

SnO₂-F Based Electrode Material for Synthesis of Sodium Hypochlorite Solutions

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Abstract – Kinetics of galvanostatic formation of hypochlorite-ions on the Pt and FTO surface can indicate the similar character, surface concentration, and the energy of adsorbed radical-type particles. FTO coating shows high electrocatalytic activity towards the synthesis of sodium hypochlorite during the electrolysis of dilute NaCl solutions.

Key words – sodium hypochlorite, electrolysis, FTO

I. Introduction

Noble metal oxides (RuO₂ and IrO₂) have attracted intensive attention due to their metallic conductivity, excellent electrochemical activity, and good stability in aggressive aqueous solutions [1,2]. These oxides have now been used as anodic materials, i.e. so-called dimensionally stable anode (DSA[®]), in a variety of electrochemical applications, including water electrolysis, chlor-alkali production, metal electrowinning, organic synthesis, and in waste water treatment, etc.

Ruthenium based DSA has acquired an excellent reputation for the electrolysis of concentrated NaCl solutions.

During the electrolysis of dilute NaCl solutions, degradation of the electrode material occurs. RuO₂ is corrosion resistant, but it is not stable enough for long term oxygen evolution [3]. Oxidation to Ru(VIII) is believed to be part of the reaction mechanism of oxygen evolution on ruthenium [4,5]

At the present time the development of new electrode materials for the synthesis of dilute sodium hypochlorite solutions for human and veterinary medicine by the electrolysis of NaCl solution (9-27 g/liter) is of substantial interest.

The objective of this work is to verify the possibility of application of fluorine doped tin dioxide (FTO) as the anode material for the electrolysis of weak NaCl solutions and oxygen evolution, as well as to study the activity of electrodes consisting of PbO₂ nanoparticles dispersed on the surface of FTO.

II. Sodium hypochlorite generation

Micromodification of FTO surface with lead dioxide leads to the decrease of oxygen evolution overpotential by 500 mV in 0.5 M MSA (shown in Fig. 1). However, in the presence of 0.15 M NaCl, the polarization of FTO modified with lead dioxide decreases only by 50-100 mV, and for non-modified FTO it decreases almost by 400 mV (Fig. 2). It denotes more substantial catalytic activity of FTO coating towards the process of chloride-ions oxidation as compared with the reaction of oxygen evolution. It makes this electrode material promising for the electrolysis of solutions containing chloride-ions.

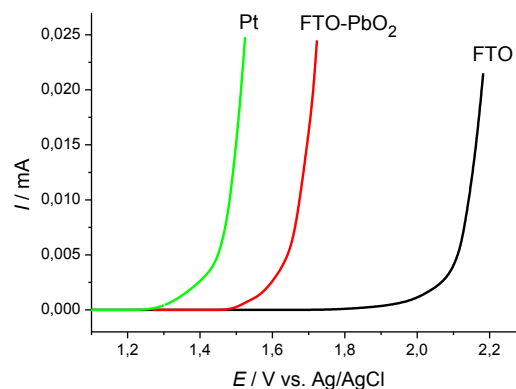


Fig. 1. Voltammograms of oxygen evolution on Pt (0.4 cm²) and on a sample with FTO and FTO-PbO₂ coating (0.4 cm²) in 0.5 M MSA; $v=10$ mV s⁻¹

The influence of micromodification of FTO surface with lead dioxide on electrocatalytic activity was shown on the example of electrolysis of dilute NaCl solution. Voltammograms obtained on the modified and unmodified FTO coating in 0.15 M (0.89%) NaCl solution are given in Fig. 2. Presence of lead dioxide nanoparticles on the FTO surface considerably improves electrocatalytic activity of the deposit towards chloride-ions discharge, although this effect is less pronounced as compared with the influence of modification on the oxygen evolution reaction (Fig. 1).

It is interesting to compare the character of voltammograms which reflect total processes of oxygen evolution and chloride-ions oxidation (shown in Fig. 2) with partial data obtained from the electrolysis of NaCl solution under galvanostatic conditions. For the comparison, we took Pt and FTO electrodes, the platinized titanium anode (Ti-Pt) which was prepared as described in [6], as well as FTO electrodes modified with lead dioxide which i) was deposited by the method of cyclic potential scanning, as it was described above (hereafter this coating is called FTO-PbO₂ (1), and ii) was deposited under galvanostatic conditions (4 mA/cm²) from 0.1 M MSA + 0.01 M Pb(MS)₂ solution during 200 sec (hereafter this coating is called FTO-PbO₂ (2)). The electrolysis of 0.15 M NaCl solution in a cell without a separator was carried out for 20 min at anodic current density of 10 mA cm⁻². Electrolyte volume was 100 cm³, 4 cm² cathode, FTO, FTO-PbO₂, Pt and Ti-Pt anodes surface area was 1,6 cm² each. Electrolysis data are given in Table 1.

