Concentration Measurement of Actinide and Lanthanide ions in LiCl-KCl Melt by Using Electrochemical Techniques

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Outline

1. Work scope in our laboratory

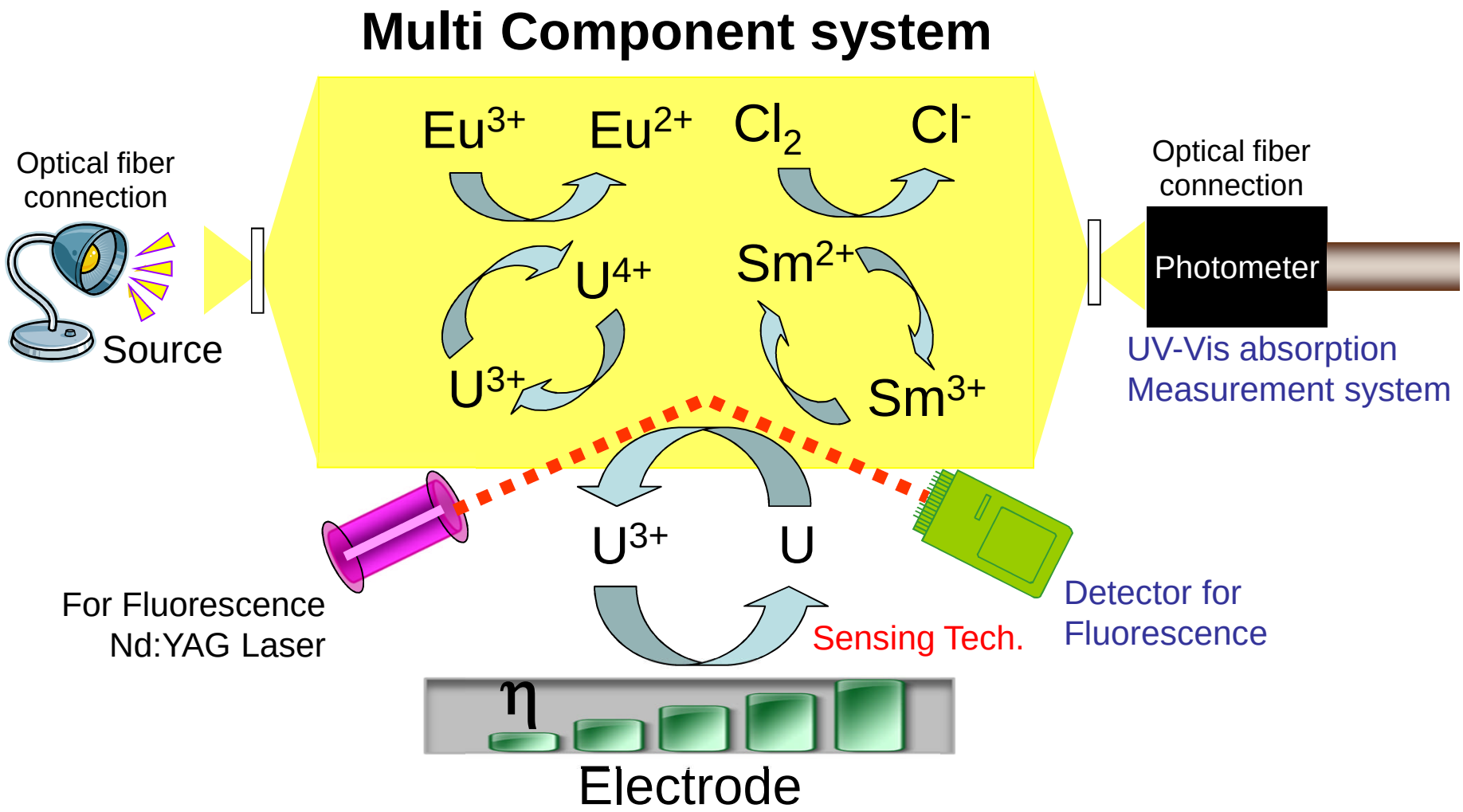
2. Some electrochemical techniques
   - -CV, CA, CP
   - -NPV, SWV

3. Apparatus and Experimental

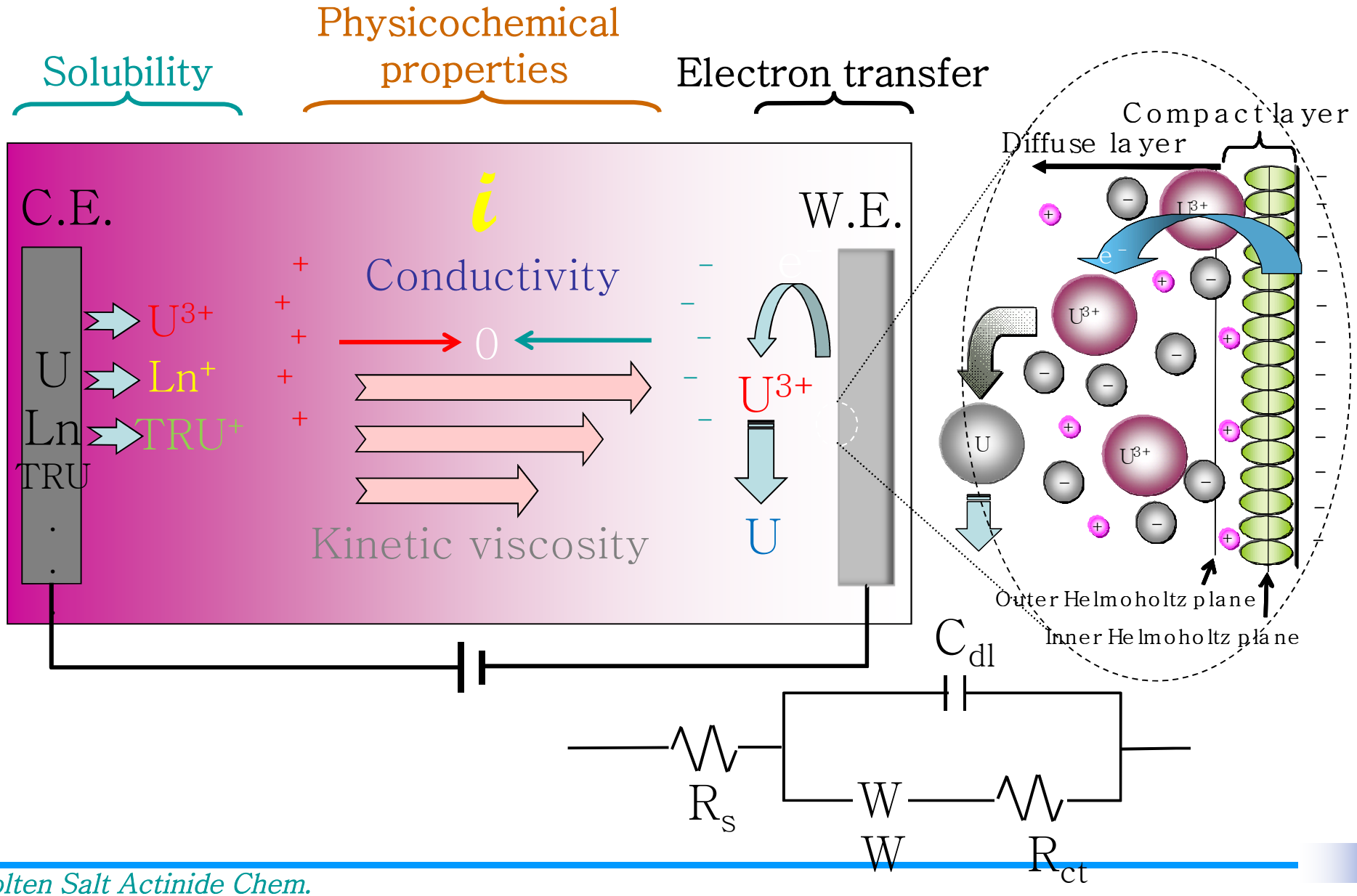
4. Results and Discussion
   - a. Conventional electrochemical measurements
   - b. Repeating chronoamperometry
   - c. UV-VIS absorption spectroscopy

5. Conclusion

Work scope in our laboratory

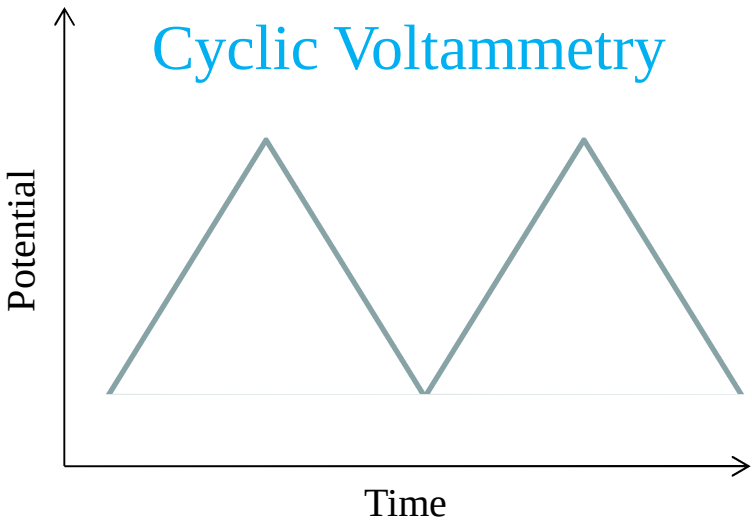


Electrochemical environment in molten salt

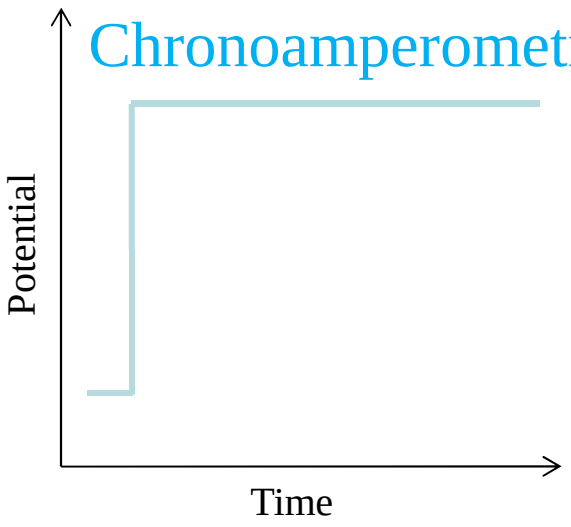


Electrochemical methodologies

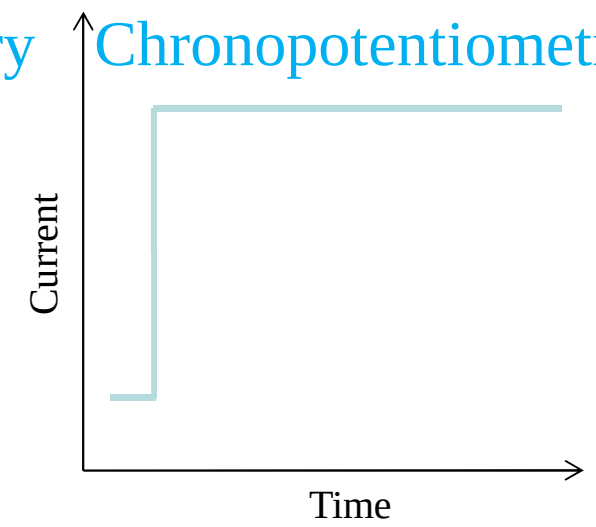
Cyclic Voltammetry



Chronoamperometry



Chronopotentiometry



Randles-Sevick equation

$$i_p = 0.4463\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A D^{1/2} C v^{1/2}$$

