STUDY OF THE ELECTRODE'S SURFACES COATED RARE EARTH OXIDES

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Abstract

Rare earth elements are widely used in metallurgy for alloying. It is known that small admixtures of these elements give unique properties to alloys. Rare earth oxides are used, for example, in optics or in solid-oxide fuel cells. In this work, the properties of electrodes based on oxides of titanium, ruthenium and rare earth oxides are investigated. The effect of organic additives on the surface properties of the electrode has also been studied. In the sample with butanol, the current density in the sodium chloride solution is almost 10 times higher than that of the electrodes without butanol. For the samples that showed the best results in electrochemical tests, the surface morphology was explored. The surface microphotographs demonstrate the cracks and the inclusions of rare earth oxides.

Keywords: Rare earth oxide, electrocatalytic activity, surface morphology, roughness

1. INTRODUCTION

Rare earth oxides are increasingly used in various high-tech industries: catalysis, optics, high-energy magnets, glass industry, etc. [1,2].

In the world research works are carried out with the purpose of the oxides using as doping additives in the electrodes, at that cerium is used more frequent [3-8]. These oxide compositions often include precious metal oxides such as ruthenium dioxide or iridium dioxide [4-6].

In this paper, we study changes of the electrochemical and physico-mechanical properties of a mixture of RuO_2, TiO_2, La_2O_3, Ce_2O_3, Nd_2O_3 obtained on titanium plates by thermal method, depending on the adding in the precursor of organic additives for modifying electrode surface morphology.

2. EXPERIMENTAL SECTION

Used reagents in the preparation of the electrodes and the electrochemical experiment: $RuCl_3$, H_2IrCl_6, $TiCl_4$, rare earth carbonates, n-butanol (BuOH), polyethyleneglycol (PEG), NaCl, Na_2SO_4, H_2O.

2.1. Synthesis of the oxides

The oxide composition of RuO_2, TiO_2, Ce_2O_3, La_2O_3 and Nd_2O_3 have been synthesized by thermochemical method. Salts $RuCl_3$ (TU 2625-050-00205067-2004), H_2IrCl_6 (TU 2625-030-57979587-2005), $TiCl_4$ (CAS # 7550-45-0), rare earth carbonates have been mixed in the desired ratio and then added BuOH (GOST 6006-78) or PEG (CAS # 25322-68-3). The resulting mixture was applied to a pre-prepared titanium substrate of the grade VT-1-00, thereafter it was poured into electric furnace at 350-450 °C for 30 minutes. The calcination operation was repeated until the desired coating thickness.

2.2. Physical and physicochemical characterization

Measurements of surface morphology were performed using scanning electron microscope (SEM) JEOL 1610LV with energy dispersive spectrometer for electron-probe microanalysis SSD X-Max Inca Energy (JEOL, Japan; Oxford Instruments, Great Britain) in D. I. Mendeleev CKP.

The 3D surface profile image is obtained on the laser scanning microscope OLYMPUS LEXT OLS4100 (OLYMPUS Corporation, Japan).

2.3. Electrochemical measurements

Electrochemical measurements (voltammetry) were performed in three-electrode electrochemical cell by using a Potentiostat-galvanostat P-20 X (Elins, Russia). The reference electrode was saturated Ag/AgCl, KCl, and counter electrode was Pt wire. All the results obtained are calculated relative to the reversible hydrogen electrode.

3. RESULTS AND DISCUSSION

For the prepared samples, the electrochemical characteristics were first measured. The comparison of the current density of the samples doped rare earth oxides with an industrial model of the DSA (Dimensionally Stable Anodes) are presented in **Table 1**. According to the obtained data, it is clear that in the presence of rare earth oxides in active layer of the electrode surface, regardless of the organic additive, current density of oxygen evolution in the Na_2SO_4 solution decrease. When butanol and polyethyleneglycol are added current, density reduces by two times, while for samples without additives it decreases almost by six times. In the NaCl solution, there is a current density increase by about 2.9 times in the presence of the butanol, and by 1.3 times with polyethyleneglycol. For a non-organic sample, the current density decreased to 1.1 $mA \cdot cm^{-2}$ versus 3.5 $mA \cdot cm^{-2}$ for an industrial type sample (DSA).

Table 1 Values of the current density in NaCl and Na_2SO_4 solutions

Organic additive	*i* at 1.4 V in NaCl ($mA \cdot cm^{-2}$)	*i* at 1.4 V in Na_2SO_4 ($mA \cdot cm^{-2}$)
BuOH	10.0	1.1
PEG	4.4	1.2
-	1.1	0.3
- (DSA)	3.5	2.0

It can be concluded that RuO_2, TiO_2, Ce_2O_3, La_2O_3, Nd_2O_3 composition electrodes prepared in the presence of butanol and polyethyleneglycol show an increase in the current density in the sodium chloride solution. In sodium sulfate solution, the samples have a lower electrocatalytic activity that samples of industrial type.

