Gas Permeability Test Protocol for Ion-Exchange Membranes

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The membrane-based electrolysis of water is a growing topic of interest due to the advantages of employing membranes in hydrogen production efficiency and system safety over the traditional alkaline water electrolysis. Ion-exchange membranes with low gas permeability are highly desirable for stable and safe operation of membrane-based water-splitting technologies, hence gas permeability through ion-exchange membranes needs to be properly assessed with standardized methods. We addressed three methods to measure gas permeability of ion-exchange membranes, a pressure permeation cell, chronoamperometry microelectrodes, and *in situ* testing of the membrane electrode assembly, and provide a guideline for choosing the appropriate method for the targeted operating conditions of the water electrolyzers.

INTRODUCTION

Electrochemical splitting of water to generate green hydrogen as an energy carrier is a promising method for sustainable fuel production. Compared to the traditional alkaline electrolyzer that uses aqueous alkaline electrolytes confined in a porous diaphragm, solid electrolyte water electrolyzers use ion-conducting membranes serving both as electrolytes and as a gas separator. This zero-gap design using non-porous membranes has distinct advantages in terms of efficiency, safety, and durability: low internal resistance, high hydrogen production rate, high-pressure operation, and the ability to prevent intermixing of the gaseous products.

The proton exchange membrane (PEM) water electrolyzer splits water at the anode into oxygen and protons, then the proton migrates through the PEM to the cathode where hydrogen is evolved. On the other hand, the anion exchange membrane (AEM) water electrolyzer splits water at the cathode into hydrogen and hydroxide ions, and the latter migrates through the AEM, liberating oxygen at the anode. Both membrane-based water electrolyzer systems allow the operation of the cell under differential pressure to produce high-pressure hydrogen and atmospheric pressure oxygen to minimize the need for additional mechanical compression for hydrogen use or storage (Motz et al., 2021). Preventing physical crossover of the gaseous products of electrolysis is of particular interest due to the flammable nature of hydrogen and possible formation of an explosive mixture of hydrogen and oxygen (Grigoriev et al., 2009; Xiang et al., 2016). In addition, interdiffusion of reactant gases may cause the formation of aggressive radical species such as peroxide, leading the chemical degradation of the ion-exchange membranes, especially perfluorosulfonic acid-based PEMs. Therefore, a proper measurement of the gas permeation rate across the membrane is necessary in the context of efficiency, safety, and durability of water electrolyzer systems.

In this protocol, three methods used for the measurement of gas permeability through an ion-exchange membrane are summarized and described in a procedure to help to establish a guideline for the ion-exchange membrane–based water-splitting technology community.

PROTOCOL SCOPE

Scope and Applicability

- This protocol is designated to develop standard procedures for the measurement of gas permeability of an ion-exchange membrane, including PEM and AEM. Hydrogen and oxygen would be the gases of the interest for the purpose.

Summary of Method

- The gas permeation rate can be measured using (A) a pressure permeation cell, (B) chronoamperometry with microelectrodes, or (C) *in situ* testing of the membrane electrode assembly (MEA). A pressure permeation cell is used with controlled humidified gas flow and gas chromatography (GC) or mass spectrometry. For the chronoamperometric technique, a microelectrode is used for hydrogen permeability, and the oxygen permeability can be calculated from the voltammetric limiting currents. *In situ* testing uses MEA configurations for fuel cell testing for hydrogen or oxygen permeability measurement, quantifying the limiting current of the electrochemical reaction through the membrane.

Personnel Qualifications/Responsibilities

- The user should be properly trained in hydrogen safety and pressure safety prior to the permeability measurement. The user should be properly trained to safely operate the instruments and able to perform the analysis to collect data used for permeability coefficient calculation.

Health and Safety Warning

- The user should be wearing appropriate personal protective equipment, including protective eyewear, gloves, and laboratory coats, in the laboratory at the time when the measurement procedure is followed. The use of compressed gases in laboratory settings need to be permitted prior to protocol implementation.

Equipment and Supplies

The following equipment and supplies are needed for each measurement:
A) Pressure Permeation Cell
  - For the measurement at low pressure, a conventional diffusion cell could be used. For high-pressure testing, an electrolyzer cell rated to a pressure greater than the highest pressure is required for the measurement, that is, EH-50 from Greenlight (rated to 50 bar).
  - A porous transport layer (PTL) and gas diffusion layer (GDL) will play an important role in H_2 permeation as they will affect the compression of the membrane. Use a Ti sinter or Ti felt for the anode PTL, that is, 2GDL10-0.25 Bekaert, and Ti PTL or carbon GDL for the cathode GDL, that is, MGL370, AvCarb.
  - A measure of 1–2 mil (1 mil = 0.001 inches or 25.4 μm) of PTFE for the sub-gasket.
  - An instrument to monitor the gas product, that is, gas chromatography (GC).

