

Humidification studies on polymer electrolyte membrane fuel cell

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Abstract

Two methods of humidifying the anode gas, namely, external and membrane humidification, for a polymer electrolyte membrane fuel (PEMFC) cell are explained. It is found that the water of solvation of protons decreases with increase in the current density and the electrode area. This is due to insufficient external humidification. In a membrane-based humidification, an optimum set of parameters, such as gas flow rate, area and type of the membrane, must be chosen to achieve effective humidification. The present study examines the dependence of water pick-up by hydrogen on the temperature, area and thickness of the membrane in membrane humidification. Since the performance of the fuel cell is dependent more on hydrogen humidification than on oxygen humidification, the scope of the work is restricted to the humidification of hydrogen using Nafion[®] membrane. An examination is made on the dependence of water pick-up by hydrogen in membrane humidification on the temperature, area and thickness of the membrane. The dependence of fuel cell performance on membrane humidification and external humidification in the anode gas is also considered. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer electrolyte membrane fuel (PEMFC) cells are attracting considerable interest as power sources for transport, stationary and portable applications. Perfluoro sulfonic acid membranes, such as Nafion[®], which are used as the solid polymer electrolyte in the fuel cell, require humidity in order to maintain proton conductivity [1–9]. One of the challenges in attaining optimum performance from PEMFCs is to achieve effective hydration of the ionomeric structure of the membrane. Less than full hydration results in a decrease in the proton conductivity of the membrane. In addition, the kinetics of the oxygen reduction reaction at the cathode are adversely affected by a decrease in water content. Maintaining an optimum hydration level for all operating conditions of the fuel cell is difficult for a number of reasons. For example, at low current density or at open-circuit when little liquid water is produced by the oxygen reduction reaction, the membrane hydration level will tend to drop. On the other hand, at high current densities, the electro-osmotic drag of water associated with the proton flux from the anode to the cathode tends to dry out the anode side of the membrane, whereas the cathode side tends to ‘flood’ because of the product water generated and the water

dragged across from the anode side. Hence, management of water in a polymer electrolyte membrane is essential for achieving stable and high-power performance in fuel cells. Humidification of the reactant gas is one of the methods employed to keep the membrane in a high state of hydration.

The simplest PEMFC system would be one where no auxiliary humidification system is required. In principle, the water produced at the cathode is sufficient to maintain adequate hydration of the fuel cell under certain conditions [10]. Relatively high performances have been obtained from fuel cells at near ambient pressure with no external humidification using thin ionomeric membranes [11,12]. Operation without humidification is based on the principle that the electrolyte absorbs and retains water under the operating conditions.

Attempts to introduce self-humidification to the fuel cell led to the introduction of a special membrane [13–15] which was recast from solubilised polymer electrolyte in the presence of SiO₂ or TiO₂. This membrane was modified by deposition of a platinum film (~0.1 mg cm⁻²) inside the membrane via cation exchange followed by reduction. The self-humidification mechanism was based on the ability of such a membrane to transport reactants, both hydrogen and oxygen, which then recombined on the embedded platinum film. Water, the product of this reaction, directly humidified the membrane. Such a mode of operation required high stoichiometries of reactants. Cisar et al. [16] developed a

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membrane cast in the presence of special micro-tubing. The embedded micro-tubes provided internal passages which provided water for membrane humidification. A similar approach based on the direct addition of water to the membrane was developed by Watanabe et al. [17]. The International Fuel Cell Corporation [18] uses water-permeable bipolar plates, water is recovered from the cathode side and directly humidifies the anode and cathode flow streams within the cells.

In a technique commonly adopted for small cell stacks, the reactant gas streams are humidified by bubbling through heated sparger bottles which contain water. One of the main drawbacks with such an arrangement is the development of a considerable pressure drop which results in a substantially lower pressure of the gases on entry to the fuel cell. Consequently, the inlet gas to the sparger has to be supplied at a higher pressure so as to achieve sufficient pressure at the fuel cell inlet.

Chow et al. [19] have reported the use of a membrane-based humidification arrangement. The fuel and oxidant gases are humidified by passing the gas on one side of a membrane and deionised water on the other side, prior to introduction to the fuel cell. Deionised water is preferred to prevent membrane contamination by undesired ions. In such arrangements, water is transferred across the membrane to the fuel and oxidant gases.

