# Reduction Behaviors of Zirconium Oxide Compounds in LiCl-$Li_2O$ Melt

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**Y. Sakamura, M. Iizuka and T. Koyama**
**Central Research Institute of Electric Power Industry (CRIEPI)**

**S. Kitawaki, A. Nakayoshi and H. Kofuji**
**Japan Atomic Energy Agency (JAEA)**

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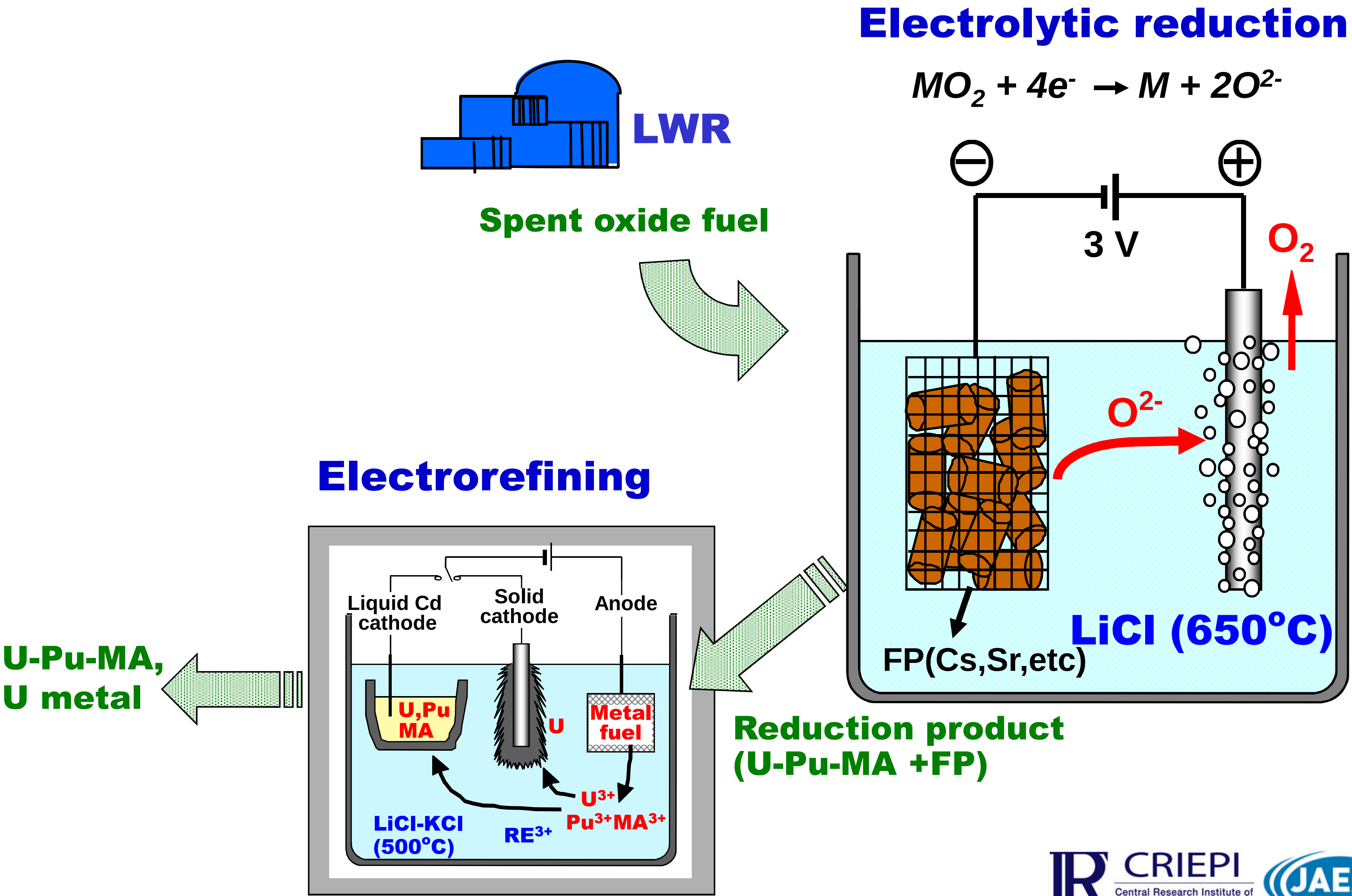
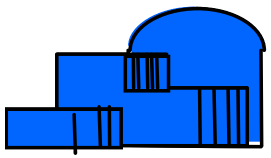
# Pyrochemical Reprocessing for Spent LWR Fuels



# *Pyrochemical Reprocessing for Spent LWR Fuels*

***Behavior of Zr in $LiCl\text{-}Li_2O$ melt needs to be clarified.***

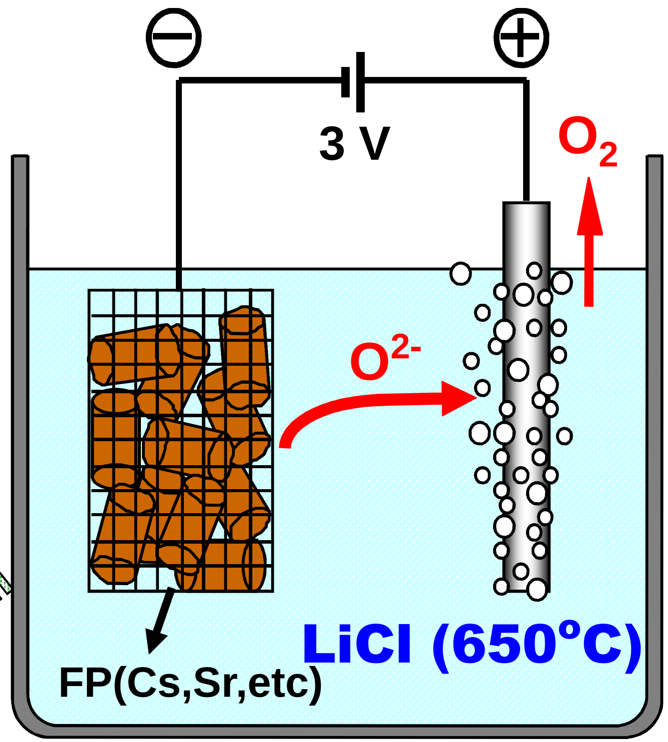
**Fukushima-Daiichi**
**Damaged fuel debris**
**[major constituent: $(U,Zr)O_2$]**




**Spent oxide fuel**

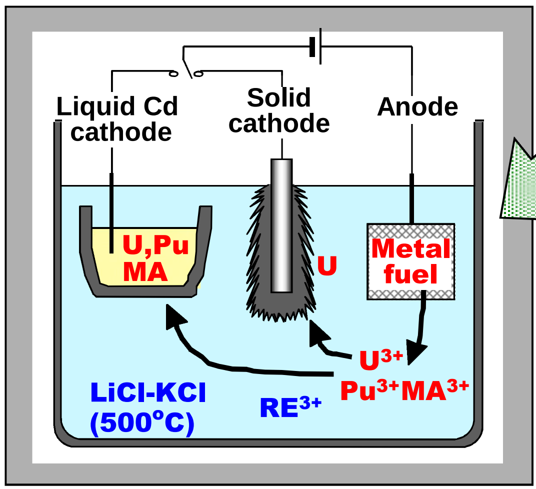
## Electrolytic reduction

$$MO_2 + 4e^- \rightarrow M + 2O^{2-}$$




**Reduction product**
**(U-Pu-MA +FP)**

## Electrorefining




**U-Pu-MA,**
**U metal**

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# Reduction Behavior of Metal Oxides

