Improvement of water management by a microporous sublayer for PEM fuel cells

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Abstract

A microporous PTFE/carbon sublayer between the carbon paper and the catalyst layer played a crucial role in PEM fuel cells. Such a layer reduced the difference among different carbon paper types made by different manufacturers or by the same manufacturer at different times. When such a sublayer was present, the carbon paper seemed to function merely as a support that provided the mechanical strength for the sublayer. A sublayer was extremely useful if the carbon paper was prone to flooding. Sublayers of different thickness containing 24, 35 and 45% PTFE were tested. A four-cell stack could operate stably at a current density of 145 mA/cm^2 using unhumidified air and hydrogen when sublayered carbon paper was employed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Microporous; Sublayer; Carbon paper; Catalyst layer; PEM fuel cells

1. Introduction

Appropriate water management is critical in order to achieve high performance of proton-exchange membrane (PEM) fuel cells [1,2]. On the one hand, water is needed to hydrate the ionically-conducting membrane and the ionic conductor in the catalyst layer for proton conductance. The higher the water content, the better the ionic conductivity [3–5]. Water can be introduced by external humidification and as a product of the oxygen reduction reaction at the cathode side. On the other hand, water can flood pores in the catalyst layers as well as in the gas diffusion layers, resulting in higher mass transport resistance. The less the water content, the lower the resistance to reactant flow. Clearly, water plays a conflicting role; therefore, delicate balance is required.

Carbon paper is one of the most prevalent gas diffusion media used in PEM fuel cells. The paper possesses good mechanical strength, high electrical conductivity, and suitable porosity. In order to increase its ability to expel water, it is normally teflonated by PTFE. Increasing the PTFE content increases the hydrophobicity, but lowers the electrical conductivity. An optimal PTFE content can be determined experimentally.

Carbon paper made by different manufacturers possesses slightly different properties. Experiments need to be performed to find the optimal PTFE content for each type of paper. Occasionally, different batches of paper purchased from the same supplier show substantially different behavior. This could cause problems when electrodes are made following a standard procedure, resulting in not only wasted materials, but also time and effort.

A microporous PTFE/carbon layer between the carbon paper and the catalyst layer has been found to be useful to increase PEM fuel cell performance [6–9]. After a large number of experiments, we found that such a microporous layer (referred to hereafter as sublayer) could diminish the differences among different carbon paper types made by the same or different manufacturers. Such a layer was extremely helpful where the carbon paper was prone to flooding. This article reports the results using both high and low Pt loading in the electrodes.

2. Experimental

Carbon paper was teflonated by soaking in a 10% PTFE suspension for a few minutes. The paper was removed from the solution and "drip-dried" at room temperature. During this drying process, the paper was constantly rotated to ensure even PTFE distribution inside the paper. The paper was then dried at 110, 280 and sintered at 350 °C for 30 min, respectively. The paper contained ca. 20% PTFE.

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A mixture of PTFE and carbon black was applied to the above teflonated carbon paper. After the applied layer was dried at room temperature, it was dried at 110, 280 and sintered at 350 °C for 30 min, respectively. Three mixtures containing 24, 35 and 45% PTFE were prepared. The sublayer thickness was reflected by the carbon loading in this layer.

Electrodes were prepared with various Pt loadings. High Pt loading electrodes (>1.0 mg/cm^2) were made using Pt black. Electrodes with lower Pt loadings were made using 20% Pt/Vulcan XC-72. The catalyst layer contained catalyst and Nafion without PTFE. Membrane-electrode assemblies

(MEAs) were made by hot-pressing electrodes onto Nafion membranes at 130 °C for 3 min.

