



# Oxygen reduction on chemically heterogeneous iron-containing nanoporous carbon: The effects of specific surface functionalities



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## ABSTRACT

Synthetic activated carbon containing iron and sulfur heteroatoms, obtained from polystyrene sulfonic acid-based organic salt, and commercial wood-based carbon containing phosphorous were tested as catalysts for oxygen reduction reactions. The carbons were characterized using adsorption of nitrogen, TA-MS, FTIR, XRD, XPS, potentiometric titration, SEM/EDX, and HR-TEM microscopy. The introduction of iron to the carbon resulted a marked electrocatalytic activity for oxygen reduction reaction (ORR) in alkaline medium. A current density was higher than that on commonly used platinum modified carbon and number of electron transfer ( $\sim 4e^-$ ) indicated a high ORR efficiency. This was accompanied by a high tolerance to methanol oxidation and a good long-term stability after 1500 potential cycles. The extensive surface characterization indicated the fast  $O_2$  adsorption and charge transfer was owed to the surface hydrophobicity, small pores and conductivity. The synergistic effect of porosity and specific iron species containing sulfur lead to high ORR activity and high kinetic current densities.

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## 1. Introduction

Platinum/carbon (Pt/C) based cathodes are commercially used for an oxygen reduction reaction (ORR), important for development of new sources of energy [1,2]. Unfortunately, such electrodes, besides being expensive, show a low tolerance to fuel crossover. This has stimulated much research on use of non-noble metal electrocatalysts for reduction of oxygen [3–17]. Heteroatom doped nanoporous carbons have been widely investigated for this purpose [16–25]. Other carbonaceous materials such as graphene oxide or graphene have also attracted significant attention of researchers [3,4,6–10,12,16]. Besides a high electrical conductivity and high surface area of such materials, the presence of heteroatoms such as nitrogen [5,6,8,9,11,15,20,21,25], sulfur [6,7,10,12,16], phosphorus [18,23,24], or boron doped to the carbonaceous matrices has been indicated as of paramount importance [23,26,27]. Such heteroatoms were shown to provide sites for oxygen adsorption and reduction [3,10,12,26]. So far the materials doped with nitrogen exhibit the highest number of electron transfer ( $n$ ) and high density

of a kinetic-current ( $J_k$ ) [28]. The calculated values from Koutecký–Levich plot for such materials were  $n = 3.96$  and  $J_k = 4.02 \text{ mA/cm}^2$  at  $-0.50 \text{ V vs. SCE}$  ( $0.51 \text{ V vs. RHE}$ ). When sulfur and nitrogen are dual-doped into mesoporous graphene  $n = 3.3$  and  $J_k = 24.5 \text{ mA/cm}^2$  at  $-0.50 \text{ V vs. Ag/AgCl}$  ( $0.48 \text{ V vs. RHE}$ ) were measured [10]. An important feature of these materials is their high tolerance to methanol crossover [10,28]. Even though the number of electron transfer can be close to 4, in the majority of studies the ORR follows an incomplete  $4e^-$  electron pathway at more positive potential [29].

Another research approach explored to decrease the costs of the ORR catalysts is an incorporation of non-precious metal oxides and nanoparticles into a carbon catalyst support. So far carbon materials containing Fe, Co, Mn, Ni, Cu oxides and nanoparticles have been investigated [14,17,20,21,30–32]. Even though the four-electrons transfer mechanism is favored on these materials, their activity is still lower than that of Pt/C [3,20,31]. For the performance of such catalysts, the distribution of active sites and also sizes, shapes, and structures of nanoparticles are of paramount importance [32]. In this group of catalysts, carbon-supported CoN/C nanoparticles synthesized by An and coworkers showed a high ORR activity and a comparable onset potential ( $0.85 \text{ V vs. RHE}$ ) to that of commercial Pt/C [17].

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Copper is a non precious metal catalyst widely investigated for ORR [33–36]. Recently, we have shown a promising performance of copper/nanoporous catalysts obtained from the copper containing polymeric salt [36]. The unique architecture of copper particles, their specific chemistry (sulfides and oxides) and a high electrical conductivity and surface hydrophobicity resulted in a high electrocatalytic activity and tolerance to methanol crossover with a  $3.5e^-$  reduction path [36]. The source of sulfur was in the sulfone-based polymer used as a carbon precursor, which even after carbonization without transition metals shows some ORR activity owing to the catalytic effect of sulfur [6,7,10,12,16,36].

Besides copper, iron containing nanoporous carbons and graphene/Fe<sub>2</sub>O<sub>3</sub> have been also investigated with encouraging results [8,20,37,38]. Their reactivity is significantly enhanced in the presence of Fe–N bonds and various iron-containing species were used as a source of these functionalities. Moreover, the superior performance of the nanocomposites was linked to a bimodal-pore structure, high surface area, as well as a uniform distribution of high-density nitrogen and metal active sites [39].

