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Electric Current Value Decreasing due to H_2 and Cl_2 Gas Formation near Electrodes during Electrolysis Calculation

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Abstract Our investigations show that the degradation rate of aluminium (Al) cylindrical anodes increases with the temperature of concentrated NaCl solution increasing from 20°C to 100°C during electrolysis at an electric current density of 3,000 A/m^2. The general quantity of Al^{3+} ions also increases with temperature. Electric current value also increases with temperature. The general quantity of H^+ and Cl^- ions decreases during electrolysis at all temperatures since H_2 and Cl_2gases are formed near electrodes. We have calculated that it decreases the electric current value by 1.3%. The degradation rate of copper (Cu) cylindrical anodes decreases with the temperature of concentrated NaCl solution increasing from 20°C to 100°C during electrolysis at an electric current density of 3,000 A/m^2. The general quantity of Cu^+ and Cu^{2+} ions also decreases with temperature. We guess that the only reason for the increasing electric current value is the average charge of copper ions, which increases from +1 at room temperature to +1.5 at 100°C and to +2 at 180°C.

Keywords: Electrolysis, Aluminium, Copper, Electrochemical corrosion, Arrhenius law.

1. Introduction

Cheaper, electrocatalytic working electrodes, compared to a novel Ni/Ni(OH)$_2$ reference electrode, can be used to increase the feasibility of hydrogen gas production in eutectic molten hydroxide (NaOH-KOH, 49–51 mol%) at a temperature of 300°C, as described in [1]. The reduction potential of the hydrogen evolution reaction using different working electrodes was in the order of (from more positive to negative reduction potential): Pt > Ni > St.st > Ag > Mo. Aluminium or copper electrodes were not used for the experiments.

2. Calculation of aluminium loss due to electrolysis per unit time

Dependence of corrosion rate (C_R), or weight-loss of aluminium per unit time, on temperature can be expressed in the form of the Arrhenius equation as [2]:

$$C_R^{Al}(T) = A_{Al} e^{-\frac{E_A^{Al}}{RT}} = k_{Al}(T)\pi L \rho_{Al} \, . \qquad (1)$$

The aluminium weight-loss per unit time can be calculated using our experimental results [3]:

$$C_R^{Al}(20^oC) = k_{Al}(20^oC)\pi L \rho_{Al} = 2.78 \cdot 10^{-7} kg \cdot s^{-1} \, ; \, k_{Al}(T_1{=}20^oC){=}7.29\cdot 10^{-10} \, m^2/s \, ; \qquad (2a)$$

$$C_R^{Al}(100^oC) = k_{Al}(100^oC)\pi L \rho_{Al} = 2.86 \cdot 10^{-7} kg \cdot s^{-1} \, ; \, k_{Al}(T_2{=}100^oC){=}8.42\cdot 10^{-10} \, m^2/s \, . \qquad (2b)$$

Here, A_{Al} is the pre-exponential factor, E_A^{Al} is the activation energy of corrosion. R is the gas constant, T is absolute temperature, and k_{Al} [m^2/s] is the aluminum cylindrical anode radius-decreasing rate constant [3]. In addition, L is the length of the anode immersed into the electrolyte at the temperature of the experiment. (L(20°C) = 45 mm; L(100°C) = 40 mm). We can calculate the aluminum activation energy of corrosion and the pre-exponential factor using experimental results during electrolysis at room temperature and 100°C:

$$E_A^{Al} = \frac{T_1 T_2 R}{T_2 - T_1} ln \frac{C_R(T_2)}{C_R(T_1)} = 322 \, J \cdot mol^{-1} = 0.003 \, eV \, ; \, A_{Al} = C_R(T) e^{\frac{E_A^{Al}}{RT}} = 3.17 \cdot 10^{-7} \, kg \cdot s^{-1} \qquad (3)$$

We can calculate the corrosion rate of aluminum at a temperature of 180°C during electrolysis in a concentrated NaCl solution:

$$C_R^{Al}(180^oC) = 2.91 \cdot 10^{-7} kg \cdot s^{-1} \, ; \, k_{Al}(180^oC) = \frac{C_R^{Al}(180^o)}{\pi L \rho_{Al}} = 8.58 \cdot 10^{-10} m^2 \cdot s^{-1}. \qquad (2c)$$

The electric current value increases due to the increasing quantity of Al^{3+} ions with temperature.
Therefore, we can propose the following equation:

$$I^{Al}(T) = I_0^{Al} e^{-\frac{E_A^{Al}}{RT}};\ I_0^{Al} = 3.538\,A;\ I^{Al}(T) = 3.538 e^{-\frac{322\,J\cdot mol^{-1}}{RT}}. \tag{4}$$

Eq. 4 gives:

$$I^{Al}(20^oC) = 3.1\,A;\ I^{Al}(100^oC) = 3.19\,A;\ I^{Al}(180^oC) = 3.25\,A. \tag{5}$$

Measured values equal [3]: $I_{exp}^{Al}(20^oC) = 3.1\,A;\ I_{exp}^{Al}(100^oC) = 3.15\,A.$

Linear assumption gives: $I_{exp}^{Al}(20^oC) = 3.1\,A;\ I_{exp}^{Al}(100^oC) = 3.15\,A;\ I^{Al}(180^oC) = 3.2\,A,$

so, the Arrhenius equation describes the increase in electric current value better.