Redox potentials, electrochemical reaction rates of the compounds, and intermediates

Cottrell's equation

$$i = \frac{n\,F\,A\,C\,D^{1/2}}{\sqrt{\pi\,t}}$$

Good precision for measuring concentration

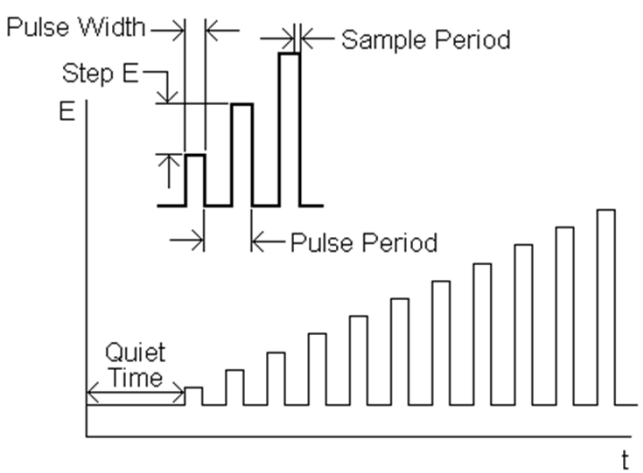
$$E = E^\circ + \frac{RT}{nF}\ln\left[\frac{1-\left(\frac{t}{\tau}\right)^{1/2}}{\left(\frac{t}{\tau}\right)^{1/2}}\right]$$

$E = E^\circ$ for $t = \frac{\tau}{4}$

Determination of E°

Electrochemical methodologies

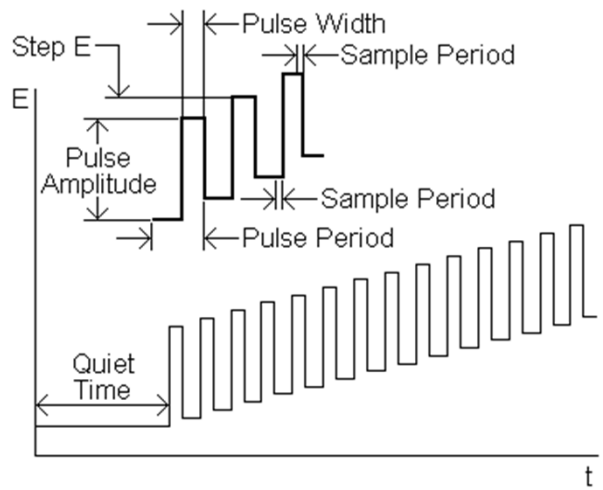
Normal Pulse Voltammetry (NPV)



$$i = \frac{n F A C D^{1/2}}{\sqrt{\pi t}}$$

Removing charging current
Good peak separation

Square wave Voltammetry (SWV)



$$\Delta I_f(j) = \frac{n F A C D^{1/2}}{\sqrt{\pi t}} \Delta\psi(j)$$

Removing charging current,
Good S/N ratio, Good detection limit (10^{-8}M)

Electrochemical analysis in LiCl-KCl

Normal Pulse Voltammetry (NPV)

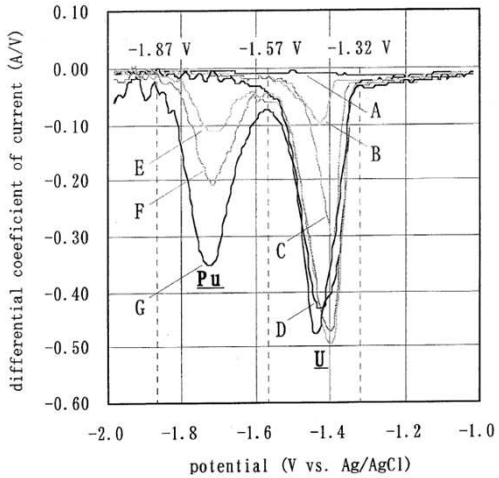


Fig. 12. Differentiated NPV curves for LiCl–KCl–UCl_3–$PuCl_3$.

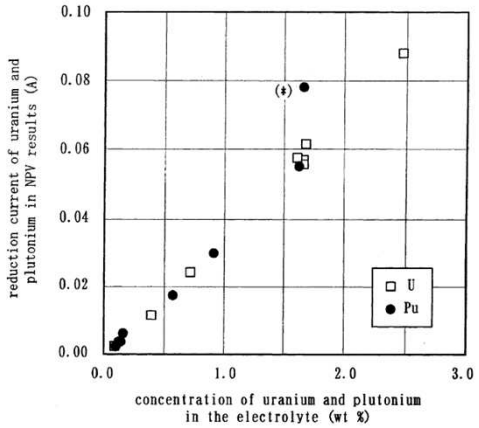


Fig. 13. Concentration dependence of reduction current in NPV curves for LiCl–KCl–UCl_3–$PuCl_3$.

Square wave Voltammetry (SWV)

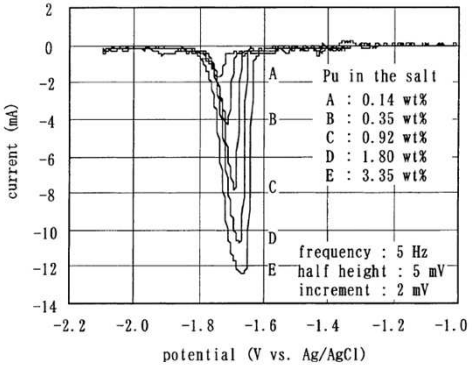


Fig. 6. SWV curves for LiCl–KCl–$PuCl_3$.

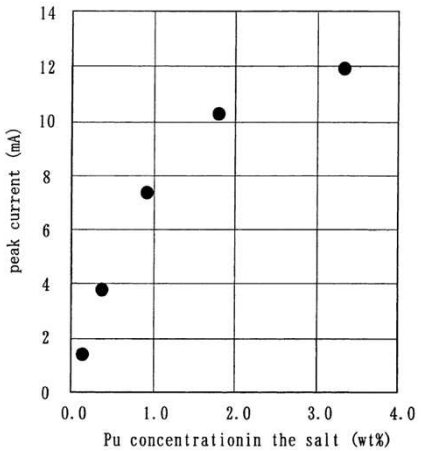


Fig. 7. Concentration dependence of peak height in SWV curves for LiCl–KCl–$PuCl_3$.

•Iizuka et al.

Differential Pulse Voltammetry

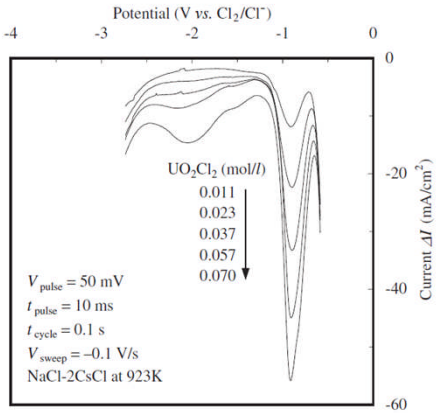


Fig. 2 Differential pulse voltammograms for uranyl dichloride in NaCl-2CsCl at 923 K

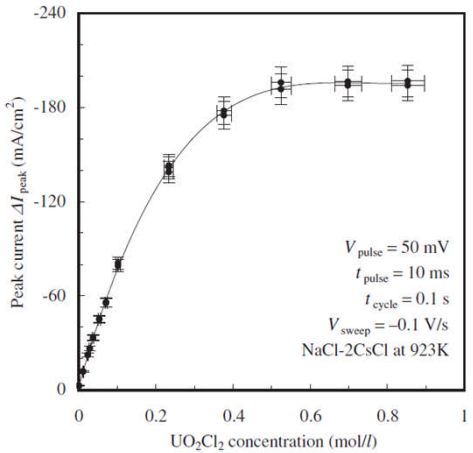
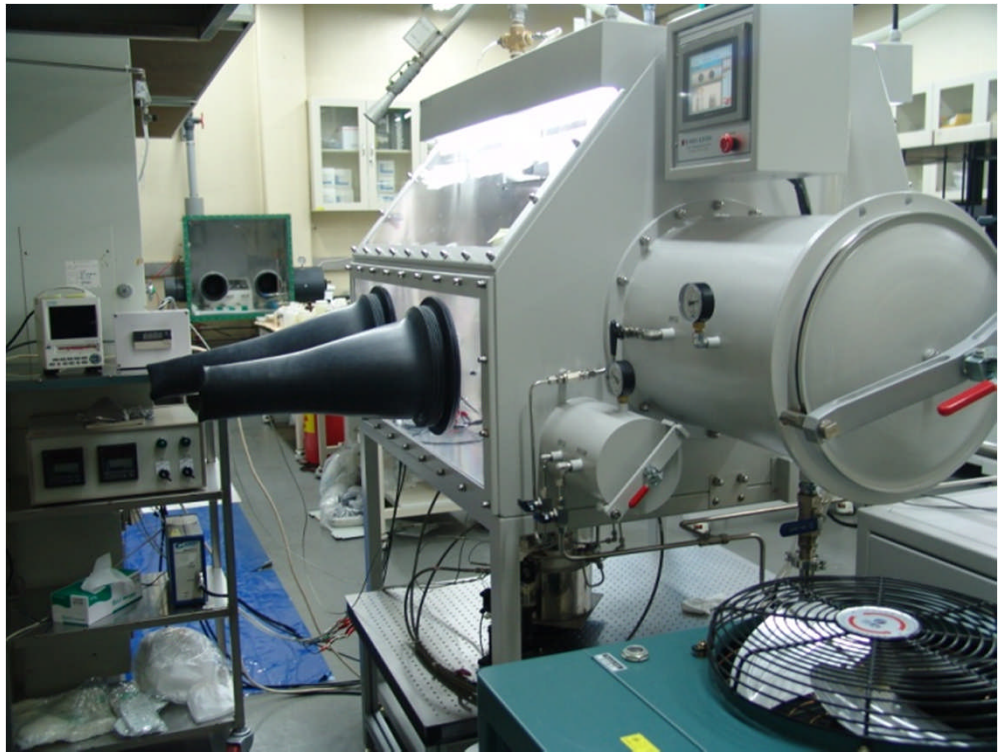
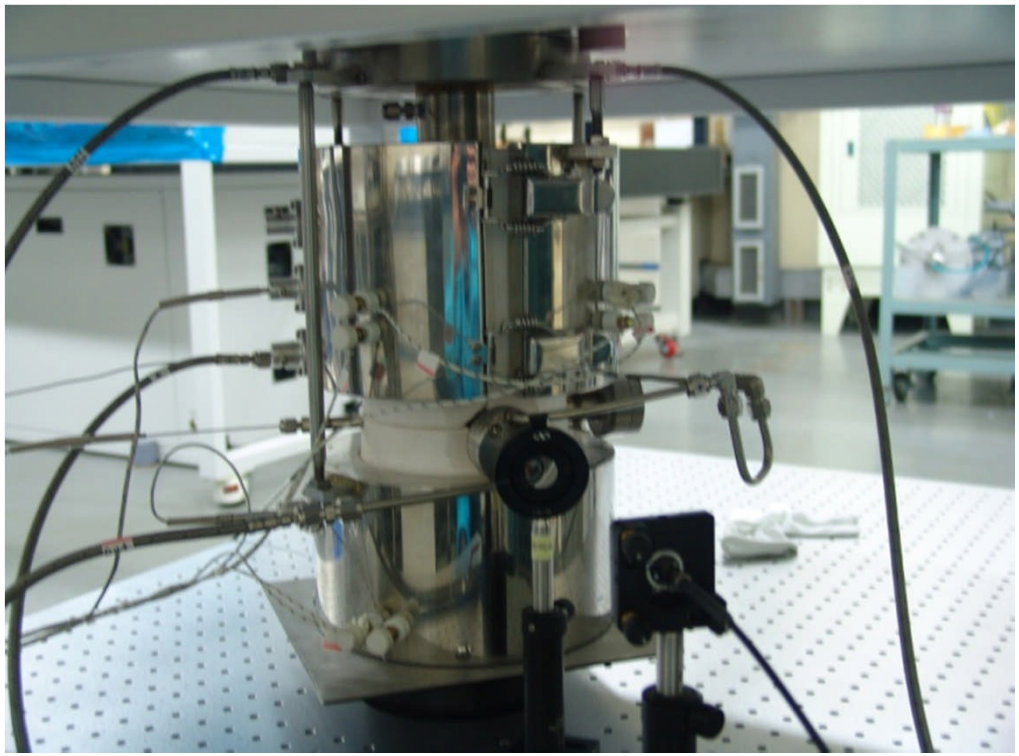


