Salt chemistry and Redox control

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Research Team

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All the experimental measurements presented were conducted at The Ohio State University

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Salt impurities/source term

- ❑ Tritium
- ❑ Noble Gas (Xe, Kr)
- ❑ Noble metals (Nb, Mo, Tc, Ru, Rh, Ag, Cd, In, Sn, Zn, Ga, Ge, As)
- ❑ Halogens (I, Br)
- ❑ Tellurium Group (Te, Sb, Se)
- ❑ Barium, Strontium (Ba, Sr)
- ❑ Rare earth/alkaline metals (Y, La, Ce, Pr, Nd, Pm, Gd, Tb, Dy, Ho, Er, Zr, Sm, Eu, Sr, Ba, Rb, Cs)
- ❑ Actinide (U, Pu, Np)
- ❑ Corrosion Products (Ni, Fe, Cr)

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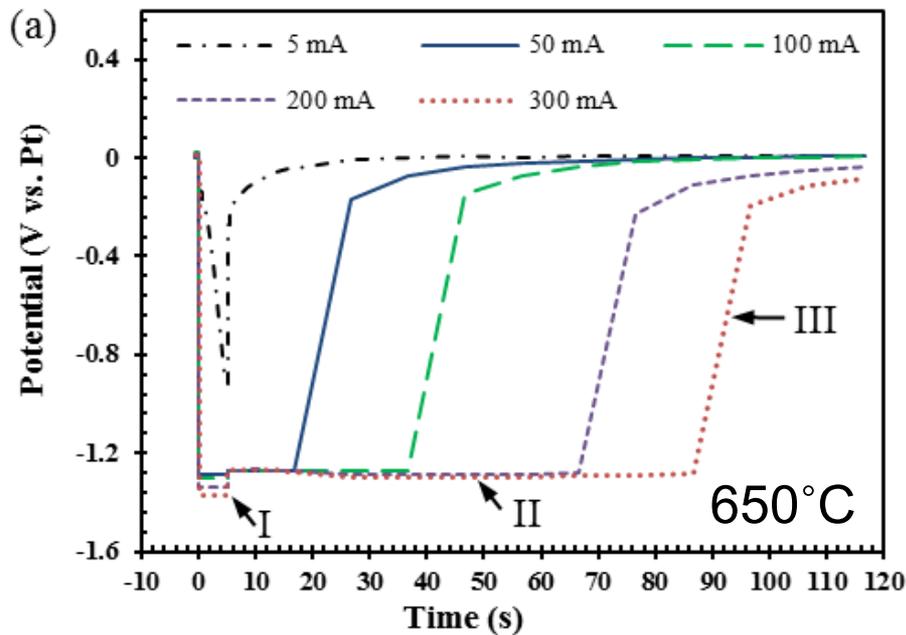
What do we have to do

- ❏ Review the available data
- ❏ Measure fundamental data of element in the salt and liquid Bi
- ❏ Develop chemical (redox) control method
- ❏ Develop and design salt purification system in operation
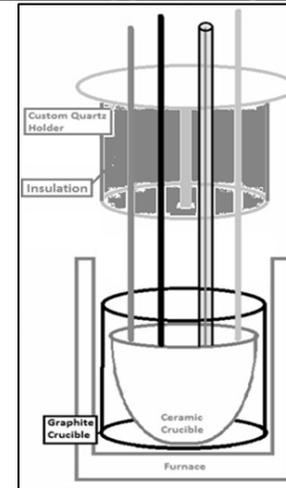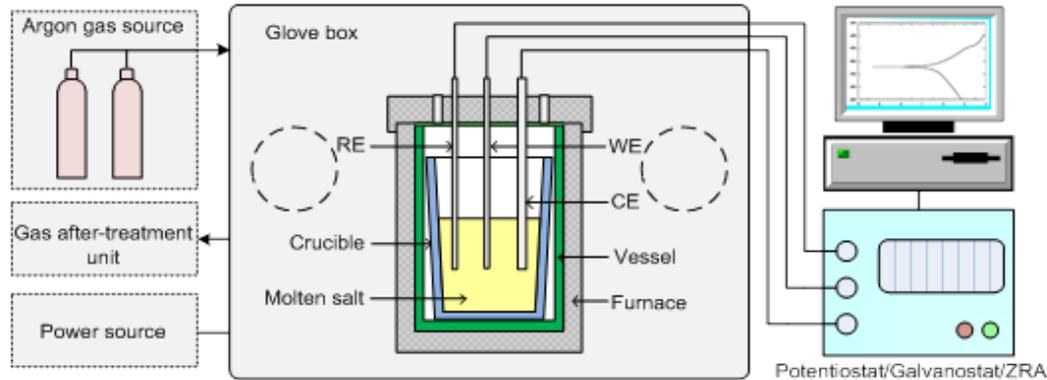
- ❑ A three-electrode system: working electrode (WE); Count electrode (CE) and Reference electrode (RE).
- ❑ Glove box (purged with Argon): the O_2 and H_2O was controlled below 4.0 during all experiments.
- ❑ Electrochemical technology: CV, EIS, LP, *etc*
- ❑ Properties measured: apparent potential, diffusion coefficient, activity coefficient, exchange current,

Determining of reference potential

(a)

Temperature (°C)	$E_{K^+/K}^{redox}$ (V vs. Pt)	Standard Deviation (mV)
650	-1.272	3.2
700	-1.270	2.9
750	-1.271	4.6

Electrolyte resistance of 0.12 Ω·cm² at 650°C, 0.11 Ω·cm² at 700°C and 0.09 Ω·cm² at 750°C

