Zirconium(IV) electrochemical behavior and electrorefining in molten fluoride salts

D. Quaranta, E. Mendes, Laurent Massot, Mathieu Gibilaro, J. Serp

FROM RESEARCH TO INDUSTRY

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2018 INTERNATIONAL PYROPROCESSING RESEARCH CONFERENCE

Electrochemical behavior of zirconium in molten fluoride

Delphine QUARANTA[1], **Eric MENDES[1]**, Laurent MASSOT[2], Mathieu GIBILARO[2], Jérôme SERP[1]

[1] CEA Marcoule, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes, 30207 Bagnols-sur-Cèze, France

[2] Laboratoire de Genie Chimique, Université de Toulouse, UPS, CNRS, INPT, 118 Route de Narbonne, 31062, Toulouse Cedex 9, France

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Context
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*

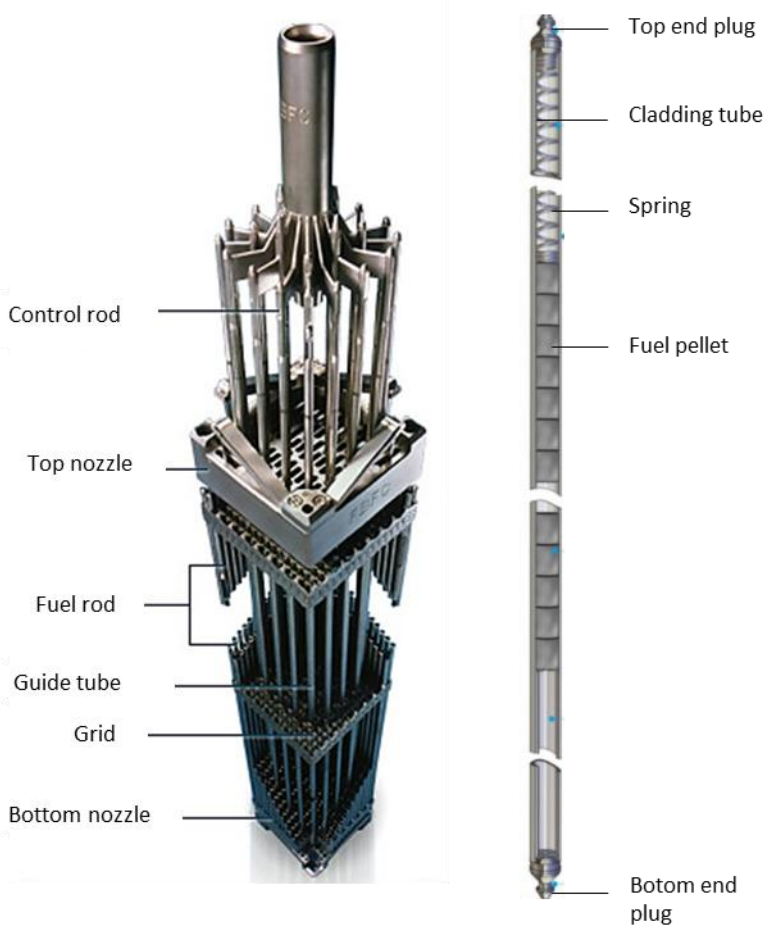
Activity coming from:

βγ elements:

Fission products (FPs): ^{3}H, ^{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

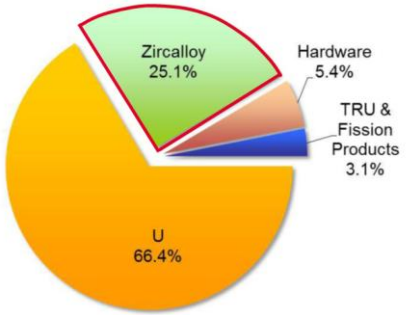


Schematic of an assembly of a French nuclear fuel

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

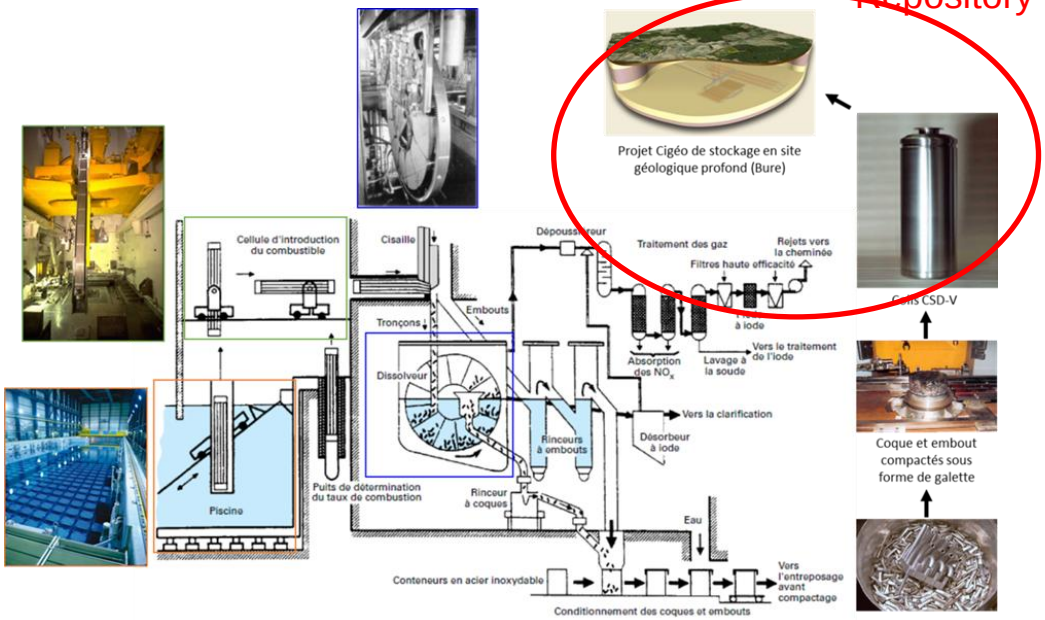
Context
Recycling Zr contained in Zircaloy cladding

