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2018 INTERNATIONAL PYROPROCESSING RESEARCH CONFERENCE

FROM RESEARCH TO INDUSTRY



Electrochemical behavior of zirconium in molten fluoride

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Tokai-mura, Ibaraki, Japan,
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Definition of Zircaloy and composition of irradiated Zircaloy cladding

➤ Zircaloy

- Material constituting nuclear fuel claddings
- Main composition of Zircaloy-4
 - *Non-irradiated*

Elements	Content (wt%)
Sn	1.20 – 1.70
Fe	0.18 – 0.24
Cr	0.07 – 0.13
O	0.09 – 0.16
Zr	~ 98

- *Irradiated claddings*

Activity coming from:

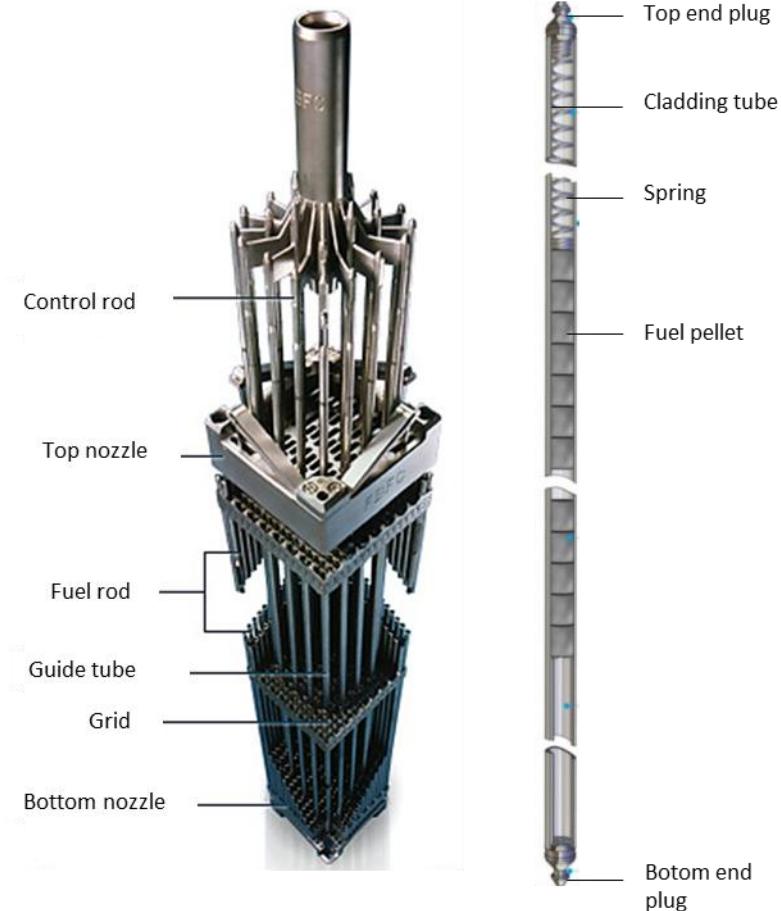
By elements:

Fission products (FPs): ^3H , ^{90}Sr , ^{106}Ru , ^{137}Cs , ^{154}Eu ...

Activation products (APs): ^{55}Fe , ^{60}Co , ^{59}Ni , ^{93}Zr , ^{94}Nb , ^{121}Sn , ^{125}Sb

α elements: Actinides Am, Pu, Cm, U

Heterogeneity : distribution of radioelements, nature of elements (metal, oxide, hydrides)

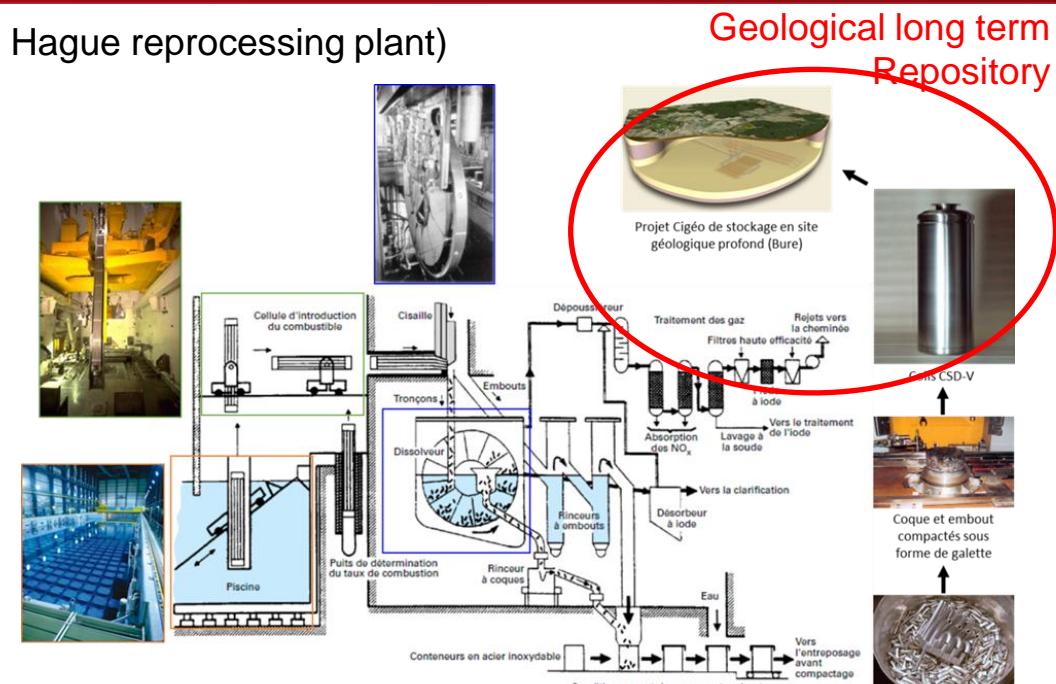
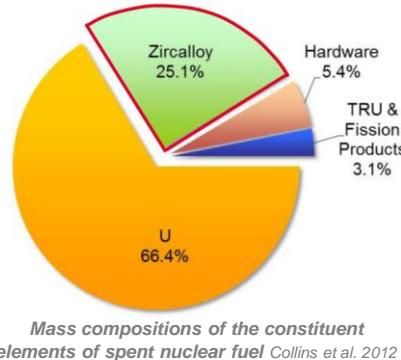


