JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 277–282

Porosity and catalyst utilization of thin layer cathodes in air operated PEM-fuel cells*

A. FISCHER, J. JINDRA‡, H. WENDT

Institute of Chemical Technology, Technical University of Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany

Received 1 November 1996; revised 14 April 1997

Better performance of and higher electrocatalyst utilization in proton-exchange membrane fuel cells equipped with thin film electrodes is achieved by exploiting pore forming additives in the electrode recipe formulation. Preparing the membrane–electrode assembly by a hot spraying procedure already provides 35% porosity. Additional coarse porosity is obtained by adding pore formers to the electrocatalyst slurry which is used for the hot spraying process. This allows for a better access of oxygen from air to the depth of the cathode. For air operation at ambient pressure and low catalyst loading of 0.15 mg Pt cm^{-2} a current density of 200 mA cm^{-2} at 0.7 V cell voltage can be obtained with such electrodes.

Keywords: *fuel cells*, *PEMFC*, *oxygen cathode*, *electrode porosity*, *mass transport*

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) are regarded as a possible alternative power source for stationary and mobile applications. They are light and allow for high power densities, but still are too expensive to compete with conventional internal combustion engines [1]. Conventional PEMFCs operate on hydrogen as a fuel and oxygen or air as an oxidant. The proton conducting membrane as an electrolyte is sandwiched between two gas diffusion electrodes. Platinum finely distributed on carbon black is regarded as the best catalyst for hydrogen oxidation and oxygen reduction in acidic media at low temperatures. The gas streams have to be humidified to keep the membrane (e.g. Nafion 117®, Du Pont de Nemours) water swollen in order to obtain sufficiently high protonic conductivity. When the cell is operated with air a drastic decrease in cell performance compared to operation with neat oxygen cannot be avoided. This is due to accumulation of nitrogen in the pores of the cathode leading to concentration polarization. Compressing the air to several bars increases cell performance sufficiently but the air compression consumes too much power, reducing the energy efficiencies of the system. Operation with uncompressed air demands high platinum loadings of about 4 mg cm^{-2} [2], but such high platinum loadings result in too high catalyst costs. As will be shown below the situation can be improved by increasing the porosity of PEMFC cathodes.

The state-of-the-art for PEMFCs involves thin film electrodes whose thickness does not exceed 10 μm and whose catalyst, consisting of commercial platinum on carbon black (E-TEK), are soaked with the ionomer and are directly glued to the membrane [3–6]. Recently catalyst loadings were reduced from 4 mg Pt cm^{-2} to as little as 0.05 mg Pt cm^{-2} for hydrogen/oxygen operation [7]. Further lowering catalyst loading seems to be unlikely and is not necessary, as the catalyst is no longer cost-determining for PEMFCs.

In this paper the effect of additional porosity of such electrodes with a low platinum loading (0.15 mg Pt cm^{-2}) on cell performance in air operated cells is presented. The investigation is performed under ambient pressure as it is presumed that using these cells for electrotraction in automobiles would demand that, for the cathode, air be used with only little overpressure in order to limit power losses due to air compression. To obtain higher electrode porosities volatile pore formers had been used, a method which previously had been applied to increase the porosity of fuel cell electrodes [8].

2. Experimental details

2.1. *Preparation of membrane electrode assemblies*

Cathodes and anodes of membrane-electrode assemblies (MEAs) according to [4–6] were prepared by spraying a slurry consisting of the catalyst (30 w/o Pt on Vulcan XC-72, E-TEK Inc.), Nafion solution (5 w/o, Aldrich), water and glycerol onto a heated Nafion 117® membrane and subsequently removing the solvents by heating to at least 150 °C. MEAs with

---

[*] This paper was presented at the Fourth European Symposium on Electrochemical Engineering, Prague, 28–30 August 1996.
[‡] Present address: Academy of Science of the Czech Republic, Vlašská 9, 11840 Prague 1, Czech Republic.

0021-891X

an active area of 25 cm^2 and a catalyst loading of 0.15 ± 0.02 mg Pt cm^{-2} were manufactured.

