Development of Metal Oxide Reference Electrodes for Oxygen Sensors in Molten Salts

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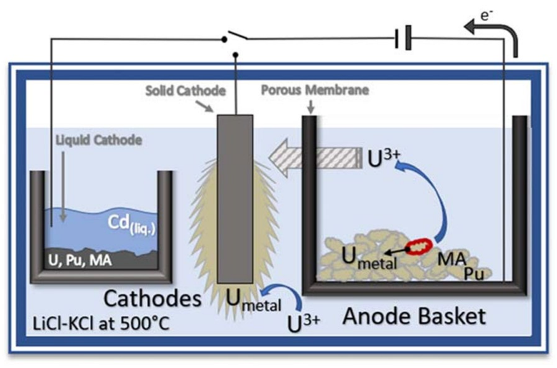
Introduction

Molten Salts

Important media for several electrochemical processes

Electrorefining of high purity metals

Pyroprocessing to recover U/TRU metal

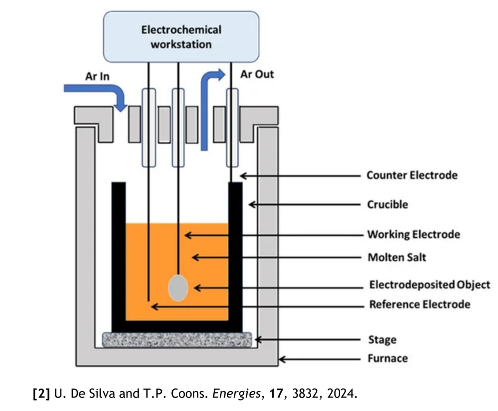


[1] N. Hege, J. Jackson, and J. Shafer. J. of the Electrochem. Soc., 170, 016503, 2023.

Voltage applied: $U_{metal} \rightarrow U^{3+} + 3e^-$

Deposition: $U^{3+} + 3e^- \rightarrow U_{metal}$

Electrodeposition of metals



[2] U. De Silva and T.P. Coons. Energies, 17, 3832, 2024.

Electrochemical cell for performing molten salt electrodeposition

Molten salts are susceptible toward oxygen contamination due to the lack of impurity level controls.

Oxygen Impurities in Molten Salts

Oxygen content in molten salts affect the operation of molten salt reactors

Oxygen Content

Increased levels of dissolved oxygen in molten salts

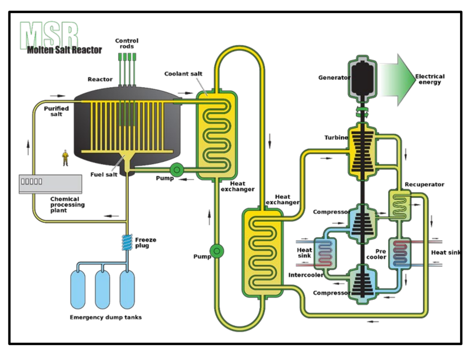
Effect on Viscosity

Increased oxygen content raises viscosity in molten salts

Impact on Reactor Efficiency

Reduced flow rate through the system

Molten Salt Reactor



Effect on Corrosion

Oxygen promotes formation of oxides, increasing corrosion rates

Material Degradation

Formation of oxide particles that contaminate the salt

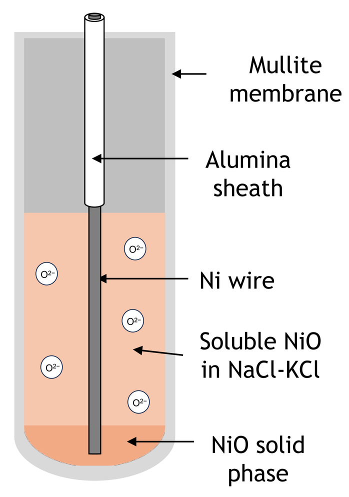
Combined Impact on Reactor Operation

Oxygen is critical to monitor in molten salt reactors.