Single cell tests were carried out using a home-made 10 cm^2 active area test fixture. The test fixture was composed of a pair of metal plates with serpentine flow-fields. The plates were coated with a metal nitride for corrosion protection. Rod-like heaters were inserted into the plates to control the cell temperature. Air and pure hydrogen were used as the reactants. If the gas needed to be humidified, it was passed through a stainless steel water bottle; otherwise, the gas bypassed the humidifier and got into the cell at room
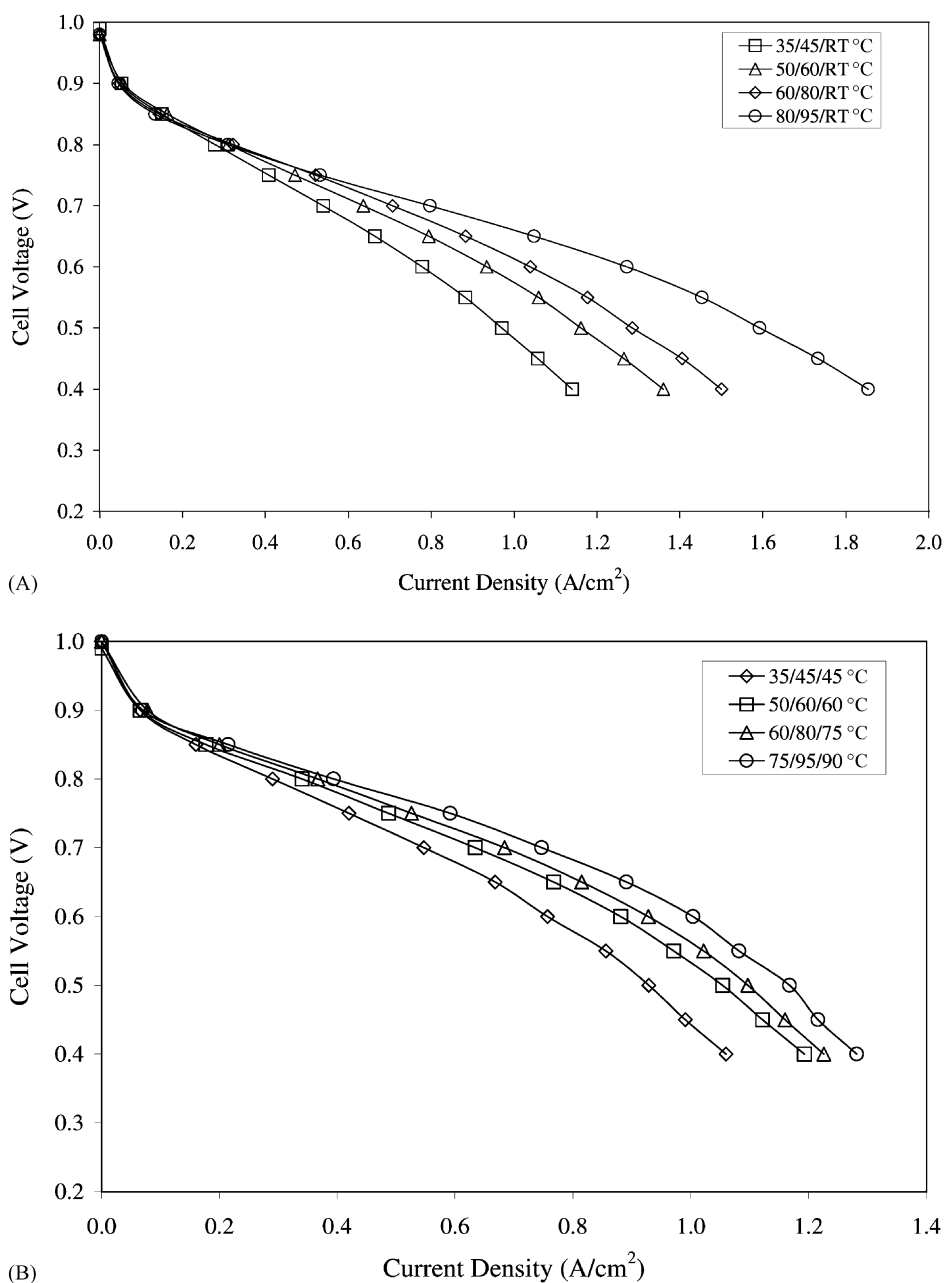

Fig. 1. Performance of teflonated batch 1 carbon paper at different temperatures: (A) hydrogen was humidified but not air; (B) both hydrogen and air were humidified. Pt = 1.7 mg/cm^2, Nafion 112 membrane.

temperature. A cell temperature of 35 °C, hydrogen inlet temperature of 45 °C, and air inlet temperature at room temperature are denoted herein as 35/45/RT °C. The stoichiometries of air and hydrogen were about 10 at the current density of 2.0 A/cm² unless otherwise specified. The load was varied using a rheostat when voltage (V)–current density (I) curves were collected. The low Pt loading electrodes made using 20% Pt/C were activated using H Power proprietary techniques before data collection.

