

Reasons for the DSA Passivation during Chlorate Electrolysis and the Means for Extending the Anode Service Life

V. I. Eberil', E. A. Novikov, and A. F. Mazanko

Sintez Research Institute, Moscow, 109432 Russia

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Abstract—Based on experiments and analysis of literature data, it is shown that a poor utilization of the active mass of the coating on metal oxide anodes of the DSA type during the electrochemical sodium chlorate production is due to pseudopassivation (an increase in the anodic potential due to a predominant corrosion dissolution of RuO_2 as compared with TiO_2 in the outer working zone of the coating), which develops with time. The true irreversible anode passivation, resulting from the formation of a stable barrier layer of higher titanium oxides at the coating/substrate interface, occurs when the DSA active mass wears out to a residual ruthenium content below 1.4 g/m^2 in it. The coating service life can be extended with no increase in the potential and with a minimum active mass consumption by using, concurrently with RuO_2 and TiO_2 , catalytically active additives with higher corrosion resistance than that of RuO_2 at pH 6 to 7. This prevents the anode pseudopassivation and, with an increased initial amount of the active mass, makes it possible to use the anodes until its residual content exceeds the limit below which the true passivation starts, and regenerate the coating by applying fresh mass on the residue of the existing mass.

INTRODUCTION

The important advantage of metal oxide anodes, in particular DSA, in the chlorine and chlorate electrolyses is a low anodic potential and its stability. However, when the anode operates to a virtually full utilization of the coating service life, at a certain stage of its operation, the anodic potential increases. This effect manifests itself as the onset of the voltage growth across the electrolyzing cell at residual ruthenium contents $M_{\text{Ru, res}}$, which depend on the anode operation conditions. In chlorine electrolyzing cells with a mercury cathode, this effect occurs earlier and is stronger than in the diaphragm cells; the effect is the strongest at high current densities and pH values [1]. The same is true for the anodes in the chlorate electrolysis [2], which is characterized by higher pH values than the chlorine electrolysis.

An increase in the anodic potential after a long-term operation should be considered as resulting from the anode passivation.¹ The passivation may result from the emergence and growth of a barrier TiO_2 layer between the active coating and Ti substrate, leading to virtual loss of conductivity at the coating/substrate interface [3]. This kind of passivation is irreversible, and an anode that is passivated by this mechanism requires the coating regeneration with the removal of its residue and the etching of the oxidized substrate. Another type of passivation can be considered as a reversible passiva-

tion or a pseudopassivation. In contrast to the irreversible (true) passivation, the pseudopassivation stems from a relative depletion in RuO_2 of a relatively thin surface coating layer, in which most anodic reactions proceed. The depletion is due to the Ru corrosion rate being higher than that of Ti, and it increases with the electrolyte's pH [4]. A relative depletion of the coating in RuO_2 and the corresponding enriching in TiO_2 increase the anodic potential, especially strongly when the RuO_2 fraction decreases below 20 mol % [5].

In real electrolyses, both DSA passivation mechanisms can occur, and the balance between them as a function of the electrolysis conditions is important primarily for selecting the active mass of the coating, its amount, and operation conditions for the anodes that would ensure their long service life with a minimum electric power consumption. In most studies dealing with this problem, the prevailing opinion is that the anodic passivation is due primarily to an increased ohmic resistance at the coating/substrate interface [3, 6–8]. However, industrial use of the anodes and the contradictions between the data reported in the studies cited require a further analysis and a more rigorous and concrete interpretation of the phenomena observed.

Here, we consider the reasons for the DSA passivation during the chlorate electrolysis.

It was shown experimentally that, during industrial use of DSA with an initial specific Ru content in the coating of $6.5\text{--}6.7 \text{ g/m}^2$ in the chlorate electrolyzing cells, the useful consumption of Ru in the coating varies between 30 and 70% of its overall initial amount M_{Ru} . Once the voltage across the cell starts increasing, $M_{\text{Ru, res}} = 2.0\text{--}4.5 \text{ g/m}^2$ [2, 6]. After a DSA operated in a

¹ The term “anodic passivation” here characterizes not a “passive state of the anode,” which in the literature implies the operation conditions corresponding to low corrosion rates of the coating, but an increase in the anodic potential of an ohmic nature.

