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Highly active metal-free nitrogen-containing carbon catalysts for oxygen reduction synthesized by thermal treatment of polypyridine-carbon black mixtures

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ABSTRACT

A straight-forward method for the synthesis of metal-free catalysts for oxygen reduction by thermal treatment of a mixture of poly(3,5-pyridine) with carbon black in helium is reported. The catalyst was characterized by X-ray diffraction and photoelectron spectroscopy, cyclic voltammetry and rotating disk electrode measurements. The new catalyst exhibited remarkable activity similar to Pt-based catalysts in alkaline media.

1. Introduction

The oxygen reduction reaction (ORR) in alkaline media is of great industrial importance. For example, it is involved in alkaline fuel cells and in modern chlor-alkali electrolysis as the cathode reaction [1–3]. The state-of-the-art electrocatalysts for the ORR are platinum-based nanoparticles dispersed on carbon. However, the high cost of platinum, let alone its scarcity inhibits commercialization of some technologies where it is essential [4]. Consequently, tremendous efforts are aimed at its replacement with cheaper and readily available materials [5]. Transition metal N4-macrocyclic complexes are among the most intensively investigated non-precious metal catalysts for the ORR [5]. Nitrogen-doped carbon nanotubes were found to be active for the ORR especially in alkaline media [6–8]. Certain types of N-containing functional groups such as pyrrolyic and pyridinic groups, particularly those at graphitic edge plane sites, have been claimed to be responsible for the high ORR activities. Here, we report the synthesis of highly active ORR catalysts by an efficient and completely metal-free route consisting of mixing carbon black and polypyridine followed by pyrolysis in helium.

2. Experimental

2.1. Catalysts synthesis

Carbon black (Vulcan® XC72) and poly(3,5-pyridine) (Aldrich) in weight ratios of: 1:10, 1:5 or 2:5 were mixed in an agate mortar and subsequently treated at 400, 600, or 800 °C for 180 min in flowing helium. After cooling, the catalysts were obtained as black powders.

2.2. Characterizations

X-ray diffraction (XRD) was measured using a PANalytical theta–theta powder diffractometer equipped with a CuKα source. X-ray photoelectron spectroscopy (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.

2.3. ORR tests

Electrocatalytic ORR measurements were performed in a single compartment glass cell with glassy carbon (Ø 3 mm; HTW, Germany) modified with a catalyst film as the working electrode (WE), a graphite rod as counter electrode (CE), and a Ag/AgCl/3 M KCl reference electrode (RE). 5.0 mg of the catalyst or 2.5 mg for the case of Pt-ETEK (20% Pt on Vulcan carbon), were dissolved in water (490 μl), ethanol (490 μl) and 20 μl of nafion (5%) followed by ultrasonication for 15 min. 5.3 μl of the resulting catalyst ink was pipetted on a polished

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glassy carbon (GC) rotatable disk electrode and left to dry in air. All measurements were recorded at room temperature in KOH (0.1 M) using a μAutolab Type III potentiostat/galvanostat (Eco Chemie, The Netherlands).

3. Results and discussion

The application of polypyridine arises from its high nitrogen content, especially of the pyridinic type. Because the activity, stability and conductivity of electrocatalysts derived from organic materials are known to increase upon thermal treatment, mixing polypyridine with carbon black and subsequent thermal treatment was considered more promising than using the polymer itself as a catalyst. Different polymer to carbon weight ratios including 1:10, 1:5 and 2:5 were applied, and the pyrolysis was performed in helium at 400 °C, 600 °C and 800 °C.

The degree of carbonization of the polymer was studied by X-ray diffraction. Similar backgrounds were observed in all the obtained XRD patterns, where the two major contributions at about 25° and 43° originate from carbon (Fig. 1). The additional peaks observed for the sample treated at 400 °C (denoted P400, Fig. 1a) are apparently from polypyridine. These peaks disappeared in the sample treated at 600 °C (P600) indicating that the pyrolysis at 400 °C was not sufficient to fully carbonize the polymer. However, the absence of these peaks does not necessarily indicate complete carbonization of the polymer. Only the carbon background was observed for the samples treated at 800 °C (P800), even for high polymer loadings up to 2:5 (Fig. 1b). Due to the low melting point and low thermal stability of polymers, polypyridine and its fragments are assumed to be mobile at high temperatures resulting in spreading of the polymer phase, thereby improving its dispersion on the substrate. In addition, solid–solid, solid–liquid or even solid–gas reactions at the carbon-polymer interface are favored at higher temperatures, hence enhancing the interaction.

