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Durability and efficiency tests for direct methanol fuel cell's long-term performance assessment

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ABSTRACT

This research assessed the long-term performance of direct methanol fuel cells. The experiment was performed at room temperature using 0.51 mol/L ~0.651 mol/L methanol with a fuel consumption rate of 0.8 ± 0.1 cc/Wh at stack temperature of 60 °C–70 °C. DuPont Nafion115 proton exchange membrane was used as the base material of MEA (membrane electrode assembly), which is then examined via a series of processes that include I–V curve test, humidity cycle test, load cycle test, and hydrogen penetration test. The study employs membrane modification and cell structure adjustment approaches to reduce the methanol crossover in the cathode and identify the cell performance effect of the carbon paper gas diffusion layer. The test results indicated an efficiency of 25% can be achieved with a three-piece MEA assembly. According to the durability test, the stack power-generation efficiency has maintained at 15% –25% level. With such efficiency, the stack voltage output has been able to stay above 7.8-V for over 5000 h. This result is in line with industry standard.

1. Introduction

The green technology has delivered important progress in three areas: LEDs (light emitting diodes) [1], organic photovoltaic cells [2], and fuel cells [3]. Responding to political, economical, and environmental constraints to reduce the fossil fuel consumption as well as consequent emissions, fuel cells are being actively studied due to their potential for high efficiency, low pollution, and a waste to energy chain [4]. The maturing technology and the vast number of LED applications have brought great hope among researchers to expect fuel cells to become the next prominent energy star. Fuel cells produce water, heat, and, depending on the fuel used, small amounts of nitrogen dioxide and other supposedly harmless emissions.

The efficiency of a fuel cell runs between 40 and 60% (PEMFC (proton exchange membrane fuel cell)), or up to 85% (Phosphoric Acid FC, Molten Carbonate FC, Solid Oxide FC, etc.) when the generated heat is reused [5]. Fuel cell-powered vehicles with market competitiveness are gradually evolving to be the vehicle of the future [6].

Most fuel cells are fueled by hydrocarbon fuels or renewable fuels such as biogas [7]. For example, simple structured methanol, after a rectification process, can be used as a hydrogen-rich fuel source of RMFC (*reformed methanol fuel cell*) for power generation.

Methanol can be mixed with steam and fed directly to the anode of DMFC (direct methanol fuel cell) for electricity generation [8,9]. DMFC is a subset of PEMFC (proton exchange membrane fuel cell) generally used for small portable power applications. DMFC is compact in design, needs no compressor or humidification, and feeds directly off methanol in liquid form. Compared to other types of fuel cells, DMFC can be made smaller and less costly. DMFC can also be more efficient as the refueling of DMFC is fast [10]. The improvements in cell structure and catalytic materials performance have allowed low power DMFC products, which are suitable for portable, mobile, and stationary applications, to enter the market and start to replace the PEMFC power system. As a result, DMFC has been found an appropriate alternative to rechargeable battery technology [11]. Unfortunately, methanol is highly toxic to humans.

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Nomenclature

AN	Anode
CA	Cathode
CL	Catalyst layers
BP	Bipolar plate
EMS	Energy management system
DMFC	Direct methanol fuel cell
GDL	Gas diffusion layer
MEA	Membrane electrode assembly
MeOH	Methanol
MPL	Micro-porous layer
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cell
RMFC	reformed methanol fuel cell

It can be easily absorbed by ingestion and inhalation, and less speedily by skin exposure. The median lethal dose is estimated to be 1–2 ml/kg [12]. As little as 0.1 ml/kg (i.e. 6–10 ml in adults) of pure methanol, when ingested, can destruct the optic nerve and cause permanent blindness. Despite such potential health hazard, DMFC's potential for higher energy density makes it a leading contender to replace the lithium-ion (Li-ion) battery as the power source of choice for mobile devices. Given a large enough market, the DMFC systems will eventually be less expensive than other alternative battery technologies. Nevertheless, to become more competitive with, and ultimately take the place of Li-ion batteries, the DMFC systems must be designed to have higher energy efficiency. As conventional batteries are becoming insufficient for the complexity and the increasing power demand of portable electronic devices, DMFC has the potential to become their replacement when:

- Its average efficiency reaches beyond 30%.
- Its life span is compatible to that of lithium-ion battery [13].
- Its high-cost platinum catalyst is replaced by a more affordable material [14,15].

