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Instituto Politécnico de Bragança & Ordem dos Engenheiros

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Highly stable noble metal-free bifunctional carbon black electrocatalysts for oxygen reduction and evolution reactions

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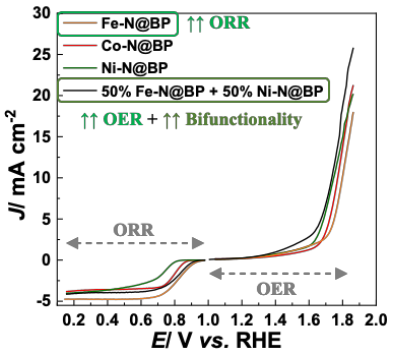

This communication features our contribution to advance the design of carbon-based electrocatalysts, focusing on the main parameters to consider when aiming precise surface tuning with highly stable transition metals as active sites. The quality and dispersion of Fe species are the main parameters governing the electrocatalytic activity. For this, a simultaneous incorporation of nitrogen (to anchor individual metal centers and modulate the charge density nearby the active sites) and glucose (as chelating agent to enhance metal dispersion) was found crucial. The optimized Fe-containing carbon black electrocatalyst revealed a superior performance in ORR (*e.g.*, higher onset potential and current density) compared to a benchmark electrocatalyst containing 20 wt.% of platinum. The best bifunctionality features for oxygen reduction (ORR) and evolution (OER) reactions were obtained when employing a physical mixture of Fe- and Ni-containing carbon blacks as a catalyst.

Introduction

In May 2021, the International Energy Agency established the Net Zero Emissions by 2050 Scenario, as landmark, detailing the sustainable energy-related goals needed to ensure the feasibility of the roadmap to a 1.5 °C stabilization in rising global temperatures [1]. Renewable electricity generation is expected to play a central role in this endeavor, accounting for 50% of the final energy consumption by 2050 [1]. However, renewable energy sources are intermittent, *i.e.*, their output is dependent upon the weather. Moreover, the storage devices currently available (*e.g.*, batteries) lack the capacity needed to store the oversupply of renewable energy until peak demands occur [2]. Therefore, new solutions are needed to balance the renewable electricity supply and demand. The use of hydrogen as an energy vector can be that solution. Excess electrical energy can be converted into storable chemical energy in an electrolyzer, yielding hydrogen and oxygen [3], through the so-called hydrogen (HER) and oxygen (OER) evolution reactions [4]. The net zero-carbon fuel and oxidant can then be converted back to electrical energy in a fuel cell, through the so-called hydrogen oxidation (HOR) and oxygen reduction (ORR) reactions [3, 4]. Under a more innovative approach, unitized regenerative fuel cells (*i.e.*, compact systems with a single electrochemical cell operating alternatively in electrolyzer and fuel cell mode) can be used to decrease capital costs and render an operation easier [4]. However, it poses the need for bifunctional electrocatalysts, *i.e.*, one suitable for ORR and OER, and another for HOR and HER. ORR is the bottleneck of a hydrogen-based energy cycle. Therefore, oxygen reactions have been the focus of our study. ORR and OER electrocatalysts have been traditionally based on noble metals-containing nanoparticles supported on carbon black – mostly platinum (Pt) and its alloys [5-8]. Thus, the widespread use of hydrogen as the energy vector has been hindered both by the scarcity (and unsustainability) of these precious metals, as well as by the major impact of their high price on the overall costs [5, 9]. Bearing this in mind, highly active and stable noble metal-free carbon black electrocatalysts were developed in this study as an alternative to traditional noble metals-containing materials. A molecular engineering approach was taken for that purpose, through which highly porous carbon black with promising features for ORR [10] was meticulously tailored with Fe, Ni, and Co species as active sites.

Experimental

Materials

Commercial carbon black – Black Pearls 2000 (BP), was purchased from Cabot Corporation (Boston, MA, USA). Iron species were introduced on the surface of BP using iron (III) nitrate, iron (II) chloride, or iron (II) acetate as precursor. Nickel (II) and cobalt (II) acetates were used as a source of nickel and cobalt, respectively. Melamine was used as a source of nitrogen and glucose was added as a chelating agent. Various ratios of the precursors were considered. The samples containing iron, nickel, cobalt, nitrogen, and/or glucose were subjected to a final thermal treatment under an inert atmosphere at 800 ºC.

Characterization

Samples were characterized by N_2 physisorption; thermogravimetric analysis (TGA) coupled with a MS detector; X-ray Diffraction (XRD); X-ray photoelectron spectroscopy (XPS); and high-resolution transmission electron microscopy (HR-TEM).

