Berkeley UNIVERSITY OF CALIFORNIA Nuclear Engineering

Molten Fluoride Salt Chemistry

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Advanced Non-Light Water Reactors –
Materials & Component Integrity Workshop

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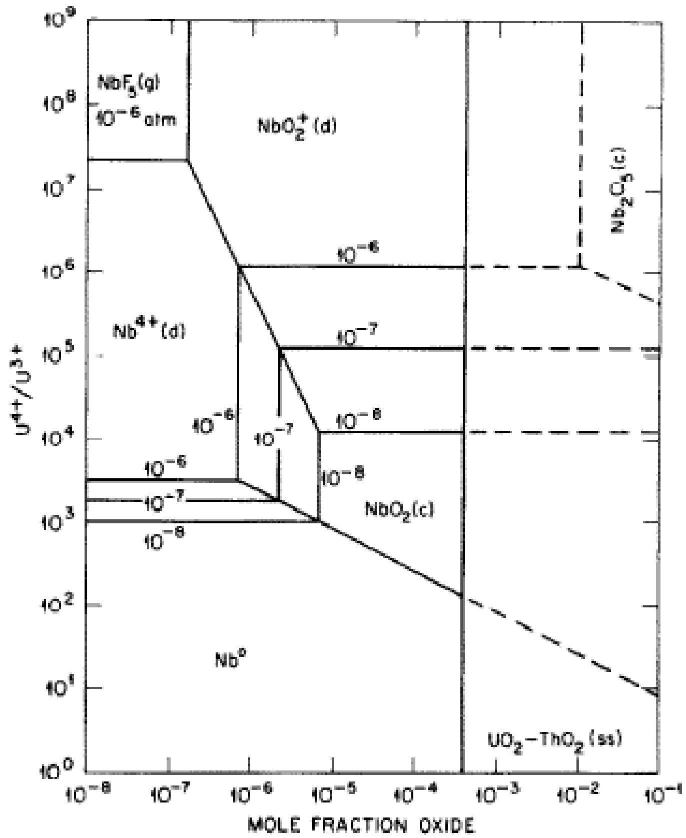
U.S. Department of Energy

Complex Ion Formation | Example: Niobium Solubility in FLiBe

Pseudo-Pourbaix Diagram



Ting, Baes, Bamberger, Mamantov. The Oxide Chemistry of Niobium in Molten LiF-BeF2 Mixtures. J. Inorg. Chem. 1977 (39) pp. 1803-1808.

Olander, Fukuda, Baes. Equilibrium Pressures over BeF_2/LiF(Flibe) Molten Mixtures. Fusion Sci. Technol. 41, (2001).

Pourbaix diagram for niobium: solubilitization of an otherwise volatile species state (Nb^{5+})

Oxidation (electron transfer) reaction:

Nb^{4+} <-> $Nb^{5+} + e^-$

Association-dissociation (complexation) reaction:

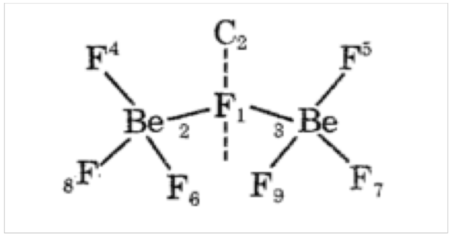
$Nb^{5+} + 2O^{2-}$ <-> NbO_2^-

Other examples:

$Be^{2+} + 4F^-$ -> BeF_4^{2-}

$2BeF_4^{2-}$ <-> $Be_2F_7^- + F^-$

$(Be_2F_7)^{3-}$



Polymeric Structures and Bridging Fluorines

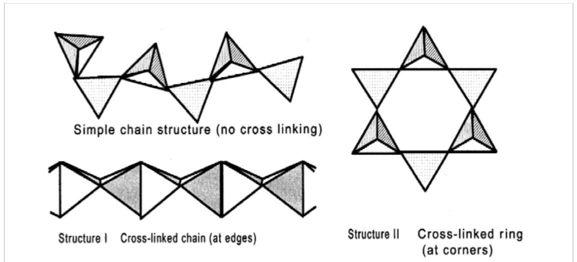


Fig. 4. Elementary polymeric structures of BeF_2 in Flibe.

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Complex Ion Formation | Speciation Diagrams and Fluoracidity

