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Enhanced Molten Salt Purification by Electrochemical Methods: Feasibility Experiments with Flibe

Alan K Wertsching
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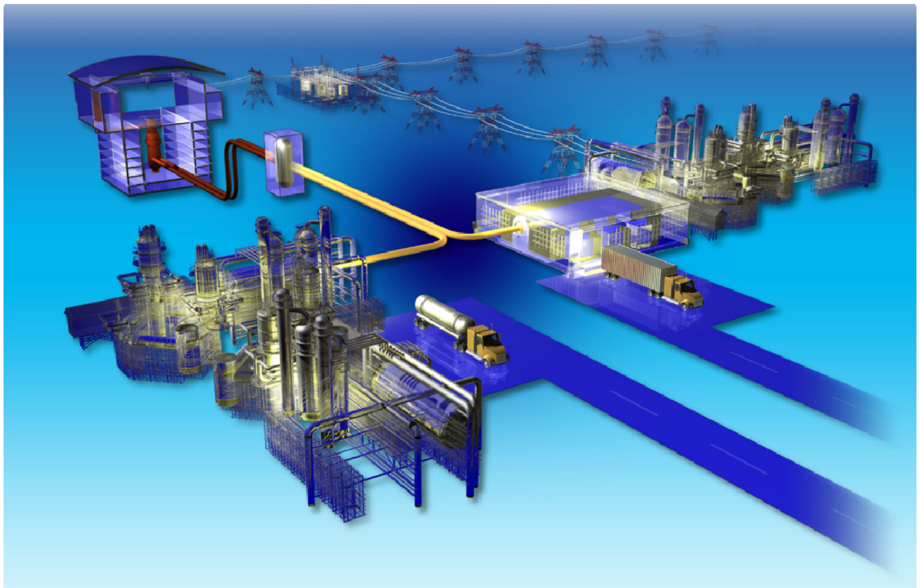

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Idaho National Laboratory
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Idaho Falls, Idaho 83415

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Approved by:

for Pattrick Calderoni
Pattrick Calderoni
Author

9/29/2010
Date

Phil Sharpe
Liquid Salt Lead

9/29/10
Date

Gary D Roberts
Gary Roberts
VHTR TDO Quality Assurance

9/29/2010
Date

Diane V Croson
Diane Croson
VHTR TDO Deputy Directory

9/29/10
Date

ABSTRACT

Molten salts are considered within the Very High Temperature Reactor program as heat transfer media because of their intrinsically favorable thermophysical properties at temperatures starting from 300°C and extending up to 1200°C. In this context, two main applications of molten salt are considered, both involving fluoride-based materials as (1) primary coolants for a heterogeneous fuel reactor core and (2) secondary heat transport medium to a helium power cycle for electricity generation or other processing plants, such as hydrogen production. The reference design concept considered in this report is the Advanced High Temperature Reactor, which is a large, passively safe reactor that uses solid graphite-matrix coated-particle fuel (similar to that used in gas-cooled reactors) and a molten salt primary and secondary coolant with peak temperatures between 700 and 1000°C, depending upon the application. However, the considerations included in this report apply to any high temperature system employing fluoride salts as heat transfer fluid, including intermediate heat exchangers for gas-cooled reactor concepts and homogenous molten salt concepts, and extending to fast reactors, accelerator-driven systems, and fusion energy systems.

The most important initial requirement for heat transfer test of molten salt systems is the establishment of reference coolant materials to use in the experiments. An earlier report produced within the same project (INL/EXT-10-18297) highlighted how thermophysical properties of the materials that directly impact the heat transfer behavior are strongly correlated to the composition and impurities concentration of the melt. It is therefore essential to establish laboratory techniques that can measure the melt composition and to develop purification methods that would allow the production of large quantities of coolant with the desired purity. A companion report titled *Experimental Test Plan for the Characterization of Molten Salt Thermochemical Properties in Heat Transport Systems* describes the options available to reach such objectives and contains extended references to published work. The report highlights how electrochemical methods are the most promising techniques for the development of instrumentation aimed at the measurement of melts composition and for enhanced purification systems. The purpose of this work is to summarize preliminary experimental activities performed at the Idaho National Laboratory Safety and Tritium Applied Research facility in support of the development of electrochemistry based instrumentation and purification systems. The experiments have been focused on the LiF-BeF_2 eutectic (67 and 33 mol%, respectively), also known as flibe.

