

An Experimental Method to Calculate Average Metal Ions Charge by Electrolysis at Different Temperatures

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Abstract An experimental method to calculate average metal ions charge by electrolysis at different temperatures is proposed. Direct electric current and anode mass decreasing were measured during electrolysis into concentrated NaCl solution at room temperature and 100°C. Average charges of copper, iron, and aluminium ions were calculated using Faraday's law of electrolysis: +3 for aluminium; +2 for iron; and +1 for copper at room temperature, and +3 for aluminium; +2 for iron; and +1.5 for copper at temperature 100°C.

Keywords: electrolysis; Faraday's law; electrochemical corrosion; copper; aluminium; iron.

1. Introduction

The container which consists of an outer copper canister and an inner carbon steel (Fe) tank is used to dispose of spent nuclear fuel [1]. Copper (Cu) coatings on an aluminium (Al) wire, that are widely used in the automobile and aerospace industries to reduce of total weight of the electric wires, can be quickly destroyed during working since they are heated up to 200°C [2]. We have planned to analyse the average charge of Cu, Fe, and Al ions that dissolve into an electrolyte at room temperature and 100°C.

2. Method of average metal ions charge calculation by electrolysis at different temperatures

The rate of cylindrical anode dissolving into electrolyte can be calculated using Faraday's law of electrolysis:

$$\frac{dm}{dt} = \frac{MI}{zF}; dm(t) = -\rho LdA(t). \quad (1)$$

Here, m is the anode mass dissolved into the electrolyte, t is the time of the experiment, M is molar mass, I is the direct electric current value, F is the Faraday constant ($F \approx 96,500 \text{ Cmol}^{-1}$), z is a charge of ions, $A = \pi R^2$ is anode cross-section area, L is anode length immersed into the electrolyte, ρ is the anode density. Cylindrical anodes (99.99 % Cu, 99.96 % Fe, and 99.99 % Al) were used for copper, aluminium, and iron electrochemical corrosion investigation. Concentrated sodium chloride (NaCl) solution was used as an electrolyte [3, 4]. Direct electric current value and the anode's radii decreasing kinetics were measured. Equations (1) give:

$$z = \frac{MI t}{F \pi \rho L (R^2(t=0) - R^2(t))}, \quad (2)$$

Charges of copper, iron, and aluminium ions were calculated at room temperature:

$$z_{Cu} = \frac{63.55 \cdot 10^{-3} \text{ kg/mol} \cdot 2.8 \text{ A} \cdot 1.2 \cdot 10^3 \text{ s}}{F \cdot \pi \cdot 8.9 \cdot 10^3 \text{ kg/m}^3 L_{Cu} \cdot (R_{Cu}^2(t=0) - R_{Cu}^2(t_4))} \approx 0.995 \approx 1, \quad (3)$$

$$z_{Al} = \frac{27 \cdot 10^{-3} \text{ kg/mol} \cdot 3.1 \text{ A} \cdot 1.2 \cdot 10^3 \text{ s}}{F \cdot \pi \cdot 2.7 \cdot 10^3 \text{ kg/m}^3 L_{Al} \cdot (R_{Al}^2(t=0) - R_{Al}^2(t_4))} \approx 2.954 \approx 3, \quad (4)$$

$$z_{Fe} = \frac{55.847 \cdot 10^{-3} \text{ kg/mol} \cdot 3.15 \text{ A} \cdot 1.2 \cdot 10^3 \text{ s}}{F \cdot \pi \cdot 7.86 \cdot 10^3 \text{ kg/m}^3 L_{Fe} \cdot (R_{Fe}^2(t=0) - R_{Fe}^2(t_4))} \approx 2.03 \approx 2, \quad (5)$$