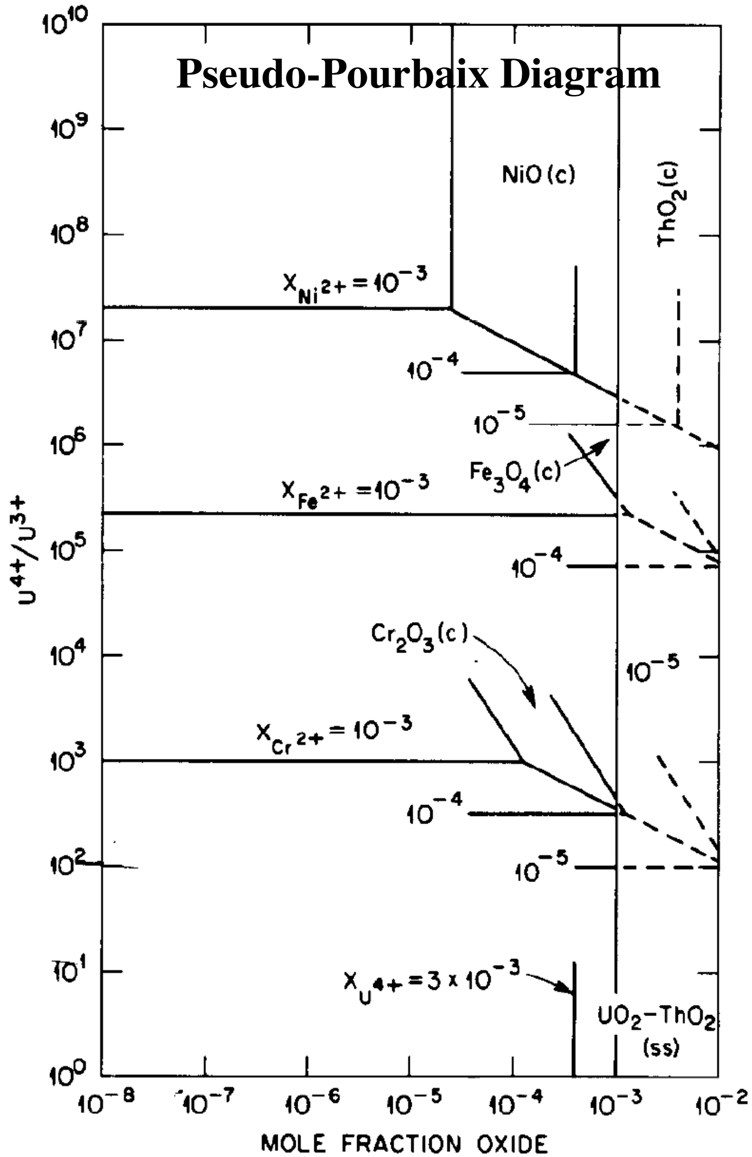
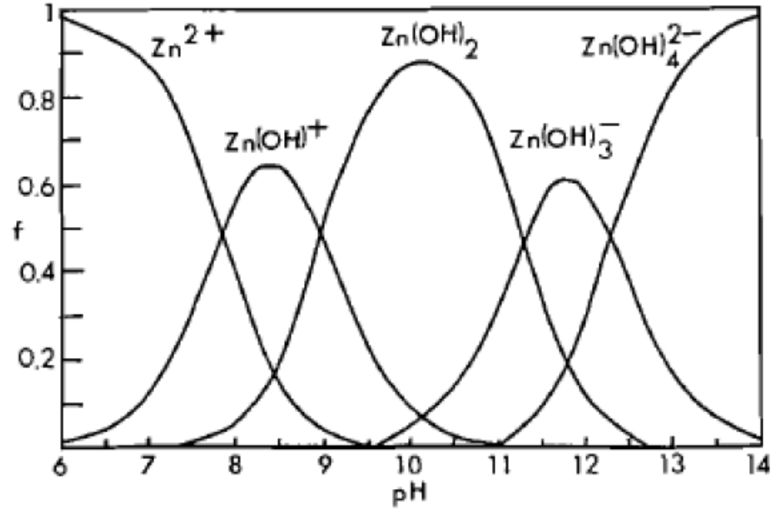


Fig. 11. Pourbaix diagram for the structural metals in LiF–BeF_2–ThF_4 (72–16–12 mol %) at 600°C.

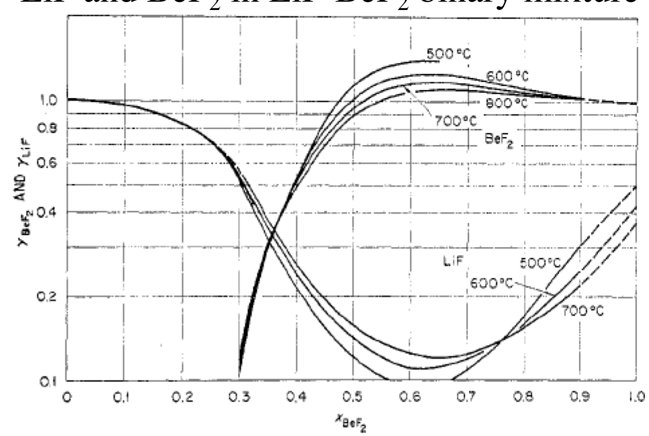
Speciation Diagram

Zinc in aqueous solution at 25°C



Activity Coefficients

LiF and BeF_2 in LiF-BeF_2 binary mixture



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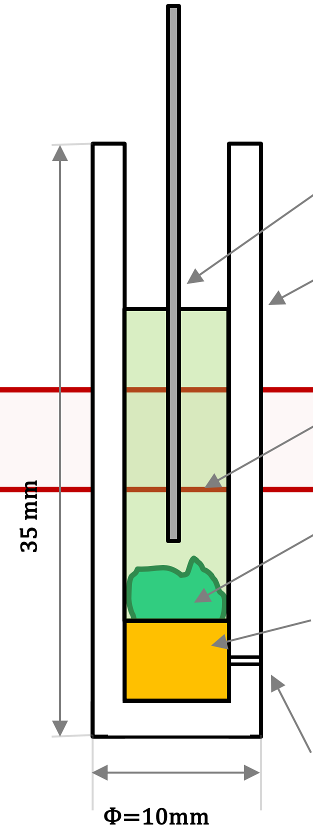
Baes, Molten Salt Reactor Fuels. *Journal of Nuclear Materials* 51 (1974) 149-162.
R. A. Reichle et al., Can. J. Chem. 53 (24) 3841–3845 (1975). [

Reference Electrodes | Thermodynamic Reference Electrode for FLiBe



Ni rod

Boron Nitride tube:

- Electrical insulator
- Stable in fluoride melts [Jenkins, 1968]

Ni^{2+}-saturated FLiBe:

- Known Solubility [Blood, 1964]

Excess NiF2

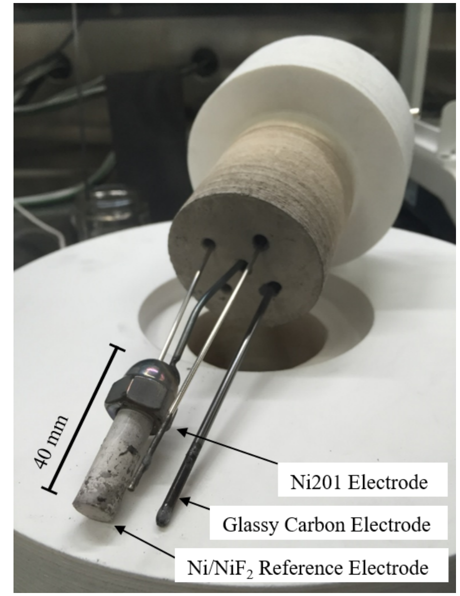
LaF3 crystal:

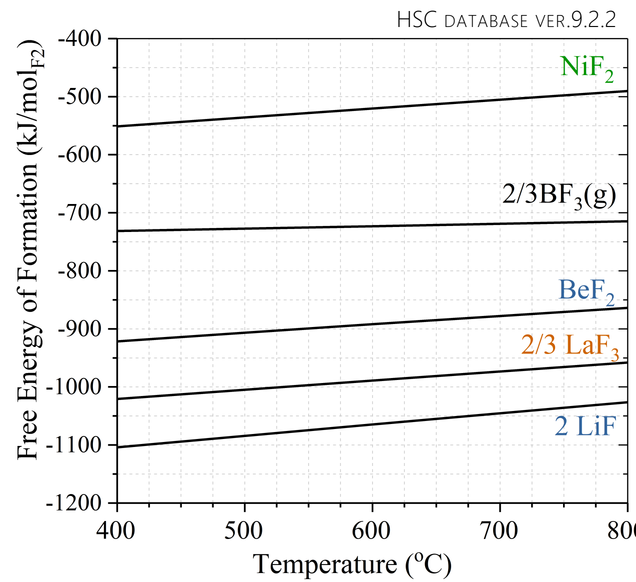
- F^- Ionic conductor [Bronstein,1972]

Φ= 0.3 mm hole

F. Carotti, H. Wu, and R. O. Scarlat. Characterization of a Thermodynamic Reference Electrode for Molten LiF-BeF2 (FLiBe). Journal of The Electrochemical Society, 164 (12) H854-H861 (2017).

F. Carotti, A. Laudenbach, H. Wu, M. Straka, R.O. Scarlat. Characterization of a Thermodynamic Reference Electrode for Molten LiF-BeF2 (FLiBe). Part II: Materials Analysis. Journal of the Electrochemical Society, 166 (15) H835-H841 (2019).

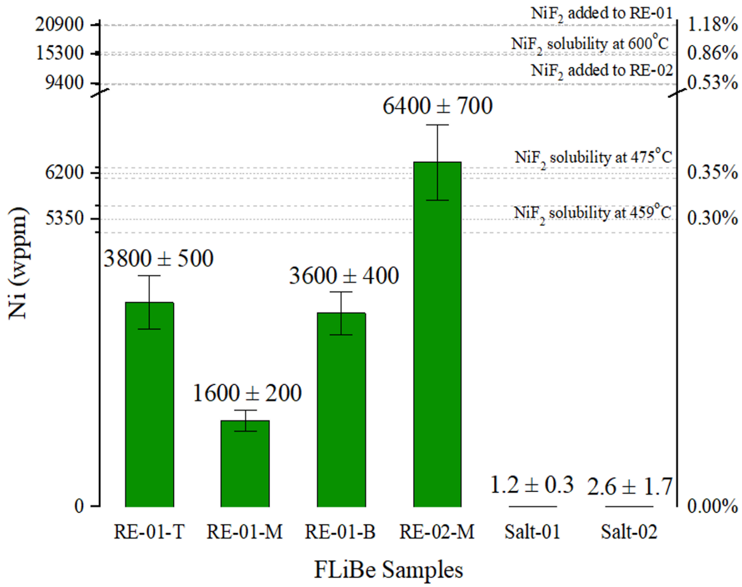


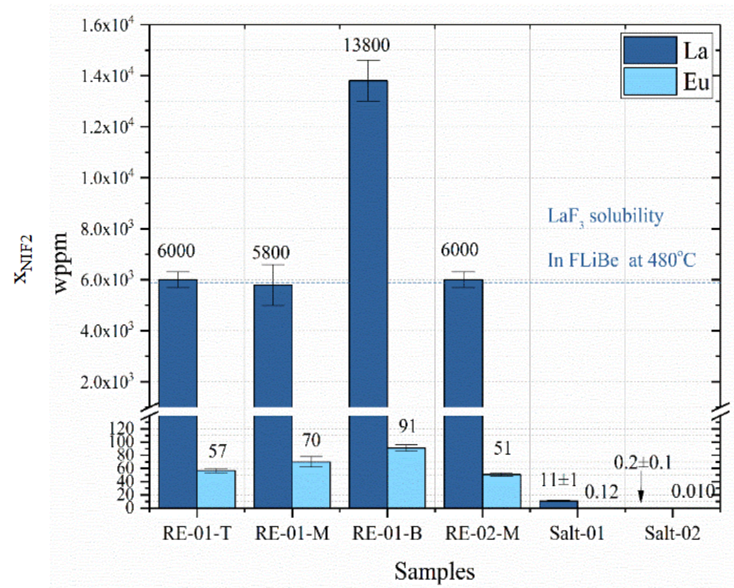


Expected chemical interaction between Ni^{2+} and BN

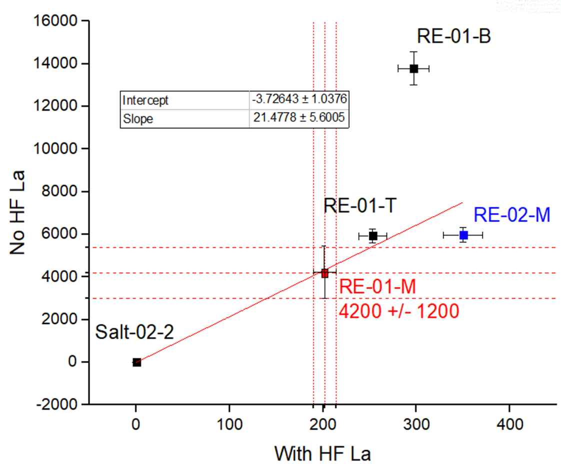
$$3\,NiF_2 + 2BN = 3Ni + 2\,BF_3(g) + N_2(g)$$

