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Platinum group metal-free electrocatalysts: Effects of synthesis on structure and performance in proton-exchange membrane fuel cell cathodes

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HIGHLIGHTS

- A set of PGM-free ORR catalysts are fabricated with varying synthetic parameters.
- Performance testing and physicochemical characterization are performed.
- Performance correlates with atomically dispersed Fe, N-Fe, and surface oxides.
- Parameters that promote favorable chemistries and increase performance are reported.

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ABSTRACT

Development of platinum group metal free catalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) requires understanding of the interactions between surface chemistry and performance, both of which are strongly dependent on synthesis conditions. To elucidate these complex relationships, a set of Fe-N-C catalysts derived from the same set of precursor materials is fabricated by varying several key synthetic parameters under controlled conditions. The results of physicochemical characterization are presented and compared with the results of rotating disk electrode (RDE) analysis and fuel cell testing. We find that electrochemical performance is strongly correlated with three key properties related to catalyst composition: concentrations of 1) atomically dispersed Fe species, 2) species in which N is bound to Fe, and 3) surface oxides. Not only are these factors related to performance, these types of chemical species are shown to correlate with each other. This study provides evidence supporting the role of iron coordinated with nitrogen as an active species for the ORR, and offers synthetic pathways to increase the density of atomically dispersed iron species and surface oxides for optimum performance.

1. Introduction/background

Many studies focus on replacing platinum group metal (PGM) catalysts for the oxygen reduction reaction (ORR) at the cathode of proton exchange membrane fuel cells. The family of transition metal-nitrogen-carbon (MNC) electrocatalysts has been investigated extensively over the years [1–25] as a PGM-free alternative, with several recent reports demonstrating dramatic improvement in ORR activity and durability in fuel cell operation [26–28]. To further these advances and understand the underlying mechanisms, continued focus is required to link structural composition with ORR activity and durability [7,8,11,29].

In order to provide insight for rational design of optimized

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catalyst materials, it is necessary to elucidate the roles various chemistries play in the activity and durability of PGM-free catalysts. The effect of different metal species, contributions of various N moieties, and impact of the C support network are of central importance. Among the various available transition metal precursors, Fe is the most frequently studied due to the high activity and stability of the resulting catalysts [30]. In these materials, Fe is primarily manifested in two forms: Fe-rich phases such as metallic particles and carbides [31–35], o or atomically dispersed Fe coordinated to N in a variety of configurations [7,36,37]. Nitrogen functionalities identified in MNCs include – but are not limited to – pyridinic, graphitic [38], hydrogenated as pyrrolic or hydrogenated pyridinic [39], cationic as quaternary or protonated, and the N coordinated with atomically dispersed Fe species (N-Fe). Multiple detailed structure-to-property and theoretical studies show that Fe coordinated to N (FeN_x) forms active sites that catalyze the complete reduction of oxygen to water, while other N types such as hydrogenated and graphitic facilitate the partial reduction of oxygen to hydrogen peroxide [7,8,29,40] In this work, “N-Fe” is used when discussing measured concentrations of N bound to Fe and “FeN_x” is used when discussing the idealized active sites. This distinction is significant because N could be bound to Fe in non-active configurations and the potential presence of atomic Fe particles cannot be discounted. Surface oxides present in the C network are important (indirect) indicators of defects which influence the formation of active FeN_x sites [29,41]. An important aspect of the C network is its contribution to hydrophilic/hydrophobic properties that are critical for the integration of catalyst powders into fuel cell catalyst layers. Length-scale specific morphology of the catalyst also plays a very important role, particularly at the point integrating the catalyst into catalyst layers [18,42]. The distribution and accessibility of active sites as well as the mass transport and water management properties of catalyst layers depend on the chemical composition, surface energy, and morphology of the catalysts themselves.

The pyrolytic routes typically employed in the synthesis of MNC catalysts result in very heterogeneous materials with a multitude of C, metal, and N moieties, as well as varying physical structure. Development of PGM-free catalysts with improved activity and durability requires elucidation of the interplay between synthesis methodologies and catalyst composition, morphology, and both electrochemical and fuel cell performance characteristics. RDE testing is important for pre-screening catalyst activity and stability, as well as for mechanistic studies [30]. Beyond RDE, it is crucial to determine correlations between catalyst synthesis, physicochemical properties, and performance in membrane electrode assembly (MEA) tests; these experiments evaluate materials upon integration into the catalyst layer, which in turn affects mass, electron, and proton transport [18,43].