Nafion[®] is a suitable and convenient humidification membrane material for fuel cell applications. One of the advantages derived in such membrane-based humidification is that it is possible to humidify the fuel and oxidant gases at temperatures close to that of the operating temperature of the fuel cell if the cooling arrangement of the stack is integrated with the humidification system. Except for the above reported study, no literature is available on membrane-based humidification. That study dealt only with integration of the humidification system with the fuel cell system and not with the amount of humidification that is possible for a given temperature, the area of the membrane, and the type of the membrane. The performance of the cell was found to be dependent more on hydrogen humidification than on oxygen humidification. Hence, the scope of the present study is restricted to the humidification of hydrogen using a Nafion[®] membrane.

2. Experimental

The electrodes for PEMFCs were made from carbon cloth, impregnated with Teflon, and provided with a layer of catalytic material of 20 wt.% Pt on carbon (from E-TEK) with 5% Nafion solution (from Aldrich). The catalyst loading for both the electrodes was at around 0.75 mg cm^{-2} , with a slightly higher loading in the cathode. Nafion, a perfluorosulfonic acid membrane, was sandwiched between two electrodes, and each membrane and electrode assembly (MEA) was hot-pressed at 150°C and under various

pressures depending upon the electrode area. Electrodes of different area (from 25 to 300 cm^2) were prepared and also two types of Nafion membrane, namely, 112 and 115, were used to prepare different MEAs. The MEA thus prepared was placed between two grooved graphite plates (for anode and cathode gas flow) and a copper current-collector. The assembly was then tightened with the help of end plates, bolts and nuts. An electrical load was applied to the fuel cell assembly with the help of Hewlett-Packard load boxes models HP6060A and HP 6050A.

The performance of the fuel cell was studied with respect to humidification of the gas streams by external humidification and membrane humidification. In external humidification, the reactant gases were bubbled through heated water prior to entering the fuel cell. In membrane humidification, the gas streams were humidified by passage over a membrane saturated with water. The main attraction of this procedure lies in the possibility of humidifying the gas streams at temperatures close to the operating temperature of the stack, and elimination of auxiliary power consumption required for humidifying the gases is achieved by incorporating this system within the stack. Such a system is also called an 'internal humidification system'. This humidification region, electrically isolated from the electrochemically active region, consists of a membrane sandwiched between two grooved graphite plates. Heated water is passed on one side of the membrane and the gas to be humidified is passed on the other side. Water diffuses through the membrane and is picked up by the flowing gas stream on the other side. In practice, coolant water from the fuel cell assembly, at a temperature close to that of the fuel cell, can also be used for humidifying the membrane. This simplifies the overall design.

For evaluation of water uptake by gases in the above two arrangements, namely, external and membrane-based humidification, two moisture traps made of glass and containing silica were connected to each gas stream at the outlet of the fuel-cell assembly. The difference between the initial and final weights of the traps gives the amount of water present in the respective gas streams. The procedure was repeated (i) under load, (ii) under no load conditions and (iii) for the fuel cell inlet gas streams by connecting the traps just after the humidification set-up, prior to the inlet of the fuel cell. From the humidity data, various parameters (e.g. water uptake by gases and by the fuel-cell membrane, water of solvation) can be calculated, based on certain assumptions, such as the entire system is held at constant temperature, the solubility of both hydrogen and oxygen in the membrane is negligible.

3. Results and discussion

3.1. External humidification

The water uptake by the fuel-cell membrane on the anode side was calculated from the difference in the moisture

contents of the inlet and outlet gas streams under no load conditions. The water of solvation was obtained from the difference in the amount of water in the inlet and outlet hydrogen streams, which has been used to solvate the hydrogen ions as they move through the MEA. The change in water content between the inlet and outlet hydrogen gas streams is attributed only to the solvation of the ions, assuming that losses due to other factors are negligible. Therefore,

$$\text{water of solvation} = \text{water at hydrogen outlet} \\ (\text{under no load} - \text{under load})$$

In order to estimate the amount of product water, i.e. the amount of water formed due to the fuel-cell reaction, it is assumed that all the water due to solvation of protons is pushed to the cathode and comes out with the oxygen outlet stream. The amount of water coming out of oxygen outlet consists of (1) product water, (2) water of solvation and (3) the residual water of humidification. Hence, the amount of product water is calculated as

$$\text{product water} = \text{H}_2\text{O} (\text{O}_2 \text{ outlet under load}) \\ - \text{H}_2\text{O} (\text{O}_2 \text{ outlet under no load}) \\ - \text{water of solvation}$$

