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W_2C-IL composite materials as promising electrocatalysts towards hydrogen evolution reaction in alkaline solution (P-16H-V)

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1. Introduction

Low-temperature water electrolysis (WE) technology is one of the most promising methods to obtain high-purity green hydrogen to use it as a new energy vector. However, the implementation of this model has several drawbacks (e.g., high economic cost of electrolyzers technology). This issue arises from the current necessity of platinum-based catalysts to get high efficiencies in the production of this gas. Therefore, researching of new non-noble materials with high catalytic activity towards hydrogen evolution reaction (HER) appears as a promising way to reduce the cost of WE.

In this sense, transition metal carbides (TMCs) are interesting due to their similarities with the platinum electronic structure close to the Fermi level. Then, similar catalytic performances are expected from these compounds towards HER [1]. However, some issues are still needed to be overcome to improve the activity of TMCs. This imply understanding the role of the particle size of the carbide as well as the existence of the respective transition metal oxides (TMOs) onto the surface of the TMCs materials [2].

On the other hand, ionic liquids (ILs) have also been studied as interesting compounds for many applications. In the case of electrocatalysis, the properties that make ionic liquids interesting for HER catalysis are good electrical conductivity and hydrophobic character. The latter is important for the integrity of an IL-based catalyst to face an electrochemical reaction in aqueous solution [2].

An important characteristic of HER is related to the kinetics of the reaction. There is a widely accepted mechanism for hydrogen electrogeneration that involves three possible steps for the entire process to take place. These steps are outlined below in basic media:

(1) $H_2O + e^- \rightleftharpoons H_{ad} + OH^-$

(2) $H_{ad} + H_2O + e^- \rightleftharpoons H_2 + OH^-$

(3) $H_{ad} + H_{ad} \rightleftharpoons H_2$

The reaction (1) is known as the Volmer step, and it involves the electroreduction of water producing an adsorbed hydrogen atom and a hydroxide anion. In the Heyrovsky step (2), another electrochemical reduction of a water molecule occurs near the previous adsorbed hydrogen to generate H_2. Finally, the mechanism can evolve by process (3), also known as the Tafel step. Here, two adsorbed hydrogen atoms chemically react to produce the hydrogen molecule [1,2]. Tafel slopes are usually employed to determine the rate-determining step (RDS) of the process. Thus, Tafel slope values of 120, 40, and 30 $mV \cdot dec^{-1}$ indicate that the RDS is the Volmer step, the Heyrovsky step, or the Tafel step, respectively.

The target of the current work is to synthesize new W_2C-ILs composites with high catalytic activity towards HER. Thus, W_2C materials have been prepared by a modification of the urea-glass route [3]. Then, composite materials have been achieved by a simple physical mixing of the W_2C phase and the IL [1,2]. The formation of composite materials has been corroborated by several physicochemical techniques and their activity towards HER has been characterized by spectroelectrochemical methods (differential electrochemical mass spectroscopy; DEMS). Moreover, DEMS has also been used to obtained reliable information on the kinetics of HER.

2. Experimental

2.1 Catalysts obtention

W_2C material has been prepared by a slightly modification of the urea-glass route [3]. Briefly, the appropriate amounts of WCl_4, EtOH and urea were mixed under argon atmosphere during 3 h to generate the urea-glass precursor. Then, it was heated up to 800 °C under argon flux in the tubular furnace. The resulting material is tagged as WC1. To obtain the composite material an IL (octylpyridinium hexafluorophosphate; OPy) was used [2]. The obtention of the composite material (WC1-OPy) has been achieved by an ultrasound-assisted physical mixing of the carbide with a 5 % w/w of OPy using isopropanol to obtain the catalytic ink.

2.2 Physicochemical characterization

X-ray diffraction (XRD) patterns were obtained using a diffractometer PANanalytical X'Pert Pro operating with Cu Kα radiation. Crystallite size was obtained from the Scherrer approximation and crystalline phase proportion was calculated by Rietveld refinement. Moreover, X-ray photoelectron spectroscopy (XPS; MultiLab 2000 equipped with a monochromatic Al Kα X-ray source) has been used to study the surface of the catalysts. Raman experiments were performed for the composite materials using an SPELEC RAMAN instrument equipped with a 532 nm laser.

