



Fundamental properties and Removal of Impurities in Molten Salt systems

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Outline

- ❑ Introduction
- ❑ New method for Red potential measurements
- ❑ New method for exchange current density measurements
- ❑ New method for lanthanides separation
- ❑ On line corrosion measurement
- ❑ Summary of what we have done

Introduction

- ❑ Tritium:
- ❑ Noble Gas:
- ❑ Halogens (iodine)
- ❑ Alkaline Metals
- ❑ Rare Earths
- ❑ Noble Metals:
- ❑ Tellurium and Antimony
- ❑ Actinides
- ❑ Corrosion Products
- ❑ Oxygen and Moisture

REVIEW

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Impurities in Primary Coolant Salt of FHRs: Chemistry, Impact, and Removal Methods

Jinsuo Zhang

The fluoride salt-cooled high-temperature reactor (FHR) is one of the Gen. IV reactor concepts. Considering the complexity of salt chemistry, radiation risk, impurity-induced material corrosion, and impurity-induced solid precipitation, the salt chemistry should be well controlled. Therefore, molten salt cleanup systems are needed in operation. Based on the experience of molten salt reactors (MSRs) and available data, the present study identifies the types of impurities, their potential sources, and their impact in FHR primary coolants. Cleanup methods for each type of impurity and future research activities are also discussed.

1. Introduction

Using molten fluorides as both fuel and coolant is the motivation behind the molten salt breeder reactor (MSBR) and other similar designs. In these schematics, the fuel (typically in the form of trifluorides or tetrafluorides) is used as a fuel blanket or dissolved directly into the primary coolant. Thus, fission products and other decay daughter products will be generated directly in the molten salt and require online removal. The fluoride salt-cooled high-temperature reactor (FHR) is a similar reactor design, except the salt is used only as a coolant and the fuel is maintained in tristructural-isotropic fuel (TRISO) particle form. The FHR offers a convenient technological bridge between today's reactors (solid fuel, water cooled) and future molten salt reactors (liquid fuel, liquid salt cooled). Detail information on the FHR status, operation performance, and current designs can be found in a report.^[1]

Of the technological gaps that inhibit progress of the FHR designs, one of the major concerns is the removal of actinides, fission products (such as rare earth metals), and other impurities (corrosion products, oxide, moisture, etc.) from the primary coolant salt. These impurities can enter into the salt through different ways including leakage from the fuels, corrosion of the structural materials, vessel gasket leakage, maintenance access, leakage of heat exchanger (HX) tubes, etc.^[1] The leakage of the HX tubes leads to the primary salt being contaminated by the molten salt in

the second or intermediate loop. The intermediate coolant may be molten LiF–NaF–KF (FLiNaK) or KF–ZrF₄. The contamination by the intermediate coolant may lead to a higher vapor pressure and introduce elements that are neutron poisons in the primary loop.

Different from the molten salt-fueled molten salt reactor (MSR), leaking radioactive nuclides such as fission products must pass through the four-layer coating of the TRISO particle to enter into the primary salt. In addition, the coating (C-based materials) has high retention capabilities for some radioactive nuclides. Therefore, the


fission product impurity levels in the FHR are low and orders of magnitude less than in an MSR. However, some contaminating elements, for example, the rare earth elements (REs)^[2] and oxygen/moisture, pollute the coolant salt and harshly affect the neutronics, heat transfer, and material compatibility. Therefore, salt purification processes for an FHR must be developed to remove these impurities from the coolant salt and also monitor various impurity concentrations during normal reactor operation.^[3]

Based on the current available knowledge and operation experience on previous MSRs and other types of nuclear reactors, the paper identifies the major impurities that are related to either material compatibility, salt properties, or radioactive source terms, and the potential contamination sources of these impurities, their transport in the primary coolant loop, and available online cleanup methodologies for a particular group of impurity. The available data on the thermodynamic behaviors of the impurities in the primary salt are also discussed as well as the mechanisms of the online removal methods of electrochemical separation and liquid metal (Bi–Li) extraction.

