Electrochemical Behaviour and Processing of CH_4 and CO_2 in Molten Salts

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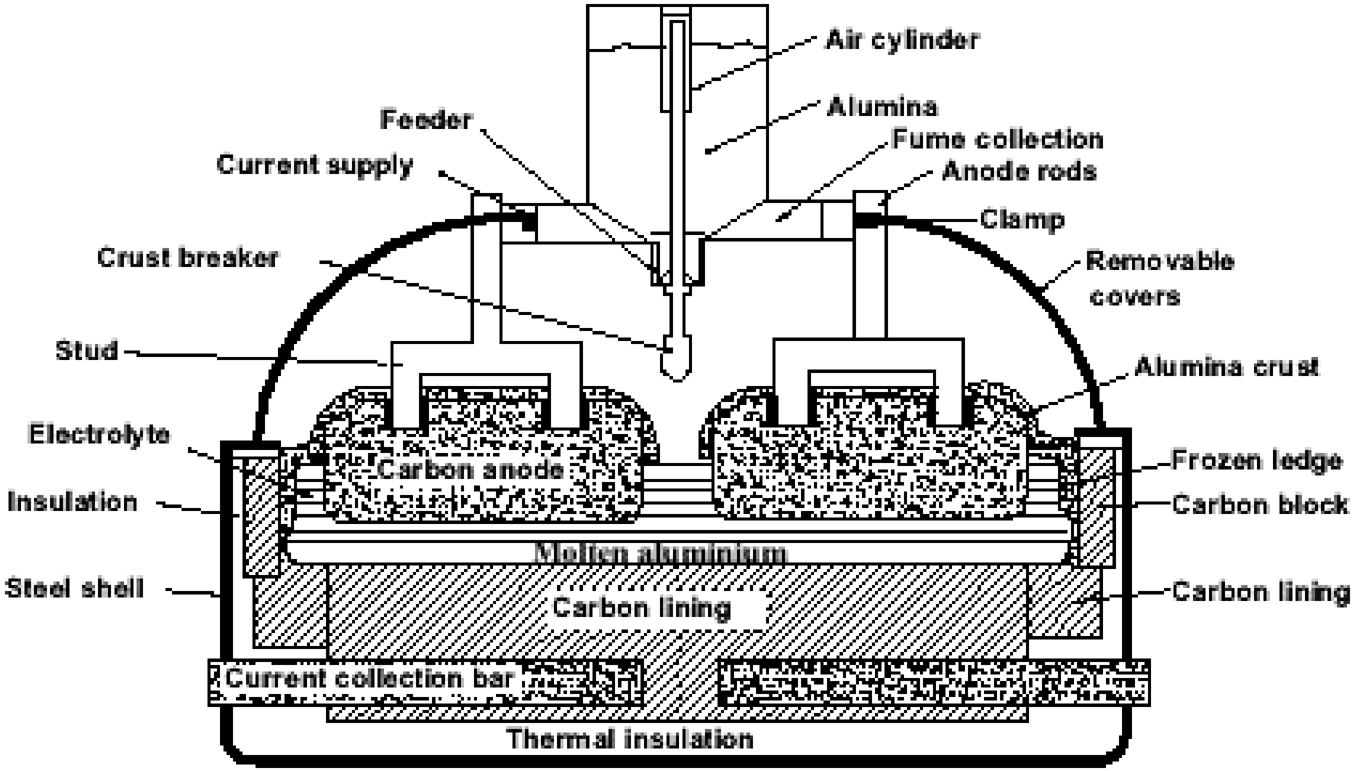
Objectives

- CH_4:
  - Electrochemical methods to utilize the energy in CH_4 for metal production
  - Example: Production of Al, Norway's largest electrochemical production
- CO_2:
  - Electrochemical methods to convert CO_2 to valuable products, (including CO_2 capture)
  - Example: C and O_2 in molten carbonate melt

