THE ELECTROCATALYTIC ACTIVITY OF $YMnO_3$-BASED ELECTRODES FOR THE O_2 AND H_2 EVOLUTION REACTIONS IN A STRONG ALKALINE MEDIUM

Bogdan-Ovidiu Taranu[1], Paula Sfirloaga[1,2]

[1]National Institute for Research and Development in Electrochemistry and Condensed Matter, Dr. A.P. Podeanu street, No. 144, 300569, Timisoara, Romania
[2]Spin-off Nattive-Senz SRL, Dr. A.P. Podeanu street, No. 144, 300569, Timisoara, Timis, Romania
e-mail: b.taranu84@gmail.com

Abstract

$YMnO_3$ perovskites synthesized using the sol-gel method were studied regarding their electrocatalytic properties for the O_2 and H_2 evolution reactions (OER and HER) in a strong alkaline medium. The highest activity was observed during HER experiments, especially for the electrodes manufactured using suspensions containing Nafion, Carbon Black and either Co^{2+} doped $YMnO_3$ or Sn^{2+} doped $YMnO_3$. For these samples, the HER overpotential value at $i = -10$ mA/cm^2 was 0.83 V. The main conclusions are the following: (a) the inclusion of Carbon Black into the electrode manufacturing process improved the HER catalytic activity of all perovskite-modified electrodes and (b) the HER activity of the samples modified with the catalysts, Nafion and Carbon Black was similar despite the different temperatures applied during perovskite synthesis.

Introduction

Two side effects of the comparatively recent and rapid global economic development consist of climate change and the global energy crisis currently facing humanity [1]. These two issues are at the heart of the present efforts to replace the fossil fuel-based infrastructure with an alternative energy-based one [2]. The ongoing research revealed hydrogen, a carbon-free energy carrier and energy source, as promising for a sustainable alternative energy-oriented infrastructure [3]. There are several known methods for generating hydrogen [4], but the one that is both eco-friendly and economically effective is water-splitting, either by photo- or electrocatalysis [5,6].

Electrocatalytic water-splitting consists of the decomposition of water – an abundant source of H_2 – using electrical current. The two half-cell reactions occurring during this process, namely the hydrogen evolution reaction (HER) taking place at the cathode and the oxygen evolution reaction (OER) unfolding at the anode, make its large-scale application difficult because of high overpotentials (which are a measure of the kinetic energy barriers) [1,7]. To resolve this issue, researchers are actively looking to identify materials that can serve as effective and stable electrocatalysts for the specified reactions. Such catalysts would minimize the overpotentials, ensuring more efficient hydrogen production [8].

The present paper describes a study in which the electrocatalytic activity for the two half-reactions involved in water-splitting of $YMnO_3$ perovskite materials synthesized at different temperatures using the sol-gel method is evaluated in a strong alkaline medium.

Experimental

The materials were synthesized by the sol-gel method, followed by thermal treatments at different temperatures. The subsequent perovskites were obtained: YMO-800 ($YMnO_3$ synthesized at 800 °C), YMO-1000 ($YMnO_3$ synthesized at 1000 °C), YMO-15 (0.005 mmol Co^{2+} doped $YMnO_3$) and YMO-16 (0.005 mmol Sn^{2+} doped $YMnO_3$). Glassy carbon

(GC) pellets were acquired from Andreescu Labor & Soft SRL, Nafion® 117 solution from Sigma-Aldrich, Carbon Black - Vulcan XC 72 from Fuel Cell Store, potassium hydroxide from Merck, and acetone and ethanol from Chimreactiv.

The role of Carbon Black was to enhance the charge transfer at the interface between the sample and the electrolyte solution [9]. Nafion was utilized as binder, ensuring adherence between the deposited composition and the substrate surface [10].

The perovskite catalysts were employed to manufacture modified electrodes by adapting a previously published protocol [11]. The samples were obtained by pursuing the steps described in what follows. The GC pellets served as conductive support. They were washed with water and detergent, water, bidistilled water, acetone and ethanol. After drying, one of their surfaces was covered with suspensions containing the catalytic materials. The suspensions were prepared following two procedures: (1) 5 mg catalyst and 50 µL Nafion solution were added to 450 µL ethanol and (2) 5 mg catalyst, 50 µL Nafion solution and 5 mg Carbon Black were added to 900 µL ethanol. The suspensions were ultrasonicated for 30 min., and a volume of 10 µL was taken from each of them and drop-casted on one of the surfaces of the GC pellets to obtain each modified electrode. The samples were used in the experiments after drying at RT. For each experiment one of the electrodes was inserted into a polyamide support which restricted its geometrical surface to 0.28 cm^2.

The names of the samples are presented in Table 1 along with the compositions of the suspensions used to obtain them.

