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Preparation of metal-free electrocatalysts from cassava residues for the oxygen reduction reaction: A sulfur functionalization approach

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ABSTRACT

Metal-free electrocatalysts for the oxygen reduction reaction (ORR) were synthesized from cassava residues through a thermal functionalization with sulfuric acid. Their electrocatalytic activities were tested through the ORR performance in basic media. Chemical composition in samples seems to play an important role in their electroactivity, more than textural properties, as the sulfur-treated high-temperature sample (Sy800) has the best performance with an onset potential of 0.69 V vs RHE (reversible hydrogen electrode) and a current of -2.32 mA cm^{-2} at 0.3 V vs RHE. These functionalized cassava residues are promising materials to be used like carbon-based metal-free electrocatalysts.

Fuel cells are devices capable to convert the chemical energy from fuels to electricity directly, with high efficiencies and zero or low emissions [1]. For many years, Pt-based electrocatalysts and other precious metals have been widely used as active catalysts for oxygen reduction reaction (ORR). However, noble metals are expensive and scarce; they present poor long-term stability and can be easily CO poisoned. Recently, nitrogen-doped carbon (NDC) has been widely studied as metal-free electrocatalyst showing high activity for ORR in alkaline media [2]. In the same manner, it has been reported that the sulfur-doped carbon structures (SDC) possess catalytic activity for the ORR [3], although SDC have been less studied than NDC. In this regard, there are theoretical studies which propose that sulfur in the carbon framework promotes the redistribution of spin and charge densities, favorable for providing more ORR active sites [4]. Some reports suggest that sulfur improves the selectivity of oxygen reduction towards the $4e^-$ process and materials are more stable than commercial Pt-C catalysts [5]. Therefore, the synthesis and study of SDC is an interesting field to obtain low cost metal-free electrocatalysts with high performance for ORR.

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The sulfur doping has been carried out over SDC through different methods and tested in several applications. Zhang et al. synthesized graphene doped with nitrogen/sulfur (N/S) using cysteine as an environmental-friendly N/S source, the ORR behaviour for these materials were better to those obtained using Pt/C [6]. Following the same research approach of co-doped materials, Zhao et al. prepared materials contain N/S over hollow carbon microspheres with electrochemical performance better than Pt/C in alkaline media [7]. Another study used residues from banana-peel to prepare porous carbons, which were co-doped with N/S, afterwards they were tested in the ORR in alkaline media and compared with the commercial Pt/C, the results were very promising as they perform better than commercial Pt/C [8].

On the other hand, carbon can be derived from abundant sources through simple processes. Cassava (*Manihot esculenta*) is considered a crop which generates huge amount of waste in the form of peel and pulp, contributing over 700 MT waste in the global upstream food waste [9,10]. Then, cassava residues can be converted into valuable products and energy in a sustainable manner. Although there are reports about sulfur-doped graphenes used as carbon-based metal-free electrocatalysts [11–13], cassava has not been studied extensively as carbon source for this application. In this work, metal-free electrocatalysts from cassava were obtained by eco-friendly methods and evaluated for ORR, providing an opportunity to give added value to local residues.

Experimental

The metal-free electrocatalysts from cassava were prepared as follows: cassava residues obtained from a local market were washed with distilled water; cut into cubes of 1 cm per edge and dry at 80 °C overnight in an oven HS60 Prendo. Dry samples were grinded using a coffee grinder and sieved through 100 ASTM sieves. 5 g of grinded cassava were mixed with 100 mL of distilled water at 72 °C during 1 h of gelatinization. Afterwards, samples were refrigerated at 4 °C for 48 h to promote retrodegradation. A mixture of gel-alcohol was formed adding 50 mL ethanol (TEDIA, 98%) and sonicated during 30 min for the solvent interchange. The material was recovered by filtration and dried at 80 °C overnight. Then, dry samples were carbonized under nitrogen atmosphere, at 300 and 800 °C during 1 h, at heating rate of 10 °C min^{-1}. The functionalization treatment was carried out according to the procedure proposed by Mena-Duran and Macquarrie, [14] in which 1 g of material was mixed with 7 mL of sulfuric acid (CTR Scientific, 95%) at 95 °C during 3 h. Afterwards, the sulfur-functionalized carbons were washed with hot water until filtrates got a pH 6. Finally, these materials were dried at 80 °C overnight. Samples were labelled as follows: Syraw, Sy300 and Sy800, where raw refers to material without any thermal treatment, 300 and 800 corresponds to the pyrolysis temperature used to prepare the materials.

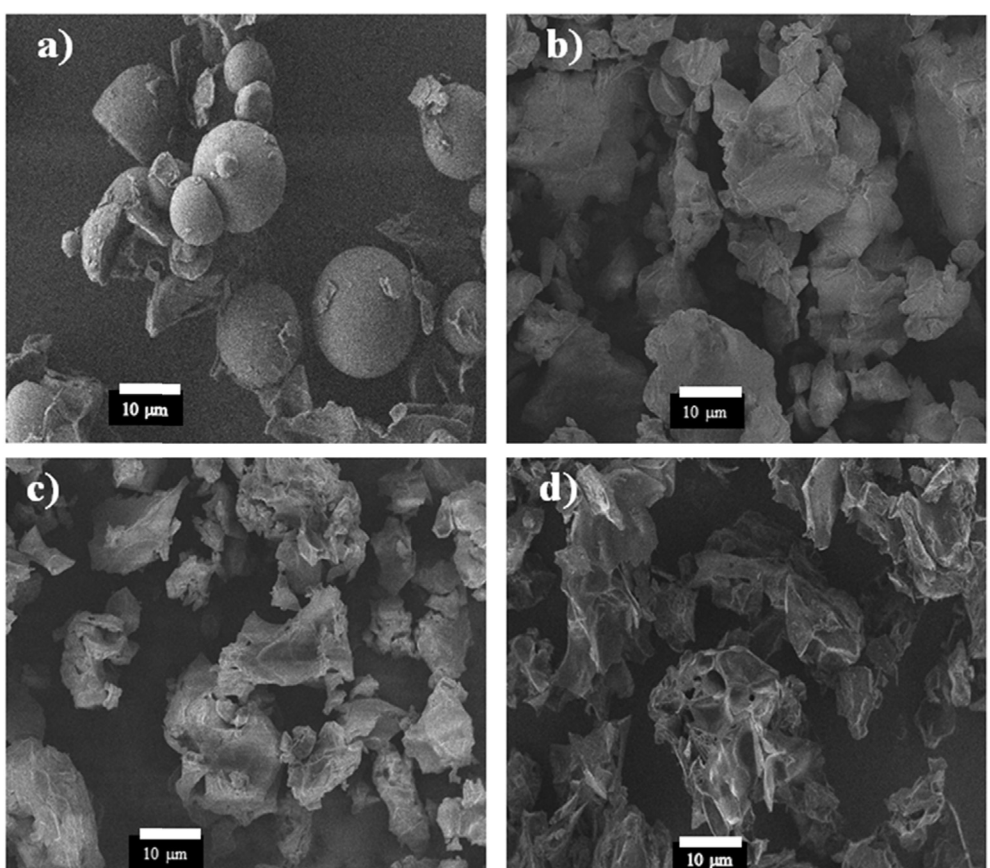

Fig. 1 – SEM micrographs of raw cassava (a), Syraw (b), Sy300 (c) and Sy800 (d).