**Table $\Delta G_f^0$ of metal oxide at 650°C**

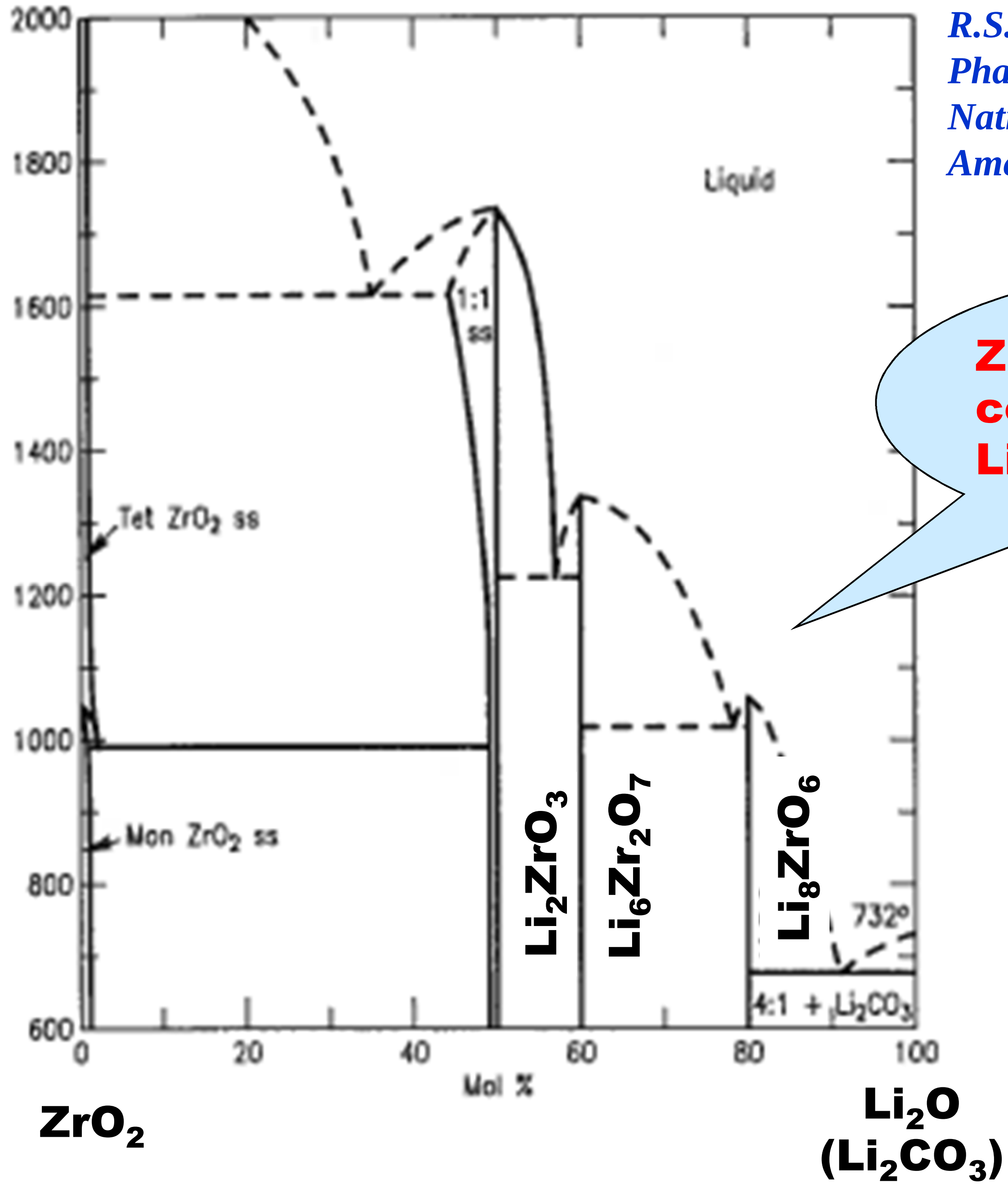
| Oxide | $\Delta G_f^0$ (kJ/mol-O) |
|---|---|
| $ZrO_2$ | -462.2 |
| $UO_2$ | -462.6 |
| $Pu_2O_3$ | -471.8 |
| $Li_2O$ | -475.8 |
| $La_2O_3$ | -509.6 |
| $Ce_2O_3$ | -506.1 |
| $Nd_2O_3$ | -515.1 |
| $Sm_2O_3$ | -518.0 |
| $Y_2O_3$ | -545.6 |

Behavior of $ZrO_2$ and its complex oxide compounds?

$UO_2$ and MOX are easily reduced to metals.

Rare-earth oxides are hardly reduced to metals.

# Binary Phase Diagram for $ZrO_2$-$Li_2O$ System



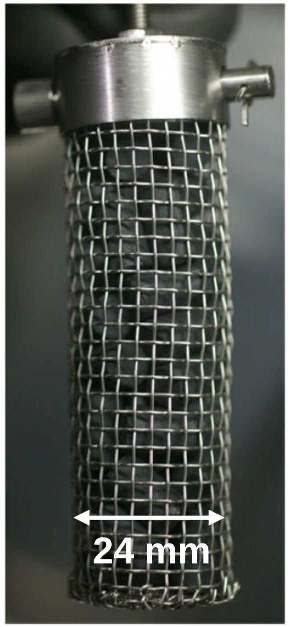

*R.S. Roth, J.R. Dennis and H.F. McMurdie, Phase Diagrams for Ceramiste Volume VI, National Bureau of Standards, The American Ceramic Soc., Inc. (1987)*

**$ZrO_2$ may form stable complex oxides with $Li_2O$.**

# *Reduction Test for Simulated Spent Oxide Fuel*

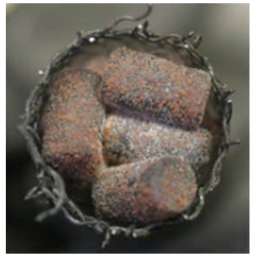
Y. Sakamura and M. Akagi, *Nucl. Technol*, **179**, 220-233 (2012).


**Oxide pellets with 31-33% porosity**
**($UO_2$ + Sr, Ce, Nd, Sm, Zr, Mo, Pd)**




**34 pellets (100.8 g) were loaded in the cathode basket.**

**Electrolysis**
**(15-1 A**
**7.6 h)**



**Cathode basket**

**Cross-sectional pellet**

- **Reduction yield of U : 99.2 %**
- **Current efficiency : 74 %**

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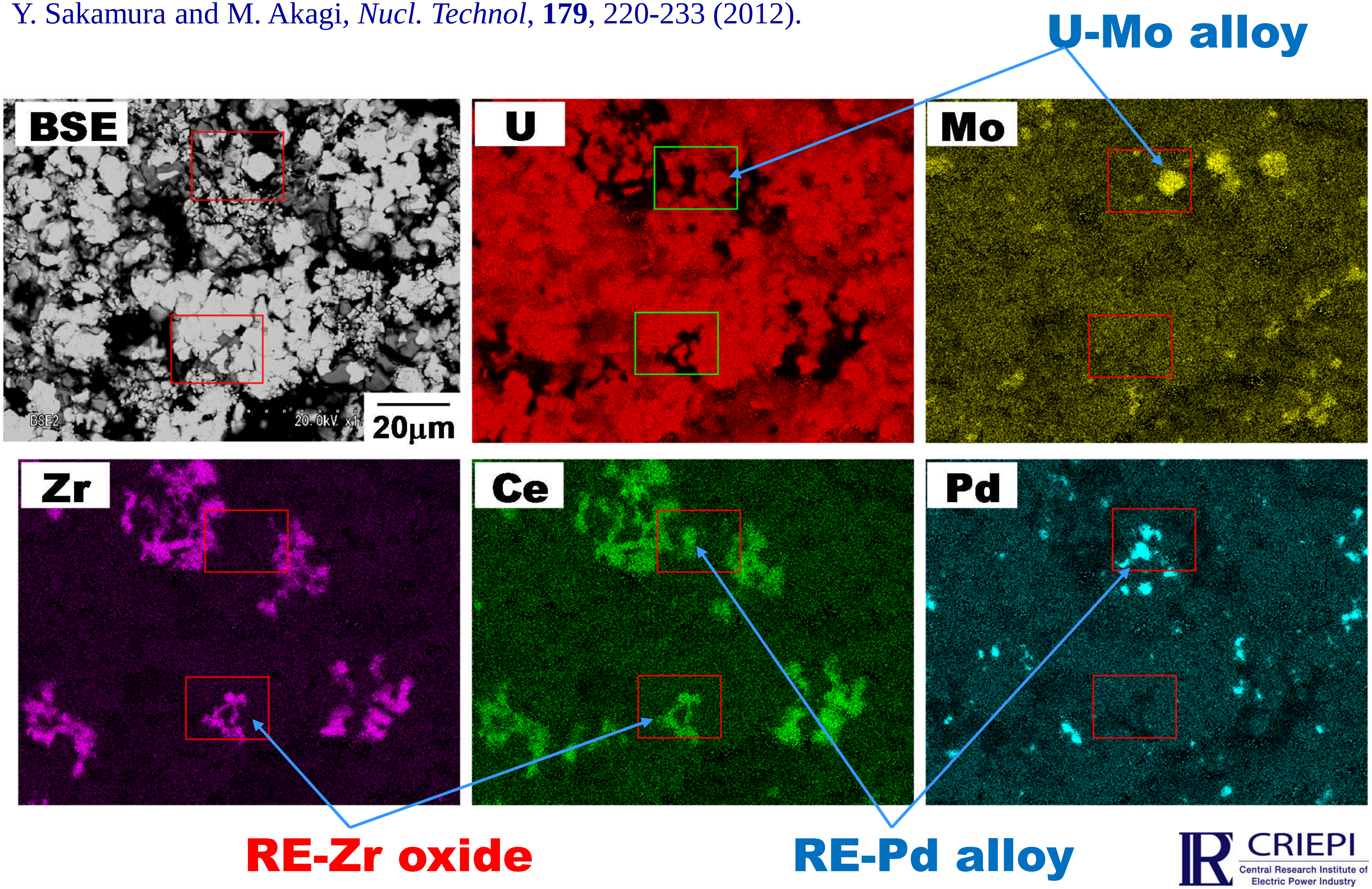
# Reduction Test for Simulated Spent Oxide Fuel

