



Oxygen reduction on SILAR deposited iron oxide onto graphite felt electrode



Branimir N. Grgur^{a,*}, Branimir Z. Jugović^b, Milica M. Gvozdenović^a

^a Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11020 Belgrade, Serbia

^b Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11000 Belgrade, Serbia

ARTICLE INFO

Article history:

Received 23 May 2016

Received in revised form 1 July 2016

Accepted 6 July 2016

Available online 6 July 2016

Keywords:

Fuel cells

Platinum

Mechanism

Hematite

Hypochlorite

ABSTRACT

The potential characteristics of graphite felt electrodes, modified by iron oxide, for oxygen reduction are evaluated. Modification is carried out by Successive Ion Layer Adsorption and Reaction (SILAR) method, using a solution of ferric nitrate in methanol for the adsorption of ions, and a solution of sodium hypochlorite for reaction. The reaction activity of the oxygen reduction from the air, in sodium sulfate based solution varying the number of SILAR cycles, as well as the influence of pH is investigated. By comparing the activity with pure platinum, similar activity is obtained at pH=9.2, as well as good electrode stability. Possible mechanism of the oxygen reduction on the graphite felt modified by iron oxide is discussed.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

A new generation of the fuel cells, e.g. photoelectrochemical [1–4], microbial [5–7] and enzymatic [8] attract growing interest. All this fuel cell can be used for the simultaneous electricity production using different biofuels, or for example wastewater treatment. Due to slow reduction kinetics in near-neutral solutions, the oxygen reduction reaction (ORR) is the main limiting factor for relatively low power of such devices. Different carbon materials were considered as a cathode material [9,10], but unfortunately on these materials the ORR proceeds via two-electron, hydrogen peroxide path decreasing the available power. To improve the performance, modifying the carbon cathode materials with a highly active catalyst, e.g., Pt, which is the most active one [9], is supposed to reduce the cathodic reaction activation energy and increase the reaction rate. However, Pt is an expensive metal and very sensitive to different impurities, as well as the decreased activity of the carbon-supported high surface area catalysts in comparison with bulk platinum [11], which limits its practical application. Many efforts were made to reduce cathode costs by decreasing Pt loading or in search for other non-Pt catalysts, like PbO₂, [12], MnO₂ [13] Co₂O₃ [14] and iron oxides [15]. Iron oxides (including Fe₃O₄, α-Fe₂O₃ and γ-Fe₂O₃) are very promising materials for electrochemical energy storage and conversion

devices, because their low cost, nontoxicity, good chemical stability [16]. Oxygen reduction reaction shows encouraging characteristics in alkaline solution on α-Fe₂O₃ spherical nanocrystals supported on CNTs [15], and on 3D nitrogen-doped graphene aerogel supported with Fe₃O₄ nanoparticles. [17] Among different procedures, hydrothermal method for iron oxide synthesis were well elaborated [15,17–19]. Typically, this procedure includes long lasting hydrolysis of the iron salt at elevated temperature in an autoclave. Recently, it was reported that α-Fe₂O₃ can be obtained by forced hydrolysis of ferric nitrate with sodium hypochlorite at ambient temperature for a relatively short period of time [20]. Hence, the aim of this paper is to investigate possible characteristics of the oxygen reduction reaction on graphite felt electrode modified with iron oxide using the simple SILAR procedure.

2. Experimental

Commercial 1.5 × 3 cm, 2 mm thick graphite felt (*ssa* = 0.6 m² g⁻¹, *ρ* = 0.09 g cm⁻³) was used. One side of electrode was glued to polyethylene sheet, and electrical contact was achieved using a graphite rod (*d* = 3 mm). The modification of the graphite felt with iron oxide was made using the successive ion adsorption and reaction (SILAR) procedure. The iron ion precursor was 0.05 M Fe(NO₃)₃ × 9H₂O (p.a. Merck) in methanol, and the reaction medium was a 3.5 wt.% sodium hypochlorite solution (Centrohém, Serbia) with a pH ~ 10.5. In a typical procedure, the graphite felt was immersed for 30 s in the ion precursor solution, dried with hot air,

* Corresponding author.

