

VACUUM DEPOSITED FILMS OF COBALT OXIDES AS ELECTROCATALYSTS FOR OXYGEN REACTIONS

V. Rashkova, S. Kitova*, T. Vitanov^a

Central Laboratory of Photoprocesses "Acad. J. Malinowski", BAS,
Acad. G. Bonchev str., bl.109, Sofia 1113, Bulgaria

^aCentral Laboratory for Electrochemical Power Sources, BAS Acad. G. Bonchev str.,
bl.10, Sofia 1113, Bulgaria

Cobalt oxides, obtained by vacuum co-evaporation of Co and TeO₂ are investigated as electrocatalysts for oxygen reactions in alkaline media. Bifunctional gas-diffusion oxygen electrodes (GDE) are prepared by direct deposition of catalyst films on gas-diffusion membranes (GDM). The influence of thermal annealing on the surface morphology, the composition and the electrochemical behaviour of the films on GDM are followed by scanning and transmission electron microscopy and cyclic voltammetry. It is found that thermal annealing of GDEs at 100 °C leads to an abrupt increase in the concentration of the active sites participating in the surface redox reactions.

(Received December 9, 2004; accepted January 26, 2005)

Keywords: Thin films, Vacuum deposition, Cobalt oxides, Electrocatalysts

1. Introduction

The search for highly efficient bifunctional oxygen electrocatalysts still remains an attractive area of investigation, because of their possible application in oxygen-evolving and reducing gas-diffusion electrodes 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 widely, according to their method of preparation [6]. Thin films of Co₃O₄ and CoO have been prepared by chemical [7] or physical [8] vapour deposition, by electrodeposition [9], by chemical spray pyrolysis [4], by cathodic sputtering [10] or by a sol-gel method [6].

We have used a new method [11,12] for preparing cobalt oxides films by vacuum co-deposition of Co and TeO₂ onto a substrate held at room temperature. During the vacuum deposition, co-evaporated substances are mixed at an atomic level, giving the possibility of obtaining catalysts with various components in the desired proportions. It has been found that a chemical reaction takes place between them, resulting in the formation of CoO and of elemental Te phases [11,13]. X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) studies have shown that the reaction proceeds until the complete oxidation of Co to Co²⁺ in films with an atomic ratio R_{Co/Te} < 2, and until the complete reduction of TeO₂ to elemental Te in films with R_{Co/Te} > 2 [11,13]. Changes in the chemical state of the cobalt were observed after thermal annealing above 300 °C, caused by the oxidation of Co²⁺ to a higher valence state.

Our previous studies have shown that films with an atomic ratio R_{Co/Te} = 1.4 - 1.8 exhibit the highest catalytic activity toward both oxygen evolution and reduction reactions in alkaline solution, even at a very small loading of about 0.05 – 0.5 mg cm⁻² [14]. It has been found that Te and TeO₂

* Corresponding author: skitova@clf.bas.bg

themselves exhibit some activity, which is significantly lower, especially for Te, than that of the oxide films [12,14].

In this paper we have studied the influence of thermal annealing on the morphology and electrocatalytic properties of films deposited by the above-mentioned method on gas-diffusion membranes.

2. Experimental details

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

Gas-diffusion membranes, consisting of Teflon-bonded carbon blacks, hot pressed on Ni-screens, were used as substrates. The system of the film deposited on GDM represents the gas-diffusion electrode. The effective loading of the catalytic film was within the range $0.05 - 0.25 \text{ mg cm}^{-2}$ of geometric surface, which corresponds to a nominal thickness of about 100 to 500 nm.

Bright and dark field TEM and microdiffraction (Philips CM20) at an accelerating voltage of 200 kV, plus scanning electron microscopy (SEM), were employed to characterize the films.

The electrochemical study was carried out by means of cyclic voltammetry. The GDEs 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 a Hg/HgO reference electrode in 20% KOH, positioned close to the test electrode by a Luggin capillary. The system was carefully de-aerated by supplying Ar through the membrane and bubbling it into the electrolyte before the measurements.

To follow the thermally induced changes, GDEs were thermally annealed for 3 hours at $100\text{-}300^\circ\text{C}$. under an air atmosphere in an oven.

3. Results and discussion

Our previous investigations of films deposited on plane substrates of carbon coated mica have shown that as a rule films with $R_{\text{Co/Te}} < 2$ are amorphous, while those with $R_{\text{Co/Te}} > 2$ are nanocrystalline [11,13]. The study of the films deposited on gas-diffusion membranes, however has indicated that they do not follow such a rule. The SEM micrographs in Fig. 1 illustrate the surface morphology of the gas-diffusion membrane and of the film with $R_{\text{Co/Te}}=1.5$, deposited on it.

