

Lab-Scale Electrodeposition Behaviors of Pr(III) and Ce(III) with Use of Quartz Cell in Molten LiCl-KCl Eutectic

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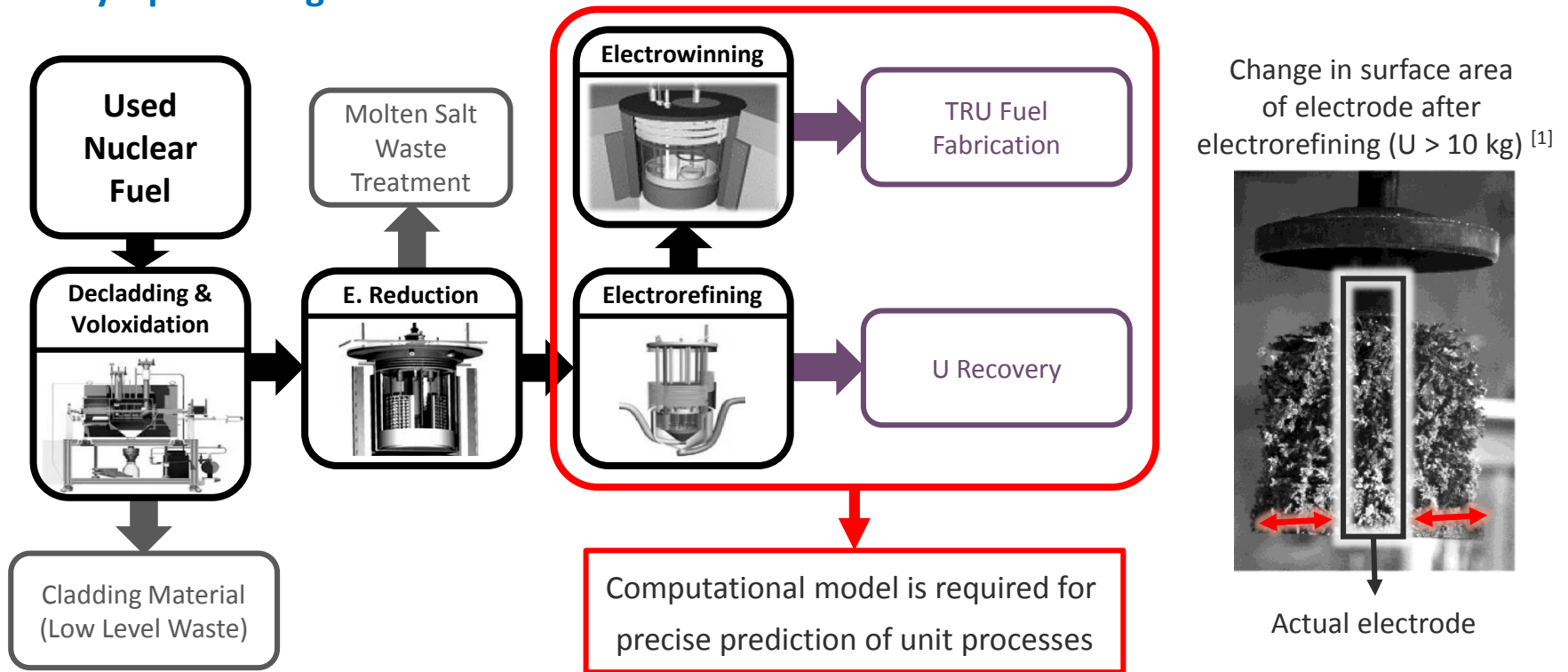
- Electrodeposition with CP and CA
- Investigation on Black Part
- Spontaneous Dissolution
- Serial Electrodeposition

4. Conclusions

Introduction

Introduction

Pyroprocessing



- Precise simulation → real-time prediction, material stream analysis, performance assessment
- Electrodeposited material → change in surface area → change in electrochemical conditions
- Absence of model reflecting change in surface area of electrodes

Research Objectives

Verification of electrodeposition behaviors of lanthanides and uranium

- ❖ Amount of deposit + change in surface area of electrodes
 - Parameters: reaction time, applied current, bulk concentration, over-potential
- ❖ Verification of electrodeposition behaviors
- ❖ One/multi-parameter empirical formula

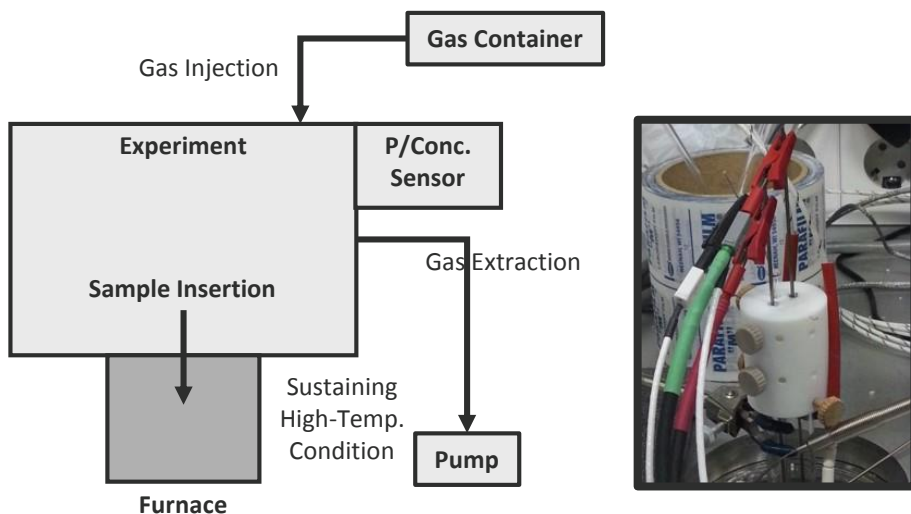


Continuous renewal of surface area information due to electrochemically deposited materials on electrodes →

Enhancement of precision in process simulation (more real-like)

Experimental

Experimental Set-ups



❖ Experimental Conditions

- Argon atmosphere
 - 99.9999 % Ar gas
 - H₂O < 1 ppm, O₂ < 1 ppm
- System temperature: 773 K (500 °C)

❖ Chemicals and Apparatus

- LiCl-KCl eutectic (99.99 %, anhydrous, Sigma-Aldrich)
- CeCl₃, PrCl₃ (99.99 %, Sigma-Aldrich)
- 1 wt. % AgCl-LiCl-KCl
- W rods for CE and WE
- Ag wire for RE

❖ Sample Cell

- Quartz cuvette (1 cm x 1 cm x 3.5 cm)
- Quartz cylindrical cell (1.6 cm i.d.)
- Pyrex guide for RE

❖ Selection of Lanthanides

O: appropriate
 Δ: partially appropriate
 X: not measurable

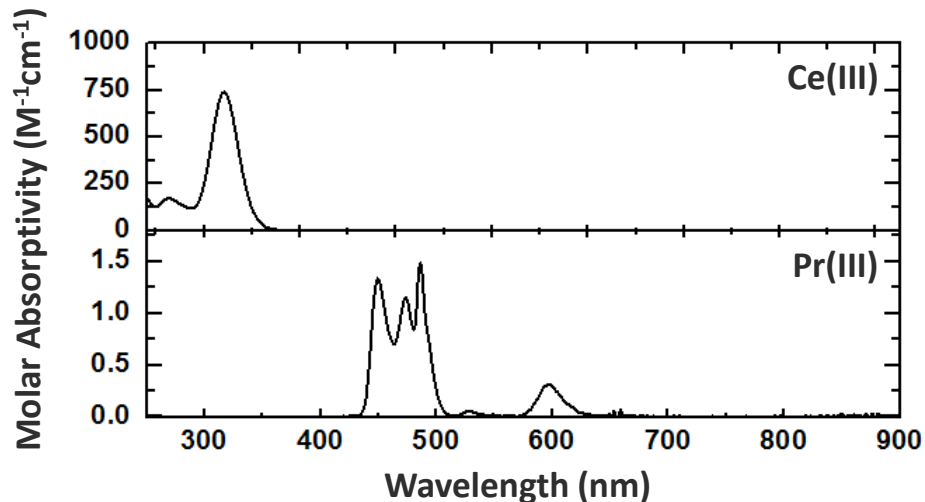
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
X	O	O	Δ	-	Δ	Δ	X	X	X	Not the region of interest				

Selection of Element

Electrochemical Properties of Uranium and Other Lanthanides

	Uranium	Cerium	Praseodymium
Diffusion Coefficient [cm^2/s]	4.29×10^{-5}	0.33×10^{-5}	6.53×10^{-5}
Exchange Current Density [mA/cm^2]	18.75	17.61	25.48
Reaction Step	+3 \rightarrow 0	+3 \rightarrow 0	+3 \rightarrow 0
Transfer Coefficient	0.68	0.55	0.54