The catalyst slurry was prepared by mixing of the catalyst and the Nafion solution. Excessively stirring the slurry in an ultrasonic bath until the slurry became viscous accomplished the desired internal wetting of the catalyst by the ionomer. To avoid precipitation of TBA–Nafion tetrabutylammonium-hydroxide was added to the slurry after all the other ingredients were mixed together. The membrane was in the sodium form to provide better thermostability. For electrode-spraying it was spread on a heated (200 °C) vacuum table. The ionomer in the catalyst slurry was in the tetrabutylammonium (TBA) form to provide thermoplastic properties in order to improve the contact between the ionomer and the catalyst by merging the ionomer in the catalyst with the membrane in the hot spray procedure. After drying, the MEA was reprotonated in boiling sulphuric acid and rinsed several times with deionized water to remove traces of acid. To provide the electrodes with an additional porosity different kinds of pore forming additives were added to the catalyst slurry. A hydrophobic graphite paper (Toray TGPH-090), serving simultaneously as a gas distributor and a current collector, was applied to the electrodes. The MEAs were finally assembled in a commercially available graphite cell frame (Electrochem Inc., FC25-02SP). The pore forming substances were always added in an amount equal to 50 wt% of the pure catalyst.

2.2. *Operating conditions*

The cells were operated at 0.1 MPa with hydrogen (300 ml min^{-1}) and dry oxygen or dry air (150 ml min^{-1} or 300 ml min^{-1}, resp.). The cell temperature was 75 °C, hydrogen was saturated with water vapour at 85 °C ($p_{\mathrm{water}} = 0.057$ MPa). For impedance measurements small, circular cathodes of 2 cm^2 were used which were operated in the same cell frame together with a common 25 cm^2 anode as the counterelectrode. To avoid cracking of the bare part of the membrane which was exposed to the cathode gas the cathode gas stream was in that case humidified according to a vapour pressure at 75 °C ($p_{\mathrm{water}} = 0.038$ MPa).

2.3. *Morphological investigations*

Scanning electron microscopy was used to investigate the electrode morphology. Cross cuts of MEAs were prepared by breaking them under liquid nitrogen. Electrode porosities were determined pycnometrically by weighing dry and soaked circular pieces of MEAs with toluene under reduced pressure and measuring the weight gain after filling the pores with toluene. It had been shown before that, on exposure of the ionomer to toluene, the uptake of the organic solvent is negligible.

2.4. *Electrochemical measurements*

Current voltage curves were measured galvanostatically with an electronic load. Impedance spectra were recorded with a Zahner IM 5d instrument at different cell voltages in the frequency range 50 kHz to 0.1 Hz. For this purpose the anode served as a counter and reference electrode. To interpret these spectra the assumption was made that the anode impedances at all current densities are negligible (cf. [9]). The electronic electrode conductivity was measured by the current interruption method.

3. Results

3.1. *Electrode morphology*

Electrodes prepared by hot spraying without pore fillers show an overall porosity of about 35% (Table 1) in contrast to hot-pressed electrodes with only 20% porosity. The micrograph of the cross cut of this MEA allows identification of pores with diameters of less than 0.5 μm (Fig. 1). The electrode surface is almost closed with only smaller cracks.

Different kinds of filler were used to confer higher porosity on the electrodes. The MEA prepared with Li_2CO_3 crystals as a pore forming additive, which was removed by dissolving the salt in aqueous sulphuric acid during reprotonation, shows a porosity of about 65% with a fissured electrode surface. Fine pores with diameters below 0.5 μm and larger pores of diameters as large as 5 μm diameter can be distinguished (Fig. 2). The specific electronic conductivity of this electrode is lower than that of electrodes of equal loading prepared without fillers (Table 1).

Table 1. Porosities and specific electronic conductivities of different kinds of electrodes

Production technology	*Hot spray of slurry without additives*	*Hot spray of slurry with a low temperature decomposable additive*	*Hot spray of slurry with a high temperature decomposable additive*	*Hot spray of slurry with a soluble additive*
Porosity of electrodes/%	35	42	48	65
Specific conductivity of electrodes/S cm^{-1}	1.64	0.83	1.04	0.44

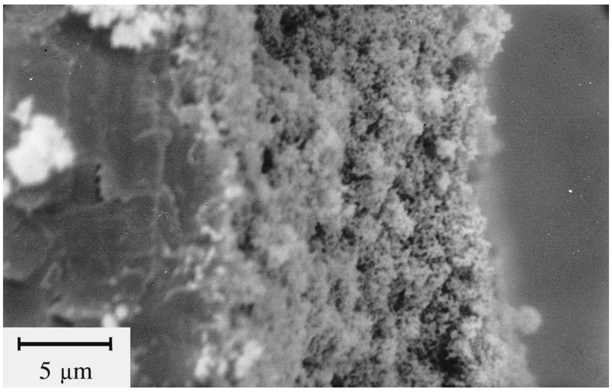

Fig. 1. SEM micrograph of a cross-cut of a MEA prepared without filler.