Some electrodes with an active area of 27.6 cm² were tested in a four-cell stack. The stack was operated with dead-ended hydrogen (i.e. the hydrogen exit was closed). Periodically, purging was performed to release liquid water that accumulated during the operation by briefly opening the hydrogen exit. Air was open-ended and was controlled at a stoichiometry of 3× using a flow meter. The inlet pressure of both gases was set at ca. 5 psig. Unless specified, neither hydrogen nor air was humidified. The stack temperature was
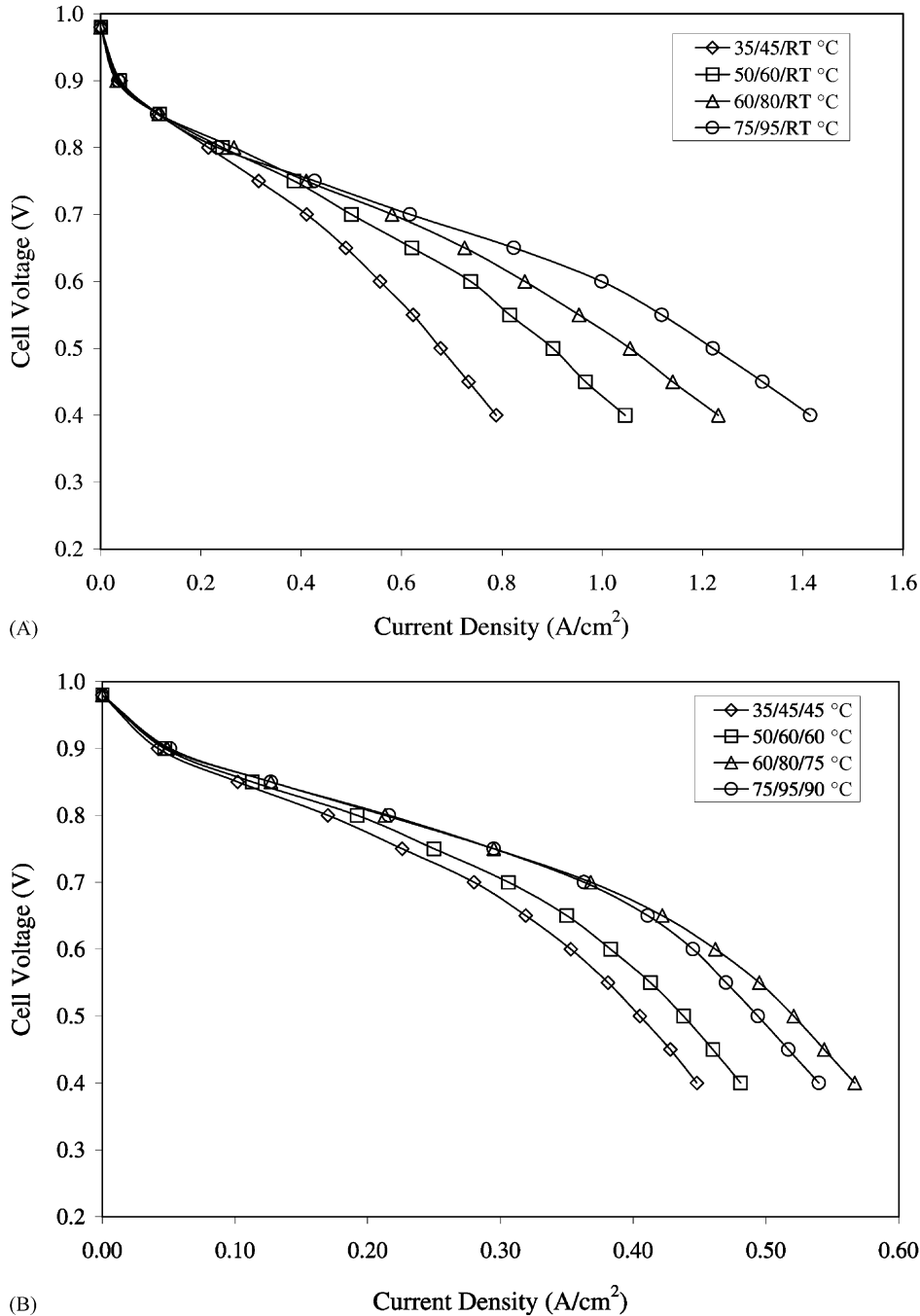

Fig. 2. Performance of teflonated batch 2 carbon paper at different temperatures: (A) hydrogen was humidified, but not air; (B) both hydrogen and air were humidified. Pt = 1.7 mg/cm², Nafion 112 membrane.