Schematic of an assembly of a French nuclear fuel

Context

Recycling Zr contained in Zircaloy cladding

- Spent fuel management in France (La Hague reprocessing plant)
 - pool storage
 - shearing in 3-5 cm section
 - dissolution of UO₂ pellet
- Treatment of remaining Zircaloy
- 25 wt.% of spent nuclear fuel



- Aim of the study: investigation on potential recycling of Zr from irradiated Zircaloy
 - Re-use of Zr for zircaloy refabrication and/or easier storage
- Identification of two promising routes
 - Chemical attack at high temperature : chlorination (Collins et al. DOE, USA)
 - **Electrochemical processes in molten salts : electrorefining**
- First step: fundamental comprehension of electrochemical behavior of Zr in salt

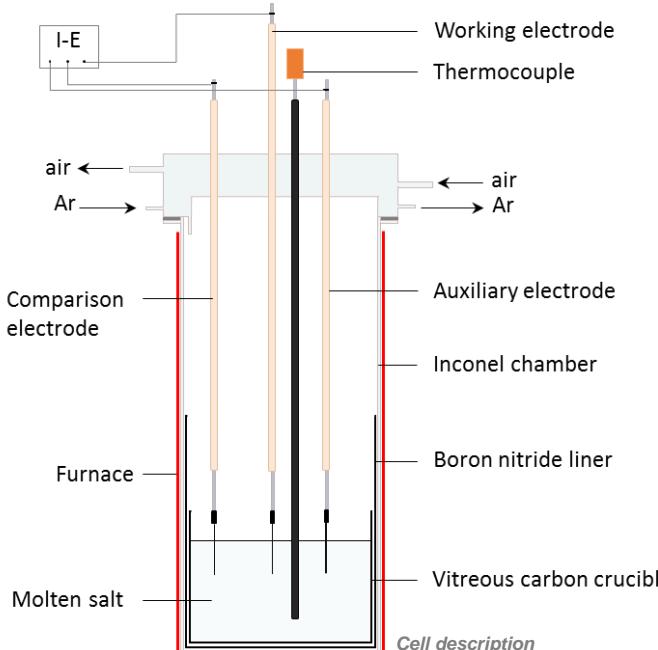
Experimental Setup

➤ Salt media

- Chlorides: several stable oxidation states (*0, I, II, IV*) of Zr reported in the literature → **Not adapted**
- Fluorides: should stabilise oxidation state → **Eutectic LiF-NaF**

➤ Equipment

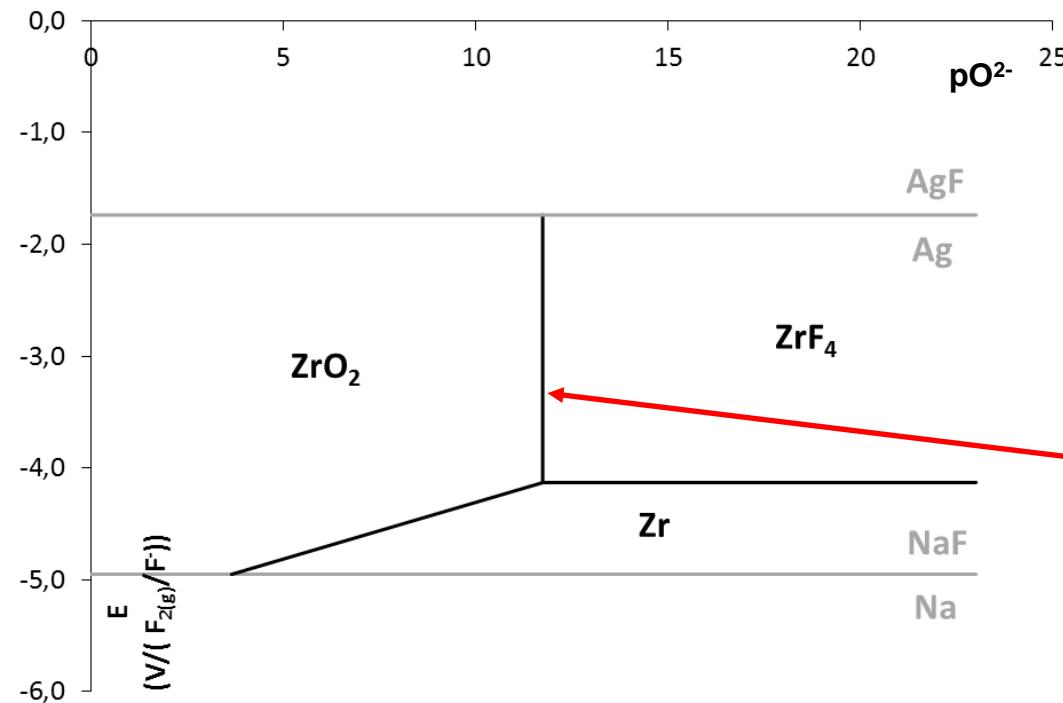
- Inactive pyrochemistry lab in gloveboxes under Ar atmosphere (< 10 ppm H₂O and < 5 ppm O₂)



