Development of Simultaneous Measurement of Water Vapor Adsorption and Proton Conductivity to PEM for PEFC

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Abstract

A new system "MSB-AD-V-FC (BEL JAPAN Inc.)" has been developed, which has made it possible to simultaneous measurement of a water vapor adsorption and a proton conductivity to PEM under various experimental conditions (Temp; 353-473K, Humidity;0-95%RH, Press; atmospheric pressure-1.0MPa). The upper mix-conditioned run to PEM enables in a single original chamber considering of both principles of a gravimetric method for the water vapor adsorption and an alternating current impedance method for proton conductivity and automatically proceeds by software, BEL FCE™. Both investigations for the Nafion 112, 1135 and 1035 was achieved under the several experimental conditions. In the case of a run, Nafion 112, 353K, 90%RH and 200kPa, the adsorbed amount for the water vapor and the conductivity (1kHz) was 0.137 (g/g) and 0.117 (S/cm), respectively.

Introduction

Polymer electrolyte fuel cell (PEFC) invented by GE Co. Ltd. in the latter of 1950's has been taking advantage of the motor vehicles and the electric power supply for civilian applications because of low operation temperature and compact size. Thereby, the demand for the PEFC will be higher and higher year by year from their point of views. The points of a membrane development are particularly to have heat resisting properties, water holding properties and high proton conductivities under the low humidity condition because it is very important for the high functional membrane in the PEFC to have a low cost and long lifetime under the various environments.

When investigating these properties for the membranes, each data for them have been gotten by the each instruments and examined them by the researcher in spite of taking too much time. For the achievement of higher efficiencies to the polymer development, we have developed simultaneous measurements between water vapor adsorption and proton conductivity to the polymer electrolyte membrane (PEM) under the various sets of experimental parameters.

Experiment

Experimental Apparatus

The process flow and the external diagram for a new system "MSB-AD-V-FC" is shown in Figure 1 and Figure 2, respectively. The total apparatus (W2500xH1500xD1000) consists of 3 parts of an experimental parameter control part, a simultaneous sample measurement part and a system control part with data logging as shown in figure 2. The inactive (inert) gas, in this case of N2, and water were mixed into the evaporator and vaporized at high temperature. The water vapor got into a bottom of sample cell (Figure 4) equipped with a sample holder for magnetic suspension balance shown in Figure 3 and an electrode cell for impedance measurements. The temperature in the cell was controlled by an oil circulation pump and the stabilization was ±0.1℃ and around the all of tubing, valves and several instruments form the evaporator to the condenser were controlled not to occur water condensation in the system by the air circulating bath or heater flexible horses. The two membranes were fixed onto the both the holder and the cell and able to pretreatment at vacuum or gas flow condition before the measurement.