Absorption Spectrum



$$\epsilon(321 \text{ nm}) = 694.13 \pm 8.13 \text{ M}^{-1}\text{cm}^{-1}$$

$$\epsilon(449 \text{ nm}) = 1.36 \pm 0.01 \text{ M}^{-1}\text{cm}^{-1}$$

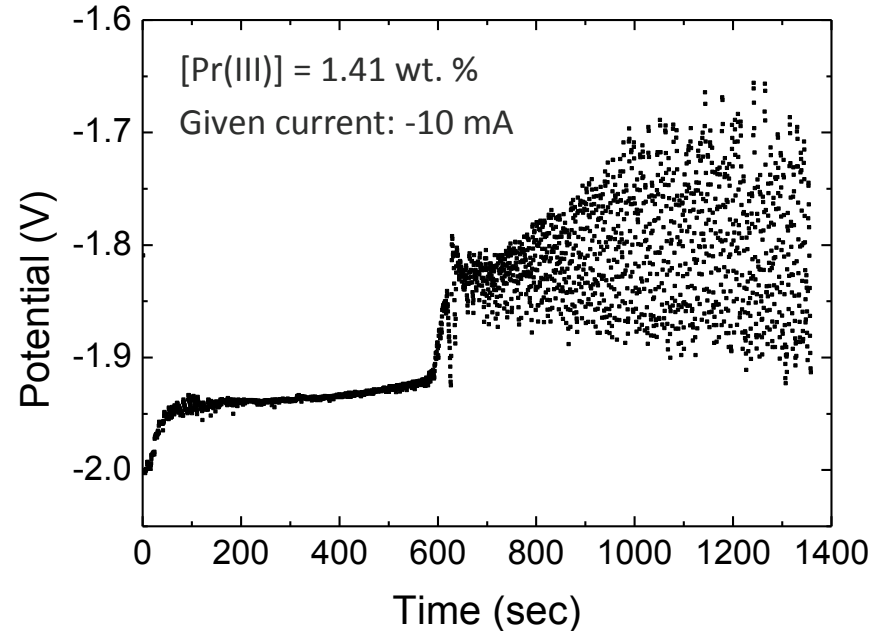
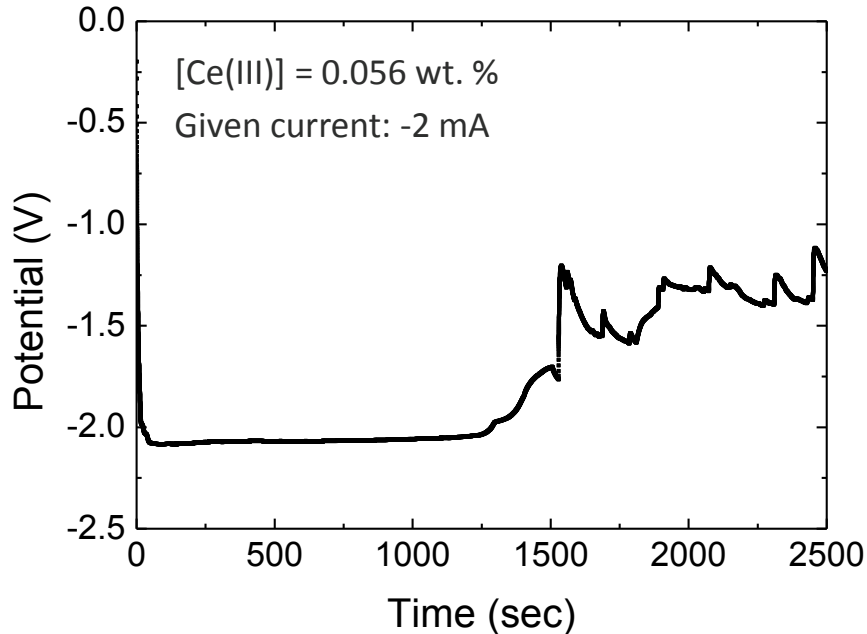
$$\epsilon(474 \text{ nm}) = 1.18 \pm 0.01 \text{ M}^{-1}\text{cm}^{-1}$$

$$\epsilon(486 \text{ nm}) = 1.52 \pm 0.01 \text{ M}^{-1}\text{cm}^{-1}$$

Results and Discussions

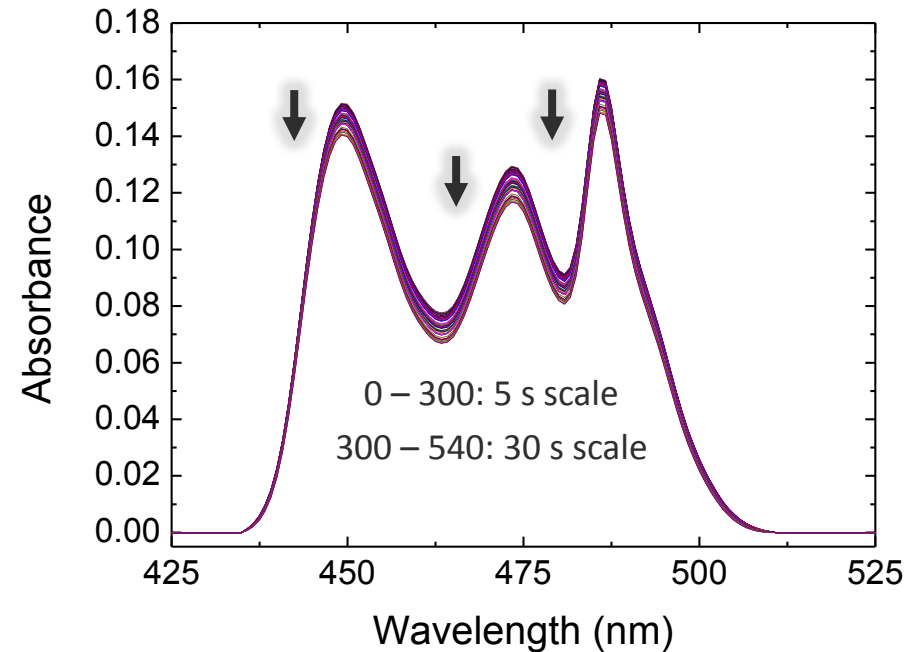
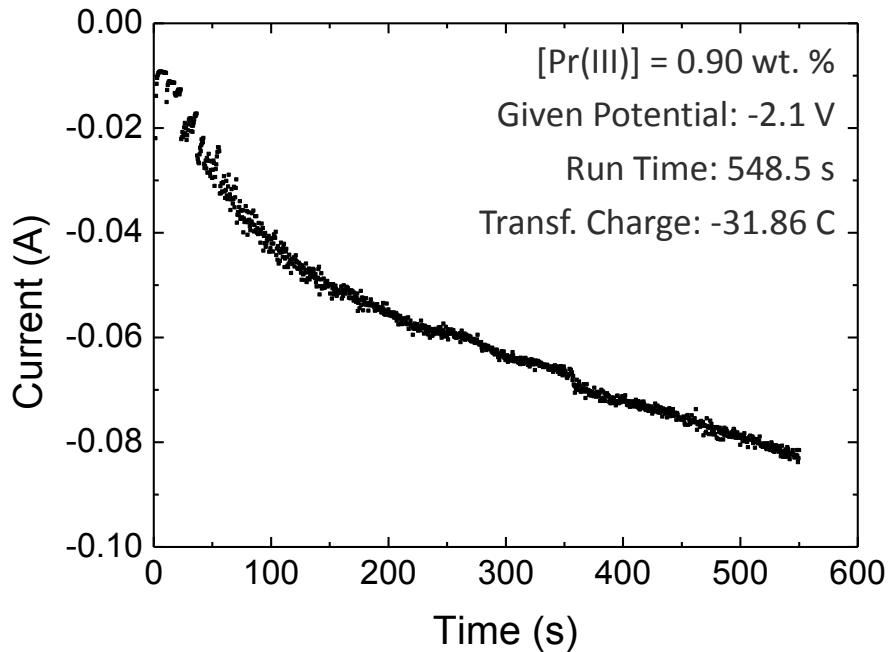
Electrodeposition of Ce(III) and Pr(III)

Chronopotentiometry



- Potential was **largely digressed** from expected potential. (-2.05 V for Ce(III), -2.1 V for Pr(III))
- Amounts of transferred charge were **not sufficient** to fully reduce Ln(III) ions.
 - Digression by something else
- For the perfect reduction condition, chronoamperometry(CA) was chosen.

