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## Communication (Special Issue on Electrocatalysis Transformation)

# Cathode catalytic dependency behavior on ionomer content in direct methanol fuel cells

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## ABSTRACT

Cathode catalyst layers (CLs) with varying ionomer (Nafion) contents were prepared and the direct methanol fuel cell structure and catalytic behavior were investigated as a function of ionomer content. CL roughness and thickness increased with increasing Nafion content. Contact angle measurements determined that CL hydrophilicity also increased as a function of Nafion content. Poor bonding between the CL, microporous layer, and the proton exchange membrane was obtained when the ionomer content was too low. The electrochemical surface areas (ESAs) were found to increase with increasing Nafion content before reaching an asymptote at elevated loading levels. However, upon increasing the ionomer content above 30 wt.%, the water and oxygen mass transfer properties were difficult to control. Considering the above conditions, N30 (30 wt.% Nafion) was found to be the optimal level to effectively extend the three-phase boundaries and enhance cell performance.

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Over the past few decades, direct methanol fuel cells (DMFCs) have attracted significant attention as a potential candidate for environmentally friendly energy conversion devices. Compared with hydrogen proton exchange membrane fuel cells (PEMFCs), DMFCs are safer to operate because of the liquid characteristics of methanol fuel [1,2]. A membrane electrode assembly (MEA) is a central part of DMFCs [3,4]. A MEA usually consists of a gas diffusion layer (GDL) having a microporous layer (MPL), a catalyst layer, and a proton exchange membrane (PEM). The GDL controls water, gas, and electron transfer [5–7]. PEMs transfer protons and separate fuel from oxygen.

The cathode catalyst layer (CL) is the crucial zone of the electrochemical reaction. The heterogeneous reaction occurs at a three-phase boundary comprising reactants, catalysts and an electrolyte [8]. The state-of-the-art catalysts used for methanol oxidation and oxygen reduction are PtRu/C and Pt/C, respectively. The electrolyte is a perfluorosulfonic acid polymer, such as Nafion [9,10]. There are numerous reports investigating the detailed structure of CLs in PEMFCs, which have led to improvements in cell performance through optimizing the CL structure [9,11–20]. Xing et al. [20] presented a two-dimensional, two-phase flow model detailing how ionomer swelling

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results in both a decrease in cathode CL porosity and an increase in the ionomer coating thickness, thereby increasing the oxygen transport resistance. Optimal cell performance in the presence of fully humidified gases utilizes an initial dry ionomer volume fraction (initial ionomer content) close to 10%, corresponding to 0.3 mg/cm<sup>2</sup>. Mashio et al. [21] employed a mathematical model to analyze the water sorption isotherm of PEMFC catalyst layers and observed water adsorption in the CLs initiates on the adsorption sites. Soboleva et al. [22] reported that ionomer co-deposition in the CL strongly influenced its porosity, covering a pore range < 20 nm, which originated from the microporous nature of the carbon particles (pore sizes < 2 nm) and the agglomeration of the carbon particles (pore sizes of 2–20 nm). Passalacqua et al. [23] investigated Nafion content in the PEMFC catalyst layer and observed the optimal ionomer content to be ~33 wt.%. Multiple investigations have reported hybrid and multi-graded catalyst layer combinations to optimize the function of the CL in PEMFCs [24–27]. Lee et al. [28] designed a hybrid anode CL to study methanol and water transport in DMFCs. However, there are few reports studying the optimization of cathode CLs in DMFCs.

Herein, cathode CLs were prepared as a function of ionomer content and the influence on the cell structure and catalytic behavior was investigated. Electrochemical surface areas (ESAs) were found to increase with increasing Nafion content until a constant value was reached. Additionally, further increasing the ionomer content beyond this threshold level results in the inability to control water and oxygen mass transfer effectively. N30 (30 wt.% Nafion content) is found to be the optimal level to effectively extend the three-phase boundaries, improving cell performance.

