Electrochemistry Communications 34 (2013) 113–116

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

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

Justus Masa [a], Anqi Zhao [b], Wei Xia [b], Zhenyu Sun [b], Bastian Mei [b], Martin Muhler [b], Wolfgang Schuhmann [a,*]

[a] Analytische Chemie und Zentrum für Elektrochemie — Elektroanalytik & Sensorik, Ruhr-Universität Bochum, Universitätsstr. 150, D-44780 Bochum, Germany
[b] Laboratory of Industrial Chemistry, Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany

ARTICLE INFO

Article history:
Received 21 April 2013
Received in revised form 25 May 2013
Accepted 28 May 2013
Available online 4 June 2013

Keywords:
Metal-free catalysts
Metal residues
Oxygen reduction
Nitrogen-modified carbon catalysts

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.

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

* Corresponding author. Tel.: +49 234 3226200; fax: +49 234 3214683.
E-mail address: wolfgang.schuhmann@rub.de (W. Schuhmann).

1388-2481/$ – see front matter
http://dx.doi.org/10.1016/j.elecom.2013.05.032

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 Kα X-ray source and a high resolution Gammadata-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 μl), ethanol (490 μl) and 5% Nafion (20 μl) 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^2. 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_2SO_4 (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_2SO_4 (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_2O_2 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_2SO_4 (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^{-2} 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),

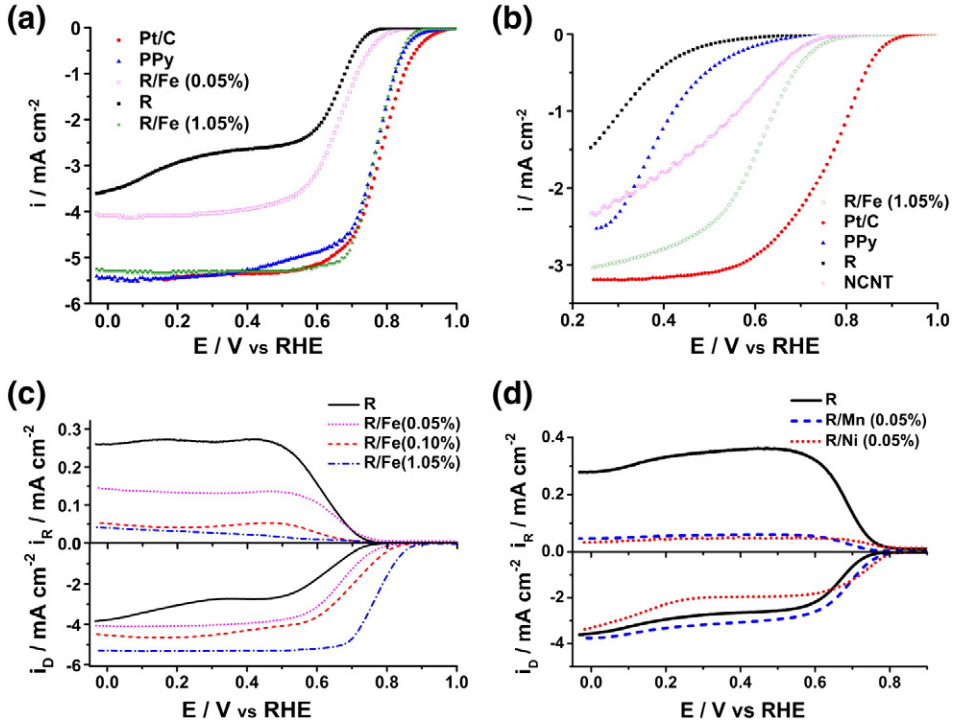

Fig. 1. RDE voltammograms recorded at 5 mV/s showing oxygen reduction by R, R/Fe (0.05%), R/Fe (1.05%), PPy, NCNT and Pt/C in (a) KOH (0.1 M) at a rotation speed of 1600 rpm and in (b) H_2SO_4 (0.5 M) at a rotation speed of 900 rpm. RRDE voltammograms recorded at 5 mV/s and 1600 rpm showing the reduction 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).

and Pt/C (0.80) respectively in KOH and in H_2SO_4. FBP represents the catalyst obtained by pyrolysis of a mixture of R and the free-base porphyrin (FBP), *meso*-tetra(4-pyridyl)porphyrin. In contrast to R/Fe and R/Mn, R, NMC and FBP showed very similar activity thus providing additional evidence of the promotional effect of metal species on the ORR activity of NC catalysts. In particular, the presence of Fe at a concentration of as low as 0.05% in the case of R/Fe (0.05%) significantly promoted the ORR activity of R.