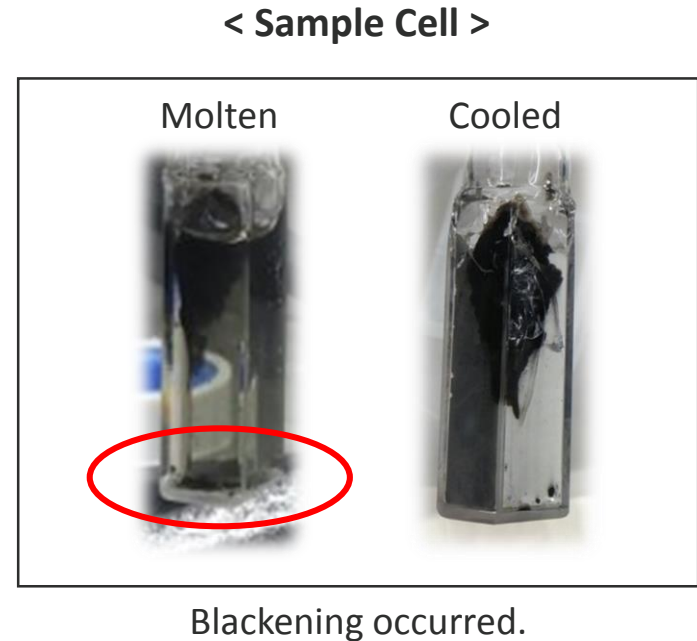
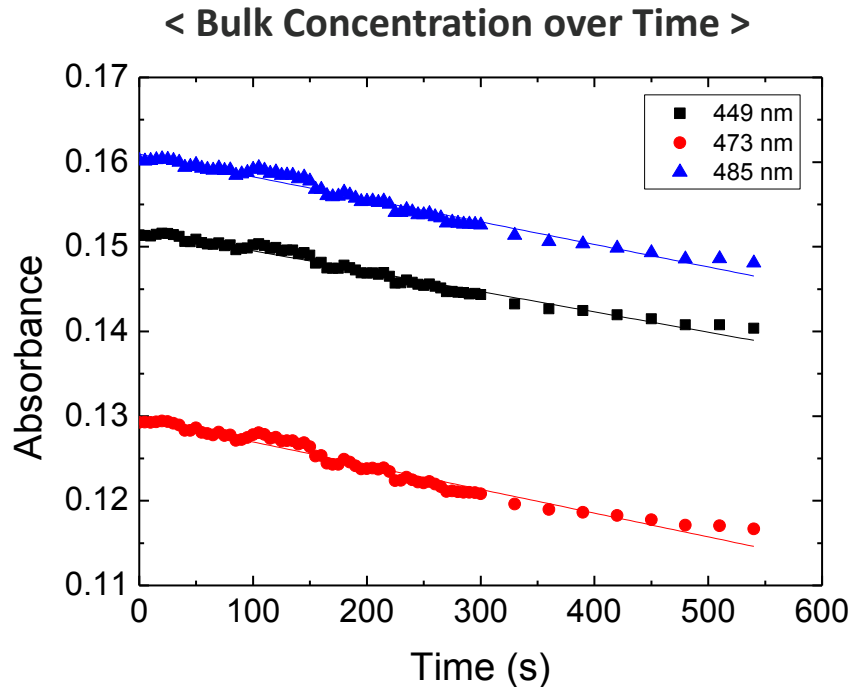
Chronoamperometry + UV-Vis Spectroscopy



- CA showed extremely deviated (and **continuously being deviated**) value of current (**-83 mA**).
- With run time of **548.5 s**, **-31.86 C** of charge was flowed.
 - $31.86 \text{ C} = 3.31 \times 10^{-4} \text{ mol e}^- \rightarrow 30 \%$ of the total amount of e^- to deposit entire Pr(III) ion.
- Only **8 %** of the bulk concentration was decreased. (**$-5.38 \times 10^{-8} \text{ mol/s Pr}^{3+}$**)

Electrodeposition of Pr(III)

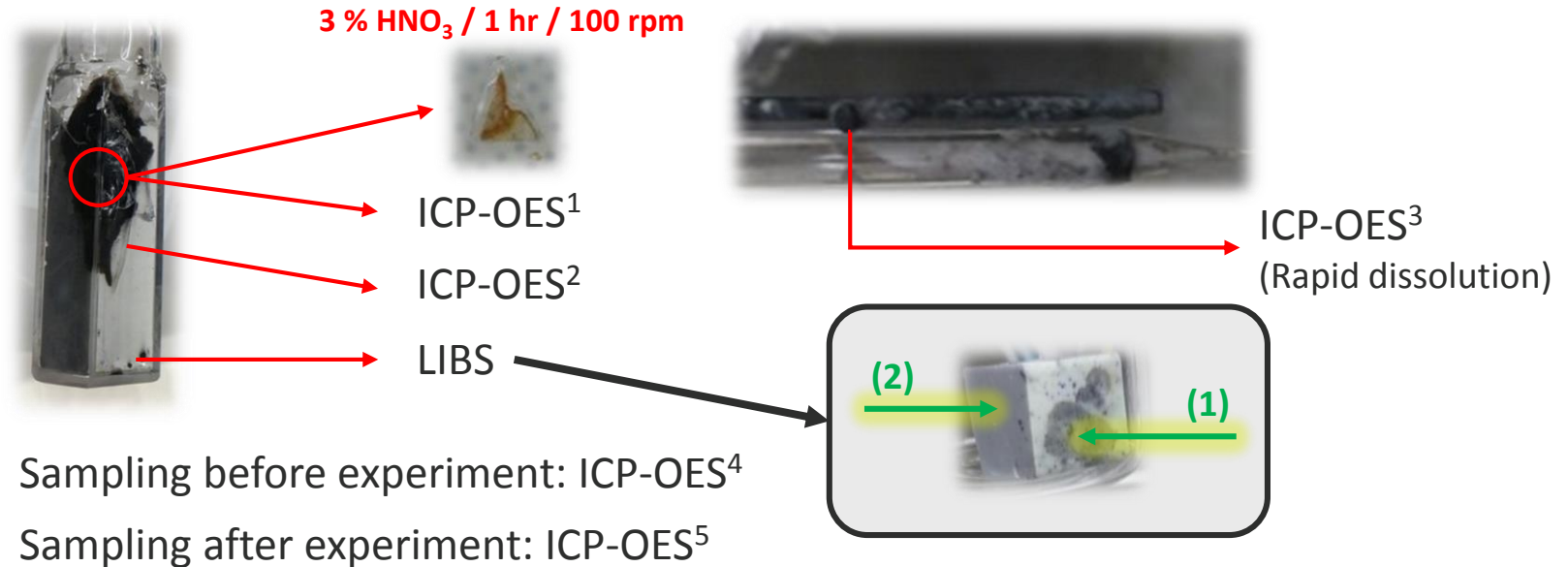
After Electrodeposition



- Rate of concentration decrement **decreased**. (**Current increased**.)
 - Charge leakage or spontaneous dissolution
- Bottom of the cell: black powder + floated dust → W(?)
- Inside of the cell: black wall + crack after cooling → W(?) or any other element

Required Analyses

Investigation of Black Part and Deposited Amount



ICP-OES¹: Black part (W/Si)

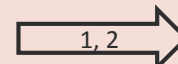
ICP-OES²: Salt + Black part (W/Si)

ICP-OES³: Deposit (Pr/W/Si)

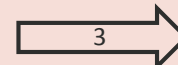
ICP-OES⁴: Initial bulk concentration (Pr)

ICP-OES⁵: Final bulk concentration (Pr)

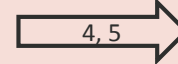
LIBS: Elemental analysis of black part



Existence of W/Si



Larger [Pr(III)]



Dissolution rate

Investigation of Blacken Part

- Possible elements: Li, K, Cl, Pr, W(?), Si(?)

I: Neutral
II: Singly Ionized

Pr II		W I (Most II peaks at vacuum-UV)		Si I	
Database	Measured	Database	Measured	Database	Measured
414.311 (1000)	414.174	294.440 (300)	-	250.617 (400)	250.659
417.939 (500)	417.807	294.699 (300)	-	251.353 (400)	251.432
418.948 (500)	418.808	361.752 (200)	-	251.532 (500)	251.611
		400.875 (1000)	-	251.833 (400)	251.920
		407.436 (600)	-	252.326 (400)	252.411
		429.461 (500)	-	252.774 (400)	252.851

Summary of ICP-OES Results

- Black part: **not homogeneous** and showed **concentrated** Pr (**1.7 wt. %**) with Si.
- Deposited material: **highly concentrated** Pr (up to **23 wt. %**) → large portion was LiCl-KCl
- Bulk: homogeneous + small amount of W (as floating dust)
- Charge balance: expected to be **0.547 wt. %**, but actual deposition was **0.217 wt. %**.

