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INFLUENCE OF THE SUPORT TYPE ON THE ELECTROCATALYTIC PROPERTIES OF THIN VACUUM DEPOSITED FILMS OF COBALT OXIDES

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Cobalt oxides, obtain by vacuum co-evaporation of Co and TeO_2 has been investigated as electrocatalysts for oxygen evolution and reduction reactions in alkaline media. Two types of bifunctional gas-diffusion oxygen electrodes (GDE) are prepared by direct deposition of catalytic oxide films on supports of teflonized carbon blacks or Ebonex (titanium sub-oxides). The influence of the nature of the support on the surface morphology and electrochemical behavior of the films are followed by scanning electron microscopy (SEM) and cyclic voltammetry. It has been found, that the films on Ebonex electrodes have significantly higher number of active sites participating in the surface redox reactions, than those on the carbon electrodes.

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1. Introduction

The search for highly efficient bifunctional oxygen elelctrocatalysts still remains an attractive area of investigation, because of their possible application in oxygen-evolving and reducing gas-diffusion electrodes (GDE) for metal/air and metal hydride/air rechargeable batteries and regenerative fuel cells [1, 2].

The cobalt oxides have shown promising properties as electrocatalysts for oxygen evolution [1, 3, 4] and reduction [1, 5] reactions. It is well known that the electrocatalytic properties of the metal oxides vary according to their method of preparation [6]. We have used a new method [7-9] for preparing cobalt oxides films by vacuum co-deposition of Co and TeO_2 onto substrate held at room temperature. It has been found that the chemical reaction takes place between them, resulting in the formation of CoO and of elemental Te phases [7, 9]. The X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) studies have shown that the reaction proceeds until the complete oxidation of Co to Co^{2+} in the films with atomic ratio $R_{Co/Te} <2$ and until the complete reduction of TeO_2 to elemental Te in the films with $R_{Co/Te} >2$ [7, 9].

It is well known the importance of catalyst support for the oxygen electrodes. Typically, the support should provide good electronic conductivity, proper physical surface necessary for achieving high surface area as well as porous structure. It should be also hydrophobic to allow gas diffusion from the gas side to the reaction surface sites through the pores. The most often used material for the support is a mixture of Teflon and carbon blacks [10, 11]. The carbon material has good electronic conductivity and provides a suitable porous structure with high accessible surface area, but it is not stable enough during oxygen evolving process.

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Our previous studies of GDEs obtained by direct deposition of the catalytic films on teflonized carbon blacks supports have shown that the films with atomic ratio $R_{Co/Te}$ =1.4 - 1.8 exhibit high catalytic activity toward oxygen evolution reactions in alkaline solution even at very small loading of about 0.05 – 0.5 mg cm^{-2} [12]. GDEs obtained with these atomic ratios Co/Te have also shown good catalytic activity with respect to oxygen reduction reaction, although the catalytic activity of the film itself was difficult to be estimated precisely due to the high activity and low reproducibility of the carbon support [12].

In order to eliminate the disadvantages of the carbon support we have replaced carbon blacks with Ebonex. Conductive oxide supports, particularly reduced titanium oxides have been used in electrolyzers and are important candidates for use in the oxygen electrodes of URFCs [13]. Ebonex (Altraverda Ltd., U.K.) is an electrically conductive ceramic consisting of several suboxides of tanium dioxide, mainly Ti_4O_7 and Ti_5O_9, which are the most conductive compounds in homologous series of structures with general formula Ti_nO_{2n-1} ($4 \leq n \leq 10$), collectively known as Magneli phases [13]. Ebonex has a unique combination of high conductivity ($\sigma \approx 10^3\ \Omega^{-1}cm^{-1}$), good corrosion resistance and it is electrochemically stable in both acidic and alkaline solutions [13]. Moreover using titanium suboxides as a support we could expect to modulate the properties of the active layer in a way to reach a hypo-hyper-d-electronic structures leading to synergetic catalytic effect [14].

In this paper we have studied the influence of the carbon blacks and Ebonex supports on the morphology and electrocatalytic properties of the cobalt oxide films deposited by the above-mentioned method.

2. Experimental

The films with various thicknesses were prepared by co-deposition of TeO_2 and Co on stationery substrates under vacuum better than 10^{-4} Pa. The evaporation of TeO_2 was carried out from Knudsen type platinum cell and that of Co - by an electron gun. The condensation rates of each substance within the range 0.02 - 0.04 μg cm^{-2} s^{-1} were controlled separately during the evaporation using quartz crystal monitors. The amount of the both substances as well as the atomic ratio $R_{Co/Te}$ at each point of the substrate were calculated from the crystal monitors data [15]. The atomic ratio $R_{Co/Te}$ was controlled by energy dispersive spectroscopy (EDS) in scanning electron microscope (JEOL, System 5000 – HNU).

