Cyclic voltammetry of $LiF\text{-}ThF_4$

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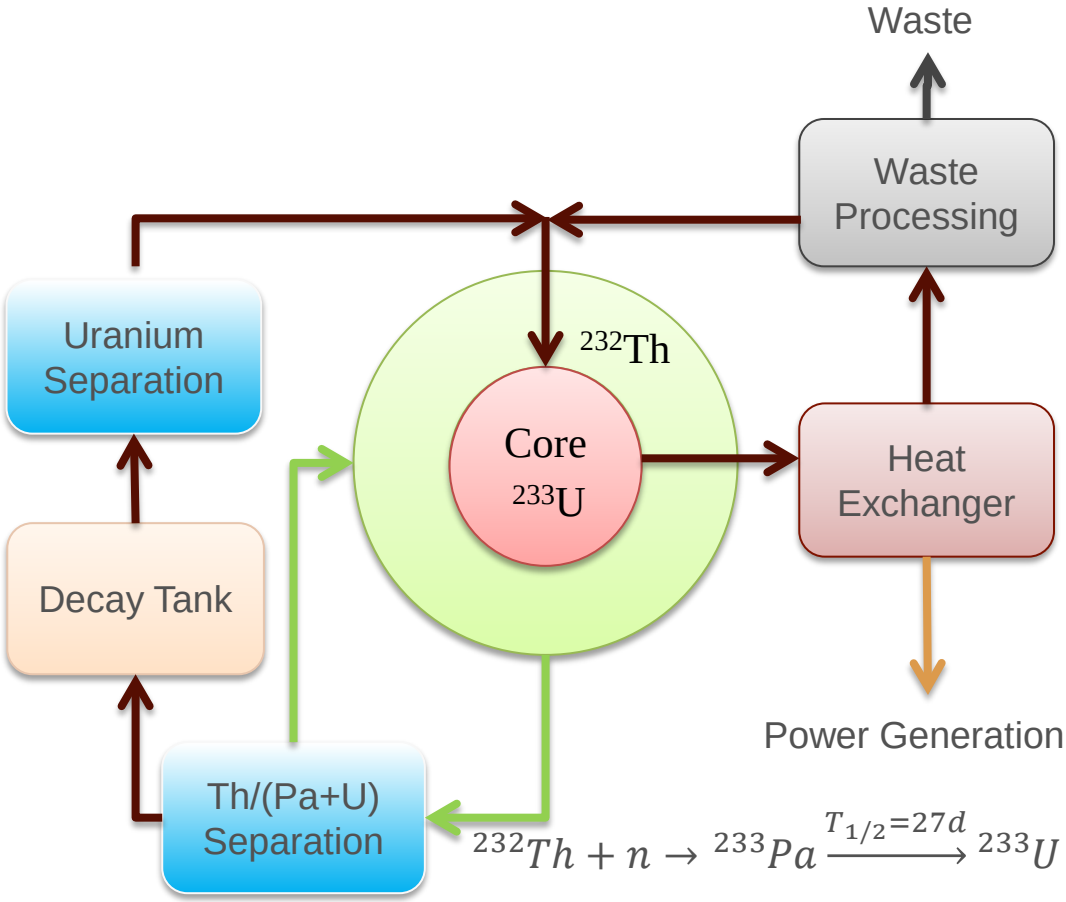
Outline

- Application of molten fluoride electrochemistry
- Objective
- Experimental setup
- Results
- Conclusions
- Future work

Application of molten fluoride electrochemistry

- ORNL MSBR – liquid fluoride salt carries Th and U, needs frequent reprocessing
- Electrochemical methods have potential to be employed for separations (either Ln/An or U/Th)
- Electrochemical methods also suitable for monitoring
- This work is focused on U/Th separation for blanket region of MSR



