SACSESS
Safety of actinide separation processes

European Commission

# Safety related to refractory oxide fuel treatment: Head-end conversion by electroreduction of CERMET fuel surrogate Mo-$CeO_2$ in LiCl-$Li_2O$

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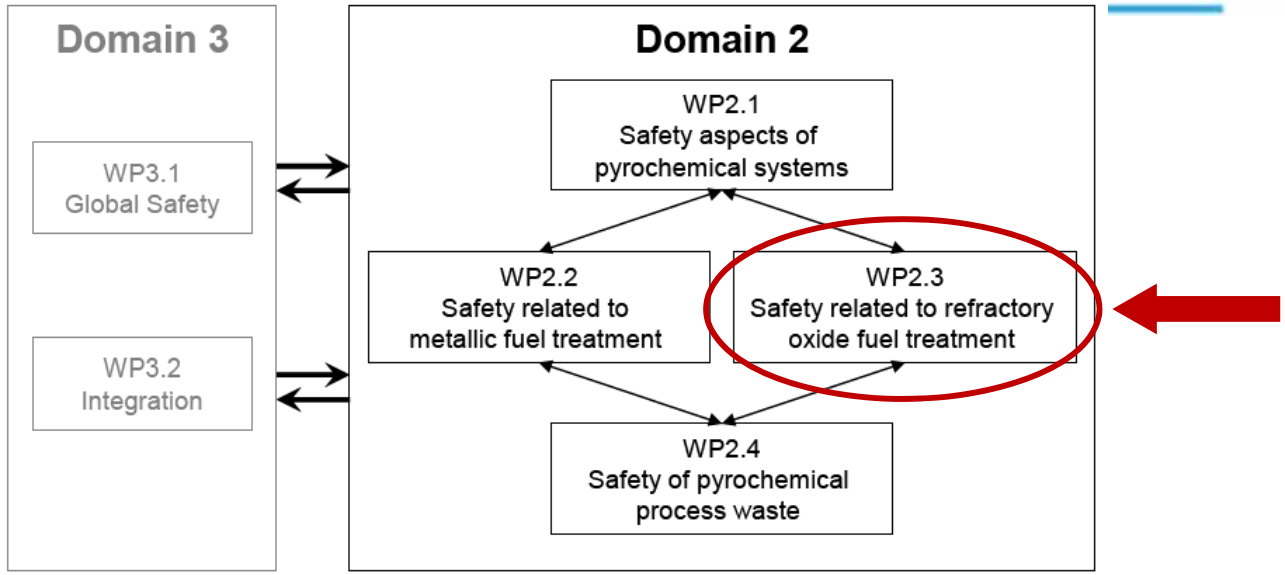
# Main ITU activities

- Fundamental and Applied Actinide Research
- Safety of Conventional/Advanced Nuclear Fuels
- Nuclear Waste Disposal
- Advanced Nuclear Fuel Cycle
- Forensic Analysis and Combating Illicit Trafficking
- Nuclear and Trace Analysis for Safeguards
- Alpha-Immunotherapy

## Advanced Nuclear Fuel Cycle

- Preparation of advanced experimental nuclear fuels (e.g., metallic, inert matrix fuels…)
- Investigation of specific properties and irradiation performance testing
- Development of efficient processes for the recovery of long-lived radionuclides
  - hydrometallurgical extraction separation processes
  - pyrochemical separation processes




## DM2 - Safety of pyrochemical processes

**WP2.3** To assess safety issues related to **refractory oxide fuel treatment**

⇒ **CERCER ($MgO-AnO_2$) and CERMET ($Mo-AnO_2$)**
– transmutation targets, multirecycling of An required

