Overcoming Challenges in Developing a High-Temperature Reference Electrode for Molten Fluoride Salts

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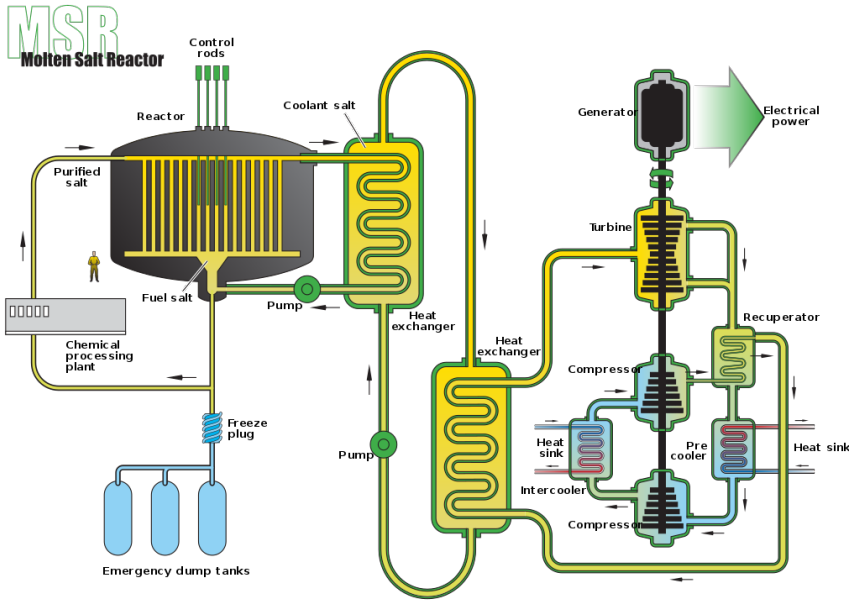
Outline:

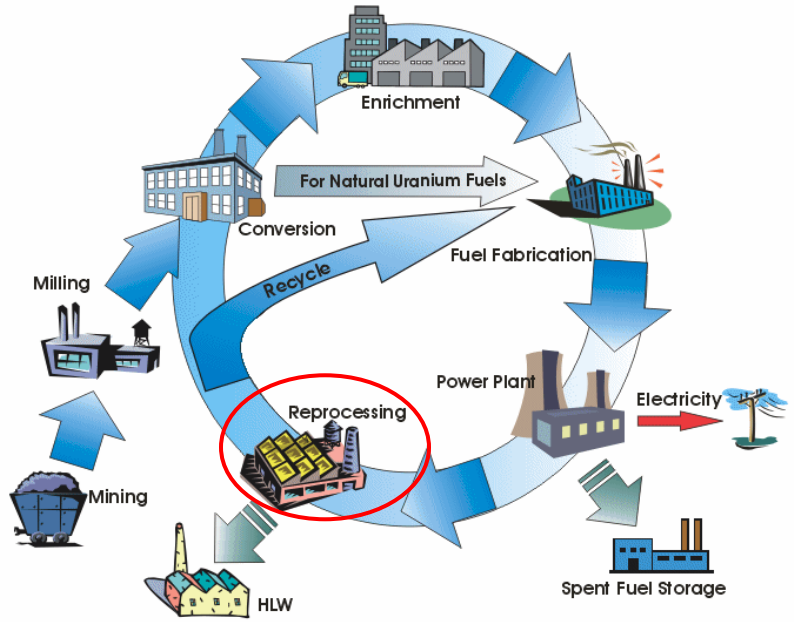
1) **Introduction** to molten salts and high-temperature reference electrodes (HTREs)
2) **Challenges**: Material compatibility, membrane robustness, design for manufacturing and assembly (DFMA), and safety considerations
3) **Solutions:** New HTRE taper seal and DIY kit designs
4) **Summary, lessons learned, and future efforts**

DOE SBIR Phase IIB, DE-SC0020579, "Stable High-Temperature Molten Salt Reference Electrodes," Jim Willit, DOE Program Manager

Uses and Importance of Molten Salts

- **Radiation resistant** with stable operating temperature range from about 400 to 800°C
- **Molten salt mixtures can be tailored** to achieve desired properties: liquidus temperature, reactivity, vapor pressure, etc. and can dissolve fissile and fertile actinides
- **Several applications** for nuclear energy and fuel cycle technology
  - **Pyroprocessing** of spent nuclear fuel
  - **Liquid fuel/coolant** for molten salt reactors
  - **Tritium breeding blankets** for sustainable fusion systems
- **Electrochemical methods for separations, corrosion control, and real-time composition monitoring are enabled by HTREs in MS**





