

Status of the development of a direct methanol fuel cell

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Abstract

In the past, most papers on direct methanol fuel cells (DMFC) reported about systems using pure oxygen instead of air supplied to the cathode. The status of the work on DMFC at Siemens was characterized by more than 200 mW/cm² at a cell voltage of 0.5 V under oxygen operation (4–5 bar abs.) at high temperatures (140°C). High oxygen pressure operation at high temperatures is only useful in special market niches. Low air pressure up to 1.5 bar abs. and therefore low operation temperatures in the range of 80–110°C are necessary technical features and economic requirements for widespread application of the DMFC. Today, our system produces 50 mW/cm² under air operation at low over pressure and at 80°C, while the cell voltage again amounts to 0.5 V. These measurements were carried out in single cells between 3 and 60 cm². First results for a cell design with an electrode area of 550 cm², which is appropriate for assembling a DMFC-stack, are shown. In the new cell it was possible to achieve the same power densities as in the experimental cells at low air over pressure. Also a three-celled stack based on this design revealed nearly the same performance. At 80°C a power output of 77 W at a stack voltage of 1.4 V can be obtained in the air mode. The low pressure air operation results in a lower performance which must be compensated by future improvements of the activity of the anode catalyst and by an adequate membrane with a low methanol and water permeation, which would be a great progress for the DMFC. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The provision of suitable fuels is an essential problem for the technical and economical application of fuel cells (see e.g., Ref. [1]). The hydrogen PEM fuel cells are supplied with gaseous hydrogen. But there is no infrastructure established yet for the distribution and storage of hydrogen, neither as a liquid nor as a gas. Another possibility could be the on-board generation of hydrogen from a liquid fuel by a fuel processor, comprising a reformer, a catalytic burner and a CO removal unit [2,3]. The hydrogen rich gas, produced by this fuel processor, is then supplied to the anode of the PEM fuel cell. Methanol is a possible candidate as a liquid fuel due to its high energy density. It would enable simple and safe handling and a low cost distribution system.

Alternatively to the PEMFC + reformer system, methanol could be mixed with water and directly supplied to the anode of a direct methanol fuel cell (DMFC). Thus, the system complexity is reduced considerably. Furthermore, the DMFC enables a quick start-up procedure, be-

cause there are no units which have to be heated to several hundred degrees centigrade as has to be done in a fuel processor. Additionally, an emission of carbon monoxide could be completely avoided in case of the DMFC, while the catalytic burner of a PEMFC + reformer system produces small amounts of CO, which are released in the exhaust gas.

The main disadvantage of the DMFC system is the relative low power density, which has to be significantly improved if the DMFC should be a viable alternative to the PEMFC plus reformer system.

The lower cell performance of a DMFC is caused by the poor kinetics of the anode reaction. Methanol is oxidized to carbon dioxide at the anode of a DMFC (Fig. 1). But the oxidation reaction proceeds through the formation of carbon monoxide as an intermediate which strongly adsorbs on the surface of a Pt catalyst [4]. Therefore, a potential, which is much more anodic than the thermodynamic value, is needed to obtain a reasonable reaction rate [5]. In contrast to the PEMFC, where it is mainly the cathode that is kinetically hindered, both electrodes of a DMFC suffer from kinetic losses. Consequently, numerous materials were studied to find an electrode material that

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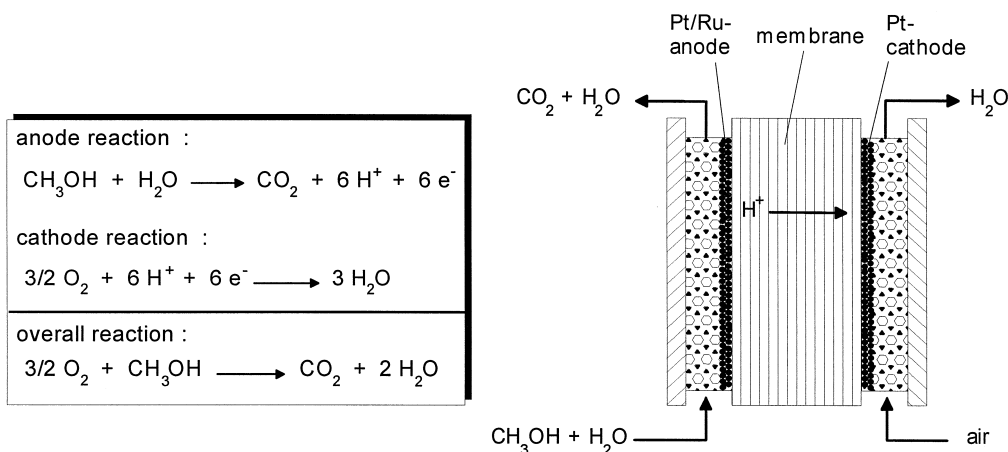