Zone I: 5s current pulse is applied, and the potential of the W electrode becomes more negative due to the formation of a potassium layer on electrode surface. More negative potential at greater current due to the potential drop in electrolyte.
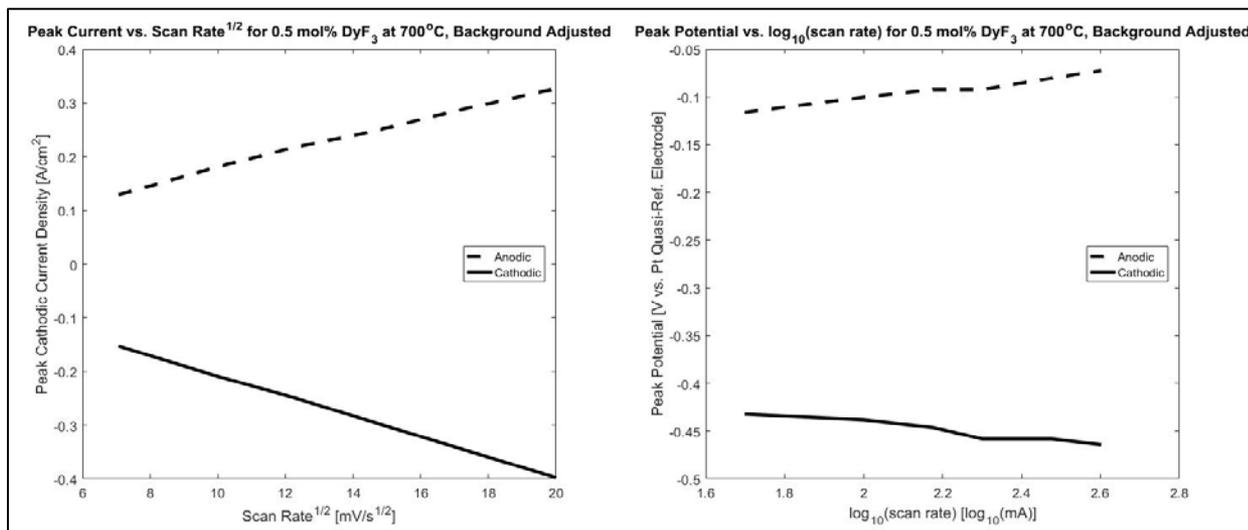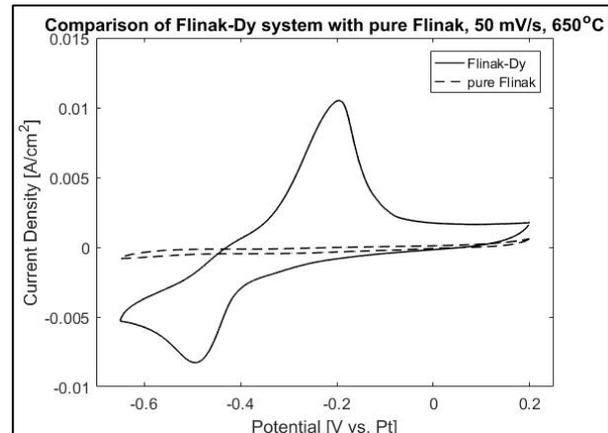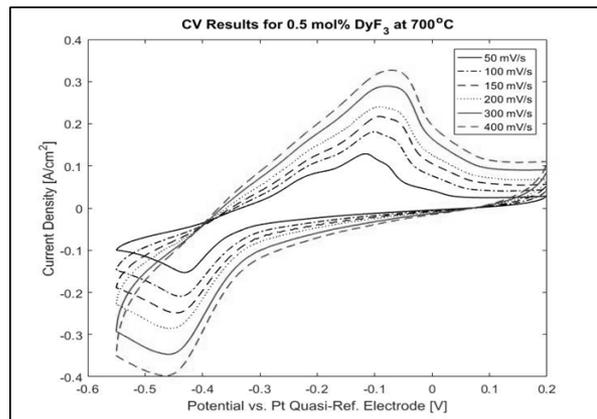
Zone II: No current applied. Consistent potential represents K⁺/K potential.
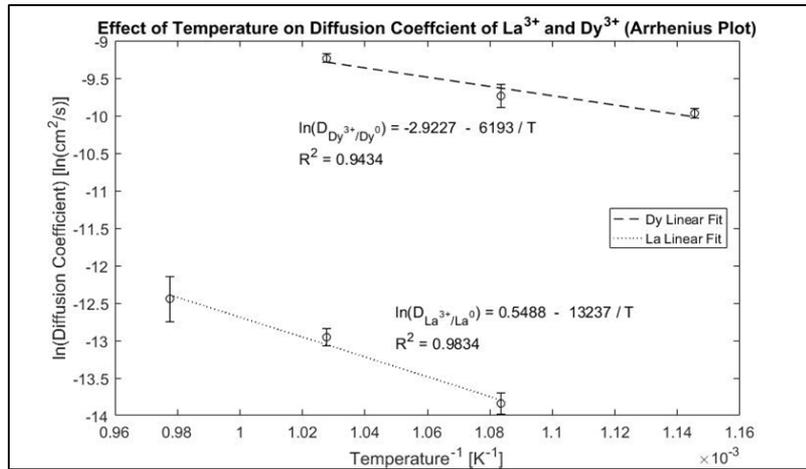
Zone III: Potential returns back due to dissolution of K.

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Measured CV signal

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Diffusion coefficient and Apparent potential of Dy and La

Effect of Temperature on Diffusion Coeffcient of La^{3+} and Dy^{3+} (Arrhenius Plot)

$\ln(D_{Dy^{3+}/Dy^0}) = -2.9227 - 6193/T$

$R^2 = 0.9434$

$\ln(D_{La^{3+}/La^0}) = 0.5488 - 13237/T$

$R^2 = 0.9834$

Effect of Temperature on Apparent Potential of LaF_3 and DyF_3

$E^{0*}_{Dy^{3+}/Dy^0} = 0.062621 + 0.0008804 * T(K)$

$R^2 = 0.98571$

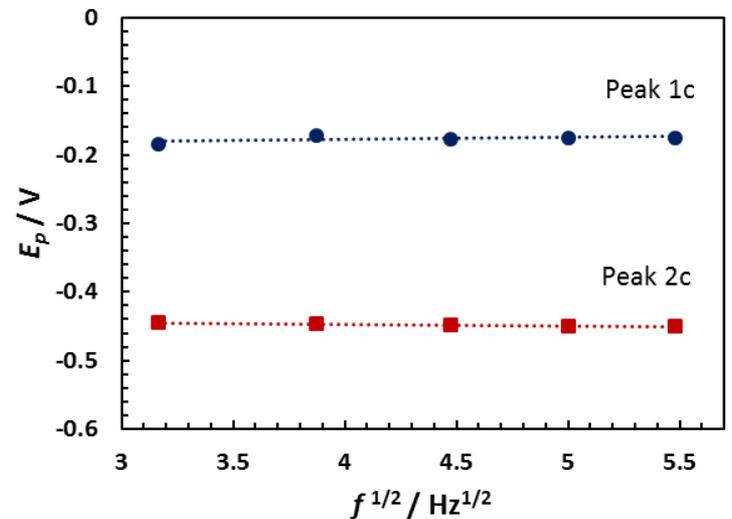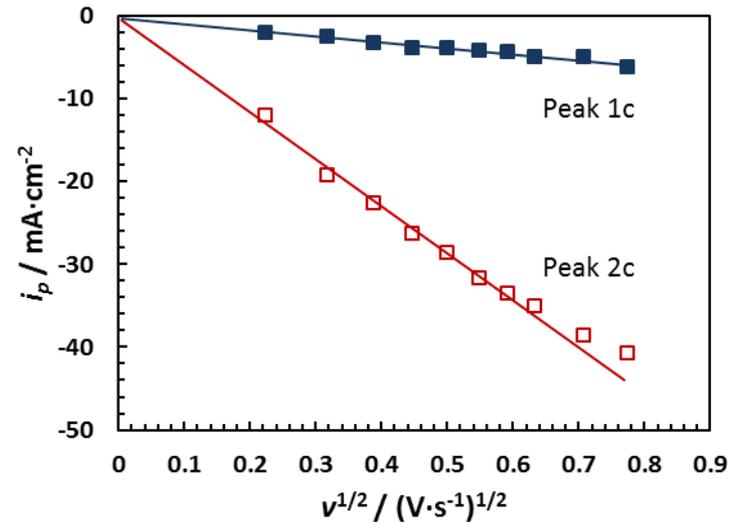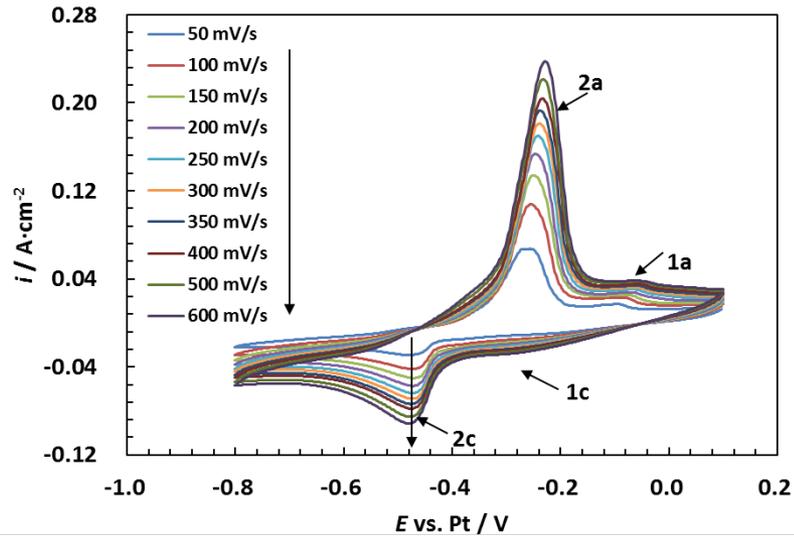$E^{0*}_{La^{3+}/La^0} = -0.36802 + 0.0011187 * T(K)$

