stability window as the added water can be split and hydrogen gas produced as seen below in Equation 2.

\[ 2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^- \]  
Eqn. 2

Figure 5a clearly demonstrates the decrease in electrochemical stability with increasing water additions. The first addition of 50 µL of water to ionic liquid decreases the cathodic breakdown potential from approximately -2.5 V to -1.5 V. Sequential additions of water produce a far smaller impact on the cathodic breakdown potential. This observation agrees well with the work of O’Mahony et al. [19] who studied the effects of water on the electrochemical windows of 12 RTIL’s. Figure 5b presents a baseline, pure IL, CV scan along with a scan of the RTIL with 500 µL of water present. After additions of 150µL of water, a second aqueous layer was observed forming above the ionic liquid layer. O’Mahony observed a similar phenomenon, noting that the saturation water content of BMP-TFSI be 11,000 ppm with further addition of water resulting in an immiscible layer. Significant changes in the breakdown potential are not seen after 100-150µL water addition as this concentration roughly coincides with the saturation content of water in the ionic liquid. Above that concentration, water is excluded from the ionic liquid and forms an immiscible layer.

Examining the CV scans presented in Figure 5b closely reveals a peak or limiting current observed in scans with water added but not in pure ionic liquid. This peak is attributed to the splitting of water and generation of hydrogen gas. To further study these reactions, the rotating disk electrode technique was utilized in combination with linear sweep voltammetry. LSV scans to examine the effect of rotation speed are presented in Figure 5c. The pure ionic liquid scan reveals no significant peaks in the potential range from 0 to -1.5 V. When 500 µL of water added, distinct peaks and limiting currents are obvious due to the reduction of water.

The peak and limiting values seen in Figure 5c were plotted against the square root of rotation speed to produce a Levich plot which is presented in Figure 5d. The Levich plot demonstrates excellent linearity (R^2 = 0.993) up to the maximum studied rotation speed of 2000 RPM. Using the Levich equation as presented below in Equation 3, the diffusion coefficient for water in the RTIL BMP-TFSI was determined to be 7.6x10^{-7} cm^2/s. Notice again, that a plot of
the peak current versus the square root of rotation speed should be linear and pass through the origin. The slope contains valuable information on the diffusion coefficient.

\[ i_{\text{peak}} = 0.62nFAD^2C\sqrt{\frac{1}{6}\omega^2} \quad \text{Eqn. 3} \]

For the calculation of the diffusion coefficient of water in BMP-TFSI the kinematic viscosity of the solution calculated to be 0.91911 cm\(^2\)/sec based on the work of Sanchez-Ramirez et al. \[20\]. For the concentration of water in BMP-TFSI, the saturation water content of ~11,000 ppm was used as reported by O’Mahony et al. [__]. This value is comparable to those reported by other researchers. Rollet et al. \[21\] measured the diffusion coefficient of water in an imidazolium-TFSI ionic liquid using pulse field NMR, reporting the diffusion coefficient of water to 2.6x10\(^{-10}\)m\(^2\)/s. Saihara et al. \[22\] reported the diffusion coefficient of water in imidazolium tetrafluoroborate to be 4.3x10\(^{-10}\) m\(^2\)/s. Menjoge et al. \[23\] reported the diffusion coefficient of water in imidazolium ionic liquids to be on the order of 10\(^{-10}\) to 10\(^{-11}\) cm\(^2\)/sec using the technique of pulse field gradient NMR.

3.4 **Effect of ethanol addition to BMP-TFSI**

Similar to water are described above, ethanol also possesses a far smaller electrochemical window than BMP-TFSI in the cathodic direction. The addition of ethanol to ionic liquid requires further study. Linear sweep voltammetry was used to determine the effects of ethanol addition on the electrochemical stability of BMP-TFSI in the cathodic region.

Figure 6a presents LSV in the cathodic region to examine the effect of incremental ethanol addition to ionic liquid. Notice from Figure 6a that additions of up to 100 µL of ethanol to a 5g sample of BMP-TFSI can be “tolerated” without a drastic change in the electrochemical stability. However, any further additions of ethanol results in a drastically reduced cathodic breakdown potential of roughly -1.5 V.

Schmidt et al. \[24\] studied the oxidation and reductions reactions of ethanol on platinum and ruthenium electrodes and alloys. The researchers extensively studied the electrochemical reaction products of ethanol on platinum and ruthenium using mass spectroscopy. Using mass
spectroscopy, they identified ethane and methane gasses as the primary reduction products of ethanol produced on platinum. A two step reduction process for ethanol was proposed and demonstrated by the authors as presented below in Equations 4 and 5. The first step in the

Figure 6: Electrochemistry of ethanol in BMP-TFSI on a Pt working electrode (a) LSV to examine effect of incremental ethanol additions to 5g BMP-TFSI (b) LSV in the cathodic region to examine the effect of RPM effect on 5g BMP-TFSI + 0.5mL ethanol (c) Levich plot of limiting/peak cathodic currents as a function of the square root of rotation speed (d) Koutecky-Levich plot of limiting/peak cathodic currents as a function of the square root of rotation speed.
reduction process was the adsorption of ethanol or an ethanol radical (negatively charged ethanol molecule) onto the platinum surface (Eqn. 4).

$$CH_3CH_2OH + e \rightarrow CH_3CH_2OH^{\text{adsorbed}}$$  \hspace{1cm} \text{Eqn. 4}

Once the ethanol molecule or radical was adsorbed, it was reduced to ethane or methane gas depending on whether or not the carbon-carbon bond was broken during the reduction process (Eqn. 5). The authors note that the splitting of the carbon-carbon bond is not likely on a platinum surface as platinum does not serve as a good catalyst for the breaking of carbon-carbon bonds, and as such this possible reaction is ignored.

$$CH_3CH_2OH^{\text{adsorbed}} + e + 2H^+ \rightarrow CH_3CH_3 + H_2O$$  \hspace{1cm} \text{Eqn. 5}

If the C-C bond remained intact, the adsorbed molecule was reduced to ethane gas. If the bond was broken, ethanol would be reduced to methane gas. The oxidation products of ethanol on platinum were reported by Schmidt et al. to be CO$_2$ gas primarily.

Similar to water, a region of distinct limiting currents can be seen around -1.2 V. Figure 6b presents LSV to examine the effect of RPM on a 5g BMP-TFSI samples with 500µL of ethanol added. A consistent increase in the limiting currents is seen with increasing rotation speed. The Levich plot shown in Figure 6c again shows excellent linearity ($R^2 = 0.992$). However, unlike the Levich plot seen in Figure 5d, a distinct, non-zero, intercept is seen in Figure 6c. This observation indicates that there is a sluggish kinetic parameter which must be taken into account. In order to determine the diffusion coefficient and the reaction rate constant, the Levich-Koutecky equation must be used as seen below in Equation 6, where the new term $i_k$ represent the current that would be expected without any diffusion control.

$$i_{\text{peak}}^{-1} = \frac{1}{i_k} + \left( \frac{1}{0.62nFACD_3^{\frac{1}{6}}} \right) \omega^{-\frac{1}{2}}$$  \hspace{1cm} \text{Eqn. 6}

Figure 6d presents a Levich-Koutecky plot to determine the kinetic parameter. Again, excellent linearity is seen in the Levich-Koutecky plot, and a distinct intercept is seen. By utilizing the Levich-Koutecky equation presented above in Equation 6, the diffusion coefficient of ethanol in BMP-TFSI was determined to be $1.8 \times 10^{-9}$ cm$^2$/s and the reaction rate constant for ethanol reduction on platinum was calculated to be $4.3 \times 10^{-4}$ cm/s. This value of the diffusion
coefficient is significantly smaller than the values reported by Raush et al. [25] who used dynamic light scattering techniques to determine the diffusion coefficients of acetone and ethanol in imidazolium RTIL’s.

