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Micro-crack formation in direct methanol fuel cell electrodes

Qing Li [1], Dusan Spernjak, Piotr Zelenay, Yu Seung Kim [*]

Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

HIGHLIGHTS

- Micro-crack formation in Nafion®-based MEAs is studied by subjecting MEAs to 100 h extended DMFC tests.
- Micro X-ray computed tomography (microXCT) images visualize the internal morphology of the MEAs before and after life tests.
- All MEAs show some initial micro-cracks; the electrode area increases in both electrodes during life tests.
- Higher methanol feed concentrations, thinner membrane, and the use metal-black catalysts generate more and larger cracks.
- Carbon-supported catalysts show better stability and improved resistance to crack formation compared to metal-black catalysts.

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ABSTRACT

This study focuses on the micro-crack formation of Nafion®-based membrane electrode assemblies (MEAs) after extended direct methanol fuel cell (DMFC) operation. All electrodes, both with metal-black and carbon-supported catalysts, contain some micro-cracks initially; the area covered by these cracks increases both in the anode and cathode after 100-hours of DMFC test. X-ray tomography shows an increase in the crack area in both anode and cathode that correlates with methanol feed concentration and methanol crossover. The MEAs with carbon-supported catalysts and thicker membrane are more resistant to the formation of micro-cracks compared to those with metal-black catalysts and thinner membrane, respectively. The impact of the micro-crack formation on cell performance and durability is limited over the 100-hour DMFC operation, with the long-term impact remaining unknown.

1. Introduction

Direct methanol fuel cells (DMFCs) are a promising technology as a power source for portable and uninterruptible power supply applications, offering the advantage of a liquid fuel with high energy density and an ease of fuel storage and transportation. In the last decade, DMFC research has focused predominantly on developing materials and operating strategies to improve performance of membrane-electrode assemblies (MEAs) [1,2]. Despite the recent progress, several inherent problems still hinder the wide spread of DMFC technology. One of the most critical issues is performance degradation in long-term operation, which prevents present-day DMFCs from achieving performance stability for thousands of hours that, together with meeting cost targets, is required of a majority of portable power systems [3].

Over the past years, significant research efforts have been devoted to DMFC performance degradation during long-term operation [4]. A PtRu black/Nafion®117/Pt-black (anode/membrane/cathode) MEA after a DMFC life test exceeding 1000 h was examined by Cheng et al. [5]. The results revealed fast performance degradation during the first 200 h, which slowed down between 200 and 704 h, only to accelerate after 1002 h of the test. Eickes et al. reported on DMFC performance loss due to the oxidation of a platinum cathode catalyst during continuous DMFC operation. This performance loss could be fully recovered by bringing the cathode potential down to a value corresponding to complete reduction of the surface Pt oxide [6]. Piela et al. reported that cathode contamination by Ru crossover inhibits oxygen reduction kinetics at the cathode resulting in up to 200 mV performance loss during DMFC operation [7]. Recently, Bresciani et al. [8] proposed a strategy to mitigate degradation effects. Steady-

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[*] Corresponding author. Tel.: +1 505 667 5782; fax: +1 505 665 4292.
E-mail address: yskim@lanl.gov (Y.S. Kim).

[1] Current address: Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA.

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state DMFC operation was interrupted periodically by refresh cycles involving open-circuit operation and cathode air interruption, which resulted in the reduction of permanent degradation (unrecoverable loss) by 28% as well as lower temporary degradation (recoverable loss) [8].

Catalyst loss and particle agglomeration have been identified as one of the main attributes of the DMFC performance loss. A 30% performance loss, attributed to the catalyst agglomeration, together with electrode delamination in the MEA, was reported by Liu et al. [9] after a 75-hour DMFC life test at a current density of 100 mA cm^{-2} using a PtRu/C/Nafion®115/Pt/C MEA. X-ray diffraction (XRD) and transmission electron microscopy (TEM) attest to an increase in the catalyst particle size in both the anode and cathode after a 500-hour test, with faster particle growth at the cathode in a PtRu/C/Nafion®115/Pt/C MEA [10]. Similar results were reported by Kim [11], Sarma [12] and Park [13], with PtRu-black/Nafion®115/Pt-black, PtRu-black/Nafion®117/Pt-black and PtRu-black/Nafion®115/Pt-black MEAs, respectively. Changes in the alloying degree of Pt and Ru in anode catalysts caused by the Ru loss over time were observed by X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and energy dispersive X-ray spectroscopy (EDX) (all with metal black catalysts) and correlated with the DMFC performance loss [12,14,15].

Other modes of MEA-component degradation have also been reported. Siroma et al. suggested that possible dissolution of recast Nafion® in mixtures of methanol and water can adversely impact the DMFC performance [16]. The degree of dissolution of recast Nafion® could be more than 30% at 80 °C at a methanol concentration of 80%. The performance decay caused by the decrease in the hydrophobicity of the gas diffusion layer (GDL) and subsequent cathode flooding was also observed with a PtRu/C/Nafion®117/Pt/C MEA [17]. Electrochemical impedance spectroscopy (EIS) was used to analyze DMFC performance decay after a 435-hour life test at a constant current density of 150 mA cm^{-2} with a PtRu-black/Nafion®115/Pt-black MEA. Contributions of various impedance components to the total cell impedance increase after the life test were as follows: ohmic resistance – 71%; cathode reaction resistance – 24%; anode reaction resistance – 5% [18]. Electrode delamination can cause DMFC performance degradation as well. Our previous studies reported on membrane-electrode delamination which increased with the water uptake of the membrane and methanol feed concentration [19–22]. The performance loss was accompanied with an increase in the cell resistance [20–23].

