Lower Carbon Footprint Process for the Production of Reactive Metals (Mg, Ca, Ti, and Ta)

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Outline

Solid Oxide Membrane (SOM) Process for Metals Production

- Lower carbon foot print process
- Generic Process (Mg, Ti, Ta, and Ca)
- Possibilities and Challenges

Magnesium (DOE-USCAR and Safe Hydrogen)

Calcium (Industrial Sponsors)

Titanium (NSF)

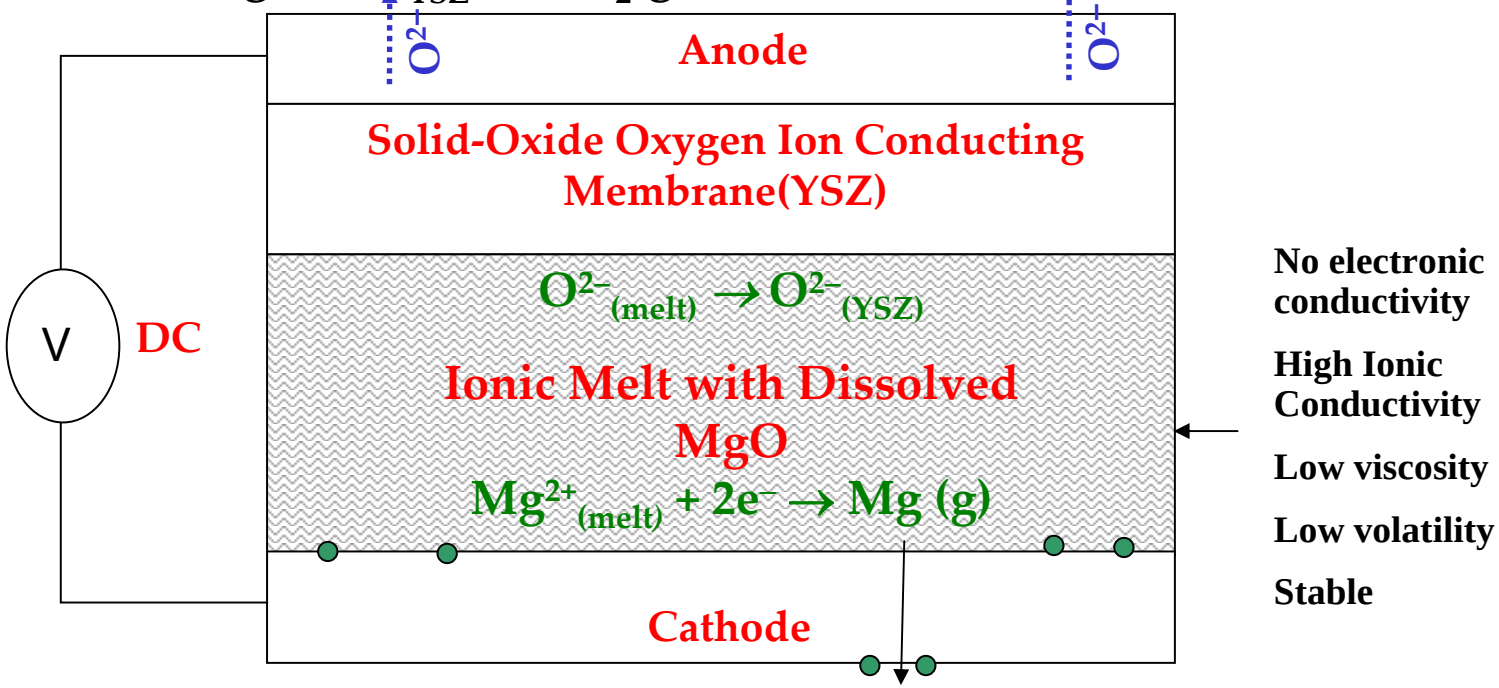
Tantalum (Tantalum Australia)

Schematic of the SOM Process for the Production of Metals

$$CH_4(g) + O^{2-}_{(YSZ)} \rightarrow CO(g) + 2H_2(g) + 2e^-$$

$$H_2(g) + O^{2-}_{(YSZ)} \rightarrow H_2O(g) + 2e^- \qquad C + O^{2-} \rightarrow CO(g) + 2e$$

$$CO(g) + O^{2-}_{YSZ} \rightarrow CO_2(g) + 2e^- \qquad O^{2-} \rightarrow \tfrac{1}{2}\, O_2(g) + 2e$$



$$Mg(g) + MeO = MgO + Me$$

Lower Carbon Footprint Process for the Production of Reactive Metals

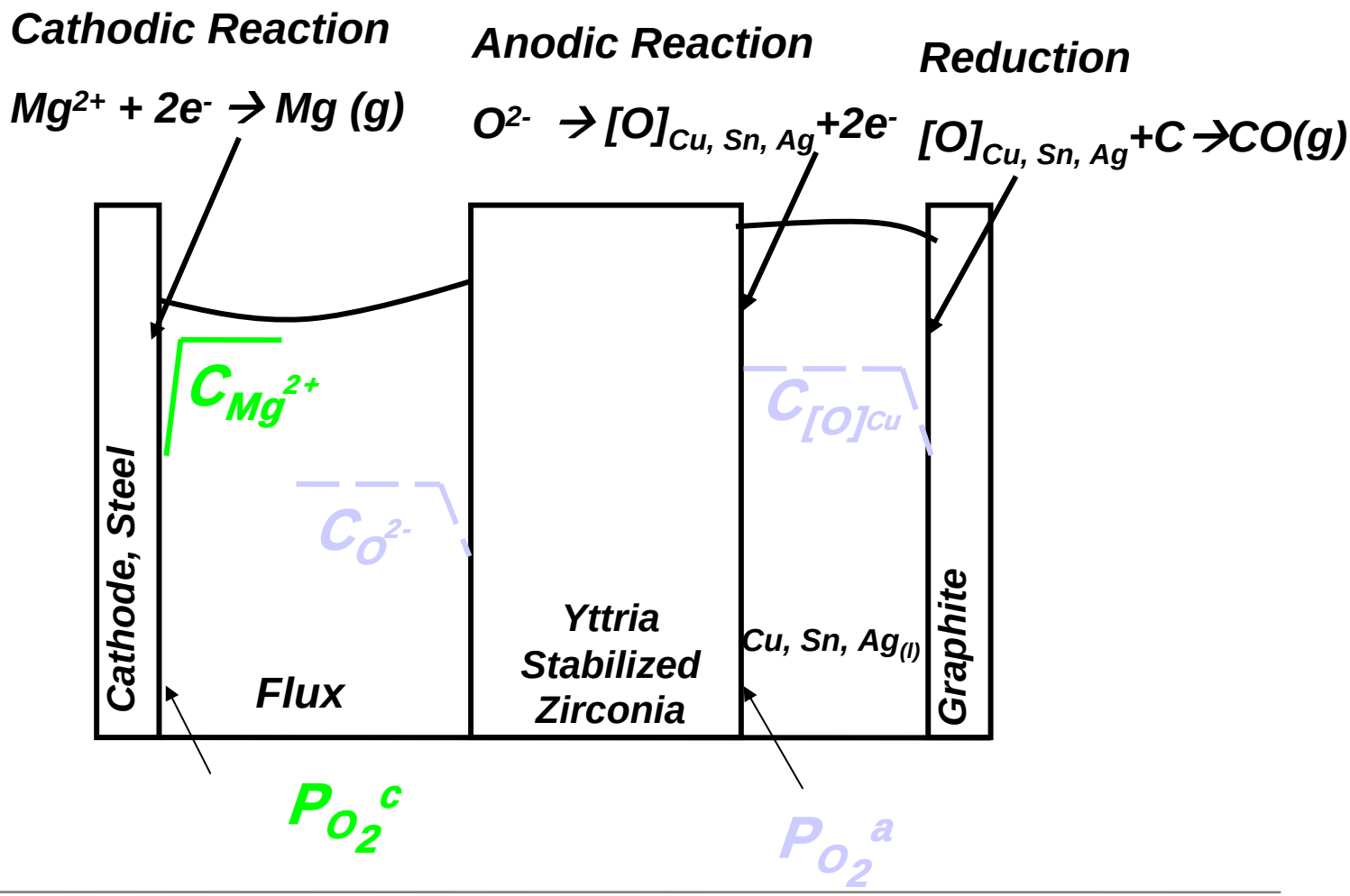
SOM Process

- Oxide feed
- Lower dissociation potential
- Higher efficiency
  - SOM process byproduct can run fuel cells to supply the needed electrical energy
  - Chemical energy can substitute for part of the needed electrical energy
- Can be CO_2 and pollutant free
  - Renewable energy
  - Oxygen evolution at the anode

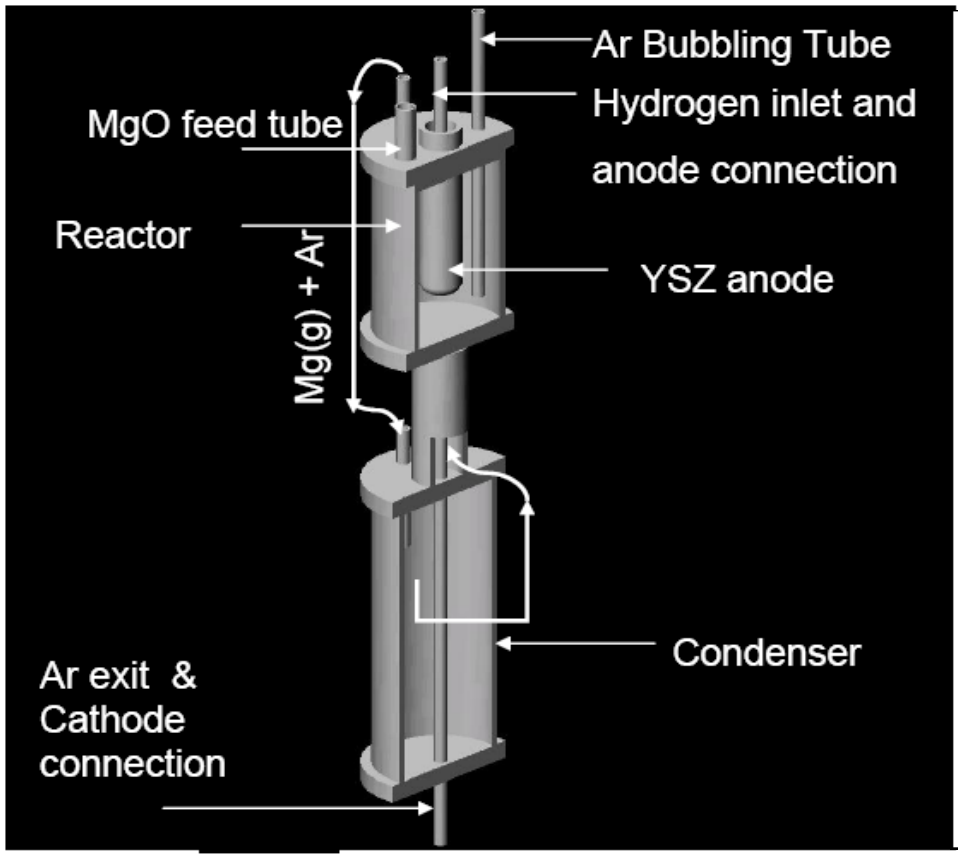
Existing Electrolytic Process

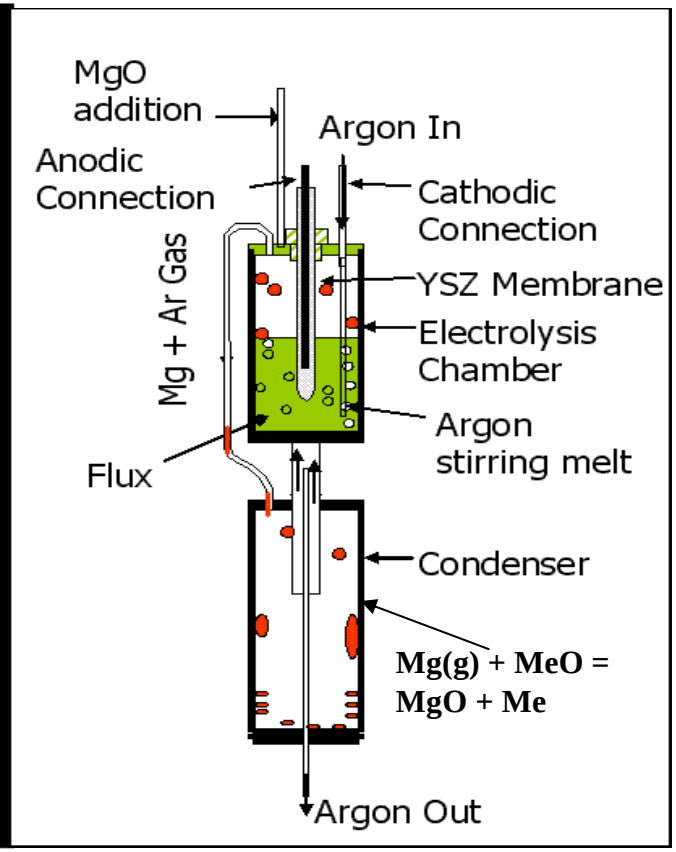
- Chloride feed preparation
- Higher dissociation potential
- Lower efficiency
  - Separate gassifier needed to run fuel cells for supplying the electrical energy
  - Process relies primarily on electrical energy
- Cannot be pollutant free
  - Chlorine and its byproducts form at the anode