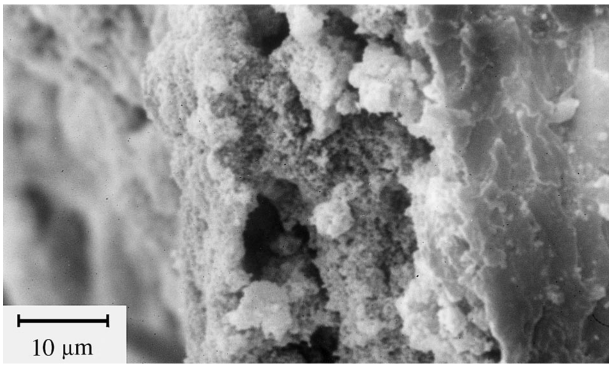

Fig. 2. SEM micrograph of a cross-cut of a MEA prepared with leachable filler.

Nevertheless, the decreased conductivity does not impair electrode performance. Further, enhanced electrode porosity has been achieved by adding volatile fillers to the catalyst slurry. Ammonium carbonate decomposes during the hot spray and drying procedure. Ammonium oxalate decomposes at about 190 °C by raising the temperature after drying of the electrode. The overall porosity of a MEA prepared by addition of ammonium oxalate is 48%. The morphology of the electrode is comparable to that of a MEA produced with little soluble lithium carbonate, a leachable filler, as a bimodal pore structure is generated. Coarser pores of micrometre dimensions stem from undissolved ammonium oxalate. Fine pores are generated by evaporation of homogeneously dissolved oxalate.

Porosities of 42% could be obtained with ammonium carbonate. With this kind of completely dissolved additive an almost homogeneous and monomodal porosity is achieved.

As expected the electronic conductivities of the electrodes increase with decreasing porosity.

3.2. *Cell performance and impedance measurements*

Figure 3 compares current–voltage characteristics typical for MEAs with electrodes prepared with and without pore forming additives for air and oxygen operation at atmospheric pressure. Performance of cells operated on air is distinctly poorer than for neat oxygen. Current voltage curves of cells produced with volatile fillers which are included in the same figure show performance with oxygen which is almost indistinguishable from that of cathodes without extra porosity. For air, however, the performance of cathodes with additional porosity is somewhat better. At a cell voltage of 0.7 V a current density of 140 mA cm^{-2} for the cell with the high temperature decomposable filler and 150 mA cm^{-2} for the cell with the low temperature decomposable filler.

Current voltage curves typical for cells provided with electrodes which had been produced with leachable fillers in comparison to the standard cell are shown in Fig. 4. Again, for oxygen operated cells there is no significant difference but performance with air shows the highest improvement with a current density

