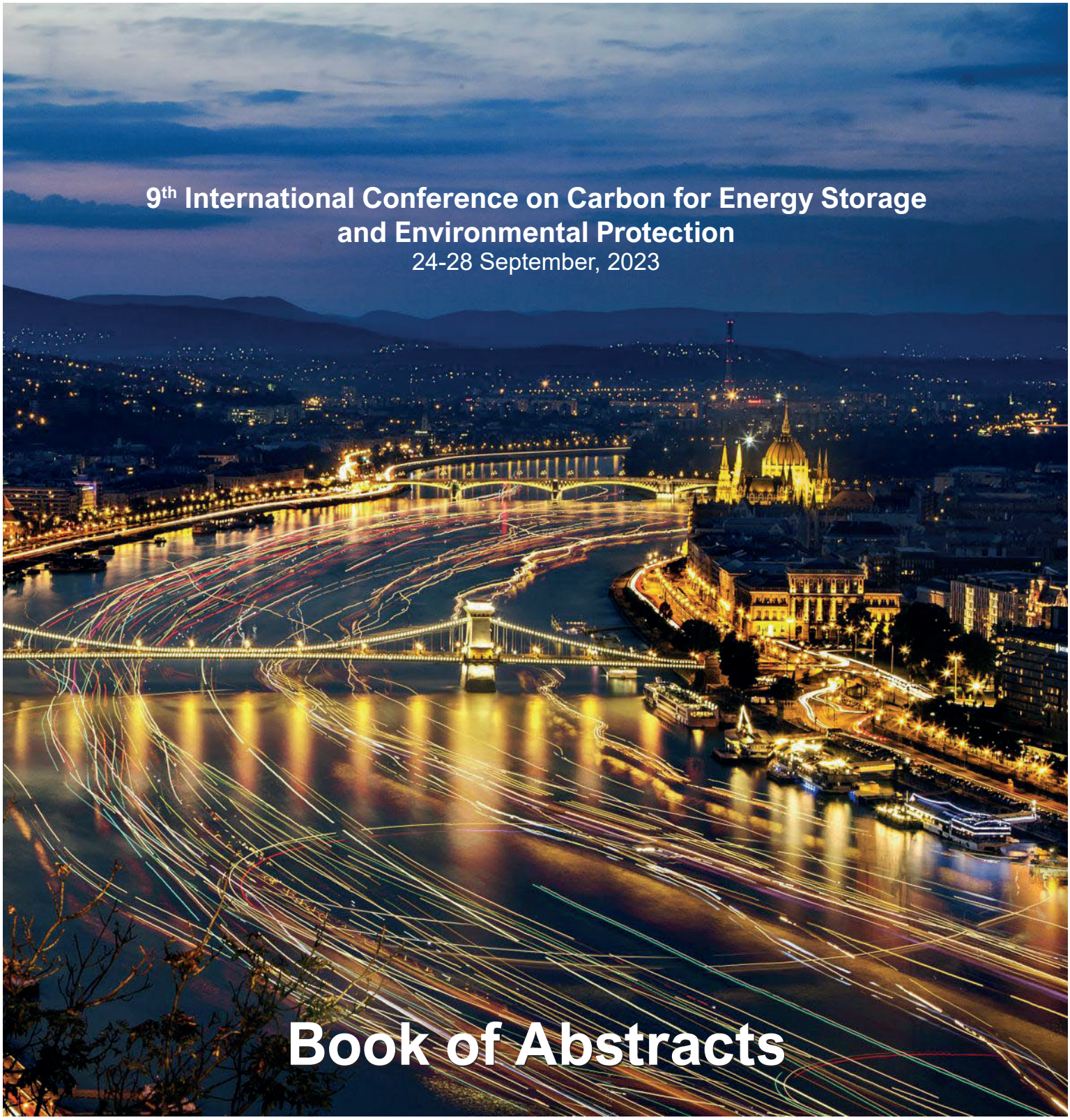

9th International Conference on Carbon for Energy Storage and Environmental Protection

24-28 September, 2023

Book of Abstracts

Carbon in the Changing World

CESEP 2023 Budapest

O-8 | BIFUNCTIONAL ELECTROCATALYSTS FOR OXYGEN REDUCTION AND EVOLUTION REACTIONS: INSIGHTS ON THE DESIGN OF HIGHLY STABLE NOBLE METAL-FREE CARBON BLACKS

Rui S. Ribeiro[1,2,3,*], Marc Florent[1], M. Fernando R. Pereira[2,3], Teresa J. Bandosz[1]

[1]Department of Chemistry and Biochemistry, The City College of The City University of New York, New York, USA
[2]LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Porto, Portugal
[3] ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Porto, Portugal
*(*corresponding author: rsribeiro@fe.up.pt)*

Keywords: ORR; OER; Single-atomic catalysts; Electrocatalysis; Unitized regenerative fuel cells

Introduction

Using H_2 as energy vector to balance renewable electricity supply and demand poses technological challenges, such as the design of cost-effective electrocatalysts, electrolyzers, and fuel cells. Unitized regenerative fuel cells allow decreasing the capital cost, but require bifunctional electrocatalysts, *i.e.*, one suitable for O_2 reduction (ORR) and evolution (OER), and another for H_2 oxidation and evolution. ORR is the bottleneck of the H_2-based energy cycle. Thus, O_2 reactions have been our main research focus.