SOM Cell – Process Reaction Schematic with Carbon as a Reductant Feed



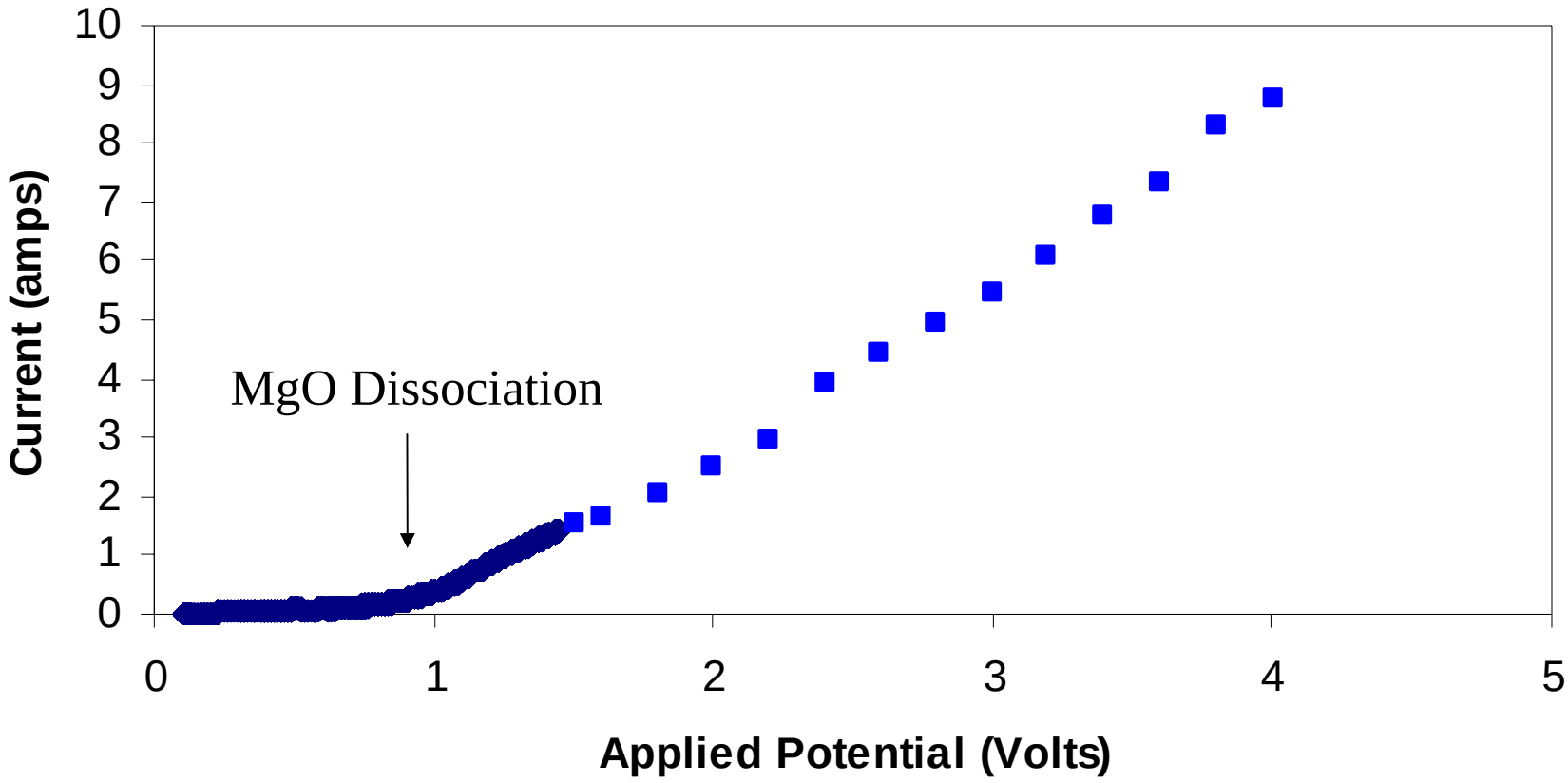
Experimental Single Tube SOM Reactor for Magnesium Production(100-200 g/day)





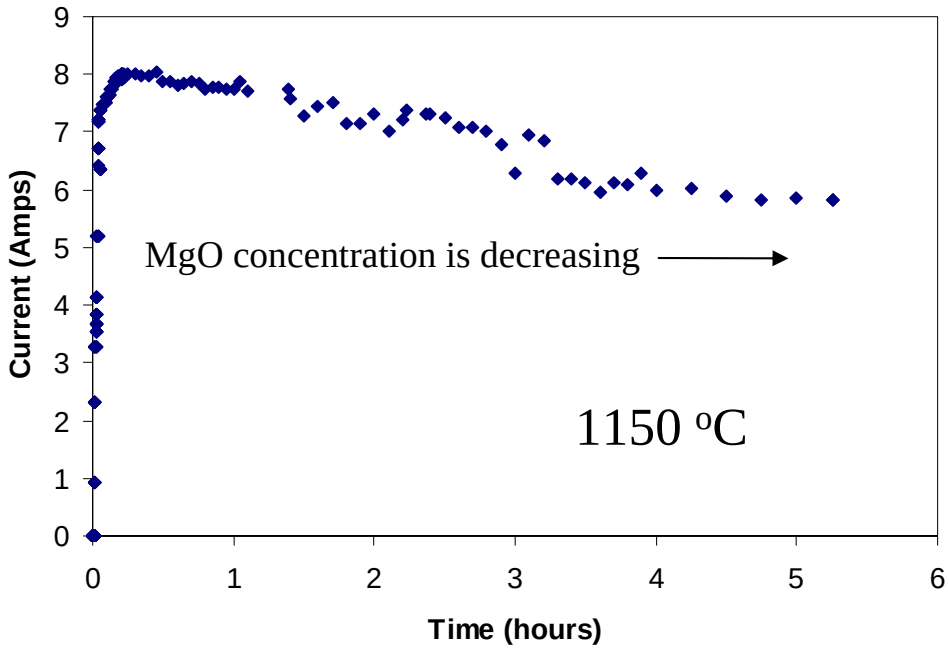
Stainless Steel construction; Single Tubular YSZ membrane;
Separate chamber for Electrolysis and Condenser; 15 g/hr of Mg at 1 Amp/cm^2; 1150 ^{o}C;
10 w% MgO in 55.5 w% MgF_2- CaF_2; Ar used as carrier and diluent for Mg vapor

Potentiodynamic Scan-Single Tube Reactor

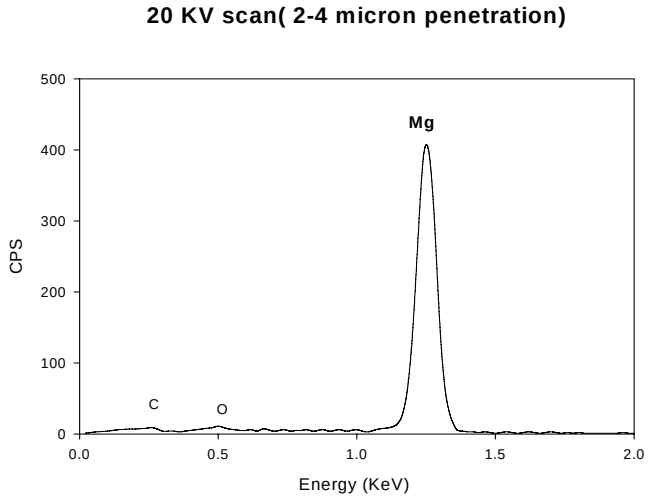


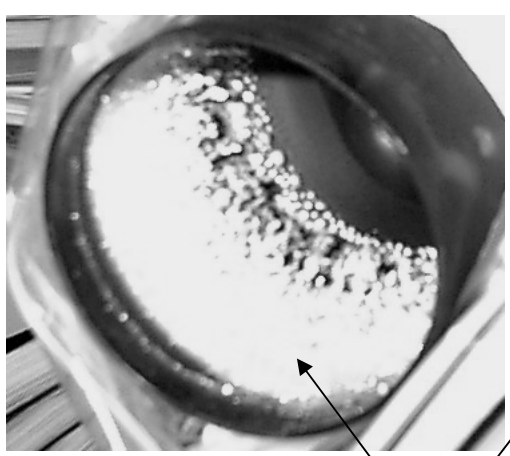
SOM Electrolysis of MgO-Single Tube Reactor

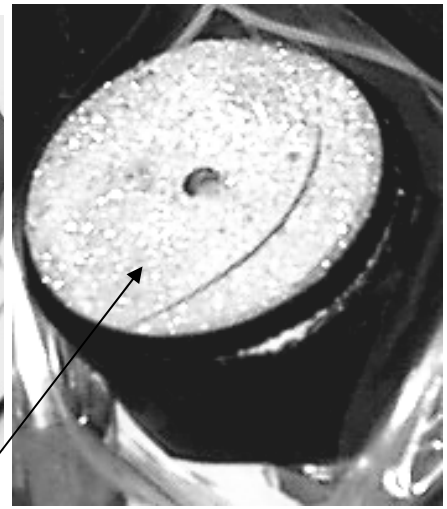
Potentiostatic Hold at 4.0 Volts



SOM Electrolysis of MgO

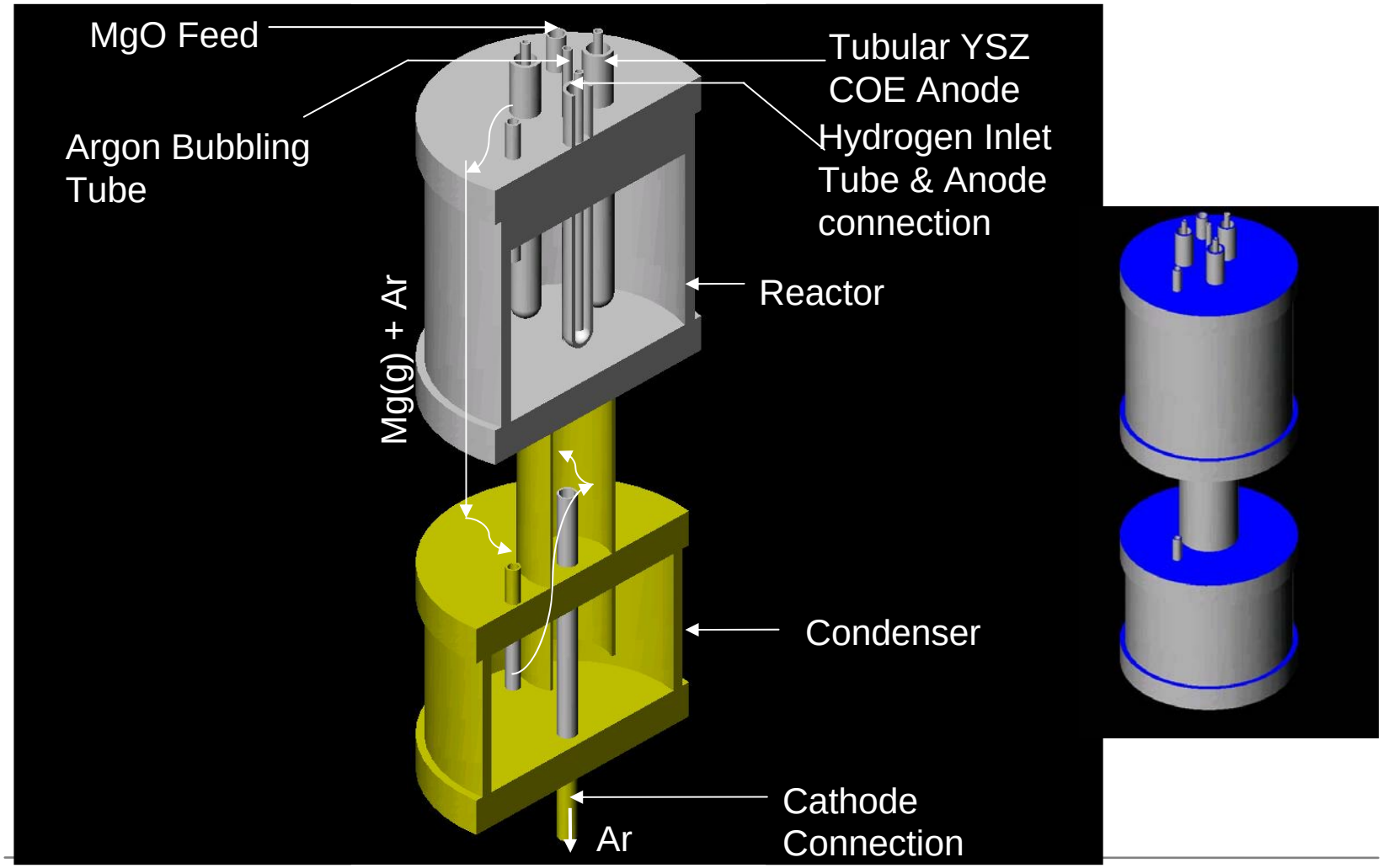






Condensed Magnesium

Experimental Tripple Tube SOM Reactor for Magnesium Production (500-1000 g/day)