Fig. 1. Schematic principle of a DMFC single cell.

displays an enhanced catalytic activity and therefore lower overpotentials towards the methanol oxidation [4]. At present, the most active catalysts are based on Pt–Ru alloys. Ruthenium reduces the poisoning effect by lowering the overpotentials at the anode and thus increases considerably the catalytic activity of pure platinum.

Moreover, the commercially available polymer electrolyte membranes, which are used for the assemblies, are not optimized for the use in a DMFC. Methanol can permeate through the membranes from the anode to the cathode [6,7] and interact with the latter electrode. Therefore, the cathode potential is decreased and a loss of the cell voltage occurs [5]. Furthermore, the diffusion of methanol to the cathode leads to a loss of fuel and thus to a diminished efficiency.

During recent years large efforts were made to develop improved catalysts, to optimize the electrode structure and to improve the fuel cell design. This has led to a rapid improvement of the performance of the DMFC so that at a cell voltage of 0.5 V power densities can be achieved in the range of 200–340 mW/cm² for the oxygen mode and 150–180 mW/cm² for air-operated cells [8–13]. But a comparison of data from different groups is difficult, as the experiments were performed by the various groups under a wide range of different operating conditions. Experimental parameters, which have a strong impact on the cell performance (such as temperature, pressure, noble metal loading, oxygen excess), differ greater.

This communication aims at summarizing the status and issues of the DMFC system, which is developed in our group. The current DMFC concept and the performance level, which is presently achieved, are described.

2. Experimental

The schematic principle of the DMFC is depicted in Fig. 1. Essentially, it is assembled in a very similar way to the hydrogen PEMFC. The central unit is the polymer

electrolyte membrane. All the results which are presented in this paper were obtained using a Nafion 117 membrane. The cathode is constituted from Pt-black (Heraeus) with a catalyst loading of 4 mg/cm².

The main difference between the PEMFC- and the DMFC-assemblies is the anode catalyst. A high surface area Pt–Ru alloy is used instead of pure Pt and methanol is supplied to this electrode as an aqueous solution. The anode catalysts were either unsupported or carbon-supported materials, both prepared by Johnson Matthey. While old data, which are shown for comparison, were obtained using an in-house prepared Pt–Ru catalyst.

Some experiments reported by our group [14] and by others [13] in the past were performed with a gaseous fuel supply at the anode. In contrast, our actual operating concept uses liquid methanol–water mixtures. Thus, the polymer electrolyte can be kept at a high level of humidification and the DMFC is easier to operate.

3. Results and discussion

During the last few years the experimental work was concentrated on a DMFC operated under high oxygen pressure and at high temperatures. Voltage–current curves recorded under such conditions are shown in Fig. 2. The power density plots, which correspond to these characteristics, are shown in the insert. The dashed curve represents the performance at 140°C and 4 bar abs. as it was measured in 1995, whereas the solid curve was recorded recently. Both characteristics are comparable, especially at intermediate and high current densities. The cell performance is characterized by a cell voltage of 500 mV at a current density of more than 0.3 A/cm². Even at 0.4 A/cm² the voltage is still more than 480 mV and that corresponds to a power density of nearly 200 mW/cm². The maximum power density, which could be achieved, was more than 250 mW/cm², but then the cell voltage drops to only 350 mV.