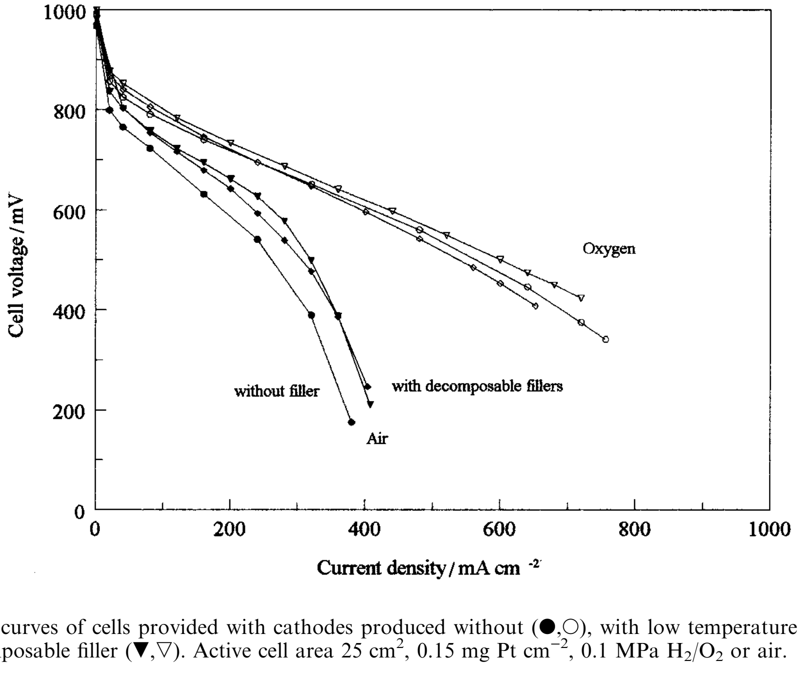

Fig. 3. Current voltage curves of cells provided with cathodes produced without (●,○), with low temperature decomposable (◆,◇), or high temperature decomposable filler (▼,▽). Active cell area 25 cm^2, 0.15 mg Pt cm^{-2}, 0.1 MPa H_2/O_2 or air.

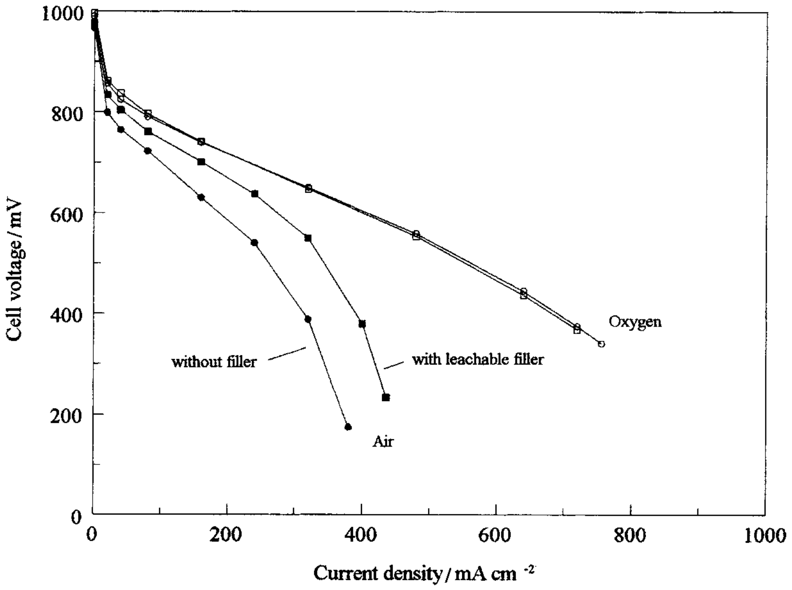

Fig. 4. Current voltage curves of cells provided with cathodes produced without (●,○) and with leachable (■,□) filler. Active cell area 25 cm^2, 0.15 mg Pt cm^{-2}, 0.1 MPa H_2/O_2 or air.

of 170 mA cm^{-2} at 0.7 V as compared with only 100 mA cm^{-2} for cathodes without added porosity.

Impedance spectra of cells produced without and with a leachable filler at different cell voltages are presented in Fig. 5. The operating conditions are different from Fig. 4 as humidified cathode gas had been used as oxidant. The spectra exhibit two distinct semicircles. The high frequency loop is almost

