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 charge of metal ions by electrolysis at different temperatures is proposed. Aluminium undergoes dissolution to the Al^{3+} ions at all temperatures. Iron undergoes dissolution to the Fe^{2+} or the Fe^{3+} ions and copper undergoes dissolution to the Cu^+ or the Cu^{2+}. It depends on temperature and electric current density. Direct electric current value and anode mass decreasing were measured during electrolysis into concentrated NaCl solution in water (5 mol/kg or 23.1%, freezing point equals -22ºC, pH 6.5–7.5) at room temperature and 100ºC. The average charges of copper, iron, and aluminium ions were calculated using Faraday's law of electrolysis at electric current density 3,000 A/m² (or 30 A/dm²): +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 100ºC. The main condition was $z_{Al}=3$. We concluded that calculations of the average metal ions charges, z_{Fe} and z_{Cu}, were correct since $z_{Al}=3$. The result is as follows: the Al^{3+}, the Fe^{2+}, and the Cu^+ ions dissolve into concentrated NaCl solution in water at room temperature; the Al^{3+}, the Fe^{2+}, the Cu^+ and the Cu^{2+} ions (50%/50%) dissolve into the solution at temperature 100ºC. We have obtained experimentally and by mathematical modelling that aluminium anodes (cylindrical or spherical) dissolve into the solution more rapidly with temperature increasing during electrolysis accordingly to the Arrhenius law, while copper anodes (cylindrical or spherical) dissolve more slowly with temperature increasing from room temperature to temperature 180°C like "inverse Arrhenius law". Iron electrochemical corrosion rate practically does not depend on temperature below 100°C (and, obviously, up to 180°C) like "zeroth Arrhenius law". The spherical anode effect is greater than the cylindrical anode effect in 1.5 times.

Keywords: electrocoagulation; 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 200ºC [2].

Copper (Cu), iron (Fe), and aluminium (Al) anodes and cathodes are used for wastewater remediating by electrocoagulation (EC) [3]. The EC process produces ions (Cu^+, Cu^{2+}, Fe^{2+}, Fe^{3+} or Al^{3+}) during electrolysis that capable of producing coagulants in water solutions.

Aluminium undergoes dissolution to the Al^{3+} ions in all types of electrodes at different temperatures [3]. Two aluminium electrodes were used for the removal of cadmium (Cd) from wastewater through the EC process and various EC tests were conducted for the different initial temperatures of 18, 30, 50 and 70 °C [4]. Cadmium (Cd) removal rate increased with temperature increasing [4]. Rate of aluminium anodes dissolving ($Al\rightarrow\{electrolysis\}Al^{3+}$) increases with temperature increasing [5 – 8], so quantity of coagulants $Al(OH)_3$ and pure Al also increases with temperature increasing, and, as result, the cadmium removal rate increases with temperature increasing too.

Iron produces the Fe^{2+} ions during dissolution. Fe^{2+} oxidation to Fe^{3+} by dioxygen becomes significant only at higher pH values (pH > 7) although Fe^{3+} is a stronger coagulant than Fe^{2+} [9, 10]. We can conclude that $Fe(OH)_3$ is better coagulant than $Fe(OH)_2$. Rate of iron anodes dissolving practically does not depend on temperature [5 – 8]. We have planned to investigate what coagulants, $Fe(OH)_2$, $Fe(OH)_3$, or/and pure Fe are formed near iron anode during electrolysis

in concentrated NaCl solution at temperatures 20°C – 100°C. It depends on electric current density [9, 10].

Some researchers believe that copper anodes dissolve into an electrolyte as the Cu^{2+} and Cu^{3+}(?) ions [11]: "Cu normally exist in either cuprous (Cu^{2+}) or cupric (Cu^{3+}) oxidation states in aqueous solution, switching between these oxidation states playing a key role in the element's speciation, transport, and bioavailability. The Cu^{2+} and Cu^{3+} ions hydrate and hydrolyse to form monomeric and polymeric species: $Cu(OH)^{2+}$, $CuOH^{2+}$, $Cu2(OH)2^{4+}$, $Cu(OH)^{4-}$, $Cu(H_2O)^{2+}$, $Cu(H_2O)_5OH^{2+}$, $Cu(H_2O)_4(OH)^{2+}$ etc". It is incorrect. We can find copper containing species in the copper-water system in Table 3 in [12]. It should be correct [12]: "Cu^+: $Cu(OH)_2^-$; Cu^{2+}: $CuOH^+$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, $Cu_2(OH)_2^{2+}$, $Cu_3(OH)_4^{2+}$ ".