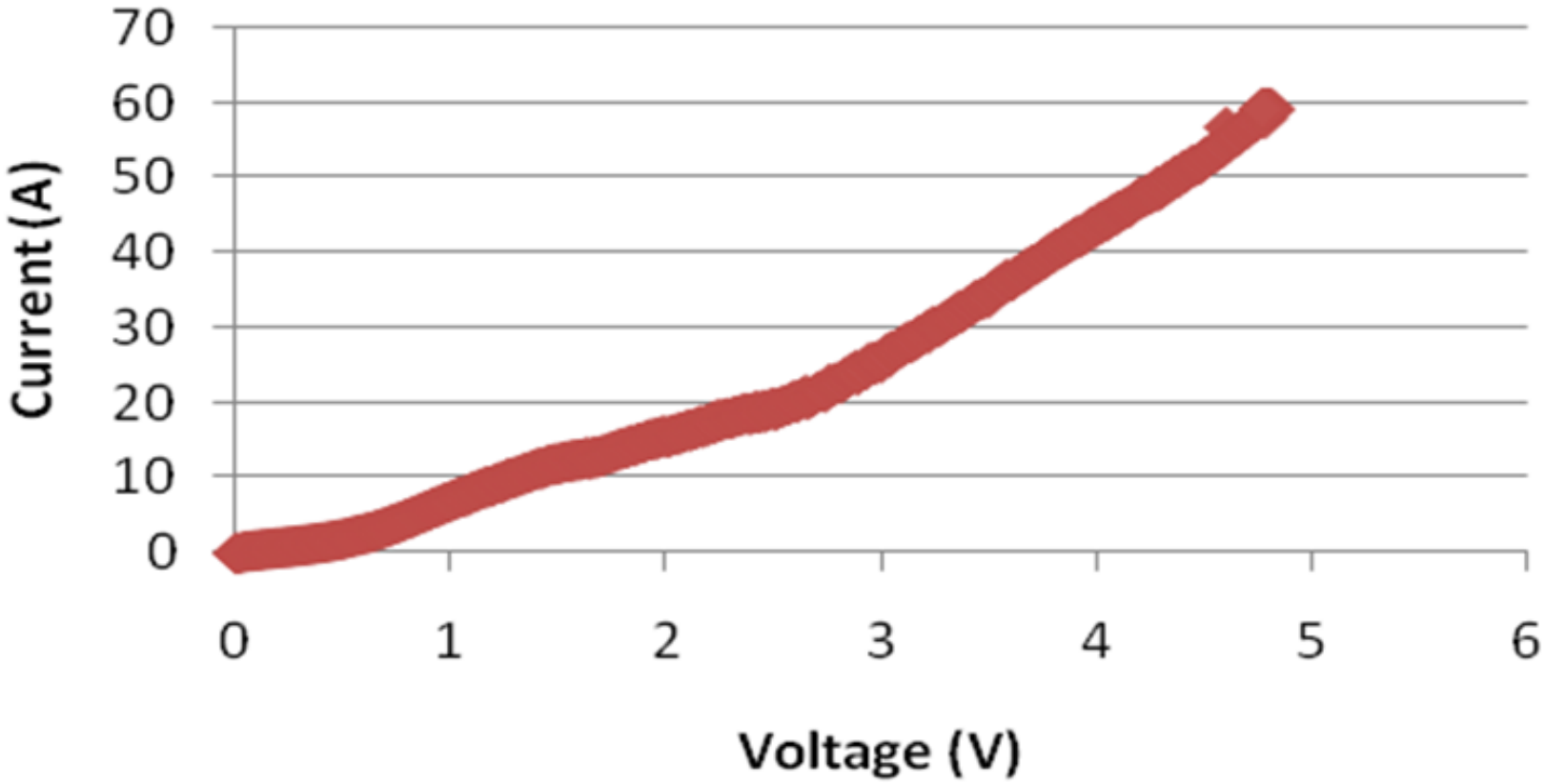


Experimental Triple Tube SOM Reactor for Magnesium Production (500-1000 g/day)

Mg-SOM cell setup

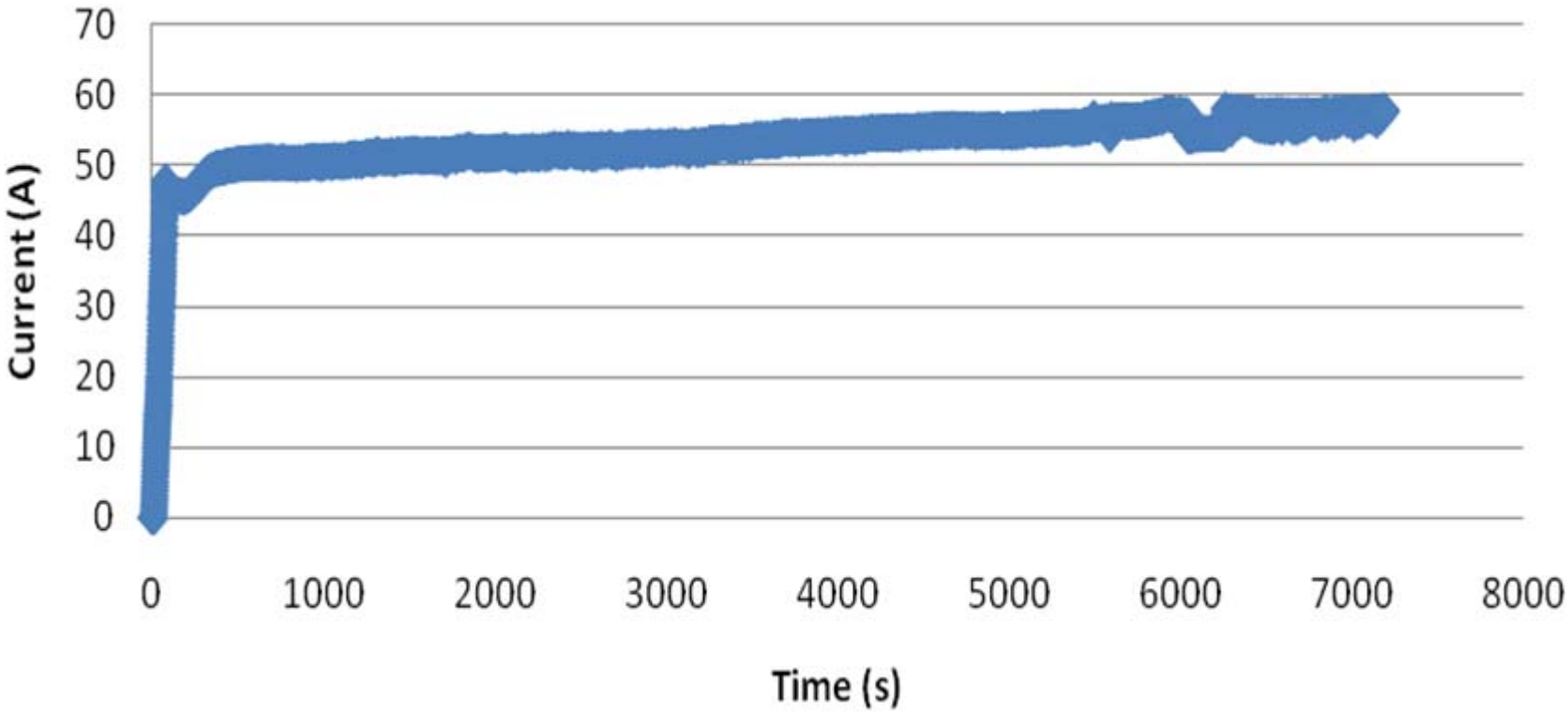
Mg-SOM cell setup inside furnace

Potentiodynamic Scan-SOM Triple Tube Reactor



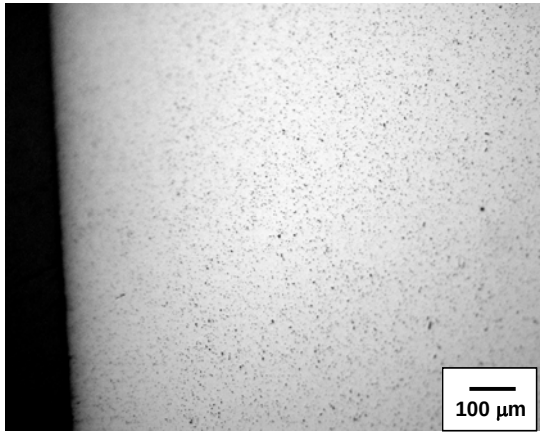
SOM Electrolysis of MgO-Triple Tube Reactor