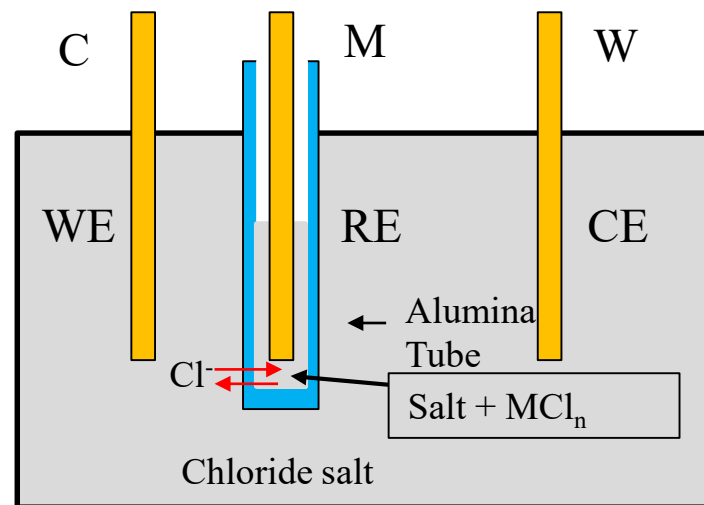
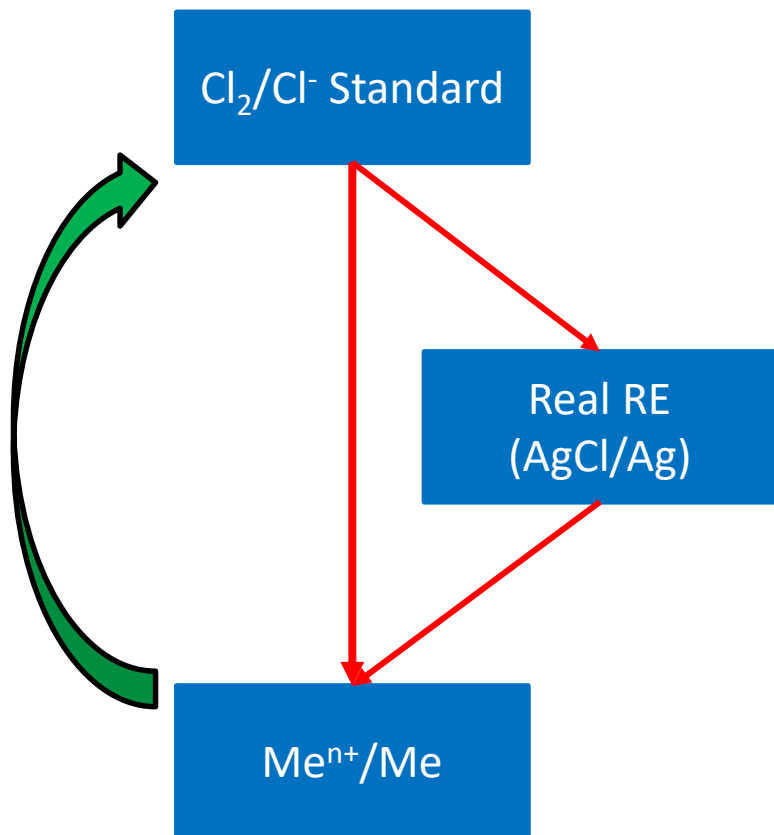
2. Impurities, Contamination Mechanisms, and Available Removal Methods

Similar to other types of advanced reactors, such as the sodium-cooled fast reactor (SFR),^[4] the impurities in the primary coolant LiF–BeF₂ of the FHR can be categorized into five groups: corrosion products from structural materials, fission products and actinides from leakage of the fuels, nuclear reaction products including transmutation products and element decay products, impurities from operation environments such as moisture and oxygen by ingress of air, and the impurities of the coolant itself such as hydrogen fluoride (HF). Although the impurity level (especially for fission products) in an FHR primary salt is much less than that in an MSR primary salt, the types and

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Redox potential measurement



Function of Alumina tube

- Isolation of the metal ion of interest to prevent it from being oxidized. E.g. Fe²⁺ and Cr²⁺
- Allowing Cl⁻ exchange between RE and bulk salt.
- If the metal ion has only one stable state (such as Ni²⁺), the alumina tube can be removed.

The Methodology of CP Data Analyze

Potential change across the interface, can be neglected when I is small

$$E_m = \left[E_{Cl_2}^0 + \frac{RT}{nF} \ln \left(\frac{a_{Cl_2}}{a_{Cl^-}} \right) \right]_{Me^{n+}/Me} + Ir + \delta(I)$$

When $I=0$

Solution resistance

$$E_m(I=0) = \left[E_{Cl_2}^0 + \frac{RT}{nF} \ln \left(\frac{a_{Cl_2}}{a_{Cl^-}} \right) \right]_{Me^{n+}/Me}$$

- $a_{Cl_2}=1$ pure substance
- $a_{Cl^-}=1$ in Chloride salt

$$E_m(I=0) = [E_{Cl_2}^0]_{Me^{n+}/Me}$$

Reverse the reference

$$E_m(I=0) = [E_{Cl_2/Cl^-}^0]_{Me^{n+}/Me} = - \left[E_{Me^{n+}/Me}^0 + \frac{RT}{nF} \ln(a_{Me^{n+}}) \right]_{Cl_2/Cl^-}$$

