Supplementary information for

On the Interface Electron Transport Problem of Highly Active IrO_x Catalysts

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Methods

Catalyst

Alfa Aesar (AA), Tanaka (TKK), and Adams-fusion (Adams) IrO_x catalysts were prepared for use as anode materials and designated as IrO_x -L, IrO_x -M, and IrO_x -S, respectively. The Adamsfusion IrO_x was synthesized using a commercial method. A precursor solution was prepared by dissolving 1 g of $IrCl_3 \cdot xH_2O$ and 10 g of NaNO₃ in 8 g of DI water. This solution was ballmilled at 300 rpm for 3 h and annealed at 400°C for 1 h to ensure complete reduction to IrO_x . The resulting product was centrifuged at 8000 rpm for 5 min and washed three times to remove residual NaOH. The Adams IrO_x was finalized by evaporating the solvent overnight in an oven at 60°C. IrO_x -S (A) was synthesized using the same process as IrO_x -S but with $Ir(acac)_3$ as the precursor instead of $IrCl_3 \cdot xH_2O$. In contrast, the Alfa Aesar and Tanaka IrO_x catalysts were used as received in their amorphous forms.

Membrane electrode assembly

All three types of IrO_x were incorporated into membrane electrode assemblies (MEAs) using the same fabrication procedure. An anode slurry was prepared by mixing 0.60 mg of IrO_x with n-propyl alcohol (NPA, Junsei Chemical), deionized (DI) water, and Nafion dispersion (D2020, IEC=1.05 mequiv g⁻¹, DuPont). The slurry was first dispersed in a 1:1 weight ratio mixture of NPA and DI water using a roll mill for 72 hours with multiple zirconia balls, then cast onto polyimide (Kapton) films and dried at 60 °C. The slurry's solid content was maintained at 20 wt. %, and the Nafion polymer content was controlled at 5, 10, and 20 wt. % of the solids. Similarly, a cathode slurry was prepared using Pt/C (Tanaka, TEC10E50E) with 9 wt. % solid content, maintaining an ionomer-to-carbon ratio of 1.0, and following the same dispersion and drying procedure as used for the anode. The anode and cathode electrodes were decal-transferred to a Nafion membrane (NR212, 50 µm, DuPont) at 138°C and 20 bar. The targeted catalyst loadings were 0.70 mg_{IrOx} cm⁻² for the anode and 0.10–0.15 mg cm⁻² for the cathode. A single cell was assembled by sandwiching the fabricated MEA with bipolar plates (BP), porous transport layers (PTL), and silicon gaskets (230 µm). The anode PTL used a Ti fiber-based material (Bekaert, 2GDL06N-025, 250 µm) and Pt-coated Ti PTL (Bekaert, 2GDL06N-025, BS02Pt, 200 nm Pt coating) while the cathode PTL employed a carbon-based material (JNTG, JNT30-A3, 210 µm) with a microporous layer (MPL). Titanium-based BP (anode) and carbon-based BP (cathode) completed the assembly, which was clamped with the end plates using eight bolt screws.

Characterization

The size distribution of the IrO_x catalysts was primarily characterized using image analysis. Field emission transmission electron microscopy (FE-TEM, Talos F200x, FEI) was employed to visualize the overall particle structure and measure particle sizes, while field emission scanning electron microscopy (FE-SEM, Magellan400, FEI) was used to examine the surface and cross-sectional morphology of the catalyst layers. The geometric surface area of each IrO_x catalyst was determined using Brunauer-Emmett-Teller (BET, 3Flex Micromeritics) analysis. High-resolution powder X-ray diffraction (XRD, RIGAKU Smartlab) was utilized to identify the crystalline structure of the IrO_x catalysts. To investigate band bending effects between TiO_x and IrOx or Nafion, a 10 nm Ir coating was deposited on Ti foil using an E-beam evaporator (A-Tech System). Cross-sectional TEM samples of Ir-coated Ti foil were prepared using a focused ion beam (FIB) (Helios G4, FEI). Nafion coatings were spin-coated onto Ti foil at 6000 rpm for 2 min using Nafion ionomer dispersions (NPA:DI water, 1:1 weight ratio) with concentrations of 5, 10, 15, and 18 wt. %. The oxidation state and atomic ratio of Ir on the surface were analyzed via X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific), employing an Al X-ray source (1486.7 eV). Ion-beam etching was performed for 2 min on the Ir-coated Ti foil to expose underlying layers. All spectra were calibrated to the sp³ carbon peak in adventitious carbon contaminants (284.5 eV, C 1s). Work functions were evaluated using ultraviolet photoelectron spectroscopy (UPS, Axis-Supra, Kratos) with He (I) radiation (21.22 eV). Additional quantitative ionomer analysis was conducted through time-offlight secondary ion mass spectrometry (ToF-SIMS, ION-TOF GmbH) by detecting Nafion and IrOx fragments (F⁻, C₅F₁₁⁻ and Ir⁻). All characterizations were performed at KARA (KAIST Analysis Center for Research Advancement).