3.5 Effect of IL addition to ethanol solutions without neodymium present

Further work was performed to understand the reactions of ethanol in BMP-TFSI. For the following set of experiments, small amounts of ionic liquid were added to a 5g sample of ethanol. The addition of ionic liquid will provide solution conductivity to the ethanol solution. Ethanol itself, due to its partly non-polar nature, is unable to provide charge carrying species to contribute to solution conductivity. With little to no solution conductivity in pure ethanol, no reactions are expected. However, incremental addition of completely ionic BMP-TFSI provides charge carrying species which help to complete the electrical circuit between the counter and working electrodes. Cyclic voltammetry was used to examine the effects of incremental BMP-TFSI addition to pure ethanol, as well as the effects of scan rate and a rotation speed of 400 RPM.

Figure 7a presents the cyclic voltammograms of an ethanol solution with incremental amounts of ionic liquid added. CV’s were performed with a scan rate of 5 mV/s, with and without rotation at 400 RPM. Notice that initially, the experiments with 400 RPM present larger current densities than those performed at stationary conditions. This observation is consistent with the fundamental concept of the Levich equation, i.e. the shrinking boundary film drives faster mass transport and thus a larger reaction rate. However, once the applied potential reaches approximately -2 V for the 50µL addition scan, the scan at the stationary condition surpasses the scans with 400 RPM rotation and presents larger current densities. For the rest of the scan towards the cathodic direction, the stationary CV scan demonstrates larger current densities than the CV scan with 40 RPM. This transition from 400 RPM to stationary conditions providing the largest current densities requires careful examination. An identical transition can be seen at -1.75 V for the 250µL IL addition, and -1.5 V for the 1000µL IL addition CV scans.
Figure 7: CV to examine the effects of incremental IL addition to a 5g sample of ethanol with no NdCl₃ present with 0 and 400 RPM rotation speeds (a) scan rate: 5 mV/s (b) scan rate: 10 mV/s (c) scan rate: 50 mV/s.

This transition can be understood in light of the observations made by Schmidt et al. [37], who proposed the two step reduction process for ethanol discussed above and reproduced below in Equations 7 and 8.

$$\text{CH}_3\text{CH}_2\text{OH} + e \rightarrow \text{CH}_3\text{CH}_2\text{OH}^\text{adsorbed} \quad \text{Eqn. 7}$$

$$\text{CH}_3\text{CH}_2\text{OH}^\text{adsorbed} + e + 2\text{H}^+ \rightarrow \text{CH}_3\text{CH}_3 + \text{H}_2\text{O} \quad \text{Eqn. 8}$$
The first step in the reduction process was the adsorption of an ethanol radical followed by reduction to ethane gas. In light of the two step process just described for the reduction of ethanol on platinum, the experimental results seen in Figure 7a can be clarified. In experiments where no rotation speed was used. The adsorbed ethanol species remained on the surface longer and were fully converted to ethane or methane reduction products. However, when rotation was present, some of the adsorbed species were removed from the surface by the rotation. Removing the adsorbed species led to smaller currents during the rest of the scan as the remaining species were converted to ethane or methane.

This concept of the adsorbed intermediate species in the reduction process of ethanol can be further seen in the experimental results presented in Figures 7b and 7c with faster scan rates of 20 mV/s and 50 mV/s respectively. Notice that in both of these figures, when no rotation speed was used, an anodic peak was detected after the scan was reversed from the cathodic to anodic scan direction. These anodic currents are not seen when 400 RPM of rotation speed was used. These anodic currents are attributed to the oxidation of the adsorbed ethanol radicals that remained on the electrode surface. These anodic currents are not seen in the 400 RPM scans as the rotation of the electrode removes the species from the surface before they can be oxidized. These anodic currents were also not seen in Figure 7a in experiments with and without rotation as the slower scan rate of 5 mV/s used in Figure 7a allowed the adsorbed species to leave the surface before they could be oxidized. In all experiments seen in Figures 7a-c, it can be seen that the currents increase consistently with increasing additions of ionic liquid. This observation is explained by the ionic liquid providing greatly increased charge carrier concentrations to the ethanol solution.

3.6 Effect of IL addition to ethanol solutions with neodymium present

Previous experiments presented in Figures 7a-c discussed the incremental addition of ionic liquid to ethanol without neodymium present. To understand the reactions of ethanol when NdCl₃ is present, an identical batch of experiments was performed using a 5g ethanol solution with 125 mg of NdCl₃ added. Ionic liquid was then added incrementally and the results are shown in Figures 8c and 8d. Due to the large electronegative potential required for neodymium
deposition (more cathodic than -2.5 V), the addition of neodymium chloride to ethanol/ionic liquid mixtures is not expected to produce any new peaks or behaviors within the voltage range studied. Experiments seen above in Figures 7a-c indicate that ethanol breakdown begins at approximately -1 V, well before any electrochemical reactions of neodymium are expected to occur.

Figures 8a and 8b present the same data as Figure 7c above, with the 0 and 400 RPM experiments plotted on separate graphs. Notice again that the anodic currents disappear with rotation speed, indicating that an adsorbed reaction intermediary is being spun away from the electrode surface. A distinct change in the behavior in the plots is seen with the addition of NdCl₃ as seen in Figures 8c and 8d. The addition of NdCl₃ suppresses the cathodic currents even with up to 1000μL of BMP-TFSI added to provide solution conductivity.

The first possible explanation for the suppression of the cathodic currents in Figure 8c and 8d is the deposition of a neodymium film achieved via a disproportionation reaction. For neodymium, the disproportion reaction first requires the single electron reduction of neodymium as seen below in Equation 9.

\[ \text{Nd}^{3+} + e \rightarrow \text{Nd}^{2+} \]  

Eqn. 9

It is generally accepted that Nd²⁺ is unstable and will decay via the disproportionation reaction as presented in Equation 10 below.

\[ 3\text{Nd}^{2+} \rightarrow 2\text{Nd}^{3+} + \text{Nd}^{0} \]  

Eqn. 10

Chou and Hussey [__] observed a cathodic peak in the cyclic voltammograms in their RTIL occurring around the potential of -1.5 V vs a Ag/Ag+ reference electrode. They proposed that this peak should be attributed to reduction of Nd³⁺ to Nd²⁺ as seen in Equation 9. Once the neodymium film is deposited, the new neodymium surface would most likely have a smaller exchange current density for the reduction of ethanol compared to the original platinum surface.
**Figure 8:** CV performed at 50 mV/s to examine the effects of incremental IL and NdCl₃ addition on the CV of EtOH (a) 0 RPM, no NdCl₃ (b) 400 RPM, no NdCl₃ (c) 0 RPM, with NdCl₃ (d) 400 RPM, with NdCl₃.

