Journal of Power Sources 272 (2014) 522–530

Contents lists available at ScienceDirect

Journal of Power Sources

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

Static friction force between catalyst layer and micro porous layer and its effect on deformations of membrane electrode assemblies under swelling

Tomoaki Uchiyama [a, *], Hideyuki Kumei [a], Toshihiko Yoshida [a], Kazuhiko Ishihara [b]

[a] Toyota Motor Corporation, Fuel Cell System Development Div., R&D Group, 1200, Mishuku, Susono, Shizuoka 410-1193 Japan
[b] Department of Materials Science, School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

HIGHLIGHTS

- MEA wrinkles did not occur at higher contact pressures under humidity cycles.
- Static friction coefficient increased with the increase in the contact pressure.
- Convex sections of the MPL generated a static friction force by contacts with the CL.
- Static friction force, which was 12% of swelling force, restricted the MEA wrinkles.

ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form
19 June 2014
Accepted 25 August 2014
Available online 3 September 2014

Keywords:
Polymer electrolyte membrane
Membrane electrode assembly
Static friction force
Contact pressure
Wrinkle

ABSTRACT

Membrane electrode assemblies (MEAs) composed of a Nafion membrane and heat-transferred catalyst layers (CLs) were employed in this study. The deformation of MEAs between micro porous layers (MPLs)/gas diffusion layers (GDLs) was investigated in response to humidity cycles. The MEA deformed into wrinkle shapes at lower contact pressures and exhibited bulge deformation at higher contact pressures. Wrinkles were generated by large in-plane swelling after buckling when swelling could not be restricted by the friction force from MPLs. Next, the static friction coefficient between the MEA and MPL was measured, and a friction mechanism was investigated. The static friction coefficient was 0.43 at the contact pressure of 0.22 MPa between the MEA and MPL and increased with the increase in the contact pressure. The surface observation of the MPL after the friction test indicated that a static friction was generated by the contact of the convex MPL and flat CL surface. The static friction force and swelling force were calculated to investigate the effect of the static friction force on the MEA deformation. The static friction force, which was more than 12% of the swelling force, could prevent wrinkles in 33 μm thick MEA.

1. Introduction

Polymer electrolyte fuel cells (FCs) are electric generators with zero emissions and expected to be utilized for FC vehicles. Durable and reliable FC stack designs need to be manufactured at low cost for FCs to be widely commercialized. FC consists of many layers. Membrane electrode assemblies (MEAs) are located in the center of the FCs and are the main component to affect its generating performance. The MEA is a hydrophilic multi-layer membrane that consists of a polymer electrolyte membrane (PEM) and catalyst layers (CLs) that sandwich the PEM. The PEM separates both CLs and inhibits gas permeation from the anode or cathode sides to the other side. Protons are conducted through the PEM from the anode to the cathode. The oxidation reaction of hydrogen occurs at the anode side, and the reduction reaction of oxygen is carried out on the cathode side in each CL. When the PEM degrades, these functions decrease. Thus, the durability and stability of the MEA is essential for its long-term use.

Many researchers have studied the mechanical and chemical durability of the MEA [1–15]. The resistance of the PEM affects the generating performance and is better for thinner membranes and higher ion-exchange capacities with the sulfonic acid moiety in the side chains. The high swelling ratio of PEM leads to mechanical degradation, and thinner PEMs tend to rapidly result in MEA failure [10]. The development of PEMs aims to generate thinner PEMs with high water absorption that ensure proton conductivity and durability.

* Corresponding author. Tel.: +81 55 997 9078; fax: +81 55 997 7120.
E-mail address: tomoaki_uchiyama@mail.toyota.co.jp (T. Uchiyama).

http://dx.doi.org/10.1016/j.jpowsour.2014.08.103
0378-7753/

The failure mechanism for laminated MEAs and gas diffusion layers (GDLs) must be understood to ensure the reliable design of the MEA. MEA failure tends to occur under channel portions of gas flow fields, and it can be prevented by applying higher contact pressure between the MEA and GDL [11–13]. Distributions of the contact pressure are generated according to the in-plane portion. Under channel portions the contact pressure would become below 0.1 MPa. Lower contact pressures are induced when the channel width is wide and the GDL rigidity is low. Although prevention methods of MEA failure have been studied [4,5,8,10–13], prevention mechanism that utilize higher contact pressures have not been adequately researched.

The PEM absorbs water into its ion cluster around the sulfonic acid moiety and swells [16–20].The MEA is constrained at the in-plane edge by a gasket and cannot freely swell. When the compressive stress in the PEM under swelling exceeds the critical stress for in-plane buckling, MEA wrinkles result [11]. The wrinkle is an initial degradation of the MEA and accelerates PEM failure. While studies about wrinkles have focused on Nafion® membranes, this phenomenon is confirmed in a PEM with in-plane swelling. Wrinkles induce large strains in the deformed portion, and CL cracks are formed [11–13,15]. Micro-structural changes, such as molecular chain scissions and the crystallinity of the molecular chain due to the large strain, would accelerate micro-void formations in the PEM.