controlled using two small fans. The *V–I* curves were collected using an HP 6050A load bank.

3. Results and discussion

Fig. 1 shows the single cell performance of batch 1 carbon paper at different temperatures. The carbon paper was teflonated but without a PTFE/carbon sublayer. In Fig. 1A,

only hydrogen was humidified, but in Fig. 1B, both hydrogen and air were humidified. In both cases, the performance increased with cell temperature since temperature has a positive effect on the kinetics of the oxygen reduction reaction (and the hydrogen oxidation reaction). When both hydrogen and air were humidified, the cell had a lower performance in the higher current density region even at the high reactant stoichiometries employed (10× at the current density of 2.0 A/cm^2). This could be due to two reasons.
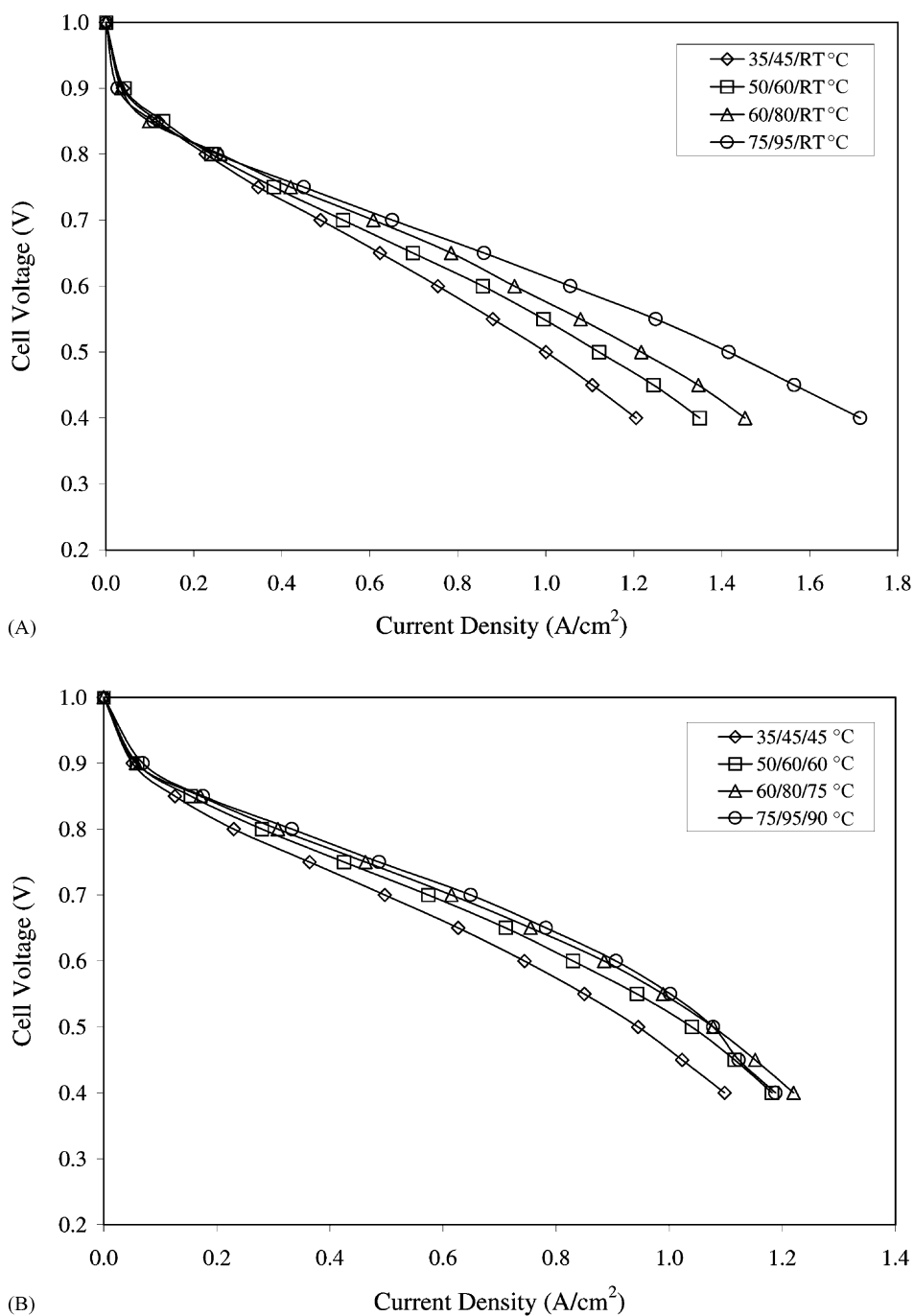