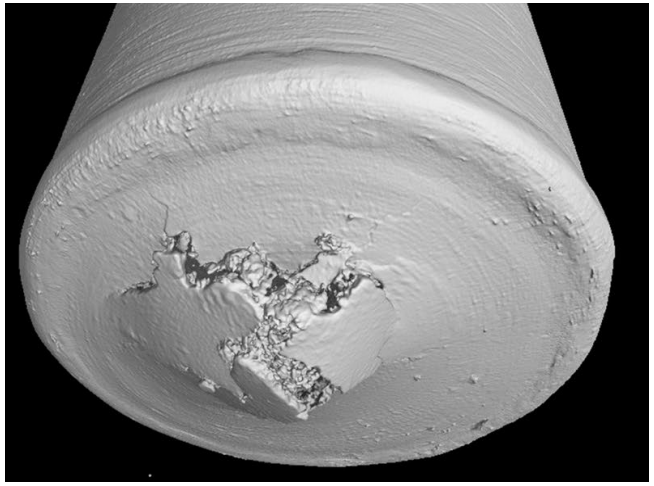
Fluoride HTMS Challenges

- Mullite, quartz, and alumina membranes used for chloride melts ***are not compatible with FLiNaK***
- Nickel membranes are compatible, but thermal expansion of FLiNaK during freeze/thaw cycles ruptured thin porous metal membranes driving requirement for additional membrane mechanical support
- Processes for fabricating controlled-porosity metal membranes are difficult with long lead times
- Safety requirements for building and shipping HTREs containing Be and radioactive materials

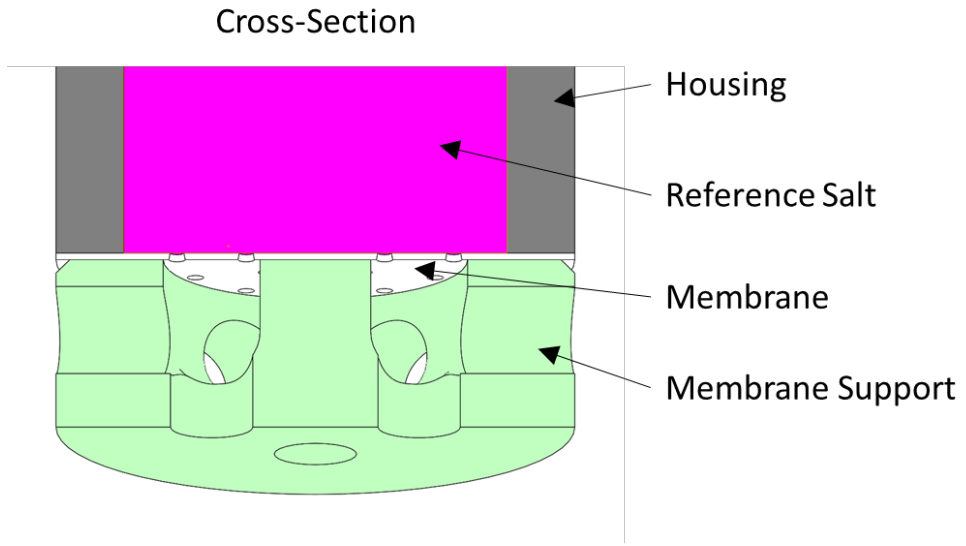
Before

After

Mullite tube images before/after
500-hours corrosion test at 750°C in FLiNaK

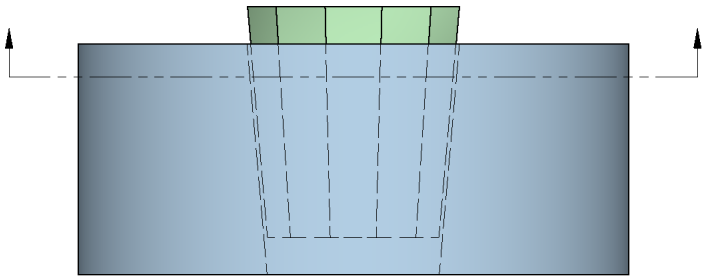


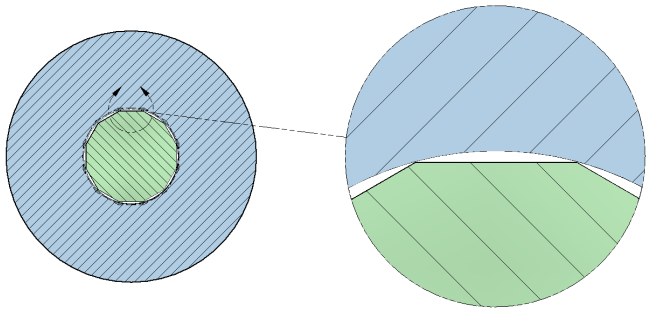
End-View XRCT Images of HTRE Number N02
After Testing in FLiNaK at INL at 664 °C



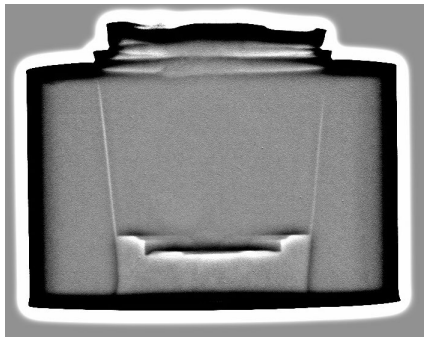
New Robust Taper Seal Membrane for HTREs