Y. Sakamura and M. Akagi, *Nucl. Technol*, **179**, 220-233 (2012).




**SEM-EDX analysis of cross-sectional pellet**

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# Objectives

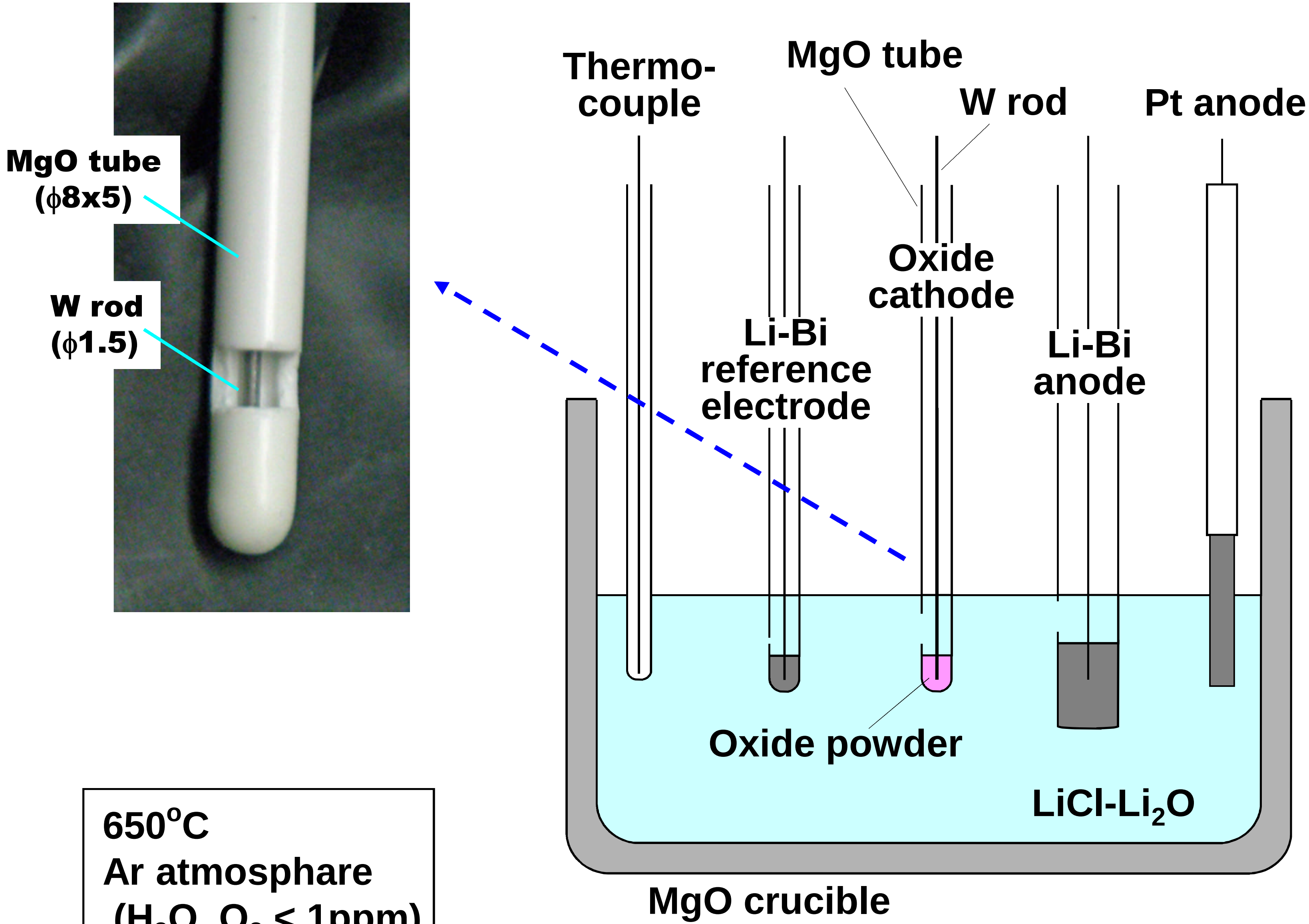
(1) To examine whether $ZrO_2$ and $(U,Zr)O_2$ can be reduced to metallic form in LiCl-$Li_2O$ melt at 650°C.

- Electrolytic reduction tests for $ZrO_2$, $Li_2ZrO_3$ and $(U,Zr)O_2$.

- Formation behavior of $Li_2O$-$ZrO_2$ complex oxides.

(2) To propose a process flow chart for damaged LWR fuel debris.

# Cell for Electrolytic Reduction Tests




$650^{o}C$
Ar atmosphare
($H_2O$, $O_2$ < 1ppm)

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# Electrolytic Reduction Test for $ZrO_2$