In order to confirm this assumption, Tafel polarizations were performed using both the bare platinum surface, as well as the platinum electrode with an electrochemically prepared neodymium surface. A Tafel polarization is a specific type of LSV experiment where the potentials scanned from -250mV to +250mV vs the equilibrium working electrode potential at a slow scan rate. The Tafel polarizations are presented below in Figure 9. Tafel polarizations
provide quick and definitive values for the exchange current densities for the possible reactions occurring on the electrode surfaces. The Tafel polarizations were performed to determine if an electrodeposited neodymium film lead to lower exchange current densities for ethanol reduction.

![Tafel polarization graph](image)

**Figure 9:** Tafel polarizations to examine effect of electrode surface chemistry on the redox reactions of ethanol. SR: 1 mV/s, T: 25 C.

The Tafel polarizations presented above in Figure 9 clearly illustrate that platinum will provide a larger exchange current density for the reduction of ethanol compared to an electrodeposited neodymium surface. The neodymium surface was prepared by cathodically polarizing the electrode in an ionic liquid with NdCl$_3$ present.

By extrapolating the linear regions of the cathodic branch of the Tafel plots, the exchange current density for the reduction of ethanol on the two different surfaces can be predicted. Notice that the linear extrapolation of the electrodeposited neodymium film is significantly steeper than that of the polished platinum surface. This indicates that the exchange current density for ethanol reduction on neodymium will be significantly smaller compared to platinum. The Tafel polarizations confirm the theory that a neodymium film deposited by
disproportionation could be the cause of smaller current densities for ethanol when NdCl₃ is present. The rare earths are commonly known to act as catalysts, however, here neodymium deposition is seen to reduce the reduction current densities. Literature is scarce on the reduction reactions of ethanol. Schmidt [__] found that the redox reactions of ethanol proceeded rapidly on platinum, but no redox reactions were observed on a ruthenium electrode. It is possible that in this situation, neodymium metal behaves in a similar fashion as ruthenium, and electrodeposits of neodymium provide greatly reduced ethanol reduction current densities.

While it has been just shown that a neodymium film by disproportionation would lead to smaller ethanol reduction currents, it is unlikely that neodymium film formation is occurring in these experiments. Close examination of the scans presented in Figures 4c and 8d reveal no appreciable peaks attributable to the disproportion of neodymium. Note also that the suppression of the currents begins at approximately -1 V. This observation is particularly prominent in Figure 8d. Comparing this potential with the work of Hussey and Chou [__] discussed above reveals that the suppression of the anodic current begins roughly 500 mV before that which has been thermodynamic established for the first electron reduction of neodymium.

A second possibility for the suppression of the anodic currents could be the strong chemisorption of a NdCl₃-ethanol solvate. This stable solvate would resist electrochemical reduction, and its occupation of the surface would shield the electrode from free ethanol molecules. These two effects would lead to the markedly small currents seen in the cathodic region in Figures 8c-d. In order to determine if this phenomenon was occurring, experiments were performed in pure ethanol with 0.2 M CaCl₂ salt added to provide solution conductivity. After a baseline CV scan was performed in this solution, a second scan was performed with 0.1 M of neodymium chloride added. The results are presented below in Figure 10.
Figure 10: CV of ethanol with 0.2 M CaCl$_2$ added to examine the effect of 0.1M NdCl$_3$ addition.

Examining Figure 10 closely indicates that the addition of NdCl$_3$ to ethanol leads to large reductions in the cathodic currents. This is opposite of the expected increase in currents with the increased solution conductivity from the extra ions of NdCl$_3$. Comparing the current values of the scans in Figure 8c and 8d with those seen above in Figure 10 show that all the scans with NdCl$_3$ added are almost identical in terms of current densities. Meanwhile, the scan without NdCl$_3$ present presents significantly larger currents. The scans in Figure 10 indicate the formation of a strongly adsorbed NdCl$_3$-ethanol solvate that screens the working electrode surface from solution. This adsorbed solvate could also explain the results seen in Figures 8c-d. Solvation occurs when the solute atoms (in this case neodymium) are surrounded by concentric spheres of the solvent species (ethanol).

This proposed ethanol neodymium solvate fits well with the experimental data in Figures 8c and 8d. Without rotation in Figure 8c, the cathodic currents are all suppressed and present roughly the same value of roughly -1 mA/cm$^2$. In Figure 8d, with 400 RPM of rotation speed,
the cathodic currents are still suppressed and with rotation all experiments virtually identical limiting current values of -0.6 mA/cm². This observation of more consistent limiting currents with rotation can be explained by the rotation of the electrode creating a more uniform surface coverage of the strongly adsorbed solvate. This uniform surface coverage leads to very similar current density values for all experiments also explains the reduction in currents with rotation. The rotation helps promote a more uniformly adsorbed solvate layer which eliminates the few remaining sites on the electrode on which ethanol reduction can occur. Neodymium chloride-ethanol solvate complexes have been reported [26, 27] with three molecules of ethanol assigned to each molecule of neodymium chloride.

3.7 CV of BMP-TFSI at low and high temperatures without NdCl₃ present

In order to understand the baseline stability of BMP-TFSI on platinum, molybdenum, and glassy carbon working electrodes, cyclic voltammetry was used to probe the electrochemical windows at 25° and 100° C.

![Graph](image)

**Figure 11:** Baseline CV scans to study the electrochemistry of BMP-TFSI on Pt-Ir, Mo, and GC electrodes at room and high temperature (a) 25° C (b) 100° C.
Figure 11a shows that at 25° C the platinum and molybdenum working electrodes perform similarly in the cathodic region. In the cathodic region, glassy carbon performs the best out of the three electrodes in terms of increasing the stability range of BMP-TFSI. While all scans show severe breakdown of ionic liquid at approximately -3.2 V, glassy carbon provides the smallest current densities in the region from -2 to -3.2 V. In the anodic region the glassy carbon again presents the smallest current densities, while platinum and molybdenum present similar values. Notice however, that the molybdenum electrode does not present significant currents due to breakdown of the ionic liquid in the anodic direction. While breakdown in the cathodic direction should be attributed to reduction of the cation, breakdown in the anodic direction should be attributed to the oxidation of the anion. Based on this observation, it can be stated that the oxidation of the TFSI anion does not proceed rapidly on a molybdenum surface.

Figure 11b presents similar scans as Figure 11a with the temperature increased to 100 C. Again, the glassy carbon electrode performs the best in the cathodic region, as it presents the smallest current densities attributable to the reduction of the BMP cation. Molybdenum presents slightly larger currents than the glassy carbon, and the platinum surface provides the largest current densities. In the anodic direction, platinum again presents the largest current densities and earliest break down. Glassy carbon presents smaller currents, while molybdenum again presents almost no anodic currents, even when scanned to +4.5 V. This observation again indicates that the oxidation of the TFSI anion does not proceed rapidly on the molybdenum surface.

