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Designing Fe–N–C single-atom catalysts using carbon black for efficient oxygen reduction reaction

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The oxygen reduction reaction (ORR) is one of the hottest reactions in sustainable energy technologies. This reaction is crucial for both fuel cells and metal-air batteries, which are essential for enabling the transition to a carbon-neutral energy future. Nonetheless, the ORR presents sluggish kinetics that significantly hinder device efficiency, posing a critical challenge in developing highly active and durable electrocatalysts. Moreover, platinum and its alloys are the most commonly used ORR catalysts to overcome these limitations, but they are very scarce and expensive, thereby increasing the overall device cost. Therefore, large research efforts have been devoted to the development of noble metal-free ORR electrocatalysts, including those from our group [1-4]. In this sense, the combination of iron and nitrogen on carbon supports surges as an optimal candidate due to their adjustable active sites and high electrocatalytic activity towards the reaction. Carbon materials are considered excellent candidates for the replacement of Pt, as they generally present a more competitive price and exhibit high versatility. In this context, this work focuses on using different carbon blacks (CBs) as support for ORR catalysts. They bring several advantages due to their high electrical conductivity, which ensures efficient electron transport, and their high surface area and tuneable porosity, which allow a uniform dispersion of active sites and facilitates the mass transport during the ORR [3, 5]. Additionally, the surface defects in the CBs provide anchoring points for coordinating iron and nitrogen species, promoting the formation of highly stable single-atom Fe-N_x active centres [3]. Moreover, their chemical robustness under electrochemical conditions ensures long-term durability, while their low cost and scalability make them highly attractive for practical fuel cell and metal-air battery applications. These combined properties make CBs a promising carbon support to develop next-generation, non-precious metal ORR catalysts. In the present study, selected CBs were modified by adapting a previously reported methodology, which has been shown effective to incorporate nitrogen-coordinated single-atom iron into different carbon frameworks by using only broadly available and low-cost precursors [3, 4]. The successful incorporation of iron was confirmed by inductively coupled plasma-optical emission spectrometry (ICP-OES), which revealed an iron content of approximately 4 wt.% in all catalysts.

The electrochemical performance of the synthesised electrocatalysts was evaluated using linear sweep voltammetry and chronoamperometry using a three-electrode cell with a rotating ring-disc electrode and a rotating disc electrode, respectively.

CBs modification led to an increase of 600-800% in the current density observed at 0.4 V vs. the reversible hydrogen electrode (RHE) and an increase in the onset potential of 300-400 mV in comparison to the bare CBs. Furthermore, the successful incorporation of single-atom iron was suggested by a shift in the reaction mechanism towards the four-electron ORR pathway with negligible by-product formation, as opposed to the indirect two-electron pathway observed on the bare CBs.

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