



Thorium fuel cycle-based Molten salt reactor  
Safeguards, and Salt Chemistry and materials

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# Outline

## ❑ Introduction

- Thorium fuel cycle
- Thorium fuel type
- Thorium-based molten salt reactor
- Some design concerns

## ❑ Safeguards and non-proliferation

## ❑ Salt chemistry and purification

- Major impurities in the primary salt
- Lanthanides fission products removal
- Non-metal impurity removal

## ❑ Molten salt corrosion

- Corrosion mechanisms
- Corrosion kinetics
- Carbon and fission products' effects
- Corrosion control

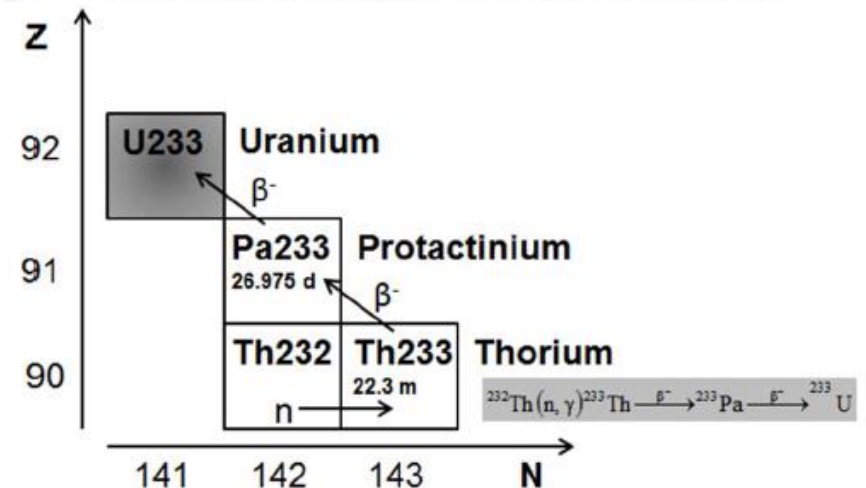
# Introduction-Thorium

- ❑ More abundant in nature than uranium
- ❑ In nature, in a single isotopic form –Th-232
- ❑ Th-232 is not a fissile materials, can not be directly use as fission materials for thermal reactor
- ❑ Th-232 is a fertile materials and can transmute to U-233 upon absorbing a neutron, U-233 is an excellent fissile material.
- ❑ Thermal-breeder reactor
- ❑ No plutonium production

**TABLE 2.1**  
CRUSTAL ABUNDANCE OF SELECTED ELEMENTS\*

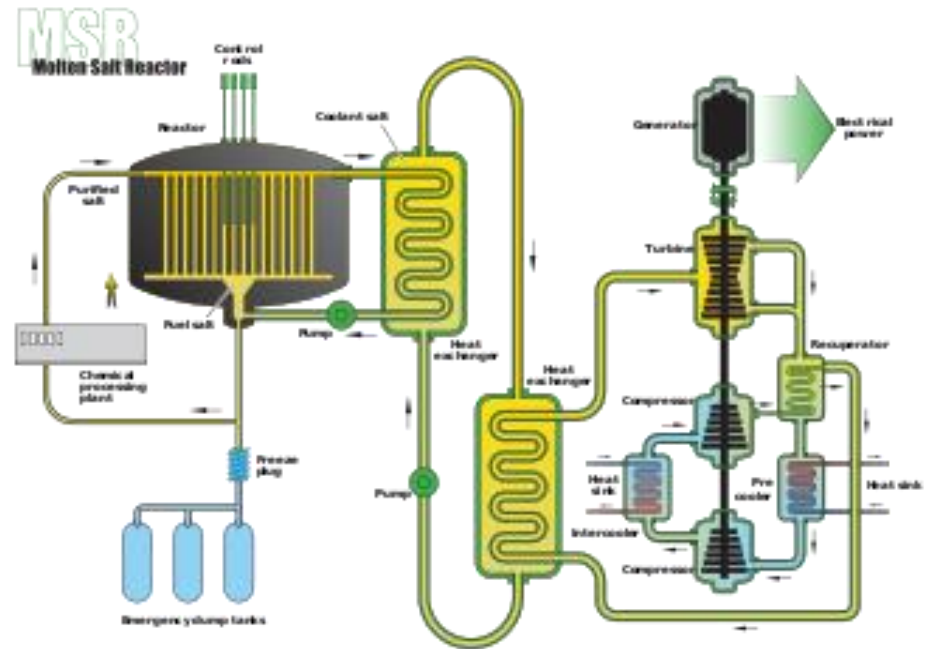
Element	Abundance (g/ton)
Gold	0.004
Silver	0.07
Tungsten	1.5
Molybdenum	1.5
Uranium	1.8
Thorium	7
Lead	13
Copper	55
Zinc	70
Iron	50,000
Aluminum	81,300

\*Source: B. Mason, *Principles of Geochemistry*, 3rd ed., John Wiley & Sons, New York (1966).



# Introduction-Thorium Fuel

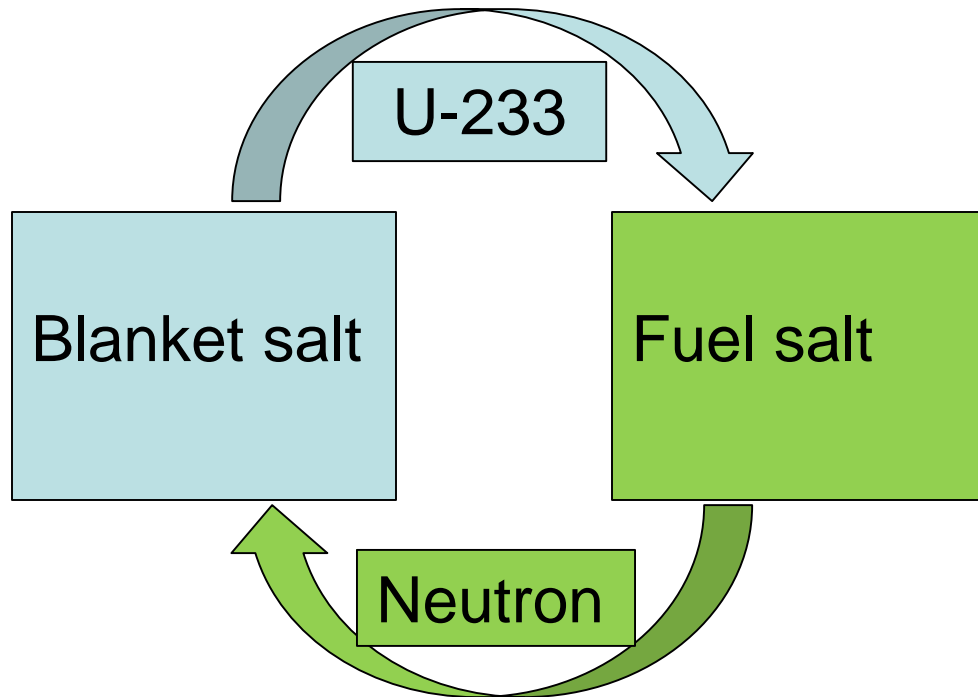
- ❑ **Solid fuel (Thorium Oxide)**
  - It is harder to fabricate
  - Do not have much experience
- ❑ **Liquid fuel (Thorium Fluoride)**
  - No fuel fabrication issue
  - Have experience
- ❑ **Thorium Fuels need a fissile material as a “driver” to maintain the “Chain Reaction”**



