

# Recent progress in performance improvement of the proton exchange membrane fuel cell (PEMFC)

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## Abstract

Research activities to improve the performance of the low platinum loading hydrogen–air proton exchange membrane fuel cell (PEMFC) operating at atmospheric pressure are described. Pore-forming additives, new types of proton exchange membranes, and higher activity platinum-on-carbon electrocatalysts have been used in low platinum loading gas diffusion electrodes (GDEs) and Membrane–electrode assemblies (MEAs) developed at this center. A method for the fabrication of an integrated GDE and light weight gas flow-field is described. As a result, a three-fold improvement in PEMFC performance at the same platinum loading has been achieved. © 2002 Published by Elsevier Science B.V.

*Keywords:* Proton exchange membrane fuel cell; Gas diffusion electrode; Membrane–electrode assembly; Pore-forming agent; Light weight material

## 1. Introduction

Commercialization of proton exchange membrane fuel cell (PEMFC) technology depends on achieving a high specific power and power density for a given cost, so that its characteristics compete cost-effectively with traditionally used energy conversion devices. Improved PEMFC performance depends on many factors, including the electrocatalytic activity of the electrocatalysts used in the gas diffusion electrodes (GDEs), improvement of the electrochemical characteristics of the latter, optimization of their structure to reduce mass transport hindrances, the amount and nature of the polymer electrolyte in the porous electrode three-phase-boundary, and the type and thickness of bulk polymer electrolyte membrane. To achieve acceptable specific performance of the cost-effective PEMFC stack, low-cost light weight materials must be used as bipolar plates and gas separators.

Extensive systematic R&D activities on the above problems have been conducted at this Center since 1988. As a result, a rapid, simple and reproducible in-house method of fabrication of low platinum loading GDEs and Membrane–electrode assemblies (MEA) has been developed [1]. Using the GDE structure as a template, new electrocatalysts,

polymer electrolytes, pore-forming additives, and other components have been introduced into the MEA at constant low platinum loading. Further results obtained have been recently presented [2–5]. This publication demonstrates how significant PEMFC performance improvements at constant low platinum loading using the above approaches may be achieved.

## 2. Experimental

### 2.1. Preparation of GDEs and MEAs

The in-house method of GDE fabrication is a modification of that of the Los Alamos National Laboratory (LANL) [6–8], and uses an electrocatalyst-Nafion<sup>TM</sup> ink to produce the active layer (AL), which is painted or printed on the GDL without chemical transformation of the Nafion<sup>TM</sup>. Platinum nanocrystallites supported on Vulcan XC-72 conducting furnace black (Cabot Corp., Boston, MA), generally supplied by E-TEK Inc. (Natick, MA) at different weight percentage loadings were used as AL electrocatalysts. Nafion<sup>TM</sup> (Du Pont de Nemours and Company, Wilmington, DE) of equivalent weight (EW) 960 Da as a 5 wt.% solution (CG Solutions) was used as the perfluorosulfonate ionomer. Shawinigan black (Chevron Corp., Houston, TX) with 35 wt.% PTFE was spread as a thin (3 mg/cm<sup>2</sup>) gas diffusion

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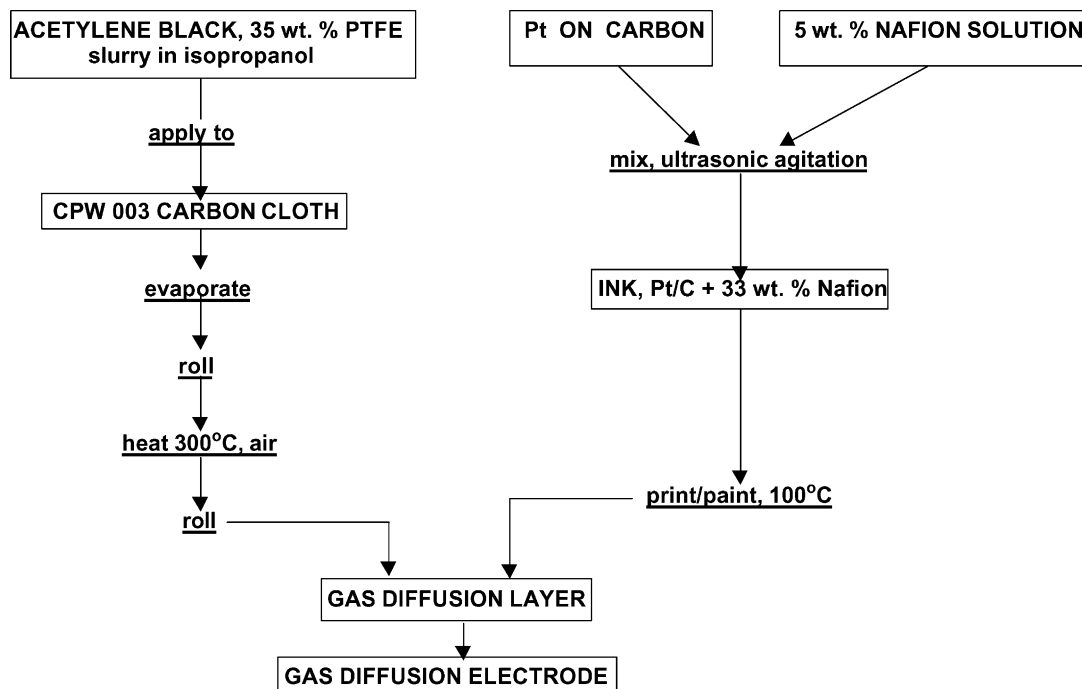


