

2D MXenes as catalysts for hydrogen evolution and oxygen reduction reactions (P-22H)

S. Delgado, Y. Remedios-Díaz, J.C. Calderón*, M.C. Arévalo, G. García, E. Pastor**

Instituto de Materiales y Nanotecnología, Departamento de Química, Universidad de La Laguna, AP 456, 38206, La Laguna, Santa Cruz de Tenerife, España

(* Pres. author: jcaldero@ull.edu.es

(** Corresp. author: epastor@ull.edu.es

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1. Introduction

The implementation of renewable energy sources constitutes a way to decrease hazardous chemical emissions such as CO₂, NO and SO_x, generated from fossil fuels combustion [1]. In this regard, water electrolysis is an alternative to produce hydrogen and oxygen as fuel and comburent, respectively, to feed proton exchange membrane fuel cells (PEMFCs), thus providing a possibility to replace fossil fuel-based energy, bearing in mind that no pollutants are involved in this process [2].

Traditionally, platinum group metals (PGM)-based materials are employed as electrodes in both water electrolyzers and PEMFCs, since they exhibit high performances. A well-known drawback associated to these materials is their high cost and scarcity, forcing the designing of novel catalysts with low/zero content of PGMs [3]. Among these materials, doped/modified-reduced graphene oxides, transition metal dichalcogenides, atomic quantum clusters and MXenes have stood out because of their novelty and low cost [4].

In particular, and due to their catalytic properties, 2D MXenes have rise as an alternative in the last years, to replace PGMs from the electrodes utilised in the mentioned applications [5]. 2D MXenes are metal (M = Ti, Mo, V, etc.) carbides or nitrides compounds consisting of few atoms' thick layers, which form stacks after deposited on different substrates [6]. Furthermore, they are transparent, stable, and allow rich chemistry, making them suitable for several electrocatalytic applications, including hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) [6]. MXenes are usually obtained following a top-down strategy, which consists of the etching of MAX phases, with M as an early transition metal (Ti, V, Cr, Mo, etc.), A as Al, Si, Sn or In and X as C or N. It means that A is removed to form the corresponding MXenes [7].

In this work, Ti₃C₂, Mo₂TiC₂ and V₄C₃ MXenes are synthesised from their commercial MAX phases and physically/electrochemically characterised to determine their suitability as catalysts for the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR).

2. Experimental

2.1 Synthesis of MXenes

The preparation of MXenes was addressed by etching of the corresponding commercial MAX phases, immersing these phases in hydrofluoric acid or LiF/HCl mixture at room temperature. Further washing, filtering, and drying of the

products were performed to obtain the MXenes Ti₃C₂, Mo₂TiC₂ and V₄C₃.

2.2 Physicochemical characterisation

A surface and structural characterisation of the obtained materials was performed applying X-ray techniques (XRD, EDX, XPS), microscopies (SEM, TEM), and spectroscopies (infrared, Raman) to determine the composition, morphology and crystallinity of the synthesised materials.

2.3 Electrochemical characterisation

HER and ORR activities of MXenes were evaluated by polarisation curves and rotating disk electrode (RDE), respectively, in 0.5 M H₂SO₄ as supporting electrolyte. A three-electrodes cell was used, controlled by an Autolab® PGSTAT302N potentiostat-galvanostat. A glassy carbon bar acted as counter electrode and the reference electrode was a reversible hydrogen electrode (RHE) in 0.5 M H₂SO₄. For both reactions, a rotating disk electrode-setup (RDE, Pine Research Instrumentation) with a glassy carbon (GC) disk supporting the synthesised catalysts acted as working electrode.

3. Results

3.1 Preparation of MXenes and physicochemical characterisation

First, Mo₂TiC₂ was prepared using the LiF/HCl mixture procedure. The XRD pattern for this material (Figure 1) shows a peak located around 7 2θ degrees (orange box) that verifies the formation of a laminar 2D structure. However, the peaks located between 33 and 46 2θ degrees (pink box) indicate the presence of residual MAX phase, suggesting an incomplete etching during the synthesis. In order to improve the route, HF was used as etching agent and in this case the MAX phase was mostly removed (Figure 1).

The last procedure was used to obtain Ti₃C₂ and V₄C₃. According to XRD patterns (Figure 1), the synthesis was optimal for the first one but in the case of the V material some residues are still present.