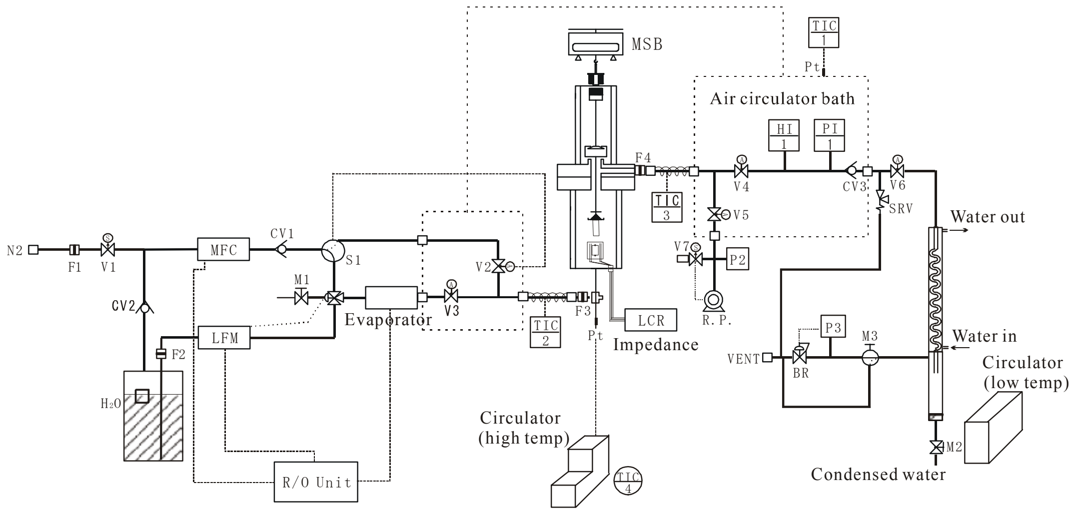

Figure 1. Process flow diagram for evaluation of high functional membrane

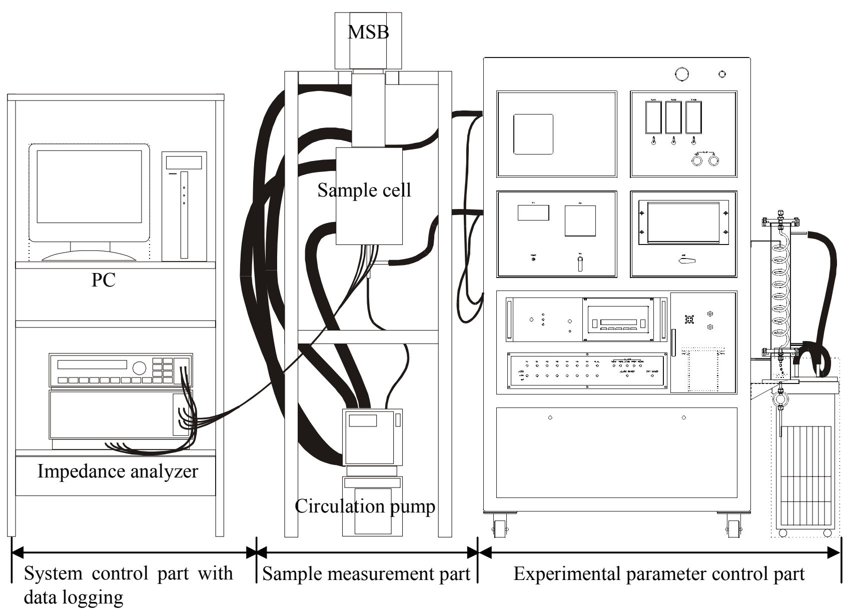

Figure 2. External diagram for MSB-AD-V-FC

When passing through the cell, the gas under the high or low temperature and humidity was supplied into the condenser to remove the part of water and the pressure of the gas was easily controlled by an automatic back-pressure regulation system. The various sets of parameters of temperature (353-473K), pressure (0.1-1.0Mpa), humidity (0-95%RH) and frequency of an Impedance analyzer etc. were automatically changed by the system control part with an original software BEL-FCE™. It was the parameters control, data logging as well as equiribulium judgment of water vapor adsorption and proton conductivity. The usual simultaneous measurements were 4steps sequence of a pretreatment, a stabilization of experimental parameters (max. 999 step), an equiliburium of the water vapor adsorption and proton conductivity and an after-treatment.

Measurement of Water Adsorption Amount & Proton Conductivity

Simultaneous measurement was achieved by the magnetic suspension balance (MSB: Rubotherm GmbH) considering of gravimetry and by an impedance analyzer (4263B: Agilent Technology Co.) utilizing the frequency response method. Each measurement was completed in the thermostatic sample cell equipped with the sample holder and 4 terminals electrode cell. Although the MSB could be done two kinds of values between the sorption amount and the density by the use of the sinker as illustrated in Figure 3, the balance without the sinker was applied because of not too much high buoyancy at the experimental conditions.

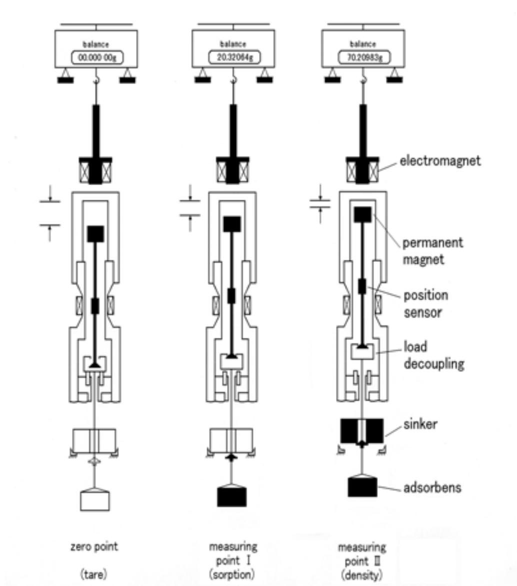

Figure 3. Principal of magnetic suspension balance (MSB)

