Seoul National University

SNUMAT Seoul National University Nuclear Materials Lab.

Computational modeling on electrorefining of irradiated Zircaloy-4 cladding in LiCl-KCl-$ZrCl_4$ at 500°C

Jaeyeong Park[a]*

Sungyeol Choi[b], Sungjun Son[a], Kwang-rag Kim[b], Il Soon Hwang[a]

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*d486916@snu.ac.kr

a: Seoul National University

b: Korea Atomic Energy Research Institute

Outline

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I Introduction

II Modeling strategy

III Modeling on multi-step reduction of Zr(IV)

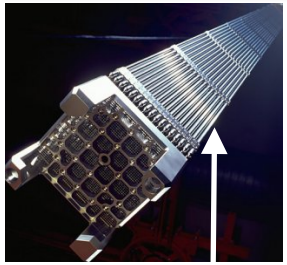
IV Simulation on irradiated Zircaloy cladding electrorefining

V Summary

Introduction

- **Zirconium uses in nuclear power industry**

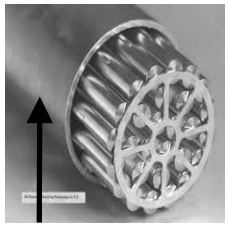
Nuclear Fuel Cladding in Thermal Reactor



Cadding
(Zircaloy)

- **Actinides and FPs** could be included because of penetration.
- **Major radioisotopes** Actinides, FPs, and activation products of Zircaloy

Pressure Tube/Calandria Tube in CANDU

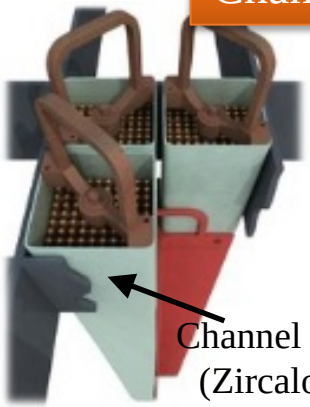


Pressure tube
(Zr-2.5Nb)

Calandria tube
(Zircaloy)

- **Actinides and FPs** are not included.
- **Major radioisotopes** Nb-94, C-14, Co-60 and others can be separated

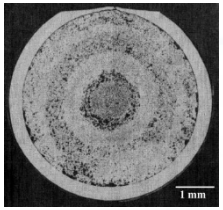
Channel Box in BWR



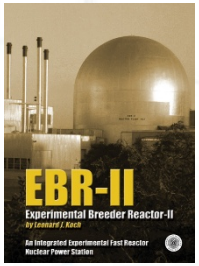
Channel Box
(Zircaloy)

- **Actinides and FPs** might not be included.
- **Major radioisotopes**
- Co-60, Sb-12 and other activation products of Zircaloy

Metallic Fuel for Fast Reactor



Metallic fuel
(U-TRU-Zr)



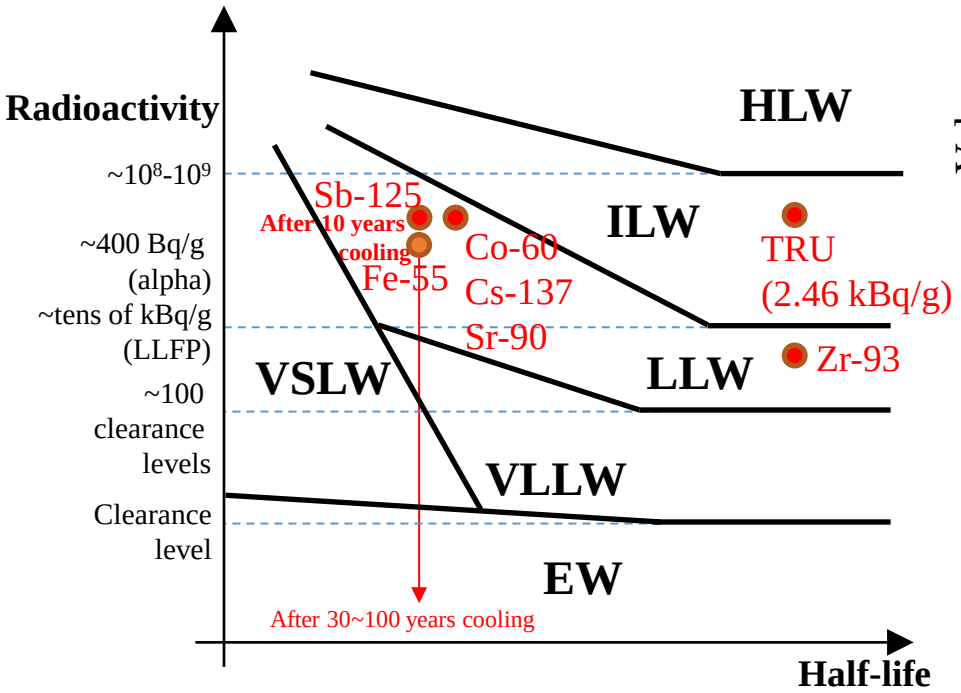
Fast Reactor

- **Actinides and FPs** compose about 90% in Fuel with 10% Zr.
- **Zr could interrupt U recovery in electrorefining.**

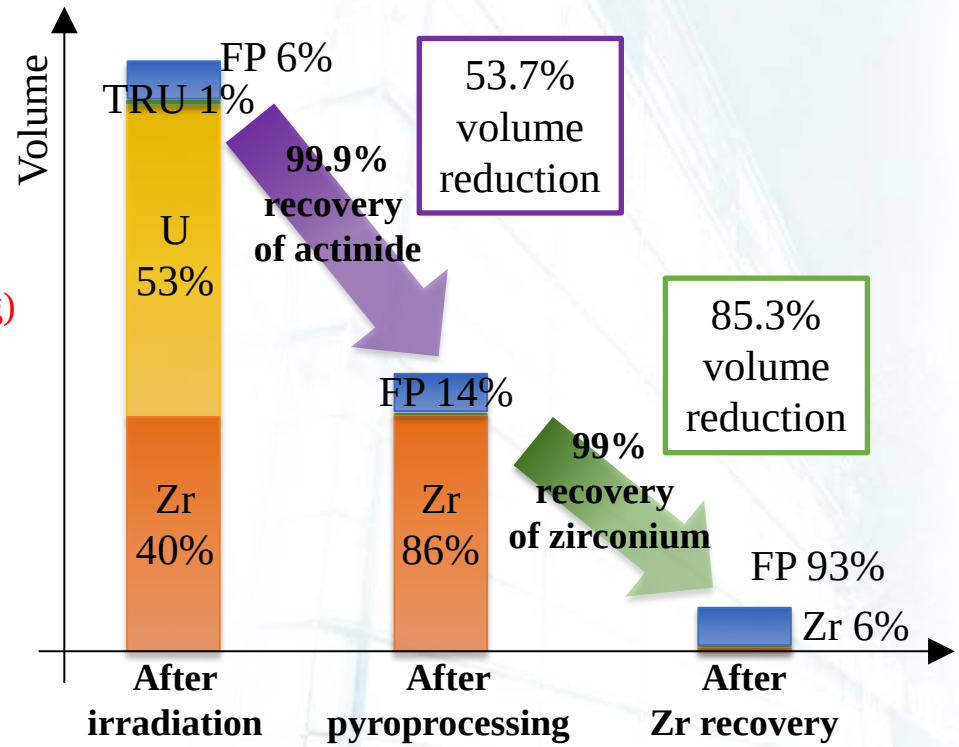
Introduction

- **Radiological Characteristics of Irradiated Zircaloy-4 Cladding**

Radioactive Waste Classification



Volume Reduction of Geological Disposal



- **Decontaminationan factor of U, TRU and Co-60 should be decontaminated.**

- **If we could recover zirconium form irradiated cladding, total volume of final waste could be reduced into 6.8%.**

Introduction

- **Electrorefining as a decontamination process for irradiated cladding**

			Pros	Cons
Surface decontamination	hydrofluoric acid process		• Simple process	• U and TRU could not be decontaminated.
Volume decontamination	Iodination process		• High decontamination factor	• ZrI_4 is very hygroscopic • Decomposition process requires long reaction time
	Hydrochlorination process			• $ZrCl_4$ reduction process
	Electrorefining in fluoride salts		• One-step reduction of Zr(IV) into Zr metal • Metal deposition with high purity of 99.93% • Coarse metal recovery	• High operating temperature • Fluoride corrosion
	Electrorefining in fluoride-chloride salts	LiCl-KCl based	• Suppressed disproportionate reaction • Metal deposition with high purity of 99.9%	• High operating temperature • Fluoride corrosion • Complicated salt purification
		CsCl, $SrCl_2$ based	• More coarse metal recovery	• Fluoride corrosion • High operating temperature • Large amount of Cs and Sr waste
	Electrorefining in chloride salts	**LiCl-KCl**	• Low operating temperature • Low corrosion problem	• Complicated redox reactions • Disproportionate reaction • ZrCl codeposition

Introduction

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Lab-Scale Expriment

1. Suggesting **possibilities of electrorefining** in LiCl-KCl-$ZrCl_4$ without ZrCl deposition and disproportionate reaction

2. Suggesting **design requirements** to secure high decontamination factor

Design criteria
Material properties

Computational model

1. Investigating **actinide deposition behavior** during irradiated Zircaloy-4 electrorefining

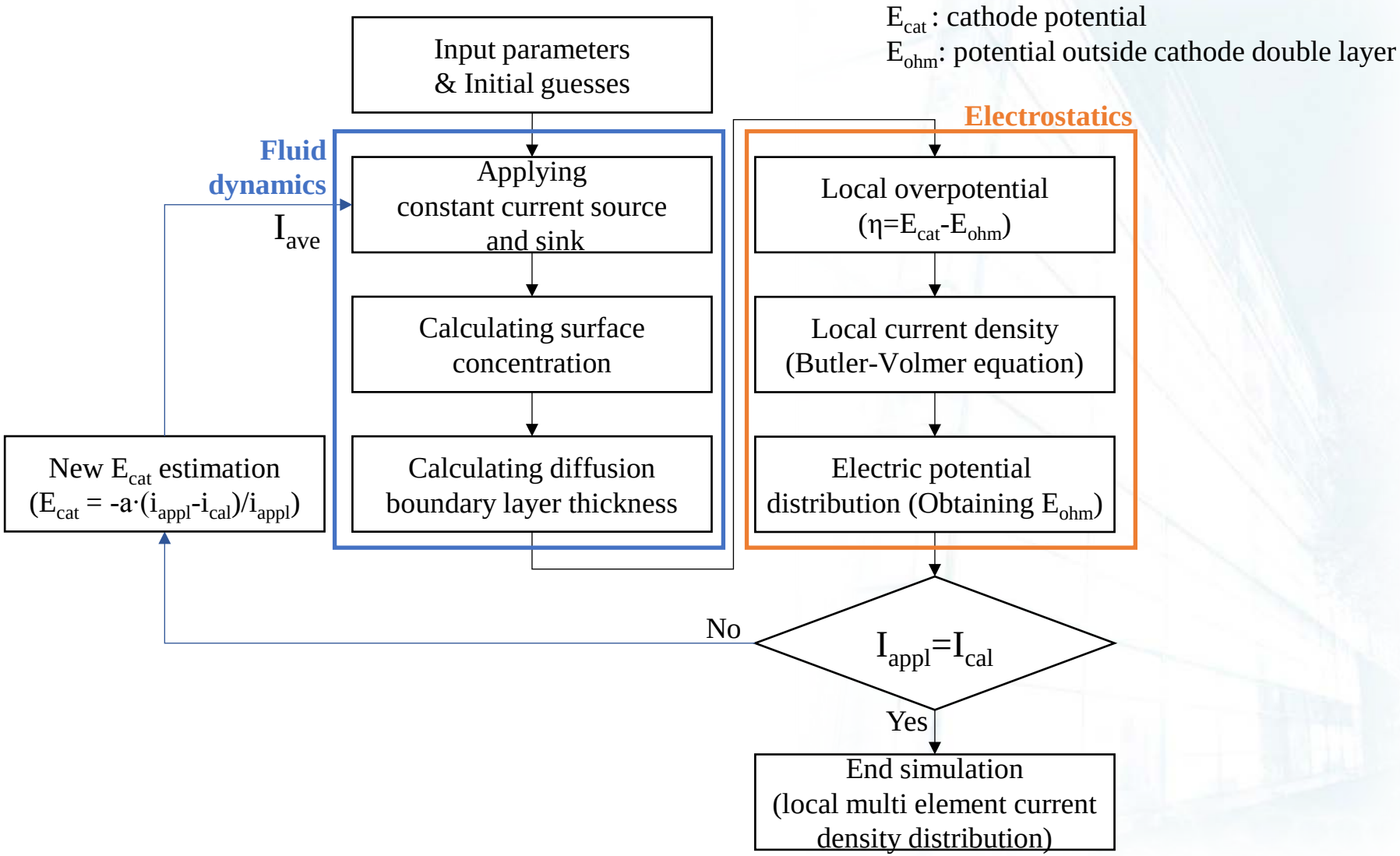
2. Investigating **local current density distribution**

