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Fan XU

Xuan CHENG

Ying ZHANG

Qin-bai FAN

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Influence of Assembly Force in a PEMFC under a Lifetime Test

XU Fan¹, CHENG Xuan^{2,3*}, ZHANG Ying², FAN Qin-bai⁴

(1. Department of Chemistry, College of Chemistry and Chemical Engineering

Xiamen University, Xiamen 361005, Fujian, China;

2. Department of Materials Science and Engineering, College of Materials

Xiamen University, Xiamen 361005, Fujian, China;

3. State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, Fujian, China;

4. Gas Technology Institute, Des Plaines, IL 60018, USA)

Abstract: The lifetime performance was investigated by assembling the single cell of PEMFC under a series of holding forces ranging from 0.45 to 11.3 MPa and reassembled under optimal holding force. The polarization and power density curves were obtained during different periods of operating time up to 2000 hours and the fuel cell catalyst activation regions in the polarization curves were analyzed to evaluate the electrochemical kinetic parameters. The results revealed that the holding forces affected not only the internal contact resistances, but also the kinetic parameters which might be caused by the change of the MEA microstructures. The apparent degradation observed at higher current densities after 2000 h lifetime test under the optimal holding force of 3.2 MPa was due mainly to the increases of the catalyst particle sizes. However, the agglomeration in the particle sizes of cathode catalyst after 2000 h lifetime test at 3.2 MPa was less severe than that without optimal assembly force control.

Key words: proton exchange membrane fuel cell; contact resistance; assembly force; membrane electrode assembly; lifetime performance

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1 Introduction

Performance and durability of the proton exchange membrane fuel cell (PEMFC) are main challenges for the commercialization of the fuel cell technology and have been actively investigated in recent years^[1-6]. The fuel cell operation conditions including gas pressure, temperature^[4,7], relative humidity, gas flow rate^[4,7-8], oxidant type and shut down procedure^[9] have all shown great influence in the cell lifetime and performance.

A PEMFC single cell comprises two major components, membrane electrode assembly (MEA) and two polar plates. During the fuel cell assembly, the MEA and the polar plates are clamped together with gaskets. Hence, a proper assembly procedure during the cell assembly is essential to ensure good performance. The MEA is a key component in a fuel cell and has a sandwich structure consisting of catalyst layers (CL)/gas diffusion layers (GDL) at an anode and a cathode side, respectively, with a proton exchange

membrane (PEM) sitting between The contacts between any two interfacial layers within MEA might affect the contact resistances between the flow field on polar plates and GDL, the gas distribution of the three phase areas (gas PEM and CL) and the inside pressure of the cell^[10]. The gasket and PEM could become deformed to different degrees under different holding forces^[10-11]. The deformation caused by clamping results in two main aspects which may significantly affect cell performance and durability: firstly, the assembly process changes the MEA microstructure of GDL^[10-12], the volume in the flow channels^[11, 13] and the catalyst utilization^[10]. It was found that the porosity decreased as the holding force increased since the GDL thickness reduced more than the incompatible gasket employed and the performance changes were also suggested to be related to changes in the GDL porosity, ultimately, too high compression force may even damage the MEA and diffusion layer^[10, 12]. A model study^[11] revealed that the porosity is a function of the holding force. The relative porosity in GDL, which represents the difference between initial porosity and strain porosity, decreased much faster than the porosity with a holding force. It was also demonstrated that the volume of the flow channel was reduced more than 10% due to the GDL sagging in. Thus, the GDL deformation and holding force had to be considered when the gas transport was analyzed^[12]. There are too many parameters involved in the fuel cell operation, and it is usually a trade off phenomena. Hence, the factors that affect the MEA microstructure have mainly been discussed by modeling analysis. Little information is available from experimental validation. Secondly, the assembly process varies the contact resistances between the polar plates and GDL, which directly influences the electron transport process^[10-11, 14-16]. The contact resistances, measured by using a 4-point method described in the literatures^[14-16] or an interrupted method^[17], decreased rapidly with the initial increase in the compression force and then remained virtually unchanged after reaching relatively larger compression force. However, these findings must be correlated to the real fuel cell performance under an optimized holding force^[10-11]. A theoretical analysis^[11] suggested that

the holding force affects the interfacial contact resistance and the porosity in two opposite ways. A higher holding force gives a lower interfacial contact resistance, but also gets a lower GDL porosity, and ultimately results in decrease of the system efficiency, which is consistent with the fuel cell results^[10, 12]. These also raise an elastic strength compatibility question of the gasket material and MEA.

