



Short communication

A study of water adsorption and desorption by a PBI-H₃PO₄ membrane electrode assembly

T. Gu^a, S. Shimpalee^{a,*}, J.W. Van Zee^a, C.-Y. Chen^b, C.-W. Lin^c^a Department of Chemical Engineering, University of South Carolina, 301 Main St., Columbia, SC 29208, USA^b Institute of Aeronautics and Astronautics, National Cheng Kung University, Taiwan, ROC^c Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-sen University, Taiwan, ROC

ARTICLE INFO

Article history:

Received 16 May 2010

Received in revised form 17 June 2010

Accepted 18 June 2010

Available online 25 June 2010

Keywords:

PolyBenzimidazole

High Temperature Membrane

Fuel cells

PEMFC

Adsorption and desorption

Phosphoric acid

ABSTRACT

Data corresponding to the isotherms for the equilibrium water content of a PolyBenzimidazole (PBI)-H₃PO₄ High Temperature Membrane Electrode Assembly (HT-MEA) are presented over a range of temperatures from 30 °C to 180 °C. The data show values for the ratio of water to acid which range from 4.0 at 70 °C to 0.2 at –160 °C at 30 kPa of water vapor pressure. In addition to the equilibrium data, rates of adsorption are shown to have time constants on the order of 500 s and 2500 s at 70 °C and 50 °C, respectively. At temperatures above 100 °C the time constants for adsorption are on the order of 100 s. These data allow for the calculation of “acid dilution” in this HT-MEA during low-temperature excursions and start up/shut down.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The phosphoric acid doped PolyBenzimidazole (PBI-H₃PO₄) Membrane Electrode Assembly (MEA) has drawn a lot of attention due to its higher operating temperature (i.e., 140–200 °C) which results in a less complicated balance of plant for reformat fueling of stationary fuel cells. A recent review [1] has updated its development for fuel cell technologies and included polymer synthesis, membrane casting, physicochemical characterizations. Because this system operates at these higher temperatures, it removes the problem of water flooding that is common in conventional proton exchange membrane fuel cell (PEMFC) systems. However, water is generated at the cathode and the extent to which it equilibrates in the membrane has resulted in concerns about dilution of the acid especially during temperature at shutdown and for unexpected interruptions of the current. Data for this water content are absent in the literature perhaps because each type of MEA has a distinct level of H₃PO₄ doping [2,3] or a different interaction between the PBI and the water formulation of polymer [4–6].

For example, Daletou et al. [6] present thermogravimetric analyses that show water vapor interacts with the H₃PO₄ in a PBI/polysulphone membrane and that the H₃PO₄ can be dehy-

drated above 120 °C to form a H₄P₂O₇; Li et al. [2] have shown that water uptake increases with the acid concentration in the membrane at room temperature and Schmidt and Baurmeister [7] concluded that the membrane in the Celtec®-P 1000 MEAs was stable during stop/start cycles and that the degradation was due to corrosion of the cathode carbon-Pt catalyst rather than a loss of conductivity of the MEA corresponding to “acid dilution.”

In an effort to complement the exiting performance data on PBI-H₃PO₄ MEAs and membranes [1–8], we report here, data suitable for understanding changes in the ratio of water to H₃PO₄ at various temperatures and water vapor pressures in a Celtec®-P 1000 MEA. These ex situ data allow modelers to understand the water content of these MEAs and experimentalists to access the dilution of acid at low temperatures such as those, which may exist during shut down with humid gases.

2. Experimental

Commercially available high temperature PolyBenzimidazole (PBI) membrane electrode assemblies (MEA) (Celtec®-P Series 1000) were obtained from PEMEAS, LLC (currently BASF Fuel Cells).¹ The MEAs were cut into 6.25 cm² samples and the weight

* Corresponding author. Tel.: +1 803 576 6140; fax: +1 803 777 8142.
E-mail address: shimpalee@cec.sc.edu (S. Shimpalee).

¹ Note that these MEAs may not be state of the art with the new company, but that they allow a baseline to be established for the purpose of PBI-HT-MEA.

