The Behaviour of Moisture in Cryolite Melts

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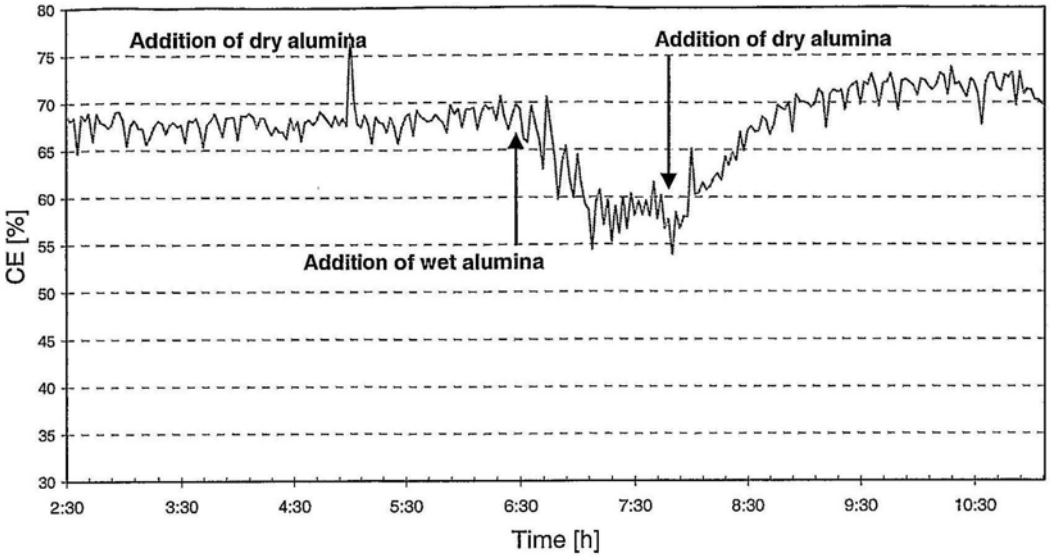
Outline

- **Motivation**
  - **Current efficiency, behaviour of moisture in molten salts – literature, aim**
- **Approach and Methodology**
  - **Gas analysis, estimation of H accumulation, voltammetry**
- **Experimental**
  - **Experimental set - up and procedures**
- **Results**
  - **Gas analysis, voltammetry**
- **Discussion**
- **Concluding remarks**

Current Efficiency



Electrolysis test with inert anodes at Hydro:

- **Addition of non-dried alumina brought about a decrease in CE**
- **The observed loss was much larger than the theoretical**
- **Hypothesis: Hydrogen containing species are soluble in the bath, and may be reduced several times in a shuttle reaction**

Julsrud, Lorentsen and Rosenkilde, US patent 2008

HF Formation

- **Fluorides present in the bath or vapour react with moisture:**

$$\tfrac{2}{3}\,AlF_3(diss) + H_2O(g) = 2\,HF(g) + \tfrac{1}{3}\,Al_2O_3(diss)$$

$$NaAlF_4(g) + H_2O(g) = 2\,HF(g) + \tfrac{1}{3}\,Al_2O_3(s) + \tfrac{1}{3}\,Na_3AlF_6(s)$$

- **Structural hydroxyl in the primary alumina and water content in the ambient air**

- **What happens in the bath?**

Wahnsiedler et al. 1978, Haupin and Kvande 1993, Hyland et al. 2004

Behaviour of Water in Molten Salts (1)

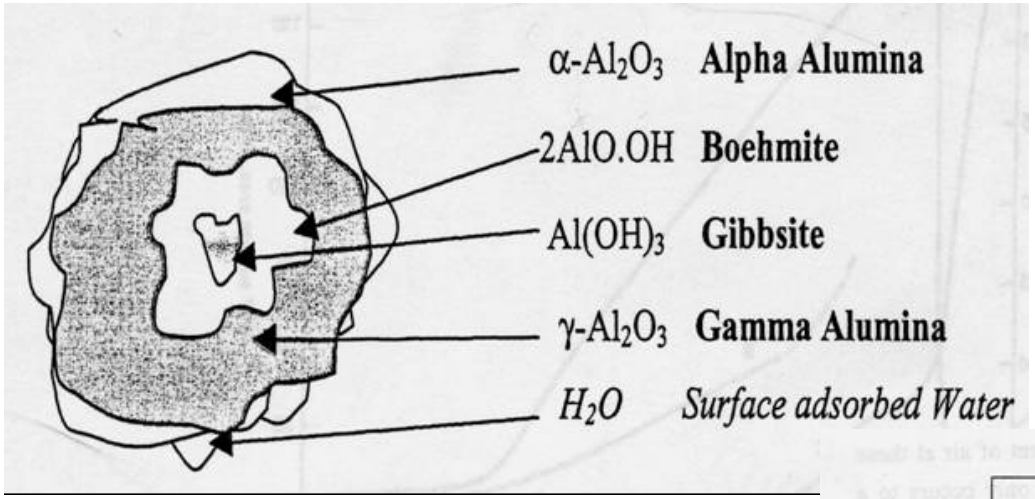
- ”Metal Mist” (Haupin 1962)

  - Cryolite melt containing molten aluminum in contact with air gave formation of hydrogen bubbles

