

Vapor-Fed Electrolysis of Water Using Earth-Abundant Catalysts in Nafion or in Bipolar Nafion/ Poly(benzimidazolium) Membranes: Supporting Information

Authors: Patrick K. Giesbrecht;^{1,2} Astrid M. Müller;^{3,4} Carlos G. Read;⁵ Steven Holdcroft;⁶ Nathan S. Lewis;⁵ Michael S. Freund^{1,2}

Affiliations: ¹Department of Chemistry, Florida Institute of Technology, Melbourne, Florida 32901, United States; ²Department of Chemistry, Dalhousie University, 6274 Coburg Road, Halifax, NS B3H 4R2, Canada; ³Beckman Institute, California Institute of Technology, 1200 E. California Boulevard, Mail Code 139-74, Pasadena, California 91125, United States; ⁴Department of Chemical Engineering, University of Rochester, Rochester, New York 14627, United States; ⁵Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States; ⁶Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

Table of Contents

1. Catalyst Films and Solution-Phase HER/OER	S3
<i>Figure S1.</i> Tafel plots of a) HER catalyst films in 0.50 M H ₂ SO ₄ (aq); and b) OER catalyst films in 1.0 M KOH(aq). Dashed lines represent predicted Tafel slopes for an HER/OER electrocatalyst under operation with $n\alpha=0.5, 1, 2$ (120, 59 and 30 mV dec ⁻¹). ^{1,2}	S3
<i>Figure S2.</i> Scanning-electron micrographs of a) Pt/C and b) IrO _x Nafion-based films on C-paper prior to MEA incorporation. Catalyst loadings of 3 mg cm ⁻²	S3
<i>Table S1.</i> Overpotentials for the Cathode and Anode Catalysts Determined in this Work.....	S4
2. TP-WS Capabilities of MEAs in this work	S4
<i>Figure S3.</i> Comparison of the TP-WS performance in a two-electrode configuration under humid-N ₂ (g) flow at room temperature of a commercially available Pt IrRuO _x sample (black trace) with that of an in-house Pt IrO _x MEA used in this work (red trace). a) Steady-state polarization data and b) constant-current electrolysis at 10 mA cm ⁻² . Catalyst loadings were 3 mg cm ⁻²	S4
<i>Figure S4.</i> a) Constant-current electrolysis (10 mA cm ⁻²) data for CoP-Ti IrO _x MEAs performing TP-WS under humid-N ₂ (g) flow at room temperature in the absence (blue trace) and presence (grey trace) of a Nafion overcoat. b) Steady-state polarization and c) constant-current electrolysis (10 mA cm ⁻²) data for CoP-C IrO _x MEAs performing TP-WS under humid-N ₂ (g) flow at room temperature with and without C black (cb) incorporated into the CoP side or a Nafion overcoat. Nafion-based Pt/C IrO _x MEA (red squares) shown for comparison. CoP loading of 2 mg cm ⁻² for C-paper-based cathodes. IrO _x loading of 3 mg cm ⁻² on C-paper for the anode.	S5
<i>Figure S5.</i> a) Steady-state polarization and b) constant-current electrolysis (10 mA cm ⁻²) data for [NiFe]-LDH samples performing TP-WS under humid-N ₂ (g) flow at room temperature with a HMT-PMBI overlayer (light blue, brown traces) and a HMT-PMBI backlayer (dark blue trace). A Nafion-based Pt/C IrO _x MEA (red) is shown for comparison. [NiFe]-LDH loading of 0.6 mg cm ⁻² on the anode; Pt/C loading of 3 mg cm ⁻² on C-paper for the cathode.....	S5
<i>Figure S6.</i> a) Steady-state polarization and b) constant-current electrolysis (10 mA cm ⁻²) data for [NiFe]-LDH samples performing TP-WS under humid-N ₂ (g) flow at room temperature with HMT-PMBI-Br (gold) or HMT-PMBI-OH (brown) as the ionomer binder. Nafion-based Pt/C IrO _x MEA (red) shown for comparison. [NiFe]-LDH loading of 0.6 mg cm ⁻² on the anode; Pt/C loading of 3 mg cm ⁻² on C-paper for the cathode.	S6