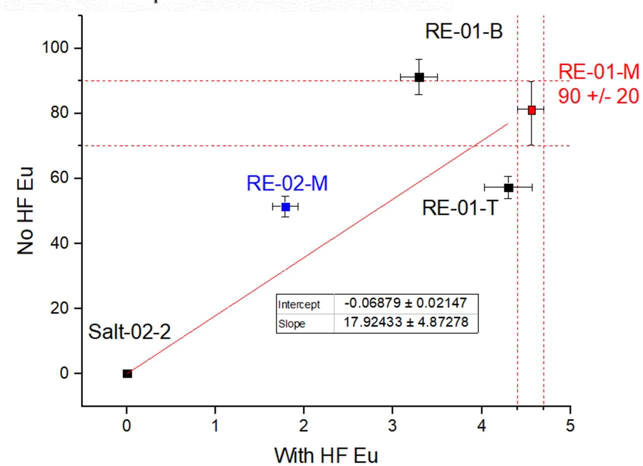
Reference Electrodes | Thermodynamic Reference Electrode for FLiBe & Salt Elemental Analysis





Standards and Standard Methods for Elemental Analysis are Needed





[1] F. Carotti, A. Laudenbach, H. Wu, M. Straka, R.O. Scarlat. Characterization of a Thermodynamic Reference Electrode for Molten LiF-BeF2 (FLiBe). Part II: Materials Analysis. Journal of the Electrochemical Society, 166 (15) H835-H841 (2019). [2] J. E. Seifried, R. O. Scarlat, P. F. Peterson, E. Greenspan. A General Approach for Determination of Acceptable FLiBe Impurity Concentrations in FHRs. Nuclear Engineering and Design. 343: 85-95 (Mar. 2019).

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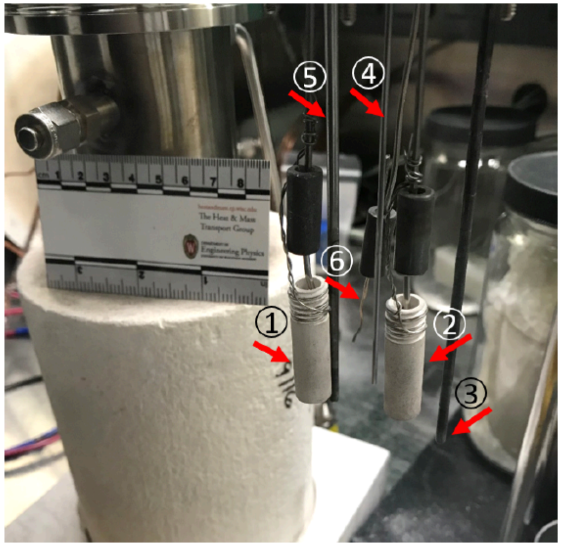
Reference Electrodes (RE) | The Value of Thermodynamic RE

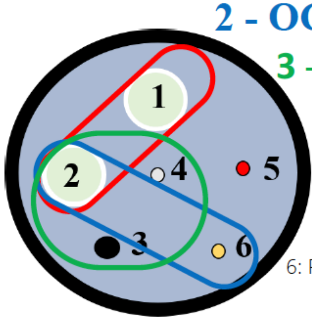
Experimental electrodes Setup:



1 OCP: RE-03 vs RE-04

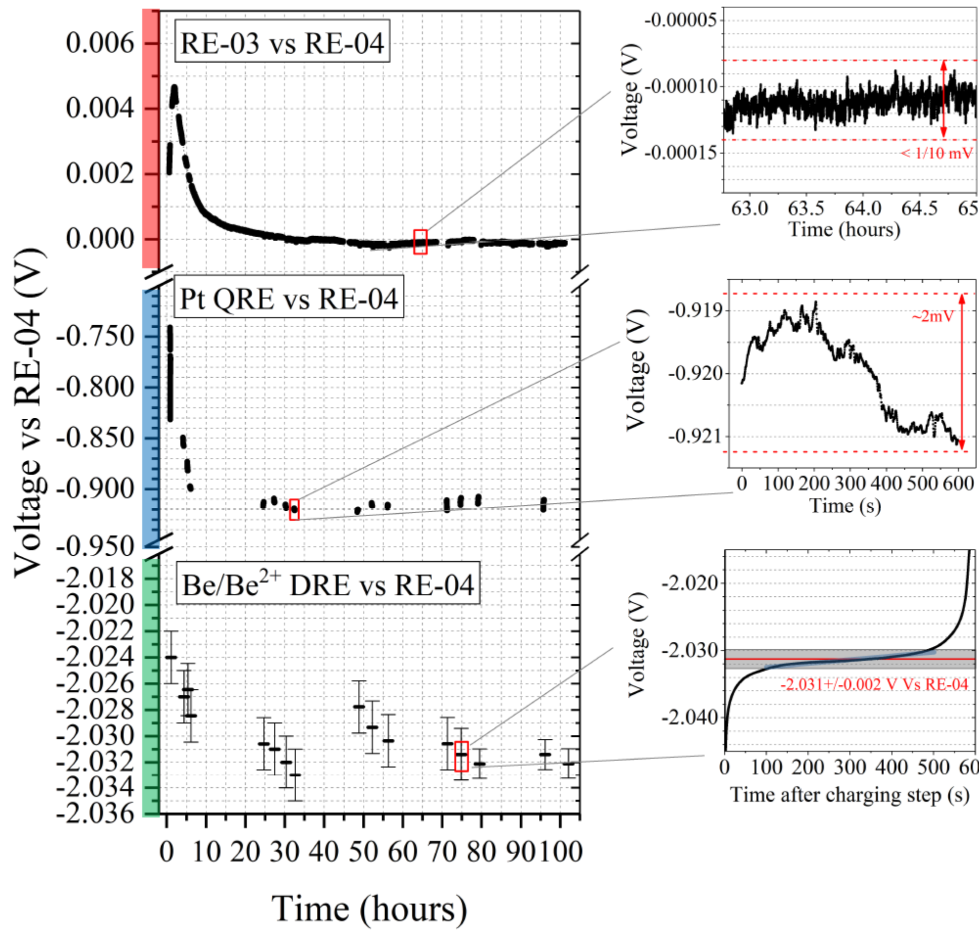
2 - OCP: Pt vs RE-04

3 – BeDRE vs RE-04



1: Ni/Ni(II) RE-03;
2: Ni/Ni(II) RE-04;
3: Glassy Carbon CE;
4: Mo electrode, BeDRE;
5: Thermocouple Mo well;
6: Pt electrode used as PtQRE.
GC crucible with FLiBe salt