The general quantity of H^+ and Cl^- ions decreases during electrolysis at all temperatures because H_2 and Cl_2 gases are formed near the electrodes. We can calculate:

$$\Delta I = I_{theor}^{Al}(100^oC) - I_{exp}^{Al}(100^oC) = 0.04\,A\,;\ \frac{\Delta I}{I_{exp}^{Al}(100^oC)} = 0.013 = 1.3\%, \tag{6}$$

so, the electric current value decreases by 1.3%.

3. Calculation of the amount of copper loss due to electrolysis per unit time

The dependence of the corrosion rate during electrolysis (C_R) or weight loss of copper per unit time on temperature could be expressed in the form of the Arrhenius equation as [2]:

$$C_R^{Cu}(T) = A_{Cu} e^{-\frac{E_A^{Cu}}{RT}} = k_{Cu}(T)\pi L \rho_{Cu}\,. \tag{7}$$

We can calculate the copper weight loss per unit time using our experimental results [3]:

$$C_R^{Cu}(20^oC) = k_{Cu}(20^oC)\pi L \rho_{Cu} = 1.75 \cdot 10^{-6} kg \cdot s^{-1}\,;\ k_{Cu}(T_1\text{=}20^\circ\text{C})\text{=}1.25\cdot 10^{-9}\ \text{m}^2/\text{s}\ ; \tag{8a}$$

$$C_R^{Cu}(100^oC) = k_{Cu}(100^oC)\pi L \rho_{Cu} = 1.29 \cdot 10^{-6} kg \cdot s^{-1}\,;\ k_{Cu}(T_2\text{=}100^\circ\text{C})\text{=}1.154\cdot 10^{-9}\ \text{m}^2/\text{s}\ . \tag{8b}$$

Here, A_{Cu} is the pre-exponential factor, E_A^{Cu} is the activation energy of corrosion, R=8.314 *J/mol* is the gas constant, T is the absolute temperature, k_{Cu} [m^2/s] is the copper cylindrical anode radius-decreasing rate constant [3], and L is the anode length immersed into the electrolyte at the temperature of the experiment (L(20°C)=50 mm; L(100°C)=40 mm). We can calculate the copper activation energy of corrosion and the pre-exponential factor using experimental results during electrolysis at room temperature and 100°C:

$$E_A^{Cu} = \frac{T_1 T_2 R}{T_2 - T_1} ln \frac{C_R(T_2)}{C_R(T_1)} = -3.464\,kJ \cdot mol^{-1} = -0.036\,eV\,;\ A_{Cu} = C_R(T) e^{\frac{E_A^{Cu}}{RT}} = 4.2 \cdot 10^{-7}\,kg \cdot s^{-1} \tag{9}$$

We can calculate the copper corrosion rate at a temperature of 180°C during electrolysis in concentrated NaCl solution.

$$C_R^{Cu}(180^oC) = 1.05 \cdot 10^{-6} kg \cdot s^{-1}\,;\ k_{Cu}(180^oC) = \frac{C_R^{Cu}(180^o)}{\pi L \rho_{Cu}} = 9.4 \cdot 10^{-10} m^2 \cdot s^{-1}. \tag{8c}$$

The electric current value increases due to the average charge of the Cu ions increasing from +1 to +2 with the temperature increasing from 20 to 100°C. Therefore, we can propose the following equation:

$$I^{Cu}(T) = I_0^{Cu} \cdot e^{-\frac{E_A^{Al} \cdot z \cdot k_z}{RT}};\ I_0^{Cu} = 1.726\,A;\ I^{Cu}(T) = 1.726 \cdot e^{\frac{3{,}464\,J\cdot mol^{-1}\cdot z\cdot k_z}{RT}};\ k_z = 0.34. \tag{10}$$

Eq. 10 gives:

$$I^{Cu}(20^oC) = 2.8\,A;\ I^{Cu}(100^oC) = 3.05\,A;\ I^{Cu}(180^oC) = 3.23\,A. \tag{11}$$

The measured values are equal to [3]: $I_{exp}^{Cu}(20^{o}C) = 2.8\ A$; $I_{exp}^{Cu}(100^{o}C) = 3.05\ A$.

The linear assumption gives: $I_{exp}^{Cu}(20^{o}C) = 2.8\ A$; $I_{exp}^{Cu}(100^{o}C) = 3.05\ A$; $I^{Cu}(180^{o}C) = 3.3\ A$,

therefore, the Arrhenius equation better describes the increasing electric current value.

Rates of cylindrical and spherical copper anodes dissolving into concentrated NaCl water solution during electrolysis and temperature increase were calculated in [4].

Conclusions

The measured values are equal to [3]: $I_{exp}^{Cu}(20^{o}C) = 2.8\ A$; $I_{exp}^{Cu}(100^{o}C) = 3.05\ A$.

The linear assumption gives: $I_{exp}^{Cu}(20^{o}C) = 2.8\ A$; $I_{exp}^{Cu}(100^{o}C) = 3.05\ A$; $I^{Cu}(180^{o}C) = 3.3\ A$,

therefore, the Arrhenius equation better describes the increasing electric current value.

Rates of cylindrical and spherical copper anodes dissolving into concentrated NaCl water solution during electrolysis and temperature increase were calculated in [4].

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