B) Microelectrode Chronoamperometry
  - Pt microdisk working electrode.
  - Pt counter electrode and Pt dynamic hydrogen electrode.
  - A controlled humidity chamber for control over gas, pressure, humidity, and temperature.
  - A potentiostat, that is, EG&G PAR Model 283.
  - Syringe filters (PTFE, 0.2 or 0.45 μm).
  - A measure of 0.1 M of H_2SO_4 or 0.1 M of NaOH aqueous solution.
C) *In Situ* Measurement in MEA
  - A standard single-cell hardware (one example is shown in **Figure 1**).
  - GDL.
  - A fuel cell station, that is, Scribner 850e.
  - An electrochemical interface potentiostat, that is, Solartron 1287.

PROCEDURE

Step-By-Step Procedure

A) Pressure Permeation Cell (Broka and Ekdunge, 1997; Bernt et al., 2020)
  1. Prepare a flat, dry membrane piece with a known thickness (wet) and a matching hardware plate (greater than the active area, e.g., 100 cm^2 plate for 50 cm^2 active area) to provide a good seal for the hardware. Any wrinkles in the membrane may lead to gas leak and hardware not being able to achieve the desired pressures.
  2. Assemble an electrolyzer cell–like standard operation with the exception of no catalyst layer on electrodes and utilizing a PTL without Pt coating (**Figure 1**), where each plate is connected to a gas inlet and outlet. Adding a sub-gasket between the PTL and the membrane is recommended to avoid PTL edges causing pinholes in the membrane. For instance, for the PTL area of 50 cm^2; the sub-gasket masks the active area up to 49 cm^2.
  3. Before starting the experiment, check the pressure to ensure proper sealing of the hardware at high pressure. Flow N_2 on both the anode and cathode side at a fixed flow rate (<300 sccm) through a mass flow controller similar to the actual experiment. Gradually increase the pressure on the cathode side to the highest operating pressure while the anode side is at 1 atm. If the anode side is not able to reach the highest