The incorporation of nitrogen into carbon has been demonstrated to accelerate not only the kinetics of O_2 electroreduction but also the chemical decomposition of H_2O_2 [12]. Separate studies by Stevenson's group [13] and Anderson's group [14] indicated that a dual site is necessary if oxygen is to be reduced to OH^- in high pH electrolytes or to H_2O in low pH electrolytes, whereby NC active sites reduce oxygen to a peroxide intermediate, which is then heterogeneously decomposed to OH^- or H_2O by metal or metal oxide sites. According to Jaouen and others [15], heterogeneous decomposition of H_2O_2 is believed to be catalyzed by $M–N_x/C$-like sites following a Fenton-like mechanism via an oxo-ferryl-like cation radical, where M is a transition metal (typically Fe or Co) and x is the number of nitrogen atoms coordinated to M. $M–N_x/C$ sites are formed when nitrogen-containing organic compounds are pyrolyzed at high temperatures (600–1000 °C) in the presence of a transition metal and are reportedly more active for ORR than the corresponding catalysts obtained in the absence of transition metals [16]. The presence of metal species in NC catalysts is therefore crucial and ought not to be overlooked. For example, it can be seen from Fig. 1a and b that the addition of a minute quantity of Fe (0.05 wt.%) to R markedly improved its ORR activity. In KOH, the activity of R/Fe (1.05%) matched that of Pt/C with their onset potentials differing by only 38 mV in contrast to 84 mV for R.

RRDE voltammetry was employed to further probe the influence of trace metals on the ORR activity of NC catalysts with regard to the generation of H_2O_2 as shown in Fig. 1c and d. The amount of H_2O_2 generated decreased from 40.8% for R to 22% for R/Fe (0.05%), 7.5% for R/Fe (0.1%), and 4.5% for R/Fe (1.05%) clearly demonstrating that traces of Fe promote the ORR, and significantly influence the selectivity of the reaction. Similarly, the addition of Mn and Ni to R at a loading of 0.05% resulted in almost negligible generation of H_2O_2 and a higher onset potential for ORR (Fig. 1d). It has to be noted that despite the important role played by Fe, we did not detect its presence in R/Fe (0.05%) using EDX coupled to SEM, whereas Fe (Kα) was only barely detectable in R/Fe (0.1%) (Fig. 2a) after prolonged scanning.

XPS is popularly used to confirm the absence of metal residues after acid washing of NC catalysts prepared using metal precursors [17]. Signals from Fe and Mn were indiscernible in the XPS survey spectra of Re/Fe (0.1%) and R/Mn (0.1%) (Fig. 2b) after a minimum of 20 scans. The insets in Fig. 2b show enlargements of the binding energy regions within which the Fe 2p3/2 and Mn 2p3/2 peaks are expected to appear. Just very weak Fe 2p3/2 and Mn 2p3/2 peaks can be seen. This example shows that the sensitivity of XPS does not suffice to guarantee the absence of metal residues in NC catalysts prepared using metal precursors.

The importance of metal species in transition metal–N/C (MN/C) type catalysts has been widely investigated [6,12,13,18,19]. Lalande et al. [18] found that the most active sites of MN/C catalysts were only formed when both nitrogen and metal precursors were present during the pyrolysis. The debate as to whether the metal is involved in constituting the active site in MN/C catalysts or that it merely facilitates the formation of active site is not fully resolved [19]. However, the common observation is that the presence of both metal and nitrogen during pyrolysis leads to higher activity than when only one of them is present [6,20], as corroborated by the results shown in Fig. 1.

