

HYDROGEN EVOLUTION REACTION ON RHENIUM MODIFIED PHOSPHATE Mo- AND PHOSPHATE W-BRONZE

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ABSTRACT

Phosphate molybdenum bronze (MoPB) and phosphate tungsten bronze (WPB) were synthesized and used as support for rhenium. Rhenium-modified bronze samples were applied at the surface of the glassy carbon electrode and tested for hydrogen evolution reaction. The electrodes were investigated by cyclic voltammetry and linear sweep voltammetry. The influence of carbon black on the electrochemical activity of starting bronze and Re-modified bronze samples was tested.

INTRODUCTION

Harvesting hydrogen energy represents a sustainable and renewable alternative to fossil fuels [1]. Hydrogen evolution reaction (HER) is a cathodic half-reaction of the electrochemical water splitting. It has been widely investigated in order to achieve hydrogen production at an industrial scale with economical acceptability. The new electrocatalysts are developed with the aim to enable HER at lower overpotentials.

The best-known HER electrocatalyst belongs to the platinum group metals. Platinum represents the state-of-the-art in this field, and the performance of new electrocatalysts is usually compared to the electroactivity of platinum under the same conditions. Due to the high cost and low abundance of platinum and the other elements from this group, new, more sustainable solutions are needed.

The effectiveness of electrocatalyst for HER depends on bonding energy employed in two successive and competitive processes: hydrogen adsorption and desorption. The hydrogen bonding strength of an efficient HER catalyst needs to be such to enable hydrogen bonding for the adsorption process and easy release of hydrogen in the next step. According to Trassati's volcano plot [3] rhenium has the required intermediate bonding energy value. So far, rhenium showed very low HER activity, but promising Re-intermetallic electrocatalysts have been investigated [4].

In this paper, the electrocatalyst based on phosphate molybdenum bronze (MoPB) and phosphate tungsten bronze (WPB) with and without added rhenium was investigated. The influence of carbon black on the efficiency of electrocatalyst for HER also was tested.

METHODS

Phosphate molybdenum and phosphate tungsten bronzes were obtained by thermal treatment of 12-tungstophosphoric, 12-molybdophosphoric heteropoly acids and their salts [5]. The defervescence speed is 10 °C per minute and it is constant until the temperature of Keggin's anion decomposition was reached (602 °C for PWB and 442 °C for PMoB), and then were held for 10 min at that temperature.

Incipient wetness impregnation method was used in order to obtain Re-bronze material. The bronze samples were heated up to 350 °C in order to remove adsorbed water and cooled to room temperature in a dry atmosphere before solution of sodium perrhenate was added. The samples were then dried at 90 °C to evaporate solvent and calcined at 350 °C for 1 h. The amount of rhenium introduced in this manner was 100 mg Re per 1 g of bronze.

The electrochemical activity of bronze samples was investigated using an Autolab PGSTAT302N (Metrohm-Autolab BV, Netherlands) and three-electrode cell with reference electrode Ag/AgCl in 3 M KCl, a platinum rod as a counter electrode and a glassy carbon electrode (GCE, diameter of 3 mm) coated with the catalyst ink as the working electrode. A catalyst ink was prepared by sonicating the bronze powder (with or without 10wt.% carbon black (Vulcan, XC 72)) in a mixture of 1 ml of isopropyl alcohol and 100 μ l of 5 wt. % Nafion solution. 5 μ l of prepared ink was applied on the surface of GCE. The electrodes were designated as WPB, MoPB, Re-WPB and Re-MoPB. The C is added at the end of the name if carbon black was used for the preparation of catalyst ink (WPB-C, etc)).