Potentiostatic Hold at 4.0 Volts

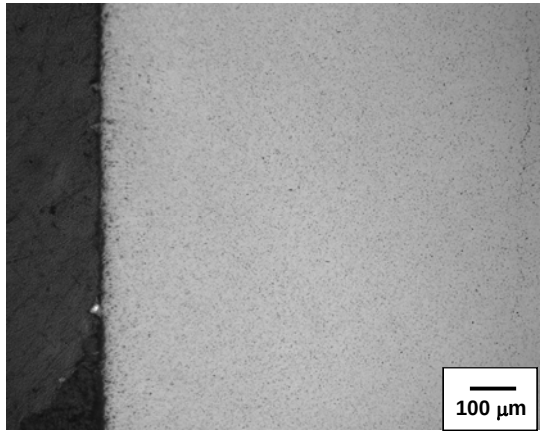


Morphology of Magnesium Deposit

Stability of Membrane



a) As Received



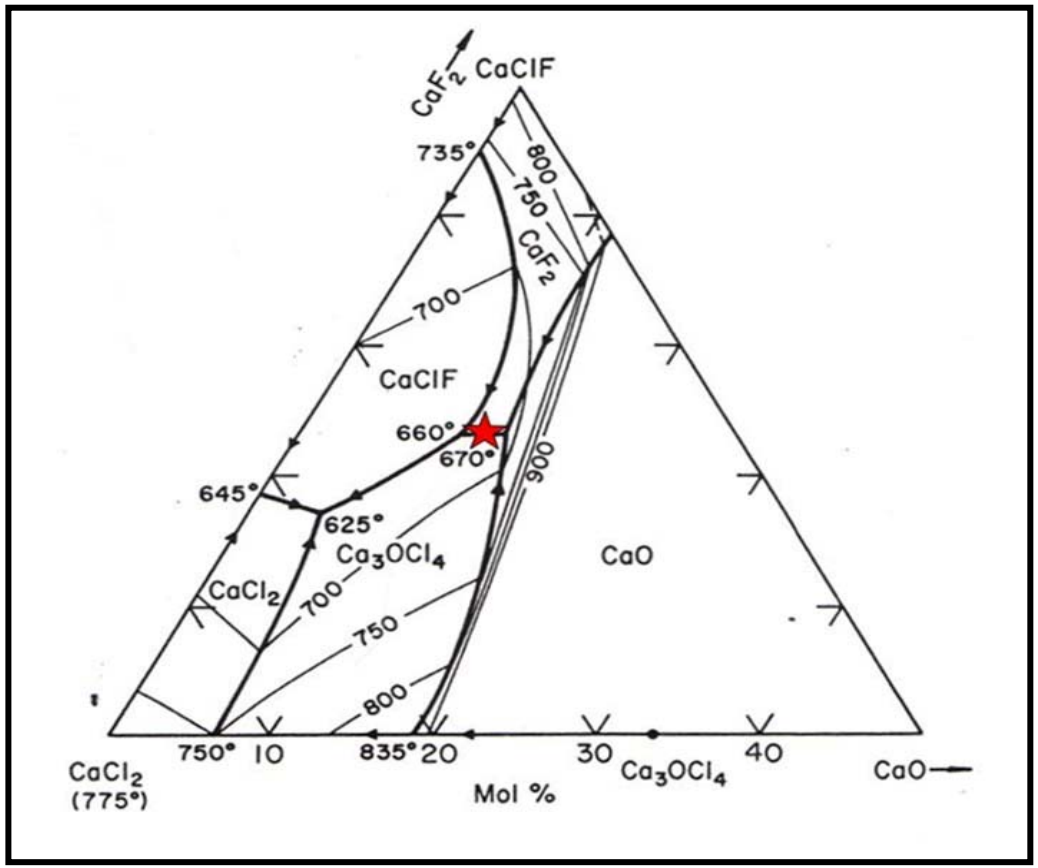
b) After Experiment

- Membrane virtually unaffected after the 20 hour experiment
- Selection of flux is critical to the process
- The operating life of Zirconia membrane will dominate overall cost of the process

Summary

- Cost Effective & Environmentally friendly
  - Direct reduction of Magnesium oxide
  - Minimize pre-processing, reduce capital and operating cost
- High Current Density (>1 Amp/cm^2) – with high applied voltages
- Good Scale up Potential
- Reformation of Natural gas due to high temperature operation
- Specific Energy consumption of MgO reduction is 10 KWh/Kg

SOM Flux Selection for Ca Production

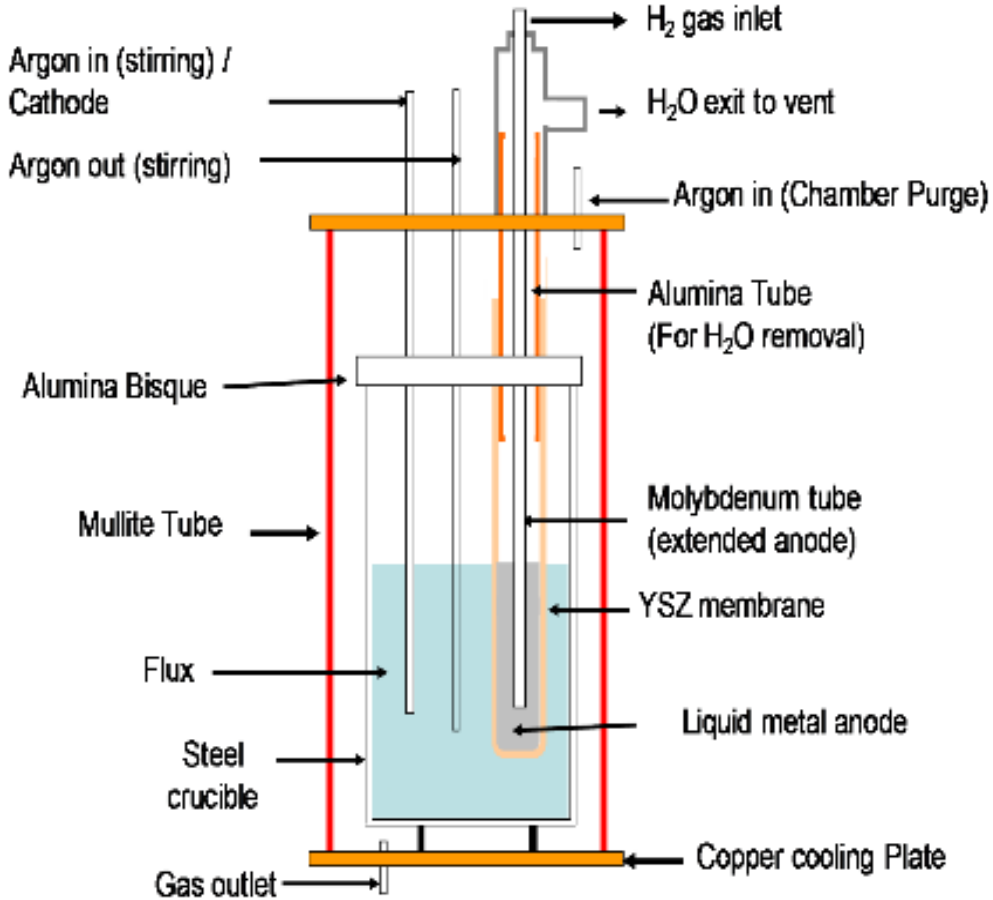


Composition - 65.12 % $CaCl_2$ - 28.31 % CaF_2 - 6.57 % CaO

Melting Point - 675°C approximately

* D.A. Wenz, I. Johnson, R.D. Wolson, "System $CaCl_2$-CaF_2-CaO, High-$CaCl_2$ portion," Journal of Chemical and Engineering Data, 14 [2] (1969), 252

SOM Experimental Set-Up for Ca Production



SOM Electrolysis Cell operating temperature = 750 ^{o}C

Inert environment was maintained flowing ultra high purity argon gas

Note : Set up schematic is not to scale

Electrochemical Characterization

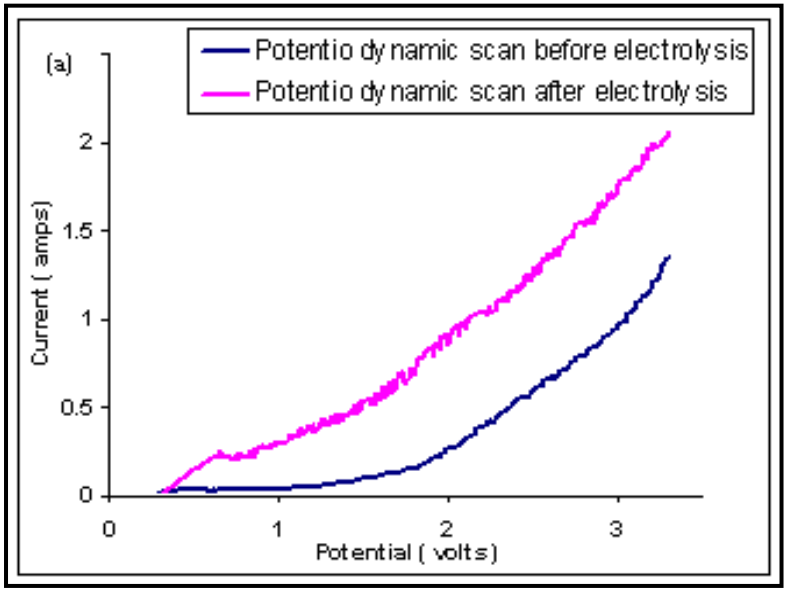


Fig A . Potentio-dynamic scan

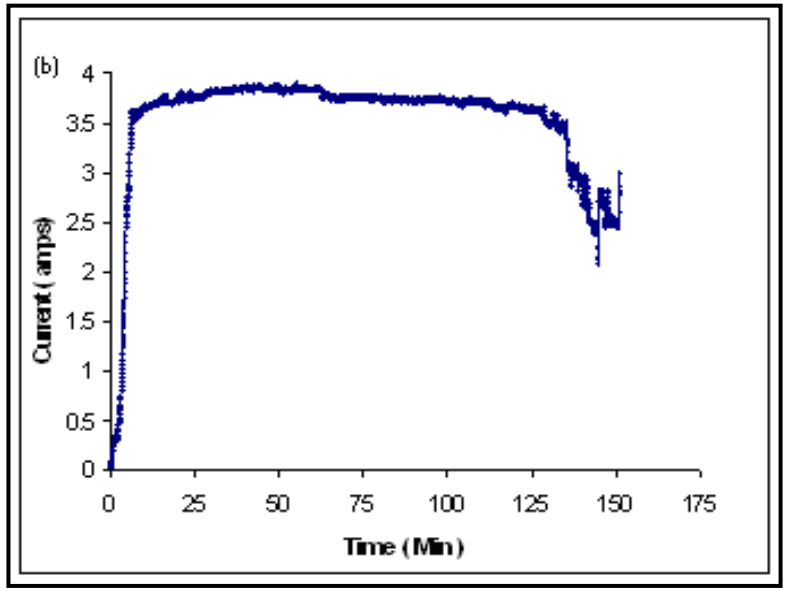


Fig B . Electrolysis

- The sharp change in slope at a potential of 1.65 V (Fig A) indicates the dissociation of CaO, which is very near to theoretical dissociation potential (1.74 V) of CaO when H_2 is used as a reductant at the anode .

- A current density of 280 mA/cm^2 is obtained when a potential of 4.5 volts was applied across the SOM cell (Fig B).

- Instability and sharp rise in current is due electronic behavior of the flux * (Fig B) which is confirmed by a potentio-dynamic scan after the electrolysis (Fig A)

Deposit on the iron cathode

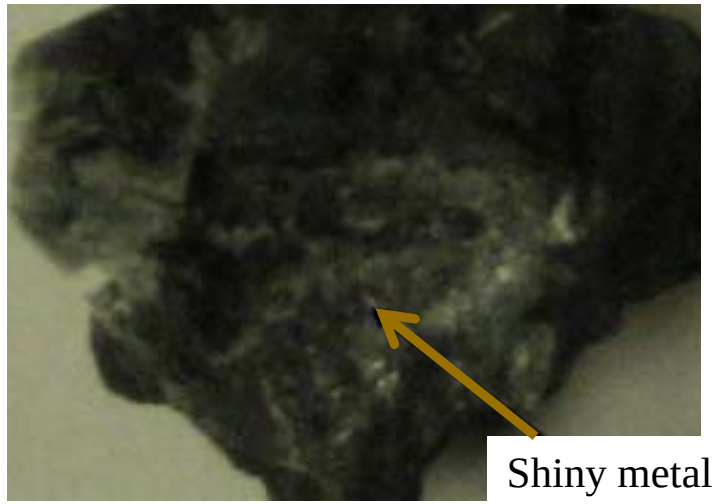
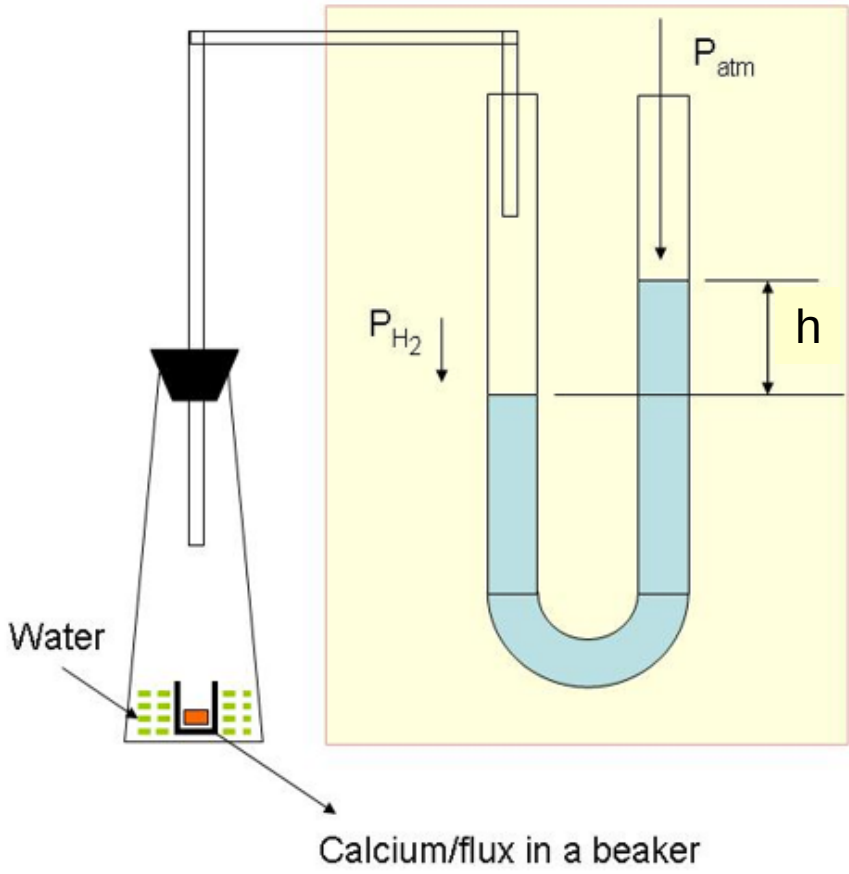