- Spent fuel management in France (La Hague reprocessing plant)
  - *pool storage*
  - *shearing in 3-5 cm section*
  - *dissolution of UO_2 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*

Geological long term Repository



➢ 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

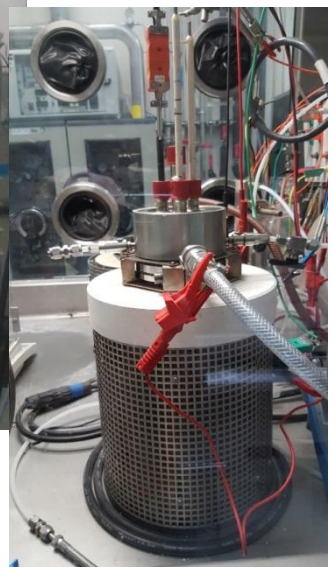
Experimental Setup

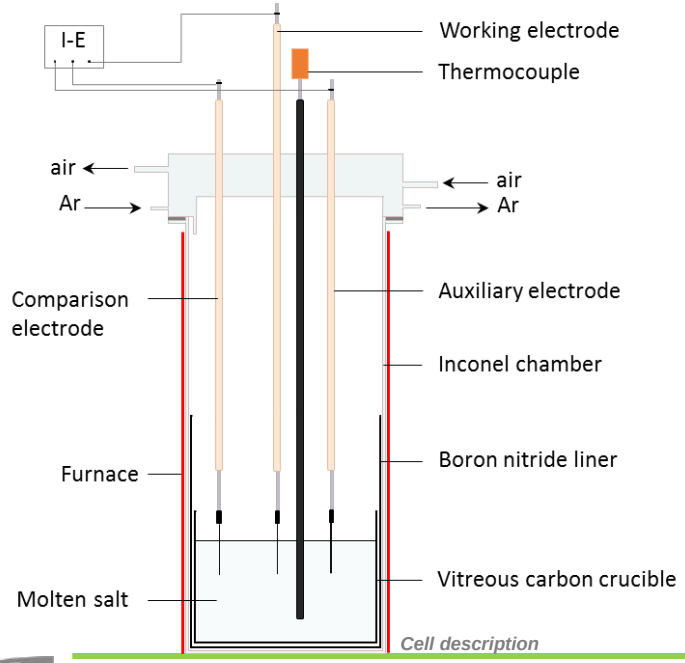
Salt media

- 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 H_2O and < 5 ppm O_2)