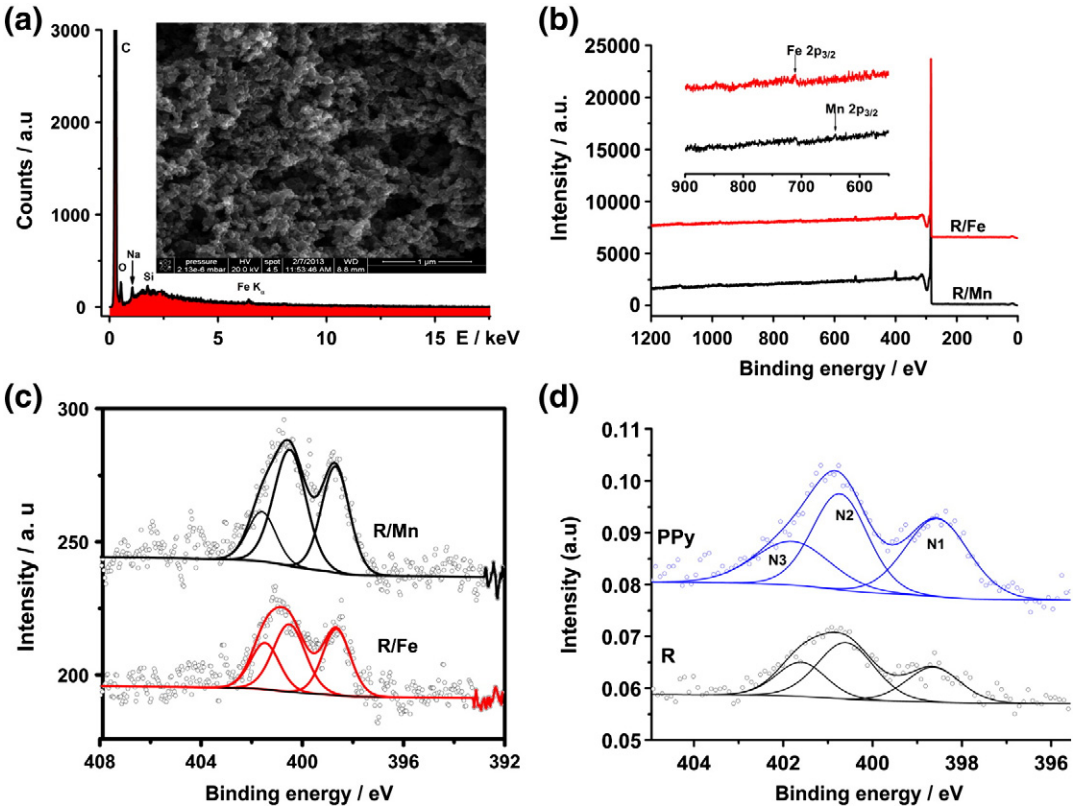

Fig. 2. (a) SEM micrograph and EDX spectrum of R/Fe (0.1%). (b) XPS survey spectra of R/Fe (0.1%) and R/Mn (0.1%) with the insets showing enlarged regions of the spectra where the $2p_{3/2}$ peaks of the corresponding metals are expected to appear. (c) High resolution N1s spectra of R/Mn and R/Fe. (d) High resolution N1s spectra of R and PPy. N1 = pyridinic, N2 = pyrrolic, N3 = graphitic.

The deconvoluted N1s spectra of R/Fe and R/Mn (Fig. 2c) were essentially similar to those of the reference catalyst R (Fig. 2d). It is therefore difficult based on XPS to assess the role played by the metal precursors in promoting the ORR activity of NC catalysts. Surprisingly, despite the similarity of the deconvoluted N1s spectra of R and PPy, the latter exhibited remarkably higher ORR activity especially in KOH (0.1 M). R and PPy were prepared by pyrolysis of polypyrrole and poly(3,5-pyridine) respectively, mixed with Vulcan XC72®. At low pyrolysis temperatures, pyridinic (N1) and pyrrolic nitrogen (N2) were the predominant groups in PPy and R respectively. However, after pyrolysis at 800 °C, the peak for graphitic nitrogen (N3) in both R and PPy became very pronounced and comparable in intensity. If only graphitic, pyridinic or pyrrolic nitrogen groups influenced ORR activity, then one would expect R and PPy to behave similarly. We observed in a previous study [8], consistent with other reports [21], that for NC catalysts, ORR activity was dependent on the relative abundance of the nitrogen functional groups and not on the absolute nitrogen content. Therefore, the large difference between the ORR activity of R and PPy implies that a hidden factor, which could not be revealed by XPS is responsible for the discrepancy. We suppose that this may partly be due to the trace amount of Ni in poly(3,5 pyridine) which may selectively promote the formation of specific NC sites, or take part in the formation of $M–N_x$/C-type active sites.

