Seoul National University

SNUMAT Seoul National University Nuclear Materials Lab.

Electrochemical Behavior of Zirconium and Electrorefining of Zircaloy-4 in LiCl-KCl at 500°C

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October 21, 2014

2014 International Pyroprocessing Research Conference

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Outline

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I Introduction

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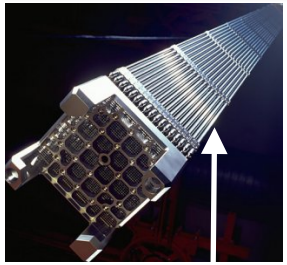
IV Electrorefining of Zircaloy-4 specimen in LiCl-KCl

V Conclusion

Introduction

- **Zirconium uses in nuclear power industry**

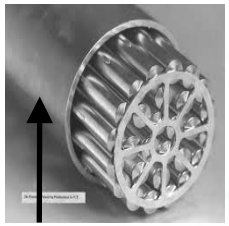
Nuclear Fuel Cladding in Thermal Reactor



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

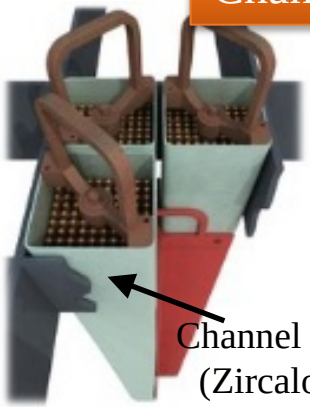


Pressure tube
(Zr-2.5Nb)

Calandria tube
(Zircaloy)

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

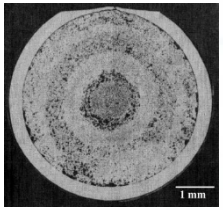
Channel Box in BWR



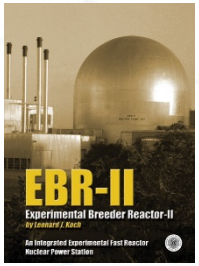
Channel Box
(Zircaloy)

- **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)



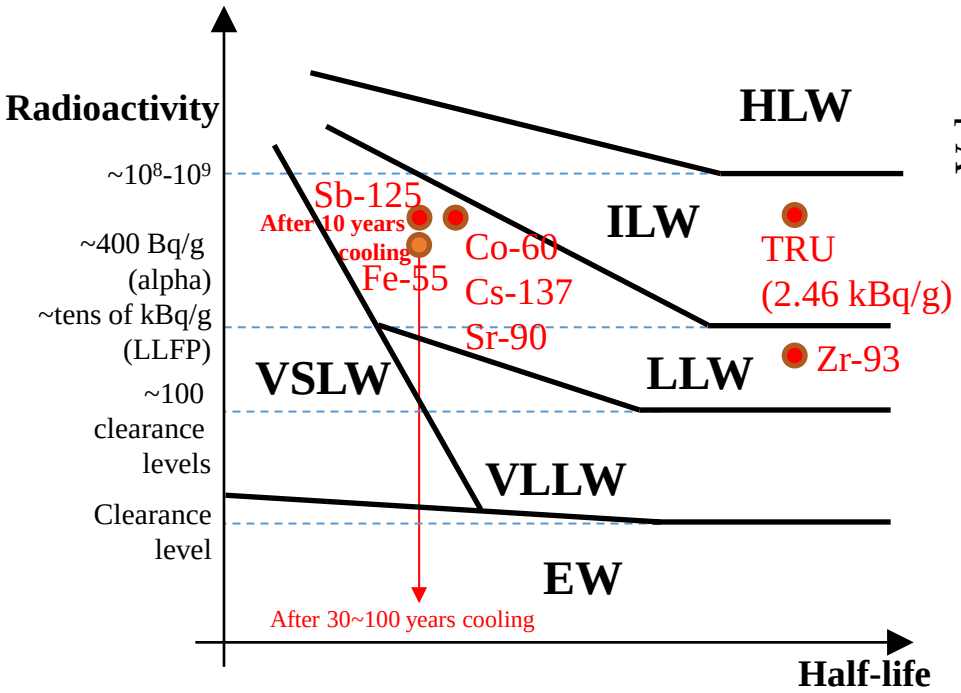
Fast Reactor

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

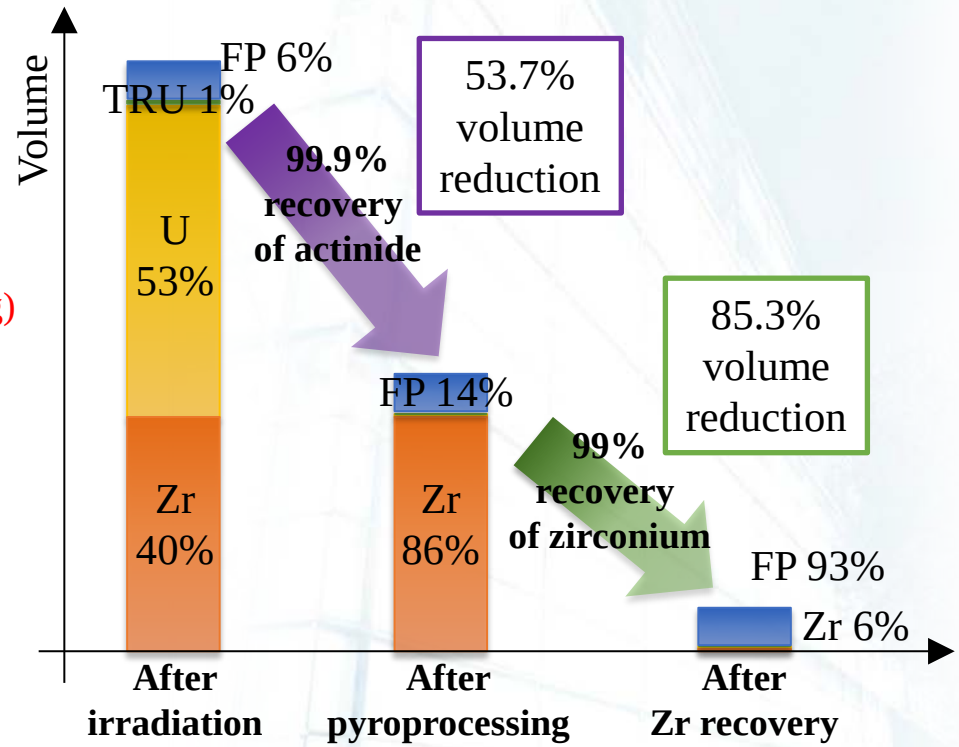
Introduction

- **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

- **Previous research on Zircaloy cladding decontamination**

			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

Objective

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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

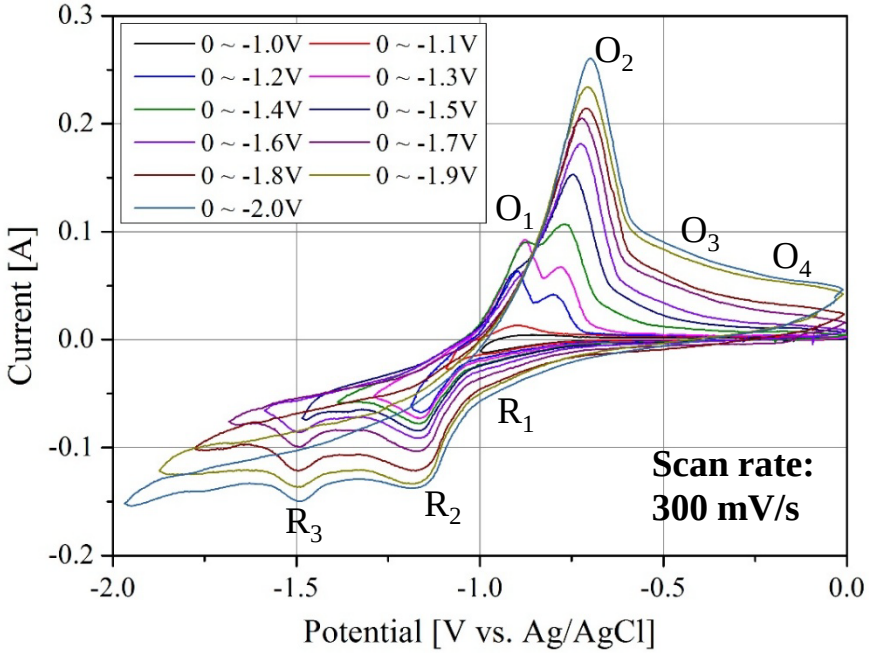
Objective

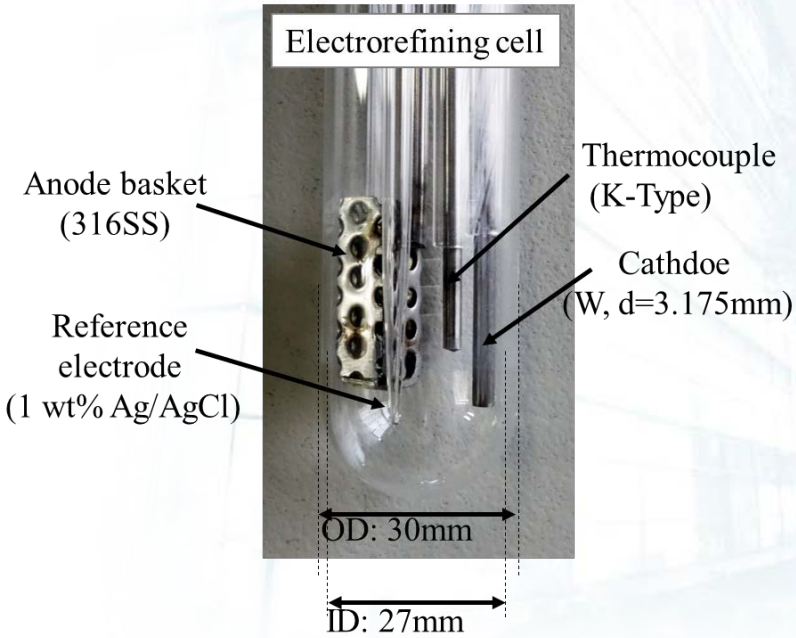
Zr redox behavior

1. Identifying Zr redox behavior in LiCl-KCl
2. Suggesting electrorefining experiment conditions to recover high purity Zr metal