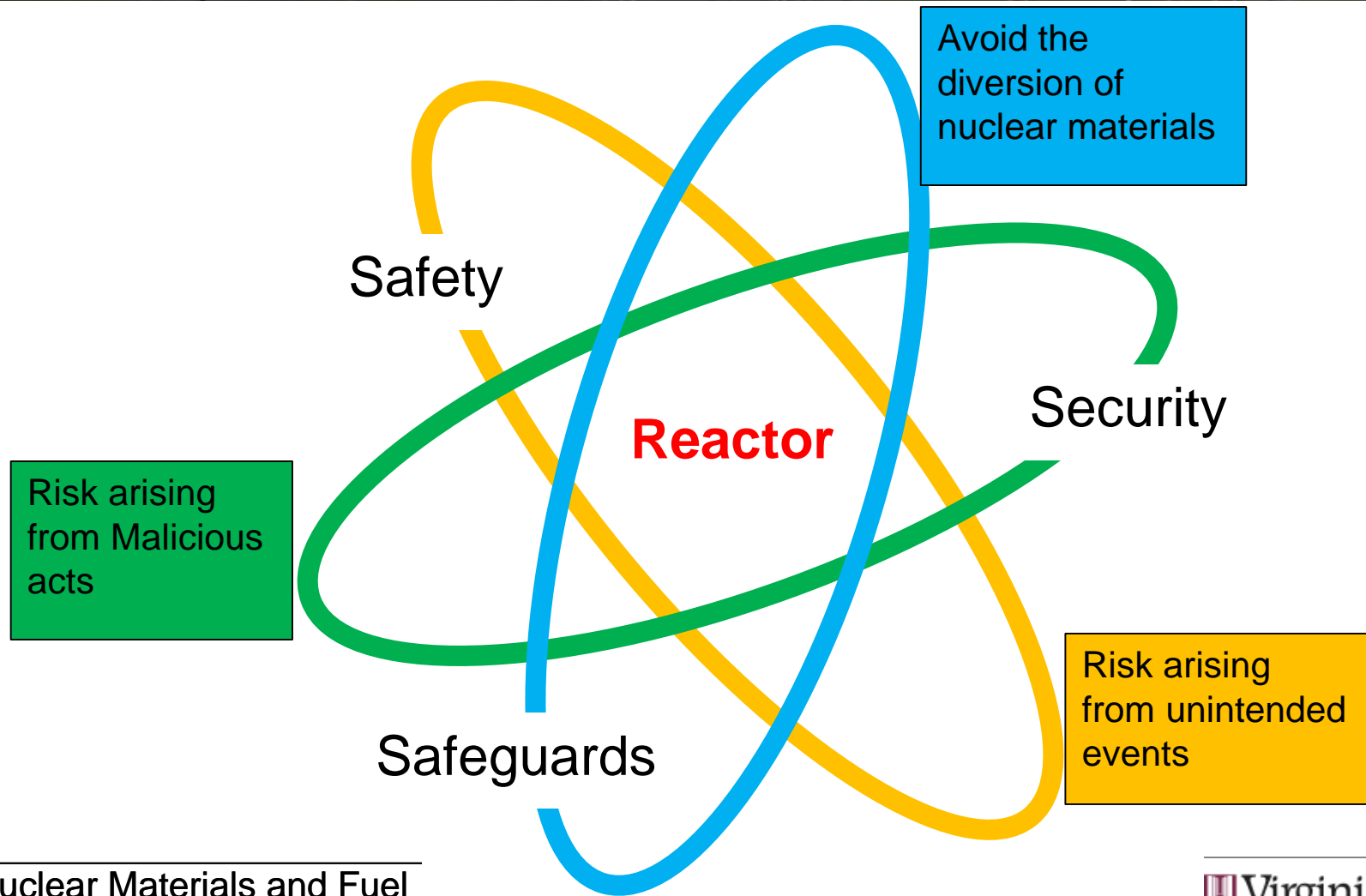
# Introduction-LFTR

## LFTR=Liquid Fluoride Thorium Reactor

- Blanket Salt:  $\text{LiF-ThF}_4$
- Fuel Salt:  $\text{LiF-BeF}_2\text{-U(233) fluoride}$



# Some Design Concerns



# Proliferation Resistance

- ❑ Th-fuel cycle should have higher proliferation resistance than U-Pu cycle (*no Pu problem*)
- ❑ The fissile inventories of a MSR are lower than in other reactor systems (*no spent fuel except at the end of life of a reactor*)
- ❑ U-233 can be weapon materials, however, obtaining the critical mass (8 kg U-233) requires the extraction of lots of salt (*the concentration of U-233 in the salt is low*)
- ❑ Self-protection (*U-233 is always together with U-232 which has a very strong gamma ray emitter*)
- ❑ Diversion is very difficult in U/spent fuel management/storage (*the amount of radioactivity by fission products and U-232 is large enough to prevent any diversion*)
- ❑ Separation of Pa-233 is possible, however, Pa-233 only has a half-life of 27 days. (if the waste is safe for a short term, weapon materials won't be an issue)

# Unique features of MSR for Safeguards

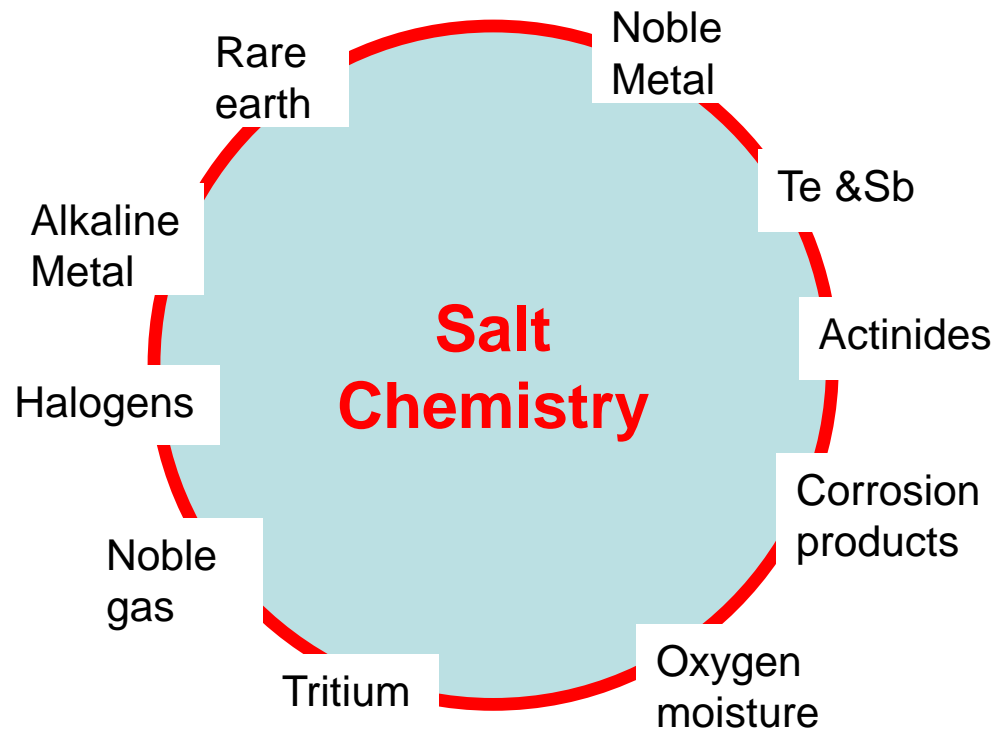
- ❑ Homogeneous fuel (*because of using liquid fuel*)
- ❑ Combination system of a reactor and a processing plant (*because of the on-line fuel treatment including salt chemistry control*)
- ❑ Low content of actinide materials (*because of large amount of molten salt and low concentration of fissile materials*)
- ❑ High temperature (*the operation temperature can be higher than 700 °C*)
- ❑ Extreme high radioactive (*Most of radioactive inventories are in the salt*)
- ❑ No discrete fuel elements (*combined with continuous transmutation prevents simple accounting*)
- ❑ High salt melting temperature



# Safeguards Challenges

- ❑ Traditional safeguards approaches can not be directly applied to MSRs
- ❑ Innovative approaches are needed
- ❑ Safeguards by design (*safeguards provisions and features are taken into account and designed into the facility from the very beginning of the design process, if SBD is applied, it will significantly improve safeguards assurances and avoid costly and time consuming redesign work*)