RESULTS AND DISCUSSION

The electrochemical performance of bronze-modified GCE in 0.5 M H₂SO₄ was studied by cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

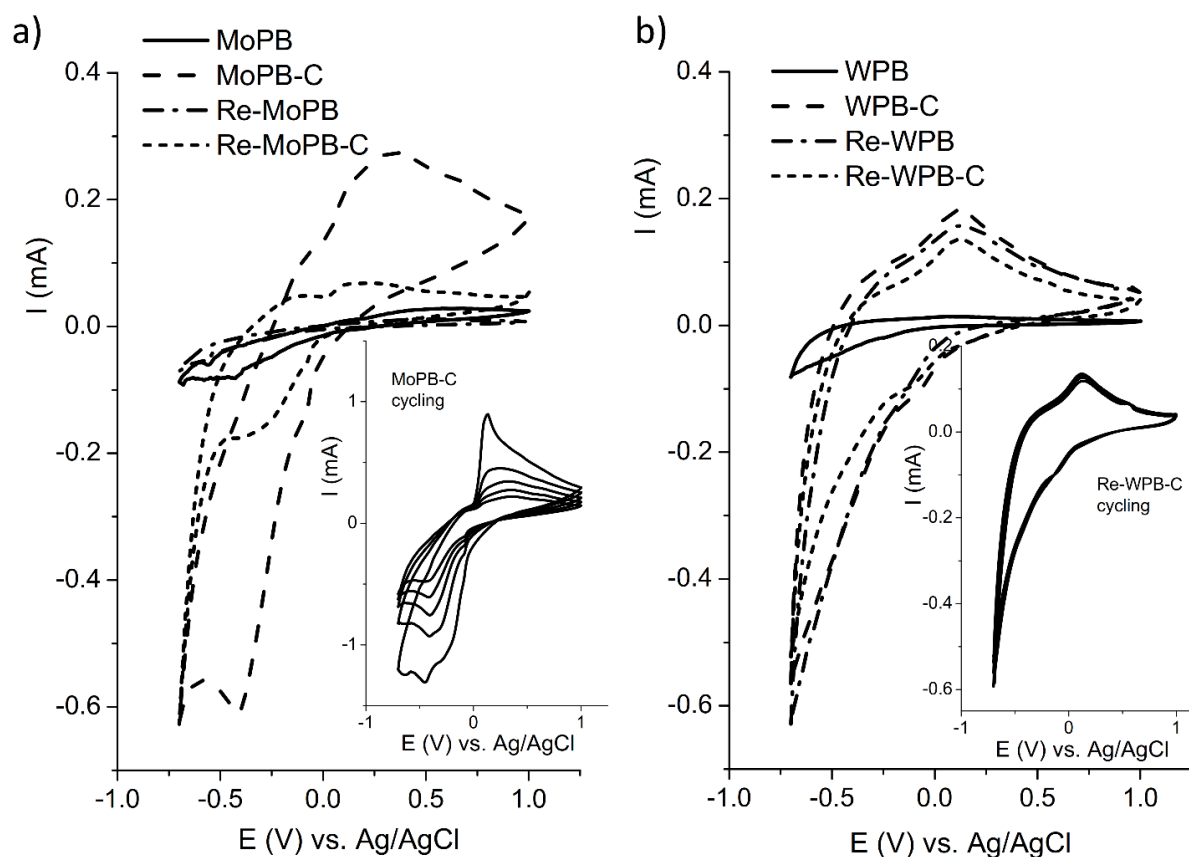


Figure 1. a) 5th cyclic voltammogram recorded in 0.5 M H₂SO₄ at a scan rate of 100 mV s⁻¹ on a molybdenum bronze samples modified GCE (inset: cycling of MoPB-C) and b) tungsten bronze samples modified GCE (inset: cycling of Re-WPB-C).

Cyclic voltammograms of molybdenum bronze material (Fig. 1a) showed that the addition of carbon black to the electrode composition showed the highest enhancement of current response, even better than the addition of rhenium and carbon black combined.

The addition of rhenium to MoPB did not have significant influence on the electrode activity. Mo-bronze electrodes were prone to corrosion in 0.5 M H₂SO₄ as can be seen in the inset of Fig. 1a, where first four cycles recorded for the MoPB-C electrode are presented. Cyclic voltammogram of tungsten bronze material (Fig. 1b) also showed the remarkable enhancing effect of adding carbon black. The addition of rhenium had a similar effect, while the addition of carbon black to the electrode that contained rhenium did not show any further enhancement. The electrodes based on tungsten were stable, without expressed corrosion behavior (inset in Fig. 1b). On the contrary, a slight increase in current was noticed with cycling that can be attributed to the conversion of surface hydroxide to oxides [6, 7].