Lab-scale electrorefing

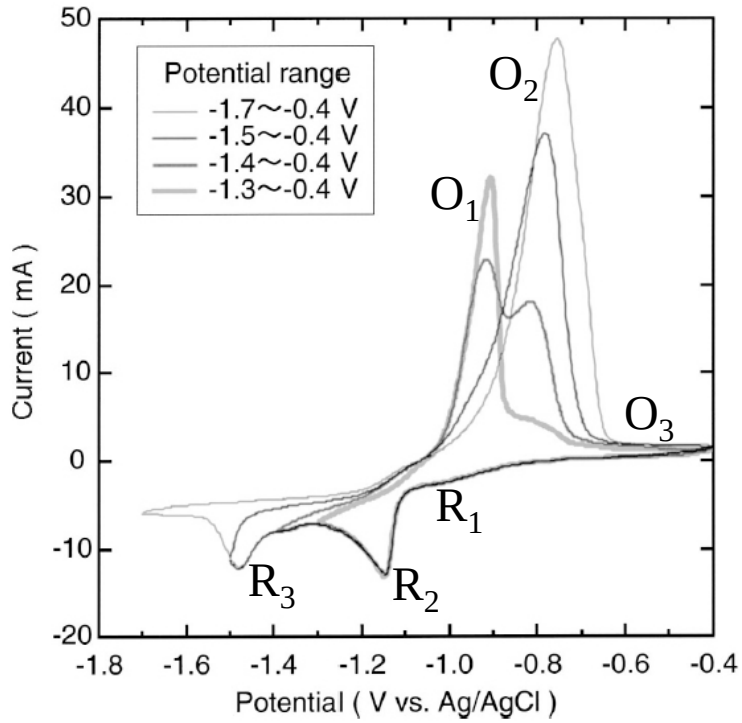
1. Confirming electrorefining conditions
2. Suggesting design requirements and points to be improved for large-scale Zircaloy-4 electrorefining





Zirconium redox behaviors in LiCl-KCl

- **Reported zirconium electrochemical behaviors in LiCl-KCl**



Sakamura (2004)

Peak	Lee (500°C, 4wt% $ZrCl_4$, W working electrode)	Ghosh (525°C, about 2.65wt% $ZrCl_4$, W working electrode)	Sakamura (500°C, about 0.514 wt% $ZrCl_4$, Mo working electrode)
O_1	ZrCl → Zr(IV) + 3e⁻ Zr → Zr(II) + 2e⁻	Zr → Zr(I) + e⁻	ZrCl → Zr(IV) + 3e⁻
O_2	Zr → Zr(IV) + 4e⁻	Zr → Zr(II) + 2e⁻ Zr(I) → Zr(II) + e⁻	Zr → Zr(IV) + 4e⁻
O_3	Zr(II) → Zr(IV) + 2e⁻	Zr(II) → Zr(IV) + 2e⁻	Not observed
R_1	Zr(IV) + 2e⁻ → Zr(II)	Zr(IV) + 2e⁻ → Zr(II)	Zr(IV) + 2e⁻ → Zr(II)
R_2	Zr(II) + 2e⁻ → Zr Zr(IV) + 3e⁻ → ZrCl	Zr(II) + 2e⁻ → Zr Zr(II) + e⁻ → Zr(I) *Zr(I)+ e⁻ → Zr (*This reaction is located at slightly more negative potent ial than other reactions.)	Zr(IV) + 4e⁻ → Zr Zr(IV) + 3e⁻ → ZrCl
R_3	ZrCl + e⁻ → Zr Zr(IV) + 4e⁻ → Zr	Not observed	ZrCl + e⁻ → Zr

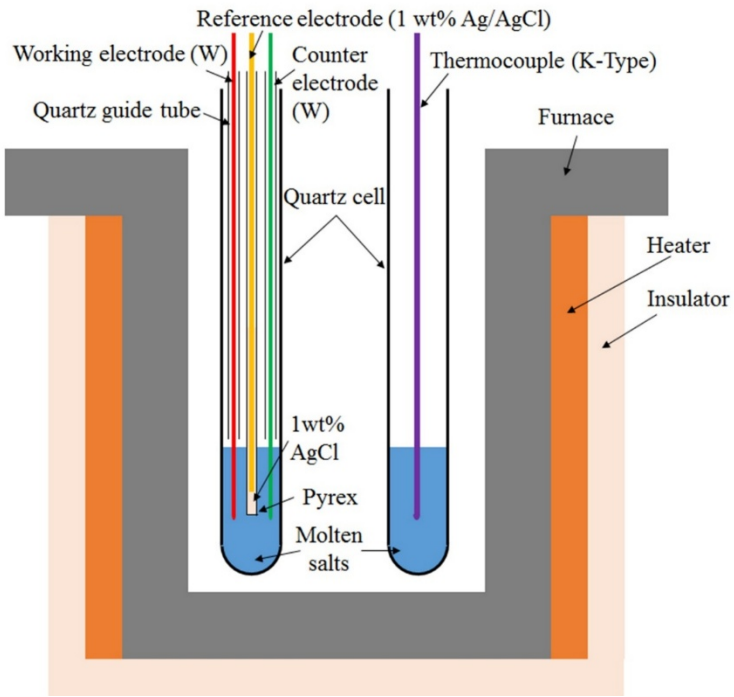
- **Zirconium redox behaviors in LiCl-KCl-$ZrCl_4$ are greatly dependent on $ZrCl_4$ concentration, temperature, working electrode materials and so on.**
- **Therefore, there would be a certain condition where Zr metal can be recovered with high purity without ZrCl.**

Zirconium redox behaviors in LiCl-KCl

- **Experimental set of $ZrCl_4$ cyclic voltammetry**

Working and counter electrode: tungsten (d=1 mm)

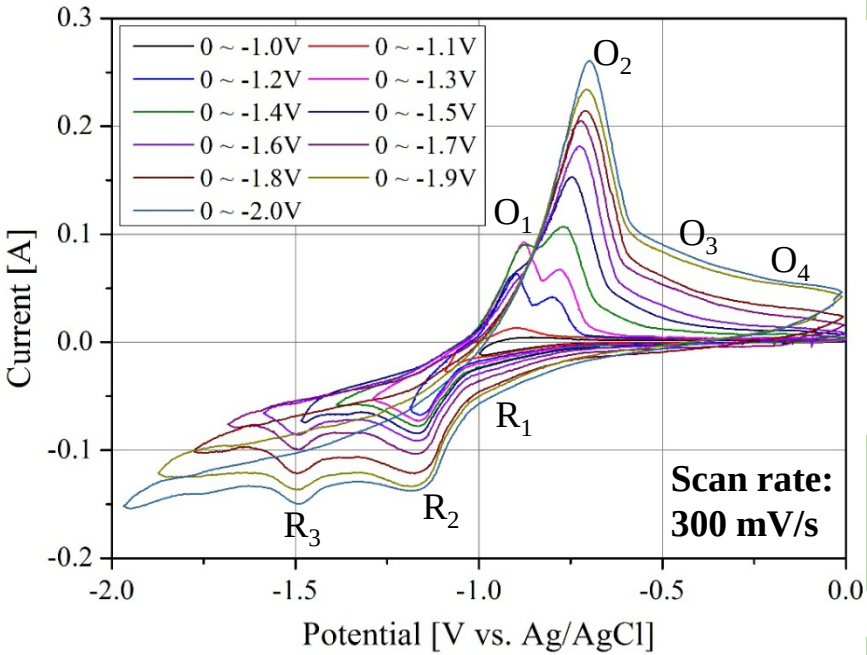
Reference electrode: 1 wt. % Ag/AgCl



	Concentration of $ZrCl_4$ (wt%)	Scan range (V vs Ag/AgCl)	Scan rate (mV/s)	Objective
#1	0.0	0.0 ~ -2.0	300	background current density
#2	1.0	11 scan ranges from 0.0 ~ -1.0 to 0.0 ~ -2.0	300	zirconium redox peaks
#3		0.0 ~ -1.3	100~1500	redox reactions for each peak
#4		0.0 ~ -1.2	100~1500	
#5		0.0 ~ -1.1	300~1500	
#6		0.0 ~ -1.6	100~1500	
#7		4 scan ranges from 0.0 ~ -1.0 to 0.0 ~ -1.3	500	
#12	0.5	0.0~-1.3	100~1500	concentration effects on redox peaks
#13	2.0	0.0~-1.3	100~1500	
#14	4.0	0.0~-1.3	100~1500	
#15	8.0	0.0~-1.3	100~1500	

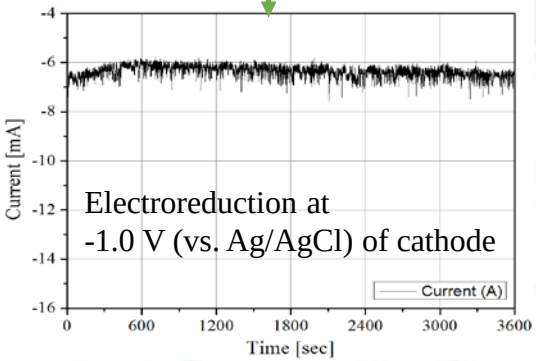
Zirconium redox behaviors in LiCl-KCl

- Cyclic voltammograms of 1wt% $ZrCl_4$
  - ✓ WE&CE: W rod
  - ✓ RE: 1 wt% Ag/AgCl



Four oxidation (O_1, O_2, O_3 and O_4) and three reduction peaks (R_1, R_2, R_3) are identified.