➤ Experimental conditions

- Temperature range 750 – 900°C
- ZrF₄ concentration: 0.2 – 1.5wt%
- Electrochemical behavior and electrocrystallisation process
 - *Working electrode : Ag wire (1mm Ø)*
 - *Counter electrode : glassy carbon rod (3mm Ø)*
 - *Quasi reference electrode : Pt wire (1mm Ø)*
- Electrodeposition
 - *Cathode : 3 different materials studied (Zr, Graphite, SS)*
 - *Anode : Zr plates*
 - *Quasi reference electrode : Pt wire*

Thermodynamic approach



- Determination of Pourbaix diagram
 - Using HSC® Chemistry database
 - Considered species : Zr , ZrF_4 and ZrO_2
 - ZrF_4 activity considered: 0.1
 - Limits of the diagram : reduction of Na^+ and oxidation of Ag working electrode

- Influence of pO_2^- on stability of Zr

Solubility limit : $pK_s = 24.5$

$$\rightarrow pO_2^- = 11.7$$

Zr very sensitive to presence of O^{2-} in the salt

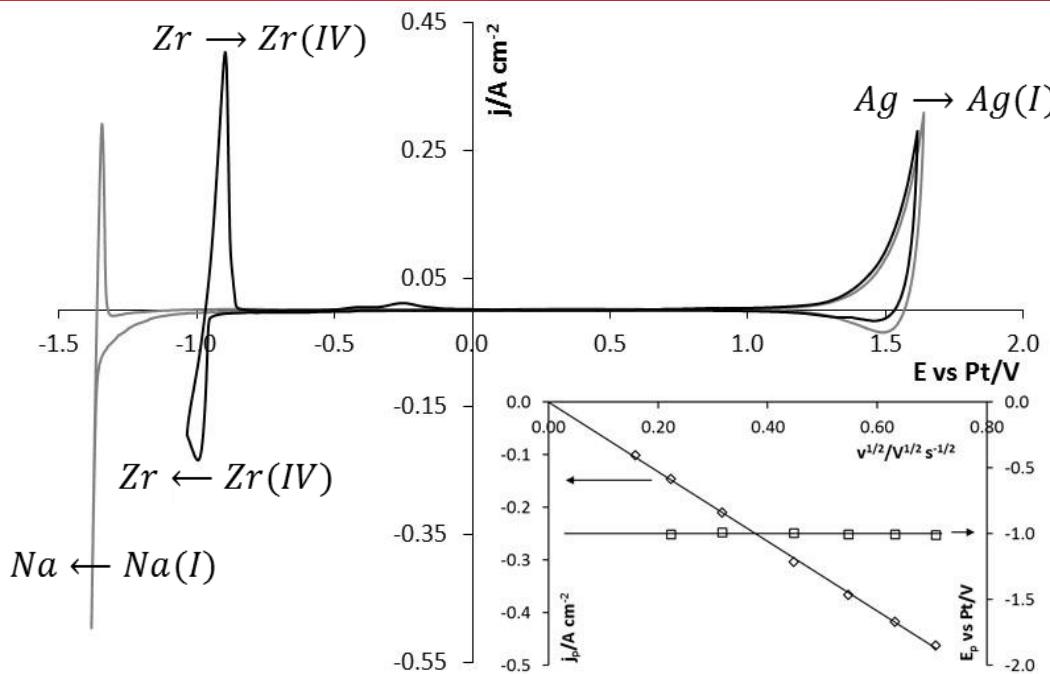


**Importance of preparation of the salt:
avoiding maximum presence of oxide**

Couples	Redox reactions Inputs HSC Chemistry	ΔG^0 (kJ/mol)	E^0 (V/ $(F_{2(g)}/F^-)$)	Expression
ZrF_4/Zr	$ZrF_4 + 4e^- \leftrightarrow Zr + 4F^-$	1574	- 4.08	$E = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{ZrF_4}}{a_{F^-}^4} \right)$
ZrO_2/Zr	$ZrO_2 + 4e^- \leftrightarrow Zr + 2O^{2-}$	2053	- 5.32	$E = E^0 + 2,3 \frac{2RT}{nF} pO_2^-$
NaF/Na	$NaF + e^- \leftrightarrow Na + F^-$	470	- 4.87	$E = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{NaF}}{a_{F^-}} \right)$
AgF/Ag	$AgF + e^- \leftrightarrow Ag + F^-$	148	- 1.53	$E = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{AgF}}{a_{F^-}} \right)$

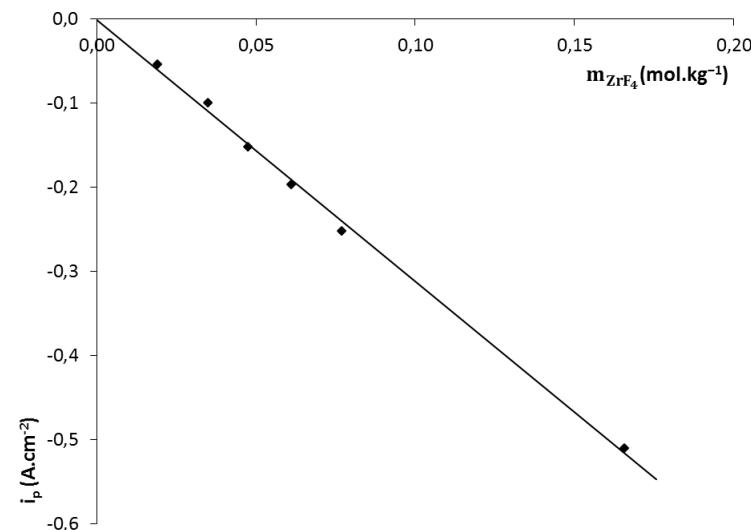
Couple	Solubility reaction input in HSC Chemistry	K	$pO_2^- = f(K)$ Expression	pO_2^-
ZrO_2/ZrF_4	$ZrO_2 + 4F^- \leftrightarrow ZrF_4 + 2O^{2-}$	$3.40 \cdot 10^{-25}$	$pO_2^- = -\frac{1}{2} \log \left(\frac{K a_{F^-}^{-4}}{a_{ZrF_4}} \right)$	11.7

