The Behaviour of Moisture in Cryolite Melts

Karen Sende Osen
Asbjørn Solheim
Egil Skybakmoen

SINTEF Materials and Chemistry

Christian Rosenkilde

Hydro Aluminium/NTNU

Workshop of Materials Process Engineering after TMS 2009

February 19, 2009, San Francisco, CA
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:

\[
\frac{2}{3} AlF_3 (\text{diss}) + H_2O(g) = 2 HF(g) + \frac{1}{3} Al_2O_3 (\text{diss})
\]

\[
NaAlF_4 (g) + H_2O(g) = 2 HF(g) + \frac{1}{3} Al_2O_3(s) + \frac{1}{3} Na_3AlF_6(s)
\]

• Structural hydroxyl in the primary alumina and water content in the ambient air

• What happens in the bath?

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":

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

\[
\begin{align*}
H_2O + F^- &= HF + OH^-, \\
cOH^- &= K(pH_2O/pHF)
\end{align*}
\]
Behaviour of Water in Molten Salts (4)

- Cathodic behaviour of HF and H$_2$O in LiF-KF-NaF (Takenaa, Ito et al. 1984)
  - Waves corresponding to HF and H$_2$O but no evidence of OH$^-$

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

  ip(H$_2$O) = K v($^{\frac{1}{2}}$) pH$_2$O
Behaviour of Water in Molten Salts (5)

- In MgCl₂ melts, water recides as the metastable species MgOHCl (Haarberg et al.)

\[ \text{H}_2\text{O} + \text{MgCl}_2 = \text{MgOHCl} + \text{HCl} \]

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

\[ \text{MgOHCl} = \text{MgO} + \text{HCl} \]
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 H₂O 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-AlF₃-Al₂O₃ (sat), CR = 6.2 and 2.2
Experimental Set-up and Procedure

Argon line

Dry Ar (g) in

H₂O line

Ar (g) sat. with H₂O into melt

Furnace with melt

H₂O and HF

Off gas cont.

Measuring cell, HF

NaOH HF-trap

Measuring cell, H₂O

To hood

H₂O analyser

HF analyser

Workshop of Materials Process Engineering after

TMS2009

138th Annual Meeting & Exhibition

February 19, 2009, San Francisco, CA
Gas Analysis

• Near infrared tunable diode laser
Results Gas Analysis and H Accumulation CR=2.2

[H] accumulated (t) = (Mass flow in – Mass flow out)Δt

[HF]

[H] accumulated

[H₂O]
Results Gas Analysis and H Accumulation CR=6.2

![Graph showing concentration of water vapor and hydrogen fluoride over time, with annotations for water vapor, hydrogen fluoride, and accumulated hydrogen concentration.]

Results Voltammetry (1)

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

![Graph showing voltammetry results with peaks labeled A, B, C, A', B', and C']

Before water addition
103 min after termination of water addition

Workshop of Materials Process Engineering after TMS 2009
138th Annual Meeting & Exhibition

February 19, 2009, San Francisco, CA
Results Voltammetry (2)

- Randles-Sevcik’s equation

\[ i_p = -0.4463 \left( \frac{nF}{RT} \right)^{\frac{3}{2}} c_o^{\frac{1}{2}} D^{\frac{1}{2}} v^{\frac{1}{2}} \]

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

![Graph showing voltammetry results with Randles-Sevcik's equation and a linear fit with a regression line equation and R^2 value.](image)
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$_2$O
- 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 metastable hydrogen containing species with very long residence times.

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

• This work was financed by Norsk Hydro. Permission to publish the results is gratefully acknowledged

• Thanks to Dr. MacKay and Mr. Viglino at Unisearch for helping with the gas analysis measurements