model chlorate electrolyzing cell for 1000 days at $i = 0.2 \text{ A/cm}^2$ and $t = 60^\circ\text{C}$ in a solution containing 100 g/l NaCl, 400 g/l NaClO_3 , and 2 g/l $\text{Na}_2\text{Cr}_2\text{O}_7$ at pH 6.5–7.0 to $M_{\text{Ru, res}} = 4.3 \text{ g/m}^2$, which corresponds to an average Ru corrosion rate of $0.9 \times 10^{-8} \text{ g/cm}^2 \text{ per h}$, the anodic potential increased prematurely [6]. This was presumably caused by the formation of a barrier layer of Ti oxides at the coating/substrate interface [6]. However, among possible reliable methods of extending the service life of the coating, a well-known expedient [9] of repeated use of the spent active mass after plating fresh active mass on it was mentioned in [6], which, according to the tests, had pronounced beneficial effect. This fact indicates that, in the case described in [6], there takes place typical pseudopassivation, which can be eliminated by reactivation of the outer coating layer without removing its residue and without etching the substrate.

However in some cases, especially under rather adverse conditions, when the coating corrosion rate is high, the true passivation and the pseudopassivation can manifest themselves virtually simultaneously.

EXPERIMENTAL

To quantitatively estimate the chlorate electrolysis conditions under which one or another type of passivation is probable, the laboratory test procedure proposed in [9] was used. The procedure involves the determination of the continuous operation time τ of an anode with a known M_{Ru} until reaching an anodic potential of 3.0 V (NHE) in a diaphragm-free cell during a continuous electrolysis in a solution of constant composition containing 550–600 g/l NaClO_3 and 2 g/l $\text{Na}_2\text{Cr}_2\text{O}_7$ at pH 6.5–7.0 and $t = 60^\circ\text{C}$. In various experiments, the current density and the NaCl concentration in the electrolyte were varied from 0.2 to 0.5 A/cm^2 and from 0 to 40 g/l, respectively.²

RESULTS AND DISCUSSION

Figure 1 gives plots of τ vs. the initial specific ruthenium content in the coating, which were obtained in the electrolysis of the above solutions at $i = 0.2 \text{ A/cm}^2$ and two NaCl concentrations. As is seen, the NaCl content strongly effects τ ; however, the plots differ. For instance, at $c_{\text{NaCl}} = 20\text{--}25 \text{ g/l}$ (curve 2), absolute values of τ are rather small, but a relative increase in τ with M_{Ru} occurs with a significant acceleration. At $c_{\text{NaCl}} = 40 \text{ g/l}$ (curve 1), the plot is more complex: at $M_{\text{Ru}} < 2.5 \text{ g/m}^2$, τ barely increases; then it abruptly rises and, as a result, at $M_{\text{Ru}} = 4 \text{ g/m}^2$ reaches 400 days, after which the growth in τ considerably slows down.

In view of a great difference between τ in curves 1 and 2, the results can be explained as follows. In solutions containing 20–25 g/l NaCl, where the Ru corro-

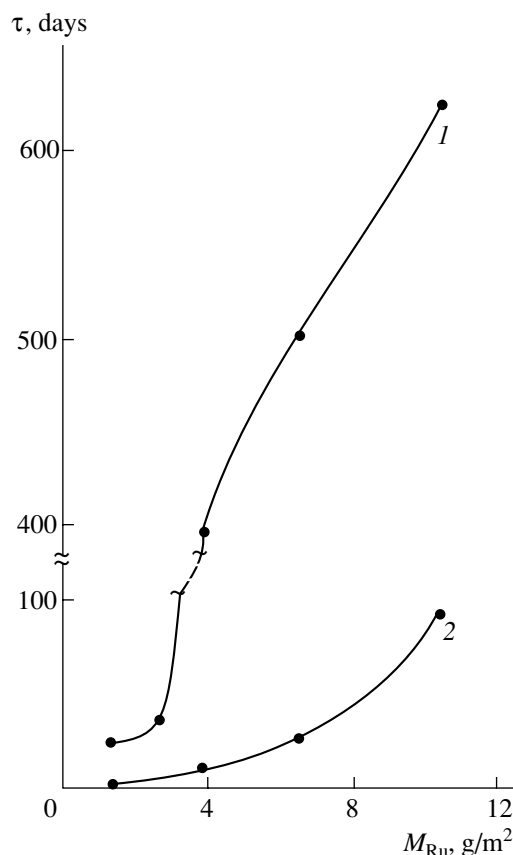


Fig. 1. Service life of DSA vs. amount of active mass (calculated for Ru metal) in accelerated tests in chlorate solutions containing (1) 40 [6] and (2) 20–25 g/l NaCl; 0.2 A/cm^2 , 60°C .