Electrochemical behavior: cyclic voltammetry



Cyclic voltammograms of the LiF-NaF system at 100 mV.s^{-1} and 750°C : without ZrF_4 (grey) and with ZrF_4 addition of 0.06 mol.kg^{-1} (black). Inset. Variation of the peak current density (\diamond) and the peak potential (\square) versus the square root of the potential scan rate.

Working electrode: Ag ($S = 0.36 \text{ cm}^2$); auxiliary electrode: glassy carbon; comparison electrode: Pt



Variation of current density of the reduction peak as a function ZrF_4 molality , at 750°C and scan rate 100mV.s^{-1} .

Reduction of Zr(IV) occurs in one step

Reduction is controlled by diffusion of Zr(IV)

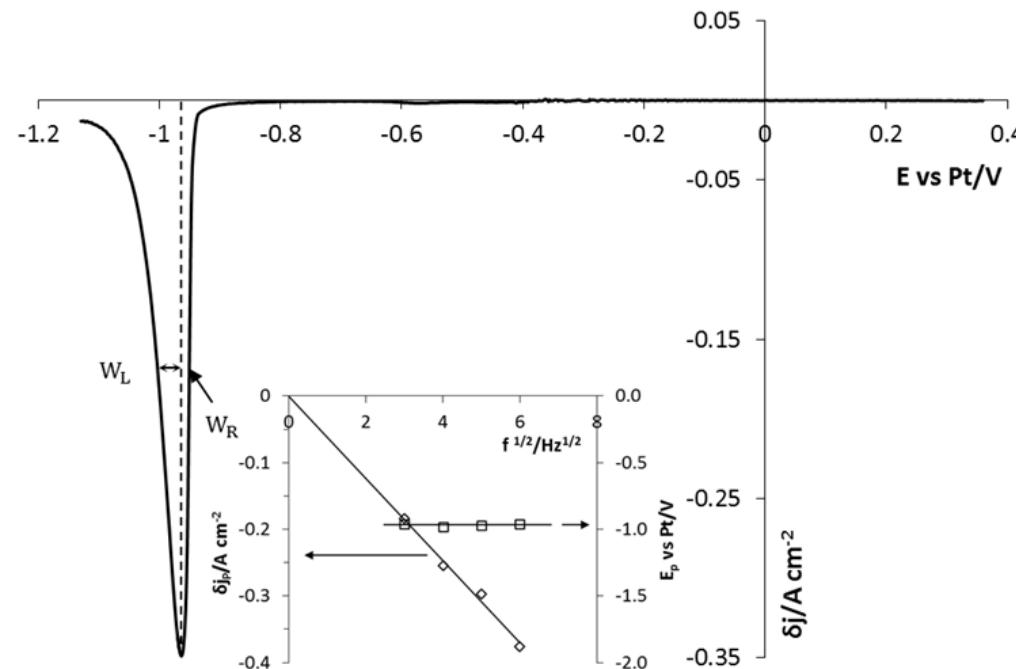
Quasi-reversible system

Diffusion coefficient $\rightarrow j_p \propto \sqrt{v}$

$$\rightarrow D_{\text{Zr(IV)}} = 1,21 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$$

$$\text{Arrhenius type law} \rightarrow \ln D_{\text{Zr(IV)}} = -7.77 - \frac{3649}{T}$$

Electrochemical behavior: square wave voltammetry



Square wave voltammogram of the LiF-NaF-ZrF₄ ($m_0 = 0.06 \text{ mol.kg}^{-1}$) at 16 Hz, pulse height: 20 mV, step potential: 2 mV and 750 °C.
 Inset. Variation of the differential of the peak current density (δj_p) and the peak potential (E_p) versus the square root of the frequency.
 Working electrode: Ag ($S = 0.35 \text{ cm}^2$); auxiliary electrode: glassy carbon; comparison electrode: Pt

