Trials of Inert Anodes for the Electrochemical Reduction of Metal Oxide Powders

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Objectives

- Investigate reduction of metal oxide powders by FFC type process
- Investigate non-consumable anodes

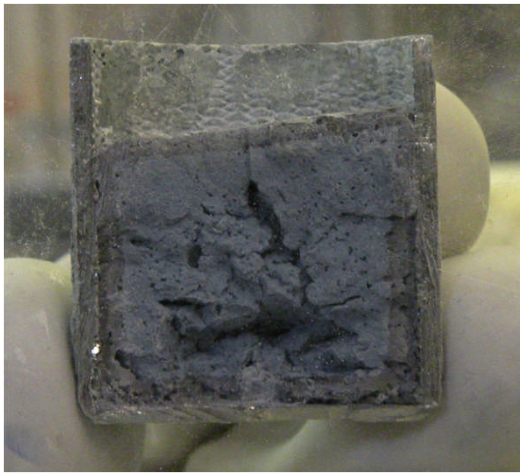
Reduction of powders

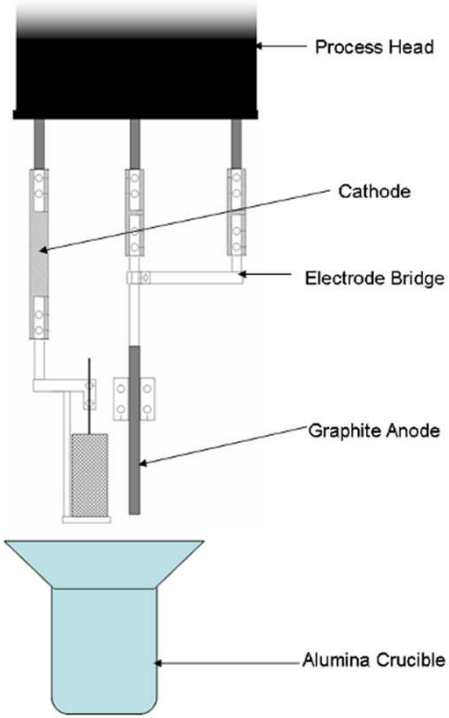
- Cavity electrodes – mechanistic studies
- UO_2 reduction in LiCl at 923K
  - Potentiostatic, E ~3.2V
  - Pt anode, Steel cathode container
  - Li generation ?
- CeO_2 reduction in $CaCl_2$-KCl at 1163K
  - Galvanostatic, E to ~3.5V, Ca generation
  - C anode, MgO cathode container
  - Some Ce and CeOCl formed

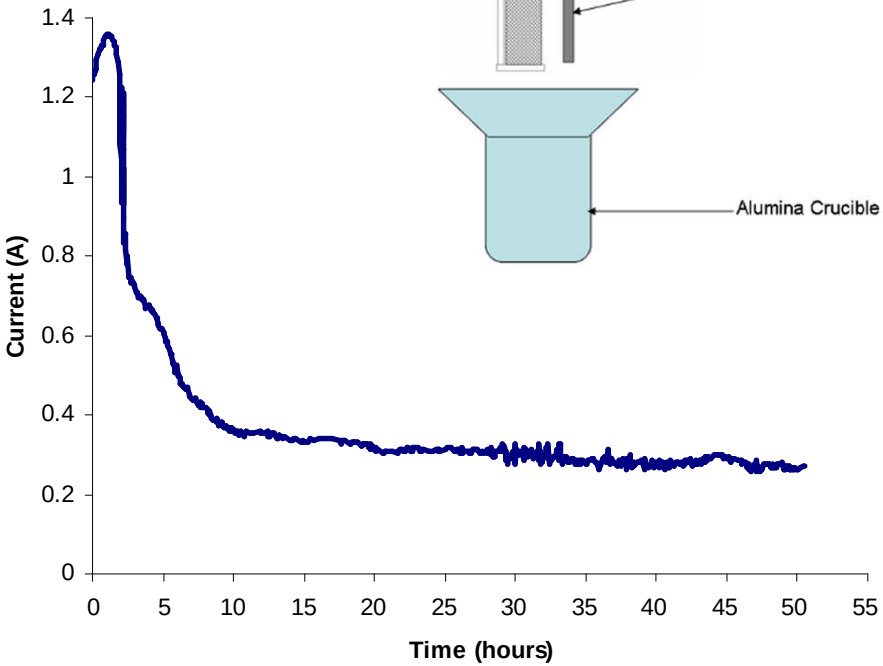
Jeong et al Electrochimica Acta 54 (2009) 6335; Claux et al Electrochimica Acta 56(2011) 2771

TiO_2 reduction

- $CaCl_2$ -1wt%CaO at ~1093K, 8g TiO_2
  - Graphite anode
  - Metal mesh cathode basket
  - -3.1V for 50 hours
  - 1.5 equivalents passed
  - Complete reduction