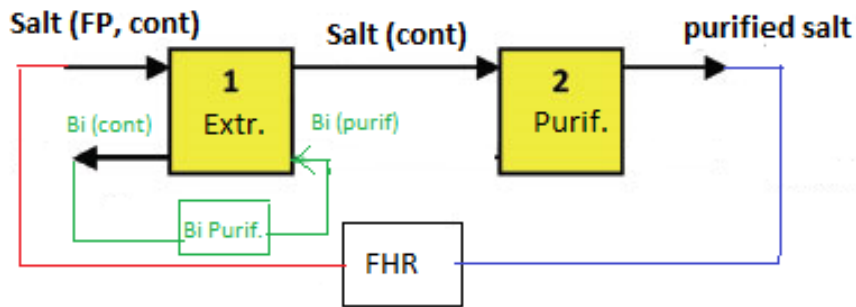
# Salt Chemistry



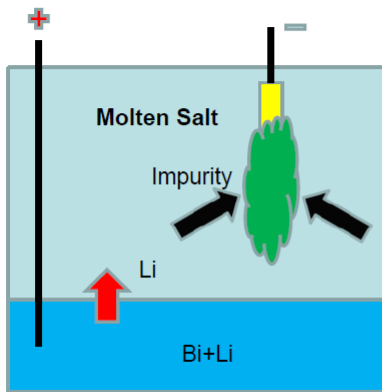
# How to purify the salt on line

- ❑ **Tritium:** Helium-hydrogen sparging, membrane reactor (Pd-Ag), double-wall heat exchanger)
- ❑ **Noble Gas:** sparging with inert gas, followed by adsorption onto a charcoal filter)
- ❑ **Halogens (iodine):** HF-H<sub>2</sub> sparging followed by accumulation in KOH solution
- ❑ **Alkaline Metals:** Liquid/liquid extraction using Bi-Li, electrochemical separation
- ❑ **Rare Earths:** Liquid/liquid extraction using Bi-Li, electrochemical separation, cold trap
- ❑ **Noble Metals:** Liquid/liquid extraction using Bi-Li, electrochemical separation.
- ❑ **Tellurium and Antimony:** Plating out, electrochemical separation if in the form of tellurides and antimonides
- ❑ **Actinides:** fluorination, Liquid/liquid extraction using Bi-Li, electrochemical separation (*need to separate first*)
- ❑ **Corrosion Products:** Removal method: liquid-liquid extraction, electrochemical separation
- ❑ **Oxygen and Moisture:** Sparging, electrochemical separation

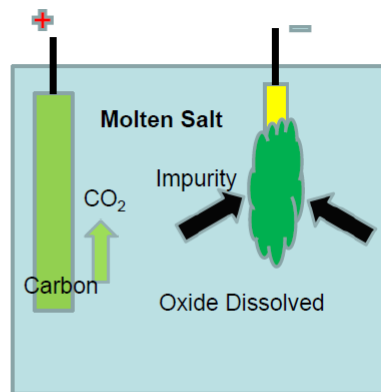
# Two Removal Methods



□ Liquid Salt/Liquid Metal Extraction



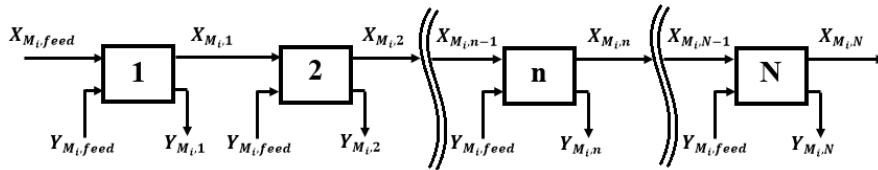
(a) Bi+Li sacrificial anode



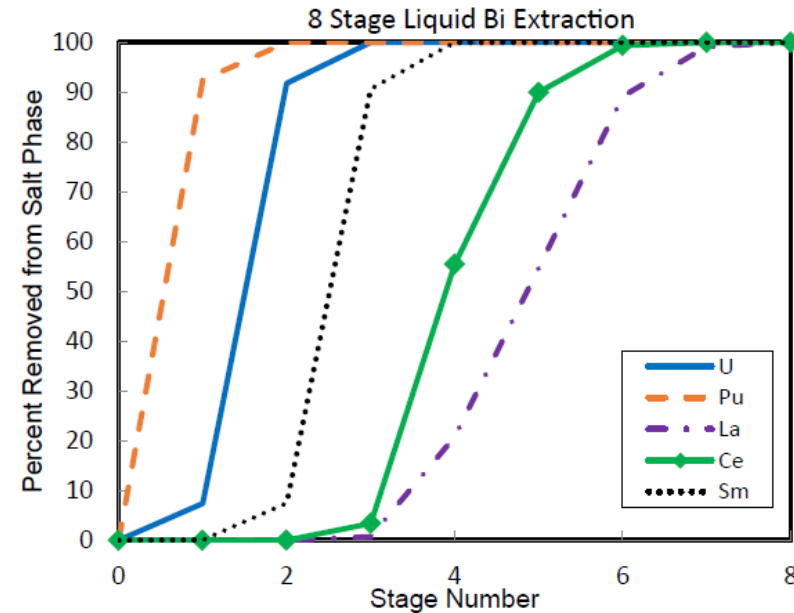
(b) Carbon sacrificial anode

□ Electrochemical Method

# Liquid/liquid Multistage Extraction Model



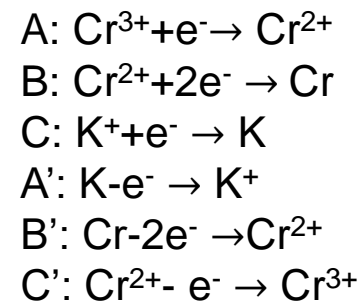
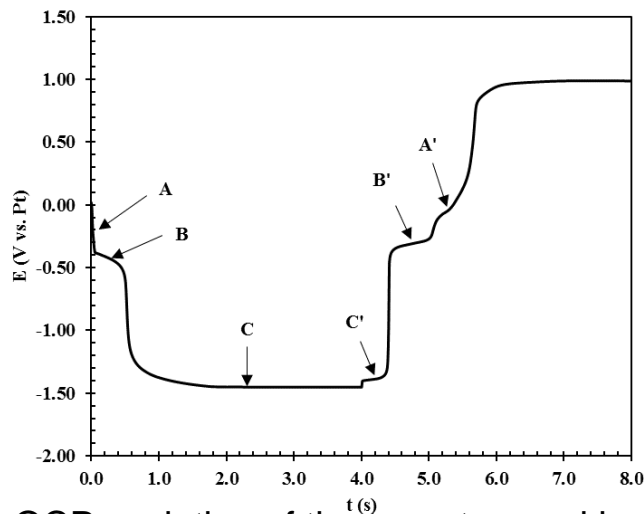
$$\sum_{i=1}^m \frac{n_i X_{M_i}^I}{Bi_{feed} + Salt_{feed} D_{M_i}} = \frac{Y_{Li}^I D_{Li} - X_{Li}^I}{Bi_{feed} + Salt_{feed} D_{Li}}$$