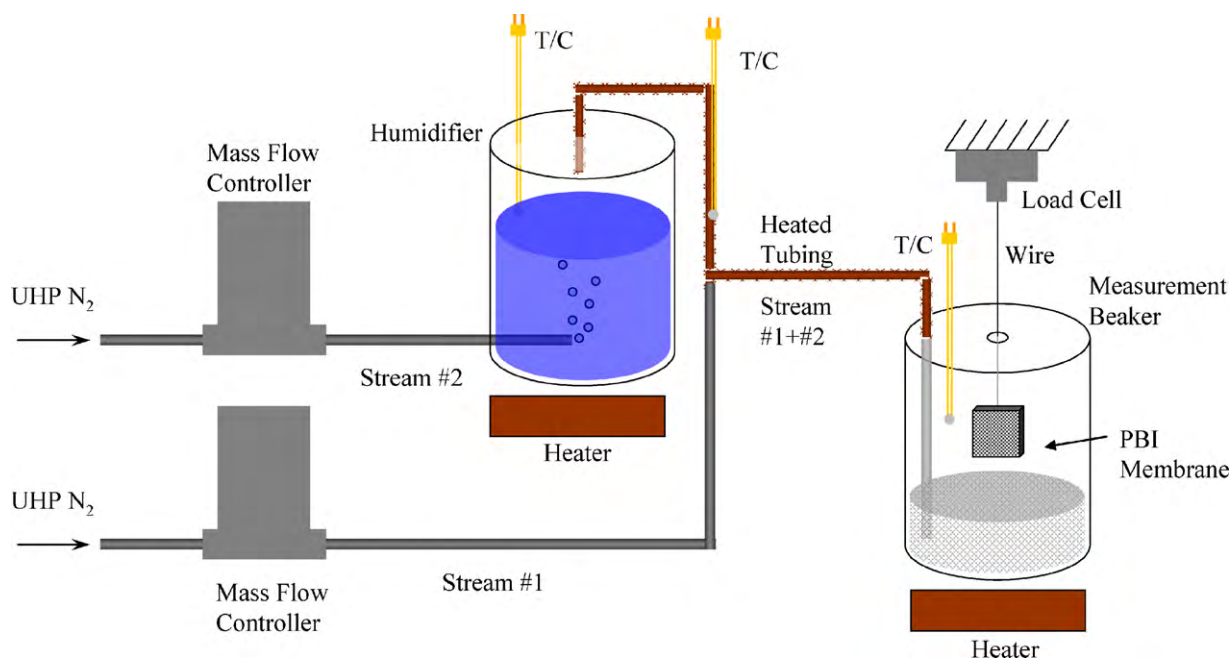


Fig. 1. Schematic experimental setup to measure water adsorption and desorption.

of each sample was measured. Since the MEA can absorb water from the environment, the samples were kept and handled in an air-tight container filled with dry, ultra-high purity nitrogen once the original package was opened.

The apparatus for measuring the water adsorption of PBI MEA is shown in Fig. 1. Two mass flow controllers (MKS1179A with a 500 sccm range) supplied ultra-high purity (UPH) nitrogen. The nitrogen stream #1 as labeled in the figure was the dry stream, which was fed directly into the measuring beaker. The nitrogen stream #2 was humidified with bottles (model #LF-HBA supplied by Fuel Cell Technology) prior to mixing with the dry stream. Water is automatically refilled into the water bottle with an Alldos 3L65 metering pump. The summation of the nitrogen flows through the two mass flow controllers and was kept at 500 sccm. The mixture gas was introduced into the measuring beaker through a heated tube to prevent condensation. Steel wool was used as a diffuser around the opening of the mixture gas inlet tube to aid with the uniformity of flow into the beaker. The measuring beaker had a glass jacket which allowed for temperature control maintained by circulating heated silicone oil in the jacket. The measurement beaker opening was covered with a piece of silicone rubber, which had a 0.3175 cm diameter hole, through which the sample could be suspended. A load cell was fixed above the measuring beaker. One end of a thin stainless steel wire was attached to the sensing point of the load cell and the other end of the wire was hooked to the sample through a small circle of stainless steel wire. The stainless steel wire was tested in situ and no corrosion due to phosphoric acid was observed. The weight of the sample was continuously monitored and recorded by a computer. A servo motor was used to adjust periodically the tare from the load cell to cancel the zero point drift. The nitrogen flow in the dry stream, the nitrogen flow in the humidified stream, and the humidifier temperature were computer controlled by mass flow meters. The dew point of the mixed steam could be set at any point below 100 °C.