Fig b . Broken piece from the deposit

- Deposit on the cathode was very brittle and the surface was grayish in appearance.
- Underneath the grayish surface the deposit was metallic

Manometer Experiments to Analyze the Cathode Deposits



Evolution of H_2 due to the following reaction

$$Ca + 2H_2O = Ca(OH)_2 + H_2(g)$$

Additional pressure (ΔP) due evolution of hydrogen and the increase in volume (ΔV) is given -

$$\Delta P = \rho * g * h$$

$$\Delta V = \pi * r^2 * h / 2$$

Moles of hydrogen gas (n_{H_2}) evolved

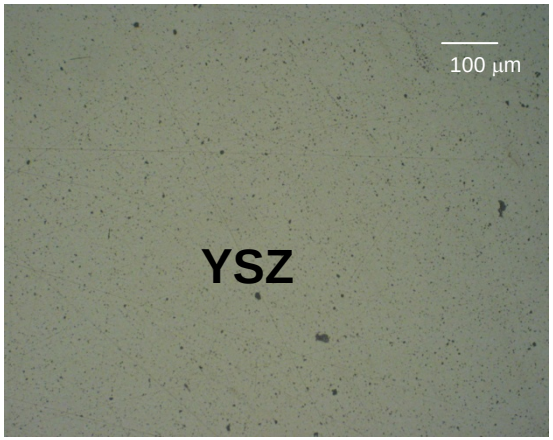
$$n_{H_2} = \frac{(P_1 + \Delta P)(V_1 + \Delta V)}{R * T} - n_1$$

$$\text{wt \% metallic Ca} = \frac{n_{H_2} * (40.078\ g) * 100}{\text{Amt of sample (g)}}$$

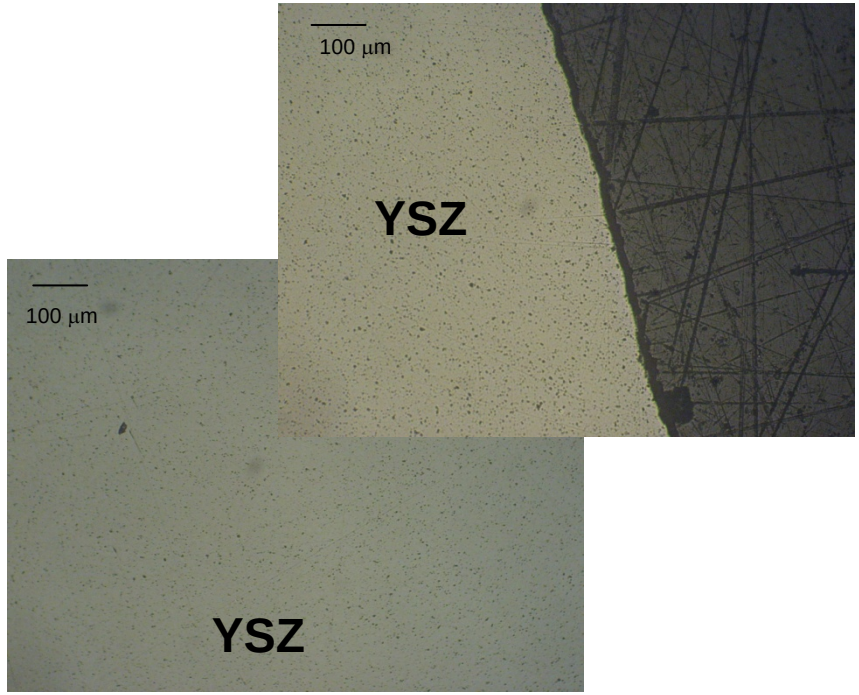
The deposit had 16 wt % of metallic calcium

W.D Threadgill, “The Calcium Chloride-Calcium Oxide Fused Salt Electrolytic System : Solubilities, Metal Contents, and Freezing Points” Journal of the Electrochemical Society,112,(1965), 632

Comparison of Membrane before and after electrolysis



Cross-section of as purchased Yttria Stabilized Zirconia (YSZ) membrane



Cross-section of the YSZ membrane after the electrolysis

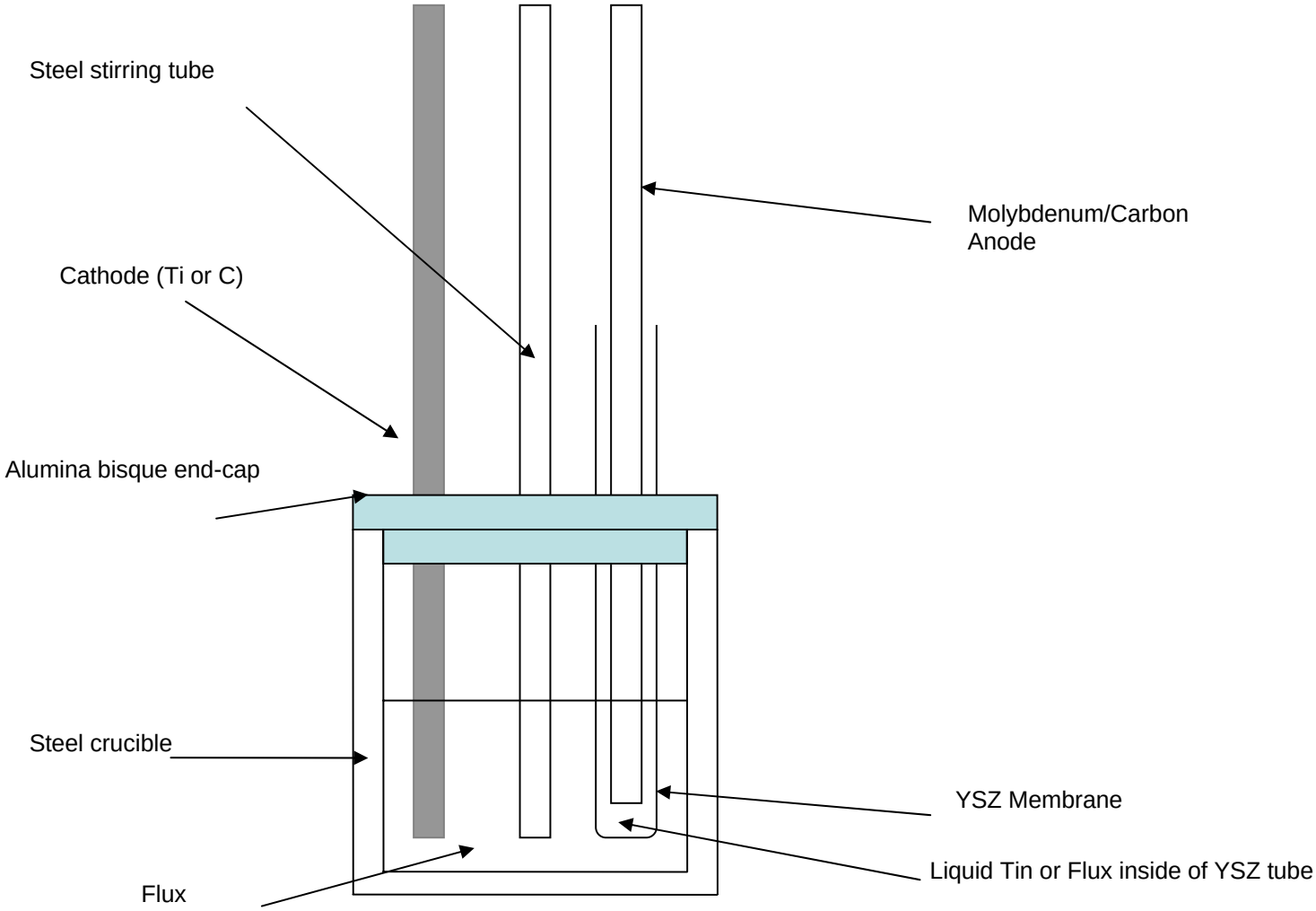
- The membrane is essentially unaffected so a thinner membrane can be used.
- The resistance offered by a thinner YSZ membrane will be lower and so higher current density in the order of 1 A/cm^2 can be achieved*.

* A. Krishnan, X.G. Lu, U.B. Pal, "Solid Oxide Membrane Process for Magnesium Production directly from Magnesium Oxide", Metallurgical and Materials Transactions,. 36B, (2005), 463.

Conclusion

- Calcium can be made by using SOM process.
- A predominantly ionic flux with composition (65.12%$CaCl_2$ - 28.31%CaF_2 - 6.57% CaO) and suitable materials required for SOM process has been identified.
- The dissociation potential of CaO in the flux was around 1.65 volts.
- Since the membrane was virtually unaffected by the process a current density up to 1 A/cm^2 can be achieved by decreasing the thickness of the membrane.
- The calcium metal made by reducing CaO in the cathode was trapped in the molten salt. So a set up where the cathode can be raised continuously during SOM electrolysis would give deposit with high metal content.
- In the SOM process Ca can be reduced and alloyed at a liquid metal cathode and subsequently removed employing a Distillation process.