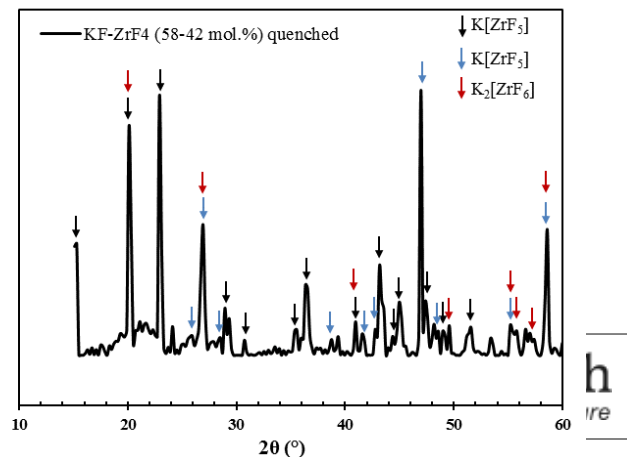
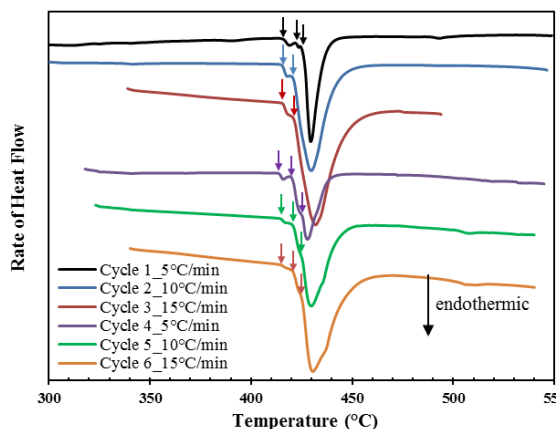
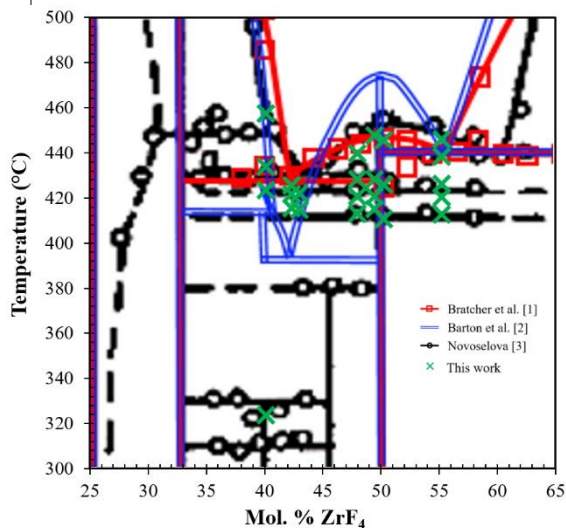
Percent removal of actinides and rare earths across extraction cascade at 700 C. 0.001 mole fraction of each impurity in the salt, flow flux ratio of liquid metal to molten is 3.

# Fundamental Property Measurement

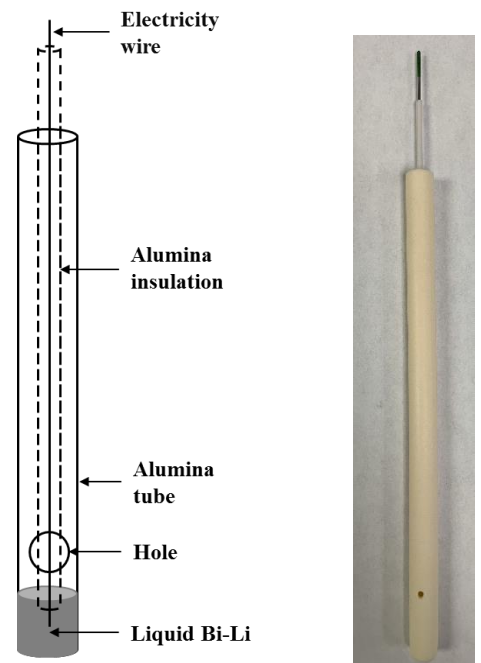
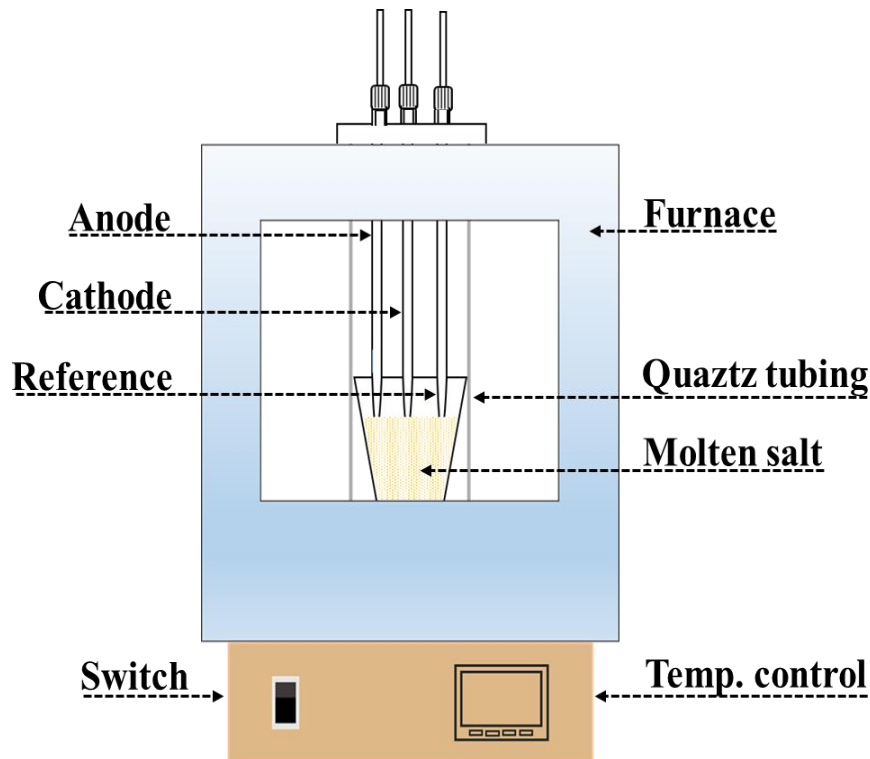
- Identify Stable ions
- Activity coefficient
- Reaction rate
- Exchange current density
- Phase diagram
- Diffusion coefficient
- Gibbs energy of formation
- Compounds formation



OCP evolution of the tungsten working electrode against platinum reference electrode over time by chronopotentiometry test at the temperature of 1023 K.



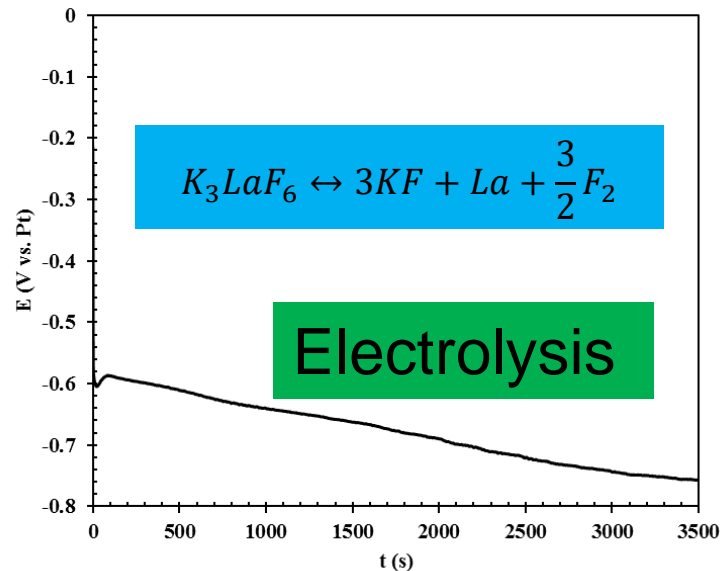
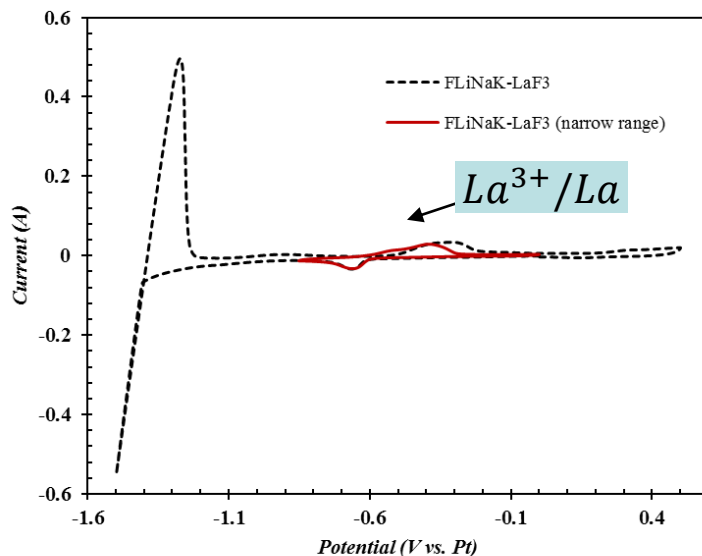
# Experiment Set up