Redox reactions for the peak of **R_1 and O_3 has been reported as a reaction between Zr(II) and Zr(IV).**

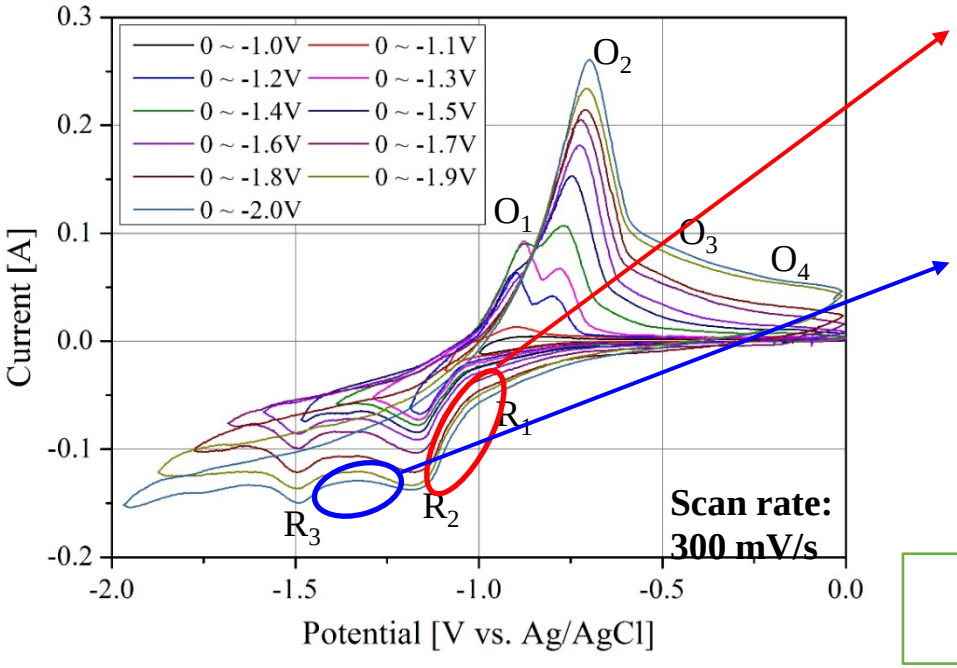


During applying -1.0 V on the cathode, total current is maintained constantly. **It could indicate that reaction at the potential of -1.0V is an soluble-soluble reaction (Zr(IV)/Zr(II)).**

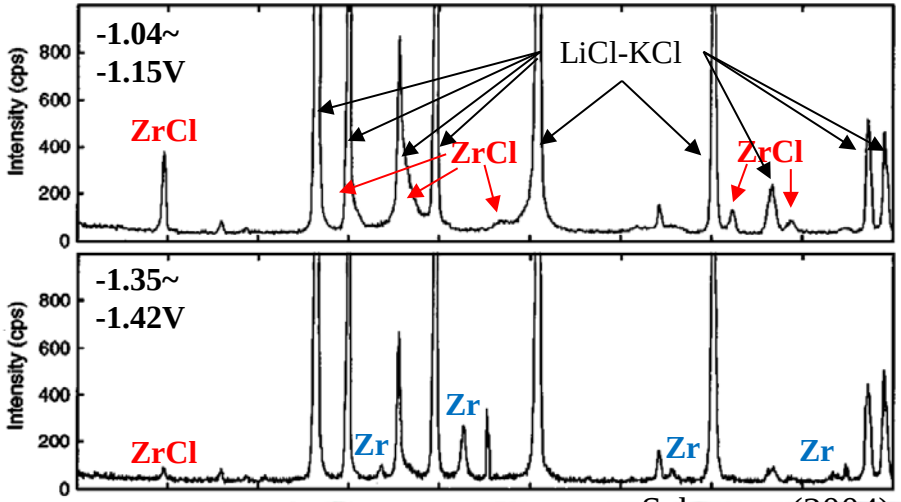
Because the peak height of R_1 and O_3 is not significant in 1wt% $ZrCl_4$-LiCl-KCl, **Zr(II) would not be a major reactant and product for other redox reactions.**

Zirconium redox behaviors in LiCl-KCl

- Cyclic voltammograms of 1wt% $ZrCl_4$
  - ✓ WE&CE: W rod
  - ✓ RE: 1 wt% Ag/AgCl



Cathode product after electrolysis in 1.08 wt. % $ZrCl_4$

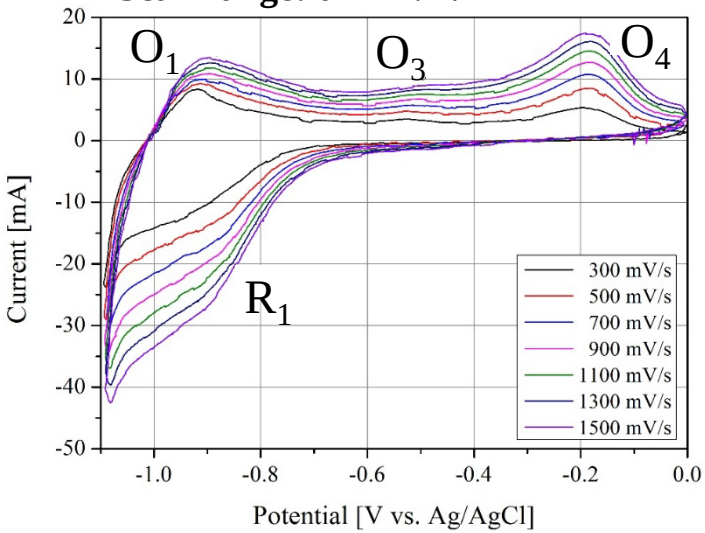


Sakamura(2004)

Major reactions of **R_2 and R_3 are related to reactions producing ZrCl and Zr metal respectively.**

Zirconium redox behaviors in LiCl-KCl

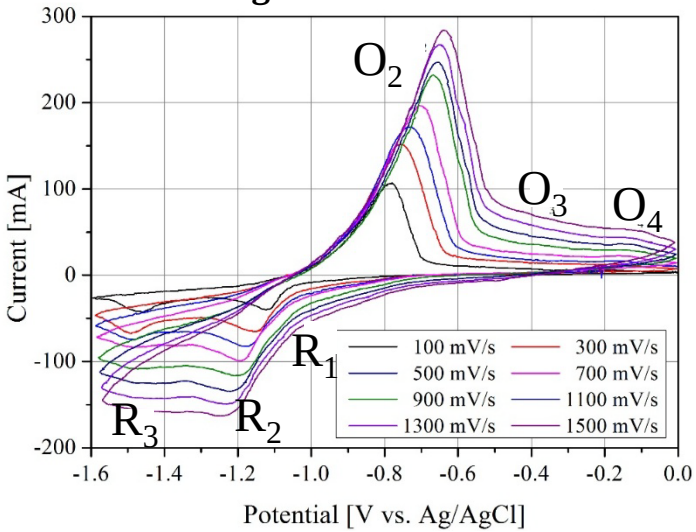
Scan range: 0 ~ - 1.1V



When potential of working electrode is scanned to -1.1V which is slightly more positive than peak R_2 (ZrCl formation) potential, peak O_2 does not appear but peak O_1 appear.

Peak O_1 might be related to the oxidation of ZrCl.

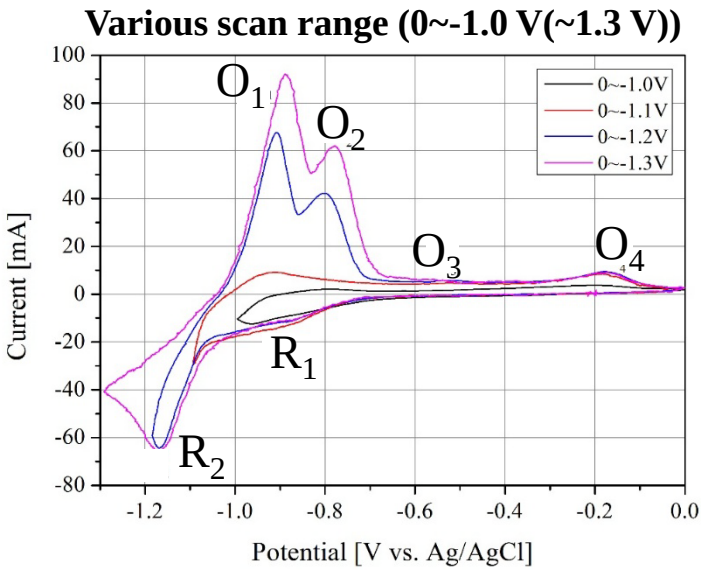
Scan range: 0 ~ - 1.6V



When potential of working electrode is scanned to -1.6V, peak O_1 (ZrCl oxidation) does not appear but peak O_2 appears.

Peak O_2 would be related to the oxidation of Zr metal and Peak R_3 related to the reduction of ZrCl into Zr metal.

Zirconium redox behaviors in LiCl-KCl

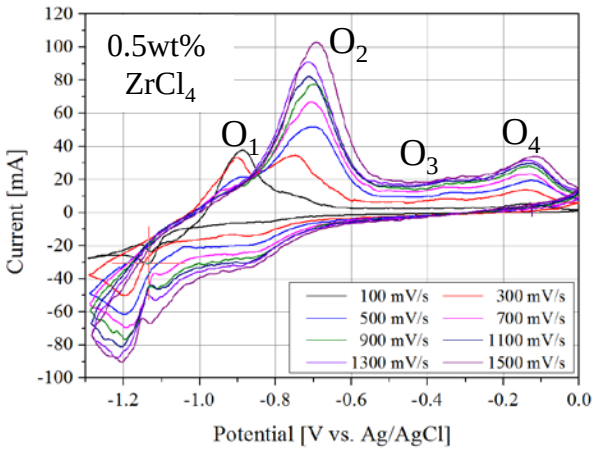


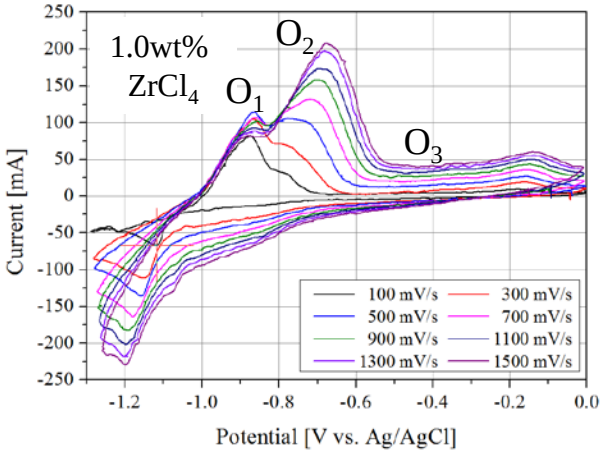
Peak O_4 starts appearing when peak O_1 becomes noticeable and peak heights are consistent regardless of scan range.

