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Templated non-PGM cathode catalysts derived from iron and poly(ethyleneimine) precursors

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ABSTRACT

A series of oxygen reduction catalysts derived from pyrolyzed iron-containing compounds and a nitrogen-containing polymeric precursor, poly(ethyleneimine), (Fe–PEI) were prepared using a sacrificial support method (SSM). The synthesis includes high-temperature pyrolysis in inert atmosphere of the precursor that has been deposited onto a highly dispersed silica support, followed by etching (dissolving) the oxide support, thus resulting in a templated, self-supported, highly porous material – the non-PGM electrocatalyst. The influence of experimental parameters on the catalytic activity of the oxygen reduction reaction (ORR) in acid media was studied, such as molecular weight of PEI, temperature of the heat treatment, duration of the heat treatment, and the ratio of metal to nitrogen precursor. This series of materials was analyzed and characterized by scanning electron microscopy (SEM), BET method (BET) and XPS in order to establish structural morphology and chemical moieties, which was then correlated to activity. Rotating ring disk electrode (RRDE) experiments were performed to evaluate catalytic activity, and the ring current data was used to conduct a mechanistic study of the material for the ORR. This work has determined that the most influential parameters on activity are the metal to nitrogen precursor ratio, and temperature of the heat treatment. Accelerated durability RDE tests (cycling between 0.2 and 1.1 V) revealed high stability of synthesized materials in acid media.

1. Introduction

Fuel cell technology is a promising alternative to conventional hydrocarbon technology for a range of applications; from automotive propulsion, to combined heat and power, to portable electric devices. There has been a significant, concerted effort by industrial and academic research centers that have greatly improved fuel cell performance and durability. However, certain challenges must be overcome before the technology can make any meaningful penetration into common use. The core of the fuel cell device, the membrane electrode assembly (MEA) typically implies the use of platinum catalysts at the anode and the cathode, which makes a major contribution to the cost of the system.

There are two distinct strategies that may alleviate the high cost of an MEA stack: use either ultra-low loadings of platinum that maximize the catalytically available surface area of the metal, or completely circumvent the use of the precious metal with other materials that perform comparably.

The later strategy has piqued the interest of research groups around the globe, and the number of organizations investigating non-platinum group metal (non-PGM) catalysts has increased dramatically. It is notable, however, that despite the amount of research pertaining to non-PGM catalysts, there has not been extensive studies of anode catalysts [1], but instead the focus has centered on cathodes [2].

It is convenient to classify non-PGM cathodes into three separate categories: materials based on transition metal chalcogenides (mainly ruthenium selenides) [3–10], heteroatomic polymeric precursors [11–13], and small molecule derived M–N–C frameworks [14–66]. The later of the classes can be further subdivided: one group based on coordinated metal macrocyclic compounds as a sole source for formation of M–N–C networks [13–27], and the second group of materials can be prepared by combining a metal precursor with a nitrogen/carbon precursor or precursors [28–66].

The common synthesis approach for all of the M–N–C classes entails the deposition of precursors (either macrocyclic or mixture of metal–nitrogen–carbon) that have been adsorbed to high surface area carbon blacks, followed by heat treatment under different conditions [2]. It has been shown that heat treatment is a critical step for creating active centers, which become the catalytic sites for the reduction of oxygen [22]. To date, there is no clear understanding about the nature of the active sites, or their role in ORR. The mechanism of oxygen reduction, which can proceed via several pathways, is not well established for this class of catalysts. Despite the fact

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that some publications have included calculations of the number of electrons participating in ORR to be close $4e^-$, the authors usually do not specify that the $n \sim 4e^-$ is the overall collected number of electrons, and it be directly related to single site $4e^-$ transfer. Based on our experience with pyrolyzed macrocyclic compounds, oxygen reduction follows a two-stage 2 × 2 electron mechanism, where first two electrons participate in electroreduction of oxygen to the hydrogen peroxide, followed by further $2e^-$ electroreduction H_2O_2 to water [67].

The present work is devoted to the preparation and characterization of new catalysts based on pyrolyzed Fe–PEI materials. To improve the surface area, porosity, and density of active sites in catalytic material, our group developed the sacrificial support method (SSM) [68,69], and this templating method was employed in this work. In contrast to conventional synthetic approaches, the SSM utilizes sacrificial supports (silica, alumina, etc.), as opposed to carbonaceous materials. After homogeneous dispersion of precursors onto the surface of silica, and the subsequent pyrolysis, the sacrificial support is removed by etching with KOH or HF. The silica etching procedure results in the creation of an inverted morphology to the sacrificial support (creation of well formed porous structures with pore sizes comparable to the diameter of individual particles of silica). Using high surface area amorphous silica allows us to synthesize M–N–C catalysts with high surface areas and densely populated active sites [68,69].

To further improve the activity of the ORR, several crucial experimental parameters were identified and conditions optimized; they are the variation of the molecular weight of PEI, the metal to nitrogen precursor ratio, and the temperature, duration, and temperature ramping rate of the heat treatment. An analysis and characterization was then performed on the synthesized catalyst material by XPS, SEM and BET methods. The reaction kinetics and mechanism of ORR on these materials was analyzed using the RRDE, and the characterized physical features were then correlated to electrochemical performance.

