Available online at www.sciencedirect.com

## SciVerse ScienceDirect

journal homepage: www.elsevier.com/locate/he

# Understanding the performance degradation of anion-exchange membrane direct ethanol fuel cells

## Y.S. Li, T.S. Zhao*

*Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China*

ABSTRACT

It has recently been demonstrated that anion-exchange membrane direct ethanol fuel cells (AEM DEFCs) can yield a high power density. The operating stability and durability of this type of fuel cell is, however, a concern. In this work, we report the durability test of an AEM DEFC that is composed of a Pd/C anode, an A201 membrane, and a Fe-Co cathode and show that the major voltage loss occurs in the initial discharge stage, but the loss becomes smaller and more stable with the discharge time. It is also found that the irreversible degradation rate of the fuel cell is around 0.02 mV h$^{-1}$, which is similar to the degradation rate of conventional acid direct methanol fuel cells (DMFCs). The experimental results also reveal that the performance loss of the AEM DEFC is mainly attributed to the anode degradation, while the performance of the cathode and the membrane remains relatively stable. The TEM results indicate that the particle size of the anode catalyst increases from 2.3 to 3.5 nm after the long-term discharge, which reduces the electrochemical active surface area and hence causes a decrease in the anode performance.

Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Direct alcohol fuel cells (DAFCs), promising to be a sustainable and efficient power source for portable and mobile applications, have attracted increasing attention over the past decade [1–6]. As compared with methanol, ethanol is less toxic and cheaper in production. Hence, tremendous efforts have been made to the development of direct ethanol fuel cells (DEFCs), including both proton-exchange membrane (PEM) and anion-exchange membrane (AEM) DEFCs. However, conventional PEM DEFCs that use Pt-based catalysts demonstrated extremely poor performance (the state-of-the-art peak power density is 30 mW cm$^{-2}$ at 60 °C) [7], primarily because it is difficult to oxidize ethanol in an acid medium. On the other hand, however, owing to the fact that the kinetics of both the ethanol oxidation reaction (EOR) and oxygen reduction reaction (ORR) can be accelerated in an alkaline medium, AEM DEFCs can yield much better performance (the state-of-the-art peak power density is 185 mW cm$^{-2}$ at 60 °C) [8], even using the Pt-free catalysts. Therefore, AEM DEFCs have recently attracted ever-increasing attention [9–14].

In developing AEM DEFCs, one of the major issues that hinder the commercialization of fuel cells is the durability. Past efforts in AEM DEFCs have mainly been focused on the development of the materials and the design of the cell system [15–17]. Relatively, few investigations have been reported to the study of the durability of AEM DEFCs [18,19]. Bianchini et al. [18] reported that the AEM DEFC showed a 15% loss of the cell voltage at a constant current density of 20 mA cm$^{-2}$ after 217-h discharge. Recently, Hou et al. [19] studied the durability of KOH-doped polybenzimidazole (PBI) membrane for air-breathing AEM DEFC. The experimental

results indicated that the ionic conductivity of KOH-doped PBI membrane degraded from initial 23 mS cm$^{-1}$ to 10 mS cm$^{-1}$ after 100-h discharge, and the degradation rate was 0.13 mS cm$^{-1}$ h$^{-1}$. However, a general understanding of performance degradation of AEM DEFCs, especially for the contribution of different components of the membrane electrode assembly (MEA) on the performance degradation, is far less understood. Being motivated by this need, in this work, we conducted a 520-h long-term durability test of the AEM DEFC. The performance of the anode electrode, cathode electrode and membrane at different time points are examined. We show that the performance loss of the AEM DEFC is mainly attributed to the anode degradation, while the performance of the cathode and the membrane remains relatively stable.

## 2. Experimental

### 2.1. Membrane electrode assembly fabrication

The MEA with an active area of 1.0 cm × 1.0 cm consisted of an anion-exchange membrane (A201, Tokuyama) and two electrodes. The cathode electrode was a single-side electrode consisting of the Fe-Co HYPERMEC™ K14 catalysts (Acta), which was attached to a backing layer made of carbon cloth. On the anode [13,20], catalyst inks were prepared by mixing the home-made Pd/C catalysts and polytetrafluoroethylene (PTFE) with ethanol as the solvent. The content of the PTFE as a binder was maintained at around 5 wt.%. The catalyst inks were stirred continuously in an ultrasonic bath for 10 min such that they were well dispersed. Subsequently, the prepared catalyst inks were directly brushed onto the nickel foam that served as the backing layer to form an anode electrode with a loading of 1.5 mg$_{pd}$ cm$^{-2}$.

