

Design of the experiments for the selection of potential electrocatalysts for both AEM Electrolyzers and Redox Flow Batteries

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Abstract. Both hydrogen production by anion exchange membrane water electrolysis (AEMWE) and energy storage by redox flow batteries (RFB) are promising technologies for dealing with the intermittency of green electricity generation. We investigated on the possibility of using the same electrocatalyst in both the systems in order to reduce production costs if industrial scale electrochemical devices are to be constructed. In this work we selected spinel-based nanostructures as promising catalysts for both oxygen evolution reaction (OER) in AEMWE and positive electrode improvement in Vanadium RFB, and design a complete experimental campaign to choose the best material.

1 Introduction

Declining gas and oil reserves, as well as global warming, have led countries to use clean and renewable energy sources. The intermittency of sustainable electricity generation poses issues of its optimal utilization and storage, leading to the search for energy carriers as hydrogen, and electricity storage systems like batteries.

The demand of hydrogen for chemical industry and transportation is increasing, so hydrogen production by water electrolysis using sustainable electricity is receiving a great attention. Among the different technological solutions, AEMWE is very promising, but it still needs to be fully developed at industrial scale, including energy efficiency, membrane stability, stack durability, robustness, ion conductivity, and cost reduction. Having the ability to operate under alkaline conditions makes AEMWE ideal for use with non-noble metals, but due to their insufficient OER and hydrogen evolution reaction (HER), non-noble metal electro-catalysts perform poorly. To overcome this barrier, new materials for OER and HER electrodes must be developed [1]. As non-noble OER catalysts, metal oxides such as CoO_x, MnO_x, NiO_x, NiFe-O_x, FeOOH have been studied. Reduced Graphene Oxide (rGO), three-dimensional Graphene (3DG) and MXene nanocomposites are expected to have a high

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specific surface area, allowing more active sites while reducing the collapsing of carbon-based active particles, thereby improving catalytic stability.

RFBs are an advanced energy storage system born from the growing demand to mitigate fluctuations in energy production and stabilize power grids. The main advantage of RFBs is the independence of the stored capacity from the power delivered. Vanadium redox flow batteries (V-RFB) are already available at industrial scale, and currently, their efficiency is about 70-85%. In order to improve efficiency and durability at large scale, research on electrode materials is still in progress. The introduction of metals, metal oxide particles and carbon-based materials (nanotubes, nanofibers) on the electrode surface acting as additional active sites can improve the overall electrode conductivity and catalytic activity [2].

The aim of this work, carried out within the industrial research project NEMESI, funded by EU-PNRR (ID: RSH2B_000002) is to select new electrocatalysts for Anion Exchange Membrane Water Electrolyzers (AEMWE) that can be also adopted inside V-RFBs. Even if the selected materials could not be contemporary the optimal ones for both the two technologies, the advantage of adopting the same production process to synthesize the materials is dramatically important at industrial scale.

We decided to start by considering a standard spinel structure of the type AB_2O_4 . This choice for the AEMWE OER electrode is largely suggested in the literature [3]. Our first investigation provides the modification of the spinel structure by using two cations, like $Ni_xFe_{1-x}Co_2O_4$, to synergistically optimize physical pore structure and increase the formation of active species on the surface of catalyst. The activity of these metals as OER catalysts, based on both bond strengths and adsorption energy is $Fe < Co < Ni$ [4].

To decrease the overpotential and improve cycle performance, oxygen in the spinel structure can be subsequently replaced with sulphur. Sulphur will create a new structure with the three cations which can increase conductivity, cycle stability and reactive sites. Also, it makes the electrocatalyst suitable for larger pH ranges, having a direct impact on AEMWE performance.

Combining the previous modified spinels with graphene-based materials can still increase the specific surface area, providing more exposure to the active sites and abundant pathways for ion (or electrolyte) diffusion. Also, the established heterojunction interfaces facilitate chemisorption of both the intermediates, thus improving the overall water splitting activity. Among the graphene based materials both rGO and 3DG [5-6] have been proposed as high-performance bi-functional electrocatalysts for OER, showing good properties and efficiency.

As regards the V-RFB, only a few works report on the use of spinel based Ni-Co oxides. In [7] NiO/Co_3O_4 and spinel-type $NiCo_2O_4$ as thin nanobelts are investigated, showing high specific capacitance and low resistance. A binary nickel cobalt oxide is proposed in [8] as a performant positive electrode on graphite felt for V-RFB. However, since there are many studies on the excellent performance of Ni, and Co oxides as supercapacitors and on the modification of both the positive and negative electrodes with nanorods, nanobelts, rGO and 3DG, our efforts in searching for a possible unique electrode material for both the applications is fully justified.