- Designed & developed DFMA process taper seal for robust controlled leak rate HTRE membranes
- Characterized leak rates via XRCT, helium leak rate, and conductivity breakthrough
- Incorporating into new smaller diameter (1/4" OD x 18") Ni/NiF_2 HTREs for electrochemical testing and characterization in FLiNaK and FLiNaZr

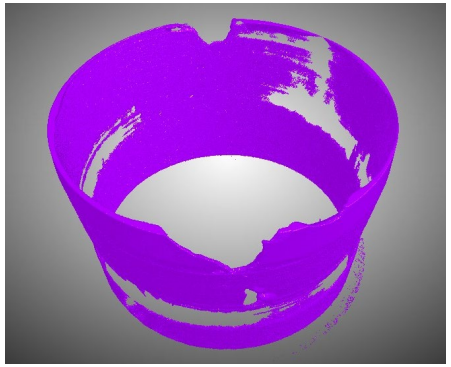




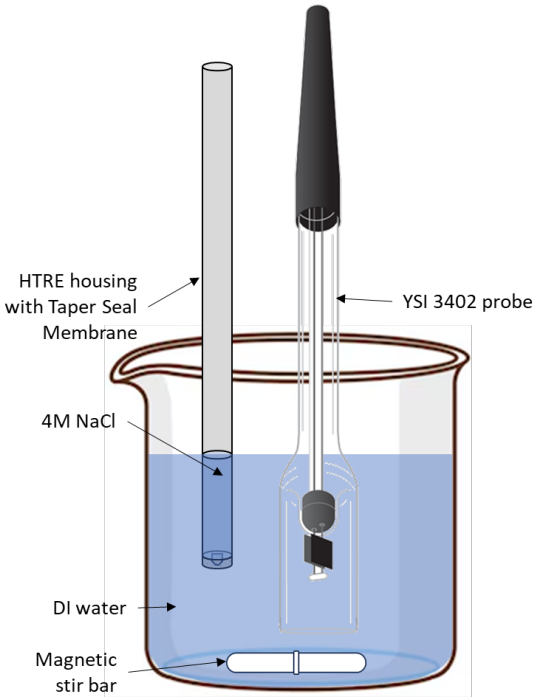
Taper Seal Design



RTXR Image of Taper Seal Subassembly



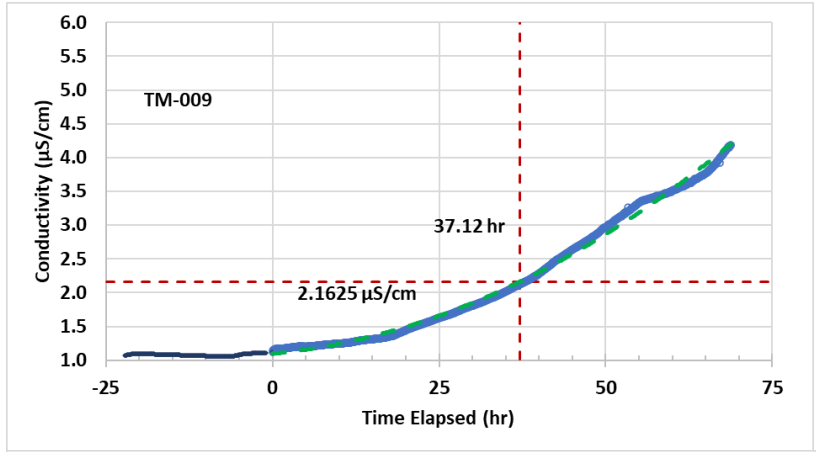
XRCT Image Taper Seal Subassembly

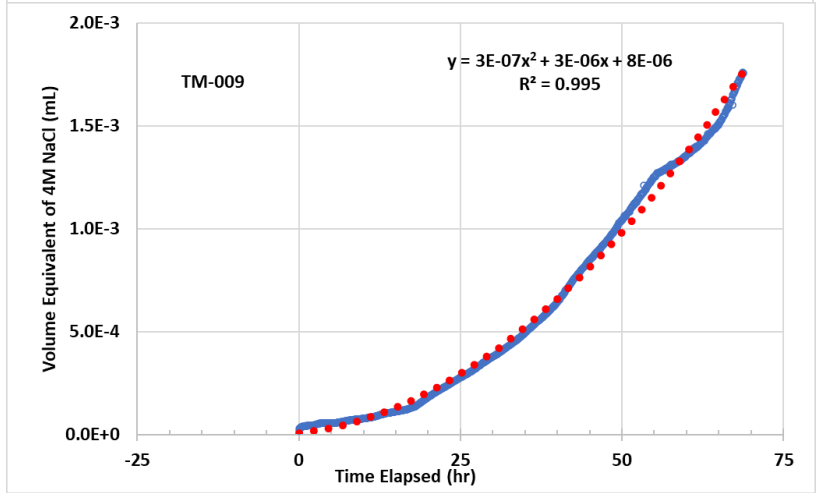


Conductivity Breakthrough Experimental Setup

