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Stability of iron species in heat-treated polyaniline–iron–carbon polymer electrolyte fuel cell cathode catalysts

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ABSTRACT

This paper describes the stability of Fe species in a heat-treated polyaniline–iron–carbon (PANI–Fe–C) oxygen reduction reaction (ORR) catalyst in an aqueous acidic electrolyte and in a membrane–electrode assembly (MEA) at various potentials. Linear combination fitting of ex situ and in situ X-ray absorption near-edge structure (XANES) spectra to the spectra for a suite of Fe standards was used to determine the catalyst iron speciation at various potentials, after potential cycling in an aqueous electrolyte, and after 200 h potentiostatic holds in MEAs. XANES edge-step analysis and inductively-coupled mass spectrometry were used to determine the amount of Fe lost from the catalyst into the aqueous electrolyte and from the MEA cathodes. Results showed that the Fe was lost from the catalyst in the electrochemical environment and the rate and extent of this loss were dependent on potential and on the type of electrolyte. The Fe specie primarily responsible for this loss was iron sulfide. Despite the large overall loss of Fe species from the catalyst that had been subjected to potentiostatic holds in an MEA at either 0.4 V or 0.6 V for 200 h, H_2–air polarization curves showed only moderate loss of cathode kinetic performance while the performance in the mass transport region improved. Correlating the performance loss to the XANES speciation, the kinetic losses may be attributed to the oxidation of active site(s) and/or loss of pyrrolic-like and pyridinic-like coordination, as well as the mass transport improvement due to removal of inactive Fe species, predominantly sulfides. Species with porphyrazin-like coordination were stable in both the aqueous and MEA environments. It is speculated that the stability of the porphyrazin is responsible for the durability of this catalyst.

1. Introduction

The oxygen reduction reaction (ORR) is the major source of efficiency loss in hydrogen–air polymer electrolyte fuel cells (PEFCs). New catalysts are necessary to enhance the kinetics of the ORR and to reduce efficiency losses. State-of-the-art catalysts in commercial PEFCs are platinum-based formulations that contribute in a major way to the cost of PEFC systems. To reduce the cost, numerous groups have focused their attention on developing catalysts based on metals with higher natural abundance, such as Fe and Co. However, the stability of non-precious metal catalysts, especially in acidic electrolyte, is typically much lower than that of Pt catalysts [1–4]. A particularly promising route to achieving both high activity and stability for Fe- and Co-based catalysts is heat treatment of carbon- and nitrogen-containing compounds of these metals. Zelenay et al. have significantly advanced both the performance and stability of heat-treated Fe- and Co-based ORR catalysts using polyaniline (PANI), an aromatic heteroatom polymer, as a nitrogen–carbon template for Fe, Co, and FeCo [5–11]. It has been hypothesized that the aromatic character of the precursor aids in stabilizing the interaction of the metal and nitrogen imbedded in the resulting graphitic carbon structure [5,12]. The PANI–(Fe, Co, FeCo)–C class of catalysts has been found to be stable in a fuel cell for up to 700 h of operation [5,8].

Various mechanisms for the degradation of non-precious metal electrocatalysts in PEFCs have been proposed and reviewed by Borup et al. [1] and Chen et al. [3]. These mechanisms include corrosion/oxidation of the active center and carbon support in the acidic environment [6,13], attack by hydrogen peroxide (an undesirable side-product of the ORR) of both the metal and N sites [6,13–17], and, in the case of heat-treated Fe and Co–carbon–nitrogen catalysts, oxidation of the pyridinic active site [6]. The contribution of oxidation and corrosion to the degradation are supported by the

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results of X-ray photoelectron studies of the PANI–Fe–C catalyst which show that the surface density of Fe and N decreases and the surface oxygen content increases after operation in a fuel cell for 500 h at 0.4 V [6].

Another phenomenon proposed to be responsible for the loss of ORR activity of Fe- and Co-based catalysts is protonation of the nitrogen centers in acidic electrolyte [14,18,19]. According to Gorbaty and Kelemen [20] and Geng [21], pyridinic nitrogen can be protonated by acidic groups, while quaternary nitrogen, which is bonded to three carbon atoms in the plane of the carbon matrix, is more resistant to protonation due to the absence of free electrons. In addition, the preferred protonation of pyridinic sites may explain why higher heat-treatment temperatures, which lead to more quaternary and less pyridinic nitrogen [22], result in more stable catalysts [6].

It has been speculated that dissolution of transition metal species from (Fe, Co)–nitrogen–carbon catalysts is responsible for the instability of these catalysts in acidic versus alkaline environments. Lefevre and Dodelet found a correlation between loss of ORR activity and Fe content in heat-treated Fe–nitrogen–carbon catalysts after treatment with H_2O_2-containing sulfuric acid solutions [13]. Little is known, however, about the extent of dissolution, the dissolution rates, and identity of the dissolved transition metal species as a function of potential in the potential range relevant to operating conditions in a real PEFC cathode. In this paper, we investigate these issues for a heat-treated PANI–Fe–C composite using ex situ and in situ X-ray absorption near-edge spectroscopy (XANES) and aqueous electrolyte dissolution measurements. As mentioned previously, this class of catalysts has been reported to have high ORR activity and relatively good stability in PEFCs [5–10]. The present study focuses on the PANI–Fe–C catalyst that was found in a previous study to have the highest ORR activity and stability among the PANI–Fe–C catalysts: the catalyst that was heat-treated at 900 °C, then acid-treated, and heat-treated again at 900 °C [10].