The water of solvation was found to decrease with increase in current density for a 25-cm² cell, as shown in Table 1. This is explained by the fact that for higher currents, the gas flow rates are gradually increased to meet the increasing gas requirements. This results in an increase in the hydrogen ion production at the anode. For a given humidification set-up, however, the moisture concentration in the hydrogen stream actually falls with increasing gas flow rates. This results in a decrease in the number of water molecules *available per hydrogen ion*. Additionally, for 100 and 300-cm² cells, development of temperature gradients due to higher operating current leads to an imbalance in the availability of water across the electrode area and this could also lead to lower solvation of protons and membrane dehydration.

It is observed that the fuel cell membrane always picks up water from the hydrogen stream even under no load conditions, which further strengthens the need for improved humidification. Table 2 gives the water picked up by the membrane on hydrogen side. It follows that for a given humidification set-up, an increase in the electrode area

Table 1
Water of solvation in external humidification

Area of the electrode (cm ²)	Current density (A cm ⁻²)		
	0.1	0.2	0.3
300	0.07	0.037	0.067
100	0.059	0.1	0.069
25	0.268	0.16	0.12

Table 2
Water uptake by the membrane at the anode side

Area of the electrode (cm ²)	Current density (A cm ⁻²) at which the electrode was equilibrated	
	0.1	0.3
300	1.3	2.8
100	2.4	1.9
25	0.45	0.18

(and hence, membrane area) and current density (necessitating higher gas flows), results in a decrease in the water of solvation due to insufficient humidification.

In the case of external humidification, the sparger in the external humidifier results in a reduced pressure in the inlet gas streams. A lower inlet pressure generally results in a fall in the performance of the fuel cell.

3.2. Membrane humidification

The absolute quantity of water uptake by the membrane alone, without fuel cell electrodes, has been quantified over a wide range of flow rates. It was found to increase with increase in the rate of gas flow up to a limiting value, for a 300-cm² Nafion 112 membrane (Fig. 1). The water uptake by hydrogen at different temperatures and flow rates is given in Fig. 2. At a constant flow rate, the water uptake by the hydrogen gas stream increases with the temperature. This is due to the evaporation-type mechanism involved in membrane humidification that is favoured by increasing temperature. It is seen that the water uptake per hour does not increase uniformly as the temperature is increased from 40 to 70°C; the increase is pronounced from 40 to 60°C, but is only marginal from 60 to 70°C. This is perhaps due to the fact that the water transfer limit across the membrane is being approached, which offsets any increase in driving forces due to diffusion and convection and, thereby, results in only marginal increase in moisture uptake by the gas at the higher temperatures.

The data in Fig. 2 also show that on increasing the gas flow rates at constant temperature, the absolute quantity of water picked up by the gas per hour (as opposed to the moisture concentration) increases, reaches a peak, and then levels off. The initial increase in water pick-up can be explained by an enhanced convective driving force due to higher flow rates. The peak represents the influence of the membrane's limitations to transfer water such that further rise in water pick-up is only marginal.

As the temperature is increased, the rate of water pick-up levels off at low flow rates, as shown in Fig. 3. This is also explained by an increased transfer rate at higher temperatures (due to the evaporation-type mechanism), even at low gas flow rates, and a subsequent levelling off due to limitations in the membrane's ability to transfer water. The concentration of water in the gas stream always decreases with