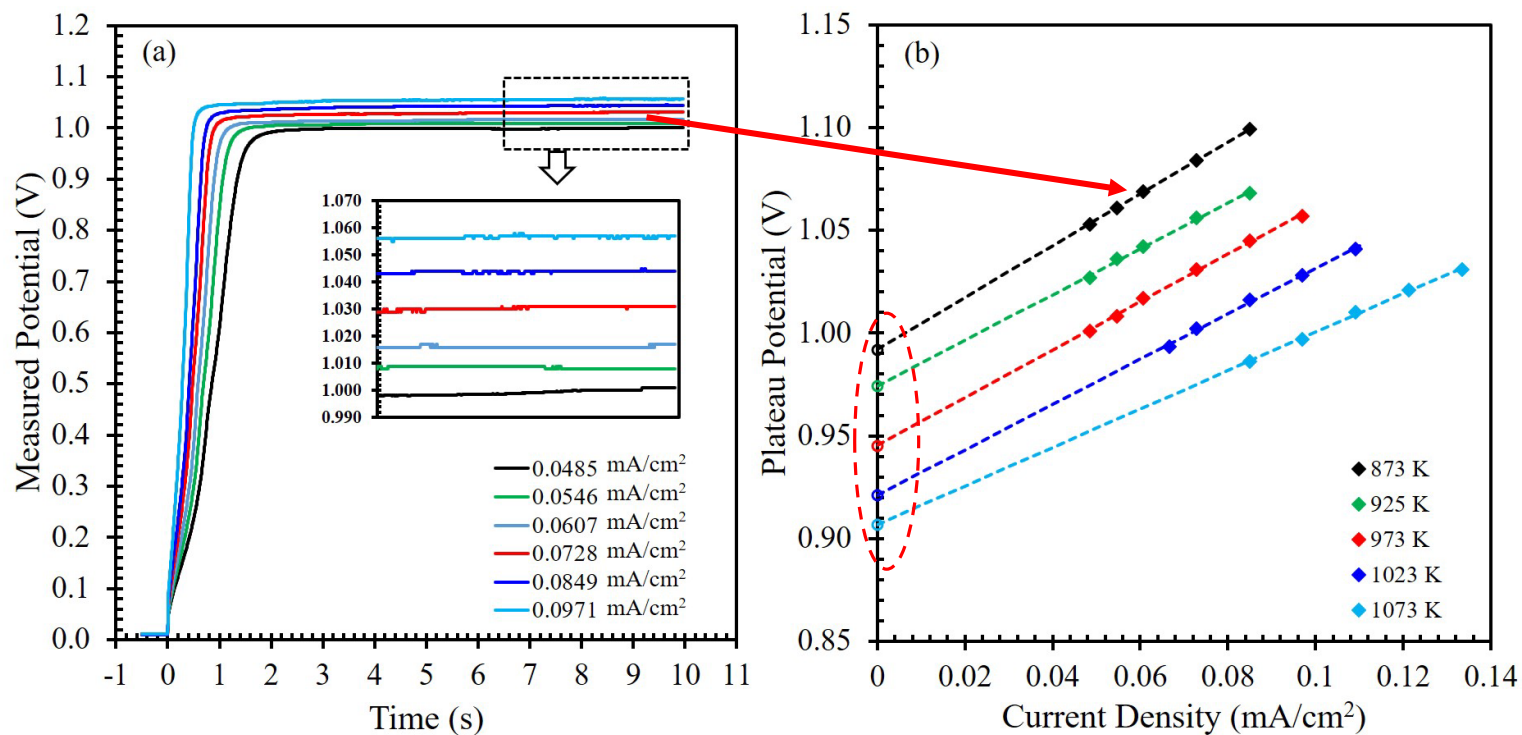
- Redox potential

$$E_{red} = [E_{Me^{n+}/Me}^0]_{Cl_2/Cl^-} + \frac{RT}{nF} \ln(\gamma_{Me^{n+}} x_{Me^{n+}}) = -E_m(I=0)$$