Based on the previously published results from our group on the ORR activity of copper containing catalyst [34,36] and activity of sulfur doped nanoporous carbons [40], the objective of this paper is to address the encouraging performance of a new ORR catalyst obtained from the polymeric salt containing iron and sulfur. The initial compound is a commodity water soluble polymer (Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt). For further studies a cation exchange with Fe<sup>3+</sup> was carried out [41]. An advance compared to state-of-the-art in this field is in providing a high surface area catalyst with sulfur doped to the carbon matrix and highly dispersed iron in a variety of chemical forms (sulfides, oxides). A highly dispersed and diverse catalyst is expected to enhance an electron transfer within the well-developed micro/mesoporous carbon texture and to provide hydrophobicity enhancing oxygen adsorption. To stress the importance of the specific chemical and structural nature of this iron-based catalyst, the surface features and the performance of the new electrocatalysts are compared to those of a catalyst obtained by heat treatment of the polymer containing sodium salt itself, of commercial wood-based carbon obtained by phosphoric acid activation and of Vulcan Pt containing carbon. The commercial wood-based activated carbon contains iron oxide as a main ash component and therefore its performance as an ORR catalyst can be affected by the trace metal impurities [14].

## 2. Experimental

### 2.1. Materials

The polymer Poly(4-styrenesulfonic acid-co-maleic acid) (Sigma Aldrich) salts containing sodium and/or iron were used as organic precursors. First, the cation exchange was done. 200 ml of 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub> were mixed with 20 g of polymer. Then the thick viscous solution was heated at 200 °C for 4 h. Dried sample was carbonized in a horizontal furnace in nitrogen as an inert gas (flow rate 300 mL/min) at 800 °C for 40 min with a heating rate of 50 °C/min [41]. The obtained materials were washed in water in a Soxhlet apparatus to remove an excess of water-soluble inorganic salts. Afterward, the carbon obtained from the iron modified polymer was heated to 950 °C for 60 min in an inert atmosphere to promote the reduction of iron species. The carbon obtained from the sodium form of the polymer is referred to as PSC, and the carbon obtained from the Fe-exchanged polymer-as PSC-Fe.

Another carbon tested for ORR activity was a wood-based WVA-900 (Mead Westvaco) obtained using phosphoric acid activation. It

is referred to as WVA. For reference Pt/Vulcan catalytic carbon with 20 wt.% Platinum (Sigma Aldrich) was used.

### 2.2. Methods

#### 2.2.1. Electrochemical characterization

The performance of our materials for electrochemical ORR was investigated in 0.1 M KOH using a three-electrode cell with Ag/AgCl/KCl (3 M) as a reference electrode. The measurements of chronoamperometry and long-term stability by applying 1500 potential cycles were carried out on VersaSTAT MC (AMETEK, Princeton Applied Research) with a scanning rate of 5 mV/s (cyclic voltammetry). The working electrode was prepared by mixing the active material with polyvinylidene fluoride (PVDF) and commercial carbon black (carbon black, acetylene, 50% compressed, Alfa Aesar) (8:1:1) in N-methyl-2-pyrrolidone (NMP) until a homogeneous slurry. The slurry was coated on a Ti foil (current collector) with the total surface area of 1 cm<sup>2</sup> of an active material. Linear sweep voltammograms were obtained in 0.1 KOH using 757 VA Computrace (Metrohm) at various rotation rates (from 0 to 2000 rpm) with Ag/AgCl (3 M KCl) and Pt wire as a reference and a counter electrode, respectively. The measurements of cyclic voltammetry were carried out under O<sub>2</sub> or N<sub>2</sub> saturation in the electrolyte in the potential range of 0.19 to –0.8 V vs. Ag/AgCl (1.17 V–0.18 V vs. RHE) at a scan rate of 5 mV/s. The working electrode was prepared by dispersing 2 mg of the catalyst in 1 ml of deionized water and 0.5 ml of 1 wt.% Nafion aqueous solution. About 5 μl of the prepared slurry was dropped (three times) on a polished glassy carbon electrode (Metrohm, Switzerland, diameter 2 mm) and dried at 50 °C in air. The potential was swept from 0.19 to –0.8 V vs. Ag/AgCl (1.17 V–0.18 V vs. RHE) at a scan rate of 5 mV/s. After each scan, the electrolyte was saturated with air (the source of O<sub>2</sub>) for 20 min. All the experiments were carried out at room temperature.

**2.2.1.1. RHE conversion.** The measured potentials versus the Ag/AgCl (3 M KCl) reference electrode were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E_{\text{Ag/AgCl}}^{\circ}$$

where  $E_{\text{RHE}}$  is the converted potential versus RHE,  $E_{\text{Ag/AgCl}}$  is the experimental potential measured against the Ag/AgCl reference electrode, and  $E_{\text{Ag/AgCl}}^{\circ}$  is the standard potential of Ag/AgCl (3 M KCl) at 25 °C (0.210 V). The electrochemical measurements were carried out in 0.1 M KOH (pH = 13) at room temperature; therefore,  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.977 \text{ V}$ .

#### 2.2.2. X-ray diffraction (XRD)

XRD measurements were conducted using standard powder diffraction procedures analyzed by CuK<sub>α</sub> radiation (tension of 40 kV and current of 40 mA) generated in a Phillips X'Pert X-ray diffractometer. The scan rate used was 2.3 deg/min. The materials were ground with methanol in a small agate mortar. Then slurry was smear-mounted on glass slide. A standard glass slide was run for the background.

#### 2.2.3. Scanning electron microscopy (SEM)

SEM images were obtained using a Zeiss Supra 55 VP. The accelerating voltage was 5 kV. Scanning was performed in situ on a sample powder without coating. Electron-dispersive X-ray spectroscopy (EDX) analysis was done at magnification 5 KX with an accelerating voltage 15 kV and the elemental content on the surface was calculated.

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