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Supplemental Information

Challenges and Strategies for Probing the Composite Interface of PEM Electrolyzers and Fuel Cells Using *Operando* AP-XPS

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Calculations of electron inelastic mean free paths (IMFP) and liquid water layer thickness

Estimates of the inelastic mean free paths (IMFP, λ) of the emitted photoelectrons through various components as a function of electron energy, E (eV) are obtained from the TPP-2M equation of Tanuma, Powell and Penn.[1,2] The relevant equations for this calculation are as follows:

$$\lambda = \frac{E}{E_p^2[\beta \ln(\gamma E) - \left(\frac{C}{E}\right) + \left(\frac{D}{E^2}\right)} \tag{1}$$

$$\beta = -0.10 + \frac{0.944}{\sqrt{E_p^2 + E_g^2}} + 0.069\rho^{0.1} \tag{2}$$

$$\gamma = 0.191\rho^{-0.50} \tag{3}$$

$$C = 1.97 - 0.91U \tag{4}$$

$$D = 53.4 - 20.8U \tag{5}$$

$$U = \frac{N_v \rho}{M} = \frac{E_p^2}{829.4} \tag{6}$$

$$E_p = 28.8\sqrt{\frac{N_v \rho}{\mathrm{M}}} \tag{7}$$

Where N_v is the number of valence electrons per atom (for elemental solids) or molecule (for compounds), ρ is the density (in g/cm^3), M is the atomic or molecular weight and E_g is the bandgap energy (in eV). Table S1 details our results for these parameters and the inelastic mean free path of photoelectrons through liquid H_2O, platinum and iridium based off of the specified peak signal (Pt 4f, Pt $3d_{5/2}$, Ir 4f, Ir $3d_{5/2}$).

	IMFP material (reference peak)				
Parameter	Water (Pt $4f_{7/2}$)	Pt (Pt $4f_{7/2}$)	Pt (Pt $3d_{5/2}$)	Ir (Ir $4f_{7/2}$)	Ir (Ir $3d5_{/2}$)
Beam (eV)	4000	4000	4000	4000	4000
peak B.E. (eV)	71	71	1878	61	2041
E (eV)	3929	3929	2122	3939	1959
density (ρ, g/cm^3)	1	21.4	21.4	22.56	22.56
band gap, Eg (eV)	7.3	0	0	0	0
Nv (valence e-s)	8	10	10	10	10
M	18.02	195.08	195.08	192.22	192.22
Ep	19.189342	30.164283	30.164283	31.200586	31.200586
U	0.443973	1.097039	1.097039	1.173712	1.173712
β	0.014979	0.025028	0.025028	0.024484	0.024484
λ	0.191000	0.041288	0.041288	0.040213	0.040213
C	1.565985	0.971695	0.971695	0.901922	0.901922
D	44.165370	30.581594	30.581594	28.986795	28.986795
λ (Å)	108.020249	33.968828	20.916871	32.687094	18.902354

Table S1: Calculated TPP-2M parameters and corresponding inelastic mean free paths of emitted photoelectrons through liquid water, platinum, and iridium as a function of electron kinetic energy (from peak referenced in parenthesis).

Using the decay of signal intensity from our metal peak, and the calculated IMFP values, we are able to obtain an estimate for liquid water thickness on our electrode. However, because the intensity of the photoelectron signal will decrease due to collisions with molecules in both the gaseous environment and the liquid phase, we need to separate these two effects. The decrease in signal intensity (I_1 from I_0) through a gaseous environment as a function of pressure can be described by:

$$\frac{I_1}{I_0} = exp\left(-\frac{\sigma_e L p}{kT}\right) \tag{8}$$

where L is the path length through the gas phase (from sample surface to the entrance cone aperture of the spectrometer, here ~ 0.35mm), *p* is the pressure (Pascal), T is the temperature (Kelvin), and *k* is the Boltzmann constant. Parameter σ_e is the total electron scattering cross section for water defined by

$$\sigma_e = \frac{1}{E}\left(1890 + 765.8\ln(E) - \frac{1}{E}38342\right)a_0^2 \tag{9}$$

with E being the electron energy and a_0^2 equal to 2.800 x 10^{-21} m^2.[3]

Parameter	Value
p	266 or 2506 Pa
T	298 K
k	$1.38 * 10^{-23}$ m^2 kg s^{-1} K^{-1}
L	$3.5 * 10^{-4}$ m
E	3929 eV
σ_e	$5.85 * 10^{-21}$ m^2

Table S2: parameters for the calculations of expected signal intensity loss from vapor phase H_2O

The intensities were taken from the peak height after background subtraction. Representative spectra for these calculations are shown below in Figure S1. We applied the expected signal decay from the vapor phase at each pressure condition above vacuum (2 Torr to 18.8 Torr) to give us our new I_1 value. This ended up being 99.9% of the intensity before our vapor phase contribution, and was thus a negligible effect when compared to that of the liquid phase. The remainder of the signal intensity loss can now be ascribed to the liquid water, and an estimate of the depth (d) of this layer on the surface is given by:

$$d = \lambda\cos(\theta) * ln\left(\frac{I_2}{I_1}\right) \tag{8}$$

which corresponds to the degree of the analyzer from normal to the surface (in our case, 0).[4,5] The data from vacuum to full humidity was taken in triplicate on a Fuel Cell Store Pt – Pt CCM.