Comparison of Taper Seal Leak Rates for Gas and Liquid Media

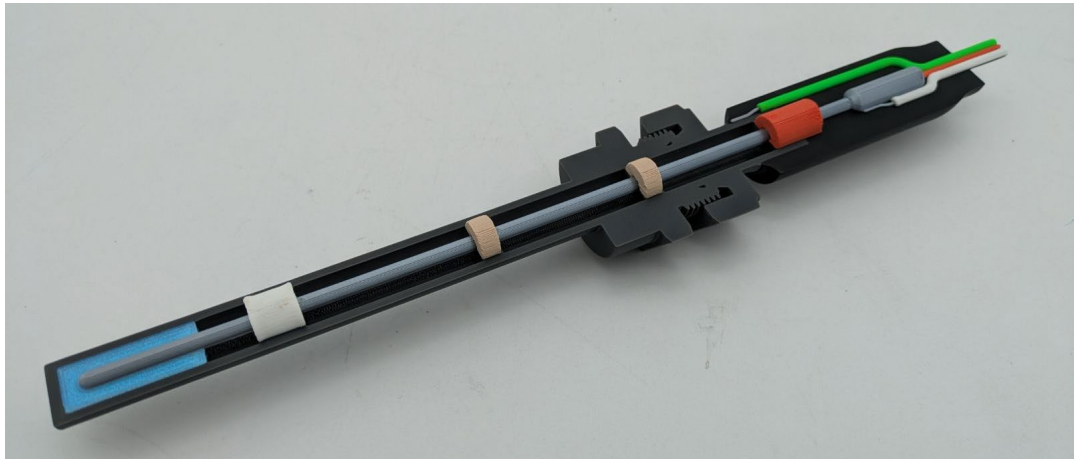
	Helium gas	4M NaCl
Membrane	He Leak Rate (atm-ccm)	Vol Rate (µL/hr)
SP-002	1.38E-01	0.011
TM-009	2.91E-01	0.050
TM-010	6.08E-02	0.067



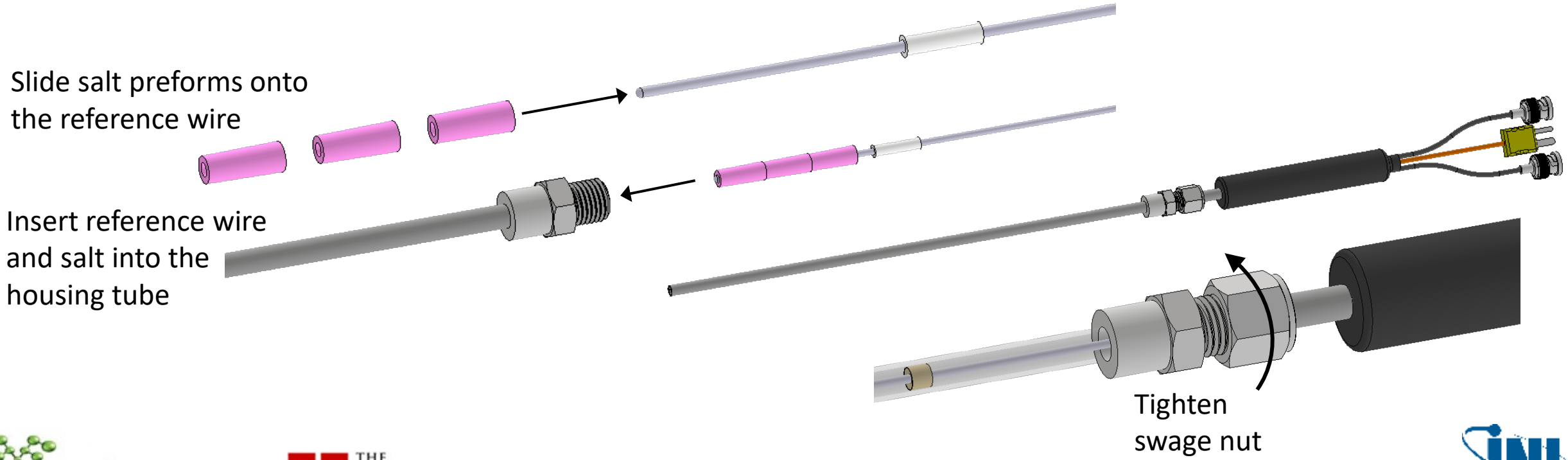


DIY Kit Enables Researchers To Add Salts of Interest To HTREs

- Designed and developed a do-it-yourself (DIY) HTRE kit for working with Be and radioactive materials
- HiFunda provides the DIY kit
- End user adds salt as powder or preforms to complete final assembly
- Looking for VOC inputs regarding DIY HTRE kit (See Survey)

