

ELECTROCHEMICAL DURABILITY OF MAGNETITE AND BIRNESSITE MODIFIED ELECTRODES WITH POTENTIAL APPLICATION IN WATER SPLITTING

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Abstract

Graphite electrodes were modified with compositions containing either Fe₃O₄ or δ-MnO₂, and their electrochemical durability was investigated using the cyclic voltammetry method. Experimental results indicate that the most stable electrode is the one modified with the composition containing magnetite and Vulcan carbon, when exposed to electrochemical potentials in the anodic domain. Given this result and the potential values at which oxygen is evolved on the electrode, it has the prospect to find application in the water splitting domain.

Introduction

With the increase in energy demand and with a global concern for the environment, the search for sustainable and renewable energy sources aimed at replacing fossil fuels has become especially important. A range of *energy* sources, including renewable ones, can be employed to generate hydrogen, which in turn is used for energy storage purposes. One way to generate hydrogen is *via* electrochemical water splitting. The two half-cell reactions taking place during this process – the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) – require a practical amount of energy in order to unfold that can be decreased with the help of catalysts. In the past five years low-cost materials with high electrocatalytic activity for the OER and HER were discovered that have the potential to replace the standard noble metal-based catalysts [1-5].

The results presented in this paper are part of a larger study aimed at developing modified electrodes using materials with electrocatalytic properties for the OER and HER. A high electrochemical durability is a characteristic that electrocatalytic materials are currently expected to possess. In this context, three graphite electrodes were modified with compositions containing either Fe₃O₄ or δ-MnO₂ and their durability was evaluated by recording sets of cyclic voltammograms. The most stable electrode is the one modified with the composition containing Fe₃O₄ and Vulcan carbon, and it has the potential to be used for electrochemical water splitting.

Experimental

Magnetite and birnessite were synthesized hydrothermally. Carbon Black – Vulcan XC 72 (Fuel Cell Store), Nafion® 117 solution (Sigma Aldrich) and KOH (analytical grade, Merck) were also used in the study. The conductive substrate modified to obtain the electrodes was spectroscopic graphite type SW.114 (“Kablo Bratislava”, Slovakia). All solutions were obtained using double distilled water. The modified electrodes were manufactured by drop-casting on the surface of graphite substrates volumes of 10 μL collected from suspensions in ethanol having different compositions. The three electrodes evaluated in terms of their electrochemical durability were selected from a series of magnetite-based electrodes and a series of birnessite-based electrodes after preliminary experiments regarding their OER and HER catalytic activity.

The compositions used to obtain the modified electrodes are presented in Table 1.

Table 1. Modified electrodes labels and the compositions applied on the graphite substrates

Electrode label	Compositions used to obtain the electrodes			
	Fe ₃ O ₄ [mg]	δ-MnO ₂ [mg]	Vulcan carbon [mg]	Nafion solution [μL]
G1	2	-	2	-
G2	-	4	-	10
G3	-	2	1	10

Cyclic voltammetry experiments were performed using a glass cell equipped with three electrodes connected to a potentiostat. The reference electrode was the Ag/AgCl (sat. KCl) electrode and the auxiliary electrode was a Pt plate ($S_{\text{geom}} = 0.8 \text{ cm}^2$). Each modified electrode was used as working electrode ($S_{\text{geom}} = 0.28 \text{ cm}^2$). Electrochemical potential (E) values were expressed in terms of the Reversible Hydrogen Electrode (RHE) and the conversion was performed using the equation employed by Zhao *et al.* [6]. All experiments presented in this paper were performed in 1M KOH solution.

Results and discussion

The cyclic voltammograms recorded on the modified electrodes are shown in Figure 1. Since the G1 electrode displays catalytic activity for both OER and HER, its electrochemical durability was investigated in both the anodic and cathodic domain. In the former domain (Figure 1a), the durability of the G1 electrode was studied by recording 150 voltammetry cycles in a potential range in which the 10 mA/cm^2 current density (i) value is reached. In OER experiments this is the value at which the OER overpotential is usually specified [7]. When the first cycle is recorded, the E value corresponding to $i = 10 \text{ mA/cm}^2$ (on the anodic branch) is $\sim 1.74 \text{ V}$. This value is higher at the 5th cycle and lower at the 100th cycle. When the 150th cycle is obtained the E value becomes $\sim 1.72 \text{ V}$. Thus, by recording 150 voltammograms the electrochemical potential corresponding to the specified i value decreases, indicating an improvement in the OER catalytic activity of the electrode. With regard to the maximum i value attained during O₂ evolution, a slight increase is observed from $\sim 21 \text{ mA/cm}^2$ (the first cycle) to $\sim 23 \text{ mA/cm}^2$ (the 150th cycle). The absence of significant change in the maximum i value indicates the relatively high electrochemical stability of the electrode.

The electrochemical durability of the G1 electrode was investigated in the cathodic domain as well (Figure 1b), by recording 120 voltammetry cycles. The shift in the potential value corresponding to the -10 mA/cm^2 current density was monitored throughout the experiment, and the following observations were made: In the case of the first cycle, on the cathodic branch of the voltammogram, the E value corresponding to $i = -10 \text{ mA/cm}^2$ is about -0.43 V . As the number of recorded voltammograms increases this E value gradually decreases, until it becomes $\sim -0.52 \text{ V}$ (120th cycle). The minimum i value obtained for the first cycle during H₂ evolution is $\sim -18 \text{ mA/cm}^2$. At the 5th cycle the value becomes -20.2 mA/cm^2 , then it increases to -11.5 mA/cm^2 (the 100th cycle) and subsequently to -10.5 mA/cm^2 (the 120th cycle). These results indicate that after the tracing of the 120 voltammograms the HER catalytic activity of the electrode depreciates significantly and its electrochemical stability in the investigated cathodic range is poor.

