Development of sustainable carbon-supported catalysts for their incorporation into electrochemical devices

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Objectives and novelty

Renewable energies have become a key alternative to conventional fossil fuels in the transition towards a more sustainable energy system, contributing to the reduction of greenhouse gas emissions and the mitigation of climate change. Nevertheless, their inherent intermittency creates the need for energy vectors capable of efficiently storing and transporting energy through time and space. Among these, green hydrogen has emerged as one of the most promising options. It can be sustainably produced through water electrolysis powered by renewable electricity, where the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) take place. Moreover, similar electrochemical devices can be employed to perform the carbon dioxide reduction reaction (CO_2RR), enabling the conversion of CO_2 into value-added products. Nevertheless, the widespread implementation of these technologies requires improving their energy efficiency and economic viability. In this regard, reducing the overpotential associated with the electrochemical reactions through the development of efficient catalysts and the optimisation of operating conditions is essential to decrease the energy demand of the processes.

Therefore, the main objective of this thesis is the development of sustainable transition-metal-based catalysts supported on carbon materials for their integration into electrochemical devices. The catalytic performance of these materials is evaluated for the three mentioned reactions: the oxygen evolution reaction (OER), the hydrogen evolution reaction (HER), and the carbon dioxide reduction reaction (CO_2RR).

The specific objectives of this thesis are:

- To develop transition-metal-based catalysts supported on reduced graphene oxide for alkaline water splitting, with a particular focus on the OER.
- To develop transition-metal-based catalysts self-supported on carbon fibre paper for alkaline seawater splitting, targeting both the OER and HER.
- To define the electrochemical operating window for CO_2RR using a copper-based catalyst under neutral and acidic electrolyte conditions.

Results

To address the first specific objective, the work focused on OER, the step with the greatest kinetic limitations. Transition-metal-based catalysts supported on reduced graphene oxide were developed for the alkaline OER. The synthesis strategy, based on freeze-casting followed by thermal reduction, enabled the preparation of aerogels with a distinctive porous structure and a homogeneous distribution of bimetallic nanoparticles (Figure 1). Furthermore, the method proved highly versatile, allowing the incorporation of different transition metal combinations, such as nickel, iron, and cobalt, in varying compositions, thereby demonstrating its potential for the tailored design of electrocatalysts.