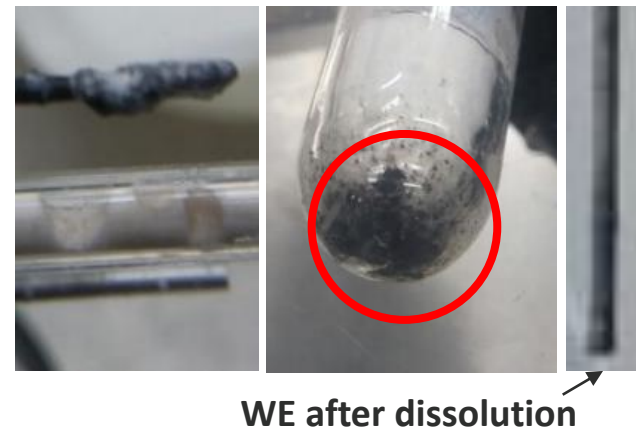
Dissolution Experiment

▪ Photographs of the Experiment

< 3-electrode system >



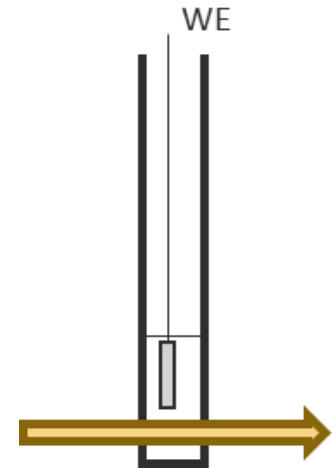
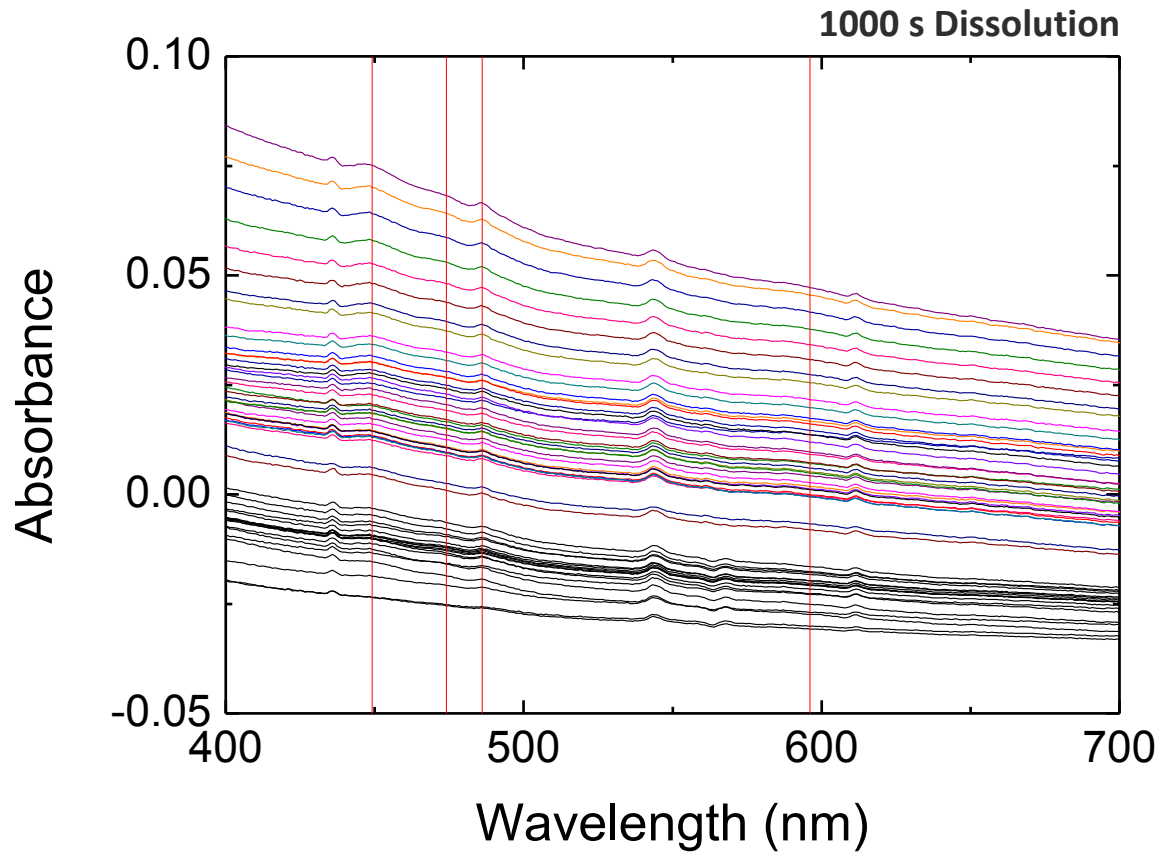
< 1-electrode system >



- Detectable amount of Pr + LiCl-KCl was successfully deposited with very clean CE.
- **Black line** appeared in dissolution experiment. (electrode-cell contact)
- Quartz cell + Pr **reacted** again even at the open circuit condition. (-0.606 V, -0.022 mA)
- Deposited materials **disappeared** and cell was **blackened**.
- **Very small** characteristic absorption peak was measured.

Dissolution Experiment

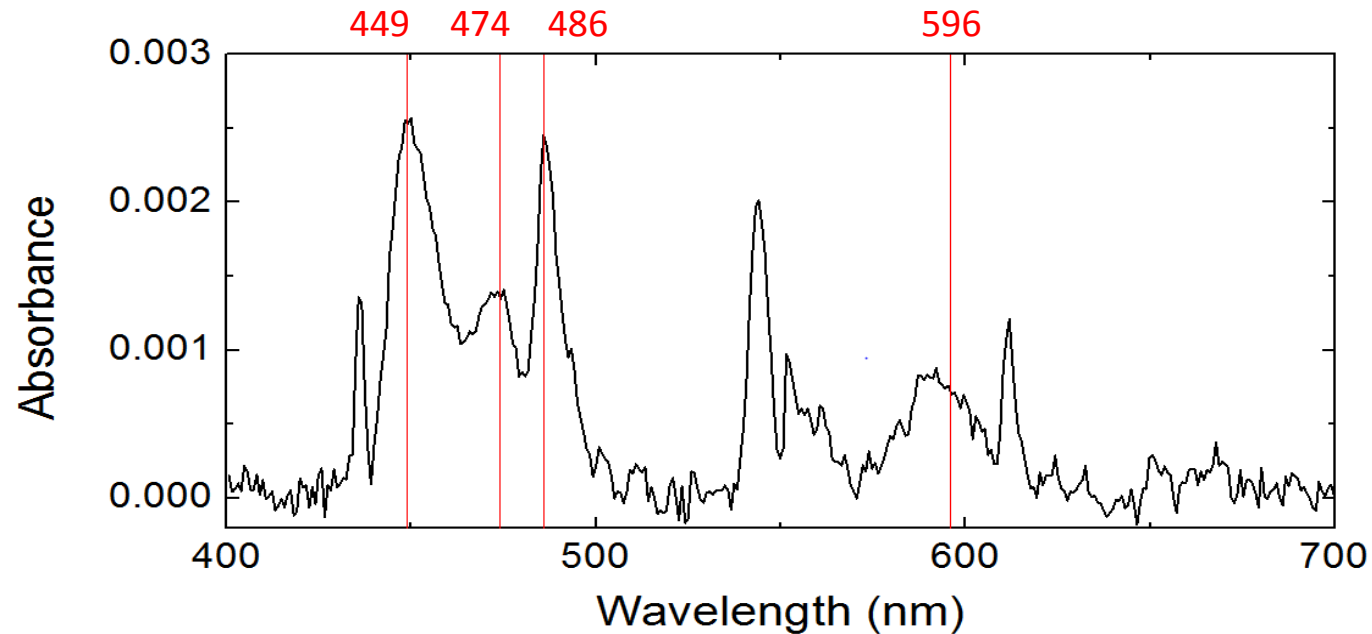
- Serial Measurement of Absorption Spectrum



➤ Really spontaneous dissolution? vs. Molten $\text{PrCl}_3\text{-LiCl-KCl}$

Dissolution Experiment

- Absorption Spectrum at Characteristic Region



- 1.6 cm optical path length: $2.18 \text{ M}^{-1}\text{cm}^{-1}$ for 449 nm peak
- 0.00208 absorbance for 449 nm peak of subtracted spectrum
- Amount of deposition: 0.034 M
- Dissolved concentration: 0.92 mM (0.008 wt. %) → **2.7 %** = almost negligible

Serial Electrodeposition

▪ Experimental Preparation and Test Matrix

- 1 mm tungsten electrodes for CE and WE
- Ag wire in 1 wt. % AgCl-LiCl-KCl for RE
- i.d. 27 mm // o.d. 30 mm large cylindrical quartz cell

Chemicals		Mass (g)
LiCl-KCl (44 wt. % LiCl)	LiCl	11.014 ± 0.001
	KCl	14.025 ± 0.001
Cerium	CeCl ₃	0.289 ± 0.001

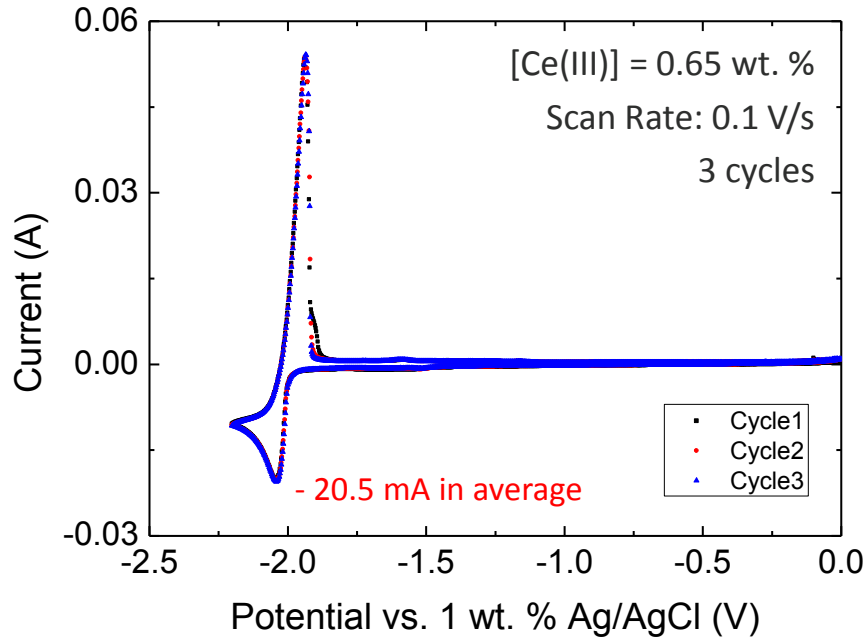
- [Ce(III)] = 0.65 wt. %

▪ Experimental Procedure

- Sample preparation → CV → CA → Sampling for ICP → electrode change → CP
w. different WE