Design and performance verification tool

Design of irradiated Zircaloy-4 cladding electrorefining in LiCl-KCl-$ZrCl_4$ molten salts

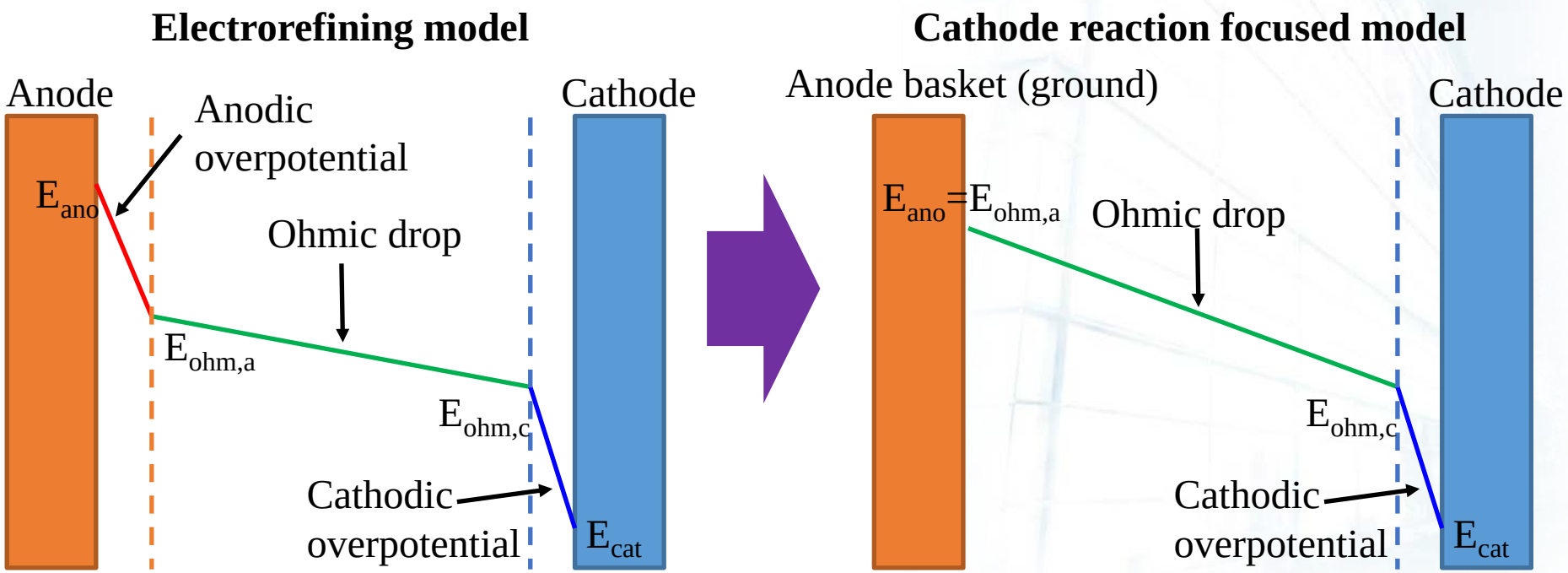
Modeling strategy

- **Flow chart of the simulation algorithm developed based on ANSYS-CFX**



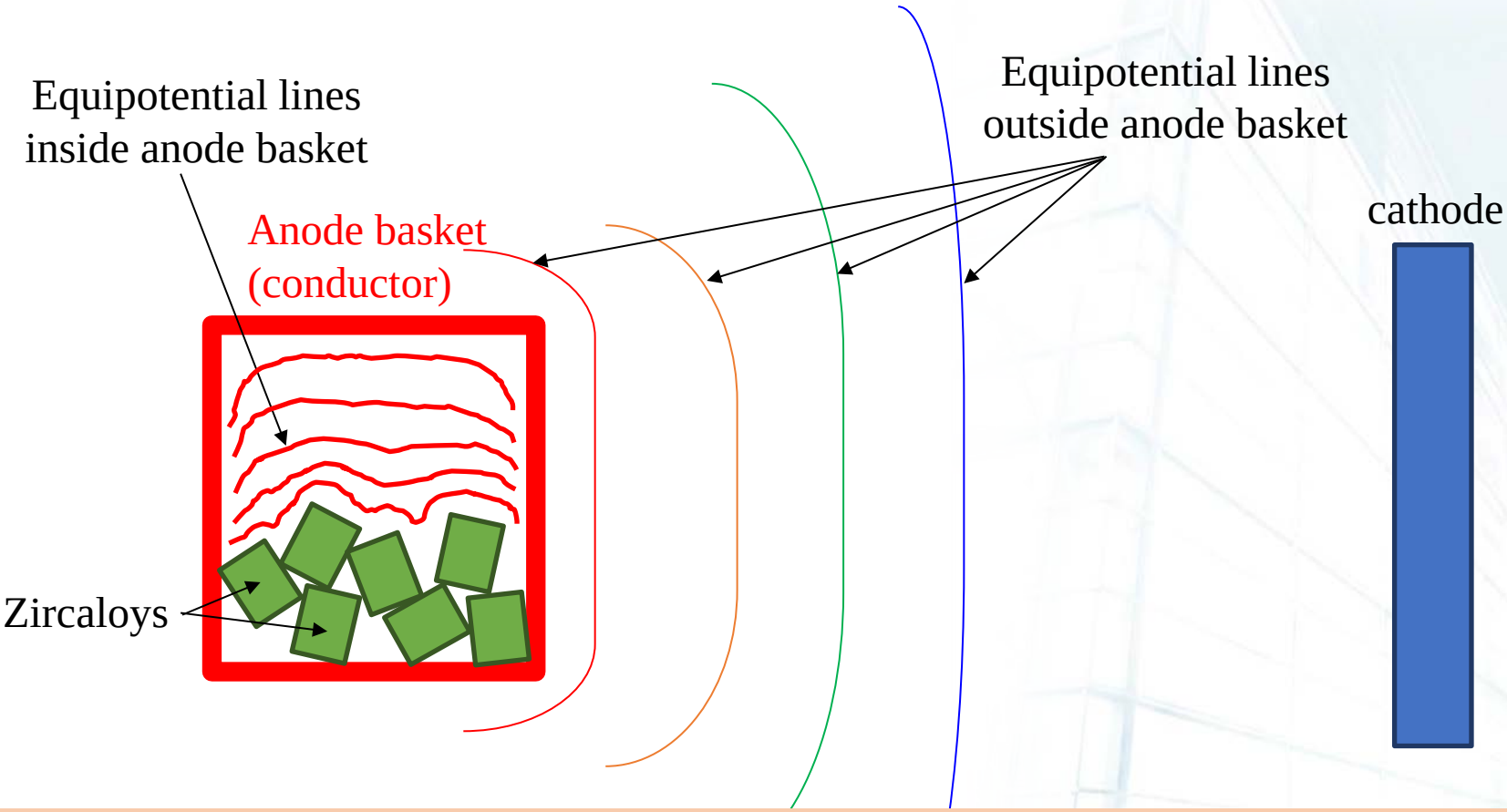
Modeling strategy

- **Cathode reaction focused model**
  1. There are large uncertainties on anodic dissolution modeling.
  2. A modeling objective is to identify modeling capability on Zr(IV) multi-step reduction.
  3. Since actinide elements are more oxidative than Zr, actinide elements can be handled in the model by assuming all actinide elements are immediately dissolved into molten salts at the initial stage of electrorefining.



Modeling strategy

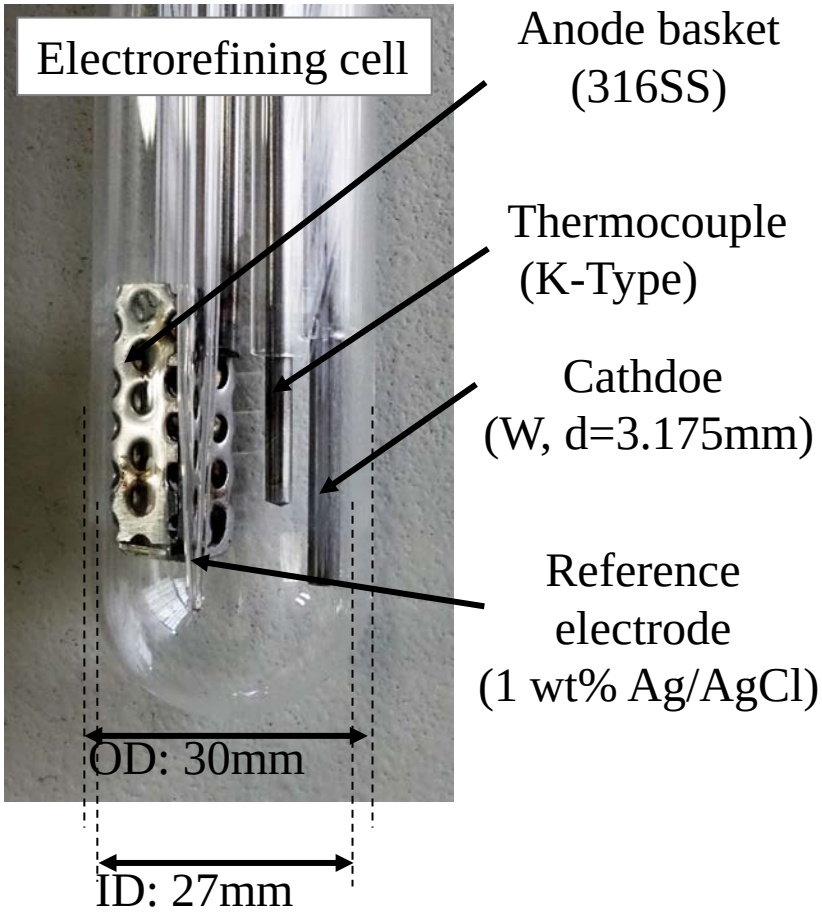
- **Cathode reaction focused model**



Potential distribution outside anode basket is determined not by geometry of Zircaloys loaded in anode basket but by that of the anode basket. **Therefore, potential distribution over the cathode could be calculated regardless of whether the anode reaction is simulated.**

Modeling on multi-step reduction of Zr(IV)

- **Objective of modeling**



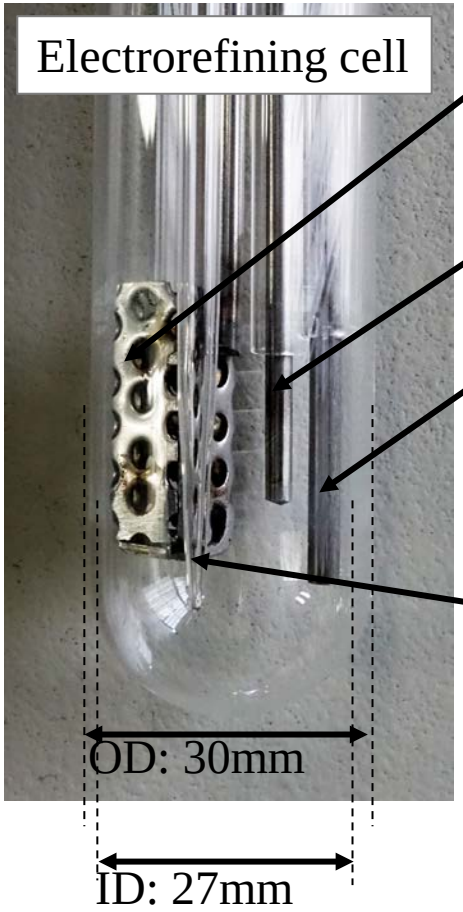
Chemical form of cathode deposits

Concentration of $ZrCl_4$	Experiment	Computational model
4.0 wt. %	ZrCl	Can be simulated?
2.0 wt. %	ZrCl	
1.0 wt. %	Zr metal + ZrCl	
0.5 wt. %	Zr metal	
0.1 wt. %	Zr metal	