CONTENTS

FIGURES

TABLES

Enhanced Molten Salt Purification by Electrochemical Methods: Feasibility Experiments with Flibe

1. SYSTEM DESCRIPTION

In the electrochemical experiments described in this report, the molten salt is contained within glassy carbon coated graphite, alumina coated metallic, or a nickel crucible. The experiments are housed in a dry inert gas glove box that is purged with Argon as shown in Figure1. The melt is initially prepared and tested using an induction heating system. The metallic crucibles (nickel) are initially chosen to better couple with the magnetic field. Longer electrochemical experiments may use standard resistance furnaces, for which a ceramic crucible may also be used. Electrochemical experiments will use metal or alloy wire for the working electrode (WE) and glassy carbon or platinum for the counter electrode (CE). The reference electrode (RE) will be either platinum wire for a pseudo-RE, gold alloy as a dynamic RE, or Ni/Ni(II) in pyrolytic boron nitride as a traditional RE. This system will be scalable for larger, more complex experiments.

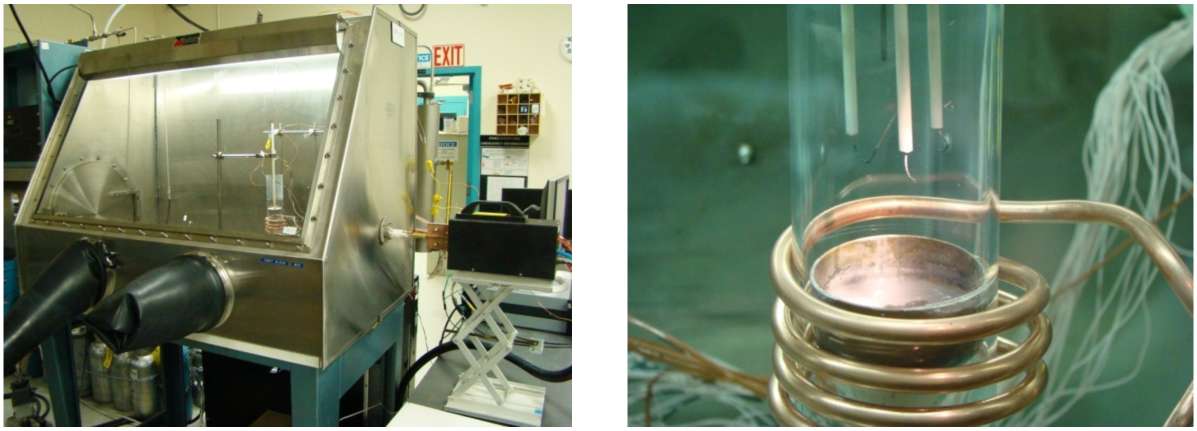


Figure 1. Glove box with induction heating system (left), molten flibe cell (right).

2. INSTRUMENTS USED IN ELECTROCHEMISTRY TESTS

Analysis of salt composition is based on electrochemical methods. An AMEL 2053 potentiostat-galvanostat with a National Instruments computer interface card (Card PCI-6259 with shielded SHC68-68-EPM cable) measures currents and potentials from a range of electrochemical experiments as shown in Figure 2. The waveforms for these experiments are generated and data are recorded from a Labview interface that was specifically designed at Idaho National Laboratory (INL) for the molten salt tests described herein. The Labview graphical user interface (GUI) allows users to design, test, and then execute simple to complex electrochemical experiments such as cyclic voltammetry, anodic stripping voltammetry, and bulk electrolysis. Utilizing the GUI’s manual mode will allow plating of dynamic reference electrodes in order to test applicability within fluoride-based molten salts. The current computer/PCI card configuration will allow scan rates from 1 to 80,000 mV/sec and measure four data points per millivolt step. Validating functions of the AMEL involves the use of the calibration side of a Gamry Universal Dummy Cell shown in Figure 2.

Figure 2. AMEL potentiostat with Labview interface (left) and dummy cell (right).

3. VALIDATING EXPERIMENTS WITH REFERENCE SOLUTION

User training and validation tests for the instrument and custom developed control interface involve the use of a simple aqueous solution of 1.0M potassium nitrate with 0.010M potassium ferricyanide (see Figure 3). The ferricyanide provides a clear, reversible, single electron oxidation/reduction for cyclic voltammetry (CV) experiments. Multiple CV scans, as shown in Figure 3, can be used to determine the concentration and diffusion coefficient of an analyte via the Randles-Sevick equation

$$I_p = 1.67 \times 10^5\, n^{3/2}\, A D^{1/2} v^{1/2} C \qquad (1)$$

where i_p is the peak current (Amp), n is the electron charge involved in the redox reaction, C is the concentration, (moles/cm^3), A is the electrode area (cm^2), D is the diffusion coefficient (cm^2/s), and v is the scan rate (volts/s).