SOM Set-up for Titanium Production



SOM Process for Ti Production

6 wt%TiO_2 Containing Flux (MgF_2-CaF_2) @ 1100-1300 ^{0}C

Non-consumable anode in reducing atmospheres

$H_2(g) + O^{2-} \rightarrow H_2O(g) + 2e$

$CO(g) + O^{2-} \rightarrow CO_2(g) + 2e$

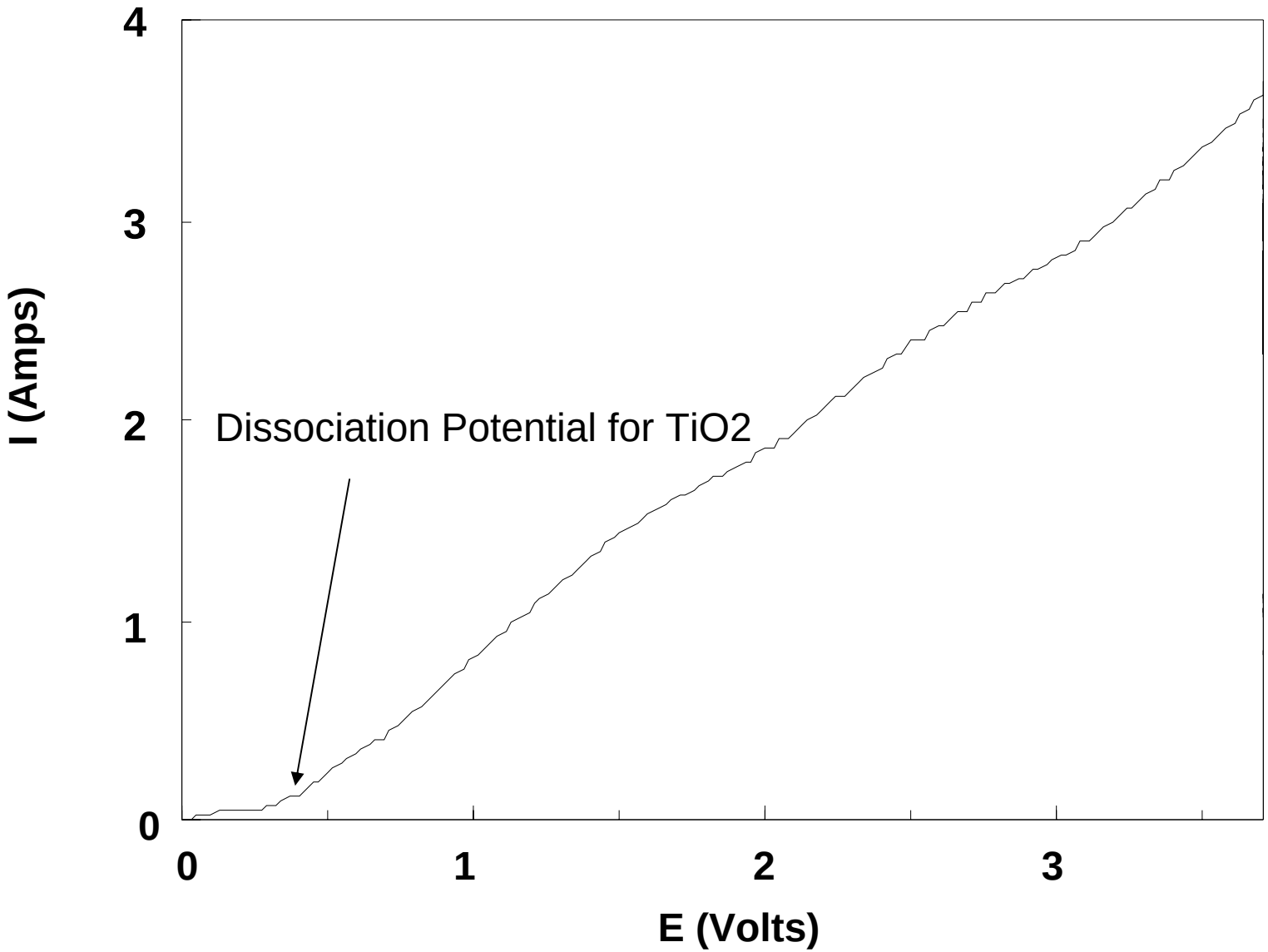
Consumable carbon anode

$O^{2-} + C \rightarrow CO(g) + 2e$

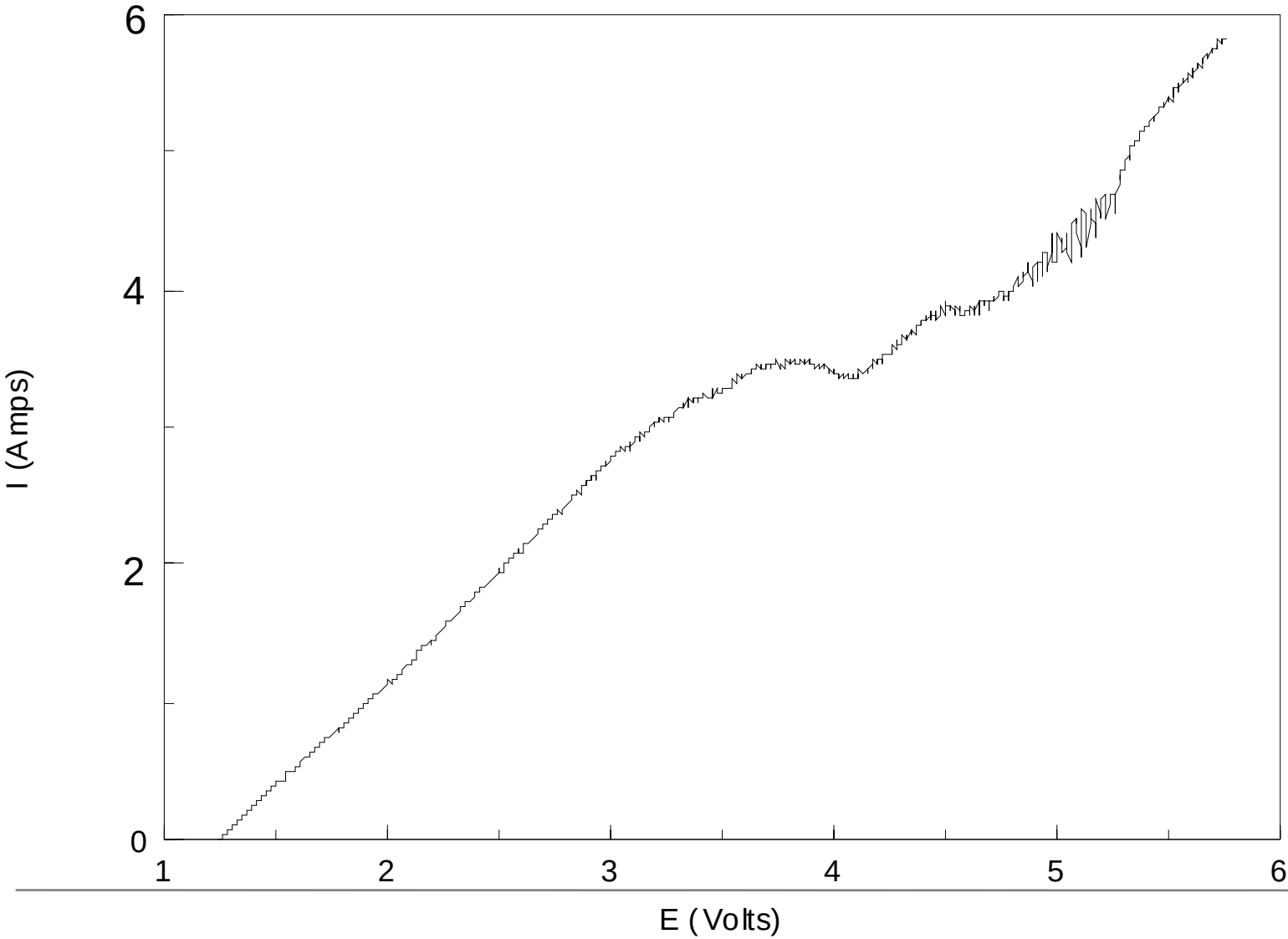
Cathode

$Ti^{n+} + ne \rightarrow Ti$ (solid)

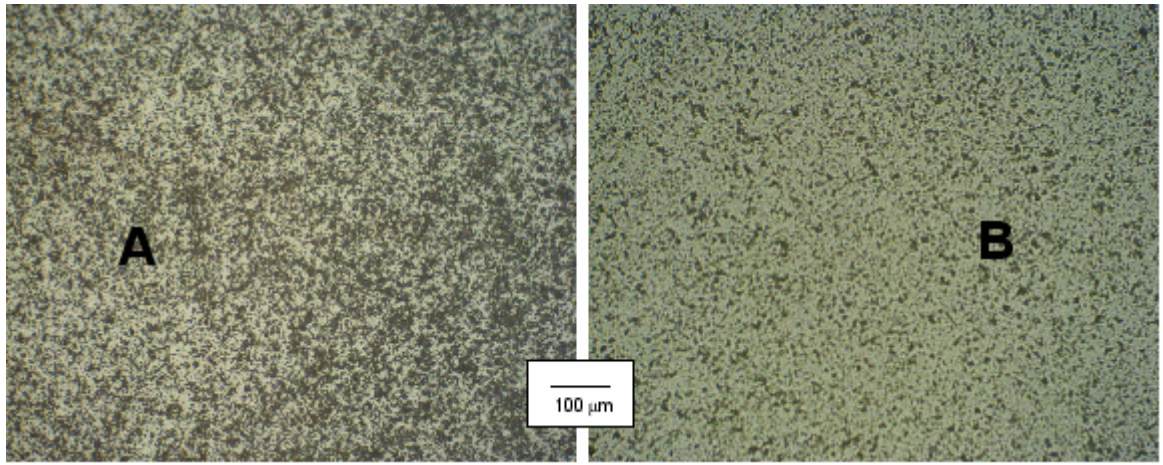
Potentiodynamic Before Electrolysis Scanned at 5mV/sec T = 1150 deg. C



Potentiodynamic After Electrolysis Scanned at 5mV/sec at 1150 deg. C



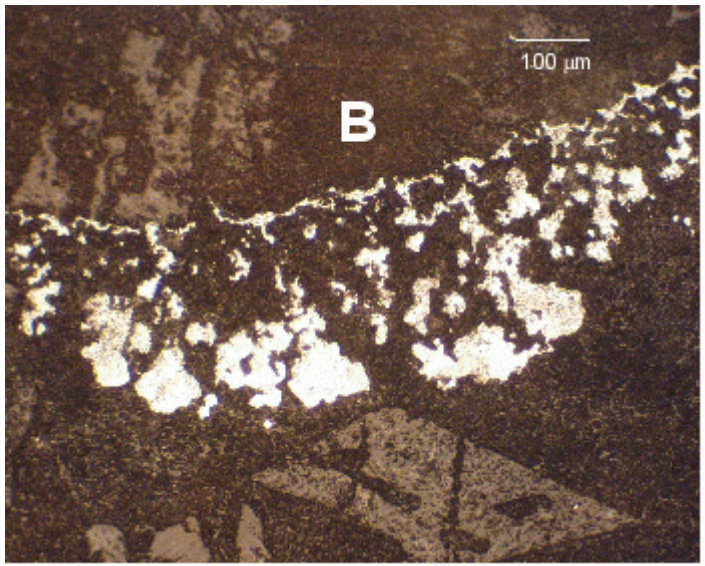
Cross-section of the Zirconia Membrane



A. In contact with the flux

B. In contact with the molten metal anode

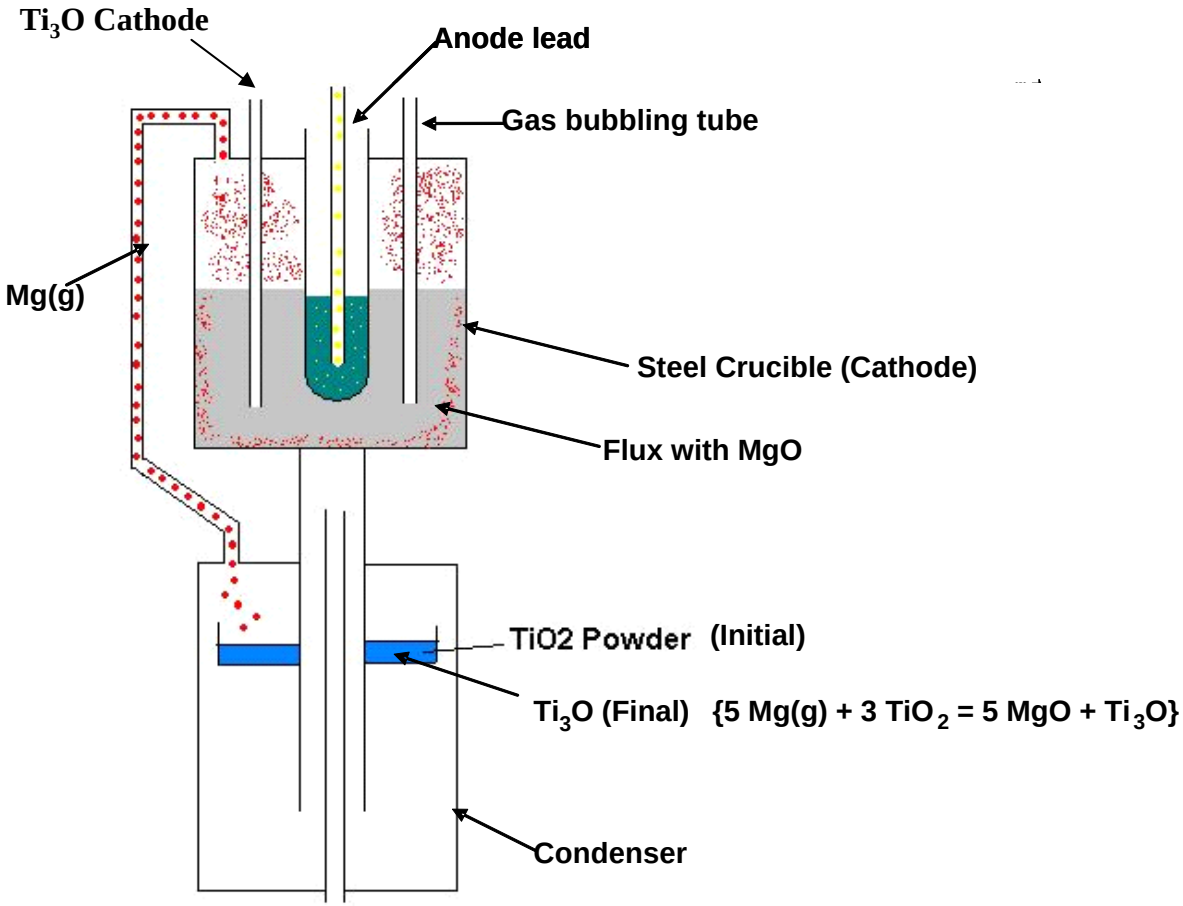
Metal Deposit at the Cathode

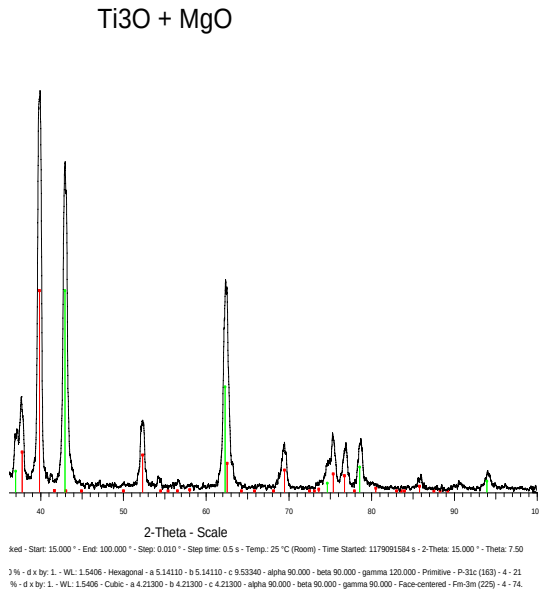


Conclusions on SOM Electrolysis of Ti

- Reduction of titanium oxide in the flux imparts electronic conductivity to the flux and results in destabilizing the zirconia
- Lower oxidation state of Ti prior to adding in the SOM cell