sion rate in the coating is significantly higher than at 40 g/l, the rates of both formation of excess phase of higher Ti oxides at the coating/substrate interface and the RuO_2 removal from the bulk coating are high and comparable. The only factor maintaining relative efficiency of the coating is M_{Ru} . However, under these conditions, even at $M_{\text{Ru}} = 10.5 \text{ g/m}^2$, the service life does not exceed 100 h. At $c_{\text{NaCl}} = 40 \text{ g/l}$ (curve 1) and $M_{\text{Ru}} < 2.5 \text{ g/m}^2$, τ increases insignificantly with M_{Ru} , but its absolute values are higher than at $c_{\text{NaCl}} = 20\text{--}25 \text{ g/l}$. With a further increase in M_{Ru} , τ steeply increases, pointing to a high protective effect of an increase in M_{Ru} , and at $M_{\text{Ru}} > 4 \text{ g/m}^2$, the growth of τ slows down.

In [6], an increase in the Ru corrosion rate in the coating was considered as a possible reason for the retardation of τ growth with an increase in M_{Ru} . It was reported that, in the electrolysis of a solution containing 60 g/l NaCl, after an 80-h test of specimens with M_{Ru} of 4.05 and 10.8 g/m^2 , the Ru corrosion rates, measured by a radiochemical method, were 2.0×10^{-4} and $3.4 \times 10^{-4} \text{ g/kA per h}$, respectively; the authors of [6] attribute this fact primarily to an increase in the true active area of the coating. We find these data rather

² Experiments were performed by L.M. Elina, V.M. Gitneva, and coworkers.

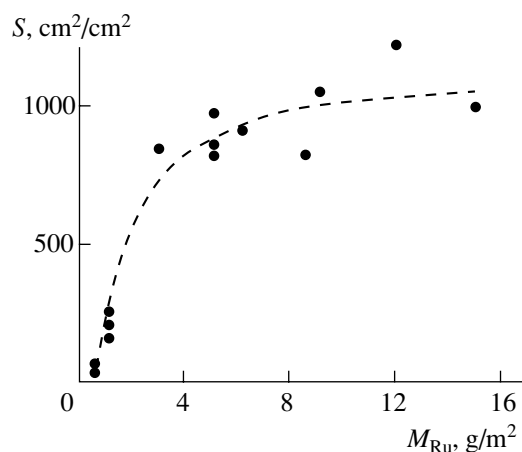


Fig. 2. Dependence of true surface area of DSA coating on M_{Ru} .

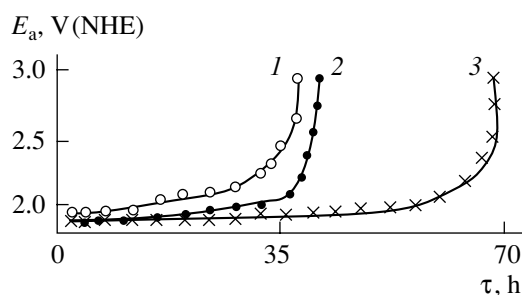


Fig. 3. Service life of DSA in accelerated tests in solution containing 650 g/l NaClO_3 and 2 g/l $\text{Na}_2\text{Cr}_2\text{O}_7$ at pH 6.5 to 7.0, 0.5 A/cm², and 60°C; active coating composition, mol %: (1) $\text{RuO}_2 : \text{TiO}_2 = 30 : 70$; (2) the same, with a platinum sublayer; (3) the same, with platinum in the active mass; $M_{Ru} = 6.5 \text{ g/m}^2$, $M_{Pt} = 1.74 \text{ g/m}^2$.

unconvincing. For instance, a more thorough study of the dependence of the Ru corrosion rate on M_{Ru} [10], showed (table) that the corrosion rate considerably increased only at low M_{Ru} , specifically, in the interval 0.45 to 1.35 g/m², and that at higher M_{Ru} , the corrosion accelerated insignificantly.

