

Effect of the Surface Chemistry of Hydrothermal Carbons on the Oxygen Reduction Reaction

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Introduction

In the last decades, researchers have focused on developing new innovative materials to enhance the performance of environmentally friendly energy conversion devices. In this context, fuel cells are considered an interesting alternative towards greener electrical energy conversion due to their high efficiency and low emission of pollutants¹. However, the overall reaction is limited by the oxygen reduction reaction (ORR) due to its sluggish kinetics. The most commonly used electrocatalysts to supply faster kinetics are platinum-based materials which, due to its high cost, should be replaced by a more economical electrocatalyst. Activated carbons (ACs) can be obtained from abundant, low-cost and environmental-friendly sources, such as biomass, which makes them good candidates to replace Pt-based electrocatalysts. Nonetheless, the physicochemical properties of ACs need to be modified to achieve outstanding electrochemical performance². These modifications can be achieved by adequate functionalization with nitrogen and the incorporation of M-N₄ (M=Metal) groups³. Accordingly, this work aims to study the role of the different nitrogen functionalities and the surface chemistry modifications caused by the incorporation of iron(II) phthalocyanine (FePc) into the structure of hydrothermal glucose-derived carbons.

Materials and Methods

Carbon electrocatalysts were prepared by hydrothermal carbonization of an initial solution containing glucose and deionized water (1:6 ratio), which was mixed and closed in a Teflon-lined stainless-steel autoclave during 12 h at 180 °C. The obtained material was then activated under a CO₂ flow of 80 cm³ min⁻¹ g⁻¹ for 4 h at 900 °C (sample AG). Nitrogen functionalities were incorporated with two different precursors: melamine and FePc. Melamine was incorporated into AG by two different approaches: i) mixing by ball milling (N-AG_{BM}) and ii) manually mixing, henceforth referred to as conventional method (N-AG_C). After the incorporation of melamine, both samples were treated at 700 °C under a N₂ atmosphere for 2 h. The FePc was incorporated by incipient wetness impregnation to achieve a nominal metal loading of 0.4 wt.%. After the impregnation, the resulting material was dried and then treated under a N₂ atmosphere at 500 °C for 2 h.

Results and Discussion

The prepared materials were directly used as electrocatalysts in the ORR using a three-electrode cell configuration with a rotating disk electrode and a rotating ring-disk electrode. The linear sweep voltammetry (LSV) curves obtained showed that the introduction of nitrogen functionalities into the carbonaceous structure improves the reaction mechanism (Figure 1). However, samples N-

AG_{BM} and N-AG_C present similar content of nitrogen (ca. 4 at.%), but different values of onset potential, suggesting that the type of nitrogen functionalities, rather than the percentage of nitrogen, might be the key factor. The conventional method incorporates a larger amount of pyridinic nitrogen, resulting in a higher pyridinic-N/quaternary-N ratio and a lower quaternary-N/pyrrolic-N ratio, improving the onset potential and the number of electrons transferred, respectively². The addition of FePc further increases the onset potential by 100 mV, as FePc incorporates a large amount of pyridinic nitrogen. In addition, the incorporation of nitrogen and iron shifts the mechanism of the reaction to the four-electron pathway, decreasing the yield of oxygen peroxide from 55 % (sample AG) to 8 % (sample N-AG_{FePc}).

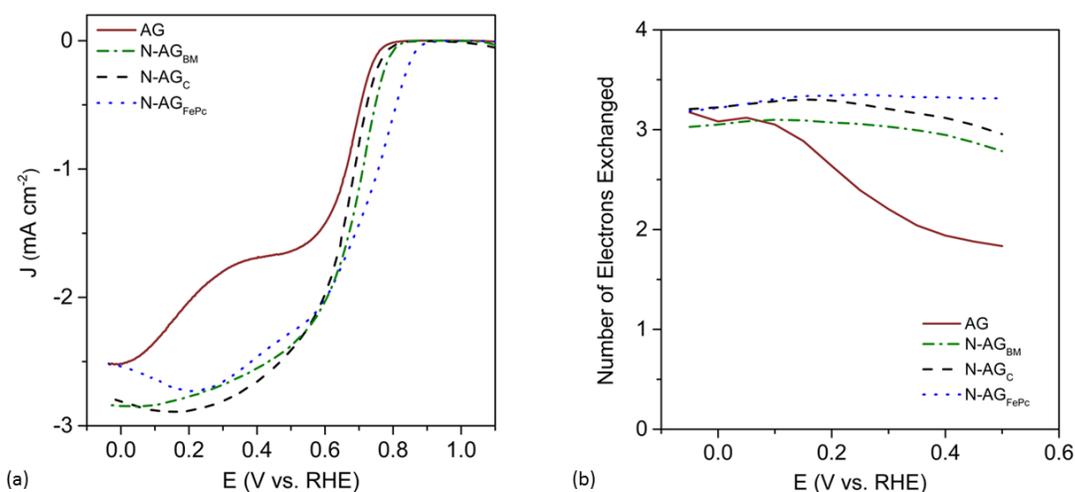


Figure 1. LSV curves (a) and number of electrons exchanged (b) of hydrothermal carbons

Conclusions

The surface chemistry of an activated hydrothermal carbon was successfully modified by the incorporation of nitrogen and iron in the carbon matrix. The incorporation of the adequate proportion between the different nitrogen functionalities is the key factor to improve the electrochemical performance of the carbon electrocatalysts, especially concerning the mechanism of the reaction. In addition, the incorporation of iron in the form of a macrocyclic compound improves the onset potential of the materials, demonstrating that the adequate combination of the chemical properties can make hydrothermal carbons competitive electrocatalysts towards ORR.

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