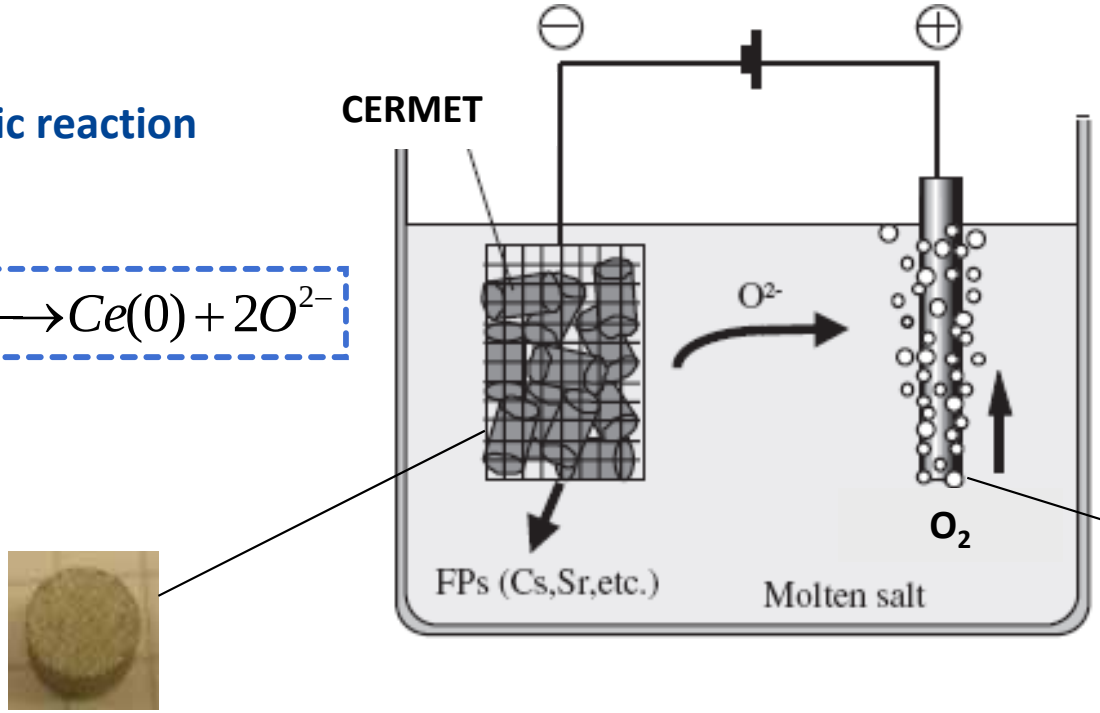
⇒ Aim: complete **recovery of the actinides from CERCER and CERMET fuels** and a separate **recycling of Mo** from CERMET fuel

⇒ the conversion and separation procedures will be optimized

# Electroreduction of $AnO_2$-Mo targets - principle

**Cathodic reaction**

$$CeO_2 + 4e^- \longrightarrow Ce(0) + 2O^{2-}$$




**Anodic reaction**
(inert anode: Pt)

$$2O^{2-} \longrightarrow O_2 + 4e^-$$

**Electrolyte**
molten LiCl-1wt% $Li_2O$ at 650°C

**Aim:** **To produce a metallic end-product from a CerMet target ($CeO_2$-Mo) for further electrorefining**

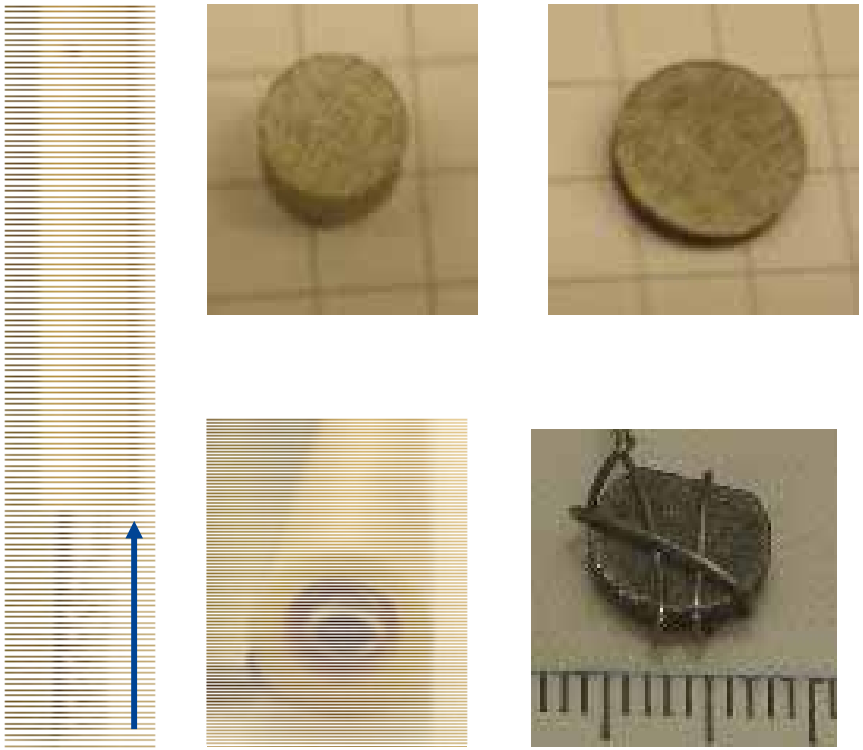
# Experimental plan

1. Experimental set-up
2. Assessment and validation of analytical scheme for characterisation of the pellets before and after electroreduction
3. Characterisation of the initial material
4. Electroreduction using different experimental conditions (charge excess, current density)
5. Characterisation of the reduced pellets
6. Evaluation of the results

