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Methods for Determining Oxygen Overvoltage and Anode Poisoning Over Time at Iron-Group Metals under High Current Densities in Alkaline Water Electrolysis

Ya. I. Tur'yan

76D Thurston Rd, Newton, MA02464. USA.

ABSTRACT: *Determination of oxygen overvoltage (η_s) is complicated by high current densities under alkaline water electrolysis. Therefore, it is desirable to develop method for advanced control of oxygen overvoltage.*

Here, we show that the modified rotating anode method offers a number of advantages for determination of oxygen overvoltage in alkaline water electrolysis under high current densities. These include elimination of the gas (oxygen) shielding anode, the electrolyte gas filling near anode, and concentrating polarization.

The mechanism of the anode material poisoning in time has been further developed by us based on the highest metal oxide surface concentration increased in time. Specifically, in a case of Ni anode: $Ni_2O_3 \longrightarrow NiO_2$ at the current density, $i = (0.1\text{-}3.0)$ A/cm^2. For Ni and Co anode: $NiO_2(CoO_2) \longrightarrow NiO_3(CoO_3)$ at i (3.0-10.0) A/cm^2.

It has been shown that the oxygen overvoltage on Ni is higher compared to Co or Fe anode, and there are no significant differences between oxygen overvoltage on Co and Fe: $\eta_s(Ni) > \eta_s(Co) \cong \eta_s(Fe)$. The difference in

oxygen overvoltage between different metals increases with the increase in current density.

Recommendations on using galvanic alloy composed of Co and Ni are given to assure the cost effectiveness of the galvanic system and better resistance to corrosion.

Keywords: *Oxygen overvoltage, methods determination, anode material poisoning.*

I. INTRODUCTION

In spite of the large interest to hydrogen production using alkaline water electrolysis, the oxygen overvoltage (η) was investigated insufficiently. Overvoltage results in higher energy consumption reducing the expected lifetime of certain equipment. Therefore, hydrogen production by water electrolysis still needs improvements in energy efficiency, safety, and durability.

In the present paper, the overvoltage values obtained by different methods under various current density (i), temperature (t), and time (τ) were compared to elucidate their impact on the overall electrolysis efficiency. The data have been applied to study behavior of the following iron-group metal anodes, i.e., Co, Fe and Ni in industrial alkaline water electrolysis using (1.0 -7.5 M) KOH electrolyte, current density, i = 0.1-10.0 A/cm^2, and t = 18 - 85° C. These metals are often used in the alkaline water electrolysis either as a pure metal, or as an alloy in conjunction with the other metals using plasma covering [1,2] or stainless steel [3].

In addition, the theory of anode poisoning has been further developed by us. Finally, recommendations for economically produced hydrogen gas via water electrolysis have been given.

II. METHODS FOR DETERMINING OXYGEN OVERVOLTAGE

It is well known that oxygen electrode does not exhibit a thermodynamically reversible behavior. This complicates the oxygen overvoltage determination. The other complication for η determinations is based on the high current densities used in the industrial alkaline water electrolysis. Under these conditions the gas (oxygen) shielding anode, the electrolyte filling near the gas-shielded anode and concentrating polarization affect oxygen overvoltage. Taking into account the indicated interferences, Hickling and Hill [4,5] have developed method for the overvoltage determination. This method is based on the polarization interrupter over different interruption time. The interruption time has been increased consecutively and the minimum potential has been measured for each interval. The dependence of the minimum potential vs. time has been further extrapolated to zero time. This potential eliminates the influence of ohmic drop potential in the electrolyte layer between the anode surface and the tip of the electrolytic switch. However, the impact of the gas shielding anode and the concentrating

polarization on the oxygen overvoltage has not been taken into account in the extrapolated method leading to the error in the η determination (see below).

We have developed method for η determination [6,7] based on using rotating wire anode ("rotating electrode method"). This allowed eliminating all interferences discussed above: the gas shielding anode, electrolyte filling with a gas and concentrating polarization. It has been shown that η is decreased with the increase of the anode rotation speed up to a definite value (530 revolutions/min for the anode construction in [6,7]). This speed was used for the η determination. Taking into account, that the gauze filling near anode was eliminated for calculation of the ohmic drop potential in indicated above electrolyte layer, the conductivity of the pure electrolyte has been used.