- Formation potential

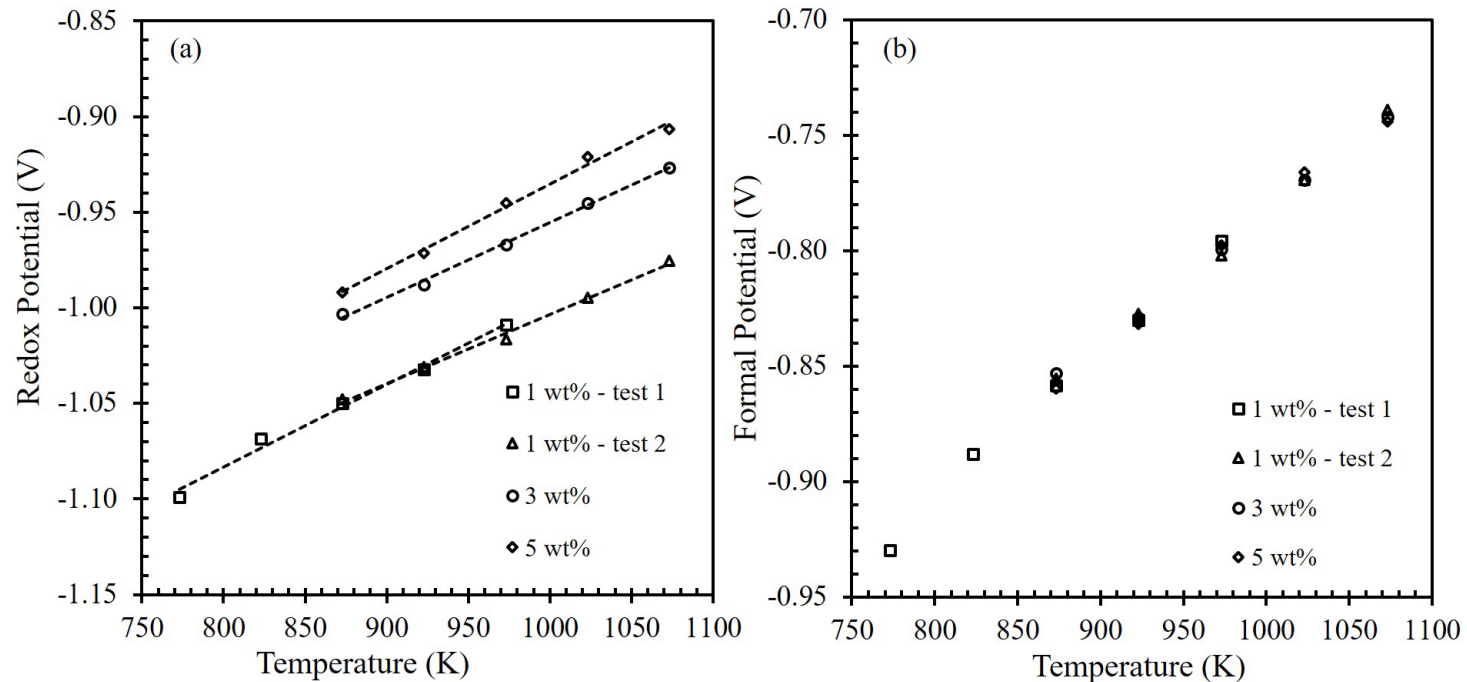
$$E_0^* = [E_{Me^{n+}/Me}^0]_{Cl_2/Cl^-} + \frac{RT}{nF} \ln(\gamma_{Me^{n+}})$$

Result example if NiCl_2 in MgCl_2 / KCl / NaCl



(a) Different current densities CP curve for 5 wt% NiCl_2 - MgCl_2 - KCl - NaCl solution at 873 K. (b) The plateau potential (zoomed-in (a)) with respect to current densities for 5 wt% NiCl_2 - MgCl_2 - KCl - NaCl at varies temperatures. WE: graphite CE & RE: nickel rod

Result example if NiCl_2 in MgCl_2 / KCl / NaCl



The summary results of NiCl_2 redox potential (a) and formal potential (b) of three different concentrations at 773 K to 1073 K. WE: graphite CE & RE: nickel rod.

- $E_0^* = 5.798\text{E-}04T - 1.363\text{E+}00$ (Formal potential is using the average value at each temperature)

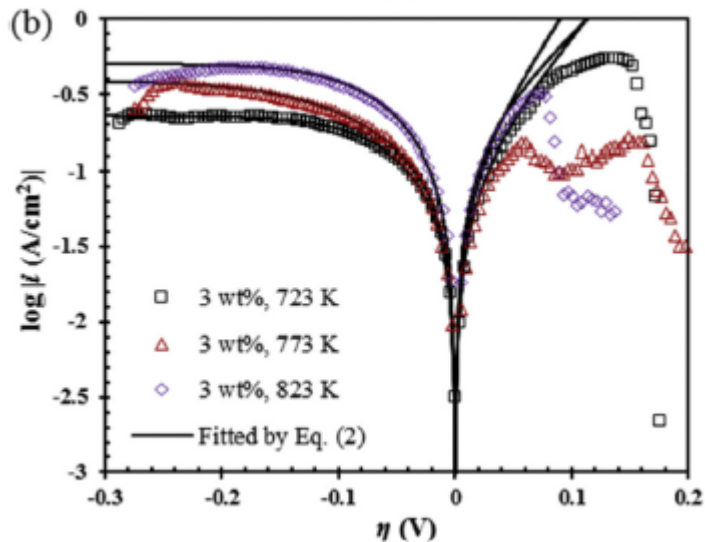
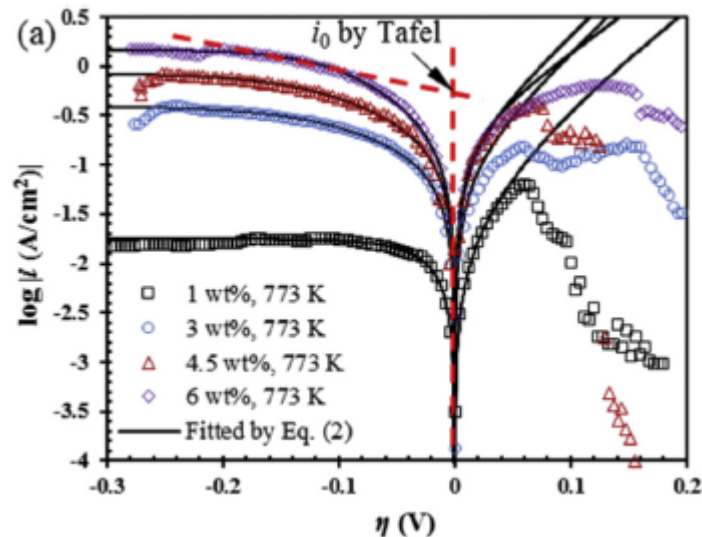
Where E_0^* is the formal potential of NiCl_2 , and T is the temperature in Kelvin