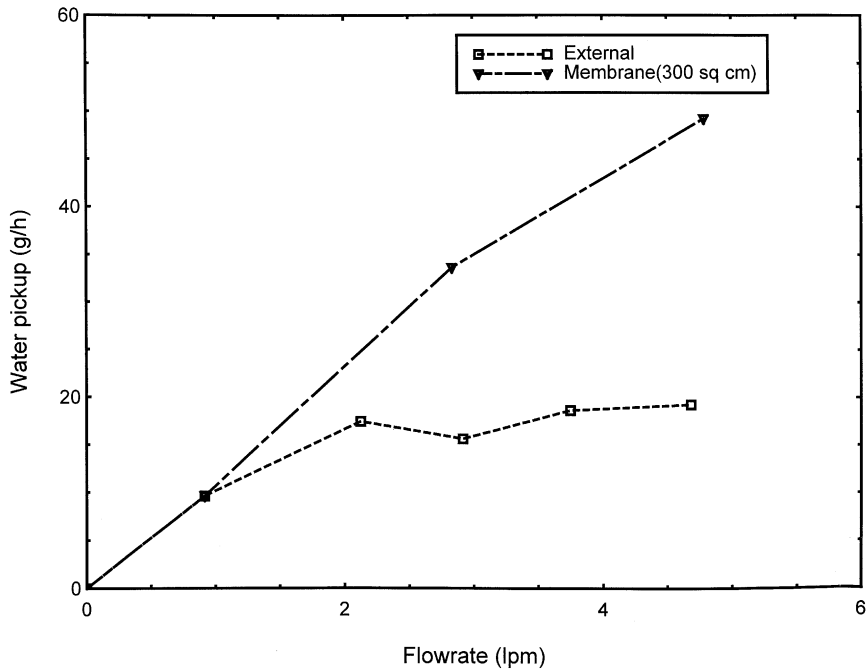


Fig. 1. Comparison of water pick-up by external and membrane humidification at 50°C.

increasing flow rate. At lower temperatures, such as at 40°C, the water pick-up by the gas does not increase appreciably with increasing flow rate. At higher temperatures (50–70°C), the initial fall in concentration is found to be steeper.

This is due to premature levelling off of the quantity of water picked up at higher temperatures due to limitations of transfer across the membrane. It also indicates that apart from the moisture concentration gradient near the membrane

(which is enhanced at higher gas flow rates) and temperature, the membrane’s ability to transfer water is a factor which affects water uptake by the gas.

Similar experiments demonstrated that water uptake by the gas streams is higher than with Nafion 115. The results are shown in Figs. 3 and 4. Being a thinner membrane, Nafion 112 is more permeable to water and, hence, makes more water available at the membrane–gas interface. Water

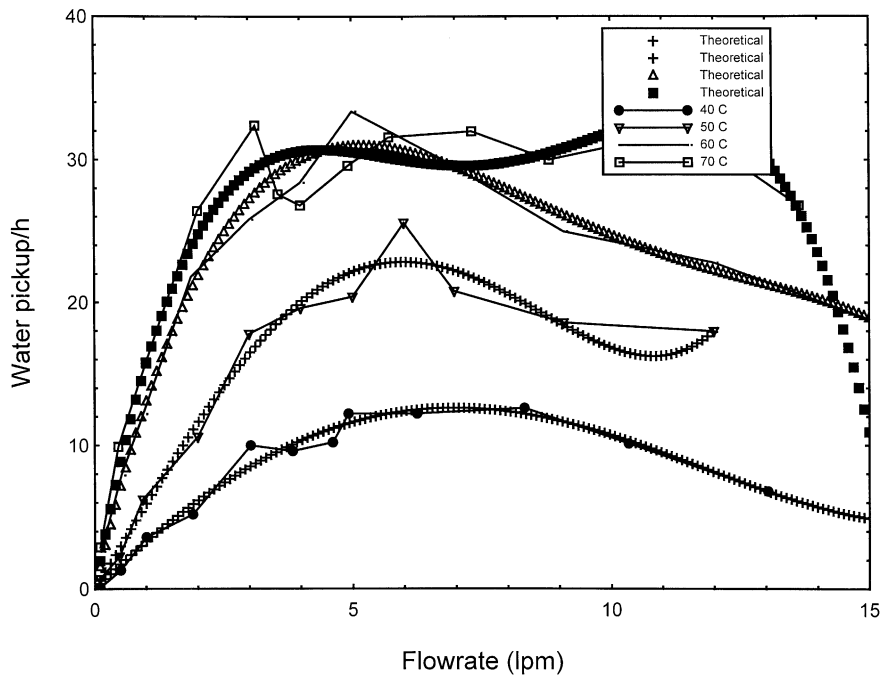


Fig. 2. Humidification of Nafion 115 membrane (100 cm²) at various temperatures.