This Work

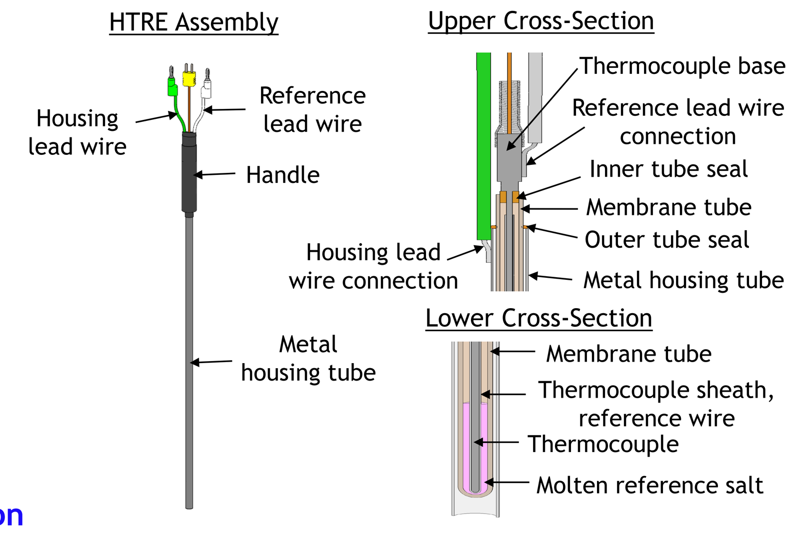
Develop a buffered and stable reference electrode (RE) using metal oxides for oxygen sensors in molten salts

Study stability of metal-oxide based RE in NaCl-KCl



Schematic representation of our reference electrode

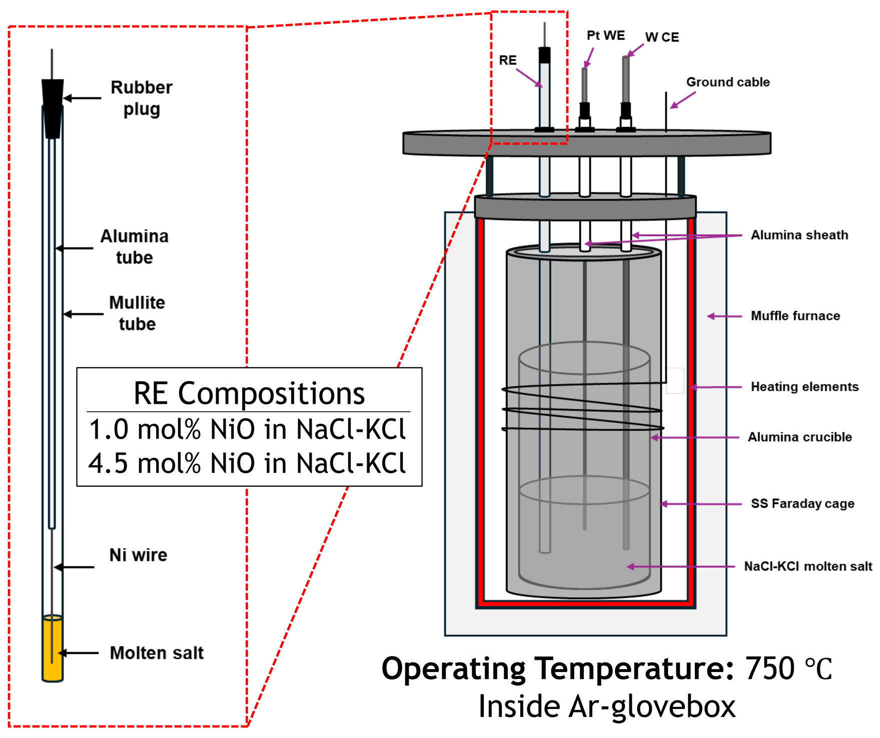
Demonstrate **electrochemical methods for quantification of oxygen** in molten salts and apply the learnings to HiFunda developed high-temperature reference electrode (HTRE)