Exchange current Density- Optimization fitting

$$i = \frac{i_0 \left\{ \exp\left[\frac{(1-\alpha)nF}{RT}\eta\right] - \exp\left[\frac{-\alpha nF}{RT}\eta\right] \right\}}{1 - \frac{i_0}{i_L} \exp\left[\frac{-\alpha nF}{RT}\eta\right]}$$

Fitting results:

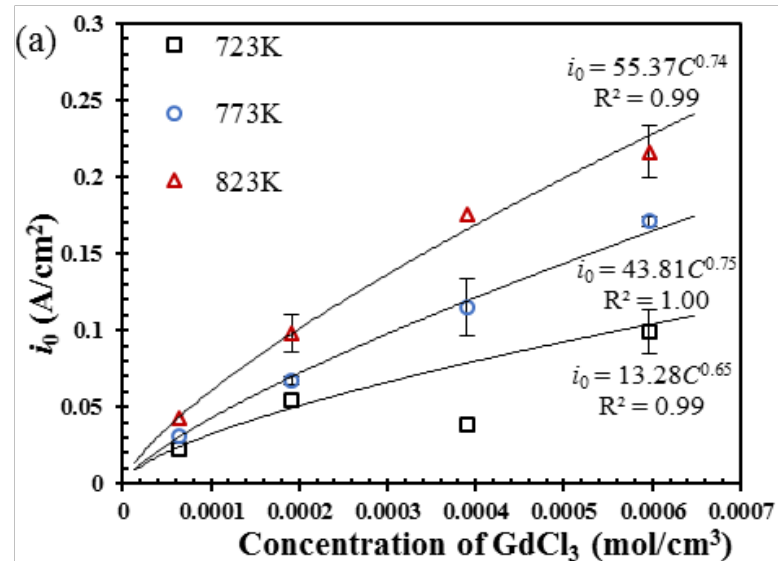
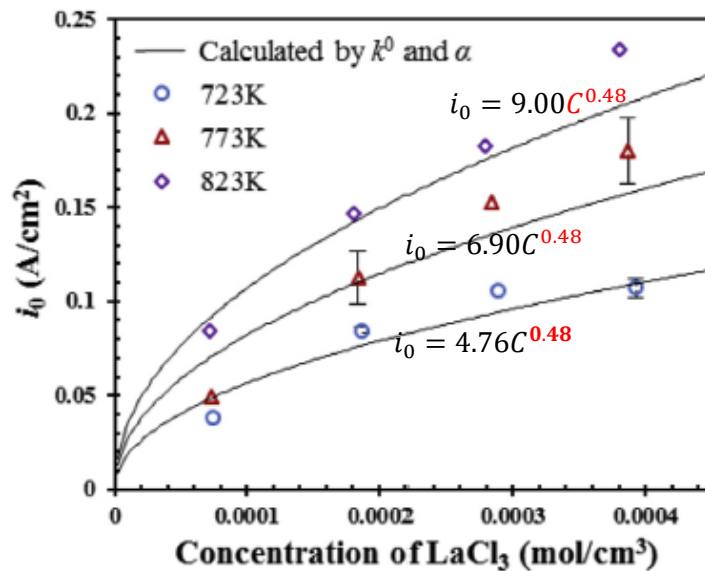
Difference between experimental and fitted data $\frac{\sum_j^N |(i_{\text{exp}} - i_{\text{cal}})/i_{\text{exp}}|}{N}$ is typically 5 -10%



Potentiodynamic polarization curves obtained in LiCl-KCl-1-LaCl_3 melts at 1 mv/s

Examine concentration correlation

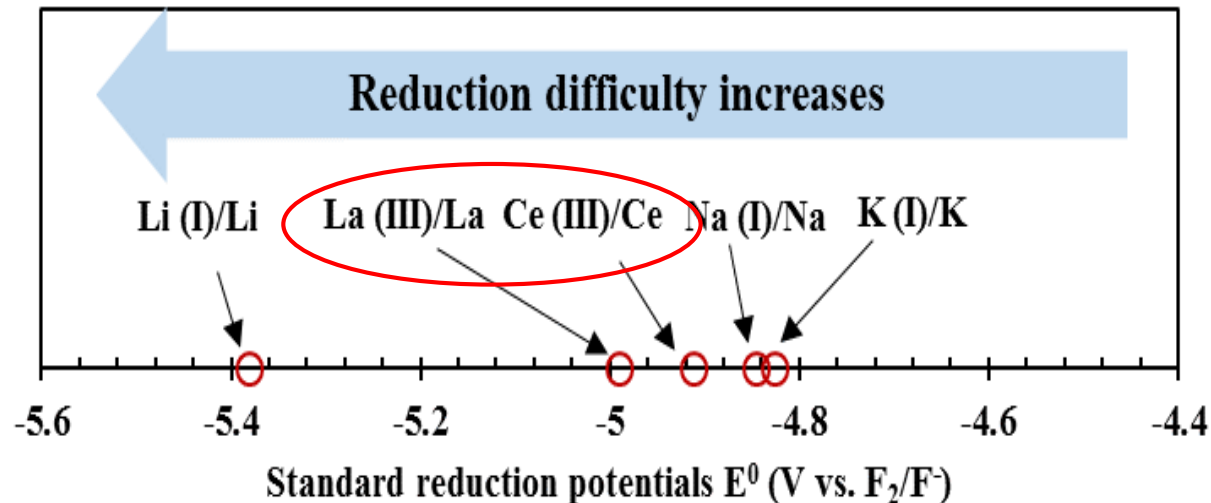
- $$i_0 = nFk^0 C_{\text{Ln(III)}}^b (1-\alpha)$$