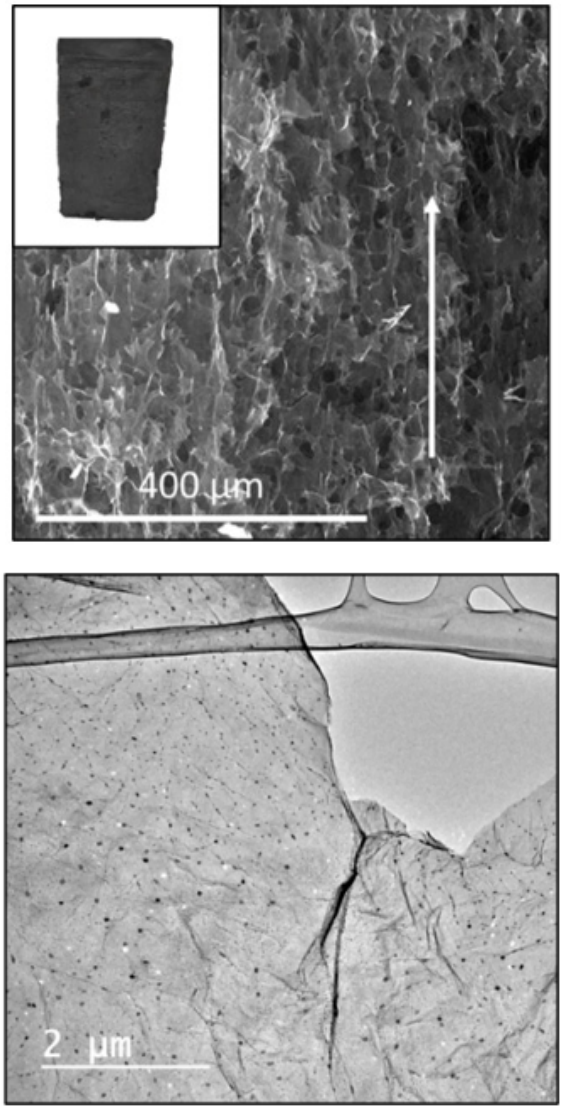

Figure 1. Morphological characterisation of the synthesised aerogels by SEM and TEM.

The aerogels with nanoparticles synthesised by this processing route exhibited activity and stability for OER comparable to a reference NiFe-LDH catalyst supported on reduced graphene oxide and synthesised by a hydrothermal route. The aerogels showed overpotentials ranging 400-450 mV at 10 mA cm^{-2}, a Tafel slope of 84.8 mV dec^{-1} and great stability for twelve hours when a low amount of catalyst is tested. An interesting finding is that doping the nickel-based nanoparticles with iron instead of cobalt resulted in a better catalytic activity towards the OER, offering valuable insight into how different dopants can tune the performance of nickel catalysts. Moreover, they showed a remarkable sensitivity to electrolyte impurities, making them particularly suitable for fundamental OER studies. This synthesis route showed great potential for producing well-dispersed nanoparticulate catalysts with tunable properties, offering a versatile platform for further development and optimisation.

To address the limitations associated with freshwater scarcity, seawater electrolysis was also explored, a process that presents additional challenges due to the presence of chlorides and other dissolved species. This study represents the second specific objective of this thesis, in this context, self-supported transition-metal-based catalysts were developed on carbon fibre paper for alkaline seawater splitting. Four catalysts, based on nickel and doped with cobalt, iron and cerium oxide (NiCo, NiCo-CeO_2, NiFe and NiFe-CeO_2), were synthesised by electrodeposition followed by thermal reduction. Electrodeposition proved to be an advantageous technique, as it is simple, efficient and allows precise control over the formation of uniform coatings. The use of carbon paper as a substrate further contributed to robustness and an open, fibre-based structure that promoted the homogeneous distribution and penetration of the deposits. This simple and scalable approach enabled the preparation of homogeneous coatings on the open fibre network of the carbon substrate that were directly used as working electrode.

The electrocatalytic performance of the catalysts was evaluated for both HER and OER in alkaline simulated seawater (1M KOH + 0.5M NaCl), showing that iron doping improved OER activity, while cobalt doping enhanced the HER. Additionally, cerium oxide further enhanced the catalytic performance, particularly in the nickel-cobalt catalyst. For HER, all materials exhibited low overpotentials and excellent long-term stability, with NiCo-CeO_2 delivering the best performance (η_{100} = 359 ± 22 mV and stable operation for 120 h at −100 mA cm^{-2}) attributed to the synergistic role of doping the nickel-based catalyst with cobalt and cerium oxide. For OER, the iron-containing catalysts showed the highest activity, particularly NiFe-CeO_2 (η_{100} = 421 ± 11 mV and stability for 120 h at 100 mA cm^{-2}) (Figure 2). In this case, cerium doping was more beneficial for the cobalt-based system, while the iron-based catalysts already exhibited superior OER performance on their own. Importantly, all catalysts operated below the potential required for the competing hypochlorite formation reaction, and iodometric analyses confirmed its suppression. These results demonstrate the potential of these sustainable and low-cost catalysts for seawater electrolysis under industrially relevant current densities.