Fig. 3. Performance of teflonated batch 2 carbon paper with a sublayer at different temperatures: (A) hydrogen was humidified, but not air; (B) both hydrogen and air were humidified. Pt = 1.7 mg/cm^2, Nafion 112 membrane. Sublayer contained 35% PTFE and 65% Vulcan XC-72 with a carbon loading of 2.4 mg/cm^2.
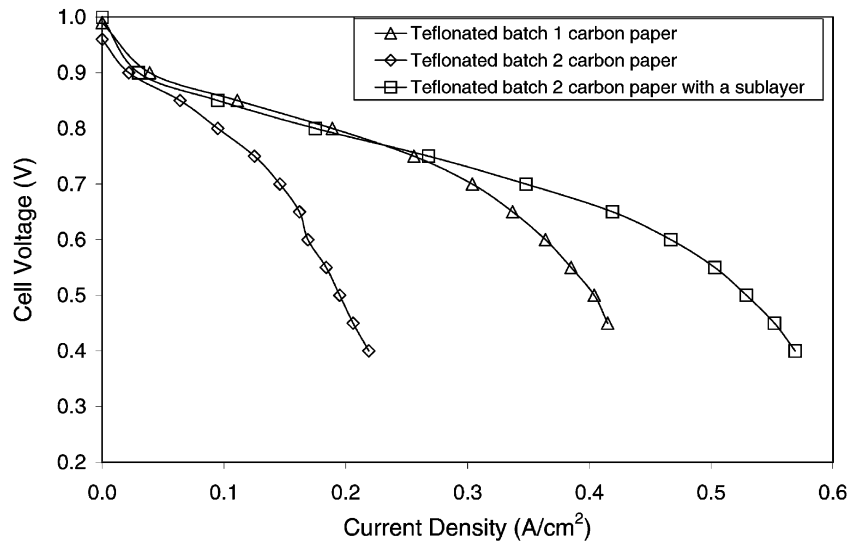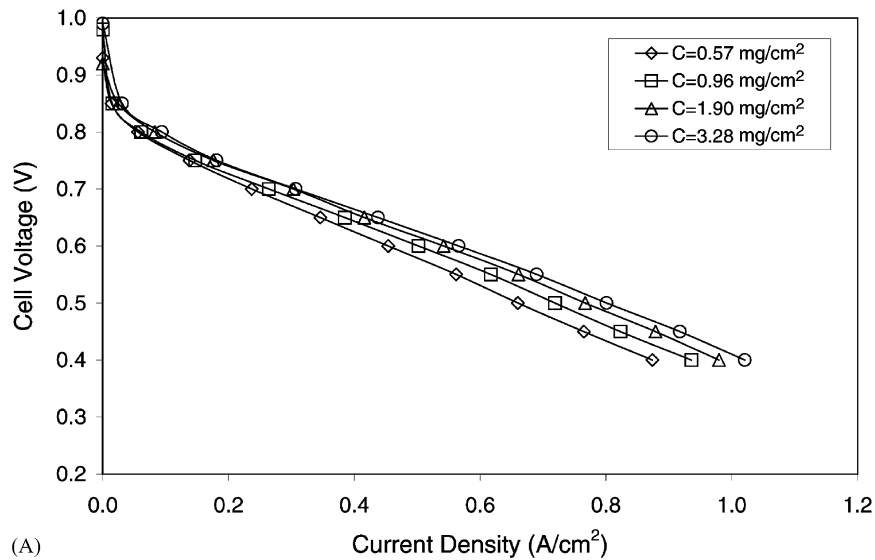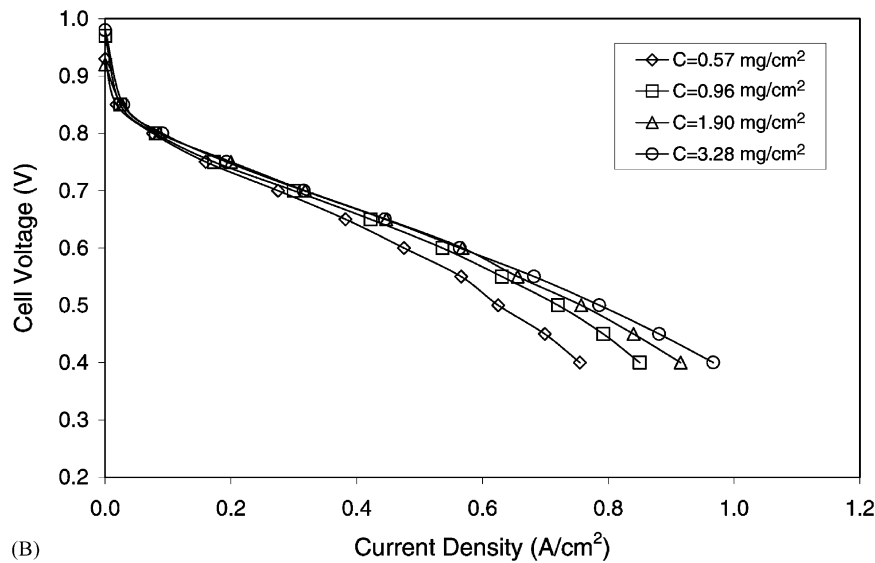
Fig. 4. Performance comparison at a lower reactant stoichiometry (3×) at 35/RT/RT (°C). Both hydrogen and air were humidified at room temperature. Pt = 1.7 mg/cm^2, Nafion 112 membrane.