# Experimental set-up

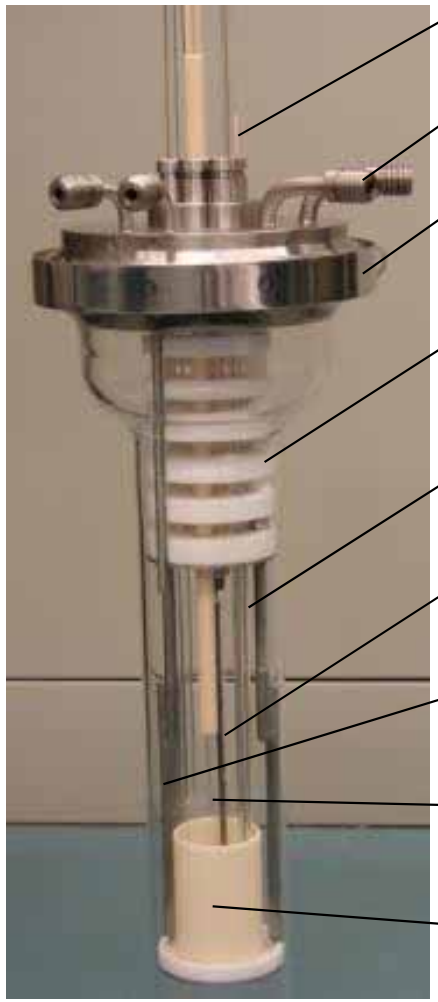
**CERMETs:** $CeO_2$-Mo

7 Pellets ~ 0.25-1.5 g



Pt anode

Mo-wired pellet



Thermocouple

Water cooling inlet / outlet

Inconel flange with gastight ports for electrodes

Quartz main body, inside ceramic thermal shielding

Cathode: Mo mesh basket

Anode: Pt wire

Reference electrode: Ag/AgCl in Mullite

Working electrode: W wire for electrochemical measurements

Alumina crucible with LiCl-$Li_2O$ melt

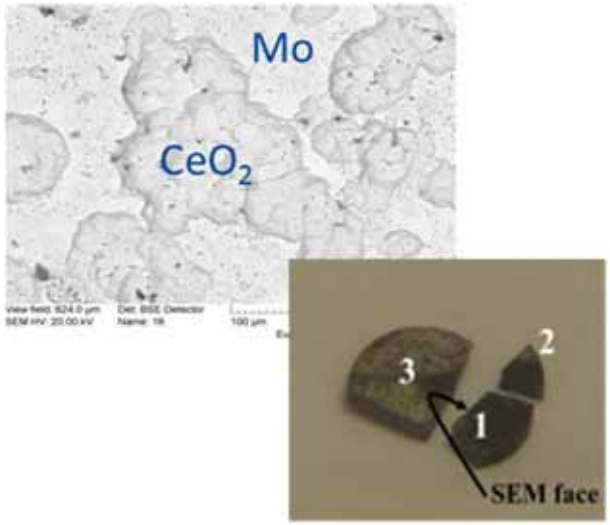
**Quartz cell with water-cooled Inconel flange**

## Pellet analyses

1. **Elemental oxygen analysis** ✓
   combustion of a sample with graphite powder → quantification of $CO_2$ released by IR spectroscopy → amount of $CeO_2$

2. **Microscopic morphology analysis**
   by SEM, BSE, EDX ✓

3. **ICP-MS** to quantify the reduced Ce metal ✓
   Ce, Mo – dissolved in 8M $HNO_3$ for analysis,
   $CeO_2$ – not dissolved



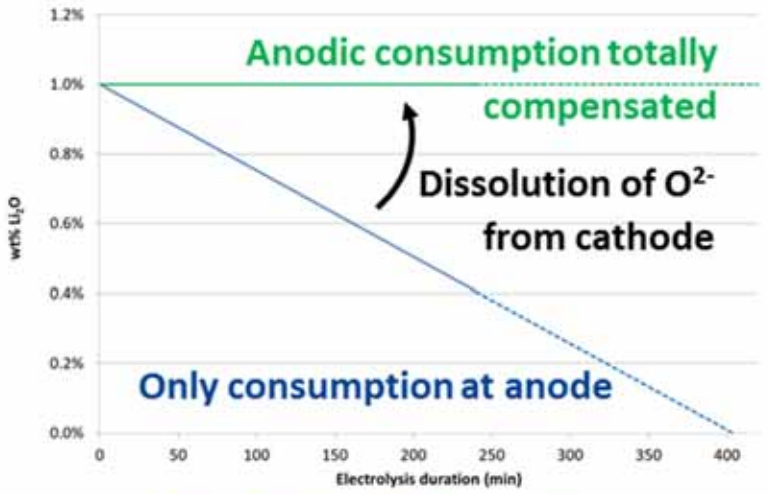
# Assessment and validation of analytical scheme