Fig. 5 Peak of current density ΔI_{peak} for various high concentrations of uranyl dichloride in NaCl-2CsCl at 923 K

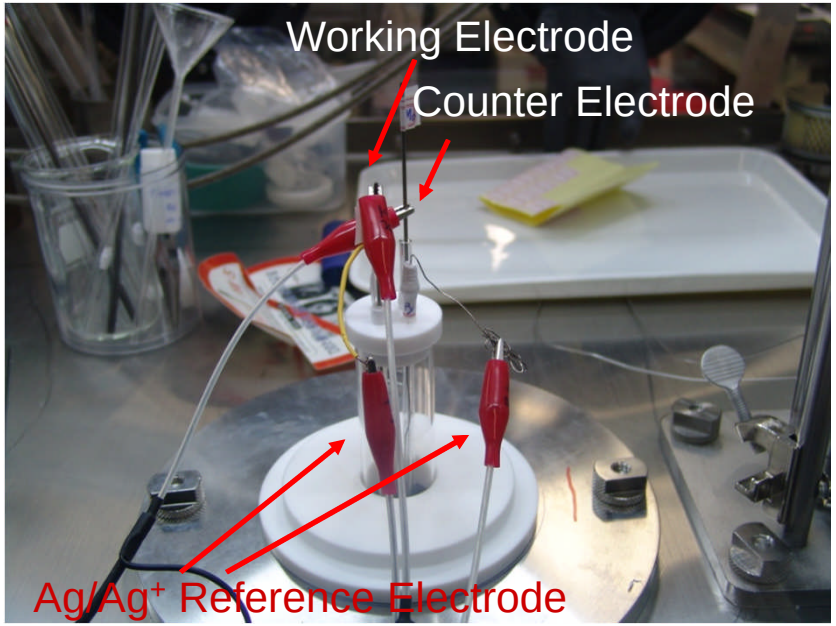
•Yamana et al.

Glove Box and Furnace for High Temperature Electrochemistry

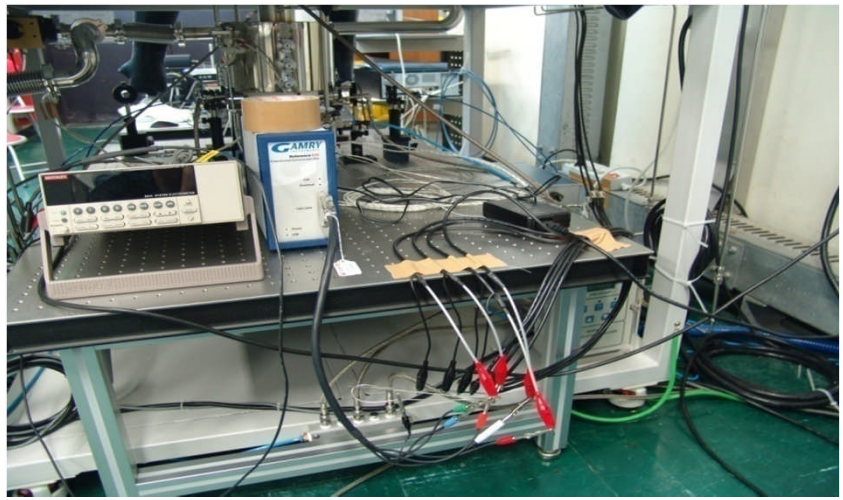




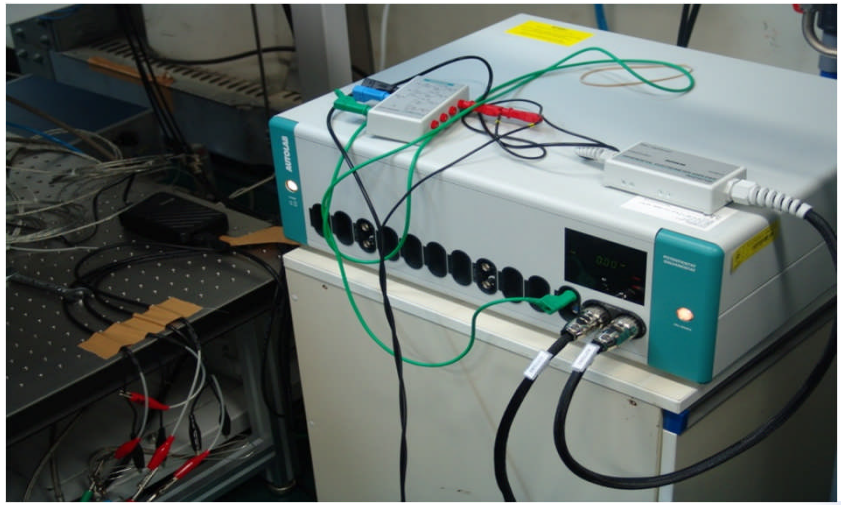
Electrochemical Measurement in Molten Salts



GAMRY Reference 600 Potentiostat/Gavanostat/ZRA



Autolab Potentiostat/Gavanostat

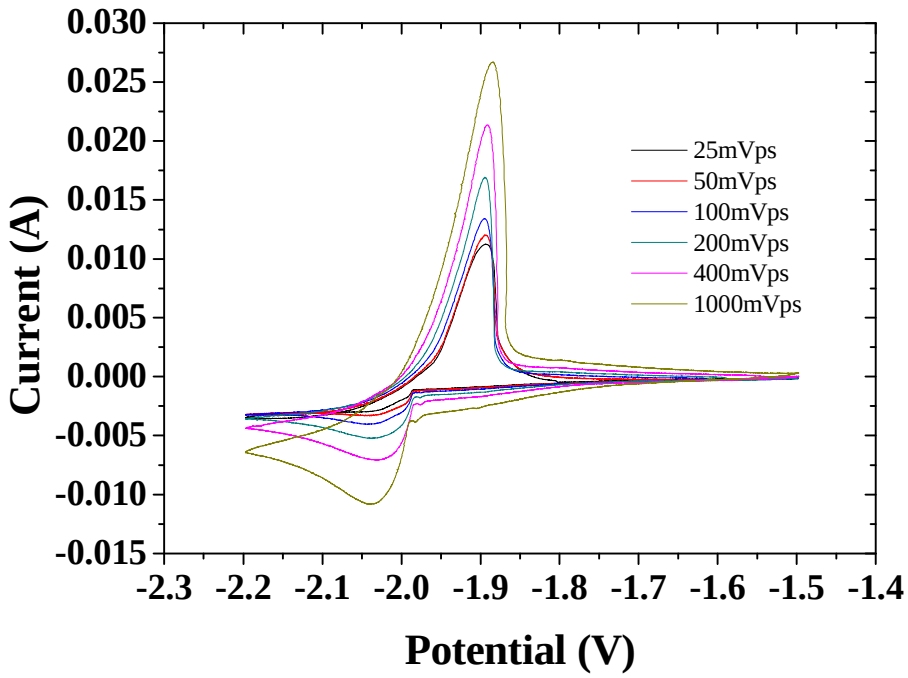


- **WE : Tungsten**
- **CE : GC**

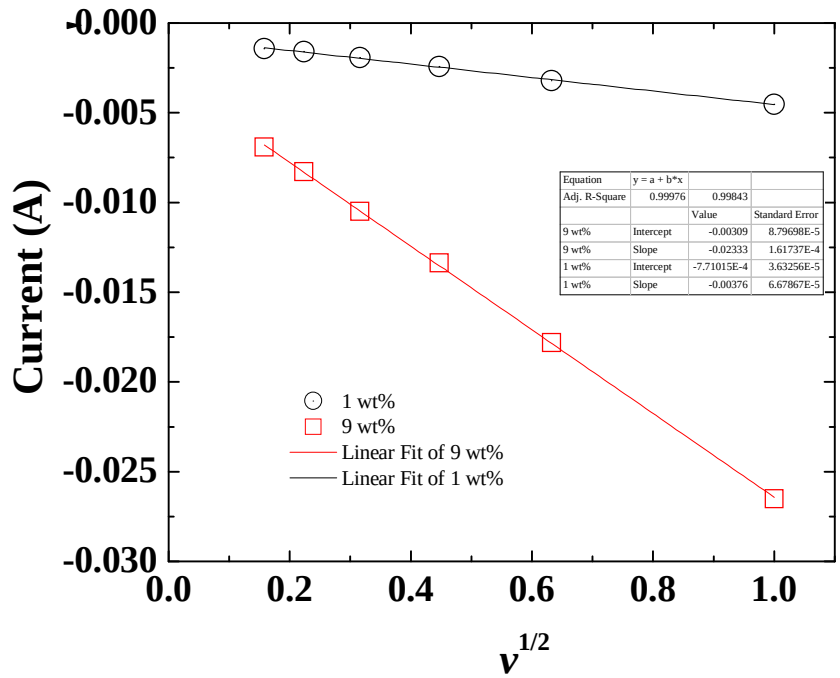
  pyrex tube (Ag|Ag+ in molten salt)
- **RE : pyrex tube (Ag|Ag^+ in molten salt)**

Results: CV (Scan rate dependence)

$$Nd^{3+} + 3e^{-} \leftrightarrow Nd(s)$$



Scan rate dependence

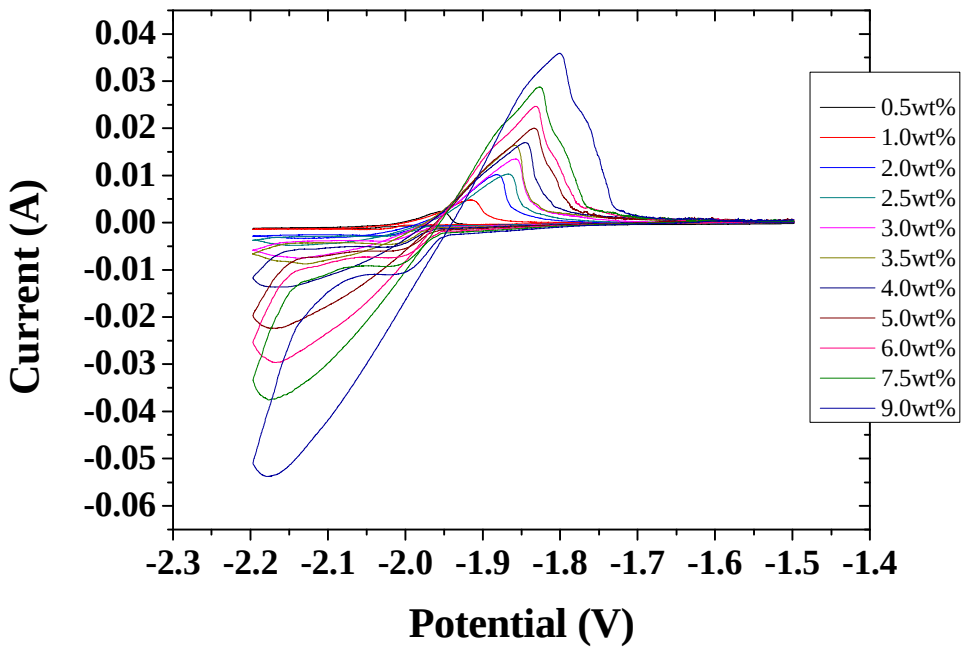


Equation	y = a + b*x		
Adj. R-Square	0.99976	0.99843	
		Value	Standard Error
9 wt%	Intercept	-0.00309	8.79698E-5
9 wt%	Slope	-0.02333	1.61737E-4
1 wt%	Intercept	-7.71015E-4	3.63256E-5
1 wt%	Slope	-0.00376	6.67867E-5

