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Optimization of ink composition based on a non-platinum cathode for single membrane electrode assembly proton exchange membrane fuel cells

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HIGHLIGHTS

- ► Effect of catalyst ink formulation on performance and stability is studied.
- ► XPS is used to study surface chemistry of various ink formulations.
- ► Statistical structure-to-property relationship is built by PCA.
- ► Better performance is linked to pyridinic N, N bounded to Co and CoO particles.
- ► Higher stability is associated with preserved moieties from carbon black and ionomer.

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ABSTRACT

Non-Pt based oxygen reduction catalyst H_2-air fuel cell performance is reported for various electrode compositions. Ink formulations for pyrolyzed Co porphyrin based cathode electrocatalysts were evaluated in a membrane electrode assembly (MEA) configuration and X-ray photoelectron spectroscopy was performed on the MEA catalyst layers. The effect of cooling time trajectories of the catalysts after pyrolysis as well as Nafion content in the ink formulation were studied. By building statistical structure-to-property relationships between XPS and MEA performance using multivariate analysis we have determined that the higher stability of fast-cooled containing inks is mainly associated with better preserved graphic carbon from the carbon black and C–F moieties of the Nafion, while better MEA performance is a result of the presence of these moieties as well as pyridinic nitrogen and nitrogen associated with metal in the pyropolymer. Optimal Nafion content is determined at 1:1 catalyst:Nafion weight ratio, while higher Nafion concentrations causes oxidation of the Nafion backbone itself as well as leaching of the Co_xO_y particles from the catalyst and formation of oxidized species of Co, O, C and F. Further, we report 1500 h of continuous fuel cell operation for two different non-platinum cathode catalysts in the optimized MEA.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) use platinum-based electrocatalysts in both the anode and cathode. Since platinum is both expensive and of limited availability, there is a need for developing and optimizing non-platinum based catalysts in order for fuel cells to be competitive with alternative energy conversion technologies. Non-platinum-based catalysts such as pyrolyzed macrocycles are a less active but inexpensive alternative material that could be used in larger quantities to meet the same power demands. The use of macrocycles as electrocatalysts has been studied for their unique catalytic properties since the 1960s. [1] More recently there have been a number of publications presenting MEA performance data using a non-platinum-based cathode catalyst [2–7].

Non-precious metal based catalysts are optimized differently than platinum-based catalysts, where for the former one strives for maximum catalyst loading, and for the latter one needs to use ultra-low metal loadings due to the cost. Freed from the constraint of the price of the catalyst metal, the best designs for non-precious metal based catalysts maximize both the number of catalytically active sites for oxygen reduction as well as the reactant transport through the catalyst layer in MEAs. Gasteiger et al suggested that if the catalyst may be consider costless, performance can be measured in volumetric currents (A cm^{-3}) with the volume depending on thickness of the catalyst layer and the geometric area of the MEA [8]. In our previous report we evaluated the H_2/air–O_2 MEA performance for different catalyst layer compositions utilizing

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a templated non-platinum oxygen reduction reaction (ORR) catalyst based on porphyrin macrocycles [5]. The effect of the non-platinum catalyst, Nafion, and 35 wt% Teflon modified Vulcan XC-72 Carbon Black (XC-35) loadings were measured under H_2/air and H_2/O_2 conditions. Transport hindrances that occur in the catalyst layers were evaluated with *E* vs. *i* analysis. It was shown that transport limitations in the cathode catalyst layer can limit the performance of the cell at relatively low current densities if the catalyst layer composition is not optimized.

Large-scale deployment of PEMFCs is facing another major challenge: increase of the lifetime. One way to improve durability is to maintain the chemical integrity, and hence, effectiveness of the catalyst layer (CL) over the lifetime of the fuel cell. CL durability is of key importance, and methodologies for improving it are being intensively pursued. CL degradation is linked to catalyst dissolution and agglomeration, ionomer degradation, carbon support degradation, and the degradation of pore morphology and surface properties [9–13].

In case of non-platinum-based, the catalyst layer is comprised of carbon particles supporting the templated catalyst. For high performance, the CL requires a sufficiently contiguous carbon matrix for good electron conductivity, and adequate surface availability of catalytically active centers for fuel/oxidant adsorption, dissociation, and electrochemical reactions. In addition, the CL must provide sufficient ionomer for proton transport, and adequate pore space for the transport of both reactant gases and removal of product water.

Although Nafion®, which is a conventionally used ionomer in PEMFCs, has demonstrated a high efficiency and a stable performance in fuel cell applications; evidence of membrane degradation is reported [14]. It is believed that membrane degradation is mainly caused by chemical attack of the polymer [12,14]. Effect of Nafion on the CL durability on non-PGM (Platinum-group metals) containing systems is under-investigation and is of critical importance in advancing the technology.