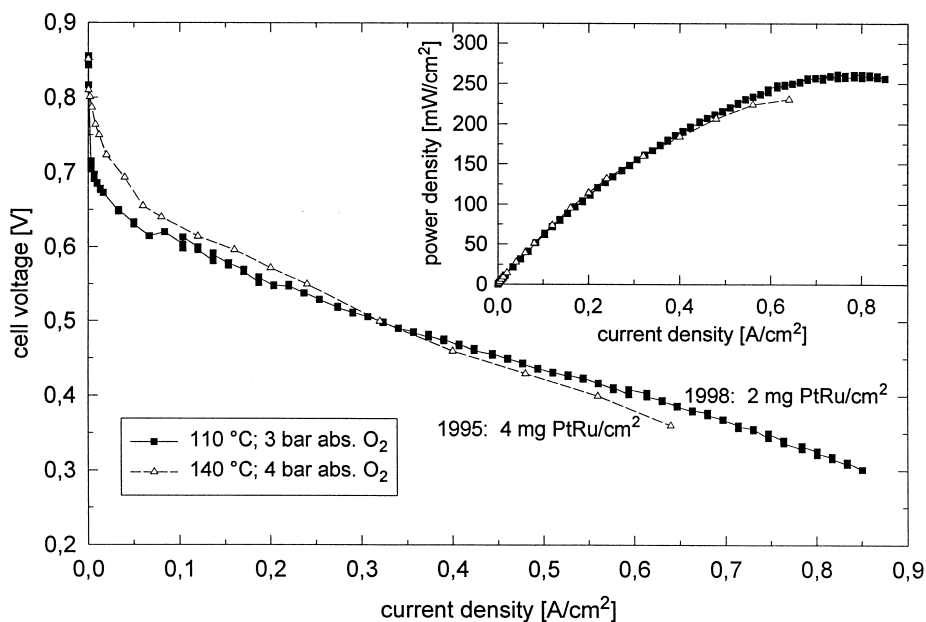


Fig. 2. Voltage–current curves and power density plots (insert) of a DMFC under oxygen operation illustrating the progress made by the development of new anode catalysts.

The good coincidence of the two curves in Fig. 2 demonstrates that we can achieve the same high cell performance today with less drastic experimental conditions. Both the temperature and the pressure are reduced significantly and the noble metal loading on the anode is reduced by half. This illustrates the progress which was made during the last years by the development of new, more active Pt–Ru catalysts and by the optimization of the electrode structure.

Nowadays, we are no more focused on running a DMFC with a high oxygen surplus under a high oxygen pressure. Today our main interest is to operate a DMFC under low pressures and to supply air instead of pure oxygen to the cathode. Due to the lower pressure, we have simultaneously to decrease the temperature. Otherwise, the water inside the cell would evaporate and the membrane would dry up. Therefore, we are limited to temperatures below 110°C, which is the boiling point of water at 1.5 bar abs. These experimental conditions seem to be more reasonable, if we want to use a DMFC as a realistic power source, which does not spend most of its energy output for compressing air to a high pressure level.

Fig. 3 represents voltage–current curves measured at experimental conditions, which meet our present requirements. The pressure was 1.5 bar abs., the temperature was 80°C and different amounts of air were supplied to the cathode. It can be seen clearly that there is a strong influence of the air flow on the cell performance at higher current densities. If a flow rate of 100 standard cubic centimeter per minute (sccm) is applied, we obtain a cell voltage of 500 mV at a current density of 0.1 A/cm². The power density plots, which correspond to these characteristics, are again shown in the insert. At 0.1 A/cm², the

power density amounts to 50 mW/cm². At a current density of 0.2 A/cm², we yield a voltage of 420 mV and this results in a power density of 84 mW/cm². The maximum power density is more than 90 mW/cm², but it again corresponds to a cell voltage of only 350 mV. All these power densities are significantly lower than those presented in Fig. 2. This decline results from the much more moderate experimental conditions and this should be considered when the power density is compared to literature data [8,9] where a higher air pressure and a considerably higher flow rate were used.

The air flow rate of 100 sccm is equivalent to an oxygen surplus of 20 at a current density of 0.1 A/cm², i.e., 20 times the stoichiometric oxygen amount was supplied to the cathode. Whereas the same air flow corresponds only to an oxygen excess of 10, if the current density is doubled.

Furthermore, it is noteworthy that the noble metal content at the anode was further reduced to 1 mg/cm², compared to 4 mg/cm² which were used in the past.

The oxidation of methanol at the Pt–Ru anode is hindered by the formation of CO. It adsorbs on the Pt-surface and forms a very stable intermediate. But this poisoning effect can be reduced at higher temperatures. Therefore, the performance of a DMFC can be improved by rising the operating temperature. Voltage–current curves measured at three different temperatures are shown in Fig. 4, while the pressure was kept constant. An increase of the temperature from 80 to 90°C results in a shift of the curve to higher voltages by about 20 mV.