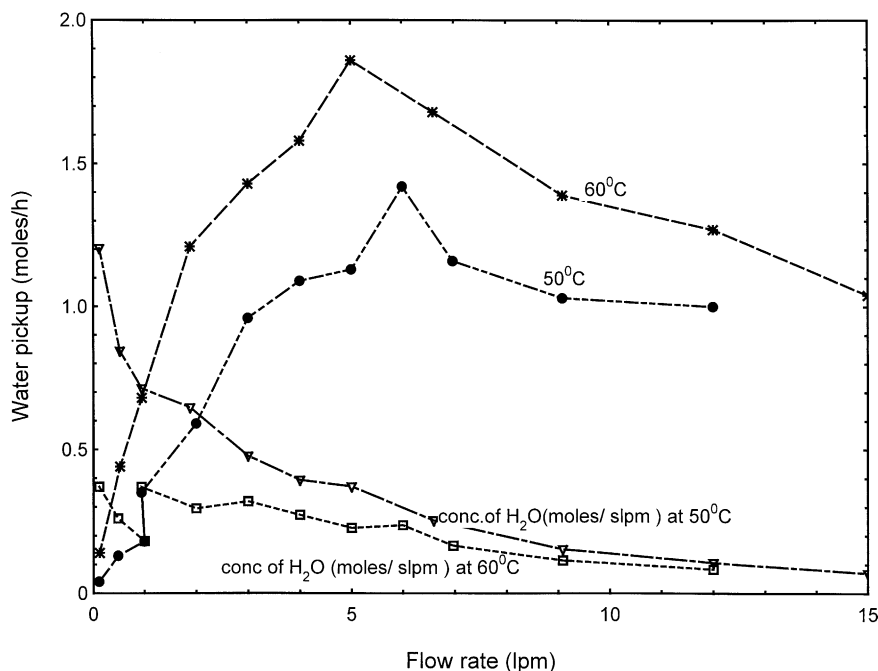


Fig. 3. Water uptake by Nafion 115 (100 cm²) at various flow rates.

pick-up was also found to increase with increase in membrane area, because of the increased area of contact.

The water picked up by hydrogen per unit area for membranes of 300 and 100 cm² was calculated at two temperatures, see Fig. 5a and b. The curves for the two membrane areas intersect at a particular flow rate of hydrogen. At flow rates less than about 10 slpm of hydrogen, the water pick-up *per unit area* for the 100-cm² membrane is

higher than that for 300 cm². This trend is reversed at flow rates above 10 slpm. This can be explained on the basis that the mass-transfer rates are primarily influenced by the phenomena of diffusion and convection. The gas stream traversing along a 300-cm² membrane has a longer residence time due to the longer traversal path and at low flow rates, the gas possibly gets saturated which, thereby, results in a lower amount of water pick-up per unit area of the