Liquid Bi-Li Electrode

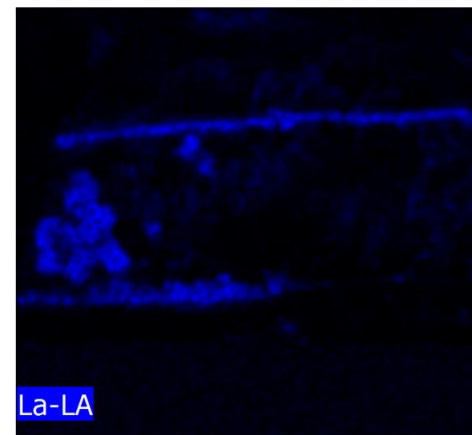
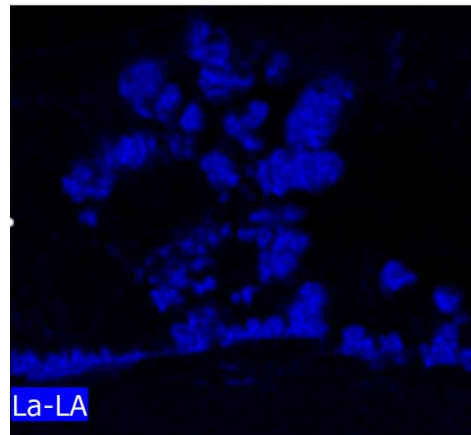
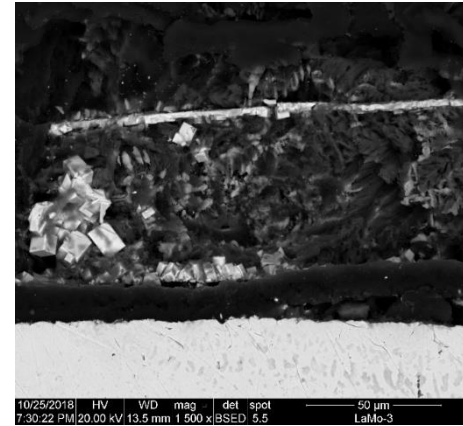
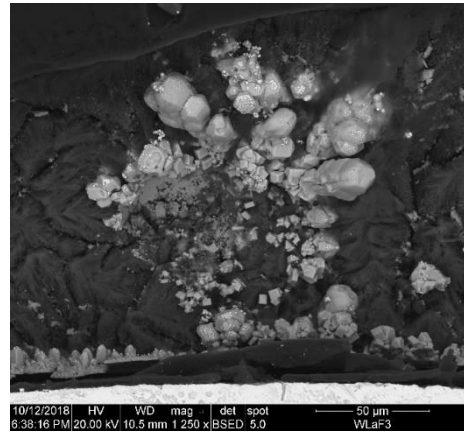
# Removal La ions from salt in metal form

- Method: Electrolysis in LiF-NaF-KF
- Working Electrode: W and Mo





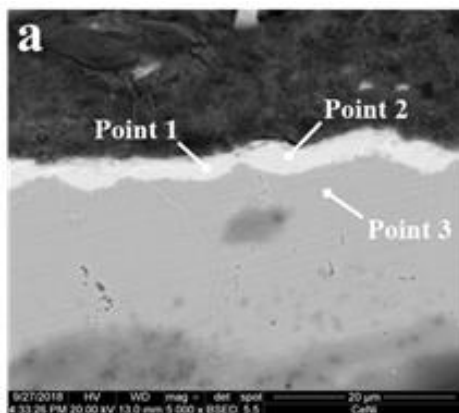
# Electrochemical Separation of lanthanide-La



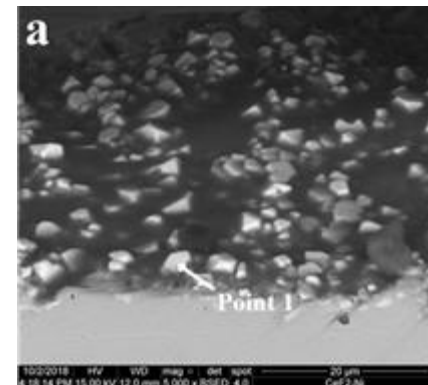
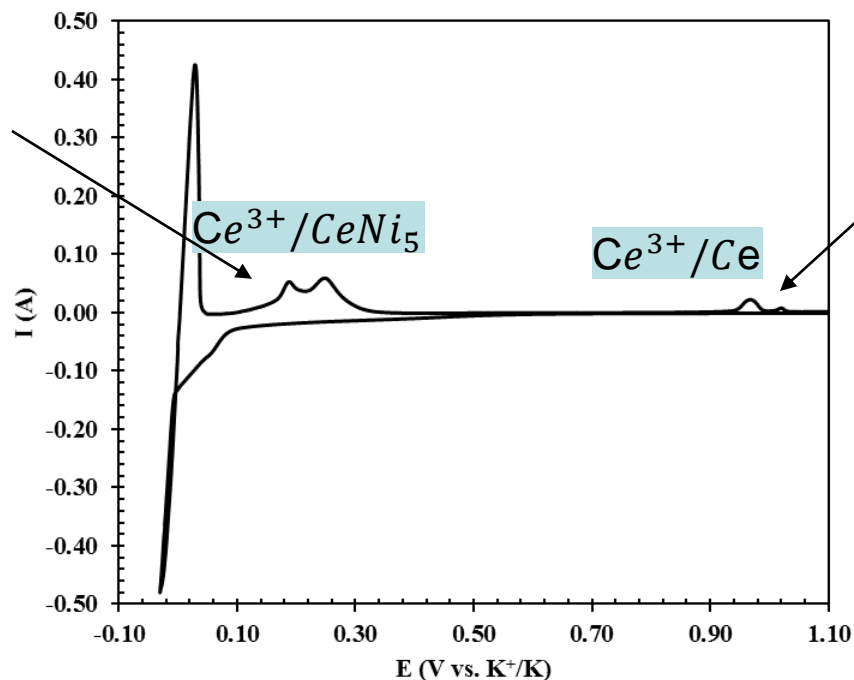
W electrode