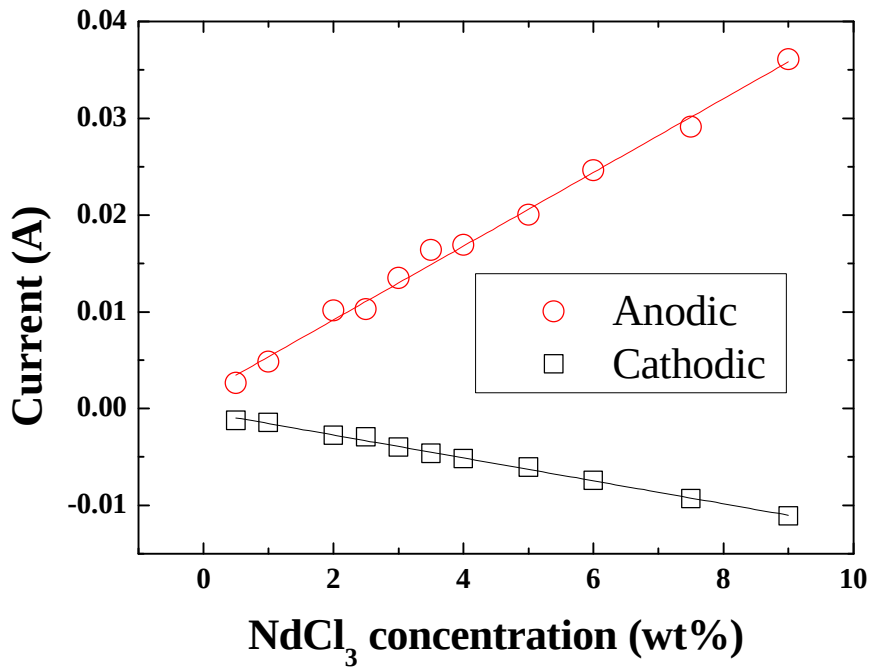
Scan rate dependence of CV in LiCl-KCl melt containing $NdCl_3$.

Results: CV (Concentration dependence)

Nd^{3+} concentration dependence of CV



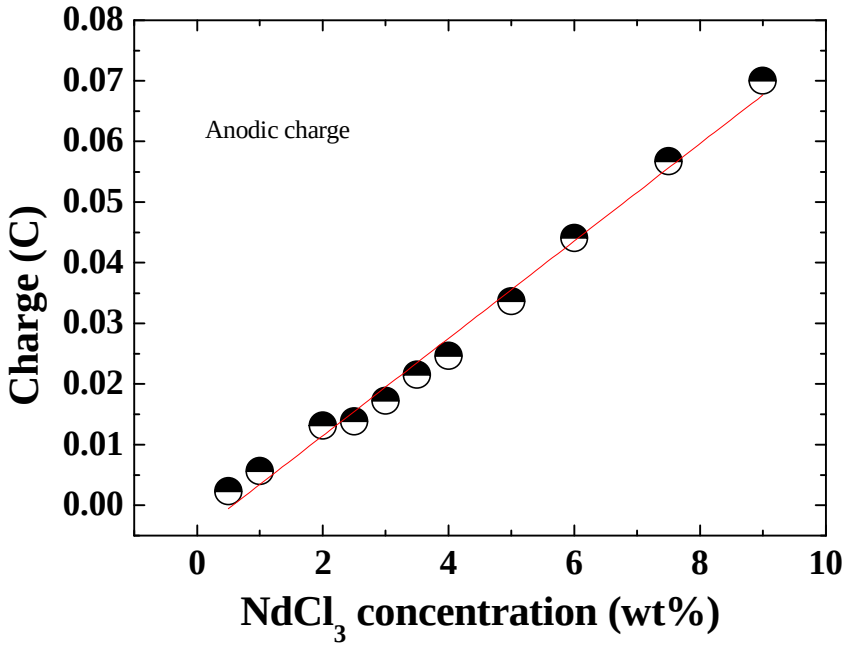
Peak current vs. $NdCl_3$ concentration

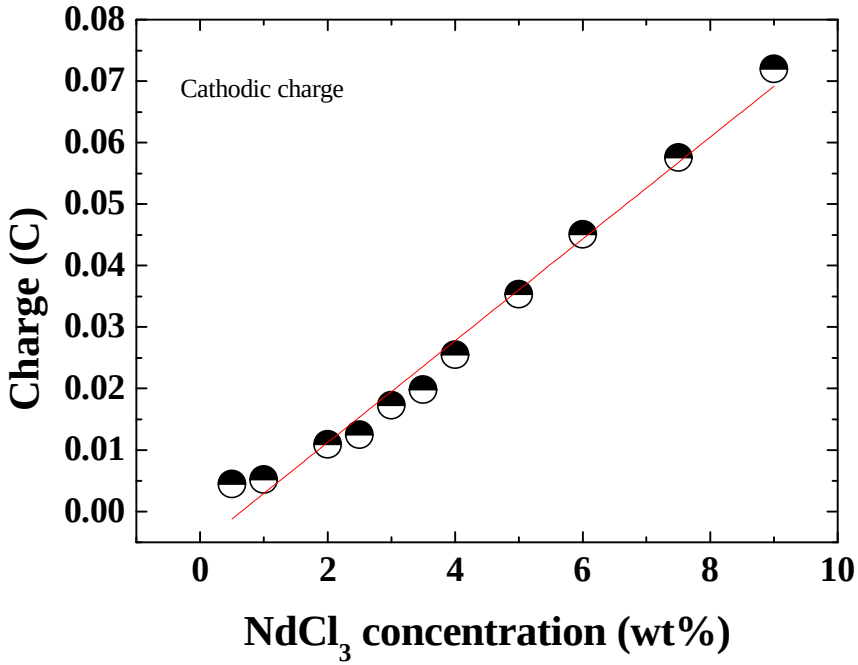


- Anodic and cathodic peak current ~ concentration
- Sometimes, the peak current at high conc. shows non linearity

Results: CV (passed charge)

Passed charge

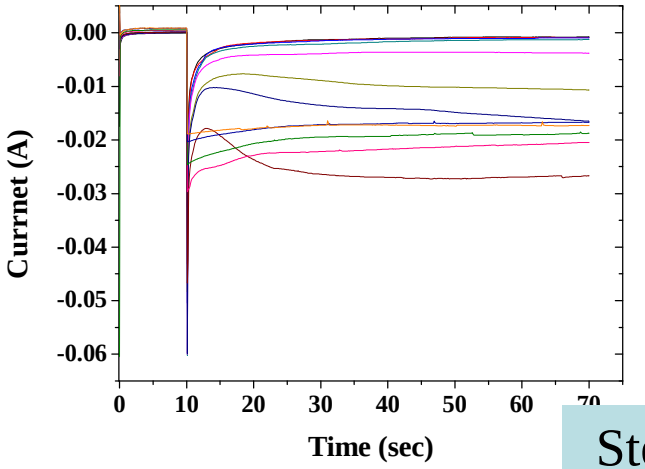




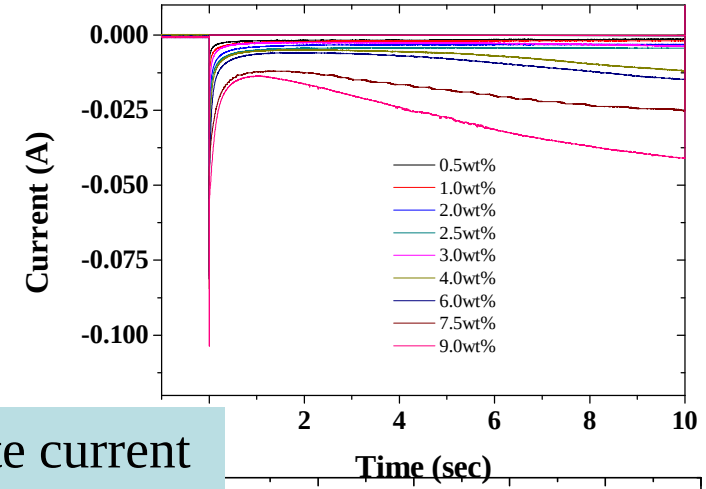
Anodic and cathodic passed charge ~ good linearity

Results: Chronoamperometry (CA)