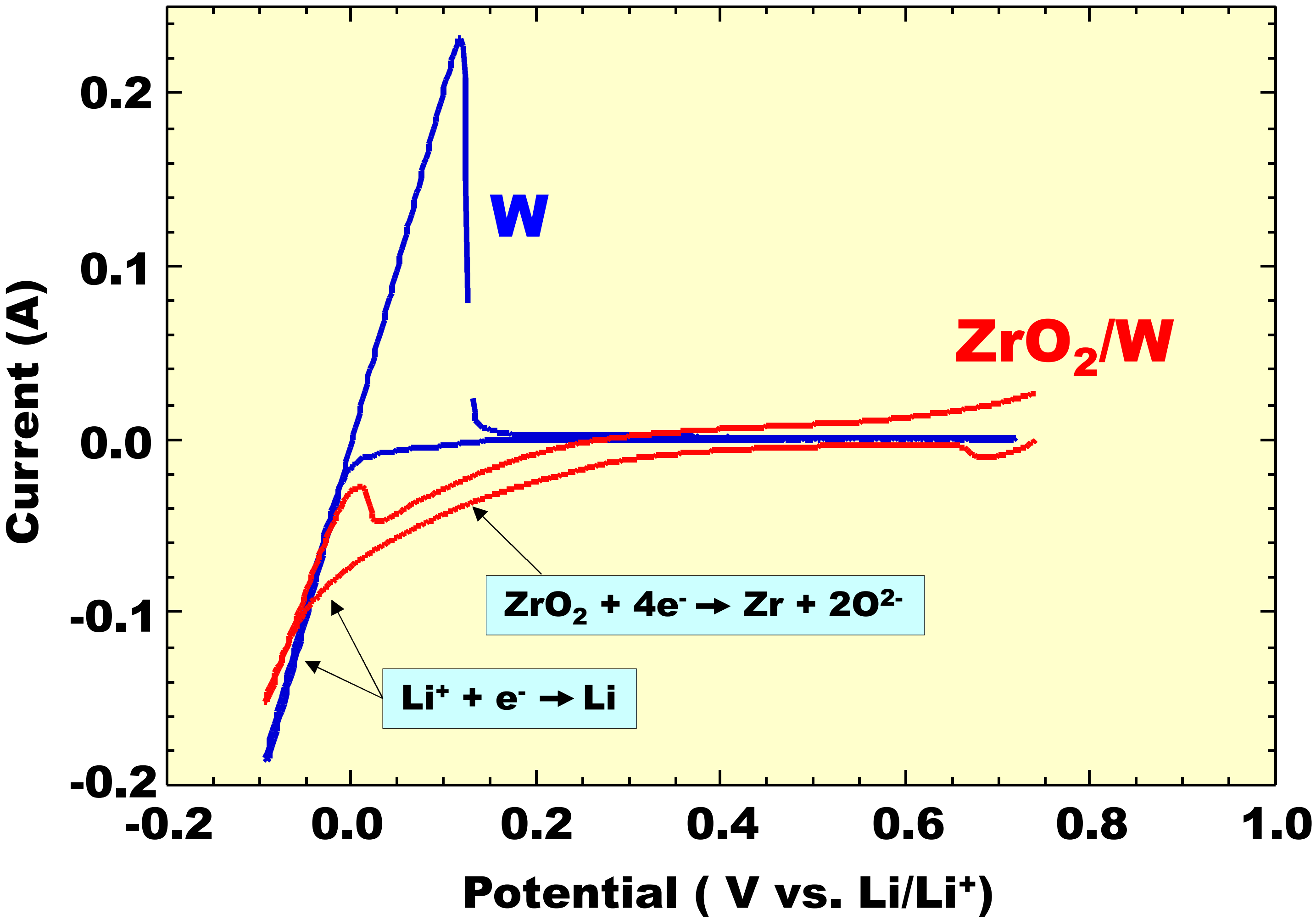
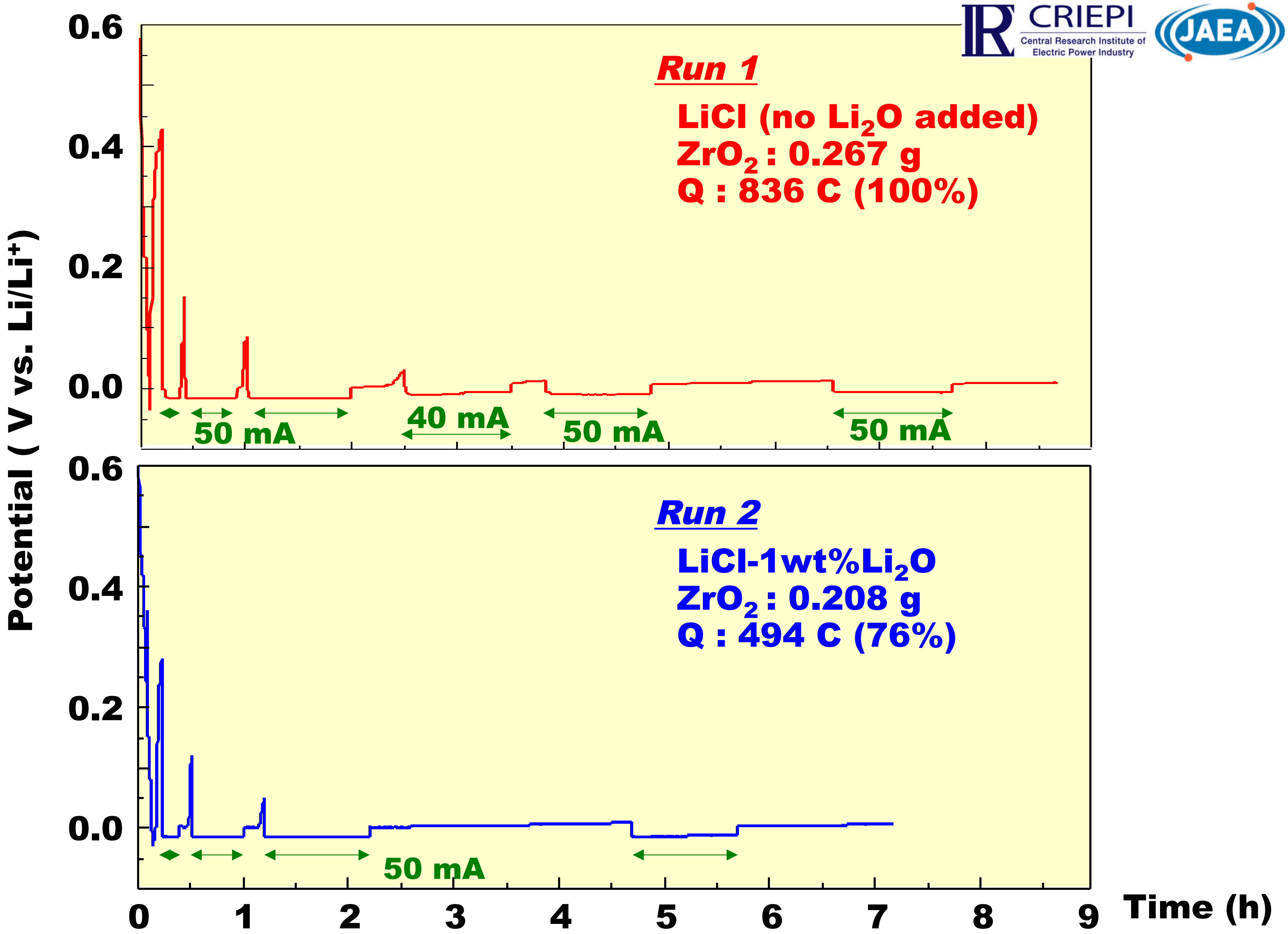
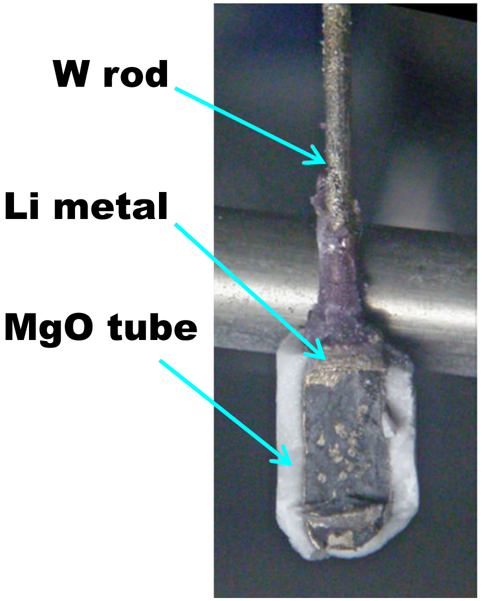



**Fig. Cyclic voltammograms in LiCl-1wt%$Li_2O$ at 650°C, SR = 0.05 V/s.**

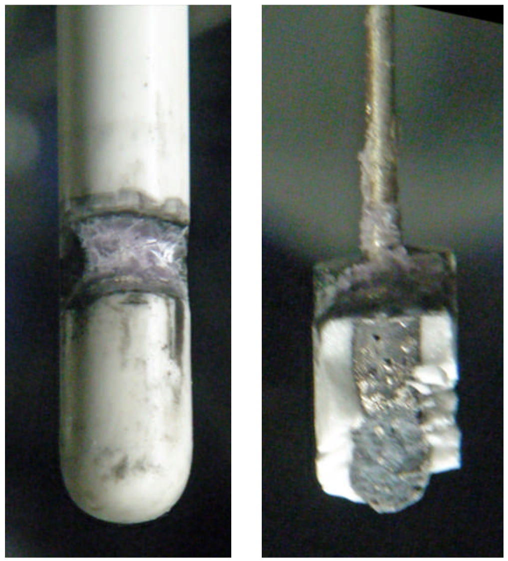
# *Electrolytic Reduction Test for $ZrO_2$*