- Existence of a meta stable hydroxide (Grjotheim 1972, Hyland 2004)

  - Kinetic behaviour with respect to HF formation

Behaviour of Water in Molten Salts (2)



”Tale”:

$OH^- + F^- = HF + O^{2-}$

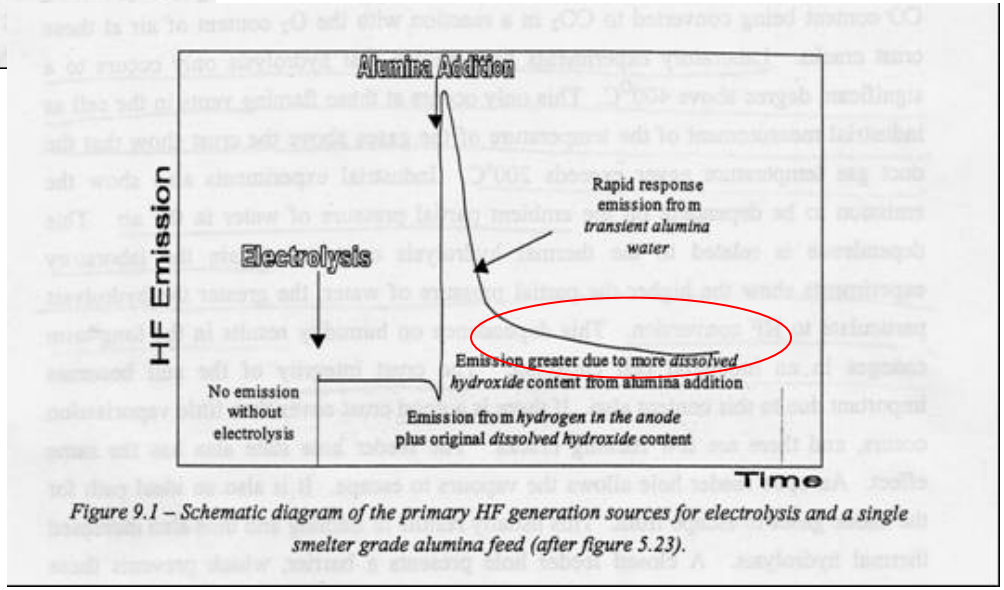


Figure 9.1 – Schematic diagram of the primary HF generation sources for electrolysis and a single smelter grade alumina feed (after figure 5.23).

Behaviour of Water in Molten Salts (3)

- **Hydrolysis reactions in LiF-BeF_2 (Matthews and Baes 1968)**

  - Observed a difference in the total proton rate in and out of the melt, signifying that H was accumulated in the molten salt as an hydroxyde

$$H_2O + F^- = HF + OH^-, \quad cOH^- = K(pH_2O/pHF)$$

Behaviour of Water in Molten Salts (4)

- **Cathodic behaviour of HF and H_2O in LiF-KF-NaF (Takenaa, Ito et al. 1984)**

  -Waves corresponding to HF and H_2O but no evidence of OH^-

  $ip(HF) = K\, v^{(1/2)}\, pHF$

  $ip(H_2O) = K\, v^{(1/2)}\, pH_2O$

Behaviour of Water in Molten Salts (5)

- In $MgCl_2$ melts, water recides as the meta stable species MgOHCl (Haarberg et al.)

  $H_2O + MgCl_2 = MgOHCl + HCl$

  - 300 minutes from addition of MgOHCl to the current wave corresponding to the hydroxychloride had vanished

  $MgOHCl = MgO + HCl$

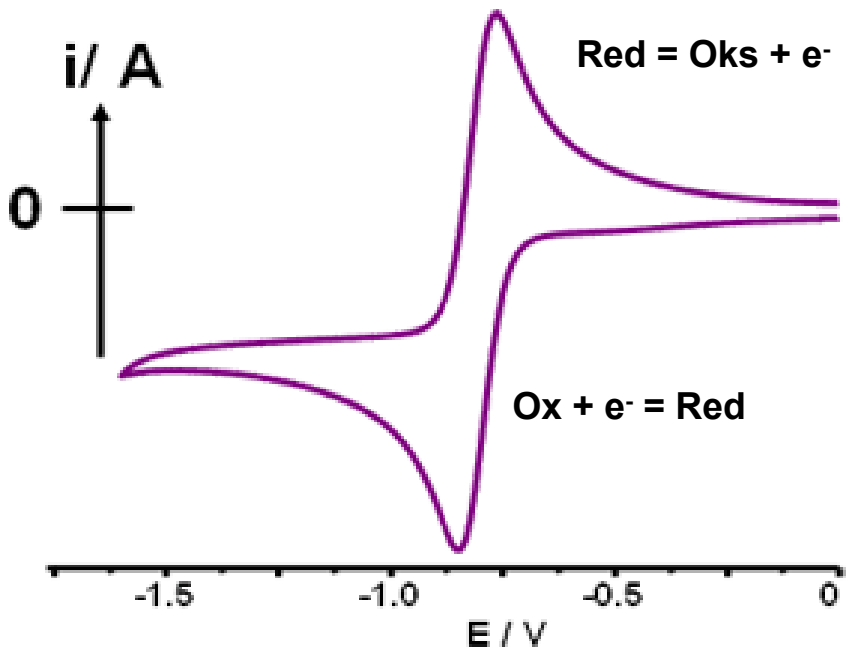
Aim

Study the behavior of moisture in cryolite, look into the stability and solubility of hydrogen containing species

