Supporting Information

Importance of Hydrogen Oxidation Reaction Current in Quantifying Hydrogen Crossover in

PEM Water Electrolyzers at High Differential Pressure

Ramchandra Gawas¹, Douglas I. Kushner¹, Xiong Peng^{1*}, and Rangachary Mukundan^{1*}

¹Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory,

Berkeley, California, United States

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1. Detailed description of experimental methods

a. Catalyst coated membrane (CCM) fabrication

127 µm PFSA membranes (Chemours, Nafion 115) were pre-treated in a two-step procedure- they were first immersed in boiling de-ionized water at 100 °C for one hour and then soaked in 0.5 M nitric acid (Sigma, 70%) for another hour followed by triple rinsing with deionized water (Millipore, 18 MΩ.cm). Soaking in nitric acid removes impurities as well as protonates sulfonic acid groups, and rinsing with DI water removes excess acid. Following pre-treatment, these membranes were stored in DI water at room temperature prior to CCM fabrication. CCMs were fabricated using the ultrasonic spray coating method by spraying dilute catalyst inks directly onto the PFSA membranes. Cathode catalyst ink was prepared using 50 wt% Pt/C (TKK TEC10V50E), deionized water (Millipore, 18 MQ.cm), and n-propanol (Sigma Aldrich, 99%) in 1:1 water and alcohol volume ratio, and 5 wt% Nafion as ionomer (Chemours, Nafion D521) with ionomer to carbon (I:C) ratio of 0.6. This cathode catalyst ink was subjected to bath ultrasonication for 30 minutes at 10 °C. Similarly, anode catalyst ink was prepared using TKK amorphous iridium oxide catalyst (TKK 77100), solvents- deionized water, n-propanol, ethanol (Sigma, 99%) in 1:2:1 volume ratio of water, n-propanol, and ethanol, and 5 wt% Nafion (Chemours, Nafion D521); ionomer to catalyst ratio for the anode catalyst ink was 0.116. Alternate anode catalysts used in this work were TKK rutile IrO₂ (TKK 77110) and Alfa Aesar mixed iridium oxide (Alfa Aesar, PremionTM, 99% metal basis) along with TKK amorphous iridium oxide. The anode catalyst ink was ultrasonicated with a probe sonicator (Cole Parmer, CEX 500) at 38% amplitude for 30 mins in an ice-bath (to avoid overheating). Both cathode and anode catalyst inks were sprayed using ultrasonic sprayer (Sono-Tek Exactacoat) at 0.2 and 0.25 ml.min⁻¹ onto the 127 µm PFSA membrane (Nafion 115, Chemours) mounted on the heated vacuum stage at 60 °C. The ultrasonic

nozzle was set to 120 kHz while spraying. X-ray fluorescence (XRF, Bruker) was used to quantify the Pt and Ir loadings on cathode and anode catalyst layers respectively. 10-15 points were measured on each side of the CCM, the loadings were quantified using a set of six calibration standards for both Pt and Ir. All CCMs used in this study have a loading of 0.1 ± 0.01 mg.cm⁻² Pt on cathode and 0.4 ± 0.04 mgcm⁻² Ir on anode.

b. <u>PEMWE single cell assembly</u>

All electrolyzer measurements in this manuscript were performed with in-house fabricated Ti flow fields (high precision machining) consisting parallel flow channels on the one side and serpentine flow channels on the cathode side with $\sim 5 \text{ cm}^2$ active area paired with aluminum end plates (fuel cell technologies) and gold-coated chrome current collectors (fuel cell technologies). Both anode and cathode flow fields were sputtered with Pt using a radio frequency sputtering System (AJA Intl. Inc., 99.999% Pt from Kurt Lasker) to eliminate ohmic losses associated with titanium passivation. The cathode side flow field was equipped with a silicone O-ring to aid with the sealing. Sintered titanium-based porous transport layers (PTL, Mott Corp., 254 µm, 37% Porosity) and Toray carbon paper with 5% PTFE (Toray 120, 370 µm, without microporous layer) were used as diffusion media on anode and cathode respectively.¹ Titanium PTLs were coated with Pt (0.2 mg_{Pt}.cm⁻²) to avoid ohmic losses due to passivation. Additionally, iridium (0.1 mg_{Ir}.cm⁻²) and gold (0.2 mg_{Au}.cm⁻²) coated PTLs were prepared using the radio frequency sputtering system (AJA Intl. Inc., 99.999% Au or Ir from Kurt Lasker). The loading of PGM coatings was confirmed using XRF (Bruker). PTLs and Toray carbon paper gas diffusion layers (GDLs) were precisely laser cut (FS Laser) to avoid any gap between the diffusion media and gaskets (Figure S1). Even a small gap between diffusion media and gaskets could lead to membrane squeezing into this gap, resulting in failure at the edge of the membrane-PTL interface during the high-pressure operation. 254 µm skived Teflon sheets (CS Hyde) were used as gasket on anode and cathode sides (31% GDL compression at cathode). Finally, the PEMWE single cells were carefully assembled using eight thread bolts with Belleville washers and torqued using a digital torque wrench following a start pattern with increments of 1.1 N-m to a final value of 4.5 N-m. The final torque (4.5 N-m) was triple checked on each bolt. The Stacked Belleville washers enable long-term, uniform compression.