$$^{232}Th + n \rightarrow {}^{233}Pa \xrightarrow{T_{1/2}=27d} {}^{233}U$$

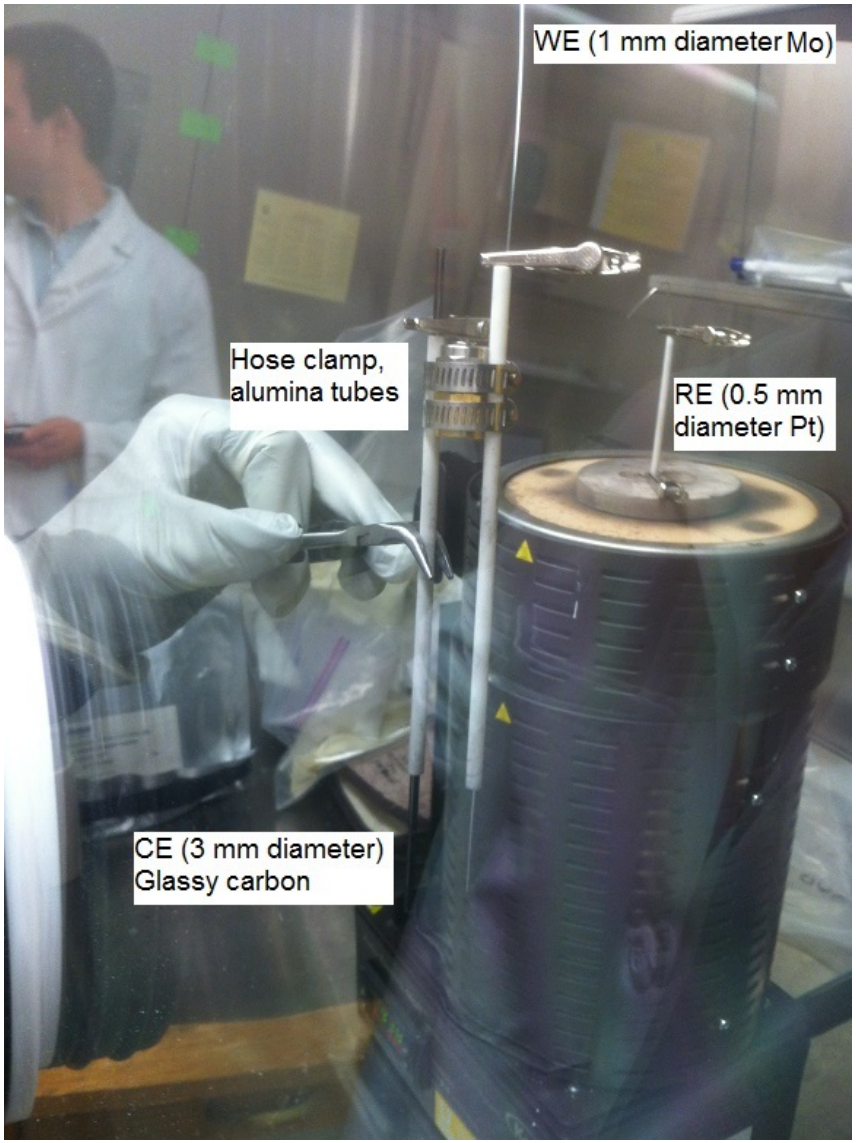
$$^{233}Pa + n \rightarrow {}^{234}Pa \rightarrow {}^{234}U$$

Objective

- Obtain concentration “calibration curve” (peak height vs. analyte concentration) usable in later salt/bismuth extraction experiments

Experimental setup

- 3 electrode setup (inert WE, Pt QRE)
- Nickel crucible
- Glove box with argon atmosphere (< 1 ppm O_2, H_2O)
- Kerr furnace operated at 900 C (1173 K)
- 99.98% LiF (Alfa Aesar)
- 99.99% ultra-dry LiF (Alfa Aesar)
- 99.99% ThF_4 (Materion)
- Autolab PGSTAT302N potentiostat
- Salt content analyzed by ICP-MS and ICP-OES