The Hall-Héroult Process for Al Production

Electrochemical decomposition of Al_2O_3 dissolved in molten cryolite

- Electrolyte: Cryolite, Na_3AlF_3, and additives : AlF_3, CaF_2, Al_2O_3. 960 °C
- Cell reaction: 2 Al_2O_3 (diss) + 3 C (s) = 4 Al (l) + 3 CO_2 (g)



Aluminium Production - Alternatives

- **Carbon anode** (H-H)

  $Al_2O_3 + 3/2\ C = 2\ Al(l) + 3/2\ CO_2(g)$ (1) $\Delta G° = 689$ kJ/mol
  - CO_2 emission (1.6 metric tons of CO_2 per ton Al produced)
  - Periodic replacement of consumed anodes
  - Regular adjustment of anode height
- **Inert anode** (e.g. SnO_2 and $NiFe_2O_4$ – based anodes)

  $Al_2O_3 = 2\ Al(l) + 3/2\ O_2(g)$ (2) $\Delta G° = 1283$ kJ/mol
  - O_2 emission
  - Non consumable anodes
  - Higher theoretical cell voltage
- **Reducing gas anode (CH_4 or H_2)**

  $Al_2O_3 + 3/4\ CH_4 = 2\ Al(l) + 3/4\ CO_2(g) + 3/2\ H_2O(g)$ (3) $\Delta G° = 683$ kJ/mol
  - 50 % less CO_2 emission
  - No anode consumption
  - Similar cell voltage to (1) and 1 V lower than (2)

Gas Anode

- Anode requirements:
  - Electrochemical and physical stability
  - Stable towards molten electrolyte, metal, and gas components
  - Electrical conductivity
- Additional requirements for a gas anode:
  - Controlled porosity → good contact between anode, gas and electrolyte
- Other challenges
  - Reaction efficiency (yield of CH_4 / H_2 oxidation)
  - Porous materials
    - Reduced electrical conductivity
    - Reduced mechanical robustness

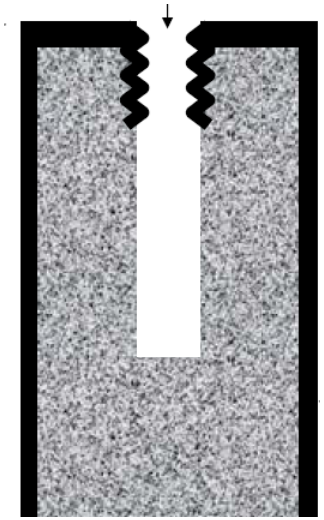
Previous Work

- Depolarization of reducing gas anode (carbon) in aluminium electrolysis has been reported [2-4]
- Initial studies by the authors have shown that the anode consumption can be reduced by introduction of methane gas during aluminium electrolysis at 880 °C [5]
- A recent US patent presents a method of aluminum electrolysis with a non-consumable anode of the type used for solid oxide fuel cells [6]

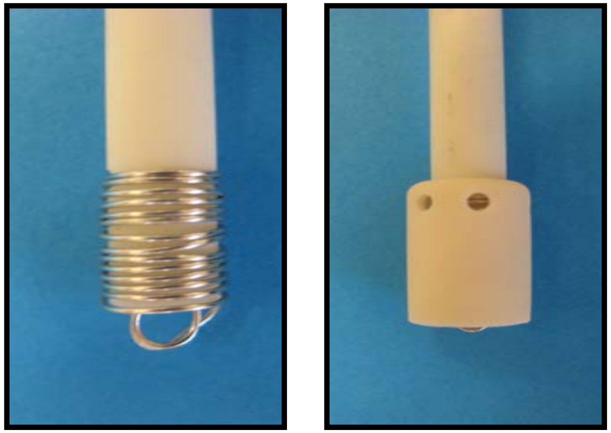
- Conclusions:
  - More systematic work with carbon is needed
  - More work with inert anodes is needed

2. M. L. Ferrand, Bull. Soc. Franc. Electriciens, ***79****, 412 (1957).*
3.V. V. Stender and V. V. Trofimenko, Khim. Tekhnol., ***12****, 41 (1969).*
4.M. L. Kronenberg, J. Electrochem. Soc., ***116****, 1160 (1969).*
5. Ratvik, A.P. and Xue, J., Norwegian Patent Application No. 2002 2617 – Anode. Patent granted 2004 – NO patent No 316925.
6. R. A. Rapp, USA patent: 6039862 (1999).