HER activity of GCE modified with investigated bronze samples was assessed using linear sweep voltammetry. LSV plots of investigated bronze samples were recorded at a scan rate of 5 mV s⁻¹ are presented in Fig. 2a and 2b.

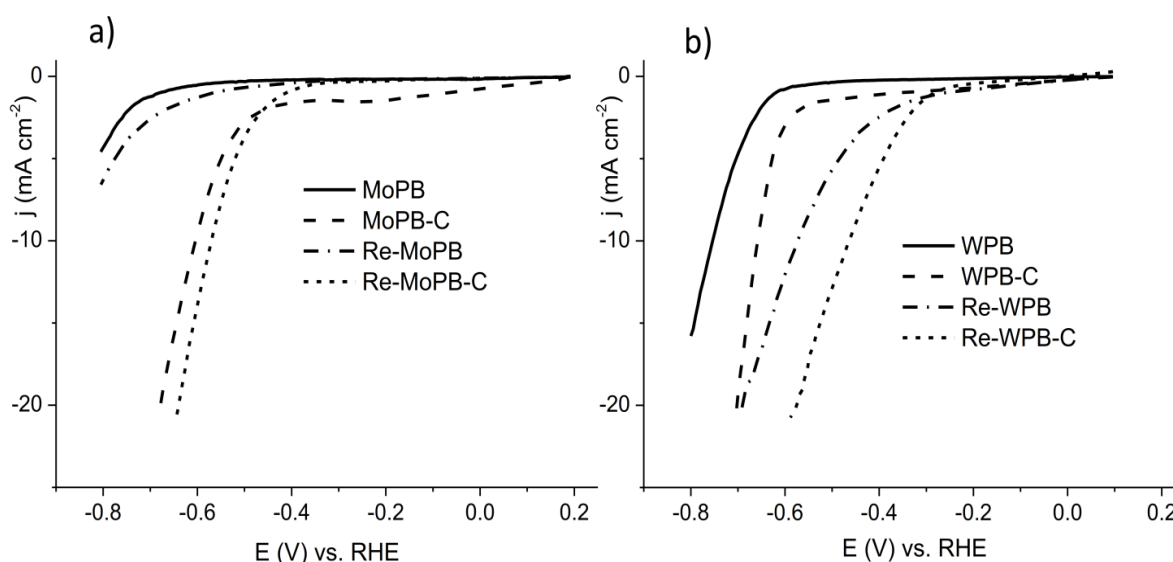


Figure 2. iR-corrected linear sweep voltammetry recorded at a scan rate of 5 mVs⁻¹ for molybdenum bronze electrodes (a) and tungsten bronze electrodes (b).

An overpotential of 605 mV and 571 mV was necessary to obtain 10 mA cm⁻² with MoPB-C and Re-MoPB-C. The activity of MoPB and Re-MoPB was too low to reach desirable value current density in a reasonable potential range. The addition of rhenium to molybdenum bronze increased the activity of bronze, but not in a significant degree. Commercial molybdenum oxide achieves the standard current density of 10 mA cm⁻² at an overpotential of 220 mV [8]. The tungsten-based samples reached 10 mA cm⁻² at an overpotential of 754 mV, 659 mV, 576 mV and 462 mV for WPB, WPB-C, Re-WPB and Re-WPB-C, respectively. The addition of carbon black lowered the overpotential for 95 mV while the addition of rhenium contributed to the lowering the overpotential for 178 mV in comparison to the starting tungsten bronze sample. The addition of carbon black to the Re-containing tungsten bronze sample contributed to further lowering of overpotential for another 114 mV. The overpotential of tungsten oxide for HER significantly depends on the structure of oxide material [9].

CONCLUSION

Phosphate molybdenum bronze and phosphate tungsten bronze were synthesized and used as a support for rhenium. The glassy carbon electrode was modified with bronze samples and tested for hydrogen evolution reaction. The addition of rhenium had a significant influence on W-bronze but not on Mo-bronze activity. The addition of carbon black significantly enhanced the performances of all investigated samples.

Acknowledgement

This work was supported by the Ministry for Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200026).

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