The data correspond to experiments in which prior to the water adsorption and desorption experiments, a sample was equilibrated at the desired experimental temperature with a 500 sccm flow of dry UPH nitrogen flow until the weight stabilized. Then the partial pressure of water vapor in the inlet stream (corresponding to a

specified dew point) was introduced and the response of the sample weight change was recorded continuously for several hours. Note that this partial pressure of water vapor was set at lower value than saturated water vapor pressure of each temperature setup. Therefore there is no liquid water presented in the experiment. The transient weight change was monitored to ensure steady state was for each step change in humidity. The change in dew point could be from low to high, in which water adsorption was measured, or, from high to low, in which water desorption was measured. Multiple samples were used to obtain the data. In addition, the data were shown to be independent of MEA thickness through experiments where three MEAs were fastened together; data for λ (described below) for the triple MEAs were within the experimental error for a single MEA.

The net weight of a sample without phosphoric acid (i.e., the polymer weight) was obtained using the following procedure. A beaker was filled with DI water and the sample was suspended partially in the water of the beaker. Because of a density difference, the heavier phosphoric acid was leached out from the bottom edge of the sample and the streak of the downward acid flow could be seen clearly. The sample was soaked overnight and then removed and soaked in a second beaker of water. The pH of the water in the second beaker was tested and used to confirm that all phosphoric acid was leached out in the first beaker. Note that one equivalent acid that neutralizes benzimidazole nitrogen cannot be removed by this method and therefore PolyBenzimidazole structure of the sample remains the same. The sample without H_3PO_4 was removed, dried with compressed air, and weighed with an analytical balance. The H_3PO_4 in the water was titrated with NaOH solution and the amount of titrate consumed was recorded and used in calculations.

The additional equipment for the experiment is as follows. The load cell was a 10 g GSO-10 from Transducer Technology. Water is automatically refilled into the humidity bottles with an Alldos 3L65 metering pump. Temperatures were controlled by Love Control PID controllers (16A and 32 DZ with 992 option). The pH value was recorded using a HI 255 meter from Hanna Instruments. A National Instruments (NI 6211 multifunctional USB I/O) was used to send control signals to the mass flow controllers and to read flow rate values.

Table 1
Measured values of λ as a function of water vapor pressure for Celtec®-P Series 1000 MEA and confirmatory data for a Nafion® 117 membrane.

H ₂ O vapor pressure (kPa)	Temperature							
	30 °C	50 °C	70 °C	70 °C Nafion®	100 °C	120 °C	160 °C	180 °C
0.00	0.28	0.19	0.14	0.0	-0.15	-0.39	-0.78	-0.80
1.01	1.66							
2.02	2.75							
3.03	4.00							
4.04	6.11							
5.05	9.32	2.08	0.96	1.71	0.27	-0.09	-0.23	-0.30
10.1		4.38	1.64	2.47	0.40	0.02	-0.12	-0.17
20.1			2.98	3.79	0.62	0.19	-0.002	-0.04
30.1			4.11	7.09	1.05	0.46	0.10	-0.06
40.1					1.24	0.55	0.18	0.09
50.1					1.66	0.77	0.26	0.15
60.1					2.12	0.94	0.27	0.15
70.1					2.73	1.09	0.27	0.17

