



Enhanced catalytic activity for the oxygen reduction reaction with co-doping of phosphorus and iron in carbon



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HIGHLIGHTS

- The P and Fe co-doped carbon (P–Fe–C) is facilely synthesized.
- The as-prepared P–Fe–C shows high catalytic activity for the ORR.
- The catalytic site of P–Fe–C for the ORR is proposed as Fe–P_x.
- The pyrolysis temperature plays an important role in the structure and activity of P–Fe–C.

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ABSTRACT

The phosphorus (P) and iron (Fe) co-doped carbon (P–Fe–C) has been facilely synthesized via an in situ sol–gel polymerization method followed by a pyrolysis process using resorcinol and formaldehyde as the carbon source, tetraphenylphosphonium bromide as the P source and iron nitrate as the Fe source. Benefiting from the high doping content of P and Fe and large specific surface area, the as-prepared P–Fe–C electrocatalysts demonstrate considerable catalytic activity for the oxygen reduction reaction (ORR) as evidenced by rotating ring-disk electrode studies and show long-term stability superior to the commercial Pt/C (20 wt.%). The catalytic site of P–Fe–C for the ORR is proposed as Fe–P_x (*x* is the coordination number of P atoms to Fe) embedded in carbon. The pyrolysis temperature is found to play an important role in the microstructure, texture and the doping content of P and Fe in carbon, which further affects the catalytic activity of P–Fe–C for ORR.

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1. Introduction

Fuel cells and metal–air batteries, as the environmental friendly energy storage and conversion devices, have attracted much attention over the past few years due to their high energy density and the potential to reduce the negative impact of climate change [1–3]. However, the sluggish oxygen reduction reaction (ORR) at the cathode, which requires highly efficient and low cost electrocatalysts, is one of the bottlenecks that restrict the wide application of these devices [4–7]. Exploring inexpensive and sustainable electrocatalysts with high efficiency to alternate the platinum-based noble electrocatalysts for the ORR is crucial for the development of these energy devices [8–11].

Carbon-based materials have emerged as a class of promising alternative electrocatalysts for the ORR due to its low price, high earth abundance and environmental friendliness. Especially the catalytic activity of carbon materials can be further improved by doping of heteroatom into carbon framework. The non-metal heteroatom doped in carbon is usually N, S, B, F and P et al., which can modify the electronic structure (like charge and/or spin density redistribution) of carbon and create the active sites favorable for the adsorption of O₂ molecule and facilitate the ORR process [12–17]. In addition, transition metal (TM) heteroatom dopants (such as Fe, Co, Ni, Cu, Mn et al.), especially being co-doped with the non-metal heteroatom mentioned above, have been reported to show great potential in improving the catalytic activity of carbon although the nature of catalytic sites in these carbon is still on debate [18–20]. Considerable efforts have been devoted to the study of transition metal (mainly Fe and Co) and N co-doped carbon (TM–N–C) catalysts for the ORR [19–23]. The catalytic sites with

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Fe–N₄/C or FeN₂₊₂/C configuration bridging two adjacent graphitic sheets hosted in micropores were proposed by Dodelet and co-workers to exist in these catalysts [19,24]. Recently, P-doped carbon is of thrive interest since P doping can modify the structure and activity of carbon more effectively due to the lower electronegativity and larger covalent radius of P as compared with N [13,25,26]. P-doped carbon with different structure, such as graphite layers [27], graphene nanosheets [28], microporous carbon [29,30] and mesoporous carbon [31,32], have been reported to show improved electrocatalytic activity for ORR. Nevertheless, there have been few reports about the ORR activity of P and transition metal co-doped carbon. In our previous work, we prepared P and Co co-doped mesoporous carbon (P–Co–MC) and studied the ORR activity of P–Co–MC in alkaline media [32]. Our results showed that co-doping of Co with P can significantly improve the catalytic activity of carbon as compared with only P-doping or Co-doping. To better understand the effect of co-doping of transition metal with P on the structure and ORR activity of carbon, other transition metal dopants need to be explored. It's reported that for the transition metal and N co-doped carbon, Fe-based catalysts show higher activity and especially higher selectivity than the Co-based catalysts [33–36]. This motivates us to explore the activity of Fe and P co-doped carbon for the ORR. To the best of our knowledge, the preparation and electrocatalytic activity of Fe and P co-doped carbon for ORR are rarely reported.