Table 1. Names of investigated electrodes and compositions of suspensions

Electrode name	Catalyst (5 mg)	Carbon Black (mg)	5% Nafion solution (µL)	Ethanol (µL)
GC_0	-	-	-	-
$GC_{YMO-800}$	YMO-800	-	50	450
$GC_{YMO-1000}$	YMO-1000	-	50	450
GC_{YMO-15}	YMO-15	-	50	450
GC_{YMO-16}	YMO-16	-	50	450
$GC_{CB-YMO-800}$	YMO-800	5	50	900
$GC_{CB-YMO-1000}$	YMO-1000	5	50	900
$GC_{CB-YMO-15}$	YMO-15	5	50	900
$GC_{CB-YMO-16}$	YMO-16	5	50	900

The electrochemical setup consisted of a potentiostat – Voltalab model PGZ 402 from Radiometer Analytical – connected to three electrodes inserted into a glass cell containing the electrolyte solution. Each modified sample, as well as an unmodified GC pellet, served as the working electrode. The auxiliary electrode was a Pt plate having a geometrical surface of 0.8 cm^2, while an Ag/AgCl (sat. KCl) electrode was utilized as reference.

The electrolyte solution employed in all experiments was 1 M KOH. Aqueous solutions were obtained with bidistilled water. Linear sweep voltammograms (LSVs) were iR-corrected and recorded at the scan rate (v) of 5 mV/s. For the HER investigations, the electrolyte solution was degassed by bubbling N_2. The electrochemical potential (E) values were represented in terms of the Reversible Hydrogen Electrode (RHE) with equation (1) [12]. The OER and HER overpotential values were obtained with equations (2) and (3), respectively [13,14].

$$E_{RHE} = E_{Ag/AgCl(sat.\ KCl)} + 0.059 \times pH + 0.197 \quad (1)$$

$$\eta_{O2} = E_{RHE} - 1.23 \quad (2)$$

$$\eta_{H2} = |E_{RHE}| \quad (3)$$

Where: E_{RHE} is the reversible hydrogen electrode potential (V); $E_{Ag/AgCl(sat.\ KCl)}$ is the potential *vs.* the Ag/AgCl (sat. KCl) reference electrode (V); η_{O2} is the oxygen evolution overpotential (V) and η_{H2} is the hydrogen evolution overpotential (V);

Results and discussion

OER investigations. Figure 1 shows the LSVs obtained on the unmodified electrode and on electrodes modified with suspensions containing the perovskite materials and Nafion. The lowest OER overpotential value at i = 10 mA/cm^2 – the current density value often considered as a measure of OER catalytic performance [15] – is 1.15 V and was determined for the $GC_{YMO-800}$ sample. The addition of Carbon Black to the suspensions utilized to manufacture the modified electrodes led to the LSVs presented in Figure 2. The presence of an oxidation peak at E values > 2.2 V hampered the determination of the η_{O2} value at i = 10 mA/cm^2. Thus, the presence of Carbon Black is not advantageous for the study of the OER activity of the perovskite-based modified electrodes.

HER investigations. Figure 3 outlines the polarization curves recorded on GC_0 and the electrodes modified with the perovskite materials and Nafion. It can be seen that the η_{H2} values at i = −10 mA/cm^2 are close to each other for all samples, including the unmodified GC pellet (η_{H2} for GC_0 = 0.9 V). The lowest η_{H2} value was determined for GC_{YMO-16} as 0.88 V. In the presence of Carbon Black in the suspensions used to manufacture the modified electrodes, an improvement in their HER catalytic activity was evidenced (Figure 4). The η_{H2} values of the modified samples remained similar, but the lowest one was determined for both $GC_{CB-YMO-15}$ and $GC_{CB-YMO-16}$ as 0.83 V. According to this result, the differences in the thermal treatment applied during the synthesis of the YMO-15 and YMO-16 perovskites did not affect their HER electrocatalytic activity.

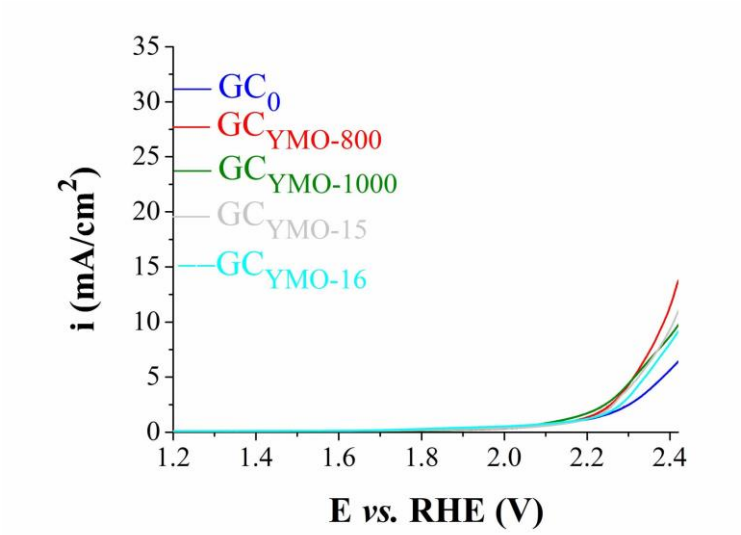

Figure 1. OER polarization curves recorded on the GC_0, $GC_{YMO-800}$, $GC_{YMO-1000}$, GC_{YMO-15}, GC_{YMO-16} electrodes, in 1 M KOH solution, at v = 5 mV/s