Electrochemical measurements

A standard three-electrode configuration was used for the electrochemical measurements, with a Ag/AgCl reference electrode; a carbon rod counter electrode; and, as a working electrode, a rotating ring-disc electrode with a glassy carbon disc and a gold ring (ORR), or a glassy carbon rotating disc electrode (OER). Incorporation of carbon materials was performed by surface modification of the working electrodes by the drop-casting method. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry measurements were carried out in basic media (0.1 mol L^{-1} KOH) pre-saturated with nitrogen or oxygen by bubbling corresponding gas through the electrolyte solution f for at least 30 min. Common indicators used to characterize the performance of electrocatalysts in ORR were determined from experiments performed with a rotation speed of 1600 rpm: onset potential (E_{onset}; defined as the

maximum of the second derivative of the current density-potential curve); half-wave potential ($E_{1/2}$; defined as the maximum of the first derivative of the current density-potential curve); limiting current density (J_L; defined as the current density at 0.2 V *vs*. RHE); hydrogen peroxide (H_2O_2) formation; and average number of electrons transferred during the ORR (n_E). The potential needed to achieve a current density of 10 mA cm^{-2} (E_{10}) was used to characterize the performance of the electrocatalysts in OER; whereas the potential gap between E_{10} and $E_{1/2}$ (ΔE) was used to evaluate bifunctionality.

Results and discussion

The synthesis methodology (Figure 1) was optimized upon introduction of Fe functionalities to the surface of BP and by a subsequent evaluation of the ORR activity. The effect of Fe precursor was studied first (results not shown), followed by the role of each synthesis precursor. The results confirmed the importance of adding nitrogen during the synthesis to anchor individual metal centers and to modulate a charge density nearby the active sites (Fe_5-N@BP *vs*. Fe_5@BP; Table 1); whereas adding glucose as a chelating agent impacts the dispersion of active sites on the carbon surface and the subsequent performance (Fe_5-N@BP *vs*. $Fe_{5,\ No\ glucose}$-N @BP; Table 1).

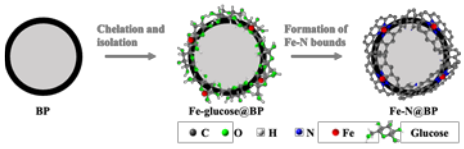

Figure 1. Strategy employed for the design of Fe-N active sites on BP.

Proper selection of the Fe load was also found important. Briefly, the performance in ORR obtained with Fe-N@BP (Table 2) was better than that of Fe_5-N@BP (Table 1), despite a 5-fold larger metal load on the latter.

Table 1. Summary of ORR results obtained with carbon black electrocatalysts prepared under various synthesis conditions.

Material	E_{onset}/ V	$E_{1/2}$/ V	J_L/ mA cm^{-2}
BP	0.772	0.727	3.480
Fe_5-N@BP	0.917	0.852	4.361
Fe_5@BP	0.767	0.717	4.066
$Fe_{5,\ No\ glucose}$-N @BP	0.822	0.742	4.740

These ORR results, together with the advanced characterization results obtained by XRD, XPS, and HR-TEM (not shown), highlight the quality and dispersion of Fe species as crucial parameters governing the electrocatalytic activity. A catalyst benchmark study revealed that Fe-N@BP enables a higher E_{onset} than that on Pt/C and similar $E_{1/2}$ (Figure 2 and Table 2). Moreover, the current density (J) yielded by the former after 24 h was still higher than that yielded by the latter at the beginning of the chronoamperometry experiment (Figure 2). The optimized synthesis methodology was employed for the introduction of Co and Ni. The best performance in OER and bifunctionality for oxygen reactions were obtained when employing a physical mixture of the Fe- and Ni-containing carbon blacks as a catalyst (Table 2 and Graphical abstract).

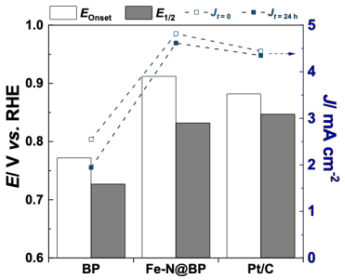

Figure 2. E_{onset} and $E_{1/2}$ (left axis); and current density (J) obtained after 0 ($J_{t=0}$) and 24 h ($J_{t=24\ h}$) at 0.4 V *vs*. RHE (right axis).

Conclusions

The methodology herein developed opens a window of opportunity for the development of electrocatalysts with enhanced bifunctionality features for ORR and OE.

Table 2. Summary of ORR and OER results obtained with Fe-, Co-, and Ni-containing carbon black electrocatalysts prepared under the optimized synthesis conditions.

Material	ORR					OER	Bifunctionality
	E_{onset}/ V	$E_{1/2}$/ V	J_L/ mA cm^{-2}	H_2O_2/ %	n_E	E_{10}/ V	ΔE/ V
Fe-N@BP	0.912	0.832	4.757	1.8	3.97	1.798	0.966
Co -N@BP	0.857	0.802	3.833	18.3	3.63	1.771	0.969
Ni-N@BP	0.787	0.747	4.037	10.6	3.79	1.747	1.000
50% Fe-N@BP + 50% Ni-N@BP	0.892	0.837	4.152	8.3	3.84	1.736	0.899
Pt/C	0.882	0.847	4.657	2.2	3.96	Not achieved	-

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