3. Results and discussion

In this work the weight change of PBI MEA was used to characterize the water adsorption and desorption ability. We used a dimensionless parameter, lambda (λ), for characterization and it corresponds to the number of water moles associated with one phosphoric acid mole at different conditions. Eq (1) is the formula to calculate the λ and again the moles of phosphoric acid for each sample was calculated from a titration experiment. In this study, approximately 1.18×10^{-3} mol of phosphoric acid were detected in a 6.25 cm^2 sample of PBI MEA.

$$\lambda = \frac{(G - G_0)/\text{molecular mass of water}}{n_{\text{total.H}_3\text{PO}_4}}$$

G : sample weight after water adsorbed (g)
 G_0 : sample weight before water adsorbed (g)
 $n_{\text{total.H}_3\text{PO}_4}$: total amount of phosphoric acid (mol)
 $= 1.18 \times 10^{-3}$ (mol)

The value of G_0 at dry conditions was 0.48053 g and it changed to 0.4722 g and 0.4640 g at 120 °C and 160 °C, respectively. Thus, λ for the dry condition at room temperature, 120 °C and 160 °C is 0.0, -0.3924, and -0.7781, respectively. These negative values are a result of the dehydration (i.e., reaction (2)) of phosphoric acid observed in Refs. [3] and [10].



Table 1 shows the data which can be summarized with the regressions in Eqs. (3)–(8):

$$\text{At } 30^\circ\text{C} : \lambda = 0.2853 + 167.7011 * P - 3952.5919 * P^2 + 83932.4486 * P^3 \quad (3)$$

$$\text{At } 70^\circ\text{C} : \lambda = 0.1483 + 16.3300 * P - 12.1791 * P^2 + 5.9968 * P^3 \quad (4)$$

$$\text{At } 100^\circ\text{C} : \lambda = -0.0737 + 5.1597 * P - 8.0942 * P^2 + 9.2425 * P^3 \quad (5)$$

$$\text{At } 120^\circ\text{C} : \lambda = -0.3292 + 3.7012 * P - 4.9455 * P^2 + 3.7064 * P^3 \quad (6)$$

$$\text{At } 160^\circ\text{C} : \lambda = -0.6382 + 5.4659 * P - 11.5761 * P^2 + 8.0637 * P^3 \quad (7)$$

$$\text{At } 180^\circ\text{C} : \lambda = -0.6737 + 5.3261 * P - 12.2678 * P^2 + 9.2177 * P^3 \quad (8)$$

Fig. 2 shows the data for the PBI MEA water content in terms of λ with dimensionless curves of water vapor pressure at different temperatures. Thus, these should be considered isotherm data for the mole fraction of water over phosphoric acid in PBI-type HT-MEA. This figure shows that the weight of sample increases with the increasing of water vapor pressure at a fixed temperature. This result reflects that the water content is not only a function of temperature, but also decreases with temperature. On the other hand, the slope of the weight change over water vapor pressure becomes higher when the temperature becomes lower. That means the PBI-type MEA becomes more sensitive to humidity at lower temperatures. Consequently, the cycles in the temperature or humidity could result in an increase of water content, which in the extreme case may result in dilution of the acid and a long-term loss in conductivity of the membrane. Note that these long-term losses were observed experimentally in situ for the given shut down and start up protocol [7].

Also in Fig. 2, two graphs of water content in the Nafion 117 membrane, which taken from Springer et al. [9], are included to compare with those data from PBI MEA at a temperature of 30 °C and 70 °C. Note that the lambda value of Nafion 117 is the water content per mole of SO_3^- . At a low temperature of 30 °C, both PBI MEA and Nafion 117 membrane show similar profiles with a steep slope. At a water activity of 1.0 ($P_{\text{H}_2\text{O}}$ kPa/101.3 kPa = 0.04), the lambda value of PBI is much lower than Nafion 117 (e.g., at a temperature of 30 °C, lambda of PBI ≈ 9 and Nafion 117 ≈ 14). When the

