SHORT COMMUNICATION

The potential–pH diagram for the Ru–H_2O–Cl^- system at 25° C

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1. Introduction

The potential–pH diagram for the system Ru–H_2O at 25° C has already been presented by Pourbaix [1] and, more recently, by Barral *et al.* [2]. Both demonstrate a comparatively wide region of thermodynamic stability for ruthenium dioxide, which constitutes the essential component in the active surface layer of activated titanium anodes (ATA). Since titanium anodes, coated with a layer of ruthenium and titanium oxides, are commonly employed in the processes of alkaline chloride electrolysis, a problem arises regarding the stability of RuO_2 in the presence of chloride ions. Therefore, the objective of this contribution is to calculate the thermodynamic stability of RuO_2 in the presence of Cl^- ions.

2. Data and calculation procedure

Owing to the scant thermodynamic data it has not been possible to carry out the calculations for the temperature of 80° C, corresponding to the conditions of industrial brine electrolysis. Therefore, all the calculations were executed for 25° C. For the same reason only the ions $RuCl_5^{2-}$ and $RuCl_5OH^{2-}$ in the system Ru–H_2O–Cl^- are considered, in addition to ruthenium compounds that may occur in the system Ru–H_2O.

The values of standard free energies at 25° C for ruthenium compounds in the system Ru–H_2O were taken from [2] and are presented in Table 1.

The values of standard free energies for H_2O(l) $\Delta G^0_{298} = -237.35\,\text{kJ mol}^{-1}$ and for Cl^-(aq) $\Delta G^0_{298} = -131.26\,\text{kJ mol}^{-1}$ were taken from [1].

The values of standard free energies for the $RuCl_5^{2-}$ and $RuCl_5OH^{2-}$ ions were calculated from the standard equilibrium potentials corresponding to the equations taken from [3]:

$$Ru + 5Cl^- \rightleftharpoons RuCl_5^{2-} + 3e^- \qquad E^0 = 0.40\,V \qquad (1)$$

$$Ru + 5Cl^- + H_2O \rightleftharpoons RuCl_5OH^{2-} + H^+ + 4e \qquad E^0 = 0.60\,V \qquad (2)$$

$$RuCl_5^{2-} + H_2O \rightleftharpoons RuCl_5OH^{2-} + H^+ + e^- \qquad E^0 = 1.30\,V \qquad (3)$$

$$RuCl_5OH^{2-} + 3H_2O \rightleftharpoons RuO_4^- + 7H^+ + 5Cl^- + 3e^- \qquad E^0 = 1.78\,V \quad (4)$$

Table 1. Standard free energies of Ru compounds at 25° C

Compound	ΔG^0_{298} (kJ mol^{-1})
RuO_2 (s)	−254.98
RuO_3 (g)	−54.43
RuO_4 (g)	−146.54
RuO_4 (s)	−146.54
RuO_4^{2-} (aq)	−295.17
RuO_4^- (aq)	−238.23
H_2RuO_5 (aq)	−378.83
$HRuO_5^-$ (aq)	−314.84

Equation 1 gives $\Delta G^0 = -540.52\,\text{kJ mol}^{-1}$ for $RuCl_5^{2-}$. Using this result it is possible to calculate for $RuCl_5OH^{2-}$ $\Delta G^0_{298} = -661.37\,\text{kJ mol}^{-1}$ from Equation 2 or, from Equation 4, $\Delta G^0_{298} = -597.64\,\text{kJ mol}^{-1}$. Substituting the data obtained from Equations 1 and 2 in the calculation according to Equation 3 results in $E^0 = 1.206\,V$, which is fairly close to $E^0 = 1.3\,V$. Using the data obtained from Equations 1 and 4 with Equation 3 gives $E^0 = 1.866\,V$. Therefore, the values $\Delta G^0_{298} = -540.52\,\text{kJ mol}^{-1}$ and $\Delta G^0_{298} = -661.37\,\text{kJ mol}^{-1}$ for $RuCl_5^{2-}$ and $RuCl_5OH^{2-}$, respectively, are used in the following. Latimer [3] reports approximate values of $-540.1\,\text{kJ mol}^{-1}$ and $-661.51\,\text{kJ mol}^{-1}$.

