DCE23 5th DOCTORAL CONGRESS IN ENGINEERING

Book of Abstracts

DCE23 - Symposium on Chemical and Biological Engineering

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of the

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Editors:
Alexandra Pinto, Cristiana Gomes, Joana Almeida, Joana Lopes, Júlia Kessler, Mariana Bessa, Sara Ferreira, Susana Fernandes

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Mono- and Bimetallic Carbon Nanotubes as Bifunctional Oxygen Electrocatalysts

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Abstract

This work aimed to develop carbon nanotube (CNT) supported electrocatalysts for electrochemical energy conversion, targeting the oxygen reactions occurring in a unitized regenerative fuel cell (URFC). A monometallic catalyst obtained by impregnation of CNT with nickel(II) nitrate followed by thermal treatment at 260 ºC under H_2 (CNT_{Ni_260H2}) displayed the best performance in the oxygen evolution reaction (OER), whereas CNT doped with iron(II) phthalocyanine (CNT_{FePc}) showed the best performance in the oxygen reduction reaction (ORR). A bifunctional catalyst prepared by physically mixing these samples in a 1:1 mass ratio (CNT_{Ni_260H2}/CNT_{FePc}) exhibited better electrocatalytic activity than a commercial benchmark electrocatalyst for OER and an ORR performance similar to that of the widely used Pt/C electrocatalyst. Ultimately, CNT_{Ni_260H2}/CNT_{FePc} presented the lowest potential gap of all the synthesized samples and benchmark catalysts, thus demonstrating its great potential to replace noble metals and be tested at a larger scale.

Author Keywords. Oxygen evolution reaction, Oxygen reduction reaction, Unitized regenerative fuel cell, Nickel, Iron(II) phthalocyanine.

1. Introduction

Modern energy supply in our society is mostly based on fossil fuels, which depends on finite resources that will be depleted in the near future. The high consumption of these fuels and consequent emissions of carbon dioxide have adverse impacts on climate change. Thus, the use of energy obtained from renewable sources is crucial to fight global warming and ensure the sustainability of the planet. Therefore, it is essential to optimize systems for energy storage when renewable energy production exceeds energy consumption and for its reconversion into electrical energy when demand surpasses instant production.

Currently, noble metals are widely used as catalysts for electrochemical energy conversion, but are associated with high costs. Carbon materials are a good alternative, as they are significantly less expensive than noble metals. Therefore, the objective of this study was to prepare highly active bifunctional electrocatalysts for the oxygen reactions occurring in a unitized regenerative fuel cell (URFC). To achieve this objective, iron phthalocyanine (FePc) and/or nickel species were incorporated onto carbon nanotubes (CNT) and tested towards the oxygen evolution and reduction reactions (OER and ORR, respectively).

2. Materials and Methods

Electrocatalysts for OER were prepared by incorporating nickel(II) nitrate hexahydrate on CNT by incipient wetness impregnation (IWI) followed by thermal treatments in two different atmospheres (N_2 and/or H_2) and at various temperatures. CNT were also modified by incorporation of FePc by IWI followed by a thermal treatment under N_2 atmosphere at 500 °C for 2 h (CNT_{FePc}). This Fe-doped CNT sample has been previously tested as ORR electrocatalyst, displaying a performance similar to that of the benchmark Pt/C catalyst. The Ni-doped samples were electrochemically characterized to determine their OER activities. Afterwards, the best-performing Ni-doped CNT (CNT_{Ni_260H2}) and CNT_{FePc} were

physically mixed using a 1:1 mass ratio ($CNT_{Ni\_260H2}/CNT_{FePc}$). The electrochemical measurements (cyclic voltammetry – CV, linear sweep voltammetry – LSV, and stability tests) were performed using 0.1 mol L^{-1} of KOH as the electrolyte in a conventional 3-electrode cell. To determine the bifunctionality of the catalysts for the oxygen reactions, the potential gap (ΔE), which corresponds to the difference between the OER potential at 10 mA cm^{-2} (E_{10}), and the ORR half-wave potential ($E_{1/2}$) was calculated.

3. Discussion

The prepared carbon electrocatalysts were tested in the OER. The OER electroactivity of the samples treated under H_2 atmosphere was higher than their N_2-treated counterparts, in which CNT_{Ni_260H2} achieved a very low E_{10} (1.59 V). Nevertheless, the best performance among all samples was obtained with the bimetallic catalyst ($CNT_{Ni\_260H2}/CNT_{FePc}$), an E_{10} as low as 1.57 V being obtained. This performance is even slightly better than that of RuO_2 (E_{10} = 1.58 V) – a conventional electrocatalyst for OER. Regarding ORR, CNT_{Ni_260H2} presents a poor performance towards this reaction. Nonetheless, $CNT_{Ni\_260H2}/CNT_{FePc}$ displays an excellent performance in the ORR, surpassing that of Pt/C ($E_{1/2}$ of 0.91 V vs 0.83 V, respectively), with negligible by-product formation. Regarding stability during the ORR, CNT_{Ni_260H2} performed better than CNT_{FePc}, but worse than Pt/C. However, the stability of the bimetallic catalyst formed by the mixture of these two samples is quite close to that of Pt/C, which is a good indication of its long-term performance as ORR electrocatalyst. Concerning oxygen bifunctionality, all the prepared samples led to a ΔE lower than that of Pt/C, which indicates that these catalysts are better suited to be used in a URFC. Among all samples prepared, the bimetallic sample stands out ($CNT_{Ni\_260H2}/CNT_{FePc}$) with a ΔE of 0.66 V, which represents almost half the value obtained for Pt/C.

4. Conclusions

The highest electrocatalytic activity towards OER among the monometallic catalysts was obtained with sample CNT_{Ni_260H2}. The bimetallic electrocatalyst ($CNT_{Ni\_260H2}/CNT_{FePc}$), which consists of a physical mixture of the catalysts with the best performance in OER and ORR, demonstrated the highest bifunctionality towards the oxygen reactions occurring in a URFC (*i.e.*, ORR and OER), even surpassing that of the commercial noble metal-containing catalysts typically used at industrial scale. Therefore, the prepared materials have high potential as a viable alternative to replace noble metal-based electrocatalysts.

References

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