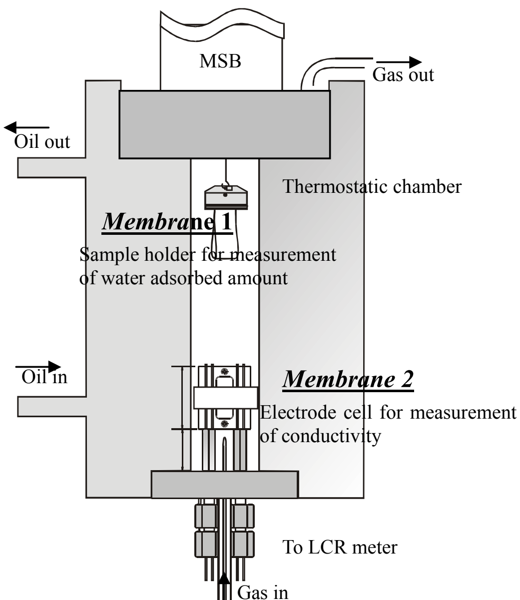

Figure 4. Sample cell for simultaneous measurement of gravimetry and impedance for high functional membrane

Differences between water adsorption and pre-adsorption to PEM are calculated by the Eq. (1)

$$q_n = (W_{MPn} - W_{ZPn}) - (W_{MP0} - W_{ZP0}) \quad (1)$$

where W_{MP} (g) and W_{ZP} (g) means the amount of water vapor sorption at an equilibrium point and of the zero point of the balance, respectively. The subscript of *n* and *0* implies the n^{th} point of the equilibrium and 0^{th} point of the following pretreatment. Finally, the water adsorbed amount (g/g) is defined as the value q_n divided by the membrane amount following the pretreatment.

Proton conductivity κ (S/ｃm) is also gotten by the Eq.(2)

$$\kappa = \frac{1}{R} \cdot \frac{\frac{B}{10}}{\frac{D}{10^4} \cdot \frac{E}{10}} \quad (2)$$

$$Z = R + Xi \quad (3)$$

$$\tan \Theta = \frac{X}{R} \quad (4)$$

where B (mm), D (μ m) and E (mm) are the distance between electrode, membrane thickness and width, respectively. Impedance Z (Ω) is defined as Eq. (3) and (4). R (Ω) and X (Ω) are the real and the imaginary component of Impedance Z. The impedance value is examined by the frequency response method (100Hz, 120Hz, 1kHz, 10kHz and 100kHz) and determined by stabilization of the angle θ (rad.) from R and X.

Result & Discussion

Influence of Ion-exchange Capacity

Relationship between the water adsorbed amount (g/g) and the proton conductivity (S/cm) of PEM to the related humidity (%RH) under the experimental conditions of 373K and 200kPa was depicted in the Figure 5. The utilized samples in the experiment were two types of membranes that were different ion-exchange capacity, so-called Nafion 1135 (N1135) and Nafion 1035 (N1035). Nafion^R (Du pont) is a typical sample of the fulurinated alkyl sulfonate ion-exchange membrane used as the electrolyte of PEFC. The ion-exchange capacity of N1135 and 1035 is 0.89 (meq./g) and 1.01 (meq./g), respectively and the both thickness is 88μm. The surface of the PEM was pretreated to stabilize membrane conditions before the measurements, which was oxidation by H_2O_2 (3.0Vol%) to remove the some organic compounds and protonation by HNO_3 (1mol/l).

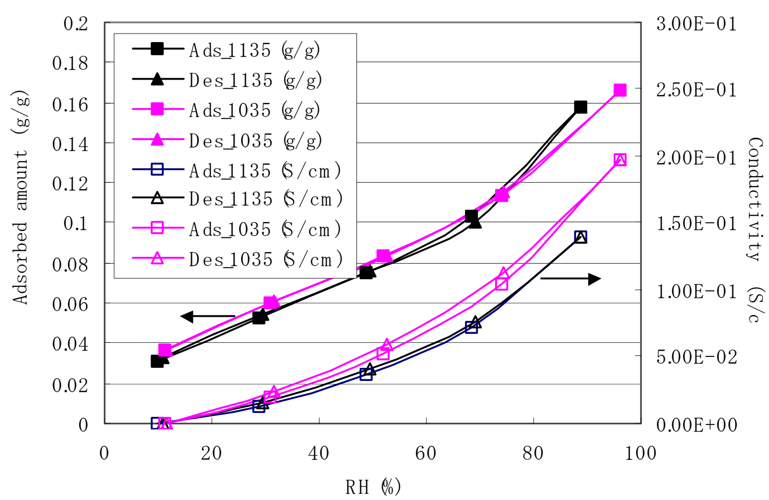

Figure 5. Influence of ion-exchange capacity to adsorption amount and proton conductivity (100℃. 200kPa)
Nafion1135 : 0.89(mequiv/g) Nafion1035 : 1.01(mequiv/g)