The contact resistances have been measured in simulated apparatus^[10-11, 14-16]. Their effects on electrode microstructures related to cell performance have been analyzed^[10, 12-13]. However, little work has been done in the correlation of contact resistances to fuel cell lifetime performance in a single cell test. The aim of this work is to systematically examine the effect of the holding forces on the durability and performance of a PEMFC single cell. The optimal holding force was then determined and the lifetime test was also performed for 2000 h. The contact resistance and cell performance are correlated by the electrochemical kinetic parameters obtained from the polarization curves. The factors related to the change in the microstructure of MEA were roughly analyzed to gain the relationship among the microstructure, the assembly force and the lifetime performance of the cell.

2 Experimental

2.1 Single Cell Assembly

A PEMFC, only for experiments, used 30% Pt-Ru/C as an anode catalyst, 40% Pt/C as a cathode catalyst and Nafion 112 as a proton exchange membrane to form an MEA. The active area of the cell is 6.5 cm². The catalyst loading was 0.5 mg • cm⁻² at anode and cathode side, respectively. The backing material was made using carbon cloth (Zoltek, 0.5 mm) and a layer of carbon black mixed with hydrophobic polytetrafluoroethylene (PTFE). Two pieces of PTFE, which was 0.3 mm in thickness, were used as the gasket. Graphite polar plates and gold-plated copper end plates were used to assemble the cell^[21].

Two sets of micrometer adjustable torque wrenches with different measuring ranges were used to quantitatively control the holding forces when assembling the cell. The single cell was first held in a simple apparatus, a desirable force was then set to lock the

nuts on the end plates which have the MEA and polar plates with gaskets between to assemble the single cell before each test

2.2 Lifetime and Performance Tests

Another same MEA was assembled with the polar plates into the single cell in a controllable holding force mentioned above. The single cell was operated using the 100% humidified hydrogen and air entered the anode and cathode of the cell at a constant flow rate of 47.16 and 186.65 mL · min⁻¹, respectively, at a cell temperature of 60 °C and ambient pressure. The polarization and power density curves were recorded and analyzed to evaluate kinetic parameters. The particle sizes of catalysts from MEA after the lifetime tests were examined by XRD using the same procedures as described previously^[2].

3 Results and Discussion

Figure 1 provides typical polarization and power density curves obtained from the hydrogen/air PEMFC single cell assembled using a series of holding forces ranging from 0.45 to 11.3 MPa. It is evident that the holding forces significantly affected the cell voltages as well as the power densities at larger current densities. The polarization curves shown in Fig 1a indicated a slight decrease in the cell voltage with increase in the holding forces up to 8.2 MPa and this became more apparent in higher current density range. The cell voltages dropped suddenly starting at very low current densities when the holding force was 11.3 MPa.

The corresponding power density curves given in

Fig 1b confirmed with the poor performance with very large holding force (11.3 MPa) at the current density higher than 60 mA · cm⁻². The peak power densities determined from Fig 1b are plotted as a function of assembly force in Fig 2. With the fitting curve the optimum holding force might be determined to be approximately 3.2 MPa.

The increase of the holding force reduced the GDL porosity^[10] and the flow channel volume^[11], but increased the inside cell pressure^[10]. Obviously, with the lower GDL porosity, the fuel became more difficult to flow through the GDL to the CL active area and harder to release the product water out of the cell, which might cause the mass transport limitation. The smaller channel volume caused the possibility of channel clogging by water droplets^[19] and produced non-uniform reactant distribution in the cell.