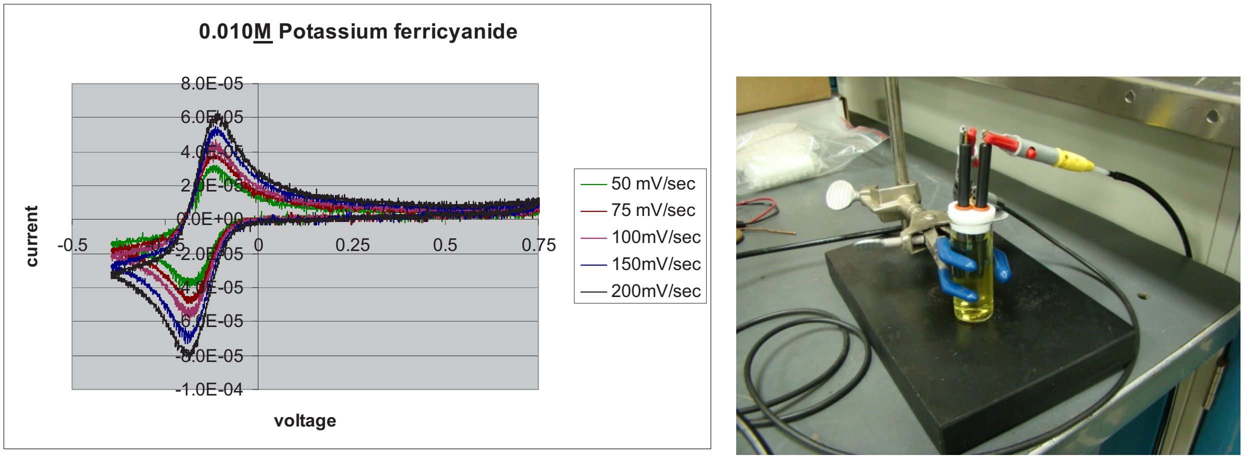


Figure 3. Multisweep scans (left) with gold WE, platinum quasi-RE and platinum CE (right).

Further experiments with the reference solution were done to validate the approach in flow conditions for their applicability to heat exchanger performance tests. Flow conditions were simulated with a commercial magnetic stirrer commonly used for solution mixing. The tests also provided initial information on the electromagnetic (EM) noise induced in the data acquisition system by magnetic field fluctuations from the stirring unit, which will be applied to minimize the effect of the induction heating system on instrument performance. Validating the tests with reference solution also provided valuable experience and solutions to problems that may arise with the actual molten salt, such as comparing the performance of various electrode materials (gold, nickel, stainless steel, glassy carbon) in various role combinations (WE, CE, RE).

An example of such scoping tests in Figure 4 shows a dramatic loss in current signal between the electrodes after the solution is stirred to simulate flow conditions. However, the disruption from the induced flow can be resolved by increasing the sweep rate of the potential (millivolts per second). Another example is how a fluctuating magnetic field can affect the measurements as shown in Figure 5. The test reported used glassy carbon as the working electrode because it was the most affected by the EM noise of the materials tested, which may ultimately limit its use with the induction heating system in the glove box.