Peak O_4 might be related to oxidation of ZrCl monolayer.

Zirconium redox behaviors in LiCl-KCl

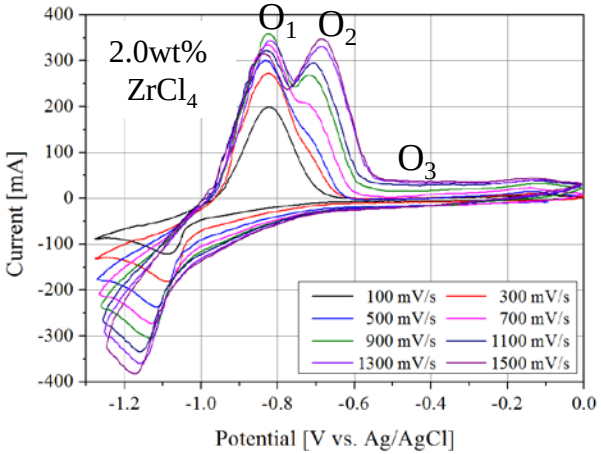
- Cyclic voltammograms in various concentration of $ZrCl_4$

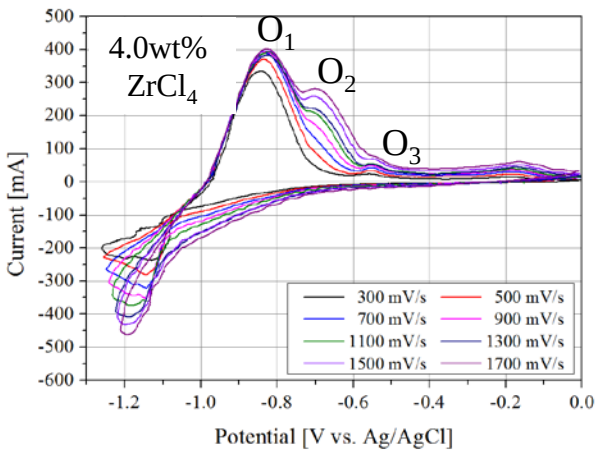


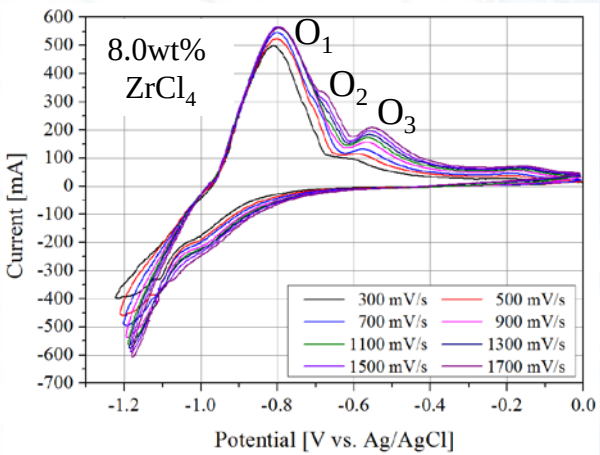


As $ZrCl_4$ concentration increases, peak O_1 does not disappear even at high scan rate and peak O_3 becomes evident.

High concentration of $ZrCl_4$ could make it hard to recover zirconium metal on the cathode and result in disproportionate reaction.







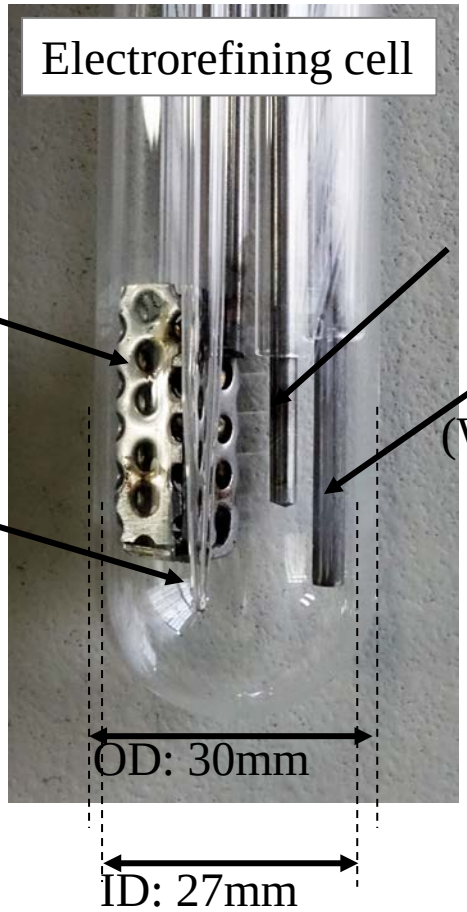
Zirconium redox behaviors in LiCl-KCl

Red: dominant in low concentration of $ZrCl_4$, Blue: increasing influence as $ZrCl_4$ concentration increases

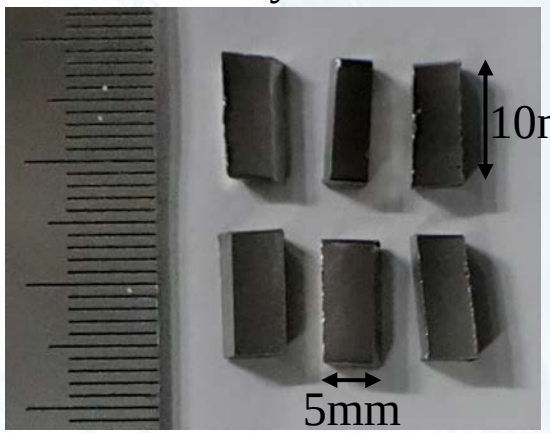
Peak	This study (500°C, 1wt% $ZrCl_4$, tungsten electrode)	Lee 500°C, 4wt% $ZrCl_4$, tungsten electrode	Ghosh 525°C, 1.84E-4 mol/cm^3 $ZrCl_4$, (about 2.6 wt.% $ZrCl_4$,) tungsten electrode	Sakamura 500°C, 0.00123 mole fraction $ZrCl_4$, (about 1 wt.% $ZrCl_4$) tungsten electrode
O_1	**$ZrCl \rightarrow Zr(IV) + 3e^-$ (major reaction)** $ZrCl \rightarrow Zr(II) + e^-$	$ZrCl \rightarrow Zr(IV) + 3e^-$ $Zr \rightarrow Zr(II) + 2e^-$	$Zr \rightarrow Zr(I) + e^-$	$ZrCl \rightarrow Zr(IV) + 3e^-$
O_2	**$Zr \rightarrow Zr(IV) + 4e^-$ (major reaction)** $Zr \rightarrow Zr(II) + 2e^-$	$Zr \rightarrow Zr(IV) + 4e^-$	$Zr \rightarrow Zr(II) + 2e^-$ $Zr(I) \rightarrow Zr(II) + e^-$	$Zr \rightarrow Zr(IV) + 4e^-$
O_3	$Zr(II) \rightarrow Zr(IV) + 2e^-$	$Zr(II) \rightarrow Zr(IV) + 2e^-$	$Zr(II) \rightarrow Zr(IV) + 2e^-$	Not observed
O_4	ZrCl (monolayer) $\rightarrow Zr(IV) + 2e^-$	Not observed	Monolayer dissolution of Zr(II)	Not observed
R_1	$Zr(IV) + 2e^- \rightarrow Zr(II)$	$Zr(IV) + 2e^- \rightarrow Zr(II)$	$Zr(IV) + 2e^- \rightarrow Zr(II)$	$Zr(IV) + 2e^- \rightarrow Zr(II)$
R_2	**$Zr(IV) + 3e^- \rightarrow ZrCl$ (major reaction)** $Zr(II) + e^- \rightarrow ZrCl$ (Zr metal formation could influence this peak height but the major reaction might be ZrCl formation.)	$Zr(II) + 2e^- \rightarrow Zr$ $Zr(IV) + 3e^- \rightarrow ZrCl$	$Zr(II) + 2e^- \rightarrow Zr$ $Zr(II) + e^- \rightarrow Zr(I)$ *$Zr(I) + e^- \rightarrow Zr$ (*This reaction is located at slightly more negative potential than other reactions.)	$Zr(IV) + 4e^- \rightarrow Zr$ $Zr(IV) + 3e^- \rightarrow ZrCl$
R_3	$ZrCl + e^- \rightarrow Zr$ $Zr(II) + 2e^- \rightarrow Zr$ $Zr(IV) + 4e^- \rightarrow Zr$	$ZrCl + e^- \rightarrow Zr$ $Zr(IV) + 4e^- \rightarrow Zr$	Not observed	$ZrCl + e^- \rightarrow Zr$

Electrorefining of Zircaloy-4 specimen

- Experimental setup for lab-scale Zircaloy-4 electrorefining



Zircaloy-4 cuts



Composition of Zircaloy-4 cuts

Elements	Composition [wt%]
Zr	98.6
Sn	1.12
Cr	0.083
Fe	0.161
Co	0.00161

Electrorefining of Zircaloy-4 specimen

- Experimental conditions for Zircaloy-4 electrorefining

All electrorefining experiments are potentiostatically conducted by controlling anode potential.