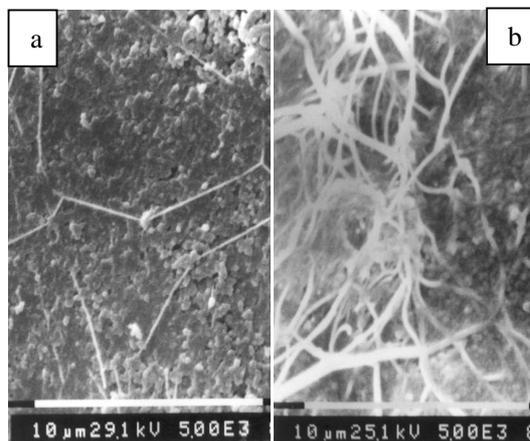


Fig. 1. SEM micrograph of: (a) a gas-diffusion membrane; (b) a 100 nm thick film with $R_{\text{Co/Te}}=1.5$.

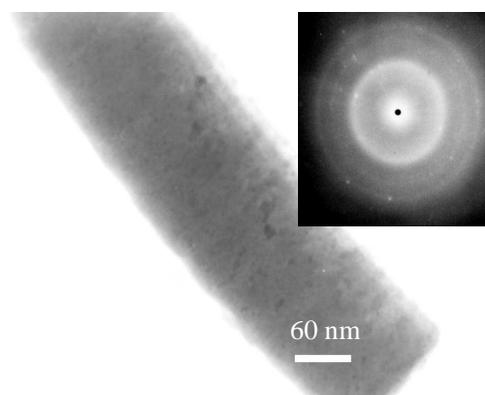


Fig. 2. TEM micrograph and ED pattern of a 100 nm thick film with $R_{\text{Co/Te}}=0.7$.

A very rough film surface, following that of the membrane, is seen for the as-deposited films. It was found that this morphology does not change after thermal annealing up to 300°C. The results obtained confirm that the surface morphology shown in Fig. 1b is typical for films deposited on the GDM, independently of the film thickness, $R_{\text{Co/Te}}$ and the thermal treatment. The only finding was an increase in the “wire” diameter with increasing film thickness. The results show that the “wires” consist of an amorphous matrix with nanosized crystals embedded in it. A TEM micrograph and an ED pattern of a typical “wire” formed on GDM are given in Fig. 2. Only rings of the hexagonal CoO phase are observed in the ED pattern.

The electrochemical behaviour of the films deposited on GDM has been studied by cyclic voltammetry. The response of the film surface is a characteristic “electrochemical spectrum”, a fingerprint of the state and composition of the surface. The resulting curve exhibits characteristic peaks in the redox potential, indicating the different oxidation states of the metal ion. Cyclic voltammograms of GDEs, fresh and thermally annealed at different temperatures are presented in Fig. 3. All the electrodes had the optimum catalyst loading of 0.2 mg cm⁻² and the atomic ratio $R_{\text{Co/Te}}=1.35$. Two pairs of broad peaks prior to the oxygen evolution are observed. They can be associated with the formation of redox couples CoO/CoO₂ (+ 195 mV vs. Hg/HgO [16]) and CoOOH/CoO₂ (+562 mV vs. Hg/HgO [16]) on the surface. Fig. 3 shows that the position of the main peaks is little influenced by the thermal treatment, although a small shift to less positive values is detected for GDE treated at 300 °C. A third pair of broad peaks at around 0 mV, which can be connected with a Co(OH)₂/CoOOH redox couple [16] is seen for GDE treated at 100 °C. The reason for its appearance only for this electrode is not clear at present.

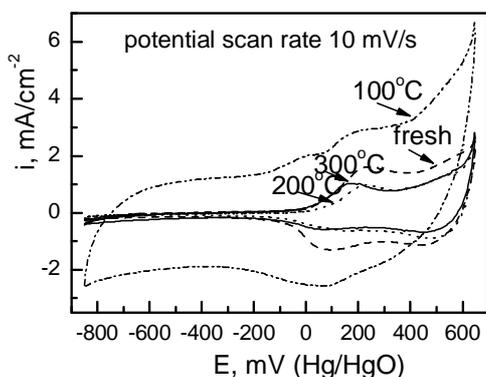


Fig. 3. Cyclic voltammograms of GDEs, thermally treated at the indicated temperatures.

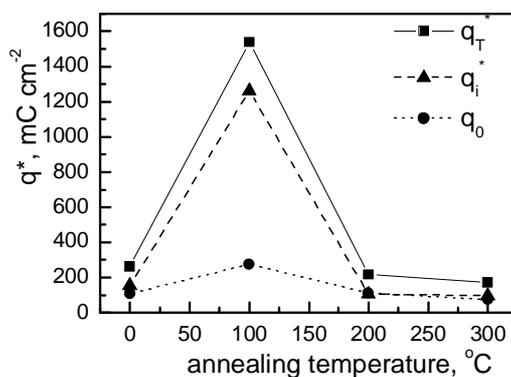


Fig. 4. The total q_T^* , inner q_i^* and outer q_o^* charges, as a function of the annealing temperature

The CV surface response is related to redox reactions at the surface active sites [17]. Thus the surface charge, q^* , derived by integration of the voltammetric curves, can be taken as proportional to the number of active sites, i.e. to the actual surface area of the oxide film [17,18]. The common observation with oxide electrodes is that q^* decreases as the potential scan rate v is increased. It has been shown, however, that q^* can be extrapolated to $v = 0$, providing the total surface charge q_T^* , as well as to $v = \infty$, giving the outer surface charge q_0^* [18]. The difference $q_T^* - q_0^* = q_i^*$ provides the inner surface charge, i.e. that associated with the less accessible surface regions (pores, cracks, grain boundaries, etc.), where protons diffuse with difficulty [18].