Serial Electrodeposition

▪ Cyclic Voltammetry



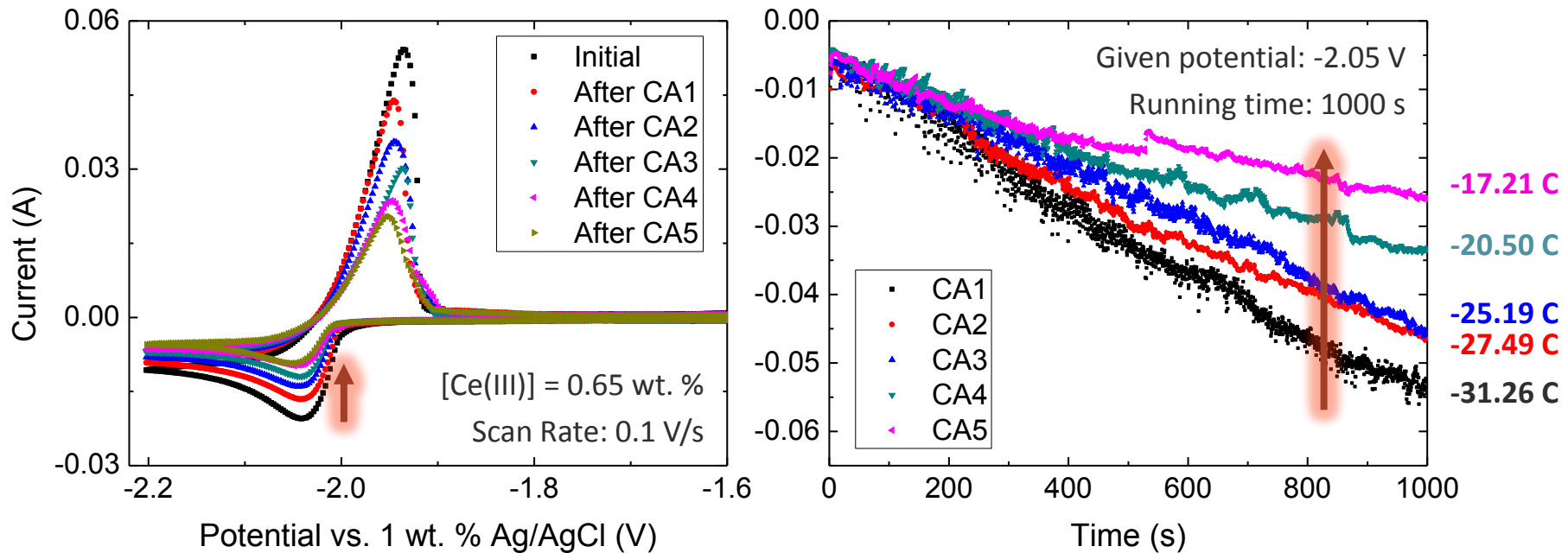
Current (mA)	Expected time (s)
5	67,976
10	33,988
20	16,994
50	6,798

- No dissolution
- No consideration of diffusion/migration
- 3 electrons / deposition of one Ce(III)
- $Q = It = nFVC$ ($F = 96485 \text{ A}\cdot\text{s/mol}$)

- $0.2894 \text{ g CeCl}_3 = 0.001174 \text{ mol Ce} = 0.003523 \text{ mol e}^-$
- 5 trials \rightarrow 1000 s running for each trial
- Reduction potential: - 2.05 V
- Expected current for stabilized electrodeposition: - 60 mA

Serial Electrodeposition

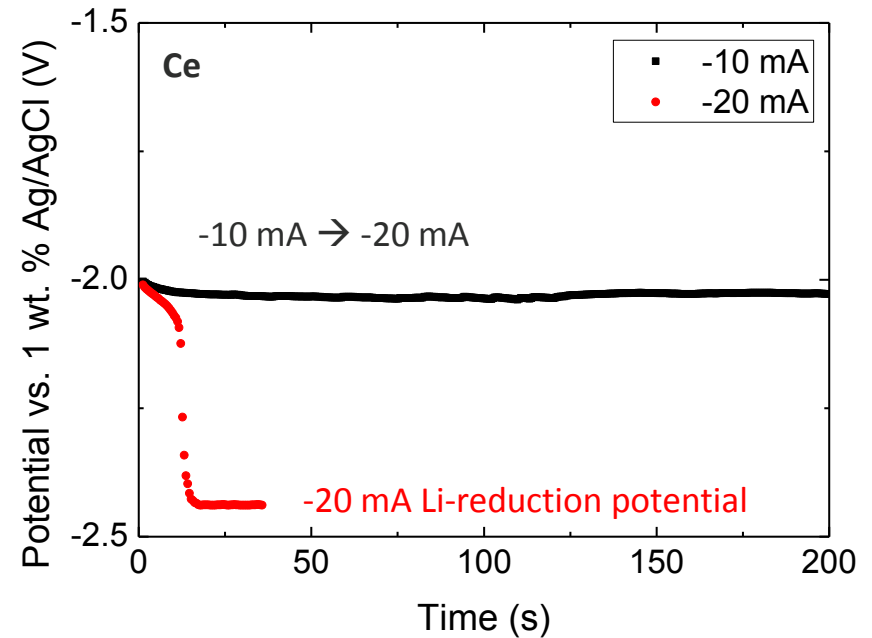
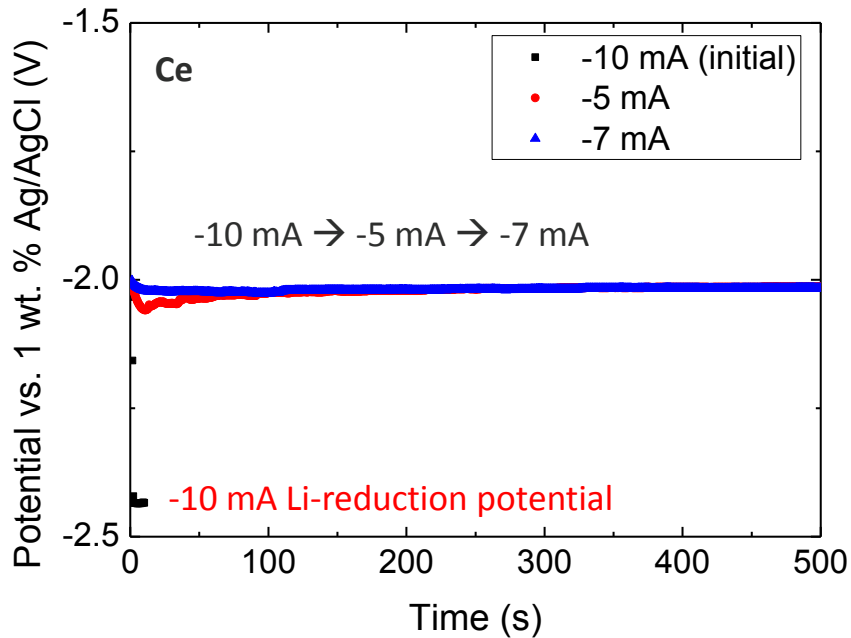
Electrodeposition



- [Ce(III)] started from 0.65 wt. %, and CV diagrams were plotted after each CA.
- Magnitudes of **CV peaks** were **decreased** due to decrease in bulk concentration.
 - Reduction peak: -20.5 mA → -9.0 mA
- CA delineated **linear decrease** in magnitude of current, and **slopes were decreased** as well.

Serial Electrodeposition

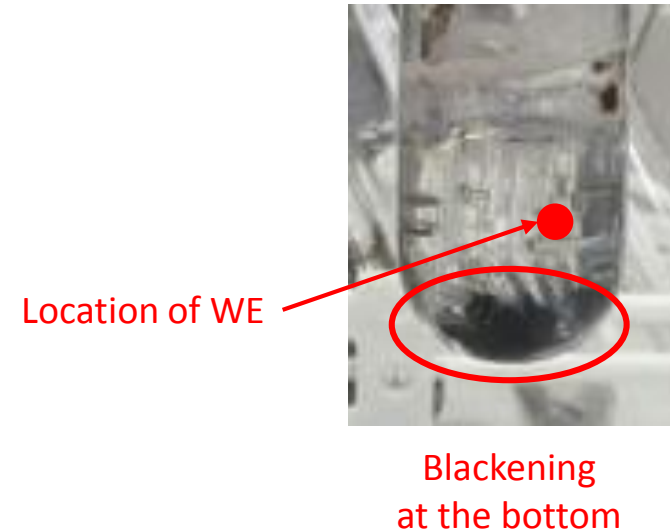
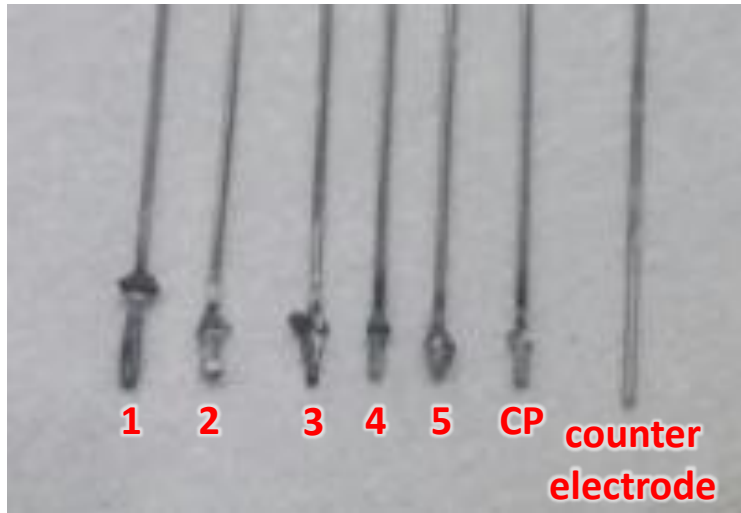
Chronopotentiometry