pressure, then repeat the cell assembly with a new membrane. For low-pressure testing, the cathode pressure should be 5 atm, and for high pressure, the cathode pressure should be 30 atm.
  4. After the pressure check, flow H_2 to the cathode side and a carrier gas to the anode side at a fixed flow rate (<300 sccm). Flow water at 2 ml min^{-1} cm^{-2} through a pump on the anode side to provide sufficient hydration to the membrane. The carrier gas can be either N_2 or O_2 depending on the membrane; if the membrane contains gas recombination catalyst, the carrier gas should be O_2 otherwise N_2 could be used. Set partial pressure of the
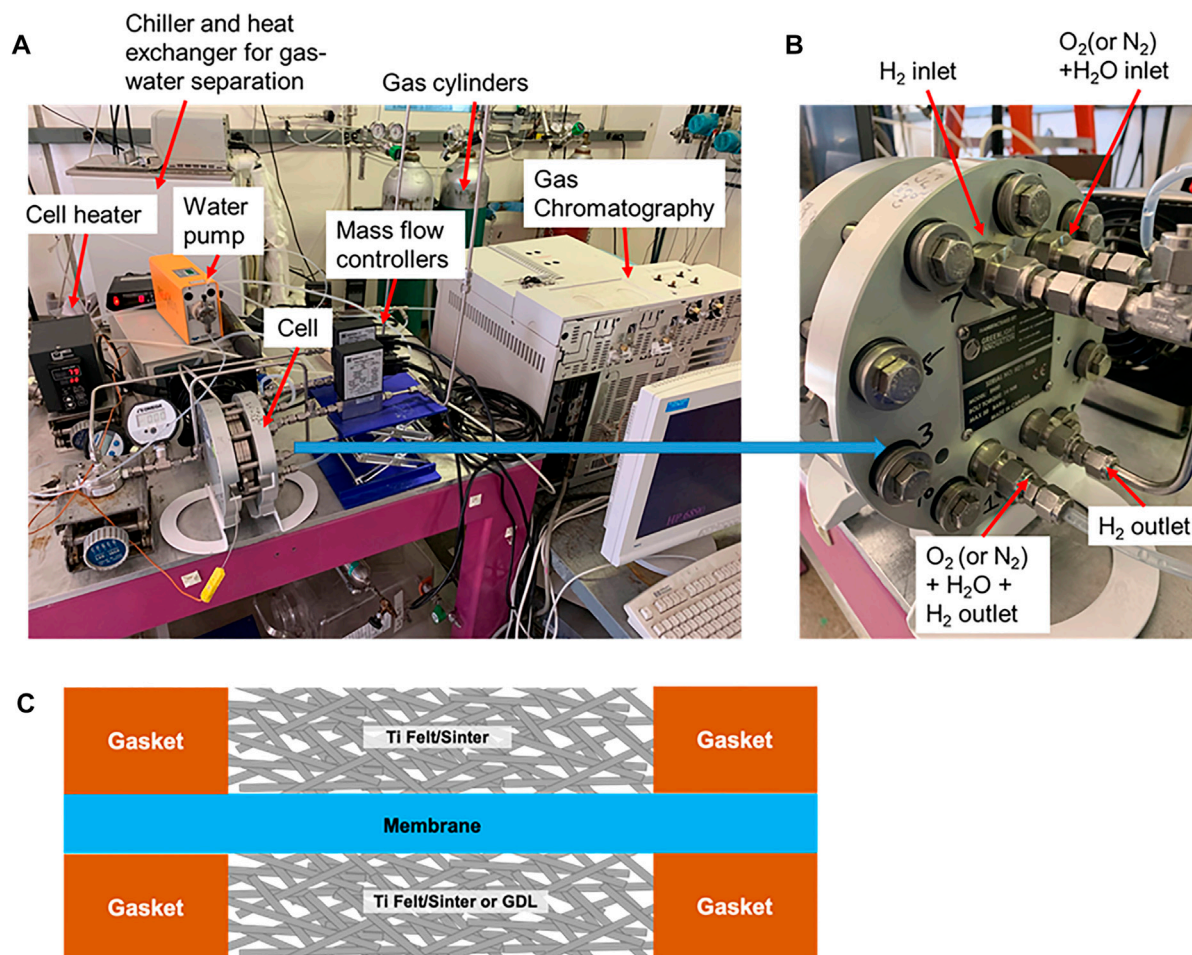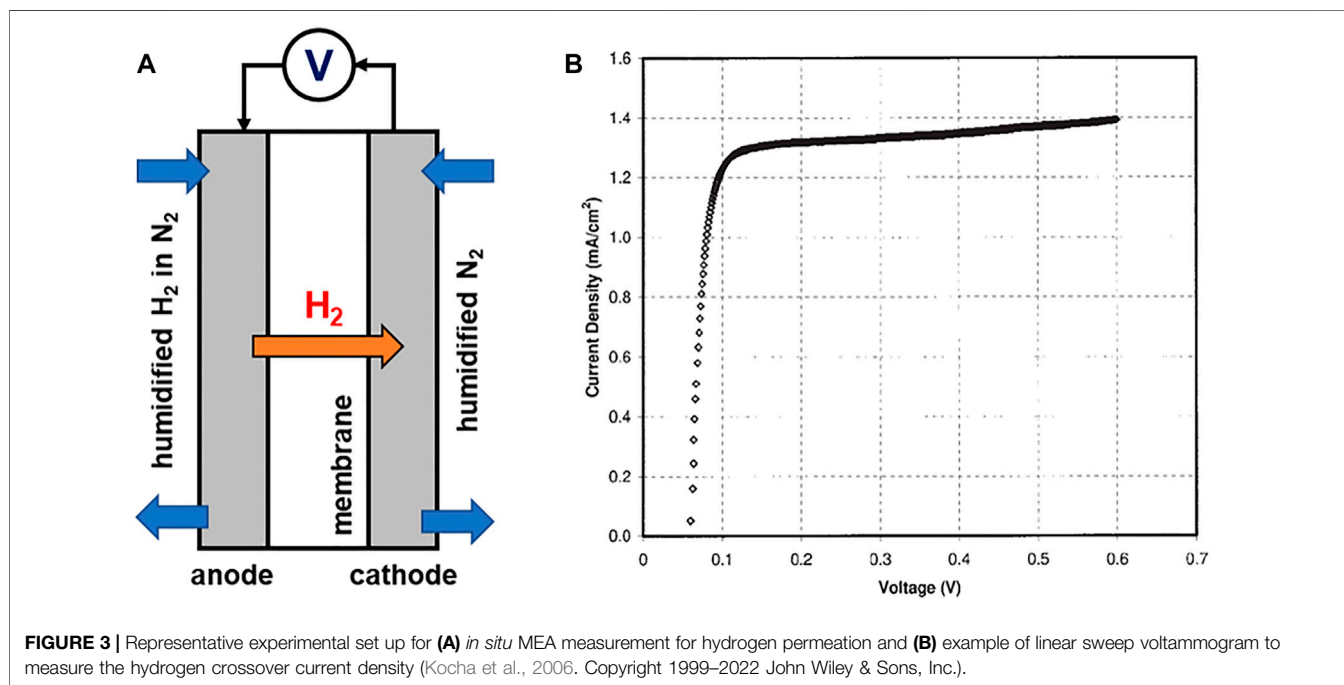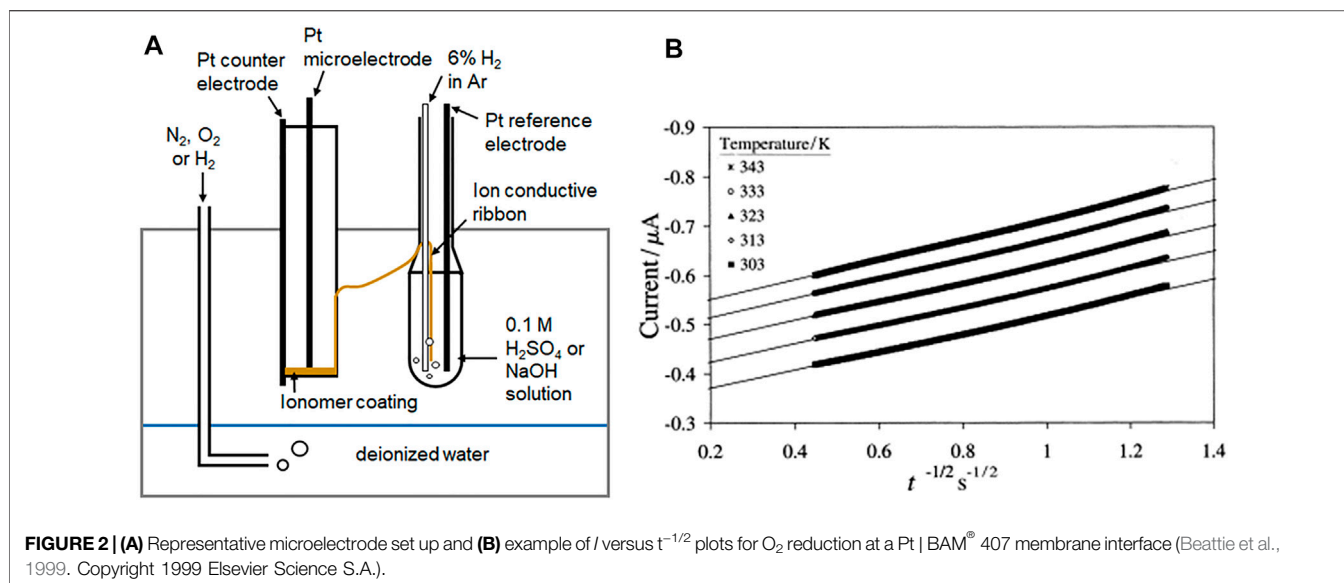
FIGURE 1 | (A) Experiment set up for *ex situ* gas permeation measurement using a pressure permeation cell, **(B)** closed-up view of the cell with gas inlet and outlets, and **(C)** cell assembly diagram.