Gas anode development



- Candidate anode materials
  - Porous carbon materials
  - SnO_2-based materials
    - Most common ceramic material with electrical conductivity
    - Proposed as the best anode material in $CaCl_2$-NaCl melts[1]
  - $NiFe_2O_4$-based materials
    - Most common cermet material
    - Corrodes in $CaCl_2$-NaCl melts[1]
    - Liquid phase sintering
      → challenging porosity control
  - Metals
    - Porous metals of Ni,
      Hasteloy C-276, Inconel 600, Pt



Pt anode for introducing reducing gas

1. K. T. Kilby *The Anodic Testing of a Tin Oxide (SnO2) Based Material for the FFC-Cambridge Process, PhD Thesis, University of Cambridge, 2008*

Experimental Approach

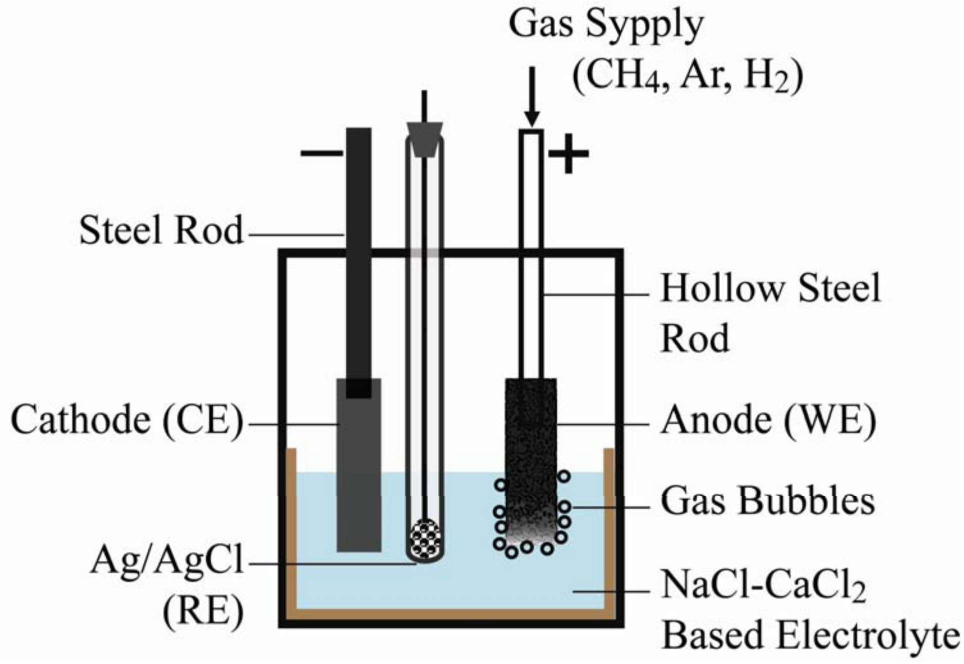
- Goal:
  Aluminum electrolysis with reducing gas (CH_4 or H_2) anode