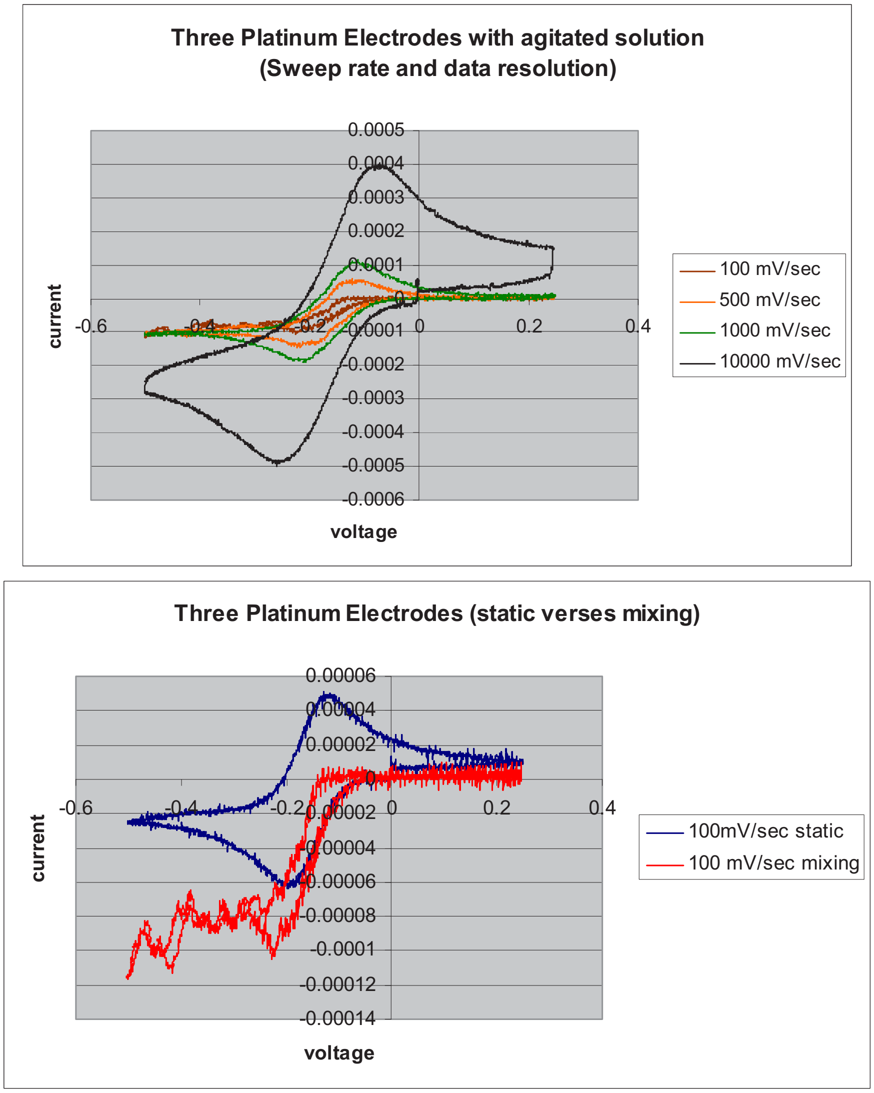


Figure 4. Differences in resolution from a static in blue and flowing solution loop in red (top) and increased resolution under flowing condition with faster sweep rates (bottom).

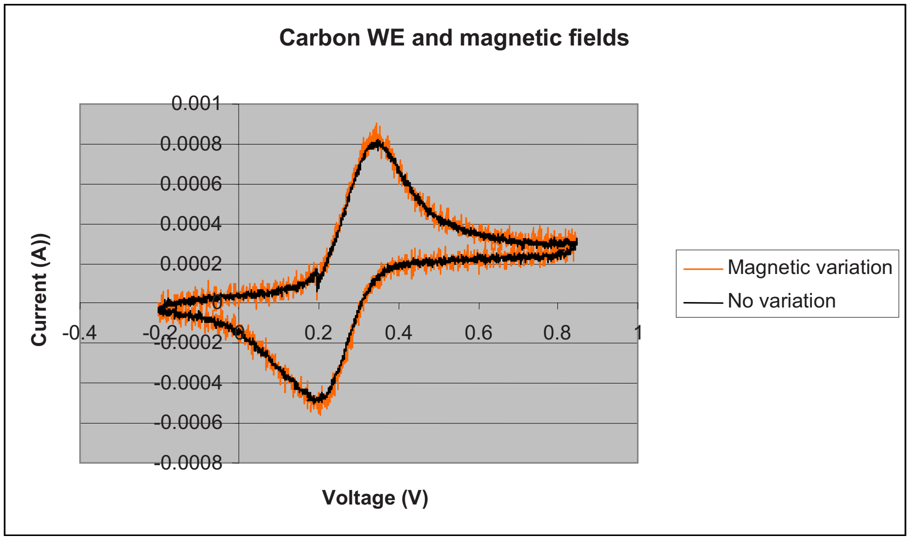
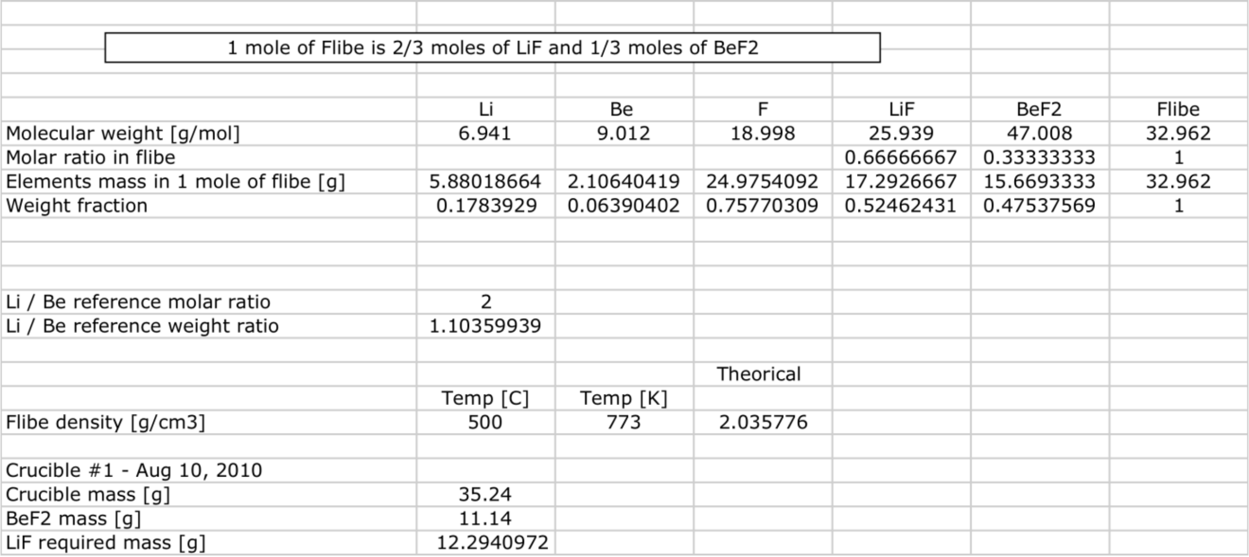


Figure 5. Noise experienced with magnetic variation and use of a glassy carbon WE.