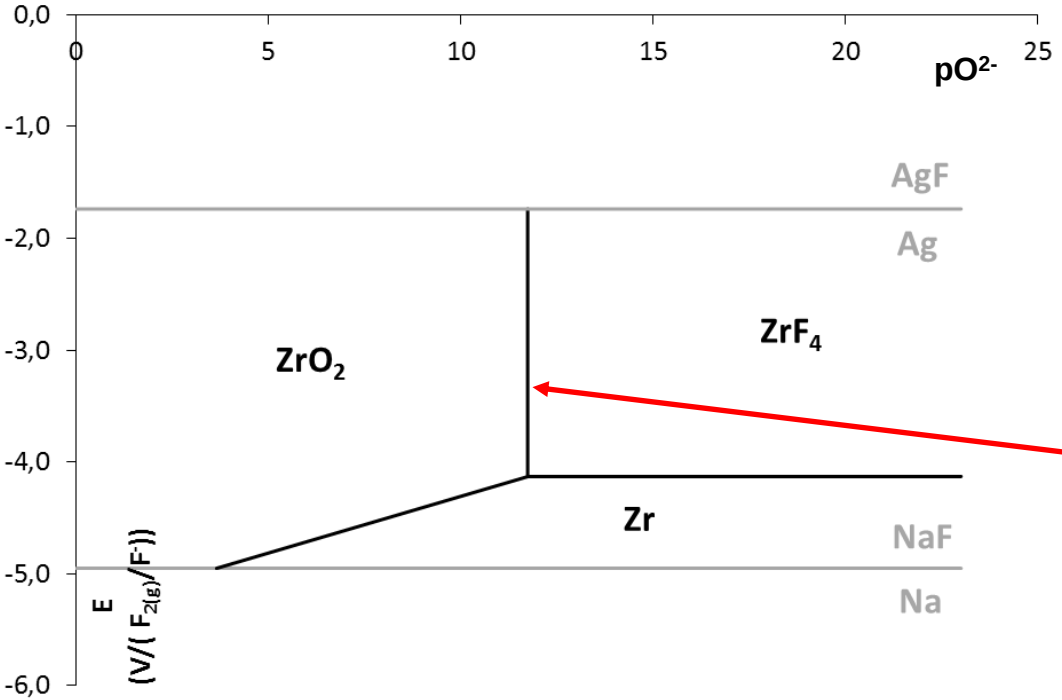


Cell description

Experimental conditions

- Temperature range 750 – 900°C
- ZrF_4 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 : pKs = 24.5

→ ***pO^{2-} = 11.7***

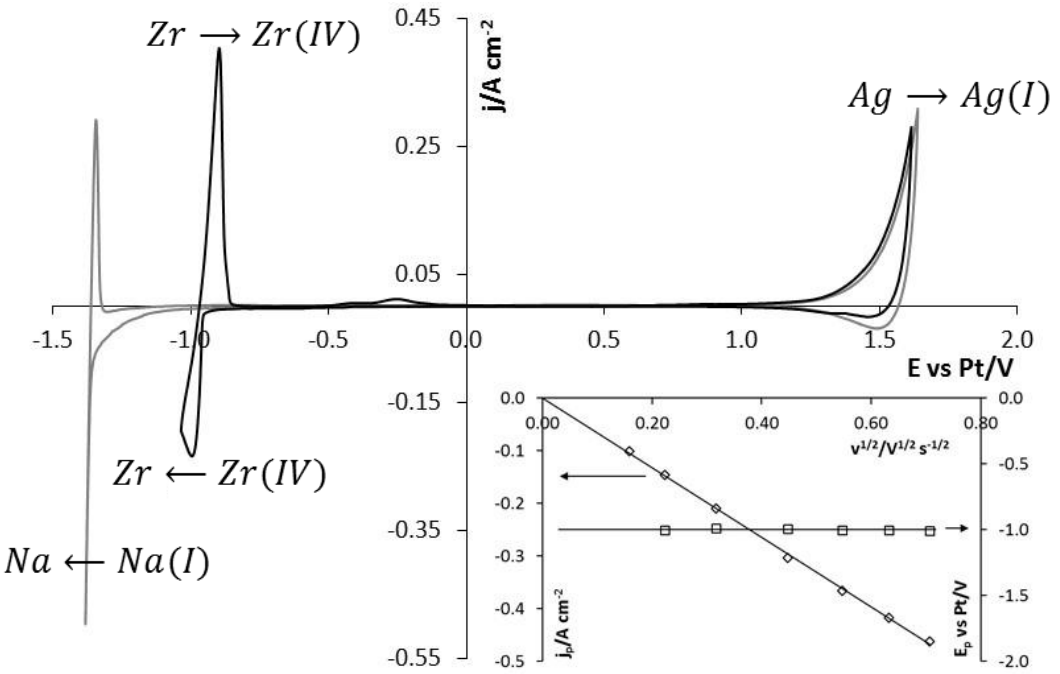
Zr very sensitive to presence of O^{2-} in the salt

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

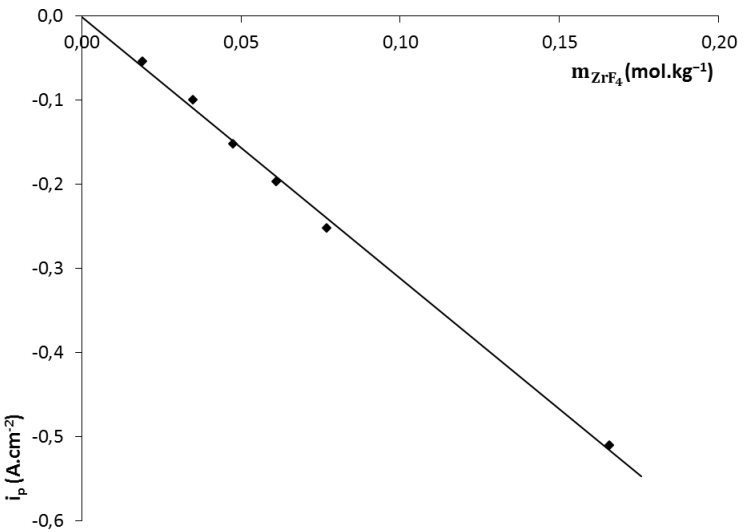
Couples	Redox reactions Inputs HSC Chemistry	ΔG^0 (kJ/mol)	E^0 (V/($F_{2(g)}/F^-$))	Expression
ZrF_4/Zr	$ZrF_4 + 4e^- \leftrightarrow Zr + 4F^-$	1574	− 4.08	$E = E^0 + \frac{RT}{n\mathcal{F}} \ln\left(\frac{a_{ZrF_4}}{a_{F^-}{}^4}\right)$
ZrO_2/Zr	$ZrO_2 + 4e^- \leftrightarrow Zr + 2O^{2-}$	2053	− 5.32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