Commonly used electrochemical and other methods to investigate degradation of the CL and membrane have failed to detect the ionomer degradation in the catalyst layer. X-ray photoelectron spectroscopy (XPS) is a powerful technique to study the chemical changes in the polymer membrane. It has been applied to quantitatively analyze catalyst layer degradation in PEM fuel cells. XPS was shown to be very useful for determining both the elemental concentrations and chemical states of C, F, Pt, O and S on the catalyst layer [11,13,14]. It has been shown that the ionomer on the catalyst layer dissolves and/or decomposes, and that characteristic XPS signals decrease after about 300 h of fuel cell operation. Ionomer degradation was characterized by a decrease of CF_3 and CF_2 species and an increase in oxidized forms of carbon (e.g. C–O and C=O).

In the current report we study the effect of catalyst preparation and ink composition on MEA performance and stability by XPS. We report 1500 h of operation for non-platinum containing cathode in MEA. By building structure-to-property relationship between XPS and MEA testing data using multivariate analysis we determine which types of chemical structures and which types of ink formulations result in better performance and better stabilities.

2. Experimental

2.1. Catalyst preparation

Catalyst porphyrin precursor CoTMPP (Co-tetramethoxyphenylporphyrin) was obtained from Aldrich Chemical Company (CAS 28903-71-1) and was used without further purification. Cab-O-Sil M-5, an amorphous fumed silica (325 $m^2\ g^{-1}$ specific surface area) obtained from Cabot Corporation, was used as the carrier. The organic solvent was tetrahydrofuran, 99.99% assay by gas chromatography, obtained from EM Science (Merck). A Lindberg Blue tube furnace with a programmable controller was used in the pyrolysis process with 99.9% pure nitrogen which was obtained from local sources. 0.5 g of porphyrin sample was weighed and dissolved in tetrahydrofuran and mixed with 0.5 g of amorphous fumed silica and sonicated for 15 min for uniform dispersion of silica in the solution matrix. The templated material was then pyrolyzed at 700 °C for 4 h under nitrogen gas flow. An adequate flow of nitrogen is supplied to provide an inert residence environment, which prevents oxidation of organics at the high temperatures. Two types of cooling were employed: slow-cooled (cooling rate 3 K min^{-1}) and fast-cooled (estimated cooling rate 20 K min^{-1}). The sample was stirred with 7.0 M KOH to etch out the silica. Finally, the sample was washed with (de-ionized) DI water and dried.

2.2. Ink fabrication

The standard anode ink was prepared as follows: 40 mg of PtRu black, 500 mg DI H_2O, and 166 mg of 5% Nafion solution was sonicated and hand painted on an 1135 Nafion membrane.

The non-platinum cathode inks were prepared as follows: 4 mg cm^{-2} geometric CoTMPP catalyst was mixed with a 20 wt% Teflon/Vulcan XC-72 (noted here as XC-35) material and 1:0.5, 1:1, 1:2 and 1:3 5% catalyst:Nafion weight ratio. Cathode inks were analyzed by XPS as is by drying them on the sample bar.

2.3. MEA fabrication and testing

The non-platinum cathode ink was then hand painted on an 1135 Nafion membrane (Ion Power) and the microporous layer of the gas diffusion layer (GDL LT 1400-W Low temperature, ELAT(R) GDL microporous layer on woven web) in a ratio of 1:9, respectively. The MEA was then pressed at 345 N cm^{-2} at 125 °C for 10 min.

The MEA was placed in a 5 cm^2 cell with serpentine flow channels and the bolts were compressed to 553 kPa (80 lb in^{-2}). The fuel cell technologies fuel cell test station was used to obtain H_2/O_2 and H_2/air polarization curves. Polarization curves were obtained galvanostatically with a 30 s delay before data acquisition. The anode and cathode gases were heated and humidified at 85 °C, and the flow rates were 266 and 466 sccm, respectively. The cell operating temperature was maintained at 80 °C. Polarization curves were acquired at 0 and 20 N cm^{-2} backpressure.

2.4. HRTEM

TEM was performed on a JEOL 2000 FX microscope operating at 200 keV.

2.5. XPS analysis

The XPS spectra were acquired using a Kratos AXIS Ultra photoelectron spectrometer equipped with a monochromatic Al Kα source operating at 300 W. The base pressure was 2.7×10^{-8} Pa, and the operating pressure was 2.7×10^{-7} Pa. Charge compensation was accomplished using low energy electrons (−2.8 V bias voltage, −1.0 V filament voltage and a filament current of 2.1 A). Survey spectra were initially acquired at pass energy (PE) of 80 eV, followed by high-resolution spectra of Co2p, C.1s, O 1s and N 1s at PE of 20 eV for all of the samples. Acquisition times for survey C.1s and O 1s spectra were 20 min, F1s 5min for N 1s 2 scans of 20 min, and for Co2p 5 scans of 30 min. Data analysis and quantification