The voltage–pH diagram was set up on the basis of

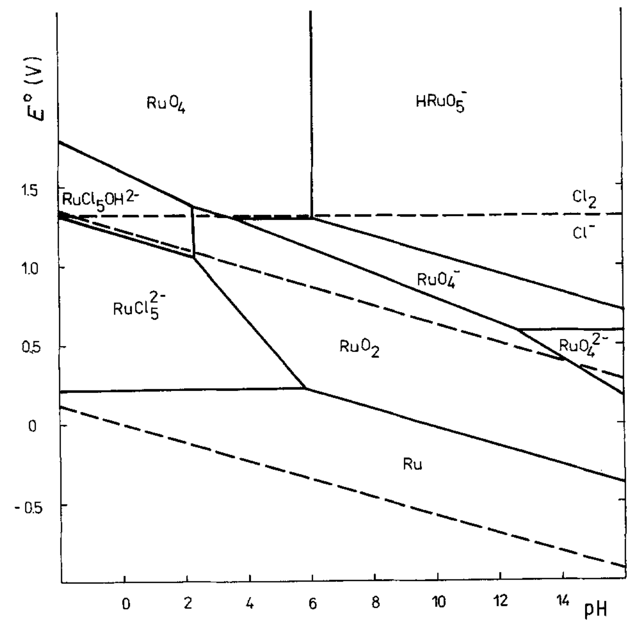

Fig. 1. Potential–pH diagram for the Ru–H_2O–Cl^-, system at 25° C in a solution of 264 g l^{-1} NaCl. Activities of the other ions are 10^{-6}.

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Table 2. Reactions considered in this study. (Square backets denote activities of the respective ions.)

1. $Ru(s) + 5Cl^-(aq) \rightleftharpoons RuCl_5^{2-}(aq) + 3e^-$	$E^0 = 0.400 + 0.020 \frac{[RuCl_5^{2-}]}{[Cl^{-5}]}$
2. $RuCl_5^{2-}(aq) + 2H_2O \rightleftharpoons RuO_2(s) + 5Cl^-(aq) + e^- + 4H^+$	$E^0 = 1.077 - 0.236\ pH + 0.059 \log \frac{[Cl^-]^5}{[RuCl_5^{2-}]}$
3. $RuO_2(s) + 5Cl^-(aq) + 3H^+ \rightleftharpoons RuOHCl_5^{2-}(aq) + H_2O$	$\log \frac{[RuOHCl_5^{2-}]}{[Cl^-]^5} = 3\ pH - 2.196$
4. $RuOHCl_5^{2-}(aq) + 3H_2O \rightleftharpoons RuO_4(s) + 5Cl^-(aq) + 7H^+ + 4e^-$	$E^0 = 1.477 - 0.103\ pH + 0.015 \log \frac{[Cl^-]^5}{[RuOHCl_5^{2-}]}$
5. $RuCl_5^{2-}(aq) + H_2O \rightleftharpoons RuOHCl_5^{2-}(aq) + H^+ + e^-$	$E^0 = 1.207 - 0.059\ pH + 0.059 \log \frac{[RuOHCl_5^{2-}]}{[RuCl_5^{2-}]}$
6. $RuO_4^{2-}(aq) \rightleftharpoons RuO_4^-(aq) + e^-$	$E^0 = 0.590 + 0.059 \log \frac{[RuO_4^-]}{[RuO_4^{2-}]}$
7. $RuO_4^-(aq) + H_2O \rightleftharpoons HRuO_5^-(aq) + H^+ + e^-$	$E^0 = 1.665 - 0.059\ pH + 0.059 \log \frac{[HRuO_5^-]}{[RuO_4^-]}$
8. $Ru(s) + 2H_2O \rightleftharpoons RuO_2(s) + 4H^+ + 4e^-$	$E^0 = 0.569 - 0.059\ pH$
9. $RuO_2(s) + 2H_2O \rightleftharpoons RuO_4(s) + 4H^+ + 4e^-$	$E^0 = 1.510 - 0.059\ pH$
10. $RuO_4(s) + H_2O \rightleftharpoons HRuO_5^-(aq) + H^+$	$\log [HRuO_5^-] = -12.10 + pH$
11. $RuO_2(s) + 2H_2O \rightleftharpoons RuO_4^{2-}(aq) + 4H^+ + 2e^-$	$E^0 = 2.250 - 0.118\ pH + 0.029 \log [RuO_4^{2-}]$
12. $RuO_2(s) + 2H_2O \rightleftharpoons RuO_4^-(aq) + 4H^+ + 3e^-$	$E^0 = 1.697 - 0.079\ pH + 0.020 \log [RuO_4^-]$

the equations compiled in Table 2, using the following simplifications:

(a) in the diagram only $RuO_4(s)$ but not $H_2RuO_5(aq)$ is considered;
(b) the concentration of Cl^- corresponding to $264\,g\,l^{-1}$ NaCl ($\gamma_\pm = 0.885$ [4]) is considered, which is near to the conditions of the brine electrolysis process;
(c) the activities of the other ions (that is, those other than Cl^-) are assumed to be 10^{-6}.

Table 2 shows the reactions under consideration. The final plot of the calculated data is presented in Fig. 1. In addition to the standard curves for hydrogen and oxygen the curve for chlorine discharge is also included. It follows from the diagram that at the equilibrium potential of chlorine discharge, RuO_2 is stable within the pH range 2.3–3.0. It should be noted that Gorodetskii *et al.* [5], studying the kinetics of the RuO_2 active layer dissolution, observed the lowest rate of dissolution in the pH range 0.3–3.0.

References

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