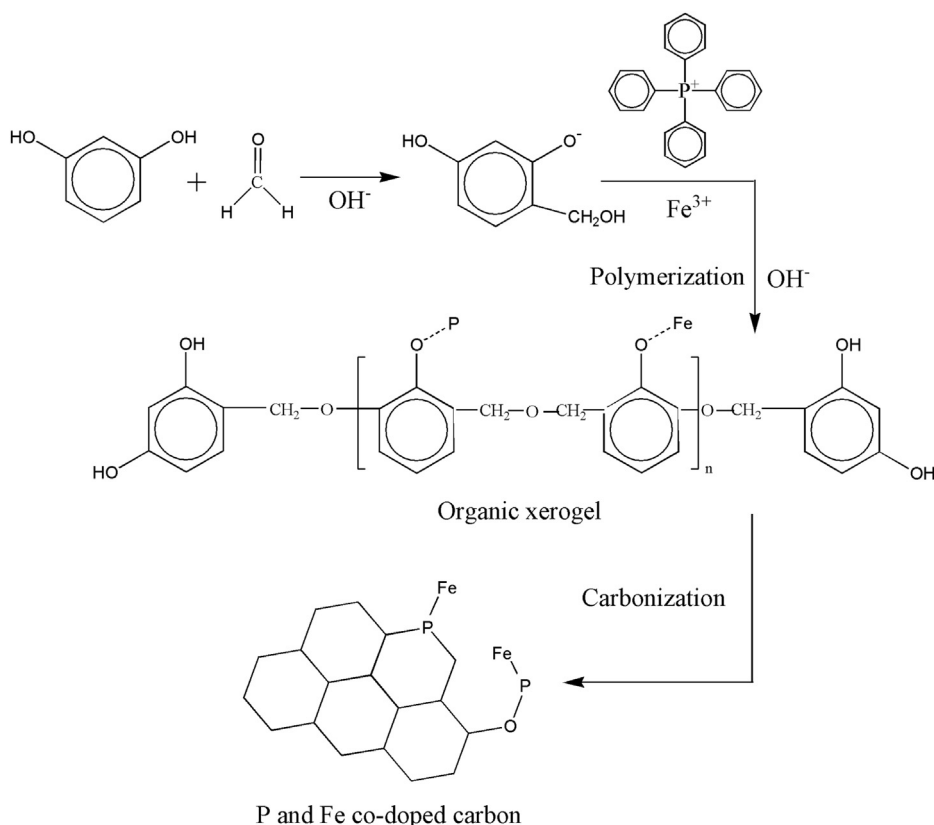
Herein, we developed a facile method to synthesize the P and Fe co-doped carbon xerogel (P–Fe–C) via an in-situ sol–gel polymerization method followed by a pyrolysis process for the first time. The resorcinol and formaldehyde were used as the carbon source. Iron nitrate and tetraphenylphosphonium bromide were used as sources of Fe and P, respectively. The P and Fe were introduced into carbon precursors during the polymerization process.

The influence of Fe and P co-doping on the electrocatalytic activity of the resulting P–Fe–C for the ORR in alkaline media was investigated. The pyrolysis temperature has a strong impact on the structure and texture of the P–Fe–C, which further affects the ORR activity and durability of P–Fe–C.

2. Experimental

2.1. Sample preparation

The P and Fe co-doped carbon xerogel was synthesized via an in-situ sol–gel polymerization method followed by a pyrolysis process. In a typical experiment, 0.05 mol of resorcinol and 0.10 mol of formaldehyde were mixed and dissolved in 25 ml of deionized water to form a homogeneous solution by stirring. Meanwhile 0.0167 mol of tetraphenylphosphonium bromide (C₂₄H₂₀BrP, ≥99.0%, Sigma Aldrich) was dissolved in 50 ml of ethanol and added to the above solution. Then 0.0025 mol Fe(NO₃)₃·9H₂O (≥99.0%, Guoyao Chemical Reagent Co. Ltd.) was added to the solution. Afterwards, aqueous ammonia solution was added and kept stirring until a wet organic xerogel was obtained. Next, the wet organic gel was dried and cured in a vacuum oven for 7 days at a temperature of 85 °C. Eventually, the organic gel was ground into uniform powder and subjected to carbonization under N₂ atmosphere at a temperature of 800 °C with a heating rate of 5 °C min^{−1} and holding time of 2 h. The pyrolyzed samples were stirred in 500 mL of 1.0 M HCl solution for 12 h to dissolve the residue Fe in the carbon. Finally, the samples were washed with ultrapure water until a neutral pH was reached and then dried in an oven at 90 °C. The sample obtained was denoted as P–Fe–C-800, where the number reflects the pyrolysis temperature. To study the influence of pyrolysis temperature on the structure and catalytic activity of



Scheme 1. Schematic illustration of the preparation of P and Fe co-doped carbon xerogels.

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