Experiment was carried out by humidification and dehumidification from 10%RH to 90%RH under the above conditions. The water adsorbed amount and the proton conductivity was getting higher and higher when increasing the humidity. There was no hysterisis in the both of them. The both properties of N1035 were larger than those of N1135 in our expected.

Effect of Membrane Thickness

Influence of membrane thickness of N112 (50μm/ 0.89meq/g) and N1135 (88μm/ 0.89meq/g) was examined at the condition of 353K and 200kPa. The results between adsorbed amount and conductivity through the humidification and dehumidification were shown in Figure 6. The both properties were almost same until 50%RH because of the same ion-exchange capacity. On the other side, the both value of N1135 were higher than those of N112 up to 70%RH. Particularly, the data of N1135 was 20% larger than that of N112 in the case of 90%RH because of the different posture swelling of the membrane, which the N112 structure of the water vapor adsorption might be a little bit unstable for the reason of thin comparing to the N1135. The maximum value of the water adsorption amount and the conductivity under the 90%RH, 353K of temperature and 200kPa of pressure were respectively 0.14 (g/g) and 0.12 (S/cm) for N 112 and 0.16 (g/g) and 0.135 S/cm for N1135.

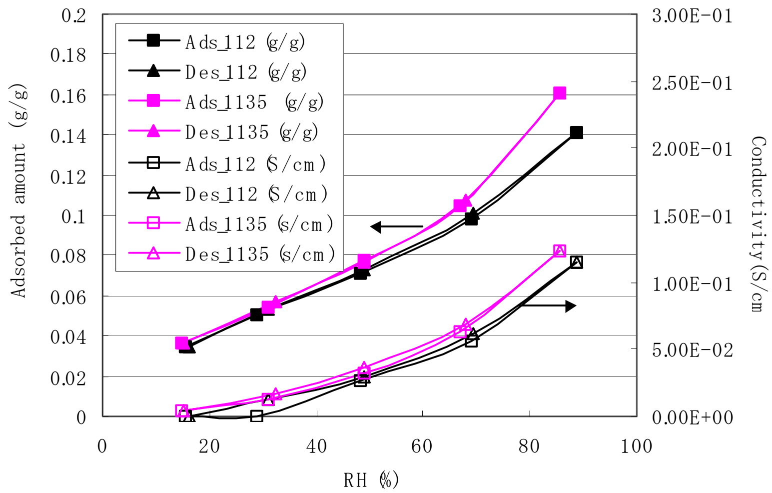

Figure 6. Dependence of membrane thickness to adsorbed amount and proton conductivity under the same ion-exchange capacity（80℃. 200kPa）(Nafion 112: 50 μ m, Nafion 1135: 88 μ m)

Temperature Dependency

The water adsorption and proton conductivity to N112 were investigated under the condition of 90%RH and 200kPa in changing the temperature from 333K to 393K. Adsorbed amount was getting

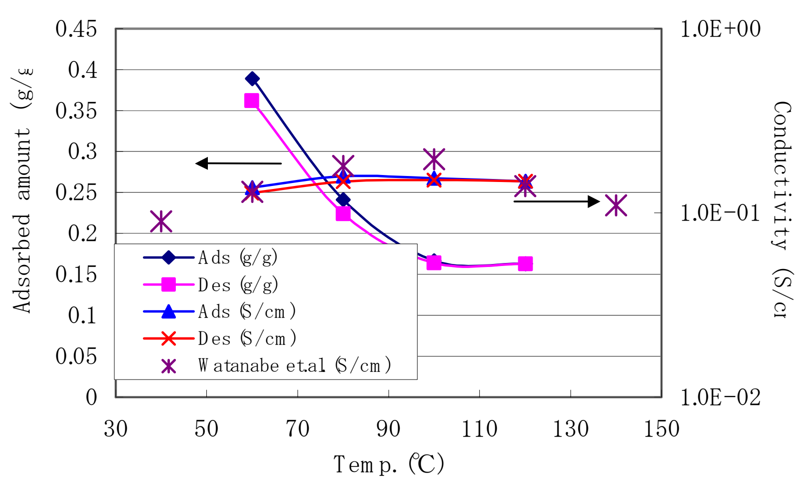

Figure 7. Water adsorption amount and proton conductivity to Nafion112 in changing measurement temperature （Present work: RH90%. 200kPa）(cf. Watanabe et. al: RH100%)