Reduction of Zr(IV) in one step

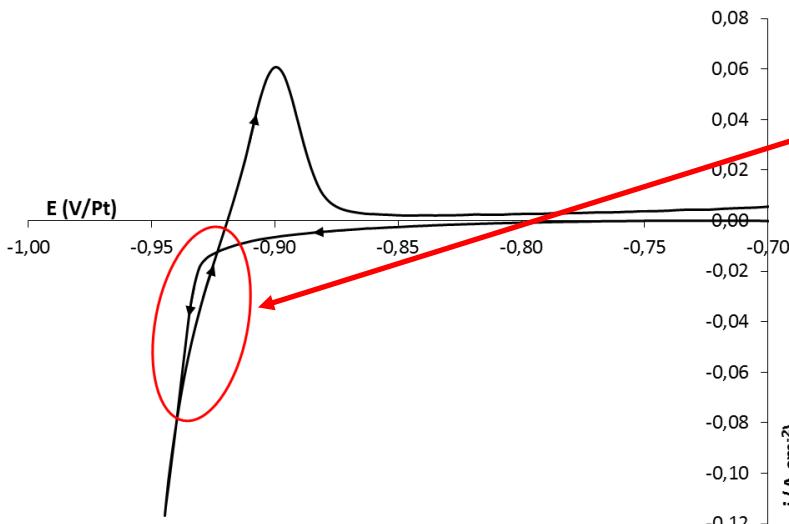
Number of exchanged electrons

$$W_{1/2} = 3.52 \frac{RT}{nF} = 2W_L$$

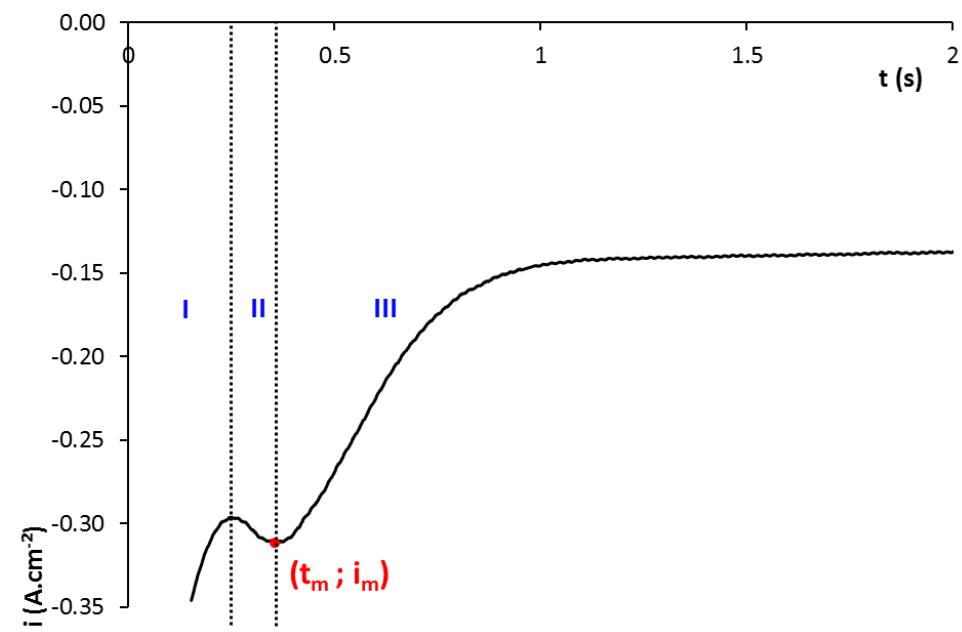
4 electrons exchange



Soluble/insoluble system



■ Crossover on cyclic voltammograms observed: **Nucleation process evidenced**



Chronoamperogram on silver electrode at $\eta = -0.969 \text{ V}$ vs Pt in LiF-NaF-ZrF_4 ($m_0 = 0.17 \text{ mol.kg}^{-1}$) at 690°C . Working electrode: Ag ($S = 0.35 \text{ cm}^2$); auxiliary electrode: glassy carbon; comparison electrode: Pt

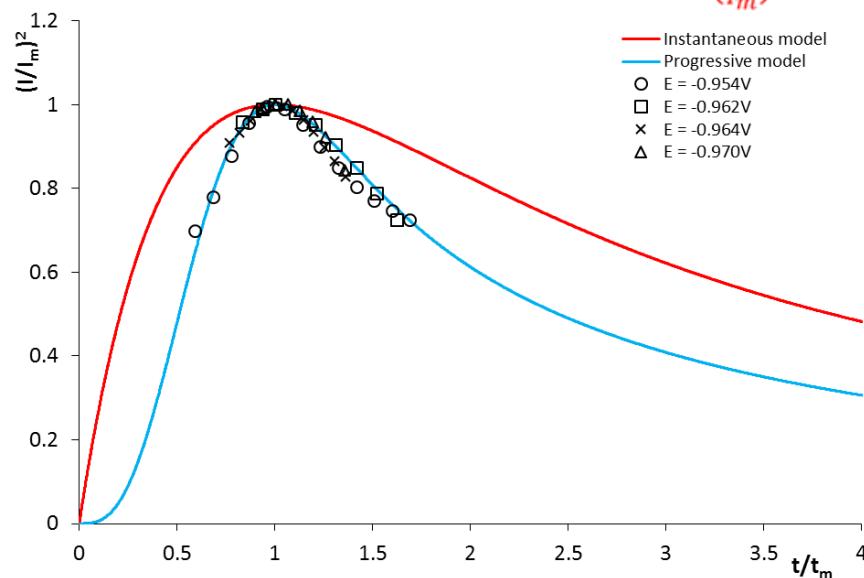
- **Chronoamperometry** → 3 areas:
- **Part 1:** charging of the double layer and the formation of the first germs
- **Part 2:** growth of the crystals
 $(t_m ; i_m) \rightarrow v_{\text{diffusion}} = v_{\text{growth crystals}}$
- **Part 3:** limitation of the reaction by the diffusion of Zr(IV) ions



Non-dimensional models : $\left(\frac{i}{i_m}\right)^2 = f\left(\frac{t}{t_m}\right)$