But a further increase of the temperature to 100°C causes a decrease of the cell performance at low current densities due to an enhanced methanol diffusion through

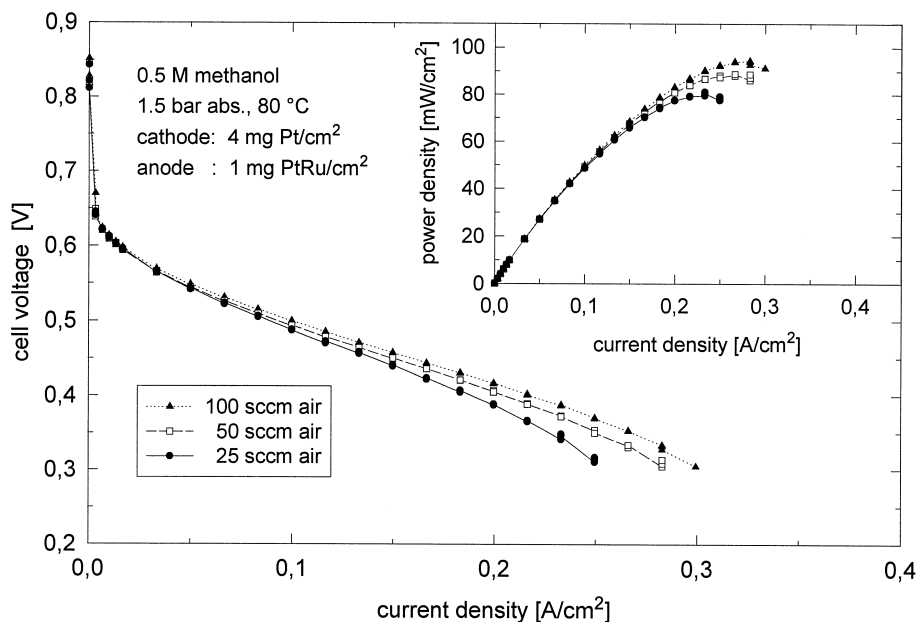


Fig. 3. Voltage–current curves and power density plots (insert) of an air-operated DMFC for different gas flow rates.

the membrane at the elevated temperature. Hence, this leads to a higher methanol concentration at the cathode which results in a steeper drop of the cathode potential and finally in a decrease of the cell performance. An increase of the cell voltage results at 100°C only at high currents, where most of the methanol is oxidized at the anode and thus the amount diffusing to the cathode is minimized.

Consequently, the optimal operation temperature seems to be 90°C, if Nafion 117 is used as the membrane material, at least for current densities up to 0.15 A/cm².

All the results, which are presented in Figs. 2–4, were obtained using experimental cells with a quite small electrode area, mainly 3 cm². But one of the major tasks of the DMFC project at Siemens is to build up a stack with a power output in the range of 1 kW. Therefore, we tested a cell design with a much larger electrode area, which totals 550 cm² per single cell. This cell design allows us to accumulate several cells in a series connection between the end plates. A three-celled stack based on this cell design was assembled and the results of the electrochemical tests,

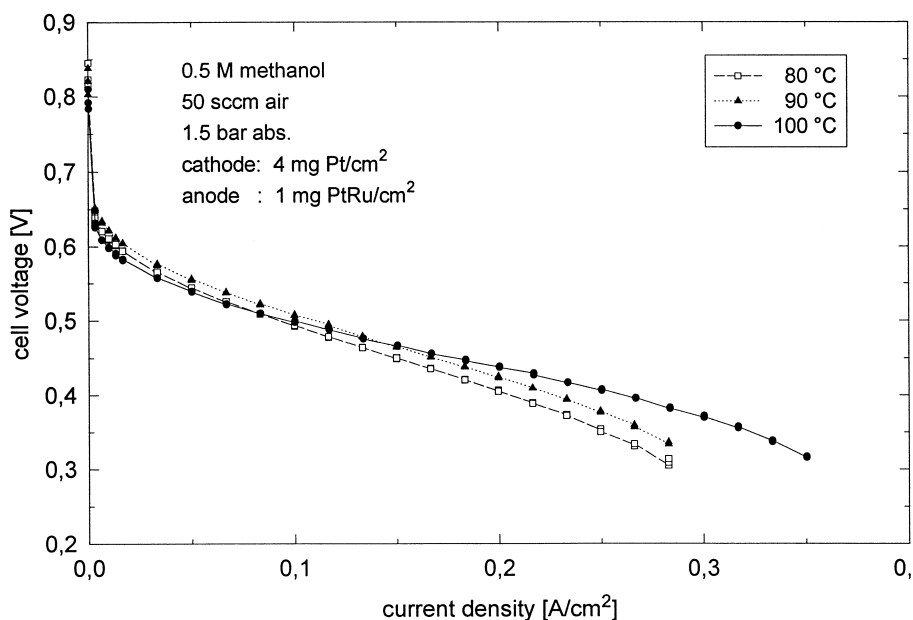


Fig. 4. Influence of the temperature on the performance of a DMFC under air operation.

