



Short communication

## Trace metal residues promote the activity of supposedly metal-free nitrogen-modified carbon catalysts for the oxygen reduction reaction



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### ABSTRACT

We show in this study that the presence of trace metal residues in some supposedly metal-free catalysts for oxygen reduction, at concentrations which are difficult to detect using conventional methods such as XPS and EDX, can profoundly promote the ORR activity of the catalysts.

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## 1. Introduction

Metal-free catalysts for the oxygen reduction reaction (ORR) have recently witnessed unprecedented interest in light of their prospective application in key technologies such as metal–air batteries, fuel cells and chlor-alkali electrolysis [1]. These catalysts are considered the “Holy Grail” in applications for energy conversion and storage with the promise of being substantially less costly than the noble-metal catalysts used nowadays. However, the important question is “How metal-free are metal-free catalysts?” A careful evaluation of the reported synthesis strategies reveals that many supposedly metal-free ORR catalysts are synthesized using metal precursors [1]. Notably, graphene which is increasingly being used for synthesis of so-called metal-free carbon catalysts modified with heteroatoms may contain metal impurities depending on the method of its synthesis [2]. The residual metal species in these catalysts are reportedly dislodged by acid leaching. However, the complete removal of metal residues is difficult to prove. Actually, even prolonged treatment with acids, termed as “super-washing”, does not rid carbon nanotubes of iron residues [4–6], which may significantly affect their electrocatalytic properties [3,5,6].

To probe the influence of trace metal residues on the ORR activity of nitrogen-modified carbon (NC) catalysts, we performed careful synthesis of a metal-free NC catalyst (R), cautiously avoiding any metal contamination. Metal precursors, in minute concentrations (0.05–1.05 wt.%) were then deliberately incorporated into R and the

resulting effect on the ORR was investigated. For comparison, nitrogen-modified mesoporous carbon (NMC) [7], nitrogen-modified carbon nanotubes (NCNT) [8], and a catalyst obtained by the pyrolysis of a mixture of poly(3,5 pyridine) and Vulcan XC72® (PPy) [9] were also included in the investigation.

## 2. Experimental

### 2.1. Synthesis of R, NMC and NCNT

The reference metal-free catalyst R was prepared by pyrolysis of a composite of polypyrrole and Vulcan XC72® (Carbot Corporation), weight ratio 2:3 respectively. Vulcan XC72® was dispersed in ultrapure water containing acetic acid (10%). After ultrasonication for 15 min, pyrrole (Acros Organics) was added to the suspension followed by further ultrasonication for 20 min. Afterwards, hydrogen peroxide (30%) was added drop-wise to the suspension leading to polymerization of the pyrrole. The polypyrrole/Vulcan XC72® composite was filtered, dried in air for 24 h and pyrolyzed at 800 °C for 2 h under helium (50 sccm) to obtain R. NMC was prepared via an entirely metal-free nanocasting method as reported previously [7]. Acid-washed NCNT were synthesized as reported in the literature [8].

### 2.2. Incorporation of Fe, Mn and Ni into R

R was impregnated with a known concentration of the corresponding *meso*-tetrakis(4-pyridyl) porphyrin (TPyP) metal complex (Porphyrin systems), dried in air and subsequently pyrolyzed at

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800 °C under He gas (50 sccm, 2 h). R/Fe, R/Mn and R/Ni denote R with traces of Fe, Mn and Ni respectively.

### 2.3. Physical–chemical characterization

XPS measurements were carried out in an ultra-high vacuum set-up equipped with a monochromatic Al K $\alpha$  X-ray source and a high resolution Gammatdata-Scienta SES 2002 analyzer. SEM images were recorded using a Quanta 3D FEG scanning electron microscope equipped with EDX. ICP-OES and AAS were used to determine the presence and level of metal impurities in all the catalysts.

### 2.4. Electrochemical measurements

Catalyst inks were prepared by dispersing the catalyst powder (5 mg) in a mixture of ultra-pure water (490  $\mu$ l), ethanol (490  $\mu$ l) and 5% Nafion (20  $\mu$ l) followed by ultrasonication for 20 min. A specific volume of the ink was pipetted onto a pre-cleaned glassy carbon electrode to form a catalyst film with a loading equivalent to 0.210 mg/cm<sup>2</sup>. The resulting films were left to dry in air and later investigated for the ORR using rotating disk electrode (RDE) and rotating-ring disk electrode (RRDE) voltammetry in KOH (0.1 M) and in H<sub>2</sub>SO<sub>4</sub> (0.5 M) using a PGSTAT302N bipotentiostat/galvanostat (Eco Chemie). The measurements were performed at room temperature using a Ag/AgCl/3 M KCl reference electrode and a platinum counter electrode. The potentials are reported against the reversible hydrogen electrode (RHE).

## 3. Results and discussion

Fig. 1a shows RDE voltammograms of R, R/Fe with 0.05% and 1.05% Fe loading, PPy, and Pt/C (20% Pt, ETEK) in KOH (0.1 M), while Fig. 1b shows results of the same catalysts including NMC and NCNT in H<sub>2</sub>SO<sub>4</sub> (0.5 M). The oxygen reduction current by R (Fig. 1a), which was very similar to NMC (not shown), increases with overpotential with a plateau between  $-0.50$  and  $-0.64$  V characteristic of the formation of

H<sub>2</sub>O<sub>2</sub> as an intermediate. The features of the voltammogram, particularly, the potential for the onset of oxygen reduction, and the magnitude of the electrocatalytic current are typical of truly metal-free NC catalysts [10]. The nitrogen content in R was 3.3% (XPS) and its N1s peak was deconvoluted into pyridinic, graphitic and pyrrolic nitrogen groups of roughly equal intensity. R was therefore a suitable choice as a reference metal-free NC catalyst.