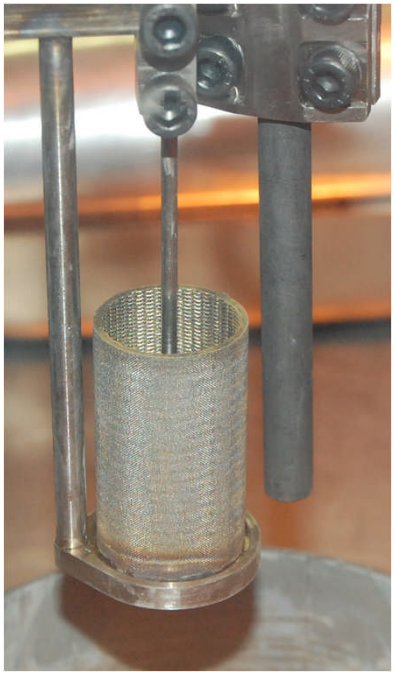






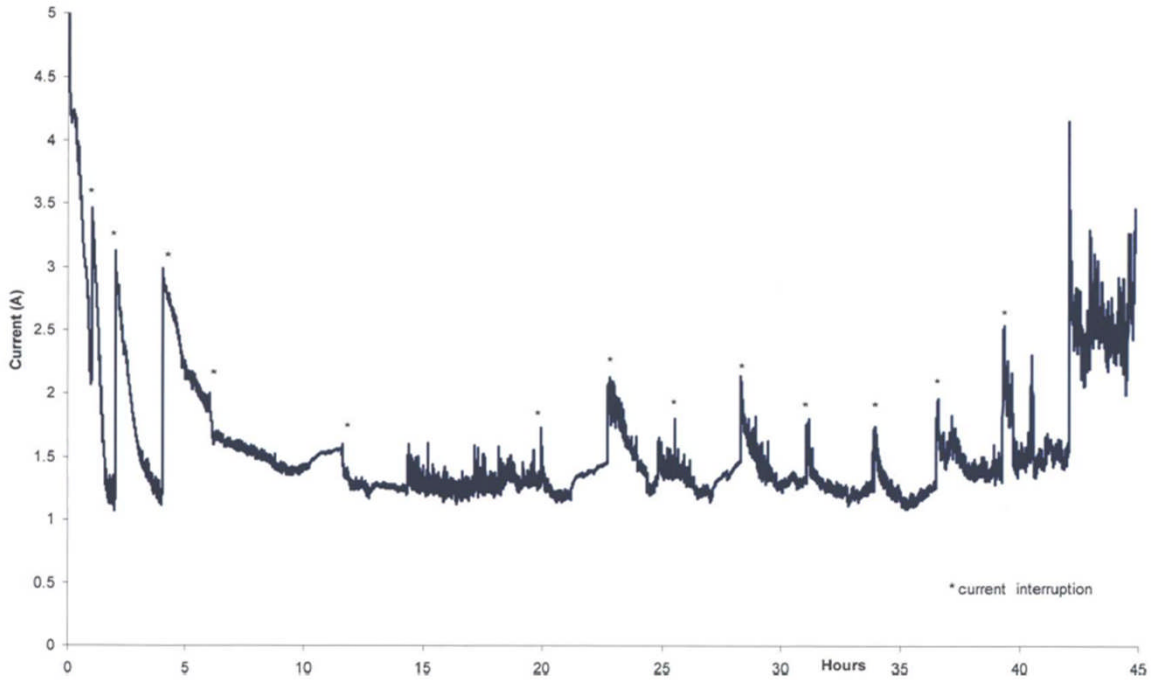
PuO_2 reduction

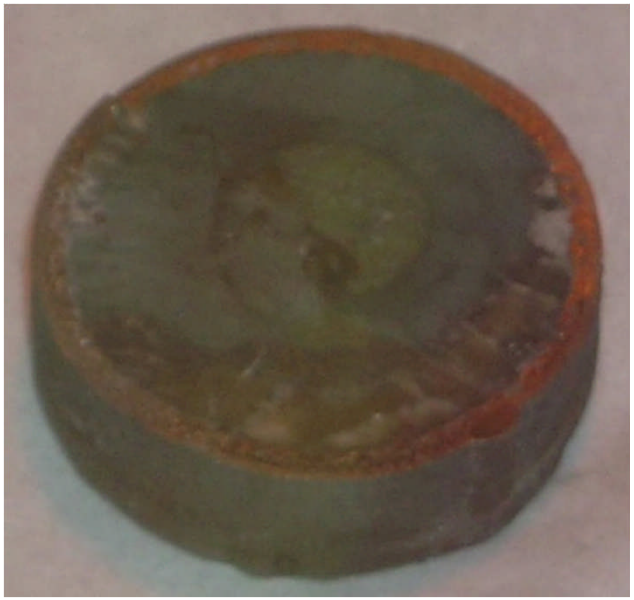
- Cathode : Mesh basket (~5µm) 26.5g PuO_2
- Anode : Graphite rod 10mm diameter
- Salt : $CaCl_2$-1wt%CaO
- Temperature : 1123K
- Applied potential -3.1V
- Pass 6.7 equivalents
- C loss -1.6g



PuO_2 reduction

- Higher current than TiO_2 reduction





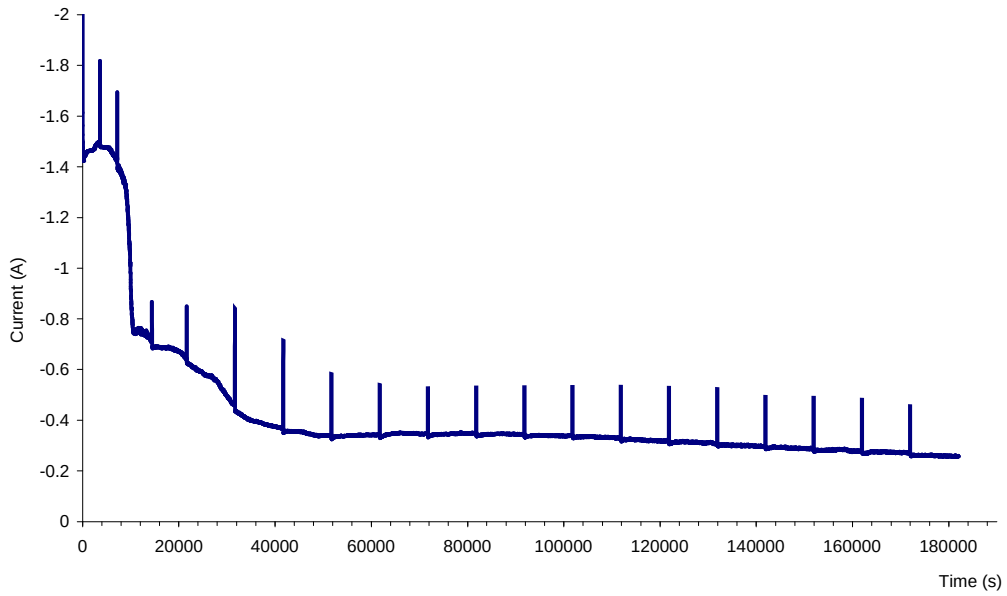
Inert Anodes

- Various materials have been proposed/trialled
  - SnO_2
  - $CaRuO_3$
  - Gold used for reduction in fluorides
    - LiF-NaF at 1023K for SnO_2 and Fe_3O_4
    - LiF-CaF_2 at 1123K for TiO_2 and UO_2
  - Pt – with UO_2 in LiCl and $CaCl_2$

Jiao et al Metall & Mater Trans B 41 (2010) 74
Gibilaro et al Electrochimica Acta 56 (2011) 5410; Gibilaro et al J.Nuc.Mater 414 (2011) 169
Sakamura et al J Electrochem Soc 153 (2006) D31

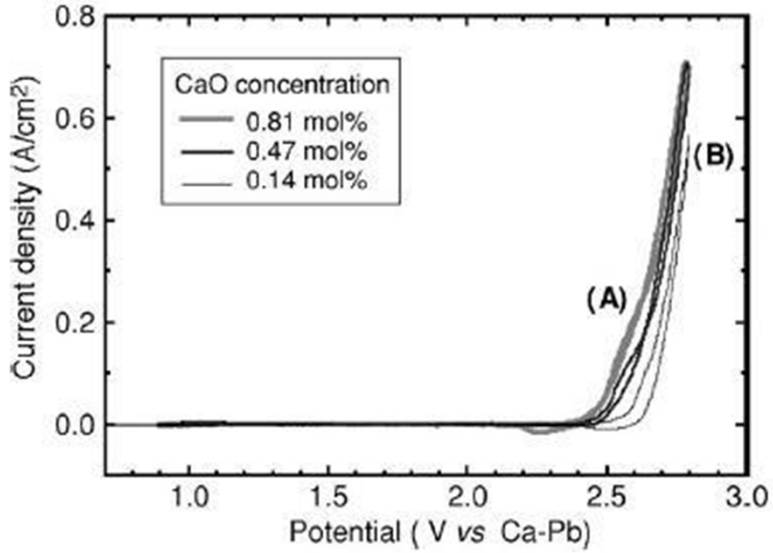
SnO_2 based anode

- Cathode : Mesh basket (15µm) 15.5g TiO_2
- Anode : SnO_2 – (Glassworks Hounsell Ltd)
- Salt : $CaCl_2$ – 1wt%CaO
- T = 1107K
- Potentiostatic, -2.9V
- SnO_2 eroded 2-3mm