Figure S7. a-c) Steady-state polarization and d-e) constant-current electrolysis (10 mA cm^{-2}) data for multiple samples of a,d) Nafion-based Pt/IrO _x and CoP-Ti/IrO _x MEAs, b) Pt/IrO _x BPM-based MEAs, c,e) Pt/[NiFe] BPM-based MEAs performing TP-WS under humid-N ₂ (g) flow at room temperature. CoP loading of 2.5 mg cm^{-2} on Ti-paper or C-paper for the cathode; IrO _x loading of 3 mg cm^{-2} on C-paper for the anode; [NiFe]-LDH loading of 0.6 mg cm^{-2} on C-paper for the anode; Pt/C loading of 3 mg cm^{-2} on C-paper for the cathode.....	S6
Figure S8. Constant-current electrolysis (10 mA cm^{-2}) data for a) Nafion-based (red) and BPM-based (blue) Pt/IrO _x MEAs; b) Pt/[NiFe] BPM-based MEA; c) CoP-C/IrO _x Nafion-based MEA; and d) CoP-Ti/IrO _x Nafion-based MEA before and after rehydration of the MEA under open-circuit voltage conditions. CoP loading of 2.5 mg cm^{-2} on Ti-paper or C-paper for the cathode; IrO _x loading of 3 mg cm^{-2} on C-paper for the anode; [NiFe]-LDH loading of 0.6 mg cm^{-2} on C-paper for the anode; Pt/C loading of 3 mg cm^{-2} on C-paper for the cathode. S7	S7
Figure S9. Bode Plots for representative MEAs at the operating voltage $V_{10 \text{ mA cm}^{-2}}$ for TP-WS in this work: a) Pt/IrO _x Nafion-based MEA; b) Pt/IrO _x BPM-based MEAs (Pt/IrO _x -10 light blue; Pt/IrO _x -30 dark blue); c) CoP-Ti/IrO _x MEA; d) Pt/[NiFe]-30 (gold) and Pt/[NiFe]-100 (brown) BPM-based MEAs; e) CoP-C/IrO _x MEA before (purple) and after (blue) constant-current electrolysis at 10 mA cm^{-2}	S8
Figure S10. Equivalent circuit model fits to EIS spectra at the operating voltage $V_{10 \text{ mA cm}^{-2}}$ for representative MEAs in this work.....	S9
Table S2. Series, polarization, mass-transport and activation overvoltages determined from EIS data at $V_{10 \text{ mA cm}^{-2}}$ for representative MEAs studied in this work.....	S9
Table S3. Values of the operating voltage $V_{10 \text{ mA cm}^{-2}}$ and the drift in the operating voltage during constant-current electrolysis at 10 mA cm^{-2} for individual MEAs studied in this work.....	S10
Table S4. EIS equivalent circuit model values for representative MEAs in this work. Uncorrected for surface area of MEA.....	S10
Determination of the mass-transport overvoltage at 10 mA cm^{-2}.....	S11
Determination of the longevity of co-ion current at 10 mA cm^{-2} in BPM-based MEAs.....	S11
Calculation of current contribution through carbonate removal.....	S11
References.....	S11

