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2018 INTERNATIONAL PYROPROCESSING RESEARCH CONFERENCE

FROM RESEARCH TO INDUSTRY

cea den

Electrochemical behavior of zirconium in molten fluoride

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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:

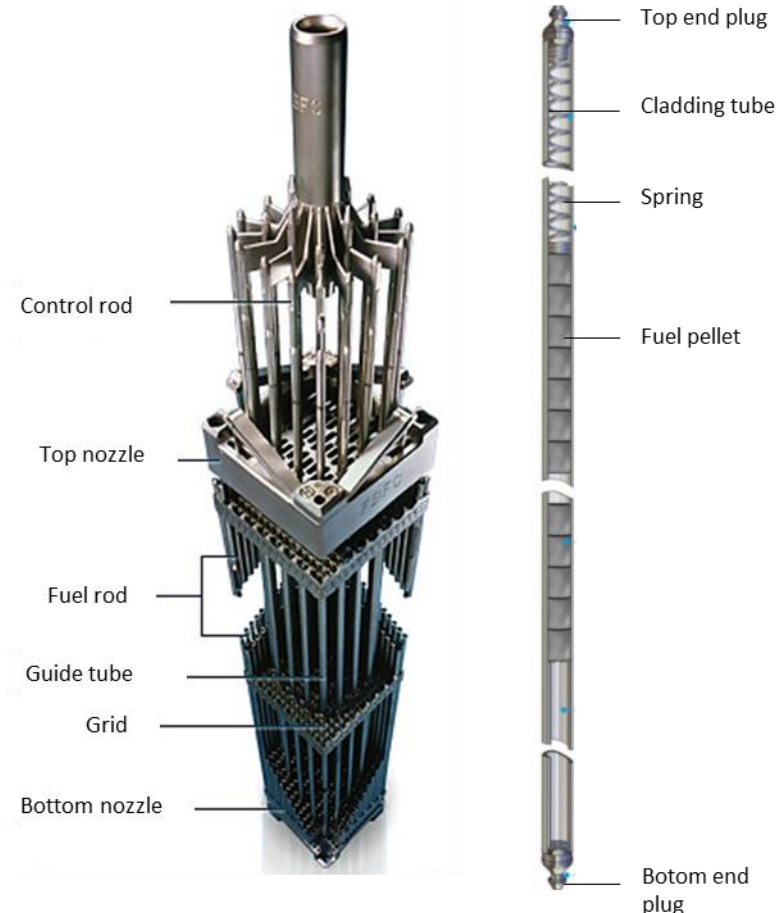
$\beta\gamma$ elements:

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)

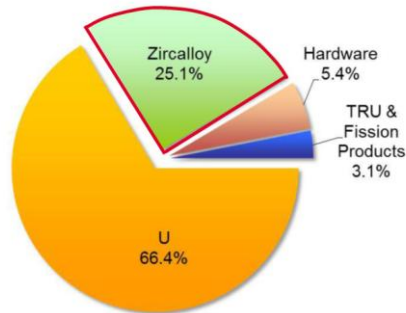


Schematic of an assembly of a French nuclear fuel

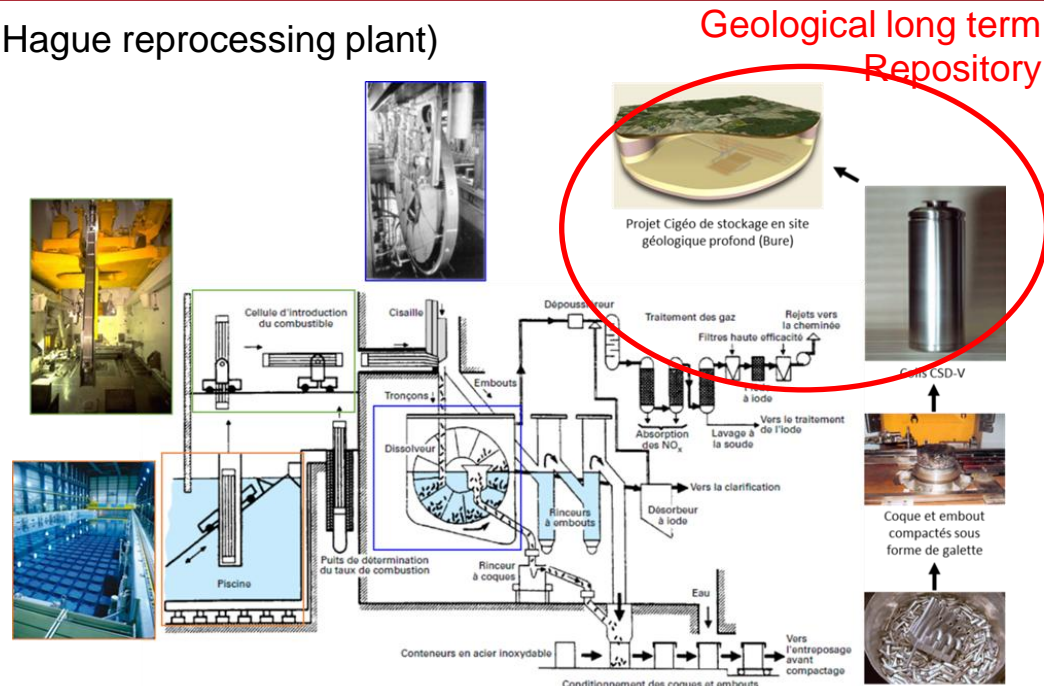
Context

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



Mass compositions of the constituent elements of spent nuclear fuel Collins et al. 2012