down when increasing the temperature as illustrated Figure 7. The adsorption amount of 333K was twice as high as that of 393K. There was a phenomenon of hysterisys when increasing and decreasing the temperature because the structure of water adsorption in the membrane occur the part of destruction for the high temperature. It was very unique that the conductivity was low in spite of high water adsorption amount at the 333K. It was higher and higher up to 353K and lower and lower from 353K to 393K. These dependencies were almost same as the examination from Watanabe et.al. that are under the experimental conditions of 100%RH.

Reproducibility and Stabilization of the Apparatus

The humidification (10-90%RH) and dehumidification (90-10%RH) was repeated to confirm the reproducibility and the stabilization of the conductivity, the adsorption amount and the θ value of N112 at

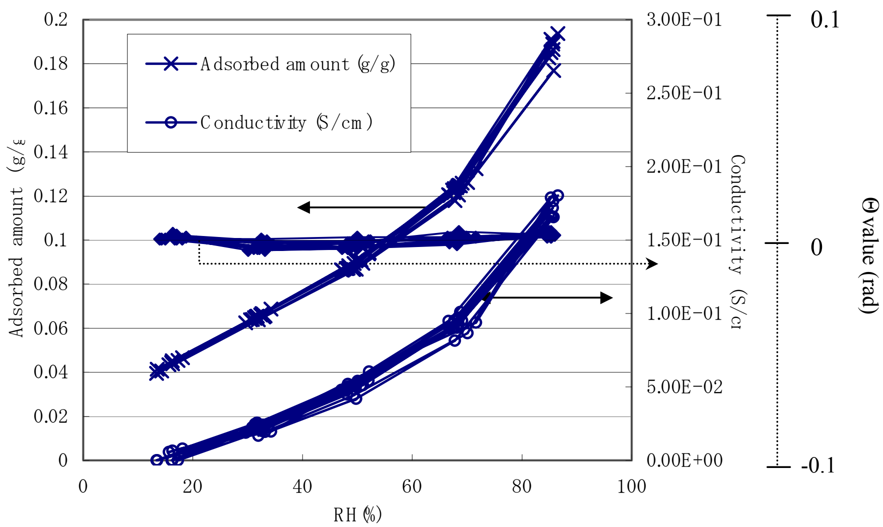

Figure 8. Examination of reproducibility and stabilization for proton conductivity with θ value at 1kHz and water adsorbed amount to Nafion 112（80℃. 200kPa）

the 200kPa and 353K. The repeatability experiment of 8 times was carried out and the results were shown in the Figure 8. The reproducibility and stabilization of both conductivity and adsorbed amount were defined as the results. The θ value (1kHz) was so stable that only the impedance from the direct current component was considered in this measurement.

Conclusion

A new system "MSB-AD-V-FC (BEL JAPAN Inc.)" has been developed, which has made it possible to simultaneous measurement of a water vapor adsorption and a proton conductivity to PEM under the various sets of experimental conditions (Temp; 353-473K, Humidity;0-95%RH, Press; atmospheric pressure-1.0MPa). The mix-conditioned run to PEM enables in a single original chamber considering of both principles of a gravimetric method for the water vapor adsorption and an alternating current impedance method for proton conductivity and automatically proceeds by software, BEL-FCE™. As the example of the experiment, investigations for the Nafion 112, 1135 and 1035 was achieved under the several experimental conditions. The both value from the difference of ion-exchange capacity between N1135 and N1035 was cleared. We also found out that the thick membrane of N1135 has larger conductivity than thin membrane of N112. There was no hysterisys of the both data through the humidification and dehumidifization. However, when changing the temperature, there was the phenomenon because of the changing the structure of the polymer for the high temperature. The reproducibility and stabilization was also examined and defined by the repeatable experiment.

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