where $L_{Cu} = L_{Fe} = 5 \cdot 10^{-2} \text{ m}$, $L_{Al} = 4.5 \cdot 10^{-2} \text{ m}$; $R_{0Cu} = R_{0Al} = 2.8 \text{ mm}$, $R_{0Fe} = 2.98 \text{ mm}$; $I_{Fe} = 3.15 \text{ A}$, $I_{Al} = 3.1 \text{ A}$, $I_{Cu} = 2.8 \text{ A}$, so copper dissolved into NaCl solution as the Cu^+ ions, iron dissolved into NaCl solution as the Fe^{2+} ions, and aluminium dissolved into NaCl solution as the Al^{3+} ions. Experimental results are as follows: $t_1 = 5 \text{ min}$, $t_2 = 10 \text{ min}$, $t_3 = 15 \text{ min}$, $t_4 = 20 \text{ min}$; $R_{1Cu} = 2.74 \text{ mm}$, $R_{2Cu} = 2.67 \text{ mm}$, $R_{3Cu} = 2.59 \text{ mm}$, $R_{4Cu} = 2.5 \text{ mm}$; $R_{1Al} = 2.77 \text{ mm}$, $R_{2Al} = 2.73 \text{ mm}$, $R_{3Al} = 2.68 \text{ mm}$, $R_{4Al} = 2.62 \text{ mm}$, $R_{1Fe} = 2.95 \text{ mm}$, $R_{2Fe} = 2.92 \text{ mm}$, $R_{3Fe} = 2.88 \text{ mm}$, $R_{4Fe} = 2.83 \text{ mm}$. Measurement precision was 0.01 mm or 10 micrometers.

Literature data show that the uncharged copper (II) chloride complex $\text{CuCl}_2(\text{aq})$ predominates at 50-100 °C [5], so the average charge of copper ions should be greater than +1 and less than +2. We have calculated at temperature 100°C:

$$z_{Cu} = \frac{63.55 \cdot 10^{-3} \text{ kg/mol} \cdot 3.05 \text{ A} \cdot 1.2 \cdot 10^3 \text{ s}}{F \cdot \pi \cdot 8.9 \cdot 10^3 \text{ kg/m}^3 L_{Cu} \cdot (R_{Cu}^2(t=0) - R_{Cu}^2(t_4))} \approx 1.47 \approx \frac{1+2}{2}, \quad (6)$$

$$z_{Al} = \frac{27 \cdot 10^{-3} \text{ kg/mol} \cdot 3.15 \text{ A} \cdot 1.2 \cdot 10^3 \text{ s}}{F \cdot \pi \cdot 2.7 \cdot 10^3 \text{ kg/m}^3 L_{Al} \cdot (R_{Al}^2(t=0) - R_{Al}^2(t_4))} \approx 2.85 \approx 3, \quad (7)$$

$$z_{Fe} = \frac{55.847 \cdot 10^{-3} \text{ kg/mol} \cdot 3.15 \text{ A} \cdot 1.2 \cdot 10^3 \text{ s}}{F \cdot \pi \cdot 7.86 \cdot 10^3 \text{ kg/m}^3 L_{Fe} \cdot (R_{Fe}^2(t=0) - R_{Fe}^2(t_4))} \approx 2.01 \approx 2, \quad (8)$$

where $L_{Cu} = L_{Al} = 4 \cdot 10^{-2} \text{ m}$, $L_{Fe} = 5 \cdot 10^{-2} \text{ m}$, $R_{0Cu} = 2.27 \text{ mm}$, $R_{0Al} = 2.6 \text{ mm}$, $R_{0Fe} = 2.83 \text{ mm}$, $I_{Al} = 3.15 \text{ A}$, $I_{Fe} = 3.13 \text{ A}$, $I_{Cu} = 3.05 \text{ A}$. Copper dissolved into NaCl solution as Cu^+ and Cu^{2+} ions, iron dissolved into NaCl solution as the Fe^{2+} ions, and aluminium dissolved into NaCl solution as Al^{3+} ions. Experimental results are as follows: $t_1 = 5 \text{ min}$, $t_2 = 10 \text{ min}$, $t_3 = 15 \text{ min}$, and $t_4 = 20 \text{ min}$; $R_{1Cu} = 2.2 \text{ mm}$, $R_{2Cu} = 2.12 \text{ mm}$, $R_{3Cu} = 2.03 \text{ mm}$, $R_{4Cu} = 1.92 \text{ mm}$; $R_{1Al} = 2.56 \text{ mm}$, $R_{2Al} = 2.51 \text{ mm}$, $R_{3Al} = 2.45 \text{ mm}$, $R_{4Al} = 2.38 \text{ mm}$; $R_{1Fe} = 2.80 \text{ mm}$, $R_{2Fe} = 2.76 \text{ mm}$, $R_{3Fe} = 2.72 \text{ mm}$, $R_{4Fe} = 2.67 \text{ mm}$. We carried out additional experiments, but the result was the same.