100 hours potential monitoring at 550°C:



Thermo dynamic RE
+/- 0.1 mV

Quasi RE
+/- 2 mV

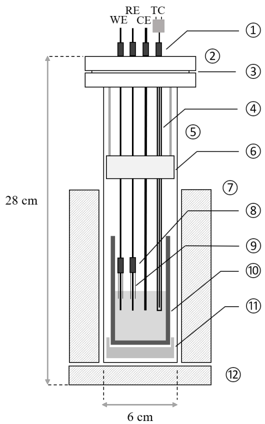
Dynamic RE
+/- 2 mV

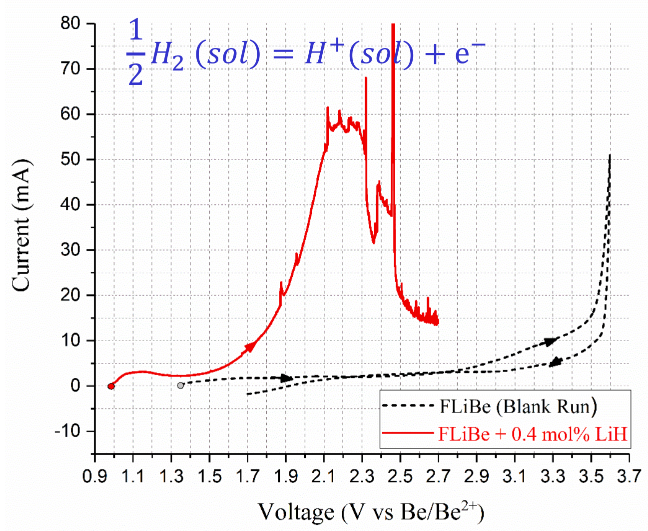
→ **Stability** and **Reproducibility** between RE-03 and RE-04 of +/- 5 mV, compared to BeDRE

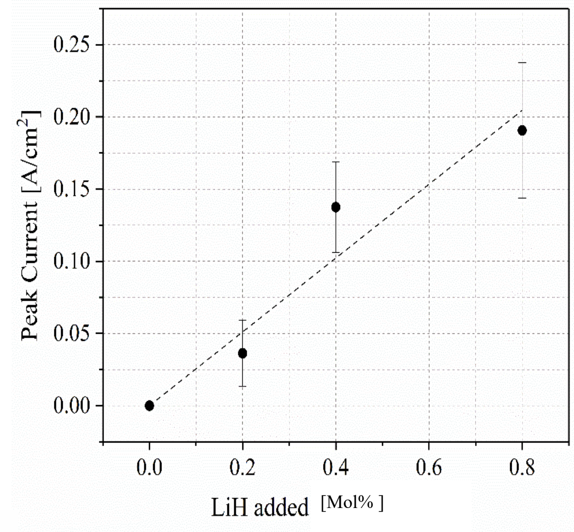
→ **Noise level** below 1/10 mV for over 100 hours.

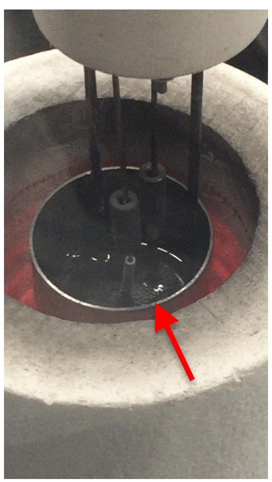
F. Carotti, Ph.D. Thesis. UW Madison. (2019).
F. Carotti, R. Scarlat. A comparison among different types of reference electrodes in FLiBe. (in preparation)