$R^2 = 0.98203$

Diffusion activation energy: 51.5 kJ/mol for Dy^{3+}, 127 kJ/mol for La^{3+}
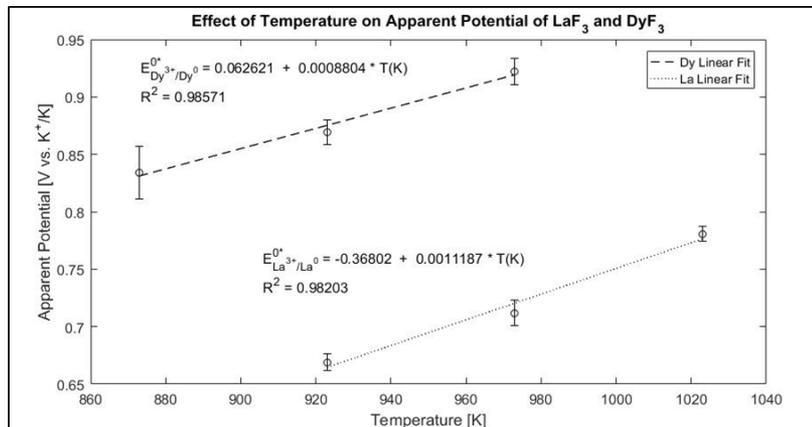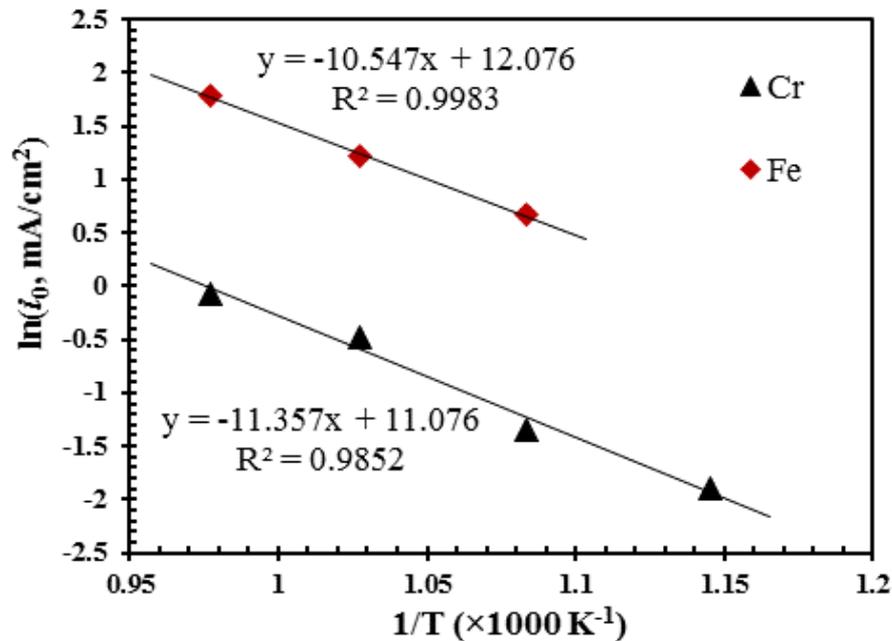
Both diffusion coefficient and apparent potential increases with temperature

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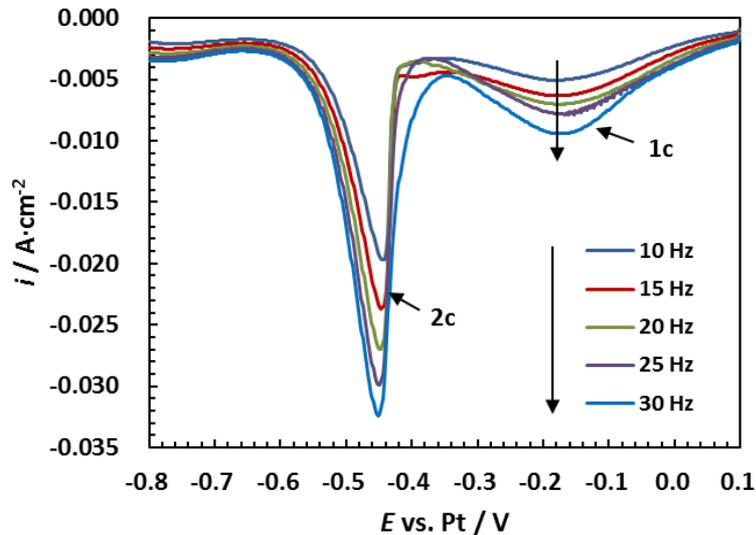
- Activation energy: 94.42 kJ/mol for Cr/Cr^{2+}, and 87.69 kJ/mol for Fe/Fe^{2+} in molten FLiNaK

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Redox Control

- Cover gas control method
- Metal control method
- Dissolved salt control method
- Refueling control method
- Cathodic protection

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Dissolved Salt control method
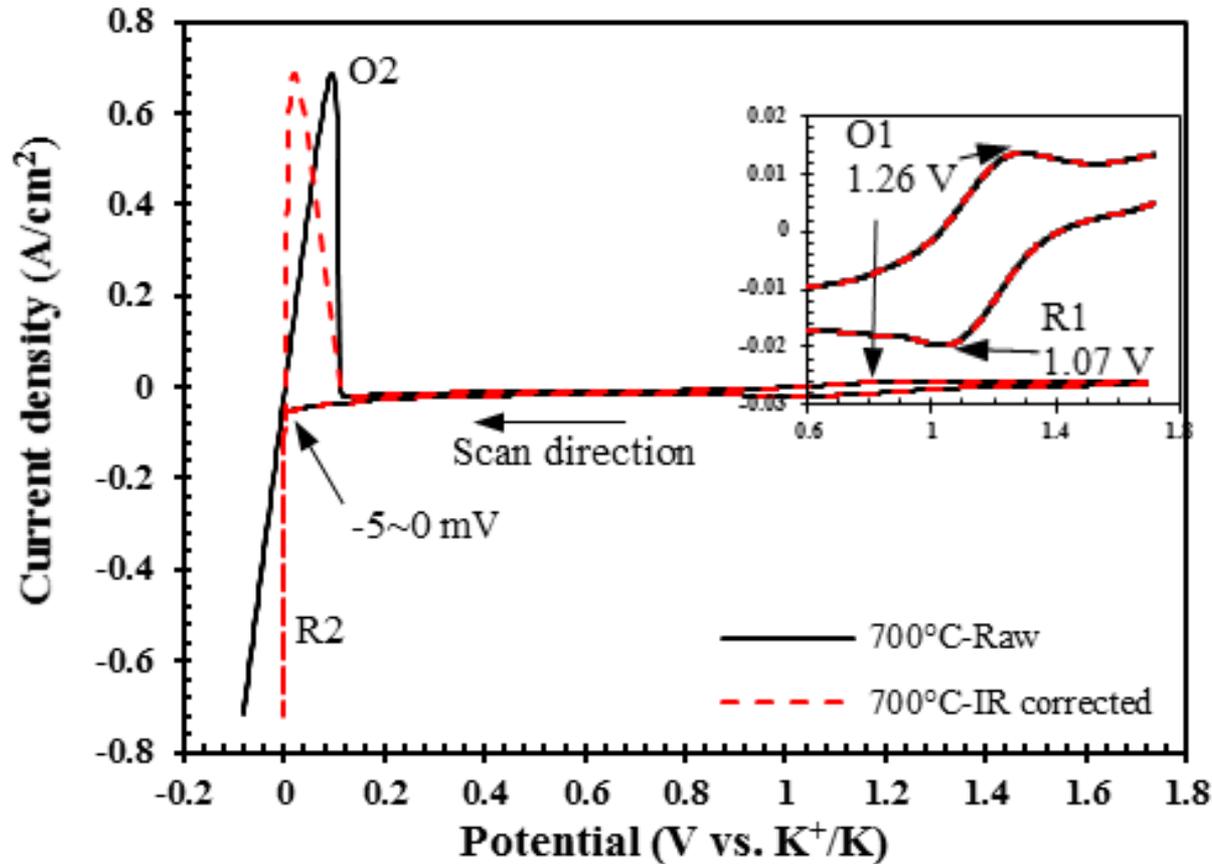
Tungsten electrode, 700˚C, FLiNaK-EuF$_3$-EuF$_2$, 200 mV/s

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Concentration ratio of Eu^{3+}/Eu^{2+}