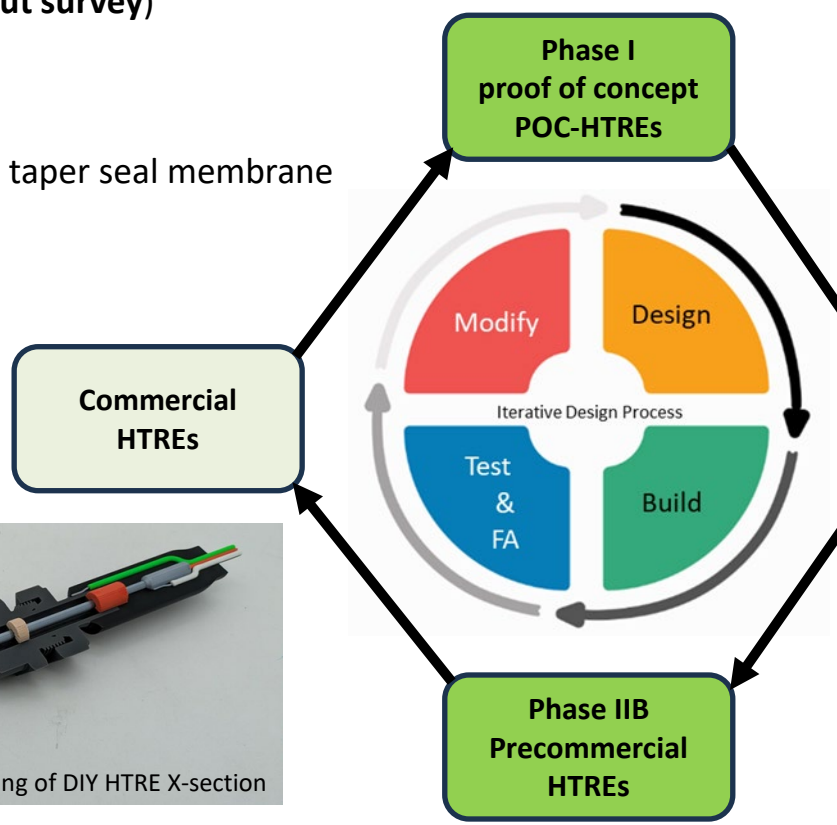


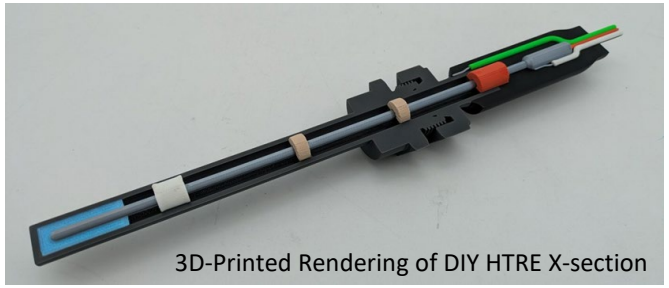
3D-Printed Rendering of DIY HTRE X-section



Summary, Lessons Learned, and Future Efforts

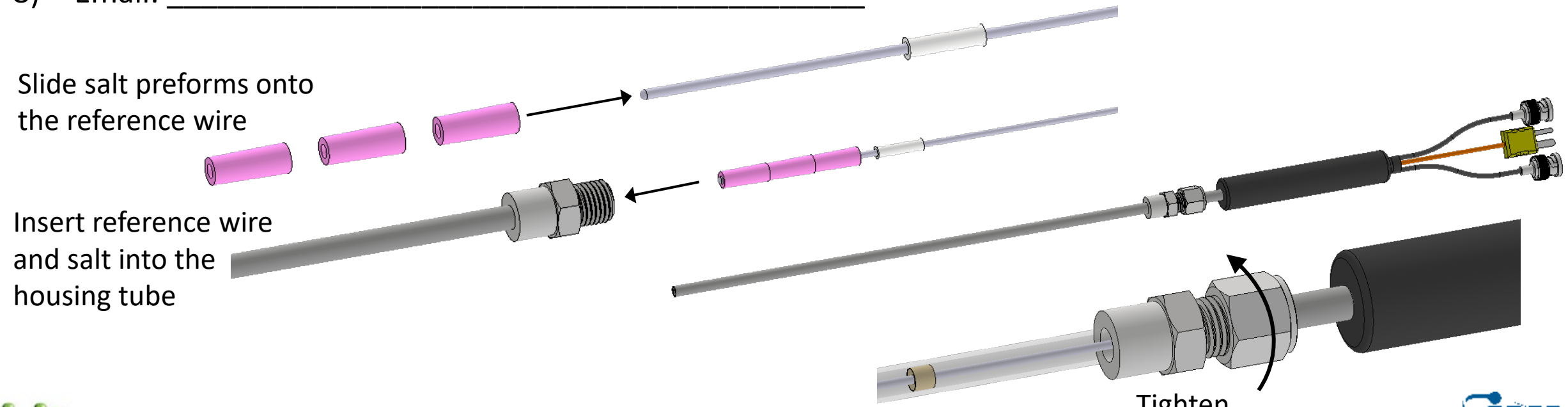
- Summary:
  1) Developed **new robust taper seal membrane and DIY kit** for HTREs
  2) HTREs can be customized for your applications (**Please see HTRE brochure)**
  3) Performed chemical compatibility tests of HTRE materials in FLiNaK up to 750°C
- Lessons Learned:
  1) **Iterate rapidly and often per iterative design process**
  2) Build and test prototypes of new proposed designs and subassemblies
  3) Pay attention to chemical compatibility and freeze-thaw properties of HTMS
  4) Leverage voice-of-customer (VOC) inputs on DIY HTREs (**Please see VOC input survey**)
  5) Leverage state (UTMMG) and federal resources
- Future Efforts:
  1) Perform short and long-term testing and characterization of DIY HTREs with taper seal membrane
  2) Testing in FLiNaZr and uranium at the UofU
  3) Testing in FLiNaK at ACU in crucibles and flow loop
  4) Building upon HTRE platform technology by adding an O_2 sense electrode as part of existing Phase I SBIR project, "In Situ Electrochemical Sensor for Oxygen Determination in HTMS" DE-SC0025051
     See Carlos Mejia's (BYU) companion poster