Another possible DMFC degradation mode is electrode micro-cracking. While in general adversely impacting DMFC performance through a buckling deformation [24], pin-hole formation in the membrane [25], inhibiting multi-phase transport [26], and affecting the three-phase interface regions [27], the crack formation can also benefit the cell performance by facilitating access of reactants to the reaction sites [28,29]. As a result, the overall effect of the catalyst layer cracks on the DMFC durability is not obvious. Furthermore, the fragility of catalyst layers makes it difficult for the post-mortem analysis and often brings experimental uncertainties. In the present work, we depict micro-crack formation in DMFC MEAs using X-ray micro-tomography technique and discuss their impact on DMFC performance durability. Cracks in Nafion®-based MEAs were systematically studied during DMFC operation for 100 h hours at methanol feed concentrations of 0.5, 1.0, and 4.0 M, using metal-black and carbon-supported catalysts, catalyst-coated membranes and gas-diffusion electrodes, and membranes of different thickness (single- and three-layer membranes). The effects of cell operating conditions on the electrode structural change and performance degradation modes are discussed.

2. Experimental

2.1. MEA preparation

MEAs were fabricated using Nafion® 212 membranes (DuPont) in acid form (single-layer membranes by default, triple-layer membranes membrane where noted) and Pt based electrocatalysts (Johnson Matthey). Three types of electrodes were used in this study:

- MEA 1: Catalyst-coated membrane (CCM) with metal-black catalysts; $Pt_{50}Ru_{50}$ black (HiSPEC® 6000) anode catalyst at 4.0 mg_{Pt}/cm^2; Pt black (HiSPEC® 1000) cathode catalyst at 4.0 mg_{Pt}/cm^2.
- MEA 2: CCM with carbon-supported catalysts; PtRu/C (75% metal loading, HiSPEC® 12100) anode catalyst at 2.7 mg_{Pt}/cm^2; Pt/C (60% metal loading, HiSPEC® 9100) cathode catalyst at 2.0 mg_{Pt}/cm^2.
- MEA 3: Gas-diffusion electrode (GDE) with carbon-supported catalysts (Johnson Matthey); PtRu/C (HiSPEC® 12100) anode catalyst at 2.7 mg_{Pt}/cm^2; Pt/C (HiSPEC® 9100) at 2.0 mg_{Pt}/cm^2 cathode catalyst.

Catalyst inks for MEAs 1 and 2 were prepared by ultrasonically mixing catalyst powders with de-ionized water (Millipore®, 18 MΩ cm) and 5% Nafion® suspension (Ion Power, Inc.) for 90 s. Catalyst inks were brush-painted onto the membrane at 75 °C and dried for 30 min. MEA 3 was obtained by hot-pressing GDEs onto the membrane at 120 °C and 45 kg cm^{-2} for 2 min. The active cell area was 5 cm^2.

2.2. Fuel cell testing

DMFC testing was carried out in a single 5 cm^2 cell using a commercial fuel cell test station (Fuel Cell Technologies, Inc.). MEA was sandwiched between two graphite bipolar plates, each with a single-serpentine flow channel. The cell was operated at 80 °C. Methanol solution (0.5, 1.0, or 4.0 M) was delivered to the anode at a flow rate of 1.8 mL min^{-1} using a high-pressure liquid chromatography pump (Shimadzu LC-10AS). The cathode side was supplied with pre-humidified air at a high flow rate of 500 sccm and ambient pressure. The temperature of cathode humidifier was set to 10 °C higher than the cell temperature. While this is not the most practical condition, it maintains the membrane humidification by pushing liquid water through cathode layer. High-frequency resistance (HFR) of the cell was measured using a sinusoidal voltage perturbation at 3333 Hz (chosen to minimize capacitance). Each cell was subjected to a two-hour break-in in a hydrogen/air fuel cell at 0.7 V using fully humidified gases at a back pressure of 1.4 bar. Long-term DMFC performance was investigated in 100-hour life tests at 0.45 V. The cell HFR was monitored during life tests. The CO_2 content in the cathode effluent was measured by a gas analyzer equipped with a calibrated non-dispersive infrared (NDIR) sensor (California Analytical Instruments, Inc.). The NDIR sensor was calibrated using certified CO_2 gas cylinder and connected to cathode effluent before the CO_2 measurement. From the down stream of the fuel cell, water was completely removed from the gas stream by Drierite® water trap. Polarization curves were recorded before and immediately after each life test. In addition, the fuel cell performance was recorded after a performance recovery process which included cooling down and drying the cell. This post-recovery cell performance is denoted as recovered performance.

Unless noted otherwise, data reported below correspond to the following operating conditions of the fuel cell: temperature 80 °C,