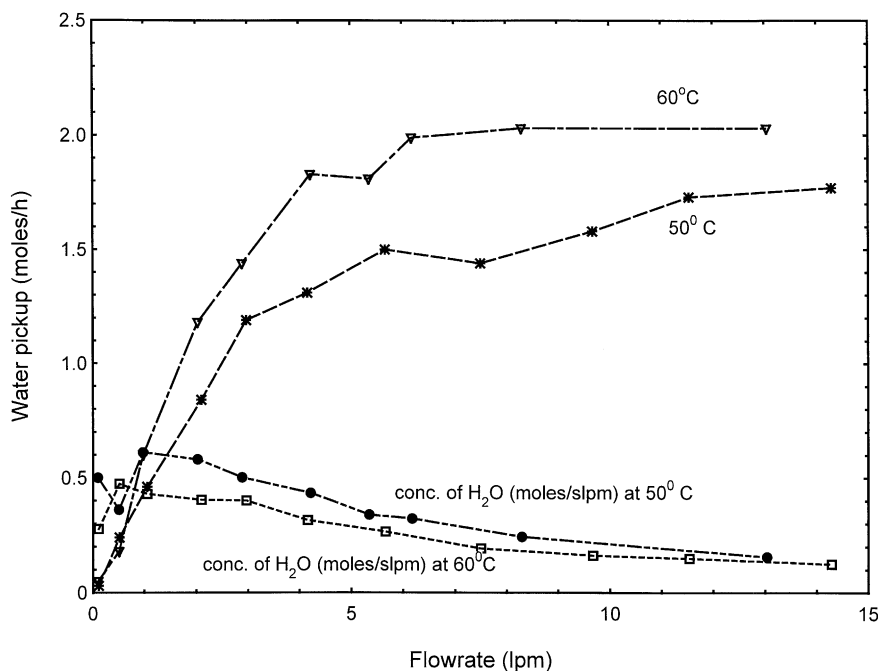
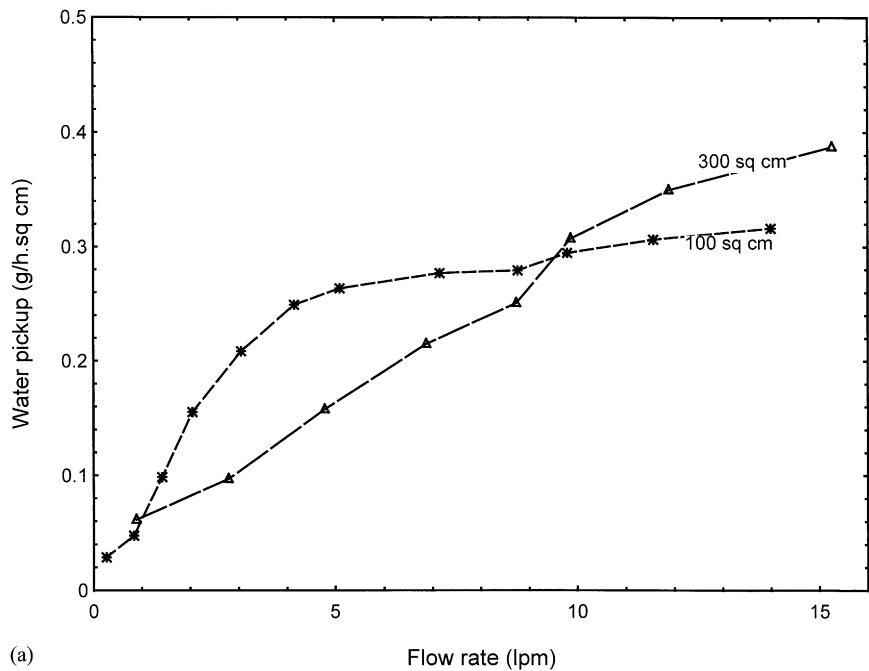
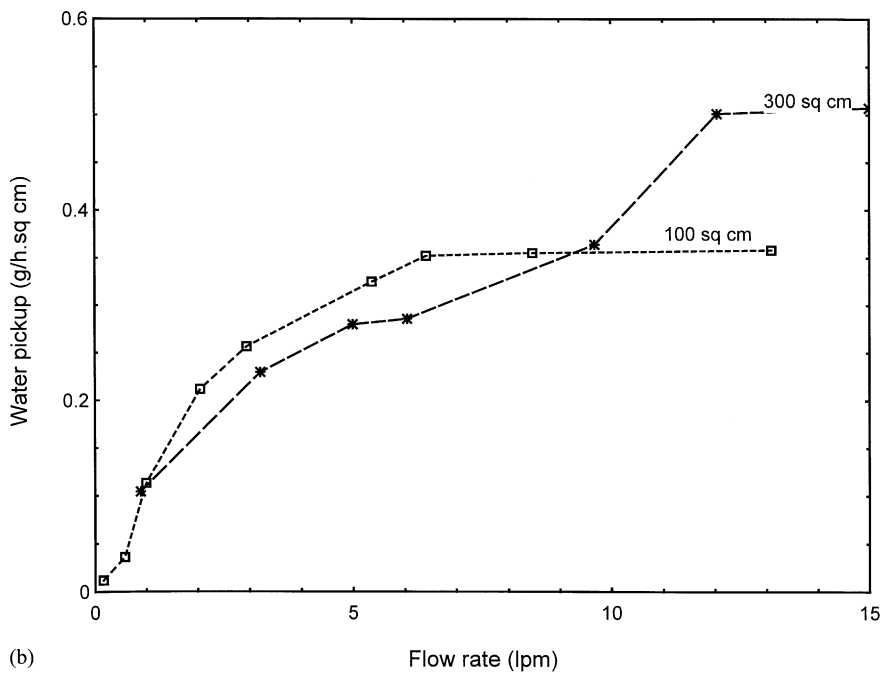


Fig. 4. Water uptake by Nafion 112 (100 cm²) at various flow rates.