The cathodic region and breakdown behavior of BMP-TFSI is of more importance than the anodic behavior as reduction of neodymium will occur in the cathodic region. Kroon et al. [28] used computational methods to simulate the cathodic breakdown products of the BMP cation. The computational results were corroborated with experiments and characterization with gas chromatography and mass spectroscopy. Kroon’s computation results yielded three possible products for the breakdown of BMP. The first and most likely outcome is the creation of methylpyrrolidine and a butyl radical group. The second most likely is the splitting of the pyrrolidine ring and the formation dibutylmethylamine radical. The final and least likely outcome is the formation of butylpyrrolidine and a methyl radical.
3.7.2 CV at 25° C and 100° C to examine the electrochemistry of BMP-TFSI with NdCl₃ present on Pt, Mo, and GC working electrodes

With the baseline behavior of BMP-TFSI on platinum, molybdenum, and glassy carbon established in Figures 11a and 11b, neodymium chloride was added to the ionic liquid to examine the electrochemistry of neodymium in BMP-TFSI. CV scans of the ionic liquid-NdCl₃ solution are presented below in Figures 12a and 12b on platinum, molybdenum, and glassy carbon working electrodes at 25 and 100° C.

![CV scans](image)

**Figure 12:** CV of BMP-TFSI on the Pt-Ir, Mo, and GC working electrodes in pure IL dried overnight with Nd present via HTFSI addition (a) 25° C (b) 100° C.

The CV scans shown above in Figure 12a present distinct peaks for Nd reduction beginning at approximately -2.75 V for platinum and ranging to -3 V for glassy carbon. As discussed above it is well known that the glassy carbon surface will require large over potentials compared to the platinum and molybdenum substrates. These peaks are not visible in the scans presented in Figure 12b when the temperature was increased to 100° C. The observation can be understood by the temperature induced instability of the BMP cation. The currents observed for
Nd reduction in Figure 12a range from -3 to -5 mA/cm². Examining Figure 12b closely indicates that currents of this magnitude would be “drowned out” by the increased electrochemical degradation of the ionic liquid. Further efforts to study the cathodic peaks seen in Figure 12a will be made using LSV scans.

Notice in Figure 12a that the cyclic voltammograms showing distinct reduction peaks for neodymium do not show any oxidation peaks. This observation indicates that either the reduction reaction of neodymium is irreversible, or that neodymium reacts chemically with species present in the ionic liquid before it can be reoxidized. Bhatt et al. [29] described the synthesis and CV response of a thorium (IV)-TFSI compound. They observed deposition of metallic thorium at -2.15 V with in a completely irreversible process. The researchers report that water was present as a contaminant from the synthesis process and they propose that the freshly deposited thorium film reacted chemically to form ThO₂ before the film could be oxidized electrochemically. Suppan [30] reported cyclic voltammograms for neodymium in BMP-TFSI and again showed no oxidation peaks on the return scan, attributed to the irreversibility of the neodymium reduction reaction.

3.8 LSV of BMP-TFSI with Nd added on Pt, Mo, and GC working electrodes

The CV scans presented above in Figure 12a present distinct cathodic peaks that correspond well with the standard potential for neodymium reduction. To further study the peaks seen during the cathodic scans at room temperature discussed above in Figure 12a, linear sweep voltammetry was performed with the three different electrodes. Linear sweep voltammetry was chosen instead of cyclic voltammetry in order to accurately study the deposits on the electrode surface directly after the peaks seen in the CV’s. LSV scans for the Pt-Ir, Mo, and GC electrodes are presented below in Figure 13.
The LSV scans presented in Figure 13 present distinct peaks in the cathodic region that correspond well neodymium reduction. The platinum electrode presents the most well defined peak with the largest current density. This is consistent with known behavior of platinum for large exchange current densities and lower over potentials compared to other substrates. The molybdenum electrode presents the next largest current densities with the peak potential shifted approximately 70 mV in the cathodic direction compared the peak potential of the platinum electrode. Finally, the glassy carbon electrode presents the smallest peak current densities and the most cathodic peak potential. It is generally known that glassy carbon requires larger over potential for deposition of metals compared to metallic electrodes like molybdenum and carbon. Notice in Figure 13 that there are no distinct peaks to be assigned to the single electron reduction of Nd\(^{3+}\) to Nd\(^{2+}\). This observation is in contrast with the work of Chou and Hussey [___] who all showed a single electron reduction step for neodymium.

Immediately following the LSV experiments just discussed, the electrodes were imaged using optical microscopy to study the effect of surface on the films formed on each electrode.
The electrodes were cleaned with methanol and methylene chloride prior to imaging. Optical micrographs of the three working electrodes are presented below in Figures 14a-c.

![Optical micrographs](image)

**Figure 14:** Optical micrographs taken at 40x magnification of working electrodes after LSV experiments (a) Pt-Ir (b) Mo (c) GC.

The optical micrographs presented above demonstrate that platinum and molybdenum provide the best film coverage, while glassy carbon provides slightly less surface coverage. This is consistent with the magnitudes of the peak current densities seen in the LSV scans in Figure 13. These scans showed platinum and molybdenum to have the largest current densities compared to glassy carbon. As stated above, molybdenum provided much smaller currents for the breakdown of ionic liquid and provided comparable peak current densities for neodymium deposition compared to platinum. For these reasons, combined with the distinct film seen in Figure 14b, molybdenum again distinguishes itself as suitable electrode for neodymium deposition.

Based on the LSV scans and optical microscopy, it is apparent that either the molybdenum or platinum substrate will provide the best results for deposition of metallic neodymium from ionic liquids. While platinum presents the largest leak current densities for the deposition of neodymium, molybdenum performed better than platinum without neodymium present by delaying the onset of ionic liquid breakdown and allowing smaller current densities for the ionic liquid decomposition.
3.9 *Optical characterization of electrodeposited films on a Pt working electrode at 25° C*

Optical microscopy allows quick and easy verification that a film has been deposited. Figures 15a-g below present the effect of applied potential on the surface films formed on the platinum working electrode following potentiostatic polarization for 3 seconds. After each experiment the electrode was dipped in two successive methanol baths to remove excess ionic liquid. Directly before optical microscopy, the surface was cleaned with methylene chloride organic solvent to remove any residue.