- 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

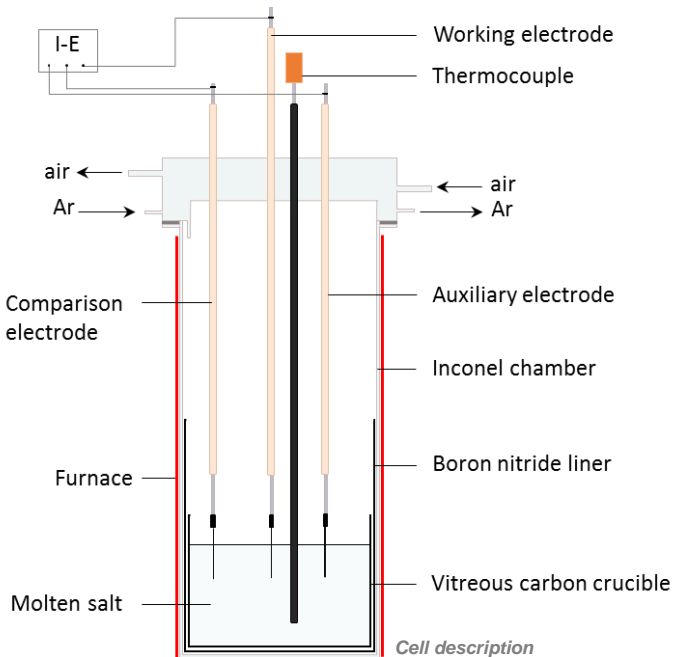
Experimental Setup

➤ 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)

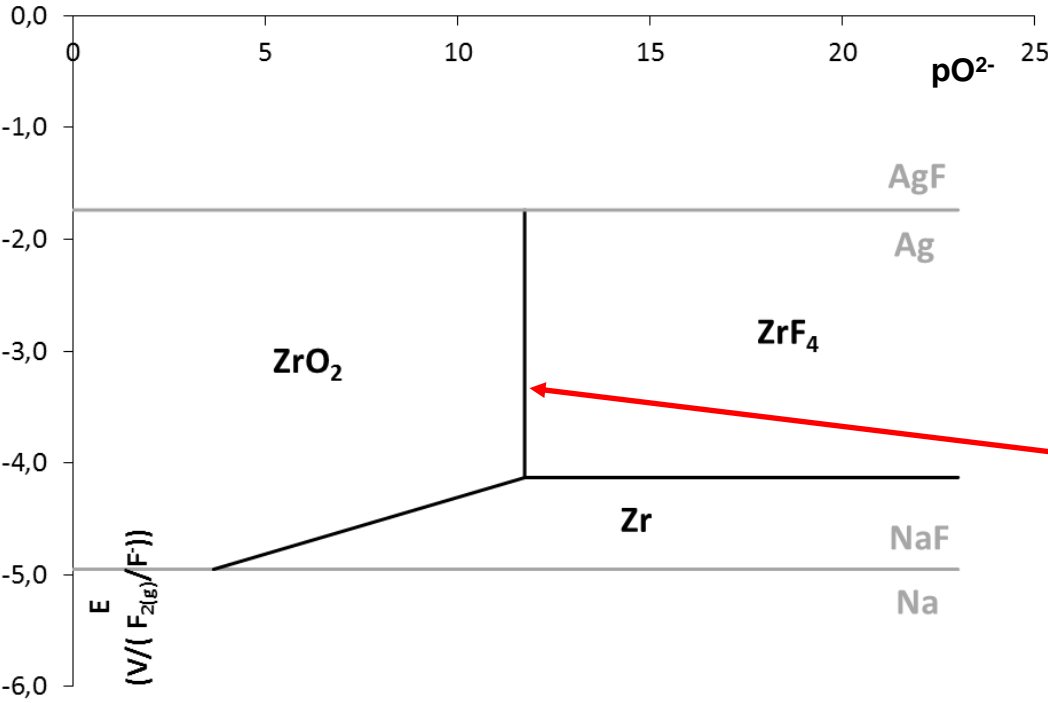


➤ Experimental conditions

- 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, ZrF₄ and ZrO₂
 - ZrF₄ activity considered: 0.1
 - Limits of the diagram : reduction of Na⁺ and oxidation of Ag working electrode