Notable differences exist between the ORR activity of R and the catalysts susceptible to be contaminated with metal residues or that were obtained by incorporation of trace metals into R. Most strikingly, the current density of R was markedly lower at all potentials compared to that of R/Fe (0.05%). Increasing the Fe content led to substantial increase in the catalytic current and to significant decrease of the overpotential for the ORR, consistent with other studies [6,10], thus underscoring the latent role of Fe on the ORR activity of NC catalysts.

All the catalysts showed significantly lower activity in H<sub>2</sub>SO<sub>4</sub> (0.5 M) compared to Pt/C (Fig. 1b). As in the alkaline medium, R showed the least activity, exceedingly lower than that of the catalysts with trace metals thus affirming that both the overpotential for ORR and the electrocatalytic reduction current are very sensitive to the presence of metal species. We attribute the relatively higher activities of PPy and NCNT in comparison to R to the likely presence of metal residues emanating from their synthesis. In particular, poly(3,5 pyridine) is commonly prepared by organometallic polycondensation using nickel or palladium complexes [11] and could therefore potentially contain traces of Ni or Pd. We confirmed using ICP-OES that poly(3,5 pyridine) contained 0.04 wt.% Ni corresponding to a loading of at least 0.01% Ni in PPy, and that NCNT contained 0.83 wt.% Fe and 0.01% Co using AAS, whereas, as expected, no metal species were detected in R (<0.01%) using both ICP-OES and AAS. The activities of all the catalysts that were investigated, expressed as the potential corresponding to a current density of  $-0.5$  mA cm<sup>-2</sup> were: R (0.71), R/Fe (0.76), R/Mn (0.74), R/Ni (0.77), FBP (0.73), PPy (0.83), NCNT (0.83), NMC (0.73), and Pt/C (0.87), and R (0.17), R/Fe (0.67), R/Mn (0.65), R/Ni (0.27), FBP (0.16), PPy (0.37), NCNT (0.58), NMC (0.12),

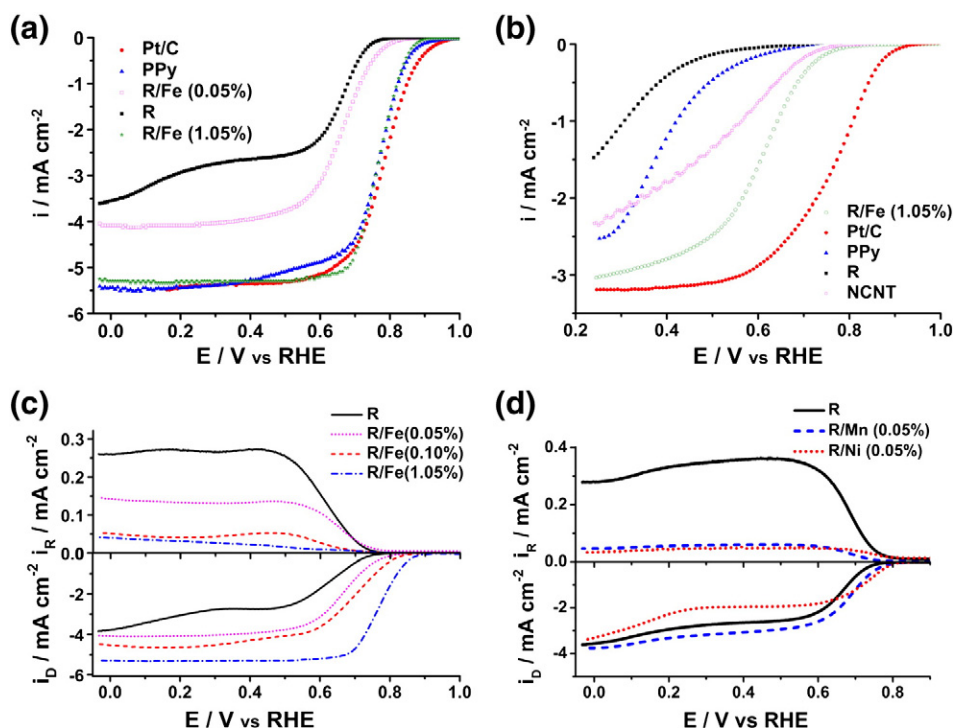


Fig. 1. RDE voltammograms recorded at 5 mV/s showing oxygen reduction by R, R/Fe (0.05%), R/Fe (1.05%), PPy, NCNT and Pt/C in (a) KOH (0.1 M) at a rotation speed of 1600 rpm and in (b) H<sub>2</sub>SO<sub>4</sub> (0.5 M) at a rotation speed of 900 rpm. RRDE voltammograms recorded at 5 mV/s and 1600 rpm showing the reduction of oxygen in KOH (0.1 M) at the disk ( $i_D$ ) and the oxidation of hydrogen peroxide at the ring ( $i_R$ ) polarized at 0.4 V, for different loadings of Fe in R/Fe (c), and for R/Mn (0.05%) and R/Ni (0.05%) (d).

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