Schematic representation of HiFunda's HTRE

Experimental

Molten Salt Electrochemical Setup

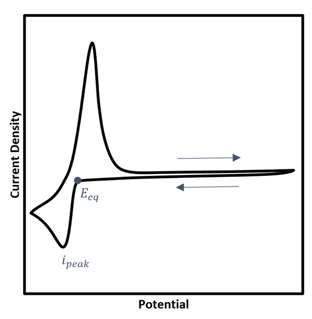


Operating Temperature: 750 °C
Inside Ar-glovebox

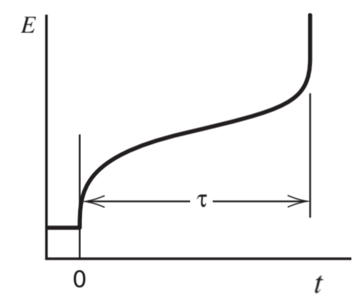
Stability test setup for REs with varying metal oxide concentrations in molten salts.

Electrochemical Techniques for Stability Tests

Cyclic Voltammetry (CV)

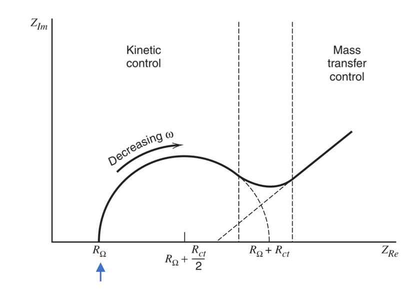


Chronopotentiometry (CP)



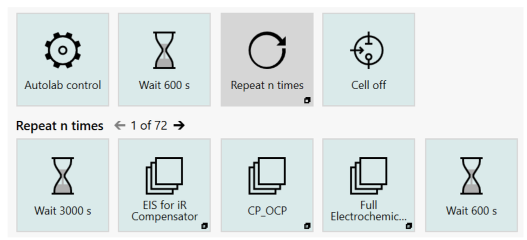
Measure open circuit potential (OCP) after CP

Electrochemical impedance spectroscopy (EIS)



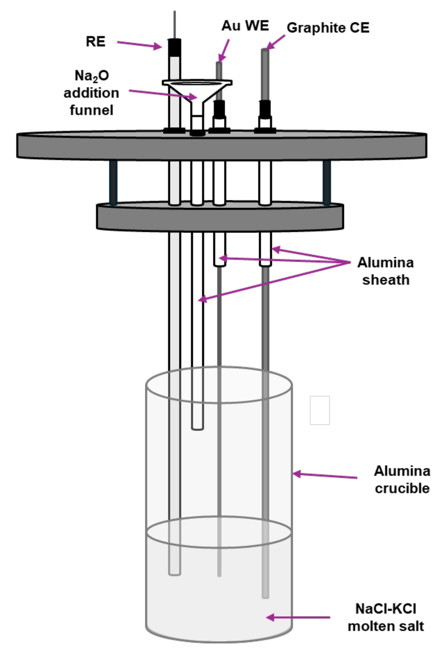
Solution resistance

Procedure to automate and collect stability data (Metrohm AUT88738 – Nova 2.1.7)



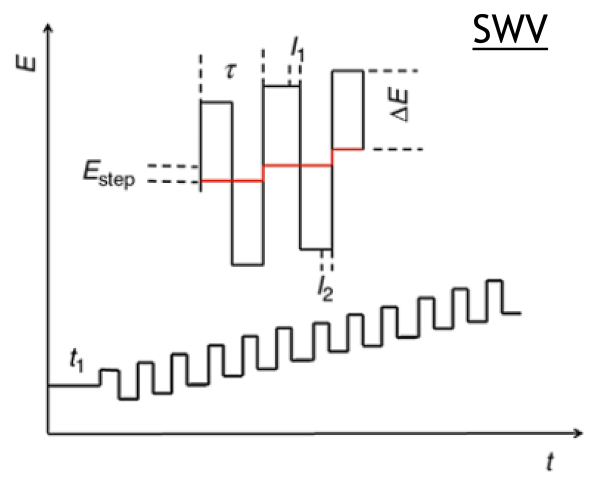
Three different electrochemical techniques to evaluate the stability of REs.