Elemental analysis by atomic absorption spectroscopy disclosed that the N content decreased from 1.62 wt.% in P600(1:5) to 1.38 wt.% in P800(1:5). A higher amount of polypyridine in P800(2:5) led to a higher N concentration of 2.20 wt.%. Elemental mapping using energy dispersive X-ray analysis indicates a homogeneous distribution of N in the obtained samples. High-resolution XPS was employed to investigate the nature of nitrogen species formed in the course of thermal treatment. Only carbon, nitrogen and oxygen were detected in the survey scans thus excluding the presence of any metallic impurities. Since carbon black is the major component of all the samples, the spectra were calibrated and normalized against the major C1s peak at 284.5 eV of graphitic carbon. Fig. 2a shows the C1s spectra of P400, P600 and P800. The C s peak of polymers and organics normally appears at binding energies higher than 284.5 eV [9]. P400 shows a relatively strong shoulder between 285 and 286 eV despite its low polypyridine loading (1:10). This can be attributed to organic carbon species from polypyridine or its fragments [10], thus confirming the XRD result that polypyridine was not fully decomposed in P400. The shoulder is weaker in P600(1:10), indicating the presence of less organic carbon species and more carbonized polypyridine. P800(2:5) shows a strong shoulder between 285–286 eV just like P400 in addition to an even stronger one at about 287 eV. Both shoulders can be attributed to carbon bound to nitrogen on the surface of the sample, which results from the relatively higher amount of the polymer in the starting material P800(2:5).

The N1s XP spectra of the three samples are shown in Fig. 2b. It is known that pyridinic nitrogen on carbon surfaces appears at about 398.6 eV [10]. Cohen et al. [11] showed that the N1s peak of pyridine weakly bound to carbon is located at 399.7 eV. Greczynski et al. [12] reported even higher N1s binding energies in poly(p-pyridine). For P400, a narrow peak indicative of a single N-containing functional group of the pyridine-type appears at about 399.3 eV, further confirming that the aromatic structure of polypyridine was not yet destroyed, although the polymer may have degraded to fragments. Thermal treatment at 600 °C led to significant broadening of the N1s peak (Fig. 2b). Decomposition of the polypyridine and its reaction with the carbon must have occurred leading to formation of new nitrogen species. Three peaks can be resolved by fitting at 401.7 eV, 400.6 eV and 399.0 eV, corresponding to quaternary N, pyrrolic N and pyridine-type N, respectively. The 0.3 eV shift in BE of the pyridine-type N compared to P400 is believed to be due to its enhanced interaction with the surface, for example, due to chemisorption by π-interactions [13]. Treatment at 800 °C resulted in nitrogen species fully consistent with nitrogen species strongly embedded in carbon materials [14]. In addition to the quaternary and pyrrolic nitrogen groups, pyridinic N was observed at 398.6 eV, which is a further shift of 0.4 eV to lower binding energies.

The ORR activity of the samples was investigated using cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements in 0.1 M KOH. The activity increased in the order: P400<P600<P800 (polymer to carbon ratio of 1:5) on the basis of onset potential (Fig. 3a). Although the reduction currents for P600 are higher than those for P800 below −0.3 V, the mass transfer limitation achieved at much lower potential for P600 implies that it is less active than P800. Since the same mass loading was applied for the two samples, the difference in diffusion limited current may arise from differences in actual surface areas. Thus, although both P600 and P800 have pyrrolic and quaternary nitrogen groups in addition to pyridine-type nitrogen, which may contribute to oxygen reduction, the enhanced activity of P800 may be due to better conductivity as a result of stronger interactions between pyrolyzed polypyridine and the carbon support as indicated by the XPS. Hence, further studies focus on sample P800.