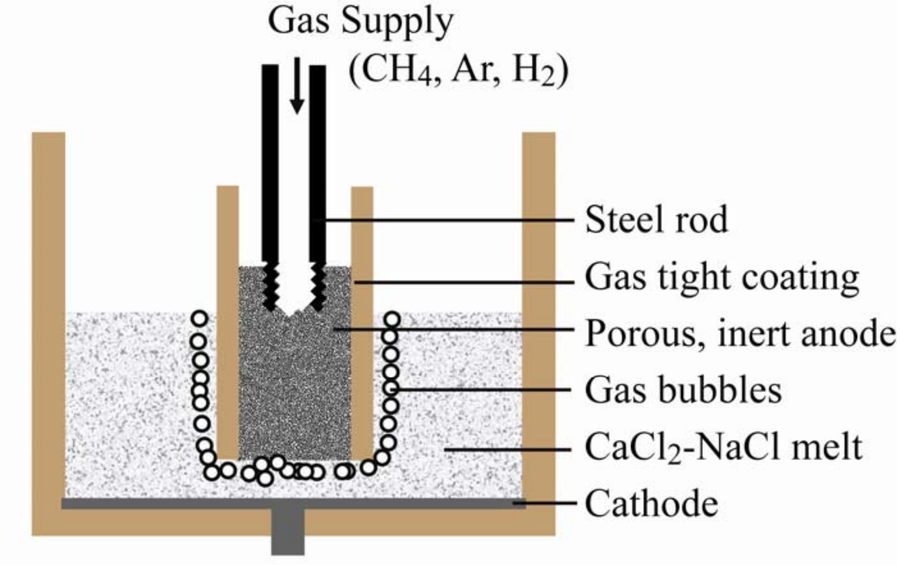
- First:
  Establish the methods in a simpler system
  - Molten electrolyte: $CaCl_2$-NaCl-CaO with $PbCl_2$ and AgCl
  - Temperature: 680 °C
  - Working electrode: Pt gas anode
Porous carbon anode
Oxide anode (SnO_2 or $NiFe_2O_4$)
  - Counter electrode: Carbon cathode
  - Reference electrode: Ag/AgCl

Experimental Techniques

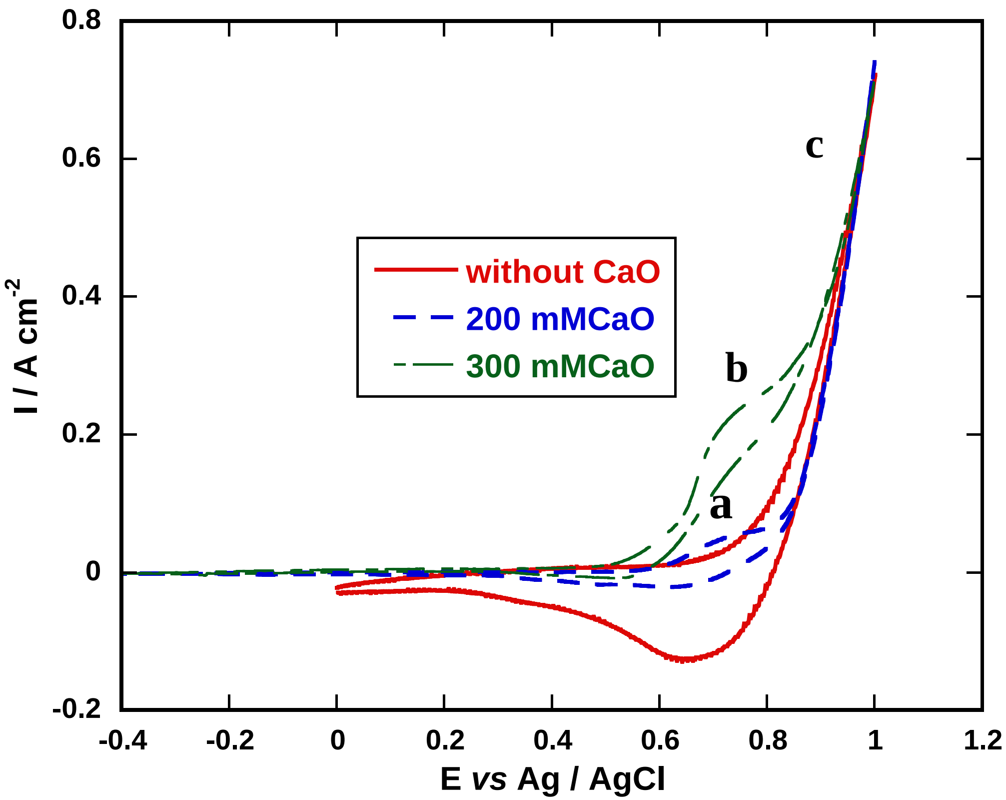
- Cyclic Voltammetry
- Constant Current Electrolysis
- Gas Chromatography Analysis