Electrochemical Studies of Hydrogen in FLiBe

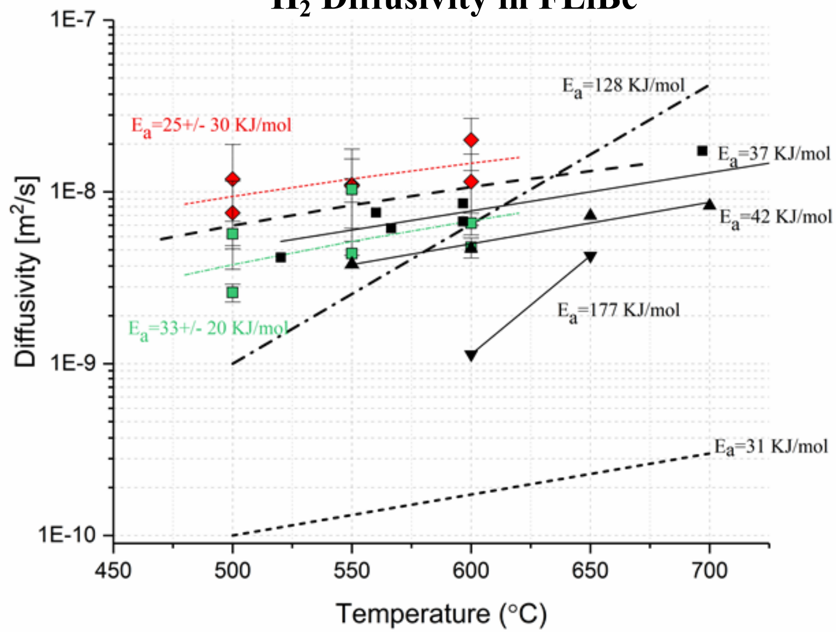




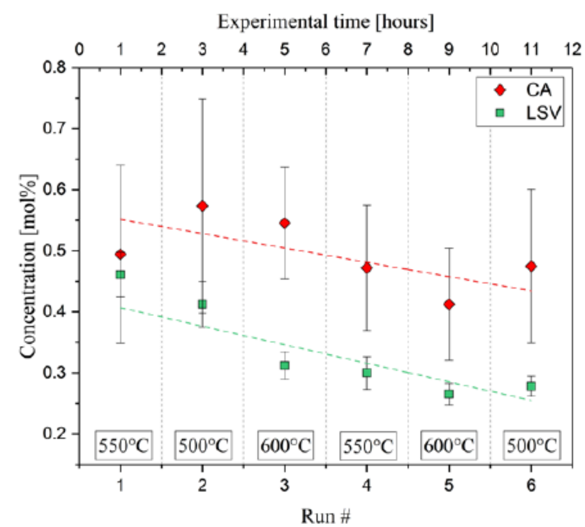




H_2 Diffusivity in FLiBe



Slow Thermal Degradation of BeH_2



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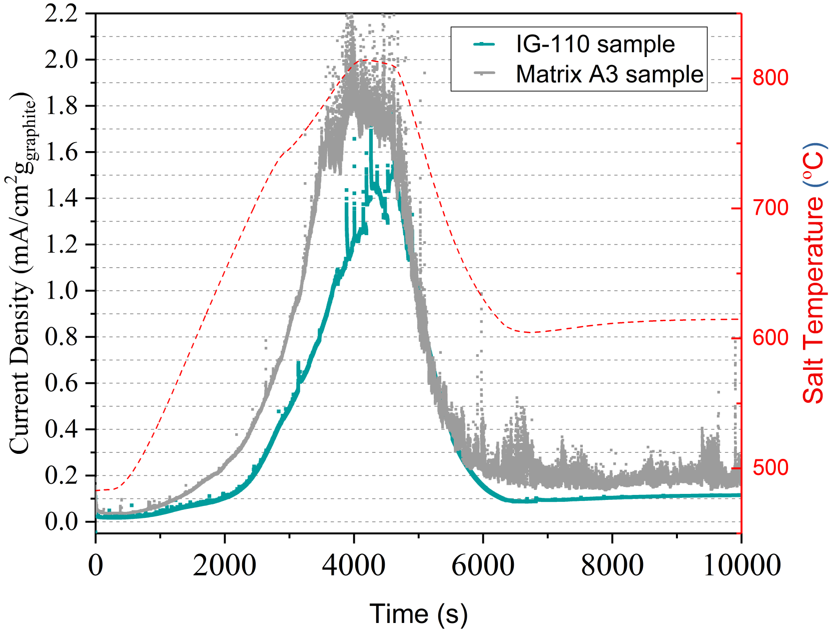
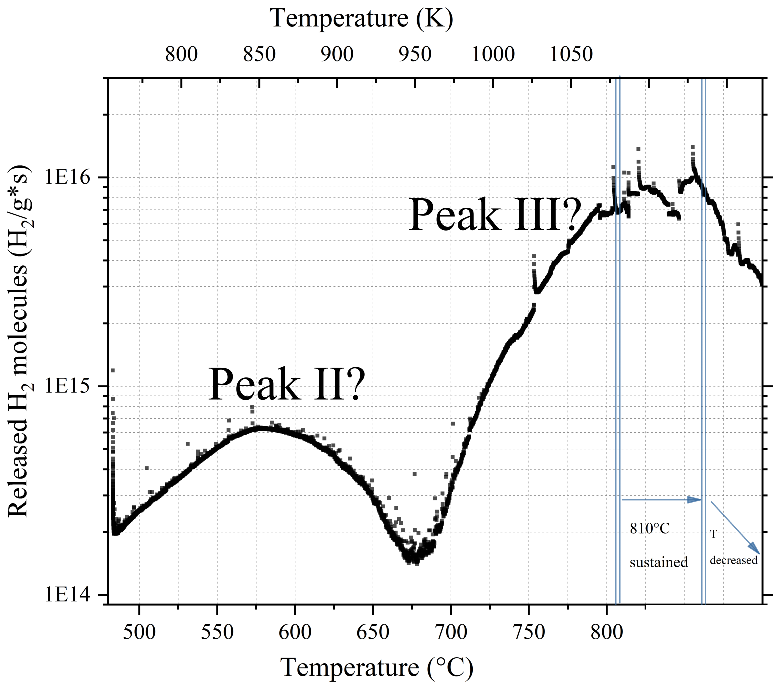
iu, Digby Macdonald, Raluca Scarlat. Electrochemical Studies of Hydrogen in Molten 2LiF-BeF2 (FLiBe). (in preparation)

Electrochemical Desorption of hydrogen pre-charged graphite

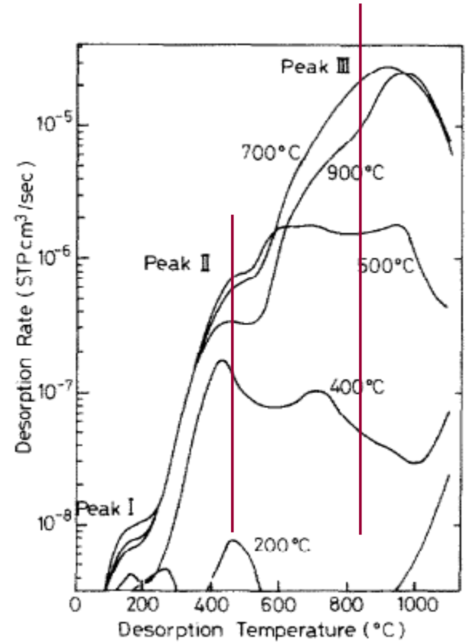


- Electrochemical Discharge (ED) of IG110 and Matrix A4 collected with temperature ramp from 480°C to 810°C.
- ED currents shows higher signal response for Matrix A3 than IG110.