■ Influence of pO₂₋ on stability of Zr
Solubility limit : pKs = 24.5

→ pO₂₋ = 11.7

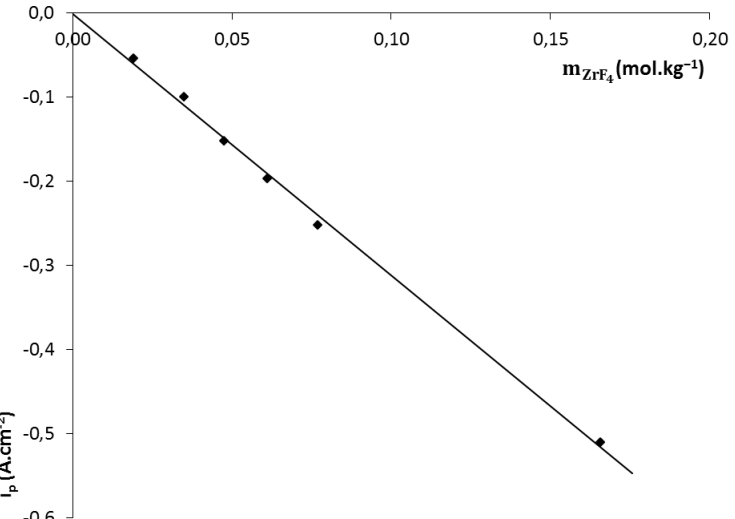
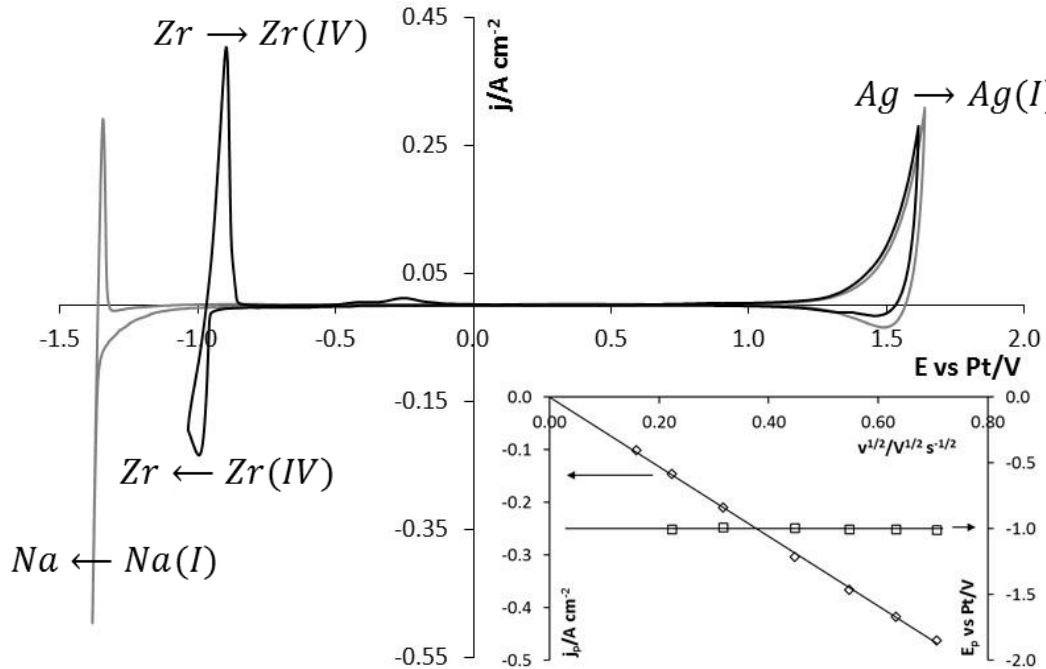
Zr very sensitive to presence of O²⁻ in the salt



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 ⁻ ↔ Zr + 4F ⁻	1574	-4.08	$E = E^0 + \frac{RT}{n\mathcal{F}} \ln \left(\frac{a_{ZrF_4}}{a_p^{-4}} \right)$
ZrO ₂ /Zr	ZrO ₂ + 4e ⁻ ↔ Zr + 2O ²⁻	2053	-5.32	$E = E^0 + 2,3 \frac{2RT}{n\mathcal{F}} pO^{2-}$
NaF/Na	NaF + e ⁻ ↔ Na + F ⁻	470	-4.87	$E = E^0 + \frac{RT}{n\mathcal{F}} \ln \left(\frac{a_{NaF}}{a_p^-} \right)$
AgF/Ag	AgF + e ⁻ ↔ Ag + F ⁻	148	-1.53	$E = E^0 + \frac{RT}{n\mathcal{F}} \ln \left(\frac{a_{AgF}}{a_p^-} \right)$

Couple	Solubility reaction input in HSC Chemistry	K	pO ²⁻ = f(K) Expression	pO ²⁻
ZrO ₂ /ZrF ₄	ZrO ₂ + 4F ⁻ ↔ ZrF ₄ + 2O ²⁻	3.40.10 ⁻²⁵	$pO^{2-} = -\frac{1}{2} \log \left(\frac{K a_p^{-4}}{a_{ZrF_4}} \right)$	11.7



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

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 (◇) and the peak potential (□) versus the square root of the potential scan rate. Working electrode: Ag (S = 0.36 cm²); auxiliary electrode: glassy carbon; comparison electrode: Pt