In this work we report the experimental design related to the selection of the potential best electrocatalysts and the details on their synthesis.

2 Materials and methods

All the chemicals are from Carlo Erba Reagents and Sigma Aldrich.

2.1 Synthesis of electrocatalysts

2.1.1 Spinel $Ni_xFe_{1-x}Co_2O_4$

The stoichiometric amount of $NiCl_2 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ is dissolved in the 50 ml deionized water (DI) and stirred for 20 min and urea is added as a hydrolysis agent (A). Simultaneously, stoichiometric amount of $CoCl_2 \cdot 6H_2O$ is dissolved in DI under stirring for 20 min (B). A is added to B drop wisely under stirring. The obtained solution is placed in ultrasound for 15min with 150W power. The solution is transferred to a 100 ml Teflon autoclave at $120^\circ-180^\circ C$ for 10hr. After being cooled to room temperature, the obtained solution is washed with DI and ethanol while collecting the powder with filtration. The precipitate catalyst is placed in a vacuum oven under $60^\circ C$ for 10hr. To obtain $Ni_xFe_{1-x}Co_2O_4$, the precipitate was calcinated in the furnace at $350^\circ-400^\circ C$ for 3h.

2.1.2 Reduced Graphene Oxide (rGO) and 3D-Graphene

The modified Hummer's method followed by reducing agent is adopted to produce rGO from pure graphite powder [5].

3DG is prepared according to [6].

2.2 Working electrode preparation and tests

Catalysts for AEMWE are tested in 1M KOH solution by using Hg/HgO as reference electrode; conversely, Ag/AgCl is adopted. Pt wire/plate is adopted as counter electrode and modified glassy carbon electrode (GCE) as working electrode.

GCE is prepared as follows: 5 mg of each catalyst is dispersed into 1.5 ml of deionized water with 0.5 ml of 5% Nafion (acting as binder); it is sonicated for 1.5 hr to get proper ink. Then after, 0.01 ml of prepared ink is deposited on GCE and dried by air blowing at room temperature with almost 0.30 mg/cm^2 amount of each catalyst.

The electrochemical measurements are carried out at ambient temperature in a 3-electrode cell system. Polarization curves are obtained with voltage range 0-1V and scan rate of 2 mV/s vs Hg/HgO. The Tafel slope is calculated from the polarization curve (LSV, Linear Sweep Voltammetry). Cyclic voltammetry (CV) allows to measure the double-layer capacitance and to determine the electrochemical surface area (ECSA), with CV curves from 0.01 V to 0.25 V at scan rate in the range 2-20 mV/s.

Electrochemical Impedance Spectroscopy (EIS) is applied at a potential of 0.5-1 V with frequency ranges from 100 kHz to 0.1 Hz. (Biologic VSP-300 potentiostat). EIS is carried out at a voltage of 5 mV in a frequency range of 100 kHz to 0.1 Hz.

Stability is evaluated at 10- 20 mA/cm² by using chrono-potentiometry technique and durability is checked before and after stability test through LSV technique.

2.3 Electrodes preparation and tests

Different materials are available as AEMWE gas diffusion layers, to be coated with the selected OER catalysts. In this study we considered one industrial grade nickel felt (99% pure nickel, porosity 0.7) and one research grade Ni fiber paper (Dioxide Materials Inc.).

As regards V-RFB, usually carbon felt and graphite felt are utilized. We selected Sigracet 39BB (SGL Carbon GmbH; 325 micro meter thickness and $12 \text{ m}\Omega \text{ cm}^{-2}$ electrical resistance) and AvCarb GDS5130 (suitable for high current density).

A 5 cm² AEM monocell (Dioxide Materials) and a 5 cm² Redox Flow Cell (Redox Flow) are adopted to test the MEA.