Porosity, conductivity, compressibility, hydrophobicity, gas penetration rate, MPL (micro-porous layer) properties are among the cathode GDL (gas diffusion layer's) specifications that may affect the stack performance. Researchers have been studying the performance impact of these parameters [16,17] to develop suitable GDLs for different fuel cell systems [18,19].

Some positive argument about the penetration of diluted methanol to the cathode (methanol crossover) is worth noticing. Well-managed methanol crossover can be used to distribute the anti-freeze additive evenly across the cell stack and is helpful during start-up or under extreme outside conditions as it rapidly heat up the unit [20].

The purpose of this study is to demonstrate certain approaches (i.e. membrane modifications and cell structure adjustment) that can help to manage methanol crossover. The study also aims to verify the significance of the effect of the carbon paper type in the cathode GDL to the fuel cell performance.

To assess the long-term performance of DMFC under conditions not as optimal as in the lab, the experiment specifications with greater than 10% fluctuations have been applied to facilitate the observation of the DMFC's functioning stabilities in the less-than-perfect environments.

2. Materials and method

Fig. 1 demonstrates the overall chemical reaction of a DMFC, where the reaction in anode is [21]:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (E_{n,a} = 0.046V) \tag{1}$$

DMFC's standard electromotive force and total power output efficiency are lower than those of RMFC since the potential of methanol oxidation in anode is higher than the standard reversible potential of hydrogen. Therefore, a second set of catalysts is needed to boost the activation and dissociation of water molecules to complement the low potential (<0.4 V) in the anode process.

Platinum and Pt–Ru, respectively, are the best electrochemical reaction catalysts for methanol oxidation in anode and O_2 reduction in cathode. The oxidation of methanol into CO_2 involves the transfer of six electrons. Incomplete reaction may generate CO that could set off platinum catalyst poisoning. As a result, oxygen from external source is required to avoid the CO generation.

$$1.5\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (E_{n,c} = 1.229V) \tag{2}$$

The combination of Eqs. (1) and (2) conclude the overall reaction:

$$CH_3OH + 1.5\ O_2 + H_2O \rightarrow CO_2 + 2H_2O \quad (E_n = 1.183V) \tag{3}$$

Temperature, flow rates, pressure drop, and relative humidity in the channels affect the removal and accumulation of water in the GDL, gas flow channels, and fuel channels [22].

A single cell comprises BP (bipolar plates), GDL, CL (catalyst layers) and electrolyte membrane, which prevents the H_2 and O_2 from mixing directly. The channels in the BP serve to distribute H_2 and O_2 on the active area. On the catalyst surface, a more homogeneous reactant concentration, which can be regulated through uniform flow rate and pressure profiles, leads to a higher power density [23]. The GDL, which is made of porous materials, allows the diffusion of H_2 and O_2 to the CL from the channels and the backflow of H_2O from the CL to the channels. Electrochemical reactions occur only in the CL but in the BP and the GDL.

The MEA (membrane electrode assembly) used in this DMFC study is assembled via stacking on a metal substrate (Fig. 2a) in the following sequence (Fig. 2b):

- a graphite BP,
- an anti-leakage lining,
- a carbon paper sheet,
- a three layers of membrane electrode,
- a carbon paper sheet, and
- an anti-leakage lining

Repeat the process to form the desired number of MEA layers, that is, three for a 3-layer MEA DMFC stack (or 3-cell stack) and 26 for a 26-layer MEA DMFC stack (26-cell stack) and then cover the set with a top metal plate. The set is then fastened with insulation-coated screws, washers, springs, and nuts to form a DMFC stack ready for testing.

2.1. GDL test for 3-piece-MEA DMFC stack

Based on the previous studies [24,25], five reasonable GDLs have been selected to use in the fuel cell stacks for the study. The stacks are tested for their I–V curve and short-time fix power output to identify which GDL leads to optimum performance. The features of the selected carbon papers are listed in Table 1. Their detailed specifications can be obtained from the supplier, SGL Group [26].