Fig. 1. Preparation of gas diffusion electrodes.

layer (GDL) on Textron (Wilmington, MA) CPW-003 light weight carbon cloth. A flow-chart for GDE preparation is shown in Fig. 1. After applying the AL, but before pressing the MEA, the surface was impregnated with ca.  $0.3 \text{ mg/cm}^2$  5 wt.% Nafion<sup>TM</sup> solution by brushing. MEAs were prepared by hot-pressing the anode and cathode GDE structures symmetrically on both sides of the proton exchange membrane (PEM) between two  $125 \mu\text{m}$  PTFE sheets (McMaster-Carr, Atlanta, GA) at  $70 \text{ kg/cm}^2$  for 5 min at  $155^\circ\text{C}$ . All of the ALs described here contained  $0.2 \text{ mg/cm}^2$  (20 wt.% Pt on carbon) and  $0.05 \text{ mg/cm}^2$  (10 wt.%) of platinum at the cathode and anode, respectively. Earlier experiments showed that the optimal amount of perfluorosulfonate ionomer in the active layer was 33 wt.%, so this was used in all cases. Unless otherwise stated, the electrolyte used was Nafion<sup>TM</sup> 112 membrane. The total thickness of the standard MEA was approximately 0.8 mm. The active area of all MEAs was  $50 \text{ cm}^2$ .

### 2.2. Electrochemical measurements

Evaluation of MEA performance used a conventional test fixture with gas flow fields consisting of Poco (Dallas, TX) graphite plates with three series-parallel ribs and channels with channel width and depth of 0.8 mm. After MEA conditioning, cell potential current density dependences were obtained at a cell temperature of  $50^\circ\text{C}$  with pure hydrogen and externally humidified oxygen or air at atmospheric pressure. The gas stoichiometry was kept constant at 1.1 for 100% hydrogen and 2.2 for oxygen in air at all cell currents. The 1.1 stoichiometry for

hydrogen simply affects the inlet and exit flow rates, since the concentration of hydrogen remains the same everywhere.

## 3. Results and discussion

### 3.1. Type of gas diffusion layer

The GDL (also called the backing layer, support layer or substrate) plays a significant role in overall GDE performance [9–12]. Generally, it contains carbon black of some type mixed with a strongly hydrophobic polymer, usually PTFE. Early work showed that the best results were obtained with acetylene black in a PTFE water dispersion, with a 0.65:0.35 weight ratio for these components [13,14]. Fig. 2 shows the performance of standard MEAs with different cathode GDLs. They include commercial E-TEK ELAT<sup>TM</sup> [15], the Improved ELAT<sup>TM</sup> GDL [16], supplied by courtesy of E-TEK, and a CESHHR-developed layer containing  $3 \text{ mg/cm}^2$  of the acetylene black/PTFE composition spread and rolled on the above carbon cloth (Fig. 1). The performance of the MEAs with the CESHHR and improved ELAT<sup>TM</sup> GDLs are similar, and both are significantly better than that of the MEA with the standard ELAT<sup>TM</sup> GDL. This results from the better gas diffusion properties of the CESHHR and improved ELAT<sup>TM</sup> GDLs because of their higher total porosity compared to that of the standard ELAT<sup>TM</sup> (Table 1). This is shown by the oxygen gain-current density plots for pure oxygen and air [17,18] in Fig. 3 taken from the results in Fig. 2.