Couple	Solubility reaction input in HSC Chemistry	K	$pO^{2-} = f(K)$ Expression	pO^{2-}
ZrO_2/ZrF_4	$ZrO_2 + 4F^- \leftrightarrow ZrF_4 + 2O^{2-}$	$3.40.10^{-25}$	$pO^{2-} = -\frac{1}{2}\log\left(\frac{K\, a_{F^-}{}^4}{a_{ZrF_4}}\right)$	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 (◊) and the peak potential (□) versus the square root of the potential scan rate. Working electrode: Ag (S = 0.36 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) →

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

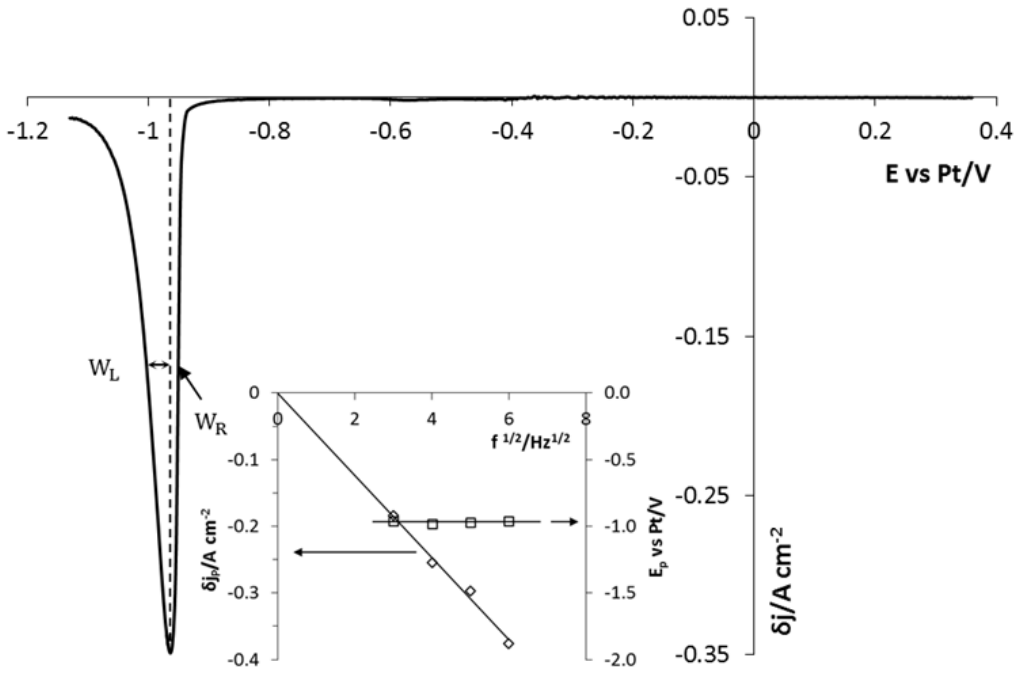
→ $D_{Zr(IV)} = 1,21.10^{-5}\ cm^2.s^{-1}$

↓

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

Quasi-reversible system

Electrochemical behavior: square wave voltammetry



Square wave voltammogram of the LiF–NaF–ZrF_4 (m_0 = 0.06 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 (◊) and the peak potential (□) versus the square root of the frequency. Working electrode: Ag (S = 0.35 cm^2); auxiliary electrode: glassy carbon; comparison electrode: Pt

Reduction of Zr(IV) in one step →

Number of exchanged electrons

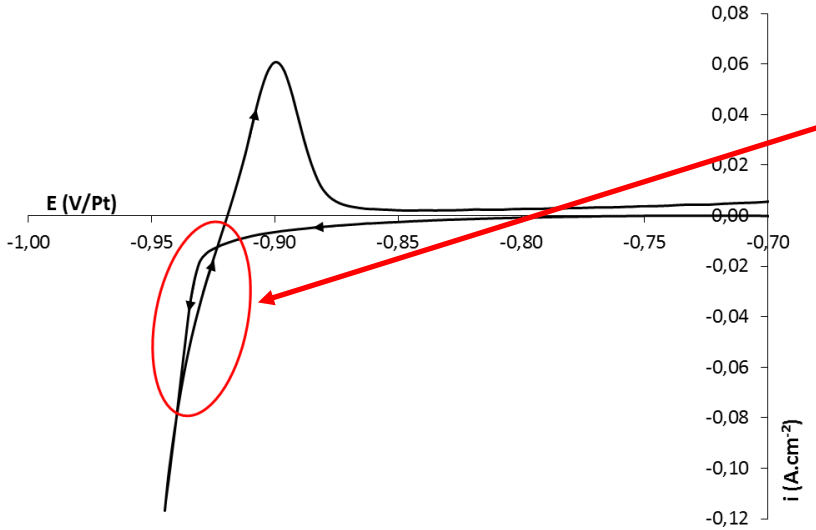
$$W_{1/2} = 3.52\frac{RT}{n\mathcal{F}} = 2W_L$$