3D-Printed Rendering of DIY HTRE X-section

VOC Survey Regarding DIY HTRE Kit

1) Are you interested in a do-it-yourself (DIY) HTRE kit for working with Be and/or radioactive materials?
2) If yes, what are your salts of interest?
3) Are you comfortable pouring your salt into a 0.19” ID tube in a glovebox? And then inserting thermocouple into melted powder with associated assembly issues?
4) Would you prefer that we provide a mold for DIY casting or hot pressing MS pellets with center hole?
5) Are you interested in an in situ electrochemical oxygen sensor?
6) Other comments: _____
7) Name: _____
8) Email: _____



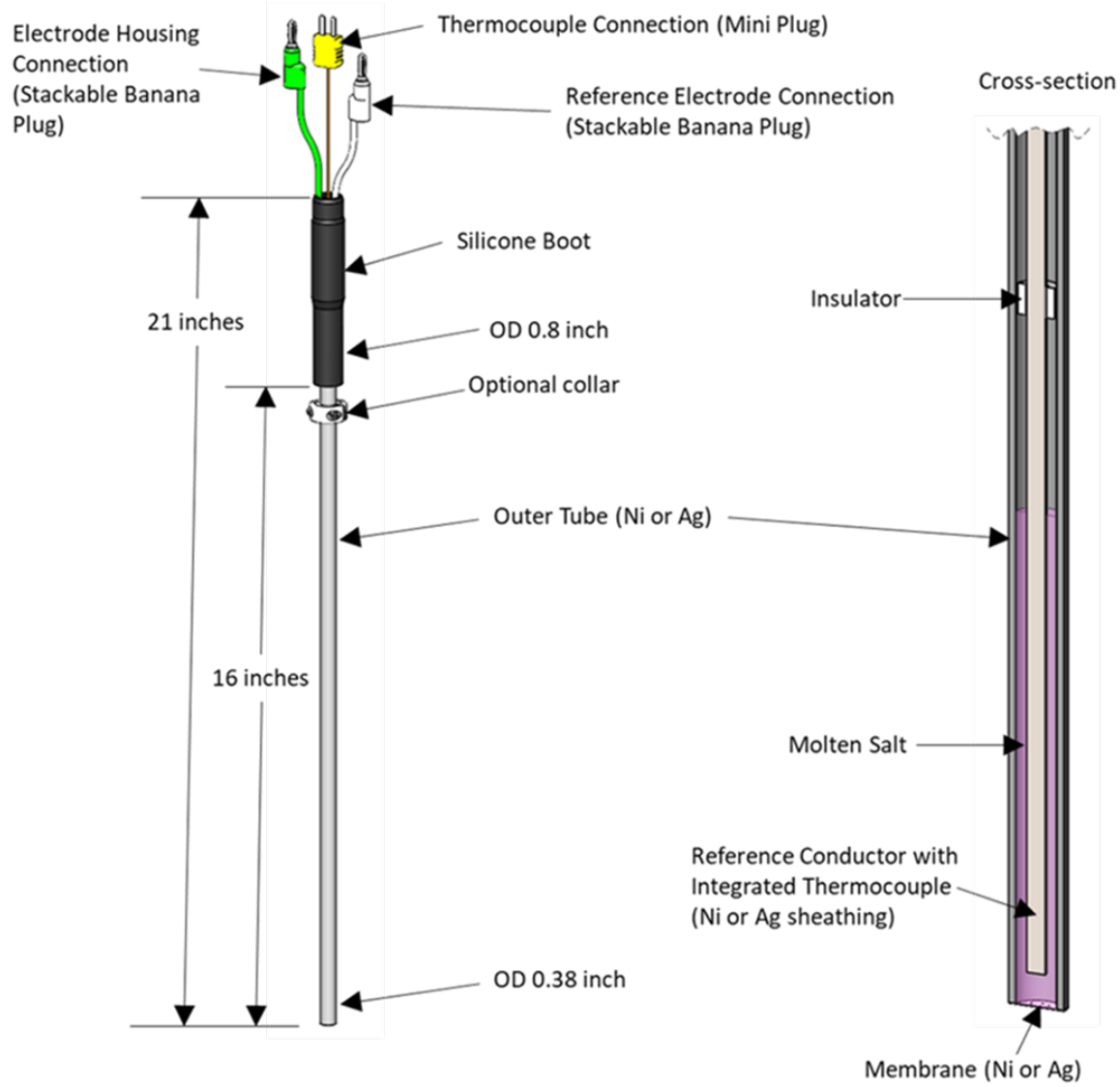
High-Temperature Reference Electrodes (HTRE) for Molten Salts