Reduction of Zr(IV) occurs in one step

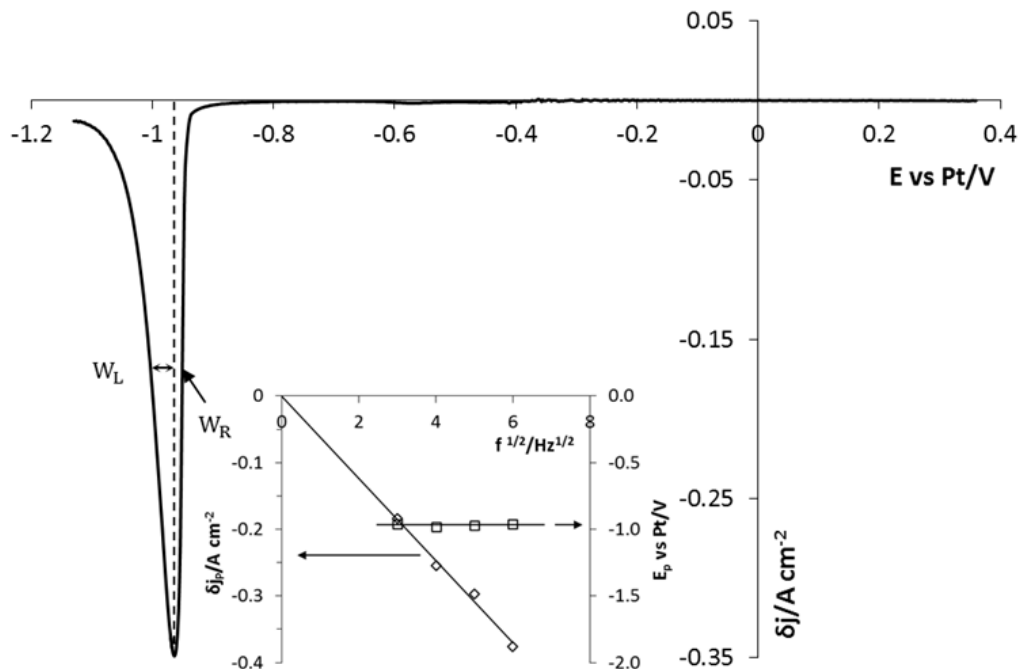
Reduction is controlled by diffusion of Zr(IV)

Quasi-reversible system

Diffusion coefficient $\rightarrow j_p \propto \sqrt{v}$
 $\rightarrow D_{Zr(IV)} = 1,21 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$

↓

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



Square wave voltammogram of the LiF-NaF-ZrF_4 ($m_0 = 0.06 \text{ mol.kg}^{-1}$) at 16 Hz, pulse height: 20 mV, step potential: 2 mV and 750 °C.
 Inset. Variation of the differential of the peak current density (\diamond) and the peak potential (\square) 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

