

## PRELIMINARY WATER SPLITTING STUDIES ON Ag AND GRAPHITE MODIFIED POROUS STRUCTURES, AS SUCH OR DECORATED WITH Pt PARTICLES

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### Abstract

Porous materials were obtained using polyether foam modified with Ag nanowires and graphite paste. Some of those modified porous structures were decorated with Pt particles *via* double step chronoamperometry. All porous materials were investigated in terms of their electrocatalytic activity for the oxygen and hydrogen evolution reactions (OER and HER) in alkaline medium, after they were inserted into supports made from sintered graphite (for the OER experiments) or Ag wire (for the HER experiments). Electrochemical stability tests were also performed. The results of the OER and HER experiments show that the most catalytically active porous structure is the one modified with graphite paste and Pt particles. Stability tests data show that the porous electrode based on this structure is very stable.

### Introduction

As the global energy demand and environmental concerns increase, there is growing interest for the energy conversion and storage domain, in which the role of hydrogen production processes cannot be overlooked. Electrochemical water splitting is one way of obtaining this useful gas and it involves two half-cell reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) [1].

In practice, in the presence of certain materials the energy required for the occurring of the two half-cell reactions decreases and, as a result, they take place at electrochemical potential values that are closer to the theoretical ones than those at which they would have occurred in the absence of the materials. They possess electrocatalytic properties for the OER and/or HER, and in the last few years several such structures with high catalytic activity have been reported in the scientific literature [2-6].

Herein, we present the preliminary results obtained using porous structures modified with Ag or graphite, as such or further decorated with Pt particles, to catalyze the OER and HER half-cell reactions in strong alkaline medium.

### Experimental

In order to manufacture porous electrodes, polyether foam cylinders ( $\phi = 12$  mm, height = 5 mm) were obtained from a polyether foam block (Jiejie, Beijing). After a cleaning stage they were covered either with Ag nanowires synthesized using a modified polyol method [7] in which the polyol was replaced with ethylene glycol (Honeywell) or with graphite paste obtained from graphite flakes (325 mesh particle size, Sigma Aldrich) that were ground using the ball mill for 12 hours. Some of the resulted modified porous structures were decorated electrochemically with Pt particles using two consecutive potential steps for different time intervals ( $E_1 = -0.5$  V and  $E_2 = 0$  V *vs.* SCE;  $t_1 = 5$  s and  $t_2 = 60$  s), in electrolyte solution obtained by adding 5 mM  $H_2(PtCl_6) \times 6H_2O$  solution (5 mL) in 0.5 M  $H_2SO_4$  solution (20 mL).

The reagents were purchased from Sigma Aldrich. For the HER experiments the porous structures were inserted into a silver support made from Ag wire processed in the form of a spiral (999 – 1,5 mm x 50 cm, Artkimia), while for the OER experiments a sintered graphite support was manufactured and coated with polyurethane resin, except for the area where the porous material was placed (Figure 1). These supports and the ensembles (modified porous structures introduced into the supports) are the electrodes investigated in the study, coded as specified in Table 1.

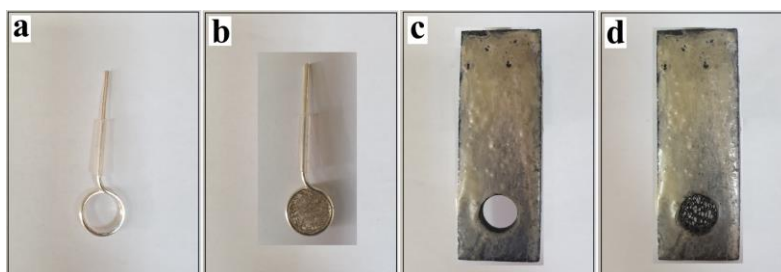


Figure 1. Ag wire support,  $\phi_{\text{int}} = 11$  mm and thickness = 3 mm (a); Ag wire support with Ag modified porous material (b); Graphite support,  $\phi_{\text{int}} = 11$  mm and thickness = 5 mm (c); Graphite support with graphite modified porous material (d)