Reaction	Formal reduction potential [V vs. Ag/AgCl]
$Zr^{4+}/ZrCl$	**-0.994**
$ZrCl/Zr$	**-1.1~-1.2**
Sn^{2+}/Sn	**-0.156**
Cr^{2+}/Cr	**-0.601**
Fe^{2+}/Fe	**-0.288**
Co^{2+}/Co	**-0.089**

Since all elements except zirconium are more reductive than zirconium, if these elements are dissolved from the anode, they will be deposited on the cathode with Zr.

LiCl-KCl salts (99.99%) used in this study contain Cr of 10 ppm.

$$E_{eq,Cr} = E_{Cr}^{0'} + \frac{RT}{nF}\ln C_{Cr(II)}$$
$$= -0.899\ V\ \text{(vs.Ag/AgCl)}$$

Therefore, **to prevent Cr dissolution at the anode, anode potential is maintained more negative than -0.9 V (vs. Ag/AgCl)**

Electrorefining of Zircaloy-4 specimen

- Experimental conditions for Zircaloy-4 electrorefining

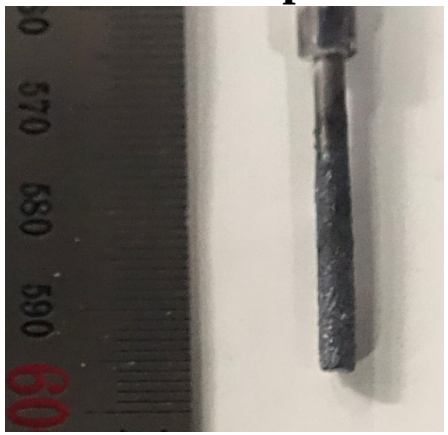
About 5 hours electrorefining at 773 K

	Molten salts	Expected purity of Zr product (without salts)	Expected chemical form of Zr product
#1	LiCl-KCl-0.1wt% $ZrCl_4$	Over 99.9%	Zr metal
#2	LiCl-KCl-0.5wt% $ZrCl_4$	Over 99.9%	Zr metal
#3	LiCl-KCl-1.0wt% $ZrCl_4$	Over 99.9%	Zr metal
#4	LiCl-KCl-2.0wt% $ZrCl_4$	Over 99.9%	Zr metal & ZrCl
#5	LiCl-KCl-4.0wt% $ZrCl_4$	Over 99.9%	ZrCl

Electrorefining of Zircaloy-4 specimen

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

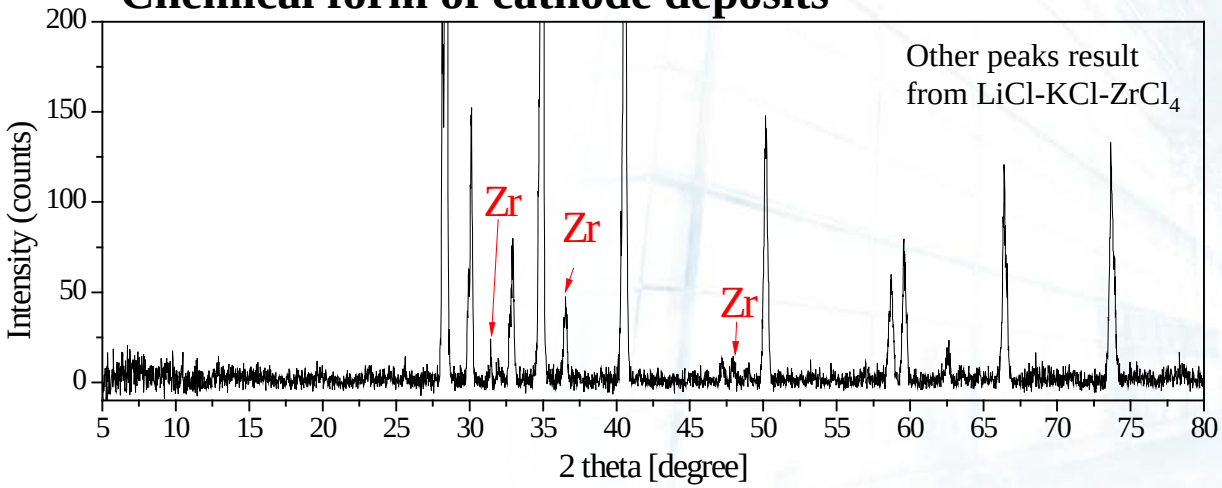
Cathode deposits



Composition of cathode deposits (ICP-MS)

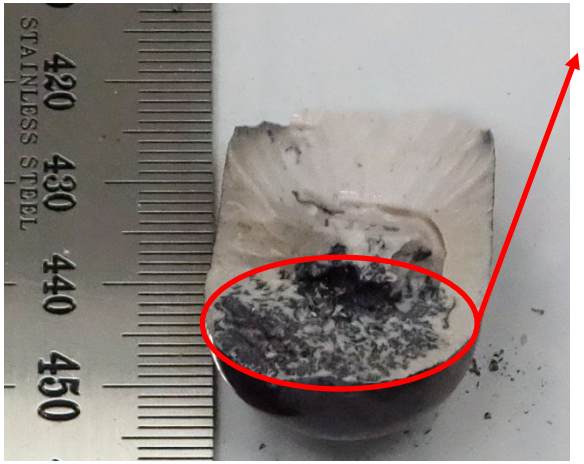
Element	Zircaloy-4 specimen [wt%]	Cathode deposit [wt%]
Zr	98.6	99.999
Sn	1.12	N/D
Fe	0.083	N/D
Cr	0.161	N/D
Co	0.002	N/D

Chemical form of cathode deposits



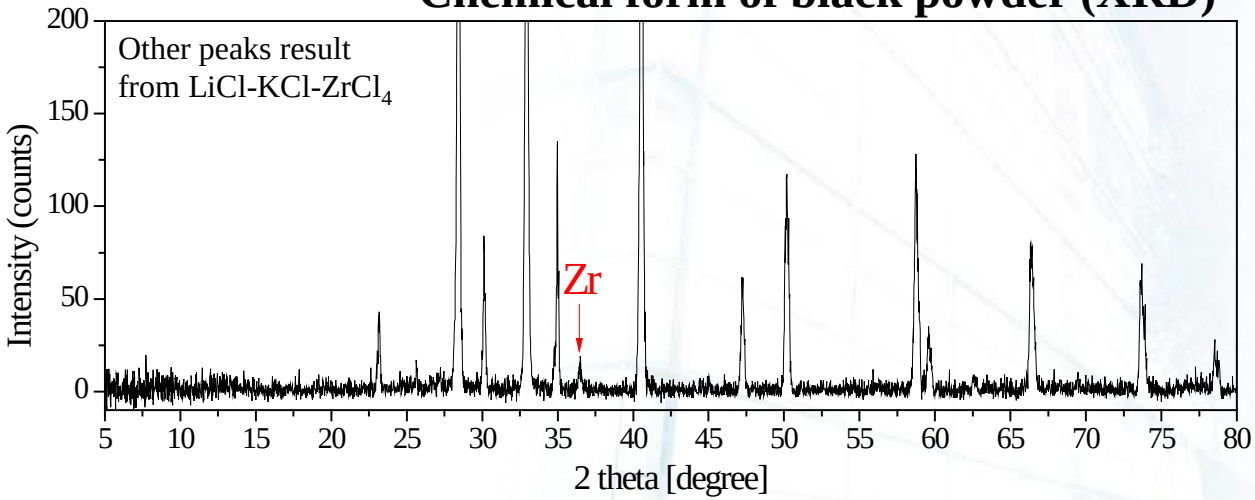
Electrorefining of Zircaloy-4 specimen

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



After electrorefining, black powders are precipitated at the bottom of salts.

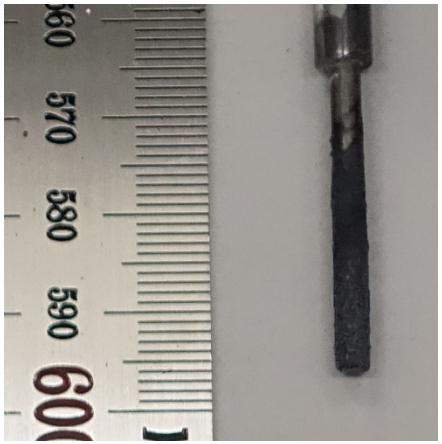
Chemical form of black powder (XRD)



Electrorefining of Zircaloy-4 specimen

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

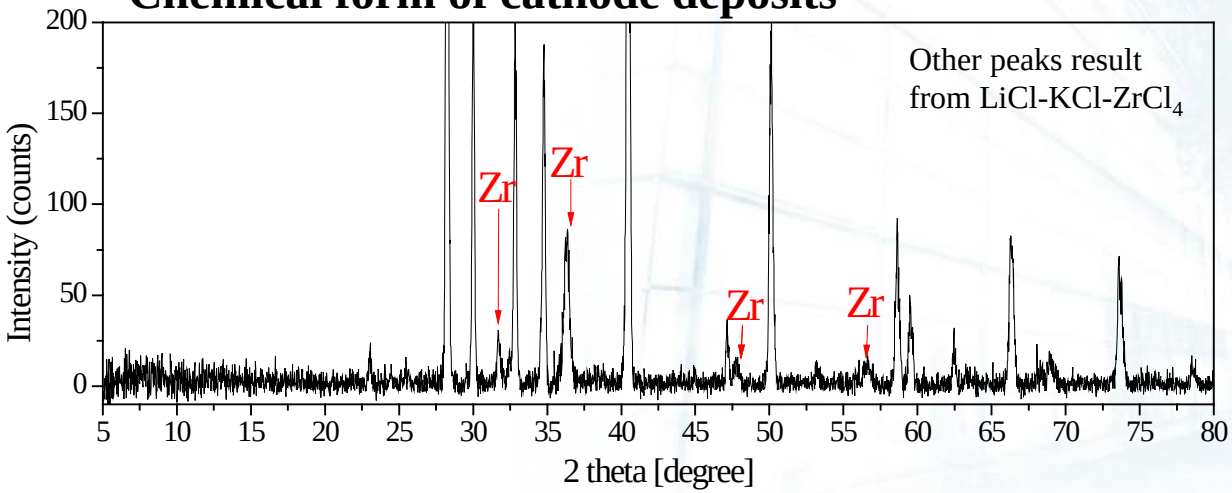
Cathode deposits



Composition of cathode deposits (ICP-MS)

