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Anodes Based on Platinized Ebonex®

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Ceramic materials consisting of Magneli phases (titanium "sub-oxides" and having the generic formula Ti_nO_{2n-1}, where n=4–10), have been commercially recognized under the Ebonex® trade name (1-3), they exhibit high conductivity, good service life (1) and electrochemical stability in a wide potential range (2). Nevertheless, application of Ebonex® as anode material is limited due to high potential values even under low current densities. Owing to this, Magneli phases materials are more commonly used as substrates for active electrocatalytic layer (3-5) among which platinum and other noble metals are often the preferred choice since they exhibit unique catalytic activity. It is generally established that deposition of a thin platinum layer on Ebonex® results in a conspicuous gain in electrocatalytic activity and decrease in potential value (2,5). In this case thermal treatment in the air can become an opportunity to vary electrocatalytic activity.

In this work we have examined the effects of amount of electrodeposited Pt and thermal treatment of platinized Ebonex® electrodes on their electrocatalytic activity and semiconducting properties.

Ebonex®/Pt-electrodes were prepared according to (4). Some of them were thermally treated in the air using tube furnace at 230, 310 or 410ºC for 1 hour.

It is known that Ebonex® shows significant charging current as a result of porosity and is characterized by high polarizability, with low activity towards reactions of oxygen/hydrogen evolution except at relatively high potentials (4,6). Electrodeposition of Pt on Ebonex® results in polarizability decrease and increase in electrocatalytic activity of electrode. Cyclic voltammogram of platinized Ebonex®-electrode is similar to one obtained for Pt. The cathodic branch of the curve shows the typical peak of platinum oxides reduction that characterizes the amount of electrochemically active platinum on the electrode surface and could be correlated with electrocatalytic activity of thermally treated Ebonex®/Pt-electrodes (4,6).

As one can see from Fig., oxygen overpotential depends on amount of electrodeposited Pt and temperature of electrode treatment. In general, increase in treatment temperature leads to increase in oxygen overpotential due to thermal diffusion of electrocatalyst (Pt) deep into substrate.

In all cases, E-log(i) curves are linear and characterized by high slope (>0.275 V). This denotes an increased semiconductive component or porosity effects. Impedance measurements were then carried out in order to investigate the semiconducting properties of Pt/Ebonex® electrodes. Solution of 1 M $HClO_4$ was used for impedance measurements to eliminate effects of adsorption. The data recorded at a frequency of 5 Hz obey Mott-Schottky relationship in wide range of potentials that denotes the semiconducting properties of investigated electrodes. Investigated materials behave as highly doped n-type semiconductors since positive slope of the C^{-2} – E plot was observed. Anodic polarization of Ebonex®/Pt above flatband potential leads to carrier depletion, decrease in electrode capacitance and increase in slope of polarization curve represented in semilogarithmic scale.

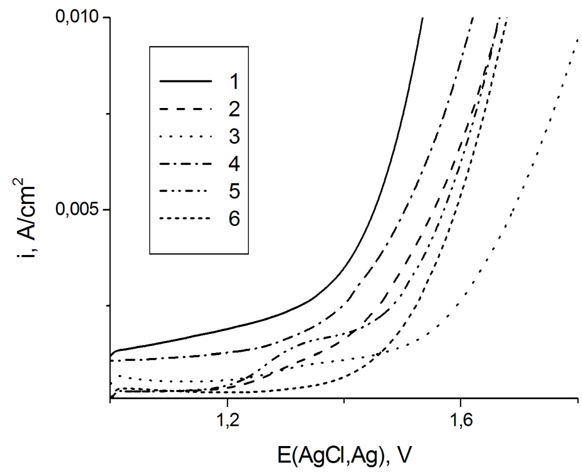

Fig. Polarization curves (5 mV/s) in 1 M $HClO_4$ for Ebonex®/Pt-anodes, obtained without thermal treatment (1,4) and thermally treated at 310 (2,5) or 410^{0}C (3,6). Amount of Pt, mg/cm^2 – 8 (1-3), 2 (4-6).

We observed an increase of the flatband potential (Table) with thermal treatment temperature, and the donor concentration decreases induced both oxidation of Pt with phase oxides formation and TiO_2 formation that leads, as a result, to reduction of free electrons number. We observed unusual behavior of electrode treated at 310°C (Table) assumed to formation of new phase Ti-O according to XRD data.

Table . Electrochemical and semiconductor properties of Ebonex®/Pt-electrodes

Amount of Pt (mg/cm^2); treatment temperature (^{0}C) of Ebonex®/Pt-electrodes	**Slopes of polarization curves in semiloga-rithmic scale**	**Flatband potentials and donor concentrations calculated from Mott-Schottky plot**	
	b, V	E_{FB}, V	N×10^{-23}, cm^{-3}
2; 25	0.381	0.550	74.0
2; 310	0.314	0.833	9.0
2; 410	0.222	0.843	1.7
8; 25	0.294	0.465	100
8; 310	0.389	0.439	6.3
8; 410	0.425	0.666	0.027

The temperature of treatment significantly affects the catalytic activity of platinized Ebonex® electrodes through surface morphology, chemical composition and semiconductor properties, i.e., shift of flatband potential to positive values and decrease in donor concentration. An increase in treatment temperature leads to rearrangement of the Pt overlayer by thermal surface diffusion (310°C) and deeper into pores of the substrate at still higher temperature (410°C).

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