Plots of i_0 versus GdCl₃ and LaCl₃ concentrations

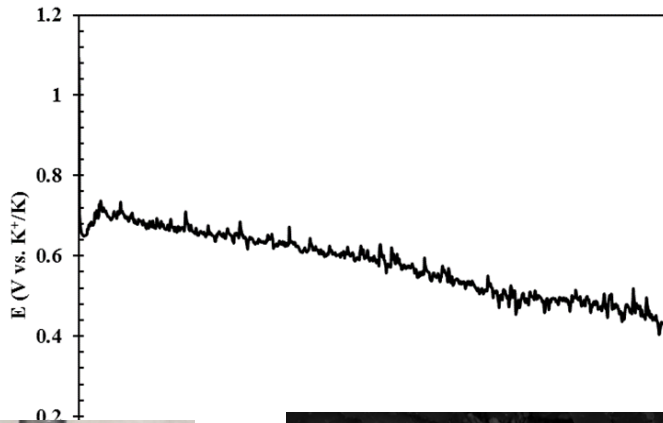
Conditions for Electrochemical Separation

- The Standard deposition potential of the impurity should be more positive than major metal ion redox potential but more negative than F/F^-

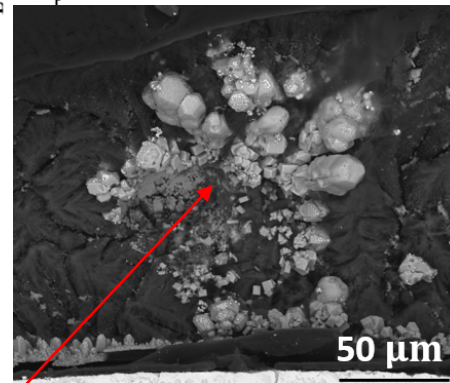
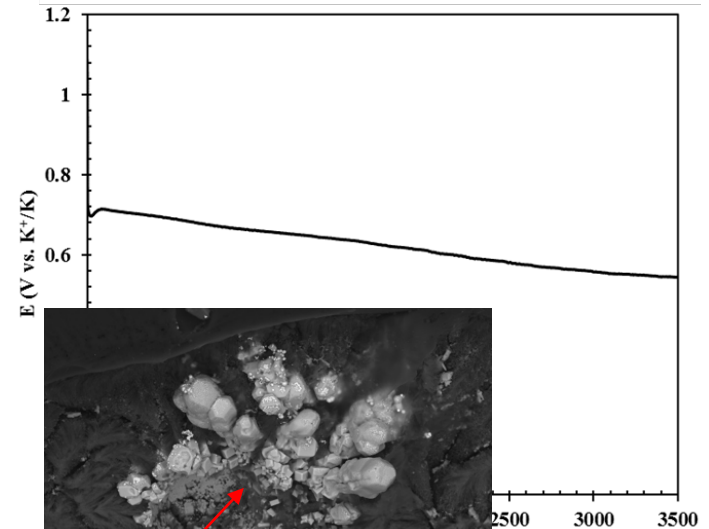
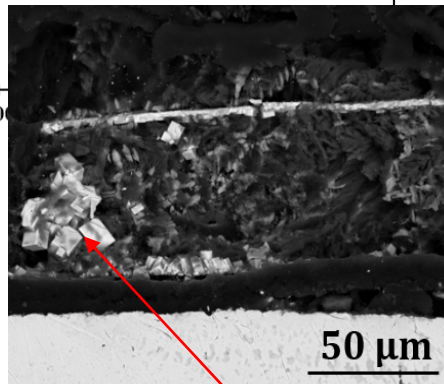


In LiF-NaF-KF, La and Ce can not be deposited

Electrochemical Separation of LaF_3 from FLiNaK Molten Salt on Inert Mo/W Electrode



400 600



2500 3000 3500

La metal

Why? Lanthanum Deposition Potential Shifts When KF or NaF Presents

- Lanthanum is found to predominantly exists in the species of LaF_6^{3-} instead of La^{3+} in molten fluoride salts when KF or NaF presents.