4 electrons exchange

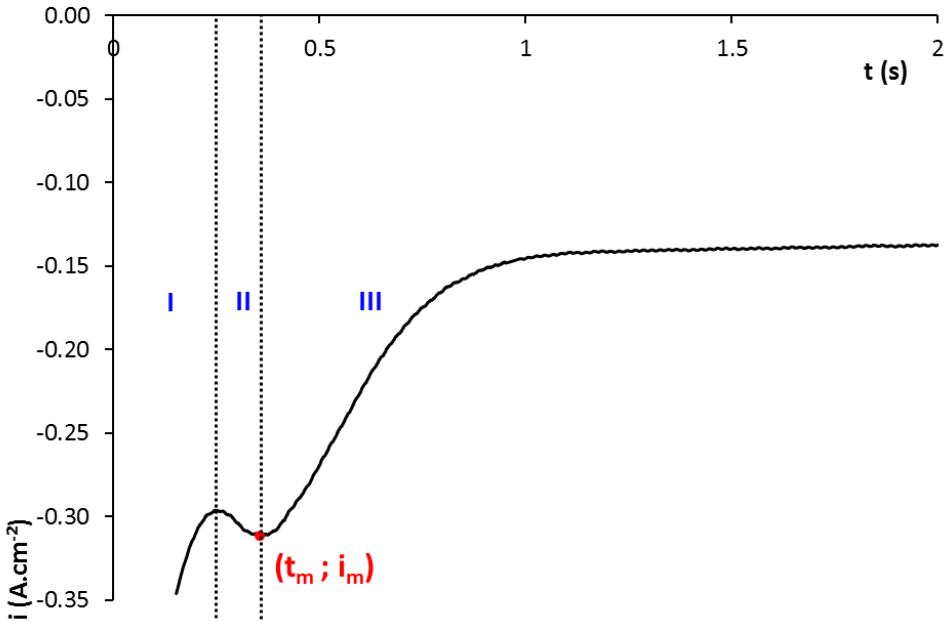
$$Zr(IV) + 4e^- \rightarrow Zr$$

Soluble/insoluble system

Electrocrystallisation process 1/2



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



Chronoamperogram on silver electrode at η = −0.969V vs Pt in LiF–NaF–ZrF_4 (m_0 = 0.17 mol.kg^{-1}) at 690 °C. Working electrode: Ag (S = 0.35 cm²); auxiliary electrode: glassy carbon; comparison electrode: Pt

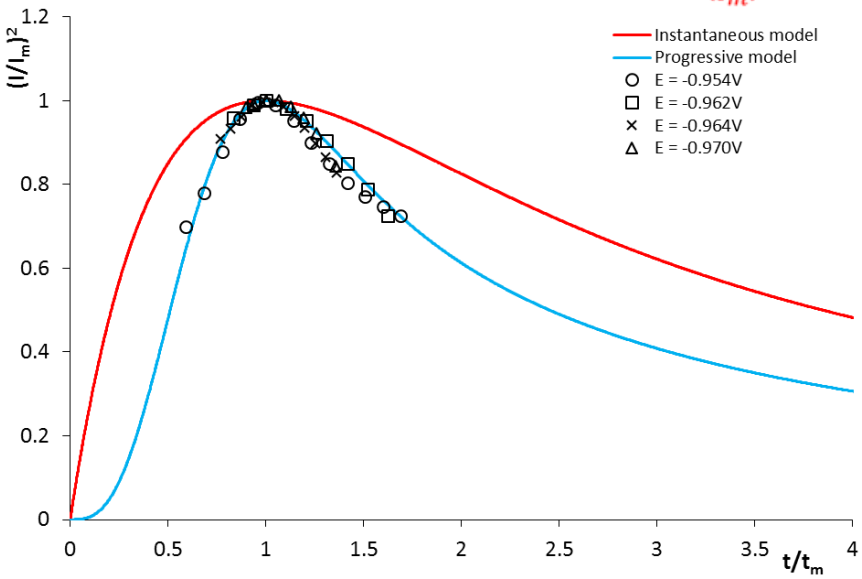
- Chronoamperometry → 3 areas:
  - **Part 1:** charging of the double layer and the formation of the first germs
  - **Part 2:** growth of the crystals