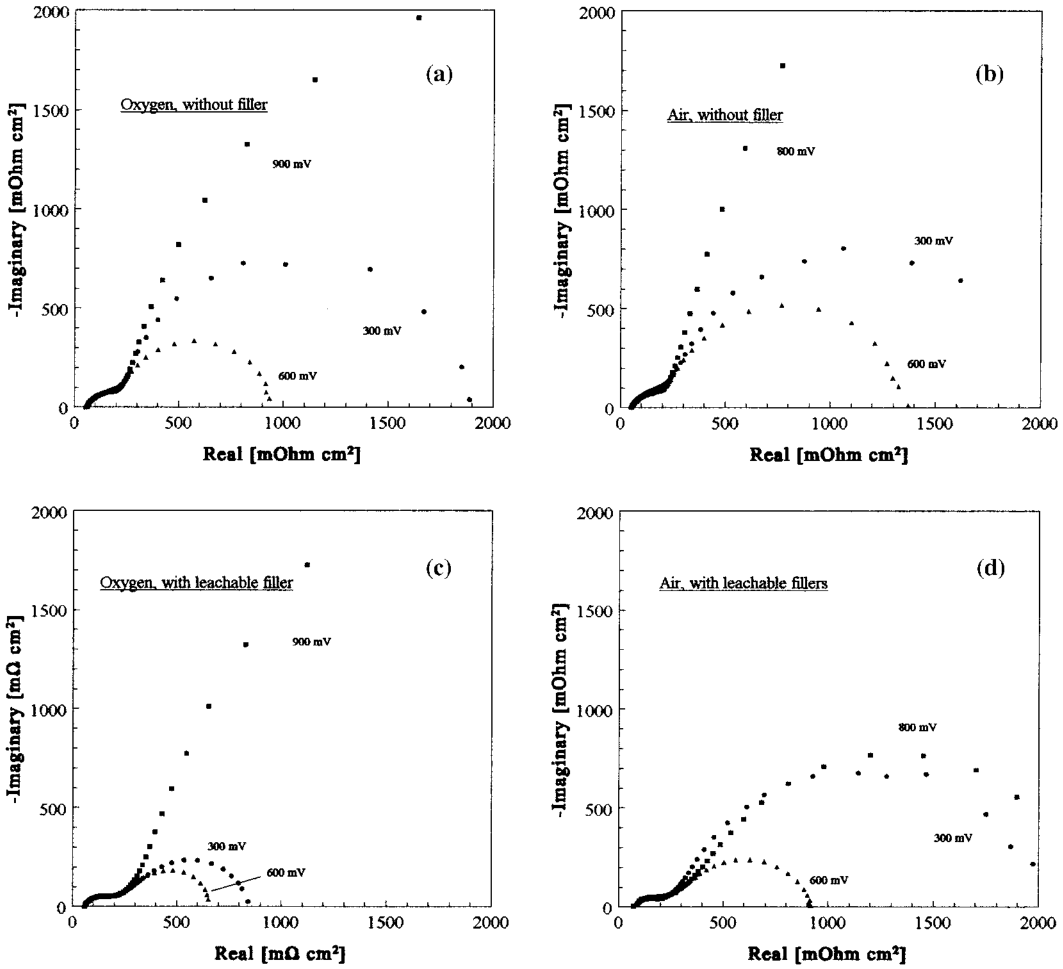

Fig. 5. Impedance spectra of cells with different cathodes and operated with oxygen or air as cathode gas. Active cell area 2 cm^2, 0.15 mg Pt cm^{-2}, 0.1 MPa H_2. (a) Electrode prepared without filler, 0.1 MPa O_2. (b) Electrode prepared without filler, 0.1 MPa air. (c) Electrode prepared with leachable filler, 0.1 MPa O_2. (d) Electrode prepared with leachable filler, 0.1 MPa air.

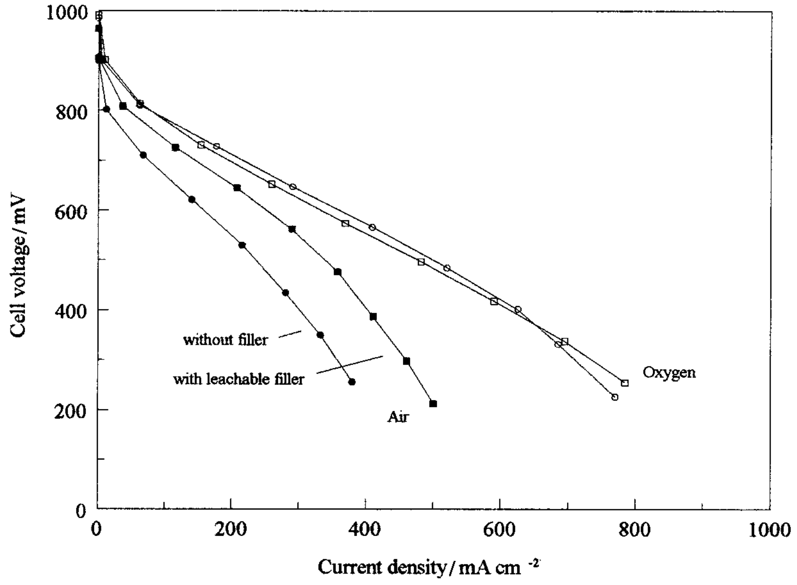

Fig. 6. Current voltage curves of cells with cathodes without (●,○) and with (■,□) leachable filler. Active cell area 2 cm^2, 0.15 mg Pt cm^{-2}, 0.1 MPa H_2/O_2 or air.

unchanged at all cell voltages. For all cells irrespective of their special design the diameter of the low frequency loop first decreases with decreasing cell voltage (i.e., increasing cathode overpotential) and starts to increase again at the highest overpotentials due to the increasing influence of mass transfer limitations for oxygen reduction. When the current voltage curve starts to become mass-transfer controlled the diameters of the low frequency loops at the corresponding cell voltages are lower for the cell prepared with a filler, indicating a lower mass-transfer hindrance of the latter cell.