## Pellet analyses

1. **X-ray diffraction** ✗
   omitted – too high uncertainty due to likely unwanted oxidation of the reduced sample during the preparation and analysis
2. **Gas-burette analysis** ✗
   quantification of released $H_2$ by hydrolysis of the reduced reactive metal
   omitted - too high uncertainty due to co-dissolution of Mo

## Salt analyses

1. **Titration** ✓
   salt sample dissolved in water,
   the dissolved $Li_2O$ titrated by 0.01 M HCl
2. **ICP-MS analysis** ✓
   Solution analysed for Ce, Mo, Pt



Hypothesis : i=200mA, $m_{salt}$=75g

# Characterisation of the pellets before reduction

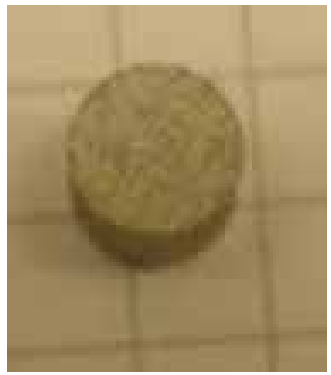
| Sample | | 014 | 015 |
|---|---|---|---|
| Measured by image treatment | %surf. Mo | 77% | 72% |
| | %surf. $CeO_2$ | 11% | 17% |
| | %surf. pores | 10% | 11% |
| | Total | 97% | 100% |
| | %vol Mo | 88% | 81% |
| | %vol $CeO_2$ | 12% | 19% |
| Pores size min (µm) | | 1 | 1 |
| Pores size max (µm) | | 30 | 20 |
| $CeO_2$ size min (µm) | | 10 | 10 |
| $CeO_2$ size max (µm) | | 200 | 200 |
| vol% $CeO_2$ | | 10% | 20% |
| m pellet (g) | | 0.774 | 0.541 |
| m $CeO_2$ (mg) | | 56 | 80 |
| O measured by ONH (wt %) | | 1.4% | 2.7% |
| O theoretical (wt%) | | 1.3% | 2.8% |
| ΔONH | | 1% | -2% |

## Main properties measured:

- Porosity: 9 -27 vol%
- Pores size: 1-30 µm
- $CeO_2$ size: 10-200 µm
- Amount of O close to theory

## Fabrication:

- 2005, pressed uniaxially at 500 Mpa, sintered at 1650C, 5 -8 h, Ar-6%$H_2$



# Electroreduction of the pellets – experimental parameters

Different initial materials and experimental conditions – possibility to compare the influence of **porosity, $CeO_2$ content and current density** on the reduction yield

| Run | $CeO_2$ (vol%) | Porosity (vol%) | Current (mA) | Current density (mA/cm²) | Charge (C) | $\%Q_{theo}$ |
|---|---|---|---|---|---|---|
| 014 | 10% | 9% | 20 | 6.4 | 236 | 189% |
| 016 | 30% | 13% | 100 | 33.6 | 840 | 197% |
| 017 | 40% | 11% | 200 | 60.1 | 1300 | 208% |
| 130b-131b | 20-40% | 14-27% | 200 | 36.3 | 554 | 98% |
| 130-131 | 20-40% | 14-27% | 200 | 28.8 | 2600 | 294% |