PEMWE single-cell electrochemical analysis

Water was pumped into the anode end plate of the PEMWE at a flow rate of 5 mL/min, while the cell temperature was maintained at 80 °C. IV polarization and electrochemical impedance spectroscopy (EIS) analyses were performed using a potentiostat (HCP-803, BioLogic Science Instrument). Cell activation involved 10 cycles of chronopotentiometry (CP) at 1 A, followed by linear sweep voltammetry (LSV) from 0 V to 1.8 V at a scan rate of 10 mV s⁻¹. The iV polarization curves were obtained by recording the voltage at each current step with a 2-min stabilization period. Current density was initially adjusted in fine increments below 0.1 A cm⁻² and subsequently measured at intervals of 0.1 A cm⁻². EIS measurements were conducted simultaneously across a frequency range of 100–100 kHz at current densities of 0.04, 0.2, 1, and 1.5 A cm⁻² to identify resistances within the OER potential window. To further investigate electron and ion transport resistance within the catalyst layer, additional EIS measurements were performed below the OER voltage by applying a voltage of 1.35 V under an H_2/H_2O atmosphere at the cathode/anode.

COMSOL simulation

The Semiconductor Module in COMSOL Multiphysics 6.2 was employed to solve the electric potential at various Schottky contact interfaces using the governing equation (Eq. S1). Two ideal Schottky contacts were modeled using semiconductor physics to represent the IrO_x/TiO_x and ionomer/ TiO_x interfaces. The TiO_x layer, with an anatase structure, simulated the PEMWE anode interface between the catalyst layer and the Ti PTL, with a thickness of 16 nm, consistent with previous research.¹ The ionomer contact was substituted by a metal contact with a 6 eV work function, based on our work function analysis of the Nafion-coated interface (**Fig. S26**). The electric potential of each interface was determined by measuring the central contact point within the TiO_x bulk region under a 1.8 V reverse bias. Additionally, the electron barrier at the TiO_x interface was compared across varying IrO_x contact sizes ranging from 5 nm to 30 nm. The electron barrier on the TiO_x surface was calculated using (Eq. S2), referenced to the Fermi energy level of TiO_x:

$$V = V_o - \phi_B - \chi_o - V_{eq, adj}$$
(Eq. S1)

Electron energy
$$(E_{CB} vs E_{fermi}) = V - \chi_o$$
 (Eq. S2)

The symbols and their definitions are provided in **Table S2**, and the parameters for each material required for the numerical simulation are summarized in **Table S3**.

Supplementary Note

The iV polarization curve was deconvoluted into three components: kinetic, ohmic, and mass transport overpotential, neglecting the cathode contribution. The ohmic overpotential was calculated by measuring the high-frequency resistance (HFR) from the GEIS Nyquist plot at each current density and applying Ohm's law (Eq. S3) to obtain the iR-compensated polarization curve.

ohmic overpotential =
$$i(A cm^{-2}) \times HFR$$
 (ohm cm^{2}) (Eq. S3)

The kinetic overpotential was determined using the Tafel equation for the OER assuming an extremely low HER overpotential (Eq. S4).

$$i = i_o exp^{mi} \left(\frac{(1-\alpha)F\eta_{kin}}{RT}\right)$$
(Eq. S4)

To minimize HER influence, the initial two points at low current densities were excluded. Subsequently, five data points below 1.48 V were selected to construct a linear Tafel plot, ensuring an R² value exceeding 0.99. The kinetic overpotential was calculated by subtracting the reversible potential of 1.18 V from the measured potential at each current density. The residual voltage difference between the iR-free polarization curve and the kinetic overpotential was attributed to mass transport overpotential. The Tafel slope was calculated while accounting for R_{CL}^{eff} , representing the ion and electron transport resistance in the tortuous CL. The R_{CL}^{eff} was determined at 1.35 V using a transmission line element (TLE) approach, corresponding to the 45° slope region in the PEIS data, as shown in **Fig. S14, S25**.