- Randles-Sevcik equation is not valid for system containing both members (e.g., both U^{4+} and U^{3+})) of the redox couple:

$$i_{\mathrm{p}} = 0.4463nFC_{\mathrm{b}}D^{1/2}\left(\frac{nFv}{RT}\right)^{1/2}$$

- Theory developed by Keightley et al. are adopted [1]:

- $\vec{\imath} = nF\left(C_{\mathrm{b}}^{\mathrm{Red}}D_{\mathrm{Red}}^{1/2} + C_{\mathrm{b}}^{\mathrm{Ox}}D_{\mathrm{Ox}}^{1/2}\right)\left(\frac{nFv}{RT}\right)^{1/2}\chi(\xi;\xi_i)$

- $\overleftarrow{\imath} = nF\left(C_{\mathrm{b}}^{\mathrm{Red}}D_{\mathrm{Red}}^{1/2} + C_{\mathrm{b}}^{\mathrm{Ox}}D_{\mathrm{Ox}}^{1/2}\right)\left(\frac{nFv}{RT}\right)^{1/2}[\chi(2\xi_r - \xi, \xi_i) - \chi(2\xi_r - \xi, \xi_r) - \chi(-\xi, \xi_r)]$

- where $\chi\,(x, \alpha) = \frac{\mathrm{d}^{1/2}}{\mathrm{d}x^{1/2}}\frac{1}{2\sqrt{\pi}}\left[\tanh\left(\frac{x+\alpha}{2}\right) - \tanh(\frac{\alpha}{2})\right];\ \xi = nF(E - E_{1/2})/RT$

[1] A.M. Keightley, et al, J. Electroanal. Chem. 322 (1992) 25-54.

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Determined concentration ratio

Predicted coordinates of cyclic voltammetric peaks and the calculated concentration ratio.

Test #	$\dfrac{nF}{RT}\Delta E_p$	$\dfrac{C_{Eu^{2+}}}{C_{Eu^{3+}}}\sqrt{\dfrac{D_{Eu^{2+}}}{D_{Eu^{3+}}}}$	$\dfrac{\lvert i_p\rvert}{C^b}\sqrt{\dfrac{RT}{n^3F^3vD^b}}$	$\dfrac{nF}{RT}(E_{1/2}-E_p^c)$	$\dfrac{C_{Eu^{3+}}}{C_{Eu^{2+}}}$†
-	2.236	0	0.4463	1.109	-
650°C #1	2.814	1.31	0.5415	1.697	1.21
650°C #2	3.102	2.13	0.5596	1.988	1.96
650°C #3	3.075	2.04	0.5581	1.959	1.88
700°C #1	2.855	1.42	0.5447	1.741	1.29
700°C #2	3.067	2.02	0.5578	1.953	1.83
700°C #3	3.119	2.18	0.5605	2.003	1.98
750°C #1	2.740	1.13	0.5356	1.623	1.08
750°C #2	2.674	0.98	0.5299	1.558	0.93
750°C #3	2.842	1.39	0.5439	1.729	1.33

†Calculated by the determined diffusion coefficient.

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XPS examination

- Eu^{3+}/Eu^{2+} ratio ≈ 2:1
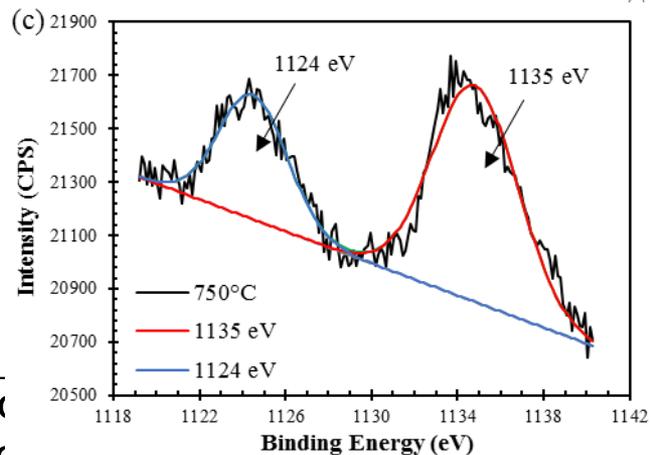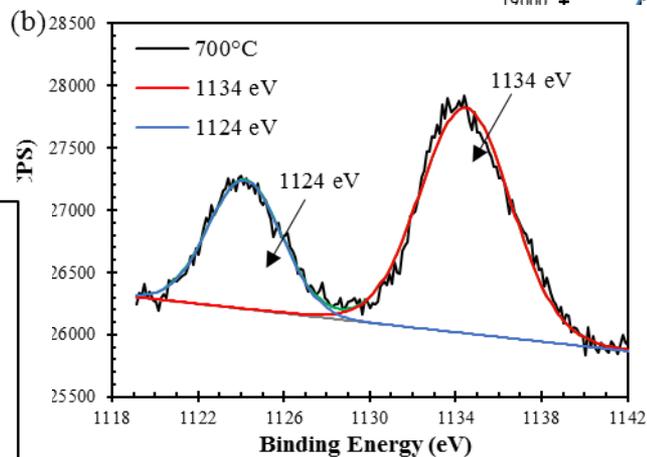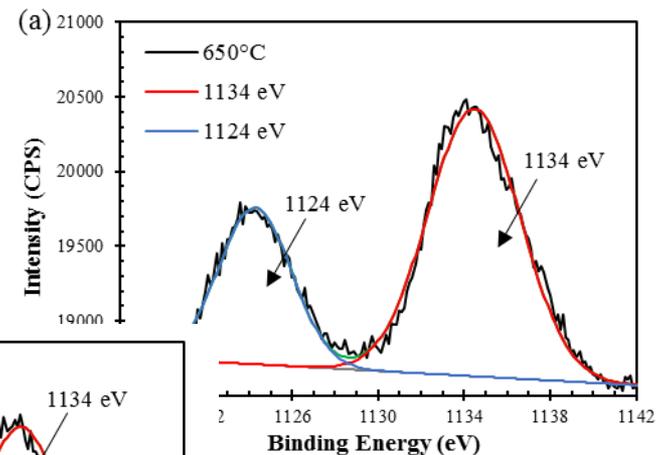
Formal potential for Eu^{3+}/Eu^{2+}

- $E^* = E_{1/2} + \frac{RT}{nF} ln\left(\frac{D_{Ox}}{D_{Red}}\right)^{\frac{1}{2}}$

**Table Summary of formal standard potential from this work and references**

Temperature (°C)	E^* (V vs. F_2/F^-)	Salt	Total concentration of Eu in salt	Source
550	-3.94 or -3.82[†]	FLiNaK	0.072 mol/kg	[1]
650	-3.836 ± 0.005	FLiNaK	0.048 mol/kg	This work
700	-3.787 ± 0.009	FLiNaK	0.048 mol/kg	This work
750	-3.732 ± 0.006	FLiNaK	0.048 mol/kg	This work
800	-3.53 ± 0.01	$LiF-CaF_2$	0.100 mol/kg	[2]
820	-3.46 ± 0.01	$LiF-CaF_2$	0.100 mol/kg	[2]
840	-3.40 ± 0.01	$LiF-CaF_2$	0.100 mol/kg	[2]
870	-3.33 ± 0.01	$LiF-CaF_2$	0.100 mol/kg	[2]

[1] W. Huang, et al. Electrochimi. Acta 147 (2014) 114-120.
[2] L. Massot, et al. Electrochimi. Acta 54 (2009) 6361-6366

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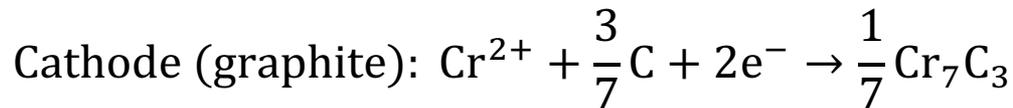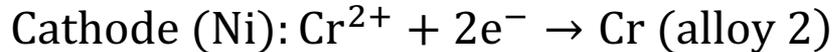*Invent the Future*

Redox potential window

- Solid line: metal dissolution at limit activity of 10^{-6}

- Dotted line: reduction of oxidants. $HF/H_2 = 0.1$: a mole ratio of $HF/H_2 = 0.1$ at 1 atm total pressure

- Double solid line: redox potential calculated based on measured apparent potential.