E-mail address: BNGrgur@tmf.bg.ac.rs (B.N. Grgur).

and exposed to the reaction medium for 60 s. Before repeating the cycle, the electrode was washed in pure methanol. The SILAR was consisted of 2 to 10 cycles, with the last immersion in HClO for 15 min, was performed. The electrode was then washed with DI water, methanol and dried in the air. The mass loading was determined separately by measuring the mass of graphite felt ($\sim 2 \text{ cm} \times 2 \text{ cm}$), before and after SILAR cycles, proper washing and drying in the oven at 80°C over night.

All the experiments were performed in three compartment glass cell. The anode compartment were separated from the working one, by the dense glass frit to avoid contamination from the Pt counter electrode [21]. Oxygen was supplied from the air by bubbling the solution thorough a glass frit, using an air pump with flow rate of 5 ml s^{-1} , with an equilibrium oxygen concentration of $\sim 0.25 \text{ mM}$. Experiments were mainly conducted in $0.1 \text{ M Na}_2\text{SO}_4$ (p.a. Merck) buffered to $\text{pH}=9.2$ with 0.01 M sodium tetraborate, prepared using distilled water. The influence of the pH was investigated in $0.1 \text{ M Na}_2\text{SO}_4$, $\text{pH}=7$, and with the addition of 0.05 M potassium hydrogen phthalate, $\text{pH}=4$. Also for $\text{pH}=11$ combination, 1:1 of 0.1 M NaOH and 0.05 M sodium tetraborate with addition of $0.1 \text{ M Na}_2\text{SO}_4$, were used. Saturated calomel electrode as the reference and platinum plate (5 cm^2) as a counter electrode was used. Experiments were carried out using Gamry PC3 potentiaostat/galvanostat.

For the characterization, iron oxide in the bulk form was prepared as follows: 10 mmol of $\text{Fe}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$ were dissolved in 20 cm^3 of methanol, and slowly added (during 5 min) to 200 cm^3 of $3.5 \text{ wt.}\%$ HClO. After 15 min, the mixture was filtrated using a Büchner funnel and a water vacuum pump. After thorough rinsing with DI water and methanol, iron oxide was dried at room temperature. Part of the bulk sample was annealed at 450°C for one hour. The XRD pattern of the samples was recorded with an Itai Structure APD2000 X-ray diffractometer in a Bragg–Brentano geometry using $\text{CuK}\alpha$ radiation and the step-scan mode (range: $10\text{--}80^\circ 2\theta$, step-time: 0.50 s , step-width: 0.02°). The program PowderCell, was used for an approximate phase analysis. Unit cell parameters were obtained by the least-squares method using the program LSUCRIPC. The mean crystallite size of $\alpha\text{-Fe}_2\text{O}_3$ phase was estimated from the most intensive diffraction peaks by the Scherrer formula using the appropriate instrumental resolution function for ZnO as a standard. Optical micrographs were obtained with an optical microscope Olympus CX41 connected to PC.

3. Results and discussion

Fig. 1 shows polarization curves of the oxygen reduction reaction onto bulk platinum and graphite felt electrodes under air saturated non-mixed, and air mixed conditions. In non-mixed electrolyte open circuit potential for platinum was 0.3 V , which was $\sim 0.14 \text{ V}$ lower than the theoretical value of 0.437 V (SCE) . After cathodic polarization, up to the potential of $\sim 0.1 \text{ V}$, the oxygen reduction reaction followed a two-electron, hydrogen peroxide, kinetics occurred:



characterized by the limiting diffusion current density of $1 \mu\text{A cm}^{-2}$. After that, at the potentials below $\sim 0.1 \text{ V}$, the Tafel slope of -130 mV dec^{-1} , can be assigned to the four-electron oxygen reduction reaction:



Observed limiting diffusion current density of $\sim 80 \mu\text{A cm}^{-2}$ correspond to partial oxygen pressure of 0.21 bar , for non-mixed electrolyte [22]. In the air mixed electrolyte, the open circuit potential was lower, probable due poisoning of active centers. The