In-Situ Oxygen Concentration in Molten Salts



Operating Temperature: 750 °C
Inside Ar-glovebox

Open circuit potential (OCP) and **square wave voltammetry** (SWV) measurements after Na_2O additions to NaCl-KCl

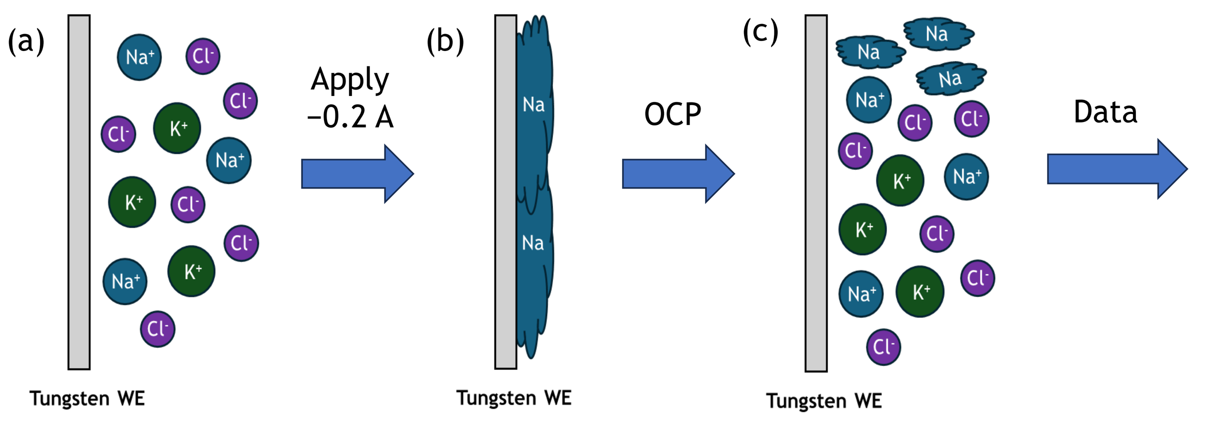


Measurements taken 30 minutes post Na_2O additions

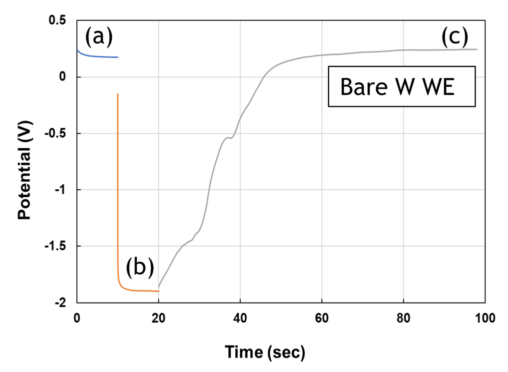
Procedure to examine oxygen potential peaks after addition of Na_2O to NaCl-KCl for development of oxygen sensors using our developed REs.