- Porosity
- Current density
- Charge

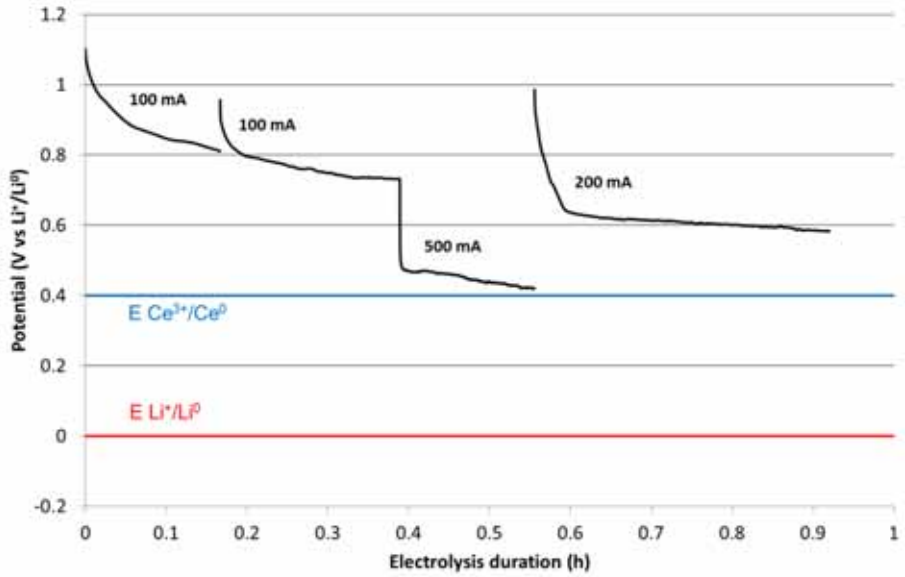
- $CeO_2$ amount
- Porosity

Runs 014 – 017: One single pellet reduced

Runs 130 – 131: Two pellets reduced together to assure exactly the same conditions for the comparison

# Electroreduction of the pellets – pre electrolysis

Galvanostatic electrolysis, only the current passed at potential lower than $CeO_2/Ce^0$ accounted for current efficiency calculation




**Pre-electrolysis on Mo basket + pellet**

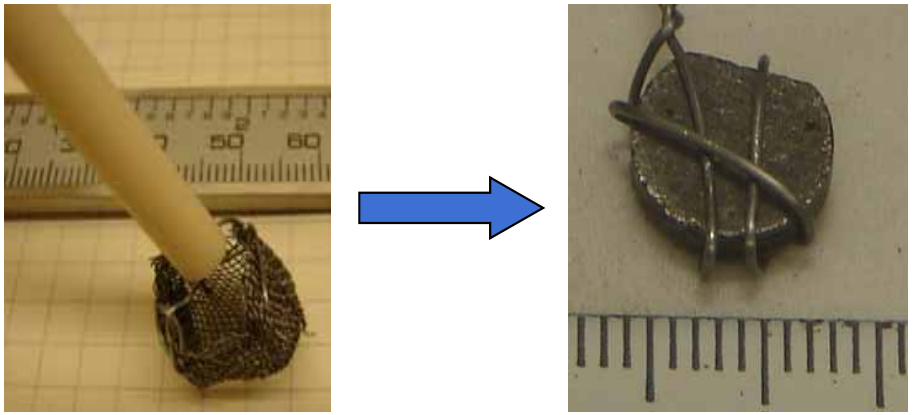
**Current due to :**

- Oxidation of the outside layer of Mo in the pellets due to a long storage (9 years)
- Oxide layer on the Mo basket used to contain the pellet (cathode)

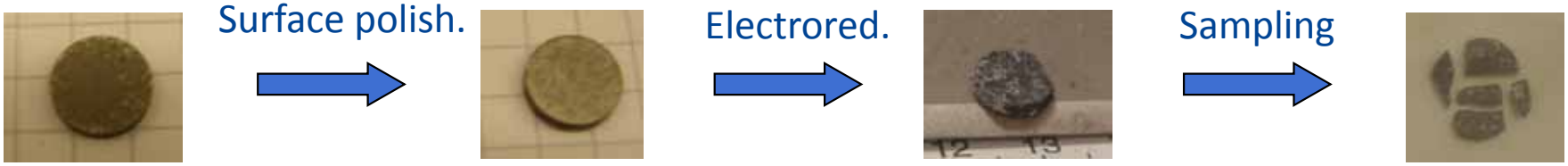
**Long electrolysis and high current needed to remove Mo oxides:**

- Risk of damaging the Pt anode (limiting anodic current: 200 mA)

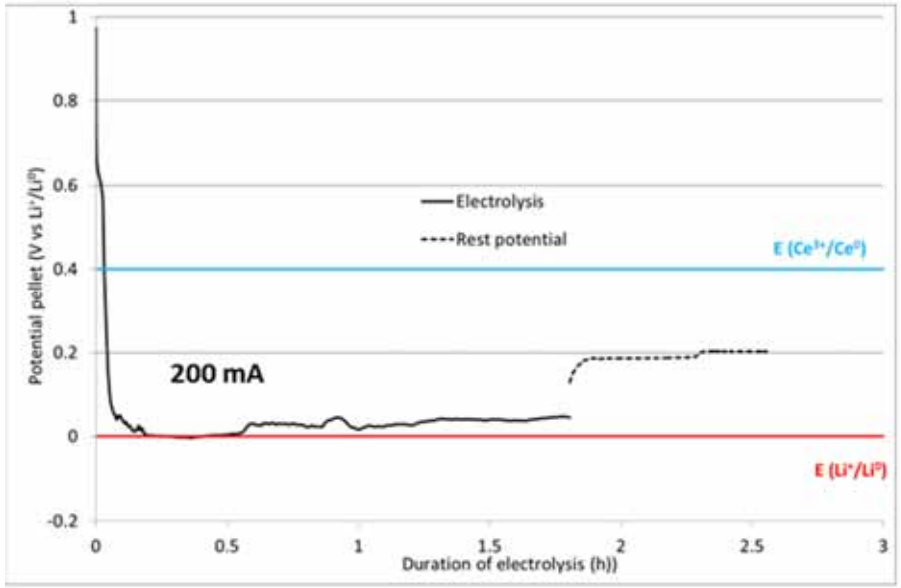
⇨ Mo basket cannot be used, pellet attached only by Mo wire