Fig. S1. Deconvolution of PEMWE overpotential and electrical resistance analysis for cells with bare Ti PTL and Pt-coated PTL. (a and c) Electric and ionic resistance analysis of ohmic resistance using 0.30 ± 0.05 mg cm⁻² anode loading (IrO_x-L) and NR212 membrane, comparing Ti PTL and Pt-coated PTL. (b) High-frequency resistance analysis for varying membrane thicknesses (NR212, N115, and N117) with 0.40 mg cm⁻² anode loading (IrO_x-L), comparing cells with Ti PTL and Pt-coated PTL.



Fig. S2. TEM images of catalysts showing irregular 0D nanoparticle shapes arranged by size: (a) IrO_x -L, (b) IrO_x -M, and (c) IrO_x -S.



Fig. S3. Particle size distribution analysis of catalysts using ImageJ software. (a) IrO_x -L exhibited a broad particle size distribution with an average size of 24 nm. (b) IrO_x -M showed a narrower distribution, with most particles under 15 nm and an average size of 14 nm. (c) IrO_x -S demonstrated an extremely narrow distribution, with particles predominantly around 4 nm.



Fig. S4. BET surface area analysis for each catalyst. IrO_x -L, with the largest particle size, had the smallest surface area (19.8 m² g⁻¹), while IrO_x -M and IrO_x -S, with smaller particle sizes, exhibited larger surface areas (92.8 and 202.2 m² g⁻¹, respectively).



Fig. S5. Overpotential breakdown and high-frequency resistance analysis for single cells with Pt-coated Ti PTL. (a) Overpotential deconvolution at 1 A cm⁻², separating kinetic, ohmic, and mass transport contributions, revealed kinetic overpotentials of 0.35, 0.31, and 0.33 V for IrO_x-L, IrO_x-M, and IrO_x-S, respectively, with consistent ohmic overpotential (0.06 \pm 0.005 V) across all samples. (b) High-frequency resistance of each catalyst.



Fig. S6. Impedance analysis at 0.04 A cm⁻² of each catalyst (IrO_x-L, M, S) coupled with Pt-coated Ti PTL. Smaller particle catalysts (IrO_x-M and IrO_x-S) exhibited reduced charge transfer resistance related to OER, with no additional variations observed.



Fig. S7. Mass activity comparison of catalysts. (a) Enlarged iR compensated polarization curves near 1.45 V. (b) Mass activity calculated at 1.45 V from iR compensated polarization curves. Smaller catalysts (IrO_x-M and IrO_x-S) demonstrated higher mass activities (132.67 and 54.30 A g⁻¹) compared to IrO_x-L (47.29 A g⁻¹).



Fig. S8. XPS Ir 4f spectra of each catalyst. IrO_x -L and IrO_x -M exhibited a larger Ir $4f_{7/2}$ Ir³⁺ peak area at 62.3 eV compared to the Ir $4f_{7/2}$ Ir⁴⁺ peak at 61.8 eV, whereas IrO_x -S showed an opposite trend, with a dominant Ir $4f_{7/2}$ Ir⁴⁺ peak area.



Fig. S9. Catalyst characterization via XRD, TEM, and FFT. (a) XRD analysis revealed that IrO_x -S exhibited higher crystallinity compared to IrO_x -L and IrO_x -M. (b) High-resolution TEM images confirmed the crystalline structure of IrO_x -S. (c) TEM images of IrO_x -L indicated lower crystallinity. (d) FFT analysis of IrO_x -L TEM images revealed a non-discrete surface structure.

Although IrO_x -L exhibited an amorphous structure corresponding to the Ir^{3+} state (as shown in **Fig. S8** XPS), it displayed distinct Ir metal peaks in XRD (**Fig. S9**), which were absent in the other samples. These peaks are likely negligible due to the low metallic content and noncrystalline structure. Willinger et al. analyzed the same commercial IrO_x , referred to here as IrO_x -L, and reported that the metallic Ir content was below 2 wt.% based on quantitative XRD analysis^{2,3}, indicating that this low content has an insignificant impact on electrical conductivity. This conclusion is further supported by the amorphous structure confirmed through TEM and FFT analyses.

The poor performance and high-frequency impedance of IrO_x -S with Ti PTL, as shown in **Figs. 1c** and 1d, indicate that crystallinity (Ir^{4+} state) has minimal influence on electron conductivity.