- Two **desorption peaks** at 575°C and above 800°C, after subtraction of the faradaic baseline.
- The total hydrogen released, estimated as 2000 appm H/C



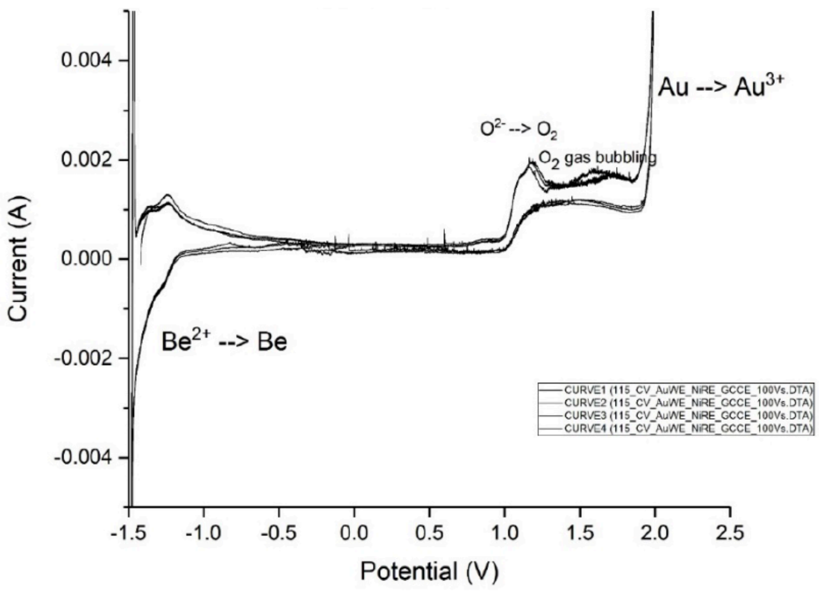
F. Carotti. Ph.D. Thesis. UW Madison. Feb. 2019.



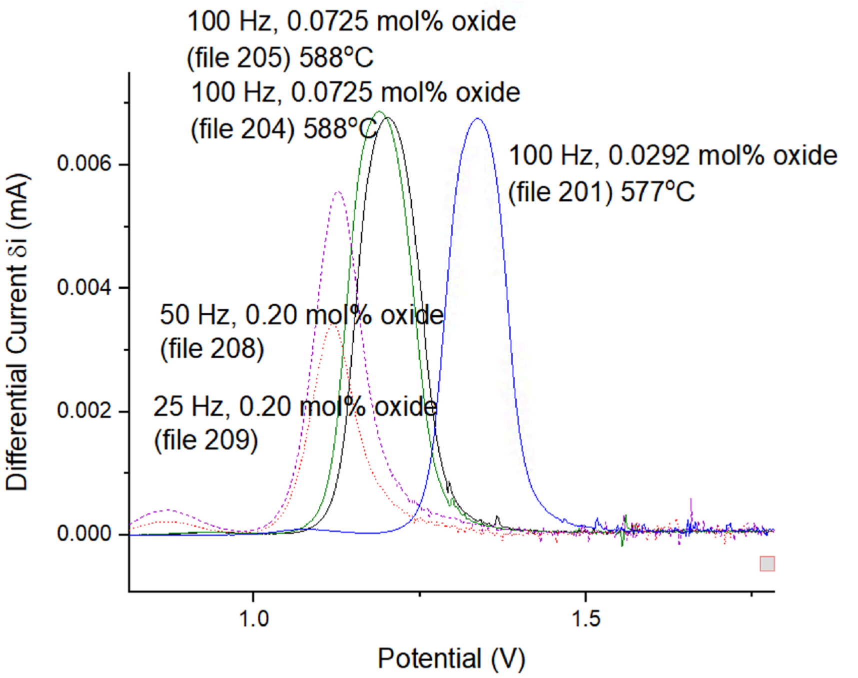
H. Atsumi et al. Journal of Nuclear Materials 417 (2011) 633–636.

Electrochemical Studies of Oxides in FLiBe

Cyclic Voltammetry



Square Wave Voltammetry



Molten Fluoride Salt Chemistry
Future Questions to Investigate

1. Fluoroacidity, speciation diagrams, and activity coefficients as tools for predicting corrosion drivers, solubility and volatility.
2. The role of oxide anions and other anions on complexation and activity coefficients.
3. Ion-specific reference electrodes can enable measurement of acidity, speciation diagrams, and activity coefficients, and generation of Pourbaix diagrams
4. Demonstrating reference electrode stability and reliability is important and it performance is melt-specific and composition-specific (i.e. an electrode that works in one salt composition, might not work in another salt composition).
5. Sensor development - references electrodes enable development and calibration of electrochemical sensors – e.g. for oxide content quantification.

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Molten Fluoride Salt Chemistry
ADDITIONAL SLIDES

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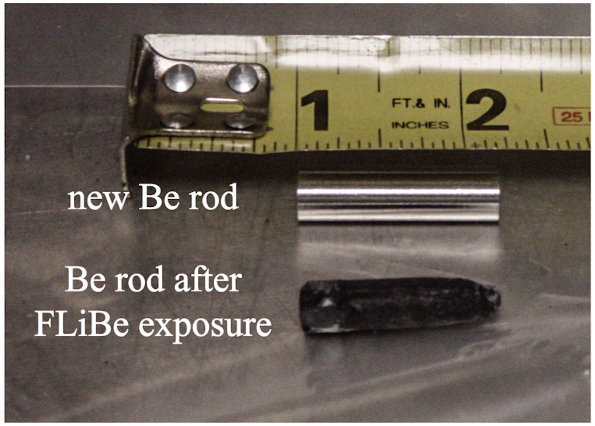
Thermodynamic Drivers for Corrosion



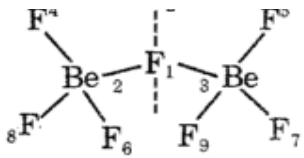
(Zhang, 2018)

1. Oxidating species: a balance among cation oxidation states.
   - Fission, activation, temperature gradients and addition of materials can have oxidative effects