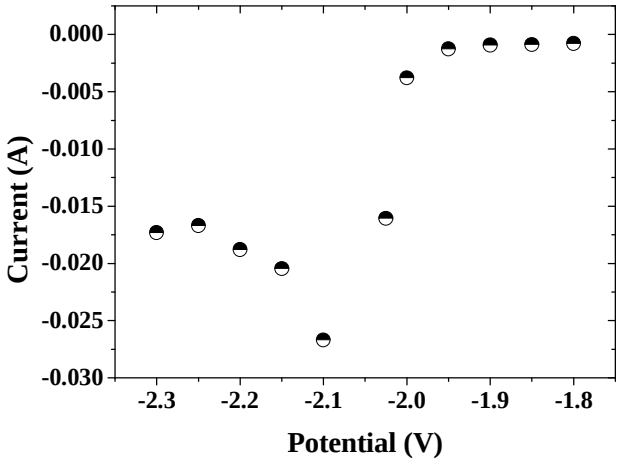
CA at various potentials

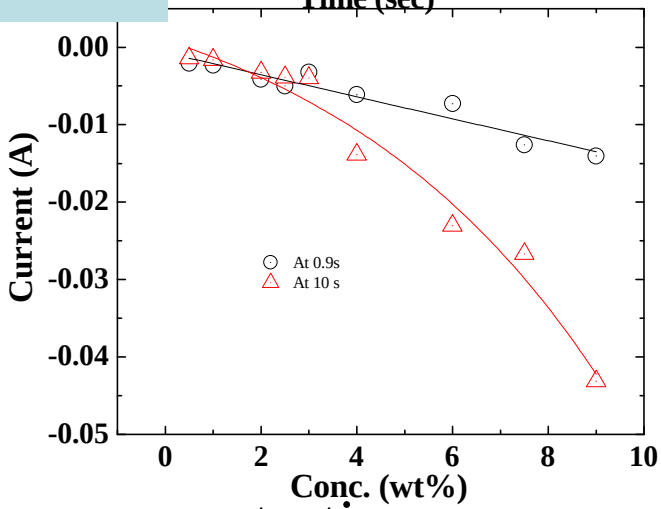


Electrodeposition at -2.1 V



Steady state current

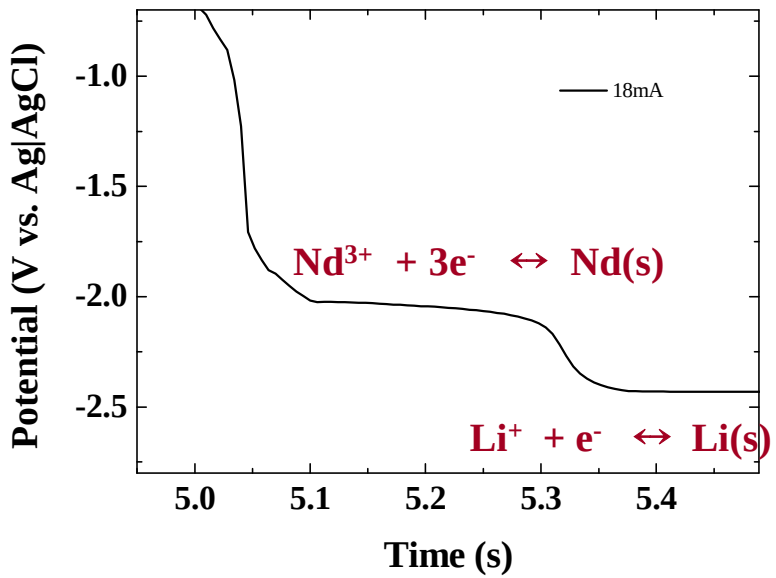




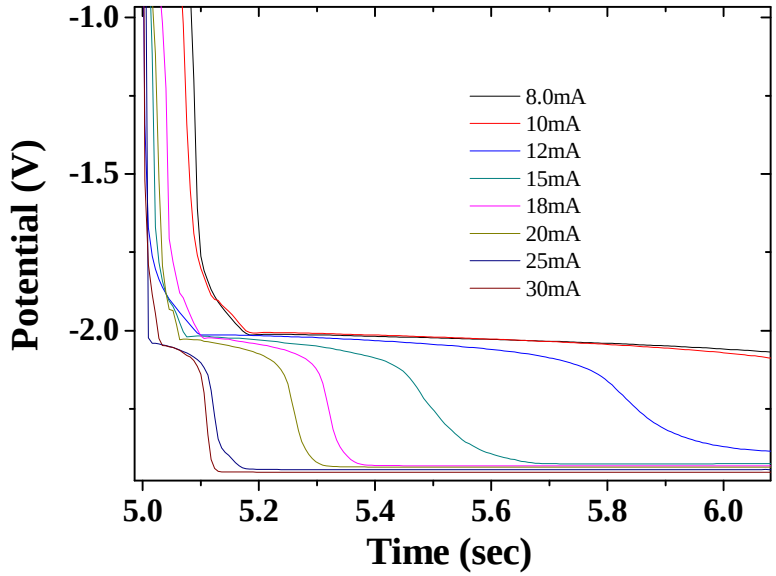
- Current at 1 s (steady state current) ~ concentration
- Current at 10 s ≠ concentration (Cl_2 evol., increasing electrode area…)

Results: Chronopotentiometry (CP)

At 18 mA in 3 wt% $NdCl_3$



At various currents

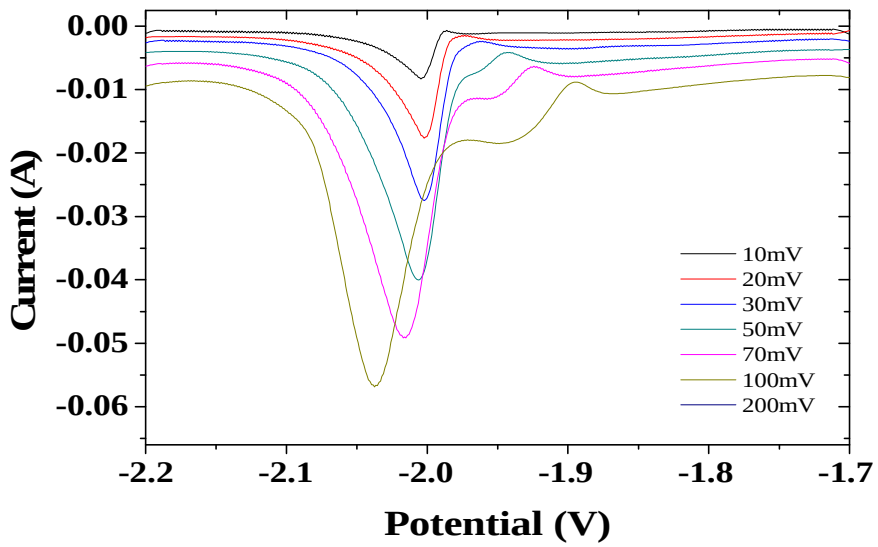


Apparent standard potential:

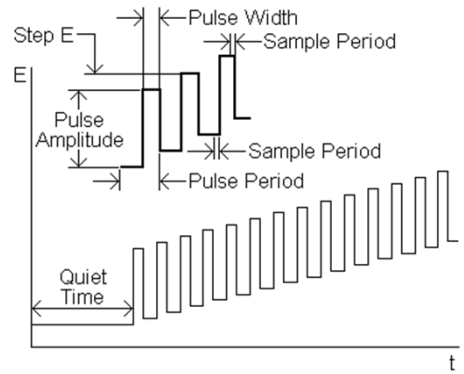
E^{o*}= -2.02 V vs. $Ag|Ag^+$

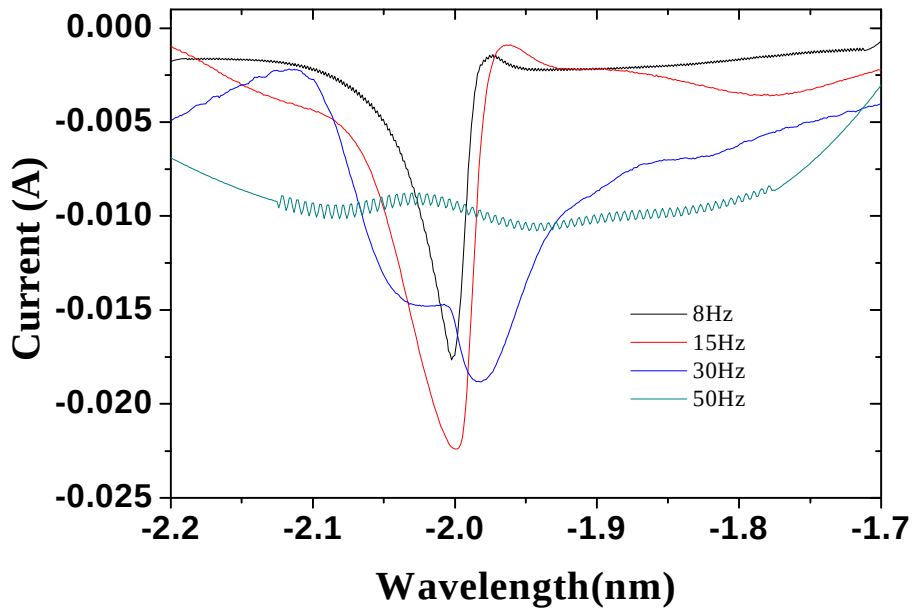
Results: Optimizing SWV condition

Parameter dependence of SWV



Pulse amplitude

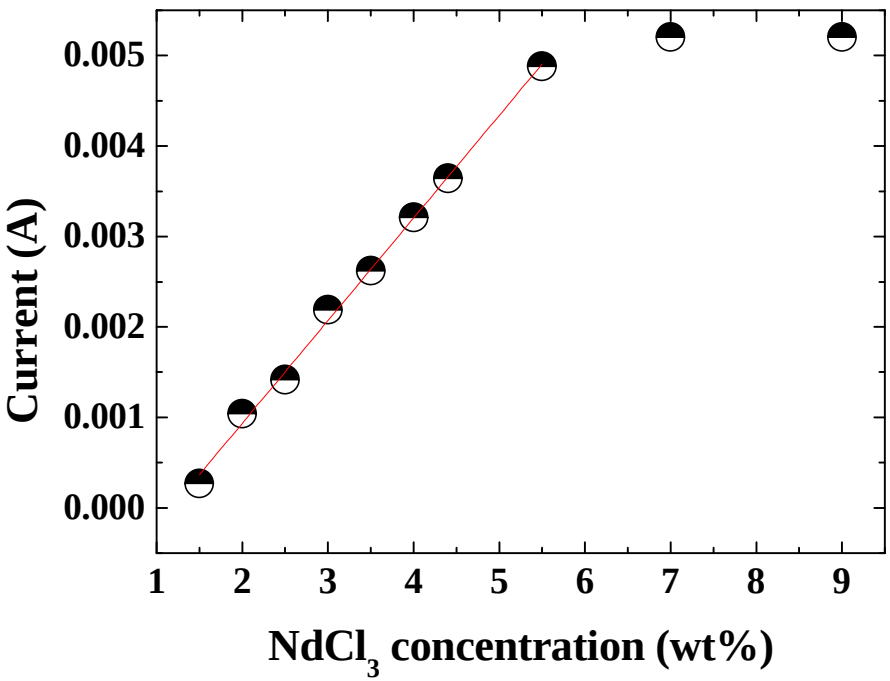




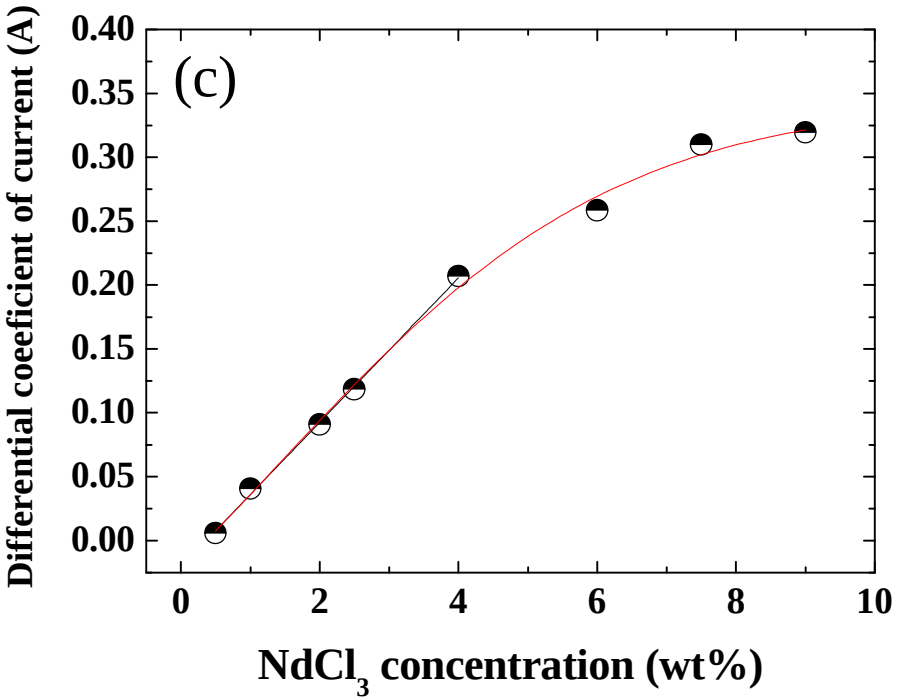
Pulse frequency

Results: Concentration depend. of SWV and NPV

Square wave voltammetry

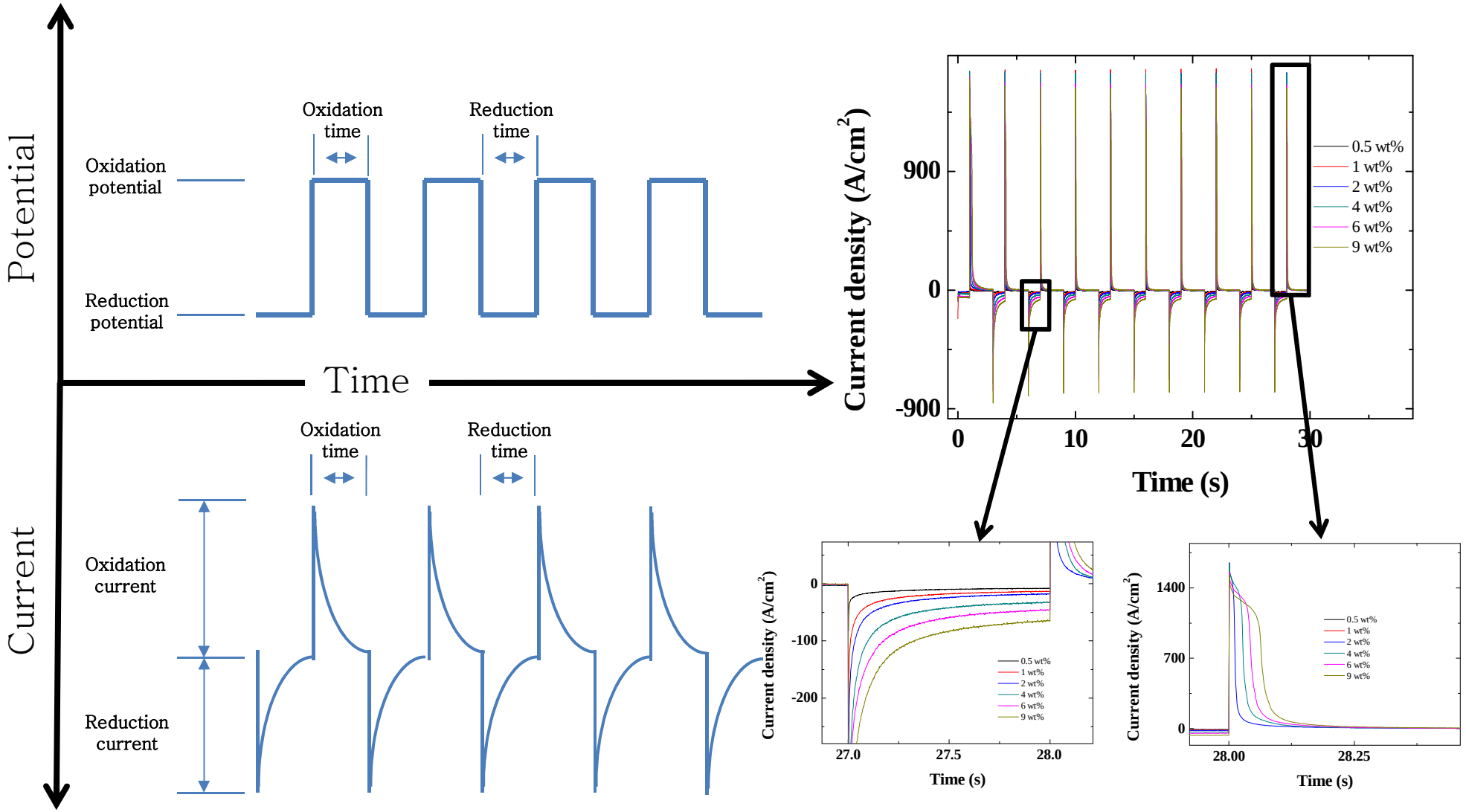


Normal Pulse voltammetry



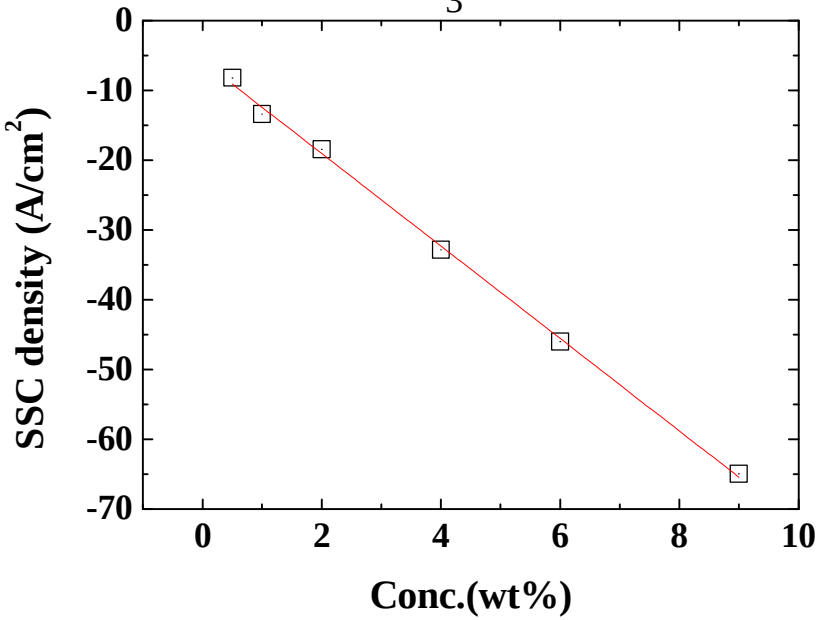
- Linear relation up to 5.5 wt%
- Linear relation up to 4 wt%

Results: Repeating CA (RCA; $NdCl_3$)

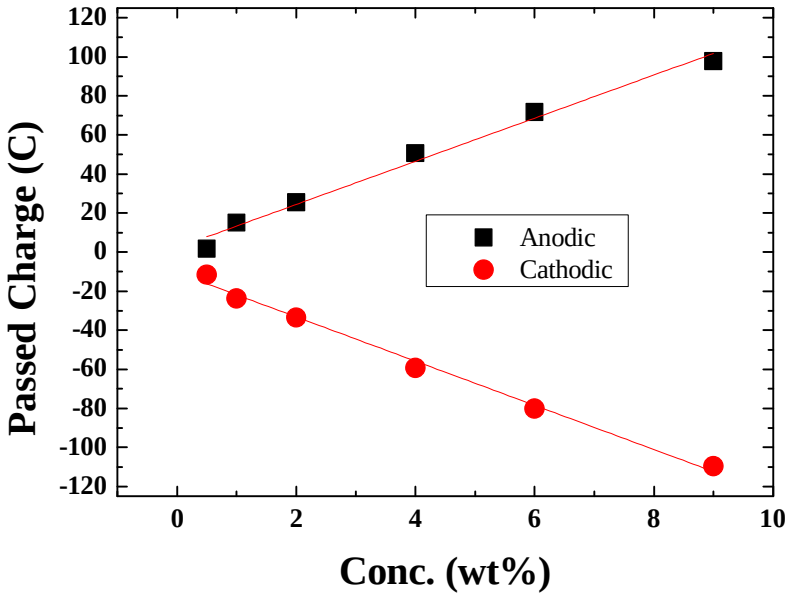


Results: Repeating CA (RCA; $NdCl_3$)

Steady state current vs. $NdCl_3$ conc.

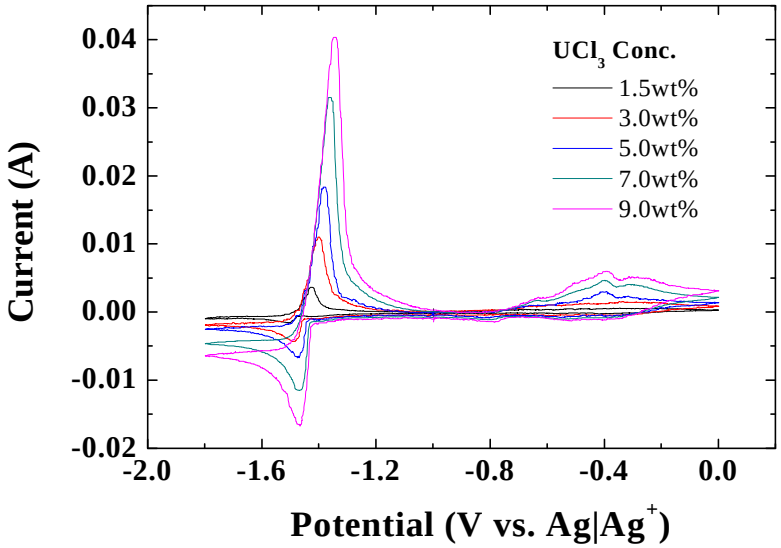


Passed charge vs. $NdCl_3$ conc.

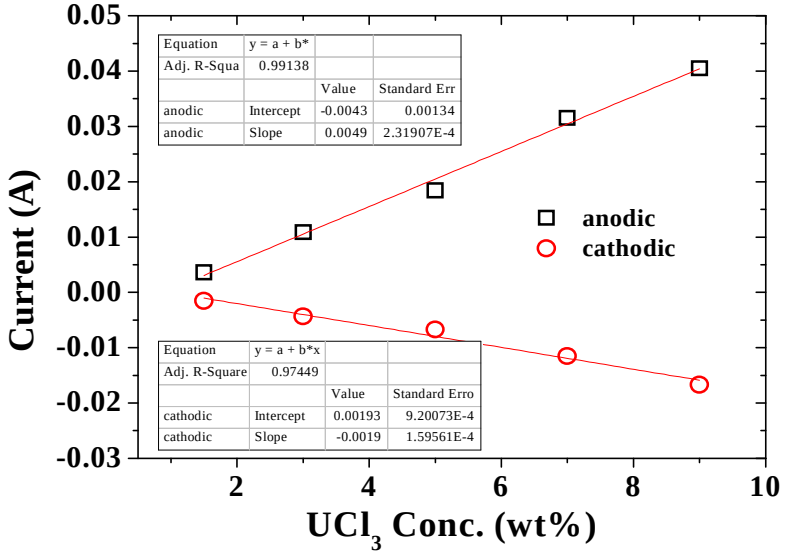


Results: Cyclic voltammetry; UCl_3

Cyclic voltammetry – UCl_3



Peak currents vs. conc.