- Procedure: -10 mA (15 s) → -5 mA, -7 mA (500 s) → -10 mA (200 s) → -20 mA (40 s)
- Initially, CP measurement with -10 mA → rapid drop of potential
- After -5 mA, -7 mA CP measurement → -10 mA showed stable electrodeposition
- Increase in surface area → increase capability of current flow

Serial Electrodeposition

- Photographs



- Immersed depth gently decreased as experiments were repeated.
- CE was clean.
- Bottom part of the cell was **blackened** (not from the side) → Detached deposit
 - Mostly remains in Ce(0); a small portion may re-dissolve to Ce(III)

Serial Electrodeposition

Concentration vs. peak current in CV vs. rate of deposition

Concentration of Ce(III) (wt. %)		Peak current (mA)	Transferred charge (C)	Calculated decrease of [Ce(III)] (wt. %)	Deposited Ce (ICP-OES) (wt. %)	Δ Electrode Mass (mg)
0.65	0.64	-12.5	-31.26	0.060	0.038 (9.7 mg)	49
0.59	0.58	-11.3	-27.49	0.053	0.024 (6.0 mg)	32
0.54	0.54	-10.2	-25.19	0.048	0.021 (5.3 mg)	17
0.49	0.51	9.5	-20.50	0.039	0.017 (4.3 mg)	16
0.45	0.49	8.9	-17.21	0.033	0.020 (5.2 mg)	21
0.42	0.47	8.5	-8.0	0.015	0.010 (2.7 mg)	11
0.41	0.46					

Left: nominal
Right: ICP-OES

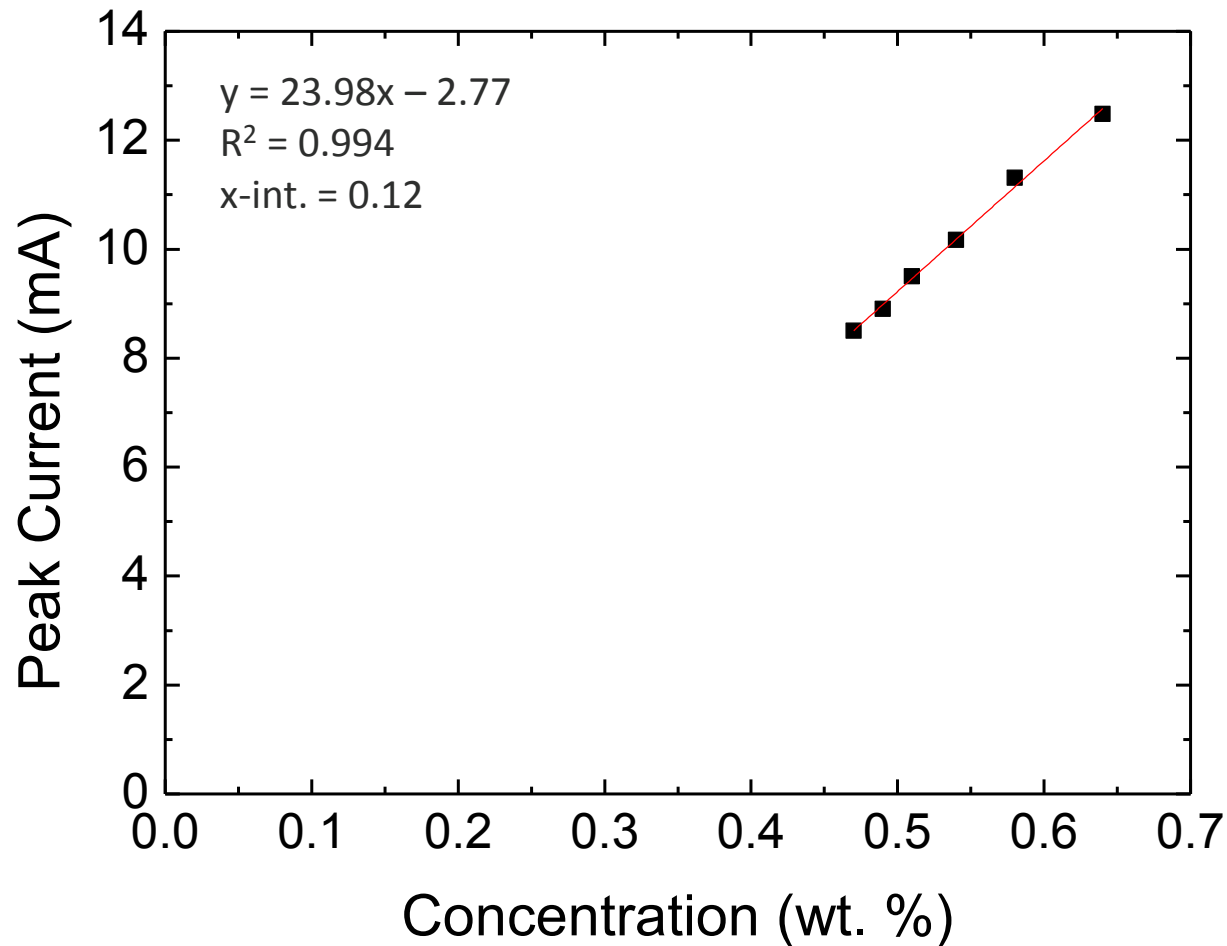
- Concentration decrement was less than the expected amount.
- Amount of deposited Ce(0) < consumed Ce(III)
- Most part of deposit = LiCl-KCl + Ce(III)



Electrodeposition
Detachment
Quartz Reaction
Release of
LiCl-KCl + Ce(III)

Serial Electrodeposition

- Concentration vs. peak current in CV



Conclusions

- **Lessons Learned in Quartz Cell Experiments**

- Electrochemically deposited material **reacts** with quartz cell. (even in an open circuit)
- Enormous amount of charge is **consumed** in this deposit-quartz spontaneous reaction.
- Indicators
 - Black wall
 - Linear decrease in current with large magnitude (more negative than -100 mA) during CA
 - Unstable fluctuation in CP measurement
- Spontaneous dissolution of electrochemically reduced metal does not occur.
 - Small portion of deposit can be re-dissolved when it reacts with quartz.
- Alumina crucible is desirable.

Conclusions

▪ CV and CA

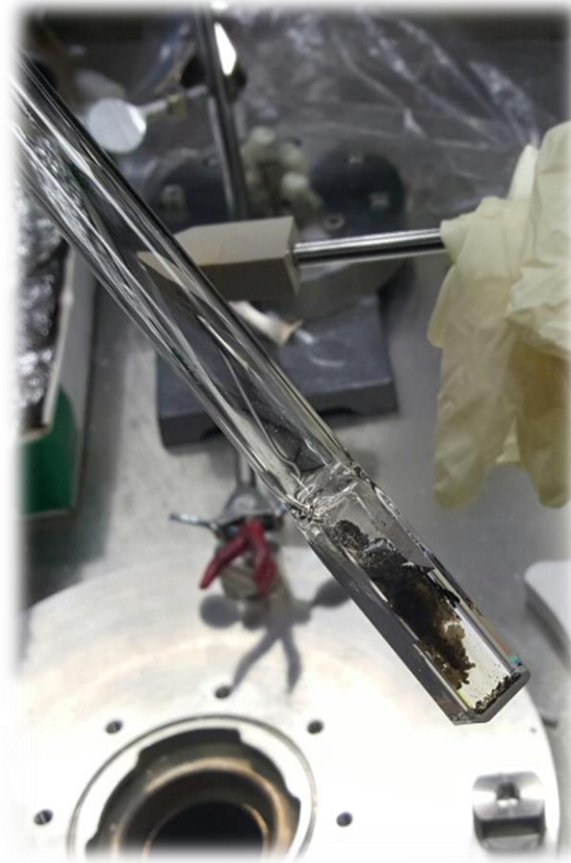
- Repetition of CV and CA with new working electrodes showed followings:
 - Magnitude of current at reduction peak: 20.5 mA → 9.0 mA
 - Amount of charge transferred: 31.26 C → 17.21 C
- Magnitude of current flow during CA **increased** due to increase in surface area.
- **Bulk concentration** is one of the significant factors in electrochemistry:
- **Decrease** in bulk conc. → **decrease** in rate of electrodeposition (more gentle slope of CA)
- **Physical detachment** of deposit happens with W electrode.

▪ CP

- Experiments with electrode **not in contact with** quartz cell showed stable CP.
- The amount of **bearable current** for e.d. increased as surface area of electrode increased.
 - Dendrite formation → large current → larger electrode with high bulk conc.