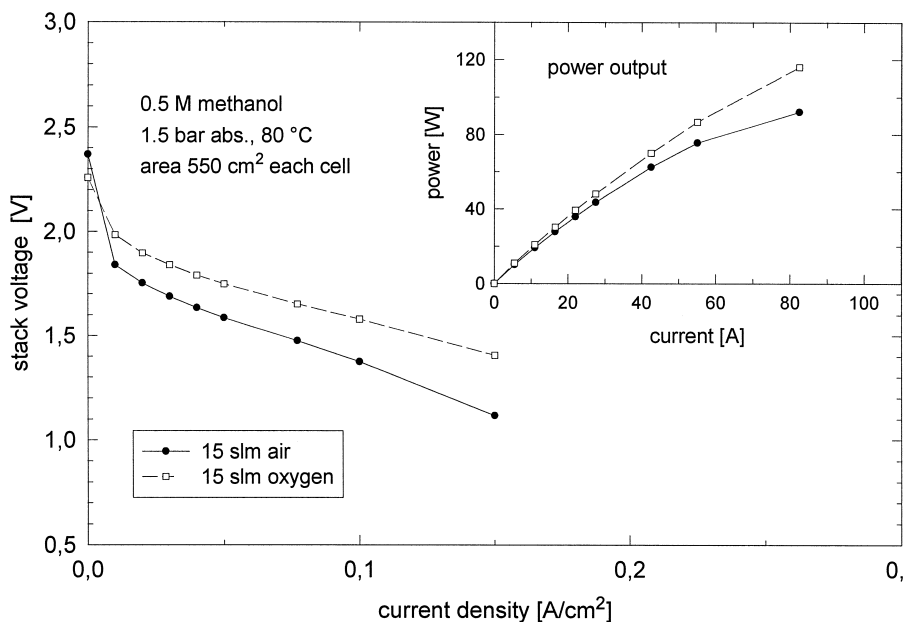


Fig. 5. Performance of a three-celled DMFC-stack under both air (—●—) and oxygen (- -□-) operation at 80°C.

which were realized with that battery, are demonstrated in Fig. 5.

The experimental conditions were 80°C, 1.5 bar abs. and an overall gas flow of 15 standard liter per minute (slm). This air flow corresponds to a very low oxygen excess compared to the values, which have been reported by other groups [8,11]. At a current density of 0.1 A/cm² the surplus is only five times the amount which is necessary on stoichiometric grounds. Fortunately, the characteristic curves of the three cells are nearly identical and this is observed not only under oxygen operation but also in the air mode. Thus, it can be concluded that the different cells in the stack are supplied equally. There were no problems caused by a different feeding of the cells with the reactants.

Furthermore, the cell performance of the 550-cm² DMFC is comparable to that of the small experimental cells. Using the above mentioned low oxygen surplus ($\lambda = 5$), a cell voltage of 460 mV was obtained at 0.1 A/cm². Thus, nearly the same power densities can be yielded as in the 3-cm² cells and therefore no losses occurred upon scaling up the electrode area. We can assume that the cell design, the manifold and the flow fields seem to be suited for assembling a multi-celled DMFC-stack.

The plot of the overall stack voltage as a function of the current density (Fig. 5) demonstrates that the stack voltage was 1.4 V under air operation and 1.6 V under oxygen conditions at 0.1 A/cm², which corresponds to a current of 55 A. The insert shows that at this current the power output amounted to 77 W in the air mode and 88 W under oxygen operation, respectively. The maximum power output exceeds 90 W for the air-operated stack and reaches

nearly 120 W, if pure oxygen is supplied to the cathode. To the best of our knowledge, these total power output data are the highest ever reported for an air-operated multi-celled DMFC stack. A five-celled stack, which was built at JPL with an electrode area of 25 cm² per cell [15], led to a performance of about 2.2 V at 0.1 A/cm² which equals a power density of 44 mW/cm². The temperature was 60°C and the air flow 23 times stoichiometry. The power density in this stack is comparable to the performance of our stack, but the power output at 0.1 A/cm² only amounted to about 6 W due to the significantly smaller electrode area.