Table 1. The codes for the studied support type electrodes and modified porous electrodes

<i>Electrode code</i>	<i>Details about the studied electrode</i>
S <sub>G</sub>	The graphite support
S <sub>G</sub> G	The graphite support with graphite modified porous structure
S <sub>G</sub> GP	The graphite support with graphite modified porous structure decorated with Pt particles
S <sub>A</sub>	The Ag support
S <sub>A</sub> G	The Ag support with graphite modified porous structure
S <sub>A</sub> GP	The Ag support with graphite modified porous structure decorated with Pt particles
S <sub>A</sub> A	The Ag support with Ag modified porous structure
S <sub>A</sub> AP	The Ag support with Ag modified porous structure decorated with Pt particles

The electrochemical experiments were performed using a glass cell equipped with three electrodes connected to a Voltalab PGZ 402 potentiostat (Radiometer Analytical). The counter electrode was a Pt plate ( $S_{\text{geom}} = 0.8 \text{ cm}^2$ ), the Ag/AgCl (sat. KCl) electrode was used as reference and each of the electrodes presented in Table 1 was used as working electrode. The measured potentials vs. the specified reference electrode were subsequently converted to the Reversible Hydrogen Electrode (RHE) using the standard equation [8]. The O<sub>2</sub> and H<sub>2</sub> evolution overpotentials were determined using equations (1) and (2). The electrolyte solution was 1M KOH (the potassium hydroxide was procured from Merck), the employed methods were linear and cyclic voltammetry, the recorded curves were iR-corrected using the Ohmic Drop Comp. option from the VoltaMaster 4 potentiostat software, the scan rate (v) was 5 mV/s, and prior to the HER experiments the electrolyte solution was deoxygenated by bubbling nitrogen 4.6 for 10 min.

$$\eta_{\text{O}_2} = E_{\text{RHE}} - 1,23 \quad (1)$$

$$\eta_{\text{H}_2} = |E_{\text{RHE}}| \quad (2)$$

Where,  $E_{\text{RHE}}$  = the RHE potential [V],  $\eta_{\text{O}_2}$  and  $\eta_{\text{H}_2}$  = the  $\text{O}_2$  and  $\text{H}_2$  evolution overpotentials [V].

## Results and discussion

**OER experiments.** The linear voltammograms recorded on the  $\text{S}_\text{G}$ ,  $\text{S}_\text{G}\text{G}$  and  $\text{S}_\text{G}\text{GP}$  electrodes are presented in Figure 2. At low current density values it is observed that an anodic signal is present on the polarization curve obtained using the  $\text{S}_\text{G}\text{GP}$  electrode. This signal corresponds to an oxidation process taking place simultaneously with the OER and makes it difficult to identify the overpotential values at which the oxygen evolution takes place in the potential range in which it is evidenced. The feature is absent from the other voltammograms and at high current density values there are no other processes taking place, on any of the traced curves, that overlap with the OER. However, despite the signal, it is clear that the electrocatalytic activity of  $\text{S}_\text{G}\text{GP}$  for the oxygen evolution reaction is significantly higher than that of the other two electrodes. The experimental results indicate that Pt particles decoration of the graphite modified porous structures has the effect of decreasing the  $\text{O}_2$  evolution overpotential.

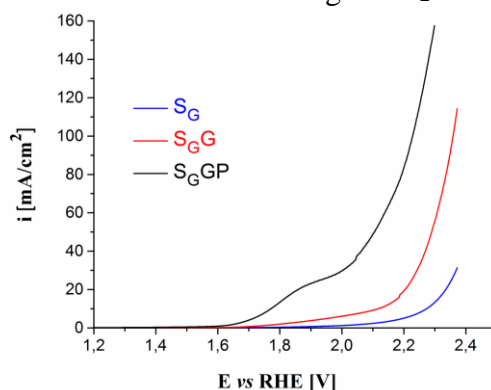


Figure 2. Linear voltammograms recorded on the  $\text{S}_\text{G}$ ,  $\text{S}_\text{G}\text{G}$  and  $\text{S}_\text{G}\text{GP}$  electrodes, in 1M KOH solution, at  $v = 5 \text{ mV/s}$