Approach and Methodology

- Water vapour added to the melt by bubbling moist argon
- Mass flow of hydrogen studied by online HF and H_2O analysis of the off gas
- The gas analysis was conducted by means of two Unisearch LasIR tuneable diode lasers
- The difference between the modelled hydrogen flow rate through an empty container and the measured hydrogen flow rate through the melt was calculated
- The accumulation of hydrogen containing species in the bath could be derived
- Voltammetry

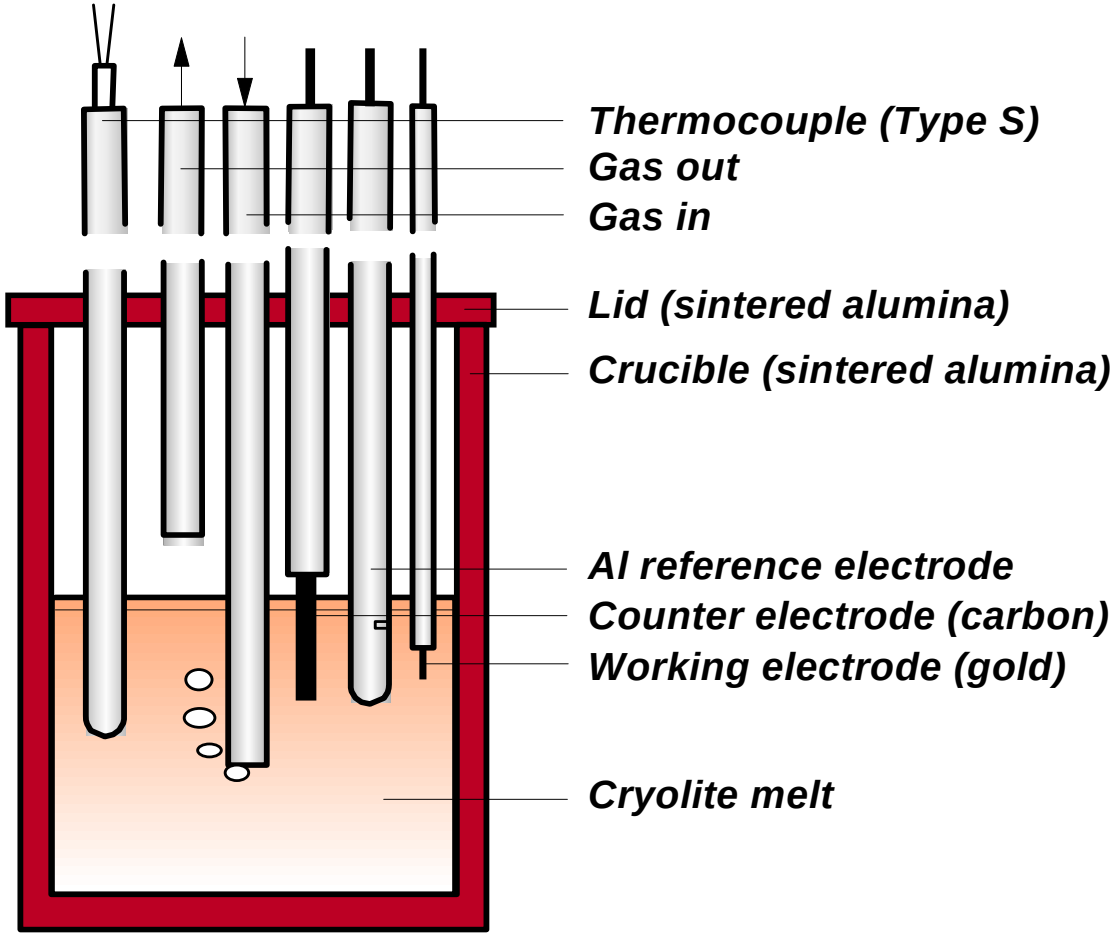
Voltammetry



- An electrochemical ”spectrum”
- Information about the types of reactions that occur in a system and at which potential they occur
- In situ analytical tool to determine which species are present in a system, and at which concentrations