Identifying computational model capability on chemical form changes according to $ZrCl_4$ concentration

Modeling on multi-step reduction of Zr(IV)

- **Geometry and mesh generation for modeling**



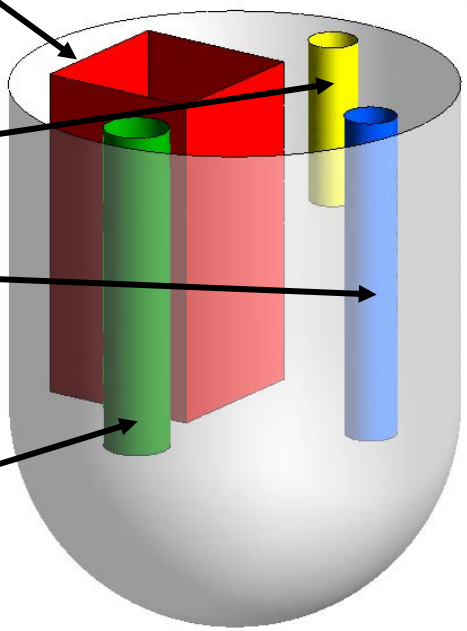
Anode basket (316SS)

Thermocouple (K-Type)

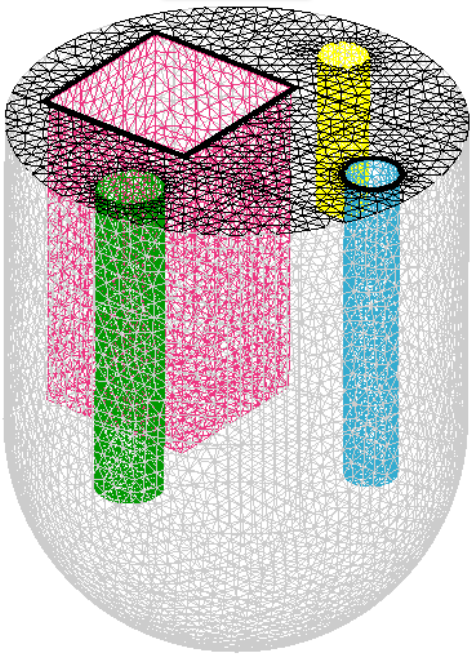
Cathdoe (W, d=3.175mm)

Reference electrode (1 wt% Ag/AgCl)

Geometry



Mesh



Modeling on multi-step reduction of Zr(IV)

- **Mathematical model on Zr electrochemical redox reactions on cathode**

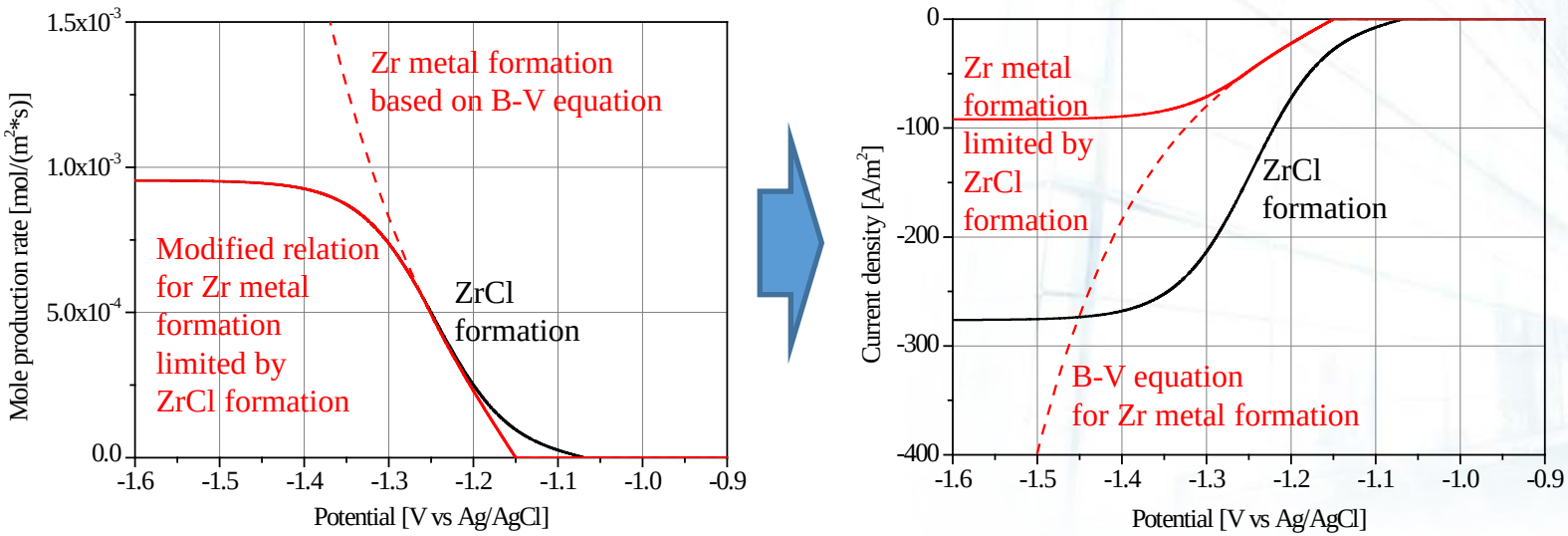
1) $Zr^{4+} + 3e^- + Cl^- \rightarrow ZrCl$

$$i_{ZrCl} = n_{ZrCl} F k_{0,ZrCl} \left[-C_{Zr^{4+}}(0,t) \exp\left(-\alpha_{ZrCl} \frac{n_{ZrCl} F}{RT} (E - E^{0\prime}_{ZrCl})\right) + \exp\left((1-\alpha_{ZrCl}) \frac{n_{ZrCl} F}{RT} (E - E^{0\prime}_{ZrCl})\right) \right]$$

2) $ZrCl + e^- \rightarrow Zr + Cl^-$

$$i_{Zr} = n_{Zr} F k_{0,Zr} \left[-\exp\left(-\alpha_{Zr} \frac{n_{Zr} F}{RT} (E - E^{0\prime}_{Zr})\right) + \exp\left((1-\alpha_{Zr}) \frac{n_{Zr} F}{RT} (E - E^{0\prime}_{Zr})\right) \right]$$

If a molar production rate of Zr metal calculated by the above equation is higher than a molar production rate of ZrCl, it is assumed that molar production rate of Zr metal is equivalent to that of ZrCl.



Modeling on multi-step reduction of Zr(IV)

- **Mathematical model on Zr electrochemical redox reactions on cathode**

1) $Zr^{4+} + 3e^- + Cl^- \rightarrow ZrCl$

$$i_{ZrCl} = n_{ZrCl} F k_{0,ZrCl} \left[-C_{Zr^{4+}}(0,t) \exp\left(-\alpha_{ZrCl} \frac{n_{ZrCl} F}{RT} (E - E^{0\prime}_{ZrCl})\right) + \exp\left((1-\alpha_{ZrCl}) \frac{n_{ZrCl} F}{RT} (E - E^{0\prime}_{ZrCl})\right) \right]$$

2) $ZrCl + e^- \rightarrow Zr + Cl^-$

$$i_{Zr} = n_{Zr} F k_{0,Zr} \left[-\exp\left(-\alpha_{Zr} \frac{n_{Zr} F}{RT} (E - E^{0\prime}_{Zr})\right) + \exp\left((1-\alpha_{Zr}) \frac{n_{Zr} F}{RT} (E - E^{0\prime}_{Zr})\right) \right]$$

Unknowns	**Material properties**			
	Property	**Value**	**Property**	**Value**
E (Electrode potential)	n_{ZrCl}	3	n_{Zr}	1
	$E^{0\prime}_{ZrCl}$	-0.994 [V vs Ag/AgCl] (experimentally measured)	$E^{0\prime}_{Zr}$	-1.15 [V vs Ag/AgCl] (experimentally measured)
$C_{Zr^{4+}}(0,t)$ (Surface concentration of Zr^{4+})	α_{ZrCl}	0.5 (assumed)	α_{Zr}	0.5 (assumed)
	$k_{0,ZrCl}$	1.69E-4 [m/s] (assumed as the value of U(III)/U rate constant)	$k_{0,Zr}$	1E-6 ~ 1E-1 [m/s]

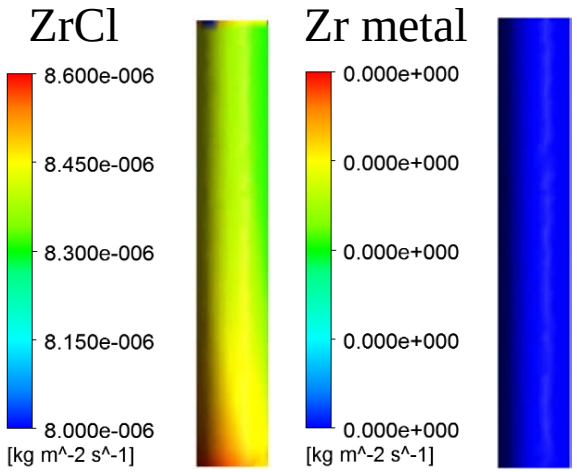
Modeling on multi-step reduction of Zr(IV)

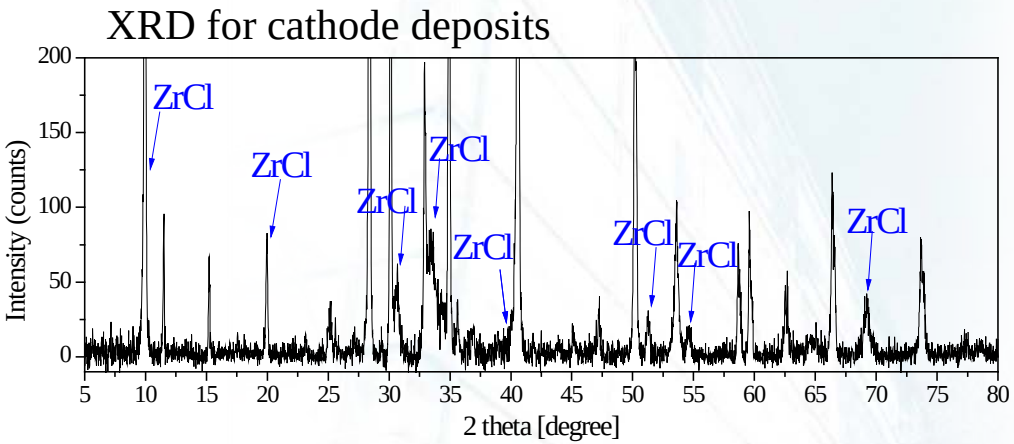
- **Comparison on chemical form of cathode deposits ($k_{0,Zr}$=1.0E-3 m/s)**