The three electrodes were further characterized in terms of their electrochemical stability using cyclic voltammetry. Figure 3 shows the 1<sup>st</sup> and 10<sup>th</sup> cycles obtained for each electrode, and it can be observed that the graphite support has the lowest electrochemical stability. This is because the maximum value of the current density reached during the  $\text{O}_2$  evolution when the first cycle is recorded changes significantly by the time the 10<sup>th</sup> cycle is obtained. The other two electrodes are much more stable and this means that the introduction of the porous structures into the graphite support leads to an increase in its stability.

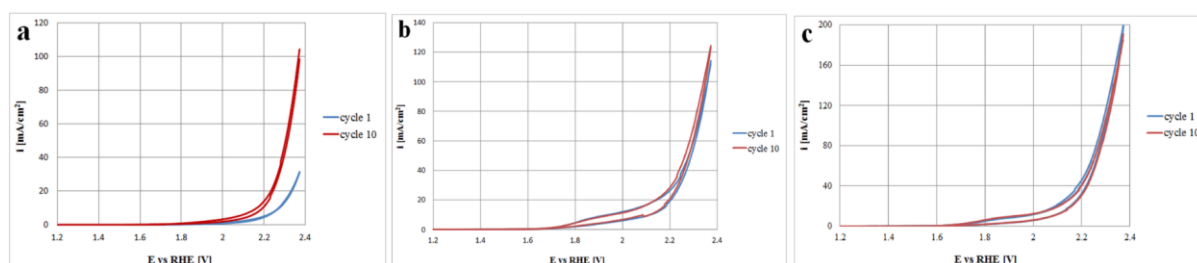


Figure 3. Cyclic voltammograms recorded on the  $\text{S}_\text{G}$  (a),  $\text{S}_\text{G}\text{G}$  (b) and  $\text{S}_\text{G}\text{GP}$  (c) electrodes, in 1M KOH solution, at  $v = 5 \text{ mV/s}$

**HER experiments.** The linear voltammetry curves shown in Figure 4a reveal that, out of the  $\text{S}_\text{A}$ ,  $\text{S}_\text{A}\text{G}$  and  $\text{S}_\text{A}\text{GP}$  electrodes, the most catalytically active for the HER is  $\text{S}_\text{A}\text{GP}$ , both at low current

density values, as well as at high ones. However, regarding the very high HER electrocatalytic activity of the  $S_{AGP}$  electrode, it is important to note that the graphite modified porous structures obtained and investigated in the present study display some disadvantages. Firstly, the paste covering them is not highly adherent to the polyether foam substrate, and secondly, after the immersion of the porous structures into the electrolyte solution and during  $H_2$  release it is strongly recommended to use a peristaltic pump to ensure the circulation of the solution through the pores for the removal of trapped gas bubbles. Addressing these issues will be the subject of future studies.

Figure 4b presents the curves obtained for the  $S_A$ ,  $S_{AA}$  and  $S_{AAP}$  electrodes during the HER experiments. It can be observed that the catalytic activity of these electrodes is not as high as that of  $S_{AGP}$ .

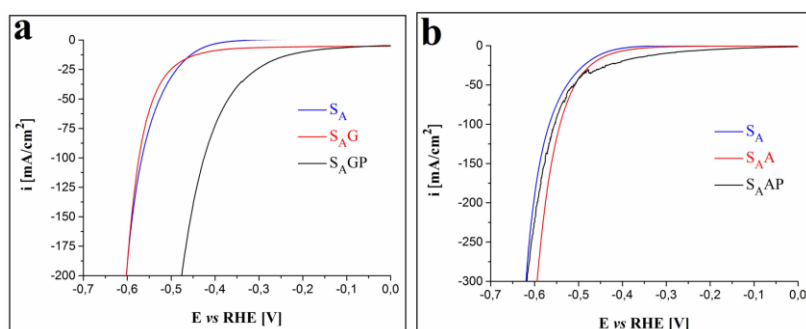


Figure 4. Linear voltammograms recorded on the  $S_A$ ,  $S_{AG}$  and  $S_{AGP}$  electrodes (a), as well as on the  $S_A$ ,  $S_{AA}$  and  $S_{AAP}$  electrodes (b), in 1M KOH solution, at  $v = 5$  mV/s