(A)

(B)

Fig. 5. Performance of teflonated batch 2 carbon paper with a sublayer composed of 24% PTFE and 76% Vulcan XC-72: (A) hydrogen was humidified but not air; (B) both hydrogen and air were humidified. Pt = 0.10 mg/cm^2, Nafion 112 membrane, $T_{cell} = 35$ °C, $T_{humidification} = 45$ °C.

Firstly, when air was humidified, its oxygen concentration (or partial pressure) decreased because of the presence of water vapor from the humidifier. Secondly, the cell produced more water at higher current density, and flooding became more pronounced in the catalyst layer and/or the carbon paper.

When a second batch of carbon paper was used as the gas diffusion medium, we were surprised by its poor performance. The paper was teflonated similarly and also contained ca. 20% PTFE. When only hydrogen was humidified, the performance was not especially poor, but it was much lower than that using the first batch of paper (Fig. 2A). When both hydrogen and air were humidified, the performance

became much lower (Fig. 2B). Obviously, the cell was seriously flooded. A range of PTFE content from 0 to 41.3% in the carbon paper was tested, but the paper's performance remained poor even at the best PTFE content. The two batches of carbon paper were supposed to be the same based on the manufacturer's specifications, but they behaved far differently.

Since the catalyst layers were the same, the performance difference must have originated from the carbon paper. Although it was important to understand why the "same" paper behaved differently, we did not focus our efforts on this. Instead, we focused on improving the performance by applying a thin carbon/PTFE sublayer between the
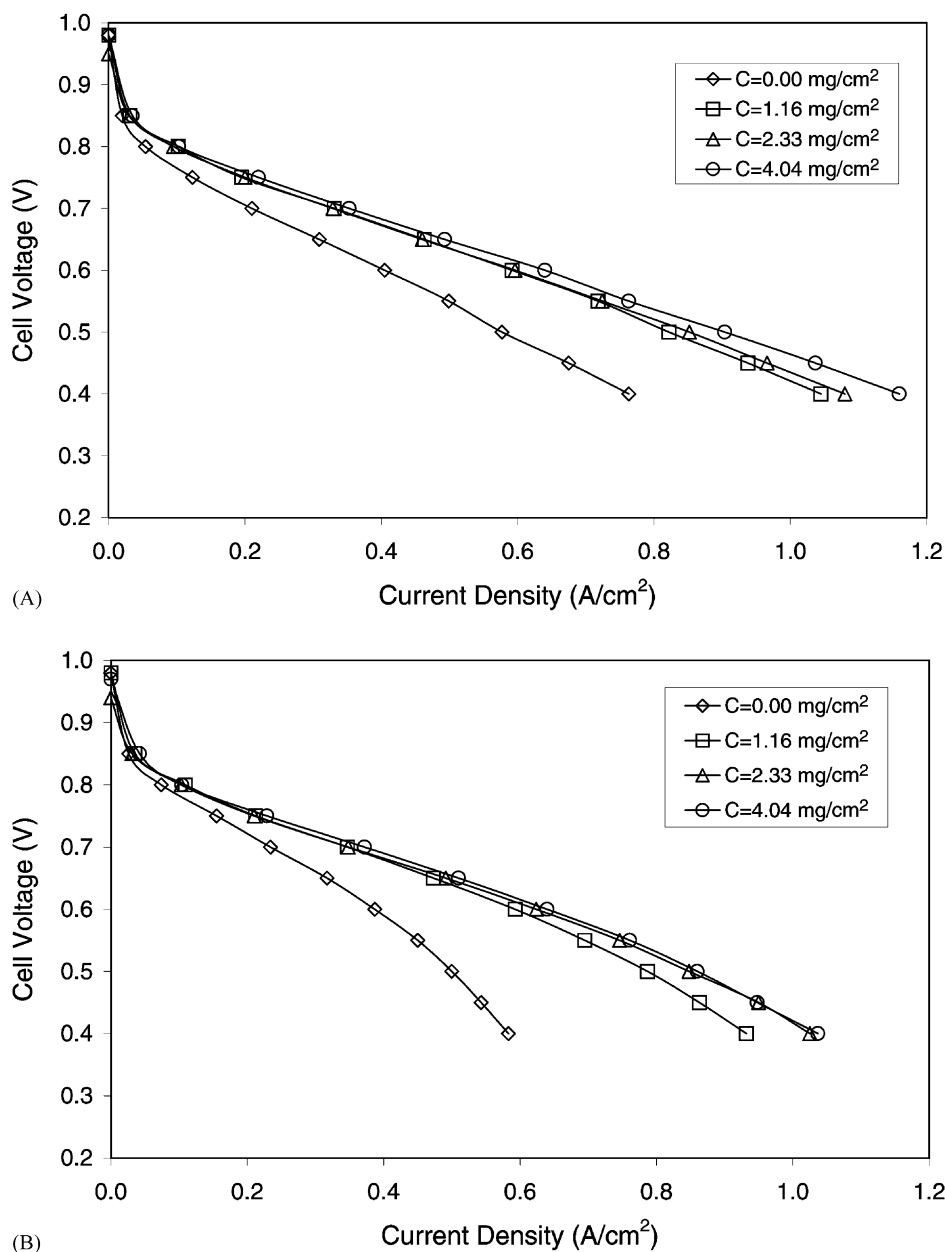

Fig. 6. Performance of teflonated batch 2 carbon paper with a sublayer composed of 35% PTFE and 65% Vulcan XC-72: (A) hydrogen was humidified but not air; (B) both hydrogen and air were humidified. Pt = 0.14 mg/cm^2, Nafion 112 membrane, T_{cell} = 35 °C, $T_{humidification}$ = 45 °C.

teflonated carbon paper and the catalyst layer. Fig. 3 shows the cell performance after a sublayer containing 35% PTFE and 65% Vulcan XC-72 was applied onto the second batch of carbon paper. The performance improved dramatically. At a high hydrogen and air stoichiometry of 10 at the current density of 2.0 A/cm^2, the performance (with a sublayer) was similar to that of the first batch of carbon paper (without a sublayer). When the stoichiometry was reduced to 3, its performance was even better than that of the first batch of paper (Fig. 4). Clearly, the sublayer not only made the carbon paper morphology itself less critical, but also improved its capacity to manage water. Carbon paper made by other manufacturers was also sublayered and tested.

The performance was dominated by the sublayer. The paper essentially became a support for the sublayer, and it was mainly the sublayer that controlled water management and mass transport. In other words, as long as the sublayer was made the same, the gas diffusion medium (carbon paper plus sublayer) behaved similarly. Hence, the effect caused by variation in the carbon paper was more or less eliminated.