4. Summary

Our DMFC system is characterized by a power density of about 200 mW/cm² at a cell voltage of 500 mV in the high temperature and high oxygen pressure mode. At low temperatures and low air pressure the power density amounts to 50 mW/cm² at a cell voltage of 500 mV.

The following results are noteworthy.

The noble metal loading was decreased to 1 mg PtRu/cm² on the anode, while it is still 4 mg Pt/cm² on the cathode.

In the 550-cm² cell, we achieve nearly the same power density as in the small experimental cells.

The three-celled stack revealed a performance of 77 W at 1.4 V at 80°C and a pressure of 1.5 bar abs., while the air flow was only five times stoichiometry.

The DMFC system offers interesting advantages.

The system complexity is reduced considerably compared to the PEMFC plus reformer system, since no fuel

processor and no humidification of gases is necessary. Furthermore, the DMFC enables a quick start-up procedure.

But the power density has to be increased in order to decrease the costs and to render the DMFC an attractive alternative. Therefore, the catalytic activity of the anode catalyst has to be further increased and the electrode structure must be simultaneously optimized. Furthermore, a specific DMFC membrane has to be developed with a low methanol permeation, which would increase the faradaic efficiency and reduce the poisoning of the cathode and thus lead to a rise of the cell voltage.

Acknowledgements

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References

- [1] K. Kordesch, G. Simader, *Fuel Cells and their Applications*, VCH, Weinheim, 1996.
- [2] N. Edwards, S.R. Ellis, J.C. Frost, S.E. Golunski, A.N.J. van Keulen, N.G. Lindewald, J.G. Reinkingh, *J. Power Sources* 71 (1998) 123.
- [3] R. Peters, J. Meusinger, Minutes of the 2nd IEA Advanced Fuel Cell Workshop held at Paul Scherrer Institute, Wislikofen, Switzerland, 29.09-01.10.1997, p. 301.
- [4] R. Parsons, T. VanderNoot, *J. Electroanal. Chem.* 257 (1988) 9.
- [5] M.P. Hogarth, G.A. Hards, *Platinum Met. Rev.* 40 (1996) 150.
- [6] S.R. Narayanan, H. Frank, B. Jeffries-Nakamura, M. Smart, W. Chun, G. Halpert, J. Kosek, C. Cropley, in: S. Gottesfeld, G. Halpert, A. Landgrebe (Eds.), *Proton conducting membrane fuel cells I*, The Electrochemical Society Proceedings Series, PV 95-23, Pennington, NJ, 1995, p. 278.
- [7] X. Ren, T.A. Zawodzinski, F. Uribe, H. Dai, S. Gottesfeld, in: S. Gottesfeld, G. Halpert, A. Landgrebe (Eds.), *Proton conducting membrane fuel cells I*, The Electrochemical Society Proceedings Series, PV 95-23, Pennington, NJ, 1995, p. 284.
- [8] S.R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M. Smart, S. Surampudi, G. Halpert, in: S. Gottesfeld, G. Halpert, A. Landgrebe (Eds.), *Proton conducting membrane fuel cells I*, The Electrochemical Society Proceedings Series, PV 95-23, Pennington, NJ, 1995, p. 261.
- [9] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. Surya Prakash, G.A. Olah, *J. Power Sources* 47 (1994) 377.
- [10] X. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) L12.
- [11] X. Ren, M.S. Wilson, S. Gottesfeld, in: S. Gottesfeld, G. Halpert, A. Landgrebe (Eds.), *Proton conducting membrane fuel cells I*, The Electrochemical Society Proceedings Series, PV 95-23, Pennington, NJ, 1995, p. 252.
- [12] H. Grüne, G. Luft, K. Mund, M. Waidhas, *Proc. Fuel Cell Semin.*, San Diego, CA, USA, 1994, p. 474.
- [13] A.K. Shukla, P.A. Christensen, A. Hamnett, M.P. Hogarth, *J. Power Sources* 55 (1995) 87.
- [14] M. Waidhas, W. Drenckhahn, W. Preidel, H. Landes, *J. Power Sources* 61 (1996) 91.
- [15] T.I. Valdez, S.R. Narayanan, H. Frank, W. Chun, *Proceedings of The 12th Annual Battery Conference on Applications and Advances held at California State University, Long Beach, CA, 14–17 January 1997*, p. 239.