- Known, fixed, **thermodynamic reference potential** is critical for HTMS electrochemical analyses and sensors

- HTREs consist of 3 essential components
  1) Metallic reference conductor (**Ni**)
  2) Reference molten salt mixture (**NiF_2/FLiNaK**)
  3) Ion conductive membrane (**Controlled porosity Ni**)

- HiFunda's HTREs have 3-fold functionality:
  1) Stable thermodynamic reference potential
  2) Integral temperature sensor
  3) Redox sensor

- Materials challenges for HTRE components in fluorides



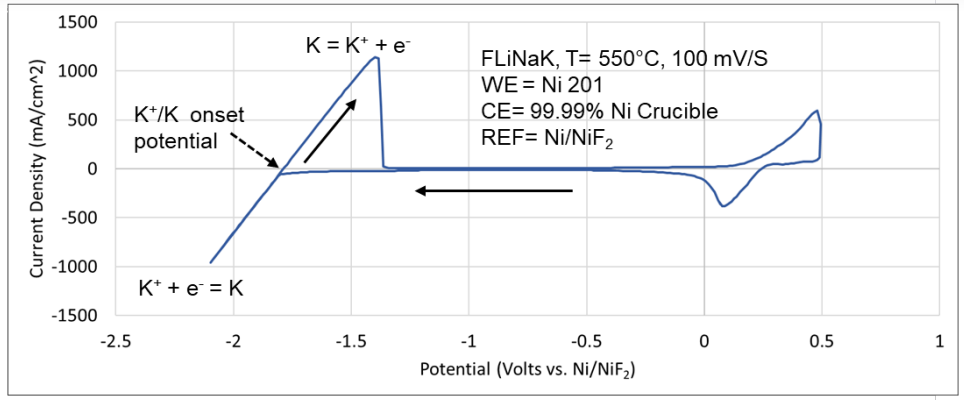
Custom High-Temperature Reference Electrodes

HiFunda has developed and demonstrated a robust thermodynamic high-temperature multi-functional reference electrode (HTRE) for performing electrochemical measurements in molten salt applications.

Until now, there have not been commercially available robust HTREs, causing scientists to make their own HTREs with inherent variability due to differences in design and fabrication methods. HiFunda can provide standard or custom HTREs for your application so your team can focus on electrochemical processing and product development.

HiFunda's Ag/AgCl, Ag/AgF, and Ni/NiF_2 HTREs are designed, built, and characterized for your application. Each HTRE has three-fold functionality 1) stable thermodynamic reference potential, 2) integral temperature sensor, 3) redox sensor.

The HiFunda HTRE technology was developed as part of DOE SBIR projects where we teamed with Idaho National Laboratory and the University of Utah to test and demonstrate HTREs for operation in molten chloride and fluoride salts.



SBIR Projects and Technical Presentations:

1) Robust, Standardized High-Temperature Molten Chloride Salt Reference Electrodes, DE-SC0021439 https://www.sbir.gov/sbirsearch/detail/2056865
2) Stable High-Temperature Molten Salt Reference Electrodes, DE-SC0020579 https://www.sbir.gov/sbirsearch/detail/2104123
3) "Robust and Standardized High-temperature Molten Chloride Salt Reference Electrode," 2022 TMS Annual Meeting & Exhibition
4) "Long Term Stability of Ag/AgCl Reference Electrode in Molten Chloride Salt," Log 254, 12th International Conference on Methods and Applications of Radioanalytical Chemistry 2022
5) "Long Term Stability of Mullite and Magnesia-Encased Ag/AgCl Reference Electrodes in Molten $MgCl_2$-KCl-NaCl," J Electrochemical Society, 170, 057505, (2023).
6) "Comparison of Ni/NiF_2 and Ag/AgF for a Stable Redox Couple for Molten Fluoride Salt Reference Electrodes, 2023 American Nuclear Society Annual Meeting, June 11-14, (2023), Indianapolis, IN.
7) "Material Challenges for Development of Long-Term Stable Reference Electrodes," The American Ceramic Society, Materials Challenges in Alternative & Renewable Energy (MCARE), August 21,2023.