Wet and dry salts

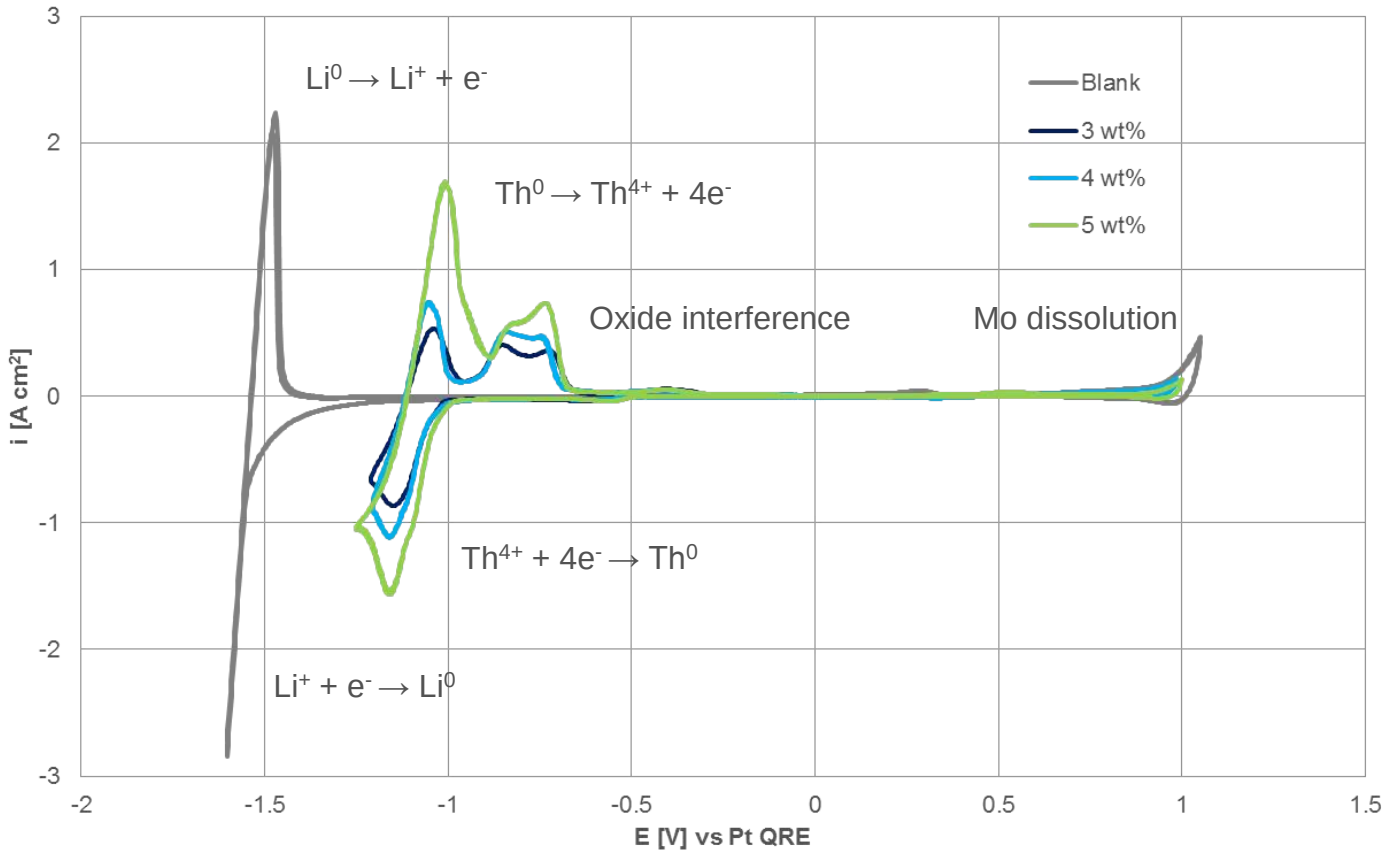
- Initial experiment performed with untreated LiF and 1 wt% ThF_4
  => no Th reduction peak!
- Analysis and literature revealed precipitated ThO_2 as a result of moisture/residual oxide reaction:

$$ThF_4 + O^{2-} \rightarrow ThOF_2, ThO_2$$

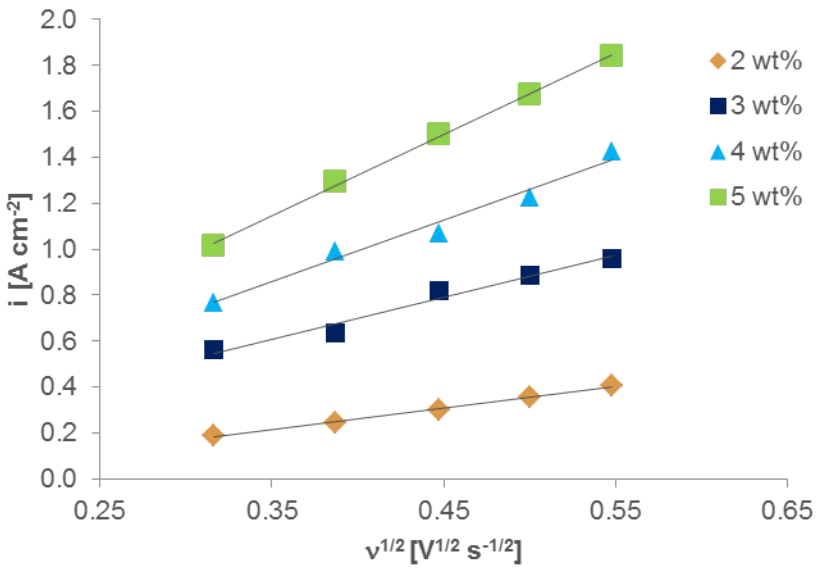
- Additional experiments performed up to 5 wt% ThF_4, subsequent analyses were used to find the true (dissolved) Th content
- Ultra-dry salt was then used to validate previous results
- => good Th reduction peak with 1 wt% ThF_4, almost no moisture reaction (analyzed content almost matched expected content)
- Results between salts not entirely compatible

