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Effect of relative humidity cycles accompanied by intermittent start/stop switches on performance degradation of membrane electrode assembly components in proton exchange membrane fuel cells

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HIGHLIGHTS

- The H_2 permeability of the PEM is doubled after the test procedure.
- Periodical thinning, cracks and pinholes formation occur after RH cycles.
- The Pt particle size increases more than 75%.
- The cathode catalyst layer becomes looser gradually.
- PEMFC performance displays a decline tendency.

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ABSTRACT

The performance degradation of membrane electrode assembly (MEA) components in proton exchange membrane fuel cell (PEMFC) is studied by designing relative humidity (RH) cycles accompanied by intermittent start/stop switches. Cathode catalyst activity, permeability and resistance of proton exchange membrane (PEM) as well as cell performance are monitored during the test procedure. The interfaces of MEA, the catalyst particle distribution near the cathode inlet are characterized by SEM and TEM, respectively. The results demonstrate both the overall H_2 permeability and crossover current of PEM are doubled compared with its initial properties. Signs of PEM degradation, including periodical thinning, cracks and pinholes formation, are observed after 300 RH cycles and 40 times of start/stop switches. The average Pt particle size increases by more than 75%, and the cathode electrochemical surface area decreases by 48% after the test procedure. Meanwhile, the cathode catalyst layer becomes looser due to the dissolution of some smaller Pt particles and catalyst agglomeration in the RH cycles and the high potential during the intermittent start/stop switches. The membrane resistance demonstrates downshift variation during the RH cycles. PEMFC performance, however, decays due to the chemical and electrochemical attack as well as the mechanical stresses.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered as one of the potential energy conversion devices for portable electronic devices, automobiles, backup power sources, residential power systems and so on. This is due to their high energy conversion, rapid startup and environmental friendliness. However, the high cost and lower durability greatly hinder widespread commercialization of PEMFC.

Durability research mainly focused on the performance degradation of membrane electrode assembly (MEA) components under PEMFC operating conditions, especially on electrocatalyst deactivation, PEM decomposition and shorting, thickness reduction of catalyst layer as well as the microstructure changes. The accelerated durability testing (ADT) included reactants starvation [1,2], high-potential cycling [3,4] or start/stop cycling [5], load cycling simulating transport operation modes [6,7], temperature fluctuation [8,9], and humidity variation [10,11], etc. The above aging conditions can lead to microstructure changes of MEA through

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destroying electrode components, such as catalyst binder decomposition (PTFE [12] and/or proton conductor [13]), carbon support corrosion [14,15], Pt agglomeration and dissolution [16–18], catalyst layer (CL) peeling from the PEM [19,20], and the occurrence of PEM defects [21,22]. The gas diffusion layer (GDL) degradation can also occur, causing mass transport problems [23,24].

In general, PEMFC operates in an intermittent start/stop mode, which means the cell starts up and shuts down irregularly with gas purging. During the intermittent start/stop switches, the cell temperature, gas humidity, and local gas makeup are all different from under steady-state conditions. The major feature during cell start/stop switches is the occurrence of local gas mixture at the anode, also known as the hydrogen/air interface [12]. The direct results of this interface presence is the high cathode potential leading to severe carbon corrosion, Pt particle sintering, Pt particle detachment from support and dissolution in the electrolyte [12,25]. Yi et al. reported that the thickness of the catalyst layers in the anode and cathode of fresh MEAs decreased 28.4% and 74.3%, respectively, after 1500 frequent startup and shutdown cycles for an open-ended fuel cell [26]. Furthermore, the formation of hydrogen peroxide radicals at the anode side during the start/stop switches can chemically facilitate decomposition of the PEM, resulting in defects formation [27].

Another important feature of intermittent start/stop switch mode is the humidity and thermal variation inside the PEMFC. With this feature, the MEA components will experience wetting and drying processes due to the variation in reactant flow rates and water content, and the PEM will undergo frequent mechanical stress and strain variations due to the repeated swelling and contraction process [28]. Because the PEM is partially fixed in the fuel cell by the catalyst layers, gas diffusion layers, sealing elements and bipolar plates, expansion and contraction of the membrane from temperature/hydration change can induce mechanical stresses [20]; repeated stresses may cause membrane breaking and PEMFC failure [21,28–31]. In recent years, humidity cycling has been used to independently characterize the strength and toughness of membranes. The commercial NRE-211 membrane showed a lifetime of only ~4500 cycles in the testing conditions [32]. The durability is not suitable for practical application of the membrane in fuel cell, and much effort is needed to achieve an improvement in this regard.