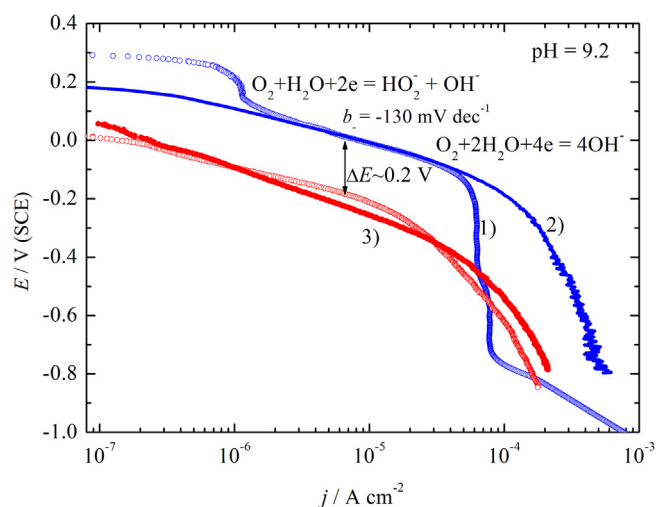
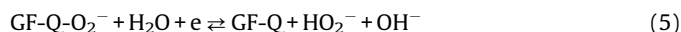


Fig. 1. Polarization curves, $v = 1 \text{ mV s}^{-1}$, for platinum (1 and 2) and graphite felt electrode (3) in non-mixed (open symbols) and air mixed (full symbols) electrolyte.

activity in the activation controlled region was the same as in non-mixed electrolyte. Limiting diffusion current density was few times higher, with the value of $400\text{--}500 \mu\text{A cm}^{-2}$.

In Fig. 1 the polarization curves of oxygen reduction on graphite felt electrode was also shown. Electrode was less active than platinum for almost 0.2 V . Mixing of the electrolyte practically did not affect reaction rate, suggesting chemical rate determining step. According to Hossain et al. [23] oxygen reduction can be described by following reaction scheme:



where GF-Q, represents quinone-like surface active centers. The rate determining step was probably chemisorption of molecular oxygen, Eq. (4), as the only chemical step in the mechanism.

To investigate the potential activity of graphite felt modified with iron oxide, graphite felt was modified by iron oxide with SILAR. The micrographs of the modified electrode, applying five SILAR cycles, was shown in Fig. 2a, as an example. From the figures, one can see that graphite fibers were covered with irregular agglomerated orange deposits of the iron oxide. The dimensions of the iron oxide deposits were roughly estimated between $10 \mu\text{m}$ up to $50 \mu\text{m}$.

Fig. 2b shows the XRD diffraction pattern of the as synthesized bulk iron oxide, and after annealing treatment. The XRD spectra of as synthesized sample correspond to poorly crystalline, almost amorphous ferrihydrite [24,25]. After FFT-filtering and smoothing (thick black line), and a comparison with standard cards for $\alpha\text{-FeO (OH)}$, $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeO(OH)}$, it could be carefully concluded that the product was a mixture of $\alpha(\gamma)\text{-FeO(OH)}$ and $\alpha\text{-Fe}_2\text{O}_3$. After annealing treatment XRD spectra reveal that the sample contained about $0.8 \text{ wt.}\%$ of the $\gamma\text{-Fe}_2\text{O}_3$ (ICSD 247035), while the predominant $\alpha\text{-Fe}_2\text{O}_3$ phase ($99.2 \text{ wt.}\%$) was confirmed by comparison of the XRD data to the ICSD 161294 card. The unit cell parameter of $\alpha\text{-Fe}_2\text{O}_3$ was 8.3813 \AA and the unit cell parameters of $\gamma\text{-Fe}_2\text{O}_3$ were $a = 5.0454 \text{ \AA}$ and $c = 13.7894 \text{ \AA}$. $\alpha\text{-Fe}_2\text{O}_3$ phase had the mean crystallite size of 32.9 nm . It should be mentioned, that annealing treatment does not affect the initial phase structure [24]. Hence, the mechanism of the iron nitrate forced hydrolysis in the

Download English Version:

<https://daneshyari.com/en/article/6605956>

Download Persian Version:

<https://daneshyari.com/article/6605956>

[Daneshyari.com](https://daneshyari.com)