4. ELECTROCHEMISTRY TESTS IN FLIBE

Flibe was prepared from single salt components beryllium di-fluoride (Alfa Aesar, Stock 35827, Lot L15J29, 100 g total of labeled 99.9% BeF_2 on metal basis) and lithium fluoride (Alfa Aesar, Stock 36359, Lot B09R001, 50 g total of labeled 99.85% LiF on metal basis). The materials were mixed according to eutectic composition (33 to 66% on molar basis, 1.1036 mass ratio) with the calculations shown in Table 1. The crucible used was a 48 mm diameter pure nickel crucible (visible in Figure 6) purchased from Metal Technology, Inc. The crucible was initially filled with 11.14 g of BeF_2 crystals. The necessary amount of LiF powder (12.30 g) was then added to reach the desired eutectic composition. The glove box condition during the mixing operation was 430.7 ppm moisture, higher than desirable for large scale preparation. Dry conditions in the glove box will need to be improved for further testing.

Table 1. Stochiometric preparation of flibe eutectic composition.



1 mole of Flibe is 2/3 moles of LiF and 1/3 moles of BeF2

	Li	Be	F	LiF	BeF2	Flibe
Molecular weight [g/mol]	6.941	9.012	18.998	25.939	47.008	32.962
Molar ratio in flibe				0.66666667	0.33333333	1
Elements mass in 1 mole of flibe [g]	5.88018664	2.10640419	24.9754092	17.2926667	15.6693333	32.962
Weight fraction	0.1783929	0.06390402	0.75770309	0.52462431	0.47537569	1
Li / Be reference molar ratio	2					
Li / Be reference weight ratio	1.10359939					
			Theorical			
	Temp [C]	Temp [K]				
Flibe density [g/cm3]	500	773	2.035776			
Crucible #1 - Aug 10, 2010						
Crucible mass [g]	35.24					
BeF2 mass [g]	11.14					
LiF required mass [g]	12.2940972					

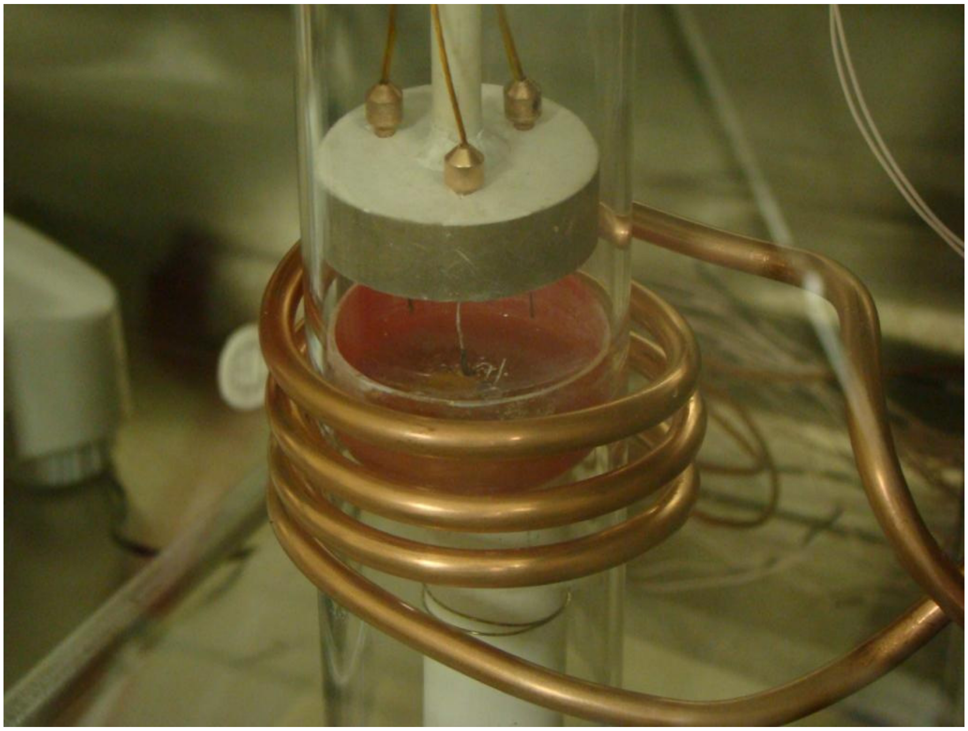


Figure 6. Induction heating of flibe (700°C) in progress.