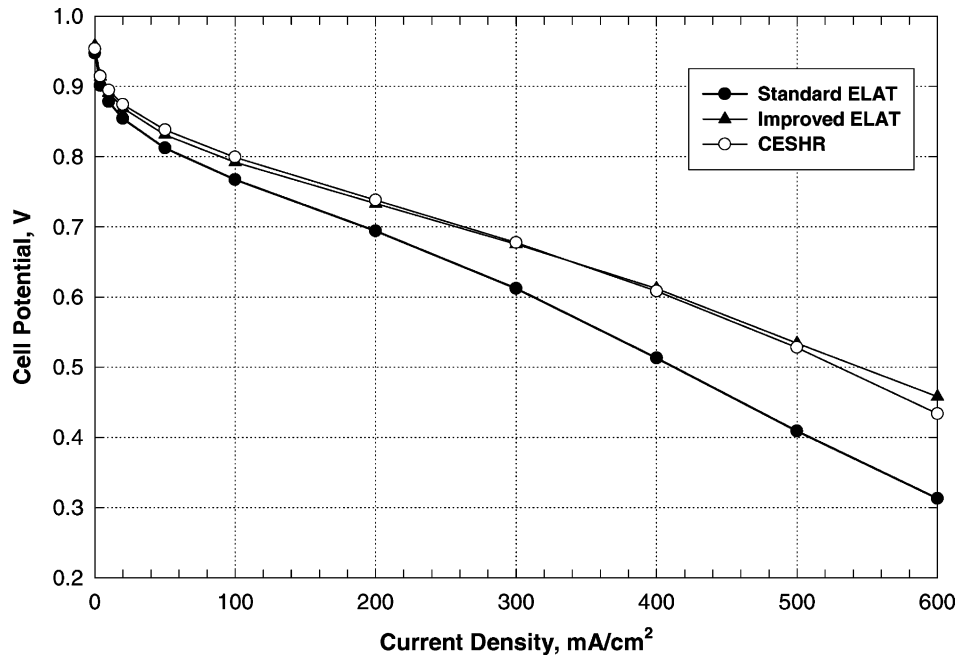


Fig. 2. Potential vs. current density for cells with different gas diffusion electrode backing layers.

Table 1  
Characteristics of gas diffusion layers used

Gas diffusion layer	Thickness (mm)	Porosity (%)
ELAT standard	0.38	45
CESH	0.30	60
ELAT improved	0.33	57

### 3.2. Pore-forming additives in the active layer

The minimization of all transport resistance in the electrochemical reaction by making appropriate changes to the overall GDL–AL is an effective method for PEMFC performance improvement. One way to minimize the gas diffusion transport resistance, especially at the cathode, is to add a range of suitable proprietary pore-forming additives to the electrocatalyst-Nafion<sup>TM</sup> ink, followed by ultrasonic

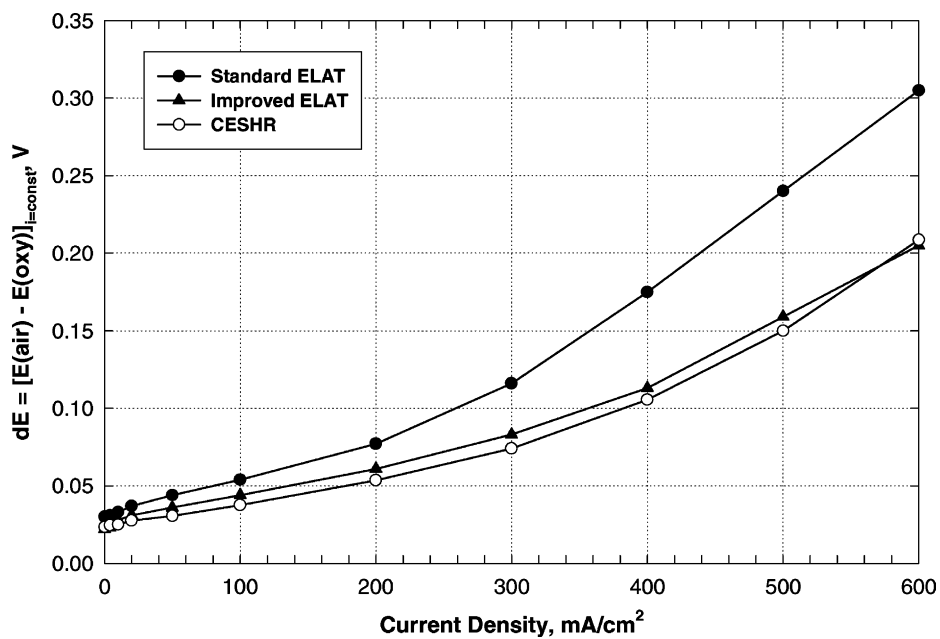


Fig. 3. Oxygen vs. air potential gain as a function of current density for cells with different gas diffusion electrode backing layers.