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HiFunda can help to solve your greatest electrochemical and materials challenges

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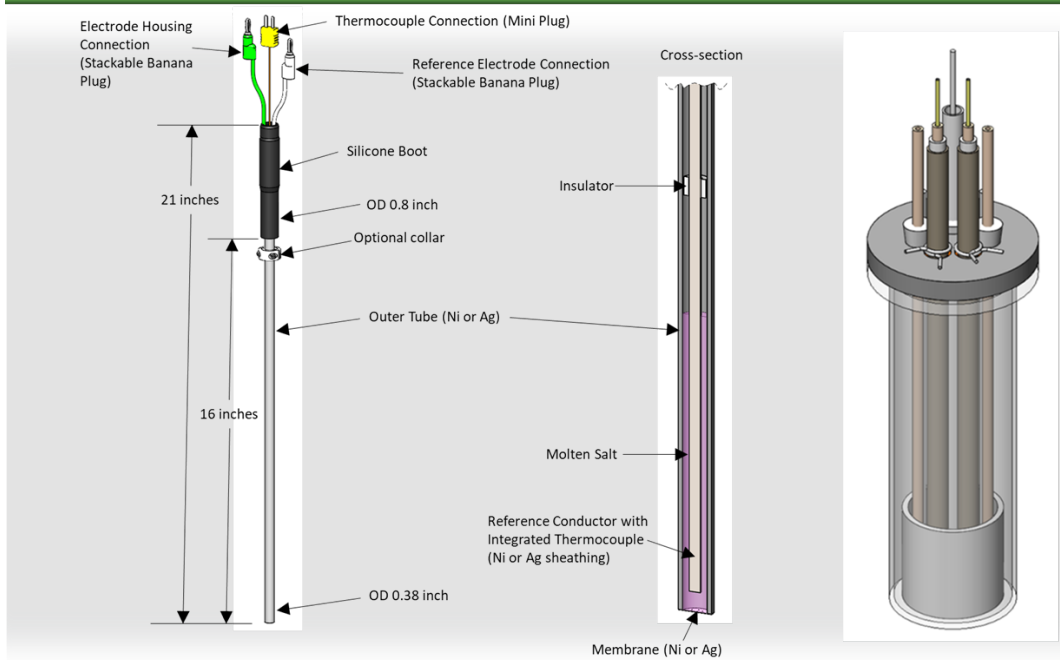
Customized HTREs for Your Molten Salt Applications



Standard HTREs

HTRE Type	Reference Wire	Housing	Membrane	Reference Melt	Wire Length (inches)	Thermocouple	HTRE length (inches)	Max Use T (°C)	Immersion Depth (Inches)	Interface	Part No.
Ni/NiF_2	Ni201	Ni201	Ni201	NiF_2/FLiNaK	36	Type K	21	750	4	Collar	Ni/NiF2-2222-3223-222-1111
Ag/AgF	Ag99.9	Ag99.9	Ag99.9	AgF/FLiNaK	36	Type K	21	750	4	Collar	Ag/AgF-1211-2123-222-1111
Ag/AgCl	Ag99.9	Ag99.9	Ag99.9	AgCl/$MgCl_2$, NaCl, KCl	36	Type K	21	750	4	Collar	Ag/AgCl-1211-2323-222-1111
Ni/$NiCl_2$	Ni201	Ni201	Ni201	$NiCl_2$/MgCl2, NaCl, KCl	36	Type K	21	750	4	Collar	Ni/NiCl2-2222-3423-222-1111

HTRE Customization Options

Feature	Description	1	2	3	4	5	6	7	8	9	Comments
A	Reference conductor	Ag99.9	Ni201	other customer specified (OCS)							Options highlighted in green correspond to standard Ag/AgF HTRE
B	Housing Diameter	0.5	0.38	0.25							
C	Housing Material	Ag99.9	Ni201	OCS							
D	Membrane type	Ag99.9	Ni201	Mullite	MgO	OCS					Mullite and MgO are not compatible with fluorides
E	Membrane leak rate (MLR, sccm)	0.0	0.1	1	10	OCS					Ni, Ag, and MgO MLR can be customized. Mullite MLR = 0
F	Reference melt	AgF/FLiNaK	NiF_2/FLiNaK	AgCl/Chloride solar salt (Future2B)	NiCl2/Chloride solar salt (Future 2b)	Nitrate solar salt (Future2B)	AgF/FLiBe (CDS)	OCS			Test melt plus reference salt
G	Reference salt composition (mol%)	0.1	1	100	OCS						Reference salt = AgF, NiF_2, AgCl, or $AgNO_3$
H	Wire length (inches)	12	24	36	OCS						
I	Thermocouple Type	None	K: single	K: triple profile	N	OCS					
J	Immersion depth (inches)	2	4	6	8						Immersion depth and total length are linked.
K	Total HTRE length (inches)	19	21	23	27						Total length is linked to maximum use temperature
L	HTRE Interface	SS316 collar for height adjustment	Isolated swagelok fitting	Nonisolated swagelok fitting							OCP of HTRE housing independent of piping OCP when isolated and the same as piping when OCP not isolated
M	Characteristic CV	T=550°C	T=650°C	T=750°C							CV at 550°C included with 3 sweeps, additional cost for other temperatures
N	Verification testing	0	1	12	24	100					Additional cost for verification testing (~$100/hr)
O	CofC	Not required	Required								Additional cost for CofC (~$50)
P	*Custom development services (CDS) available to benchmark or optimize the RE and to demonstrate electroanalytical determination of Cr or Fe for each customer's salt mixture of interest*										
Q	*Turnkey services available to design and build HT electrochemical test setups*										

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HiFunda works with customers to solve their most demanding technical challenges to develop and commercialize new materials and technologies

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