Two types of supports were studied - the first one consists of hydrophobized carbon (45% Teflon and 55% acetylene carbon blacks) and the second one is a sandwich system made by two layers: hydrophobized carbon blacks/ hydrophobized Ebonex (20%Teflon +80% Ebonex -300 μm powder, Atraverda Ltd.). Both supports were hot pressed on Ni-screen which plays role of a current collector. The system of the film deposited on support represents the gas-diffusion electrode (GDE). The effective loading of the catalytic film was in the range 0.05 to 0.25 mg cm^{-2} of geometric surface, which corresponds to a nominal film thickness of about 100 to 500nm.

Scanning electron microscopy was applied for the characterization the surface morphology of the films.

The electrochemical study was carried out by means of cyclic voltammetry. The GDE were tested in a three-electrode cell at room temperature. The electrolyte was 20% KOH, prepared with twice distilled water. High surface area platinum wire was used as a counter electrode. All the potential was referred to Hg/HgO reference electrode in 20% KOH, reaching close to test electrode by a Luggin capillary. The system was carefully deareated by supplying Ar through the membrane and bubbled it in the electrolyte before measurements.

3. Results and discussion

SEM micrographs in Fig. 1 (a-d). illustrate the surface morphology of the carbon and Ebonex supports and of the catalytic films deposited on them. It is seen from Fig. 1a and 1c that the Ebonex surface is rougher with larger ceramic particles and pores than that of carbon due to the greater particle size of Ebonex powder used. One very rough film surface following the rough surface of the substrates is also seen for the as-deposited films deposited on the both supports. In both cases “wires” with different diameters are formed, which leads to one very large surface area. The results obtained show that the surface morphology illustrated in Fig. 1b and 1d is typical for the films deposited on both supports, independently of the their thickness, atomic ratio $R_{Co/Te}$ and the thermal treatment. The only finding was an increase in the mean “wire” diameter with increasing film thickness. The EDS analysis indicates that $R_{Co/Te}$ of the “wires” and of the rest of the film is almost the same. TEM analysis of films on carbon substrates, carried out in our previous work [16] has shown that the “wires” consist of amorphous matrix with nanosized crystals of hexagonal CoO phase embedded in it.