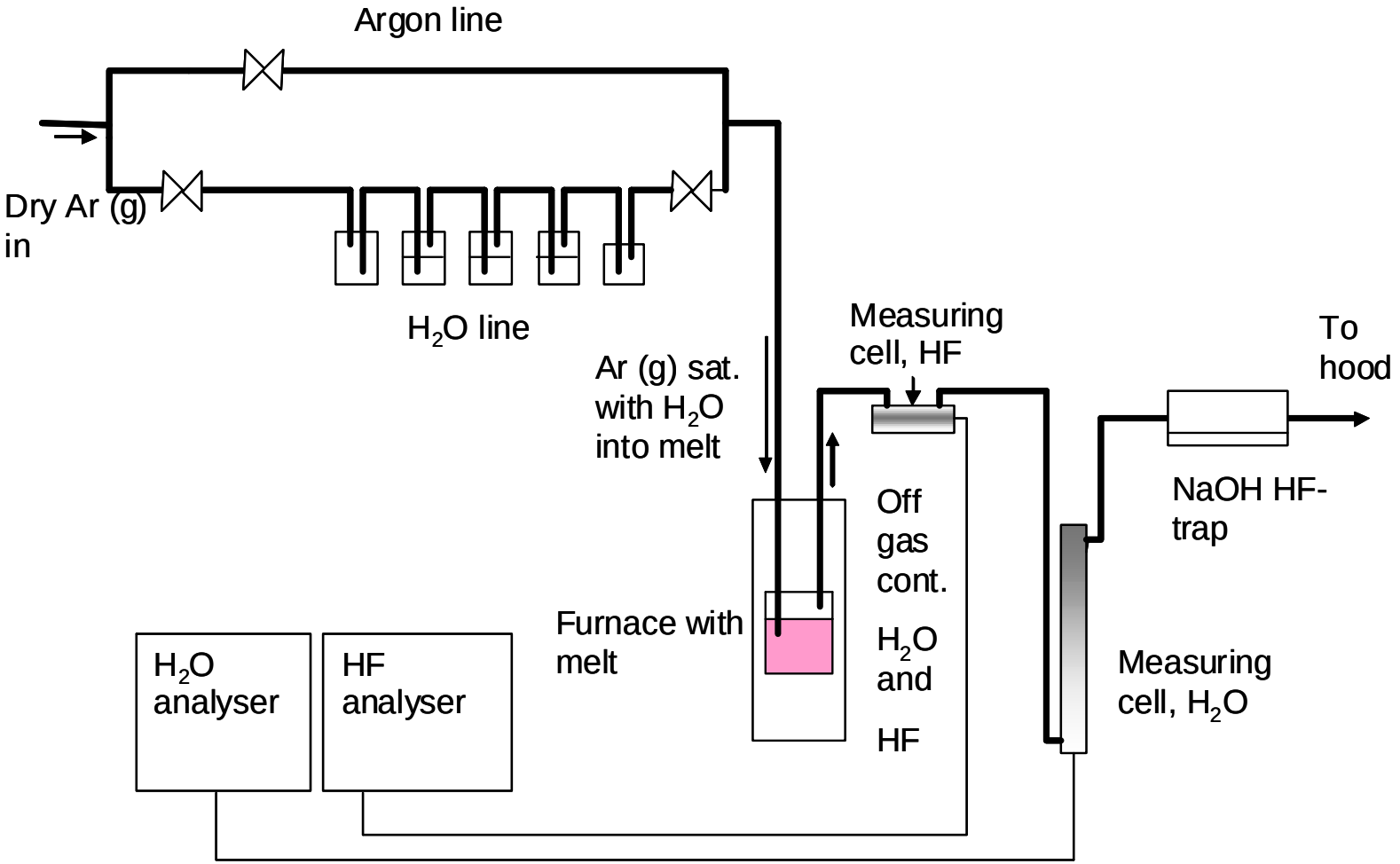
Greef et al. 1985/1990

Experimental Reactor/Electrochemical Cell

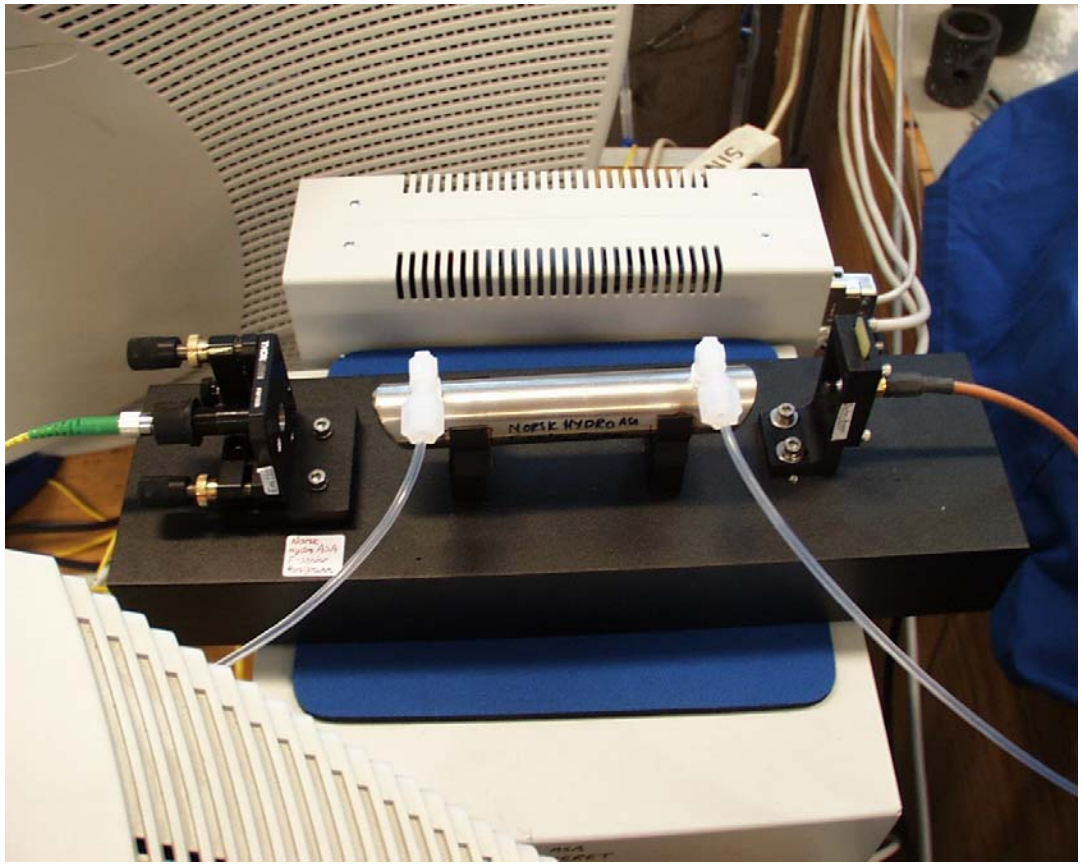


- T=960°C