Results & Discussion

Choice of Working Electrode (WE) for Testing



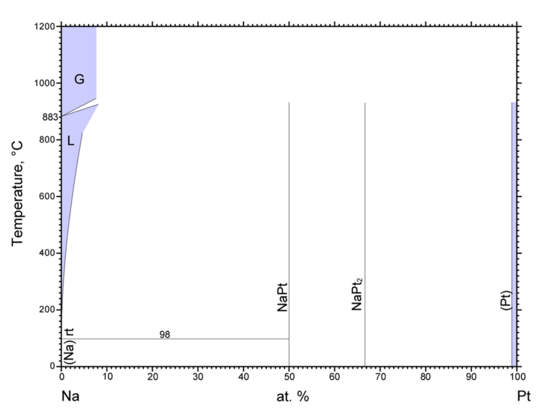
CP-OCP Measurement



Not a stable potential
Redox potential of salt

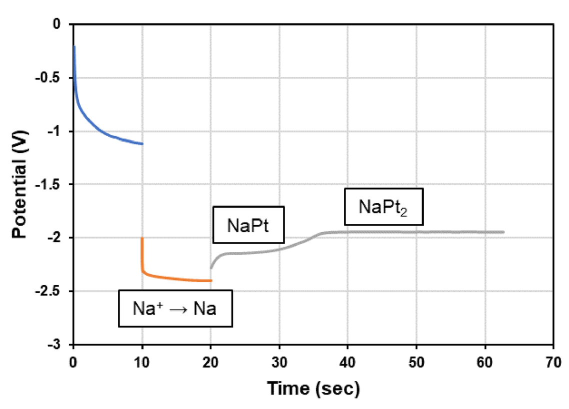
Sodium-Platinum Binary Alloy Phase Diagram

Change of WE material



Replacing Tungsten WE to Platinum WE

Apply −0.2 A, then OCP



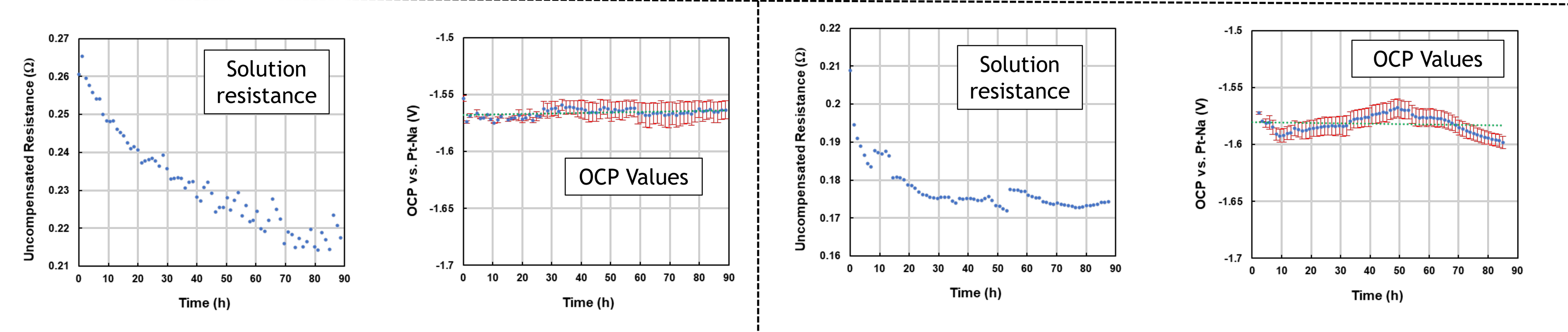
Stable potential
Redox potential of Na-Pt alloy

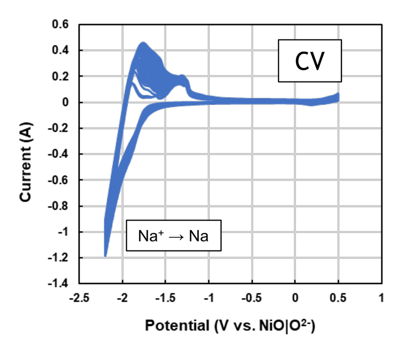
Long-Term Electrochemical Data for Stability Testing

Reference Electrode
1 mol% NiO|O^{2-} in NaCl-KCl

WE: Pt CE: W
Temperature: 750 °C

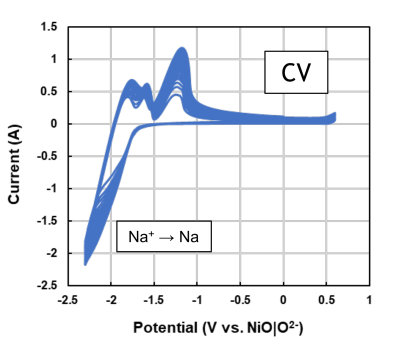
Reference Electrode
4.5 mol% NiO|O^{2-} in NaCl-KCl