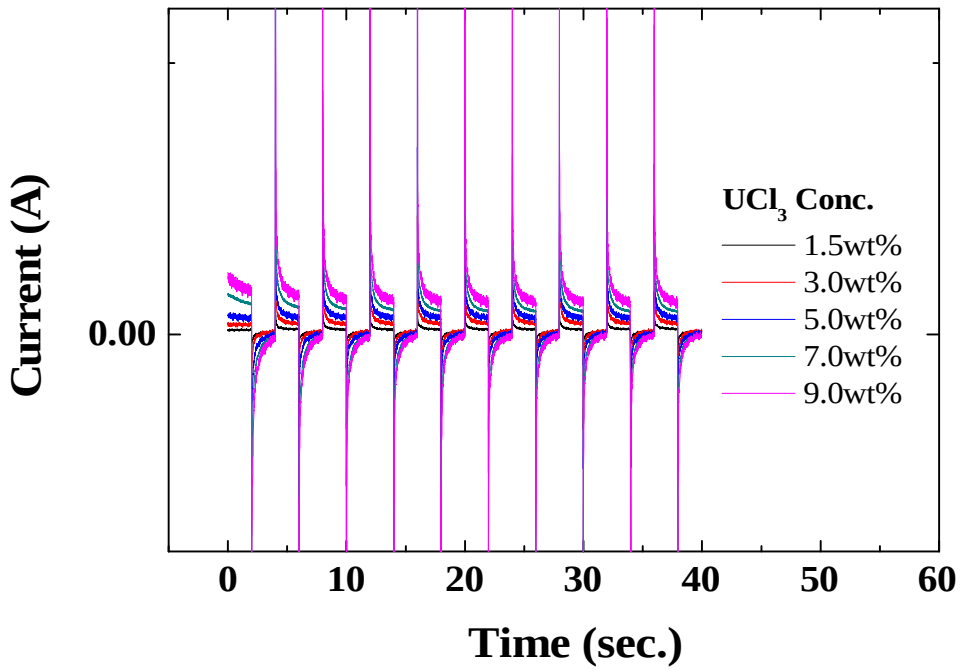


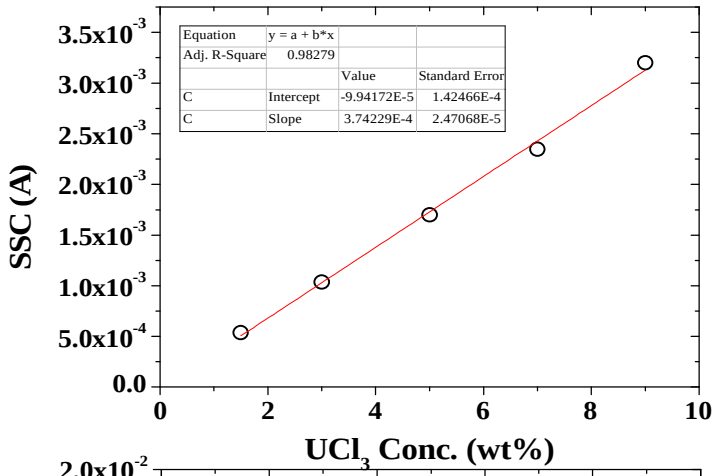
Electrodeposition reaction at -1.45 V

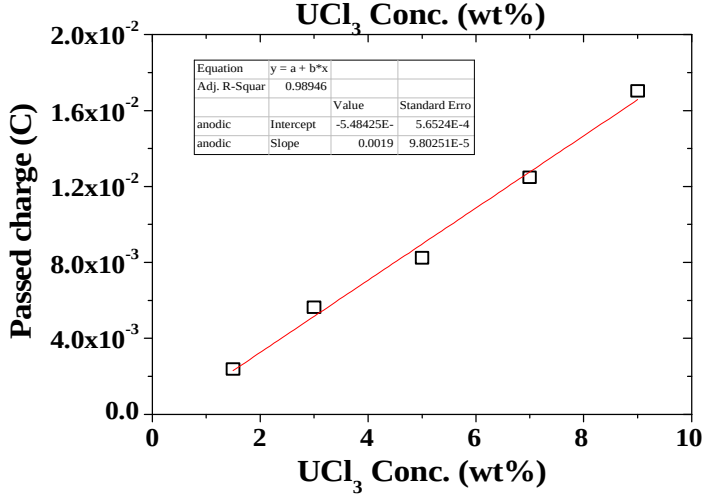
$$U^{3+} + 3e^- \rightarrow U^0$$

Results: Repeating CA (RCA; UCl_3)

$$U^{3+} \leftrightarrow U^{4+} + e^-$$

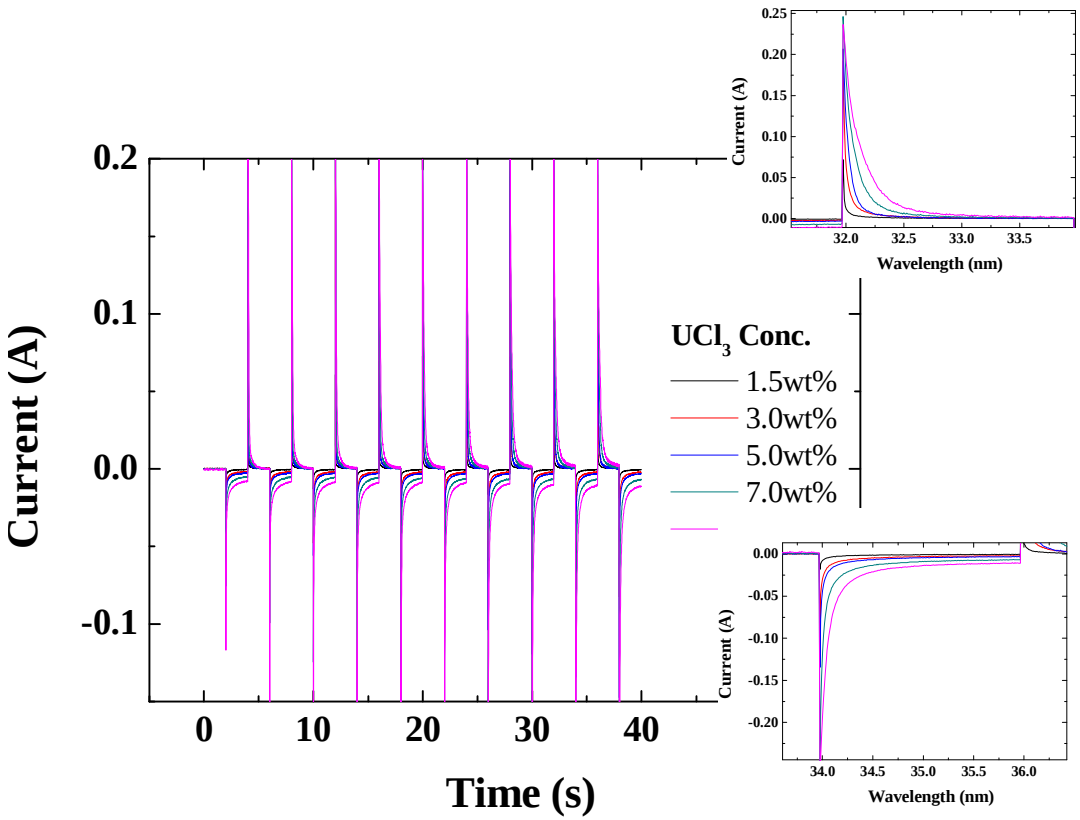


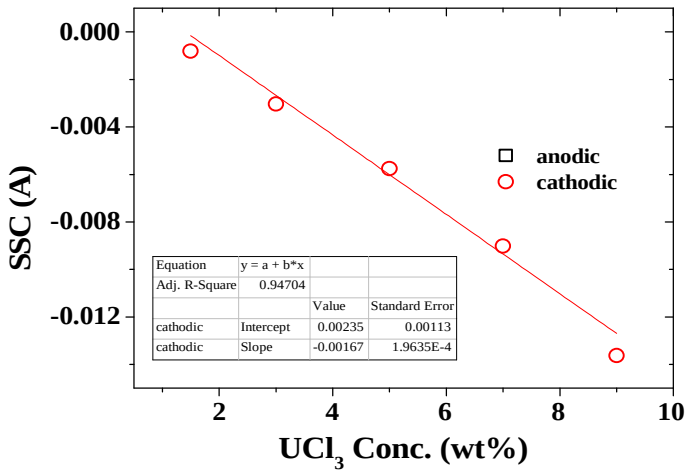


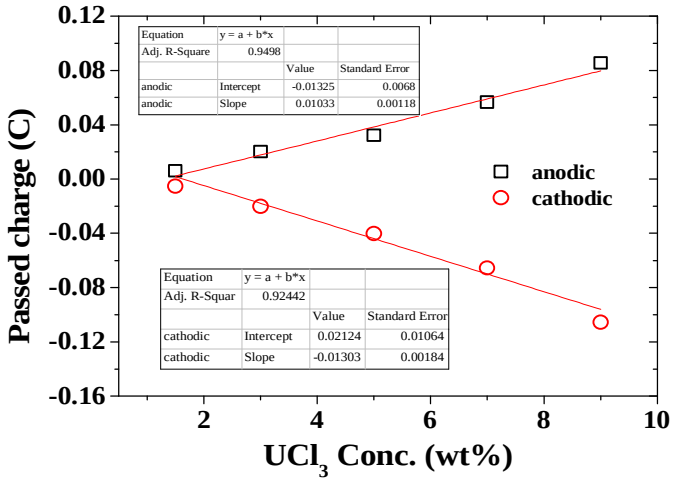


Results: Repeating CA (RCA; UCl_3)

$$U^{3+} + 3e^- \leftrightarrow U^0$$

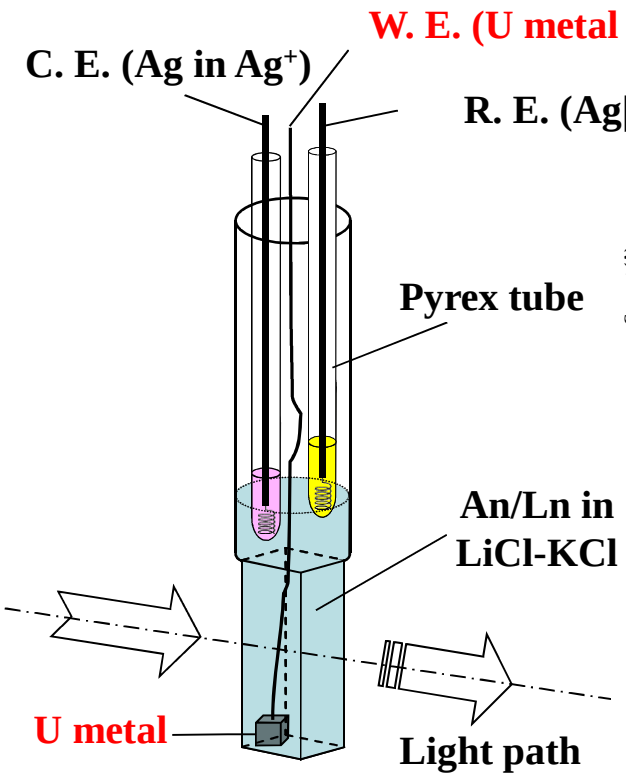


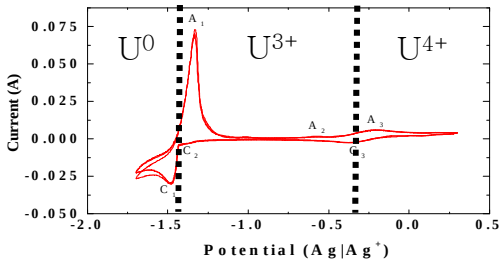


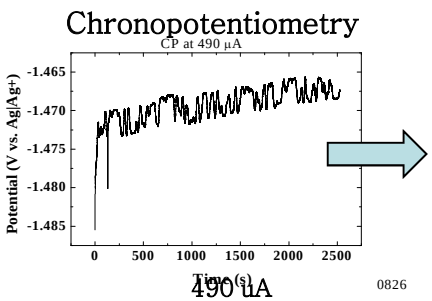


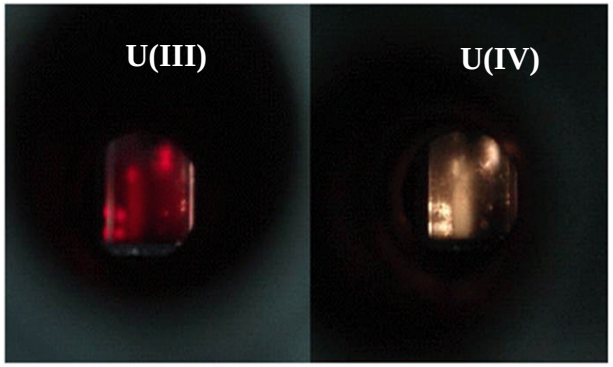
On-line monitoring with UV-VIS spectroscopy