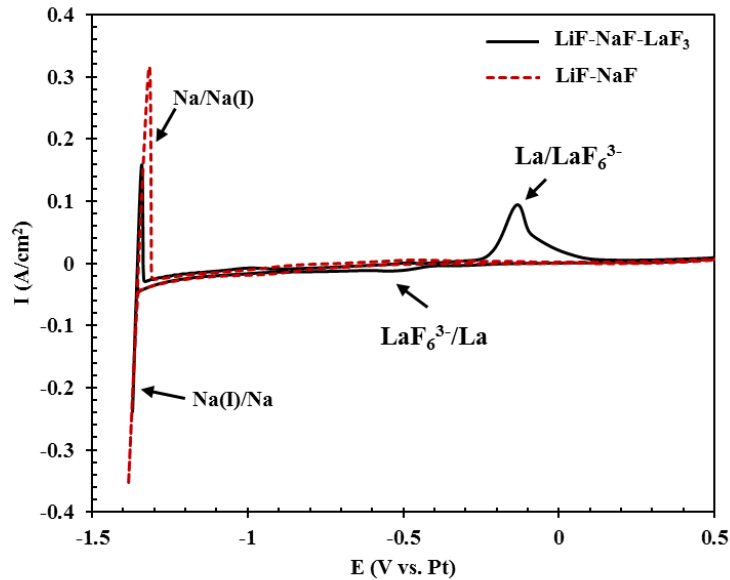
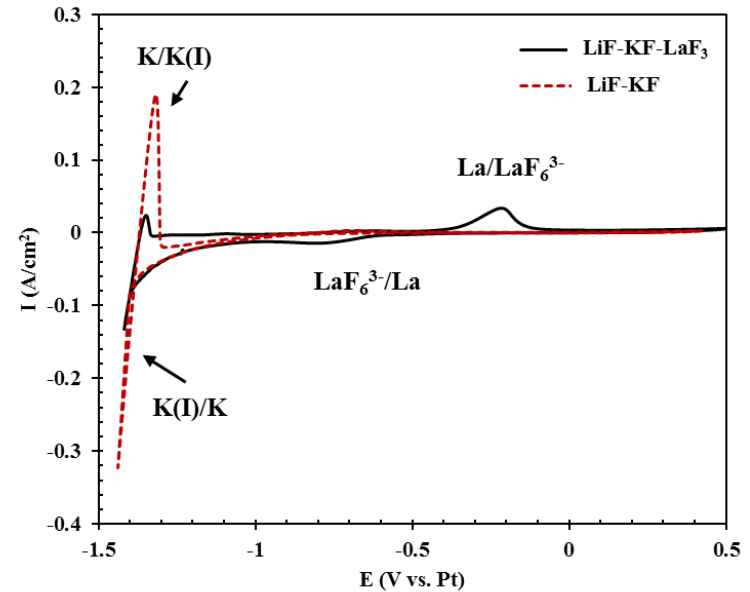
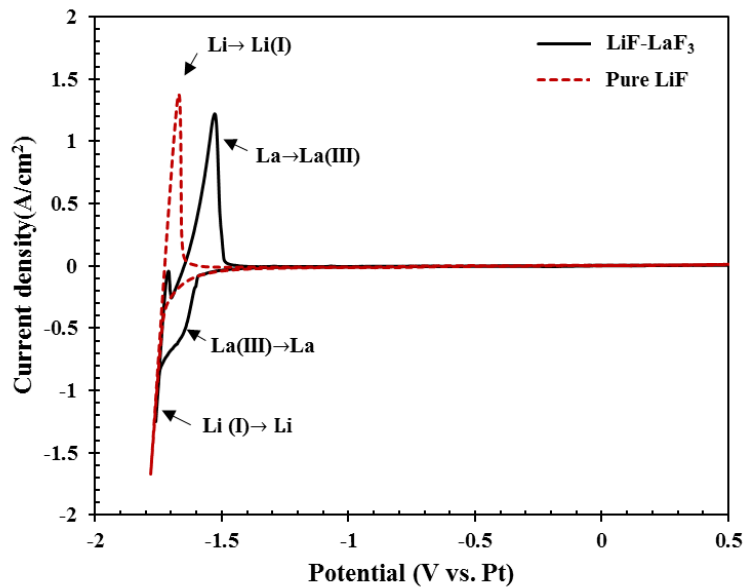


$$E_{\text{K}_3\text{LaF}_6/\text{La}}^0 = E_{\text{LaF}_3/\text{La}}^0 + \frac{\Delta G(\text{K}_3\text{LaF}_6)}{nF}$$

$$\Delta G(\text{K}_3\text{LaF}_6) = G(\text{K}_3\text{LaF}_6) - 3G(\text{KF}) - G(\text{LaF}_3)$$