3 Experimental Design

Since a full factorial design is highly time demanding due to the time necessary to validate the prepared materials by both electrochemical tests and EIS, and subsequently test the best ones in both AEMWE cells and in Redox Flow cells, we propose to adopt a step-oriented fractional factorial design. The experimental activity on the potential catalysts is designed as follows:

3.1 Catalysts for OER and V-RFB positive electrode

Three factors are considered: A: spinel composition, B: structuring type and C: structuring composition. Five levels are initially selected for spinel composition ($x=0$, $x=0.25$, $x=0.50$, $x=0.75$, $x=1$), for both $\text{Ni}_x\text{Fe}_{1-x}\text{Co}_2\text{O}_4$ and sulphur substituted $\text{Ni}_x\text{Fe}_{1-x}\text{Co}_2\text{S}_4$ (for a total of 10). Process conditions, resulting from optimization, are kept identical for the synthesis of all the catalysts, i.e. during hydrothermal (power of sonication, reaction time, temperature), drying (temperature, residence time) and calcination (environment, temperature, residence time). Among these 10 spinels the best two (one for Oxygen and one for Sulphur in the spinel structure) are selected, depending on the results obtained with the three-electrode cell system.

Furthermore, we choose two levels for graphene structuring (rGO and 3DG), and four levels for spinel structuring composition (quantity of rGO and 3DG equal to 1%, 2%, 5%, 10% respectively). Then a fully factorial design is adopted.

3.2 Electrodes

Regarding AEMWE, we must consider three factors: A: coating method, B: GDL material and C: catalyst loading. The material of the cathode catalyst layer (CCL) is fixed, made by industrial grade Ni felt so as the ink composition (ionomer/binder and solvents).

The following three processes are proposed to coat the GDL: spray coating, hand painting and direct hydrothermal deposition (on Ni felt). They are scalable, unlike other more performing ones at the laboratory scale (as ultrasonic spray coating) that are currently too expensive to be adopted for industrial scale electrodes production. The best method is decided in terms of uniformity of layer thickness and SEM analysis. Subsequently, the other factors are investigated by fully factorial design. Two levels (Ni felt, Ni paper) are considered for the anode GDL and three levels ("lower than", "initially designed", "higher than") for catalysts loading.

The factors considered for studying the V-RFB electrodes are: A: coating method, B: positive electrode material and C: catalyst loading.

After choosing the best coating method (the selected method can be different from the previously selected one, due to the different electrode material), 3 levels (graphite felt, Sigracet, AVcarb) are considered for factor B; while catalyst loading is investigated at two levels. The negative electrode is fixed, made by graphite felt.

3.3 Membranes

The MEA are constructed with the combinations of the investigated electrodes and different membranes, at the following three levels, representing 3 different commercial anion

exchange membranes: Fumasep® FAA-3-PK-75 (Fumatech), Sustanion® 37-50-RT (Dioxide Materials) and Aemion+® AF3-HWK9-75-X (Ionomr Innovations).

As regards the V-RFB, research works report good performance of both Aemion® and Sustanion® membranes. Anyway, we decided to substitute Fumasep with Nafion 115 in the experimental design since comparison with classical PEM could be more representative to evaluate the electrocatalyst performances in V-RFB.

4 Results and Discussion

The total of tests required in the three –electrode cell to select the spinels is 10. The total of tests required in the three–electrode cell with the selected spinels modified with graphene is 16. Other 16 coating tests are necessary to select the coating method. A total of 96 electrodes must be prepared for AEMWE and a total 96 for V-RFB. If we want to test all the prepared electrodes with the different membranes in 5 cm² prepared MEA, the number of runs with the 5cm² cells is too high, so again fractional factorial design has been proposed, by focalizing only on the low/high level of catalyst loading (and using Response Surface Methodology). A scheme of the main experimental steps is shown in Figure 1.