- Systems studied: $NaF-AlF_3-Al_2O_3$ (sat), CR =6.2 and 2.2

Experimental Set-up and Procedure

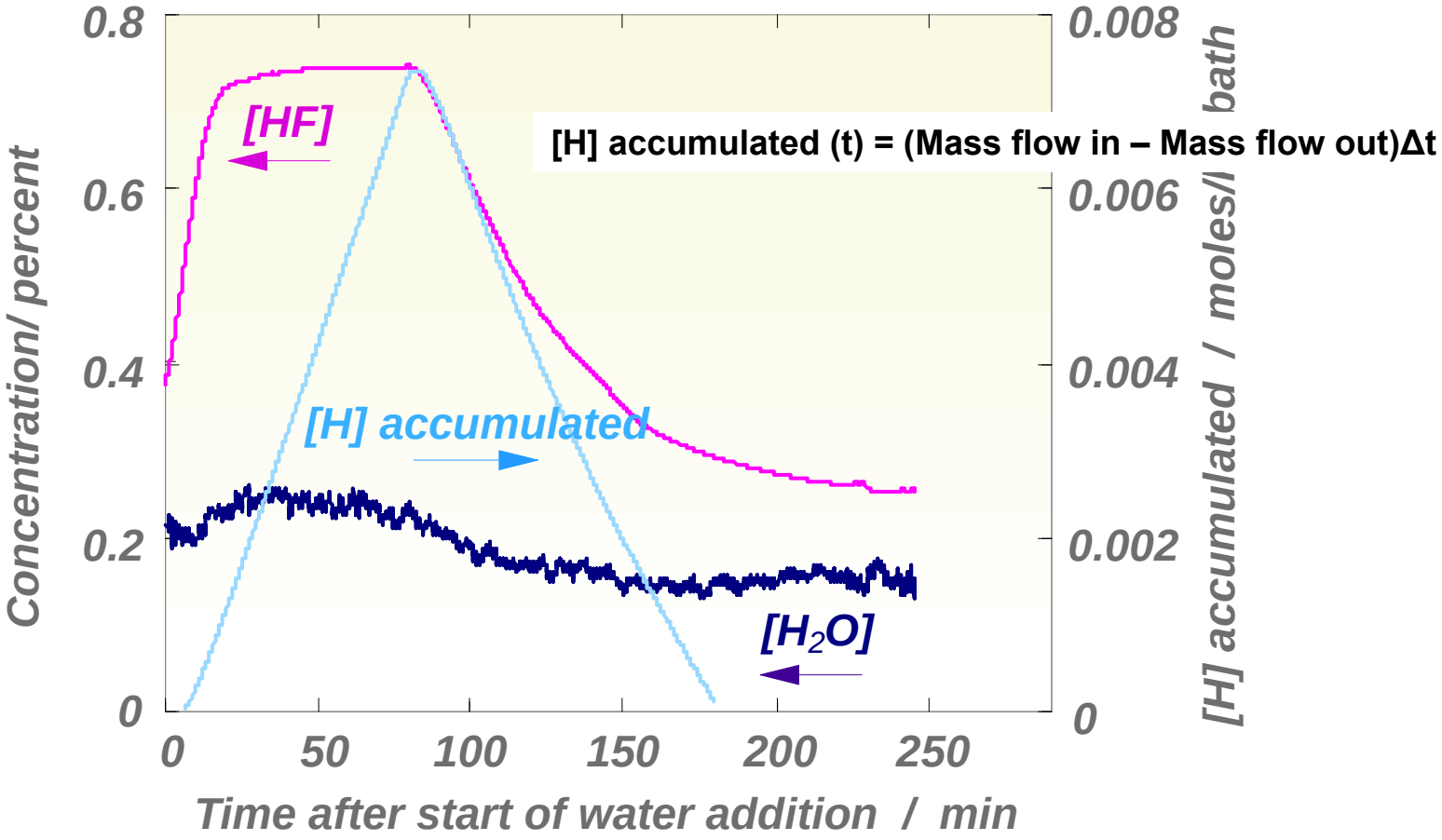


Gas Analysis