We speculate that the major factor that contributes to the improved water management in the presence of a sublayer is the microporosity of the sublayer. Since this layer is composed of carbon black and PTFE, the macropore size is primarily determined by the size of carbon particle aggregates. For Vulcan XC-72, the primary particle size is about
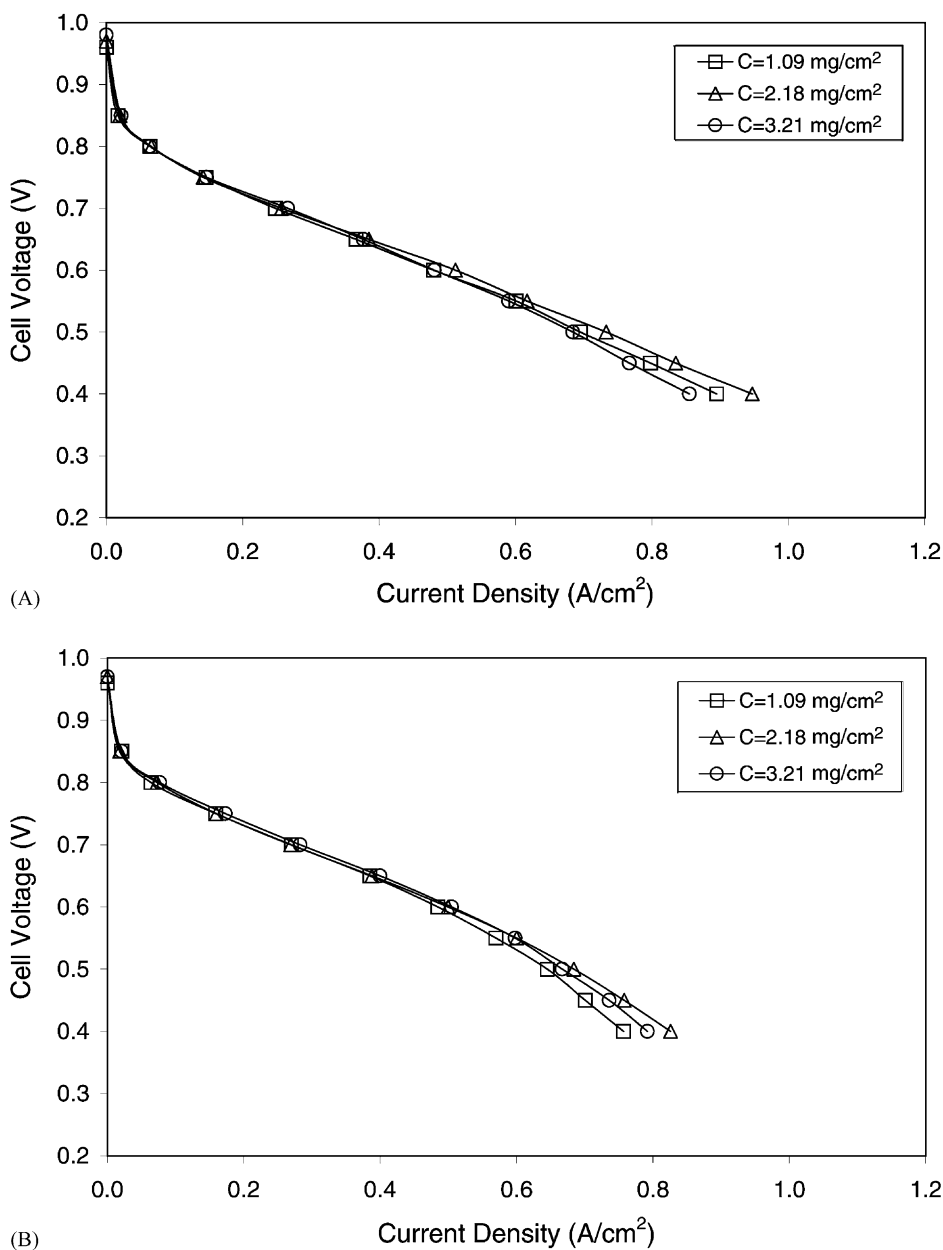

Fig. 7. Performance of teflonated batch 2 carbon paper with a sublayer composed of 45% PTFE and 55% Vulcan XC-72: (A) hydrogen was humidified, but not air; (B) both hydrogen and air were humidified. Pt = 0.10 mg/cm^2, Nafion 112 membrane, T_{cell} = 35 °C, $T_{humidification}$ = 45 °C.
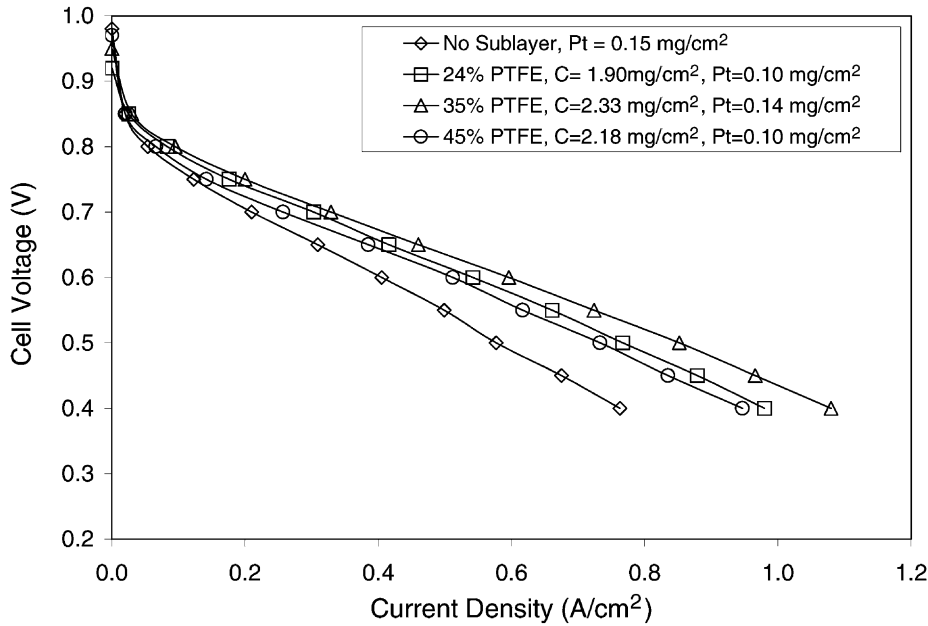
Fig. 8. Effect of PTFE content in the sublayer on performance. Hydrogen was humidified but not air. Nafion 112 membrane, $T_{cell} = 35\,^\circ C$, $T_{humidification} = 45\,^\circ C$.

30 nm [10]. These primary particles form aggregates of micron size. So, the largest pore dimension would be on the magnitude of microns in the sublayer, and the pore size distribution should be quite uniform. Water may not be able to form stable droplets inside such small and hydrophobic pores; therefore, the sublayer is less likely to be flooded. The catalyst layer that is in direct contact with the sublayer will in turn be less likely to be flooded. The sublayer also prevents the catalyst from penetrating deeply into the carbon paper when the catalyst is applied, so the loss of active

catalyst due to such penetration becomes less. In addition, the contact between the sublayer and the catalyst layer may be more intimate. These latter two factors may also play a role in the improved fuel cell performance.