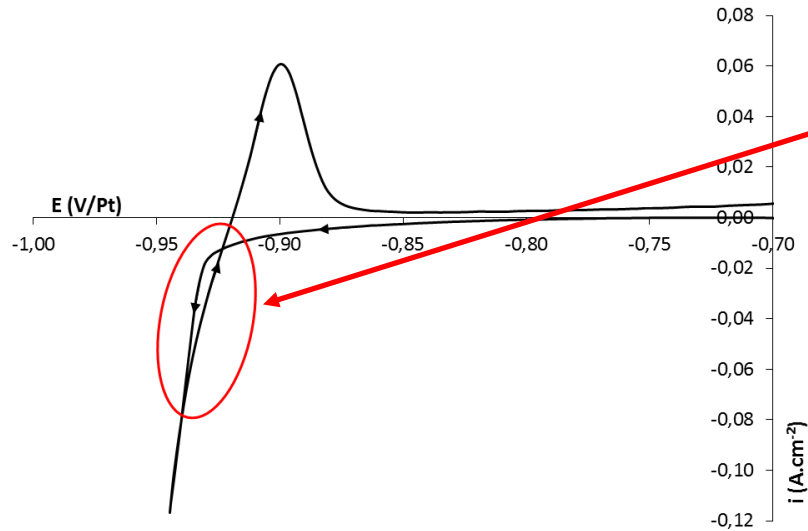
Number of exchanged electrons

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

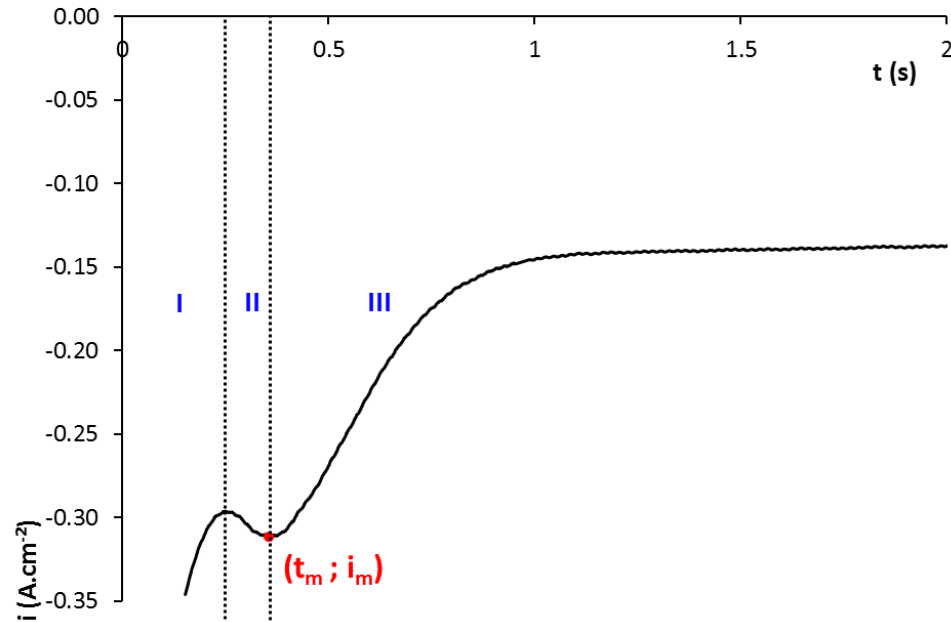
4 electrons exchange



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 $690\text{ }^\circ\text{C}$. 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
 $(t_m ; j_m) \rightarrow v_{\text{diffusion}} = v_{\text{growth crystals}}$
- **Part 3:** limitation of the reaction by the diffusion of Zr(IV) ions

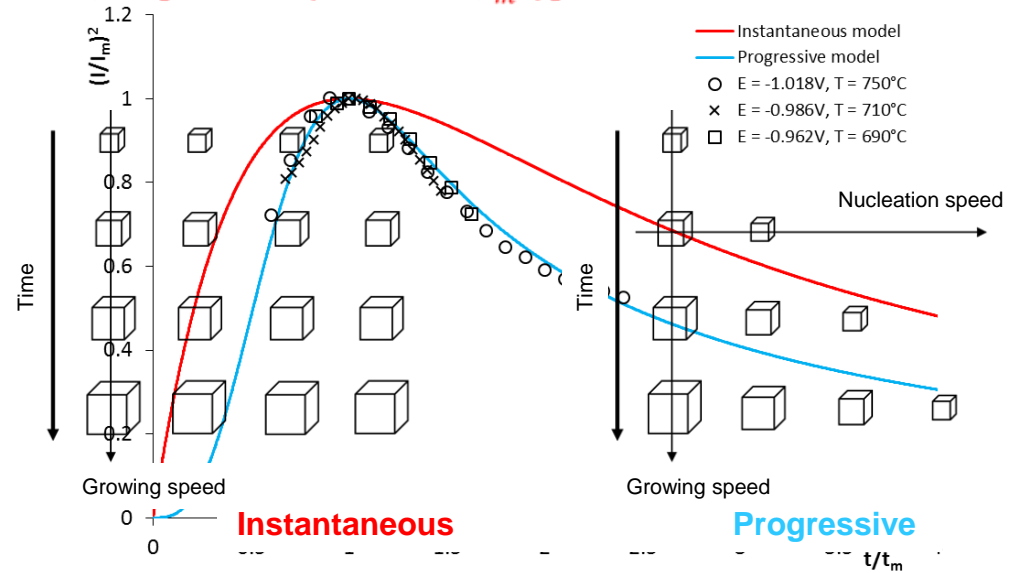
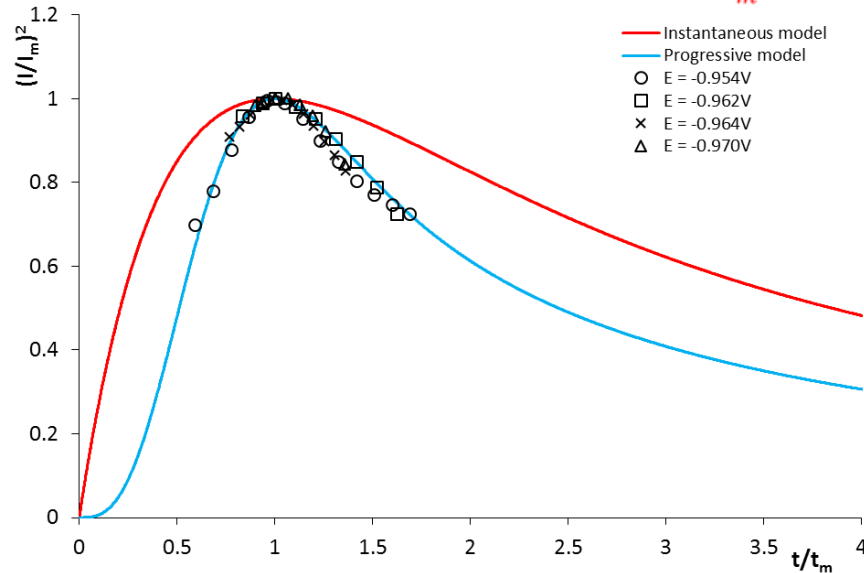