Mo electrode

# Electrochemical Separation of lanthanide-Ce: Ni Electrode



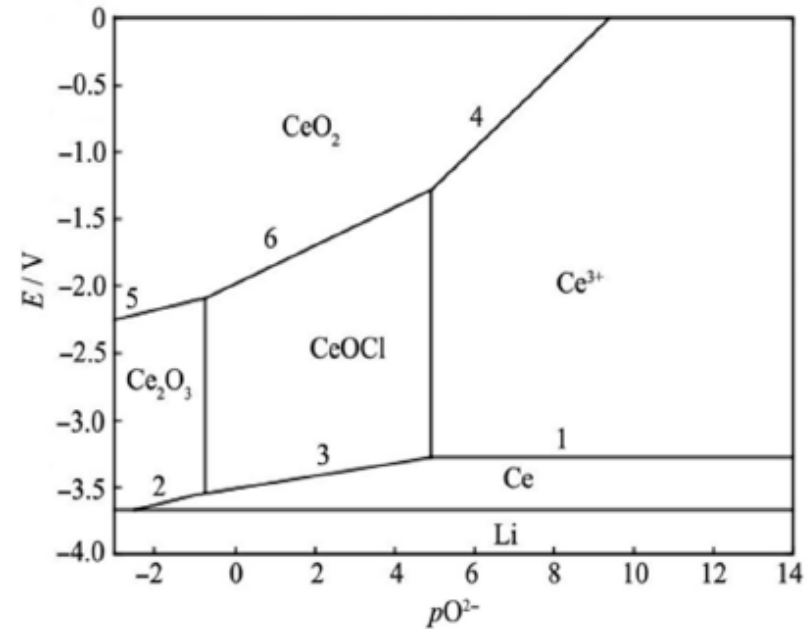
Ce-Ni compounds  
on Ni Electrode



CeF<sub>2</sub> near the Ni or  
W electrode

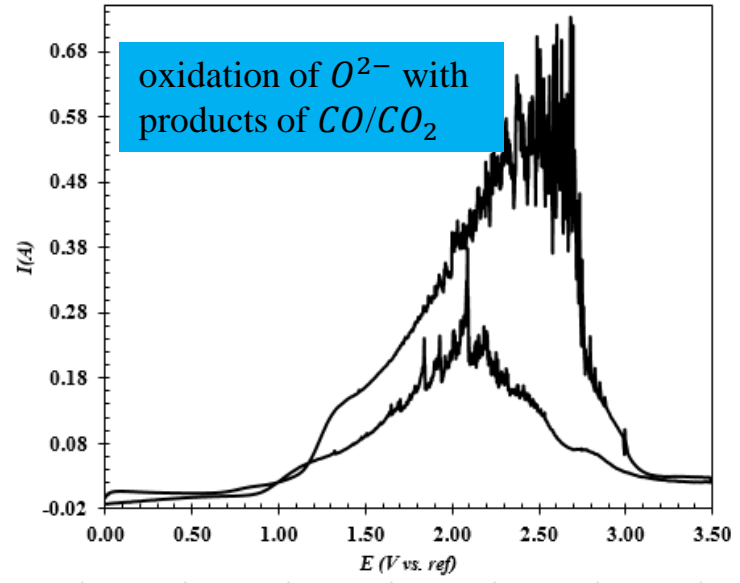
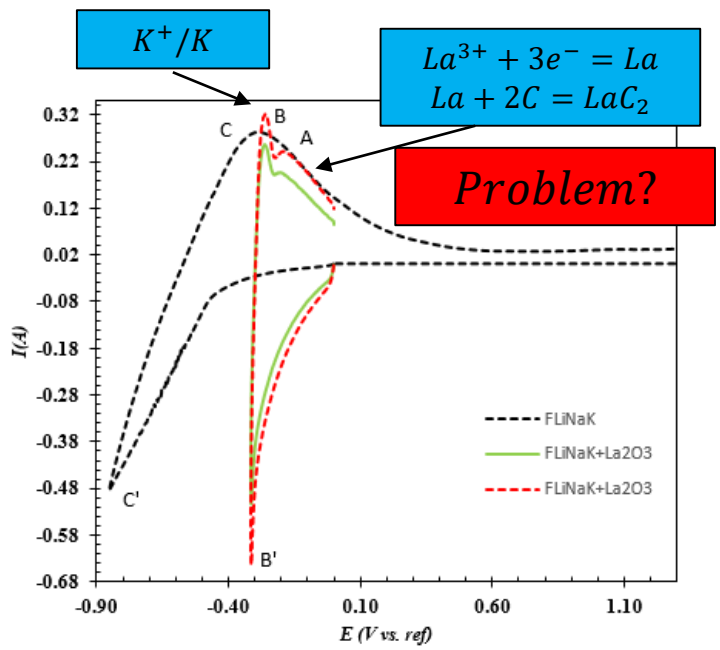
# Oxide Removal-Why remove Oxygen ions

Form non-soluble compounds:  $\text{UOF}_2$ ,  $\text{LnOF}$ , etc



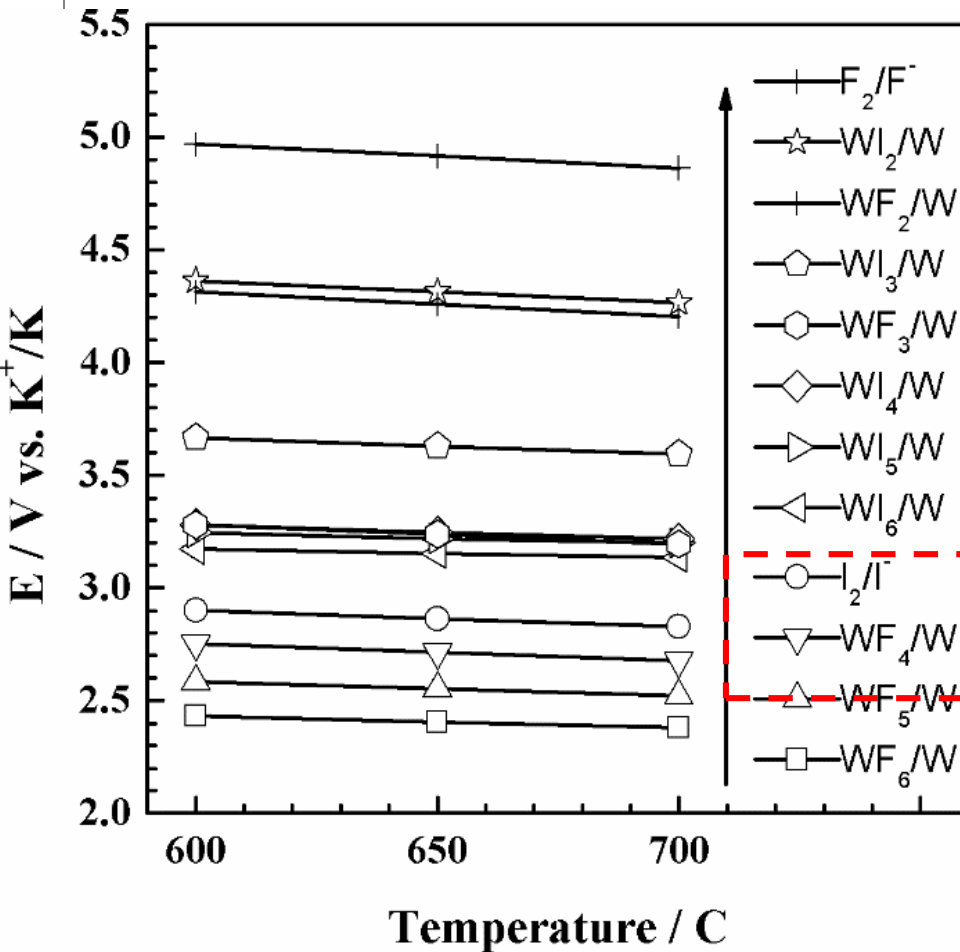
E-pO<sub>2</sub>- diagram for Ce in molten KCl-LiCl at 723K

# Oxide Removal-How to removal Oxygen ions, Graphite electrode?



Cyclic voltammetry: WE: graphite, CE: tungsten, RE: tungsten.  
 Black curve is pure FLiNaK without La<sub>2</sub>O<sub>3</sub>, green and red curves are FLiNaK with La<sub>2</sub>O<sub>3</sub>.

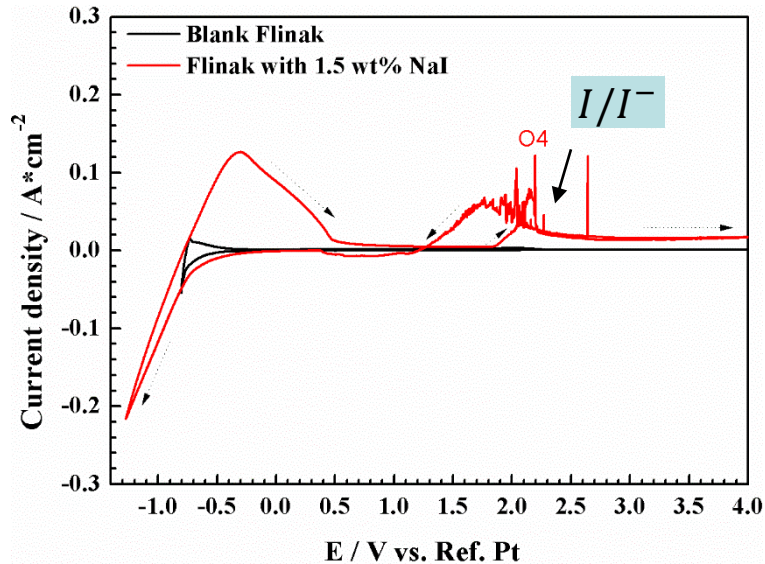
# Iodine Ion Removal-How to removal Iodine ion



Redox potential (E vs. E<sub>Na+/Na</sub>) at different temperatures for various redox couples in molten FLiNaK-NaI salt with a W electrode.