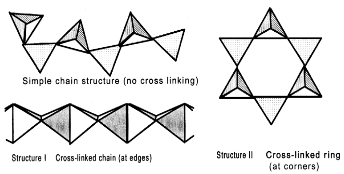
1. Standard states can have SEVERAL definitions
2. Molecular weight of FLiBe (i.e. *xi*) can have several definitions
3. The activity coefficient provides conversion among standard states
4. In order of significance: $\Delta G_f^0, T, \gamma_{BeF_2}, x_i$

J. Zhang, C. W. Forsberg, M. Simpson, S. Guo, S. T. Tang Lam, R. O. Scarlat, F. Carotti, K. J. Chan, P. Singh, W. Donniger, K. Sridharan, J. R. Keiser. Redox Potential Control in Molten Salt Systems for Corrosion Mitigation. Corrosion Science. 144: 44-53. (2018)

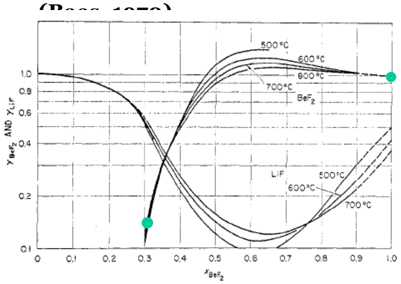
More on Activity Coefficients: Complex Ion Formation and Acidity



(Quist, 1972)



(Baes, 1970)

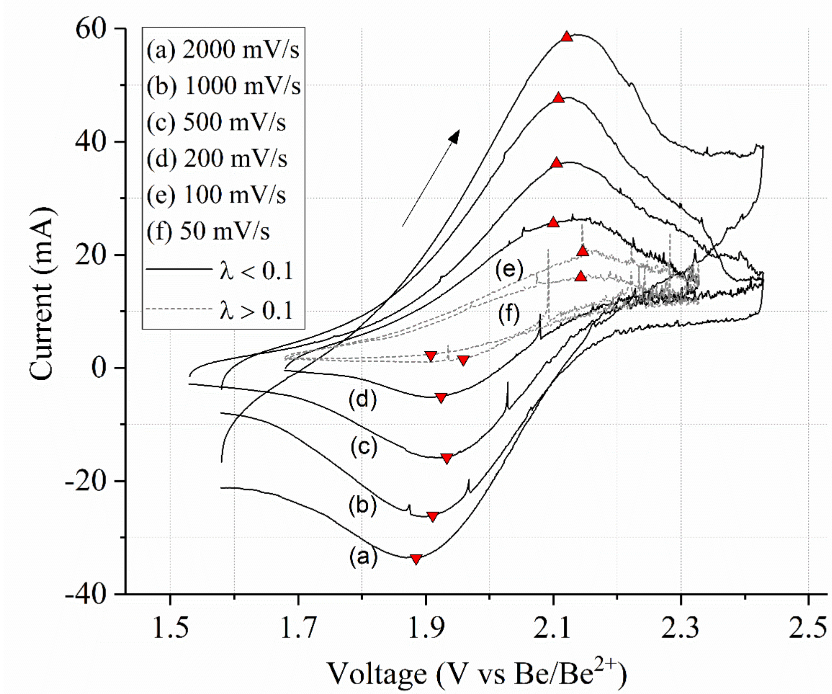


(Baes, 1969)

1. New complex ionic species can form in the melt
2. An equilibrium exists among many complexes, and it is temperature and composition-dependent.
3. Effect on activity coefficient:
   - The Gibbs energy of formation is captured in the activity coefficient.
   - The interaction energies of the new species with their surroundings are captured in the activity coefficient.
4. Effect on other solutes:
   - Solubilities and Gibbs energy of dissolution are affected
   - Solvation mechanism can change, affecting reaction kinetics and diffusivity

CHARACTERIZATION OF THE HYDROGEN ELECTROCHEMICAL REACTION IN FLIBE

Cyclic voltammogram and analysis



Reaction:

$$\frac{1}{2}H_2(sol) = H^+(sol) + e^-$$

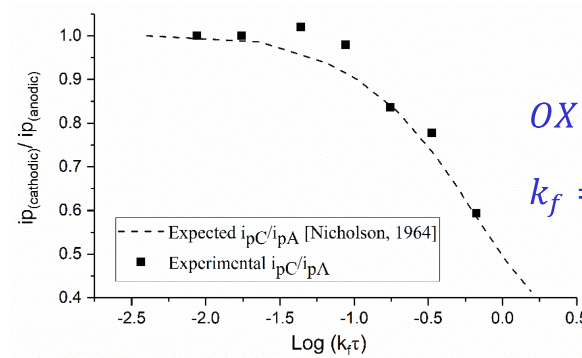
Half-wave potential:

$$E_{1/2} = 2.010 \pm 0.050\ V\ vs\ Be/(BeF_2)$$

Peak Separation:

$$\Delta E_p = 200 \pm 30\ mV$$

*1 – A chemical Reaction follows the electrochemical reaction (**EC mechanism**)*



$$OX(d) \xrightarrow{k_f} Z$$

$$k_f = 0.208\ s^{-1}$$

$$HF(sol) \xrightarrow{k_{f1}} HF(g)$$

$$HF(sol) + Be(m) \xrightarrow{k_{f2}} H_2(g) + BeF_2$$

2 – Potential and electrons exchanged support hypothesized electrochem reaction

$$E = E^0 - \frac{RT}{nF} ln\left(\frac{p_{H_2}\ a_{BeF_2}}{p_{HF}^2\ a_{Be}}\right) > \mathbf{1.870\ V}$$

$$\Delta E_p = 2.3\frac{RT}{nF} \rightarrow \boldsymbol{n = 0.8\ +/-0.5}$$

Francesco Carotti, Leo Liu, Digby Macdonald, Raluca Scarlat. Electrochemical Studies of Hydrogen in Molten 2LiF-BeF2 (FLiBe). (in preparation)