Wet salt results

- 200 mV/s

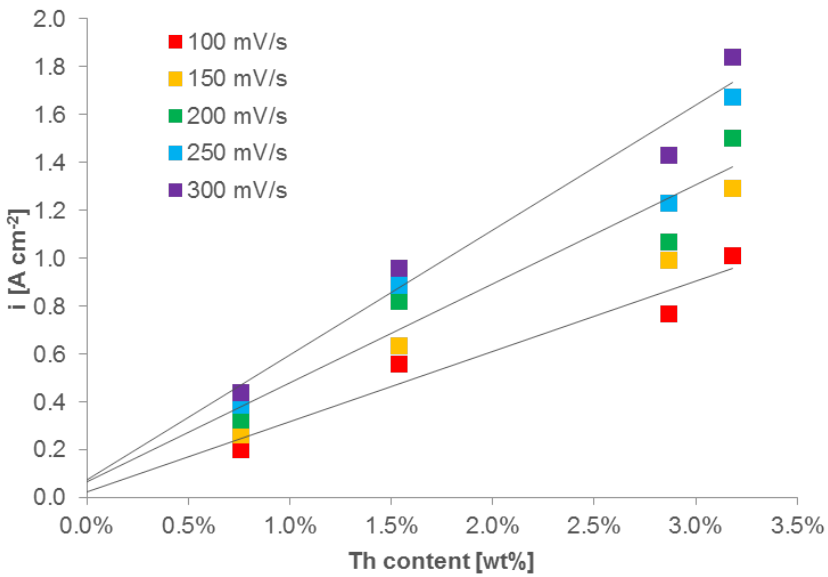


Wet salt results II



- Linearity of peak current versus square root of scan rate verified
  => process is diffusion controlled
  => process is reversible
- Berzins-Delahay equation valid for this case:
- $I = -061nFSc(\frac{nF}{RT})^{1/2}D^{1/2}\nu^{1/2}$
- Used to calculate diffusion coefficient (later slide)