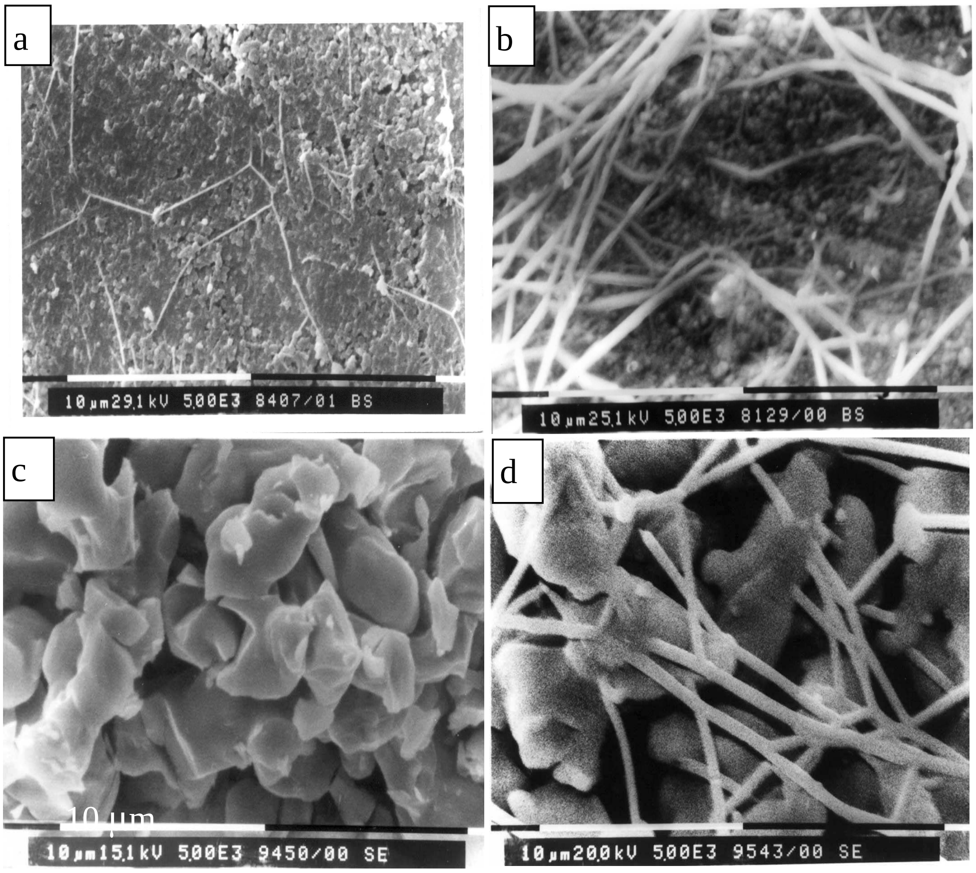

Fig. 1. SEM micrographs of: (a) bare carbon support; (b) a film with $R_{Co/Te}$=1.5 and loading of 0.2 mg cm^{-1} deposited on carbon support; (c) bare Ebonex support; (d) a film with $R_{Co/Te}$=1.5 and loading of 0.2 mg cm^{-1} deposited on Ebonex support.

The electrochemical behavior of the films deposited on carbon and Ebonex support has been studied by cyclic voltammetry. The resulting curve exhibits characteristics peaks at the redox potential, indicating the different oxidation states of the metal ion. Cyclic voltamograms of GDEs are given in Fig. 2a. The electrodes have the optimum atomic ratio $R_{Co/Te}$=1.5 and the catalyst loading of 0.2 mg cm^{-2}. For comparison in Fig. 2b the CV curves of bare carbon and Ebonex electrodes without catalytic films are also given. It is seen that they have not contribution for the peaks observed on the electrode’s CVs.

Two pairs of very broad peaks prior to the oxygen evolution are observed for the films deposited on carbon blacks. The pairs can be associated with formation of a redox couples CoO/CoO_2 (+ 195 mV vs. Hg/HgO according the calculated electrode potentials by Bell et al [17]) and $CoOOH/CoO_2$ (+562 mV vs. Hg/HgO [17]) on the surface. The detailed analysis shows, that for the films on Ebonex the positions of these peaks are slightly shifted to less positive potential values, which is not very well seen in the figure because of the peaks broadness. It should be noted that the

Ebonex electrodes show several pairs of peaks in the negative potential region (at -650, - 270, and -100 mV) which are not observed on the curves of the oxide films, deposited on carbon blacks. These peaks can be associated with redox transitions between Co^{2+}/Co^{3+} and Co/Co^{2+} [17]. The CV curves of the Ebonex electrodes show also relatively well defined oxidation peak at +87 mV which most probably can be also connected with Co^{2+}/Co^{3+} transition [17].

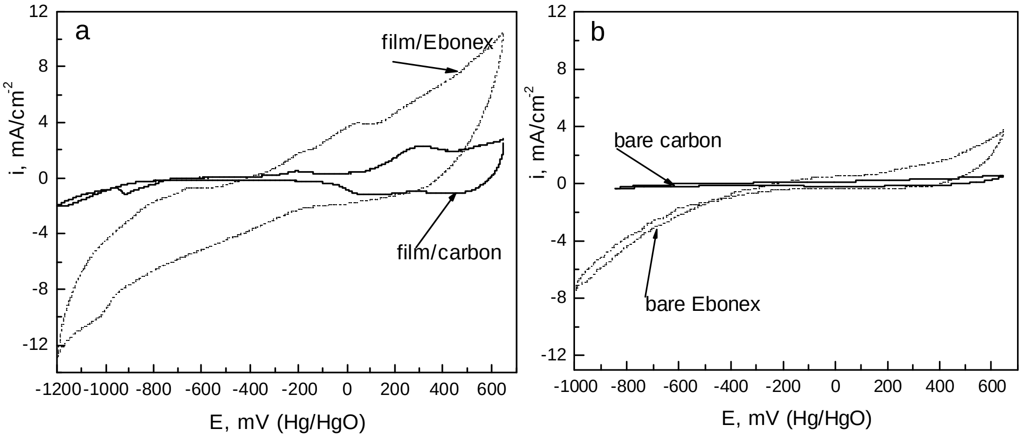

Fig. 2. Cyclic voltamograms of:a) GDEs with catalytic films having atomic ratio $R_{Co/Te}$=1.5 and loading of 0.2 mg cm^{-2} on carbon and Ebonex supports; b) bare carbon and Ebonex electrodes at potential scan rate of 10 mV s^{-1} in Ar atmosphere.

It is clearly seen from Fig. 2 that generally all peaks are broad which can be due to the heterogeneity of the size distribution of the active surface sites [18] or it is an effect of the high degree of porosity or/and roughness which effects the energy of the active sites, thus leading to broadening of the peak [19]. The position of the peak is indicative of the site's chemical nature, while the area under the peak is proportional to the numbers of sites oxidized or reduced [18]. However, the resolution of broad, not well defined peaks is very difficult. In this case the voltammetric charge over the whole potential range (q^*) can be taken as relative measure of the electrochemically active surface area. The values of q^* obtained cannot be easily converted into an absolute value since the precise nature of surface redox transitions is unknown, but q^* has proved very useful when different electrodes or different preparation procedures are being compared [18, 20, 21].