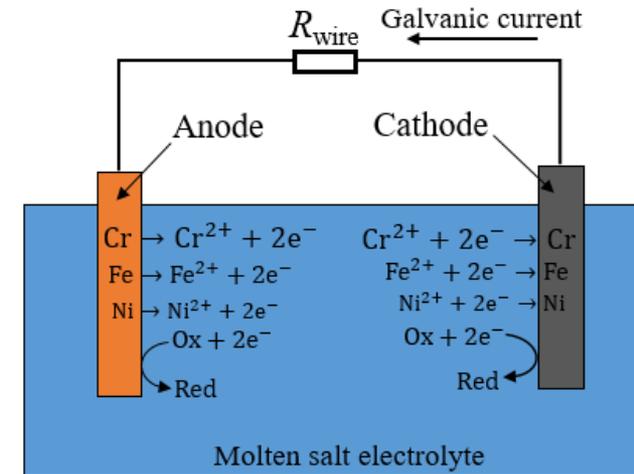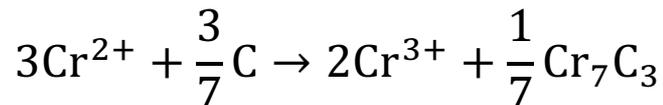- All potentials calculated based on ΔG° of fluorides at supercooled state except gaseous MoF_5, MoF_6, WF_6, and HF.

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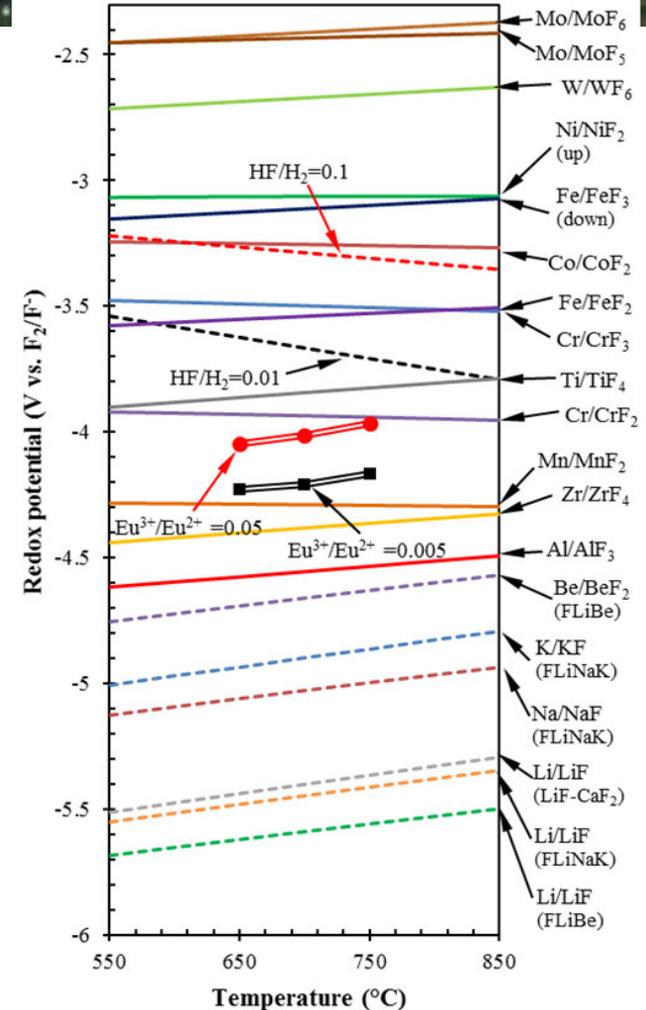
Acceleration mechanisms of Cr Dissolution

❑ Galvanic Corrosion

❑ Direct reduction of Cr^{2+}

Anode: $Cr \text{ (alloy 1)} \rightarrow Cr^{2+} + 2e^-$

Cathode (Ni): $Cr^{2+} + 2e^- \rightarrow Cr \text{ (alloy 2)}$

Cathode (graphite): $Cr^{2+} + \frac{3}{7}C + 2e^- \rightarrow \frac{1}{7}Cr_7C_3$

❑ Disproportionation reaction of Cr^{2+}

$$3Cr^{2+} \rightarrow 2Cr^{3+} + Cr$$

$$3Cr^{2+} + \frac{3}{7}C \rightarrow 2Cr^{3+} + \frac{1}{7}Cr_7C_3$$
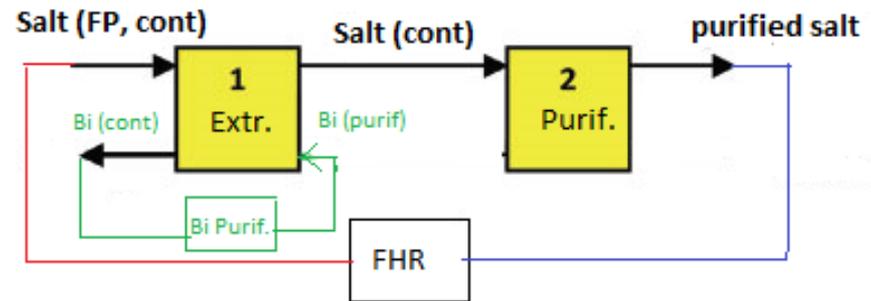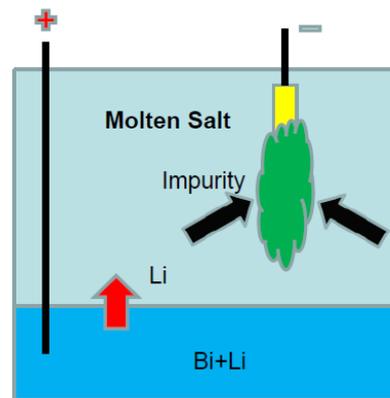

Schematic of the direct reduction of the corrosion products on the cathode during galvanic corrosion. Ox represents the residual oxidants.
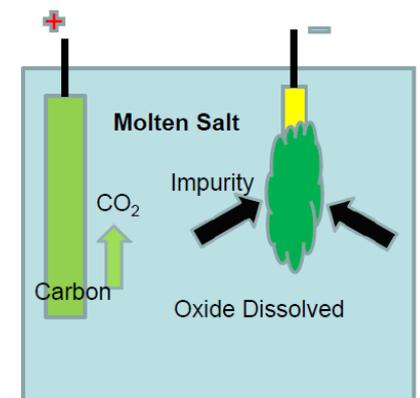
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Salt Purification Method

❑ **Bi-Li Extractor**

❑ **Sacrificial Electrode**

(a) Bi+Li sacrificial anode   (b) Carbon sacrificial anode

Rare earth metals	Solid in equilibrium with the liquid	$\ln X_s = A - (B/T)$		Temperature range (K) (T_{min}, T_{max})	Reference
		A	B		
Y	YBi	0.8549	6195	588–1000	(Schweitzer and Weeks, 1961b)[a]
	YBi	−2.8783	5941	648–948	(Kober et al., 1971a)
La	LaBi$_2$	2.1359	5366	548–933	(Schweitzer and Weeks, 1961b)
	LaBi$_2$	5.8391	8044	648–948	(Kober et al., 1968)
	LaBi$_2$	3.9875	6705	548–948	Overall fitting[a]
Ce	CeBi$_2$	2.4958	5804	573–723	(Schweitzer and Weeks, 1961b)
	CeBi$_2$	4.4073	6978		(Pleasance, 1959 −1960)
	CeBi$_2$	2.9748	6289	648–948	(Kober et al., 1971b)
	CeBi$_2$	2.7353	6046	573–948	Overall fitting[a]
Pr	PrBi$_2$	0.4704	4502	548–623	(Schweitzer and Weeks, 1961b; Weeks, 1971)
	PrBi$_2$	3.3100	6287	623–723	(Schweitzer and Weeks, 1961b)
Nd	NdBi$_2$	2.2366	5873	573–773	(Schweitzer and Weeks, 1961b)
	NdBi$_2$	3.3813	6287	573–923	(Smith, 1972a)
Sm	SmBi$_2$	5.6721	7492	573–773	(Schweitzer and Weeks, 1961b)
Eu	EuBi$_2$	6.0346	6847	598–823	(Smith, 1972b)
Ho	HoBi	−0.65	1818	673–873	(Antonchenko et al., 2009)
Er	ErBi	2.7927	7054	775–975	(Petrashkevich et al., 1976)
	ErBi	1.0378	5509	890–1090	(Yamshchikov et al., 1982)
	ErBi	1.9153	6281	775–1090	Overall fitting[a]
Yb	YbBi$_2$	4.6154	5527	553–673	(Weeks, 1965, 1971)
Lu	Unknown	0.9790	6587	623–773	(Weeks, 1965, 1971)