We have previously shown that electrocatalysts synthesized from Fe and nicarbazin precursors using the sacrificial support method (SSM) demonstrate excellent activity and durability [26,27]. The SSM involves using templates to create free-standing, highly porous materials with tunable pore size distributions. These materials are formed from pyrolytic treatment of C, N, and metal sources [18,26,27,41,44,45]. After pyrolysis, the materials are leached in order to remove the template and undesired residual metal-rich phases. A second heat treatment improves catalyst activity and durability. Type and size of the template, mixing method, etching conditions, and pyrolysis conditions (temperature, gas, duration) all affect catalyst chemistry and morphology and its subsequent performance in both RDE testing and MEA operation. Because the type of template used affects the resultant catalyst structure and porosity, it also affects catalyst-ionomer interactions in the catalyst layer [46]. The ratio of ionomer to catalyst, as well as the method of the catalyst layer fabrication, also play critical roles in MEA performance [47]. Optimized procedures for ink preparation and MEA fabrication have previously been reported for this class of materials [27,48].

The goals of this study are to elucidate: 1) chemistry-structure-performance relationships in nicarbazin-derived PGM-free catalysts, and 2) the effects of various synthetic parameters on catalyst composition, structure, and performance. A series of electrocatalysts with the same carbon/nitrogen precursor and Fe loading are fabricated under different synthetic conditions and tested for electrochemical performance in both RDE and MEA. The materials are characterized by x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDS) on a transmission electron microscope (TEM) to build correlations between synthetic parameters, performance, and surface and bulk composition of these catalysts, with focus on their heterogeneity at multiple length scales. Additional studies into the effects of catalyst and electrode morphology on performance are ongoing.

We observe that performance is strongly correlated with the concentration of N species coordinated with Fe, as well as the amount of surface oxides present. Catalyst performance is hindered by Fe-rich phases, even in the presence of the ideal, atomically dispersed Fe species. Specific synthetic parameters that affect these chemistries and can be used for tuning catalyst performance are laid out. Finally, we show that these materials are fairly chemically homogenous at scales of over ~100 nm, but are highly heterogeneous at the few-nanometer scale. Therefore, caution should be exercised in drawing structural or chemical conclusions based on high-resolution observations.

2. Experimental

2.1. Synthesis

Iron-Nicarbazin (Fe-NCB) electrocatalysts were prepared as follows: First, a calculated amount of silica (Stöber spheres synthesized in-house with a diameter of 370 nm, plus Cab-O-Sil® LM-150 and OX-50) was combined with multi-wall carbon nanotubes (Cheaptubes® 30–50 nm × 10–20 μm), iron nitrate ($Fe(NO_3)_3{*}9H_2O$, Sigma-Aldrich) and nicarbazin (1,3-bis(4-nitrophenyl)urea; 4,6-dimethyl-1H-pyrimidin-2-one, Sigma-Aldrich). The reagents were mixed with sufficient water to wet the powder and form a viscous gel, which was then dried with continuous stirring at 45 °C, then heated at 85 °C overnight. The resulting solid material was ground to a coarse powder in an agate mortar, then to a fine powder in an agate ball mill. This powder was then subjected to heat treatment (HT) in a controlled atmosphere of 7% H_2/93% N_2 (flow rate 120 cc min^{-1}). HT 1 consisted of insertion into a furnace at 525 °C then immediately setting the furnace temperature to 900 °C. Once the furnace reached 900 °C, the temperature was increased to 975 °C at a rate of 10 °C min^{-1}. The temperature was held at 975 °C for 45 min, then the catalyst was quenched by removing the tube from the furnace. After HT 1, the sample was ground in an agate ball mill then leached with a 2:1 mixture of 25% HF:35% HNO_3 for 3 days. The catalysts were then washed with DI water until neutral pH was reached and dried at 85 °C overnight. A second HT was performed at 950 °C for 30 min in reactive (7% NH_3/93% N_2) atmospheres. The final product was ground in an agate ball mill for 1 h. The varied synthetic parameters are shown in Table 1.

2.2. Rotating disk electrode

RDE measurements were performed with a glassy carbon working electrode and a graphite counter electrode. Ink composition was 5 mg of catalyst in 850 μL 4:1 water:isopropanol and