Pt anode in $CaCl_2$-CaO

- Electrochemical window > 2.5V
- Demonstrated UO_2 reduction at <0.6V vs Ca/Ca^{2+} in $CaCl_2$ at 1093K
- Pt_3O_4 on anode



T=1083K, 200mV/s

Peak A : $2\ O^{2-} \rightarrow O_2 + 4\ e^-$

: $3Pt + 4\ O^{2-} \rightarrow Pt_3O_4 + 8\ e^-$

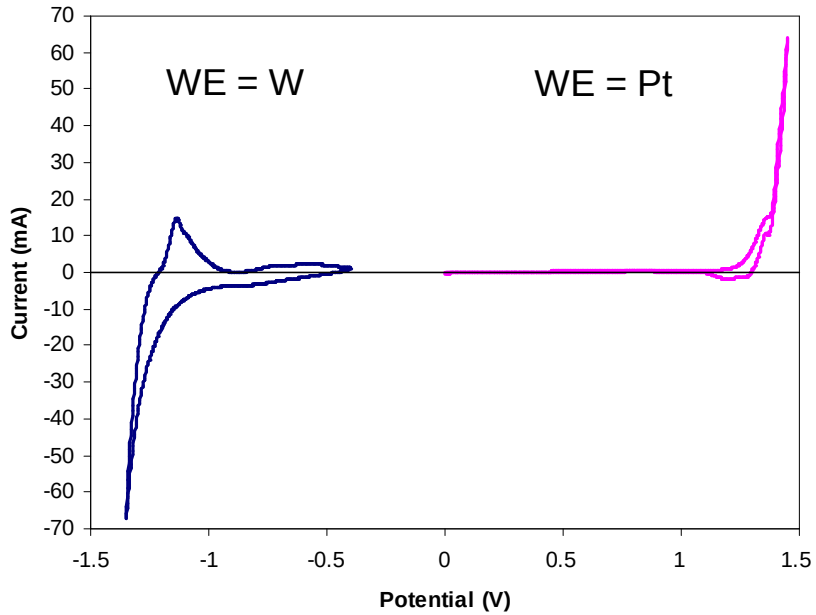
Peak B : $2Cl^- \rightarrow Cl_2 + 2e^-$

: $Pt \rightarrow Pt^{2+} + 2e^-$

Sakamura et al J.Electrochem.Soc 153 (2006) D31

Electrochemistry at Pt anode

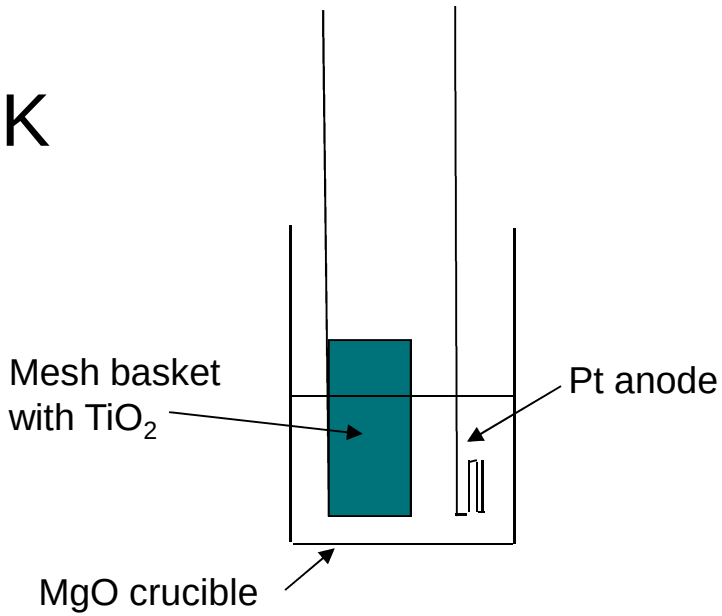
- Electrochemical window ~ 2.5V
- 2 or more reduction/oxidation process near anodic limit



$CaCl_2$-1wt% CaO, 1083K, QRE=Mo, 100mV/s

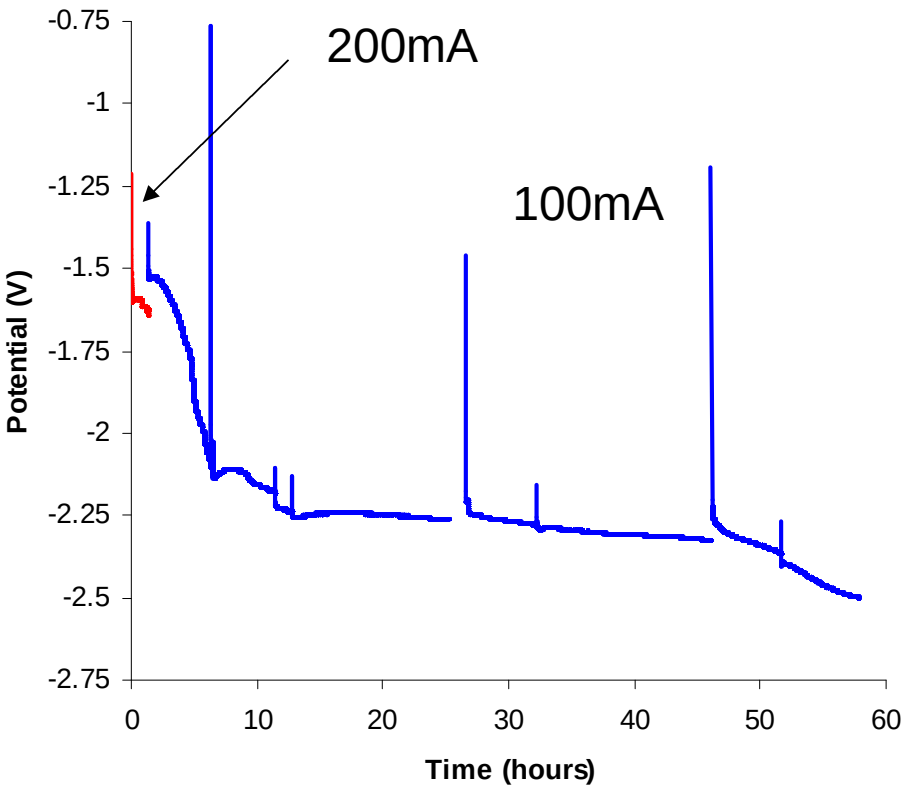
Pt anode (I)