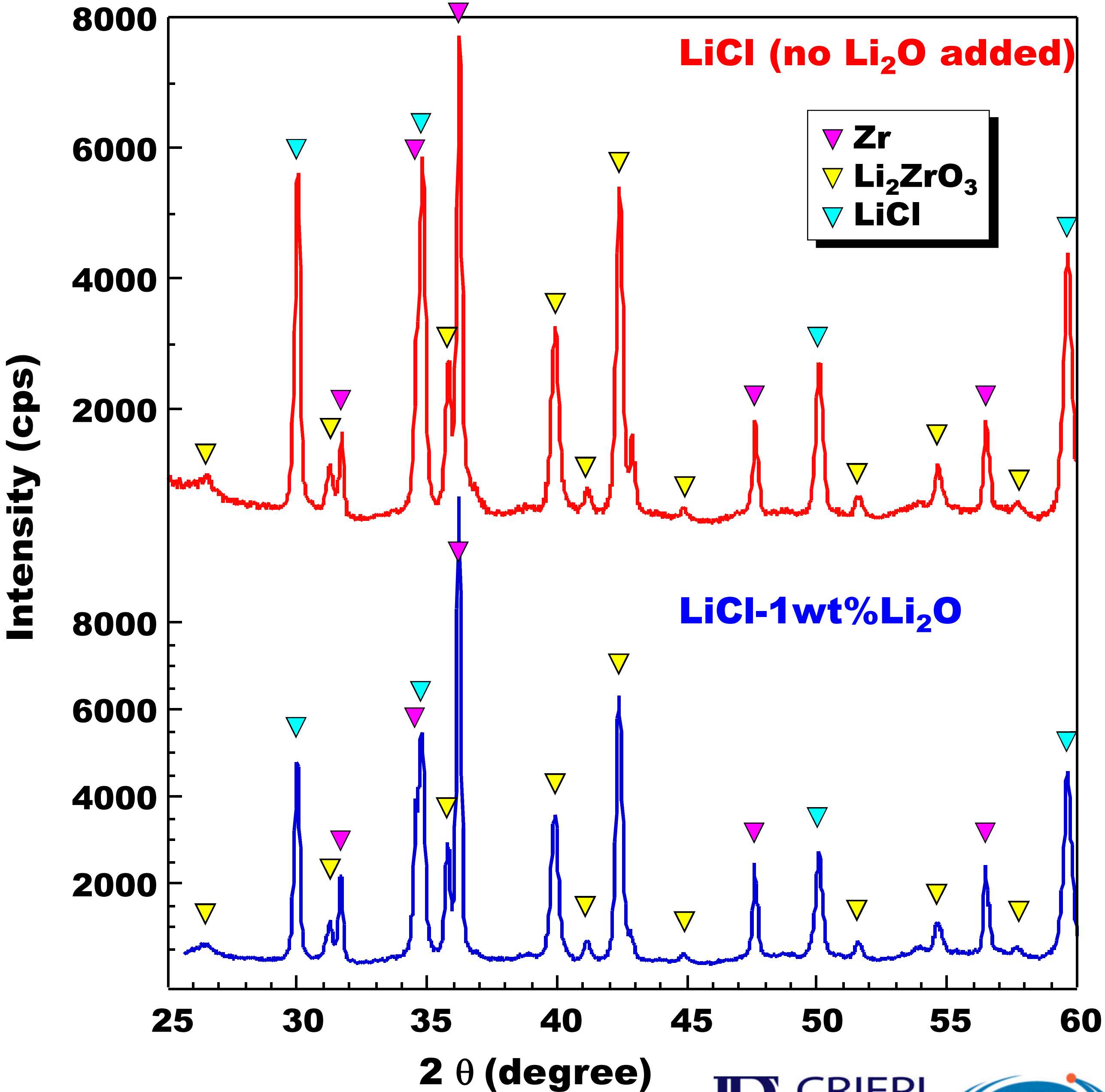
# Electrolytic Reduction Test for $ZrO_2$




Product in LiCl



Product in LiCl-1wt%$Li_2O$

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# Electrolytic Reduction Test for $Li_2ZrO_3$

**Reduction of $Li_2ZrO_3$ to Zr metal did not proceed even in LiCl without $Li_2O$ addition.**

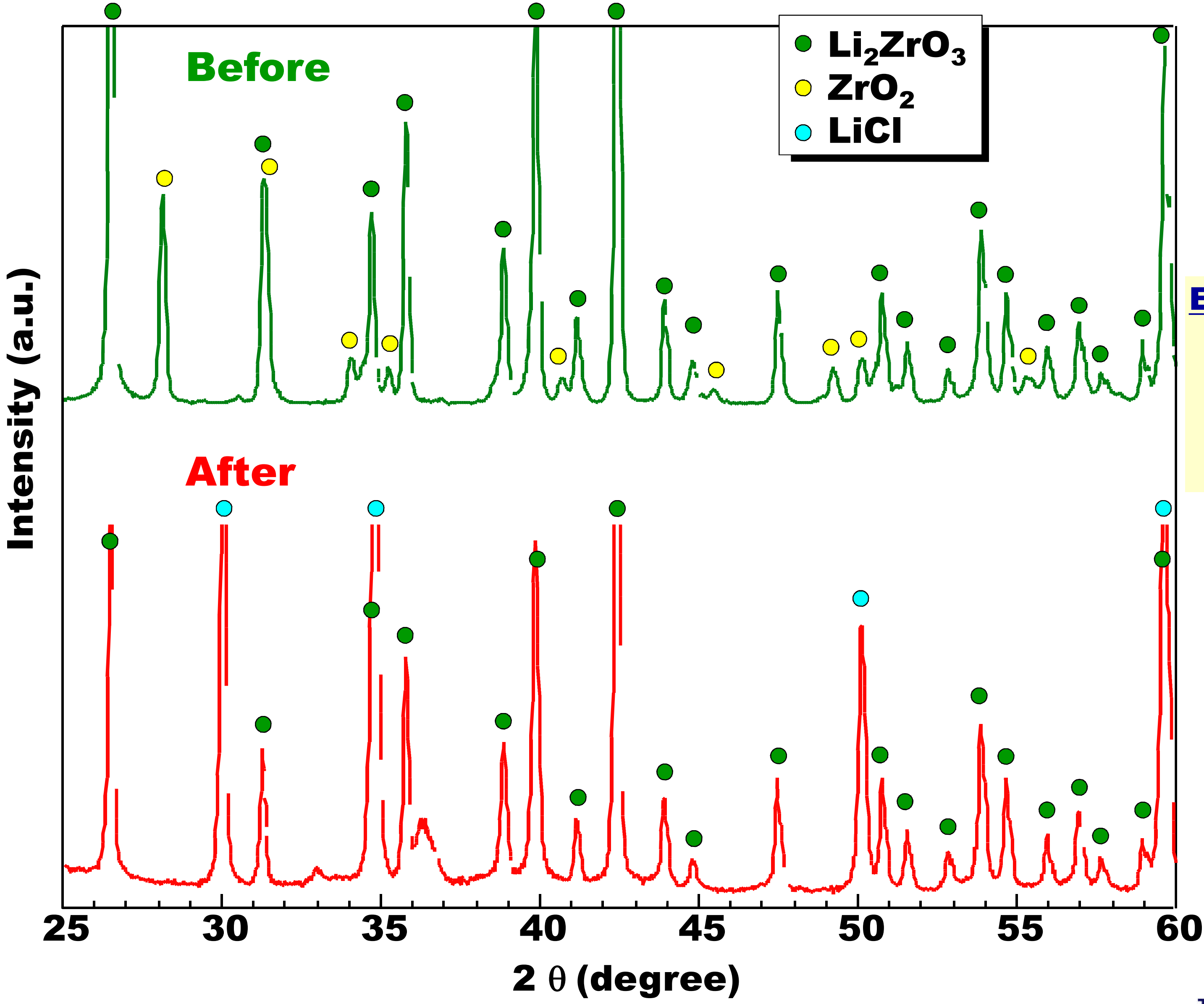
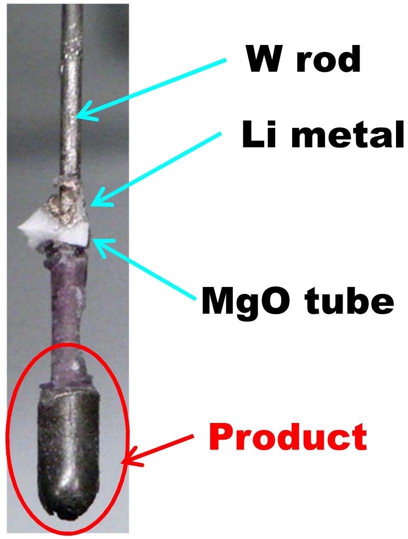



Fig. XRD patterns of $Li_2ZrO_3$ before and after electrolysis.

$Li_2ZrO_3$ reagent

**Electrolysis conditions**

- LiCl (no $Li_2O$ added)
- $Li_2ZrO_3$ : 0.160 g
- Current : 50 mA
- Q : 372 C (92%)

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# Results of Electrolytic Reduction Tests for $ZrO_2$

- $ZrO_2$ was reduced to Zr metal in LiCl-$Li_2O$ melt.

$$ZrO_2 + 4\,e^- \rightarrow Zr + 2\,O^{2-}$$
$$Li^+ + e^- \rightarrow Li$$
$$ZrO_2 + 4\,Li \rightarrow Zr + 4\,Li^+ + 2\,O^{2-}$$

- $Li_2ZrO_3$ was formed during electrolytic reduction.

$$ZrO_2 + O^{2-} + 2\,Li^+ \rightarrow Li_2ZrO_3$$

- $Li_2ZrO_3$ was hardly reduced to Zr metal.