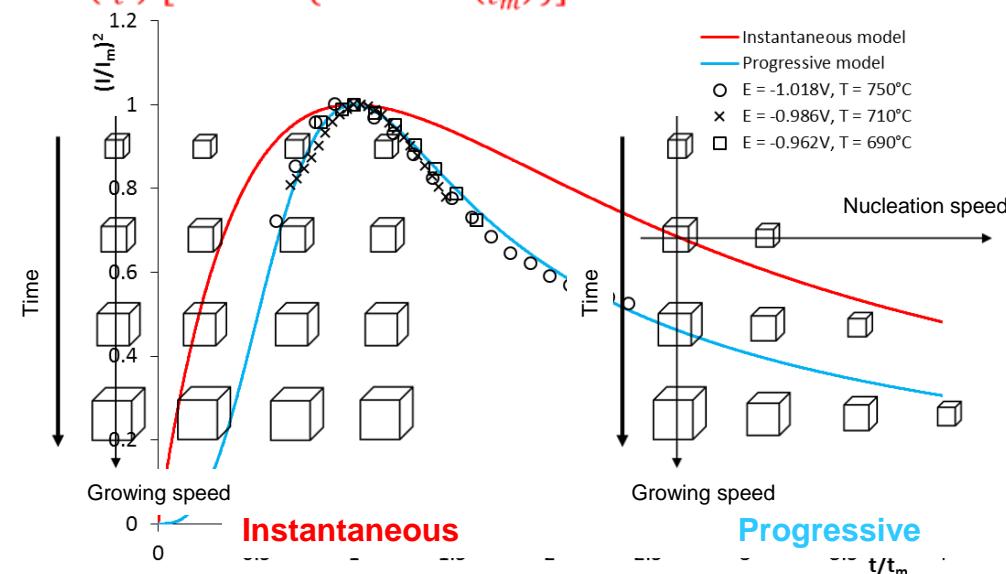
- Non-dimensional theoretical models → 2 nucleation modes (Scharifker et al. 1983)

- Progressive nucleation → $\left(\frac{I}{I_m}\right)^2 = 1.2254 \left(\frac{t_m}{t}\right) \left[1 - \exp\left\{-2.3367 \left(\frac{t}{t_m}\right)^2\right\}\right]^2$
- Instantaneous nucleation → $\left(\frac{I}{I_m}\right)^2 = 1.9542 \left(\frac{t_m}{t}\right) \left[1 - \exp\left\{-1.2564 \left(\frac{t}{t_m}\right)\right\}\right]^2$



Comparison of the dimensionless experimental data obtained from the current-time transients at various overvoltages and temperature with the theoretical models for instantaneous and progressive nucleation in LiF-NaF-ZrF_4 ($m_0 = 0.17 \text{ mol.kg}^{-1}$).

Working electrode: Ag; auxiliary electrode: glassy carbon; comparison electrode: Pt



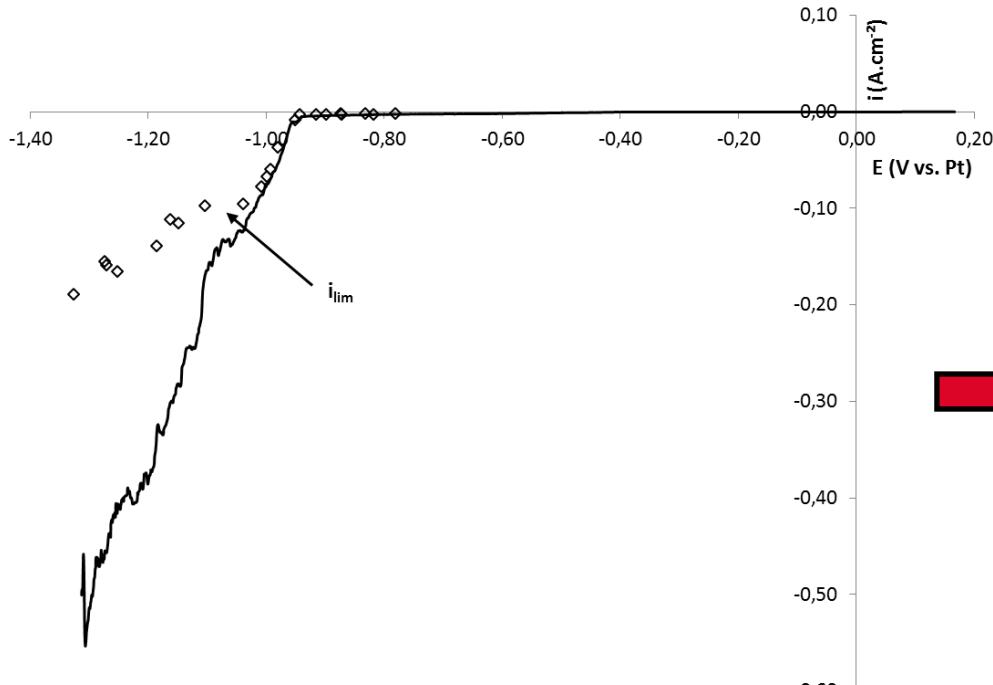
Progressive nucleation mode whatever the overvoltage imposed and the working temperature
Cristal growth in the three dimensions and limited by the diffusion of Zr(IV) ions

Progressive nucleation: high temperature, high concentration and high overvoltage → best deposit conditions

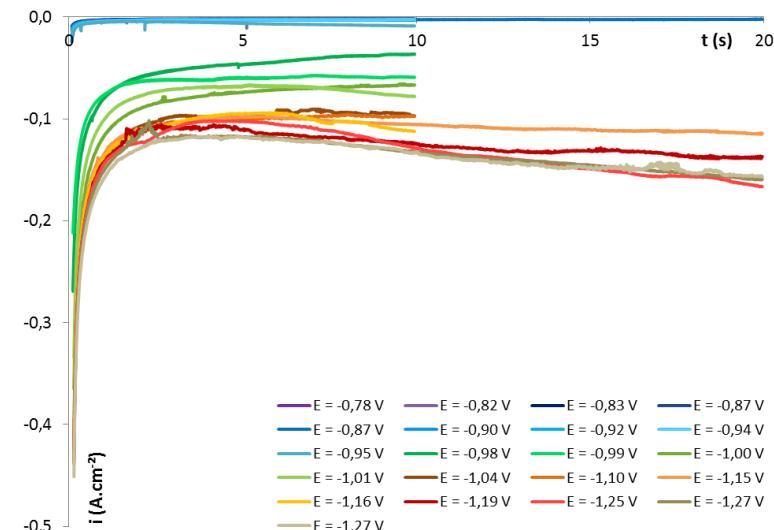
Determination of the limiting current

- Fluoride media : No reference electrode
⇒ Galvanostatic electrodeposition
- System limited by Zr diffusion**
⇒ **Determination of the limiting current needed**

Tow technics: Voltammetry (low scan range) or polarisation



Linear Voltamperogram on LiF-NaF-ZrF₄ (C = 7.46.10⁻²mol/kg), scan range: 1mV/s at 750°C and polarisation plots.