- Cathode : mesh basket containing 3.15g TiO_2
- Anode : Pt wire (0.76mm dia), Area = 6.2 cm^2
- Salt : $CaCl_2$ – 1wt% CaO
- Process temperature : 1108K
- Operate galvanostatically
  - limit potential to -2.5V
- Pass 1.4 equivalents



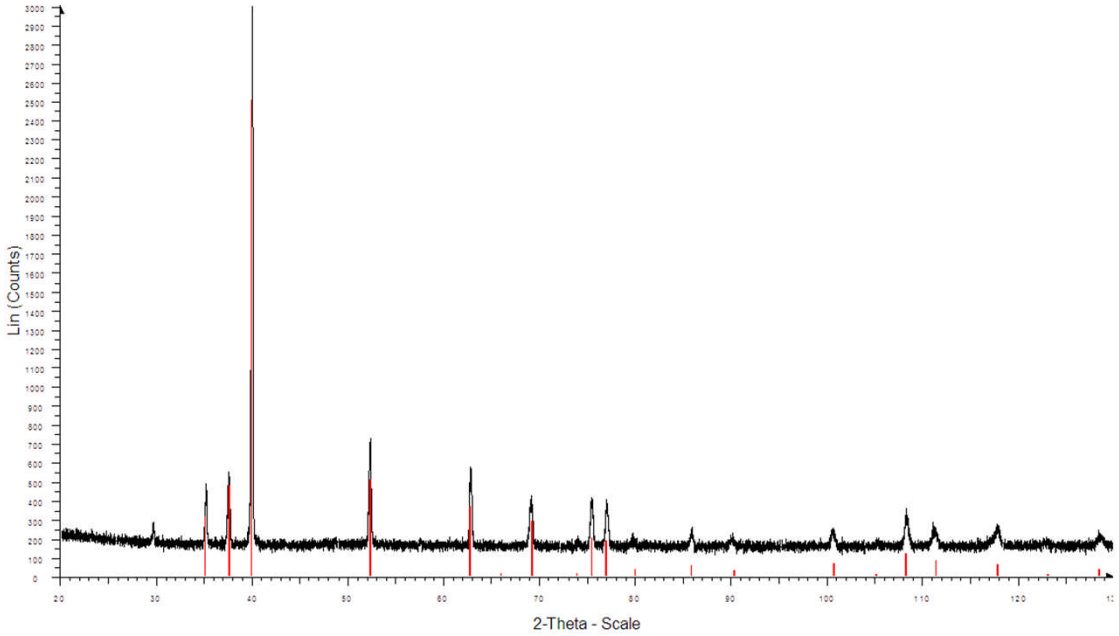
Pt anode (I)

- Terminate when potential reaches -2.5V

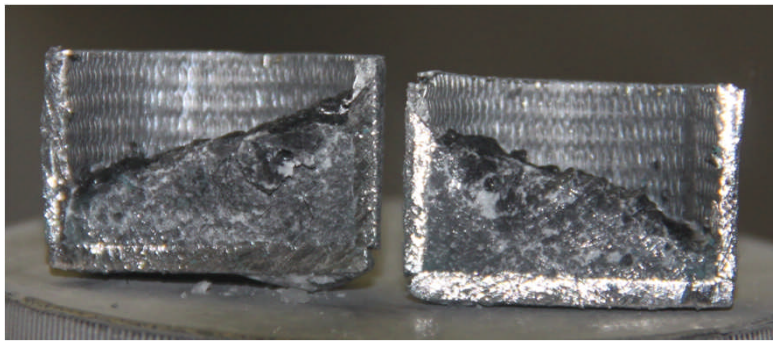


Pt anode (I)

Cathode basket



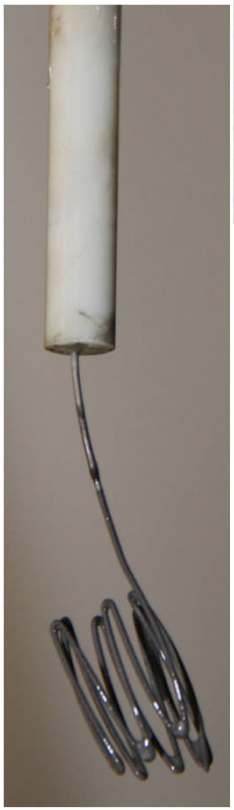
XRD shows Ti / Ti[$O_{0.42}$]

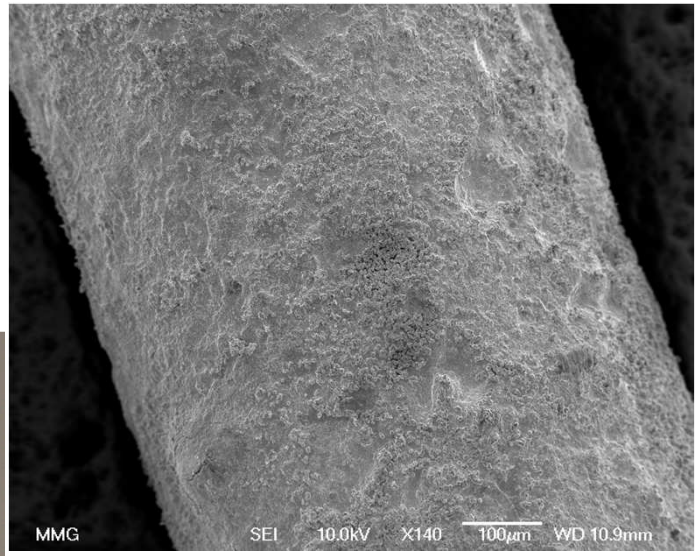


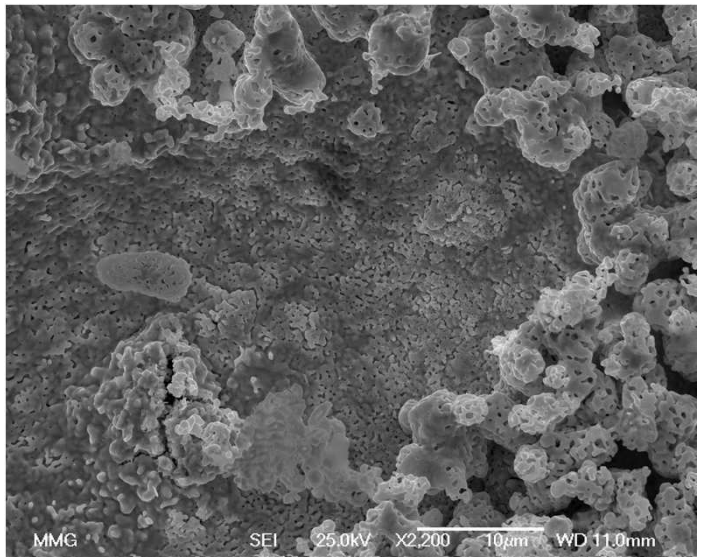
Process product :
Water wash to remove salt.