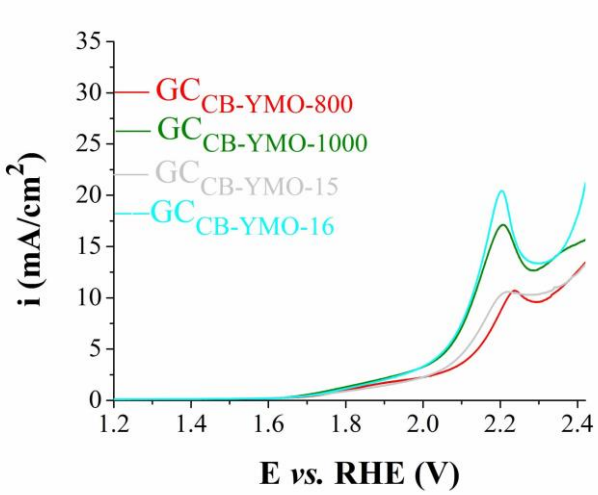

Figure 2. OER polarization curves recorded on the GC_0, $GC_{CB\text{-}YMO\text{-}800}$, $GC_{CB\text{-}YMO\text{-}1000}$, $GC_{CB\text{-}YMO\text{-}15}$, $GC_{CB\text{-}YMO\text{-}16}$ electrodes, in 1 M KOH solution, at v = 5 mV/s

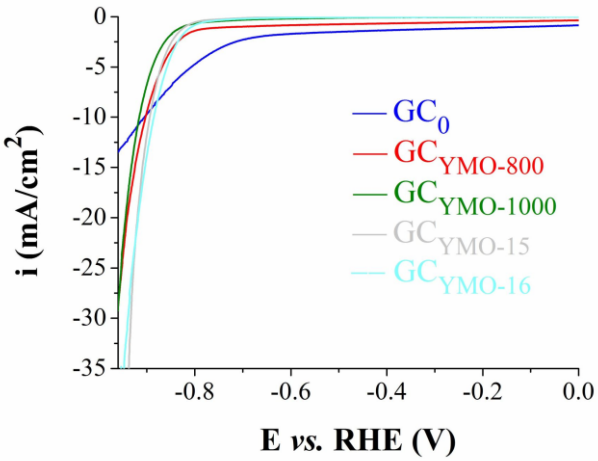

Figure 3. HER polarization curves recorded on the GC_0, $GC_{YMO\text{-}800}$, $GC_{YMO\text{-}1000}$, $GC_{YMO\text{-}15}$, $GC_{YMO\text{-}16}$ electrodes, in 1 M KOH solution, at v = 5 mV/s

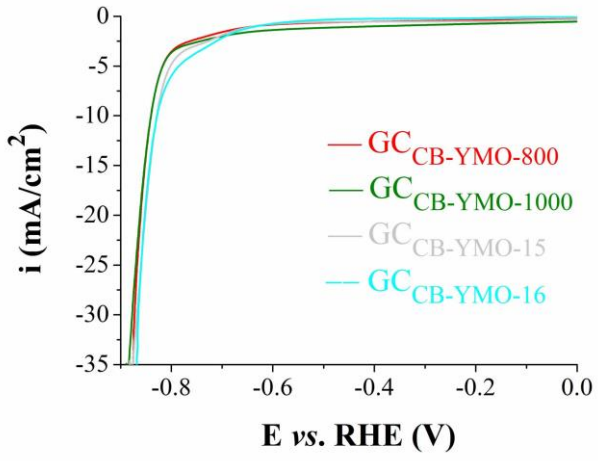

Figure 4. HER polarization curves recorded on the $GC_{CB\text{-}YMO\text{-}800}$, $GC_{CB\text{-}YMO\text{-}1000}$, $GC_{CB\text{-}YMO\text{-}15}$, $GC_{CB\text{-}YMO\text{-}16}$ electrodes, in 1 M KOH solution, at v = 5 mV/s

Conclusion

The OER and HER experiments performed in a strong alkaline medium (1 M KOH) on modified electrodes manufactured using $YMnO_3$ perovskite materials synthesized at different temperatures revealed that these electrodes are more suitable for the HER. The highest electrocatalytic activity was evidenced for the GC_{YMO-15} and GC_{YMO-16} samples. However, despite different temperatures being applied during the synthesis of the perovskites no significant differences in the HER electrocatalytic activity of the materials were observed. Compared to the samples obtained without using Carbon Black the ones containing this type of conductive carbon displayed lower HER overpotentials.

Acknowledgements

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