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Repetitive bending test of membrane electrode assembly for bendable polymer electrolyte membrane fuel cell

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ABSTRACT

Membrane electrode assemblies (MEAs) with carbon paper and cloth for bendable polymer electrolyte membrane fuel cell were characterized as it is subject to repetitive bending. The performance of the MEA with carbon paper was decreased significantly while the MEA with carbon cloth remained constant after repetitive bending. Electrochemical impedance spectroscopy revealed ohmic and charge transfer resistances of the MEA with carbon paper were increased by repetitive bending. Such performance degradation is due to physically observed damages in carbon paper and its detachment from the MEA, which was not in the MEA with carbon cloth due to its intrinsic flexibility.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered as one of the portable power sources of the future on account of their potential high energy density as well as high efficiency and scalability [1–6]. Although, the current technologies for miniaturization of PEMFCs are not yet fully matured, the aforementioned characteristics enable them to be used as portable auxiliary power sources [7–10]. Even if it may not be easy to employ a PEMFC as a direct power source in portable applications, this technology is undoubtedly a strong candidate for achieving a higher energy density than the current market-leading lithium-ion batteries.

With this variation in the power sources, 'flexible' or 'bendable' electronic devices are emerging as interesting future electronics. The development of such flexible electronics has been motivated by their use in a variety of applications such as wearable and epidermal electronics [11–15]. Consequently, research on flexible electronics has been actively pursued for decades. Given that fuel cells are capable of attaining higher energy density than lithium-ion batteries, a 'flexible and bendable fuel cell' can be a part of future portable power sources.

That is why there have been several studies on bendable fuel cells [16–22]. Among these, bendable fuel cells based on polydimethylsiloxane (PDMS) coated with Ag nanowires even showed usable power (>1 W) [23–27]. This suggests that the technological advancements of bendable fuel cells are close to commercialization. Interestingly, a characteristic common to all the bendable fuel cells was the employment of normal membrane electrode assemblies (MEAs), which are generally used in normal PEMFCs, without any modifications. Although a MEA is composed of a Nafion® membrane, Pt/C catalyst layers, and gas diffusion layers (GDLs), which are types of bendable materials, each component could be damaged by repetitive bending. Here, a bendable fuel cell will be exposed to repetitive bending in a real operation environment. Thus, if normal MEAs need to be used in any bendable fuel cell templates, performance variation of the MEA under repetitive bending should be investigated. Furthermore, the issue with previous flexible PEMFCs was their fabrication using brittle carbon papers as GDLs. In this case, it is possible that such GDLs will get damaged under real operating conditions of flexible electronics, such as repetitive bending. Therefore, it is necessary to investigate the bending durability of carbon papers. However, to the best of our knowledge, such research has not yet been reported.

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Thus, in this study we have investigated the performance variation of normal MEAs as they were subjected to repetitive bending cycles. As mentioned earlier, because carbon paper has been widely used as a GDL material, a MEA with carbon paper was first examined. A carbon cloth, which is another representative GDL material, was also tested, because being a kind of fabric, it is not brittle unlike carbon paper. This implies that the carbon cloth will be bent easily without any damages. Our results showed that the carbon-paper-based MEA was fragile to repetitive bending, while the carbon-cloth-based MEA showed good bending-durability. The difference in the behavior of the two MEAs was analyzed *via* electrochemical measurements and by observing digital camera images of a physically damaged carbon-paper-based MEA. Interestingly, the repetitive bending increased both the ohmic and charge transfer resistances of the carbon-paper-based fuel cell. It was observed that the damages to carbon paper by repetitive bending resulted from its detachment from the MEA and extrinsic deterioration due to the generation of macro-scale cracks. However, no noticeable damages were detected for carbon cloth, due to its softness. This result signifies the need for further development of carbon cloths as GDLs in PEMFCs, which have not been in use due to the high performance of PEMFCs with carbon paper.

Experimental

Flow-field plates were fabricated using PDMS. The weight ratio between PDMS and a curing agent was 10:1. It was solidified at 70 °C for 4 h. This gel-state PDMS solution was poured over a specially designed mold in which the structure of flow-channels was made to protrude inversely so that the channels could be etched on the solidified PDMS. The etched flow-channels were 1 mm in both width and height. The width of the rib was also 1 mm. The flow-channels were of mixed parallel-serpentine style: three channels comprised one main reactant stream from inlet to outlet. The resulting thickness of a single PDMS plate was 7 mm. The reactive area defined by the flow-channels was 3 cm × 3 cm.