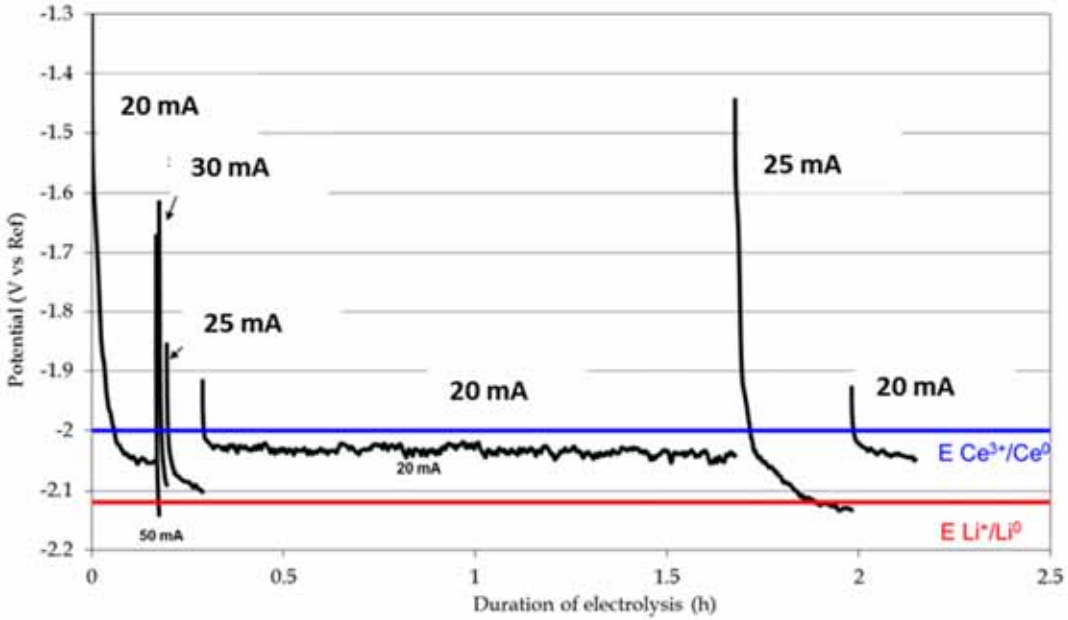


# Electroreduction of the pellets - electrolysis




Development of potential of the pellet during the electroreduction using different currents




Very low currents – potential above Li reduction, usable currents – Li reduction takes place

Likely not only direct electroreduction, but combined with chemical reduction by the formed Li metal

# Characterisation of the reduced pellets – problems of evaluation

B: Bulk S: Surface (<600µm) A: Average ρ: reduction yield

| Pellet | 017 | | | 130b | | | 131b | | |
|---|---|---|---|---|---|---|---|---|---|
| Origin | B | S | A | B | S | A | B | S | A |
| $\rho_{SEM}$ | 50% | 100% | 80% | 15% | 100% | 68% | 55% | 55% | 55% |
| $\rho_{O}$ | 44% | 49-58% | 50% | 47-65% | | | 68-69% | | |
| $\rho_{ICP-MS}$ | 44% | 51-78% | 60% | 25% | | | 40% | | |
| $\rho_{estim.}$ | **60 %** | | | **55 %** | | | **55 %** | | |
| Faradic yield | 29% | | | 54% | | | | | |

**Main identified problems of the evaluation:**

**SEM:** difficult to discriminate the porosity on reduced samples from images with poor contrast = likely overestimation of the reduction yield

**O content analysis:** trustworthy, but official uncertainty is high (1%, but official value up 20%, not validated method yet)