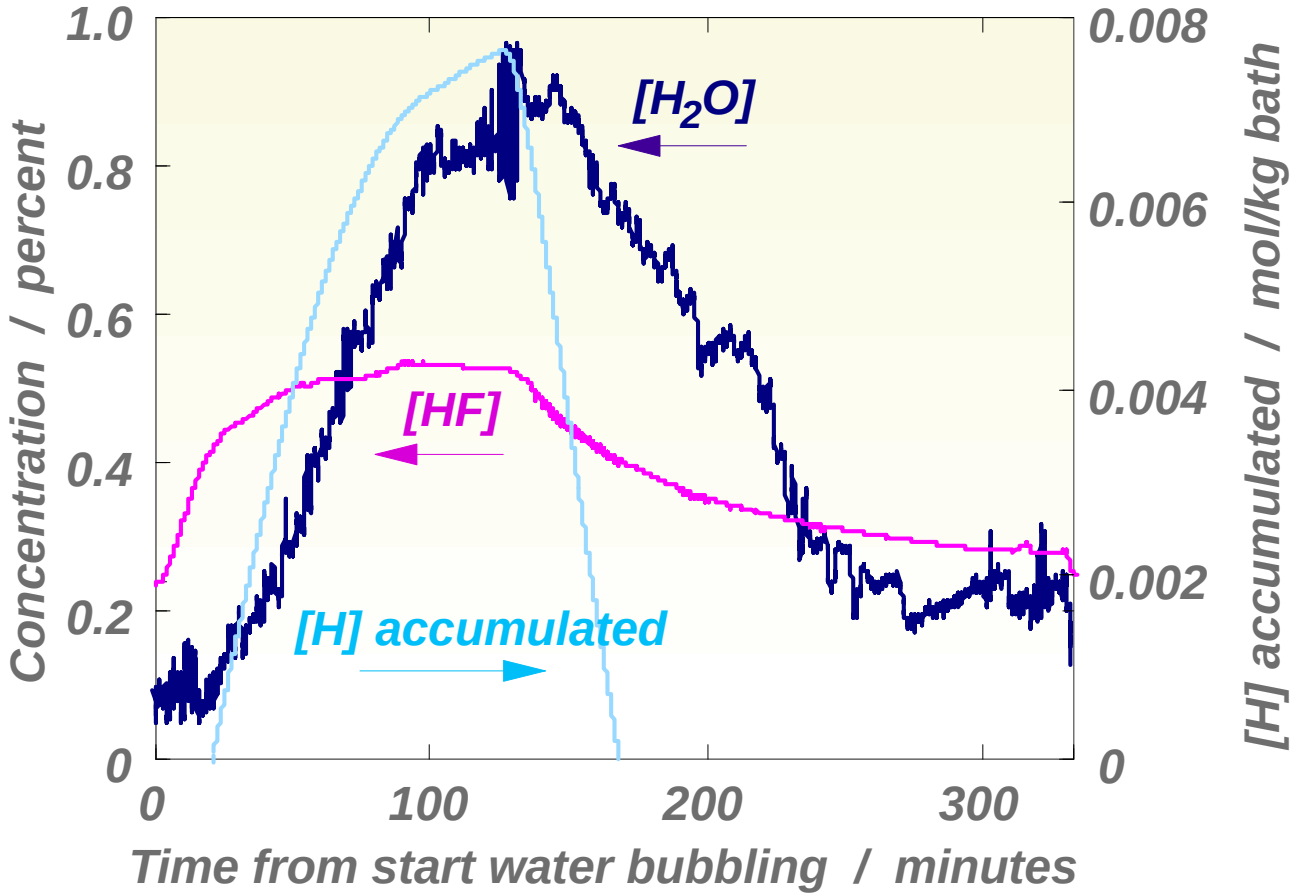


- **Near infrared tunable diode laser**

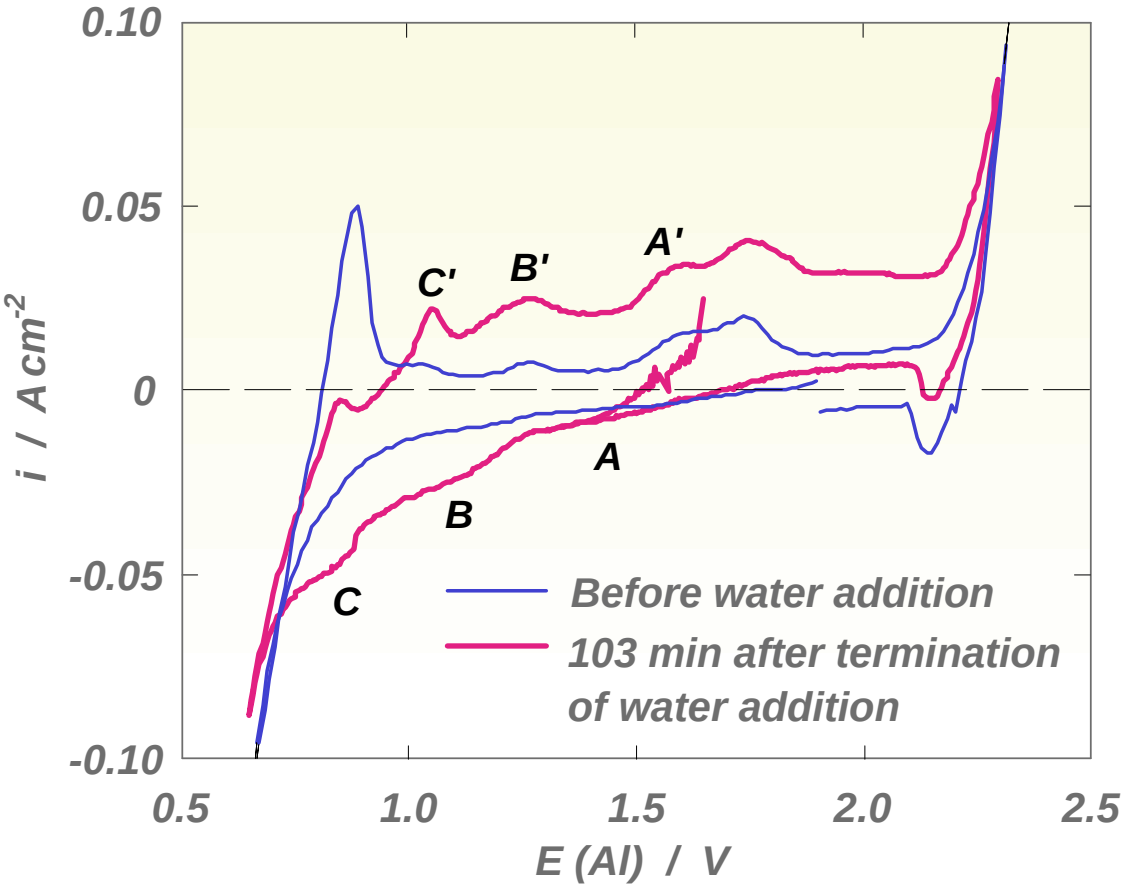
Results Gas Analysis and H Accumulation CR=2.2



