Electrochemical Technologies for Energy Production and Storage

Electrocatalysts for Fuel Cells and Electrolysers

A detailed catalyst design, based on the in-depth experimental and theroretical understanding of the surface reactions and interactions involved in the oxygen reduction and evolution reactions (ORR and OER, respectively), has allowed us to provide promising alternatives to the use of unsustainable noble metals in these processes.

Introduction

A transition to sustainable energy sources can only be achieved through the increase of renewable electricity consumption. However, the intermittent nature of renewable energy sources poses some challenges, such as the need to develop proper strategies to store the electrical surplus until such energy is needed. The use of hydrogen as energy vector has been proposed as the solution needed to balance renewable electricity supply and demand, and thus ensure system reliability and flexibility. Hydrogen can be obtained by splitting water in an electrolyser, using the electric surplus otherwise lost; and then converted back to electricity in a fuel cell when needed. Both the reactions occurring in electrolysers and fuel cells need suitable catalysts to operate efficiently. These have traditionally been based on noble metals, mostly platinum and its alloys, which are costly and scarce. Seeking alternatives to the use of noble metals through the development of unexpensive carbon-based electrocatalysts is the main goal of this research topic. A special focus has been given to those needed for the oxygen reduction reaction (ORR), which is the most challenging among all the reactions involved in the hydrogen-based energy cycle herein described.

Under a more innovative approach, an electrolyser and a fuel cell can be combined into a single, compact device: a unitized regenerative fuel cell. However, this approach poses the need for bifunctional catalysts, *i.e.*, one suitable for the ORR and the oxygen evolution reaction (OER), and another for hydrogen oxidation and evolution reactions (HOR and HER, respectively). Therefore, as secondary objective, we have also been seeking for catalysts suitable for the oxygen evolution reaction (OER).

Current Development

12 original research articles were published in high-impact international peer-reviewed journals under this research project. These include contributions to the advancement of knowledge on the use of very different carbon-based materials as ORR, OER, and/or HER electrocatalysts; and significant international collaboration (8 research groups from 5 countries). Nevertheless, for the sake of conciseness, only 5 studies reflecting our research trend (Table 1) will be briefly discussed.

Metal-free glucose-derived carbons were considered first due to their very low cost [1]. Important correlations between the properties of the electrocatalysts and their performances in ORR were found, such as that between the specific surface area and the limiting current density (Fig. 1). Nitrogen-doping was found to enhance the ORR performance further. However, it was still well-below the performances obtained with the metal-containing electrocatalysts reported in the literature. Carbon modification with transition metals was thus the next step.

In a series of subsequent studies, carbon nanotubes (CNTs) were found to be a better support for iron and cobalt phthalocyanines. This approach was very successful, as the iron phthalocyanine-containing CNTs revealed a higher activity towards ORR than that of a benchmark platinum-based electrocatalyst [2]. Our main objective was in this way partially achieved. Nevertheless, we have decided to optimize the catalyst design focusing on developing a

Table 1. Key results obtained in this research project.

Catalyst	Highlights
Metal-free glucose-derived carbons [1]	- Limiting current density increases linearly with the specific surface area of the carbons
	- N-doping enhances the ORR performance
Carbon nanotubes (CNTs) [2]	- Iron and/or cobalt phthalocyanines were sucessfully introduced to the carbon surface
	- Iron phthalocyanine-containing CNTs revealed an ORR activity above that of a platinum-containing benchmark catalyst
CNTs [3]	- Using a physical mixture of cobalt- and iron phthalocyanine-supported CNTs as a catalyst led to enhanced bifunctionality for the oxygen reactions (ORR and OER), its performance surpassing those of noble metals-containing benchmark catalysts
Hollow carbon spheres [4]	- A bottom-up construction strategy for the introduction of single-atom Fe-N active sites to the carbon was reported
	- High electrocatalytic stability towards ORR was observed
Carbon black [5]	- Preserved porosity, single-atom Fe-N centers, Fe nanoclusters, and other N-containing sites contribute to a high electrocatalytic ORR activity and stability

bifunctional catalyst for both ORR and OER. That was accomplished by taking advantage of the synergies arising from the use of a physical mixture of cobalt- and iron phthalocyanine-supported CNTs as a catalyst (Fig. 2). In fact, its performance surpassed those of noble metals-containing benchmark catalysts [3], thus our secondary objective being partially achieved.