Cannot be removed by using W

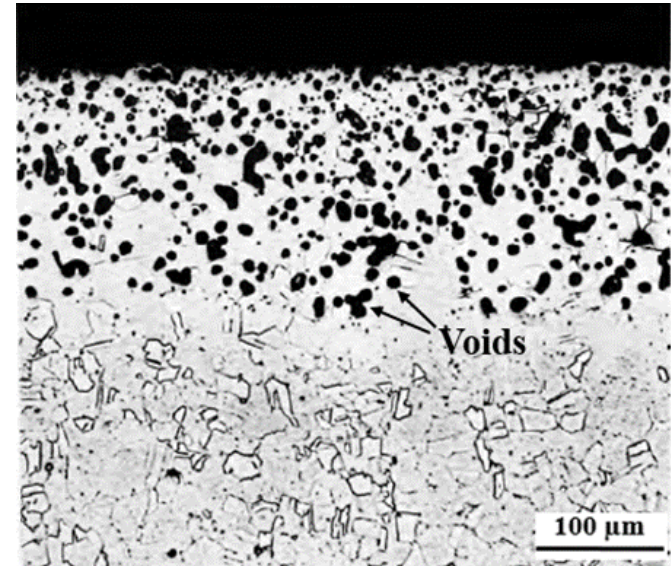
# Electrochemical Separation of Iodide-NaI



First cycle of CVs recorded from a Graphite WE (area: 0.7 cm<sup>2</sup>) in both FLiNaK and FLiNaK-NaI (1.5 wt%) melts at 600 °C under argon atmosphere. Scan rate: 200 mV/s. CE and RE: Graphite and Pt

# Typical Molten salt corrosion attack

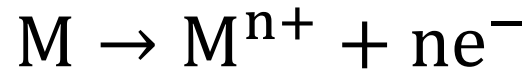
As formation of the passivating oxide layer becomes thermodynamically unfavorable in molten halide salts, corrosion proceeds as active metal dissolution, resulting in depletion of less noble alloying element and formation of void.



Inconel 600 in molten fluorides, reproduced from ORNL-2349

# Corrosion reaction

- ❑ Corrosion is an electrochemical process involving the anodic metal dissolution and cathodic reduction of oxidants



- ❑ To make the reaction occur spontaneously

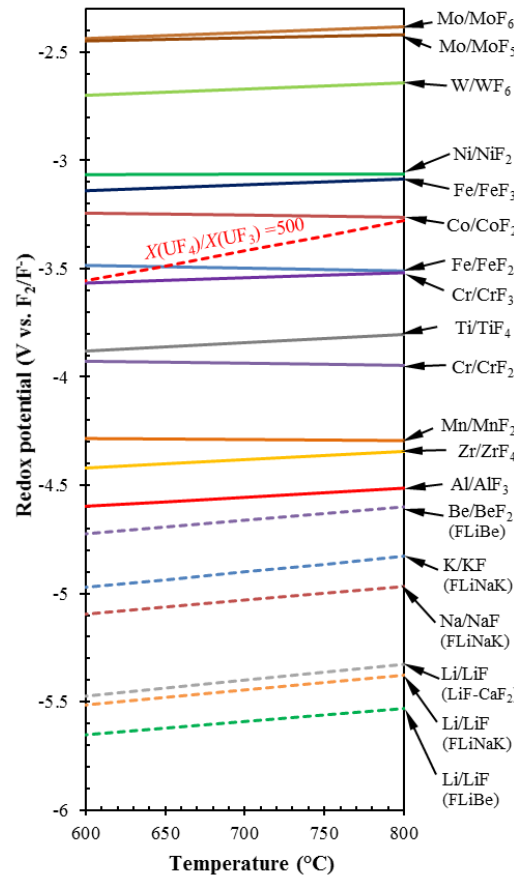
$$\Delta G = -nF(E_c - E_a) < 0$$

$$\text{Where } E_a = E_a^{\circ} + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M} \text{ \& } E_c = E_c^{\circ} + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}}$$

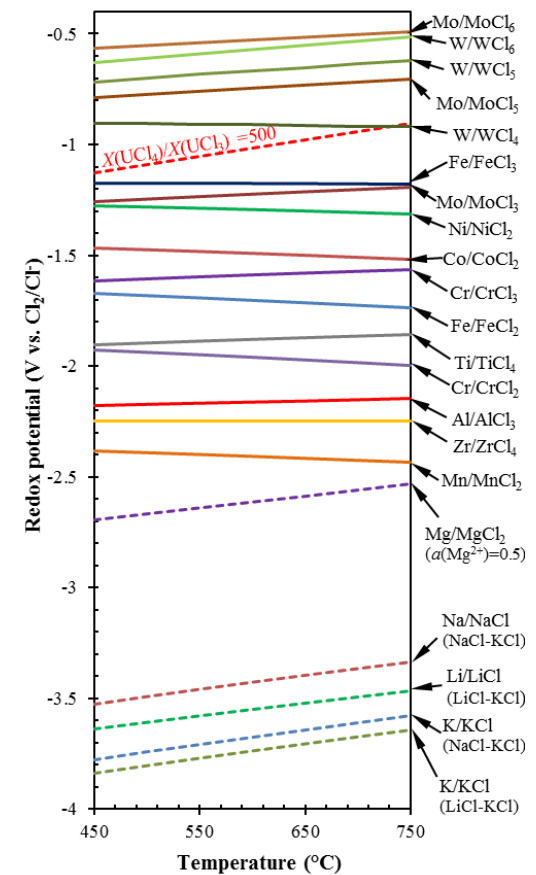


# Redox potentials

- $E_{M^{n+}/M}^{\circ}$  (vs.  $X_2/X^-$ ) =  $\Delta G_f^{\circ}(MX_n)/nF$
- Fluorides and chlorides of alkali and alkaline earth are typically not oxidizing
- However, fuel components (U), fission products (Te), and other impurities (TF,  $H_2O$ ,  $Ni^{2+}$ , etc.) are effective oxidants



Fluoride salts



Chloride salts

# Electrode kinetics

- Charge transfer rate at metal surface

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

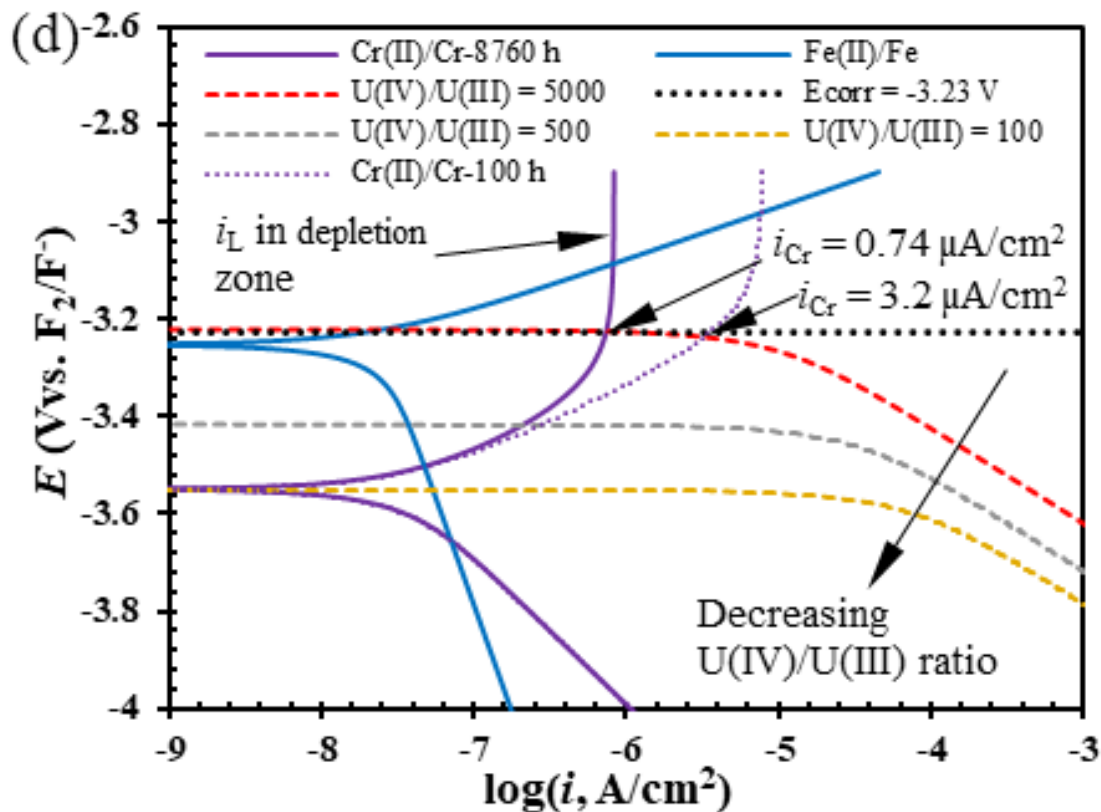
- When mass-transfer of oxidants in the salt solution is limited, oxidant reduction rate is expressed by