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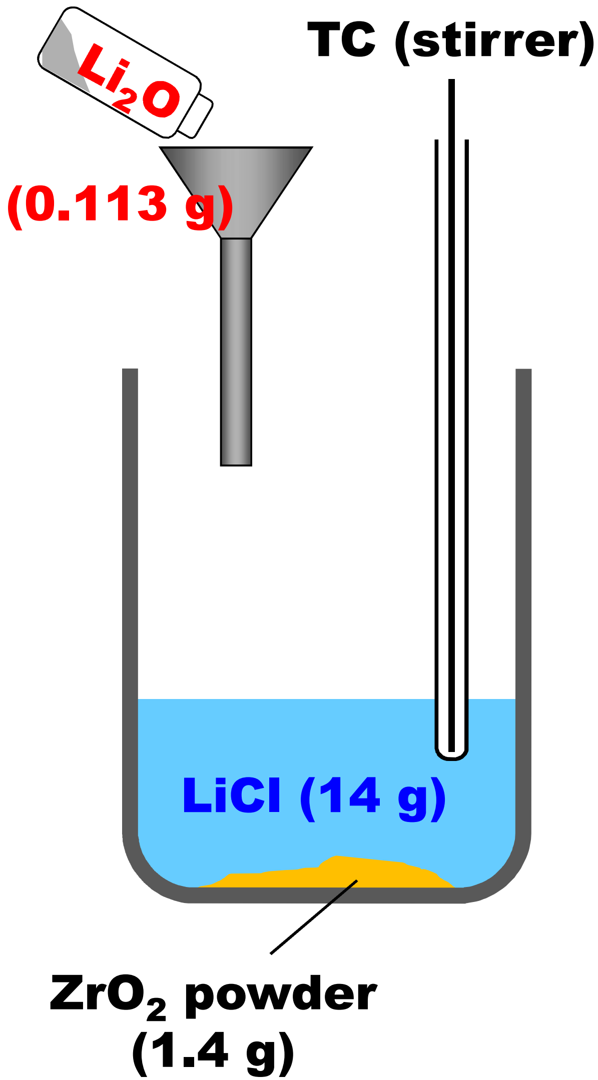
# Formation of $Li_2O$-$ZrO_2$ Complex Oxides



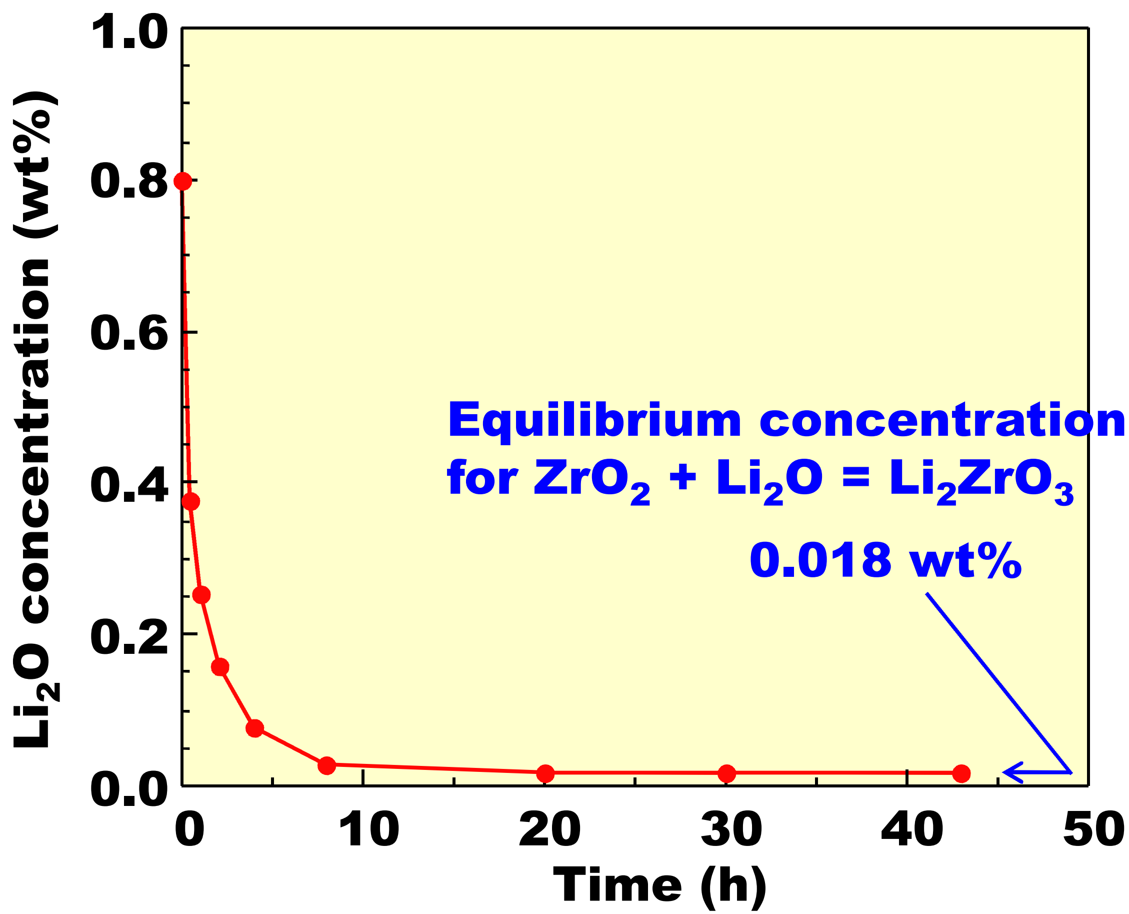




Fig. $Li_2O$ concentration after 0.113g of $Li_2O$ was added to the LiCl/$ZrO_2$ system at 650°C.

