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# A study on corrosion and deactivation mechanism of Pt/Nb anodes in sodium chlorate containing solution using EIS

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ABSTRACT

Due to their high price, the corrosion resistance and lifetime of Pt/Nb anodes, which are usually manufactured through an electrodeposition process, in the sodium perchlorate production is important. In this research, the effect of electrodeposition parameters on the corrosion behaviour of these anodes has been studied. The samples were produced through electrodeposition of platinum on niobium at current densities, electrolyte temperatures and, finally, electrodeposition time extensions. The coated samples were then exposed to accelerated life testing in sodium chlorate containing solution at different extensions. EIS spectra of the samples were obtained in sodium chloride solution at the above-mentioned time intervals. The analysis of EIS spectra showed that the highest corrosion resistance was for the sample electrodeposited for 75 min at current density of 5 $\mathrm{mA \cdot cm^{-2}}$ and electrolyte temperature of 93 °C. The low thickness of the niobium oxide passive layer in this sample and the presence of more catalytic platinum coating are the reasons for its higher corrosion resistance compared to the samples electrodeposited under other conditions. Therefore, the passive layer of the other samples is thick and more platinum has been dissolved in the solution.

## 1. Introduction

Good electrical conductivity, excellent corrosion resistance and proper catalytic properties are the main reasons for employing platinum in manufacturing of platinum-coated niobium or titanium anodes. These anodes have high applicability in electrochemical industries, such as in the production of hypochlorates and perchlorates. In all mentioned applications, catalytic properties and long service life of the anodes are very important for users [1].

Ion plating, electrodeposition, thermal decomposition, chemical vapor deposition (CVD) and physical vapor deposition (PVD) are the main methods by which platinum can be coated on the substrate [2,3]. Of these, electrodeposition is the simplest method by which to electrodeposit platinum on the substrate, thereby rendering a coating with controlled structure obtainable [4]. Of the electrolytes available for electrodeposition of platinum, platinum tetraammine with a phosphate buffer is recommended for obtaining a thick deposit on niobium [5–7].

The properties of coatings produced by electrodeposition are a function of current density, electrolyte temperature, electrodeposition time, electrolyte type and metal concentration in the electrolyte. Studies have demonstrated that electrodeposition, even in ammine solutions, is incapable of producing a compact coating, so a porous and rough coating will be produced by this process [8].

As noted above, the electrochemical production of sodium perchlorate is one of the main applications of Pt/Nb or Pt/Ti anodes. These anodes are known as DSAs[1] in the context of the mentioned application [9].

As mentioned for mixed metal oxide (MMO) anodes which are a branch of DSA's, passivation of substrate and degradation of coating in the solution are the main reasons by which they are deactivated in industrial applications [10,11]. However no mechanism was found for deactivation of Pt/Nb anodes up to now. Salunke and his co-workers [11] believe that galvanic coupling will be created between the coating and the substrate while the solution diffuses through the crack, which tends the metal with more negative potential to dissolve in the solution. However, this cannot be correct if the Pt/Nb is polarized anodically. Therefore, a more accurate method is necessary for studying the corrosion mechanism of Pt/Nb anodes.

EIS is one of the most complete methods by which the behaviour of both the substrate and the coating can be studied. In one of studies, Yang and his co-workers utilized EIS method to study the corrosion behaviour of Pt/Ti anodes in a sodium chloride solution. Their analysis of the presence of Warburg impedance in their impedance plots concluded that the corrosion of these anodes is diffusion-controlled [12,13].

Juchniewicz described the effect of superimposed a.c. on the corrosion of anodically polarized platinum in sodium chloride solutions, using capacitance and resistance measurements to study the formation

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[1] Dimensionally stable anodes.

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and destruction of oxide films on the electrode surfaces. Increased corrosion was found when up to 30% a.c. was superimposed on d.c. The importance of reducing the a.c. component in rectified currents used in cathodic protection and electrolytic processes was shown [14].

As mentioned above, the industrial importance of Pt/Nb anodes requires a deep study of their deactivation mechanism. Deactivation of these anodes is a function of coating morphology, which itself adheres to electrodeposition parameters. Regarding the lack of information in this subject, the aim of this research is to determine the optimum current density, electrolyte temperature and electrodeposition time to obtain an anode with highest possible corrosion resistance and subsequently highest service life in chlorate-containing medium.

## 2. Materials and methods

The niobium substrates with purity of 99.07 wt% were sandblasted with $SiO_2$ particles of sizes less than 30 μm and pressure of 2.5 bars and then degreased in acetone with ultrasonic cleaning at 20 kHz for 30 min. The samples were etched using a solution containing 60 vol.% $HNO_3$ (65% purity, specific gravity of 1.4 $g\cdot cm^{-2}$) and 20 vol.% HF (48% purity, specific gravity of 1.27 $g\cdot cm^{-2}$) at 60 °C, then rinsed in distilled water. The sample then electrodeposited in platinum Q salt solution with $Pt(NH_3)_4(HPO_4)$ formula (Jhonson Matthey Co.) and with platinum concentration of 0.02 M. For decreasing the hydrogen ion concentration in the electrolyte and obtaining a low crack deposit on the substrate, the pH of the electrolyte was adjusted in 10.5 with 10 vol.% NaOH solution during the electrodeposition. Electrodeposition was carried out at current densities of 3, 5 and 8 $mA\cdot cm^{-2}$ for different electrodeposition times, by which a platinum coating with thickness of 10 μm was obtained.