The materials were melted using the induction heater assembly visible in Figure 1. A quartz tube was situated between the coils and the crucible to prevent accidental contact and possible spills while allowing unobstructed view. Two type K thermocouples were installed on the system: one, inserted within the mixed crystal and powder materials, measured the melting temperature of the eutectic; the other, embedded in the boron nitrate rod holding the crucible, measured the crucible temperature. The induction heater was set in stable condition for a desired current in the coils of 88.2A, resulting in 101kW of power coupled with the crucible at a natural frequency of 328 kHz. After about 10 minutes of operation, the salt started to melt (based on visual observation) for a measured temperature of 470°C compared to the theoretical eutectic melting point of 459.1°C. At the time of melting the glove box conditions had improved to 248 ppm moisture under Argon gas flow. Figure 6 shows the salt at 700°C in a subsequent melting operation prior to an electrochemical test run. The immersed thermocouple was retracted from the bath through the central alumina tube visible in the picture.

The three-electrode assembly used in the test, as shown in Figure 6, was constructed from a boron nitride disc. All electrodes were made of a 0.5 mm diameter platinum wire. The working and reference electrodes are simple, straight wires. The immersed portion of the wire is not accurately defined during the tests since their objective is a qualitative validation of the proposed method. The estimated immersed length is 5 mm. Accurate immersed surface assessment is necessary for quantitative evaluation of ionic species concentrations and will be implemented in the second test phase. Both wires were 29 mm long, including the section going through the ceramic holder. In any electrochemical setup, the counter electrode must have a substantially larger immersed surface area compared to the working electrode. This ensures that the electrode surface area does not impact the conclusions derived from ionic current saturation. To allow a larger immersed area, the counter electrode is bent horizontally and folded twice as shown in Figure 7. The difference in immersed length between CE and WE is at least 33 mm.

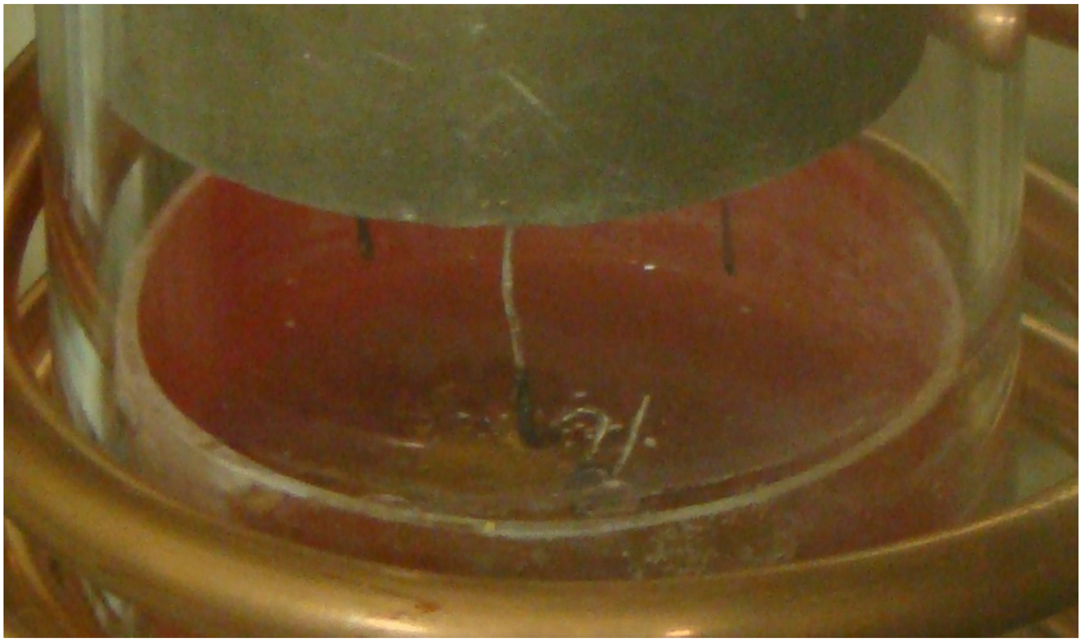


Figure 7. Platinum electrodes during operation; the counter electrode bent shape is visible.

During previous experiments on fluoride salts at the STAR facility, batches of similar constituent materials (BeF_2 and LiF) were analyzed to characterize as-received metallic impurities with inductively coupled plasma analysis. The representative sample of results, presented in Table 2, show that iron and nickel are the dominant impurities in the as-received material. It was decided to focus on nickel for this initial scoping test because of its anticipated reversible behavior at the platinum electrode surfaces because of the low solubility in the melt. The objective of the test was therefore to identify and analyze the nickel peak in the voltammetry (CV) scan obtained from the flibe prepared during the operation described above. This was done by repeating the CV scan with the same parameters and electrodes after the addition of 0.14 g of nickel fluoride (NiF_2) to the melt. The comparison of the two CV scans is shown in Figure 8. The cathodic and anodic peaks grew at -1.7 and -1.0 volts, respectively. The reduction of nickel is relatively close to the cathodic limit of flibe, and the overall chemical window of flibe with this electrochemical cell is 4 volts.