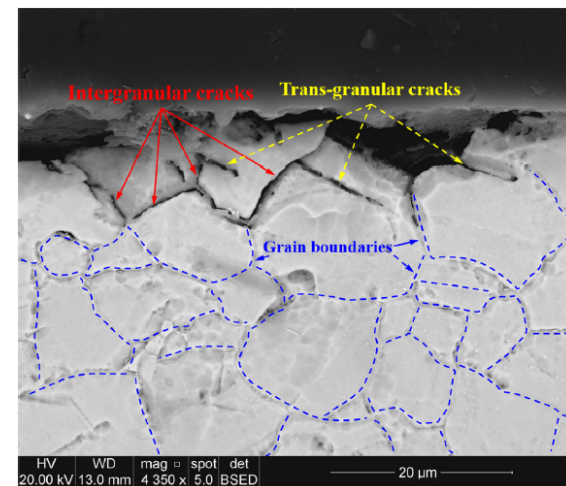
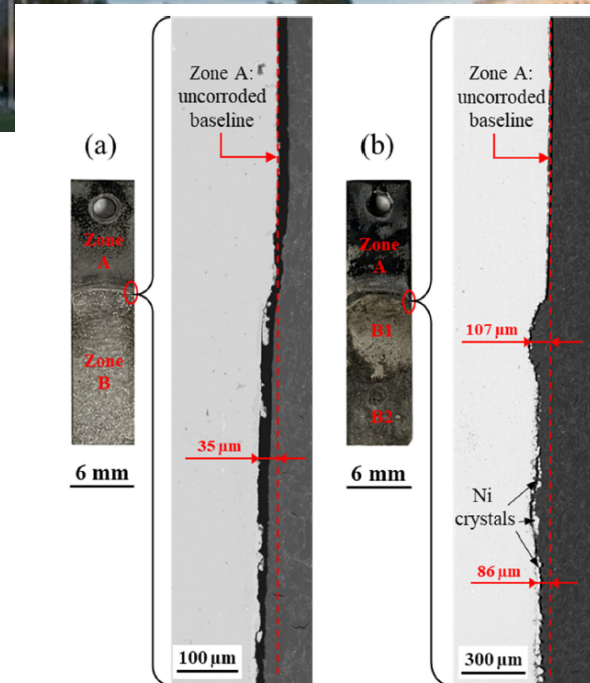
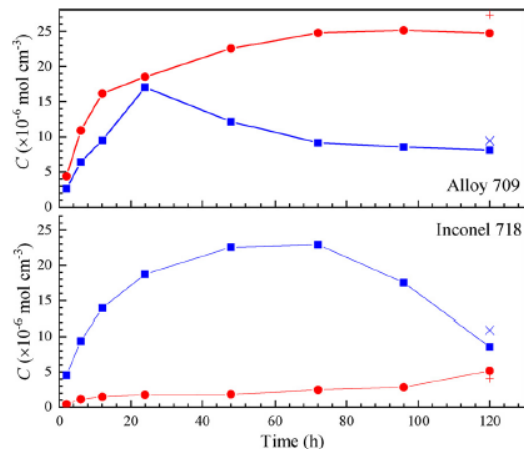
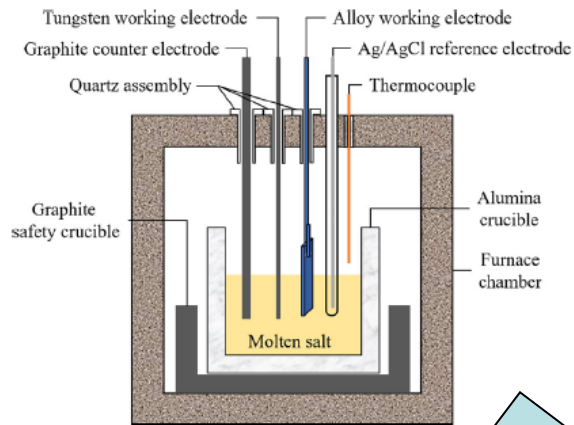
| Redox couple | Standard reduction potential E^0 (V vs. F_2/F^-) |
|-------------------------------------|---|
| LiF/Li | -5.38 |
| NaF/Na | -4.85 |
| KF/K | -4.83 |
| LaF ₃ /La | -4.99 |
| K ₃ LaF ₆ /La | -3.97 |

Does this happen for all the molten fluoride?



With the presence of the KF or NaF in molten fluoride salts, the deposition potential of lanthanum shifts to the positive direction greatly.

On-line corrosion Measurement-Eu effects on Alloy 709 and Inconel 718



What we have done/will do

- ☐ Redox Control
- ☐ Separation Kinetics
- ☐ Materials Transport in Primary Salt loop
- ☐ Materials Corrosion by Fission Products
- ☐ Flow induced corrosion (loop tests)
- ☐ Compound formation and Plating out

- ☐ Available facilities in our lab
 - ☐ Molten salt flow loop
 - ☐ 4-High-temperature Electrochemical cell (Up to 1000 C)
 - ☐ DSC machine
 - ☐ CALPHAD saltware
 - ☐ Corrosion model, materials transport model in flow loop
 - ☐ Static corrosion test autoclave (can work at high pressure)
 - ☐ Radioactive laboratory

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