As seen in the table, the relative difference between the Ru corrosion rates at M_{Ru} of 4.05 and 10.8 g/m² (according to [6], it equals $3.4/2.0 = 1.7$) lies within the limits determined by the confidence intervals of the

Dependence of the Ru corrosion rate in DSA on M_{Ru} ; 5 M NaCl, pH 6.5–7.0, 0.2 A/cm², 80°C, time of continuous tests 80 h

M_{Ru} , g/m ²	Ru corrosion rate, g/cm ² per h
0.45	$(2.0 \pm 0.3) \times 10^{-8}$
1.35	$(0.75 \pm 0.2) \times 10^{-7}$
4.05	$(1.0 \pm 0.2) \times 10^{-7}$
10.8	$(1.4 \pm 0.3) \times 10^{-7}$
27.0	$(1.2 \pm 0.4) \times 10^{-7}$

measurement accuracy for these M_{Ru} values: $(1.4 + 0.3)/(1.0 - 0.2) = 2.1$.

An increase in the Ru corrosion rate with its specific initial content at low M_{Ru} can be explained by an increase in the true working area of the anode coating and, consequently, a decrease in the true current density. This assumption was supported by a decrease in the DSA potential with an increase in M_{Ru} , which was observed predominantly at $M_{Ru} < 2 \text{ g/m}^2$ [3], and by the results of direct measurements of true DSA area, which were conducted by a gas-adsorption method (Fig. 2).³

Thus, it is unlikely that different Ru corrosion rates in a coating at different M_{Ru} should be considered as a factor strongly affecting τ at different M_{Ru} , except at very low M_{Ru} . At low M_{Ru} , by contrast, all other factors being equal, they will favor a relative increase in τ with M_{Ru} . On this basis, the pseudopassivation phenomenon, which manifests itself under a long-term polarization of the anode, is to be considered the most probable reason for the decreased growth rate of τ at $M_{Ru} > 4 \text{ g/m}^2$ (Fig. 1, curve 1).

Let us estimate values of $M_{Ru, \text{res}}$, at which the true anodic passivation sets in. At $c_{\text{NaCl}} = 100 \text{ g/l}$, an average Ru corrosion rate is $0.8 \times 10^{-8} \text{ g/cm}^2 \text{ per h}$ [6]. With c_{NaCl} decreasing to 40 g/l, the Ru corrosion rate in DSA increase approximately three-fold [11]; i.e. under conditions corresponding to curve 1 in Fig. 1 it will be approximately $2.7 \times 10^{-8} \text{ g/cm}^2 \text{ per h}$. According to the calculated Ru loss from the coating under these conditions, $M_{Ru, \text{res}}$ equals 1.15, 2.30, 1.40, 3.10, and 6.10 g/m² for M_{Ru} of 1.3, 2.6, 3.9, 6.5, and 10.4 g/m², respectively. These data can be interpreted as follows. There is a maximum permissible value of M_{Ru} below which the passivation, which is caused by the formation of a barrier layer at the coating/substrate interface, occurs too soon. Under severe electrolysis conditions corresponding to the above experiments, this value is about 2.5 g/m². At higher M_{Ru} , the protective action of the active mass, which prevents a premature passivation of the coating/substrate interface, drastically increases during the electrolysis of solutions with $c_{\text{NaCl}} \geq 40 \text{ g/l}$. However, with increasing polarization time (but not M_{Ru} !), the pseudopassivation starts to manifest itself. In Fig. 1 (curve 1) it starts at $\tau > 400$ days.

According to the above calculation, at M_{Ru} exceeding the maximum permissible value, the minimum residual ruthenium content in the coating corresponding to the onset of true passivation is 1.4 g/m². This value agrees well with a similar value determined in [12] during the DSA operation in the diaphragm chlorine electrolyzing cells, where, due to rather soft operation conditions, the pseudopassivation did not manifest itself, and the anodes lost their activity as a result of the true passivation.

At low c_{NaCl} , the Ru corrosion rate is very high, and at $M_{Ru} > 3 \text{ g/m}^2$ the test time is insufficient for the for-

³ The measurements were carried out by A.S. Kulyasova.