Element	Zircaloy-4 specimen [wt%]	Cathode deposit [wt%]
Zr	98.6	99.999
Sn	1.12	N/D
Fe	0.083	N/D
Cr	0.161	N/D
Co	0.002	N/D

Chemical form of cathode deposits



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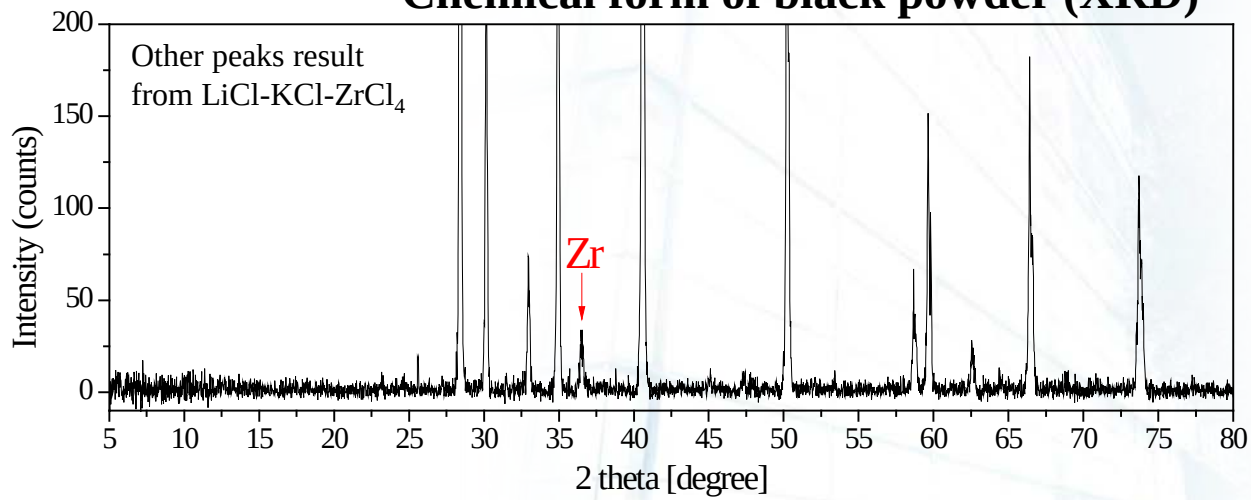


Electrorefining of Zircaloy-4 specimen

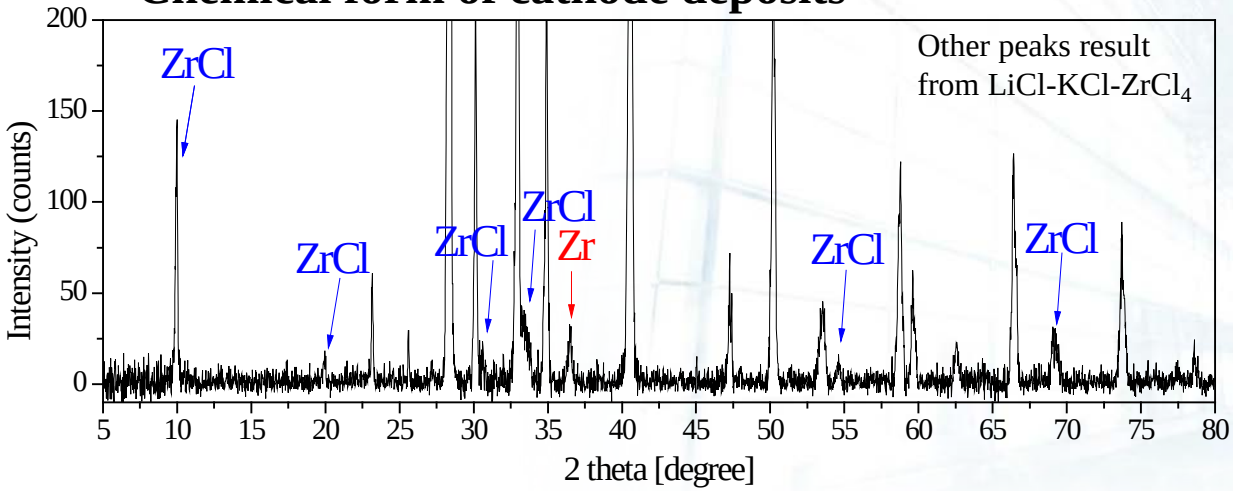
- Electrorefining in LiCl-KCl-1.0 wt. % $ZrCl_4$

Cathode deposits

Composition of cathode deposits (ICP-MS)

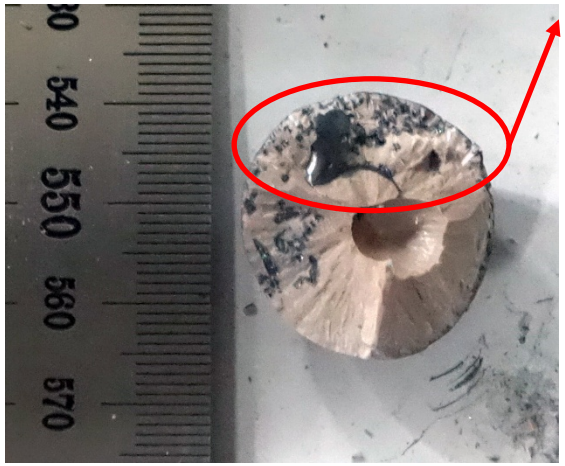
Element	Zircaloy-4 specimen [wt%]	Cathode deposit [wt%]
Zr	98.6	99.999
Sn	1.12	N/D
Fe	0.083	N/D
Cr	0.161	N/D
Co	0.002	N/D

Chemical form of cathode deposits



Electrorefining of Zircaloy-4 specimen

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



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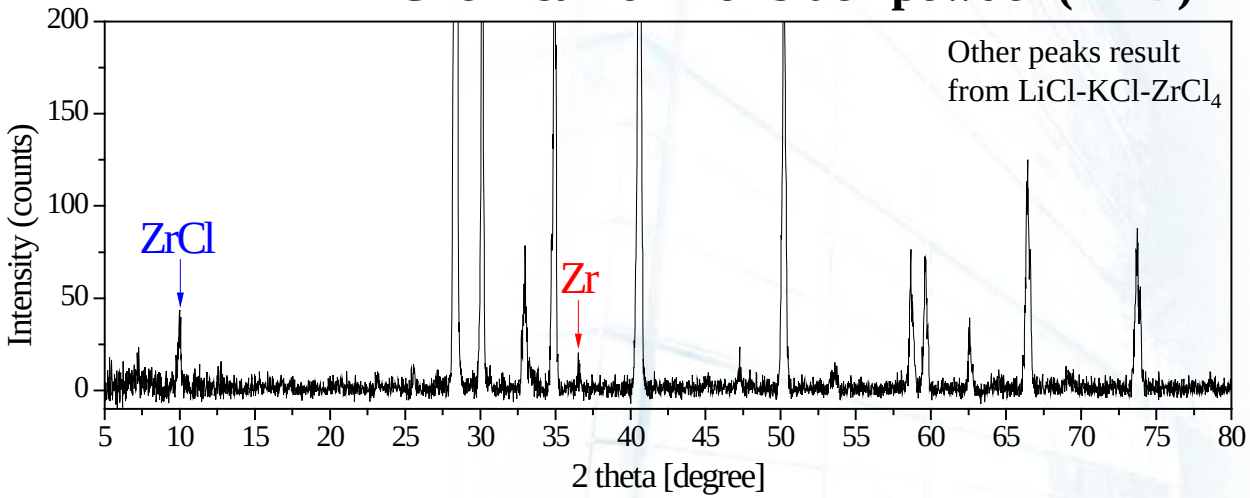


Electrorefining of Zircaloy-4 specimen

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

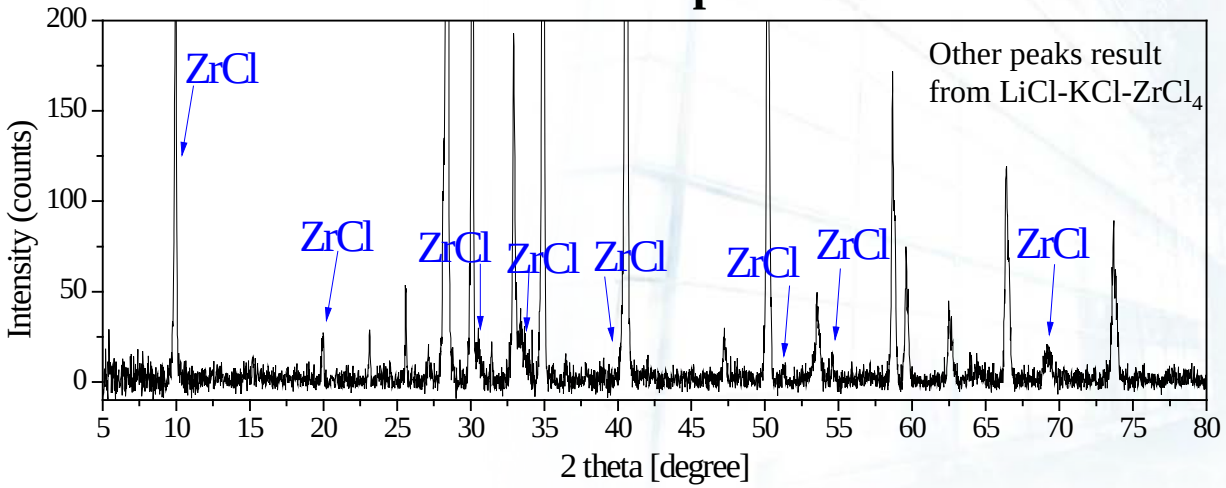
Cathode deposits

Salt after electrorefining

Composition of cathode deposits (ICP-MS)