Wet salt results III

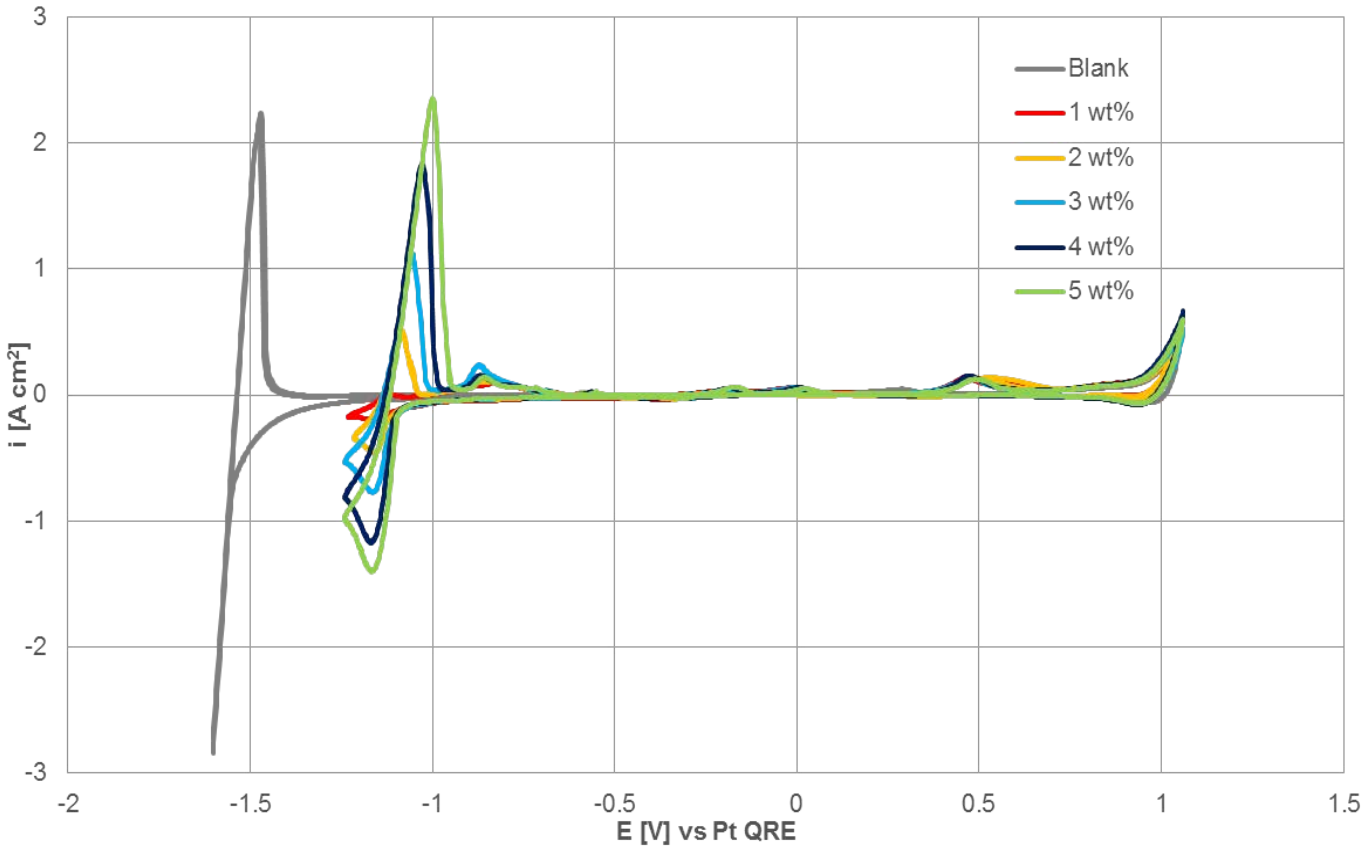


- Linear increase of peak current density with thorium content
- Intercept close to zero

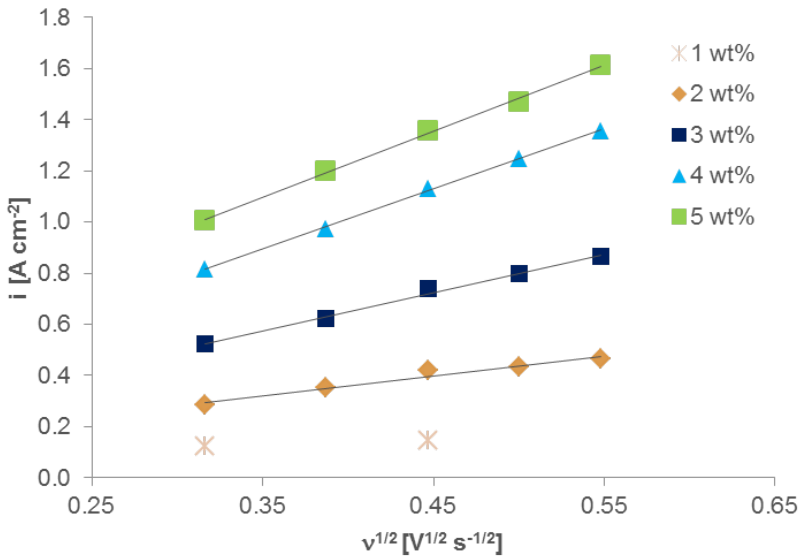
Expected Th content [wt%]	0.74%	1.52%	2.20%	2.96%	3.70%
Actual content (ICP-MS) [wt%]	0.24%	0.81%	1.57%	2.93%	-
Actual content (ICP-OES) [wt%]	0.30%	0.76%	1.54%	2.87%	3.18%