Stability response based on OCP values

Reference Electrode	Na-Pt Potential (V)	Standard Deviation (mV)	Potential Drift (mV/day)
1 mol% NiO|O^{2-}	−1.5659	3.8	1.1631
4.5 mol% NiO|O^{2-}	−1.5825	8.3	1.5959

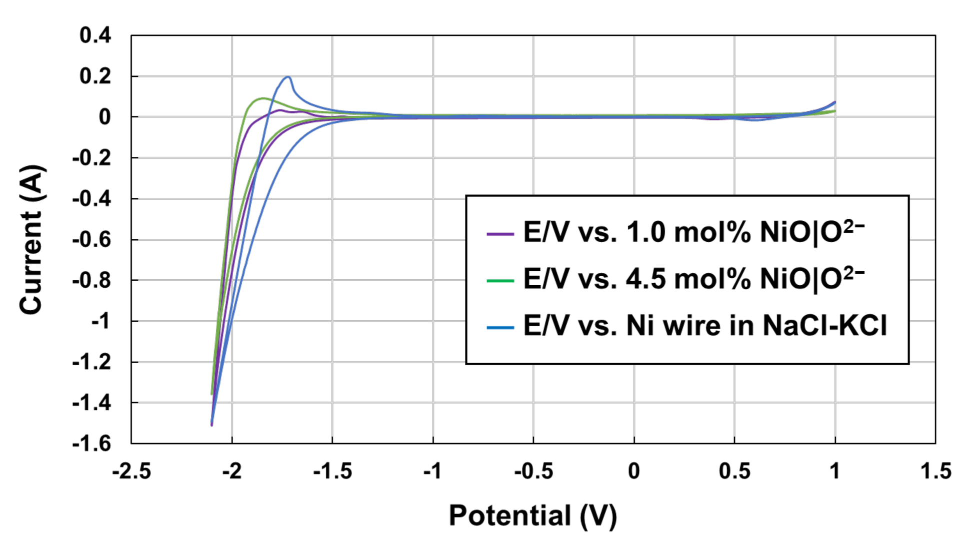


Run EIS → CP-OCP → CV × 72 times every hour using different REs in NaCl-KCl

Full Electrochemical Window for Metal Oxide RE

Electrodes	
Working Electrode	1.5 mm W rod
Counter Electrode	3.175 mm W rod

Experimental Conditions	
Temperature	750 °C
Scan Rate	0.1 V/s
Molten Salt	NaCl-KCl



Full electrochemical window comparisons with and without NiO in REs.

Electrochemical Analysis of Oxygen

Redox reaction of NiO in NaCl-KCl

$$NiO + 2e^- \rightleftharpoons Ni + O^{2-}$$

Nernst Equation

$$E = E_i^0 - \frac{RT}{nF}\ln\frac{a_{R,i}}{a_{O,i}}$$

E : Electrode potential relative to RE
E_i^0 : Standard potential of redox couple
R : Ideal gas constant
T : Absolute temperature
n : Number of electrons transferred in redox reaction
F : Faraday's constant
$a_{R,i}$: Activity of reducing species in equilibrium
$a_{O,i}$: Activity of oxidizing species in equilibrium