Experimental setup for electrochemical measurements





Cyclic Voltammetry Test



Cyclic voltammograms in $CaCl_2$-NaCl(80-20 mol%)-CaO melts with different concentration of CaO at 750 ℃

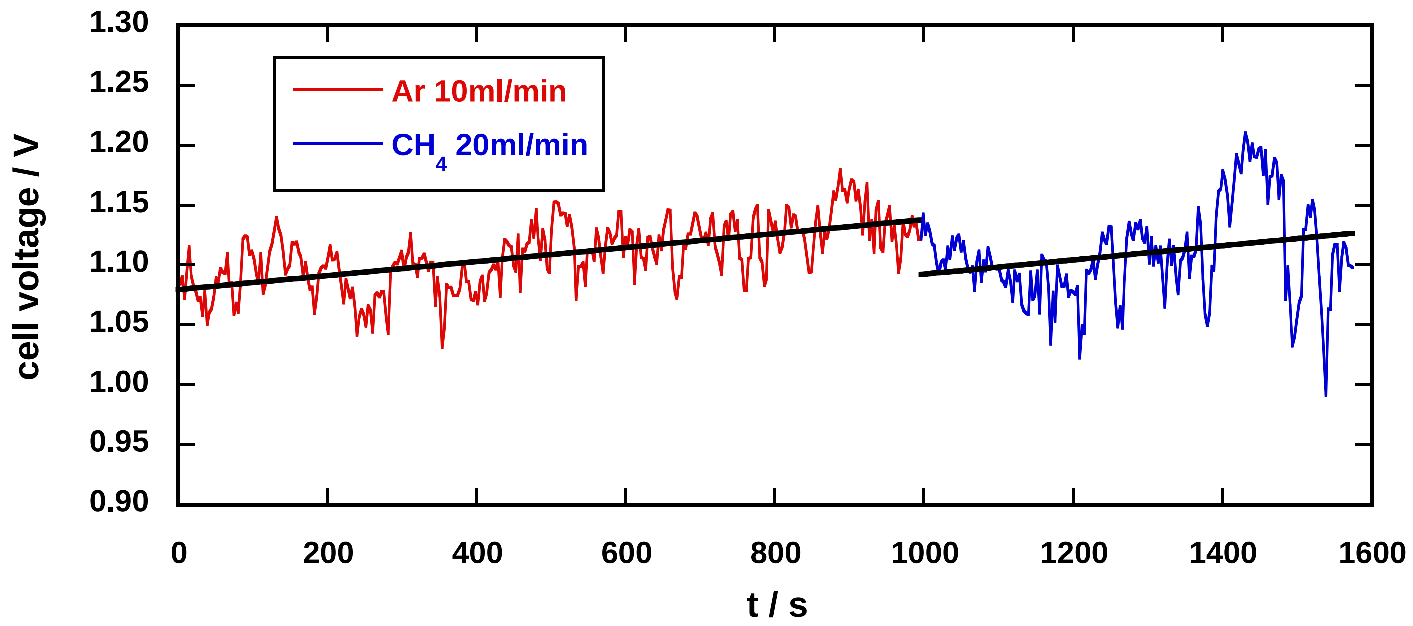
WE – *Pt*

Peak a,b: $2O^{2-} = O_2 + 4e$

Peak c: $4Cl^{-} = 2Cl_2 + 4e$

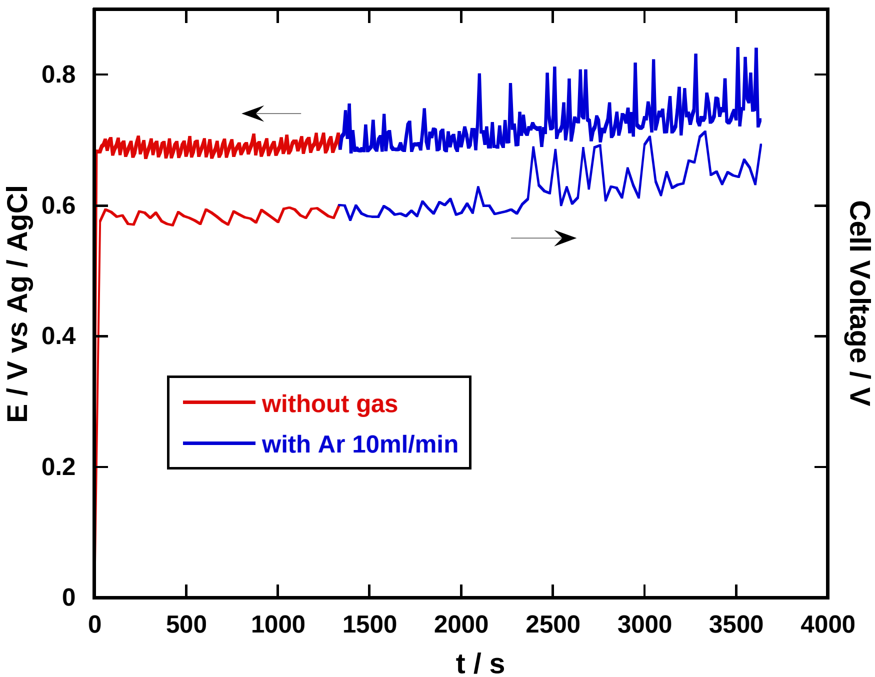
Early Results

- $NiFe_2O_4$-based anode in NaCl-$CaCl_2$ melt with CaO and AgCl
  - A larger shift is anticipated – competing reactions