Figure 15a-g presents optical micrographs captured at 40x magnification for all images. Figure 15a was polarized at -2.2 V for 3 seconds and no substantial film is seen on the surface. In Figures 15b and 15c a distinct film is seen on the electrode surface with polarization potentials of -2.4 and -2.6 V respectively. These potentials correspond well with the onset of neodymium deposition beginning to occur at -2.5 V. With a larger over potential of -2.8 V, a more distinct film is observed on the electrode surface as seen in Figure 15d. Notice also in this figure the circular areas present mainly around the edge of the electrode. These areas are attributed to the formation of bubbles on the electrode surface during polarization. The bubbles are explained by the presence of dissolved ethanol in the system as ethanol was used as an intermediate in the solution preparation process. The bubbling could also be produced from the electrolysis of water absorbed from the open atmosphere. Both of the reduction products of water and ethanol are gaseous species. As discussed above, ethanol is proposed to follow a two-step reduction process to methane or ethane, and hydrogen gas produced from water will also create bubbles on the surface. During CV experiments, bubbles were frequently observed on the electrode surfaces which were easily removed by tapping the electrode. These bubbles will obscure the surface area underneath and lead to an inconsistent film. Continued increase in applied over potential leads to complete coverage of the electrode surface with a polarization of -3 V as shown in Figure 15e, but again evidence of bubbling is present on the electrode surface. Polarization at -


Figure 15: Film formation as a function of applied potential as characterized by optical microscopy. Films formed by CA performed for three seconds at 25° C with potentials of (a) -2.2 V (b) -2.4 V (c) -2.6 V (d) -2.8 V (e) -3 V (f) -3.2 V (g) -3.4 V (h) control sample polarized at -3 V for 3 seconds in pure IL with no Nd present. All micrographs taken at 40 x magnification.
3.2 V and -3.4 V in Figures 15f and 15g leads to further increased bubbling on the electrode surface, disrupting neodymium layer formation. Figure 15h presents the electrode surface after polarization at -3 V for 3 seconds in a pure ionic liquid solution with no neodymium present. The bare surface evident in Figure 15h indicates that even up to -3 V, the deposits seen in Figure 15b-g should be attributed to the reduction of neodymium. This observation is critical as one considered explanation for the films seen was the deposition of the BMP cation from ionic liquid. The lack of deposits in Figure 5.1h indicates that the deposits must be attributed to neodymium related deposition rather than simple reduction and deposition of the BMP cation.

3.10 SEM characterization of electrodeposited films on Pt, Mo, and GC working electrodes following LSV scans at 25° C

Immediately following the LSV scan shown in Figure 13, the platinum working electrode was cleaned in two successive methanol baths for at least five minutes each. The electrode was then cleaned using methylene chloride. Optical microscopy was first performed, followed by characterization using SEM. SEM micrographs of the Pt electrode surface are presented below in Figures 16a-c.

Figures 16a-c above present SEM images of the platinum working electrode surface following linear sweep voltammetry in the cathodic region. In all three images above, the presence of white clumps is noted that appear to be charging under the SEM. These clumps are attributed to agglomeration of ionic liquid breakdown product. It should be noted that this breakdown product is very stable as soaking in methanol for at least 10 minutes and rinsing with methylene chloride did not completely remove the deposits. Of importance to note are the micro scale porosities seen in the film present. These porosities are particularly evident in Figure 16c. These porosities are attributed to the evolution of a gaseous product on the electrode surface. In this case these gaseous species are likely the generation of hydrogen gas from moisture that the ionic liquid absorbed from the atmosphere. It is unlikely that any breakdown products of the ionic liquid as discussed earlier would lead to the formation of gaseous products. Figures 16a and 16b indicate that the deposited film uniformly covers the entire platinum surface.
Figure 16: SEM characterization of the Pt working electrode after LSV in BMP-TFSI with NdCl$_3$ present at 25° C (a) 1,000x magnification (b) 3,000x magnification (c) 5,000x magnification.

In a similar fashion as the platinum electrode just discussed, SEM characterization was performed on the glassy carbon and molybdenum electrodes following LSV scans in BMP-TFSI with NdCl$_3$ present. The results are presented below in Figures 17a and 17b.
Figure 17: SEM characterization at 1,000x magnification of electrode surfaces after LSV to -3.5 V in BMP-TFSI with NdCl₃ present at 25°C (a) Molybdenum electrode (b) Glassy carbon electrode.

The electron micrograph of the film deposited on the molybdenum electrode provides almost total coverage. The film is also very dense, as the electrode surface cannot be seen in Figure 17a. However, it should be noted that there are thousands of tiny pores present which are evident of a gaseous product during the deposition process. This observation agrees well the film seen on the platinum working electrode. This gaseous product could be the electro-generation of hydrogen gas from moisture adsorbed into ionic liquid from the open atmosphere. EDX imaging of the surfaces is planned to characterize the chemical composition of the films. There are also cracks present in the films seen on the molybdenum electrode (seen as lighter lines). It is proposed that these cracks arise from the preferential generation of hydrogen gas at the electrode’s grain boundaries. These bubbles eventually crack the film as they escape. No such cracks are observed on the glassy carbon electrode, as should be expected due to the amorphous nature of glassy carbon. The white residue present particularly on the glassy carbon electrode is again proposed to be a breakdown product of the ionic liquid. This breakdown
product is very difficult to remove as mentioned above. Even prolonged soaking in methanol followed by air blow drying was unable to remove it.

3.11 *SEM characterization of electrodeposited film on a Pt working electrodes following potentiostatic deposition at 100° C*

Figures 18a-d below present electron micrographs of the platinum working electrode after CA performed in BMP-TFSI with NdCl₃. This electrode was polarized at -3.5 V for 3 hours with the temperature increased to 100° C. The increased temperature could encourage film formation by weakening the adsorption of BMP cations on the working electrode surface. With the extra thermal energy supplied, the cations would be forced off the surface, which would leave openings for metal deposition.

Notice in Figures 18a-d that there appear to be two separate films deposited on the surface of the electrode, one on top of the other. The lighter film covers almost the entire electrode surface, while only patches of the darker layer are visible underneath. Examining Figure 18d indicates that the darker layer is also a film on the electrode surface and not the bare

(a)  
(b)
Figure 18: SEM characterization of electrodeposited morphology on the platinum working electrode. Potentiostatic deposition performed for 3 hours at -3.5V at 100 C. (a) 600x (b) 4,000x (c) 6,000x (d) 10,000x.

Electrode surface itself. Even in the darker patches on either side of the scratch, a rough surface is seen which is not the well polished electrode surface. Also in Figure 18d, notice the many tightly clustered spheres that line the deeper scratch. These spheres are consistent with metallic nucleation which is drawn to scratches on the electrode surface. Scratches on an electrode surface are well known to provide the highest energy density, and thus nucleation occurs first along the scratches.

