Iron-tetracyanobenzene complex derived non-precious catalyst for oxygen reduction reaction

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A B S T R A C T

Non-precious metal oxygen reduction reaction (ORR) catalysts were prepared by pyrolyzing a carbon supported complex consisting of iron acetate coordinated with 1,2,4,5-tetracyanobenzene (TCNB) in an iron phtalocyanine-like polymer arrangement. The effect of heat treatment temperature is systematically investigated from 700 to 1000 °C, with ORR activity investigated by half-cell electrochemical evaluation in 0.1 M HClO$_4$. The highest ORR performance is obtained for the sample heat treated at 1000 °C, with this sample demonstrating high (>98%) selectivity towards the efficient 4 electron reduction mechanism, comparable with some of the best non-precious metal catalysts reported to date. The physical and surface properties of the prepared catalysts were investigated by high-resolution transmission electron microscopy (TEM), fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and BET surface area analysis. After heat treatment, a thin (<10 nm) coating was observed on the surface of the carbon supports, attributed to residual species remaining from the heat treated precursor complex that provide the source of ORR activity.

1. Introduction

The development of efficient oxygen reduction reaction (ORR) catalysts is essential for the widespread commercialization of polymer electrolyte fuel cells (PEFCs) due to the importance of the reaction kinetics in controlling device performance [1–3]. Platinum and platinum-alloy based catalysts are conventionally used owing to their high intrinsic ORR activity and stability; however the high cost and monopolized global distribution hinders the long term economic feasibility of PEFC systems. This has inspired significant research efforts to the development of low cost, non-precious metal based catalysts to replace platinum-based materials.

Since the initial discovery in 1964 by Jasinski et al. [4] that demonstrated cobalt phtalocyanine (CoPc) materials were active for the ORR, significant progress has been made towards the development of transition metal (M=Fe or Co)-nitrogen-carbon complexes, commonly referred to as M—N—C systems. Early investigations illustrated the importance of heat treating transition metal macrocycles at temperatures up to 1000 °C to realize significant performance and stability gains [5–7]. Years later the discovery was made that pyrolyzing a mixture of relatively inexpensive transition metal, nitrogen and carbon precursor materials could produce highly active M—N—C catalyst materials [8,9]. Owing to the heterogeneous complexity of the resulting catalyst structures, there still remains debate in the literature over the exact identity and nature of the catalytically active sites, with contrasting opinions over whether the transition metal species comprises the active site, or merely plays an integral role in active site formation [3]. Regardless, it has been well established that the structure, properties and resulting ORR activity of heat treated M—N—C complexes is directly governed by the particular precursor materials employed and synthetic processes utilized [10–16].

While several catalysts have been prepared by pyrolyzing transition metal-phtalocyanine (i.e. FePc, CoPc) macrocycles absorbed on the surface of carbon supports [17–21], the bulky sheet-like structure of these molecules can arise some challenges including poor dispersion on the carbon support and molecular overlap resulting in iron agglomeration during the heat treatment. Alternatively it is possible to prepare FePc polymer sheets in situ

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from relatively inexpensive iron acetate and 1,2,4,5-tetracyano-benzene (TCNB) [22–24]. By employing these small precusursor molecules, it is expected that more uniform and complete coverage of the carbon support material can be obtained, and by using the *in situ* formation and polymerization of FePc, effective iron-center segregation can be achieved. Herein, we heat treat iron acetate and TCNB adsorbed on the surface of Ketjen black carbon supports at 300 °C and then subsequently at 400 °C to promote the formation of polymeric FePc sheets with planar geometry over the carbon support and form strong molecular interactions. After collection, the obtained materials were systematically pyrolyzed at temperatures ranging from 700 to 1000 °C and then were characterized and investigated for ORR activity in an acidic electrolyte to determine synthesis-property-performance relationships for this newly developed non-precious catalyst.

2. Experimental

2.1. Catalyst synthesis

The Ketjenblack EC-600J (AkzoNobel Corporate) carbon black support was first functionalized to increase solvent dispersion and precursor reactions [25] by a procedure described in our previous work [26]. Briefly, 5 g of the carbon black was first dissolved into 6 M HCl for 2 hours at room temperature to remove metal impurities. The sample was air filtered and washed with copious amounts of D.I. water. This treatment was followed by refluxing the carbon black in 70% HNO_3 at 80 °C in air for 8 hours before filtering. The precipitate product was washed with copious amounts of D.I. water and dried at 60 °C overnight to obtain the functionalized Ketjenblack EC-600J (KJ600).