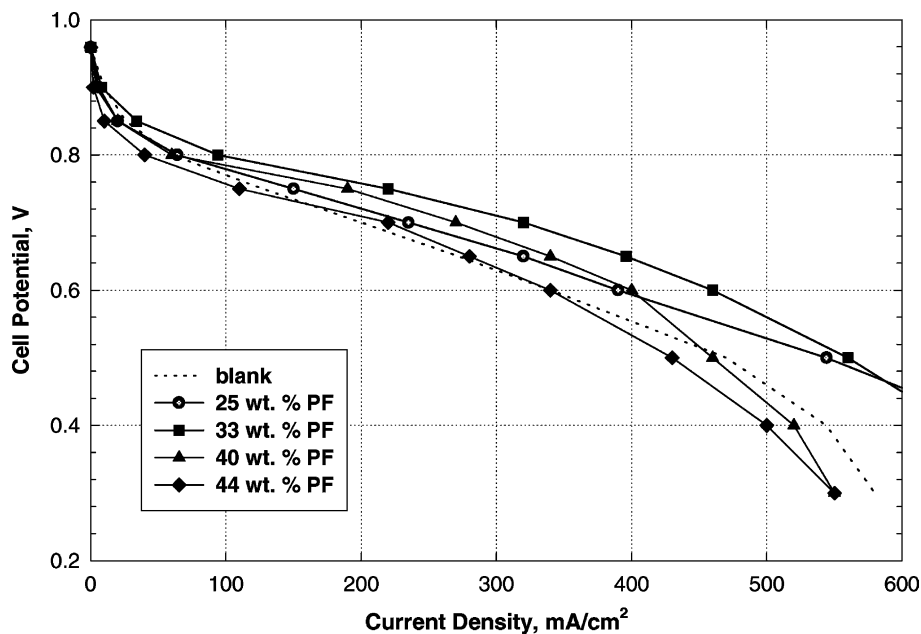


Fig. 4. Potential vs. current density for cells with different amounts of pore-forming additive in the active cathode layer.

agitation [19]. After painting the active layers onto the GDL, the electrodes were treated to extract the pore-former (PF) and MEAs were pressed by the procedure described above. In Fig. 4 are presented cell potential–current density plots for MEAs with standard-loading cathodes containing from 25 to 44 wt.% PF in the cathode AL. The results show that the optimal amount of PF results in a performance improvement on air from 210 mA/cm<sup>2</sup> at 0.7 V to 340 mA/cm<sup>2</sup> at the same potential. A detailed analysis of the data obtained shows that the PF largely acts by increasing the

hydrophilic (i.e. Nafion<sup>TM</sup>-wetted) porosity of the AL. This is illustrated in Fig. 5, which shows the MEA electrical resistance as a function of PF content in air cathodes. The resistance was calculated from the slopes of long linear part of the polarization curves for MEAs operating on pure oxygen. Since the platinum loading, the ionomer in the AL, and the electrolyte were identical for all MEAs, their effective resistance depended only on the volume of the hydrophilic AL porosity, which is determined by the amount of PF.

