$NiFe_2O_4$ hollow spheres electrocatalysts for anion exchange membrane electrolysers (O-7H-V)

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1. Introduction

Among various energy systems that work through electrochemical reactions, electrochemical water splitting is today one of the most efficient and reliable methods. It is one of the greenest ways to produce pure hydrogen without any greenhouse gases which makes it a sustainable, pollution-free, eco-friendly method when powered by renewable sources such as wind or solar. Among the different electrolysis types, low-temperature systems (< 100°C) are more promising since they allow flexibility, high current density, and long-term durability, depending on the employed technology. Liquid alkaline electrolysis is the most developed and mature technology [1]; the advantages are related to the cost since the high pH allows the use of platinum group metal (PGM)-free catalysts [2–4] whereas the disadvantages include a low current density due to the more considerable physical distance between electrodes, and maintenance costs associated with the caustic electrolyte [5–7]. For proton exchange membrane (PEM)-based systems, the electrodes are physically in contact with a polymeric membrane to form a membrane-electrode assembly (MEA). The zero-gap approach can improve performance by minimizing the electrode distance and ohmic loss [8,9]. Compared with liquid alkaline systems, the PEM electrolysis is more recent. Still, it allows for a higher operating current density, better efficiency and dynamic behaviour in terms of rapid response, fast start-up and broader operating range. PEM electrolysis technology is favourite in terms of safety and high gas purity with the possibility to work under high differential pressure conditions. However, the need for PGM catalysts and component coatings can increase costs [10]. Compared with the other technologies, AEM electrolysis systems have less commercial history and are developmental, but they share similarities with liquid alkaline and PEM electrolysis [11]. As with PEM systems, AEM electrolyzers use a zero-gap approach, but the membrane conducts hydroxide [12]. AEM electrolyzers should combine the advantages of both the liquid alkaline and PEM technologies in terms of the higher purity of generated H_2, better efficiency and dynamic behaviour [13,14]. Furthermore, using an alkaline solution of lower concentration, they are less prone to corrosion, and, finally, they can use inexpensive catalysts [15]. For the water splitting process, two reactions are fundamental: the anodic oxygen evolution reaction (OER) and the cathodic hydrogen evolution reaction (HER). To satisfy the efficiency of both reactions, the research to develop new and functional catalysts is mandatory. In particular, the OER is the rate determing step and requires very active electrocatalysts to decrease the overpotential for this reaction. Several proposals emerged in recent years through which various combinations of electrocatalysts were evaluated in a half-cell configuration to investigate the catalytic activities for the reactions occurring at the electrodes. Even noble metal-based catalysts deposited on polymeric membranes were tested in the electrolyzers. Abundant availability, strong activity, cost-effectiveness, and substantial electrocatalytic activities of transition metals make them an alternative to replace the noble-metal electrocatalysts.

The use of transition metals in an oxide form have been widely developed in recent years. Simple structures such as Co_3O_4 [16], NiO QDs [17] and MnO [18] with overpotentials of 339, 320, 540 mV, respectively, prove to be acceptable competitors in the electro-oxidation of water. The window of opportunity opened by these variants of transition metals in the OER has led to incorporate these into nanostructures such as NiCo nanosheets, which yielded 332mV results compared to their Ni-Co oxide bulk structure with an overpotencial close to 340 mV [19]. Nanostructured morphologies offer the advantage of larger amounts of active sites for OER; this advantage has increasingly led to the development of 2D and 3D nanostructured materials which in theory provide a greater number of active sites exposed to the OER. This is the case of $NiCo_2O_4$ hollow microcuboids [20] with 290 mV overpotential and a tafel slope of 53 mV dec^{-1} very close to IrO_2. Some of these promising mixed oxides such as 3D $NiFe_2O_4$ hollow spheres have been brought to real-life conditions in water electrolysis micro-fuel-cell tests where significant micro-scale hydrogen production of 2.5 $x10^{-5}$ mg s^{-1} [21]. This work explores the activity in an anion exchange membrane electrolyzer of a 3D $NiFe_2O_4$ with hollow spheres morphology.

2. Experimental

Anodes were prepared mixing for 30 minutes, under sonication, an exact amount of the catalysts with 20 wt.% of ionomer. The obtained ink was then applied by spray coating technique directly onto the FAA3-50 membrane, with a loading of 3 mg/cm^2, forming a catalyst-coated membrane (CCM). Cathodes were made using a commercial Platinum on carbon. The ink was deposited by spray coating technique onto the Sigracet 25-BC Gas Diffusion Layer (SGL) to obtain a gas diffusion electrode (GDE) with 0.5 mg/cm^2 Pt/C. Ni felt was coupled to the CCM (at the anode side) for all the tests performed.
The CCM and cathodes were previously exchanged in a 1M KOH solution for 1h before assembling them.
Electrochemical characterizations were carried out in a temperature range between 30 - 60°C at atmospheric pressure. Electrochemical measurements were realized 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. An alkaline solution (KOH 1M) was supplied by a peristaltic pump to the anode section of the single cell, with a flow rate of 5 ml/min.

3. Discussion

Once the electrodes were prepared, the $NiFe_2O_4$ sample was evaluated in an anion exchange membrane electrolyzer, using a FAA3-50 membrane (from FumaTech). The unique morphology of the hollow spheres makes the catalyst highly active for the OER, thus it showed excellent performance (Figure 1). A current density higher than 2.5 A cm^{-2} was reached at 2.2 V, larger than the value obtained with IrO_2 catalyst (2 A cm^{-2}). Further results will be presented at the conference and analysed in details.

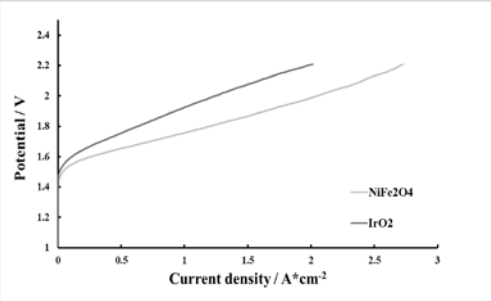

Figure 1 Linear sweep voltammetries for the cells based on $NiFe_2O_4$ hollow spheres and IrO_2 at the anode.

4. Conclusions

A $NiFe_2O_4$ catalyst characterized by a hollow sphere morphology showed very promising performance in an AEM electrolyzer, compared with a commercial IrO_2 catalyst.

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