In our previous study, we correlated the ORR activity of PANI–Fe–C catalysts with the morphology and chemical speciation using XRD, XPS, and ex situ XANES at various stages of synthesis and for different heat-treatment temperatures (600–1000 °C) [10]. In that study, the 900 °C heat-treated catalyst was found to have the highest ORR activity. By principal component analysis (PCA), the ORR activity was found to correlate well with the BET surface area, microporous surface area, and Fe–N content, especially in porphyrazin and pyridinic coordination, as determined by XANES.

This paper focuses on the stability of Fe species in the 900 °C-heat-treated PANI–Fe–C catalyst following constant potential (voltage) holds and potential cycling in aqueous acidic electrolytes and in membrane-electrode assesmblies (MEAs). Linear combination fitting of ex situ and in situ XANES spectra of the catalyst to the spectra for sixteen Fe model compounds was used to determine the Fe oxidation state and speciation in the catalyst at various potentials, as well as after potential cycling in an aqueous acidic electrolyte and after 200-h voltage holds in MEAs. XANES edge-step analysis and inductively-coupled mass spectrometry (ICP-MS) were used to determine the amount of Fe lost from the catalyst into the aqueous electrolyte and from the cathodes in MEAs. The XANES studies allowed for the correlation of the chemical speciation with ORR activity and fuel cell performance. Also evaluated were the short-term dissolution rates of Fe in aqueous H_2SO_4 electrolyte under potentiostatic and potential cycling conditions, as well as the fractions of Fe removed from the catalyst during long-term potential cycling over the potential range typically encountered during fuel cell operation. The Fe loss induced by potential cycling is compared to the loss after long-term open circuit holds in H_2SO_4 electrolyte, which is a typical pre-treatment for this type of catalyst prior to cell fabrication. The loss of Fe upon potential cycling in $HClO_4$ electrolyte was determined for comparison with the H_2SO_4 results to distinguish the effects of complexing and non-complexing anion. In addition, $HClO_4$ has been reported to more closely mimic the non-adsorbing characteristics of the perfluorosulfonic acid ionomer used in MEAs than H_2SO_4 [23].

2. Experimental

2.1. Catalyst synthesis

A detailed description of the catalyst synthesis was presented previously [8], thus an only abbreviated version is given here. Ketjenblack EC 300J (KJ-300J), a high-surface-area carbon black was used as the catalyst support. The carbon black was pre-treated in an aqueous HCl solution for 24 h to remove possible impurities. Aniline (2.0 mL) was first dispersed with acid-treated carbon black (0.4 g) in HCl solution (0.5 M). The suspension was kept below 10 °C while the oxidant, ammonium peroxydisulfate (APS, $(NH_4)_2S_2O_8$), and the transition metal precursor ($FeCl_3$) were added. The molar ratio of aniline to APS was 1:1 during the in situ aniline polymerization. After continuous mixing for 24 h to allow the polyaniline (PANI) that was formed to uniformly combine with the carbon black particles, the suspension containing carbon, polymer, and transition metal was vacuum-dried using a rotary evaporator. The subsequent heat treatment was performed at 900 °C in an inert atmosphere of nitrogen gas for 1 h with a heating ramp of 30 °C/min. The heat-treated sample was acid-leached in H_2SO_4 (0.5 M) at 80 °C for 8 h to remove unstable and inactive species from the catalyst, and then thoroughly washed in de-ionized water. In the final step, the catalyst was heat-treated again at 900 °C but for 3 h instead of 1 h. The amount of iron precursor required in the synthesis to give the highest activity and the most reproducible results was demonstrated to be 10 wt% in a previous study [9]. That amount of Fe was used in the present study.

2.2. Fuel cell testing

PANI–Fe–C catalysts were tested in fuel cell cathodes to evaluate their activity and durability under PEFC operating conditions. Catalyst inks were prepared by ultrasonically mixing catalyst powders with 5 wt% suspension of Nafion® in alcohols (Aldrich) for 4 h. Cathode inks were applied to the gas diffusion layer (GDL, ELAT LT 1400W, E-TEK, 5 cm^2) to form a gas diffusion electrode (GDE). The catalyst application process was repeated until the cathode catalyst loading reached 4.0 mg cm^{-2}. The Nafion® content in the dry catalyst was 30 wt%. A commercially-available Pt-impregnated cloth GDE (E-TEK, 0.25 mg cm^{-2} Pt, 5 cm^2 active area) was used as the anode.

The cathode and anode were hot-pressed onto two separate pieces of a Nafion® 1135 membrane and later these two halves were combined to form a two-layer membrane–electrode assembly (MEA, 5 cm^2 active area). This approach minimized the risk of possible cross-contamination of the cathode with platinum from the anode and also facilitated post mortem characterization of the cathodes. Fuel cell testing was carried out in a single cell with serpentine flow channels (Fuel Cell Technologies, Inc.). Pure hydrogen and air, both humidified at 85 °C, were supplied to the anode and cathode at a flow rate of 200 and 600 mL/min, respectively. Fuel cell electrodes were maintained at the same backpressure of 2 bar (~2.8 bar absolute pressure at the Los Alamos altitude). Fuel cell polarization plots were recorded using standard fuel cell test stations (Fuel Cell Technologies, Inc.). The voltage data obtained with the two-membrane sandwich were corrected for the resistance of one of the membranes, which means that all fuel cell polarization