The electrochemical stability of the  $S_A$ ,  $S_{AG}$ ,  $S_{AGP}$ ,  $S_{AA}$  and  $S_{AAP}$  electrodes during the  $H_2$  evolution was also investigated. The first and 10<sup>th</sup> voltammetry cycles obtained on these electrodes are shown in Figure 5 and evidence the fact that the most stable ones are  $S_{AA}$  and especially  $S_{AGP}$ . In their case, the minimum value of the current density reached during the HER when the first cycle is recorded doesn't suffer any significant changes by the time the 10<sup>th</sup> cycle is obtained.

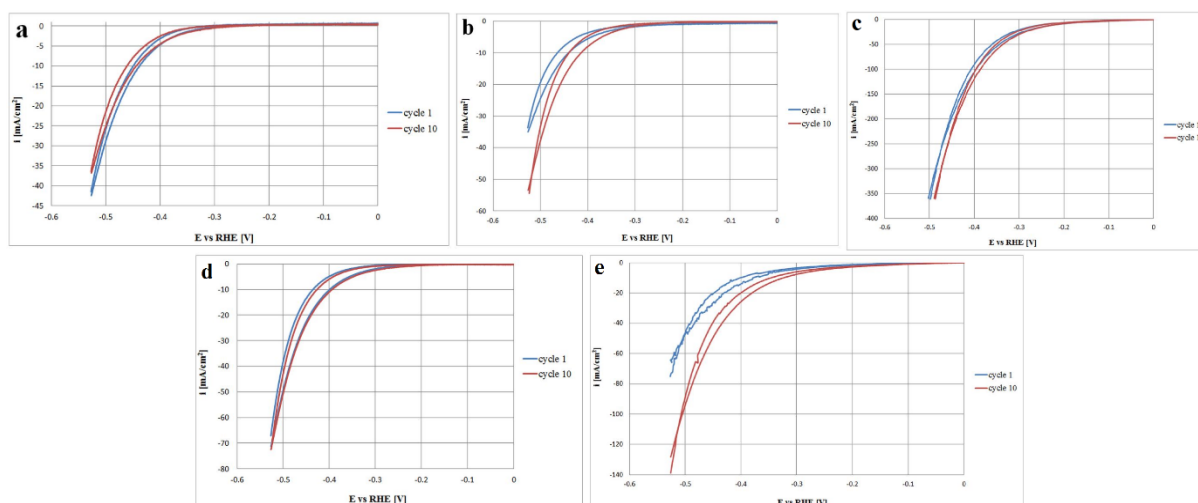


Figure 5. Cyclic voltammograms recorded on the  $S_A$  (a),  $S_{AG}$  (b),  $S_{AGP}$  (c),  $S_{AA}$  (d) and  $S_{AAP}$  (e) electrodes, in 1M KOH solution, at  $v = 5$  mV/s

## **Conclusion**

Using the experimental data obtained in strong alkaline medium during the OER and HER catalytic activity and electrochemical stability investigations of porous electrodes (modified with Ag, graphite, Ag and Pt, and graphite and Pt), it was possible to identify the most performant of them. In the case of the OER, the electrode consisting in a porous structure modified with graphite paste and Pt particles, inserted into the graphite support, is the most catalytically active. It also evidenced a high degree of stability during the electrochemical stability tests. The HER experiments aimed at finding the most catalytically active porous electrode outlined the same type of porous structure - but inserted into the Ag support. Furthermore, the electrochemical stability tests revealed this electrode to be the most stable. However, there are some issues that need to be addressed regarding the modified porous material in question and they will be the subject of future studies.

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