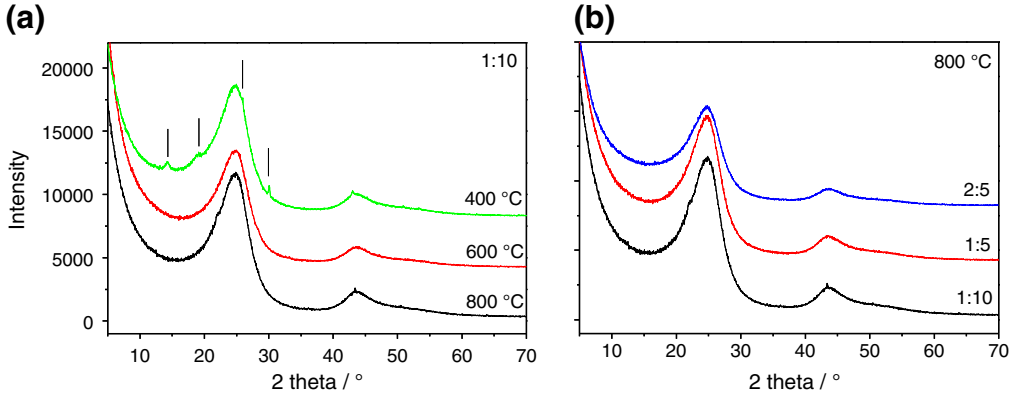

Fig. 1. XRD patterns; (a) sample with a fixed polypyridine to carbon ratio (1:10) prepared at different temperatures; (b) samples prepared at 800 °C with different polypyridine to carbon ratios.

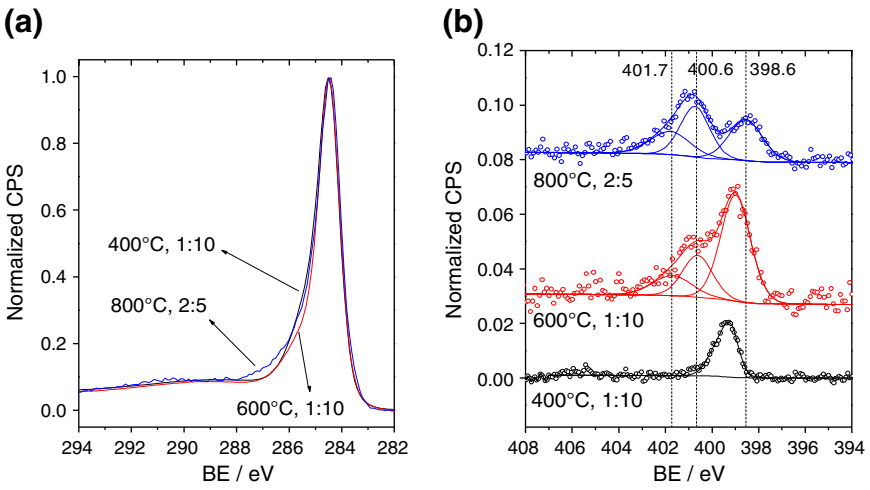

Fig. 2. XP C1s (a) and N1s (b) spectra of samples with varied polypyridine to carbon ratio (1:10 to 2:5) pyrolyzed at 400 °C, 600 °C and 800 °C.

The effect of polypyridine loading on the activity of P800(1:5 or 2:5) is shown in Fig. 3b by means of linear sweep voltammograms. A voltammogram for Pt-ETEK under the same conditions is provided for comparison. It is clear that the diffusion limited currents increase with loading in agreement with the higher average number of electrons transferred per oxygen molecule (see below). The onset potential of the synthesized catalyst is only about 50 mV less than that of the Pt-ETEK catalyst. However, although the magnitude of the catalytic currents for P800(2:5) is similar to that for Pt-ETEK, the specific loading of Pt-ETEK (0.187 mg/cm^2; normalized against the geometric area of the electrode), was only half that of P800(2:5).

The performances of P800(1:5) and P800(2:5) were further evaluated for mechanistic and kinetic performance using the Koutecky–Levich analysis (Fig. 3c) and Tafel plots (Fig. 3d). The average number of electrons transferred at −0.4 V was 3.6 and 3.8 for P800(1:5) and P800(2:5), respectively. This shows a high propensity of this catalyst to reduce O_2 nearly exclusively to OH^-. The kinetic currents for the Tafel plots were corrected for mass-transport effects [15]. The Tafel slopes in the low current density regions of P800(2:5), for the potential region from −0.075 to −0.137, and P800(1:5), for the potential range −0.125 to -0.151, were 67.3 mV/decade and 69.4 mV/decade, respectively, which corresponds to the transfer of the first electron as the rate-determining step under Temkin conditions for the adsorption of intermediates [16]. In the high current density regimes, the Tafel slopes for P800(2:5), in the potential range −0.144 to −0.178, and P800(1:5), in the potential range −0.158 to −0.185, were 122.9 mV/decade and 115.4 mV/decade, respectively. This is consistent with the commonly reported Tafel slope on Pt surfaces at high current densities and is attributed to a change in the mechanism of the ORR from Temkin to Langmuir adsorption conditions [16]. Importantly, the transition points between the two regimes of the Tafel slopes were not sharply distinct, and were different for each of the catalysts. The locus of P800(1:5) is