Magnesiothermic Reduction of TiO_2 Using the SOM Process





SOM Process for Ta Production

Ta_2O_5 Containing Electrolyte (MgF_2/MgO/CaF_2/Ta_2O_5-Other minor constituents) @ 1100-1300 ^{0}C

Non-consumable anode in reducing atmospheres

$H_2(g) + O^{2-} \rightarrow H_2O(g) + 2e$

$CO(g) + O^{2-} \rightarrow CO_2(g) + 2e$

Non-consumable anode in oxidizing atmospheres

$O^{2-} \rightarrow \frac{1}{2} O_2(g) + 2e$

Consumable carbon anode

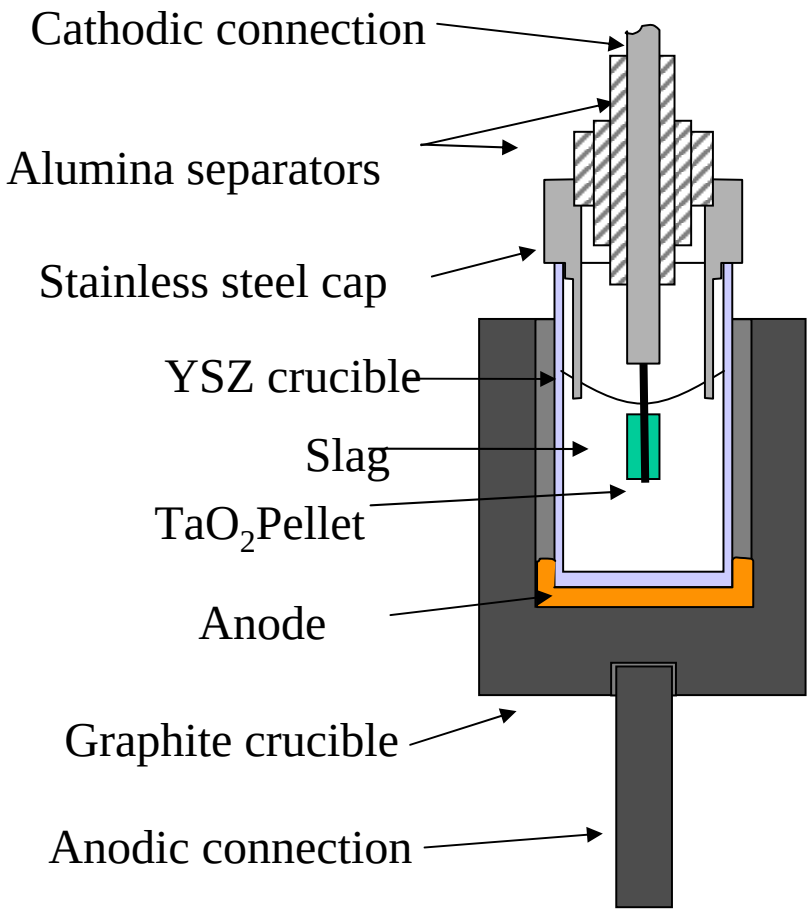
$O^{2-} + C \rightarrow CO(g) + 2e$

Cathode

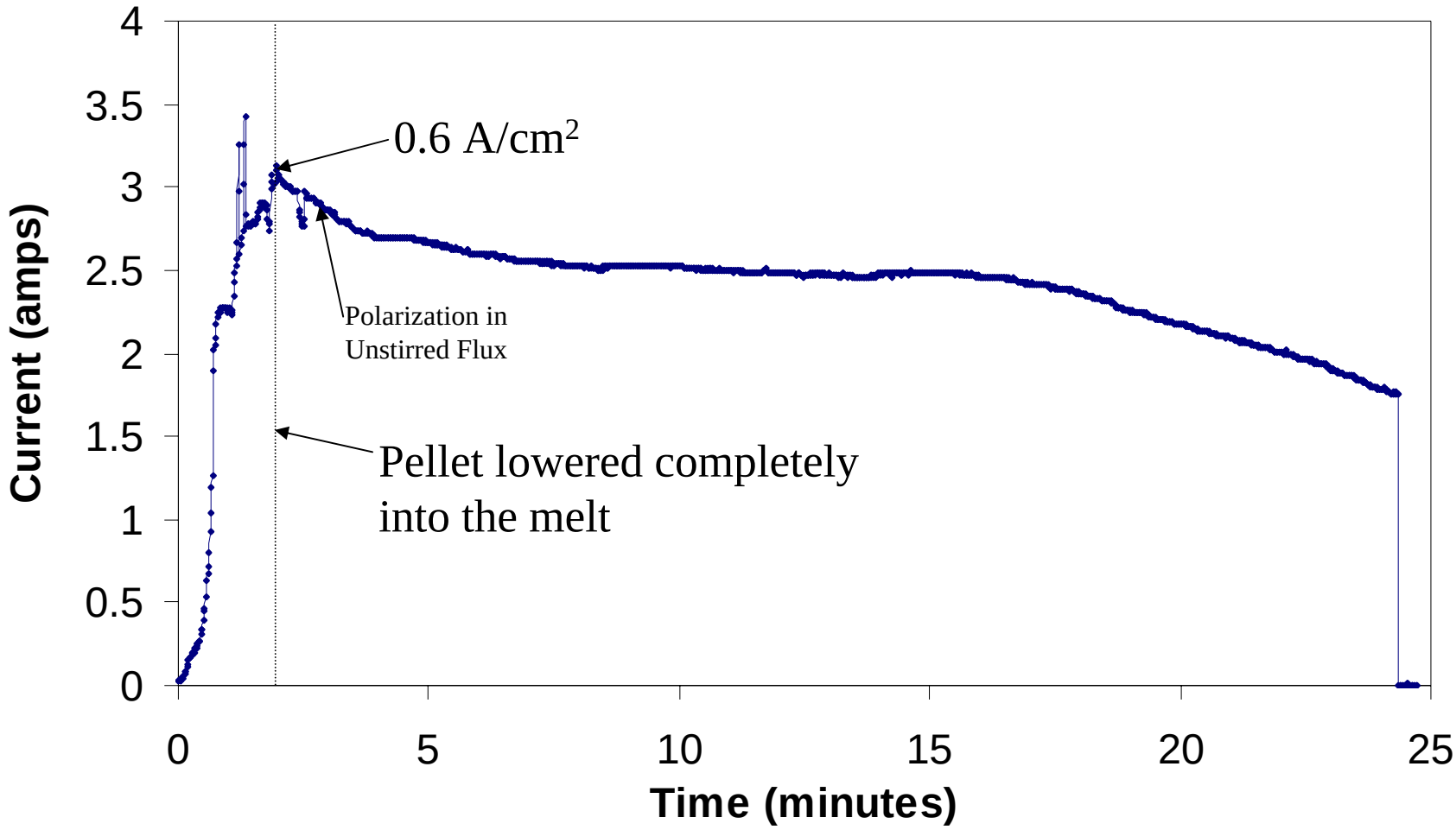
$Ta^{n+} + ne \rightarrow Ta$ (solid)

Measurements: Potentiodynamic and potentiostatic

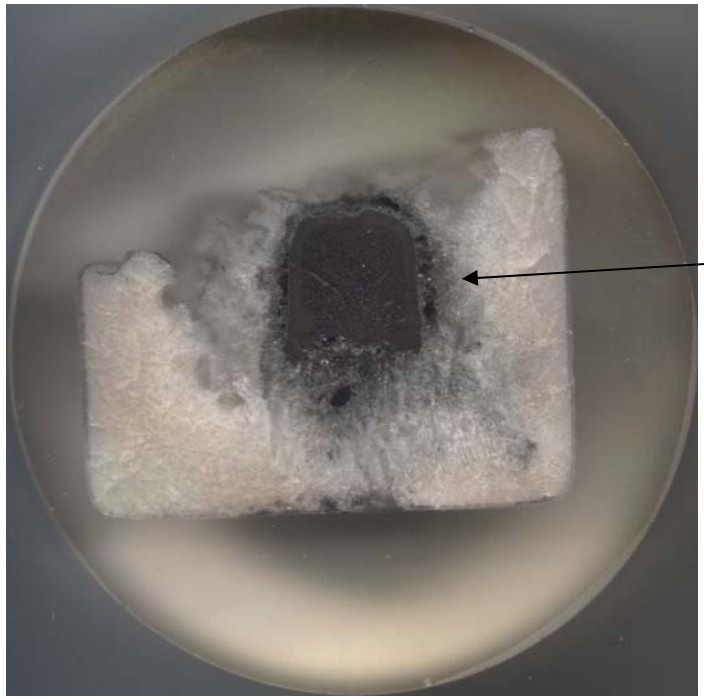
SOM Electrolysis with One Tantalum Oxide Pellet (2.5 g) as Cathode at 1300 C