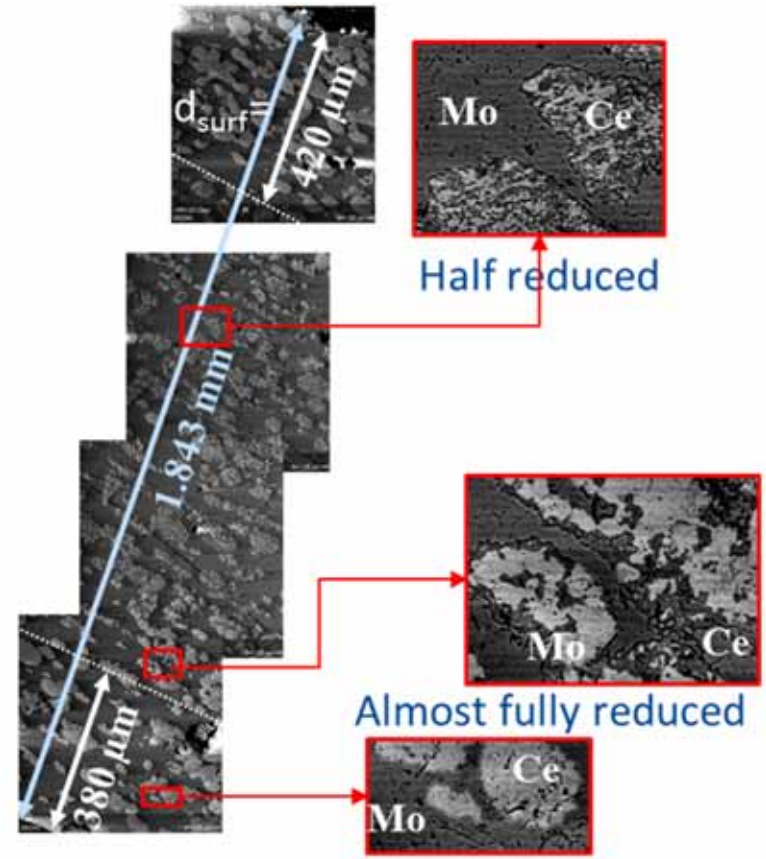
**ICP-MS:** very sensitive to the dissolution time

- short time = poor dissolution of Mo and embedded Ce
- long time = dissolution of $CeO_2$ starts

+ difficulty in averaging on the whole pellet

# Evaluation of results - effect of porosity

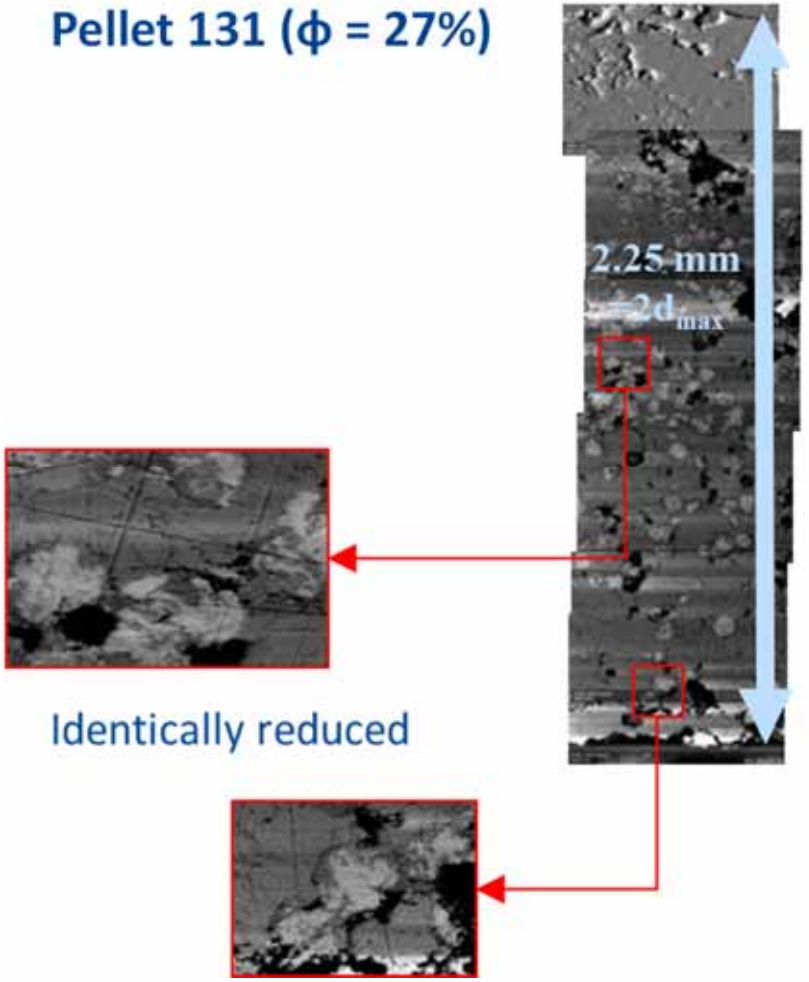
## Pellet 017 (ϕ = 14%)




