



Sulfonated silica-based fuel cell electrode structures for low humidity applications



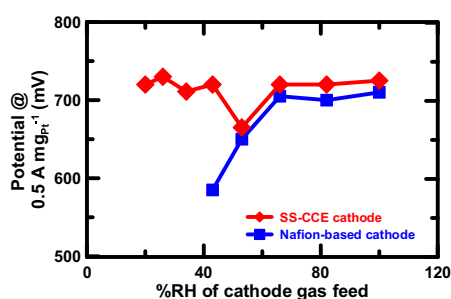
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HIGHLIGHTS

- Sulfonated silica ceramic carbon electrodes (SS-CCE) were tested as PEM fuel cell cathodes.
- Nafion-based cathodes were also tested.
- Nafion-based cathodes severe performance losses when with cathode gas feed RH drops below 60%.
- SS-CCE cathodes showed no change in performance when cathode gas feed RH was decreased down to 20%.
- SS-CCE performance stability arises from enhanced water retention & redistribution in the MEA.

GRAPHICAL ABSTRACT



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ABSTRACT

Ceramic carbon electrodes (CCEs) are prospective candidates for use in proton exchange membrane fuel cells due to their high surface area, water retention properties, and durable nature. We have determined that incorporating small amounts of sulfonated silane in the CCE structure can lead to a profound enhancement of catalytic activity and proton conductivity. To evaluate the usefulness of a new catalyst layer for practical use, performance of the materials under various conditions must be considered. We have compared the properties of membrane electrode assemblies (MEA) prepared with CCE cathode catalyst layers to that of an MEA prepared with Nafion-based cathode catalyst layers. The MEAs were characterized via transmission electron microscopy, thermogravimetric analysis, infrared spectroscopy, and BET analysis. Fuel cell performance using different cathode gas relative humidity (RH) feed conditions was monitored using electrochemical impedance spectroscopy and polarization curves. Our CCE cathode materials maintained stable performance and had improved water management capabilities at low relative humidities, whereas Nafion-containing cathodes have performed poorly. The enhanced performance and tolerance to low RH is explained in terms of water retention within the CCE-based MEA.

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1. Introduction

The energy requirements of modern civilization are rapidly consuming our natural resources, and society must look at

alternatives to fossil fuels in order to maintain current output and satisfy energy demand. Proton exchange membrane fuel cells (PEMFCs) are one technology with the potential to help meet both current and future energy needs [1]. The heart of a PEM fuel cell is the membrane electrode assembly (MEA) which consists of anode and cathode electrodes separated by a proton exchange membrane. Typical commercial catalyst layers contain a carbon-supported platinum catalyst combined with Nafion[®] ionomer

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[2]. The role of the ionomer is two-fold, as it supplies proton conductivity to the catalyst layer to increase catalyst utilization [3] as well as bind the carbon support. Several ionomers are commercially available but suffer from shortcomings such as high cost [4], restriction of gas pores [5], and poor performance in low water environments (low relative humidity and high temperature) [6]. Reduction or replacement of Nafion[®] and other perfluorosulfonic acid ionomers in the catalyst layer is essential to diminish these issues. The use of surface-modified carbon supports has been shown to be a somewhat effective method reducing catalyst layer Nafion[®] content [5,7–13]. Hydrocarbon-based ionomers such as sulfonated poly(ether ether ketone) (SPEEK) [4,14–18], sulfonated polyphosphazene [19], and poly sulfones [20] have been explored as Nafion[®] replacements but each one has its own unique set of challenges to be conquered.

Another approach to improving catalyst layer performance is by modification of the electrode support structure [21]. Electrodes are generally prepared by mixing Pt-supported carbon and Nafion ionomer solution without any additional treatment, which does not ensure suitable access to platinum particles throughout the catalyst layer. Several methods of electrode modification include use of organic-inorganic hybrid materials [22–25] to improve the accessibility to platinum and, in turn, the abundance of triple-phase sites. Ceramic carbon electrodes (CCEs) are promising candidates for fuel cell electrodes in this regard. The tuneable nature of CCEs makes them suitable candidates for use in a number of energy applications such as fuel cells [26–28], sensors [29,30], hydrogen production [31–33], and supercapacitors [34,35]. CCEs consist of electronically conductive carbon particles bound by a ceramic binder prepared via the sol–gel process to produce a gel from colloidal suspensions [36]. The sol–gel synthetic method allows for numerous conditions (e.g. pH, solvent, concentration) to be varied in order to modify material properties such as microstructure. The ceramic component is chosen to provide specific properties dependent upon the desired application. Our previous research demonstrated that introduction of the hydrophilic SiO₂ backbone affects the proton conductivity of CCEs without the addition of a functionalized side chain [27]. We have since incorporated an organosilane which has sulfonic acid moieties and hygroscopic properties to allow for enhanced proton conduction and water retention [37].