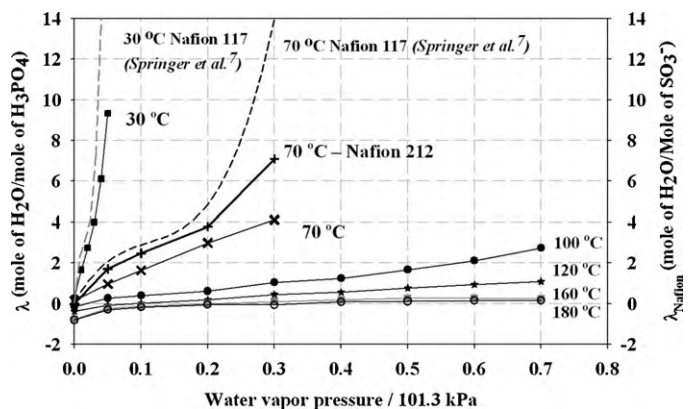


Fig. 2. Change of lambda (mole fraction of water/phosphoric acid) with water vapor pressure.

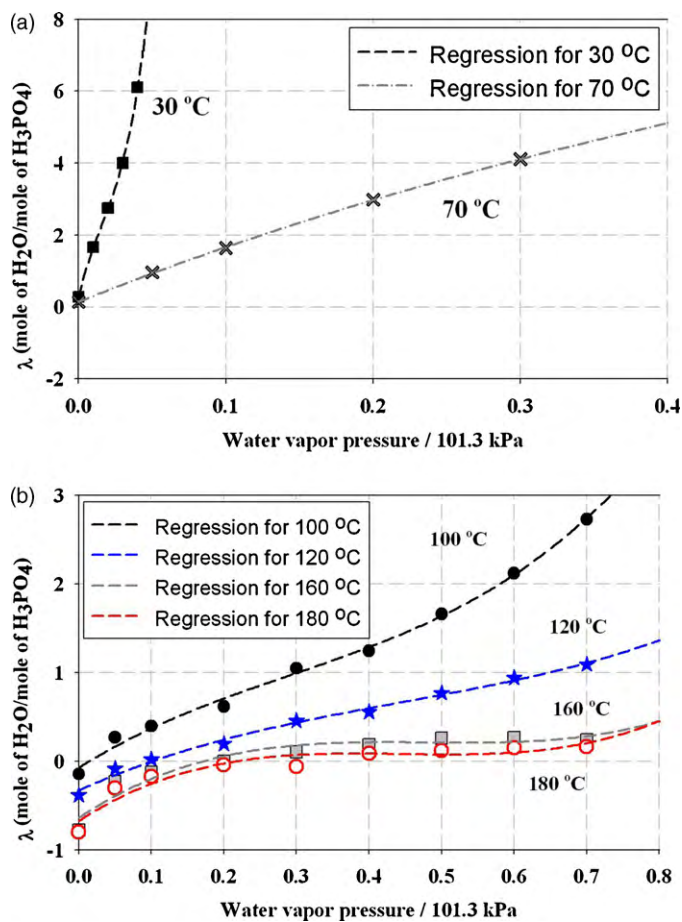


Fig. 3. (a) Comparison of regression equations with data from Table 1 for 30 °C and 70 °C. (b) Comparison of regression equations with data from Table 1 for temperatures above 100 °C.

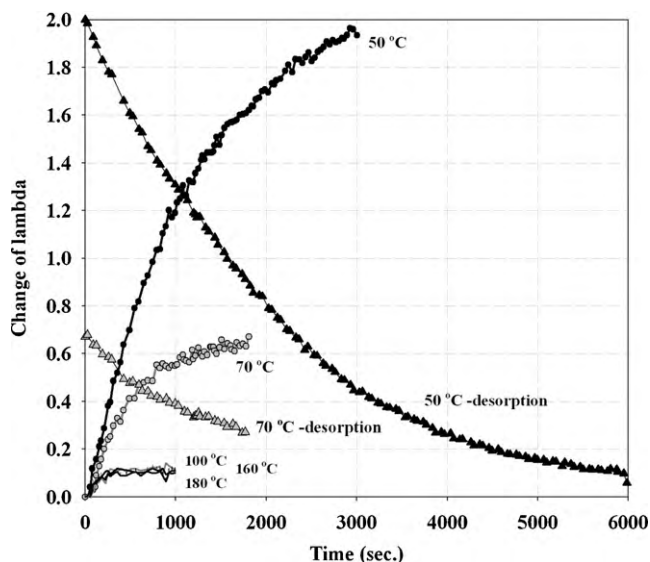


Fig. 4. Transient response of water content for water partial pressure changes from 5.05 kPa to 10.1 kPa at different temperatures.

temperature is increased to 70 °C, both samples have a less steep slope than those values at a lower temperature. The value of λ at a water saturation level of the PBI MEA was consistently lower than Nafion 117.