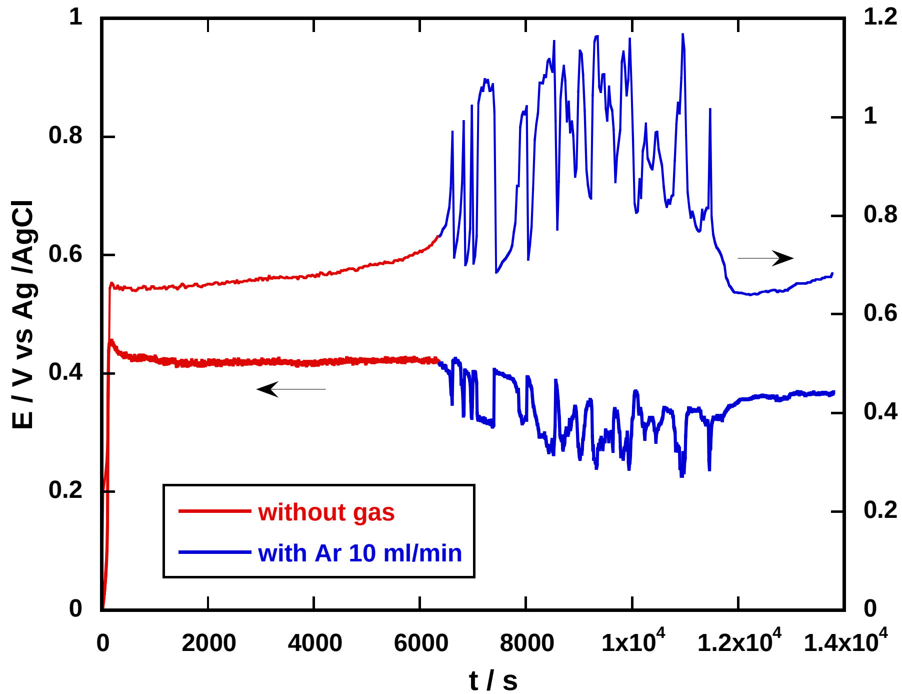
Constant Current Electrolysis

WE - *Pt*



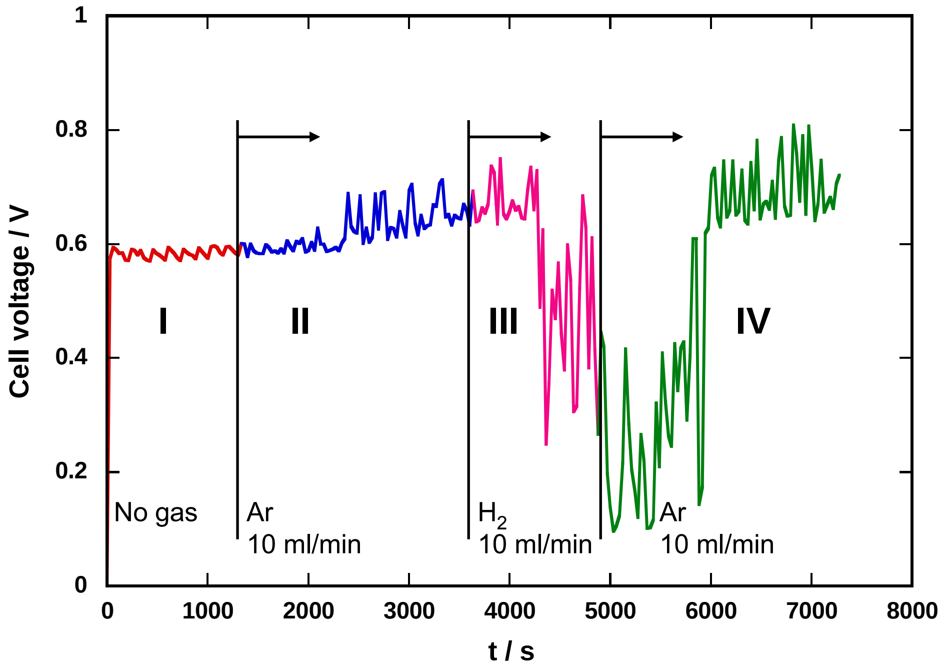
Electrolysis with constant current 0.1A
$CaCl_2$-NaCl(70-30 mol%)-CaO(16 mol%) melt with AgCl (4.7 mol%); current density, 30 mA/cm^2

WE - *Porous carbon*



Electrolysis with constant current 0.8A
$CaCl_2$-NaCl(70-30 mol%)-CaO(16 mol%) melt with $PbCl_2$ (3.4 mol%); current density 100 mA/cm^2

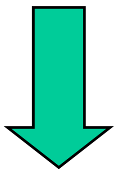
Constant Current Test w/H_2



Electrolysis with constant current 0.1A in $CaCl_2$-NaCl(70-30 mol %)-CaO(16 mol %)-AgCl (4.7 mol %) melt; current density, 30mA cm^{-2}

WE – *Pt*

Introduction of H_2



around 0.3 V decrease in anode potential and cell voltage

Anode reactions:

I, II, and IV: $2O^{2-} = O_2 + 4e$

III: $2O^{2-} + 2H_2 = 2H_2O + 4e$

Summary and Further Work

- Different gas anode configurations have been tested
- Some promising results, however, anode design is challenging
- 0.3 V reduction of cell voltage during constant current electrolyis with H_2 in $CaCl_2$-NaCl-CaO-AgCl melt

- Main challenge is to design an anode with good contact properties between anode, gas, and electrolyte

- Redesigned Pt anode in progress
- More test with less reactive carbon materials
- Online gas chromatography analysis during the electrolysis
- More work on inert anodes (e.g. SnO_2)

Acknowledgement

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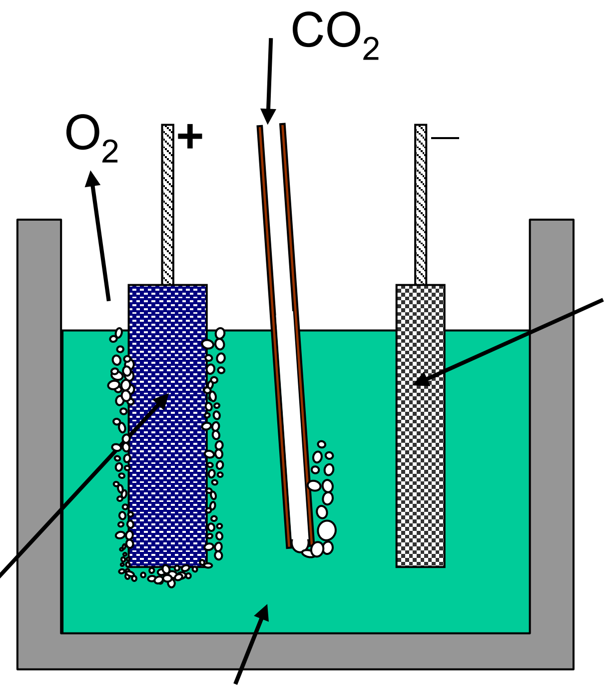
for financial support !