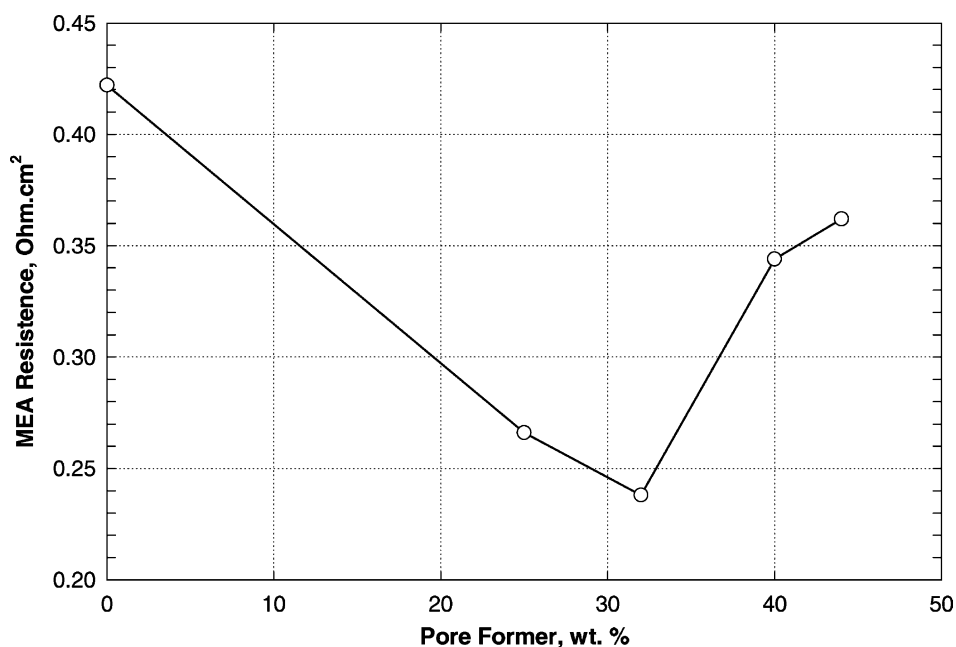


Fig. 5. Dependence of gross cell resistance on the amount of pore-forming additive in the cathode active layer.

Table 2  
Characteristics of Nafion™ membranes

Membrane	Thickness <sup>a</sup> (mm)	Equivalent weight
Nafion 112	0.050	1100
Nafion 111	0.025	1100
Nafion 1135	0.087	1100
Nafion 1035	0.087	960

<sup>a</sup> As received

### 3.3. Recent versions of Nafion membranes

New versions of Nafion™ membranes (see Table 2) have recently been made available by Ion Power Inc. (Bear, DE). MEAs incorporating these membranes with standard GDL–ALs were pressed and their performances were evaluated and compared to those with Nafion 112 membranes. The results are shown in Fig. 6. As expected, for membranes of the same EW, MEAs with thinner membranes show better performance, and at the same thickness MEA with low EW membranes also have better performance. In both the cases, this results from lower overall proton resistance. Surprisingly, the best performance was obtained with the thickest, but low EW, membrane, Nafion 1035. This results shows that equivalent weight of membrane, i.e. the concentration of charge carriers, is the predominant factor determining MEA performance when other parameters remain constant.

### 3.4. High activity electrocatalysts

Platinum supported on high surface area carbon is most commonly used electrocatalyst for both hydrogen oxidation and oxygen reduction in the PEMFC. Usually, these electrocatalysts are prepared by solution precipitation, followed

by reduction of a platinum salt in the liquid or gas phase. Recently, Superior MicroPowders L.L.C. (SMP, Albuquerque, NM) has developed a new manufacturing approach for production of platinum/carbon catalysts for PEMFC application. Fig. 7 show the performance of MEAs containing 20 wt.% Pt on carbon cathode catalysts made at SMP. The results are compared with performance of MEAs containing commercial platinum/carbon catalysts from E-TEK with the same weight percentage of platinum and the same platinum air cathode loadings. For all samples evaluated, a significant performance improvement between 50 and 80% of MEAs with SMP catalysts was observed. This improvement may be explained by the platinum particle size and its distribution on the carbon surface. Electron microscopy data show that SMP catalyst possesses a significant amount of smaller particle size platinum particles (1–2 nm) compared with E-TEK electrocatalysts. This probably results in increased platinum utilization, giving a larger reaction interface in the active layer of the oxygen electrode.

### 3.5. Light weight materials

Development of low-cost, light weight construction materials for gas flow fields and bipolar plates is a major hurdle for the broad commercialization of PEMFCs. Its solution will also increase further increase specific power and power density and reduce cost. High porosity carbons, carbon cloths, stainless steel felts, and nickel foams were examined as alternatives to machined graphite gas flow fields. The sources and porosity of these materials are shown in Table 3. These materials were evaluated by first determining the performance of an MEA in ribbed Poco graphite plates described above. Following this, the MEA was tested under

