3DOM $Mn_{0.5}Ni_{0.5}Co_2O_4$ Electrocatalyst for Anion Exchange Membrane Water Electrolysis (O-3H-V)

Angela Caprì[1], José Béjar[2], Lorena Álvarez Contreras[2], A. Martinez Lazaro[3], J. Ledesma Gárcia[3], Irene Gatto[1], Vincenzo Baglio[1] and L.G. Arriaga[1,4]**

[1] *Institute for Advanced Energy Technologies "Nicola Giordano" - CNR-ITAE, Via S. Lucia sopra Contesse 5 - 98126 Messina, Italy*

[2] *Centro de Investigación en Materiales Avanzados S. C., Complejo Industrial Chihuahua, Chihuahua, Chihuahua C. P. 31136, México.*

[3] *División de Investigación y Posgrado, Facultad de Ingeniería, Universidad Autónoma de Querétaro, 76010, Santiago de Querétaro, México.*

[4] *Centro de Investigación y Desarrollo Tecnológico en Electroquímica, 76703, Santiago de Querétaro, México.*

Keywords: Hydrogen production, oxygen evolution reaction, water splitting, anion exchange membrane.

1. Introduction

Water splitting is a process that enables the production of hydrogen by direct water decomposition in its elements. The energy required to cleave H-O-H bonds can be supplied by different power sources: electrical (current), thermal (heat), or light (electromagnetic radiation). Generally, the difference in water splitting processes is made whenever one or another type of energy source is applied to conduct the reaction, referred to as electrolysis, thermolysis, or photolysis[1]. Electrolytic water splitting is driven by passing the electrical current through an electrolyser, where conversion of the electrical energy to chemical energy takes place at the electrode-electrolyte interface through charge transfer reactions. These devices have attracted attention because of their high energy density, safe operational mode, and high abundance of water. However, this promising energy storage technology is limited by the sluggish kinetics of oxygen evolution reaction (OER) [2]. The current benchmark of electrocatalysts for OER applications is based on precious metals (Ir and Ru) and their oxides (IrO_2 and RuO_2) [3]. Yet, their low abundance, high cost, poor chemical stability in alkaline media obstruct them from the tenable application. Therefore, it is vital to develop a more efficient, stable, and low-cost non-noble electrocatalyst for OER. Over the past few years, remarkable efforts have been devoted to explore electocatalysts based on transition metals oxides (TMOs), which have been proven to present high catalytic activity towards OER [5, 6]. In addition, TMOs are environmentally friendly and abundant in the Earth's crust, and mixtures of TMOs can be made to promote synergistic effects to overcome typical issues of TMOs, such as poor electrical conductivity or limited stability. In this work, the synthesis of a trimetallic spinel ($Mn_{0.5}Ni_{0.5}$ Co_2O_4) with a 3DOM morphology using a poly– methylmethacrylate (PMMA) template made of spheres with an average diameter of 160 nm is reported [4]. This material was physicochemically characterized by different techniques to corroborate the incorporation of Mn and Ni into the Co_3O_4 crystal structure and the formation of the 3DOM morphology. This material was evaluated in an electrolyser based on an anion exchange membrane (FAA3-50 from FumaTech) as the electrolyte. Additionally, the performance was compared to that obtained using benchmarked IrO_2 electrocatalysts.

2. Experimental

Anodes were prepared using $Mn_{0.5}Ni_{0.5}$ Co_2O_4 samples with 20 wt% ionomer, spraying the anodic catalytic ink directly on the FAA3-50 membrane, with a final loading of 3 mg/cm^2. The cathodes were prepared by mixing, in an ultrasonic ice bath for 30 minutes, a commercial (Alfa Aesar) 40 wt.% Platinum on carbon (Pt/C), as the electro-catalyst, and the FAA3 ionomer (with an amount of 20 wt.% of the total solid content). The ink was deposited by spray coating technique onto the Sigracet 25-BC Gas Diffusion Layer (SGL) to obtain a gas diffusion electrode (GDE). Anode and cathode were made with geometrical area equal to 5 cm^2. Before the assembly, the anodes and cathodes were exchanged, separately, in a 1 M KOH solution for 1 h. Then they were coupled by a cold-assembling procedure to realize a membrane-electrode assembly (MEA) and tested in an electrolyser. The electrochemical characterizations were carried out in single cell configuration with a size of 5 cm^2, in terms of polarisation curves, in a temperature range between 30°C and 60°C and atmospheric pressure. A 1 M KOH solution was supplied by a peristaltic pump to the anode compartment, at a flow rate of 5 ml/min. The electrochemical measurements were carried out using a potentiostat-galvanostat device PGSTAT302N equipped with an FRA module (Autolab). I-V curves were performed at a scan rate of 5 mV/s.