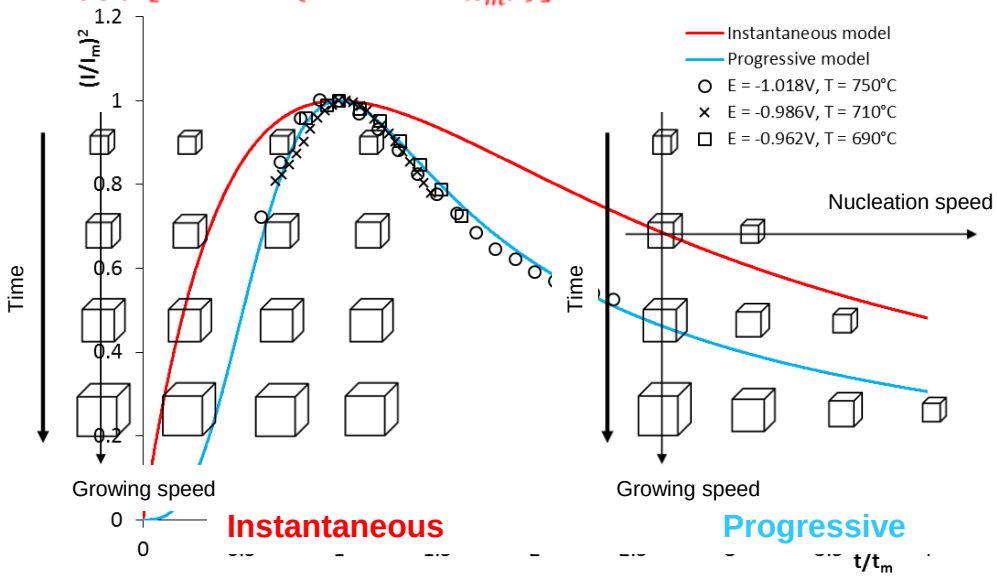
    $(t_m ; j_m) \rightarrow v_{diffusion} = v_{growth\ crystals}$
  - **Part 3:** limitation of the reaction by the diffusion of Zr(IV) ions

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

Electrocrystallisation process 2/2

- 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 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

ELECTRODEPOSITION OF ZR 1/4

Determination of the limiting current

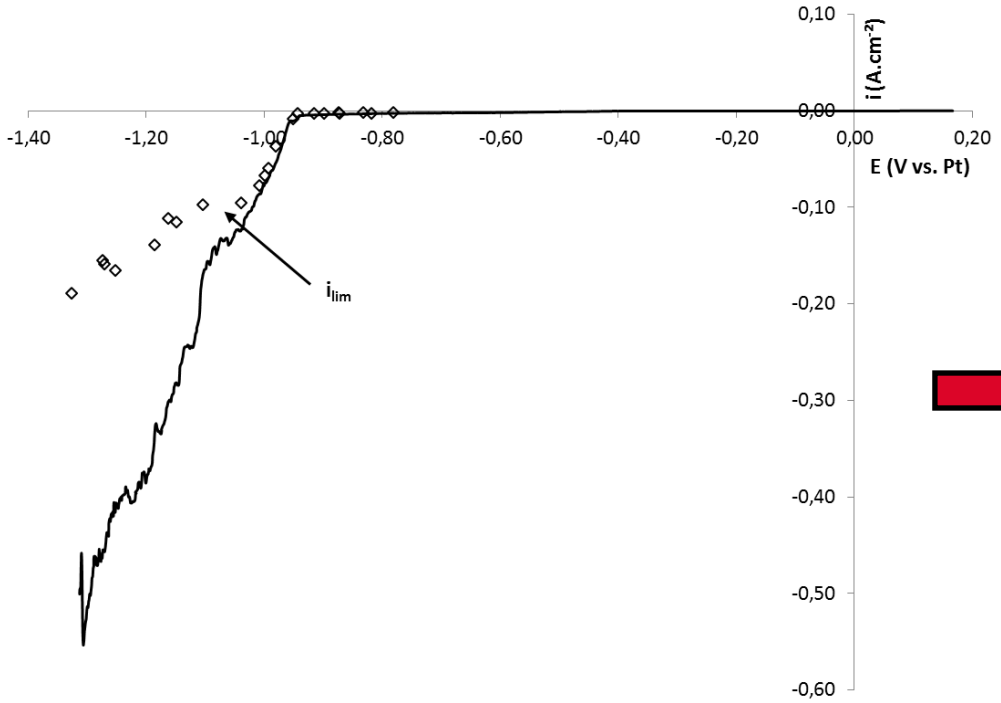
- Fluoride media : No reference electrode

  ⇒ Galvanostatic electrodeposition

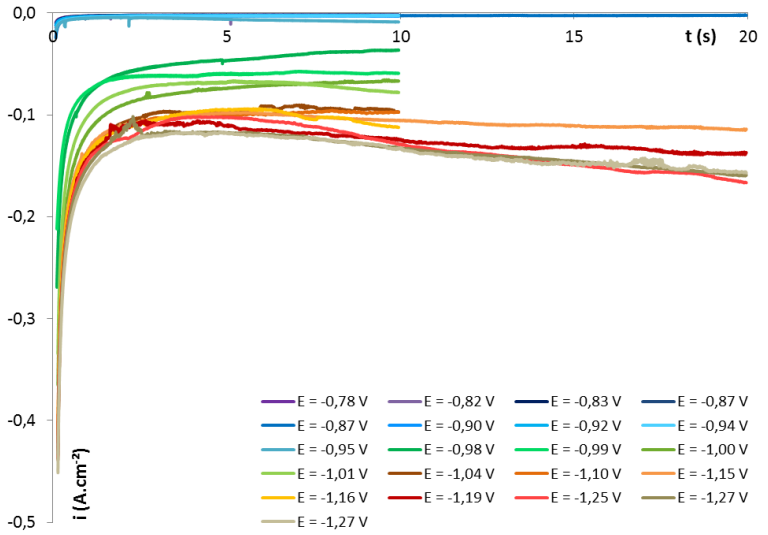
- **System limited by Zr diffusion**

  ⇒ **Determination of the limiting current needed**

Tow technics: Voltammetry (low scan range) or polarisation



***Linear Voltamperogram** on LiF-NaF-ZrF_4 (C = 7.46.10^{-2}mol/kg), scan range: **1mV/s** at 750°C and polarisation plots.*