### 2.2. Durability test

The durability of the fuel cell was tested by observing the transient voltage at a constant current density (50 mA cm$^{-2}$) that was measured with an electric load system (Arbin BT2000, Arbin Instrument Inc.) [16]. 99.5% oxygen without humidification at ambient pressure at a flow rate of 60 standard cubic centimeters per minute (sccm) was supplied to the cathode by a mass flow controller (Omega FMA-78P4 and FMA-765A). The aqueous solution, containing 3.0 M ethanol and 1.0 M KOH, was fed to the anode by a peristaltic pump at a flow rate of 1.0 ml min$^{-1}$. To test the variation in polarization curves with the discharge time, the stop/restart procedure was used at the time point of 25, 100, 200, 300, 400, and 500 h to collect the voltage and current. The cell resistance was measured by the d.c.-pulse method. The cell operating temperature was measured with a thermocouple installed at the anode fixture plate.

### 2.3. Electrode characterization

#### 2.3.1. Electrode potentials
A Hg|HgO|KOH (1.0 M) (MMO, 0.098 V vs. SHE) reference electrode was placed at the inlet of the anode flow channel [16]. The anode potential was measured by the MMO reference electrode, while the cathode potential was obtained by adding the anode potential to the iR-corrected cell voltage.

#### 2.3.2. Electrochemical active surface area measurement
The electrochemical active surface area (EASA) of the anode electrode was measured by cyclic voltammetry (CV) using a potentiostat (Autolab PG30) [20]. The three-electrode electrochemical cell was used with a Pt foil and a MMO reference electrode as the counter and reference electrodes, respectively. The anode electrode was used as the working electrode. CV tests were conducted at 50 mV s$^{-1}$ in the potential range between −0.926 and 0.274 V vs. MMO in 1.0 M KOH solution.

#### 2.3.3. Microscopic morphology
The morphology, microstructure and particle size of the anode catalyst were investigated by transmission electron microscopy (TEM) images using a high-resolution JEOL 2010F TEM system operating with a LaB6 filament at 200 kV. The anode catalyst was dispersed in ethanol under sonication and dropped on the carbon-coated grid and then imaged.

### 2.4. Membrane characterization

#### 2.4.1. Ionic conductivity
The OH$^-$ conductivity of the anion-exchange membrane, $\sigma$, can be determined from:

$$\sigma = \frac{l}{RS} \tag{1}$$

where $l$ and $S$ representing the thickness and area of the membrane, respectively. $R$ is the membrane resistance obtained from the real axis intercept of the impedance Nyquist plot. Membrane samples were immersed in 1.0 M KOH solution for three days, and then dipped in DI water that was saturated by nitrogen gas for two days to remove the redundant hydroxyl ions. The treated membrane sample, with an area of 1.0 cm × 1.0 cm, sandwiched between a pair of gold-coated stainless steel plates, was measured by the electrochemical impedance spectra (EIS) at frequency range from 100 kHz to 1 Hz with 10 mV amplitude.

#### 2.4.2. Content ratio of nitrogen to carbon
The XPS was used to measure the elemental information of the surface of membrane samples at the nanometer scale [21,22]. The content ratio of nitrogen to carbon was used to characterize the functional group (quaternary ammonium) charge of the anion-exchange membrane during the discharge process. The XPS peak intensities after being normalized by the atomic sensitivity factors can be used to determine the composition by using the following equation:

$$C_i = \frac{I_i/S_i}{\sum I_i/S_i} \tag{2}$$

where $C_i$ is the concentration of the element $i$, $I_i$ and $S_i$ are the peak area and the atomic sensitivity factor of the element $i$, respectively.

#### 2.4.3. Ion-exchange capacity
The ion-exchange capacity (IEC) of the anion-exchange membrane was measured by the conventional acid-base