According to the literature, the effects of humidity variations on cell performance include the following aspects: (1) insufficient water causes MEA drying, which increases the ohmic losses and charge transfer resistance [33]; excessive water may impede gas transport to the catalytic sites. (2) Increasing water content in PEMFC lowers the concentration of oxidizing H_2O_2 species [34], and the H_2O_2 formed in the aging condition [35] will be more concentrated in MEA under low humidification. (3) Carbon corrosion is suppressed while the rate of Pt nanoparticle growth increases with RH cycles [36], and the loss rate of electrochemical surface area (ECSA) of the cathode Pt at higher RH is higher than that at lower RH [37]. (4) Higher humidity in the cell improves the catalyst utilization [38], but leads to increase of the crossover current. (5) Inadequate humidification is detrimental to the membrane, because lack of water makes the membrane brittle and fragile. (6) The uneven mechanical stresses imposed during RH cycling facilitates the formation of pinholes, tears, and cracks of the PEM [11,39].

Although MEA components degradation by chemical and electrochemical attack to the key materials from cell start/stop switches and mechanical degradation from RH cycling have been relatively well understood, respectively, further investigation is required to understand the combined effects of the above two aspects, which is close to the real operation for transportation vehicles. Herein, the membrane expansion and contraction cycles are simulated through periodically changing the inlet humidity of reactants under higher current densities to simulate the real operation condition of transportation vehicles. The chemical and electrochemical attacks are simulated by H_2/air purging to the anode and cathode under intermittent cell start/stop switches, which involve temperature variations, high potential corrosion and chemical attacks with more intermediates, such as HO_2^- and HO*. By performing these simulations, we will study the loss of electrocatalytic activity, thickness reduction of catalyst layer, variation of the PEM thickness and permeability, fluctuation of cell resistance as well as the interfacial bonding strength between CL and the PEM to explain the reason of the cell performance degradation. Our work is expected to provide basic information for understanding the combined effects of chemical attack, electrochemical corrosion and mechanical stress on the durability of MEA components and key materials.

2. Experimental

2.1. Membrane electrode assembly (MEA) fabrication and single cell assembling

The MEA was fabricated by hot-pressing the home-made cathode, NRE 212CS (Dupont corp.) and home-made anode together under 10 MPa at 140 ± 2 °C for 2 min. Before hot pressing, the assembly was pre-conditioned at 140 ± 2 °C under 0.3 MPa for 1 min to allow the homogeneous distribution of the components temperature. The Pt loading in the anode and cathode was 0.14 mg cm^{-2} and 0.46 mg cm^{-2}, respectively.

The single cell was assembled by placing MEA between two graphite blocks with serpentine gas channels. The width of the shoulders and channels was 0.9 mm, and the channel depth was 0.5 mm. The clamping force was 10 N m. The geometry electrode area was 50 cm^2.

2.2. Description of test conditions and RH cycling procedure accompanied by H_2/air purging under intermittent start/stop switches (the RH- start/stop switches)

The RH cycling procedure was shown in Fig. 1. It was designed to simulate the PEM expansion and shrinkage cycles in the intermittent operating mode of PEMFC. During the RH cycling, the electrochemical and chemical effects under the RH-start/stop switches

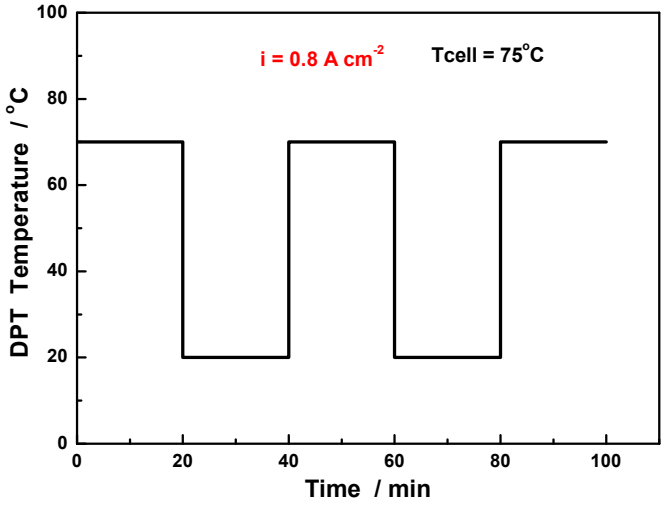

Fig. 1. The procedure of RH cycles.