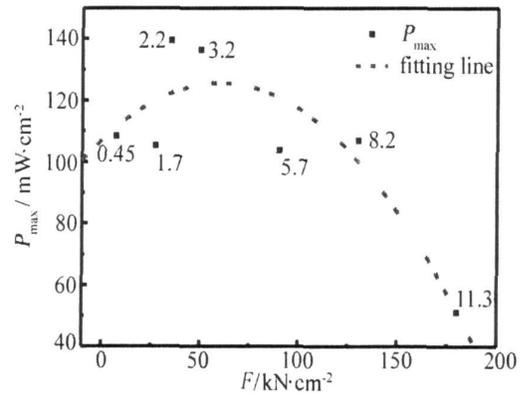


Fig 2 The peak power densities determined from Fig 1b vs the assembly forces

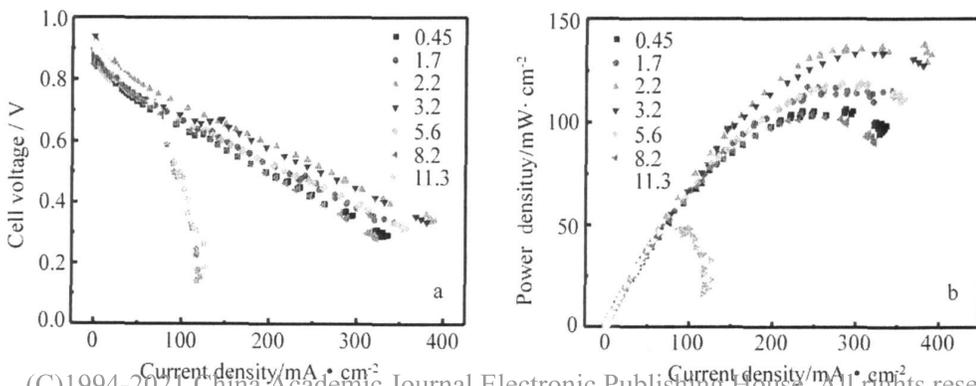


Fig 1 Effect of assembly forces on the performance of PEMFC single cell anode and cathode catalysts were PRu/C and Pt/C respectively, with Nafion 112 membrane, cell temperature at 60 °C, ambient pressure and 100% relative humidity

When the holding force is relatively large the mass transport process limitation reduces and the GDL porosity becomes the main factor to affect the cell performance. As is seen from Fig 1, the performance with 5.7 MPa was better than that with 8.2 MPa until the current density was greater than $220 \text{ mA} \cdot \text{cm}^{-2}$, where the mass transport limitation becomes serious. When the assembly force was relatively small the internal pressure decreased. This was also reflected in the comparison of the polarization curves with 1.7 and 0.45 MPa. It was also reported that the MEA might be damaged when the holding force was too big^[10]. If the holding force was too small (e.g., 0.45 MPa in this study), the gas and water leaked. Hence, too large or too small assembly forces are not good to the cell performance.

It is noticed that in Fig 1 the performance with 2.2 and 3.2 MPa was better than that with other holding forces when the current density was greater than $120 \text{ mA} \cdot \text{cm}^{-2}$. The difference appeared in the range where ohmic polarization controlled. The contact resistance is one of the important factors which are directly affected by the holding force. The linear region in Fig 1a can be analyzed by the following equation:

$$E_i = E_0 - b \log(i) - R \tag{1}$$

where

$$E_0 = E_r + b \log(i) \tag{2}$$

R represents the ohmic resistance which causes a linear variation of the potential with current and is the sum of the cell electrolyte, electrodes, current collectors and lead wires in the system. The R in Eq (1) is not only the pure contact resistance as measured with the 4-point method (only measures the contact resistances between polar plates and GDL), but also includes the PEM resistance in the single cell, hence it represents the overall resistance existed in the cell. b is the Tafel slope and E₀ is the open-circuit voltage.

The electrochemical kinetic parameters (E₀, R and b) at different holding forces were evaluated from the linear regions of Fig 1a and are summarized in Table 1. The E₀ values varied slightly while the R value almost doubled at 11.3 MPa as compared to that at the optimal holding force of 3.2 MPa. The variation rates of R with the holding forces were $0.0096 \Omega \cdot \text{cm}^2 \cdot (\text{MPa})^{-1}$ from 8.2 to 3.2 MPa and $0.016 \Omega \cdot \text{cm}^2 \cdot (\text{MPa})^{-1}$ from 3.2 to 0.45 MPa, respectively.