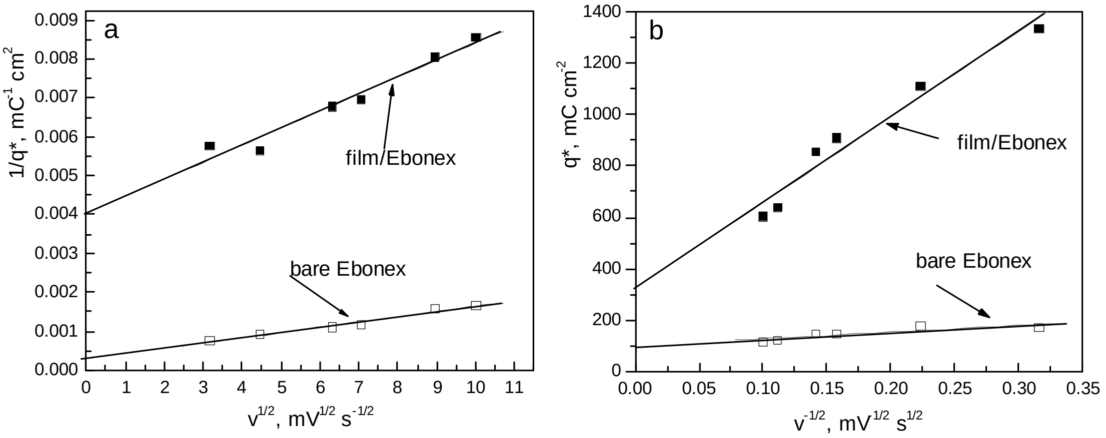

Fig. 3. Extrapolation of the voltammetric charge, obtained for Ebonex electrode with and without catalytic film to: a) υ =o and b) υ =∞.

To estimate the actual surface area of the oxide films taking place in the surface redox reactions we have calculated the surface charge q^* by integrating the voltammetric curves applying the CV technique, proposed by Trassati et al [20, 21]. The common observation with oxide electrodes is that q^* decreases as the potential scan rate υ is increased. It has been shown that q^* can be extrapolated to υ = 0, thus providing the total surface charge q_T^*, as well as to υ = ∞, giving the outer surface charge q_0^* [21]. The example of extrapolation procedure for Ebonex electrodes with and without catalytic film is illustrated in Fig. 3.

The difference $q_T^* - q_0^* = q_i^*$ provides the inner surface charge, i.e. the charge associated with the less accessible surface regions (pores, cracks, grain boundaries, etc.), where protons diffuse with difficulty [21]. If the inner charge q_i^* is related to the whole active surface (total charge) the ratio q_i^* / q_T^* can be taken as representing the "electrochemical porosity" of the electrode [21]. The total, outer and inner surface voltammetric charges and the ratio q_i^* / q_T^* of the carbon and Ebonex electrodes, bare and with catalytic films are given in Table 1.

Table 1. The total, outer and inner voltammetric charges and ratio q_i^* / q_T^*.

GDE	Voltammetric charges [mC cm^{-2}]			q_i^* / q_T^*
	q_T^*	q_0^*	q_i^*	
Bare carbon	200	0	200	1
Bare Ebonex	250	106	144	0.57
Film/carbon	498	54	444	0.89

It is seen that the both bare electrodes exhibit almost equal, relatively low number of active sites. These sites are, however, distributed preferentially in the inner surface of carbon support, while in the case of the Ebonex support they are uniformly distributed between the outer and inner surface. In this sense the bare carbon electrode exhibits more "electrochemical porosity" than the bare Ebonex most probably as a result of the significantly smaller particle size of the carbon powder used and higher teflon content in it. The results obtained clearly show that electrochemical porosity of the films on the both substrates is the same, but the total, outer and inner voltammetric charges obtained for Ebonex electrode with catalytic film are of about in order of magnitude higher than those of carbon electrode with film. This abrupt increase in the number of active sites participating in the surface redox reactions could be regarded as an indication for synergetic effect due to some interactions between Ebonex and catalytic film, although the influence of the geometry can not be excluded. This suggestion, however, must be verified by further investigations.

4. Conclusion

The results obtained show that the surface morphology of the catalytic films deposited by vacuum co-evaporation of Co and TeO_2 on carbon or Ebonex supports is the same. The films have very rough surface, following the surface of the supports. In both cases "wires" with different diameters are formed, which leads to one very large surface area. The results obtained show that the replacement of the carbon blacks with titanium sub-oxides in the catalyst support leads to of about in order of magnitude increase in the number of the active sites, participating in the surface redox reactions.

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