						Concentration of Various Elements (ppm)									
				Be	Li	Cr	Mn	Fe	Ni	Cu	Zn	Mo	Ag	Ba	Pb
Salt	Lot No.	Analyses													
BeF_2	A13K03	ICP-AES	1	155390	10	38	11	249	42	3		<16			
		ICP-AES	2	139720	3	16	6	201	28	2		<11			
BeF_2	A13K03	ICP-MS	1			9	6	403	11	4	10	1	4	9	2
		ICP-MS	2			9	6	322	10	4	8	1	4	6	2
BeF_2	L15J29	ICP-AES	1	140770	<4	8	6	180	116	<2		<13			
		ICP-AES	2	130350	2	4	6	162	47	<2		<9			
		ICP-AES	3	127160	3	3	6	174	36	2		<9			
BeF_2	L15J29	ICP-MS	1			10	7	317	11	4	9	1	<0.01	5	10
		ICP-MS	2			8	6	296	10	4	10	1	<0.01	6	3
		ICP-MS	3			10	7	265	11	4	9	1	<0.01	15	4
			2												
LiF	09809AO	ICP-AES	1	<3	14130	2	2	110	88	<1		<4			
LiF	09809AO	ICP-MS	1			5	4	141	11	3	15	2	<0.01	15	10
			2			5	4	104	5	3	13	2	<0.01	4	3
			3			2	2	43	4	2	6	1	<0.01	5	4

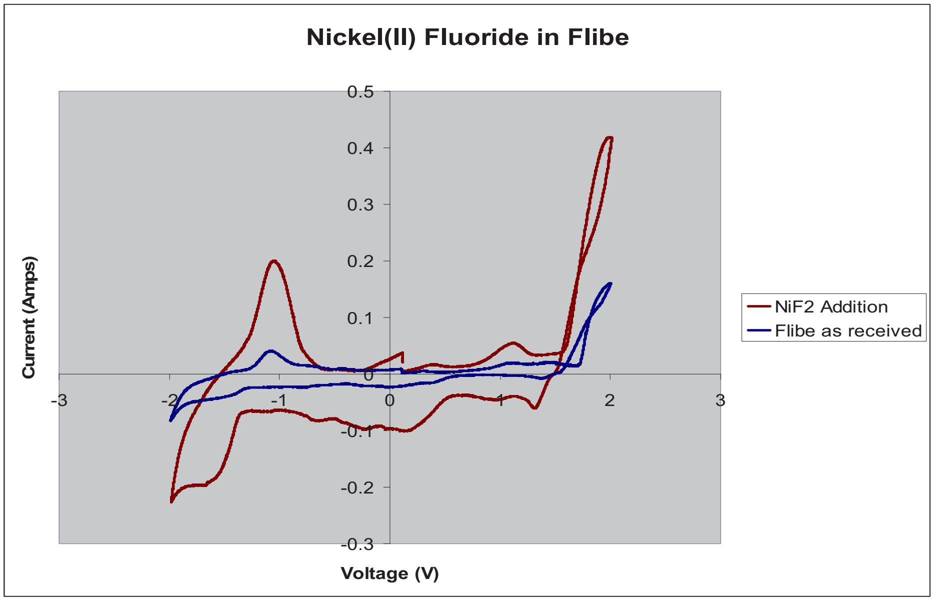


Figure 8. Flibe CV scans before and after nickel(II) fluoride addition.

A second qualitative test to validate the electrochemical method employed as a technique to characterize flibe composition was performed by adding a further 0.07 g of silver fluoride (AgF) to the same melt. Figure 9 shows the result of the last addition alone, comparing CV scans and flibe after the addition of NiF_2 with that after the addition of NiF_2 and AgF. Figure 10 compares the initial CV scan of the 'as-melted' eutectic with the final melt after both additions. The analysis of the scans in Figures 9 and 10 is not straightforward because of the addition of different materials to the same melt. Furthermore, the thermodynamic and chemical properties of silver fluoride in flibe melts are not as well know for nickel, so it is hard to anticipate the impact on the voltammetry scans.