Higher CE of oxygen on platinized titanium anode (Ti-Pt) in comparison with metal platinum can be explained by larger true surface and, as a result, lower true current density. FTO samples, modified with lead dioxide in two ways, showed close catalytic activity towards the synthesis of sodium hypochlorite and chlorite.

As follows from the analysis of figure 2 and table 1, Pt and FTO electrodes, having considerably different overpotential of oxygen evolution, showed similar catalytic activity towards synthesis of hypochlorite. The main processes, occurring under these conditions, are oxygen evolution and chloride-ions oxidation. According

THE CONCENTRATION OF SODIUM HYPOCHLORITE AND SODIUM CHLORATE, THEIR CURRENT EFFICIENCY AND ANODIC POTENTIALS AFTER 15min ELECTROLYSIS OF 0.15 M NaCl SOLUTION; ANODIC CURRENT DENSITY IS 10 mA cm^{-2}

| Anode (1.6 cm^2) | C(NaClO), mg/l | C(NaClO ₃), mg/l | CE(NaClO), % | CE(NaClO ₃), % | CE(O ₂), % | pH |
|---------------------------------|-------------------|---------------------------------|-----------------|-------------------------------|---------------------------|-----|
| Pt | 43.6 | 1.9 | 59 | 5 | 36 | 7.7 |
| FTO | 42.2 | 3.4 | 58 | 10 | 32 | 7.6 |
| FTO-PbO ₂ (1) | 28.8 | 3.4 | 39 | 10 | 51 | 7.5 |
| FTO-PbO ₂ (2) | 28.6 | 4.1 | 39 | 12 | 49 | 7.6 |
| Ti-Pt | 28.5 | 2.1 | 39 | 6 | 55 | 7.1 |

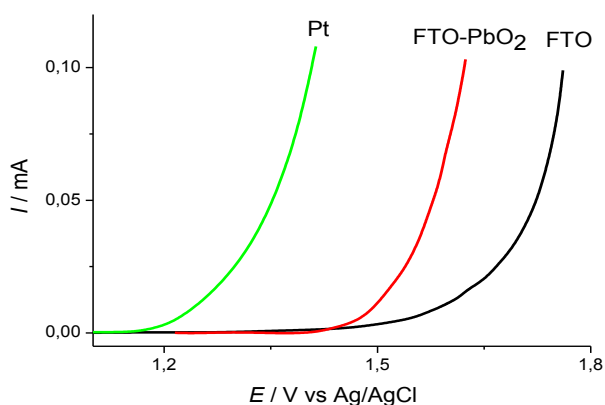
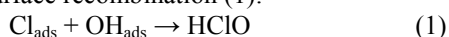
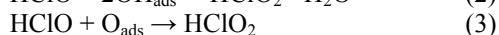


Fig. 2. Voltammograms on Pt (0.4 cm^2) and FTO-coating (0.4 cm^2), modified and unmodified with lead dioxide, in 0.15 M NaCl ; $v = 10 \text{ mV s}^{-1}$

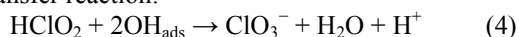
to the general opinion [1,2,7], in the region of high anodic potentials the processes of anodic oxidation run through the formation of radical-type particles like OH_{ads} , O_{ads} and Cl_{ads} which are adsorbed on an electrode. These particles can take part in the formation of oxygen-containing chlorine compounds. One of the most probable reactions is formation of hypochlorous acid according to the mechanism of surface recombination (1):



Accumulation of ClO_3^- ions as impurity in the solution most probably occurs through the formation of chlorous acid:



The following transformation of chlorous acid into chlorate is a fast stage. This stage can be written as an oxygen transfer reaction:



As a result of fast reactions (4) at high anodic polarization, chlorous acid does not have time to desorb from the electrode surface and turns fast into chlorate. Thus, we do not discover accumulation of chlorous acid and chlorite-ions in the solution during the electrolysis. In any case, accumulation of chlorate in the solution starts from the beginning of the electrolysis and its amount grows proportionally to time. It proves the supposition about common mechanism of chlorate and hypochlorite

formation through the radical-type particles which form on the surface and are adsorbed. Similar kinetics of hypochlorite-ions formation under galvanostatic conditions on the Pt and FTO surface indicates the similar character, surface concentration, and energy of the adsorbed radical-type particles.

Conclusion

FTO coating has shown high electrocatalytic activity towards sodium hypochlorite synthesis during the electrolysis of dilute NaCl solutions. This electrode material can be used in water disinfection systems, for the synthesis of disinfectant solutions, as well as for the production of sodium hypochlorite solutions for human and veterinary medicine.

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