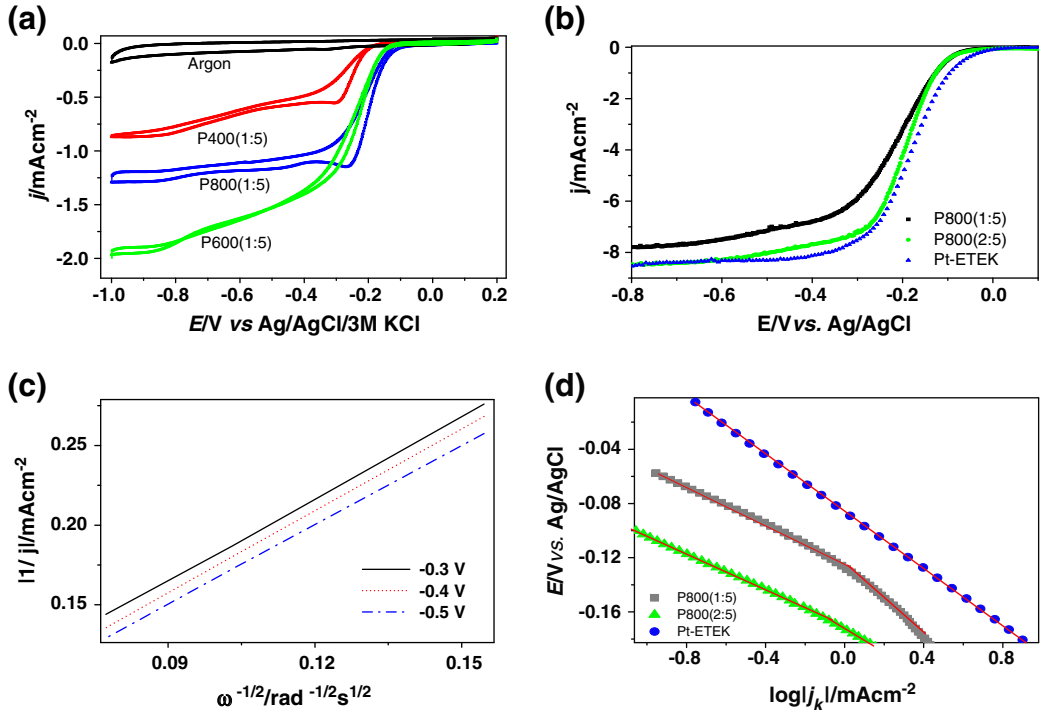

Fig. 3. (a) CVs recorded in argon- and oxygen-purged KOH (0.1 M) at a scan rate of 5 mV/s without rotation of the electrode; (b) Linear sweep voltammograms at a scan rate of 5 mV/s and rotation of 1600 rpm; (c) $j^{-1}/cm^2(mA)^{-1}$ versus $\omega^{-0.5}/(rads^{-1})^{-0.5}$ plots of P800(2:5); (d) Tafel plots extracted from (b).

very similar to that of Pt over a wide potential range (Fig. 3d). From a mechanistic point of view, this would imply close similarity of the mechanism for the oxygen reduction on both catalysts. This finding supports the suggestion by Chen et al. [2] that the mechanism for oxygen reduction on N-doped carbon in 0.1 M KOH might be similar to that for Pt-based catalysts.

The kinetic current densities at −0.15 V (normalized to the geometric electrode area) determined from Koutecky–Levich graphs were 4.41×10^{-3} mA/cm^2, 2.21×10^{-3} mA/cm^2 and 4.91×10^{-4} mA/cm^2 for Pt-ETEK, P800(2:5) and P800(1:5), respectively. Because the rate constant is directly proportional to the kinetic current density, the ORR is about 9 times slower on P800(1:5) and only about 4.5 times slower on P800(2:5) than on Pt-ETEK. Obviously, the kinetics of the ORR is dependent on the nitrogen content of the catalyst.

4. Conclusions

In summary, a highly efficient method based on thermal treatment of polypyridine-carbon black mixtures was developed for synthesis of metal-free N-containing carbon catalysts for the ORR in alkaline media. It was found that both a higher treatment temperature and a higher polypyridine loading, lead to higher activities. Samples treated at 800 °C exhibited remarkable activities similar to Pt-based catalysts. Not only pyridinic, but also pyrrolic or quaternary groups formed at high temperatures may contribute to the oxygen reduction activity.

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