Fig. 4 shows the total, inner and outer surface voltammetric charges as a function of the annealing temperature of the GDEs studied. It is seen that the total charge q_T^* , representing the concentration of active sites, goes through a maximum at 100 °C. This is due mainly to the increase of the inner voltammetric charge, since the outer charges are almost similar. This suggests that the external morphology (macro-roughness) is not very dependent on the annealing temperature, as is confirmed by the SEM studies. It should be noted that the annealing at 100 °C does not lead to any changes in the voltammetric (q_T^* , q_0^* and q_i^*) charges of the pure gas-diffusion membrane, which is known to also have some catalytic activity toward the oxygen reduction reaction. On the other hand, XPS analysis did not show any changes in the chemical state of the catalytic films annealed at temperatures up to 300 °C. Therefore, most probably, the increase in the concentration of the active sites for electrodes annealed at 100 °C is caused by full crystallization of the catalytic film, but the size of the crystallites remains very small. The abrupt drop in the inner active surface area of electrodes annealed at 200 and 300 °C can be explained with changes, caused by both melting of the Teflon in the GDM at temperatures above 200 °C and the increasing size of the catalyst crystallites. These suggestions, however, must be verified by further investigations.

4. Conclusions

The results obtained show that catalytic films, deposited on gas-diffusion membranes by vacuum co-evaporation of Co and TeO₂ have very rough surfaces, following the surfaces of the membranes. As-deposited films consisted of small nanocrystallites of CoO embedded in the amorphous matrix. Thermal annealing causes a pronounced change in the concentration of the active sites participating in the surface redox reactions, with maximum observed at 100°C.

Acknowledgments

Support by the World Federation of Scientists, and by the Science Fund of the Bulgarian Ministry of Education and Science (contract No MY-X 1402) is gratefully acknowledged.

References

- [1] M. Tarasevich, B. Efremov, in S. Trasatti (Ed.), *Electrodes of Conductive Metallic Oxides*, Part A, Elsevier, Amsterdam (1981)
- [2] S. Trasatti, *Electrochim. Acta* **26**, 329 (1981).
- [3] I. Nicolov, R. Darkaoui, E. Zhecheva, R. Stoyanova, N. Dimitrov, T. Vitanov, *J. Electroanal. Chem.* **429**, 157 (1997).
- [4] R. Singh, J. Koenig, G. Poilerat and P. Chartier, *J. Electroanal. Chem.* **314**, 2411 (1991).
- [5] S. Jiang, Z. Lin, A. Tseung, *J. Electrochem. Soc.* **137**, No. 3, 764 (1990).
- [6] J. Marco, J. Gancedo, M. Gracia, J. Gautier, E. Rios, F. Berry, *J. Solid State Chem.* **153**, 74 (2000).
- [7] T. Maruyama, S. Arai, *J. Electrochem. Soc.* **143**, 1383 (1996).

-
- [8] M. Heiler, A. Chasse, K. Schindler, M. Hollering, H. Neddermeyer, *Surface Science* **454-456**, 36 (2000).
- [9] G. Barbero, G. Planes, M. Miras, *Electrochem. Communication* **3**, 113 (2001).
- [10] B. Nkeng, G. Poillerat, J. Koenig, P. Chartier, B. Lefez, J. Lopitiaux, M. Lenglet, *J. Electrochem. Soc.* **142**, 1777 (1995).
- [11] S. Kitova, V. Rashkova, I. Konstantinov, *Vacuum* **69**, 405 (2003)
- [12] V. Rashkova, S. Kitova, I. Konstantinov, T. Vitanov, *Electrochim. Acta* **47**, 1555 (2002).
- [13] V. Rashkova, S. Kitova, L. Litynska, T. Vitanov, *Vacuum* **76**, 147 (2004).
- [14] V. Rashkova, S. Kitova and T. Vitanov, *Nanoscience & Nanotechnology* **4**, eds. E. Balabanova, I. Dragieva, Heron Press, Sofia, in press (2004).
- [15] I. Podolesheva, P. Gushterova, V. Platikanova, I. Konstantinov, *J. Vac. Sci. Technol. A* **16**, 674 (1998).
- [16] W. Behl, J. Toni, *J. Electroanal. Chem.*, 31, 63 (1971).
- [17] R. Boggio, A. Carugati, S. Trasatti, *J. Appl. Electrochem.* **17**, 828 (1987)
- [18] G. Spinolo, S. Ardizzone, S. Trasatti, *J. Electroanal. Chem.* **423**, 49 (1997).