***Chronoamperograms** on LiF-NaF-ZrF_4 (C = 7.46.10^{-2}mol/kg) at 750°C **different applied potentials**.*

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

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

Higher applied current densities:

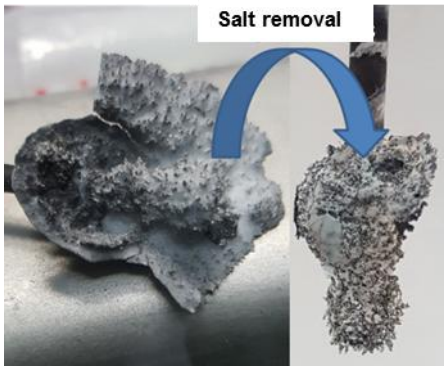
→ ***possible co-reduction of Na^+***

ELECTRODEPOSITION OF ZR 2/4

➢ Electrodeposition experimental results:

Deposit loss can be observed on several experiments

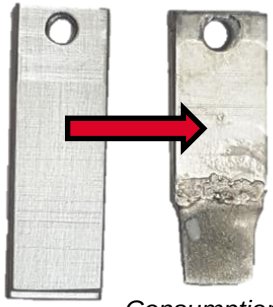
Important faradic yields reached > 80%
Difficulties to estimate it *(salt remaining removal)*