In our experiment, MEAs were prepared as follows: the MPL ink was prepared by mixing Vulcan XC-72 carbon with PTFE (25 wt.%), followed by spraying onto carbon paper (anode: TGPH060, 20 wt.% PTFE; cathode: TGPH090, 20 wt.% PTFE). The carbon loading was 1 mg/cm<sup>2</sup>. The MPL-treated carbon paper was heat-treated at 320 °C for 0.5 h to prepare the GDL. The anode and cathode catalysts were Pt40%Ru20%/C and Pt60%/C (Johnson Matthey Corp.), respectively. The catalyst ink was prepared by dispersing the catalysts and 5 wt.% Nafion solution in a solution composed of water and isopropanol (v:v = 2:3). Subsequently, the ink was sprayed onto the prepared GDL at 60 °C to form the gas diffusion electrode (GDE). Precious metal loading with respect to the anode was controlled at 2 mg/cm<sup>2</sup>, and the content of Nafion was fixed at 25 wt.%. Pt loading at the cathode was also 2 mg/cm<sup>2</sup>; however, the Nafion content varied at: 15, 25, 30, 35 and 45 wt.%, respectively. Thereafter, the MEA was prepared by hot-pressing the electrodes on two sides of Nafion 115 at 135 °C at 7.5 MPa for 2 min. The electrode area was 9 cm<sup>2</sup>, and the MEAs were named as N15, N25, N30, N35 and N45 corresponding to the Nafion content at the cathode.

The cyclic voltammetry (CV) tests of MEAs were performed with an EG&G model 273 potentiostat/Galvanostat (Oak Ridge, USA). The cathode was employed as the working electrode and the dynamic hydrogen electrode (DHE) at the anode was used as the reference electrode and counter electrode. Deionized

water at 35 °C was bubbled to the cathode at a flow rate of 8.5 mL/min, whereas hydrogen was bubbled to the anode at a flow rate of 150 mL/min. The cell remained at a constant temperature of 35 °C throughout the duration of the test. The potential window was 0–0.8 V at a scan rate of 50 mV/s.

The polar curve of the single cell having an active area of 9 cm<sup>2</sup> was evaluated using an Arbin FCT test station (Arbin Instrument Inc., USA). Methanol flow rate (2 mol/L) and O<sub>2</sub> were fixed at 6 mL/min and 0.5 L/min, respectively. All performance measurements were performed at 60 and 70 °C. Electrochemical testing measurements and operating conditions are shown in Table 1.

The CL hydrophobic character with varying Nafion content was investigated using a drop-shape analysis system, DSA30 (KRÜSS, Hamburg, Germany). CL surface morphology and roughness was observed by a 3D non-contact optical surface profilometer (Nanovea, California, USA) and scanning electron microscope (SEM, Philips XL30, field emission gun environmental SEM operating at 20 kV, Amsterdam, Netherlands).

The surface morphologies of the GDEs possessing varying Nafion contents were investigated using SEM and a 3D non-contact optical surface profilometer. 2D contour plots and the 3D surface morphology of the CLs are shown in Fig. 1. The CL roughness and thickness increased as a function of increasing Nafion content. As shown, the surfaces of N15 and N25 are relatively flat. Further increases in Nafion content result in a greater degree of surface roughness, as indicated by the higher peak densities homogeneously distributed across the sample. The area of sample studied, as indicated by the scale bars, is 5 × 5 mm<sup>2</sup>; therefore it can be observed that as surface roughness increases, the resulting micrometer-sized pores also increase; this may facilitate the mass transfer process. As shown in Fig. 2, increasing Nafion content resulted in the formation of a cracked surface with the gap between the islands extending farther apart as a function of increased Nafion content. The surface of N15 and N25 were relatively flat when compared with higher Nafion loadings. Significant gaps initially appear upon increasing Nafion loading to between 30 wt.% (N30) and 45 wt.% (N45). The results were consistent with 3D surface morphology observations of the CLs. Regarding the microstructure, observations reveal that the granular structure changed to a flocculent-type structure with increased Nafion loading. The granular structure mainly reflected the microstructure of the catalysts, whereas the flocculent-type structure originated from the microstructure of the Nafion ionomer. Ad-

**Table 1**  
Electrochemical test measurements and operating conditions.

Measurement	Operating conditions
CV	Working electrode: the cathode with flowing water Reference and counter electrode: DHE at the anode Operating temperature: 35 °C Potential window: 0–0.8 V Scan rate: 50 mV/s
Polarization curve	Active area of the single cell: 9 cm <sup>2</sup> Methanol flow rate: 6 mL/min O <sub>2</sub> flow rate: 0.5 L/min Operating temperature: 60–70 °C

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