Water is essential to facilitate good proton conduction, and as such, the ability to retain water is imperative for MEA function at high temperatures (>80 °C) and low relative humidity conditions. Electrodes containing Nafion require hydration to ensure optimal performance [25], which limits the operating conditions of the MEAs. Additionally, extra power is required to maintain humidified gas flows [25]. Thus, it is desirable to operate a fuel cell under lower humidity conditions, but the maintenance of a water balance in the MEA can be a difficult task. Too little water in the membrane can hinder proton conductivity while excess water can flood the catalyst layer and limit gas transport [25,38]. In order to operate in dry environments, the MEA requires a mechanism to maintain moisture content [39]. Excess water at the cathode can result in back-diffusion of water from the cathode across the membrane to alleviate flooding by minimizing the water concentration gradient [38]. Therefore, it is possible that under low humidity conditions, water in the catalyst layer could aid in membrane hydration [39]. In this work, an organosilane precursor with sulfonic acid groups has been used to increase proton conduction within CCEs. The hygroscopic properties of the chosen organosilane not only ensure good hydration within the catalyst layer but may promote membrane hydration via back-diffusion. Nafion, by contrast, is known to be at peak performance when fully hydrated and conductivity decreases with reduced water

content [39]. Our fabrication method involves adding the organosilane precursors to the carbon in monomer form and initiating polymerization [37]. Polymerization *in situ* allows the organosilane to chemically bond to surface hydroxyl groups on the carbon support to facilitate efficient proton transport.

We have previously demonstrated that sulfonated silane-CCE (SS-CCE) fuel cell cathodes outperform SiO₂-based CCE cathodes [40] and can perform on par with Nafion-based cathodes at 80 °C using fully humidified gases [27], conditions where Nafion-based MEAs perform at their best. This performance was explained in terms of the high water retention and proton conductivity using sulfonated silica-based ionomers. Here, we report the dependence of fuel cell performance of SS-CCE cathodes on the low relative humidity (RH) of the cathode gas feed. The results have been compared to the performance of a commercial Nafion-based cathode under the same conditions. The hygroscopic nature of the silicate material in the electrodes appears to provide a mechanism for water retention within the MEA that is normally tailored within the membrane. Water retention in the catalyst layer may provide a source of hydration for the membrane at low RH via back-diffusion of water, while ensuring flooding of the membrane pores at higher RH is minimal.

2. Experimental

2.1. CCE preparation

CCE materials for spray deposition were prepared via the sol–gel method as outlined in our previous publications [37,40]. Briefly, dry 20% Pt on Vulcan XC72 carbon black (ETEK BASF) was combined with deionized water, methanol, and 6 M ammonium hydroxide. Deionized water was added first to prevent platinum ignition upon subsequent addition of methanol. The catalyst mixture were mechanically stirred, after which additions of tetraethylorthosilicate (TEOS) and 3-(trihydroxysilyl)-1-propanesulfonic acid (TPS, 30–35% in water) were added drop-wise to achieve a 5:95 TPS-to-TEOS mole ratio at a constant total silane concentration of ca. 40%, which was previously determined to be optimal for fuel cell performance.[27,40] After several days, the partially gelled CCE was spray deposited onto a gas diffusion layer (GDL) using an air brush. Following deposition, the resulting electrodes was dried for 30 min at both room temperature and 135 °C. The electrode had a platinum loading of 0.34 mg cm⁻² and a total silicate loading of 40 wt%, and will be referred to as SS-CCE.

2.2. Materials characterization

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q600 SDT thermal analyzer. Samples were heated from room temperature to 800 °C at a rate of 20 °C min⁻¹ under flowing air (50 mL min⁻¹), which enables the determination of the weight percent of the individual components [27,32,41]. Based on this, SS-CCE had an overall silicate content of 40 wt%, of which 6 mol% was TPS (balance TEOS), and 60 wt% platinumized carbon. Further details of the thermal analysis behavior of these materials are reported elsewhere [40].

Fourier-transform infrared (FTIR) spectroscopy was performed (PerkinElmer Spectrum 100 FTIR) to verify the presence of sulfonic acid groups with KBr pellets at room temperature. Brunauer–Emmett–Teller (BET) surface areas and pore size data was collected using a Micrometrics ASAP 2020 V4.00 physisorption analyzer. Transmission electron microscopy (TEM) images of the ETEK catalyst material and the CCE layer were acquired using a Philips CM 10 instrument equipped with an AMT digital camera system.

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