H_2 and carrier gas at 1 atm accounting for the saturation pressure of water at the operating temperature (50–80°C).

5. The exhaust of the anode should be connected to a gas–water separator or chiller to remove the water from the gas.

6. If O_2 is used as carrier gas, an inert gas (N_2) should be introduced at a known flow rate after the anode exhaust and before the gas–water separator. When the carrier gas is O_2, gas dilution with N_2 is added, to prevent the exhaust gas from the gas–water separator from reaching flammable concentration levels of H_2. For safety, it is advised to maintain the H_2 concentration in the exhaust stream to less than 1% using dilution. This step is not required if N_2 is used as a carrier gas.

7. The gaseous exhaust from the gas–water separator could be connected directly to the analyzer (GC).

8. After the desired pressure is set on the anode and cathode, let the cell stabilize for about 30 min before taking measurement in GC. Repeat the measurement until a stable concentration reading is reached, that is, at least five measurements.

9. Take measurements of the H_2 concentration in the carrier gas at different partial pressures of H_2 up to the operating conditions or system limitation.

10. If N_2 dilution is utilized, ensure to correct the H_2 concentration for the dilution with the N_2 flow rate used.

B) Chronoamperometric Technique Using Microelectrodes (Beattie et al., 1999; Gode et al., 2002; Astill et al., 2009; Chlistunoff, 2014; Yim et al., 2015)

1. Dissolve an ion-exchange membrane in a solvent to prepare a 5 wt% ionomer solution. Filter through the solution with a syringe filter (PTFE, 0.2 or 0.45 μm) to remove any dust particle.

2. Drop-cast a thin layer of the solution on the Pt microdisk electrode.

3. Connect the microelectrode to the other sides of the glass body of the electrode by an ion conductive ribbon, for example, Nafion™ for PEM or quaternized Diels–Alder polyphenylene (Hibbs, 2013) for AEM, which acts as an electrolytic bridge between the external reference and working electrode (**Figure 2A**).

FIGURE 2 | (A) Representative microelectrode set up and **(B)** example of *I* versus t$^{-1/2}$ plots for O$_2$ reduction at a Pt | BAM® 407 membrane interface (Beattie et al., 1999. Copyright 1999 Elsevier Science S.A.).

FIGURE 3 | Representative experimental set up for **(A)** *in situ* MEA measurement for hydrogen permeation and **(B)** example of linear sweep voltammogram to measure the hydrogen crossover current density (Kocha et al., 2006. Copyright 1999–2022 John Wiley & Sons, Inc.).

4. Connect the microelectrode to the hydrogen reference electrode (6% H$_2$ in Ar | Pt | 0.1 M H$_2$SO$_4$ or NaOH) and place it in a controlled humidity chamber.

5. Before the experiments, cycle the electrode potential at 50 mV s^{-1} between 0 and +1.4 V using a potentiostat until a stable voltammogram is obtained. In order to provide a consistent electrode pretreatment and a clean Pt surface for every experiment, keep the microelectrode for 10 s at 1.4 V before applying a cathodic potential step or voltammetric scan.

6. Hold the potential of the microelectrode at 1.2 V for 20 s, and then proceed to 0.4 V where O$_2$ reduction is diffusion controlled for 5 s.

C) *In Situ* Measurement in MEA (Kocha et al., 2006)

1. Prepare a flat, dry membrane piece with a known thickness (wet) and a matching hardware plate.

2. Assemble a standard fuel cell MEA with GDLs. Flow humidified H$_2$ (4% in N$_2$) on the anode side of the electrochemical cell, which acts as the reference and counter electrode. Flow humidified nitrogen to the cathode at 300 sccm (**Figure 3A**).

3. Apply voltage with a potentiostat and measure the resulting currents from 0 to 0.6 V with 1 mV s^{-1} scan rate. H_2 that crosses over to the other side of the membrane gets oxidized at the cathode by the application of a voltage.
4. Obtain the H_2 oxidation current density generated from the voltammogram by the y-axis intercept of a linear fit between 0.25 and 0.35 V (**Figure 3B**).
5. For oxygen permeability measurement (Baik et al., 2013; Zhang et al., 2013), flow humidified O_2 to the anode instead of H_2 in N_2. Apply voltage with a potentiostat and measure the resulting currents from 0.4 to 1.1 V in increments of 0.1 V. Obtain the O_2 crossover limiting current between 0.8 and 1.1 V.

Data Collection and Analysis

All raw experimental data should be recorded in a laboratory notebook with the date of measurement. Any observation during the measurement and analysis should be also noted for future references.

A) Pressure Permeation Cell

Calculate the corresponding permeation rate of hydrogen, p (mol cm^{-1} s^{-1}), using the following equation:

$$P = 22.4 \cdot x_{H2} \cdot \frac{Q}{1000} \frac{\delta}{A},$$

where 22.4 is the conversion factor (1 mol = 22.4 L at standard temperature and pressure), x_{H2} is the hydrogen concentration in the carrier gas (mol L^{-1}), Q is the flow rate of the carrier gas (sccm, kmol s^{-1}), δ is the membrane thickness (wet, cm), and A is the permeating area of the MEA (cm^2).