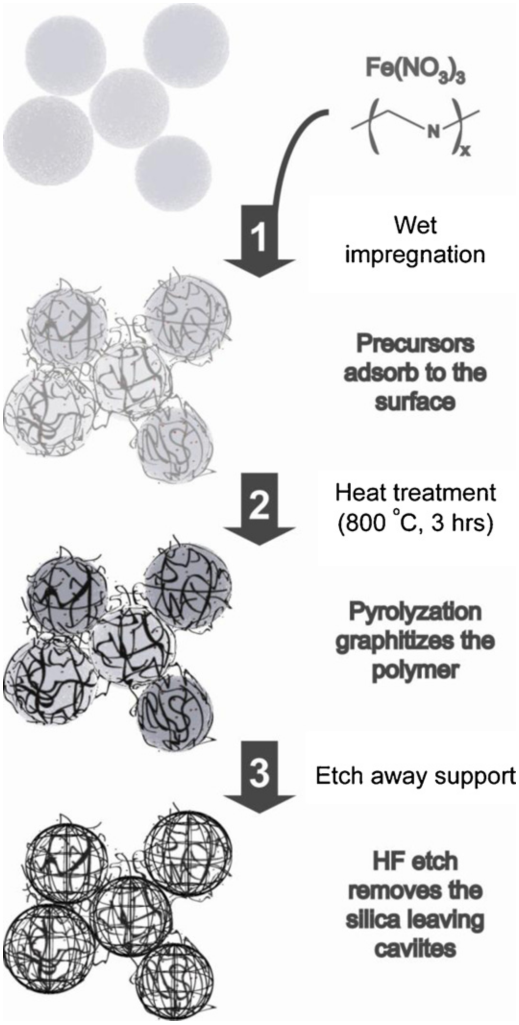

Fig. 1. Schematic representation of the sacrificial support method (SSM).

2. Experimental

2.1. Catalysts preparation

Fe–PEI catalysts were prepared via wet impregnation of iron and poly(ethyleneimine) precursors onto the surface of fumed silica (Cab-O-Sil^{TM} EH-5, surface area: $\sim 400\,m^2\,g^{-1}$). Schematic representation of sacrificial support method is shown in Fig. 1. First, a calculated amount of silica was dispersed in water using the sonobath. Then, a solution of poly(ethyleneimine) (the molecular weights (MW) used were: 2000; 25,000; 600,000; 1,000,000) (Sigma–Aldrich was the source of the PEI and it was used as obtained) in water was added to silica, and sonicated for 20 min. Then, an aqueous solution of iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Sigma–Aldrich) was added to the SiO_2–PEI solution (the total metal loading on silica was calculated to be ~15 wt.%), and then sonicated for 8 h in the sonobath. After sonication, a viscous solution of silica and Fe–PEI was dried overnight at $T = 85\,^\circ C$. The solid was ground to a fine powder in an agate mortar, and then subjected to the heat treatment (HT). The general conditions of HT were: UHP N_2 atmosphere flowing at a rate of $100\,cc\,min^{-1}$, HT temperatures of 700, 800, and 900 °C, HT temperature ramp rates of 10, 20, and $30\,^\circ C\,min^{-1}$, and HT durations of 1, 2 and 3 h. Finally, the silica was leached out by means of excess amount of 20 wt.% of HF for 24 h and resulting powder was washed with DI water until neutral reaction. Final metal content after washing with HF was found to be ~0.2–0.3 at.%.

Initially, the iron to PEI ratio selected was 1:2 (by mass), and the catalyst was denoted as Fe–2PEI. In the experiments involving the variation of Fe:PEI ratios, catalysts with Fe–PEI, Fe–2PEI, Fe–3PEI and Fe–4PEI were synthesized (again, the ratios were by mass).

In order to investigate the influence of the SSM on oxygen reduction activity, we synthesized Fe–PEI catalyst by the conventional method whereby it is deposited onto a carbon support (Vulcan XC72R), which has been denoted as sample Fe–2PEI/XC72R. After pyrolysis the prepared material was washed with 20 wt.% of HF.

2.2. Characterization

Scanning electron microscopy was performed on a Hitachi S-800 instrument.

XPS spectra were acquired on a Kratos Axis Ultra X-ray photoelectron spectrometer using a Al Kα source monochromatic operating at 150 W with no charge compensation. The base pressure was about 2×10^{-10} torr, and operating pressure was around 2×10^{-9} torr. Survey and high-resolution spectra were acquired at pass energies of 80 eV and 20 eV, respectively. Acquisition time for survey spectra was 2 min, for C 1s and O 1s spectra – 5 min, for N 1s and Fe 2p – 30 min. Data analysis and quantification were performed using CasaXPS software. A linear background subtraction was used for quantification of C 1s, O 1s and N 1s spectra, while a Shirley background was applied to Fe 2p spectra. Sensitivity factors provided by the manufacturer were utilized. A 70% Gaussian/30% Lorentzian line shape was utilized in the curve-fit of N 1s.