Pt anode (I)

- Pt appeared unconsumed
  - Diameter reduced by 0.1mm
  - SEM shows porous surface and fine particulate
- Dark deposit in bottom of salt





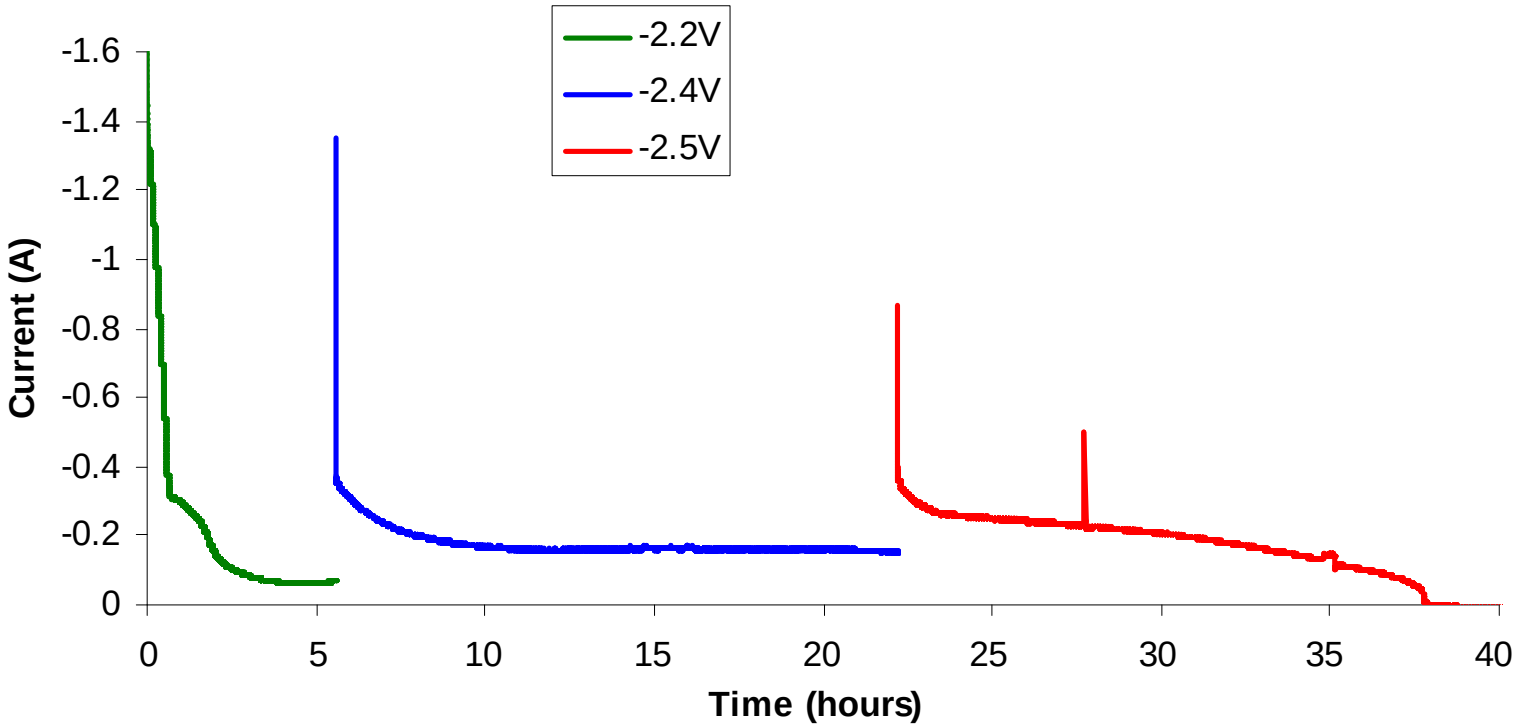


Pt anode (II)

- Cathode : Al_2O_3 crucible containing 2.9g TiO_2
- Anode : Pt wire (0.76mm dia), Area = 3.8 cm^2
- Salt : $CaCl_2$ – 1wt% CaO
- Process temperature : 1173K
- Operate potentiostatically (max -2.5V)
- Pass 1.8 equivalents

Pt anode (II)

- Process terminates on current going to zero

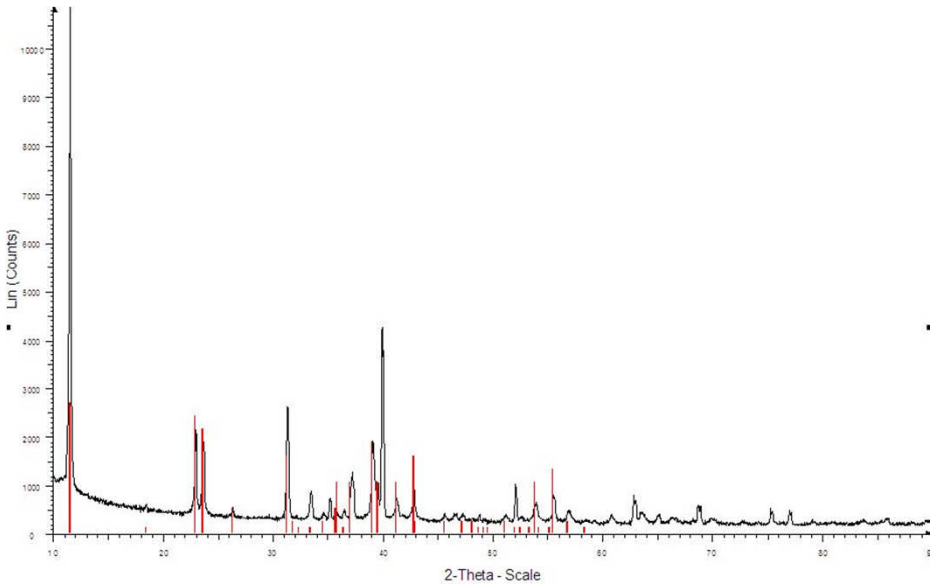


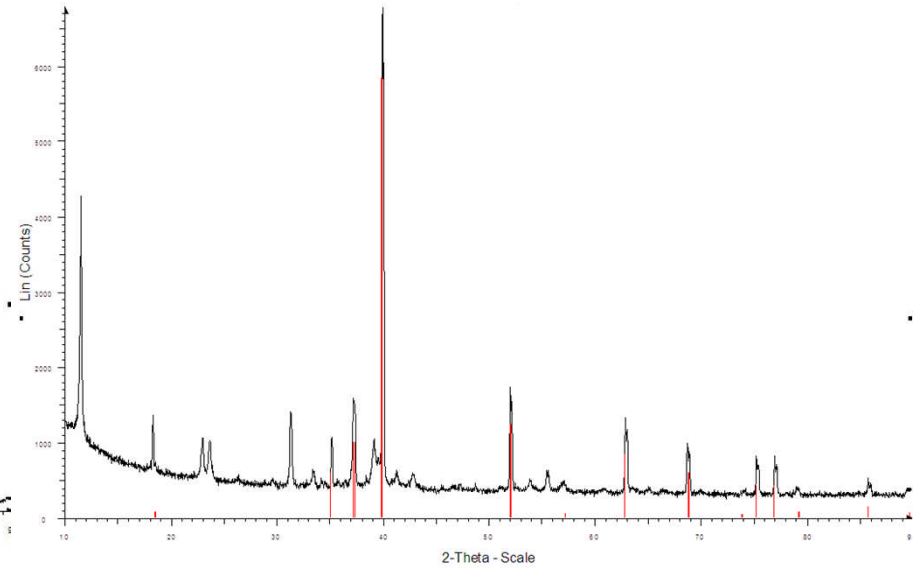
Pt anode (II)