The corrosion resistance of the coated aluminum alloy in a 3.5 wt.% NaCl solution (pH 6.5–7.5) and the influence of different surface treatment processes on the corrosion resistance of different samples were studied by scanning electron microscope (SEM) and electrochemical workstation in [13]. For this reason, we have planned to investigate copper, iron, and aluminium electrochemical corrosion rate dependence on temperature during electrolysis in concentrated sodium chloride (NaCl) solution in water (5 mol/kg [12] or 23.1%, freezing point equals -22°C [14], pH 6.5–7.5). $AlCl_3$, $FeCl_2$, $FeCl_3$, and $CuCl_2$ dissolve in water, but CuCl does not dissolve in water, so we should expect appearance of such coagulants: $Al(OH)_3$ (white colour), pure Al, $Fe(OH)_2$ (grey-green colour), $Fe(OH)_3$ (brown colour), pure Fe, $Cu(OH)$ (yellow colour), $Cu(OH)_2$ (blue-green colour), CuCl (white or greenish colour), and pure Cu.

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:

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

(1)

Here, m is anode mass dissolved into the electrolyte, t is a time of the experiment, M is molar mass, I is the direct electric current value, F is the Faraday constant ($F \approx 96,500$ 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 anodes radii decreasing kinetics were measured. Equations (1) give:

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

(2)

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

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

(3)

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

(4)

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

where $L_{Cu} = L_{Fe} = 5 \cdot 10^{-2}$ m, $L_{Al} = 4.5 \cdot 10^{-2}$ m; $R_{0Cu} = R_{0Al} = 2.8$ mm, $R_{0Fe} = 2.98$ mm; $I_{Fe} = 3.15$A, $I_{Al} = 3.1$A, $I_{Cu} = 2.8$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: $t_1 = 5$ min, $t_2 = 10$ min, $t_3 = 15$ min, $t_4 = 20$ min; $R_{1Cu} = 2.74$ mm, $R_{2Cu} = 2.67$ mm, $R_{3Cu} = 2.59$ mm, $R_{4Cu} = 2.5$ mm; $R_{1Al} = 2.77$ mm, $R_{2Al} = 2.73$ mm, $R_{3Al} = 2.68$ mm, $R_{4Al} = 2.62$ mm, $R_{1Fe} = 2.95$ mm, $R_{2Fe} = 2.92$ mm, $R_{3Fe} = 2.88$ mm, $R_{4Fe} = 2.83$ mm. Measurement precision was 0.01 mm or 10 micrometers.

Literature data show that the uncharged copper (II) chloride complex $CuCl_2$ (aq) predominates at 50-100 °C [5], so average charge of copper ions should be greater than +1 and less than +2. We have calculated at temperature 100°C:

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

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

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

where $L_{Cu} = L_{Al} = 4 \cdot 10^{-2}$ m, $L_{Fe} = 5 \cdot 10^{-2}$ m, $R_{0Cu} = 2.27$ mm, $R_{0Al} = 2.6$ mm, $R_{0Fe} = 2.83$ mm, $I_{Al} = 3.15$ A, $I_{Fe} = 3.13$ A, $I_{Cu} = 3.05$ 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: $t_1 = 5$ min, $t_2 = 10$ min, $t_3 = 15$ min, and $t_4 = 20$ min; $R_{1Cu} = 2.2$ mm, $R_{2Cu} = 2.12$ mm, $R_{3Cu} = 2.03$ mm, $R_{4Cu} = 1.92$ mm; $R_{1Al} = 2.56$ mm, $R_{2Al} = 2.51$ mm, $R_{3Al} = 2.45$ mm, $R_{4Al} = 2.38$ mm; $R_{1Fe} = 2.80$ mm, $R_{2Fe} = 2.76$ mm, $R_{3Fe} = 2.72$ mm, $R_{4Fe} = 2.67$ mm. We carried additional experiments, but 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]:

$$C_R = A \, e^{-\frac{E_A}{RT}}, \tag{9}$$

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]:

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

$$A_{Al} = \pi k_{Al} L \rho_{Al} e^{\frac{E_A}{RT}} = 5.45 \cdot 10^{-7} \, kg/s; \quad C_R^{Al} = 5.45 \cdot 10^{-7} \, e^{-\frac{197\,K}{T[K]}} \, kg/s, \quad (11)$$

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

4. Conclusions

Copper electrochemical corrosion is higher than aluminium or iron electrochemical corrosion at room temperature $T_1 \approx 20^\circ C$ (average charge of copper ions equals +1) and at temperature $T_2 = 100^\circ C$ (average charge of copper ions equals +1.5). The ratio of electrochemical corrosion rates, k_{Cu}/k_{Al} (or k_{Cu}/k_{Fe}), decreases with temperature increasing. Iron electrochemical corrosion rate practically does not depend on temperature below 100°C (average charge of iron ions equals +2). It is obvious because the melting point of iron is higher than the melting point of copper or aluminium (Fig. 7).

Increasing temperature leads to dissolution rate value of copper anodes decreasing while the electric current value increases since average charge of the Cu ions increases too.

Increasing temperature leads to dissolution rate value of aluminium anodes increasing and electric current value increases too.

The dissolving rate value of the copper anodes decreases approximately in 4 times due to the temperature increasing effect while the dissolving rate value of the aluminium or iron anodes increases all the time due to the cylindrical shape effect.

Increasing temperature practically does not influence on rate value of iron anodes dissolving as on the direct electric current value too.

The spherical shape effect is greater than the cylindrical shape effect in 1.5 times.

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