4 Conclusions

Based on the electrochemical experiments presented in this work, the following conclusions have been made. Water and ethanol both drastically reduce the electrochemical window of BMP-TFSI from approximately 6 volts to 2 volts. The diffusion coefficients of water and ethanol were evaluated to be 7.6x10^{-7} cm^2/sec and 1.8x10^{-9} cm^2/sec respectively. The
reduction of ethanol on platinum in BMP-TFSI exhibited sluggish kinetics and the rate constant was calculated to be $4.3 \times 10^{-4}$ cm/sec. Based on CA and optical microscopy, Nd deposition on platinum from BMP-TFSI begins between -2.2 V and -2.4 V vs the Ag/AgCl reference. Larger over-potentials lead to thicker surface coverage but also to gaseous product generation on the electrode surface. LSV experiments indicate no single electron transfer step from Nd$^{3+}$ to Nd$^{2+}$ is evident in these experiments. A single cathodic peak is evident on Pt, Mo, and GC working electrodes beginning at approximately -2.75 V which is consistent with the required overpotential for Nd deposition from trivalent neodymium. SEM characterization indicated the formation of a two layered film on the electrode surface. The layer closest to the electrode surface was observed to have micro-porosities present which indicate the generation of a gaseous product. On top of this porous layer, a second layer was observed attributed to deposition of reaction product from the breakdown of the ionic liquid.
TASK A1.2 Electrodeposition of Lanthanum in the Room Temperature Ionic Liquid 1-Ethyl-3-methylimidazolium dicyanamide and the Effects of Water and Ethanol: A Rotating Disk Electrode Study

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Introduction

In nuclear engineering, the accumulation of lanthanides as the main fission products has detrimental effects on the efficiency of nuclear fuel because of strong neutron absorption properties. Therefore, the lanthanides need to be separated from actinides, a difficult task due to the similarity of chemical and electrochemical properties. One of the avenues for reprocessing nuclear fuels is electrometallurgy from ionic liquids. Ionic liquids can be classified according to temperature of application into (1) high temperature and (2) low temperature. High temperature ionic liquids are eutectic inorganic salts, such as LiCl-KCl. They are operational in the range 400 – 600 °C. Low temperature ionic liquids are made of an organic (cation) and inorganic (anion) components. They are fully ionized, stable, conductive and liquid in a much lower temperature range than ionic liquids based on inorganic salts, typically 25 - 100 °C. For that reason, they are often termed as room temperature ionic liquids (RTILs).

Due to lanthanide’s large electronegative deposition potential (~ -2.4 V vs. SHE) traditional aqueous electrodeposition processes cannot be used as hydrogen evolution from water occurs prior to any lanthanide metal deposition. RTIL’s provide a unique solution to this problem as these salts are liquid at room temperature and provide a wide electrochemical window (up to 5 V) for deposition of electronegative metals without the detrimental effects from hydrogen ion reduction, as present in aqueous systems.

The goal of this study was to examine the electrochemistry and deposition morphology of lanthanum metal in the RTILs 1-ethyl-3- methylimidazolium dicyanamide (EMIM-DCA) and 1-butyl-3-methylimidazolium dicyanamide (BMIM-DCA) ionic liquids. These particular RTILs are stable in the cathodic direction up to -2.4V vs. Ag/AgCl, providing the adequate stability to observe the electrodeposition of lanthanum metal.

Reduction mechanisms were characterized on the basics of cyclic voltammetry technique. For the determination of kinetic parameters, such as diffusion rate constant and reaction rate constant the rotating disk technique was employed. The effects of water and ethanol concentration were studied in details. The role of water was important to determine in order to evaluate its effect during its eventual absorption from open atmosphere. Ethanol gained in importance because of the solubility of rare earth salts in alcohols, as the only viable route toward solubilization of rare earths in ionic liquids. The diffusion coefficient of water in EMIM-DCA was calculated to be 2.6x10^{-7} \text{ cm}^2/\text{sec}. The reduction of water on platinum in EMIM-DCA
exhibited sluggish kinetics and the rate constant was calculated to be $2.15 \times 10^{-5}$ cm/sec. Both water and ethanol additions slightly reduced the stability window of the RTIL.

Morphology of lanthanum electrodeposits, observed around -2.0V, was characterized by using scanning electron microscope (SEM). Thin dense films were generally produced. However, the organic components of ionic liquids were also intermixed with metallic deposit, which were removed by washing with alcohol.

**Experimental:**

Electrolyte: EMIM-DCA (1-Ethyl-3-methylimidazolium dicyanamide) was procured from Merck, (not in this business any longer). The ionic liquid was dried under vacuum for 48 hours before use to remove any residual moisture. LaCl$_3$ was used as received from Arcos Organics. Reagent grade ethanol was used to dissolve LaCl$_3$ for addition to EMIM-DCA. All solution preparation was carried out in the glove box under argon atmosphere.

Electrochemical Cell: A three electrode electrochemical cell was used consisting of a Pt90-Ir10 working electrode, carbon counter electrode, and Ag/AgCl reference electrode. The working electrode seen in Figure 1a was encased in a ceramic sleeve and secured in place with epoxy with a working electrode area of 0.0415 cm$^2$. The electrode was polished using metallographic papers followed by 1µm alumina polishing compound.
Figure 1: Experimental setup used in these experiments (a) Pt90-Ir10 WE (b) electrochemical setup

Electrochemical Setup: Lanthanum electrochemistry was studied using the rotating disk technique inside and outside a glove box. The rotator used was specially designed to work in and outside the glove box. It was transferred into the glove box in dismantled form through a small transfer chamber and assembled in the glove box. The rotator consists of: a vertical optical mount bar with a moving stage, a glued PVC tube for the accommodation of electrode cell and clamping of a counter electrode through a hole on the side of the tube, Pittman DC Motor, and Dremel shaft for accommodating the working electrode. The speed of rotation was controlled by EZCommander by AllMotion. A picture of the complete electrochemical setup can be found in Figure 1b.

Results and Discussion

Baseline linear sweep voltammetry (LSV) scans of EMIM-DCA containing lanthanum chloride are shown below in Figures 2a-b.
Figure 2: EMIM-DCA on Pt90-Ir10 with LaCl$_3$ present. Effect of RPM and temperature on the electrodeposition of La (a); Room Temperature (b) 80 ºC.

The voltammograms in Figure 2 show EMIM-DCA with lanthanum chloride at multiple temperatures and RPMs. The IL was colored yellow but was still clear and no particulates were seen. These scans show limiting currents around -2.2V. Bubbles were formed on the working electrode as the potential was scanned cathodically around -2 V vs Ag/AgCl. Lanthanum films were deposited during the LSV scans. Figure 3 provides a Levich plot of EMIM-DCA with lanthanum chloride between 200 and 2000 RPM. An intercept is seen in the Levich plot which consistent with a reaction with a kinetic controlling parameter.

When temperature increases the viscosity of EMIM-DCA decreases, limiting currents and film deposition start at less cathodic potentials. The viscous effect is definitely shown when comparing Figure 2a to 6a. The current also increases with temperature, from the increase of fluidity and conductance of EMIM-DCA. Figures 5b and 6 were used to determine limiting currents for Levich and Koutecky-Levich plots. Figure 3 provides a Levich plot of EMIM-DCA with lanthanum chloride between 100 and 2000 RPM at various temperatures. An intercept is seen in the Levich plot which consistent with a reaction that has a kinetic controlling parameter. The diffusion coefficients of lanthanum in EMIM-DCA were calculated via the Levich equation. Table 1 shows the data used to create the Levich plots and the diffusion coefficients and rate constants of lanthanum at various temperatures.
Table 1: Values obtained from LSVs and rotating disk studies of EMIM-DCA with LaCl₃ under various temperatures.