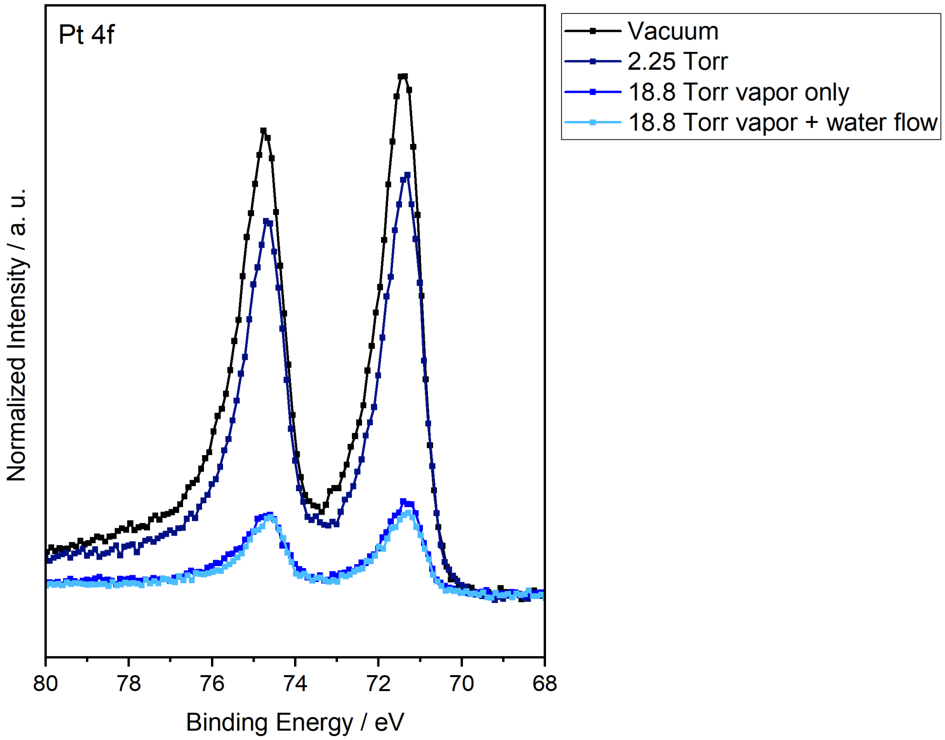

Figure S1: representative Pt 4f spectra from spot #2 used for calculated depth of liquid water layer.

Trial	1	2	3	Average
Pressure / condition	d (nm)			
2 Torr	0.39	0.89	-	0.64
18.8 Torr	4.86	5.93	5.72	5.50
18.8 Torr + water flow	5.77	7.20	5.99	6.32

Table S3: Calculated depth, d (nm), of the liquid water layer on the exposed CCM.

Slit cell full schematic:

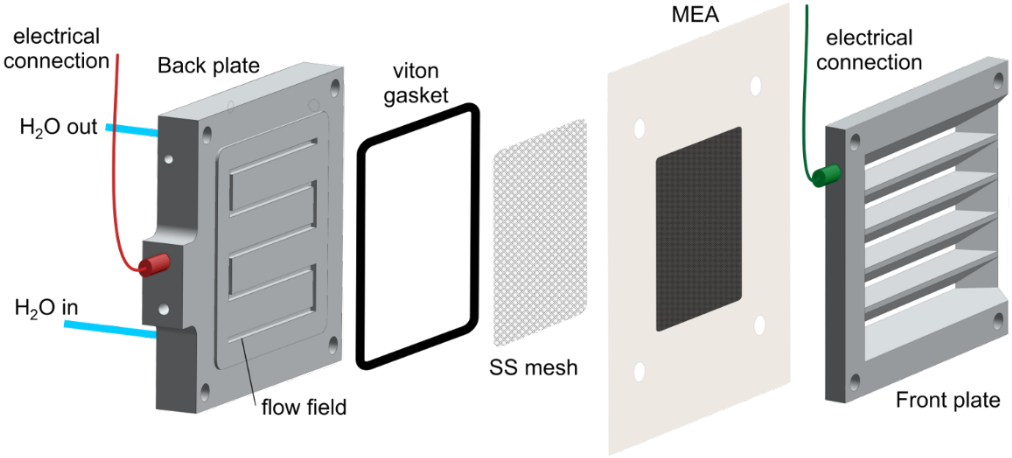

Figure S2: Schematic of the slit cell.