(a)



(b)

Fig. 5. Comparison of water uptake by Nafion 112 with various areas at 50°C (a) and 60°C (b).

membrane. In the high flow region, it is likely that the gas is well below its saturation level in the available residence time. The larger area of contact now becomes beneficial and results in a higher amount of moisture uptake by the gas, compared with that in a 100-cm² assembly. Though the gas flowing in the latter would also be below saturation level at high flow rates, a shorter residence time can account for the lower moisture pick-up per unit area of membrane.

4. Conclusions

From Section 3, it appears that an optimum set of parameters, such as the area of the membrane and the gas flow rates (or residence time), apart from temperature, need to be chosen so as to achieve effective membrane-based humidification of hydrogen gas. This aspect has also been observed in the operation of stacks which are internally humidified

using a membrane assembly. It may be noted that the membrane humidification unit is most likely to be incorporated in the stack assembly itself (hence the name ‘internal humidification’). It is therefore convenient to make the outer dimensions of this membrane humidification unit the same as that of the stack components. Additionally, the coolant water itself can be used for humidifying the hydrogen gas. This obviates the need for an external heating arrangement for water. Therefore, one of the design parameters for such a system is the number of such membrane assemblies, since the water temperature and membrane area are now fixed. The number of membrane assemblies, in turn, depends on the operating conditions and the performance characteristics of the stack.

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References

- [1] R.S. Yeo, *J. Electrochem. Soc.* 140 (1993) 3190.
- [2] M.W. Verbrugge, R.F. Hill, *J. Electrochem. Soc.* 137 (1990) 886.
- [3] D.M. Bernardi, *J. Electrochem. Soc.* 137 (1990) 3344.
- [4] T.E. Springer, T.A. Zawodzinski Jr., S. Gottesfeld, *J. Electrochem. Soc.* 138 (1991) 2334.
- [5] T.A. Zawodzinski Jr., T.E. Springer, J. Davey, J. Valerio, S. Gottesfeld, in: R.E. White, M.W. Verbrugge, J.F. Stockel (Eds.), *Modelling of Batteries and Fuel Cells*, PV 91-10, The Electrochemical Society Proceedings Series, Pennington, NJ, 1991, pp. 187–196.
- [6] T.F. Fuller, J. Newman, *J. Electrochem. Soc.* 139 (1992) 1332.
- [7] D.M. Bernardi, M.W. Verbrugge, *J. Electrochem. Soc.* 139 (1992) 2477.
- [8] Y.M. Tycon, M.C. Kimble, R.E. White, *J. Electrochem. Soc.* 139 (1992) 1939.
- [9] P. Staiti, Z. Poltarzewski, V. Alderacci, G. Maggio, N. Giordano, A. Fasulo, *Appl. Electrochem.* 22 (1992) 663.
- [10] D.M. Bernardi, M.W. Verbrugge, *J. Electrochem. Soc.* 139 (1992) 2477.
- [11] H.P. Dhar, U.S. Patent No. 5,242,764, 7 September 1993.
- [12] H.P. Dhar, U.S. Patent No. 5,318,863, 7 June 1994.
- [13] M. Watanabe, H. Uchida, Y. Seki, M. Emori, Extended abstract no. 606, in: *Proceedings of the Electrochemical Society Meeting*, Miami Beach, FL, 9–14 October 1994,.
- [14] M. Watanabe, H. Uchida, Y. Seki, M. Emori, P. Stonehart, *J. Electrochem. Soc.* 143 (1996) 3847.
- [15] M. Watanabe, H. Uchida, M. Emori, *J. Electrochem. Soc.* 145 (1998) 1137.
- [16] A.J. Cisar, A. Gonzalez-Martin, O.J. Murphy, in: O. Savadogo, P.R. Roberge, T.N. Veziroglu (Eds.), *Proceedings of the 1st International Symposium on New Materials for Fuel Cell Systems*, Montreal, Canada, 9–13 July 1995, p. 104.
- [17] M. Watanabe, Y. Satoh, C. Shimura, *J. Electrochem. Soc.* 140 (1993) 3190.
- [18] A.P. Meyer, G.W. Scheffler, P.R. Margiott, U.S. Patent No. 5,503,944, 2 April 1996.
- [19] C.Y. Chow, B.M. Wozniczka, U.S. Patent No. 5,382,478.