



Plasma deposited thin-film sandwich-like bifunctional electrocatalyst for oxygen reduction and evolution reactions



L. Jozwiak, J. Balcerzak, A. Kubiczek, J. Tyczkowski*

Department of Molecular Engineering, Faculty of Process and Environmental Engineering, Lodz University of Technology, Wolczanska213, 90-924 Lodz, Poland

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ABSTRACT

The thin-film sandwich-like system consisting of catalytic films and highly electrically conductive films arranged alternately one on top of the other was prepared using the cold plasma deposition method. The catalytic films were based on cobalt oxide while the electrically conductive carbon–nitrogen films were produced from acrylonitrile. The electrocatalytic activity of the system was tested for both the oxygen reduction reaction (ORR), on O₂ gas, and the oxygen evolution reaction (OER), from H₂O₂. Studies on the molecular structure showed that the catalytic films contained only a fraction of CoO without Co₃O₄ spinel. It was found that the catalytic activity of the sandwich-like system, for both the ORR and OER, was a several-fold higher compared with a film containing the same amount of the catalyst without the conducting films. It confirms the predictions on the possibility of increasing the catalytic activity by constructing the sandwich-like systems.

1. Introduction

In recent years there has been a sharp increase in interest in oxygen electrode catalysts for the oxygen reduction (ORR) and oxygen evolution (OER) reactions, which play a key role in a wide range of renewable energy technologies [1, 2]. The ORR catalysts are used in fuel cells [3], while the OER catalysts are mainly utilized in the water splitting technology [4].

The proton exchange membrane fuel cell (PEMFC) is one of the most efficient types of fuel cells. Its simple structure and high output current density make this fuel cell a very versatile design for mobile and stationary energy sources. Unfortunately, the use of such cells is problematic, especially in the portable applications, due to the need to supply gases, often from high pressure containers. Intensive efforts to improve the hydrogen supply have led, for example, to the design of direct methanol fuel cells. In this way, half-closed systems were created. On the other hand, atmospheric oxygen is abundant enough in many cases, but not in all of them (e.g. at space stations). Moreover, the impurities present in the air can have a negative effect on the catalyst life and efficiency. Thus, extensive studies have been performed on the replacement of gaseous oxygen with a liquid precursor and the creation of completely closed fuel cell systems. Hydrogen peroxide is one of the promising candidates for this purpose [5–7].

In general, precious metals and their alloys have been found to be the best catalysts for both the ORR and OER. Thus, they can be used as bifunctional catalysts in such processes [8]. However, the scarce

resources and high cost of these metals limit their practical applications. Therefore, it is extremely important to develop inexpensive bifunctional catalysts having high activity for the use, inter alia, in closed fuel cell systems.

Cobalt oxides have been proven to be some of the most promising catalysts for the ORR and OER [9–12]. Recently, cobalt oxides prepared in the form of thin films by plasma deposition from metalorganic precursors, have been investigated for the catalysis of ORR in hydrogen fuel cells [13, 14]. It was found that the electrocatalytic activity of the films depended on their thickness. With the growing thickness, the activity first increased and then decreased, reaching the maximum value at the optimum thickness. The initial increase in activity was related to the increase in surface density of the electrocatalytic centers. On the other hand, the decrease in activity was caused by increasingly difficult transport of electrical carriers in the increasingly thick films.

To obtain a more effective system, we designed a thin-film sandwich structure consisting of both cobalt oxide catalytic films and electrically conductive films, which were plasma-deposited alternately one on top of the other. Such a structure was supposed to provide more efficient transport of electrical carriers. The catalytic films were deposited with the electrocatalytically optimal thickness. Acrylonitrile was selected as the precursor for the deposition of the conductive films. After pyrolysis in an oxygen-free atmosphere, the as-deposited plasma polymerized acrylonitrile (pp-AN) films were partially decomposed, forming a nitrogen rich carbon phase with a strong conjugated π electron structure, which exhibited high conductivity and good permeability [15]. It was

* Corresponding author.

E-mail address: jacek.tyczkowski@p.lodz.pl (J. Tyczkowski).

also important to prepare the sandwich structure so that it was permeable to substrates and products of the ORR and OER.

In this paper, we present the results concerning the thin-film sandwich-like system plasma deposited from a cobalt-organic precursor and acrylonitrile and tested as a bifunctional catalyst for the ORR in a hydrogen fuel cell of the PEMFC type and for the OER in an oxygen generator using hydrogen peroxide.

2. Experimental details

2.1. Catalytic system preparation

The catalytic thin-film sandwich-like system was prepared by cold plasma deposition of cobalt-based and pp-AN films, laid alternately one on top of another. Both deposition processes were performed in a cylindrical, parallel plate reactor with RF (13.56 MHz) glow discharge having a power of 40 W. More details about the reactor and the deposition technique are presented elsewhere [16]. Cobalt(I) cyclopentadienyldicarbonyl, $\text{CpCo}(\text{CO})_2$, (Strem Chemicals Inc., min. 95%) and acrylonitrile, AN, (Sigma-Aldrich, $\geq 99\%$) were used as the precursors. Argon (Linde, 99.999%) was used as the carrier gas. The total pressure in the plasma reaction chamber during the plasma deposition of Co-based films was 4.5 Pa, and the flow rates of $\text{CpCo}(\text{CO})_2$ and Ar were 0.036 sccm and 0.71 sccm, respectively. On the other hand, the pp-AN films were deposited under a pressure of 3.9 Pa, with the flow rate of acrylonitrile equal to 0.45 sccm (without the carrier gas).