To study the effect of electrolyte temperature, the electrodeposition was carried out at a current density of 5 $mA\cdot cm^{-2}$ for 75 min and temperatures of 85, 93 and 97 °C. The effect of coating thickness was also studied through the electrodeposition of platinum at a current density of 5 $mA\cdot cm^{-2}$, a temperature of 93 °C and a time extension of 35, 75 and 145 min.

The coated samples with 4.9 $cm^2$ area then were exposed to an accelerated life test (ALT) in a typical sodium perchlorate production cell with a solution containing 4.6 M sodium chlorate, 0.001 M sodium chloride and 0.01 M sodium dichromate at a temperature of 35–45 °C and pH = 6.8. A constant current density of 1.2 $A\cdot cm^{-2}$ was applied to the sample and voltage between the anode and cathode were monitored in terms of time. AISI 304 stainless steel was used as a cathode in this cell and the platinum-coated samples were utilized as an anode. The distance between the anode and cathode was adjusted by 3 cm. This test was interrupted in time intervals of 1, 10, 30 and 60 h and the sample was evaluated by the EIS method.

EIS spectra were obtained using an IVIUMSTAT instrument in a frequency range of 100 kHz to 10 mHz and a perturbation amplitude of ± 10 mV while the sample was in its open circuit potential. The EIS experiments were conducted in sodium chloride solution in which saturated calomel was used as a reference electrode and a platinum plate was used as a counter.

The impedance data was then analysed using Zview2 software. The surfaces of the samples after the ALT test were also studied using a Philips XL30 ESEM model.

## 3. Results and discussion

### *3.1. The effect of electrolyte current density*

Fig. 1 shows the results of the EIS study on the sample electrodeposited at a current density of 3 $mA\cdot cm^{-2}$ after different ALT time intervals.

As shown, two time constants are observable in the Bode phase plot of Fig. 1(b). In addition, in the Bode plot of Fig. 1, the impedance of the system had increased after 60 h of ALT. It seems that two phenomena are responsible for this rising itself which should be looked for.

The platinum coating does not cover the entire surface of the substrate, because of the cracks that may be created during electrodeposition. Therefore, in accordance with all the coated anodes which are anodically polarized, the corrosive solution, which includes oxygen and chloride ions, can diffuse through the cracks and cause a passive layer to form on the substrate or the platinum coating to dissolve into $PtCl_6^{2-}$ or both [14].

Based on the above-mentioned reactions and the number of time constants in the Nyquist and Bode plots of Fig. 1, the electrical equivalent circuit represented in Fig. 2 was proposed for the corrosion and passivation process of the sample. The shown equivalent circuit has the greatest degree of compatibility with the experimental results among the probable circuits. It reveals that we should follow the mentioned guessed deactivation mechanism.

$R_s$ in this figure is uncompensated resistance between the working and reference electrode, $C_{dl}$ is the capacitance in the electrical double layer at the interface of the platinum coating and the solution, $R_{ct}$ is charge transfer resistance at the interface of the platinum coating and the solution, $C_f$ is the capacitance of films on the substrate and $R_f$ is the resistance of the mentioned film. It is notable the noted film can be composed of platinum coating and the passive film both. However, refer to low electrical resistance of platinum compared to the resistance of $Nb_2O_5$ passive film [15], the resistance of platinum layer can be neglected. Therefore $R_f$ is the sum of passive film and platinum layer resistances.

A squeezed semicircle in the Nyquist plot indicates a quasi capacitive behaviour in the system. This is because the surface has been sandblasted before electrodeposition. Therefore, CPE should be used instead of capacitance in equivalent electrical circuits of the system. The impedance of CPE is calculated in accordance with Eq. (1), in which n is the power of the constant phase element and identifies the physical significance of surface [12,16].

$$Z_{CPE} = \frac{1}{CPE(j\omega)^n} \quad (1)$$

The results of EIS study on the corrosion behaviour of the samples electrodeposited at current densities of 5 and 8 $mA\cdot cm^{-2}$ after 60 h ALT has been presented in Fig. 3. The same equivalent circuit shown in Fig. 2 was recognized as suitable for the analysis of impedance data in this figure.

Fig. 4 shows the variations of $R_{ct}$, $CPE_{dl}$, $R_f$ and $C_f$ with electrolysis time at different time intervals for the coatings electrodeposited in current densities of 3, 5 and 8 $mA\cdot cm^{-2}$. These data have been resulted of analysis of EIS spectra in Figs. 1 and 3.

It can be seen in this figure that $R_f$ in the sample electrodeposited at a current density of 5 $mA\cdot cm^{-2}$ is less than that of the other samples; however, $C_f$ in this sample is greater compared with the other samples. SEM micrographs from the samples shown in Fig. 5 show that the coating on the surface of the sample electrodeposited in current density of 5 $mA\cdot cm^{-2}$ has fewer cracks compared with the other samples. In other words, the oxygen has few ways to reach the substrate in this sample. Therefore, low magnitude of $R_f$ and high magnitude of $C_f$ in this sample implicates low thickness of the passive layer ($Nb_2O_5$) on the substrate. This layer grows by increasing the accelerated life testing time; however, the compact layer of the coating produced by electrodeposition at current density of 5 $mA\cdot cm^{-2}$ reduces the growth rate of the passive layer, which tends to cause $R_f$ and $C_f$ to vary with a low slope.

Higher magnitude of $CPE_{dl}$ and reduced magnitude of $R_{ct}$ for the sample electrodeposited at a current density of 5 $mA\cdot cm^{-2}$ is also