Thank You

Appendix 1

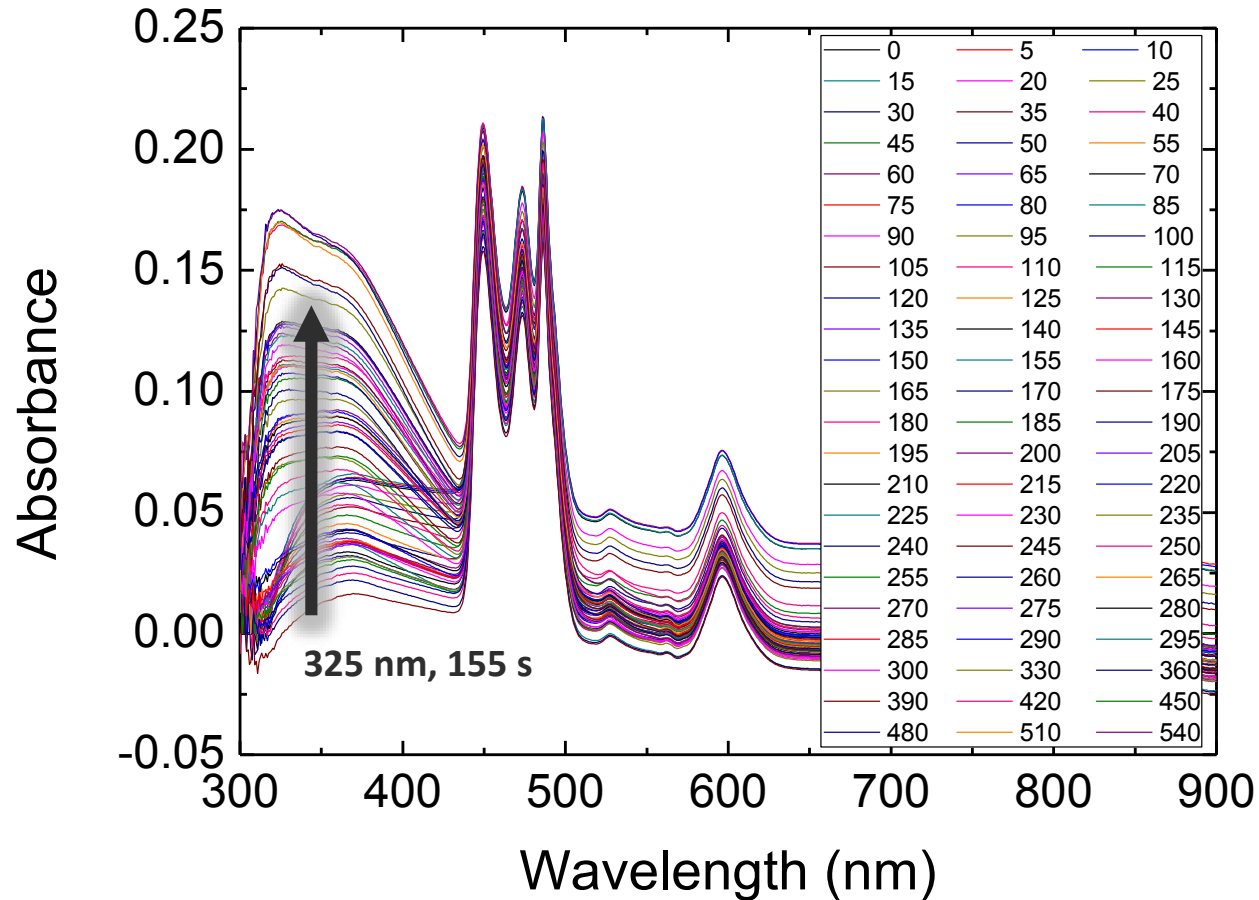


Pr(III) sample cell after the experiment

Appendix 2

- Entire Absorption Spectra from 0 s to 540 s

➤ 5 s interval (from 0 s to 300 s) // 30 s interval (from 300 s to 540 s)



Appendix 3

Red Solid: Blackened

Black Solid: White

Investigation of Blackened Part (G.D. 1 us; G.W. 5 us; Gain 2500)

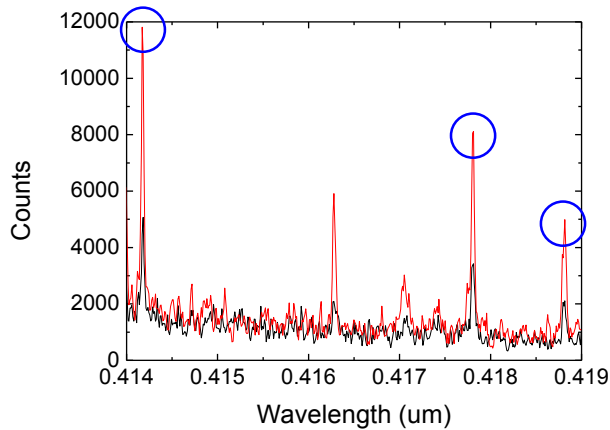
➤ Possible elements: Li, K, Cl, Pr, W(?), Si(?)

I: Neutral
II: Ionized

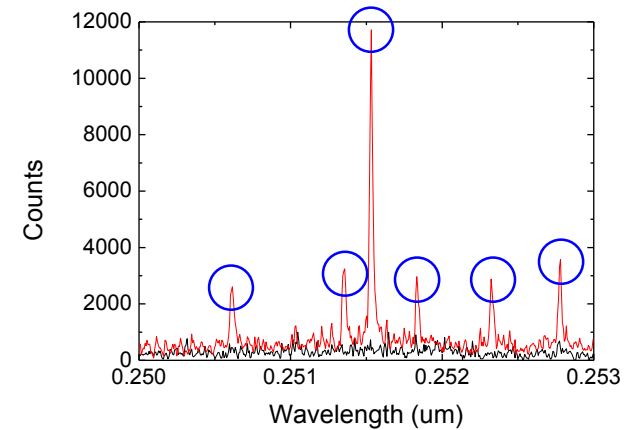
Pr II	
Database	Measured
414.311 (1000)	414.174
417.939 (500)	417.807
418.948 (500)	418.808

W I (Most II peaks at vacuum-UV)	
Database	Measured
294.440 (300)	-
294.699 (300)	-
361.752 (200)	-
400.875 (1000)	-
407.436 (600)	-
429.461 (500)	-

Si I	
Database	Measured
250.617 (400)	250.659
251.353 (400)	251.432
251.532 (500)	251.611
251.833 (400)	251.920
252.326 (400)	252.411
252.774 (400)	252.851



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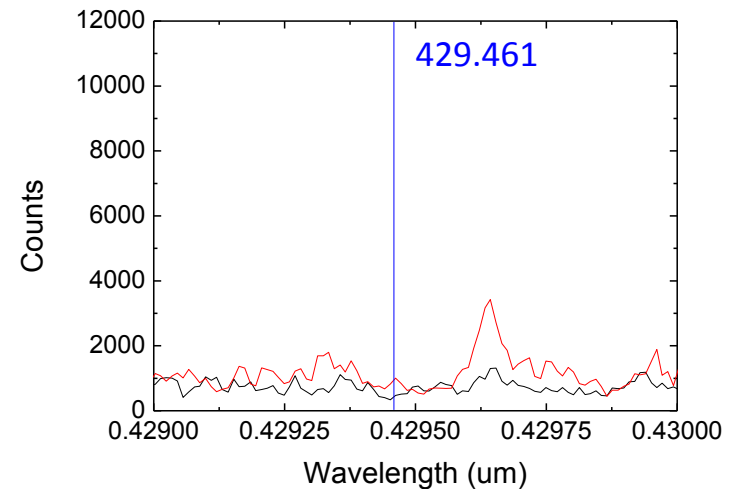
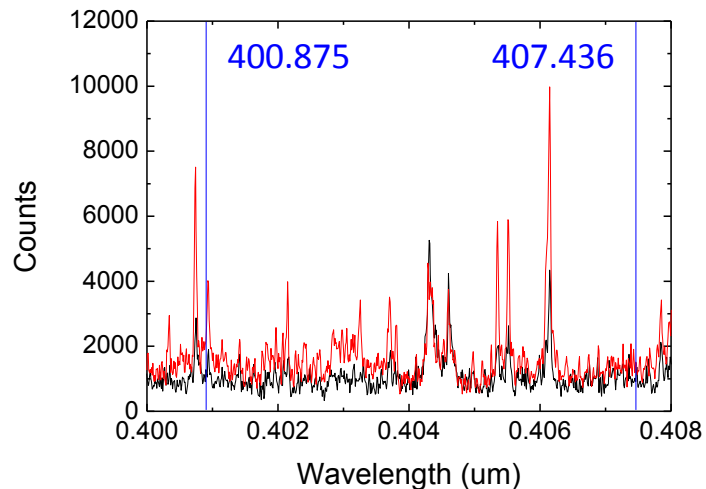
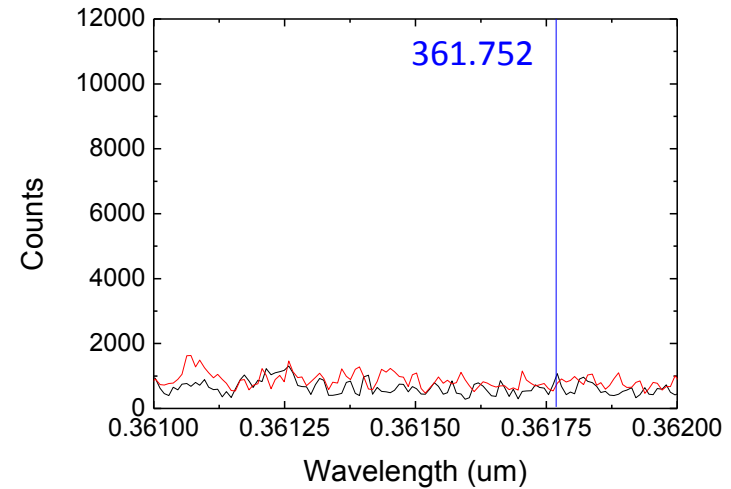
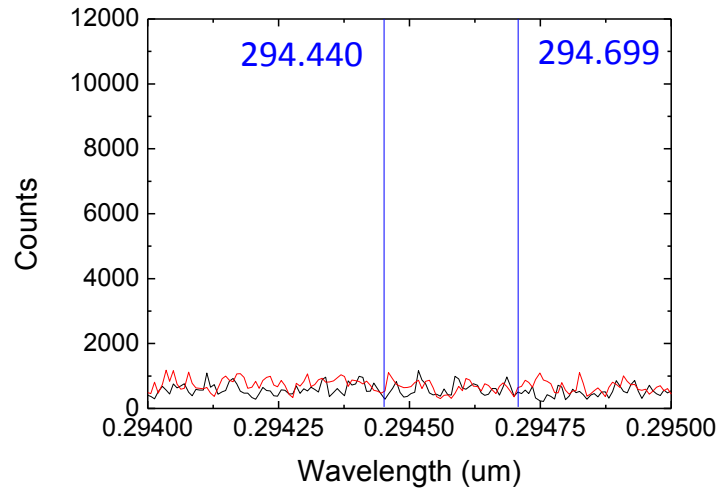