Non-dimensional models : $\left(\frac{I}{I_m}\right)^2 = f\left(\frac{t}{t_m}\right)$

➤ 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

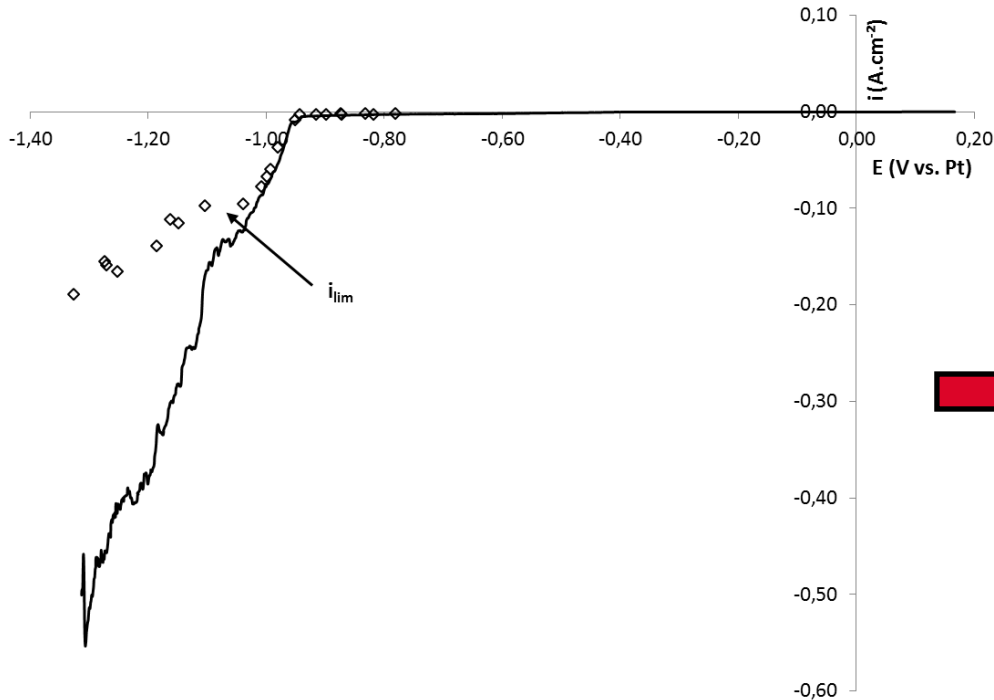
Determination of the limiting current

- Fluoride media : No reference electrode
⇒ Galvanostatic electrodeposition

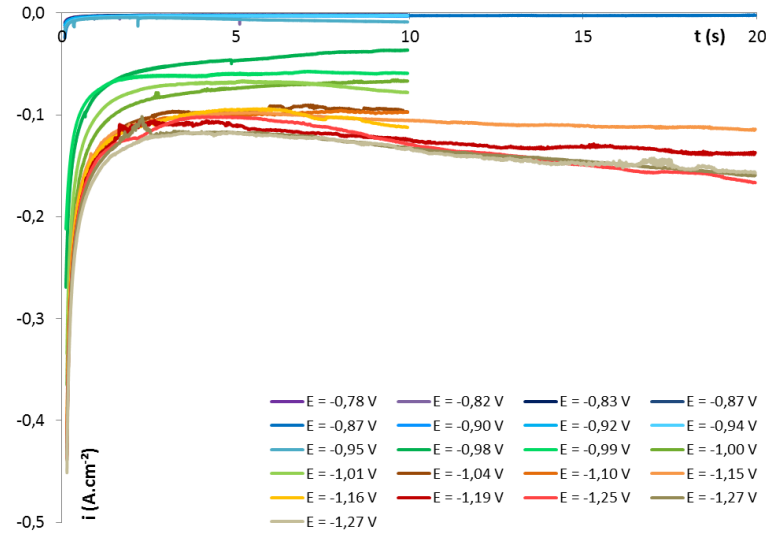
- System limited by Zr diffusion

⇒ Determination of the limiting current needed

Two techniques: Voltammetry (low scan range) or polarisation



Linear Voltamperogram on LiF-NaF-ZrF_4 ($C = 7.46 \cdot 10^{-2} \text{ mol/kg}$), scan range: 1 mV/s at 750°C and polarisation plots.



Chronoamperograms on LiF-NaF-ZrF_4 ($C = 7.46 \cdot 10^{-2} \text{ mol/kg}$) at 750°C different applied potentials.