Ultra-dry salt results

- 200 mV/s



Ultra-dry salt results II



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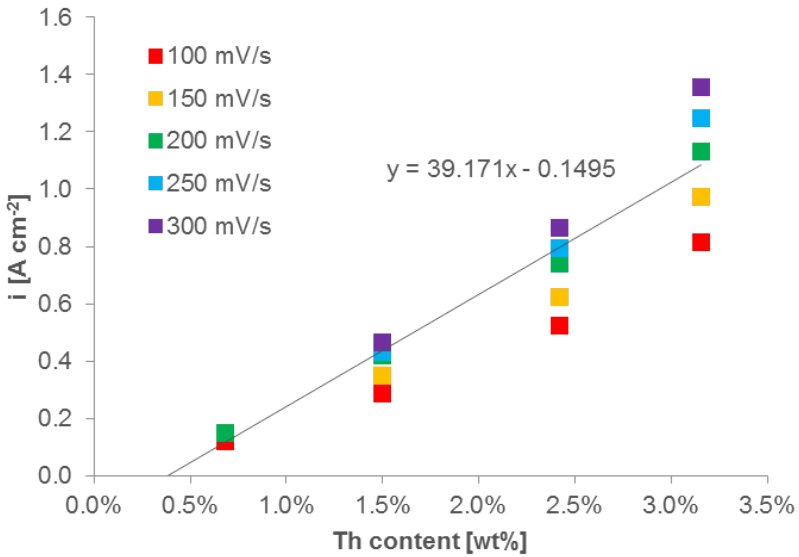
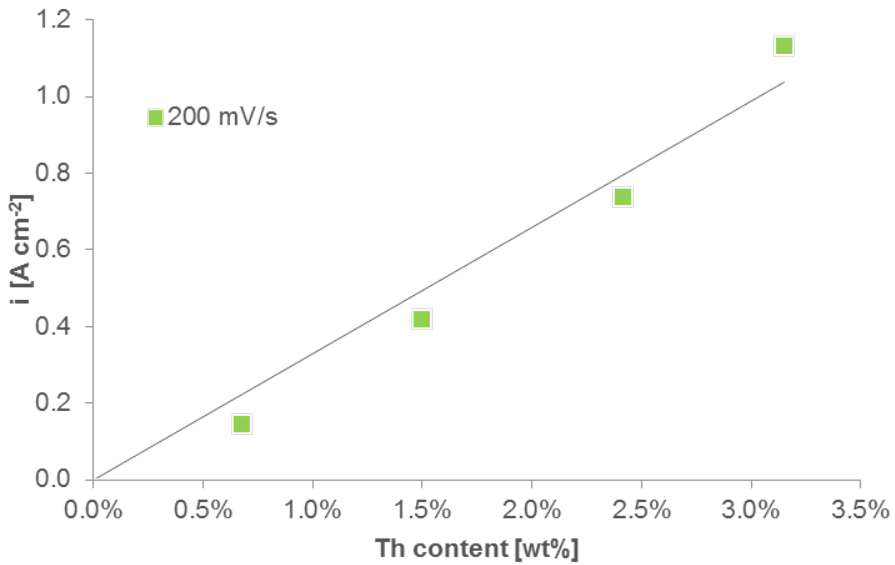
Ultra-dry salt results III



- Linear increase of peak current density with thorium content
- Intercept not close to zero

Expected Th content [wt%]	0.79%	1.55%	2.48%	3.25%	3.98%
Actual content (ICP-OES) [wt%]	0.68%	1.50%	2.42%	3.15%	3.40%

Ultra-dry salt results IV



- Linear increase of peak current density with thorium content
- Intercept fixed to be zero in order to use this regression as a calibration curve