Chronoamperograms on LiF-NaF-ZrF₄ (C = 7.46.10⁻²mol/kg) at 750°C different applied potentials.

→ $i_{lim} = -0,097 \text{ A.cm}^{-2}$

$i_{lim} = -0,14 \text{ A.cm}^{-2} \cdot \text{wt\%}^{-1}$

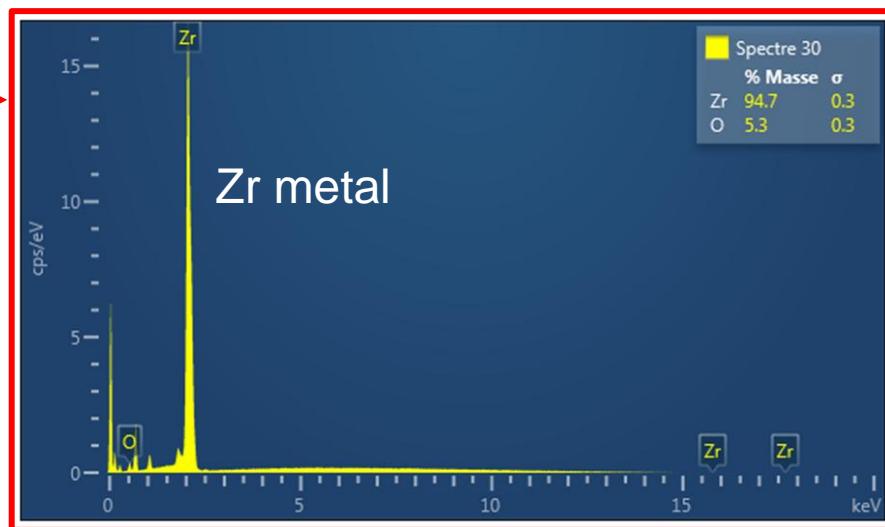
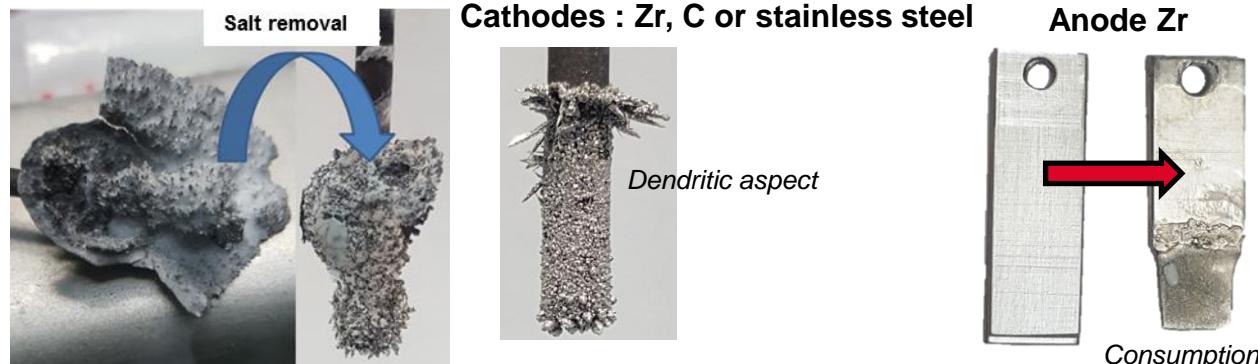
Higher applied current densities:

→ **possible co-reduction of Na⁺**

➤ Electrodeposition experimental results:

Deposit loss can be observed on several experiments

Important faradic yields reached > 80%
Difficulties to estimate it (*salt remaining removal*)