Scaling-up from a three-electrode assembly to a more realistic application was then performed under a collaboration with Prof. Bastian Etzold (Technical University of Darmstadt, Germany). Specifically, R.G. Morais engaged in a 3-month Erasmus+ student placement in which the most promising bifunctional electrocatalysts were tested in a gas diffusion half-cell operating at potentials within the fuel cell application range. The performances obtained were similar to those of noble metal-containing
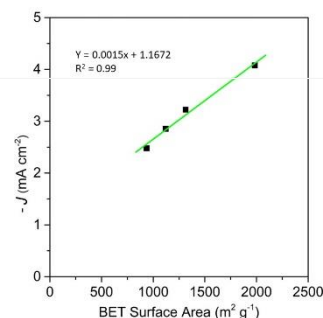

Fig. 1. Correlation between the specific surface area and the limiting current density yielded during ORR on the activated glucose-derived carbons [1].
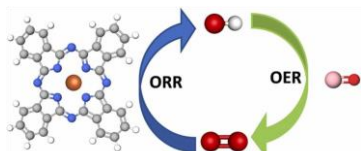
Fig. 2. Representation of the synergies arising from the combination cobalt- and iron phthalocyanine-supported carbon nanotubes (CNTs). Colors represent O (red), Fe (orange), Co (pink), N (dark blue), C (dark gray), and H (ligh gray) [3].

benchmark catalysts.

Despite the outstanding results obtained and the lower cost of phthalocyanines when compared to the price of noble metals, iron phthalocyanine is still an expensive precursor. Therefore, less expensive strategies to introduce Fe-N active centers (like that of the $Fe-N_X$ moiety in iron phthalocyanine) to the surface of carbon materials were sought. Accordingly, a bottom-up construction strategy was designed for the introduction of single-atom Fe-N active centers to the surface of hollow carbon spheres by employing only broadsly available and inexpensive precursors such as iron nitrate, melamine, and glucose [4]. The electrocatalytic activity of the resulting materials towards ORR was explained and discussed based on computational studies considering different possible active centers (Fig. 3).

The synthesis methodology developed for Fe-N-modification of hollow carbon spheres was then optimized under a collaboration with Prof. Teresa J. Bandosz (The City College of New York, NY, USA). In this case, R.S. Ribeiro was a visiting Scholar for 6 months under a Fulbright Grant for Professors and PhD Researchers. It allowed the transfer of knowledge on carbon materials between both research groups and thus engaging carbon black with high conductivity and abundant ultramicropores in enhancing the incorporation of Fe-N active centers and the ORR activity (Fig. 4). As a result, the current density yielded by our optimized electrocatalyst after 24 h of continuous operation was still above that yielded by a fresh benchmark platinum-based electrocatalyst [5].

As shown above, international presence is at the core of this research project. This is reflected by the amount of collaborative work and the 4 invitations received to present our results to well-
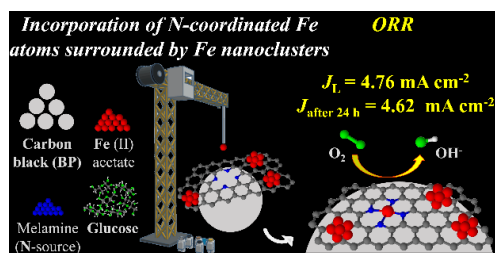

Fig. 4. Table of contents of our study on the conversion of carbon black into an efficient and multi-site oxygen reduction reaction (ORR) electrocatalyst [5].

stablished conferences, advanced schools, and seminars. In addition, R.S. Ribeiro received a nomination as the Portuguese Candidate to the 2023 EFCATS Young Researchers Award.