Potentiostatic hold at 1.9 volts

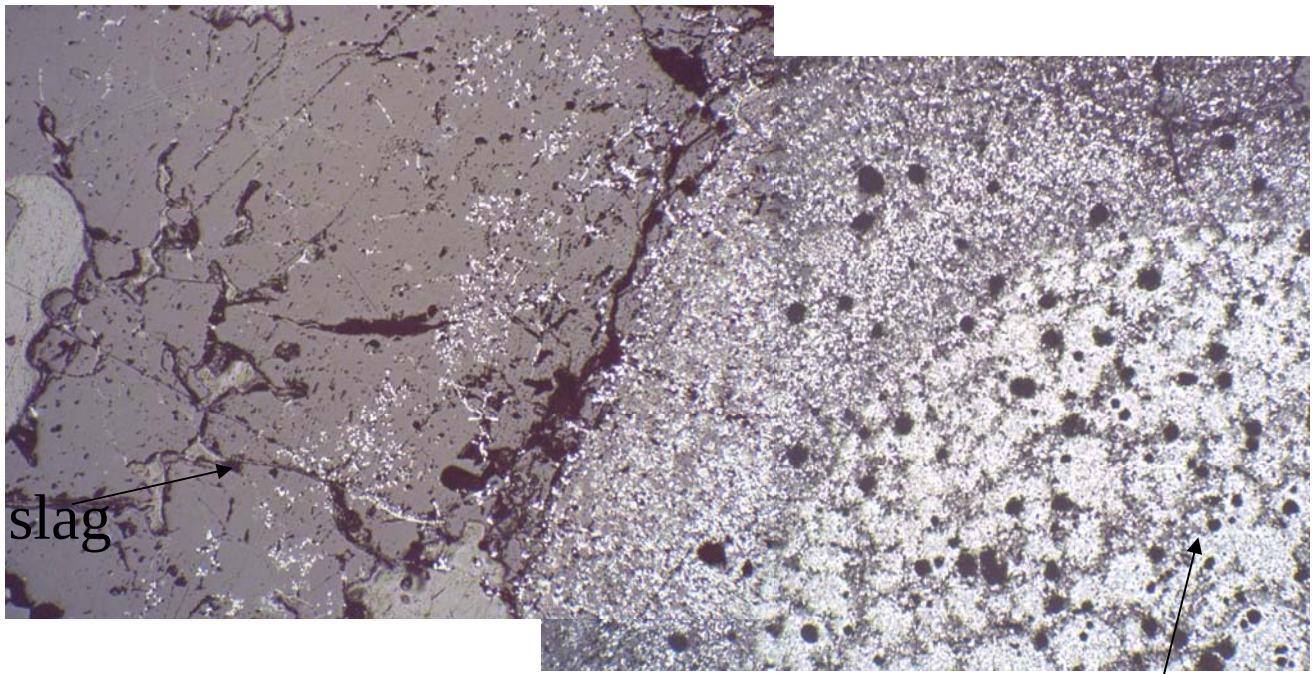


Reduced Tantalum Oxide Cathode



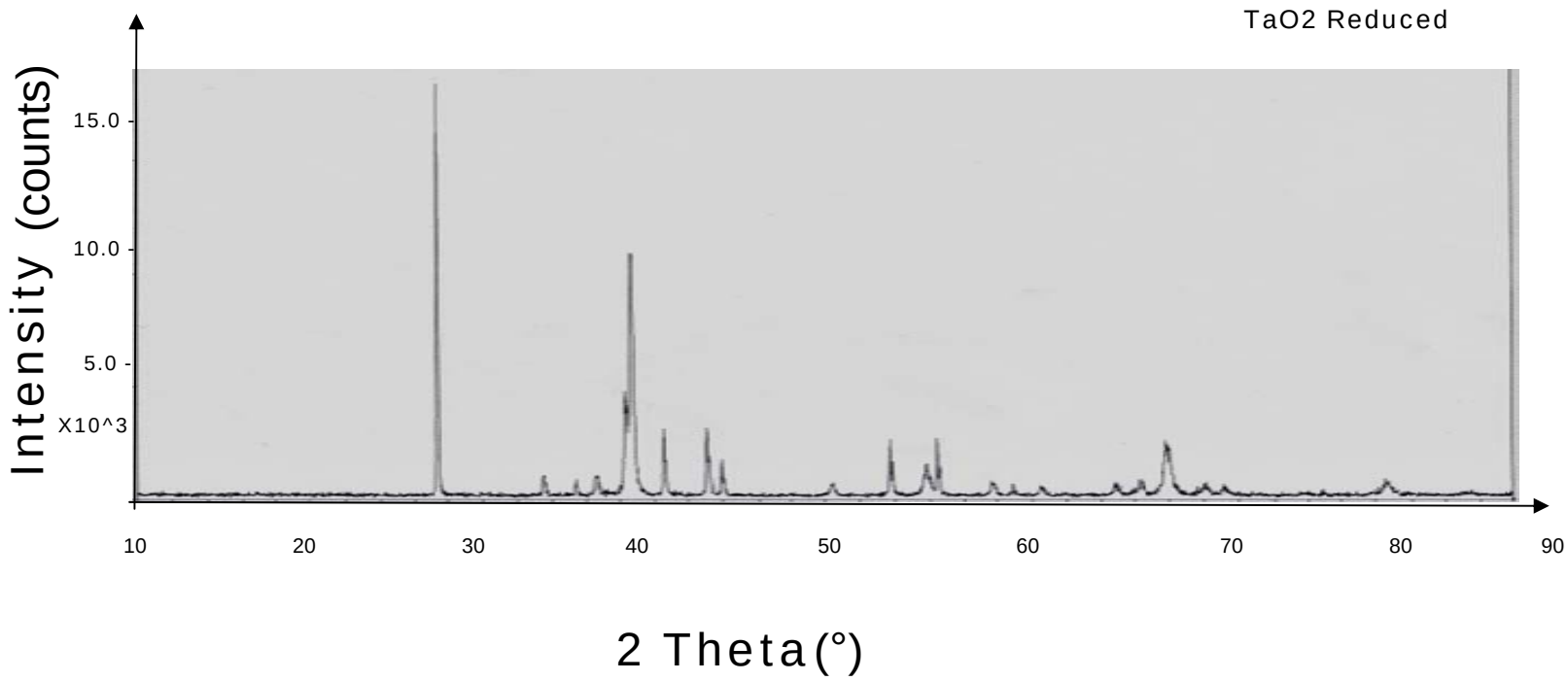
Reduced Tantalum Oxide Cathode

Top left corner of the reduced tantalum oxide cathode



X-Ray Data of Reduced Tantalum Oxide Cathode Pellet After SOM Electrolysis at 4.0V and 1300 C

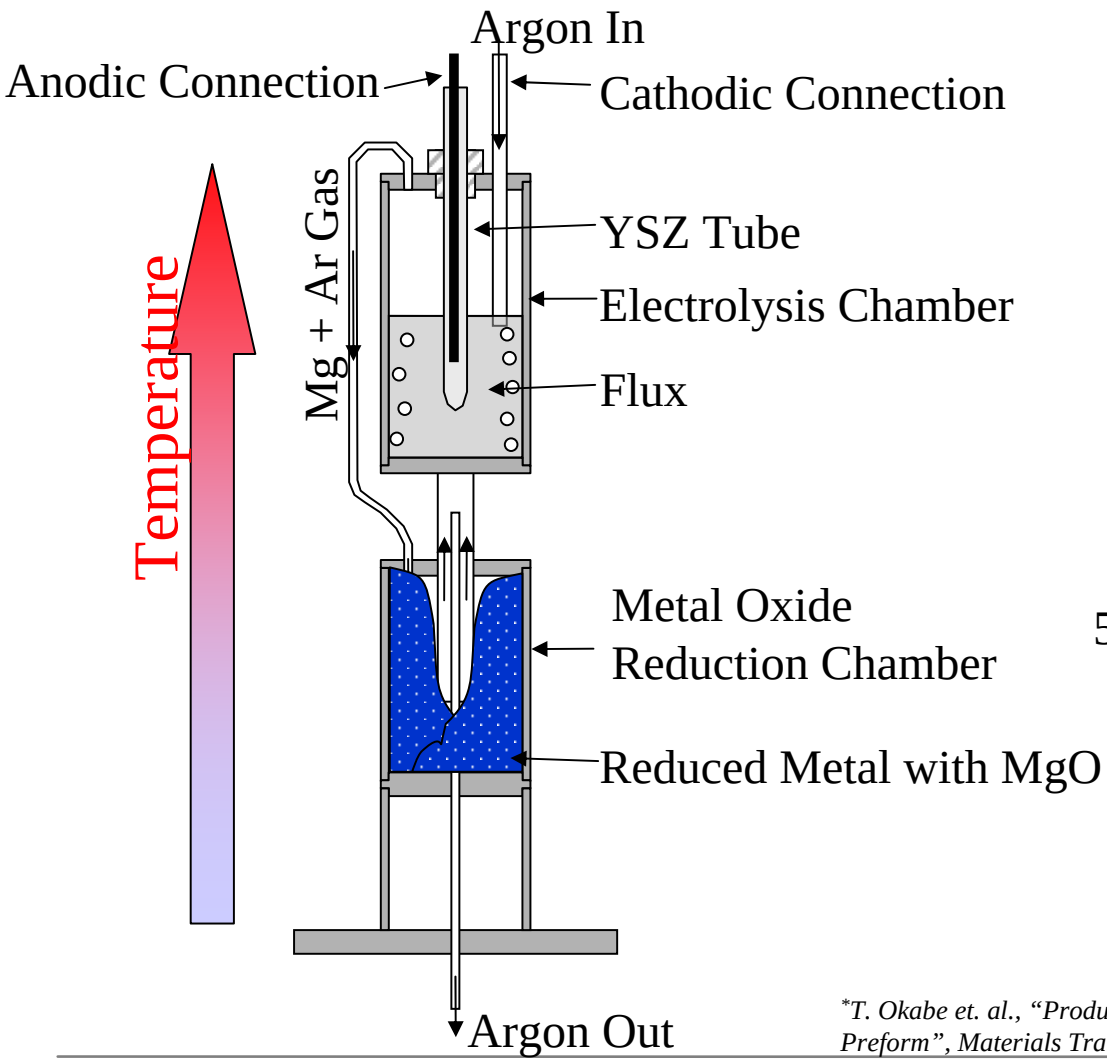
Reduced Tantalum Oxide shows Ta metal, residue flux and unreduced tantalum oxide



Conclusions on SOM Electrolysis of Ta

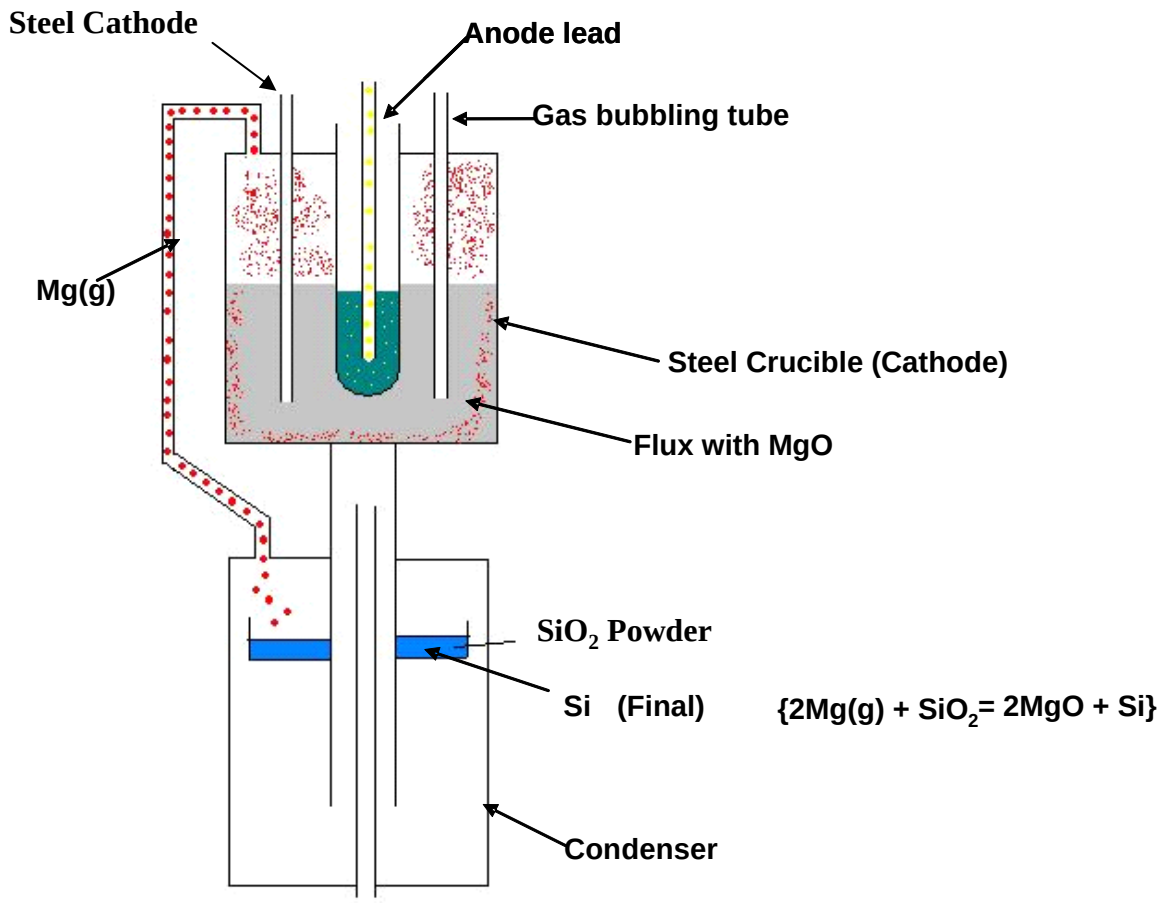
- Ta production by the SOM process is also possible by employing tantalum oxide as the cathode and sufficient stirring of the flux
- Ta Production by Magnesiothermic SOM process is possible

SOM Process Experimental Setup for Magnesiothermic Production of Ta from its Oxides



$5Mg(g) + Ta_2O_5 = 5MgO + 2Ta$

Back into the SOM Reactor

*T. Okabe et. al., "Production of Ta Powder by Magnesiothermic Reduction of Feed Preform", Materials Transaction, vol. 44, No. 12, p. 2646, (2003)

Magnesiothermic Reduction of SiO_2 Using the SOM Process