

ANODIC BEHAVIOUR OF THE Co_3O_4 – TiO_2 ACTIVE LAYERS

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Abstract

The Co_3O_4 films deposited onto titanium base by thermal decomposition technique, are known to have high selectivity with regard to chlorine release. However, because of Co_3O_4 film high wear, no industrial anodes could be obtained.

We have proposed the anode active layer that contains the mixture of Co_3O_4 (25% mol.) and TiO_2 (75% mol.) oxides. Active layer was deposited onto the titanium base by thermal decomposition of cobalt and titanium salt solution/ [Anode agent effect on electrochemical synthesis of sodium hypochlorite solutions. Gorbachev A.K., Brovin A.Yu., Tulskey G.G., Vaulin E.N. In: Voprosy khimii i khimicheskoi tekhnologii. Dnepropetrovsk, UGKhTU, 2003, No. 1, p. 112-116].

To study chlorine release and ionization on oxide cobalt-titanium active layer, the potentiostatic voltammetry technique was used. The commutation technique was used for recording and elimination of anode potential ohmic constituent. To realize reversible chlorine electrode, electrolyte was saturated with chlorine gas. The measurements were conducted in 0.1 – 5 M NaCl + 0 – 1 M Na_2SO_4 solutions, with pH = 2 and 0/075–1 atm. dissolved chlorine pressure.

The clearly pronounced Tafel zones are the most typical feature of anode polarization curves. With small chloride concentrations (0.1...0.2 M) the polarization curve slopes amounted to 70...73 mB. When C_{NaCl} rises to 0.5 M and above, Tafel slopes of 62 ± 3 mB have been obtained, close to the theoretical value of $2.3RT/F$.

The results obtained witness that with $E = \text{const}$ the anode process of chlorine release accelerates with chloride concentration growth, whereas the cathode one – its reduction – decelerates.

In small-chloride-concentration area (up to 1 M) the anode reaction was 0.75...0.8; with concentration increase up to 4.3M, the value dropped down to 0.4...0.5. The cathode reaction order also changed by chloride concentration rise: from – 0.3...– 0.35 with $C_{\text{NaCl}} = 0.2...0.6$ M to – 0.6...– 0.65 with $C_{\text{NaCl}} > 1$ M.

The reaction orders obtained could be distorted by some side effects, the most significant one being chloride specific adsorption on the active layer spinel phase surface.

The refinement of chlorine reaction orders was made in the presence of SO_4^{2-} anion,

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which displaces chloride ion from spinel surface by its adsorption, and virtually completely suppresses Cl^- -specific adsorption.

The Cl^- anode reaction order on sulfate background equaled to 0.85 – 0.95, i.e. close to 1. The cathode reaction order in Na_2SO_4 background solutions was within – 0.75...– 0.85.

Polarization curves of chlorine release and ionization have been obtained for various chlorine molecule pressures in the solutions of 3.16 M NaCl concentration and pH = 2. The chlorine molecule pressure in the solution was changed by the chlorine-saturated air blow through the electrolyte. The chlorine pressure value was determined from the changes in the potential of equilibrium chlorine electrode.

With $E_a = 1.430$ V, anode reaction order is equal to – 0.15, thus witnessing the anode reaction deceleration with increased chlorine molecule pressure in the solution. By cathode reaction of chlorine ionization, the increase in Cl_2 pressure accelerates the effect. The cathode process order for $P_{\text{Cl}_2}^- = 0.8...0.9$.

Cathode and anode branches of the polarization curve are extrapolated to the same exchange current, both by chlorine pressure change and by chloride concentration change. Hence, it can be inferred that the reaction occurs by the unique route with one slow stage that coincides in anode and cathode directions.

Analysis of kinetic data, Cl^- and Cl_2 reaction orders allow to assume that a two-stage mechanism of chlorine discharge and ionization is realized on the proposed $\text{Co}_3\text{O}_4\text{--TiO}_2$ coatings such as discharge – electrochemical desorption. For the cathode process the proposed mechanism is electrochemical adsorption – recombination.

The anodes with proposed $\text{Co}_3\text{O}_4\text{--TiO}_2$ active layer have been tested in sodium hypochloride electrical synthesis. In NaCl starting solutions, with the concentration of above 100 g/l, η NaClO current yield on the proposed anodes compared favorably with ORTA (oxide ruthenium titanium anode), and by the concentrations of below 50 g/l, NaCl even exceeded the results obtained for the ORTA/ The anode coating wear was 1.5-1.8 g/A·h.

The studies conducted have demonstrated high activity of the proposed anode with oxide cobalt-titanium active layer by chloride solution electrolysis within the broad scope of NaCl concentrations.