Electrochemical data:

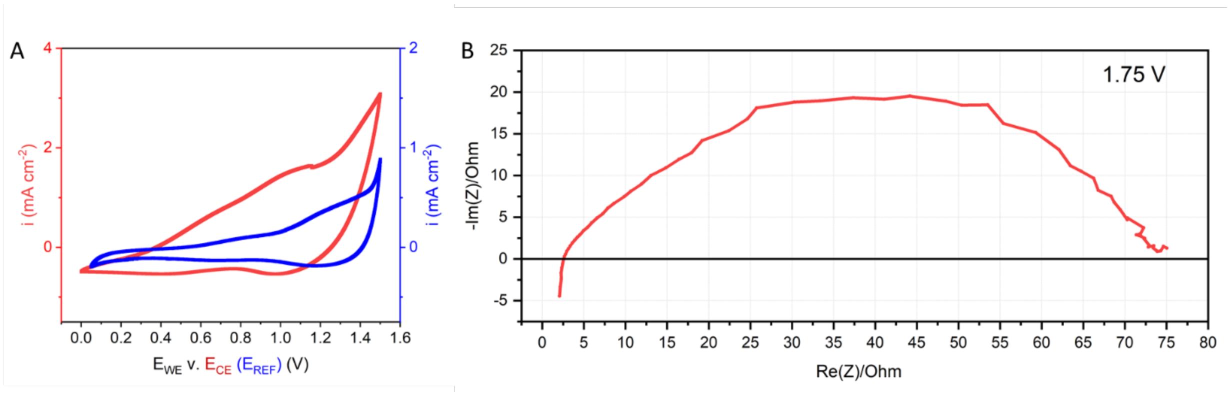

Figure S3: (A) Cyclic voltammetry (CV) and (B) impedance spectrum at a 1.75 V hold for the TKK IrO_2 sample with corresponding *operando* data displayed in Figure 2. The red CV was taken as part of a 2-electrode system (E_{WE} v. E_{CE}) in the same experiment as that of the *operando* data from Figure 2. The blue spectrum was taken at a later date (without beam), of the same sample, cell, and operating conditions and environment but while using a Pt-Hydrogen reference (E_{WE} v. E_{REF}) with hydrated hydrogen flow at the Pt cathode.

The CV with the hydrogen reference was included to compare between the two and three electrode systems, the latter allowing for a more accurate measurement and more commonly used in other studies.[1-3] At a primary level, they show similar features, including two subtle oxidation waves in the anodic sweep and a larger reduction feature as the voltage is reduced from OER conditions. However, these all shift up slightly to higher voltages and there is an overall narrowing of the current-voltage hysteresis with use of hydrogen. The two oxidation features are suggested to be a transition from Ir^{3+} to Ir^{4+} (~0.8 V) and deprotonation of hydroxide groups to form electrophilic O^{1-} species (~1.2 V).[3] The current density for the cyclic voltammetry is calculated from the electrode area in contact with the front collector plate and the slit openings, together equaling 1 cm^2. Generally, the high frequency resistance is found to be consistent at voltages in the OER regime, and here yields an ohmic drop of 0.007 V.

Connected v. disconnected trials:

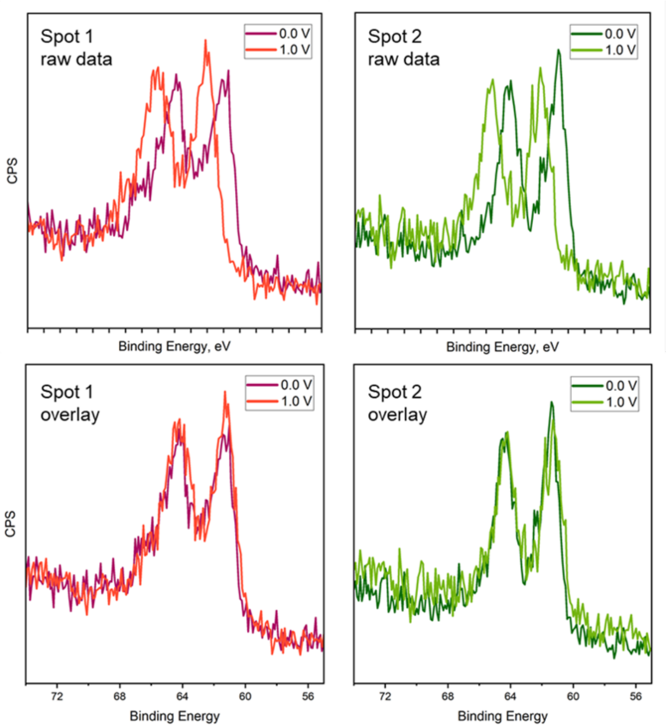

Figure S4: Ir 4f spectra obtained with forced bias on the working electrode of an MEA from two different sample spots. All spectral changes will come from applied bias to the front plate and not due to any electrochemical process. The top row shows the raw data (not calibrated) and the bottom row is an overlay of the spectra after calibration to the Fermi edge to better compare line shapes.

References:

1) S. Siracusano, et al., *J. Power Sources*, 2017, **366**, 105–114.

2) J. J. Velasco-Vélez, et al., *J. Am. Chem. Soc.*, 2021, **143**, 12524–12534.

3) V. Pfeifer, et al., *Chem. Sci.*, 2017, **8**, 2143–2149.