Fig. S10. Single-cell performance of a low-loading $(0.10 \pm 0.05 \text{ mg}_{\text{IrOx}} \text{ cm}^{-2})$ catalyst layer. (a) iV polarization curves for each catalyst using Pt-coated PTLs, with iR-compensated polarization curves shown in the inset. (b) Nyquist plots at 0.04 A cm⁻² using Pt-coated PTLs. (c) iV polarization curves and (d) Nyquist plots at 0.04 A cm⁻² using uncoated Ti PTLs.



Fig. S11. Cross-sectional SEM images of low-loading catalysts. Uneven and disconnected areas, highlighted with red arrows, can increase the ionomer/PTL interface.



Fig. S12. Characterization of IrO_x-**S (A).** (a) TEM image of IrO_x -S (A) with particle size distribution shown in the inset. (b) SEM surface analysis of the IrO_x -S (A) MEA. (c) BET surface area analysis for each catalyst. (d) XPS Ir 4f spectra of IrO_x -S (A). (e) XRD analysis confirming the comparatively low crystallinity of IrO_x -S (A). (f) UPS analysis of each catalyst.



Fig. S13. Single-cell performance of IrO_x -S (A) and its comparison with other catalysts. (a) iV polarization curves and (b) iR-compensated polarization curves using Pt-coated PTLs. The inset in (b) shows the mass activity of each catalyst at 1.45 V. (c) iV polarization curves and (d) Nyquist plots at 0.04 A cm⁻² for catalysts using uncoated Ti PTLs. All anodes employed CLs with an IrO_x loading of 0.70 ± 0.05 mg cm⁻² and 20 wt. % ionomer content.



Fig. S14. Impedance analysis at 1.35 V for R^{eff}_{CL} . The electron/ion transport resistance in the catalyst layer was measured using a Pt-coated PTL. This resistance was subtracted before calculating the Tafel slope.



Fig. S15. Four-point probe analysis. Sheet resistance measurements of the casted catalyst layer on a PI film with 20 wt. % ionomer content for each catalyst.



Fig. S16. Model experiment structure. (a, b) Schematic illustrating the preparation of Ir- and Nafion-ionomer-coated Ti foil using E-beam evaporation and spin coating. (c) Cross-sectional TEM image of Ir-coated Ti foil prepared via FIB.



Fig. S17. UPS analysis to determine the intrinsic work function of each catalyst. (a) Photoelectron signals across the full spectrum and at the Fermi energy level for a 10 nm deposited Ir film and other IrO_x catalysts. (b) Smaller catalysts exhibited lower work functions: IrO_x -L (5.0 eV), IrO_x -M (4.9 eV), and IrO_x -S (4.7 eV). This trend is not consistent with ohmic resistance behavior, which is more significantly influenced by the ionomer-induced pinch-off effect.



Fig. S18. UPS analysis of Ti foil and Ir-coated Ti foil. (a) UPS data for bare Ti foil and 10 nm Ir-coated Ti foil. (b) Enlarged UPS spectra showing an increase in the work function of Ti foil following Ir coating.



Fig. S19. UPS analysis of Ti foil and Nafion-coated Ti foils. (a) UPS data for bare Ti foil and Ti foils coated with Nafion ionomer dispersions at varying concentrations (5, 10, 15, and 18 wt%). (b) Enlarged UPS spectra indicate an increase in the work function of Ti foil with higher Nafion content.



Fig. S20. Cumulative intrusion pore volume measured by mercury intrusion porosimetry (MIP) for IrO_x -L and IrO_x -S. IrO_x -L exhibited a pore volume of 0.27 mL g_{IrOx}^{-1} , while IrO_x -S showed a slightly lower value of 0.25 mL g_{IrOx}^{-1} for pore diameters up to 5 nm.



Fig. S21. Surface distribution analysis of Nafion ionomer using the F⁻ ratio relative to total fragments via ToF-SIMS across MEAs with IrO_x -L, IrO_x -M, and IrO_x -S. Anodes with 0.70 mg cm⁻² IrO_x loading and 5 wt. % ionomer content were analyzed.



Fig. S22. Surface distribution analysis of Nafion ionomer using the C_5F_{11} fragment (originating from the Nafion backbone) via ToF-SIMS across MEAs with varying Nafion contents (5, 10, and 20 wt%) for IrO_x -M. (a) The C_5F_{11} ratio within the overall fragment corresponds to the input Nafion content. (b) The C_5F_{11} ratio confirms an increased exposure of Nafion ionomer with higher Nafion input.