c. <u>PEMWE setup with backpressure unit</u>

All PEMWE single cells were tested at 80 °C on a custom-built electrolyzer test station (modified fuel cell test station from fuel cell technologies). A diagraph liquid pump (KNF, NFB25) was used to circulate deionized water (Millipore, 18 M Ω .cm) at 80 °C to anode flow fields at 60 ml/min throughout the electrolyzer testing. Additionally, rod heaters were used to maintain the cell temperature at 80 °C. The cathode inlet was capped, and outlet was connected to an in-house designed backpressure unit equipped with a pressure transducer. This backpressure unit was used to control the cathode backpressure between 0-30 bar_g using the hydrogen gas generated at cathode. The cathode backpressure unit. Typically, the cathode backpressure was set to the desired value while operating the electrolyzer at 1 A.cm⁻². Once the electrolyzer is set at a desired backpressure value, all electrochemical characterization and online gas crossover measurements were conducted while monitoring the pressure.

d. Electrochemical characterization

All electrochemical measurements were carried out using a Biologic Potentiostat (Biologic, VSP-300) with a 20 A current booster. Prior to electrochemical and hydrogen permeation characterization, all PEMWE single cells were pre-conditioned in three steps:

- 1. 40 CV linear scans from 1.2 to 2 V at 50 mV.s⁻¹
- 2. 5 x Galvanostatic polarization curves (defined below)
- 3. A Galvanostatic 5-hour hold at 1 A.cm⁻²

Electrolyzer performance was assessed using galvanostatic polarization curves at current densities ranging from 5 mA.cm⁻² to 4 A.cm⁻². During the polarization curves, one minute hold was applied at each current density to ensure steady state; the voltage recorded in the last 30 seconds was averaged for the analysis. At each current density step in the polarization curve, a galvanostatic EIS was recorded between 1 MHz to 100 mHz. These GEIS were further analyzed to extract the high frequency resistance (HFR) at each step. HFR was used to calculate ohmic losses at each current density and these ohmic losses were subtracted from the cell voltage to get the HFR-free polarization curves.

$$E^{HFR-free}_{Cell} = E_{Cell} - i * HFR_i$$

Electrolyzer potential at each current density can be written as

$$E_{cell} = E_{rev}^{\ 0} + \eta_{ohmic} + \eta_{kinetic} + \eta_{residual}$$

Where E_{rev}^{0} is the reversible cell potential, and η_{ohmic} , $\eta_{kinetic}$, and $\eta_{residual}$ represent the ohmic, kinetic and residual overpotentials. Considering the facile hydrogen evolution kinetics and sluggish oxygen evolution kinetics, cathodic contributions are neglected in the kinetic overpotential. Using the Nernstian equation, reversible cell potential is defined as,

$$E_{rev} = 1.2291 - 0.008456 (T - 298.15) + \frac{RT}{2F} ln \left(\frac{a_{H_2} \sqrt{a_{O_2}}}{a_w}\right)$$

Where T is the temperature in Kelvin (353.15 K in this case), R is the universal gas constant, F is the Faraday's constant, a_w is the water activity (assumed to be 1), a_{H_2} and a_{O_2} are activities (or partial pressures of) hydrogen and oxygen respectively.

At 80 °C, the saturation pressure of water is 0.47 bar_a (a stands for absolute). Therefore, partial pressures of H_2 and O_2 under ambient operating conditions are both 0.53 bar_a. As the anode is operated at ambient pressure, the partial pressure of oxygen is always 0.53 bar_a. At high differential pressures (or high cathode backpressures), the partial pressures of H_2 are calculated as,

$$p_{H_2} = P_{cathode} - p_w$$

Where $P_{cathode}$ is absolute pressure of cathode and p_w is the saturation pressure of water at cathode (0.47 bar_a). The cathode partial pressures and reversible cell potentials at 0-30 bar_g (g stands for gauge) cathode backpressures are summarized in Table S1. The increase in reversible cell potential clearly shows the expected Nernstian shift at high differential pressures.