The Tafel slope b fluctuated in the range from 20 to 30 mV per decade with all the assembly forces except that of 11.3 MPa. The minor change in the b values agreed with the previously reported result that at low current density/high cell voltage the effect of GDL compression was negligible when the carbon cloth was used as the GDL^[12]. The b value at 11.3 MPa was much larger than others. However, the changes of b values did not show an obvious trend with the assembly force.

The polarization and power density curves measured periodically during the PEMFC 2000 h lifetime testing at the optimized assembly force (3.2 MPa) are given in Fig 3. It is evident that the polarization and power density curves tested before 2000 h were almost overlapped. There was no apparent mass-transfer process observed (Fig 3a) and no apparent peak power density was observed as well (Fig 3b). However, the performance after 2000 h operation significantly decayed at the current density higher than $180 \text{ mA} \cdot \text{cm}^{-2}$, and the peak power density was only $110 \text{ mW} \cdot \text{cm}^{-2}$ at $240 \text{ mA} \cdot \text{cm}^{-2}$.

To find out possible causes for this remarkable reduction in the cell performance after 2000 h operation, the electrochemical kinetic parameters were determined using Eq (1) by analyzing the linear region in the polarization curves shown in Fig 3a. The calculated results are summarized in Table 2 as a function of operating time.

Tab 1 The electrochemical parameters under different assembly forces for a PEMFC single cell

Calculated parameter	Assembly force / MPa						
	0.45	1.7	2.2	3.2	5.6	8.2	11.3
E ₀ / V	0.86	0.87	0.86	0.93	0.85	0.87	0.92
R / Ω · cm ²	1.61	1.57	1.30	1.18	1.34	1.67	2.28
b / mV · dec ⁻¹	25.5	18.8	29.3	27.7	29.4	20.4	50.3

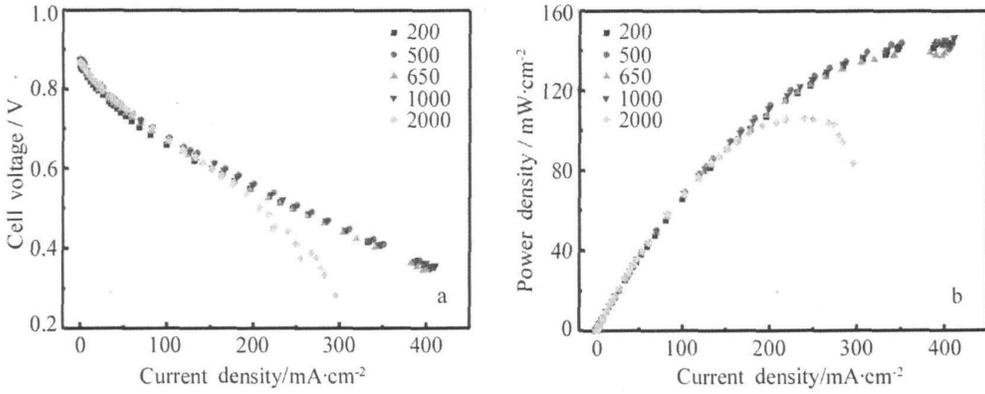


Fig 3 Polarization and power density curves of a PEMFC single cell obtained during different operation time at the optimized assembly force of 3.2 MPa

Tab 2 The electrochemical parameters under various operating time

Calculated parameter	Operating time / h				
	200	500	650	1000	2000
E_0 / V	0.90	0.90	0.90	0.90	0.90
$R / \Omega \cdot cm^2$	1.04	1.03	1.09	1.09	1.90
$b / mV \cdot dec^{-1}$	37.0	37.0	36.7	31.9	51.9

Evidently both the R and b values varied little up to 1000 h and became relatively large after 2000 h test. Therefore the mean particle sizes of the catalysts after 2000 h operation were calculated from XRD data and the results are presented in Fig 4. The solid fitting lines in Fig 4 represent the particle sizes of cathode (top) and anode (bottom) catalysts obtained without optimal assembly force control which clearly indicate the increase in the particle sizes with the operating time. The broken lines in Fig 4 are made to compare the particle sizes of both cathode (top) and anode (bottom) catalysts at the optimized assembly force of 3.2 MPa with those solid lines which show the similar increase trend. However the agglomeration of catalysts in particular the cathode catalyst was less severe when the assembly force was controlled. Hence the significantly decayed performance at the optimized assembly force after 1000 h was thought to be attributed to the changes in the MEA microstructure and physical-chemical properties as discussed previously^[2].