Computational modeling | **Experiment**

1. 4 wt%

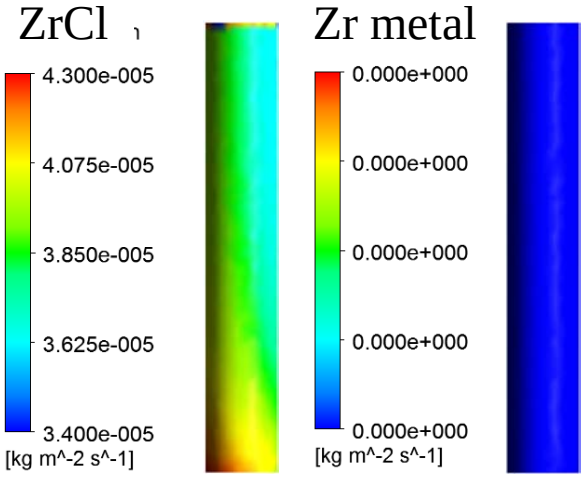
5 mA

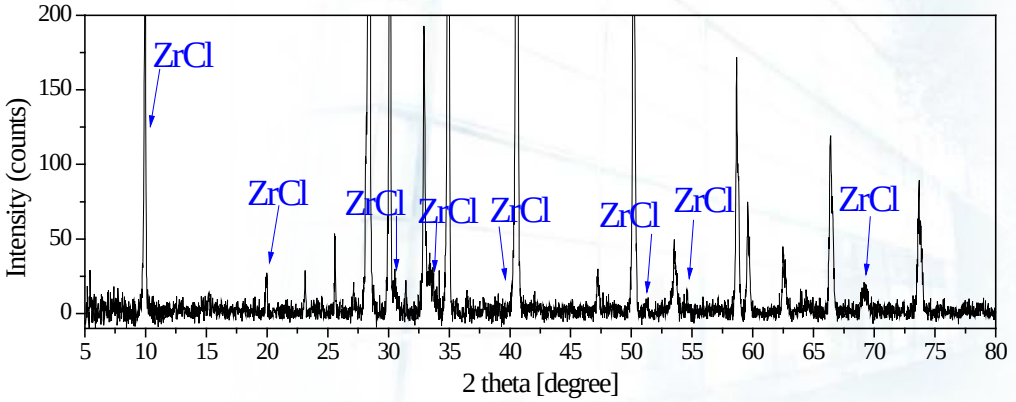




2. 2 wt%

27 mA





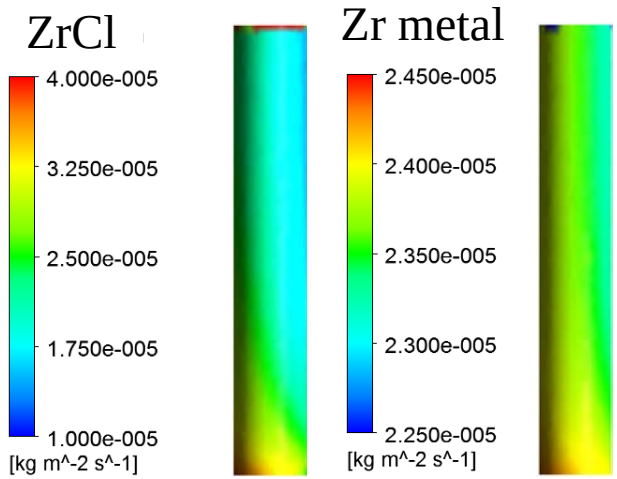
Modeling on multi-step reduction of Zr(IV)

- **Comparison on chemical form of cathode deposits ($k_{0,Zr}$=1.0E-3 m/s)**

Computational modeling

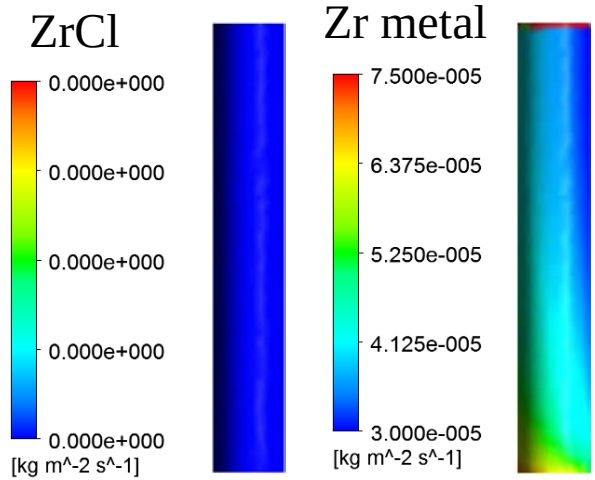
3. 1 wt%

57 mA

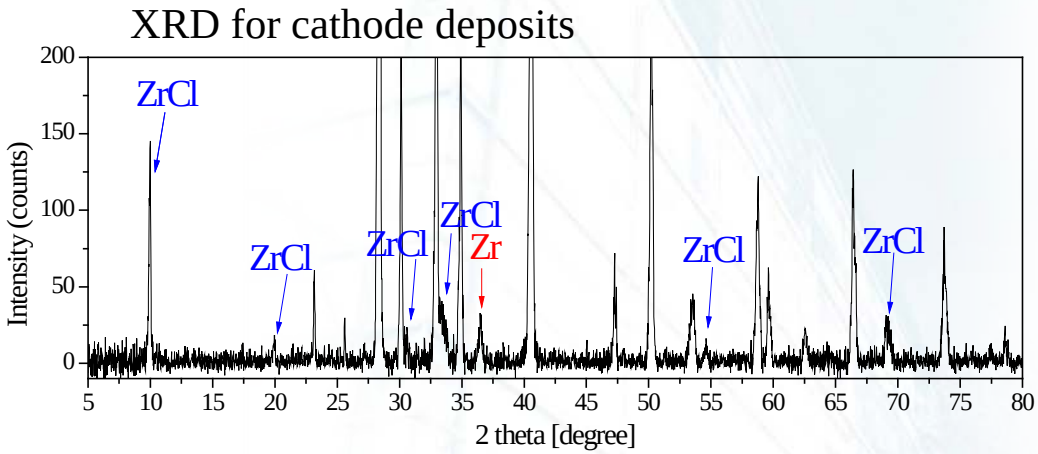


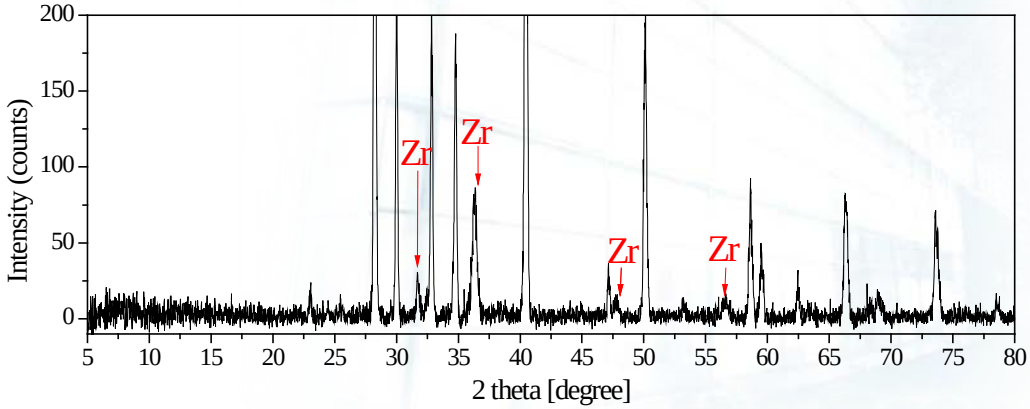
4. 0.5 wt%

90 mA



Experiment





Modeling on multi-step reduction of Zr(IV)

- **Chemical form of cathode deposits according to $k_{0,Zr}$**

		Weight percent of Zr metal in cathode deposits				
$k_{0,Zr}$ (ZrCl/Zr)	$k_{0,ZrCl}$ (Zr(IV)/ZrCl)	**0.1 wt%**	**0.5 wt%**	**1 wt%**	**2 wt%**	**4 wt%**
1.00E-06	1.69E-4	100	100	0	0	0
1.00E-05		100	100	0	0	0
1.00E-04		100	100	0	0	0
1.00E-03		**100**	**100**	**45**	**0**	**0**
1.50E-03		**100**	**100**	**50.554**	**0**	**0**
2.00E-03		100	100	57	10.037	0
1.00E-02		100	100	90	62.18	0
1.00E-01		100	100	100	72.01	0
Experimental results		100	100	100> and >0	0	0

- **Rate constant for the reaction between ZrCl and Zr metal would be much larger than the rate constant for the reaction between Zr(IV) and ZrCl.**

Simulation on irradiated Zircaloy cladding electrorefining

- **Objective of simulation**
  - ✓ Design of simple geometry electrorefiner for irradiated Zircaloy-4 cladding
  - ✓ Searching operating condition for the electrorefiner to recover Zr metal without ZrCl and actinide deposition.

- **Reactions used for simulation**

① $Zr(IV) + 3e^- + Cl^- \rightarrow ZrCl$, ② $ZrCl + e^- \rightarrow Zr + Cl^-$ and ③ $U(III) + 3e^- \rightarrow U$

① : $i_{ZrCl} = n_{ZrCl}Fk_{0,ZrCl}\left[-C_{Zr^{4+}}(0,t)\exp(-\alpha_{ZrCl}\frac{n_{ZrCl}F}{RT}(E - E^{0\prime}_{ZrCl})) + \exp((1-\alpha_{ZrCl})\frac{n_{ZrCl}F}{RT}(E - E^{0\prime}_{ZrCl}))\right]$

② : $i_{Zr} = n_{Zr}Fk_{0,Zr}\left[-\exp(-\alpha_{Zr}\frac{n_{Zr}F}{RT}(E - E^{0\prime}_{Zr})) + \exp((1-\alpha_{Zr})\frac{n_{Zr}F}{RT}(E - E^{0\prime}_{Zr}))\right]$

③ : $i_U = n_UFk_{0,U}\left[-C_{U^{3+}}(0,t)\exp(-\alpha_U\frac{n_UF}{RT}(E - E^{0\prime}_U)) + \exp((1-\alpha_U)\frac{n_UF}{RT}(E - E^{0\prime}_U))\right]$

Simulation on irradiated Zircaloy cladding electrorefining

- **Assumptions for simulation on irradiated Zircaloy-4 cladding**

1. Immediate dissolution of uranium in irradiated Zircaloy-4 cladding

- The initial concentration of UCl_3 in molten salts is determined as

$$C_{U,initial} = \frac{\text{Amount of U in Zircaloy−4 cladding loaded in anode basket}}{\text{Volume of molten salts}} \text{ [mol/m}^3\text{]}$$

- This could lead more conservative results because potential difference between Zr and U is reduced.

2. Steady state

- Since surface area changes of anode and cathode would be hard to be handled in 3D computational model, steady state is assumed.

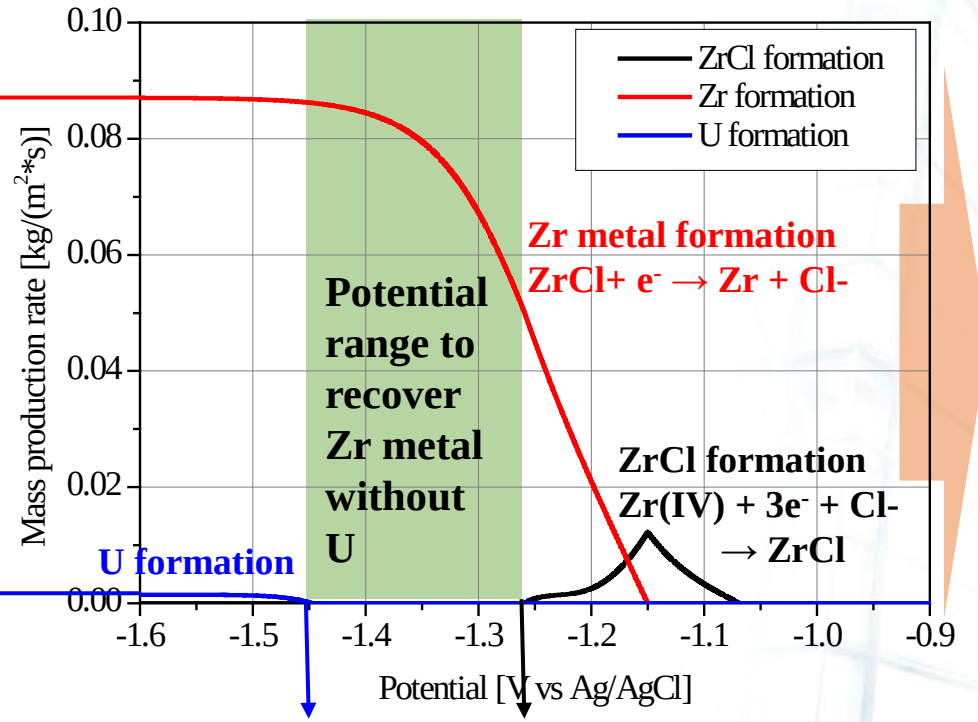
Simulation on irradiated Zircaloy cladding electrorefining