U(III) and U(IV) in molten salt

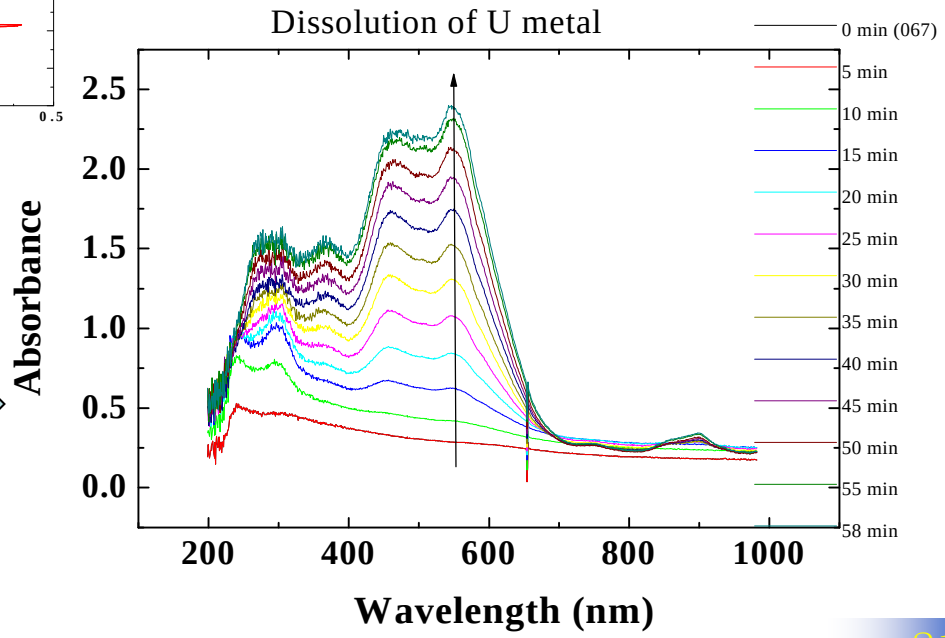






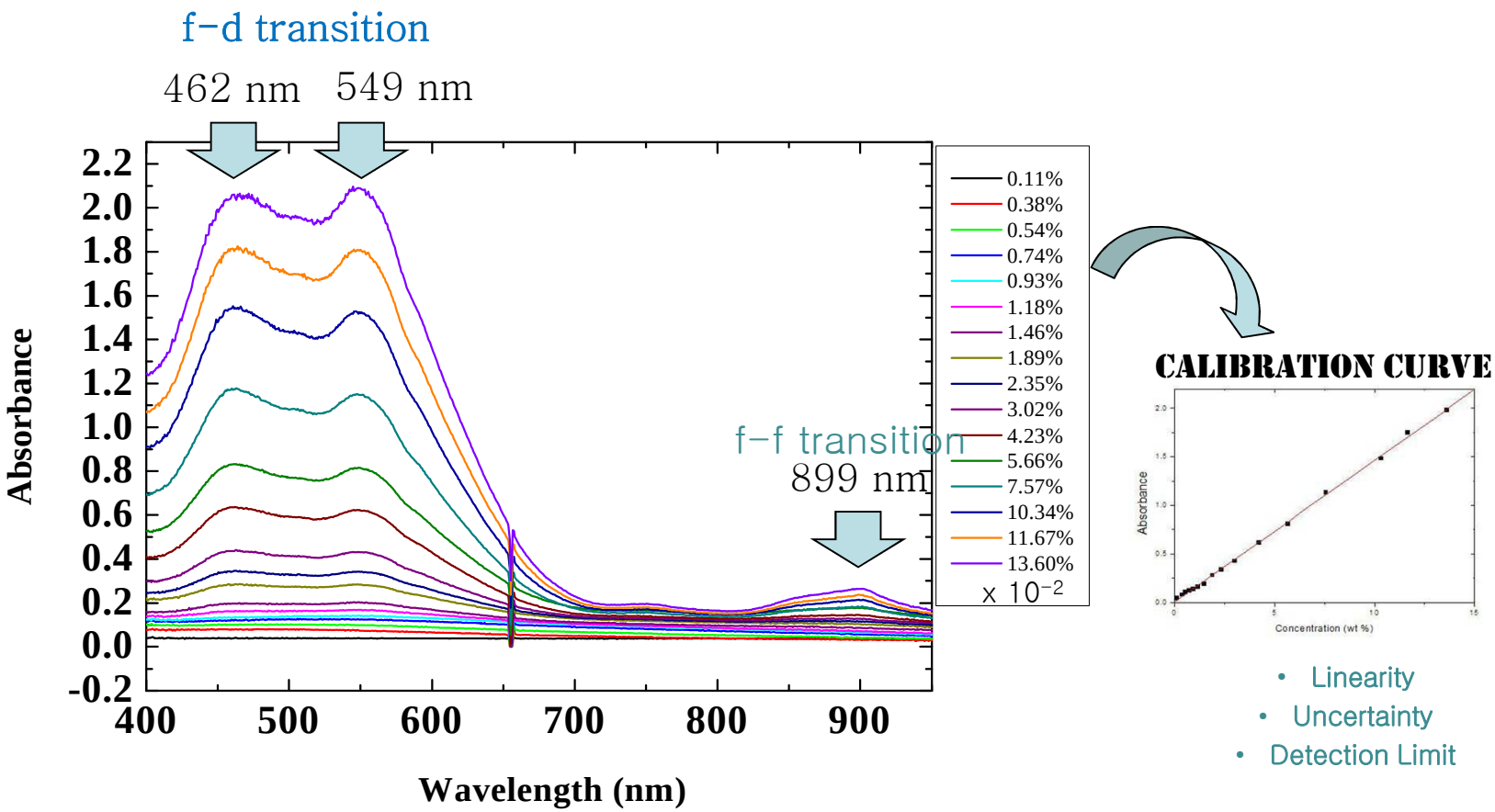


Dark wine Pale green



Electrochemical oxidation of U metal

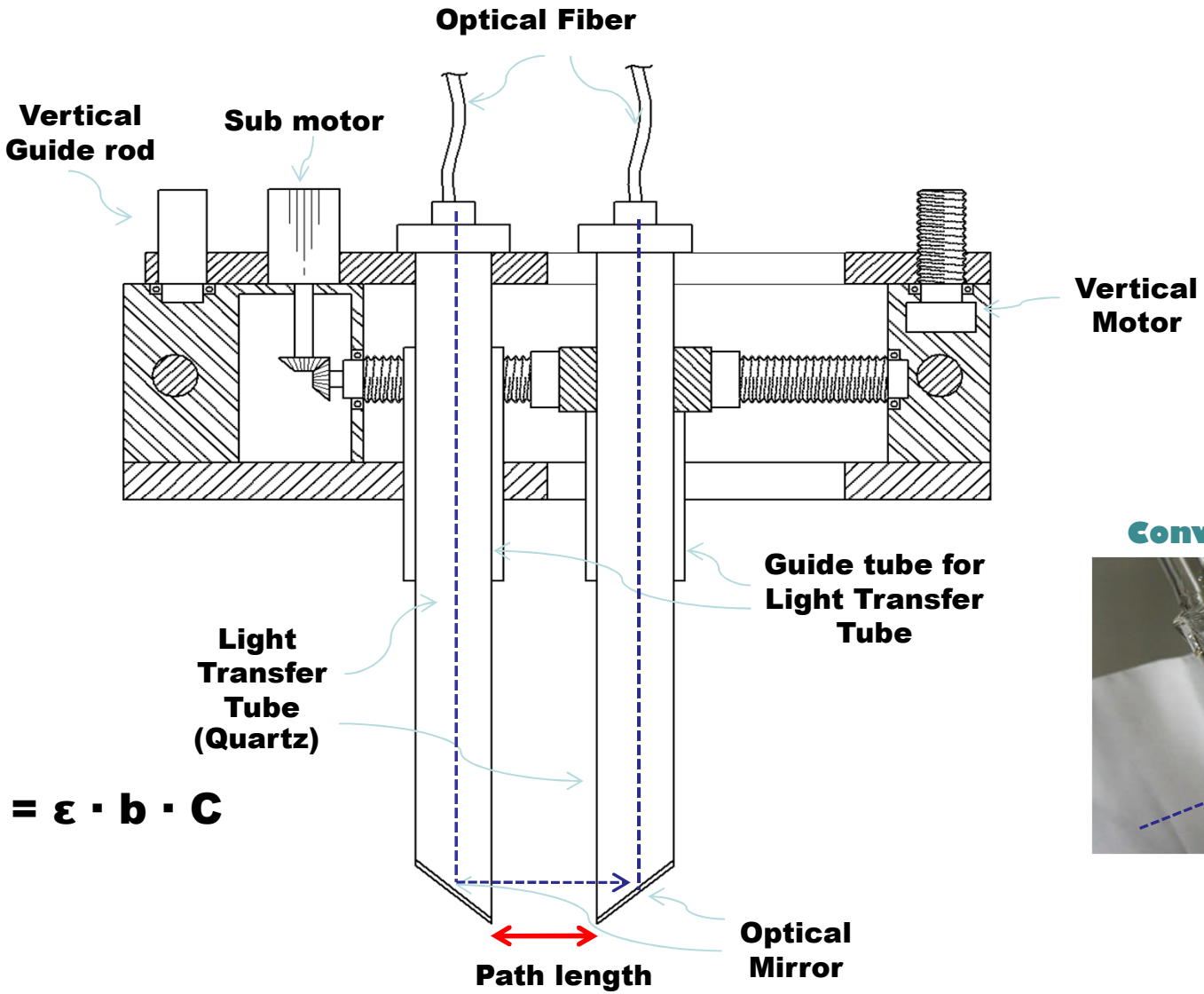
Quantitative analysis of U(III)



- Linearity
- Uncertainty
- Detection Limit

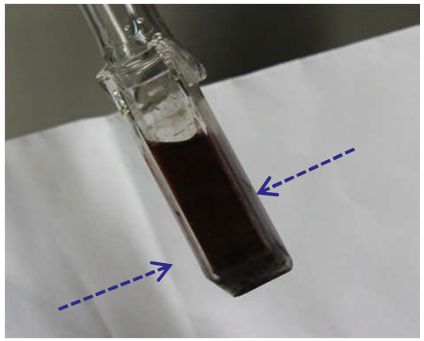
UV-VIS absorption spectra of various concentration of U^{3+} in LiCl-KCl eutectic

Design of on-site measurement cell



$$A = \varepsilon \cdot b \cdot C$$

Conventional Cell



Conclusions

- **Various electrochemical techniques have been tested to measure the concentrations of Nd^{3+} or U^{3+}in LiCl-KCl.**
- **CV results showed that the electrochemical reaction of Nd^{3+} is not only limited by diffusion rate but the cathodic peak currents are also linearly proportional to the Nd^{3+} concentration in LiCl-KCl.**
- **From CP results, apparent standard potential of Nd^{3+} deposition was measured, -2.02 V vs. $Ag|Ag^{+}$.**
- **Repeating chronoamperometry results showed a good linear relationship between the current and concentration (up to 9wt%) while the pulse methods (SWV and NPV) exhibit linear increase up to about 4 wt%.**

Thank you for your attention

Acknowledgment

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