The effects of sublayer thickness and PTFE content in the sublayer were studied using low Pt loading electrodes. Fig. 5 shows single cell performance using sublayers containing 24% PTFE (and 76% carbon). Four different sublayer thickness was studied. When only hydrogen was humidified, the performance increased gradually with carbon loading
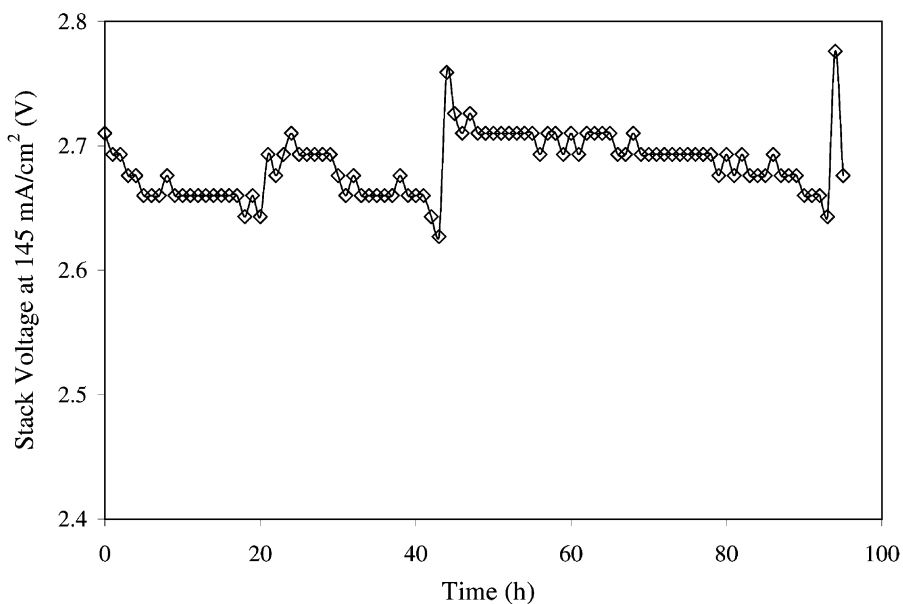

Fig. 9. Continuous performance of a four-cell stack in 5 days. Sublayer contained 35% PTFE and 65% Vulcan XC-72 with a carbon loading of 2.4 mg/cm^2. Pt = 1.7 mg/cm^2, Nafion 1135 membrane, $T_{cell} < 40\,^\circ C$. Both hydrogen and air were not humidified.

from 0.57 to 3.28 mg/cm^2. When both hydrogen and air were humidified, an apparent increase was observed when carbon loading was increased from 0.57 to 0.96 mg/cm^2. A further increase in carbon loading resulted in only very little change. In Fig. 6, the sublayer contained 35% PTFE (and 65% carbon). All the gas diffusion media with a sublayer performed much better than the one without a sublayer. Although the performance increased with carbon loading, the difference was small. Fig. 7 shows sublayers containing 45% PTFE (and 55% carbon). Little difference was observed when carbon loadings ranging from 1.09 to 3.21 mg/cm^2 were used. Fig. 8 shows the effect of PTFE content (percentage) in the sublayer on performance, while the carbon loading in the sublayer and the Pt loading in the catalyst layer were kept similar. All the sublayered electrodes gave similar performance, although it appeared that the one with 35% PTFE performed best (its Pt loading was slightly higher than other electrodes), and the one with 45% PTFE performed worst.

Electrodes with 35% PTFE in the sublayer were tested in a four-cell stack having a cell active area of 27.6 cm^2 per cell (Fig. 9). The hydrogen was dead-ended with an inlet pressure of ca. 5 psig. Air flows through double-path flow-fields [11]. In such flow-fields, one flow-field's inlet is located near the other's outlet; and, within any section of the electrode's active area, there are always adjacent channels with reactant flowing in opposite directions. Such a design enables the dry entering gas to become hydrated by picking up some of the moisture from the exiting wet gas; and, within any section of the active area, the drier gas in one channel can share the moisture in the wetter gas flowing in the other channel. Neither hydrogen nor air was humidified during the experiment. The stack could run stably at a current density of 145 mA/cm^2 without showing signs of drying out. The only water that hydrated the membrane and the catalyst layers was produced from the oxygen reduction reaction at the cathode.

4. Conclusions

Different batches of carbon paper made by the same manufacturer exhibited large variations in their ability to manage water. After a PTFE/carbon sublayer was added between the carbon paper and the catalyst layer, the resulting gas diffusion medium showed a greatly enhanced ability to manage water. Sublayers containing 24, 35 and 45% PTFE with different thickness were evaluated. The performances were similar, although it seemed that the one with 35% PTFE performed best and the one with 45% PTFE performed worst. A carbon loading of 2.0 mg/cm^2 in the sublayer was sufficiently high to achieve the maximum performance. A stable performance was achieved at a current density of 145 mA/cm^2 when the electrodes were tested in a four-cell stack using unhumidified hydrogen and air.

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