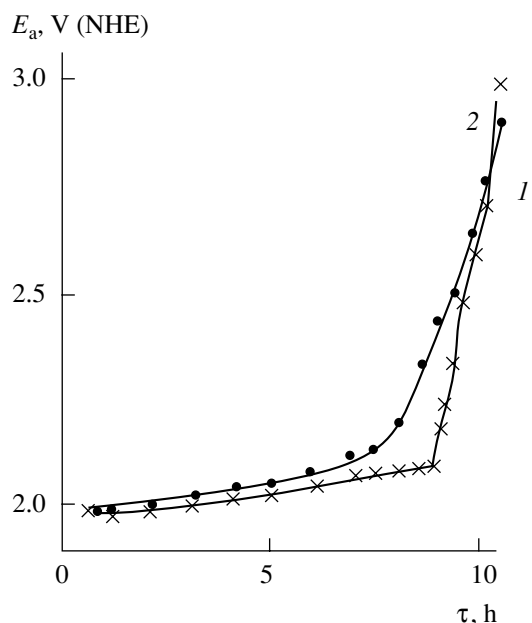


Fig. 4. Service life of DSA in accelerated tests in conditions of Fig. 3; active coating composition, mol %: (1) first layer: $\text{RuO}_2 : \text{TiO}_2 = 39 : 61$; second–sixth layers: $\text{RuO}_2 : \text{TiO}_2 = 5 : 95$; (2) all five layers: $\text{RuO}_2 : \text{TiO}_2 = 30 : 70$; $M_{\text{Ru}} = 3.9 \text{ g/m}^2$.

mation of a barrier layer with the electrical resistance required for an irreversible passivation at the coating/substrate interface. Therefore, it is possible to reactivate the anode by plating the active mass onto the coating with $M_{\text{Ru}} = 6.5 \text{ g/m}^2$ upon reaching a potential of 3.0 V at it once more [9]. This indicates that, under these conditions, at high M_{Ru} , the potential increases, most probably, due to the reversible pseudopassivation.

Figure 3 gives the results of accelerated tests of DSA whose coating containing platinum. It is seen that, when platinum is used as the sublayer, an increase in τ is not large, while the introduction of platinum into the active mass raises τ almost by two times. It is known that the introduction into the DSA coating of oxides (for example, IrO_2 [13]) whose corrosion resistance is higher than that of RuO_2 provides a higher electrocatalytic activity of the coating and ensures a virtually complete consumption of the active mass, i.e. primarily prevents the pseudopassivation. Therefore, we assume that introducing such a highly corrosion-resistant component as platinum and its oxides into the coating has a similar effect and increases τ . Platinum, when used as the sublayer in accelerated tests, where τ was short and the pseudopassivation was of primary importance in an increase in the potential, showed no protective action. Nevertheless, this fact does not exclude the possibility of hampering the true anode passivation by a corrosion-resistant sublayer during long-term anode operation under conditions where the pseudopassivation does not occur.

The experimental results presented in Fig. 4 also support the assumption that the pseudopassivation is the main reason for the premature loss of DSA activity in a chlorate electrolysis. Comparing curves 1 and 2, one can see that τ is virtually the same for anodes with a five-layer coating and the same $\text{RuO}_2 : \text{TiO}_2$ ratio of 30 : 70 or for anodes with nonuniformly applied coatings.

These results suggest that an additional protection of the coating/substrate interface by increasing the RuO_2 amount in the layers adjacent to it does not extend the anode's lifetime.

CONCLUSIONS AND RECOMMENDATIONS

The obtained results indicate that the incomplete utilization of the active mass of the DSA coating in the chlorate electrolyzing cells is due to the loss of the coating activity caused by a relative depletion of its working zone in the surface layer in RuO_2 .

In this case, the anode lifetime cannot be increased by increasing the initial amount of the active mass in the DSA coating or by the formation of highly corrosion-resistant sublayer between the substrate and the coating. The problem can be solved only by introducing into the coating a component, which enhances the corrosion resistance of the coating as compared with the DSA and eliminates the pseudopassivation, for example, IrO_2 , [13–15]. In this case, an increase in the initial amount of the active mass becomes advantageous, because it can not only extend its service life, but also makes it possible to regenerate the coating without removing the residue, thus cutting down the specific consumption of its components. This two-pronged effect can be achieved by use of anodes with a high content of a highly corrosion-resistant active mass and by using them until the coating's mass wears out to a value, which is still high enough to prevent the true anode passivation at the coating/substrate interface.

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