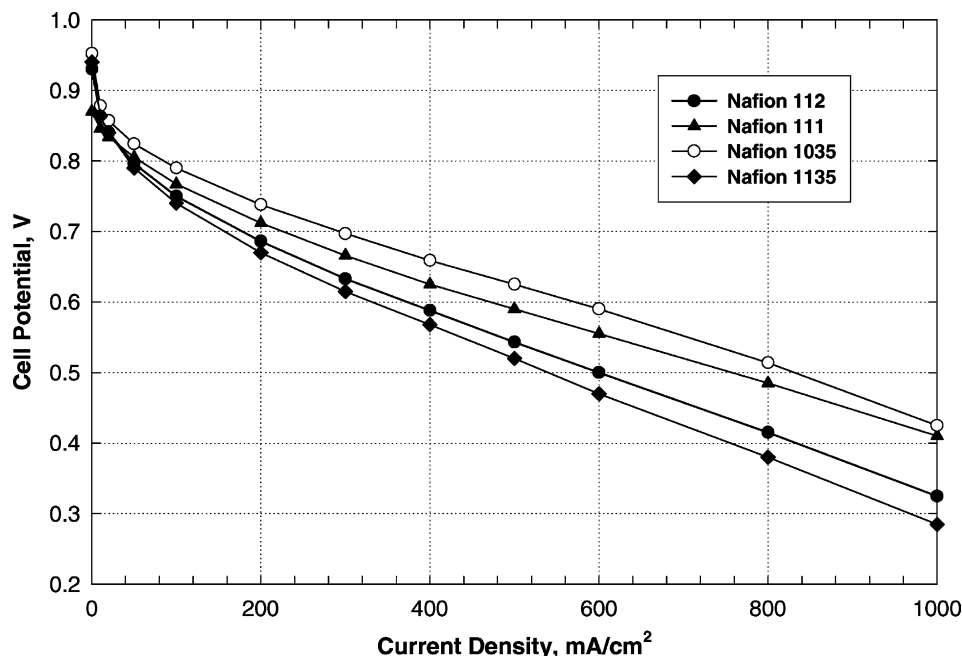


Fig. 6. Potential vs. current density for cells with different Nafion™ membranes.

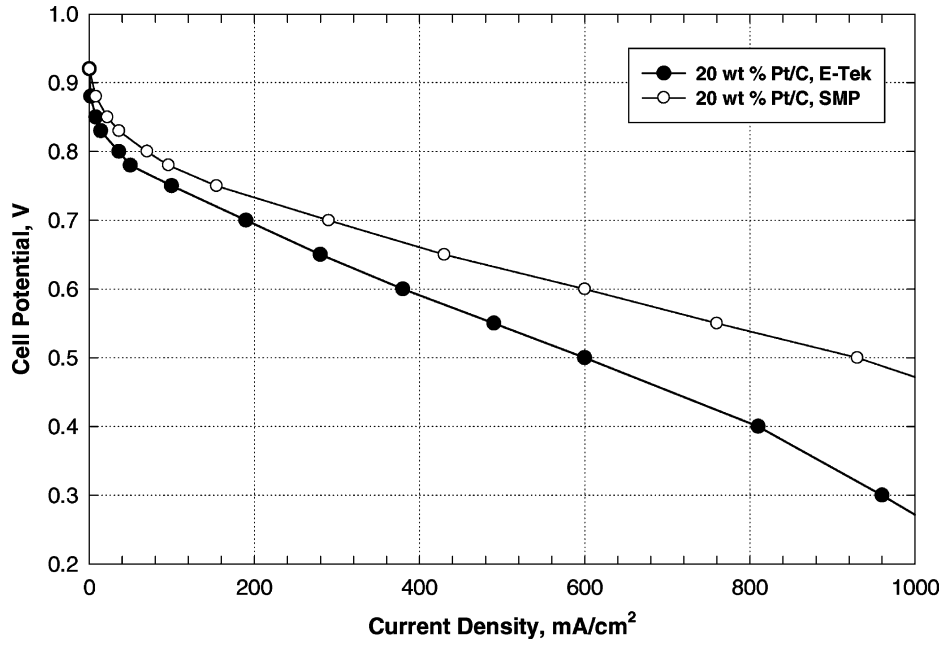


Fig. 7. Potential vs. current density for cells with 20 wt.% platinum on carbon cathode electrocatalyst.