<table>
<thead>
<tr>
<th>Celsius</th>
<th>Current Density mA/cm²</th>
<th>RPM</th>
<th>Diffusion Coefficients</th>
<th>Rate Constants</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>cm²/sec</td>
<td>cm/sec</td>
<td>200</td>
<td>400</td>
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<tr>
<td>20</td>
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<tr>
<td>80</td>
<td>130.4</td>
<td>140.56</td>
<td>175.11</td>
<td>190.5</td>
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</table>

Ethanol is used to dissolve the lanthanum chloride for addition to the ionic liquid, the next work done with ionic liquid was to study the stability of ethanol in the ionic liquid with and without any metal present. CV was performed in the cathodic region to study the reduction behavior of ethanol in EMIM-DCA and the results are shown in Figure 5a. Figure 5b shows the CV performed on the addition of ethanol to EMIM-DCA with lanthanum chloride. Figures 5a-b show no distinct peaks or limiting currents. Bubbles were formed on the working electrode as the potential was scanned cathodically around -2 V vs Ag/AgCl. This shows that ethanol has no drastic change seen to pure EMIM-DCA ionic liquid.
In order to further study the ethanol and EMIM-DCA reduction reactions, CVs were performed using 5mL of ethanol as the electrolyte with incremental additions of ionic liquid to supply conductivity. CVs were performed in the range where ethanol is active, to study the reduction behavior of EMIM-DCA in EtOH. Figures 6a shows a CV performed on the addition
of EMIM-DCA to ethanol without LaCl3. The effect of 400 RPM rotation speed on the CV of EtOH + EMIM-DCA is shown in Figure 6b. As the concentration of EMIM-DCA rises, an increase is seen in the cathodic currents combined with an anodic shift in the breakdown potential. Two possible reactions are proposed for the adsorbed ethanol radical. The radical can either be reduced to form ethane or methane, or it could react with EMIM cation. The scans below also show a distinct effect of rotation. A consistent increase in currents is seen with increasing IL concentration when no lanthanum is present.

Figures 7a-b show CVs performed on the addition of EMIM-DCA to ethanol with LaCl3, where Figure 7a shows the CV without rotation and Figure 7b shows the CV at 400 RPM. When a small amount of EMIM-DCA is added to ethanol (50 μL), lanthanum film production is observed at a scan range (-2V to 2V). This is interesting since the lanthanum shouldn’t deposit until all ethanol is consumed. Figure 7b shows two distinct peaks as a result of the lanthanum morphology. The scans without rotation have larger cathodic currents because of the rough lanthanum deposit. Where as under stirring condition, lanthanum film is smooth and has smaller surface area.

**Figure 6:** Effect of EMIM-DCA addition on the LSV of EtOH (no LaCl3). (a) CV performed at 20 mV/s at 0 RPM; (b) CV performed at 20 mV/s at 400 RPM.
Figure 7: Effect of EMIM-DCA addition on the LSV of EtOH with LaCl₃. (a) CV performed at 20 mV/s at 0 RPM; (b) CV performed at 20 mV/s at 400 RPM.

Figures 8a-b show CVs performed on the addition of EMIM-DCA to EtOH with LaCl₃ at 10mV/s and 100 mV/s. The scans show that at slower scan rates, peaks from EtOH and LaCl₃ are more distinct.

Figure 8: Effect of EMIM-DCA addition on the LSV of EtOH with LaCl₃. (a) CV performed at 10 mV/s at 0 RPM; (b) CV performed at 100 mV/s at 0 RPM.
Similar experiments to the addition of ethanol to EMIM-DCA were carried out with water. Water is known to be absorbed from the atmosphere by previous ionic liquids, interfering with processes and properties of the ionic liquid. Even the structure of an ionic liquid may be altered by the presence of water from decreasing the viscosity and the density. Therefore, the stability of water in the ionic liquid with and without lanthanum metal present should be determined. Figures 9a-d show CVs performed on the addition of H_2O to EMIM-DCA with and without LaCl_3. CV of water addition to EMIM-DCA at 0 RPM is shown in Figure 9a, and CV of water addition to EMIM-DCA with LaCl_3 at 0 RPM is shown in Figure 9b. CV of water addition to EMIM-DCA at 400 RPM is shown in Figure 9c, and the CV of water addition to EMIM-DCA with LaCl_3 at 400 RPM shown in Figure 9d.

CVs were performed in the range where water is active, to study the reduction behavior of EMIM-DCA with moisture. Figure 9a shows no distinct peaks or limiting currents. The effect of moisture on the ionic liquid EMIM-DCA therefore is small. However, when water is added to EMIM-DCA with LaCl_3 a unique reaction is demonstrated. Figure 9b shows this reaction by a distinct peak at around -1.3 V after about 200 uL of water is added. Upon looking at the microstructure, a film is made from the reaction between water and LaCl_3. Note that this reaction is unique because the current remains the same (~10 mA/cm^2) but the potential at which the reaction occurs shifts with addition of water. Figures 9c,d show that the same reactions occur with the electrode under rotation, therefore, the reaction is not intercepted by bubbling.

To further evaluate the reaction between water and EMIM-DCA with LaCl_3, CVs of water addition were performed on EMIM-DCA with twice the initial amount of LaCl_3. Figure 10a,b shows the same reaction, although the current density is doubled (~20 mA/cm^2) and the reaction shifts cathodically to about -1.55 V, confirming that the reaction is between water and lanthanum. A film is created about this potential and electrolyte was further studied by the chronoamperometry.
Figure 9: Effect of $\text{H}_2\text{O}$ addition on the CV of EMIM-DCA with and without LaCl$_3$. (a) CV without LaCl$_3$ performed at 50 mV/s at 0 RPM. (b) CV with LaCl$_3$ performed at 50 mV/s at 0 RPM. (c) CV without LaCl$_3$ performed at 50 mV/s at 400 RPM. (d) CV with LaCl$_3$ performed at 50 mV/s at 400 RPM.
Figure 10: Effect of H₂O addition on the CV of EMIM-DCA with double the concentration of LaCl₃. 
(a) CV with LaCl₃ performed at 50 mV/s at 0 RPM. (b) CV with LaCl₃ performed at 50 mV/s at 400 RPM

The effect of RPM on EMIM-DCA-LaCl₃ with water is shown in Figure 11. Figure 12 provides a Levich plot of EMIM-DCA-LaCl₃ and 500 uL H₂O between 200 and 1500 RPM. Figure 13 provides a Koutecky Levich Plot of EMIM-DCA-LaCl₃ and 500 uL H₂O. An intercept is seen in both the Levich and Koutecky Levich plot which is consistent with a reaction that has reaction controlling parameter similar to the system without water.

The electroactive windows and working potential for morphology were determined for each electrolyte by the following cyclic voltammograms. Different electrodes such as platinum, copper and glassy carbon were used, to analyze the morphology of lanthanum on the different surfaces. Before analyzing the morphology the reduction limit at each electrode needed to be determined. CVs on BMIM-DCA without and with La were measured on three different electrodes (Figures 14 a, b and Figures 15 a,b).
**Figure 11:** LSV of EMIM-DCA-LaCl₃ with 500 µL H₂O. Effect of RPM on the electrodeposition of water.