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

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

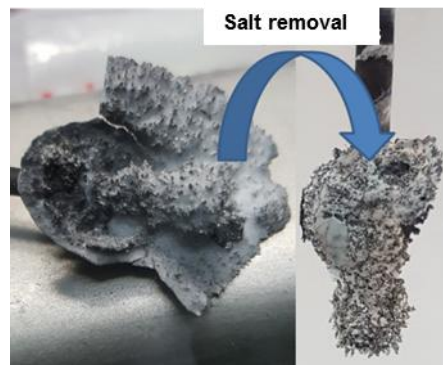
Higher applied current densities:

→ 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)

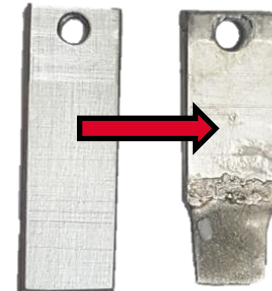


Cathodes : Zr, C or stainless steel

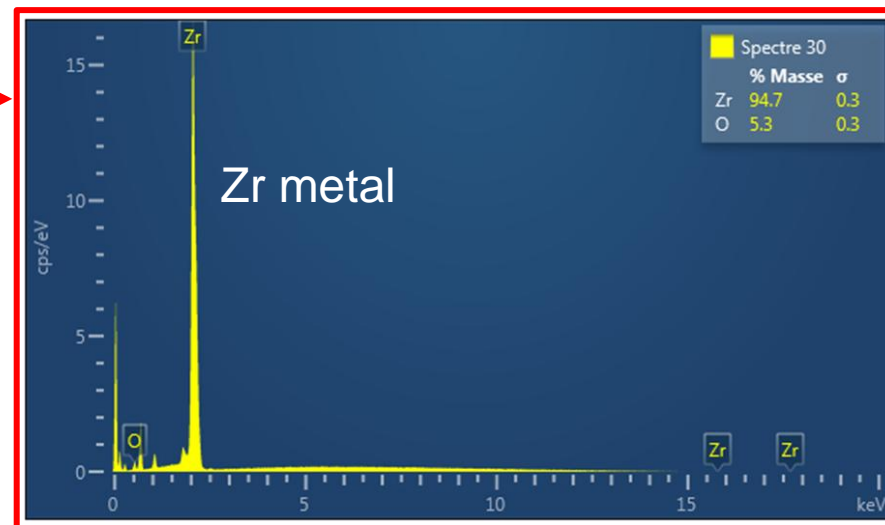
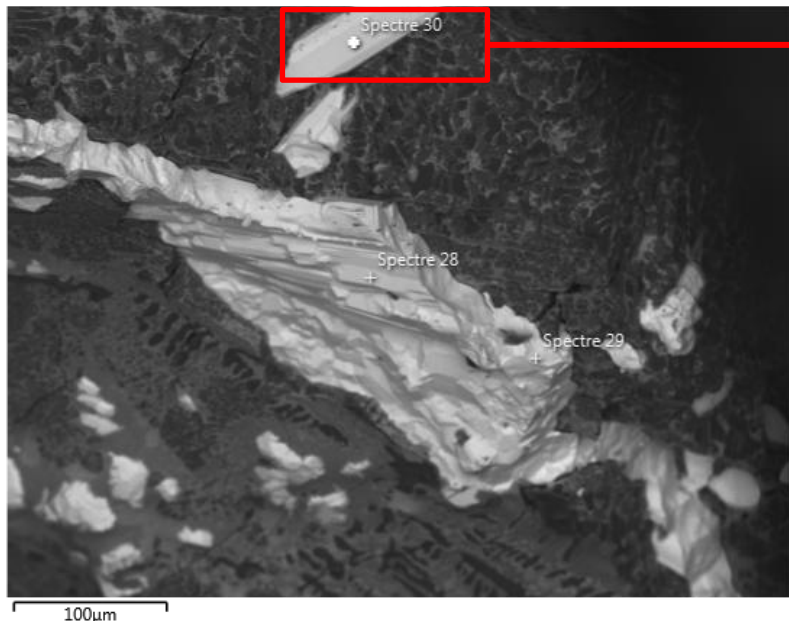