4. SURFACE MORPHOLOGY

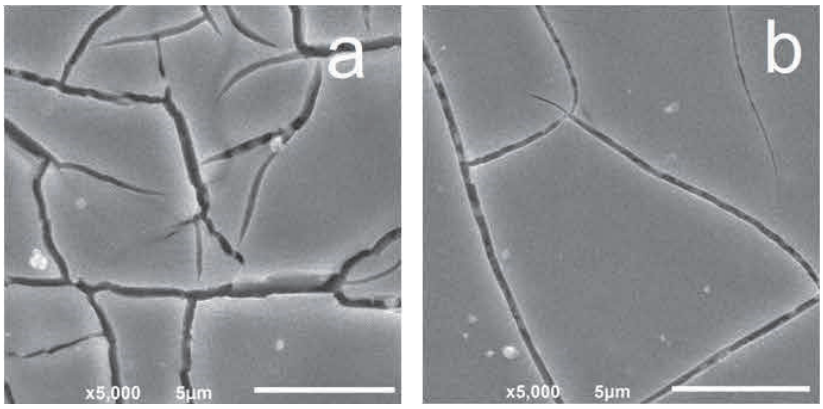

Figure 1 SEM-image of the surface of Ti/TiO_2+RuO_2+Ce_2O_3+La_2O_3+Nd_2O_3 samples, zoom x5000: (a) with butanol; (b) non-organic

Figure 1 demonstrates SEM-images of surface of the samples with butanol and without one including titanium, ruthenium, cerium, lanthanum and neodymium oxides that cover titanium plates.

Butanol and polyethyleneglycol were added to increase the surface of the metal oxide electrode due to loosening effect on the coating during thermochemical synthesis. For a sample with the addition of butanol, a multiple increase in the number of microcracks can be observed. They are deeper and wider as compared to the sample without the organic additive. This change in morphology can significantly increase the surface of the electrode.

Figure 2 shows a three-dimensional visualization of the surface of the studied anode materials for three samples: without an organic component, with butanol and polyethylenglycol. 3D-images of the surface of the oxide coating with and without butanol are comparable to each other. Both samples have peaks, cracks and stalagmite growths, but for the sample with butanol number of them is significantly more. The sample containing polyethylenglycol has a similar morphology in the practically absence of the stalagmitic growths.

Thus, it can be seen that the oxide coating with PEG also has a sufficiently developed surface structure.

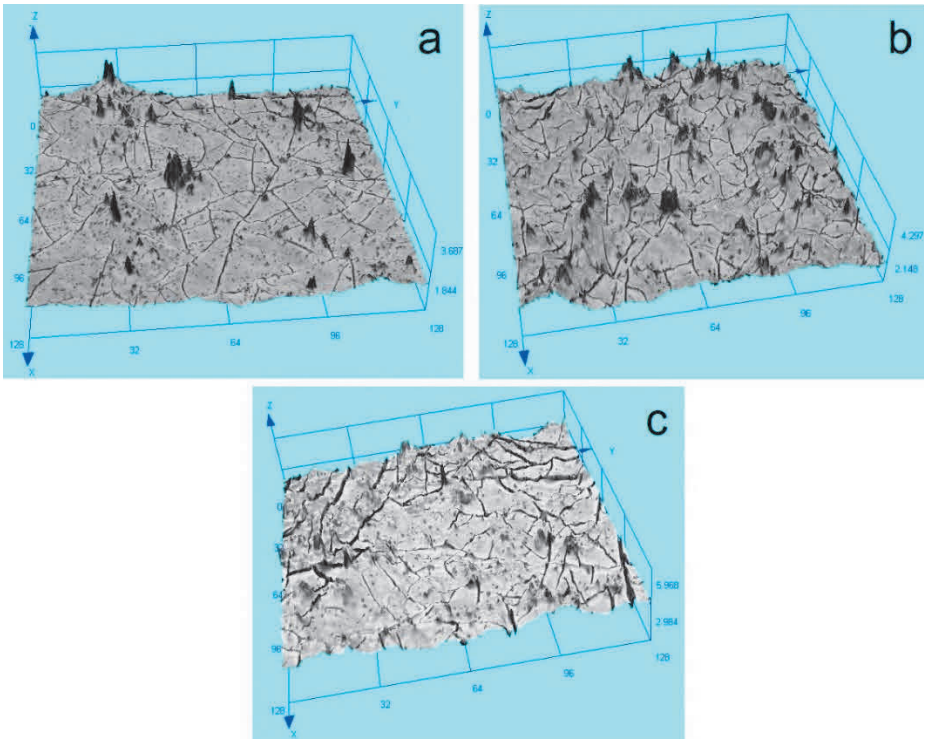

Figure 2 3D surface visualization of Ti/TiO_2+RuO_2+Ce_2O_3+La_2O_3+Nd_2O_3 electrodes: (a) non-organic; (b) with butanol; (c) with polyethylenglycol

The device software OLYMPUS LEXT OLS4100 allows to determine the roughness by ISO 4287 including such parameters as the height of the hill - Rz, the arithmetic average roughness - Ra. **Table 2** presents the values of these quantities for the test specimens.

Table 2 Indicators of roughness

Organic additive	Rz (μm)	Ra (μm)
-	1.505	0.199
BuOH	2.985	0.334
PEG	3.034	0.319

Note: the average values of the parameters from the five dimensions are given.

According to the obtained data, roughness is higher of samples with organic additives. This fact agrees with the data of surface morphology of SEM and 3D visualization (**Figures 1 - 2**) and the results of electrochemical experiment.

5. CONCLUSION

Summing up the obtained results, it can be concluded that the addition of organic components (butanol, polyethyleneglycol) in the precursor solution used for the thermochemical synthesis of RuO_2-TiO_2-Ce_2O_3-La_2O_3-Nd_2O_3 increases the roughness of the oxide coating. Samples with butanol and polyethyleneglycol have a greater electrocatalytic activity in the chloride system than without organic additives electrodes and a sample of industrial type due to the developed surface.

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