ORR electrocatalysts have been traditionally based on noble metals-containing nanoparticles supported on carbon black – mostly platinum (Pt) [1-3]. Thus, the widespread use of fuel cells has been hindered both by the scarcity and high cost of these precious metals. Seeking alternatives to the use of noble metal-containing materials through the development of noble metal-free carbon-based electrocatalysts has been the focus of our research [4-7]. In the present study, highly porous carbon black was meticulously tailored with Fe, Ni, or Co and N species as active sites and tested for ORR and OER in basic media.

Experimental

Commercial carbon black – Black Pearls 2000 (BP), purchased from Cabot Corporation (Boston, MA, USA), was enriched with active sites containing iron, cobalt or nickel and nitrogen. 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. The electrocatalysts were obtained upon thermal treatment under an inert atmosphere at 800 ^{o}C and characterized by N_2 physisorption, thermogravimetric analysis (TGA), X-ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HR-TEM).

All electrochemical measurements were performed in an alkaline medium (0.1 mol L^{-1} KOH), using a standard three-electrode configuration in which the carbons blacks were used as working electrodes (considering a catalyst load of 0.25 mg cm^{-2}). ORR performance was evaluated considering onset potential (E_{onset}), half-wave potential ($E_{1/2}$), limiting current density (J_L), 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 OER performance. The potential gap between E_{10} and $E_{1/2}$ (ΔE) was used to evaluate bifunctionality for O_2 reactions.

Results and discussion

Optimization of synthesis conditions was first performed focusing on the introduction of iron active sites for ORR. The quality and dispersion of iron species were found as the crucial parameters governing the electrocatalytic activity. In fact, we have observed that, despite being a relatively synthesis methodology, only the proper understanding of the precursors' role allows obtaining highly active and stable carbon black electrocatalysts. The optimized carbon black electrocatalyst (Fe-N@BP) outperformed a commercial platinum-based electrocatalyst (Pt/C) in almost all the ORR parameters under consideration, including E_{onset} and J_L (Table 1).

The optimized synthesis conditions were then employed for the introduction of cobalt and nickel species on BP. The best performance in OER and bifunctionality for O_2 reactions were obtained when employing a physical mixture of the Fe- and Ni-containing carbon blacks as a catalyst (Table 1).

Table 1. *Summary of ORR and OER results obtained with different electrocatalysts.*

Material	ORR				OER	Bifunctionality
	E_{onset}/ V	$E_{1/2}$/ V	J_L/ mA cm^{-2}	n_E	E_{10}/ V	ΔE/ V
BP	0.772	0.727	3.480	3.36	n.a.	-
Fe-N@BP	0.912	0.832	4.757	3.97	1.798	0.966
Co-N@BP	0.857	0.802	3.833	3.63	1.771	0.969
Ni-N@BP	0.787	0.747	4.037	3.79	1.747	1.000
50% Fe-N@BP + 50% Ni-N@BP	0.892	0.837	4.152	3.84	1.736	0.899
Pt/C	0.882	0.847	4.657	3.96	n.a.	-

n.a.: not achieved.

Conclusions

The modified carbon black materials herein reported are a promising alternative to the use of noble metal-containing electrocatalysts in fuel cells and electrolyzers.

Acknowledgments

This work was financially supported by project BiCat4Energy (PTDC/EQU-EQU/1707/2020), funded by national funds (PIDDAC) through FCT/MCTES; LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM) funded by national funds through FCT/MCTES (PIDDAC). R.S.R. acknowledges the Fulbright Grant for Professors and Researchers with PhD awarded by Fulbright Commission Portugal and FCT funding under Stimulus of Scientific Employment, Individual Support Call (CEEC IND) 5th Edition (2022.04079.CEECIND).

References

[1] M.K. Debe, Nature 486 (2012) 43-51.

[2] K.C. Tsao, H. Yang, Oxygen reduction catalysts on nanoparticle electrodes, in: Encyclopedia of Interfacial Chemistry, K. Wandelt (Ed.), Elsevier, Oxford, 2018, pp. 796-811.

[3] C. Fu *et al.*, Comput. Mater. Sci 170 (2019) 109202.

[4] R.S. Ribeiro *et al.*, Carbon 213 (2023) 118192.

[5] D. Barrera *et al.*, ACS Appl. Energy Mater. 2 (2019) 7412-7424.

[6] J.-W. Zhang *et al.*, Front. Chem. Sci. Eng. 15 (2021) 279-287.

[7] R.G. Morais *et al.*, Appl. Surf. Sci. 572 (2022) 151459.