① $Zr(IV) + 3e^- + Cl^- \rightarrow ZrCl$, ② $ZrCl + e^- \rightarrow Zr + Cl^-$ and ③ $U(III) + 3e^- \rightarrow U$

- **Major design parameters**

Production rate of Zr is related to
1) Diffusion boundary layer thickness
2) $ZrCl_4$ concentration

Production rate of U is related to
1) Diffusion boundary layer thickness
2) Amount of irradiated cladding loaded in anode
3) Volume of molten salt



Potential where U starts to be deposited is related to
1) Amount of irradiated cladding loaded in anode
2) Volume of molten salt

Potential for that only Zr metal is deposited is related to
1) Diffusion boundary layer thickness
2) $ZrCl_4$ concentration

Zr metal recovery
1. $ZrCl_4$ concentration
2. Diffusion boundary layer thickness

U metal deposition
1. Amount of irradiated cladding loaded in anode
2. Volume of molten salt
3. Diffusion boundary layer thickness

Simulation on irradiated Zircaloy cladding electrorefining

- **Design of irradiated Zircaloy-4 cladding**

1. $ZrCl_4$ concentration in LiCl-KCl molten salts

0.5 wt% $ZrCl_4$ in initial molten salts

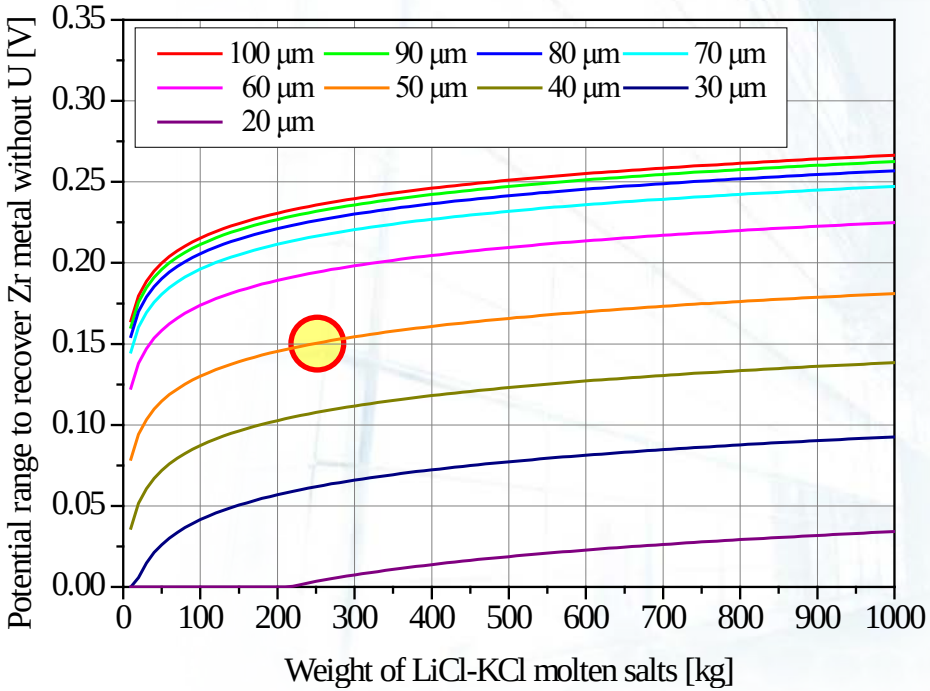
2. Amount of irradiated Zircaloy-4 cladding loaded in anode

Zircaloy-4 of 10 kg

3. Volume (Weight) of LiCl-KCl molten salts and diffusion boundary layer thickness

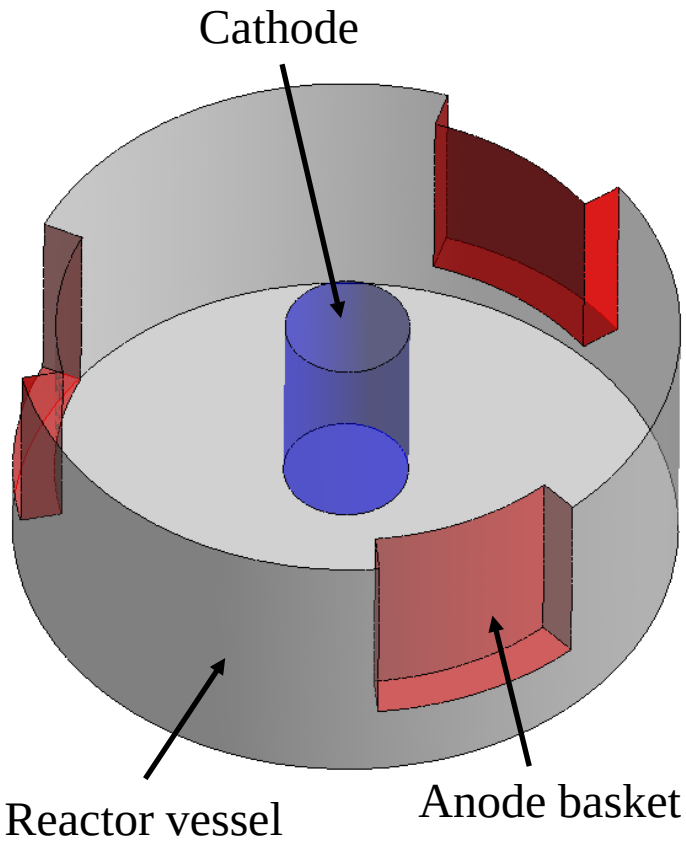
To secure potential range of 0.15 V for recovering Zr metal without ZrCl and U, **the weight of LiCl-KCl molten salt is determined as about 250 kg.**

Under this condition, diffusion boundary layer thickness **could not be thinner than 50 μm.**



Simulation on irradiated Zircaloy cladding electrorefining

- **Design of irradiated Zircaloy-4 cladding**



Design feature

1. Reactor vessel

- Height: 35 cm
- Diameter: 80 cm
- Volume (including anode basket): 175,929 cm^3
- Volume (except Zircaloy-4 cladding of 10 kg): 174,395 cm^3

2. Anode basket

- Height: 25 cm
- Basket thickness: 5 cm
- Angle of anode basket : 27.75~111°
- Number of anode baskets: 1~4
- Volume of anode baskets: 9081 cm^3
- Volume of Zircaloy-4 cladding: 1533 cm^3
- Volume of Zircaloy-4 cladding including hollow : 6799 cm^3
- Zircaloy-4 cladding loading efficiency: 75%
- Area of Zircaloy-4 cladding: 53,820 cm^2

3. Cathode

- Height: 25 cm
- Diameter: 15 cm
- Area : 1,355 cm^2

❖ To investigate electric field symmetry in circumferential direction, 4 anodes basket arrangements are tested.

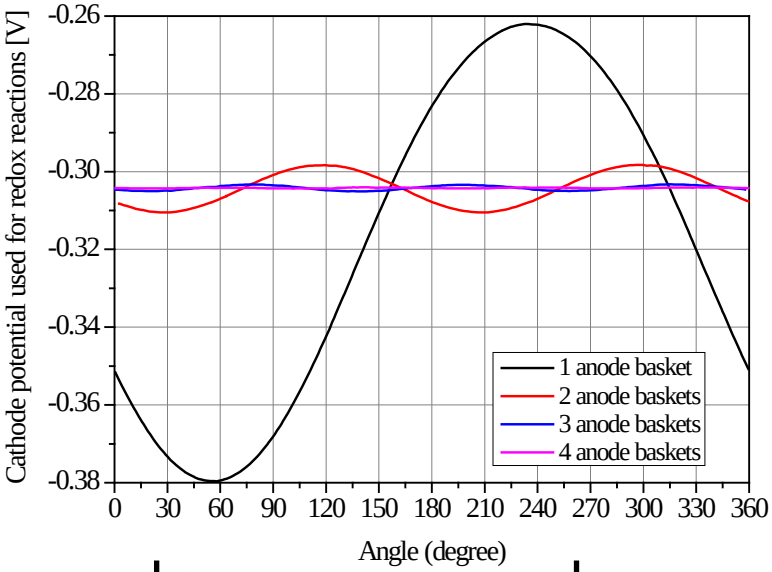
❖ To minimize cross-flow near the cathode, only cathode rotation is considered.

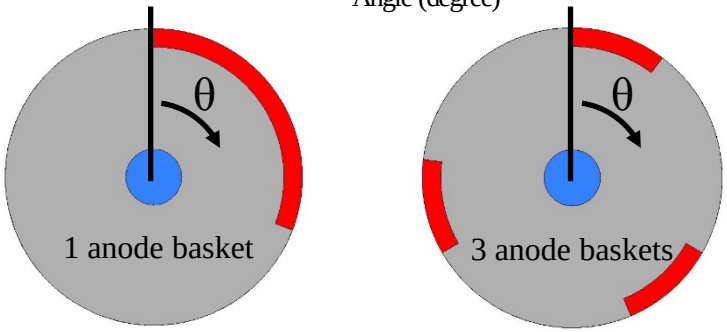
Simulation on irradiated Zircaloy cladding electrorefining

- **Simulation results on irradiated Zircaloy-4 cladding**

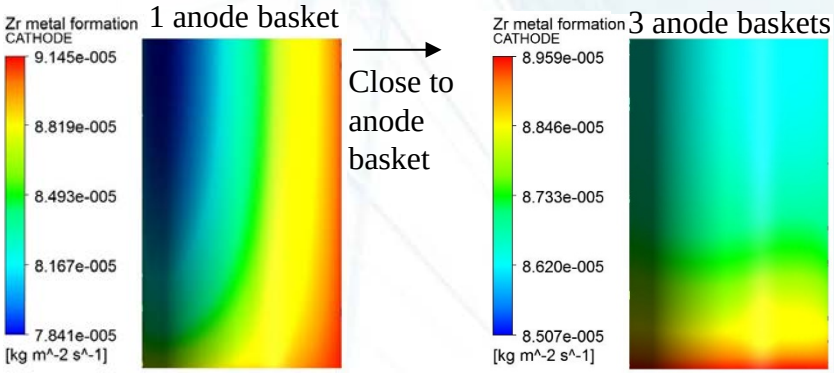
Effect of number of anode basket

- Applied current: 50 A
- Rotating speed of cathode: 100 rpm

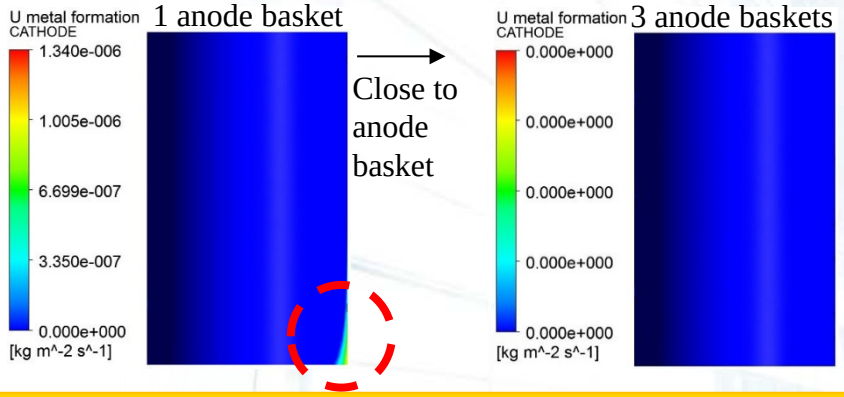




- **Zr metal formation**



- **U metal formation**



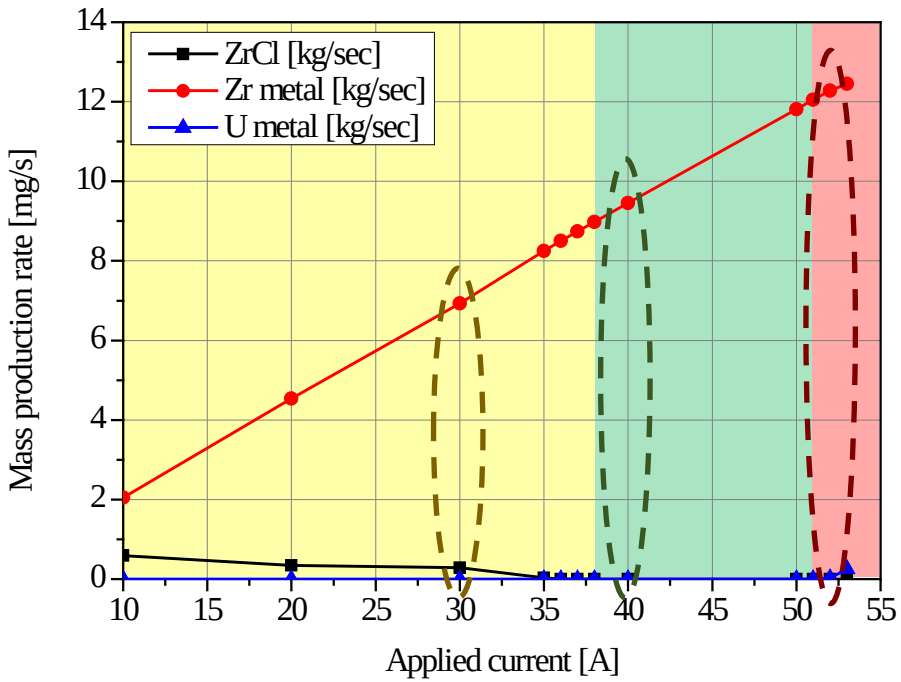
If there are **more than three anode baskets**, variation in circumferential direction could be diminished enough.