Element	Zircaloy-4 specimen [wt%]	Cathode deposit [wt%]
Zr	98.6	99.999
Sn	1.12	N/D
Fe	0.083	N/D
Cr	0.161	N/D
Co	0.002	N/D

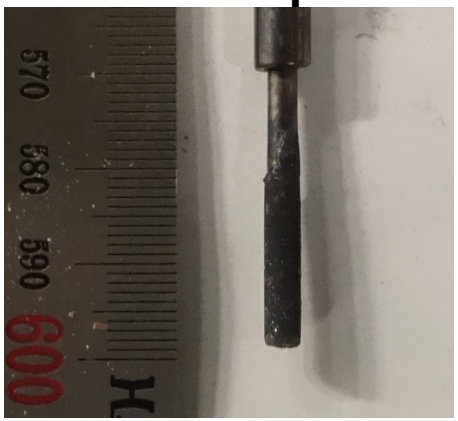
Chemical form of cathode deposits



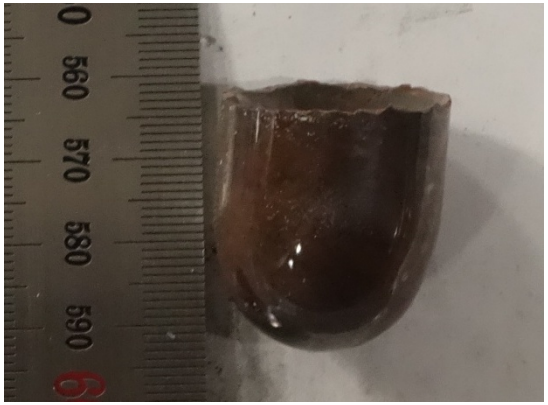
Electrorefining of Zircaloy-4 specimen

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

Cathode deposits



Salt after electrorefining



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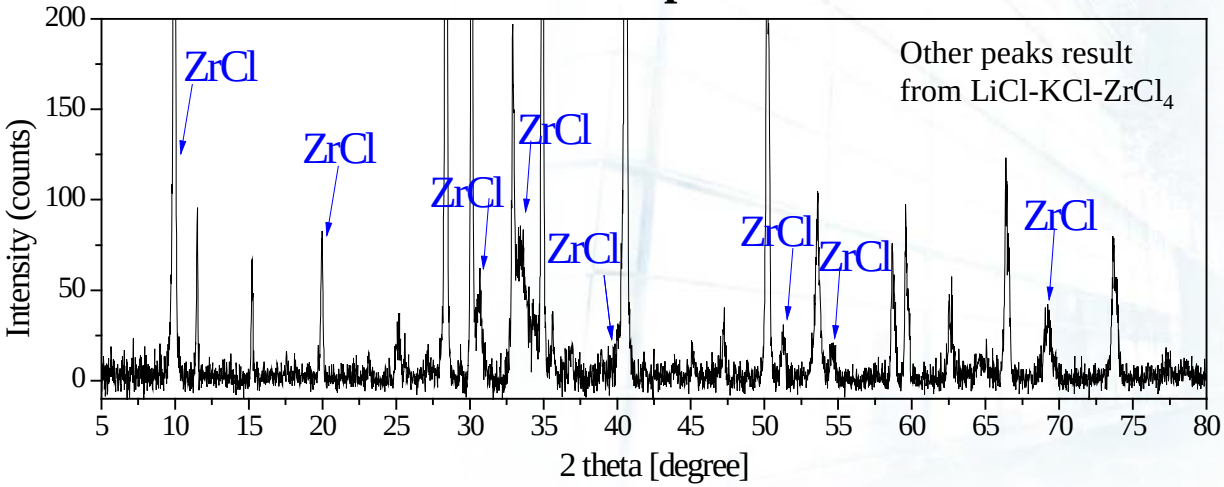


Electrorefining of Zircaloy-4 specimen

- Comparison to previous results on electrorefining in LiCl-KCl molten salts

		This study					Lee (2012)	
$ZrCl_4$ concentration		0.1 wt%	0.5 wt%	1.0 wt%	2.0 wt%	4.0 wt%	4.0 wt%	4.0 wt%
Operating condition		Anode potential is maintained below -0.9V to prevent dissolution of impurities					Cathode potential is maintained at -1.15V	Cathode potential is maintained at -1.55V
Composition of Cathode deposits	Element	wt%	wt%	wt%	wt%	wt%	Wt%	Wt%
	Zr	Over 99.999	Over 99.999	Over 99.999	Over 99.999	Over 99.999	99.44	98.95
	Sn	N/D	N/D	N/D	N/D	N/D	0.56	0.87
	Fe	N/D	N/D	N/D	N/D	N/D	N/D	0.14
	Cr	N/D	N/D	N/D	N/D	N/D	N/D	0.04
	Co	N/D	N/D	N/D	N/D	N/D	Not analyzed	
Chemical form of zirconium deposits		Zr	Zr	Zr and ZrCl	Zr and ZrCl	ZrCl	ZrCl	ZrCl and Zr

Conclusion

- **Zirconium redox behaviors in LiCl-KCl**

Zr(IV) reduction reactions related to Zircaloy electrorefining

$Zr(IV) + 3e^- + Cl^- \rightarrow ZrCl$ $\quad E^{0'}_{ZrCl/Zr(IV)} = -0.994$ V (vs. Ag/AgCl)

$ZrCl + e^- \rightarrow Zr + Cl^-$ $\quad E^{0'}_{Zr/ZrCl} = -1.1 \sim -1.2$ V (vs. Ag/AgCl)

$Zr(IV) + 2e^- \rightarrow Zr(II)$ at high concentration of $ZrCl_4$

Zr oxidation reactions related to Zircaloy electrorefining

$Zr \rightarrow Zr(IV) + 4e^-$

$Zr \rightarrow Zr(II) + 2e^-$ at high concentration of $ZrCl_4$

$Zr(II) \rightarrow Zr(IV) + 2e^-$ at high concentration of $ZrCl_4$

- **Zircaloy-4 electrorefining in LiCl-KCl**

✓ Major elements of Zircaloy-4 and some fission products which are more reductive than Zr in irradiated cladding can be separated by controlling anode potential.

✓ Low concentration of $ZrCl_4$ is preferred for recovering Zr metal without ZrCl.

Thank you for your attention

Tomorrow Presentation

3-D computational modeling on Zircaloy-4 electrorefining will be presented. Multi-step reduction of Zr(IV) and actinide codeposition with Zr during electrorefining of irradiated cladding will be handled.

Appendix

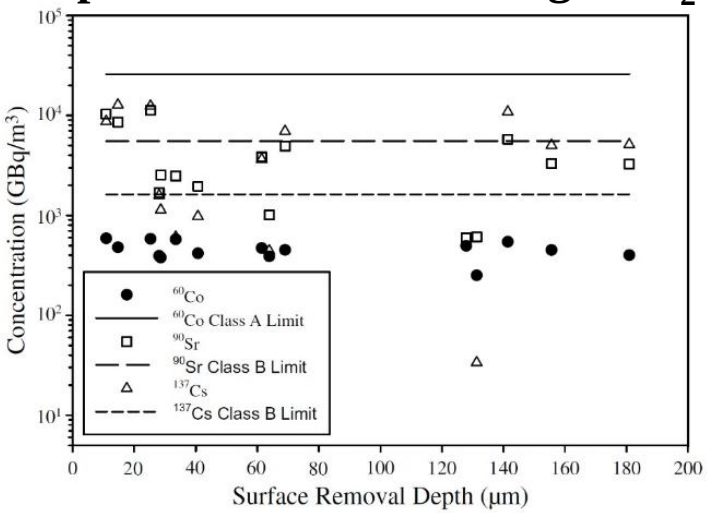
- **Electrorefining of Zircaloy channel box in chloride-fluoride salts**

Cs waste problem in case of using CsCl based salts

30,000 MWD/MTU, 50 years cooling		
Cs-137 in Zircaloy-4 cladding	192	mCi/kg-Zry
	7.107E+06	Bq/g-Zry
	2.211E-06	g/g-Zry
Half life of Cs-137	30.07	year
Cs in Zircaloy-4 cladding	1.052E-05	g/g-Zry
IAEA clearance level for Cs-137	0.1	Bq/g

Cs is more oxidative than Zr. Therefore, if a molten salt based on CsCl is used, Cs-137 will be dissolved from irradiated Zircaloy-4 cladding into the molten salts and **this could result in large amount of radioactive Cs waste.**

Sr waste problem in case of using $SrCl_2$ based salts



For a similar reason, **$SrCl_2$ based molten salts would not be preferred because of Sr waste generation.**

Zirconium redox behaviors in LiCl-KCl

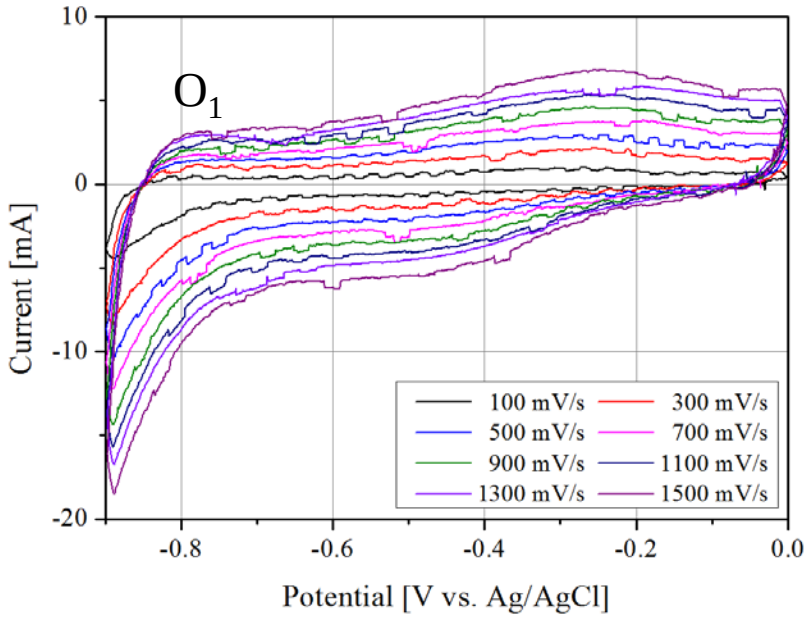
- Formal reduction potentials of zirconium redox reactions