Results Gas Analysis and H Accumulation CR=6.2

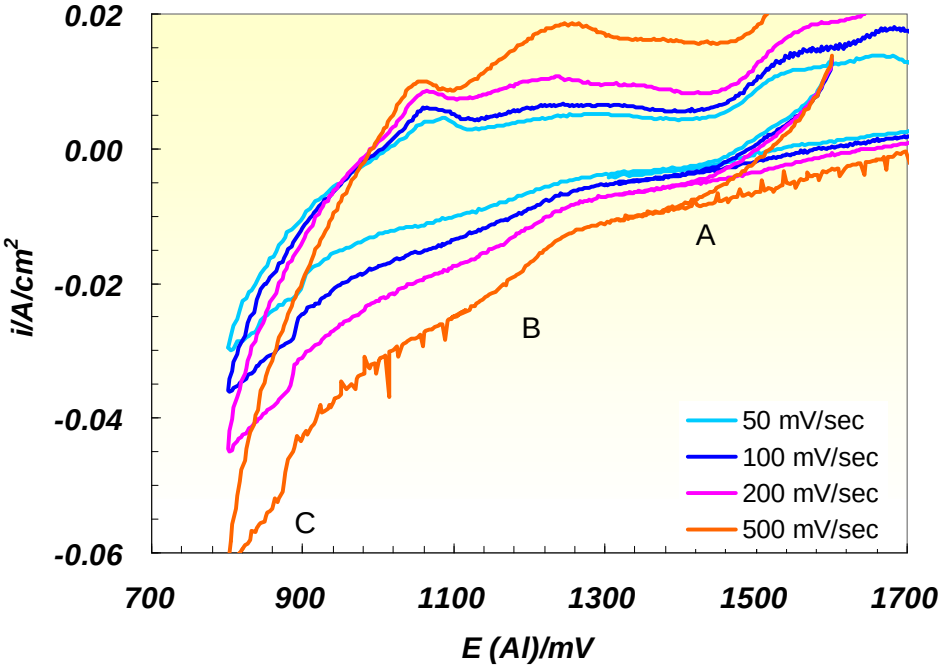


Results Voltammetry (1)



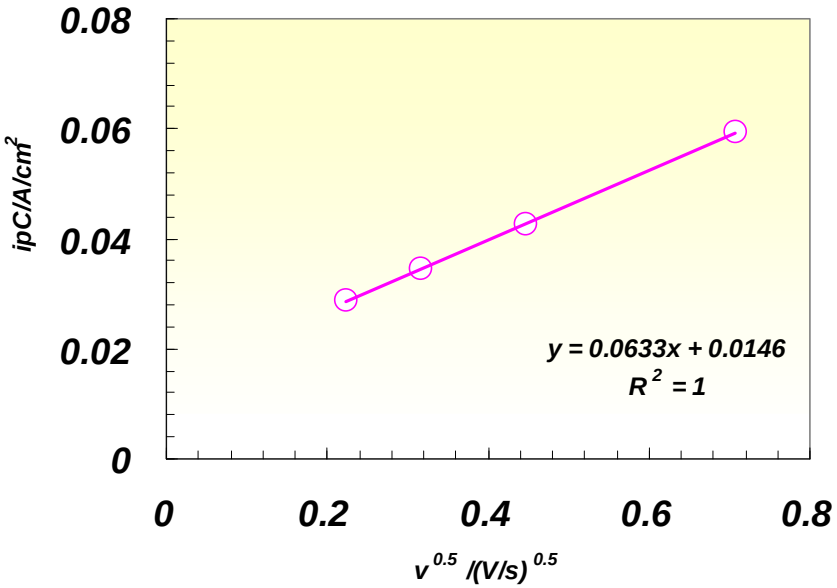
- **Cathodic waves A, B and C: One or several Hydrogen containing species are present and being reduced**
- **Long recidence time**