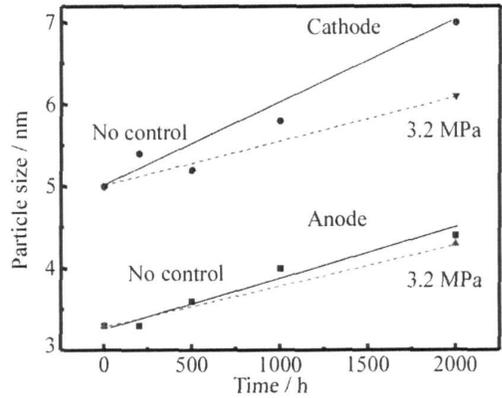


Fig 4 Average particle sizes of catalysts in a single cell of PEMFC calculated from XRD data after different periods of time during continuous 2000 h operation (broken line, at optimized assembly force of 3.2 MPa; solid line, without optimized assembly force)

the material loss (membrane, catalyst, carbon and bipolar plate) and the changes in pore properties in MEA, and other engineering problems such as water management. In addition, it is evident from the above discussion that the effect of assembly force on cathode was much more pronounced than that on anode. Un-

The optimal assembly force might greatly reduce

der conventional cell operation, the cell performance loss is predominantly determined by the degradation of cathode, thus the cell operated under the optimal assembly force might perform better due mainly to its improving in water management and cathode microstructure. Further study is undertaking in order to provide more accurate explanations.

4 Summary and Conclusions

The effect of assembly force on the lifetime performance of a PEMFC single cell was systematically studied. A single cell was constructed using a series of assembly forces ranging from 0.45 to 11.3 MPa and tested using humidified H_2 /air reactants. An optimal assembly force was determined to be 3.2 MPa based on the cell performance. The electrochemical kinetic parameters including E_0 , R and b were evaluated by analyzing the linear regions of polarization curves. It was found that the assembly force directly affected the contact resistance and the cell performance. Under the optimized assembly force of 3.2 MPa the cell degraded less significantly after prolong testing time (e.g., 2000 h), which might be mainly contributed by the minimized change in the cathode microstructures.

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质子交换膜燃料电池的组装 (锁紧力) 对其寿命性能的影响

许 帆¹, 程 璇^{2,3*}, 张 颖², 范钦柏⁴

(1. 厦门大学化学化工学院化学系, 福建 厦门 361005; 2. 厦门大学 材料学院材料科学与工程系, 福建 厦门 361005; 3. 固体表面物理化学国家重点实验室, 福建 厦门 361005; 4. 美国气体技术研究院, 美国 伊利诺伊斯, 60018)

摘要: 系统考察质子交换膜燃料电池组装 (锁紧力, 0.45~11.3 MPa) 对其性能和寿命的影响, 并确定了最佳锁紧力. 以最佳锁紧力 (3.2 MPa) 的单电池作 2000 h 寿命测试, 根据该单电池不同运行时间下的极化和功率曲线分析, 得到与其活化区对应的电化学参数. XRD 检测表明, 电池组装施加的锁紧力不但影响电池的接触电阻, 而且还影响由 MEA 微观结构决定的电池反应动力学性能. 在最佳锁紧力作用下运行 2000 h 后的单电池在大电流密度区出现了明显的性能衰减, 这主要是由于催化剂的团聚效应引起的. 但在非最佳锁紧力作用下, 阴极催化剂的团聚作用远大于阳极催化剂.

关键词: 质子交换膜燃料电池; 接触电阻; 电池锁紧力; 膜电极; 寿命性能