# Formation of $Li_2O$-$ZrO_2$ Complex Oxides

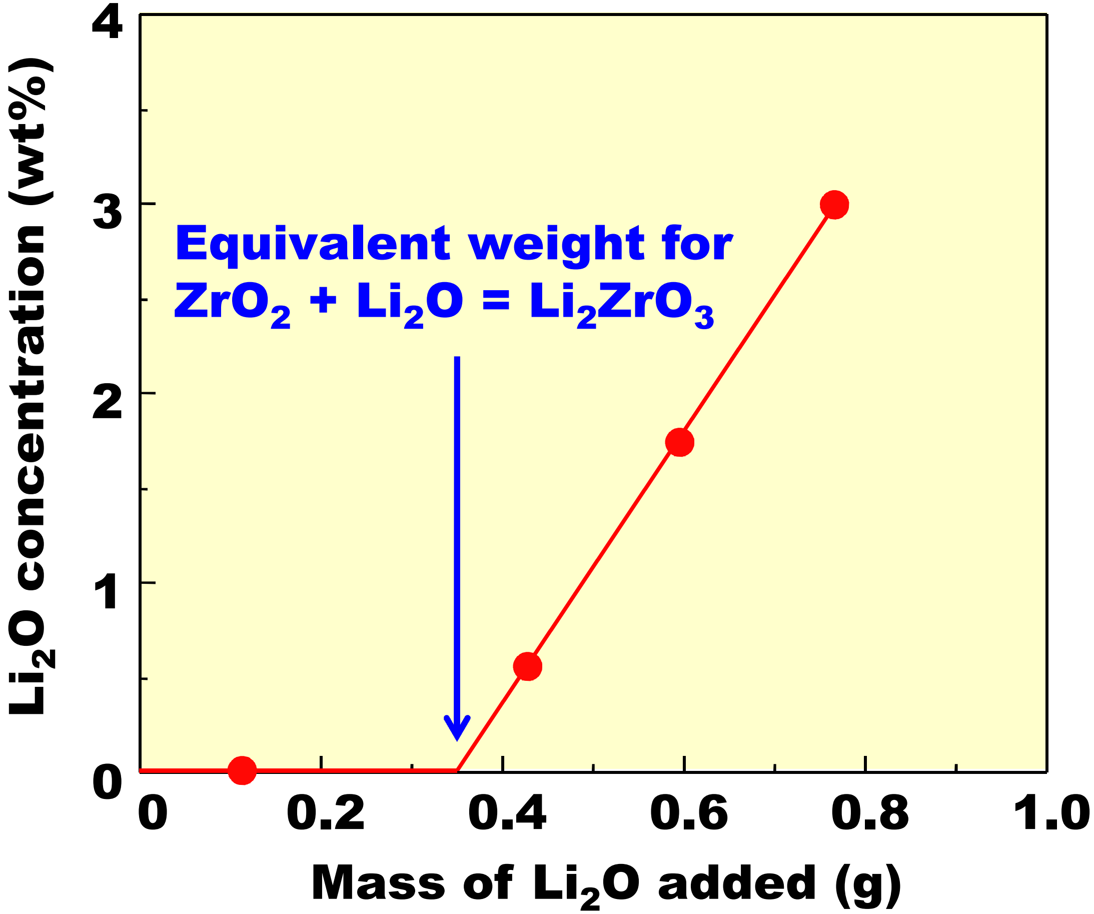



**Fig. $Li_2O$ concentration against amount of $Li_2O$ added into the LiCl/$ZrO_2$ system at 650°C.**

# *Formation of $Li_2O$-$ZrO_2$ Complex Oxides*

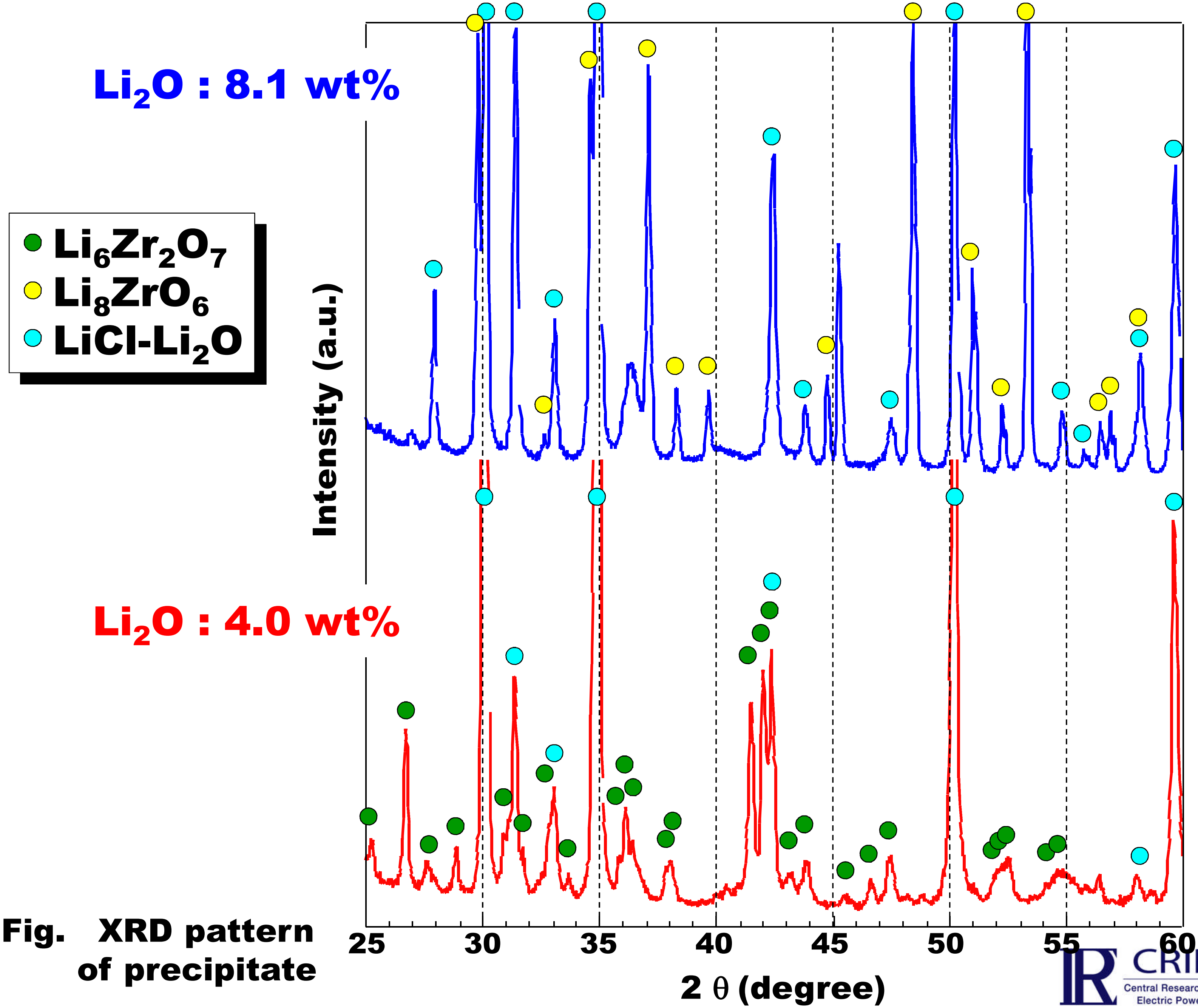



Fig. XRD pattern of precipitate

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# Formation of $Li_2O$-$ZrO_2$ Complex Oxides

## $ZrO_2$/LiCl-$Li_2O$ system at 650°C

(Equilibrium $Li_2O$ concentration)

$ZrO_2$

↓ + $Li_2O$ (0.018 wt%)

$Li_2ZrO_3$

↓ + 1/2 $Li_2O$

$Li_6Zr_2O_7$

↓ + 5/2 $Li_2O$

$Li_8ZrO_6$

**$ZrO_2$ can be used as an absorbent to remove dissolved $Li_2O$ from LiCl melt.**

***e.g.,*** **to remove $Li_2O$ in the LiCl adhering to actinide metal product of electrolytic reduction process.**

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# Electrolytic Reduction Test for $(U,Zr)O_2$

**Simulated fuel debris of $(U,Zr)O_2$ was prepared by Kato *et al.* through the study on melting temperature.**

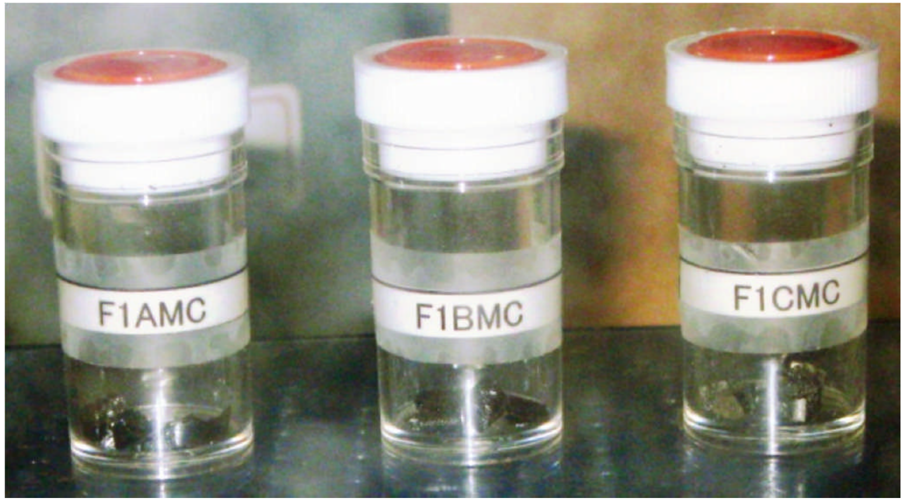
M. Kato, *et al*., MRS Online Proceedings Library, 1444 , mrss12-1444-y10-09 doi:10.1557/opl.2012.987

**(1) $UO_2$ and Zircaloy-2 powders were mixed (atom ratio, U:Zr = 1:3, 1:1 and 3:1) and compacted into green pellets.**

**(2) The green pellets were heated at 1650°C for 4 h in Ar-0.05%$H_2$ with added moisture.**

**(3) The measurement of melting temperature was conducted at 2600-2750°C in a tungsten capsule.**

**(4) The $(U,Zr)O_2$ were crushed into powder (<100 μm) for electrolytic reduction test.**




**U:Zr = 3:1 1:1 1:3**

**Simulated fuel debris of $(U,Zr)O_2$**

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# Electrolytic Reduction Test for $(U,Zr)O_2$

**Electrolysis conditions**

- $LiCl$-0.88 wt% $Li_2O$
- $(U_{0.5}Zr_{0.5})O_2$ : 0.344 g
- Current : 50-30 mA
- Time : 6.6 h
- Q : 675 C (105%)