Table 3  
Porosity of PEMFC gas flow-field materials

Material	Carbon paper	Carbon cloth	Stainless steel felt	Nickel foam
Source	E-TEK	E-TEK	Technetics Corp.	RPM Ventures
Porosity (%)	87	80	90	97

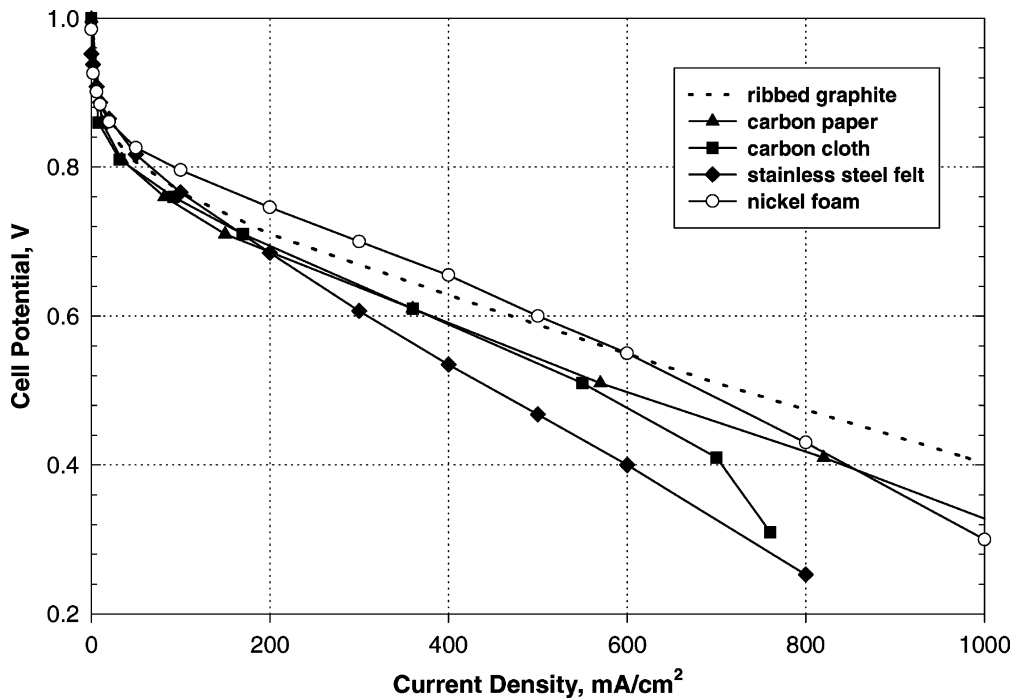


Fig. 8. Potential vs. current density for cells with different light weight materials as gas flow fields.

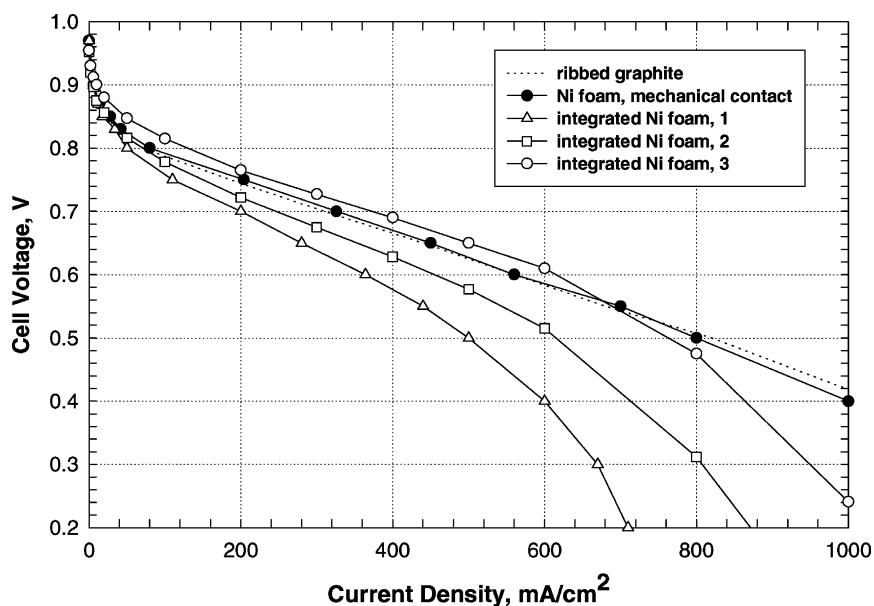


Fig. 9. Potential vs. current density for cells with different types of integrated gas diffusion electrodes and gas flow fields.

the same conditions with flow fields consisting of one of above light weight materials. Results obtained are summarized in Fig. 8. Performance with porous carbon paper was lower than that with ribbed graphite over the whole range of current densities because of the higher contact resistance between the GDL and the carbon paper. The performance of the cell with carbon cloth flow fields showed curvature of the potential–current density plot at high current densities due to gas diffusion limitations resulting from the low porosity of this material (Table 3). With stainless steel felt, performance was significantly reduced compared with ribbed graphite, because of higher specific electrical resistance of stainless steel. Performance also fell with time, due to oxide film growth. The best results were obtained with nickel foam, which showed some decrease of performance only at current densities in excess of 600 mA/cm<sup>2</sup> (Fig. 8) caused by non-uniform gas flow distribution through the foam. This effect may be easily eliminated by suitable gas manifold design.