- Pt missing !
- Ti retained in cathode compartment
- Black layer on bottom of salt

Pt anode (II) : Product – XRD Data

- Dissolve salt away from product – lighter and more dense solid phases
- XRD shows Ti_2O and $Ca_2Al(OH)_6Cl.2H2O$



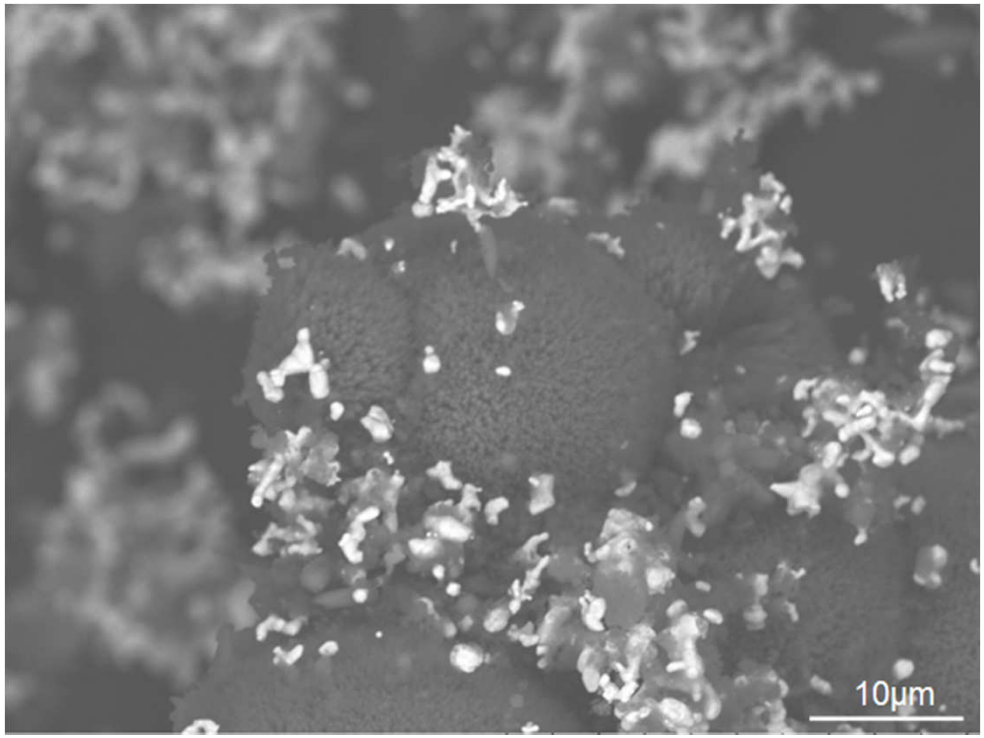


Less dense phase – more Ca/Al hydrate

More dense phase – more Ti_2O

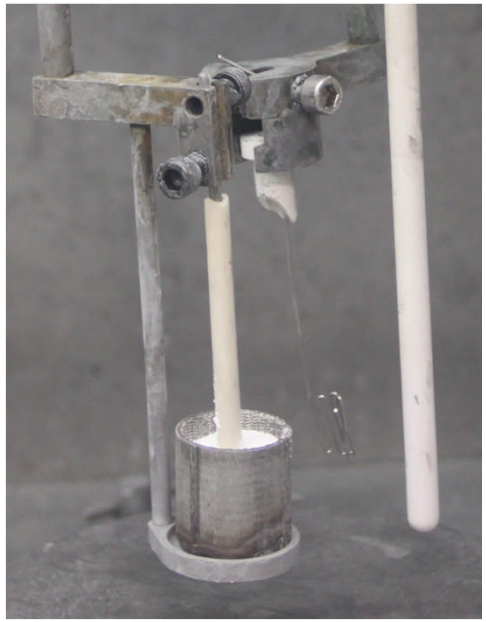
Pt anode (II)

- Black solids at bottom of salt – contain Pt



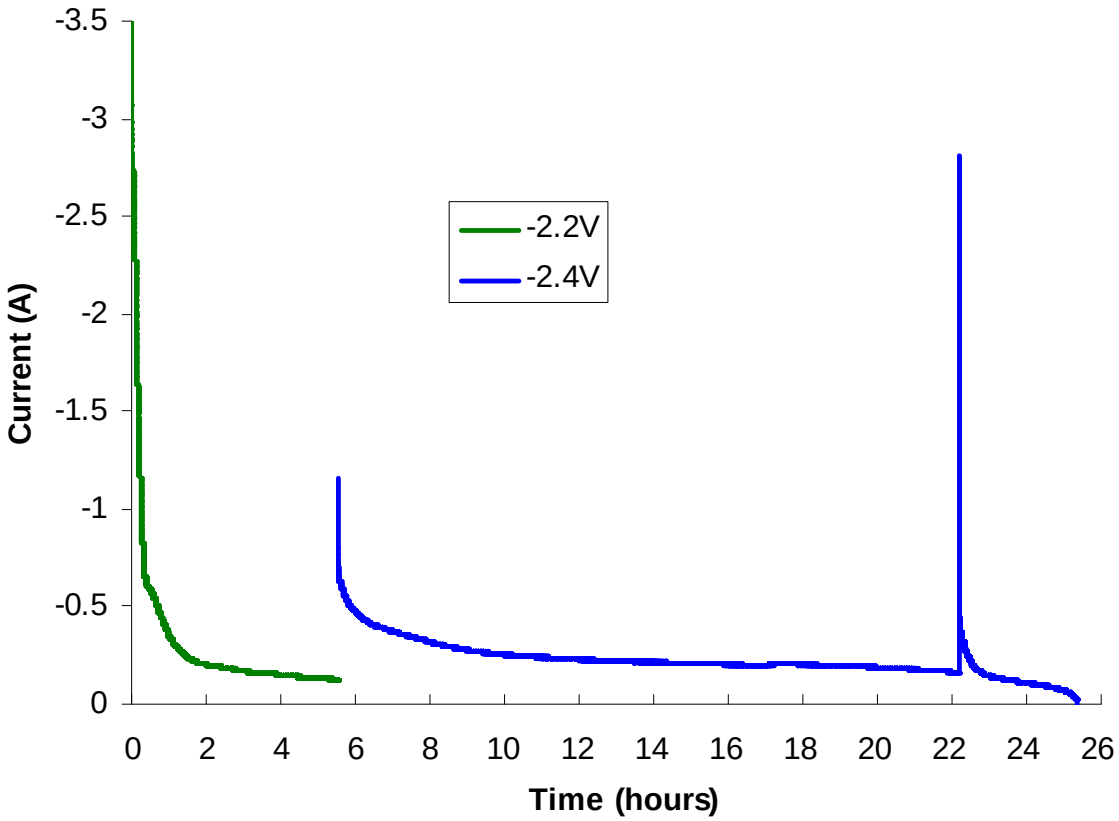
Pt anode (III)