**Figure 12:** Levich plot of EMIM-DCA-LaCl₃ with 500 µL H₂O.

**Figure 13:** Koutecky-Levich plot of EMIM-DCA-LaCl₃ with 500 µL H₂O.
For BMIM-DCA and EMIM-DCA, the reduction limit appeared at about -1.8 V on platinum. However, on glassy carbon, the reduction potentials is about -2.4 V vs. Ag/AgCl. The reductive limit also seemed to vary slightly towards more positive potentials with an increasing amount of RTIL. The major difference in platinum vs glassy carbon, is their ability to reduce...
hydrogen. Platinum is a good reducer of hydrogen; therefore bubble formation and cation reduction occurs much earlier on platinum. Glassy carbon on the other hand has an amorphous surface preventing the formation of cation on the electrode surface.

For the optical characterization of electrodeposited films on a Pt working electrode, chronoamperometry was used to create the films at various potentials (Figure 16). The choronamperograms did not show any peaks, however a slight decrease of the current sometimes occurred due to a non-constant bubbling. No peak formation occurred since organic and lanthanum deposition occurred at the same time, therefore Scharifker-Hills model could not be used to determine if the nucleation was instantaneous or progressive (Figure 17).

Optical microscopy was first used to evaluate the effect of applied potential on the surface morphology of lanthanum formed on platinum electrode, shown by Figures (18 a-f). The electrode was cleaned by three methanol washes to remove any organics or ionic liquid from the surface and dried with air before any microscopy. If needed the surface was also cleaned via methanol chloride to remove residual methanol from the surface of the electrode.

Figures 18a-f present optical micrographs at 40x for chronoamperometry performed at room temperature with EMIM-DCA with and without LaCl₃. At -1.7 V vs. Ag/AgCl, the current of the CA (Figure 16) did not decrease but stayed constant zero during the deposition time. This
means that no deposition occurs at -1.7 V which was confirmed by the absence of visible deposit on the electrode (Figure 18a). Lanthanide deposition should not occur until a potential of -2.4 V is applied at room temperature. In Figures 17b and 17c a distinct film is seen on the electrode surface with polarization potentials of -1.8 and -2.0 V respectively. These potentials correspond well with the onset of lanthanum deposition beginning to occur at -2.0 V.

![Figures 18a-f: Optical microscopy of film developed by chronoamperometry performed at room temperature with EMIM-DCA for 3 sec at various potentials. Clean via methanol wash procedure.](image)

At the potential of -2.0 V the formation of bubbles starts to occur intercepting film formation, as seen in Figure 18c around the edge of the electrode. The bubbles are explained by the presence of hydrogen from the open atmosphere or the reduction products of EMIM, and BMIM. As discussed above, the cation is proposed to follow a two-step reduction process to carbene via removal of hydrogen, and hydrogen gas is also produced from water. When the potential is increased more than -2.0 V in applied over potential more bubbling is present on the electrode surface. Polarization at -2.4 V in Figures 18e leads to further bubbling on the electrode surface, completely disrupting the lanthanum film. Figure 18f presents the electrode surface after polarization at -3 V for 3 seconds in pure EMIM-DCA with no lanthanum present. The bare surface evident in Figure 18f indicates that even up to -3 V, the deposits seen in Figure 18a-
should be attributed to the reduction of lanthanum. This demonstrates that the film is not deposited EMIM cation or an organic compound.

A high temperature setup was used to study the film morphology at higher temperature. Figure 19a-b below present electron micrographs of the platinum working electrode after CA performed in BMIM-DCA with LaCl₃. This electrode was polarized at -2.0 V for 2 hours with the temperature increased to 80° C. The increased temperature prevents BMIM cations from covering the surface of the working electrode allowing more places for lanthanum deposition. The higher temperatures should also increase the mass transfer and conductance of ionic liquid. The temperature also can reduced the amount of hydrogen absorb from the atmosphere by the ionic liquid as well as remove impurities already in the ionic liquid.

Figure 19a-b: SEM images presenting surface morphology of deposit on the platinum working electrode. CA performed for 2 hours at -2.0V at 80 C. Magnification (a) 500x, (b) 10,000x.

Two films are deposited on the surface of the platinum electrode, as shown in Figures 19a-b. Both films cover the entire electrode surface, however the darker film underneath and is only shown in small regions. Examining Figure 18b the dark film can be seen on and around the sides of the scratches located on the electrode. This indicates that the dark film is actually a film not the base metal of the electrode. Gaseous product formation during the reduction of lanthanum is shown by tiny pits everywhere on the film. This gaseous product could be the
electrogeneration of hydrogen gas from moisture adsorbed into ionic liquid from the open atmosphere, ethanol leftover from solvation step reducing to methane, or the reduction of BMIM cation to carbene. The white residue present particularly on the platinum electrode is ionic liquid that did not come off after the methanol rinse.

Similar to the high temperature experiments performed on platinum, SEM characterization at high temperatures was performed on the glassy carbon. Figure 20a-b below present electron micrographs of the glassy carbon working electrode after CA performed in BMIM-DCA with LaCl₃. This electrode was polarized at -2.0 V for 1 hour with the temperature increased to 80° C. In Figures 20a-b, notice the many tightly clustered spheres especially those that line the scratch. These spheres are consistent with metallic nucleation which is drawn to scratches on the electrode surface. Scratches on an electrode surface provide the highest energy density, thus nucleation starts and occurs more often along the scratches.

![Figure 20a-b](image)

**Figure 20a-b:** SEM images presenting surface morphology of deposit on the glassy carbon working electrode. CA performed for 1 hours at -2.0V at 80 C. Magnification (a) 500x, (b) 1,000x, (c) 2,000x.

The propose of Figure 21 was to show that we attempted x-ray diffraction to characterize the film. The XRD (Seimens 5000) used was effective enough to confirm that the film is lanthanum not an organic compound. Table 2 (inset in Figure 21) shows 2θ for HCP lanthanum. Note that the peaks’ 2θ-s in the Figure 20 are very close to the values demonstrated by the red lines.
Figure 21: XRD characterizing the surface morphology of deposit as La on the Mo working electrode. CA performed for 1-hour at -2.2V at 80°C.

Table 2: Lanthanum 2θ

<table>
<thead>
<tr>
<th>2θ (Degrees)</th>
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<tr>
<td>14.57</td>
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<tr>
<td>27.32</td>
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<td>31.09</td>
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<td>35.3</td>
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Conclusions

- Cyclic voltammetry demonstrated the electrochemical stability of DCA ILs in open atmosphere.
- Ethanol was demonstrated to be an effective solvent for LaCl₃ and created no adverse electrochemical effects when added to DCA ionic liquids.
- EMIM and BMIM electrochemically reduced to form carbene.
- The addition of water to EMIM-DCA-LaCl₃ showed an irreversible reaction between water and lanthanum.
- The rotating disk studies revealed that the reduction of La in DCA ILs was not controlled purely by mass transfer.
- SEM and Optical analysis showed film formation only with the presence of lanthanum.
- XRD was conclusive that the film contains metallic lanthanum.
REFERENCES