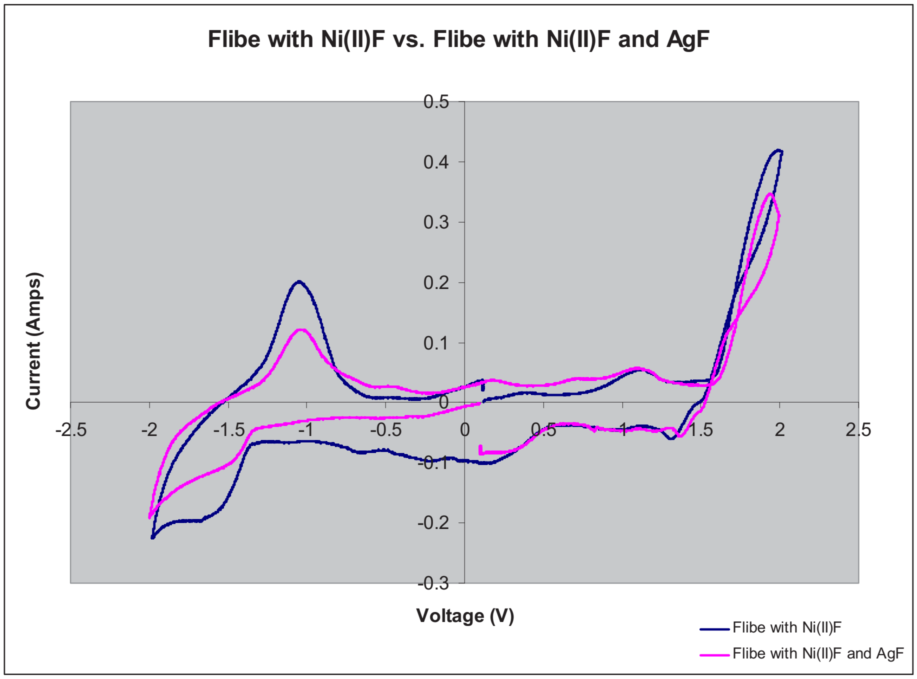


Figure 9. Flibe CV scans before and after the addition of AgF, additional NiF_2 already present.

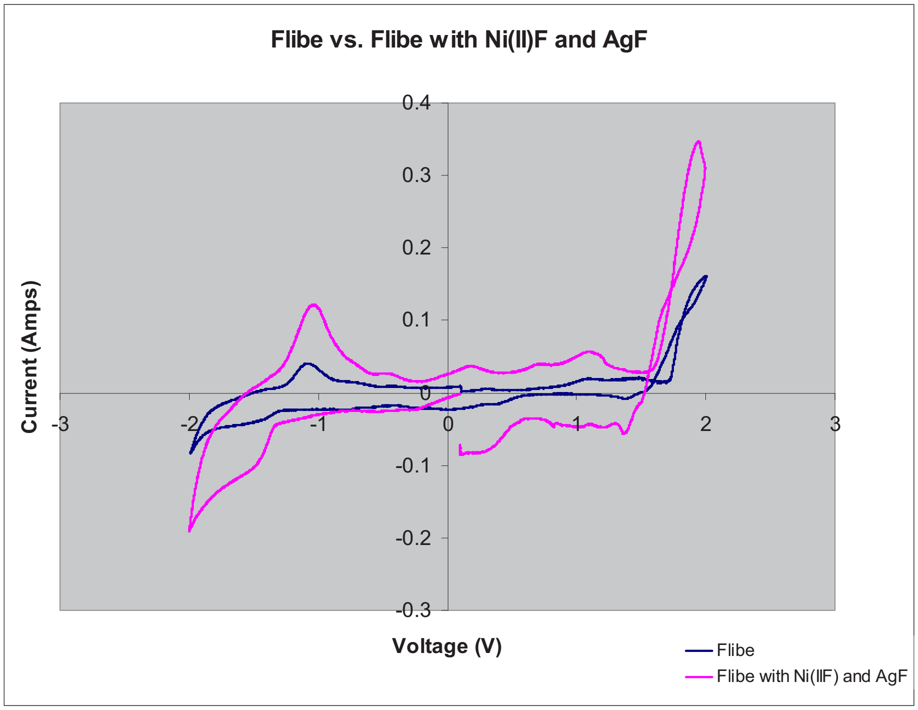


Figure 10. As received flibe CV scan compared to after Ni(II)F_2 and AgF addition.

5. CONCLUSION

Experimental activities started at the INL Safety and Tritium Applied Research facility in support of the development of electrochemistry based instrumentation and purification methods for molten salt hest transfer systems within the Very High Temperature Reactor program. The experiments have focused on the LiF-BeF_2 eutectic (67 and 33 mol%, respectively), also known as flibe. A batch of flibe has been prepared from the constituent materials using an innovative induction-heating setup with nickel crucibles housed inside an inert gas glove box. A diagnostic system based on a commercial potentiostat and a custom developed software interface for control and real-time data acquisition has been developed and its behavior validated with reference solutions and electrodes. The instrument has then been successfully applied to the generated high-temperature flibe melt. The capability of detecting peak for specific impurities in the melt and with intensity proportional to their concentration has been demonstrated with the addition of nickel fluoride.