Rare earth metals	$\ln \gamma = A - (B/T)$		Temperature range (K) (T_{min}, T_{max})	Reference
	A	B		
Y	−2.1049	16,502	673–773	(Kurata et al., 1996)
	0.8291	20,063	773–1023	(Kober et al., 1971a)
La	1.9437	25,494	673–953	(Gschneidner and Calderwood, 1989a; Kober et al., 1968)
	3.8249	−26,750	653–823	(Castrillejo et al., 2007)
	3.2836	−26,437	673–773	(Kurata et al., 1996)
	3.3810	−26,646	850–1100	(Yamana et al., 2001)
	3.1083	−26,332	653–1100	Overall fitting[a]
Ce	4.6751	−26,254	773–923	(Kober et al., 1971b)
	2.8145	−25,235	673–773	(Kurata et al., 1996)
	3.7046	−26,089	653–823	(Castrillejo et al., 2007)
	5.5280	−27,155		(Yamana et al., 2001)
	2.3606	−25,612	735–937	(Dong et al., 2008a)
	3.8165	−26,067	653–937	Overall fitting[a]
Pr	6.2425	−27,315	673–823	(Castrillejo et al., 2005a, 2007)
	2.8386	−24,994	673–773	(Kurata et al., 1996)
	6.6995	−27,496		(Kober et al., 1985)
	7.6137	−28,554		(Lebedev, 1993)
	5.8486	−27,090	673–823	Overall fitting[a]
Nd	5.1335	−26,470		(Yamana et al., 2001; Lebedev, 1993)
Sm	4.0293	−27,111		(Kurata et al., 1996; Lebedev et al., 1975)
Eu	3.4520	−20,002		(Kurata et al., 1996; Dybinin et al., 1985)
Gd	3.1689	−23,060	775–1055	(Sheng et al., 2001a)
	4.4311	−24,326	850–1100	(Yamana et al., 2001)
	3.7226	−24,163		(Lebedev, 1993)
	2.8386	−22,697		(Kober et al., 1983)
	1.2268	−20,724	673–773	(Kurata et al., 1996)
	3.0776	−22,994	673–1100	Overall fitting[a]
Tb	4.6295	−24,035	850–1100	(Yamana et al., 2001)
Dy	3.3305	−23,310	850–1100	(Yamana et al., 2001)
	2.3099	−21,811	850–1101	(Sheng et al., 2002)[a]
Er	3.9391	−21,946	850–1100	(Yamana et al., 2001)
	−3.7677	−15,082	773–973	(Gschneidner and Calderwood, 1989a)