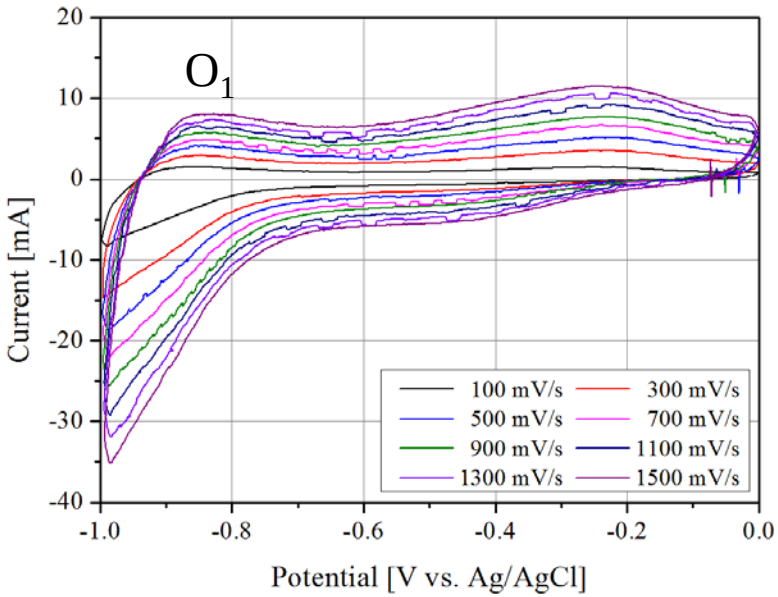
For reversible electrodeposition of insoluble products,

$$E_p = E^{0\prime} + \frac{RT}{nF}\ln C_{M^{n+}} + 0.8540\frac{RT}{nF}$$

$E^{0\prime}_{Zr4+/ZrCl}$ = -0.994 V (vs. Ag/AgCl)

(calculated at the scan rate of 100 mV/s)



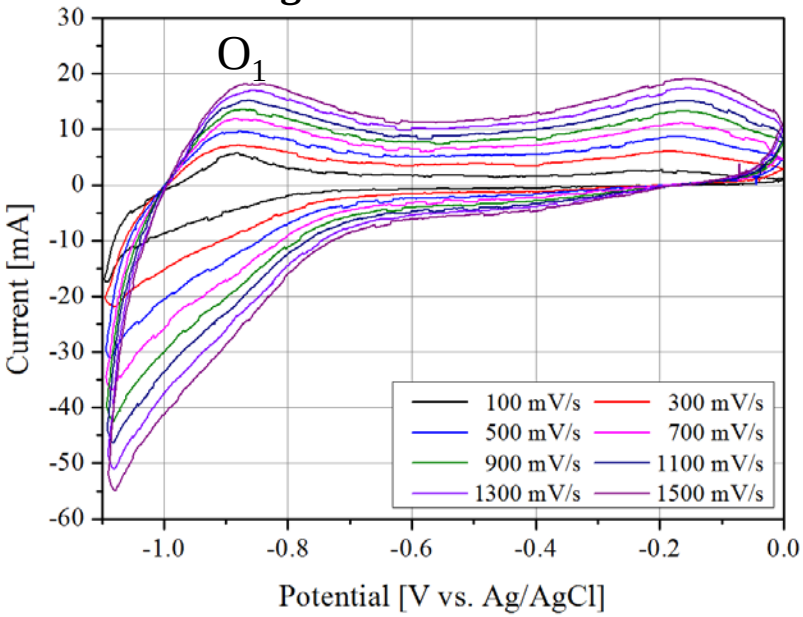


Since peak O_1 (oxidation of ZrCl into Zr(IV)) starts appearing when working electrode potential is scanned to -1.0 V, the equilibrium potential of ZrCl formation from Zr(IV) might be between -0.9 and -1.0 V (vs. Ag/AgCl). This observation agrees with the formal potential calculated from the Peak R_2 potential.

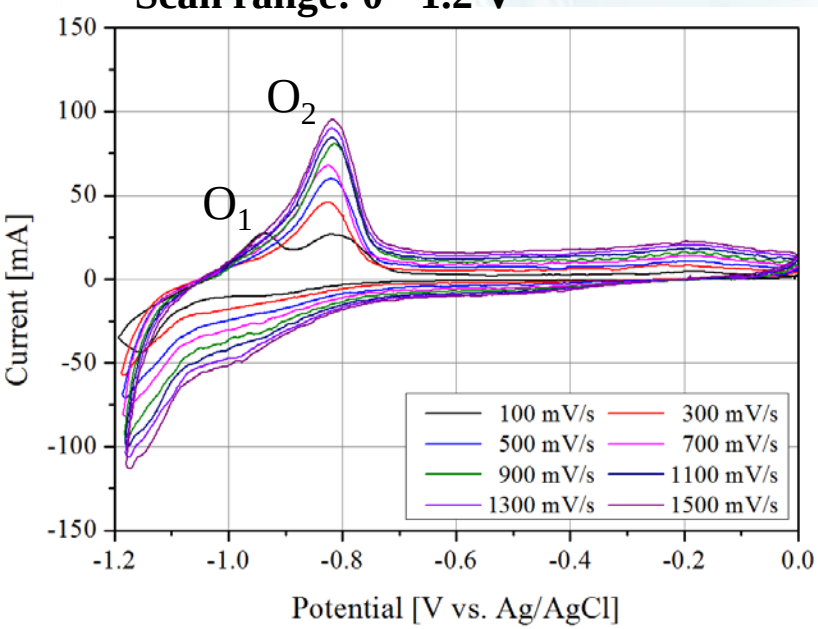
Zirconium redox behaviors in LiCl-KCl

- Formal reduction potentials of zirconium redox reactions

Scan range: 0~-1.1 V



Scan range: 0~-1.2 V



Since peak O_2 (oxidation of Zr metal) starts appearing when working electrode potential is scanned to -1.2 V,
the formal potential of Zr formation from ZrCl might be between -1.1 and -1.2 V (vs. Ag/AgCl).

$$E^{0'}_{ZrCl/Zr} = -1.1\sim-1.2\ V\ (vs.\ Ag/AgCl)$$

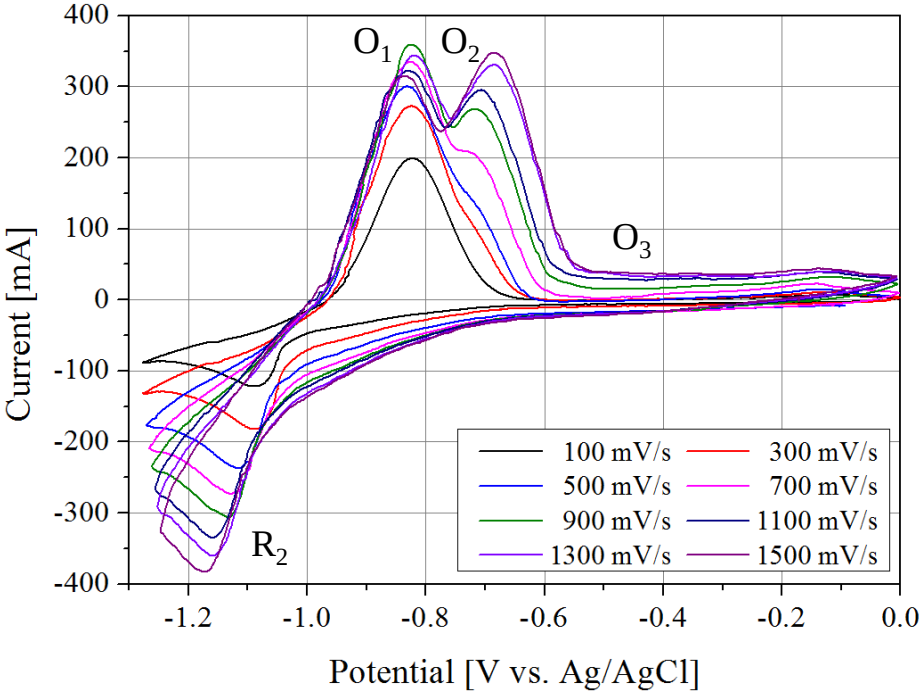
Zirconium redox behaviors in LiCl-KCl

- **Zr(IV) diffusion coefficient from CV**

For the reversible electrodeposition of insoluble products,

$$i_p = 1.082nFAC\sqrt{\frac{nFDv}{RT\pi}}$$

Numerically driven by D.J. Schiffrin (1986)



$E_p(R_2)$ at 100mV/sec = -1.0879 V (vs. Ag/AgCl)
$E_p(R_2)$ at 300mV/sec = -1.0880 V (vs. Ag/AgCl)

=> Reversible assumption could be applied.

In addition, the cyclic voltammogram at scan rate of 100mV/sec does not have O_2 and O_3 peak. It could means that peak R_2 is mainly related to the reduction of Zr(IV) into ZrCl.

$I_p(R_2)$ at 100 mV/sec = 193.15 mA/cm^2

$D_{Zr(IV)}$ = 1.373E-9 m^2/sec (this study)

$D_{Zr(IV)}$ = 1.13E-9 m^2/sec (Yamada, Capiliary method, 2007)

$D_{Zr(IV)}$ = 1.50E-9 m^2/sec (Fabrian, CV simulation, 2013)