$$\begin{aligned} i_c &= -i_{c0} \frac{c_{\text{Ox}}^s}{c_{\text{Ox}}^b} \exp \left( -\frac{\alpha_c nF}{RT} \eta_c \right) \\ &= -\frac{i_0 \exp \left( -\frac{\alpha nF}{RT} \eta \right)}{1 - \frac{i_0}{i_L^{\text{Ox}}} \exp \left( -\frac{\alpha nF}{RT} \eta \right)} \end{aligned}$$

where  $i_c = nFk_m(c_{\text{Ox}}^b - c_{\text{Ox}}^s)$ ;  $i_L^{\text{Ox}} = nFk_m c_{\text{Ox}}^b$

# Corrosion simulations

- Calculated polarization curves for alloy corrosion in molten fluoride salts containing 0.01 mol% Cr(II) and 0.001 mol% Fe(II) and Ni(II)

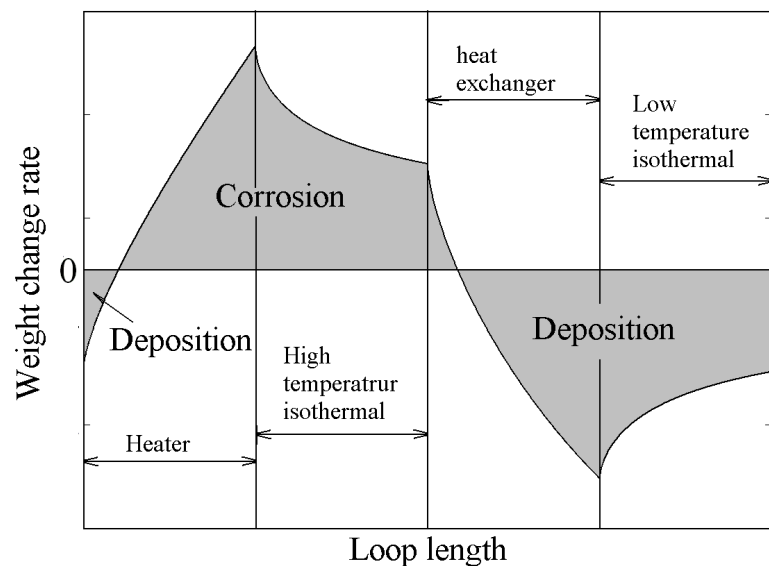


Hastelloy N after 1-year Cr depletion in salt containing 0.13 mol% U

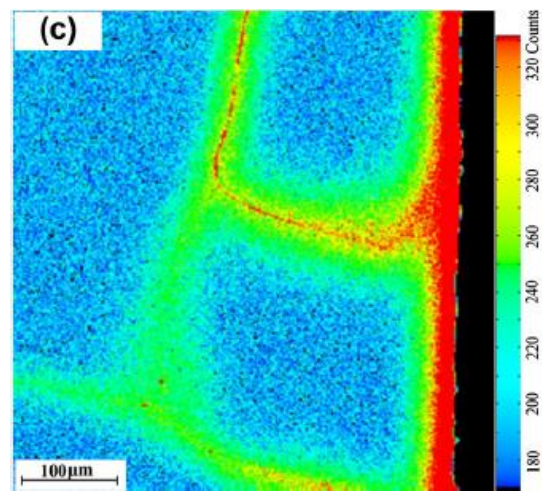
# Key factors that affects corrosion

- Oxidants and impurities in the melt
- Te-induced IGC
- Interaction with dissimilar materials
- Temperature gradient
- Radiation
- Alloying elements

# Temperature gradient and Te Effects



Corrosion rate distribution along the loop



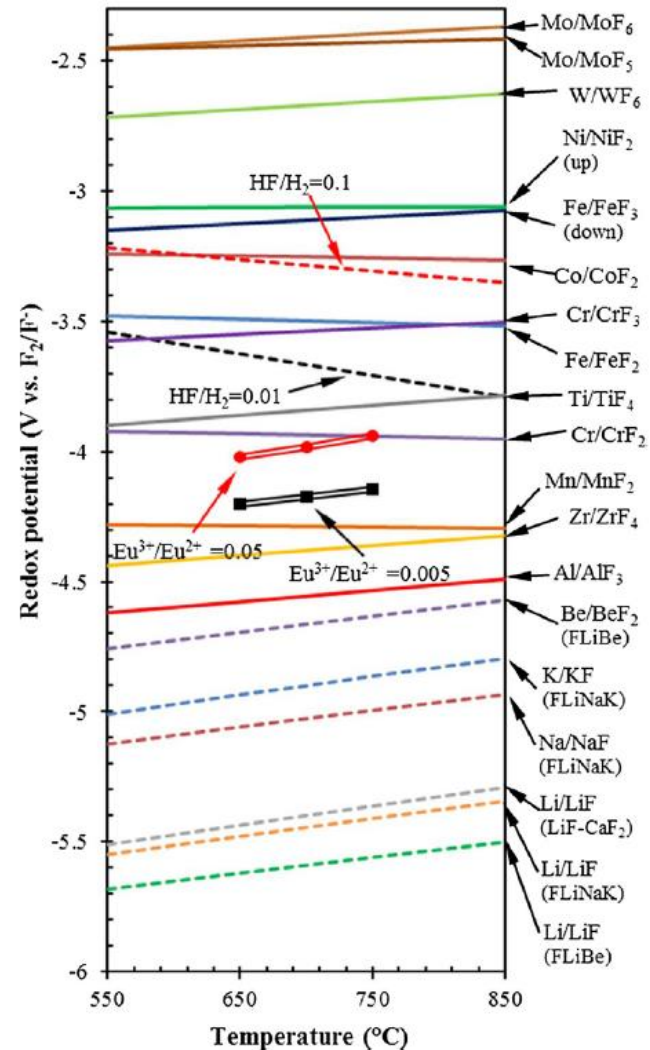
Intergranular diffusion of Te  
(Y. Jia, et al. J. Nucl. Mater. 441  
(2013) 372)

# Principles and methods

- Redox control principles
  - Lower redox potential to make salt less oxidizing
  - Faster reaction rate to consume oxidants
- Redox control methods
  - Dissolved salt control (e.g.,  $\text{UF}_4/\text{UF}_3$ )
  - Major metal control (e.g.,  $\text{BeF}_2/\text{Be}$ )
  - Gas phase control (e.g.,  $\text{HF}/\text{H}_2$ )

# Dissolved salt control

- ❑ MSRE experience indicated negligible corrosion when U(IV)/U(III) was controlled under 100.
- ❑ Increase of U(IV)/U(III) ratio during reaction with oxidants and fission can be decreased by contacting salt with reductive metals such as Be and U.
- ❑ For coolant salt, Eu(III)/Eu(II) are promising redox buffer candidate due to its appropriate formal potential.
- ❑ The monitoring of concentration ratio/redox potential can be performed by an electrochemical sensor



# Some conclusion points

- ❑ Th-Based fuel cycle generally has higher proliferation resistance
- ❑ New safeguards approaches are needed
- ❑ The salt chemistry is complex, but is controllable
- ❑ Many factors influence the material corrosion, by controlling the redox potential, the corrosion can be mitigated



# Acknowledgement

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