Simulation on irradiated Zircaloy cladding electrorefining

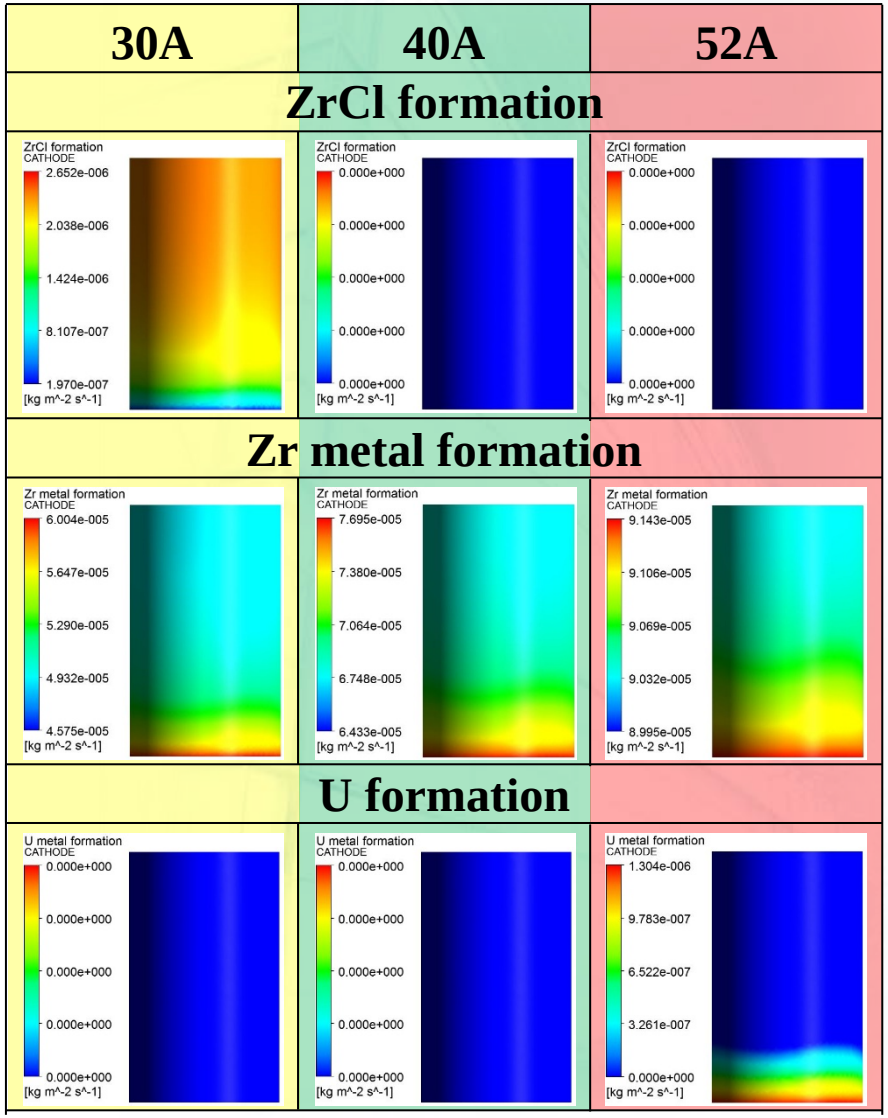
- **Simulation results on irradiated Zircaloy-4 cladding**

Effect of applied current

- 3 anode baskets
- Cathode rotating speed: 100 rpm



If applied current is between 38 A and 51 A, Zr metal could be obtained without ZrCl and U.



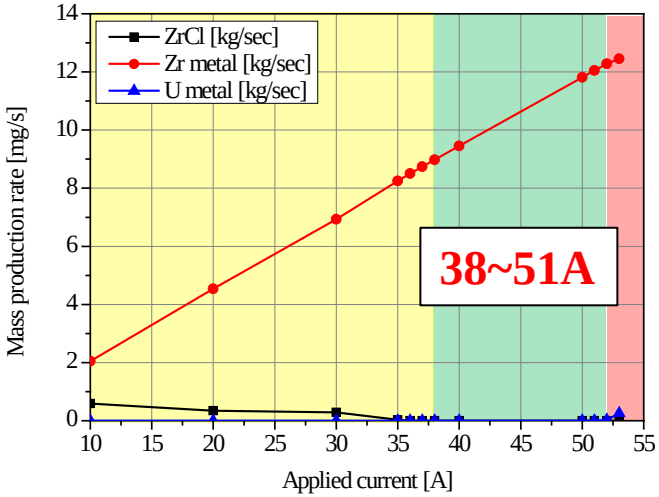
Simulation on irradiated Zircaloy cladding electrorefining

- **Simulation results on irradiated Zircaloy-4 cladding**

Effect of rotating speed of cathode

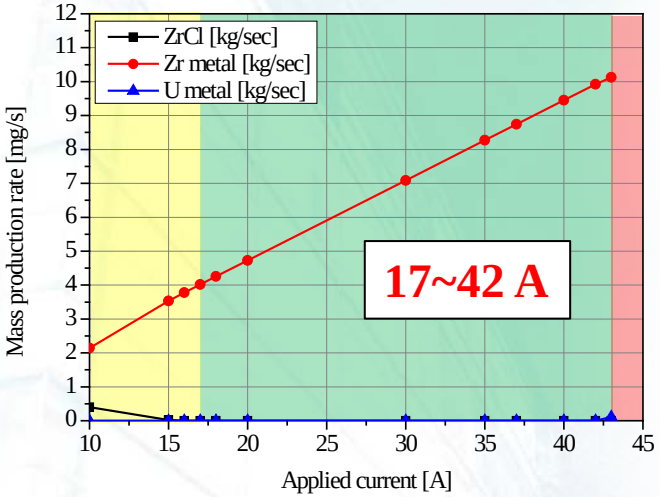
1. 100 rpm

δ = 47.25 μm



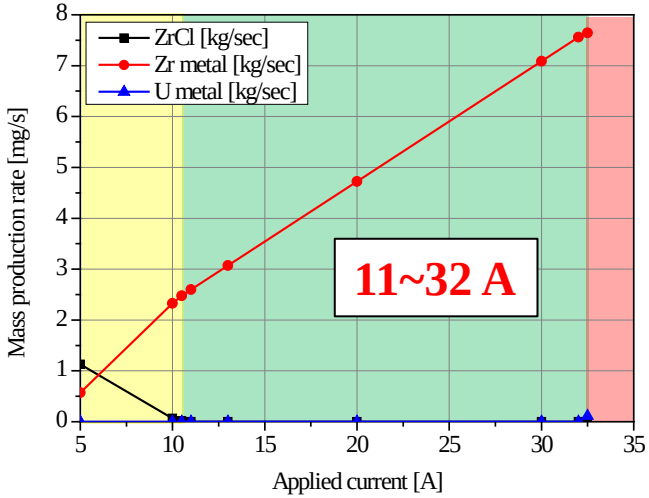
2. 75 rpm

δ = 57.79 μm



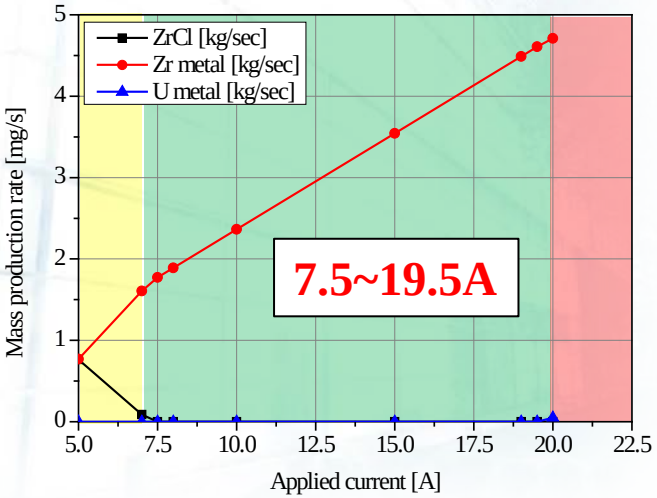
3. 50 rpm

δ = 76.75 μm



4. 25 rpm

δ = 124.7 μm



Summary

- Three-dimensional electrochemo-hydrodynamic model for electrorefining of irradiated Zircaloy cladding has been developed.
- Chemical forms of cathode deposits according to concentration of $ZrCl_4$ were simulated with multi-step reduction model of Zr(IV) and the modeling results agreed well with experimental results.
- Based on computational model, electrorefiner for irradiated Zircaloy-4 cladding was preliminarily designed and operating conditions to recover Zr metal without ZrCl and U metal deposition were derived.
- The developed computational model can be utilized for designing and improving an electrorefiner.
- In addition, it can be also used for evaluating proliferation-resistance of electrorefining or electrowinning by simulating U-Pu-MA deposition on the cathode.

Future work

Quantitative comparison on the ratio of Zr metal and ZrCl in cathode deposits

Consideration of more redox and chemical reactions

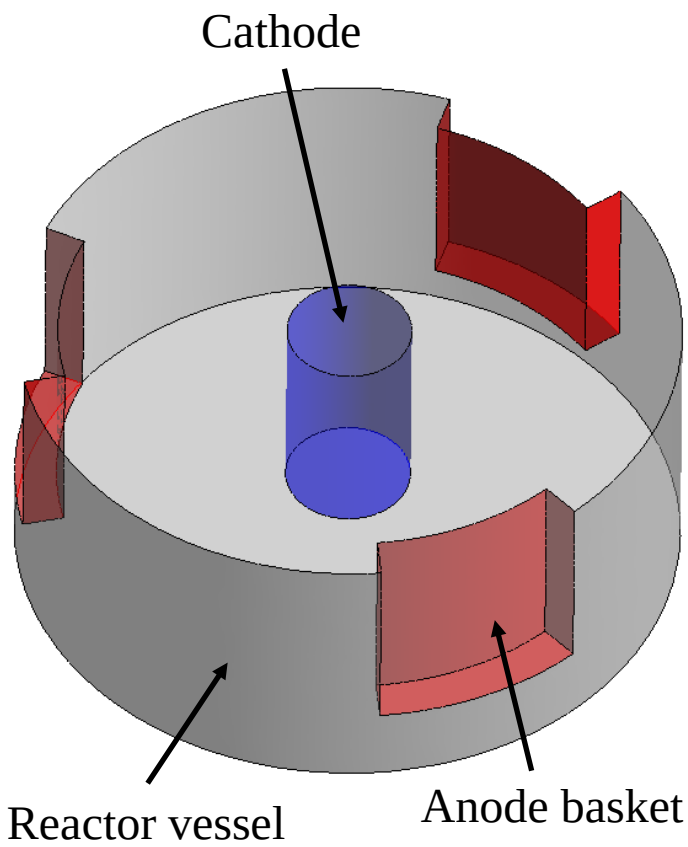
- $Zr(IV) + 2e^- \leftrightarrow Zr(II)$
- $Zr(IV) + Zr \leftrightarrow 2\ Zr(II)$
- More actinide elements