- Cathode : Metal basket containing 2.8g TiO_2
- Anode : Pt wire (0.76mm dia), Area = 2.8cm^2
- Salt : $CaCl_2$ – 1wt% CaO
- Process temperature : 1173K
- Operate potentiostatically (max -2.4V)
- Pass 1.8 equivalents



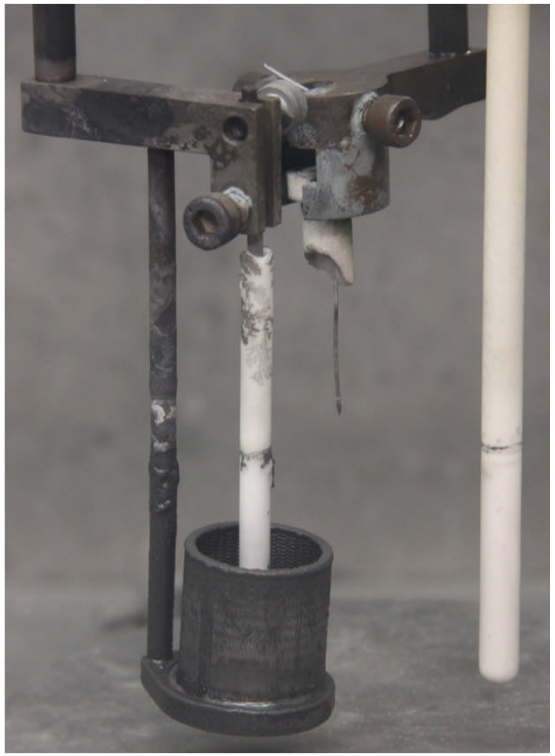
Pt anode (III)

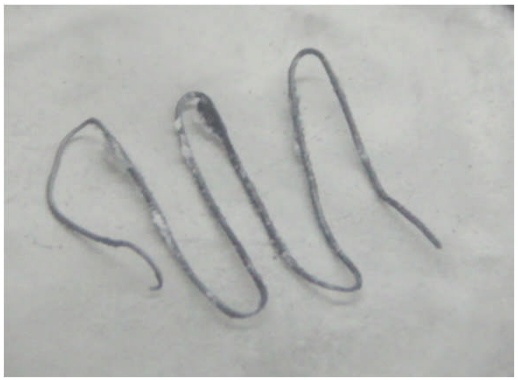
- Process terminates on current going to zero



Pt anode (III)

- Pt consumed
- Black layer in bottom of salt
- Pt wire recovered from salt,
  - thinned by 47%
  - 5cm length missing

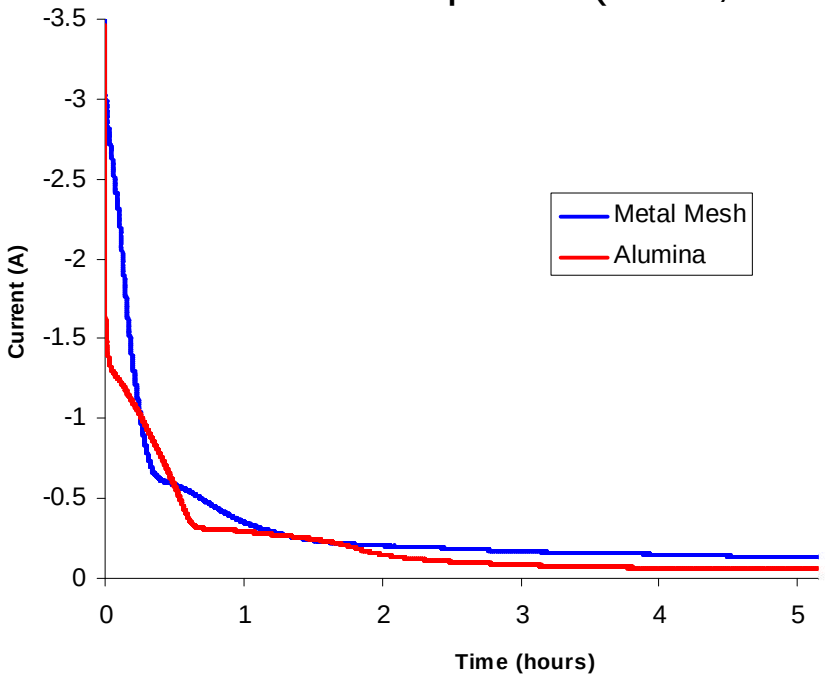


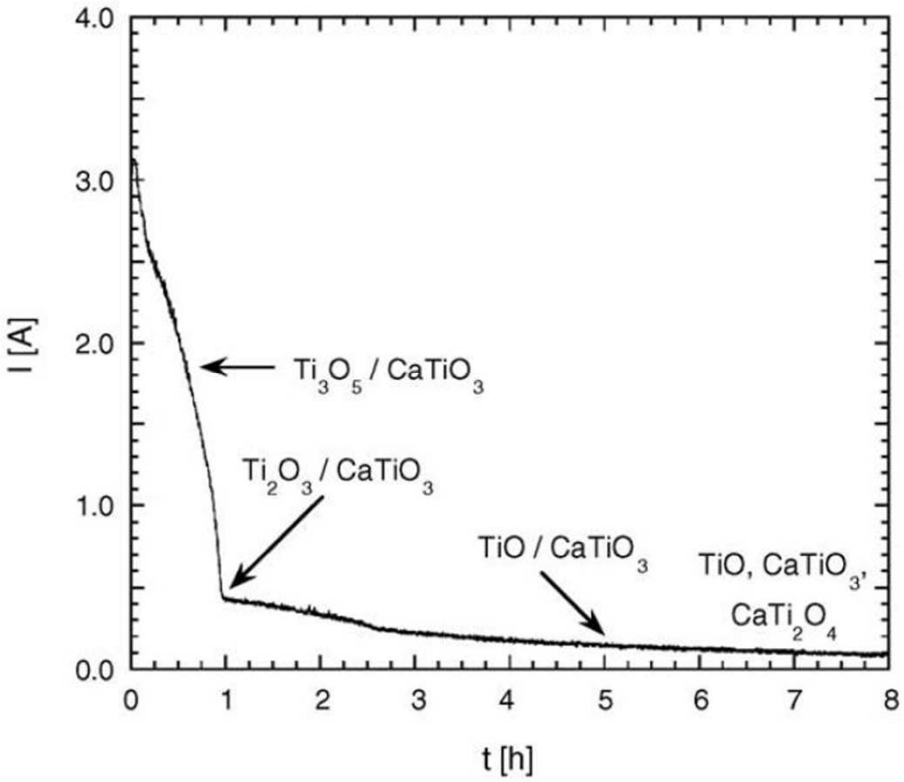


Compare TiO_2 powder / pellet reduction

- Similar current / time profiles

Initial reduction phase (-2.2V, 1173K)