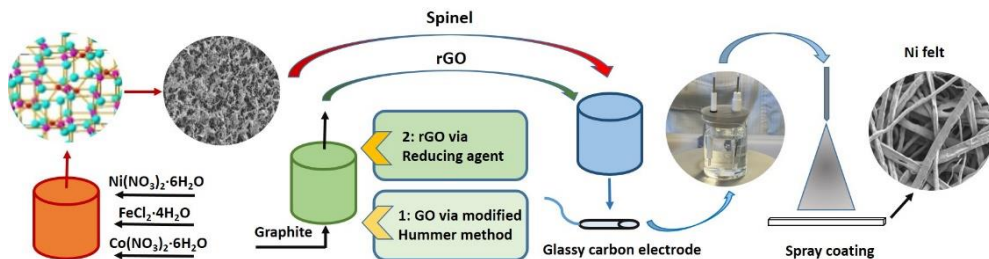


Fig. 1. Scheme of the experimental tests for selecting the electrocatalysts

The first synthesized NiCo_2O_4 samples (named NiCo1 to NiCo8) were obtained by varying three factors, namely urea content, hydrothermal temperature, and calcination temperature at two levels for a total of eight samples. These samples are synthesized to select the optimal process conditions. Through XRD and SEM analysis, the best ones were identified as NiCo3 and NiCo4. These samples were selected for further analysis, spinel $\text{Ni}_x\text{Fe}_{1-x}\text{Co}_2\text{O}_4$ fabrication and electrode fabrication. SEM analysis of the samples (Figure 2) revealed a mum-flower-like catalyst structure with homogeneous particle distribution. XRD analysis confirmed that samples 3 and 4 possessed a single-phase structure (Figure 3a). Figure 3b shows the details of the structure and the dimension of the nano-needles of catalyst deposited on the Ni-Felt electrode. A significant increase in the specific surface area of the Ni-Felt is observed, and enhanced electroconductivity, attributed to the unique characteristics of the needles. The results suggest that the synthesis conditions significantly influenced the morphology and crystalline structure of the NiCo_2O_4 samples. The selected NiCo3 and NiCo4 samples exhibit promising characteristics for further investigation and potential application in electrode fabrication for using in both AEMWE and VRFB.

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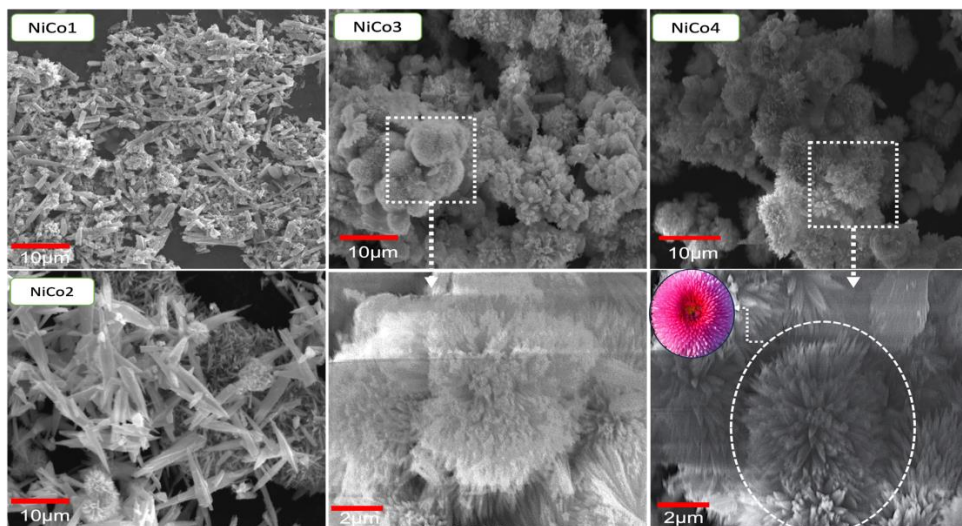


Fig 2. SEM Analysis for Nano Mums- flower like NiCo_2O_4 Catalysts

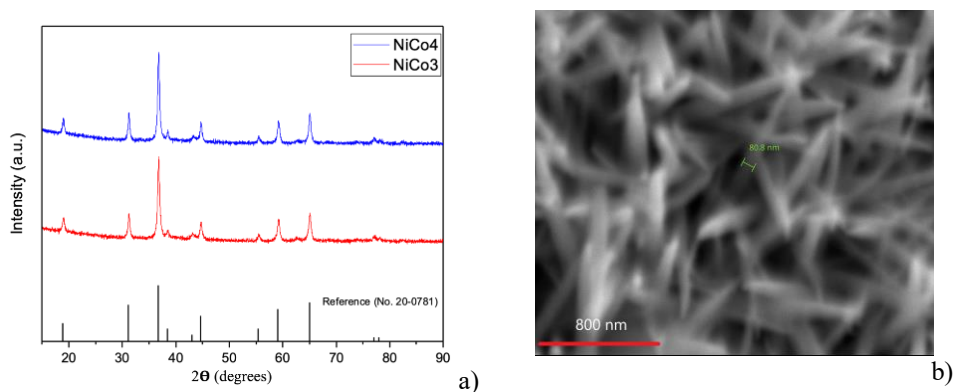


Fig. 3. a) XRD analysis for NiCo_3 and NiCo_4 ; b) SEM analysis for NiCo_4 deposited on Ni-Felt

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