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Bi-Ce

Fundamental data of Fission products in liquid Bi-Enthalpy of mixing

Bi-Ce
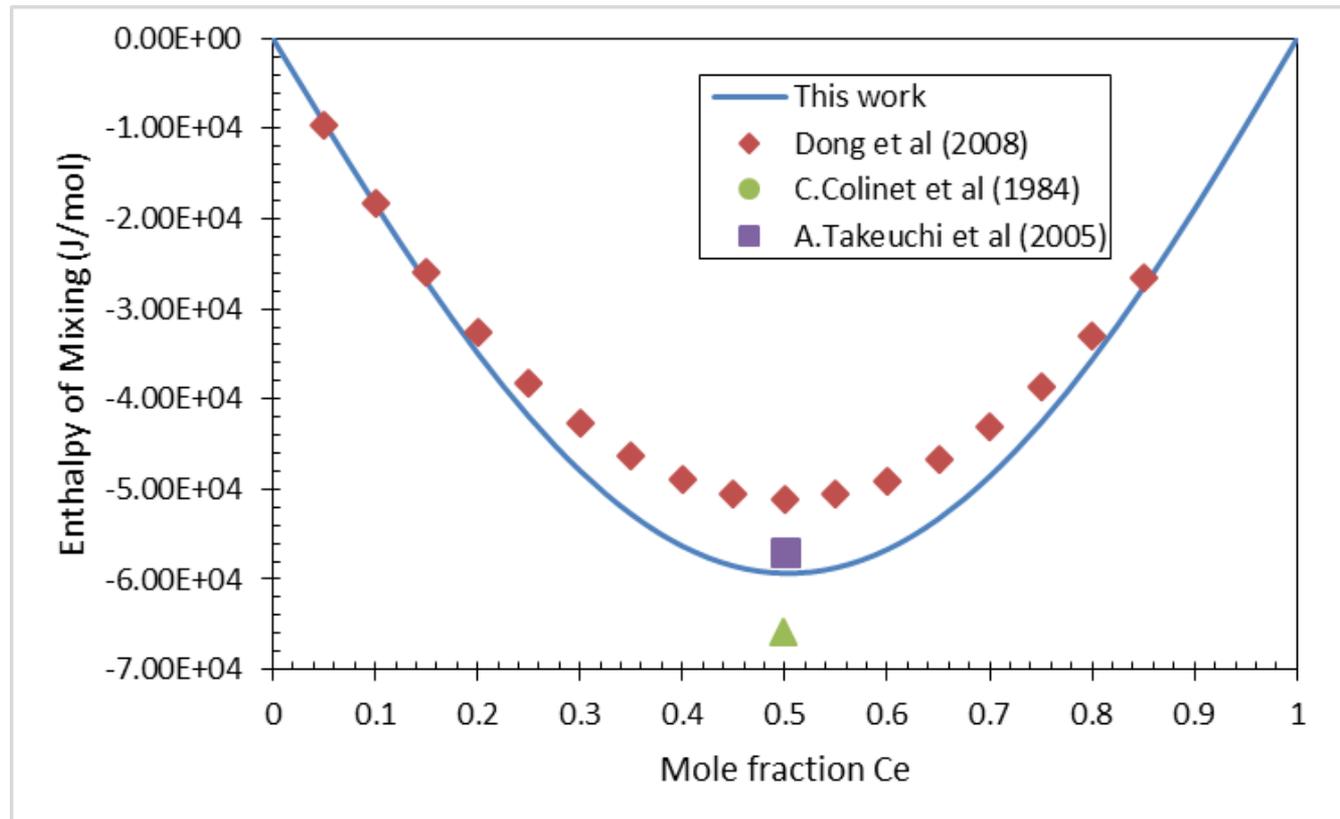
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Activity coefficient of Fission products in liquid
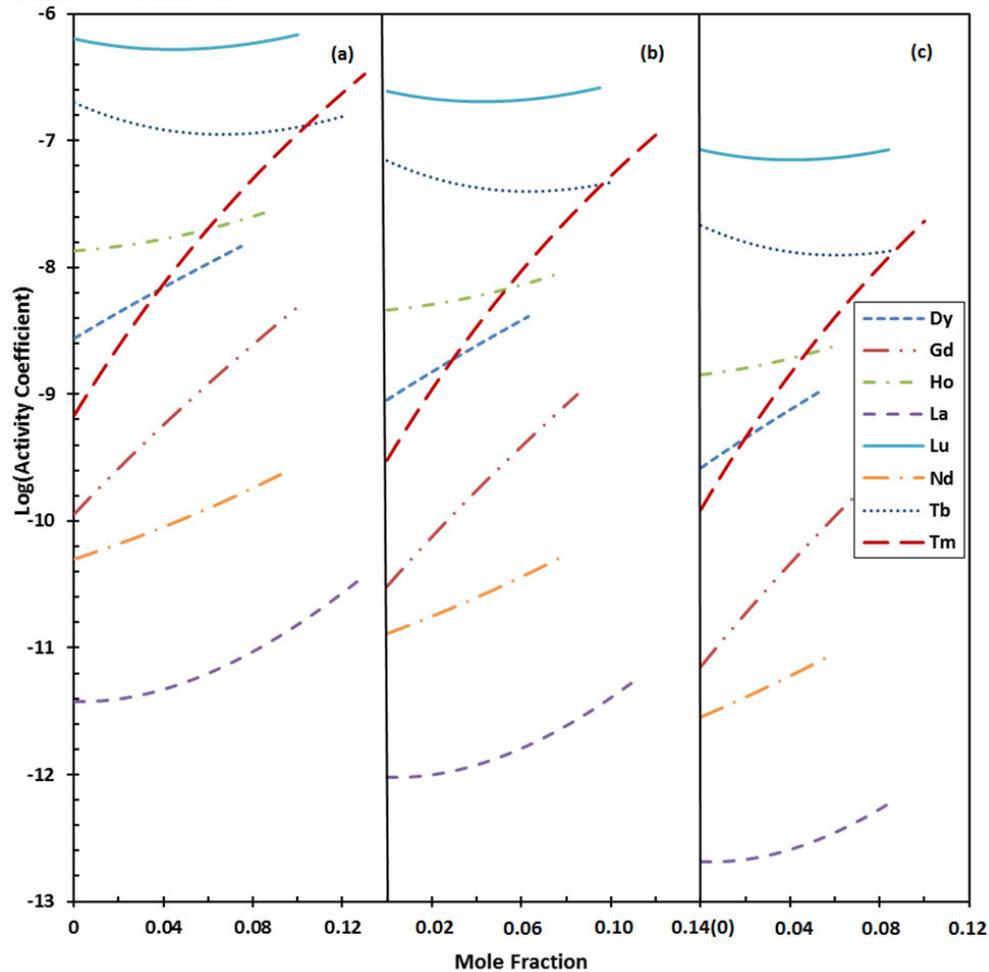
973 K   923 K   873 K
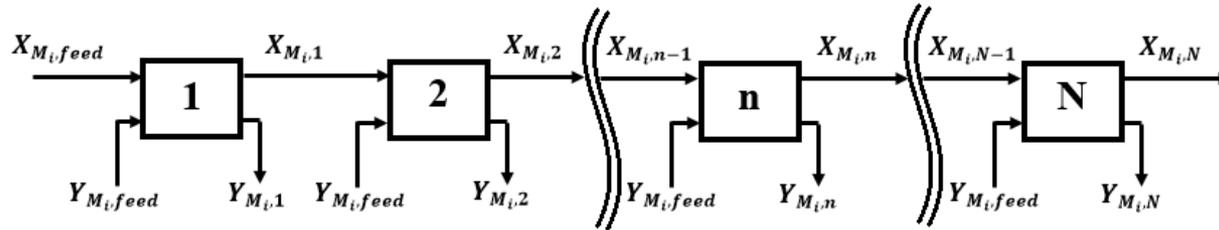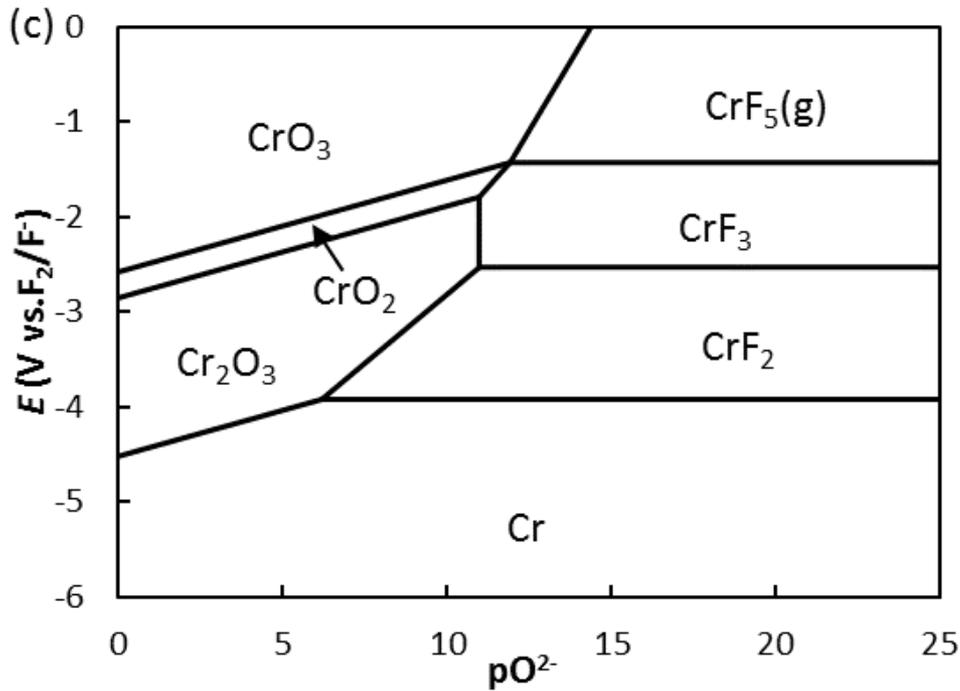
$$\sum_{i=1}^{m} \frac{n_i X_{M_i}^{I\,n_i+}}{Bi_{feed} + Salt_{feed}D_{M_i}} = \frac{Y_{Li}^{I}D_{Li} - X_{Li+}^{I}}{Bi_{feed} + Salt_{feed}D_{Li}}$$
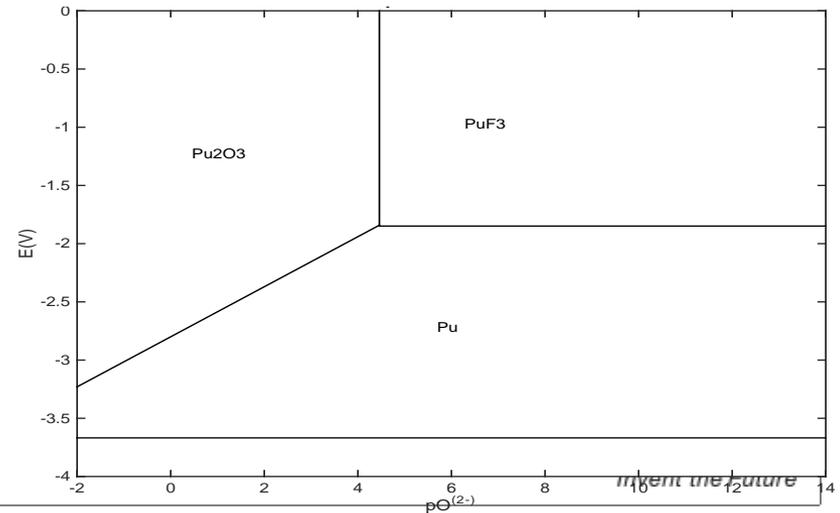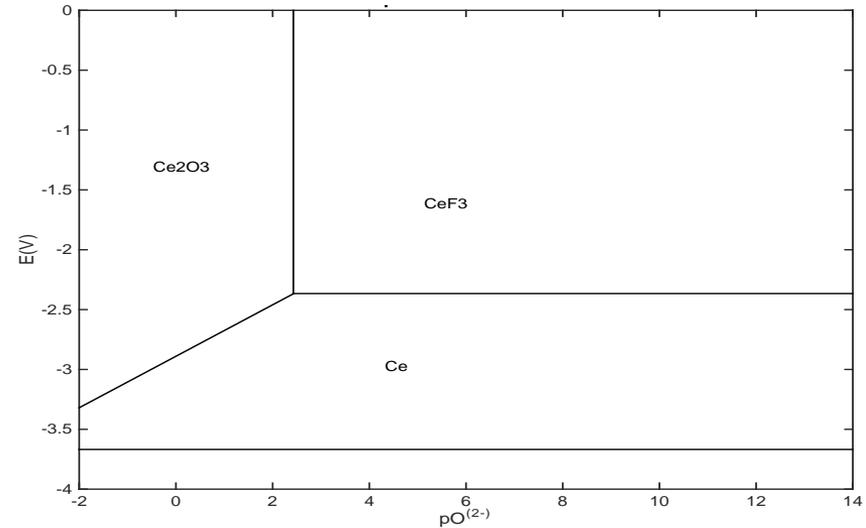
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One Example