0.0178 g of TCNB (Sigma Aldrich, 97%) and 0.0174 g of iron(II) acetate (FeAc) (Sigma Aldrich, 95%) were dissolved in 10 mL of quinoline for 30 minutes under N_2 protection and at room temperature. 0.3168 g of KJ600 was added to the mixture and stirred for 30 minutes. Still under N_2 protection, the temperature was raised to 210 °C for 24 hours and continuously refluxed. After cooling, 200 mL of methanol was added to precipitate out the solid, which was then filtered, washed with methanol and dried in an overn at 60 °C overnight. The sample was then heat-treated in a reaction furnace at 300 °C for 1 hour, at 400 °C for 1 hour and finally for 1 hour at a final heat-treatment temperature ranging from 700–1000 °C. N_2 was used to flow through the reaction chamber during pyrolysis. The furnace was allowed to cool before the samples were removed and utilized as the final catalyst product. The catalysts are denoted as Fe-TCNB/C-X where X is the final heat-treatment temperature. The catalyst obtained without the final heat-treatment is denoted as Fe-TCNB/C-0.

2.2. Physicochemical characterization

Catalyst samples were analyzed using TEM through a Philips CM300 operating at 300 kV to observe the surface morphology. A Thermal Scientific K-Alpha XPS spectrometer (150 eV) was used to investigate the relative content of different elements on the surface of the synthesized catalysts. Narrow range XPS scans of the N1s peaks were conducted to determine the relative amounts of each nitrogen species present in the catalysts. TGA was conducted using a TGA Q500 to determine the thermal behaviour of the phthalocyanine polymer formed with TCNB and the thermal stability of each of the catalyst samples. Monochromatic CuKα X-rays were used with an Inel XRG 3000 diffractometer to conduct XRD to observe the crystal structures present in the catalysts. A broad range scan of 2θ from 0.288–80.0° was carried out at a rate of 5° min^{-1}. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 FTIR spectrometer in KBr media. The BET surface area and the pore volume of the catalysts were analysed using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer.

2.3. Electrochemical characterization

Electrocatalytic ORR activity for each synthesized catalyst was evaluated using rotating ring disk electrode (RRDE) voltammetry. The instruments used include a bipotentiostat and a rotation speed controller (Pine Research Instrumentation). The RRDE experiment was carried out in 0.1 M $HClO_4$ electrolyte and using an Ag/AgCl reference electrode. The disk potential was varied from −0.25 to 0.95 V *vs.* Ag/AgCl at a potential sweep rate of 10 mV s^{-1}, and the ring potential was held constant at 1.0 V *vs.* Ag/AgCl. All figures are reported against the reversible hydrogen electrode (V *vs.* RHE).

The catalyst ink deposited on the glassy carbon disk consisted of 4 mg of catalyst suspended in 2 mL of 0.2 wt% Nafion solution. For each RRDE experiment, 40 μL of catalyst ink was deposited onto the glassy carbon electrode with a diameter of 5 mm and allowed to dry. Electrochemical potential sweeps were first conducted with the electrolyte saturated in nitrogen as a background. Bubbling oxygen gas was then used to saturate the electrolyte solution for 30 minutes before potential sweeps were conducted at 1600 rpm to evaluate the ORR activity.

3. Results and discussion

Catalyst morphology and surface structure following synthesis was investigated by TEM with results from Fe-TCNB/C-900 displayed in Fig. 1. For comparison, a TEM image of the carbon support pyrolyzed under the same conditions, albeit in the absence of TCNB precursor materials is given in Fig. 1a. For both the pyrolyzed Ketjenblack and Fe-TCNB/C-900, carbon black supports with particle sizes of ca. 30–50 nm in diameter are clearly observed, while the Fe-TCNB/C-900 catalyst shows a coating layer of less than ca. 10 nm in thickness on the surface. This coating is expected to comprise the residual products remaining after the pyrolysis of the iron and nitrogen precursors that occurs at these elevated temperatures. The coating is relatively uniform over the entire surface of the carbon support
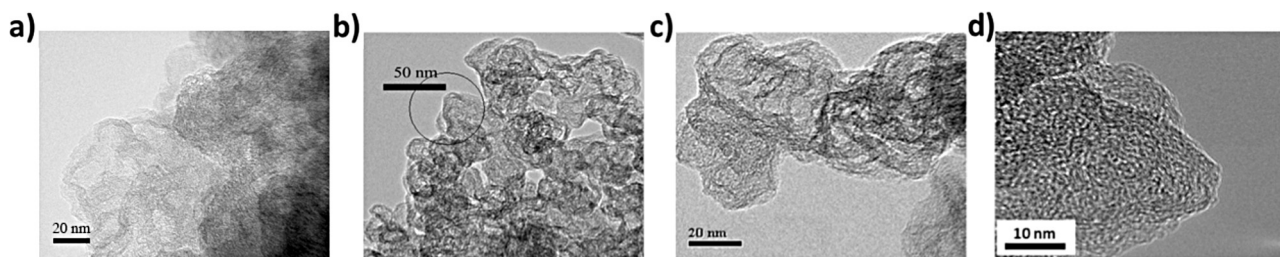

Fig. 1. TEM images of (a) KJ600 pyrolyzed at 900 °C and (b) Fe-TCNB/C-900 with area of (c) high resolution TEM image indicated by the black circle.