3. The amount of aluminium loss due to electrochemical corrosion per unit time calculation

The dependence of corrosion rate (C_R), or the amount of aluminium (only Al, not Fe or Cu) electrochemical corrosion per unit time, on temperature could be expressed in the form of Arrhenius equation in the following way [6]:

$$C_R = A e^{-\frac{E_A}{RT}}, \quad (9)$$

where A is the pre-exponential factor, E_A is the activation energy, R is the gas constant and T is temperature. We can calculate the aluminium activation energy and the pre-exponential factor using experimental results during electrolysis at room temperature and 100°C [3, 4]:

$$E_A^{Al} = \frac{T_1 T_2 R}{T_2 - T_1} \ln \frac{k_{Al}(T_2)}{k_{Al}(T_1)} = 1.637 \text{ kJ / mol} = 0.017 \text{ eV}, \quad (10)$$

$$A_{Al} = \pi k_{Al} L \rho_{Al} e^{\frac{E_A}{RT}} = 5.45 \cdot 10^{-7} \text{ kg / s}; \quad C_R^{Al} = 5.45 \cdot 10^{-7} e^{\frac{197K}{T[K]}} \text{ kg / s}, \quad (12)$$

where k_{Al} is the aluminium anode radius-decreasing rate constant, L is the anode's length immersed in the electrolyte, and ρ_{Al} is the aluminium density.

4. Conclusions

Copper electrochemical corrosion is higher at room temperature $T_1 \approx 27^\circ\text{C}$ (average charge of copper ions equals +1), and aluminium electrochemical corrosion is higher at temperature $T_2 = 100^\circ\text{C}$ (average charge of copper ions equals +1.5). The ratio of electrochemical corrosion rates, k_{Cu}/k_{Al} , decreases with temperature increasing, although iron electrochemical corrosion rate practically doesn't depend on temperature below 100°C (average charge of iron ions equals +2). It is obvious, because of the higher melting point of iron than the melting point of copper or aluminium.

References

1. Lilja, C., King, F., Puigdomenech, I., & Pastina, B. (2021). Speciation of copper in high chloride concentrations, in the context of corrosion of copper canisters. *Materials and Corrosion*, 72, 293–299. <https://doi.org/10.1002/maco.202011778>
2. Kizaki, T., O, M., & Kajihara, M. (2020). Rate-Controlling Process of Compound Growth in Cu-Clad Al Wire during Isothermal Annealing at 483–543 K. *Materials Transactions*, 61(1), 188. https://www.jstage.jst.go.jp/article/matertrans/61/1/61_MT-M2019207/html-char/en
3. Yarmolenko, M. V. (2022). Copper, Iron, and Aluminium Electrochemical Corrosion Rate Dependence on Temperature. In F. Zafar, A. Ghosal, & E. Sharmin (Eds.), *Corrosion - Fundamentals and Protection Mechanisms* (pp. 35-50). IntechOpen. <https://doi.org/10.5772/intechopen.100279>
4. Yarmolenko, M. V. (2021). Intrinsic Diffusivities Ratio Analysis in Double Multiphase Systems. *Defect and Diffusion Forum*, 413, 47–64. <https://doi.org/10.4028/www.scientific.net/ddf.413.47>
5. Beverskog, B., & Pettersson, S.-O. (2002). Pourbaix Diagrams for Copper in 5 m Chloride Solution. *SKI Report 02: 23*. <https://www.stralsakerhetsmyndigheten.se/contentassets/4b1ef76c4151413998c76becb6da0570/0223-pourbaix-diagrams-for-copper-in-5-m-chloride-solution-pdf-320-kb>
6. Olasunkanmi, O. L. (2022). Corrosion: Favoured, Yet Undesirable - Its Kinetics and Thermodynamics. In *Corrosion - Fundamentals and Protection Mechanisms* (pp. 15-33). IntechOpen. <https://doi.org/10.5772/intechopen.98545>