**Low porosity**

– surface reduced, bulk 50% reduced

## Pellet 131 (ϕ = 27%)




**High porosity**

– surface and bulk reduced identically

# Evaluation of results - effect of porosity

| Pellet | $d_{max}$ (µm) | $d_{surf.}$ (µm) | $\rho_{surf.}$ (%) | $\rho_{bulk}$ (%) | $\rho_{tot}$ (%) | Porosity (vol%) |
|---|---|---|---|---|---|---|
| 014 | 750 | 350 | 100% | 0% | 53% | 9% |
| 017 | 920 | 400 | 100% | 60% | 81% | 11% |
| 130b | 1500 | 600 | 100% | 35% | 68% | 14% |
| 131b | 1500 | N/A | | 55% | 55% | 27% |
| 130 | 3100 | 550 | 100% | 14% | 36% | 14% |
| 131 | 2100 | N/A | | 43% | 43% | 27% |

**Porosity effect :**

- No bulk reduction for $\phi \leq 9$ vol%
- Depth of the reduction depends on the limited salt diffusion: d > 350-600 µm
- No difference between the surface and bulk reduction at $\phi \geq 27$ vol% (down to 2.1 mm)

o **Impossible to evaluate the minimum required porosity for in-depth reduction**

# Evaluation of results - effect of $CeO_2$ amount, current density, charge

## $CeO_2$ content

- seems to have no effect on overall reduction yield (proven for "low" reduction yields)
- has only an effect on the porosity → helps to reduce the inside of the pellet

## Current density

- no important effect observed on all reduction yield, reduction depth and faradic yield
- shown for 6 to 60 mA/cm² and similar charge passed
- not possible to evaluate the highest applicable current density

## Charge

- no more than 60 % reduction observed even at high charge excess
- Li metal deposition during run 130-131 prevents conclusions on higher charges
- **Limitation of the process: poor removal of $Li_2O$ from the pellet, proven by the monitoring of oxygen content of the salt**

# Conclusions

**Electroreduction of Mo-$CeO_2$ pellets in LiCl-$Li_2O$ melt**

- Is feasible and progresses gradually from the surface toward the bulk of the pellet
- The mechanism is likely combination of direct electroreduction and chemical reduction by the electrochemically deposited Li metal
- The porosity has a major impact on the reduction yield of the bulk due to salt penetration (inexistent at $\phi \leq 9$ vol%, unlimited at $\phi \geq 27$ vol%)
- Any amount of $CeO_2$ from 10 to 40 vol% can be used if the porosity is high enough: only 40 vol% represented enough porosity to allow homogeneous reduction to 2.1 mm depth
- At reduction yields below 60 %, the current density does not have any effect on the faradic yield or the reduction depth

**Problems encountered:**

- Faradic yields are low and large excess of charge is required
- The reduction does not proceed if $Li^0$ hinders the surface of the pellet
- Removal of the formed $Li_2O$ from the pellet is the reduction rate limiting step
- Optimisation of the process conditions is needed to achieve a complete reduction

# Summary results

| Pellet | $CeO_2$ amount (vol%) | Porosity (vol%) | j ($mA/cm^2$) | Charge passed (C) | d salt-inside (mm) | $[O^{2-}]$f th. electr.+pre-electr. (wt%) | $[O^{2-}]$f th. electr. alone (wt%) | $[O^{2-}]$f meas. (wt%) | $\rho_{SEM}$ | | | $\rho_O$ | $\rho_{ICP-MS}$ | $\rho_{estimated}$ | Faradic yield |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | B | S | A | | | | |
| 014 | 10% | 9% | 6.4 | 236 | 0.75 | 0.92 | 0.94 | 0.75 | 0% | 100% | 53% | 52% | 14% | 50% | 33% |
| 016 | 30% | 13% | 33.6 | 840 | 0.88 | 0.83 | 0.83 | 0.84 | N/A | | | 25% | N/A | 25% | 13% |
| 017 | 40% | 11% | 60.1 | 1300 | 0.92 | 0.53 | 0.74 | 0.71 | 50% | 100% | 80% | 60% | 60% | 60% | 29% |
| 130b | 20% | 14%* | 36.3 | 554 | 1.5 | 0.60 | 0.88 | 0.63 | 15% | 100% | 68% | 47-65% | 55% | 55% | 54% |
| 131b | 40% | 27%* | | | 1.5 | | | | 55% | 55% | 55% | 68% | 40% | 55% | |
| 130 | 20% | 14% | 28.8 | 2600 | 3.1 | 0.26 | 0.46 | 1.00 | 10% | 100% | 36% | 4-19% | 27% | 25% | 8.5% |
| 131 | 40% | 27% | | | 2.1 | | | | 45% | 45% | 45% | 28% | 47% | 40% | 13.6% |