Results Voltammetry (2)



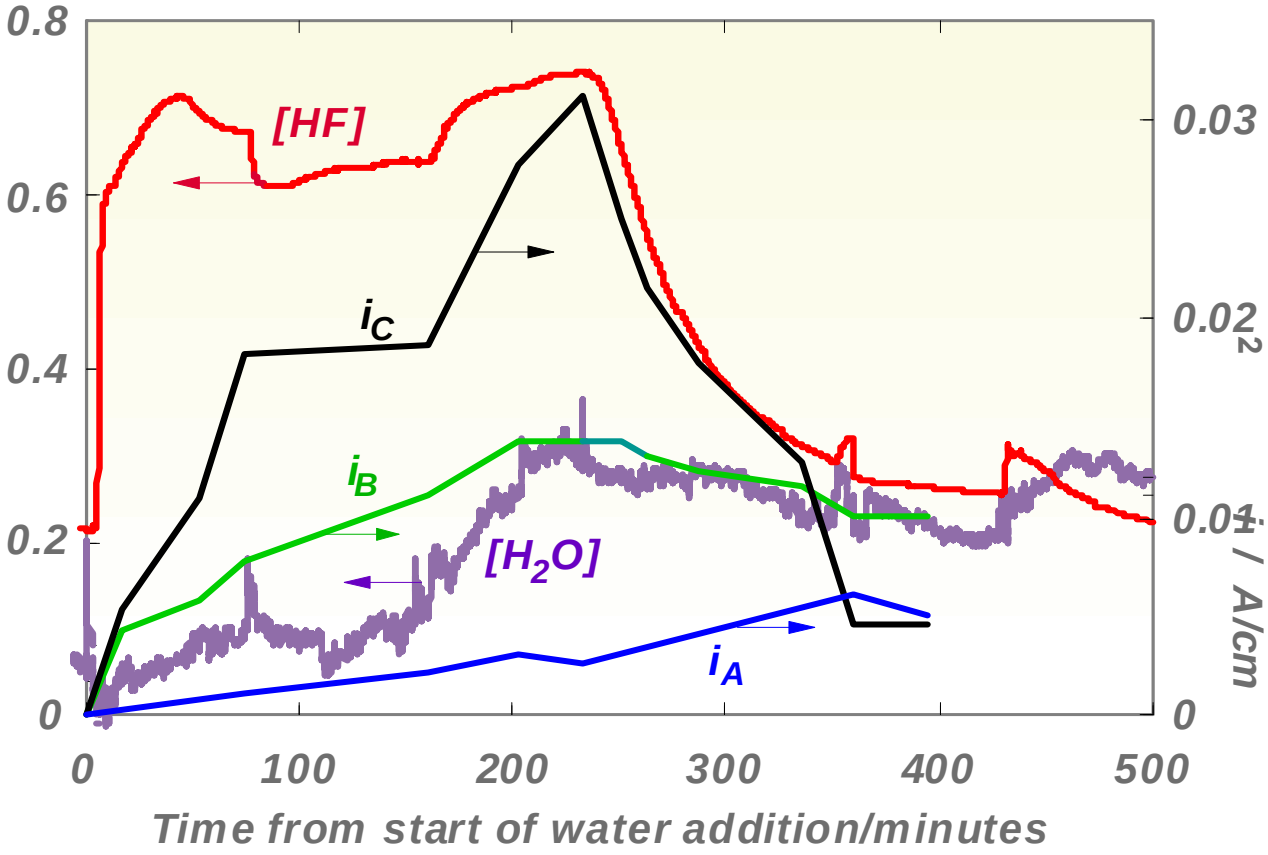
- **Randles-Sevcik's equation**

$$i_p = -0{,}4463 \frac{(nF)^{\frac{3}{2}}}{(RT)^{\frac{1}{2}}} c_o^{\infty} D^{\frac{1}{2}} v^{\frac{1}{2}}$$



- **Cathodic peak current densities proportional to the concentration of electroactive species in melt, in our case "H^+"**

Results: Compare Peak Current Densities with Gas Analysis



- Correlation between the peak current densities i_B, i_C and the concentration of HF and H_2O
- Further measurements and improvement of apparatus may help understand what species are involved

Discussion

- Loss in current efficiency might be related to loss of sodium from the cathode
- If hydrogen exists in reduced and oxidized forms “H” and “H^+” in the bath, there may be a shuttle reaction
- At anode: “H” = $H^+ + e^-$
- At cathode: Na (diss) +“H^+” = Na^+ + “H”
- Total reaction: Na (diss) = $Na^+ + e^-$

Sterten et al. 1994

Discussion Cont.

- The total reaction represents a loss of “useful” electrons, and thereby, a loss in CE
- Possibly reduction in CE due to the presence of water also in conventional aluminium cells, but this remains to be resolved

Concluding Remarks

- **Both the mass balance from the gas analysis results and the voltammetry curves gives evidence of one or several meta stable hydrogen containing species with very long residence times**

- **By improving the apparatus, more quantitative data may be obtained**

Acknowledgement

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