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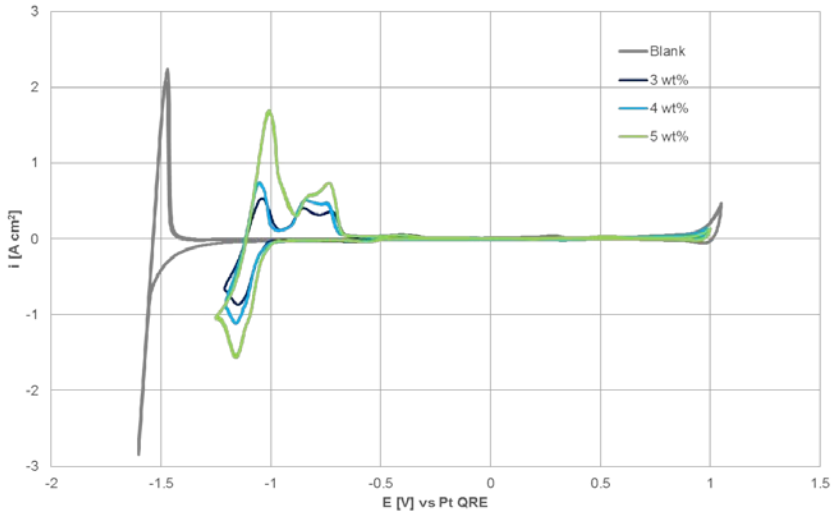
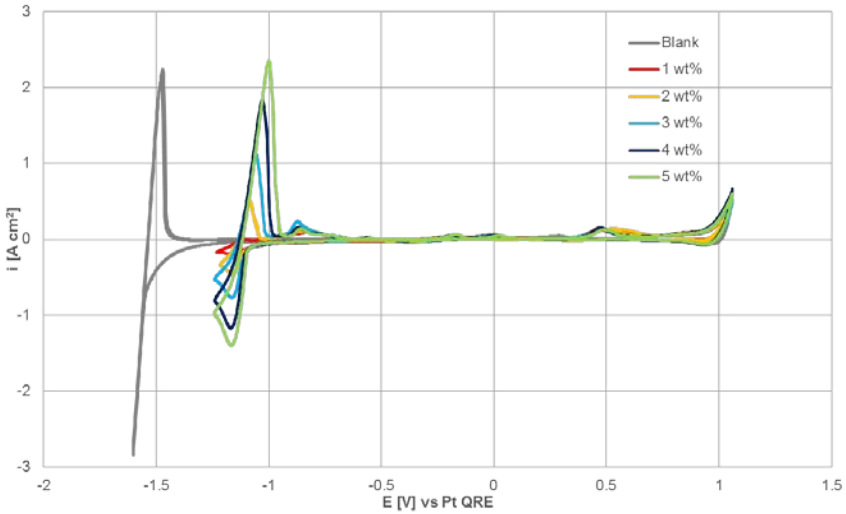
Comparison

Wet salt



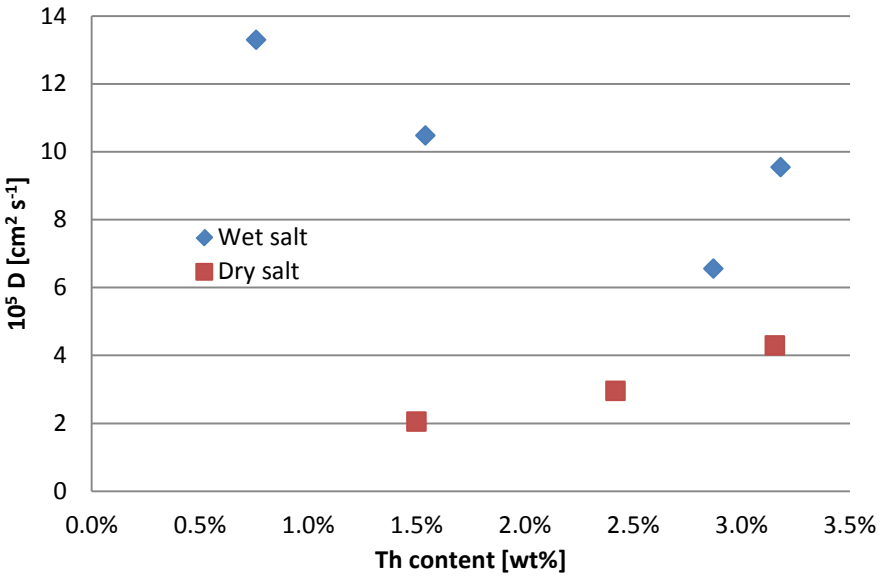
Ultra-dry salt



Comparison II

- Diffusion coefficients vary between salts and also with concentration
- Diffusion coefficients should decrease with concentration

10^5 Diffusion coefficient [cm^2/s]	Mean	±
Wet salt only	9.97	2.4
Dry salt only	3.09	0.9
Wet + dry	7.02	3.9



Massot obtained 10^5 D = 6.7 [cm^2 s^{-1}] (in $LiF\text{-}CaF_2$)

Ln D = - 3.92 - 6668.5/T

Electrochemical behaviour of thorium(IV) in molten $LiF\text{-}CaF_2$ medium on inert and reactive electrodes, Electrochimica Acta, 2010