Appendix 3 Cont.

Red Solid: Blackened
Black Solid: White

Investigation of Blackened Part (G.D. 1 us; G.W. 5 us; Gain 2500)

➤ W (Blue labels are in nm-scale)



Appendix 4

Sample 1 and 2: Cuvette Cell

Sample #	Dilution Factor	[Pr] (wt. %)	HNO ₃ (g)	Samp. (g)	ICP-OES Results (ppm)			Concentration (wt. %)		
					Pr	Si	W	Pr	Si	W
Blank	-	-	-	-	-0.002	0.004	0.001	-	-	-
1	10	0.90	21.642	0.0175	1.408	0.192	0.008	1.742	0.237	0.010
2	5	0.82		0.104	6.085	0.048	0.014	0.636	0.005	0.002

- Sample 1 and 2 are both **not homogeneous**.
- Sample 1 (black part) showed **highly concentrated** Pr with Si.
- W was observed in both samples but with very small amount.
 - < 2 % of original Pr amount

Appendix 4 Cont.

- Sample 3, 4, and 5: Deposited material (Cylindrical)

Sample #	Dilution Factor	[Pr] (wt. %)	HNO ₃ (g)	Samp. (g)	ICP-OES Results (ppm)			Concentration (wt. %)		
					Pr	Si	W	Pr	Si	W
Blank	-	-	-	-	-0.002	0.004	0.001	-	-	-
3	100	0.83 ↓ ?	7.214	0.004	1.256	0.043	0.009	22.66	0.775	0.162
4	50			0.0029	0.835	0.028	(0.003)	10.38	0.348	(0.037)
5	50			0.003	0.722	0.025	(0.003)	8.684	0.300	(0.036)

- Deposited materials (highly concentrated Pr) were obviously **not homogeneous**.
- **Large portion** of deposition was **LiCl-KCl**. (Ideally, [Pr] = 100 wt. %)
- Si was observed to be nearly **3 % of Pr amount**.
- W was observed with very small amount at some local spots.
- Rapid and vigorous reaction with bubble generation occurred at dissolution step.

Appendix 4 Cont.

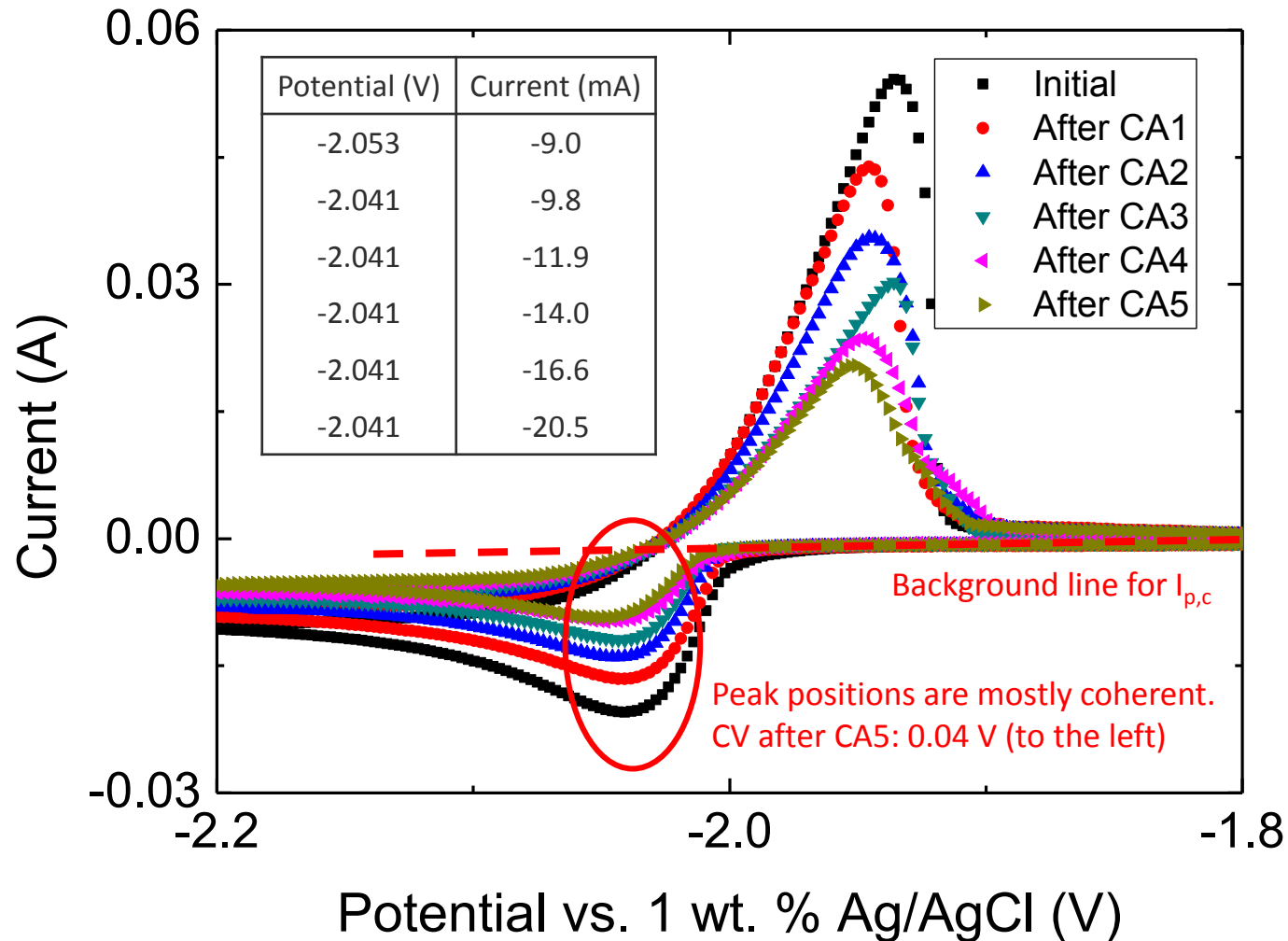
- Sample 6, 7, 8, and 9: Before/After the Experiment (Cylindrical)

Sample #	Dilution Factor	[Pr] (wt. %)	HNO ₃ (g)	Samp. (g)	ICP-OES Results (ppm)			Concentration (wt. %)		
					Pr	Si	W	Pr	Si	W
Blank	-	-	-	-	-0.002	0.004	0.001	-	-	-
6	2	0.901 ↓ 0.684	7.214	0.0169	4.261	(0.012)	0	0.877	(0.001)	0
7	1			0.005	4.288	(0.009)	(0.002)	0.925	(0.001)	0
8	2			0.0222	5.814	0.014	0.030	0.668	0.001	0.002
9	1			0.009	6.601	(0.007)	0.044	0.700	(0.001)	0.003

- Homogeneous; black impurities were included in sampling process.
- **0.217 wt. %** (in average) of Pr(III) from the bulk was deposited. (**Expected**: 60.8 %, 0.547 wt. %)
- **Dissolution (or charge-loss) rate** in terms of Pr(III) concentration: **5.48 ppm/s**
- Small amount of Si was measured, and relatively large amount of W was measured from the bulk.

Appendix 5

▪ Cyclic voltammetry



Appendix 5 Cont.

Chronoamperometry