The MEAs were prepared as follows: first, a Nafion® 212 membrane (Dupont Co., United States) was employed as an electrolyte without pre-treatment. It was mounted on a suction-type hot-plate. The temperature of the hot-plate was 80 °C. The catalyst ink for the anode and cathode catalyst layers was prepared by mixing water, 5 wt.% Nafion® solution (Dupont Co., United States), and isopropyl alcohol (IPA) (Sigma-Aldrich Co., USA) with 40 wt.% Pt/C (Johnson Matthey Co., United Kingdom). The prepared catalyst ink was blended by ultrasonic treatment and sprayed onto the anode and cathode sides of the mounted Nafion® 212 membrane. Pt loading of the as-fabricated catalyst-coated membrane (CCM) of each electrode was 0.45 mg/cm^2 and the active geometric area of the MEAs was 9.0 cm^2. After this process, the carbon papers (10BC, SGL Carbon Co., Germany) or carbon cloths (A-type cloth, E-Tek Inc., United States) were hot-pressed on this CCM. The temperature and pressing time were 110 °C and 10 min, respectively. A Ti gauze (280 μm thick, Alfa Aesar Co., USA) was used as the current collector in the fabricated MEAs. The width of the Ti mesh was 3 cm and it covered the entire surface of the GDLs. The Ti mesh was placed between the PDMS plates and MEA as illustrated in Fig. 1.

The as-fabricated fuel cell was mounted on a vise to bend it. The fuel cell performance was measured for four shapes, namely, flat and bent with bending radii of 83, 58, and 47 mm. The volumetric rate of both the hydrogen and air streams for the fuel cell was 3.33 cm^3/s. They were humidified by flowing through water at room temperature, which corresponds to the relative humidity and temperature of 94% and 25 °C, respectively. The single cell performance and the corresponding electrochemical impedance spectroscopy (EIS) data were measured using Solartron 1260/1287

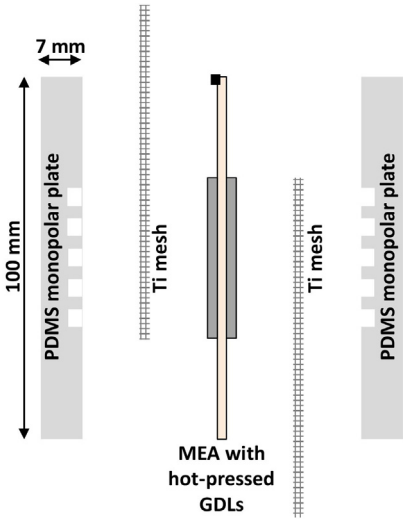

Fig. 1. Architectural schematic of the MEA-bending test setup (bendable PEMFC).

(Solartron Analytical Co., United Kingdom) at room temperature (25 °C). Before measuring the performance, it was activated by measuring current–voltage (I–V) curves repetitively. The I–V curves were measured in the voltage range from the open circuit voltage (OCV) to 0.25 V. Potentiodynamic mode was used to measure it. The voltage scan rate was 15 mV/s. Right after measuring the I–V curves, the corresponding EIS were investigated at 0.5 V *vs.* RHE. A sinusoidal input with an amplitude of 30 mV was applied and the resulting current response was monitored. The frequency range was 10^5–0.1 Hz, from high to low frequency and the corresponding ohmic and charge transfer resistances were calculated. After measuring the performance, the assembled MEA was removed from the fuel cell. It was then repetitively bent more than 100 times. The bending radius was <47 mm in this deliberate bending process (hereafter, 'before' and 'after' in all the figures refer to the MEA before and after repetitive bending test, respectively.). This bending-treated MEA was characterized again by following the same process as described above.

Results and discussion

The results of the repetitive bending test performed for the MEAs in the bendable PEMFCs are shown in Fig. 2. According to Fig. 2(a) and (b), the OCVs of the PEMFC with carbon cloth (CC-FC) are ~0.89 V while the PEMFC with carbon paper (CP-FC) are ~0.99 V. It has been commonly reported that the OCVs are typically more or less than 0.9 V if the PEMFCs are operated with ambient air at room temperature [28–31]. Accordingly, it can be inferred that sealing of the bendable PEMFCs is not problematic. In addition, there was no mass transport loss in the high current density range equivalent to low voltages of <0.3 V. Because of the high flow rates of hydrogen and air (3.33 cm^3/s), they are abundant stoichiometrically, which ensures the sealability of the fuel cell. The OCVs of the CP-FC of all shapes are higher than those of the corresponding CC-FC before the repetitive bending test (Fig. 2(c) and (d)). We believe that this difference between the OCVs of the two types of PEMFCs resulted from the unoptimized structure and lower electric conductivity of carbon cloth. Recently, carbon papers have become the chief materials for GDLs in the MEAs of PEMFCs instead of carbon cloths that were previously used, since their material characteristics, such as microstructures, relative diffusivity, and electric conductivity are superior to those of carbon cloths [32–34]. That is why in the development of GDLs, the focus has been on carbon papers. The aforementioned poor characteristics of carbon cloths might lead to insufficient supply of

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