Conversion of CO_2 in molten salts

- An alternative method of CO_2 capture?

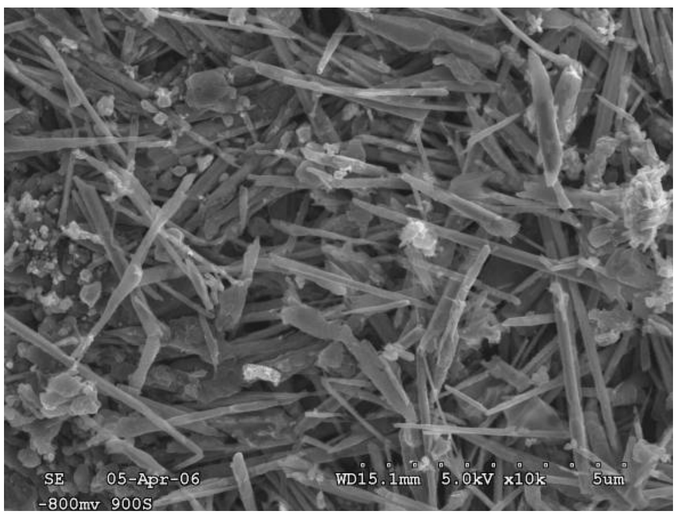
- Dissolution of CO_2:
  $CO_2 + O^{2-} = CO_3^{2-}$
- Cathode reaction:
  $CO_3^{2-} + 4\ e^- = C(s) + 3\ O^{2-}$
- Anode reaction:
  $2\ O^{2-} = O_2(g) + 4\ e^-$
- Total reaction:
  $CO_2 = C(s) + O_2(g)$

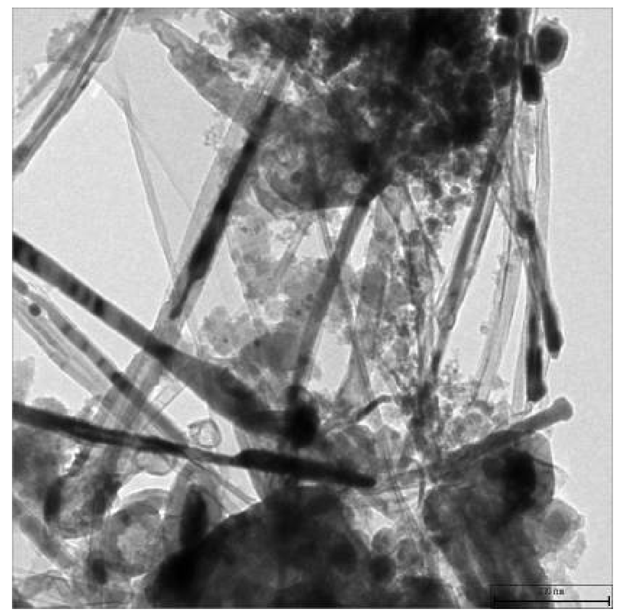
- $E_{rev} = -1.0$ V
- $W_{el} \sim 3.5$ kWh/kg CO_2



Some Results

- Formation of different carbon nanostructures
- Challenges
  - Avoid unwanted structures
  - Obtain high yield





Acknowledgement: S. Rolseth, C. Marioara

Summary and Challenges

- Simple experimental set-up and cheap chemicals
- Readily available raw material, CO_2
- Inert electrodes available
- Easy to clean products for electrolyte

- Process conditions to obtain higher selectivity and yield of valuable C products
- Current efficiency to secure low processing costs

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