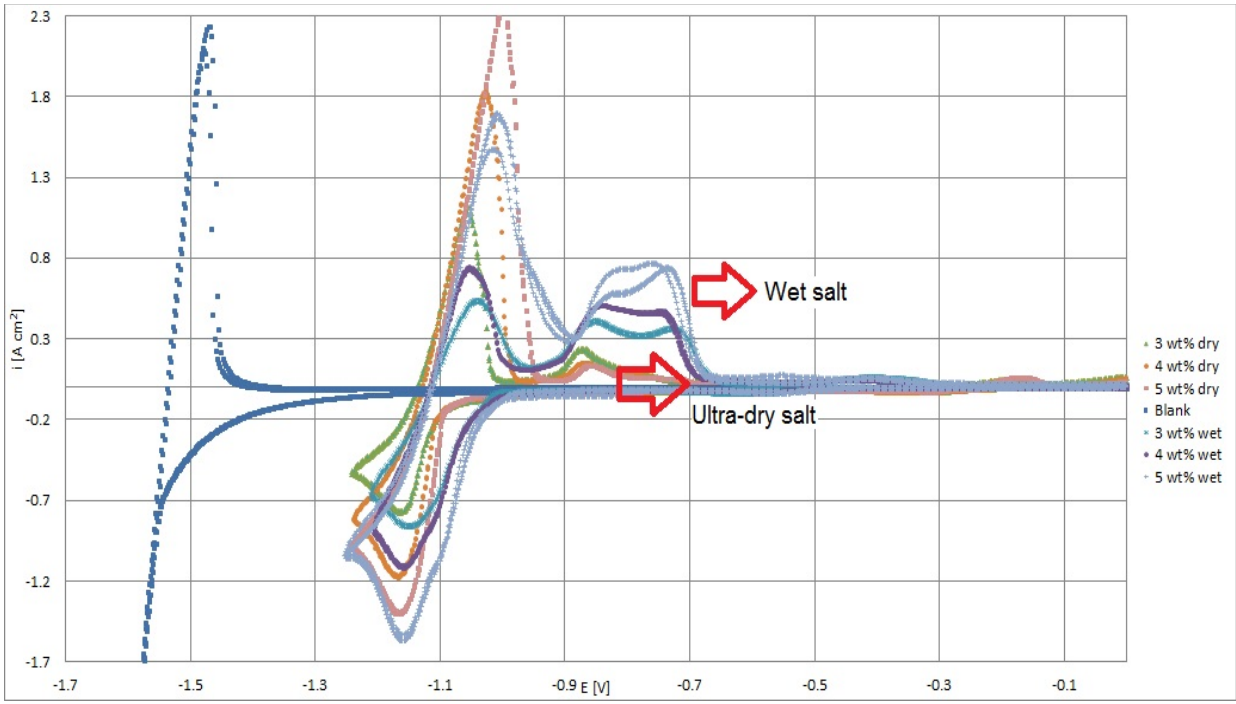
Conclusions

- Cyclic voltammetry has been performed in LiF @ 900 C for 1-5 wt% ThF_4 concentrations and for 100-300 mV/s scan rates
- Reduction mechanism has been verified as single-step soluble/insoluble process (4 electron exchange)
- Oxidation mechanism depends on oxide content, without oxide contamination single-step (4 electron exchange) dominates
- Diffusion coefficients vary with concentration and with salt dryness
- Salts offer different slopes for “calibration curves” of current peak height vs. Th concentration (obtaining this curve was the main purpose of these experiments)

Future work

- Dry ‘wet’ salt by heating it to ~ 650 C for 72 hours to get rid of moisture
- Repeat the same experiments for UF_4 to obtain diffusion coefficient and calibration curve of peak height vs. U concentration
- With both Th and U calibration curves ready, introduce liquid Bi into the system and perform extraction experiments
- Monitor progress/extent of extraction by U/Th peak heights in salt
- Assess feasibility of this method for U/Th separation
- => Directly applicable to MSR blanket circuit (lot of Th, very little U that needs to be extracted away while Th stays in salt)

Thank you

Back-up slides

- 200 mV/s
- Wet salt: Interference oxide peaks increase with Th concentration
- Ultra-dry salt: Interference oxide peaks are low and stay the same throughout Th additions