To compare the extrapolated method [4,5] with the rotating electrode method [6,7] the oxygen overvoltage (η_s) values at i=const and t=const have been chosen (Table 1). The η_s are the overvoltage values taking into consideration the poisoning effect. These values are characterized by the methods comparison under the same i and t and different C_{KOH} ([OH⁻] = 1.0M and 7.5M). The impact of C_{KOH} ([OH⁻]) on the η_s value could be neglected for Ni in the indicated interval of KOH concentrations [8.9]. We will show that this conclusion is also equitable for Co. The following theoretical confirmation has been used previously [7]:

$$\eta_s = \text{Const.} + (RT/F) \ln i \qquad (1)$$

Unlike work [7], the Const. could be expressed using the standard potentials φ^0(ox/red):

$$\text{Const.} = (RT/F) \ln(f_{OH}/k) + \varphi^0(OH/OH^-) - \varphi^0(O_2/OH^-), \qquad (2)$$

where: k- rate constant of $Co(OH)3 + OH$ reaction; f_{OH} – activity coefficient ($f_{OH} \cong 1$ due to the charge absence).

Using (1) and (2) it follows that η_s values for Co are practically independent on the C_{KOH}([OH⁻]) similar to Ni [9.10] (Table 1). Hence, there is a possibility to use the η_s values for different C_{KOH}([OH⁻]). On the basis of Table 1 it can be seen smaller η_s values for the rotating electrode method compared to the extrapolated method. This confirms the advantages of the rotating electrode method for the η_s determination allowing eliminate the gas shielding anode and concentrating polarization. The substitution of the rotating wire electrode with the rotating disk electrode using a pressed to the electrode surface thin, polymeric thread [10] should allow obtaining more effective device for the η_s determination at high current densities.
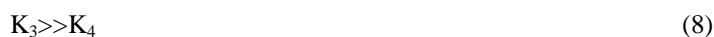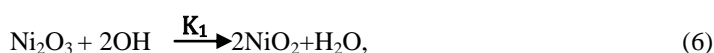
III.   THE ANODE POISONING IN TIME

Among anodes of the iron group metals (Ni, Co, Fe) considered for the alkaline water electrolysis, the only Ni anode is subjected to the poisoning over time (τ) at i ≤ 3.0 A/cm². This leads to the increase in η over time from $\eta_{\tau=0}$ up to $\eta\{\tau=\tau(\lim)\}$ at i=const and t =const. The $\tau(\lim)$ is the limiting time when η rises up to η_s = const.

On the basis of the η vs. τ dependences [8], we have obtained the general characteristics of the Ni anode poisoning in time (Table 2). The two conclusions (A and B) could be drawn using the data in Table 2:

A.   The $\tau(\lim)$ values of the Ni anode poisoning are decreased under increased i and decreased t values.

B.   The constant value of $(\eta_s - \eta_{\tau=0}) = (0.42\pm0.02)$ V is observed at i=0.1-3.0 A/cm² and t ≥18°

These conclusions have been drawn using the kinetics and mechanism of Ni anode poisoning developed by us in [8] (reactions (3-9), below). Thus, the anodic oxygen evolution and Ni anode poisoning could be described by the reactions (3-5, 8) and (6, 7, 9), respectively:

$$OH^- - e^-(Ni_2O_3) \xrightarrow{K_3} OH \qquad (3)$$

$$OH^- - e^-(NiO_2) \xrightarrow{K_4} OH \qquad (4)$$

$$4OH \longrightarrow O_2 + 2H_2O, \qquad (5)$$

$$Ni_2O_3 + 2OH \xrightarrow{K_1} 2NiO_2 + H_2O, \qquad (6)$$

$$4 NiO_2 \xrightarrow{K_2} Ni_2O_3 + O_2, \qquad (7)$$

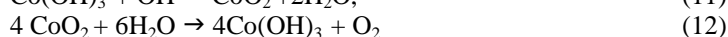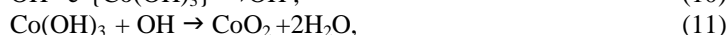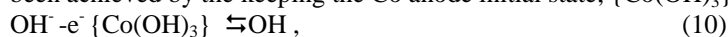$$K_3 \gg K_4 \qquad (8)$$
$$K_1 \gg K_2 \qquad (9)$$

where OH are radicals near the Ni anode surface or adsorbed radicals, OHads.

The sum of reaction rates (3) and (4) determines the rate of the entire process. Discounting (8) and (9), the Ni anode poisoning is caused by the NiO_2 formation on the anode surface (reactions 6 and 7). The full coverage of the Ni anode surface by NiO_2 takes place in the interval of i=0.1 - 3.0 A/cm^2.