The goal of this study was to understand the mechanism of wrinkle suppression at higher contact pressures between the MEA and micro porous layer (MPL)/GDL. The relationship between the wrinkle generation and the contact pressure was investigated. To this end, a MEA wrinkle test was conducted while varying the thickness of the PEM. The static friction coefficient between the MEA and MPL was measured, and their friction mechanism was considered. The swelling force was calculated from Young's modulus and the swelling ratio of the MEA, and the swelling force of the MEA was compared with the static friction force to consider effect of the friction on the wrinkle. The MEA used in this study was a catalyst layer-coated membrane. MEA contacted the MPL/GDL via a fastening force from the gas flow fields, and the MEA and MPL were not adherent.

2. Experimental procedures

2.1. Materials

The commercial Nafion® membranes [16–20] NR211, NR212 and N115 (Dupont, USA) were used in this study. These materials are sulfonated tetrafluoroethylene copolymers and consist of a hydrophobic poly(tetrafluoroethylene) (PTFE) backbone and side chains ending with hydrophilic sulfonic acid (SO_3^-) ionic groups. NR211 and NR212 are cast manufacturing membranes, and their thicknesses are 25 μm and 50 μm, respectively. N115 is an extrusion type membrane that is 125 μm thick. Catalyst ink was mixed with a Nafion solution and carbon-supported Pt at a weight ratio of 1:1. The ink was coated on the Teflon sheet at 0.2 mg cm^{-2} of Pt. The CLs on the Teflon sheet were laminated on both sides of the PEMs via the heat transfer method at 130 °C for 10 min. Commercial product SGL 25BC, which has a MPL in Sigracet® (SGL, Germany), was used as the GDL. The average thickness was 236 μm. GDL was used without treatment, e.g., pressing. Images of the surfaces of NR211-CL and MPL/GDL were captured using a scanning electron microscope (SEM, Keyence, Japan). The oblique views of the surface are described in Fig. 1. The surface of the CL was very flat, and its asperities did not exceed 1 μm. The surface of the MPL was rough, showing concave structures that were several tens of micrometers in height and several hundred micrometers in width.

2.2. MEA properties

The swelling ratios of NR211-CL and NR212-CL in liquid water at 80 °C have been previously measured [11,12]. The swelling ratio of N115-CL was measured in two samples using the same method. Sections (50 × 50 mm^2) were cut from the samples, and the thicknesses were measured with a micrometer (Mitutoyo, Japan) at 23 °C and 50 relative humidity (RH) %. After soaking the samples in de-ionized water at 80 °C for 2 h, the dimensions were measured. The samples were then dried at 80 °C for 1 h, and the dimensions were measured again. The dimension changes were measured twice during these phases. The swelling ratios of MEAs in swollen state were referenced to initial dimensions at 23 °C and 50 RH%.

Tensile tests were conducted using a tensile machine with a custom-designed environmental chamber (Instron, USA). Dumbbell-shaped samples (gage length of 33 mm and width of 6 mm) were used. Two specimens of NR211-CL were tested at each condition. After 2 h (at 40, 80 RH%) or 1 h (at 100 RH%, in liquid water) of stabilization at 80 °C in the chamber, the tensile tests were performed at strain rates of 1.39×10^{-1}, 1.39×10^{-2}, 1.39×10^{-3} and 1.39×10^{-4} s^{-1}. The stress-strain curves at each humidity value were calculated by referencing the sample size with humidity changes, which was determined via correlations between the swelling ratio change and relative humidity [11,12].

2.3. Humidity cycle test of membrane electrode assemblies

MEAs consisting of NR211, NR212 and N115 were exposed to humidity cycles at several contact forces, and the criteria of the contact pressure that prevented wrinkle generation were

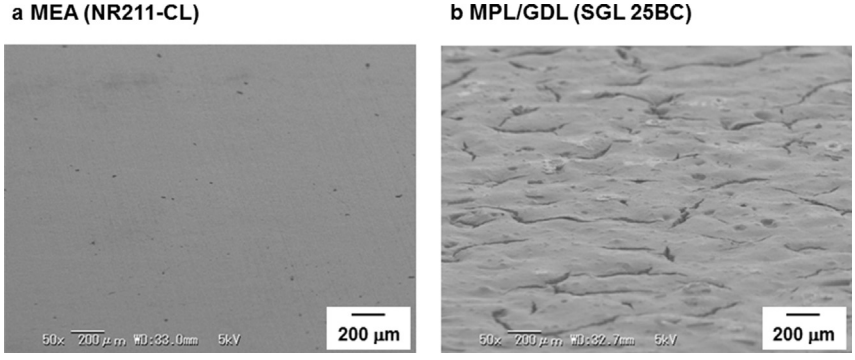

Fig. 1. SEM observations of sample surface: (a) MEA (NR211-CL), (b) MPL/GDL (SGL 25BC).