Product

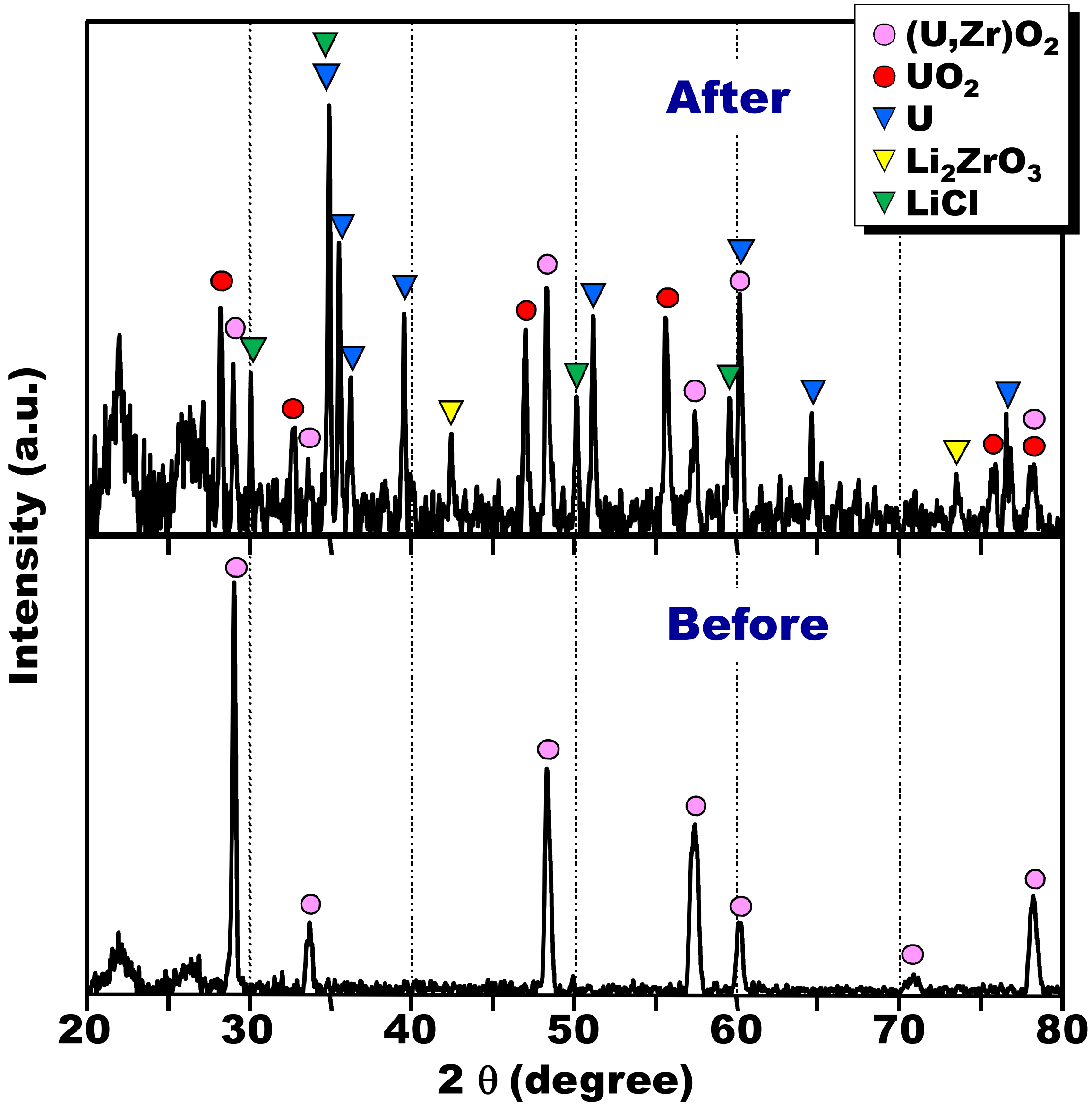


Fig. XRD patterns of $(U_{0.5}Zr_{0.5})O_2$ before and after electrolytic reduction.

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# *Electrolytic Reduction Test for $(U,Zr)O_2$*

- **The results for three oxides of $(U_{0.75},Zr_{0.25})O_2$, $(U_{0.5},Zr_{0.5})O_2$, $(U_{0.25},Zr_{0.75})O_2$ were similar.**

- **U metal, $UO_2$ and $Li_2ZrO_3$ were identified in the reduction products. $UO_2$ might be formed by the following reaction.**

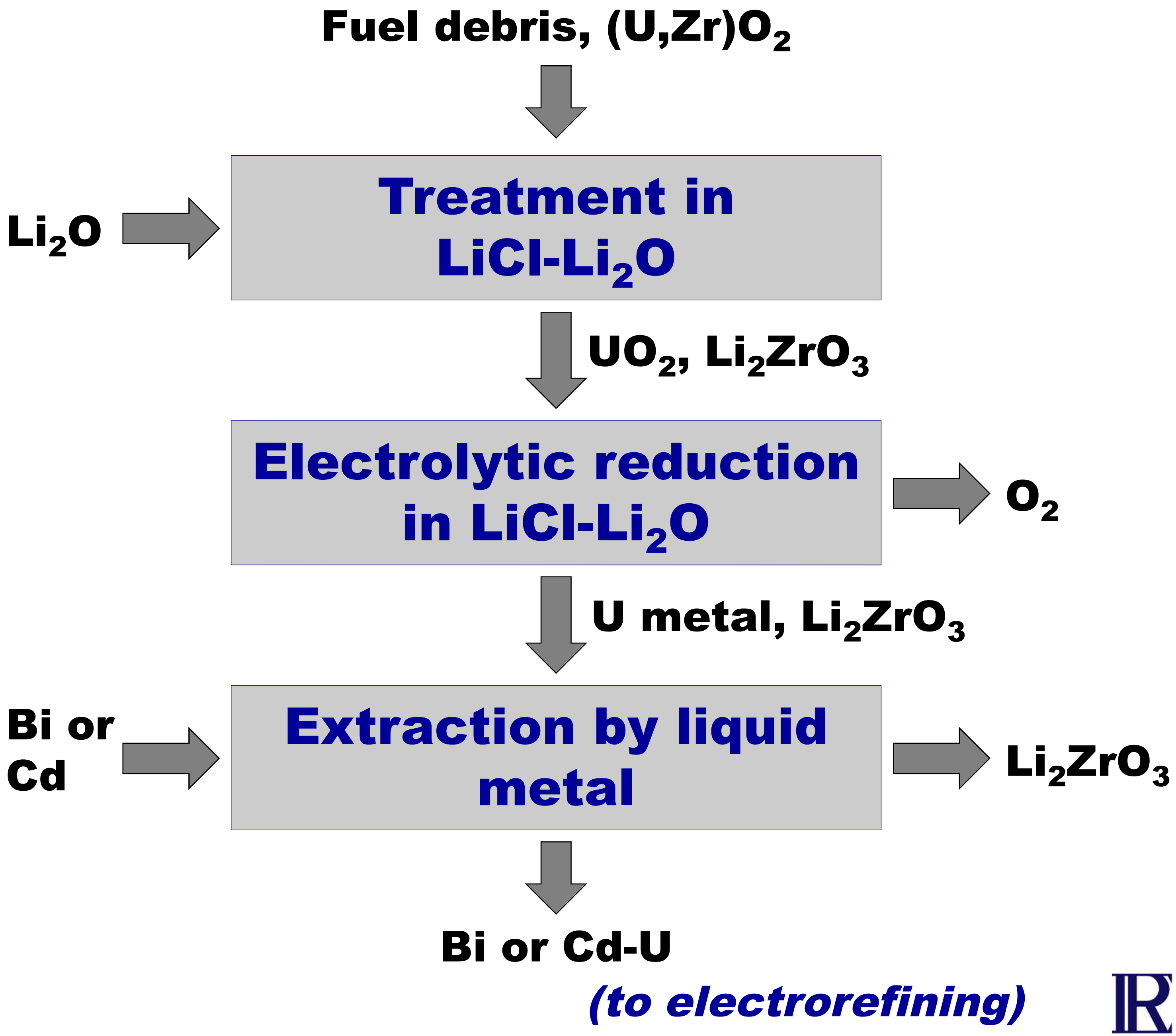
$$(U_x,Zr_y)O_2 + y\ Li_2O \rightarrow x\ UO_2 + y\ Li_2ZrO_3$$

- **Formation of $Li_2ZrO_3$ might not hinder the reduction to U metal.**

- **$Li_2ZrO_3$ will react with dissolved $UCl_3$ to give $UO_2$ and $ZrO_2$ precipitates in the subsequent electrorefining process.**

- **U metal can be separated from $Li_2ZrO_3$ by using a liquid metal (e.g., Cd, Bi).**

# *Process flow chart for damaged LWR fuel debris*

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# Summary

- $ZrO_2$ can be reduced to Zr metal by electrolytic reduction in LiCl melt, during which part of $ZrO_2$ is converted to $Li_2ZrO_3$.
- $Li_2ZrO_3$ is hardly reduced to Zr metal.
- The equilibrium $Li_2O$ concentration for $ZrO_2/Li_2ZrO_3$ is no more than 0.018 wt%, indicating $ZrO_2$ can be used to remove dissolved $Li_2O$ from LiCl melt.
- $Li_2ZrO_3$ is converted to $Li_6Zr_2O_7$ and then to $Li_8ZrO_6$ at higher $Li_2O$ concentrations.
- U metal was obtained by electrolytic reduction of simulated fuel debris, $(U,Zr)O_2$, during which $Li_2ZrO_3$ was formed.
- A process flow chart for fuel debris was proposed.