To draw the A conclusion we accepted the presumable participation of OH_{ads} in eqs.(3)-(6). Hence, with the increase of i(t=const) and decrease of t (i=const), [OH_{ads}] rises and the rate of the reaction (6) increases. This causes the τ (lim) decreases, leading to the A conclusion. To draw the B conclusion we took into account the full coverage of the Ni anode surface by NiO_2 and nearness of the slopes η vs. ln i at $\eta = \eta_{\tau=0}$ and $\eta = \eta_s$ [8]. This gives the constant difference ($\eta_s - \eta_{\tau=0}$) independently from i and t, and allowing us to draw B conclusion. To accelerate the Ni anode poisoning the dependents of η_s vs. ln i has been achieved by the preliminary anode polarization at i = 2.0 A/cm^2 during 5 min.

Under indicated conditions for the Ni anode (i $\leqslant$ 3.0 A/cm^2), the Co poisoning was absent. This has

been achieved by the keeping the Co anode initial state, {$Co(OH)_3$}, due to the regeneration of $Co(OH)_3$:

$$OH^- - e^- \{Co(OH)_3\} \leftrightarrows OH , \qquad (10)$$
$$Co(OH)_3 + OH \rightarrow CoO_2 + 2H_2O, \qquad (11)$$
$$4 CoO_2 + 6H_2O \rightarrow 4Co(OH)_3 + O_2 \qquad (12)$$

The reaction (11) is the rate determining reaction. At the same time the reaction (10) as unlikely analogous reaction for Ni anode, is close to the reversible reaction.

In the interval of i=3-10A/cm^2 , the first and the second poisoning observed for Co and Ni, respectively, are the most probably related to the new oxides CoO_3 or NiO_3 formation. The OH^- discharging deceleration increases in the following direction: $Ni_2O_3 \rightarrow NiO_2(CoO_2) \rightarrow NiO_3(CoO_3)$, that essentially widens the conclusion on $Ni_2O_3 \rightarrow NiO_2$ from this work.

IV. RECOMMENDATIONS FOR APPLICATIONS OF THE IRON GROUP ANODES

Using Table 1 the $\Delta\eta_s = \{\eta_s(Ni) - \eta_s (Co)\}$ values have been compared at different i for industrial conditions of 7.5 M KOH, 70° C (the conductivity is closed to the maximum). The current density (A/cm^2) values are corresponding to the following $\Delta\eta_s$ (V) values: (0.10; 0.10), (1.0; 0.48), (10.0; 0.64). This shows that $\eta_s(Co) < \eta_s(Ni)$. Thus, using cobalt anode assures economy of the electric energy. For the Fe anode, the η values are close to that of Co anode. However , the Fe anode passivation is insufficient leading to the more preferable usage of the Co anode. It is known that the cobalt electrode material is more expensive compared to Ni or Fe. Therefore, it is desirable using the galvanic alloy [11], i.e., Co+Ni anode.

The advantages of using rotating anode method (eliminations of the gas shielding anode, electrolyte gas filling and concentrating polarization) are also important for industrial electrodes. In this case the considerable intensification of the electrolyte circulation is necessary. The electrolyte circulation for bipolar electrodes in the filter press type electrolyze was proposed [12] and it could be achieved by using of a steam injector. The condensate in the injector compensates the water consumption during production of hydrogen and oxygen by water electrolysis.

V. CONCLUSION

It has been shown that the rotating anode method using a rotating disk anode with a polymeric thread is a method of choice for determining oxygen overvoltage.

The efficient production of hydrogen through water electrolysis requires: (1) using of galvanic alloy consisting of Co and Ni as a material for industrial anode, (2) operating with the current density of less or equal than 3.0A/cm2 to avoid poisoning of Co, (3) magnification of the industrial electrolyte circulation by using of a steam injector.

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Table 1 Comparison of oxygen overvoltage values obtained by the different method for anodes of the iron group

Anodes	Co					Fe	Ni			
$t^0 C$	20			70		20	20		70	
C(KOH),M	1.0		7.5	1.0	7.5	1.0	1.0	7.5	7.5	5.6
i A/cm^2	η_s, V [4]	η_s, V [5]	η_s, V [7]	η_s, V [5]	η_s, V [7]	η_s, V [4]	η_s, V [4]	η_s, V [6]	η_s, V [6]	$\eta_{\tau=0}$, V [1]
0.1	0.54	0.58	0.37	0.43	0.30	0.56	0.91	0.88	0.40	0.29
1.0	0.61	0.71	0.44	0.61	0.37	0.63	1.04	1.01	0.85	0.39
10.0	–	–	0.68	–	0.48	–	–	1.56	1.12	–

Table 2 Generalized description of the Ni-anode poisoning process in time at i=const in 7.5 M KOH

i A/cm^2	t ^{0}C	τ(lim) Hours	$\eta_s - \eta_{\tau=0}$ V
0.1	18	100	0.40
0.1	60	204	0.40
0.3	25	26	0.46
0.3	80	62	0.42