Extension of Nernst Equation for NiO redox couple

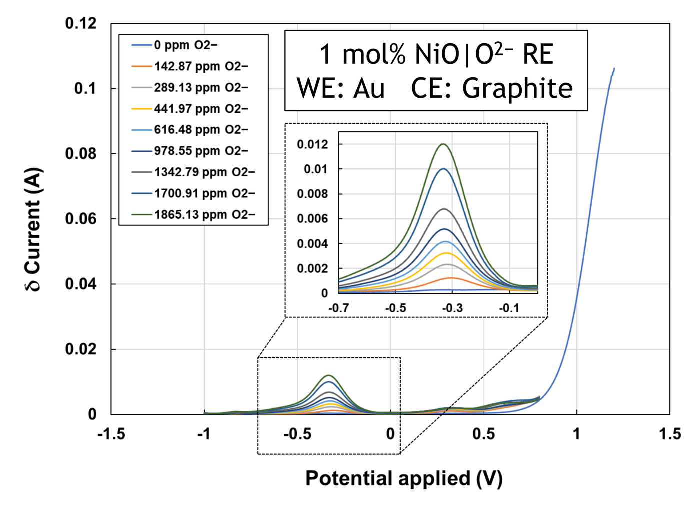
$$E = E^o_{NiO/O^{2-}} - \frac{RT}{nF}\ln\left(\frac{\alpha_{Ni}\cdot\alpha_{O^{2-}}}{\alpha_{NiO}}\right)$$

$$= E^o_{NiO/O^{2-}} - \frac{RT}{2F}\ln(\alpha_{O^{2-}}) = E^o_{NiO/O^{2-}} - \frac{RT}{2F}\ln([O^{2-}])$$

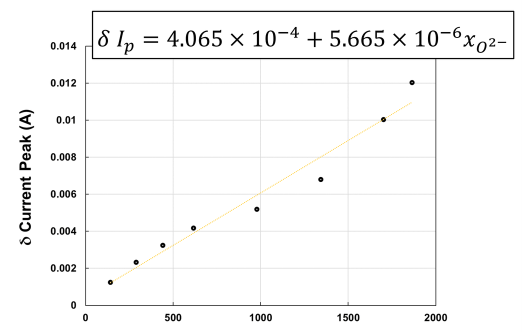
Potential is based on the concentration of oxygen ions.
From back titration, NaCl-KCl had 2.624 ppm O^{2-} and NaCl-KCl-NiO had 43.125 ppm O^{2-} by weight.
Low solubility of NiO in NaCl-KCl ensures saturated concentration of O^{2-} ions.

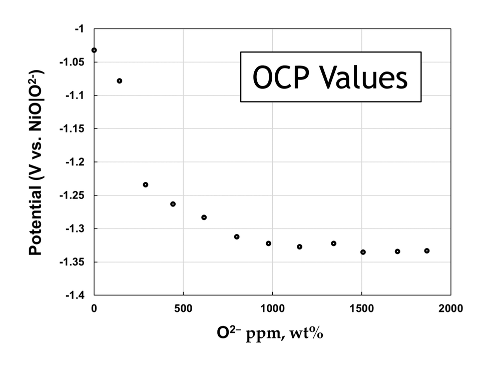
Development of Electrochemical Sensors for Oxygen Content in Molten Salts

Preliminary data using our developed RE



Performed at 36 Hz, step size of 2 mV, and amplitude of 20 mV





Increasing concentration of Na_2O increases the current peak of the O_2 redox reaction.

Summary

- REs containing metal oxides were developed and tested for their stability using different electrochemical methods.
- The reduction potential using metal-oxides were the same in NaCl-KCl.
- The developed RE was analyzed for potential applications as oxygen sensors.

Future Work

- Electroanalytical measurements for oxygen content using the developed HTRE from HiFunda.
- Study the oxygen content in fluoride salts using a compatible RE.
- Develop a model for the oxygen content in chloride and fluoride salts.

Acknowledgements

This project was funded by **Los Alamos National Laboratories** (LANL/DOE-NNSA, 212M02-BYU) and **HiFunda** (SBIR/DOE Phase I, DE-SC000025051).

Citation Details: Mejia, C., Essilfie, A., & Rappleye, D. S. (2024, November). Development of Metal Oxide Reference Electrodes for Oxygen Sensors in Molten Salts. *2024 Molten Salt Reactor Workshop*, Knoxville, TN.