Cathode backpressure	Partial Pressure of Hydrogen (abs)	Reversible Cell Potential at 80 °C
[bar _g]	[bar _a]	[V]
0	0.53	1.1633
10	10.53	1.2088
20	20.53	1.219
30	30.53	1.2251

Table S1: Partial Pressure of H_2 and Reversible cell Potentials at 80 °C and 0-30 bar_g cathode

backpressures

The ohmic and kinetic overpotential were calculated using following equations,

 $\eta_{ohmic} = i * ASR_i$

$$\eta_{kinetic} = b * log\left(\frac{i}{i_0}\right)$$

Here, b is the Tafel slope and i_0 is the apparent exchange current density for OER. b and i_0 were calculated by fitting the low current density data (<80 mA.cm⁻²) to this equation. HFR-free overpotential, which includes kinetic and residual overpotentials, is defined as,

$$\eta_{HFR-free} = E_{cell} - E_{rev}^{\ 0} - \eta_{ohmic}$$

Lastly, the residual overpotential was calculated by subtracting reversible, ohmic and kinetic losses from the cell voltage,

$$\eta_{residual} = E_{cell} - E_{rev}^{0} - \eta_{ohmic} - \eta_{kinetic}$$

e. On-line gas chromatography measurements

Hydrogen concentration at the anode outlet, H_2 vol fraction in O_2 , was quantified using gas chromatography (SRI Instruments, 8610C) with a thermal conductivity detector (Figure S2). A typical gas chromogram and calibration curve used for quantifying %H₂ volume fraction are shown in Figure S3(a) and S3(b) respectively. The water vapor in the hydrogen and oxygen gas mixture was removed with the help of condenser prior to GC injections. H₂ vol fraction in O_2 was measured at nine different current densities- 0.25 A.cm⁻², 0.5 A.cm⁻², 0.75 A.cm⁻², 1 A.cm⁻², 1.5 A.cm⁻², 2 A.cm-2, 2.5 A.cm⁻², 3 A.cm⁻², 3.5 A.cm⁻² at four different cathode backpressure- 0 bar_g, 10 bar_g, 20 bar_g, 30 bar_g. (Figure S3(c)) At least three injections were recorded at each condition following a 5-min hold to ensure steady state. These 3 injections were averaged and converted to H₂ conc using a calibration curve (Figure S3(b)). Calibration curve was obtained by quantifying at least three calibration standards under identical conditions. %H₂ in O₂ values and the corresponding error bars reported in this paper were calculated from measurements on three independent MEAs. Hydrogen vol. fraction at anode was further converted to H₂ flux at anode using the following equation,

$$N'_{H_2}^{An} = \frac{i}{2} \frac{\varphi_{H_2}}{1 - \varphi_{H_2}}$$

... Equation S1

where $N_{H_2}^{An}$ is H₂ flux at anode in mA.cm⁻², *i* is the operating current density in mAcm⁻², \emptyset_{H_2} is the H₂ in O₂ vol. fraction, and *F* is the Faraday's constant (i.e., 96485 J/mol). The H₂ flux at anode can also be written in mmol.m².s⁻¹

$$N_{H_2}^{An} = \frac{i}{4F} \frac{\phi_{H_2}}{1 - \phi_{H_2}}$$

 $N_{H_2}^{An}$ here is the H₂ flux at anode in mmol.m².s⁻¹, *i* is the operating current density in mA.m⁻².

The H₂ permeation rate was calculated by combining the hydrogen oxidation current with the H₂ flux at anode.

$$N^{'Crossover}_{H_2} = i_{HOR} + N^{'An}_{H_2}$$

N^{'Crossover} represents the H₂ crossover or permeation rate in mA.cm⁻², i_{HOR} represents the H_2 Here. HOR current density in mA.cm⁻² and $N_{H_2}^{An}$ represents the H₂ flux at anode in mA.cm⁻²

The hydrogen flux due to HOR mmol.m².s⁻¹can be written as,

$$N_{H_2}^{HOR} = \frac{i_{HOR}}{2F}$$

The H₂ concentration at anode during HOR and at OCV was quantified with the help of Ar as the purge gas at anode.

f. Rotating disk electrode measurements

The hydrogen oxidation reaction rate was evaluated using rotating disk electrode experiments on catalyst thin films in 0.1 M H₂SO₄ (acidic) electrolyte. Catalyst thin films were prepared by drop casting the catalyst ink on an Au disk to achieve 0.1 mg.cm⁻² of Pt or Ir loading. Catalyst ink solutions were prepared by dispersing the appropriate amount of catalysts in DI water and isopropyl alcohol (1:1 volume ratio) with 0.5 wt% ionomer (Nafion D521, Chemours) subjected to ultrasonication in ice bath for about 25 minutes. Cyclic voltammograms and the HOR performance of three different electrocatalysts were evaluated- metallic Ir, TKK amorphous IrO_x , and Pt/C. TKK amorphous IrOx was chosen to represent the commercial OER electrocatalyst. Since the permeated hydrogen can reduce iridium oxide catalyst at anode, TKK amorphous IrO_x catalyst was annealed under 2% H₂ at 80 °C for 6 hours to obtain the reduced IrO_x catalyst (referred as Ir). This reduced catalyst represents metallic Ir surface. A dynamic hydrogen electrode (Gaskatel) was used as a reference electrode for all RDE measurements.