Material property acquisition

- Rate constant (k)
- Transference number (α)
- Diffusion coefficient (D)
- Standard potential (E^0)

Thank you for your attention

Appendix



Irradiated Zircaloy-4 cladding ER operating condition

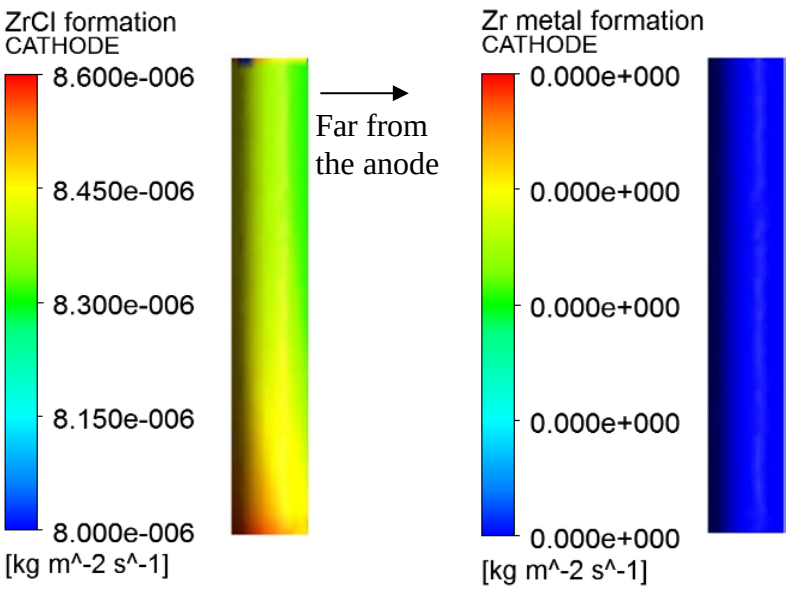
	Condition 1	Condition 2
Throughput [ton/year]	**0.1~0.15**	**0.15~0.2**
Operating hours [hours/day]	24	24
Operating days [days/year]	250	250
Applied current [A]	**20~30**	**30~40**
Number of anode baskets	3	3
Zircaloy-4 cladding loaded into anode baskets [kg]	10	10
Rotating speed of cathode [rpm]	**50**	**75**
Cathode diameter [cm]	15	15
Cathode height [cm]	25	25
Cell diameter [cm]	80	80
Cell height [cm]	35	35
DF for U and TRU	**Might not be deposited by managing applied current**	
DF for penetrating elements		
DF for activation products	**Might not be dissolved by monitoring anode potential**	

5. Computational ER Model Development

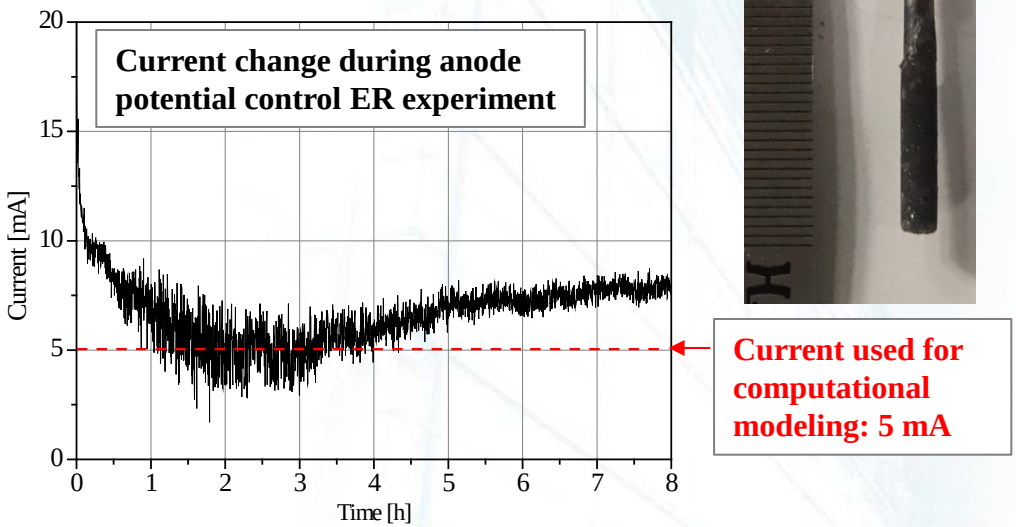
5.4 Zircaloy-4 Electrorefining system benchmark

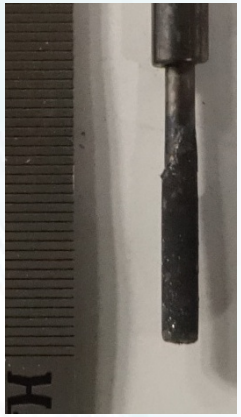
- Electrorefining in LiCl-KCl-4.0wt% $ZrCl_4$

Applied current: 5 mA

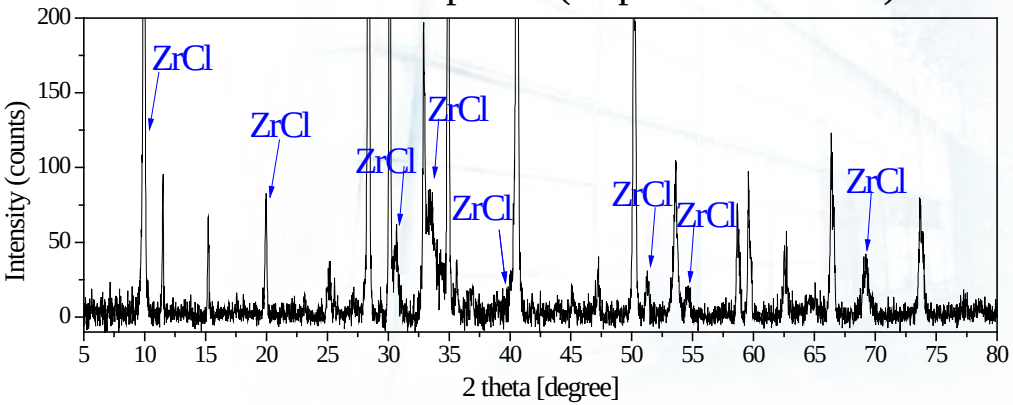


Zr metal in cathode deposits: 0.00 wt%





XRD for cathode deposits (Experimental data)

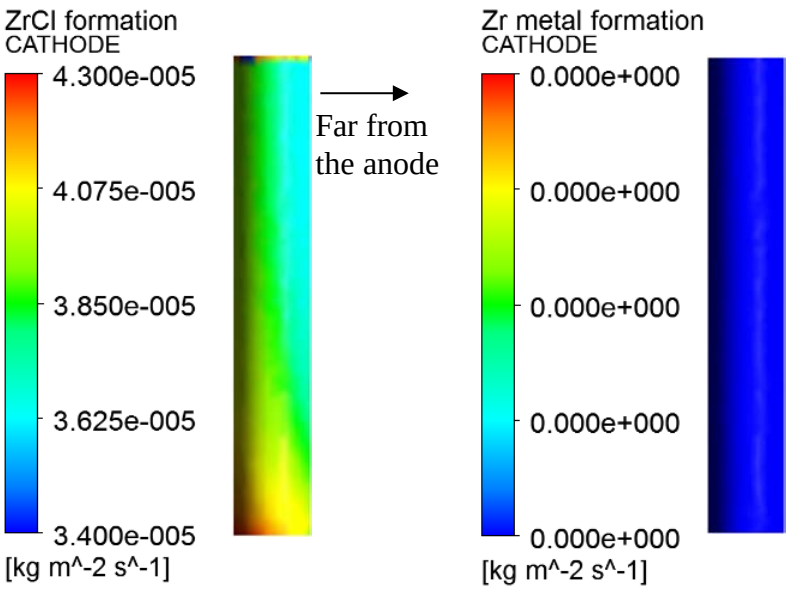


5. Computational ER Model Development

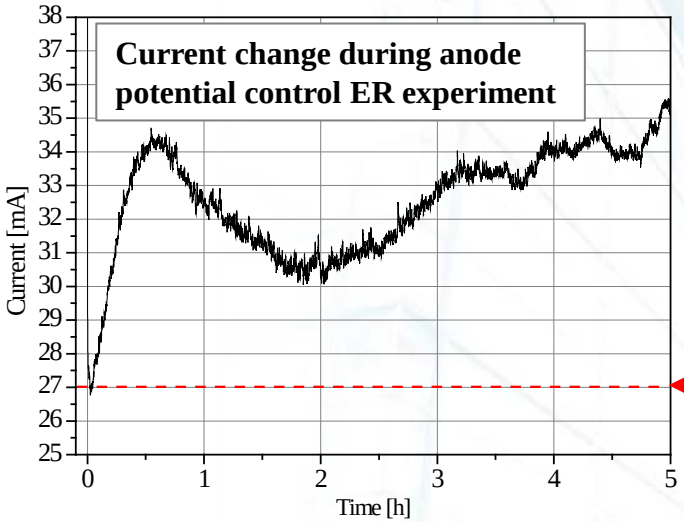
5.4 Zircaloy-4 Electrorefining system benchmark

- Electrorefining in LiCl-KCl-2.0wt% $ZrCl_4$

Applied current: 27 mA

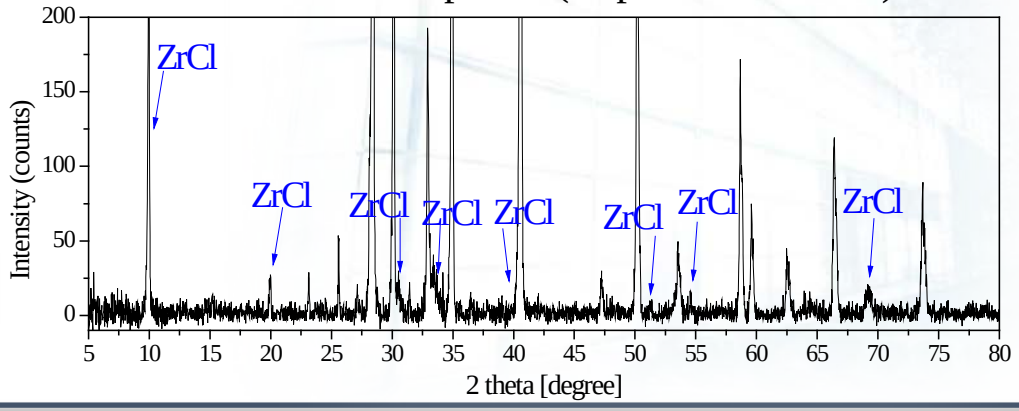


Zr metal in cathode deposits: 0.00 wt%



Current used for computational modeling: 27 mA

XRD for cathode deposits (Experimental data)