B) Chronoamperometric Technique

Chronoamperometric determination of diffusion coefficient (D_b, cm^2 s^{-1}) and solubility (C_b, mol cm^{-3}) of hydrogen or oxygen in the membrane can be determined from the linear regression analysis of the experimental slope and intercept (int) of I vs. $t^{-1/2}$ plots (**Figure 2B**).

$$D_b = \frac{r^2 (int)^2}{\pi (slope)^2}, \qquad C_b = \frac{(slope)^2}{\pi n F r^3 (int)},$$

where r is the radius of the microdisc electrode (cm), n is the number of electrons, F is the Faraday constant (96,485 s A mol^{-1}), and n is the number of electrons (mol).

D_b and C_b are used to calculate gas permeability ($p=D_b C_b$, mol cm^{-1} s^{-1}) of the membrane.

C) *In Situ* Measurement in MEA

The hydrogen permeation rate, p (mol cm^{-1} s^{-1}), of the membrane can be expressed as:

$$P = \frac{i_{H2}}{nF} \frac{th}{p_{H2}},$$

where i_{H2} is the crossover current density of hydrogen (A cm^{-2}), p_{H2} is the feed partial pressure of hydrogen (mol^{-1}), th is the wet

thickness the membrane (cm), F is the Faraday constant (96,485 s A mol^{-1}), and n is the number of electrons (mol).

QUALITY CONTROL AND QUALITY ASSURANCE
Instrument or Method Calibration and Standardization

- It is recommended to start the measurement with the commercially available membranes with the reported hydrogen and oxygen permeation rate in the literature (Nafion 112, Nafion 117 (Sakai et al., 1985; Beattie et al., 1999; Kim and Lee, 2015) or commercially available AEMs (Henkensmeier et al., 2021)) as a reference point.

- The GC for the pressure permeation cell needs to be properly calibrated with the gas standards prior to the analysis.

Cautions

- Special cautions needed during the measurement include avoiding inhalation of vapor or mist, ensuring adequate ventilation of the space, and removing all sources of ignition, heat, open flames, and sparks. No smoking or electrostatic charge is allowed. An oxygen cylinder has to be separated from hydrogen or combustible materials. All gas cylinders must be kept tightly closed in a dry, well-ventilated place.

- When using a membrane with gas recombination layers and O_2 is used as a carrier gas, it is necessary to monitor the H_2 content in O_2 with a combustible gas detection system.

Interferences

- The pressure effect on the gas permeation rate is significant to the measurement. The gas permeation rates measured under pressurized conditions, such as pressure cells and microelectrodes with pressurized gases, are higher than those measured by non-pressurized techniques. For the systems operating under pressurized conditions, it is appropriate to measure the gas permeation rate under a similar pressure condition. Other non-pressurized methods such as diffusion cells and microelectrodes without pressurized gases can be used for general screening or comparing the gas permeation rate of different ion-exchange membranes.

- Gas permeability strongly depends on the hydration level of membranes. The membrane needs to be in the fully hydrated state for the measurement, and insufficient hydration to the membrane can result in a low permeation measurement.

- Gas permeability as membrane properties is measured in pure water. In a practical system, AEM water electrolyzers often circulate alkaline solution, for example, NaOH, KOH, or K_2CO_3 solution (0.1–2 M) (Kraglund et al., 2016), and a high concentration of the solution may significantly impact the gas permeability by lowering diffusivity.

DISCUSSION

This protocol describes three methods that can be used to measure gas permeability across membranes of interest. All three methods can be applied to measure hydrogen permeability. Oxygen

permeability can be measured by either microelectrodes or *in situ* measurement in MEA, yet, it is of less concern than hydrogen crossover due its production at ambient pressure and the lower permeation rate of oxygen than that of hydrogen (Sakai et al., 1985).

For a membrane used in high differential pressure operations or a membrane with recombination layers, a pressure permeation cell would be suitable. Microelectrode chronoamperometry would be favored when the membrane is available in an ionomer solution. Using MEA configuration would be preferred when hardware for the fuel cell testing set up is available. Running different methods on the same membrane sample would result in similar gas permeabilities (Kim and Lee, 2015). It is recommended to identify the operating conditions of water electrolyzers to select the appropriate gas permeation measurement methods for the membranes.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

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AUTHOR CONTRIBUTIONS

EP and YK wrote the first draft of the manuscript. SK provided the setup and procedure for pressure permeation measurement. EP revised the manuscript with help from SK and YK.

ACKNOWLEDGMENTS

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NOMENCLATURE

Abbreviations

AEM anion exchange membrane.

GC gas chromatography.

GDL gas diffusion layer.

MEA membrane electrode assembly.

PEM proton exchange membrane.

Pt platinum.

PTFE polytetrafluoroethylene.

PTL porous transport layer.