Fig. S23. Catalyst layer structure as a function of ionomer content. (a) Surface SEM images of IrO_x -M catalyst layers containing 5, 10, and 20 wt. % ionomer at a loading of 0.70 mg_{IrOx} cm⁻². (b) Cross-sectional SEM images of each catalyst layer. (c) Cross-sectional SEM images at low magnification. The 5 wt. % ionomer content exhibited lower mechanical hardness, leading to the formation of cracks.



Fig. S24. Electrochemical performance of IrO_x -M with different Nafion contents (5, 10, and 20 wt%) in the catalyst layer using a Pt-coated Ti PTL. (a) iV polarization curves. (b) Nyquist plots from impedance analysis at 0.04 A cm⁻², (c) Overpotential deconvolution at 1.5 A cm⁻² showing no evidence of the pinch-off effect and a minimal influence of ionomer content.



Fig. S25. Impedance analysis at 1.35 V for R^{eff}_{CL} . The electron/ion transport resistance in the catalyst layer using a Pt-coated PTL at different Nafion ionomer contents (5, 10, 20 wt. %).



Fig. S26. UPS analysis of MEA. (a) Schematic illustrating the surface-exposed ionomer for varying catalyst layer structures. (b) UPS analyses of catalyst layers containing 10 wt. % and 30 wt. % ionomers, and an ultralow loading catalyst layer (0.07 mg cm⁻²). (c) Enlarged UPS spectra reveal an increased work function (6 eV) compared to pristine IrO_x (5 eV).



Fig. S27. Durability test using bare Ti PTL with 20 wt. % Nafion. (a, b) Voltage-time curves for 1 A cm⁻² constant current long-term operation of IrO_x -L and IrO_x -M at 20 wt. % Nafion loading with 0.50 mg_{IrOx} cm⁻². (c, d) iV polarization curves and (e, f) Nyquist plots at 0.04 A cm⁻² for IrO_x -L and IrO_x -M.



Fig. S28. Durability test using bare Ti PTL with 5 wt. % Nafion. (a, b) Voltage-time curves for 1 A cm⁻² constant current long-term operation of IrO_x-L and IrO_x-M at 5 wt. % Nafion loading with 0.50 mg_{IrOx} cm⁻². (c, d) iV polarization curves and (e, f) Nyquist plots at 0.04 A cm⁻² for IrO_x-L and IrO_x-M.

Catalyst	CL thickness (µm)	IrO _x volume fraction (%)	Ionomer (hydration) volume fraction (%)	Porosity (%)
IrO _x -L	3.48	17	13	70
IrO _x -M	2.68	21	16	63
IrO _x -S	2.26	26	20	54

Table S1. Volume fractions of IrO_x (95 wt. %) and ionomer (5 wt. %) in each catalyst layer, along with porosity values.

The volume fraction of each component is calculated using Eq. S5.⁴

$$V_{cat} = \frac{L_{cat}}{\rho_{cat} \times t_{an}}, \quad V_{ion} = \frac{L_{ion}}{\rho_{ion} \times t_{an}}$$
(Eq. S5)

where L represents the loading (0.70 mg cm⁻²) of each component, and ρ represents the density of IrO_x (11.7 g cm⁻³) and ionomer (1.58 g cm⁻³).^{5,6} t denotes the thickness of the anode catalyst layer. The hydrated volume fraction was calculated as 1.8 times the dry state volume, as reported by Gasteiger et al.⁷

Symbol	Unit	Description	
V _o	V	Bias	
ϕ_B	V	Schottky barrier	
χ _o	V	Electron affinity of semi-conductor	
V _{eq, adj}	V	The temperature-dependent offset	
E _{CB}	eV	Electron energy state of the conduction band	
E _{fermi}	eV	Electron energy state of aligned fermi energy	

 Table S2. COMSOL simulation symbol descriptions.

	Symbol	Unit	Value
IrO _x	Work function	eV	5.00
Nafion ionomer (replaced with metal contact)	Work function	eV	6.00
	Work function	eV	4.35
	Band gap energy	eV	3.20
	Electron affinity	eV	3.9
T 'O	Relative permittivity	V	10
1102	Conduction band effective density of states	1/cm	2×10 ¹⁷
	Valence band effective density of states	1/cm	6×10 ¹⁷
	Electron mobility	cm ² /Vs	100
	Shallow uniform donor density	1/cm ³	1017

Table S3. Parameters used for the Anatase TiO_2 in COMSOL simulation.⁸

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