4. Discussion

4.1. *Internal ohmic resistances*

The results from the impedance spectroscopy data gave two distinct loops. The high frequency loop may be attributed to the internal ohmic resistance and the contact capacitance in the granular electrode structure [10]. It is about the same size for both cells and remains almost unchanged for all cell voltages indicating that the internal processes determining the impedance of the porous electrode are almost unaffected by the electrode morphology or by the electrode polarization.

4.2. *Kinetic and mass transfer processes at the cathode*

The low frequency semicircle can be attributed, at low overpotentials, to the electrode kinetics of the cathode. Its decreasing diameter with increasing overpotential is associated with the accelerated kinetics of the oxygen reduction reaction, that is, with decreasing negative slope of the current voltage curve.

At higher cathode overpotentials, however, electrode kinetics become increasingly mass transfer controlled, resulting in an increase in the diameter of the low frequency loop. This effect can be attributed to the formation of a diffusion barrier for oxygen in the case of air operation due to a nitrogen cushion and an increasing flux of liquid water from the interior of the cathode. For oxygen operation it is only this increased production of water at the cathode, which establishes increasing mass transfer hindrance with increasing current density. This detrimental effect is still more enhanced if the air for the cathode is saturated with water vapour at 60 °C.

4.3. *Catalyst utilization*

The electrode with coarse pores gives higher current densities at all cell voltages, when operated with air (Fig. 4). This may be explained by the higher degree of utilization of the catalyst. The fine pore system of the cathode produced without pore forming additives seems to be almost completely filled with liquid water at high current densities ($i > 1$ A cm^{-2}). If air is used one would expect approximately five times lower current densities than with oxygen, since oxygen reduction is first order with respect to oxygen. Indeed this is observed at current densities lower than 50 mV cm^{-2} or 1 to 0.7 V cell potential, respectively. In the range between 700 and 650 mA cm^{-2} however, the ratio is not 1/5 but 1/1.3 to 1/2, which suggests improved utilization of the catalyst in the electrodes with extra porosity. First, less water is produced and therefore the percentage of water clogged pores is lower at the lower current densities achieved with air. Second, coarse pores provide better removal of water from the cathode, so that atmospheric oxygen penetrates more easily into the depth of the electrode.

5. Conclusions

The introduction of an additional porosity into thin film electrodes commonly used in PEMFCs improves cell and cathode performance, in particular with air as oxidant. With oxygen no improvement in performance occurred at current densities up to 800 mA cm^{-2} with dry cathode gases. Due to the higher and additional coarse porosity of the electrodes access of oxygen to the inner surface of the electrode is improved and improved catalyst utilization is achieved.

Acknowledgements

One of the authors (J.J.) is grateful to the Alexander von Humboldt Foundation, Bonn (Germany) for the financial support of a six months scholarship at Darmstadt. All authors acknowledge financial support by the Center for Solar and Hydrogen Research Ulm/Suttgart and the Ministry of Commerce and Technology of the Federal State of Baden-Würtemberg.

References

[1] S. Birkle, R. Kircher, C. Nölscher, H. Voigt, B. Ganser and B. Höhlein, *Energ.wirtsch. Tagesfr.* **7** (1994) 441–8.
[2] R. Mosdale, S. Gamburzev and S. Srinivasan, *in* Extended abstracts Vol. 95–2 (Oct. 1995), The Electrochemical Society, NJ, pp. 1031–2.
[3] M. S. Wilson and S. Gottesfeld, *J. Appl. Electrochem.* **22**, (1992) 1–7.
[4] M. S. Wilson, *US Patent 5 234 777* (1993).
[5] *Idem*, *US Patent 5 211 984* (1993).
[6] M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.* **139** (1992) L28–L30.
[7] I. D. Raistrick, U. S. Patent 4 876 115 (1989).
[8] A. J. Appleby and F. R. Foulkes, 'Fuel Cell Handbook', Van Nostrand, New York (1989), chapter 9.
[9] T. E. Springer, T. A. Zawodzinski, M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.* **143**, (1996) 587–99.
[10] S. Ahn, B. J. Tatarchuk, *ibid.* **142** (1995) 4169–75.