### 3.6. Integrated gas diffusion electrode–gas flow-field unit

The interest of using nickel foam as an alternative to graphite suggested integration of the gas diffusion electrode structure with nickel foam during electrode preparation to obtain an integrated electrode–gas flow-field unit. However, initial attempts to do this were unsuccessful [5]. Fabrication of a successful integrated unit was performed in two steps: (i) formation of a GDL on a nickel foam plaque, and (ii) application of the electrocatalyst-Nafion<sup>TM</sup> ink to the substrate latter. MEAs integrated to the flow fields were then pressed by the procedure described above. Fig. 9 shows cell potential–current density plots for MEAs fabricated in this manner. The plots are compared with the performance of MEAs with the same type of electrodes in simple mechanical

contact with the ribbed graphite and nickel foam gas flow fields, where electronic conductivity is maintained by pressure. The initial results in Fig. 9 (integrated Ni foam, 1) show that the overall performance of an integrated unit was considerably less than with both ribbed graphite and nickel foam with mechanical contact. Detailed analysis of the data obtained shows that there are at least two reasons for this performance loss: (i) high contact resistance between the nickel foam and the GDL, and (ii) increased gas diffusion resistance because of the required GDL thickness, which was over twice that of the usual GDLs for free-standing MEAs fabricated in this laboratory. As shown (Fig. 9, integrated Ni foam, 2, and 3) these problems have been progressively successfully overcome.

## 4. Conclusions

The results obtained show that significant improvement of PEMFC performance can be achieved by use of new cell and MEA components, including electrocatalysts, proton exchange membranes, and light weight structural materials incorporated into the previously developed MEA with optimized GDEs. The improvement in cell performance represents a threefold increase in current density at 0.7 V from 200–600 mA/cm<sup>2</sup> at constant low total platinum loading (0.25 mg/cm<sup>2</sup>, cathode 0.2, anode 0.05 mg/cm<sup>2</sup> respectively). This progress is illustrated by the results summarized in Table 4 and presented in Fig. 10.

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Table 4

Composition of standard and improved MEAs

Type of MEA (years)	Total Pt (mg/cm <sup>2</sup> )	Source of Pt/C electrocatalyst	PF additive (%)	Membrane	Gas flow-field
Standard (1998)	0.25	E-TEK	No	Nafion 112	Ribbed
Improved (2001)	0.25	Pt alloy	33%	Nafion 111	Nickel foam

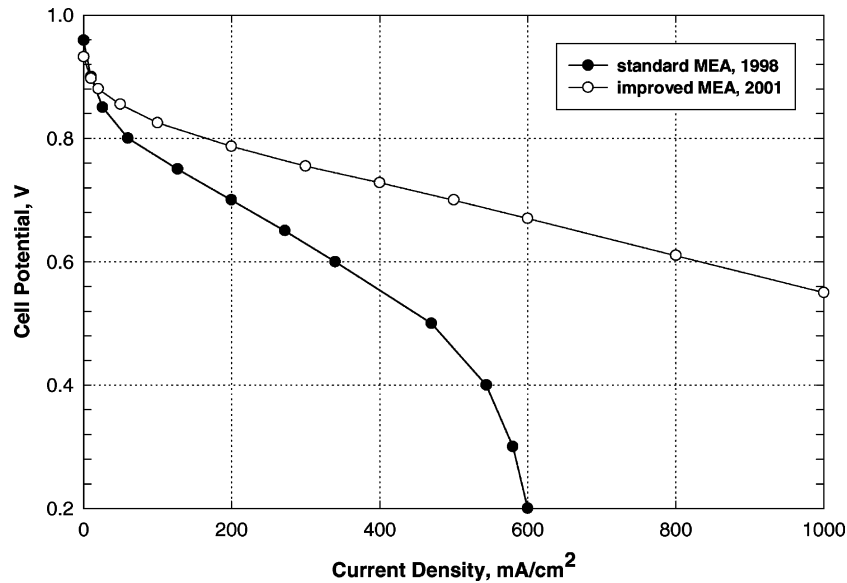


Fig. 10. Potential vs. current density for cells with standard and improved Membrane–electrode assemblies.

Technetics Inc. (DeLand, FL) for the supply of metal foams and felts.

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