3.2 Electrochemical characterisation

HER was evaluated on the MXenes and MAX phases and the results are depicted in Figure 2. All the MXenes (dashed lines) displayed more positive onset potentials and potentials at 10 mA cm⁻² than those developed by their corresponding MAX phases (full lines), indicating that the 2D carbides are more active toward HER than the precursors. In

particular, Mo_2TiC_2 presents a high activity. Surprisingly, similar results were obtained for this material for both preparation routes, that is, in the presence of residual MAX phase.

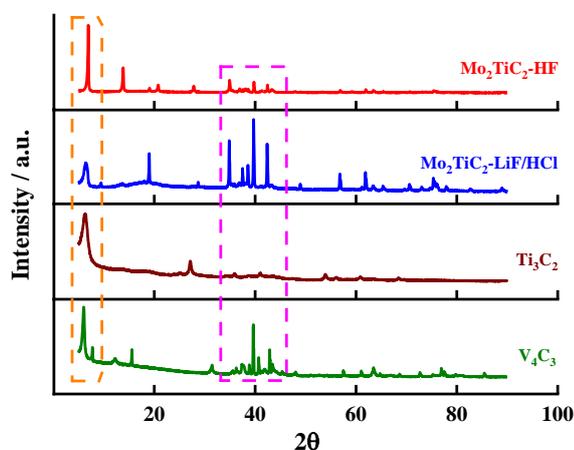


Fig. 1. XRD patterns of the synthesised 2D MXenes.

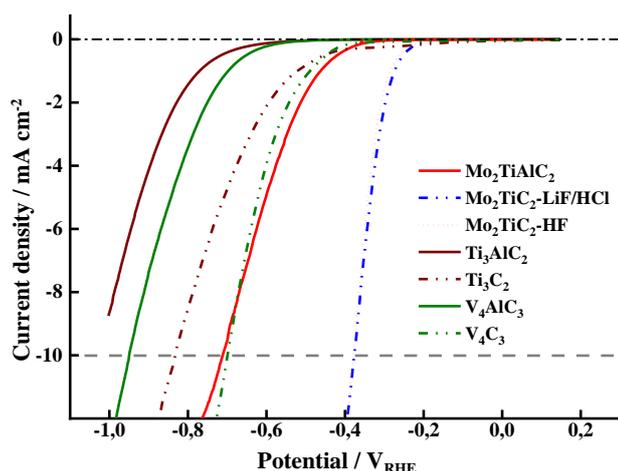


Fig. 2. Polarisation curves obtained for the HER reaction performed on the synthesised catalysts and MAX phases. Supporting electrolyte: 0.5 M H_2SO_4 . Scan rate: 2 mV s^{-1} .

On the other hand, the performance for the ORR is quite low both in acid and alkaline media for all catalysts. Hybrid materials with metal organic frameworks (MOFs), first with the ZIF67, were prepared increasing the response.

4. Discussion

From the results presented in this work, it is possible to suggest that the synthesis routes employed are suitable to synthesise 2D MXenes, since the reflections observed in the XRD patterns demonstrated the presence of layered structures, because of the etching step. However, it is necessary to improve the procedure used to remove A from the MAX phases, bearing in mind that some reflection peaks corresponding to the precursors are still detected in the XRD patterns.

On the other hand, the polarisation curves for the HER performed in acidic media indicated that the remove of A produces an increase of the activities in the MXenes with

respect to the corresponding MAX phases. However, it seems that the improvement of the performance is related to the 2D structure and the presence of residues of the precursors, that is, a complete etching is not needed to generate an active material.

This good behaviour towards the HER is not obtained for the ORR, even in alkaline media that usually present higher activity for this reaction. For this reason, hybrid materials are prepared. Preliminary results with ZIF67 has shown a notorious improvement of the response.

5. Conclusions

2D MXenes have been obtained from the chemical etching of MAX phases containing Mo, Ti and V as transition metals. XRD analysis suggests the obtaining of layered structures after the etching and removal of A element, especially when HF is employed during the etching treatment. Furthermore, the MXenes developed higher HER activities in terms of onset and 10 mA cm^{-2} -potentials than those of the MAX phases. Results for the ORR are not relevant, but the preparation of hybrid materials with MOFs appears as a possibility to be explored.

Acknowledgements

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