4. Conclusions

The metal-free catalysts that were synthesized without the involvement of any metal precursors over the entire synthesis cycle did not show as high ORR activity as the catalysts that were prepared by deliberate addition of trace metal precursors, or via synthesis routes that involved the use of metal precursors. In particular, the addition of Fe to a metal-free NC catalyst in concentrations as low as 0.05%, significantly influenced the activity and selectivity of the catalyst. These findings therefore underscore the importance of employing ultra-sensitive methods for trace metal analysis in order to avoid misleading classification of metal-free catalysts for the ORR.

References

[1] D. Yu, E. Nagelli, F. Du, L. Dai, Journal of Physical Chemistry Letters 1 (2010) 2165.
[2] A. Ambrosi, S.Y. Chee, B. Khezri, R.D. Webster, Z. Sofer, M. Pumera, Angewandte Chemie International Edition 51 (2012) 500.
[3] B. Sljukic, C.E. Banks, R.G. Compton, Nano Letters 6 (2006) 1556.
[4] K. Jurkschat, X. Ji, A. Crossley, R.G. Compton, C.E. Banks, The Analyst 132 (2006) 21.
[5] C.E. Banks, A. Crossley, C. Salter, S.J. Wilkins, R.G. Compton, Angewandte Chemie International Edition 45 (2006) 2533.
[6] Y. Li, W. Zhou, H. Wang, L. Xie, Y. Liang, F. Wei, J. Idrobo, S.J. Pennycook, H. Dai, Nature Nanotechnology 7 (2012) 394.
[7] T.C. Nagaiah, A. Bordoloi, M.D. Sánchez, M. Muhler, W. Schuhmann, Chemsuschem 5 (2012) 637.
[8] A. Zhao, J. Masa, M. Muhler, W. Schuhmann, W. Xia, Electrochimica Acta 98 (2013) 139.
[9] W. Xia, J. Masa, M. Bron, W. Schuhmann, M. Muhler, Electrochemistry Communications 13 (2011) 593.
[10] J.-S. Lee, G.S. Park, S.T. Kim, M. Liu, J. Cho, Angewandte Chemie International Edition 52 (2013) 1026.
[11] T. Yokozawa, Y. Nanashima, Y. Ohta, ACS Macro Letters 1 (2012) 862.
[12] S. Maldonado, K.J. Stevenson, The Journal of Physical Chemistry. B 109 (2005) 4707.
[13] J.D. Wiggins-Camacho, K.J. Stevenson, Journal of Physical Chemistry C 115 (2011) 20002.
[14] K.A. Kurak, A.B. Anderson, Journal of Physical Chemistry C 113 (2009) 6730.
[15] F. Jaouen, J.-P. Dodelet, Journal of Physical Chemistry C 113 (2009) 15422.
[16] F. Jaouen, J. Herranz, M. Lefèvre, J.-P. Dodelet, U.I. Kramm, I. Herrmann, P. Bogdanoff, J. Maruyama, T. Nagaoka, A. Garsuch, J.R. Dahn, T. Olson, S. Pylypenko, P. Atanassov, E.A. Ustinov, ACS Applied Materials & Interfaces 1 (2009) 1623.
[17] K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, Science 323 (2009) 760.
[18] G. Lalande, R. Cote, D. Guay, J.P. Dodelet, L.T. Weng, P. Bertrand, Electrochimica Acta 42 (1997) 1379.
[19] J.-P. Dodelet, in: M. Shao (Ed.), The controversial role of the metal in Fe- or Co-based electrocatalysts for the oxygen reduction reaction in acid medium, a non- and low-platinum approach, Lecture Notes in Energy, 9, Springer, 2013, pp. 271–337.
[20] G. Liu, X. Li, J.-W. Lee, B.N. Popov, Catalysis Sciences Technology 1 (2011) 207.
[21] L. Lai, J.R. Potts, D. Zhan, L. Wang, C. Poh, C. Tang, H. Gong, Z. Shen, J. Linc, R.S. Ruoff, Energy & Environmental Science 5 (2012) 7936.