Dendritic aspect

Anode Zr



Consumption

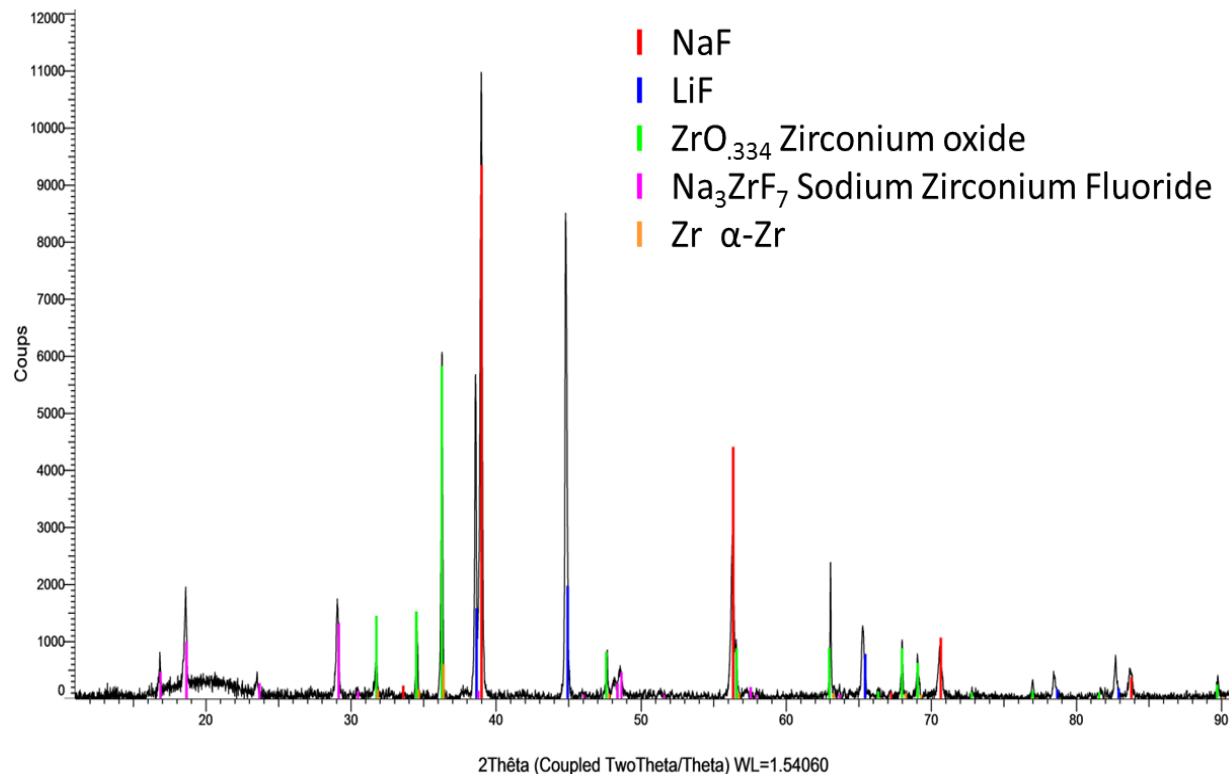


SEM analysis of Zr deposited on graphite electrode in LiF-NaF-ZrF_4 ($C = 0.55 \text{ mol.kg}^{-1}$) at 750°C , $J = -0.72 \text{ A.cm}^{-2}$

➔ Feasibility of pur Zr metal deposition demonstrated in LiF-NaF

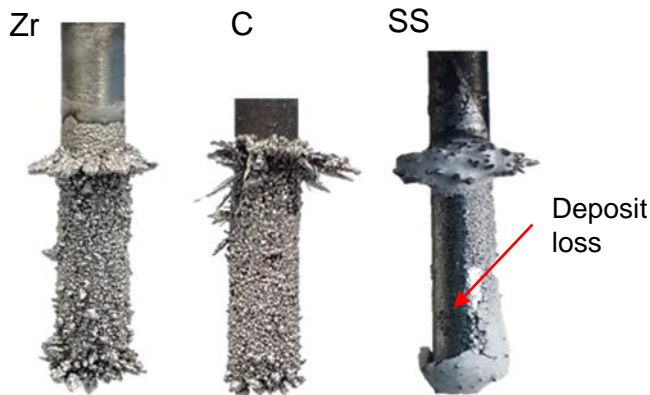
➤ XRD analysis:

- 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

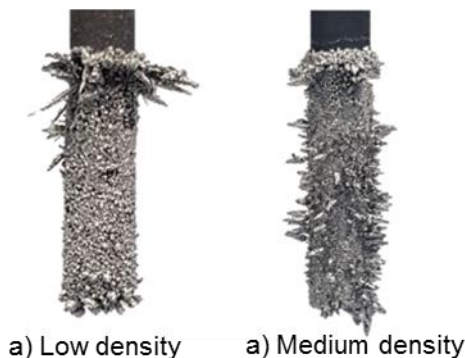


Photographs of cathodes after electrolysis runs in LiF-NaF-ZrF_4 on different substrate

Dense, compact and adherent deposit on Zr and C cathodes

Selection of the cathode material

Current density

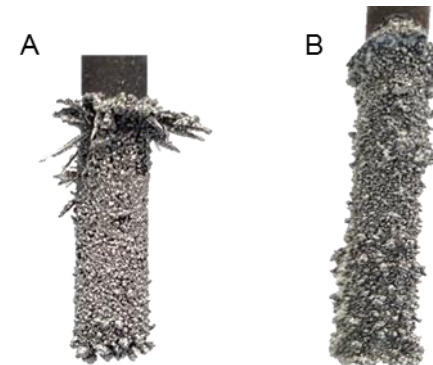


Photographs of cathodes after electrolysis runs in LiF-NaF-ZrF_4 at different current density

Strong effect of current density on the regularity

↑ current density ⇒ ↑ nuclei formed

ZrF_4 concentration



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

Moderate influence of concentration on the regularity

↑ concentration ⇒ ↑ nuclei formed

In good agreement with the Zr nucleation study

■ Electrochemical behavior in fluoride salts

- *Zr(IV) reduction in one step*



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

■ Electrocrystallisation 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*

→ \uparrow current density or \uparrow concentration \Rightarrow \uparrow nuclei formed

■ Next step

- *Tests with non irradiated Zircaloy*

Thank you for your attention

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