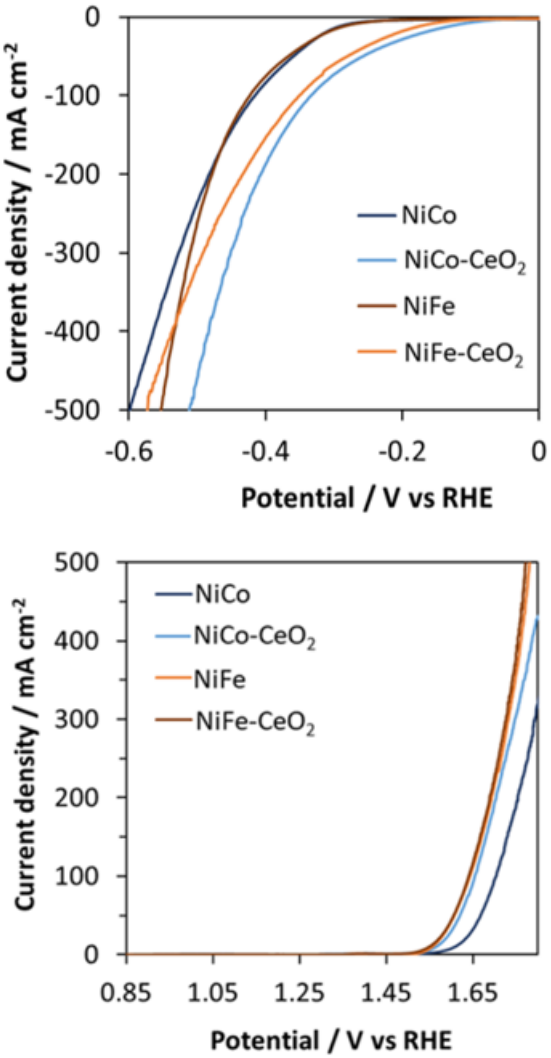

Figure 2. Catalytic activity of the catalysts determined by LSV in synthetic seawater electrolyte towards HER and OER.

Finally, a systematic study was conducted to map the CO_2 electroreduction (CO_2RR) operational window on a copper nanocubes catalyst in a series of electrolytes with markedly different physicochemical properties, with the objective of correlating electrolyte composition and applied current density with catalytic selectivity, reaction feasibility, and the stability of CO_2RR performance under acidic conditions.

Four electrolytes were investigated: bicarbonate, oxalic acid, hydrochloric acid, and sulfuric acid, each providing distinct buffering behaviour, proton availability, and interfacial transport conditions.

Across the tested current density range, clear electrolyte-dependent selectivity regimes were identified: bicarbonate enabled high CO_2RR selectivity at low current densities (40-80 mA cm^{-2}), oxalic acid and hydrochloric acid performed best at intermediate current densities (80-120 mA cm^{-2}), and sulfuric acid became more favourable at high current

densities (160-200 mA cm^{-2}), where stronger proton activity supports sustained operation. When the working electrode potential was considered, several of these windows narrowed due to unfeasibly high potentials, showing that practical operation requires optimising selectivity and energy cost. These results demonstrate that efficient CO_2RR in acidic media is governed primarily by the ability of each electrolyte to establish a favourable interfacial environment (balancing local pH and CO_2 availability under operating current), rather than by the preservation of a specific catalyst morphology.

Conclusions

Catalysts supported on carbon-based materials were successfully developed and evaluated for three key electrochemical reactions: OER, HER and CO_2RR. Carbon materials played a central role in electrode performance by enabling homogeneous dispersion of catalyst precursors, providing electrical conductivity, chemical and thermal stability, and increasing the effective surface area, all of which enhanced catalytic activity. The versatility of carbon materials enabled their compatibility with different synthesis routes, including water-based methods, thermal reductions and electrodeposition. All catalysts developed in this thesis were based on earth-abundant transition metals, avoiding noble metals and aligning with sustainability principles. Overall, the electrochemical results for the three reactions (OER, HER and CO_2RR) contribute to the development of advanced carbon-supported catalysts and represent a step forward towards sustainable electrochemical technologies for energy conversion and climate-change mitigation.

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References

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