Fig. 3(a and b) compares the regression lines (i.e., Eqs. (3) and (4) and Eqs. (5)–(8)), respectively, with the data from Fig. 2 and Table 1. The fit is relatively good. It should be noted that we chose to use water vapor pressure rather than activity for the presentation and the regression because the temperature exceeds the boiling point of water and representation of the data against activity condenses the x-axis as the P^{sat} at 120 °C, 160 °C and 180 °C increases substantially.

As a measure of the speed at which the equilibrium is obtained for the thickness of the Celtec 1000-P MEA, Fig. 4 shows the transient response of λ to a step change of water partial pressure from 5.05 kPa to 10.1 kPa. The results show an increase in the response time to reach steady-state at lower temperatures. This figure also shows that the effect of temperature is more obvious at a lower temperature than at a higher one.

4. Conclusions

The isotherms for adsorption and desorption of water in PBI-type HT-MEA were successfully obtained between 30 °C and 180 °C. There is evidence that H_3PO_4 acid would be diluted at lower temperature and/or higher water vapor pressure. However, the data also show a rather rapid rate of attainment of equilibrium for this MEA. Thus, short excursions to low temperatures in a humid environment, will probably not result in an accumulation of water in the MEA and a subsequent “dilution” of the acid in this MEA. Further, these data support previous work which indicated that loss in long-term durability is not a function of water adsorption by the MEA. On the other hand, laboratory experiments should carefully document the procedures for start up and shut down of this PBI- H_3PO_4 MEA system. This documentation should reveal the extent of time at low temperature under high humidity since these data presented here indicate that as much as six moles of water can equilibrate with the MEA at 30 °C and this could lead to the loss of acid at those low temperatures.

Acknowledgements

This project was supported by the US Department of Energy (DE-FC36-06G086041). The authors also appreciate the financial support from the Graduate Students Study Abroad Program sponsored by the Taiwan National Science Council (NSC), which sponsors Chen-Yu Chen and Chih-Wei Lin’s research at the University of South Carolina. (NSC-096-2917-I-006-108 and NSC-097-2917-I-110-108).

References

- [1] Q. Li, J.O. Jensen, R.F. Savinell, N.J. Bjerrum, *Polym. Sci.* 34 (2009) 449–477.
- [2] Q. Li, R. He, R.W. Berg, H.A. Hjuler, N.J. Bjerrum, *Solid State Ionics* 168 (2004) 117–185.
- [3] Y.-L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, *J. Electrochem. Soc.* 151 (2004) A8.
- [4] G. Qian, D.W. Smith, B.C. Benicewicz, *Polymer* 50 (2009) 3911–3916.
- [5] S. Yu, H. Zhang, L. Xiao, E.-W. Choe, B.C. Benicewicz, *Fuel Cells* 9 (4) (2009) 318–324.
- [6] M.K. Daletou, J.K. Kallitsis, G. Voyiatzis, S.G. Neophytides, *J. Membr. Sci.* 326 (2009) 76–83.
- [7] T.J. Schmidt, J. Baurmeister, *J. Power Sources* 176 (2008) 428–434.
- [8] S. Yu, L. Xiao, B.C. Benicewicz, *Fuel Cells* 8 (3–4) (2008) 165–174.
- [9] T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, *J. Electrochem. Soc.* 138 (1991) 2334.
- [10] J. Lobato, P. Canizares, M.A. Rodrigo, J.e.J. Linares, *Electrochim. Acta* 52 (2007) 3910–3920.