2.3 Scpectroelectrochemical characterization

DEMS measurements were carried out in a three-electrode half-cell at room temperature controlled by an AutoLab (Metrohm Autolab) potentiostat. A hydrophobic PTFE membrane (Cobetter) was placed at the interface between the cell and the mass spectrometer chamber (Hiden Analytics). A graphite rod was used as a counter electrode, while the reference electrode was Ag/AgCl. 0.1 M NaOH was used as supporting electrolyte. All potentials in this work are referred to reversible hydrogen electrode (RHE). The working electrode consisted of 10 µL of the catalyst ink deposited as a thin layer onto a glassy carbon disc. Then, the working electrode was introduced into the cell at a controlled potential of 0.1 V and the potential was sweep towards cathodic potential at a scan rate of 1 $mV \cdot s^{-1}$ (LSV) while the spectrometer was set to detect the m/z = 2 (MSLSV).

3. Results

3.1 Physicochemical characterization

XRD difractograms and XPS spectra of the materials show the obtention of several phases for the synthesized materials identify as a mix of crystalline W_2C and W^0, but also amorphous WO_3 onto the surface. Rietveld refinement has revealed a W_2C/W^0 ratio of 45/55 % for WC1 and a crystallite size of 19 nm was obtained from Scherrer's approximation. Raman spectra presents the W-O bending (δ) and stretching (ν) vibration modes for the surface oxides. Thus, the addition of OPy to the composite materials is affecting these vibrations. This is revealed by a shifting of the δ(W-O) and ν_a(W-O) modes towards higher Raman shift. These signals also change in the width of the peaks (decreasing of the full width at half maximum of the peak; FWHM).

3.2 Spectroelectrochemical characterization

DEMS voltammograms (depicted in Figure 1) display the faradaic currents (top panel) and the ionic currents (m/z = 2) detected in the mass spectrometer during the potential sweep at the bottom panel. Thus, it is possible to avoid the contribution of the oxide reduction currents to allow an accurate onset determination for the HER. Indeed, WC1 has an overpotential of 120 mV while the addition of OPy to the WC1 downshift the overpotential to 65 mV. Moreover, Tafel slopes values have been obtained from MSLSVs. A slope values of 67 $mV \cdot dec^{-1}$ has been determined for WC1 changing to 38 $mV \cdot dec^{-1}$ for the composite material.

4. Discussion

The proposed modification of the urea-glass route allows the obtention of W_2C nanopowders (crystallite size = 19 nm). A close inspection of XPS spectra reveals an important quantity of WO_3 generated onto the surface of the material, probably produced by the exposure of the phase to the atmosphere. Thus, the oxide may hide the carbide surface, which is the site of interest for the HER. Nevertheless, the oxide is modified when the ionic liquid is added to the material. So, the mentioned change in the FWHM is related to an increase of the metal atoms exposure, and the upshifting of the peaks is related to changes in the length of the oxide vibration modes. Therefore, the addition of OPy affects the WO_3, changing the nature of the surface. These changes lead to the obtention of smaller particle size [2], but also to an increase of the catalytic activity of the composite material. Indeed, DEMS measurements reveal a difference of 55 mV of overpotential from WC1 to WC1-OPy. The presence of IL is also conditioning the kinetics of the reaction. Thus, Tafel slope values for the reaction (obtained from MSLSVs to avoid the oxide contributions that might exist in the LSVs) present a clear change in the RDS from a mix of Volmer/Heyrovski steps for the WC1 to a pure Heyrovski step for the composite material.

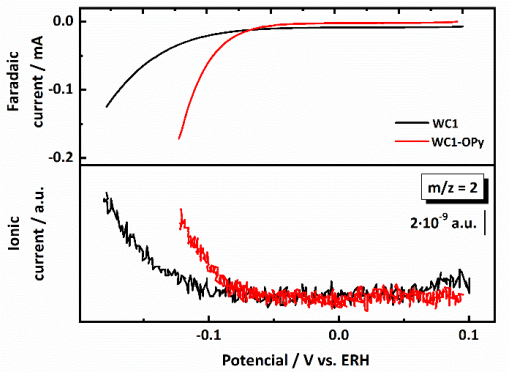

Fig. 1. LSVs (top panel) and MSLSVs (bottom panel) recorded for the studied materials in 0.1 NaOH solution at a scan rate of 1 $mV \cdot s^{-1}$.

5. Conclusions

The route proposed to generate W_2C-IL composite materials is proposed to be acceptable for the obtention of electrocatalyst with high catalytic activities towards HER. Thus, the addition of OPy to the carbide boosts the catalytic activity and change the RDS of the HER. This is probably caused by an interaction of the IL with the surface oxides of the material, producing a different reaction surface which is more active than the starting material towards HER.

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