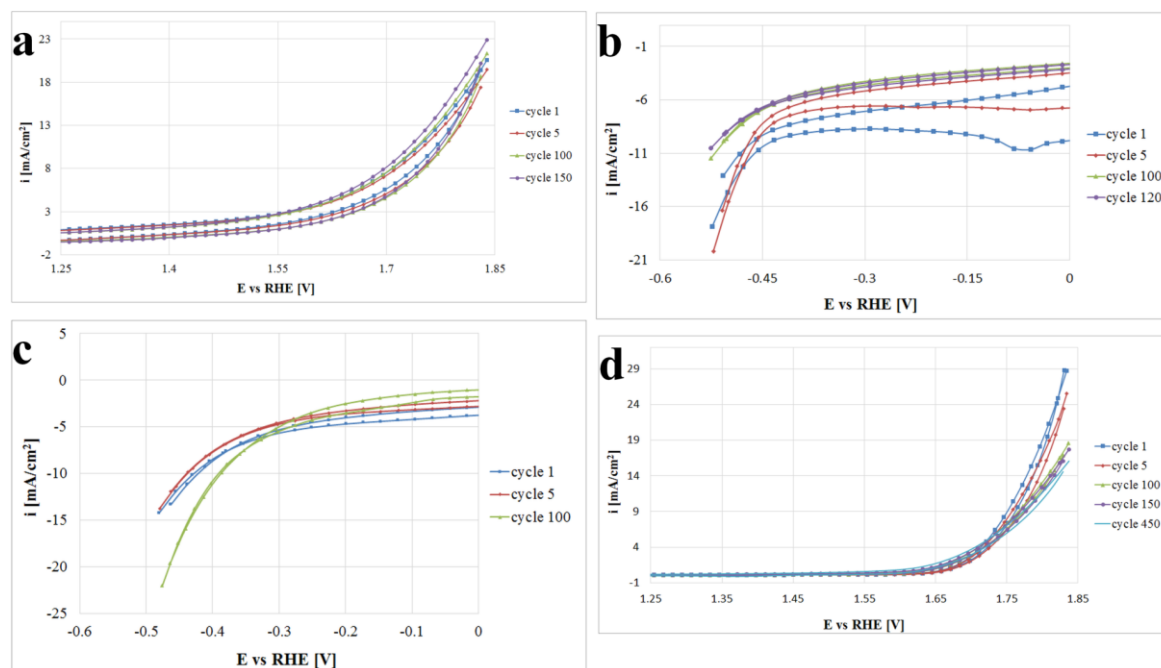


Figure 1. Cyclic voltammograms (iR corrected) obtained in 1M KOH solution, at a scan rate of 5 mV/s, on the (a) G1 electrode, in the anodic domain; (b) G1 electrode, in the cathodic domain; (c) G2 electrode, in the cathodic domain and (d) G3 electrode, in the anodic domain

Regarding the G2 electrode (Figure 1c), because it displays catalytic activity for the HER its durability was studied in the cathodic domain by recording 100 cycles. The E value corresponding to $i = -10 \text{ mA/cm}^2$, observed on the cathodic branch of the first cycle, is about -0.43 V. This value decreases (as can be seen on the 5th cycle) and then it increases up to -0.39 V (at the 100th cycle), indicating that the recording of the voltammetry curves improves the HER catalytic activity of the electrode. The minimum value of the current density obtained for the first cycle during H₂ evolution is -14.2 mA/cm². This value suffers a slight increase (the 5th cycle), but by the 100th cycle it becomes -22 mA/cm². Even though it should remain about the same throughout the voltammetric study in order for the electrode to be electrochemically stable, it is worth noting that the providing of a low current density value is desirable in HER studies [8].

Since it displays OER catalytic activity the electrochemical durability of the G3 electrode was evaluated in the anodic domain (Figure 1d). A total of 450 voltammetry cycles were obtained on this electrode, and the data show that the potential value corresponding to the 10 mA/cm² current density keeps increasing, starting from ~ 1.76 V and stopping at 1.785 V. This indicates that the OER catalytic performance of the electrode decreases. The maximum current density value obtained during the O₂ evolution, in the case of the first cycle, is ~ 29 mA/cm². This value keeps decreasing as the remaining voltammograms are traced and it becomes 25.6 mA/cm² (5th cycle), then 18.5 mA/cm² (100th cycle), 17.5 mA/cm² (150th cycle), and eventually 16 mA/cm² (450th cycle). Basically, the electrode has poor electrochemical stability in the given experimental conditions.

Conclusion

The electrochemical durability study performed on the G1, G2 and G3 modified graphite electrodes has led to the identification of the most stable electrode. This is the electrode obtained by drop-casting on the surface of the graphite substrate a composition containing both magnetite and Vulcan carbon, denoted G1. However, even though it displays a relatively good catalytic

activity for the OER and HER, its electrochemical stability is restricted to the anodic domain. Because of this, the electrode has the potential to be used as OER catalyst in the water splitting field.

Acknowledgements

This work was financed by the National Program NUCLEU, Project Code PN 19 22 01 01, Contract No. 40N/2019

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