8 Stage Liquid Bi Extraction
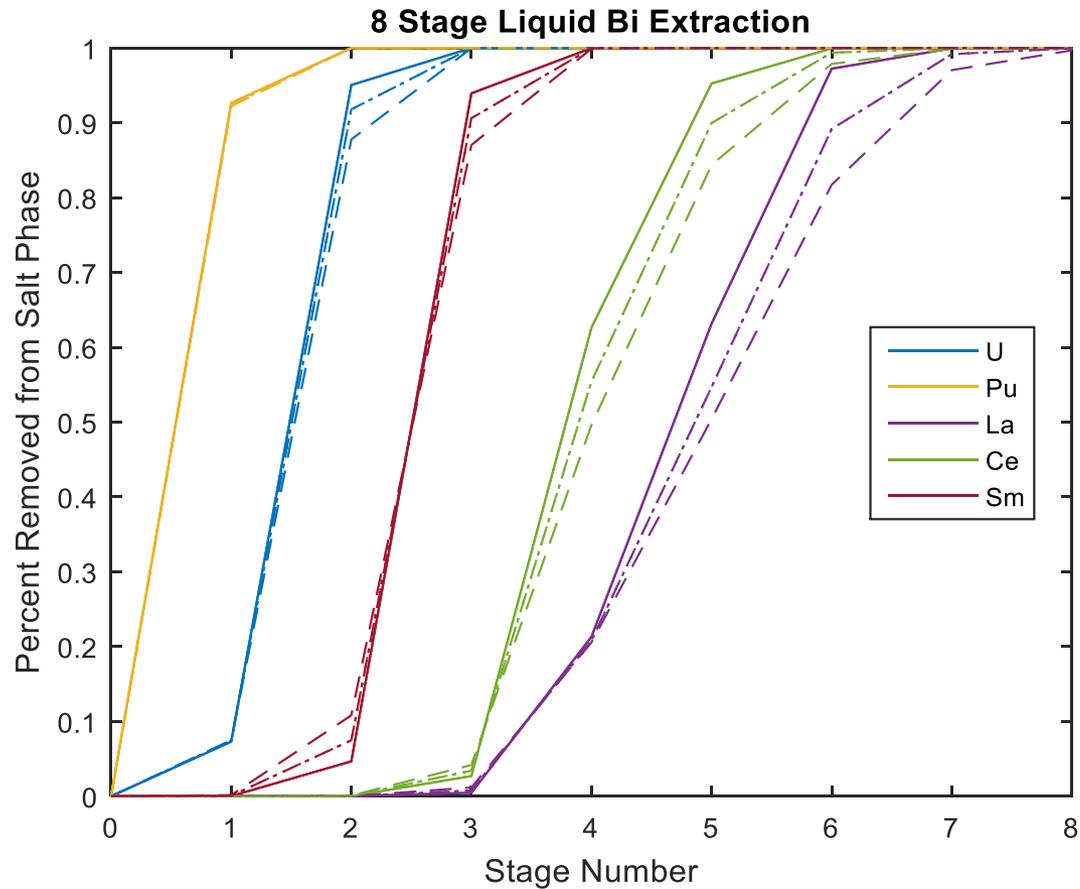
700C in FLiBe. $a_{M^{n+}}$ of 10^{-6} is used for the calculation of related equilibrium lines
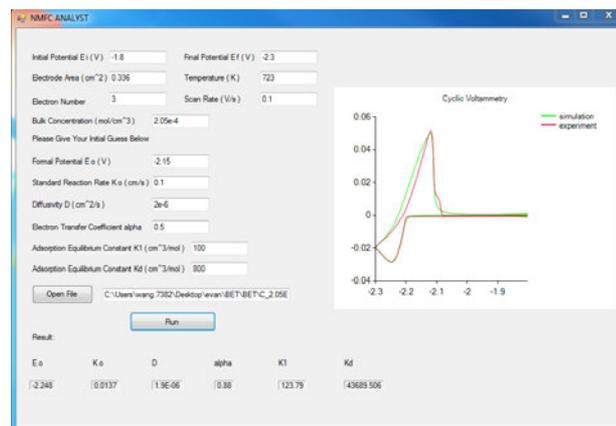
Chloride Salt Chemistry

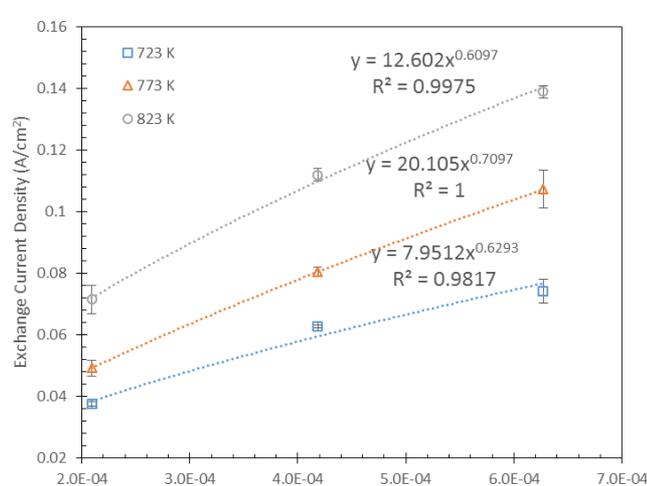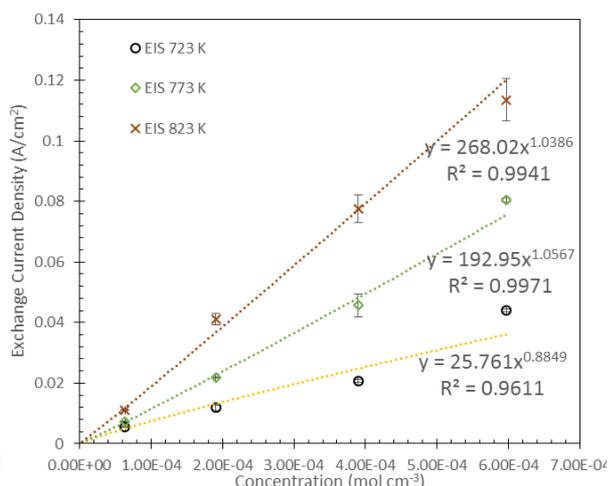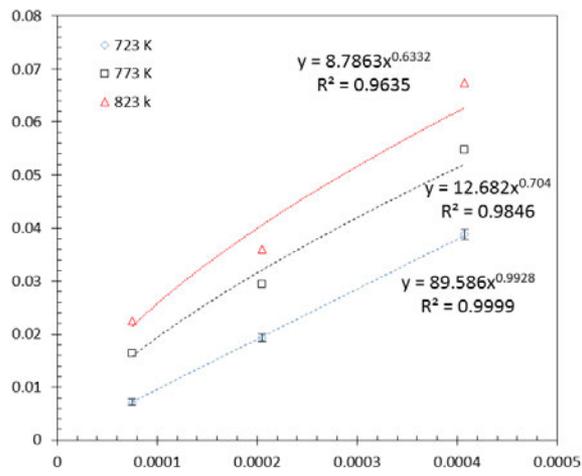❑ Nd, Gd, and La for high concentration up to 9wt% in KCl-LiCl

La^{3+}

Gd^{3+}

Nd^{2+}

Questions?

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