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Fe—N doped carbon materials from oily sludge as electrocatalysts for alkaline oxygen reduction reaction

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ABSTRACT

Alkaline oxygen reduction reaction (ORR) presents an important role for energy conversion technologies and requires the development of an efficient electrocatalyst. Pt-based catalysts provide suitable activity; however, Pt production accessibility and high costs create hurdles to their commercial implementation. Fe coordinated within N-doped carbon materials (Fe—N—C) are a promising alternative due to their high ORR catalytic activity, although the currently commercially available Fe—N—C materials rely on harsh synthetic protocols which can lead to increased environmental impacts. In this work we target this issue by taking advantage of an oily sludge waste currently generated in refineries to synthesize Fe—N—C materials, thus, avoiding the environmental impact caused by the management of this waste. The solid particles within oily sludge, which present a high concentration of C and Fe, were combined by different nitrogen sources and pyrolyzed at high temperatures.

The prepared materials present a hierarchical pore structure with surface areas up to 547 $m^2\ g^{-1}$. X-ray photoelectron spectroscopy analysis found that the impregnation of N using phenanthroline promotes the formation of pyridinic-N structures, which enhances the ORR performance compared to melamine doping. Additional doping of Fe with phenanthroline results in an ORR mass activity of 1.23 ± 0.04 A g^{-1}_{FeNC} at 0.9 $V_{RHE,\ iR\text{-}free}$ in a rotating disc electrode (0.1 M KOH). This catalyst also shows a lower relative loss in activity at 0.9 V_{RHE} after 8000 cycles in O_2-saturated conditions compared to a commercial FeNC catalyst, PMF D14401, (−63.5 vs −69 %, respectively), demonstrating promise as a cheap and simple route to Fe—N—C catalysts for alkaline ORR.

1. Introduction

The oxygen reduction reaction (ORR) is an essential process in energy conversion technologies, such as low temperature polymer electrolyte fuel cells, metal–air batteries [1,2], and alkaline exchange membrane fuel cells (AEMFC), which have gained rising prominence [3]. The ORR in AEMFC involves the reduction of oxygen molecules via the transfer of two or four protons to form hydrogen peroxide or OH^-, respectively [3,4] . The ORR is limited by the overpotential that arises from the slow kinetics at the cathode, and therefore an efficient electrocatalysts is needed. To date, Pt-based catalysts display the highest activity owing to its suitable binding energies to the ORR intermediates [5]. Nevertheless, Pt is expensive, and the majority is produced in South Africa [6]. Consequently, in the EU, Pt is considered a critical raw material due to its high global supply risk and economic vulnerability [7]. Additionally, 0.75 g Pt catalyst in a 1 kW proton exchange membrane fuel cell is predicted to provide 60 % of the total environmental impacts from manufacturing [8]. Therefore, alternative sustainable electrocatalysts derived from cheap and abundant sources are crucial for the practical implementation of fuel cells. Atomic transition metals coordinated to nitrogen-doped carbon (M—N—C) are currently the most active non-Pt based electrocatalyst for the ORR [8,9]. These materials are typically obtained by pyrolysis of a metal, carbon, and nitrogen precursors or by adsorption of macrocycles in commercial carbon materials (such as carbon black or graphene) [10–12]. However, novel techniques have recently emerged that entail the utilization of metal–organic frameworks or the ionothermal synthesis followed by cation exchange [13–16].

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