Carbon paper (SpectraCarb 2050-L, Fuel Cell Store) and stainless steel (SS type 316) mesh (500 mesh U.S.) were used to support the catalytic system. The carbon paper was pretreated by immersion in aqua regia (1 h), flushed with deionized water and dried. The stainless steel mesh was cleaned with n-hexane (POCH, $\geq 99\%$ analytic grade) two times in an ultrasonic bath to remove random impurities.

The deposition of each film lasted 10 min and between these processes the reactor chamber was pumped out below 0.20 Pa. The prepared sandwich-like system consisted of three Co-based films and two pp-AN films. For comparison of the electrocatalytic properties, the single Co-based films (without pp-AN) were produced in three consecutive deposition processes (10 min each) to obtain exactly the same amount of the catalyst as in the sandwich-like system. The single Co-based and pp-AN films were also prepared for electrical measurements. The single films with a thickness of 100–250 nm were deposited on the Corning 7059 glass plates.

All the produced samples were pyrolyzed in an electric tube furnace at 723 K for a period of 2 h in nitrogen (Linde, 99.999%). In the remaining part of the paper, the pyrolyzed Co-based and pp-AN films will be denoted as CoO and C/N, respectively. The thicknesses of single films were determined using the interference method (Nikon Eclipse LV150N) while the thicknesses of the films in the sandwich-like system were estimated from cross-section micrographs.

2.2. Characteristics of the sandwich-like system

The morphology of the sandwich-like system and the elemental composition of the component films were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a SEM FEI Quanta 200FEG microscope equipped with an EDX Oxford INCA 250 spectrometer. An electron energy of 3.5 keV was used in all the EDX measurements. A Kratos AXIS Ultra spectrometer XPS (X-ray photoelectron spectroscopy) equipped with an Al anode monochromated $\text{K}\alpha$ line = 1486.6 eV was used for a more thorough analysis of the molecular structure of the catalytic films.

The measurements of the electrical conductivity of single CoO and C/N films were carried out in coplanar geometry formed by two parallel gold strips (1 mm apart and 18 mm long) vacuum thermally evaporated on the films. The current-voltage characteristics were measured at room temperature in ambient air using a Keithley 6517 electrometer

equipped with a voltage source. A step-by-step procedure was employed, where constant current was obtained for each subsequent voltage level. For the CoO films, the polarization time was approximately 60 min while for the C/N films, it was 10 min.

2.3. Electrochemical tests

2.3.1. ORR test

For the ORR activity evaluation, the samples were prepared as complete membrane electrode assemblies (MEA) and examined by the single cell test. The test was performed at 293 K, using an electrochemical workstation Autolab PGSTAT302N working in the linear sweep voltammetry mode (LSV). The voltage was changed at a rate of 50 mV s^{-1} from the open circuit voltage to 0 V. The cell was fed with hydrogen (Linde, 99.999%) and oxygen (Linde, 99.999%).

The MEA was prepared by assembling a cathode electrode, a proton exchange membrane (Nafion 212, Fuel Cell Store) and an anode electrode, and then squeezing all together in a hot press at 390 K under a pressure of 1.2 MPa for 15 min.

The cathode was prepared from the samples under study (with the carbon paper support) covered with 0.025 g cm^{-2} of Nafion solution (Nafion D 520 – 5 wt% solution in lower aliphatic alcohols and water, Sigma-Aldrich) and dried at room temperature to complete evaporation of the solvent. On the other hand, the anode was prepared by coating the carbon paper with Pt (60% of Pt on Vulcan XC-72, Fuel Cell Store) and perfluorosulphonated ionomer identical with Nafion (15% LIQUion™ solution, Ion Power). The average amount of platinum was approximately 1.8 mg cm^{-2} .

2.3.2. OER test

The OER activity evaluation was performed at 293 K in a typical three-electrode corrosion system. The working electrode was prepared from the samples under study (with the stainless steel mesh support), a graphite rod 2 mm in diameter was the auxiliary electrode, and Ag/AgCl/KCl 3 M was used as the reference electrode. The measurements were carried out using the LSV method. An aqueous solution containing 0.05 M H_2O_2 (the active component), and 0.1 M K_2SO_4 , which improved the ionic conductivity and ensured iR compensation in the electrode system, was used as the electrolyte.

3. Results and discussion

3.1. Examination of the sandwich-like system

Fig. 1a shows a SEM image of the stainless steel mesh with the plasma deposited catalytic thin-film sandwich-like system after pyrolysis, which was intentionally damaged to confirm the presence of the coating. Fig. 1b shows a cross-section of this system. As one can see, the system was composed of five films, i.e. three CoO films, each having a thickness of about 500 nm, and two C/N films with an average thickness of 780 nm.

The elemental compositions of the films, measured with EDX for both types of materials prepared separately (CoO and C/N), are summarized in Table 1. The results showed that the CoO films, apart from cobalt and oxygen, contained also 10.5 at.% residual carbon derived from the $\text{CpCo}(\text{CO})_2$ precursor, which was not removed during pyrolysis. On the other hand, the C/N films revealed, in addition to carbon and nitrogen, the presence of some oxygen that was most likely incorporated into the film after the deposition process, via contact with air. The low nitrogen to carbon ratio (0.15) indicates a significant carbonization process occurring during pyrolysis, leading to a complex structure consisting of a mixture of different chemical species [17, 18].

More details on the molecular structure of the Co-based films were provided by the XPS investigations. Fig. 2a and b show the Co 2p spectra for the films before and after pyrolysis. The Co $2p_{3/2}$ spectra deconvolution was performed similarly to that described by Biesinger

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