3. Discussion

A novel and highly durable electrocatalyst for water splitting are presented. This work demonstrated the feasibility of synthesizing a trimetallic spinel with a 3DOM morphology

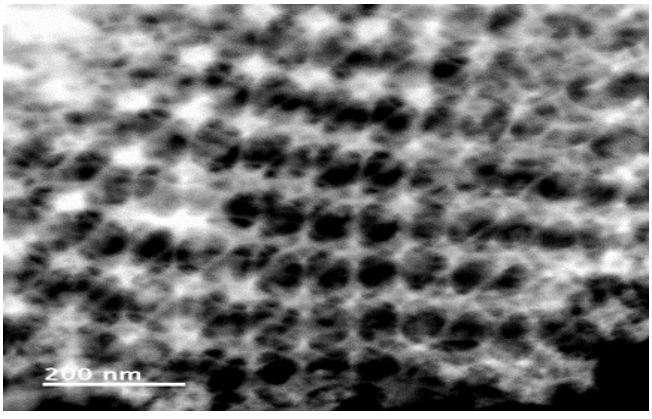

Figure 1 TEM images of 3DOM $Mn_{0.5}Ni_{0.5}Co_2O_4$ Electrocatalyst

The synthesis method allows obtain spheres with diameters close to 160 nm allowed us to obtain a surface area of 65.73 $m^2 g^{-1}$, a kind of netting is formed as shown in Figure 1. Once the electrodes are prepared, the catalyst samples were evaluated in an electrolyser, showing a very high current density (2.5 mA cm^{-2}) at 2.2 V (Figure 2). This value is even better than that obtained with an IrO_2 as anode catalyst (2 A cm^{-2}).

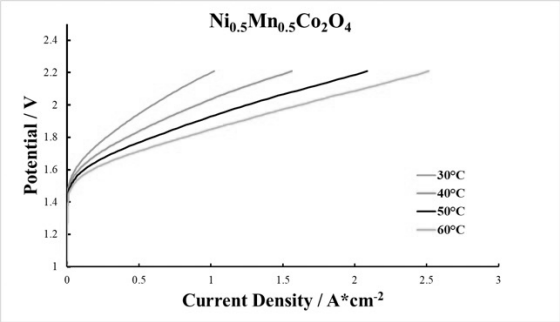

Figure 2 Linear sweep voltammetry at diferrent temperatures the MEA equipped with $Mn_{0.5}Ni_{0.5}$ Co_2O_4 anode catalyst.

4. Conclusions

The $Mn_{0.5}Ni_{0.5}$ Co_2O_4 electrocatalyst with a 3DOM morphology showed an excellent actitvity towards OER in an anion exchange membrane electrolyser, paving the way for decreasing the cost of green hydrogen production.

Acknowledgements
The authors thank the Italian ministry MUR for funding through the FISR2019 project AMPERE (FISR2019_01294).

References

[1] M. Tahir, L. Pan, F. Idrees, X. Zhang, L. Wang, J.J. Zou, Z.L. Wang, Electrocatalytic oxygen evolution reaction for energy conversion and storage: A comprehensive review, Nano Energy. 37 (2017) 136–157.

[2] K. Feng, D. Zhang, F. Liu, H. Li, J. Xu, Y. Xia, Y. Li, H. Lin, S. Wang, M. Shao, Z. Kang, J. Zhong, Highly Efficient Oxygen Evolution by a Thermocatalytic Process Cascaded Electrocatalysis Over Sulfur-Treated Fe-Based Metal–Organic-Frameworks, Adv. Energy Mater. 10 (2020) 1–8.

[3] A.S. Arico, S. Siracusano, N. Briguglio, V. Baglio, A. Di Blasi, V. Antonucci, Polymer electrolyte membrane water electrolysis: status of technologies and potential applications in combination with renewable power sources, J. Appl. Electrochem. 43 (2013) 107–118.

[4] J. Béjar, L. Álvarez, F. Espinosa, J. Ledesma, N. Arjona, L. Gerardo, Electrochimica Acta Zn – air battery operated with a 3DOM trimetallic spinel ($Mn_{0.5}Ni_{0.5}Co_2O_4$) as the oxygen electrode, 391 (2021).

[5] X. Wang, M. Qin, F. Fang, B. Jia, H. Wu, X. Qu, A.A. Volinsky, Solution combustion synthesis of nanostructured iron oxides with controllable morphology, composition and electrochemical performance, Ceram. Int. (2017) 0–1.

[6] J. Jiang, C. Zhang, L. Ai, Hierarchical iron nickel oxide architectures derived from metal-organic frameworks as efficient electrocatalysts for oxygen evolution reaction, Electrochim. Acta. 208 (2016) 17–24.