Future Perspectives

Tasks ahead can be divided into 3 main topics: (i) continuous optimization of catalyst design seeking for effective yet less expensive solutions; (ii) deepen the use of computational tools seeking for a better understanding of the processes; and (iii) scaling-
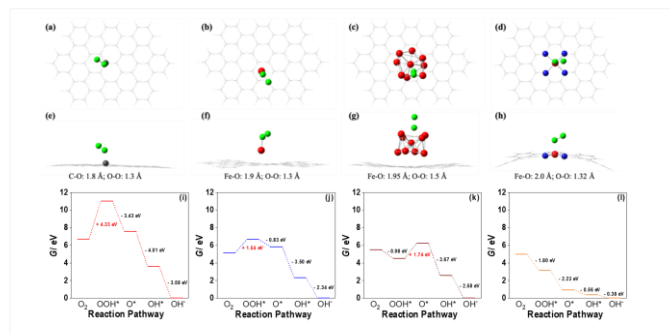

Fig. 3. (a-h) Schematic representation of the optimized molecular structures obtained for the adsorption of oxygen and (i-l) Gibbs free energy diagrams for the four-electron associative oxygen reduction reaction (ORR) on possible electrocatalytic active sites on a graphene sheet: (a,e,i) bare graphene sheet, (b,f, j) single-atom Fe, (c,g,k) Fe cluster with 9 atoms, and (d,h,l) single-atom FeN_4. (a-d) front views, and (e-h) lateral views. Colors in (a-h) represent O (green), Fe (red), N (dark blue), and C (gray) [4].

up both the catalyst synthesis processes and the electrochemical tests. Regarding the latter, a gas diffusion half-cell system is currently being assembled in our facilities to ensure that the electrochemical systems can be quickly tested at a larger scale. The most promising electrocatalysts will then be tested in fuel cells, electrolyzers, and, ultimately, in unitized regenerative fuel cells under collaborations such as those with Prof. Tompos and Prof. Alexandra Pinto (CEFT, University of Porto, Portugal). Moreover, under a collaboration with INL – International Iberian Nanotechnology Laboratory, Portugal, (iv) additional electrocatalysts will be prepared and employed in compact proton exchange membrane (PEM) electrolyzers, fosusing both on HER (with transition metal phosphides-carbons) and OER (with reduced amounts of iridium oxide supported on conductive oxides). Replacing costly noble metal-containing electrocatalysts by less expensive options will enhance the perspectives of widespread using hydrogen as energy vector within the global energy transition and decarbonization agenda.

Related Sustainable Development Goals

Outputs

PhD Theses

R.G. Morais, *Noble-metal free carbon-based materials for energy conversion*, Doctoral Program in Chemical and Biological Engineering, FEUP, 2023

Master Dissertations

J.F.G. Brito, *Implementation of critical-raw-material-free catalysts for membrane-based hydrogen generation systems*, Integrated Master's in Chemical Engineering, FEUP, 2021

M.I.S. Soares, *Estudo da operação de um eletrolisador de membrana permutadora de aniões*, Integrated Master's in Chemical Engineering, FEUP, 2023

Selected Publications

[1] R.G. Morais *et al.*, Beilstein Journal of Nanotechnology 10, 1089 (2019)
[2] R.G. Morais *et al.*, Applied Surface Science 572, 151459 (2022)
[3] R.G. Morais *et al.*, Catalysis Today 418, 114057 (2023)
[4] R. S. Ribeiro *et al.*, Carbon 213, 118192 (2023)
[5] R. S. Ribeiro *et al.*, Nanoscale 15, 18592 (2023)

Team

M. Fernando R. Pereira, Full Professor/ Group Leader; **José L. Figueiredo**, Emeritus Professor; Salomé G.P. Soares, Auxiliar Researcher; **Krzysztof Biernacki**, Researcher (Doctorate Initial Level); **Natalia Rey-Raap**, former Researcher (Doctorate Initial Level); **Rafael G. Morais**, Researcher (Doctorate Initial Level); **Rui S. Ribeiro**, Researcher (Doctorate Initial Level); **Mafalda Pina**, PhD student; Ana L.S. Vieira, former PhD student

Funding