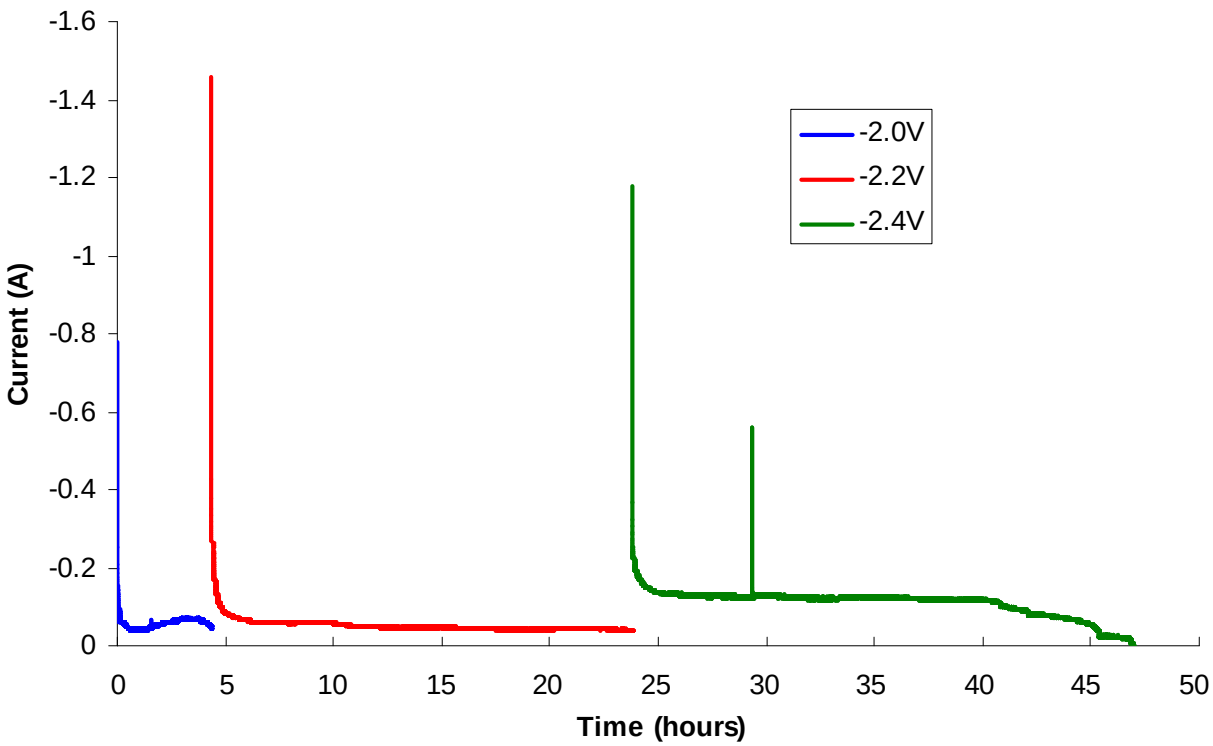
Schwandt : Electrochim Acta 51 (2005) 66

SnO_2 reduction

- Cathode : Al_2O_3 crucible with 4.5g SnO_2
- Anode : Pt wire (0.76mm dia), Area=3.3cm^2
- Salt : $CaCl_2$-1wt%CaO
- Temperature : 1173K
- Operate potentiostatically
- 1.2 equivalents passed

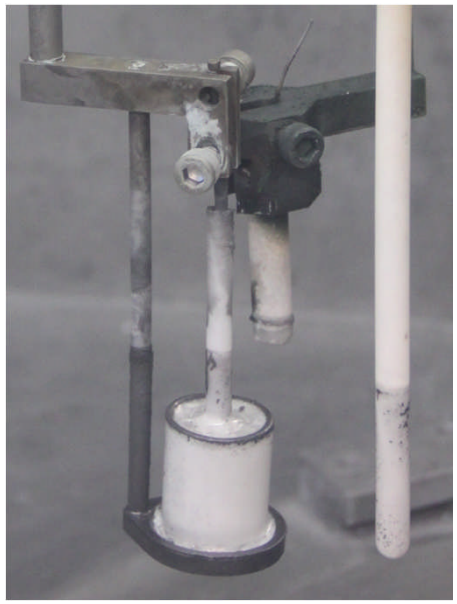
SnO_2 reduction : Pt anode

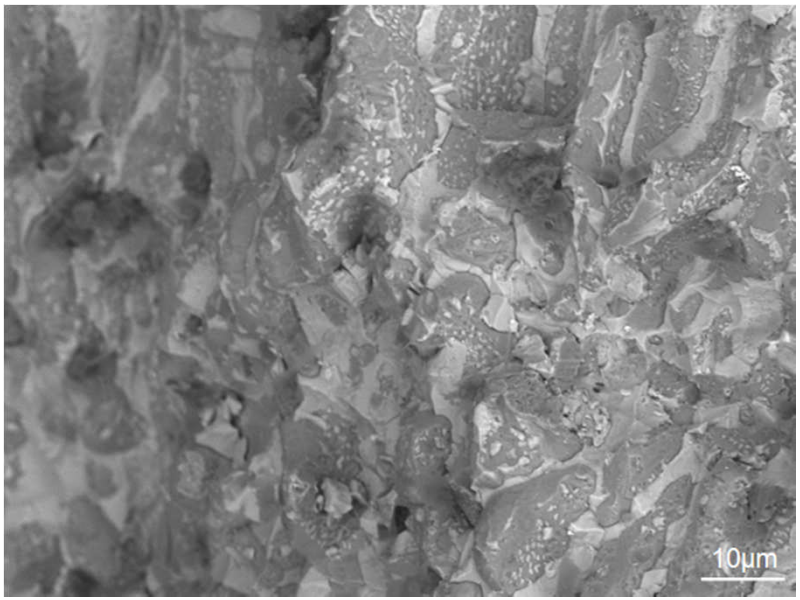
- Process terminates on current going to zero at -2.4V



SnO_2 reduction : Pt anode

- Pt consumed
- Evidence of liquid metal forming
- Sn/Fe alloy phases formed.





Conclusions

- Initial trials with graphite anode and metal oxide powders demonstrated reduction to Ti and Pu possible.
- SnO_2 anode not inert in TiO_2 reduction.
- Initial trials with Pt show reduction of TiO_2 to at least Ti[O] is possible but Pt is consumed.
- Reduction pathway with powder similar to sintered pre-forms.
- Reduction of SnO_2 to liquid product demonstrated.
- Further work required to determine conditions to minimise Pt consumption.

- Thank you for your attention
- Any Questions ?