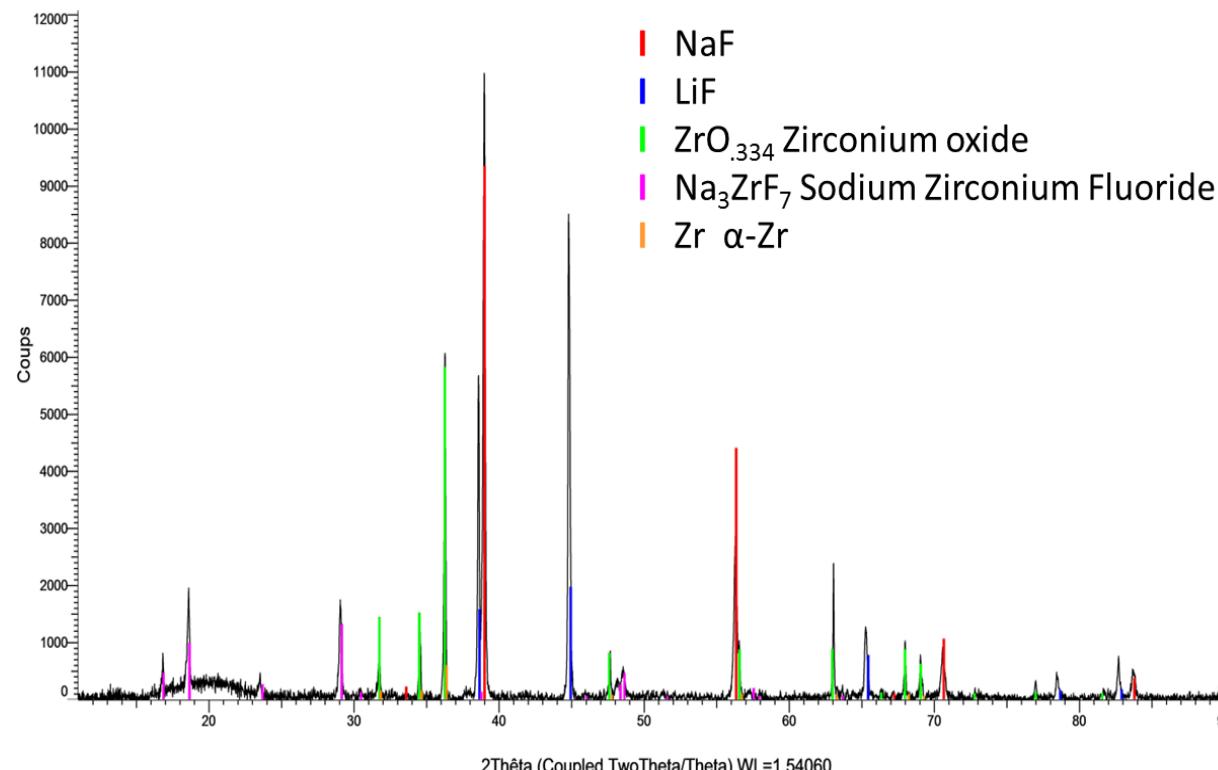


SEM analysis of Zr deposited on graphite electrode in LiF-NaF-ZrF_4
($C = 0.55 \text{ mol.kg}^{-1}$) at 750°C , $J = -0.72 \text{ A.cm}^{-2}$

Feasibility of pur Zr metal deposition demonstrated in LiF-NaF

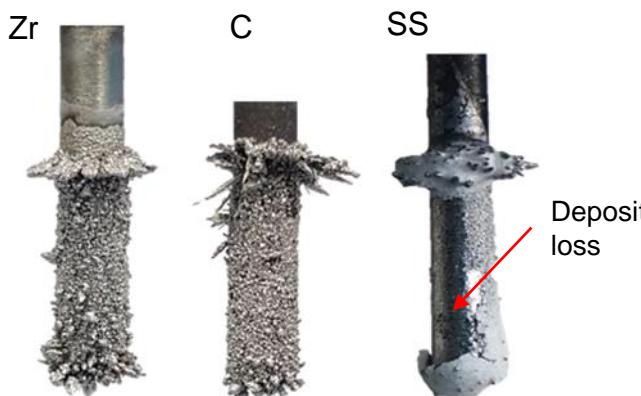
➤ XRD analysis:

- Confirmation of the SEM analysis
- Residual salt adhered onto the electrode
- Presence of oxygen: contamination of the deposit during sample preparation (*under air atmosphere*)



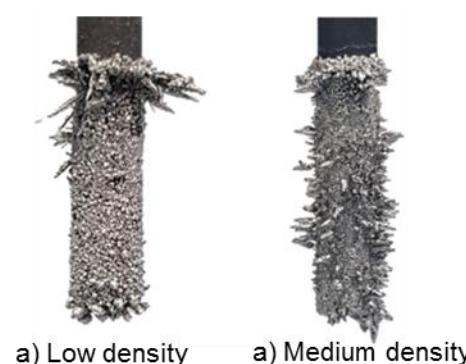
➤ Influence of the operating parameters

Substrate of cathodes



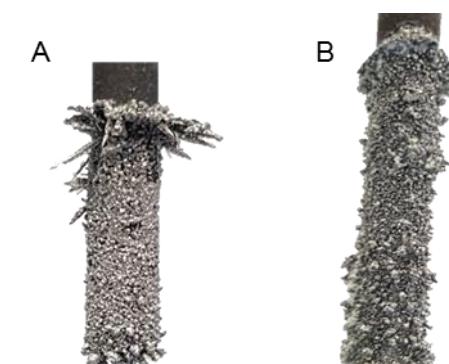
Photographs of cathodes after electrolysis runs in LiF-NaF-ZrF_4 on different substrate

Current density



Photographs of cathodes after electrolysis runs in LiF-NaF-ZrF_4 at different current density

ZrF_4 concentration



Photographs of cathodes after electrolysis runs at in LiF-NaF-ZrF_4 at different molality ($C_A > C_B$)

Dense, compact and adherent deposit on Zr and C cathodes

Selection of the cathode material

Strong effect of current density on the regularity

↑ current density \Rightarrow ↑ nuclei formed

In good agreement with the Zr nucleation study

Moderate influence of concentration on the regularity

↑ concentration \Rightarrow ↑ nuclei formed

Conclusions and prospects

■ Electrochemical behavior in fluoride salts

- *Zr(IV) reduction in one step*



- *Reduction is limited by diffusion of Zr(IV) ions* → Arrhenius type law : $\ln D_{\text{Zr(IV)}} = -7.77 - \frac{3649}{T}$

■ Electrocristallisation process

- *Progressive nucleation mode*
- *Cristal growth*
 - in the three dimensions
 - limited by the diffusion of Zr(IV) ions

■ Electrodeposition

- *Observations are in agreement with the Zr nucleation study*

→ ↑ current density or ↑ concentration ⇒ ↑ nuclei formed

■ Next step

- *Tests with non irradiated Zircaloy*

Thank you for your attention

Acknowledgments:

Pierre CHAMELOT ([LGC Toulouse](#))

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David RUDLOFF ([CEA Marcoule](#))

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