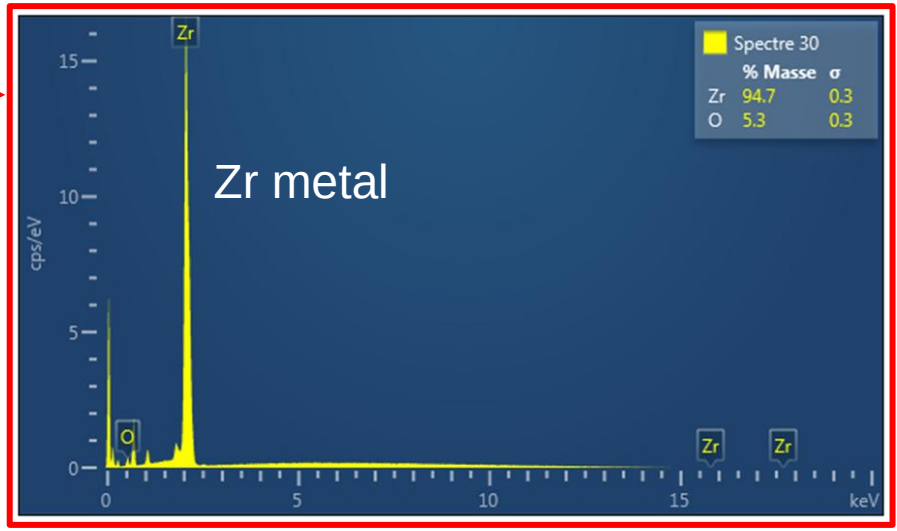
Cathodes : Zr, C or stainless steel

Dendritic aspect

Anode Zr



Consumption



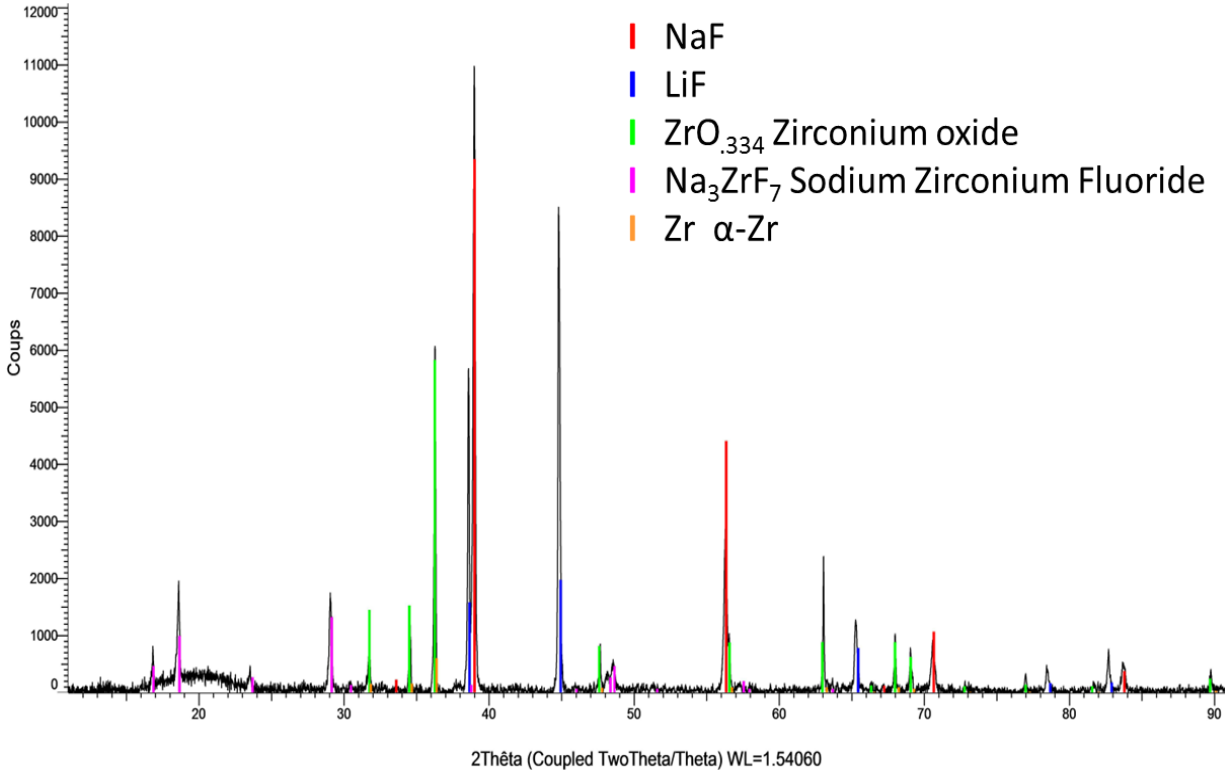
SEM analysis of Zr deposited on graphite electrode in LiF-NaF-ZrF_4 (C = 0.55 mol.kg^{-1}) at 750°C, J = – 0.72 A.cm^{-2}

Feasibility of pur Zr metal deposition demonstrated in LiF-NaF

ELECTRODEPOSITION OF ZR 3/4

➢ XRD analysis:

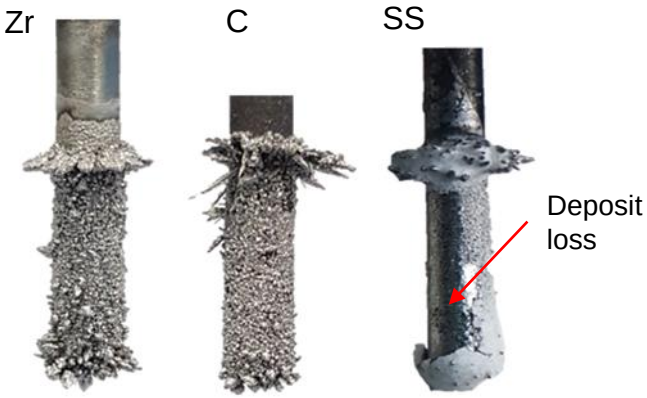
- Confirmation of the SEM analysis
- Residual salt adhered onto the electrode
- Presence of oxygen: contamination of the deposit during sample preparation *(under air atmosphere)*



ELECTRODEPOSITION OF ZR 4/4

➢ Influence of the operating parameters

Substrate of cathodes

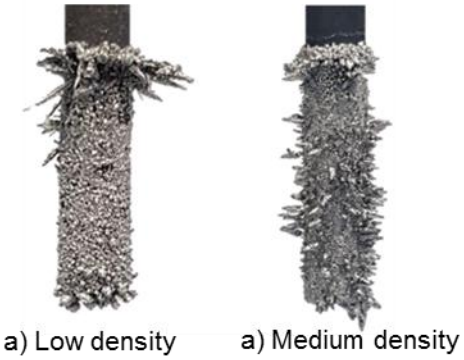


Photographs of cathodes after electrolysis runs in LiF–NaF–ZrF_4 on different substrate

Dense, compact and adherent deposit on Zr and C cathodes

Selection of the cathode material

Current density

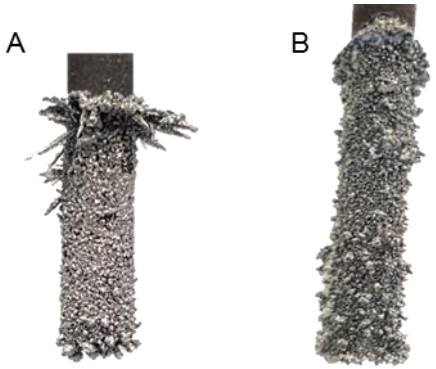


Photographs of cathodes after electrolysis runs in LiF–NaF–ZrF_4 at different current density

Strong effect of current density on the regularity

↑ current density ⇒ ↑ nuclei formed

ZrF_4 concentration



Photographs of cathodes after electrolysis runs at 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

Conclusions and prospects

- Electrochemical behavior in fluoride salts
  - *Zr(IV) reduction in one step*

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

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

    → *↑current density or ↑ concentration ⇒ ↑ nuclei formed*
- Next step
  - *Tests with non irradiated Zircaloy*

Thank you for your attention

Acknowledgments:

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Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Marcoule | 30207 Bagnols sur Cèze
T. +33 (0)4 66 79 62 51 | F. +33 (0)4 66 79 65 67

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

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