2. Supporting results and discussion

a. RDE analysis

Cyclic voltammograms (CVs) for these catalyst thin films were recorded in Ar-saturated 0.1 M H_2SO_4 at 50 mV/s. Figure S7 (a), (b), and (c) show distinct CVs for Ir, TKK amorphous IrOx and Pt/C catalyst thin films. These CVs exhibit faradaic processes occurring on the catalyst surface under inert environment in acidic electrolyte. CVs of Pt/C and Ir show a clear H-UPD region between 0.05 to 0.4 V vs. RHE whereas IrO_x CV does not exhibit any faradaic features in the H-UPD region. IrO_x CVs show three peaks at 0.6, 0.9 and 1.2 V typically observed for amorphous IrO_x surfaces. The HOR performance was recorded in H_2 saturated 0.1 M H_2SO_4 at 10 mV/s. A background current recorded in Ar-saturated 0.1 M H_2SO_4 electrolyte at 10 mV/s was subtracted from the HOR current. Figure S7 (d) shows HOR polarization curves of Ir (green), TKK amorphous IrOx (Red), Pt/C (blue) thin films as well as the Au disk (black). Au disk shows negligible HOR current and therefore can be used as an electrode substrate for these measurements. Consistent with existing literature, Pt/C and Ir thin films exhibit facile HOR kinetics reaching diffusion limited currents under 50 mV overpotential.^{2,3} Here, we observed that TKK amorphous

IrOx also exhibits similar HOR activity and reaches a diffusion-limited HOR current (slightly lower than Ir and Pt/C) under 50-60 mV overpotentials. The mechanism of HOR on iridium oxide surfaces needs to be investigated in detail.

3. Supporting Figures



Figure S1: (a) anode and (b) cathode side of the PEMWE MEA 30 bar_g operation, (c) anode, and (d) cathode flow fields used for differential pressure testing



Figure S2: Schematic of the setup used for online gas chromatography measurements in PEMWEs at high differential pressure during (a) electrolyzer operation, (b) HOR measurements



Figure S3: (a) Typical chromatogram recorded during GC measurements (b) Calibration curve for quantifying $%H_2$ in O₂ (c) On-line GC measurements at various operating current densities at 20 bar_g differential pressure.



Figure S4: Voltage breakdown analysis of PEMWEs (at ambient cathode backpressure)



Figure S5: PEMWE performance, Cell voltage vs. Current Density (log scale) at 0-30bar_g cathode backpressures; PEMWE operates as a hydrogen pump at low current densities (< HOR current) and high differential pressure (> 0 bar_g)



Figure S6: Anodic cyclic voltammograms (CVs) vs. cathode recorded at 0-30 bar_{g} cathode backpressures, 0.05 to 1.2 V vs. cathode at 50 mV/s.



Figure S7: Cyclic voltammograms recorded in Ar-saturated 0.1 M H₂SO₄ electrolyte on (a) Ir (reduced IrO_x), (b) TKK amorphous IrOx and (c) Pt/C thin films deposited on Au disk, (d) shows HOR polarization curves on Pt/C (blue), Ir metal (green), and TKK amorphous IrO_x (red) recorded in H₂ saturated 0.1 H₂SO₄ at 10 mV/s rotating at 1600 RPM; Au disk (black) under identical conditions does not show any oxidation current. All measurements were recorded using dynamic hydrogen reference electrode (DHE) at the catalyst loading of 0.1 mg.cm⁻² and 0.5 wt% ionomer.



Figure S8: Hydrogen oxidation reaction (HOR) current in PEMWEs at 0-30 barg cathode backpressure; HOR current at anode was measured using linear sweep voltammetry (LSV) from OCV to 1.5 V vs. cathode at 1 mV.s⁻¹



Figure S9: (a) H_2 flux at the anode calculated using online GC measurements (triangles) and HOR current (crosses) representing H_2 permeation rate at zero OER current, (c) hydrogen permeation rate calculated by combining the H_2 flux at anode and HOR measurements for various operating current densities at 0-30 bar_g cathode backpressures for MEAs containing Ircoated PTLs

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