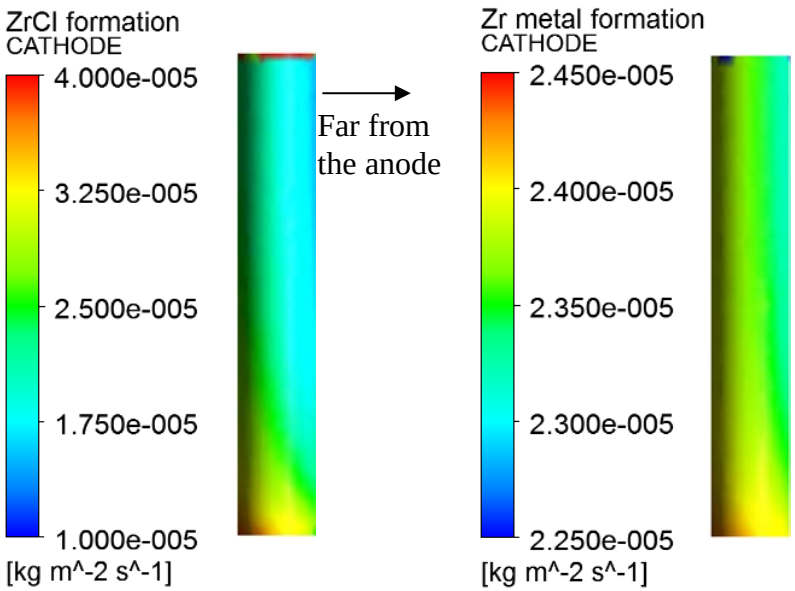


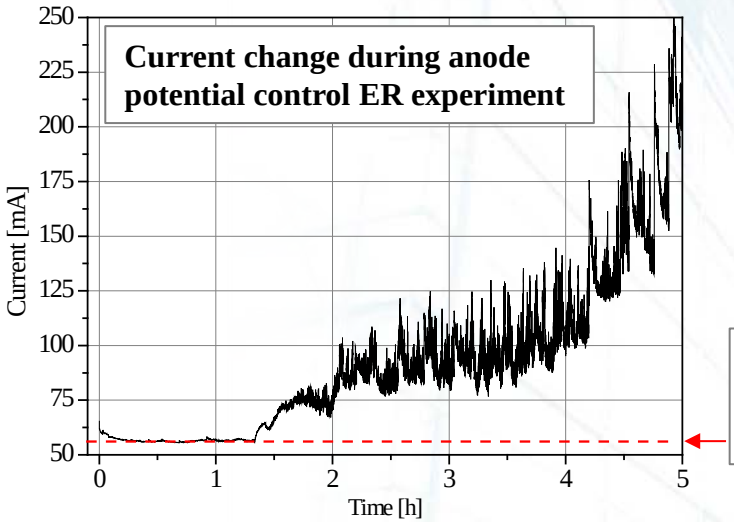
5. Computational ER Model Development

5.4 Zircaloy-4 Electrorefining system benchmark

- Electrorefining in LiCl-KCl-1.0wt% $ZrCl_4$

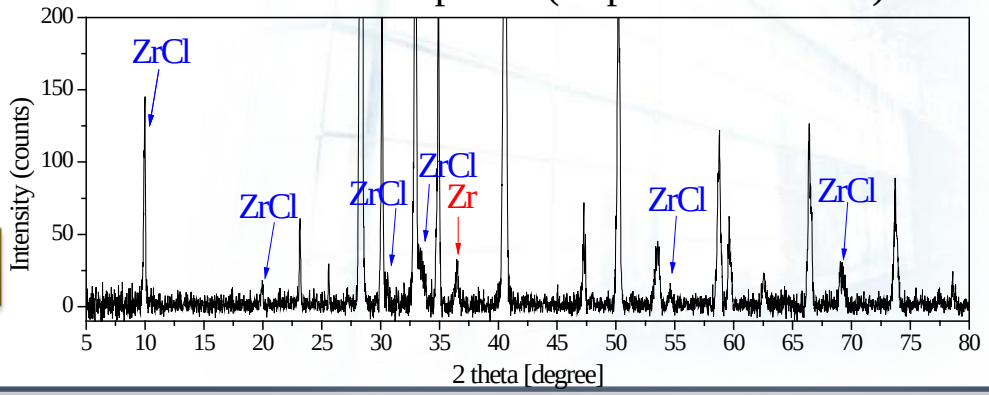
Applied current: 57 mA





Current used for computational modeling: 27 mA

XRD for cathode deposits (Experimental data)



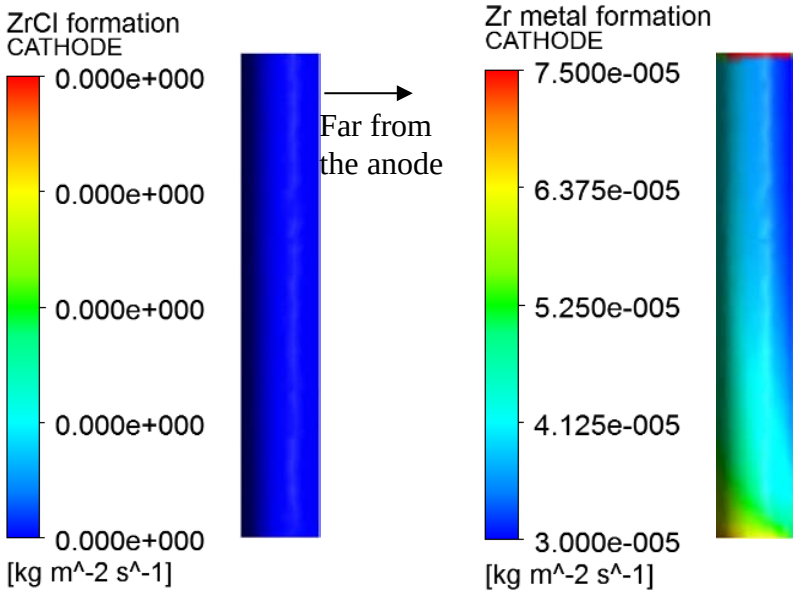
Zr metal in cathode deposits: 50.554 wt%

5. Computational ER Model Development

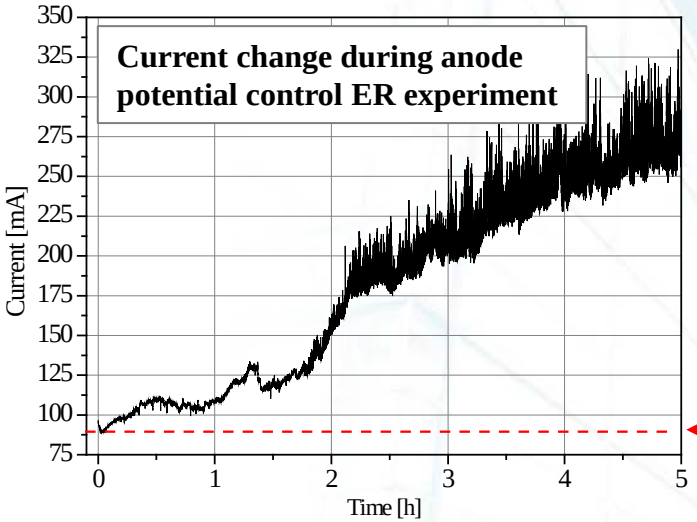
5.4 Zircaloy-4 Electrorefining system benchmark

- Electrorefining in LiCl-KCl-0.5wt% $ZrCl_4$

Applied current: 90 mA

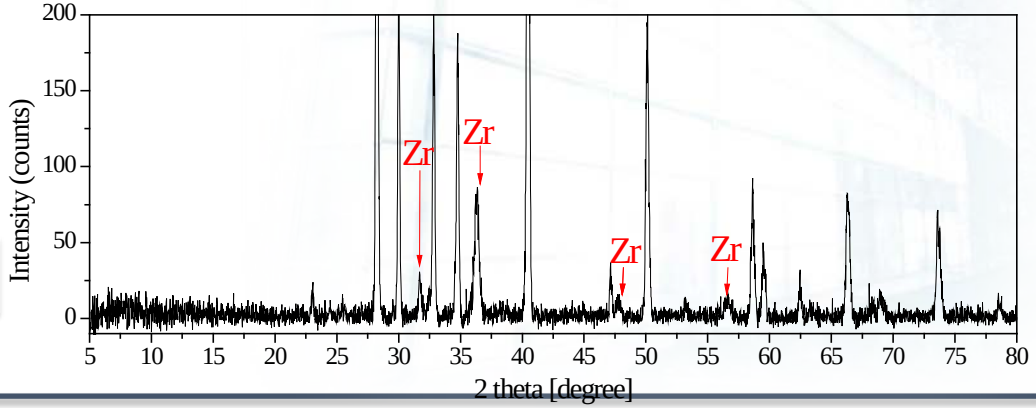


Zr metal in cathode deposits: 100 wt%



Current used for computational modeling: 90 mA

XRD for cathode deposits (Experimental data)

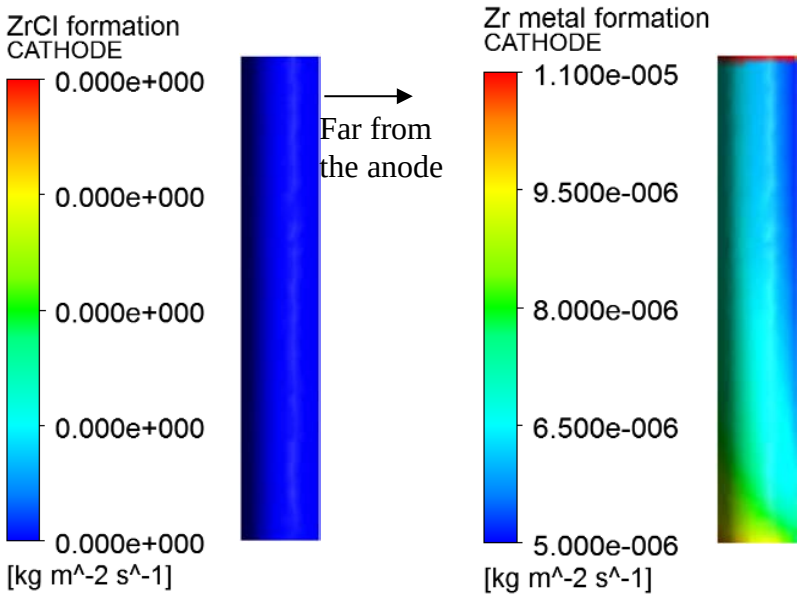


5. Computational ER Model Development

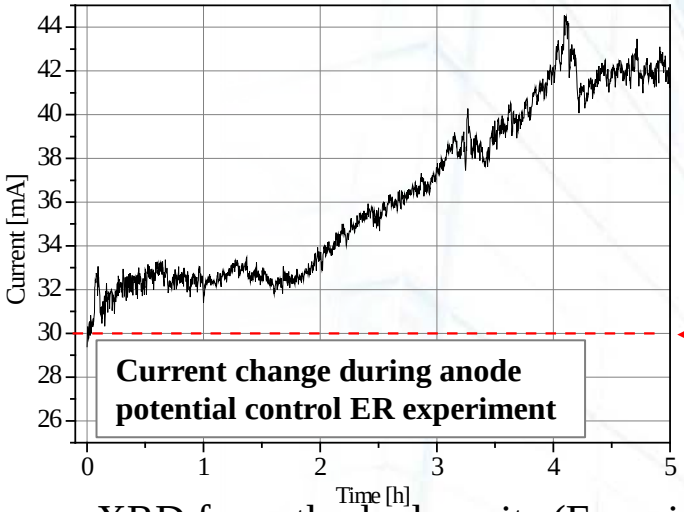
5.4 Zircaloy-4 Electrorefining system benchmark

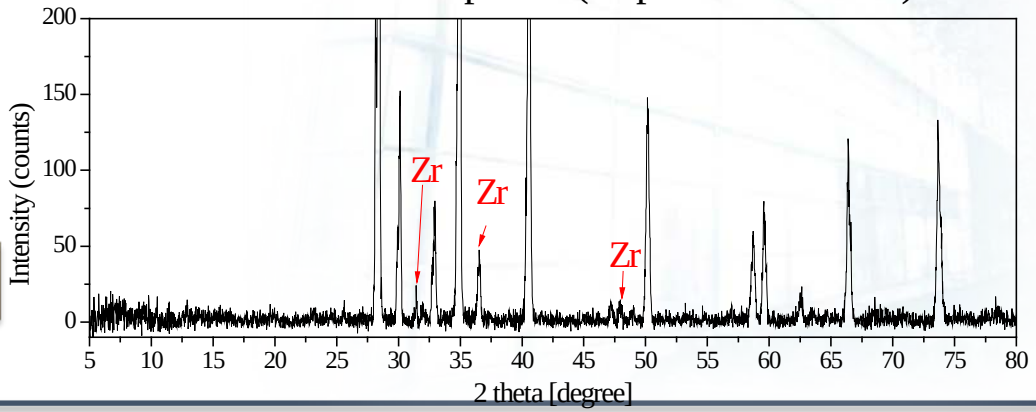
- Electrorefining in LiCl-KCl-0.1wt% $ZrCl_4$

Applied current: 30 mA



Zr metal in cathode deposits: 100 wt%



Current used for computational modeling: 30 mA

XRD for cathode deposits (Experimental data)