1. Catalyst Films and Solution-Phase HER/OER.

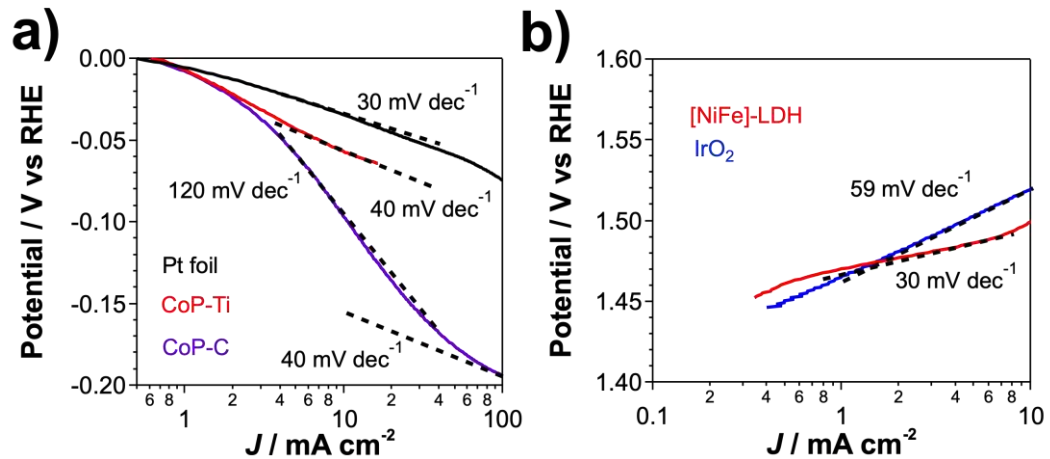


Figure S1. Tafel plots of a) HER catalyst films in 0.50 M H₂SO₄(aq); and b) OER catalyst films in 1.0 M KOH(aq). Dashed lines in a) represent predicted Tafel slopes for an HER electrocatalyst under operation (120, 40 and 30 mV dec⁻¹). Dashed lines in b) represent predicted Tafel slopes for an OER electrocatalyst under operation with $n(1-\alpha) = 1, 2$ (Tafel slopes of 59 and 30 mV dec⁻¹).^{1,2}

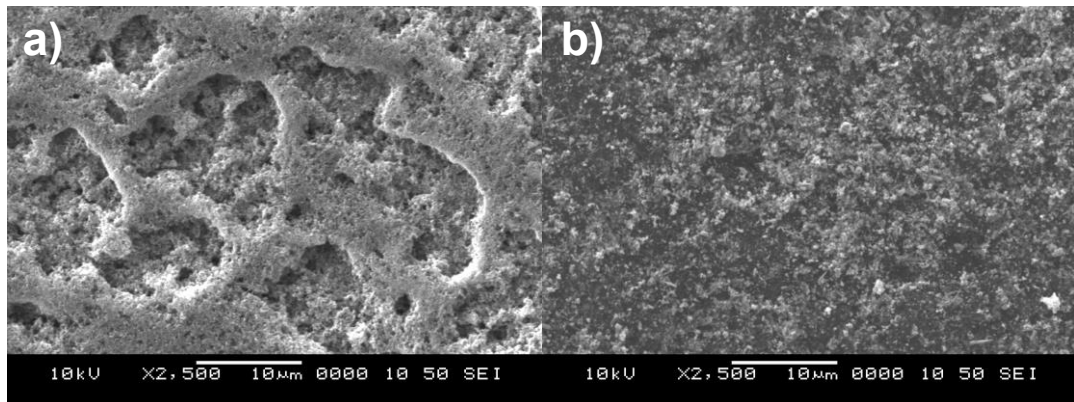


Figure S2. Scanning-electron micrographs of a) Pt/C and b) IrO_x Nafion-based films on C-paper prior to MEA incorporation. Catalyst loadings of 3 mg cm⁻².

Table S1. Overpotentials, Tafel slope, and exchange current densities for the cathode and anode catalysts determined in this work.

Catalyst	Loading (mg cm^{-2})	$\eta_{-10 \text{ mA cm}^{-2}}$ (HER, V) ^a	$\eta_{10 \text{ mA cm}^{-2}}$ (OER, V) ^b	Tafel Slope (mV dec^{-1}) ^c	J_0 (mA cm^{-2})
Pt foil	-	-0.045	-	29	0.9
CoP-Ti ^d	2.5	-0.062	-	49	0.1
CoP-C ^e	2	-0.068	-	132; 44	- ^g
IrO _x ^f	2	-	0.300	55	5×10^{-5}
[NiFe]-LDH ^f	0.4	-	0.286	25; 63	2×10^{-11}

^aHER in 0.50 M H₂SO₄(aq). ^bOER in 1.0 M KOH(aq). ^cTafel slope reported at low and high overpotentials if potential-dependent. ^dCoP deposited on Ti paper. ^eCoP deposited on C-paper. ^fDropcast film on glassy-carbon-disk electrode. ^gPotential-dependent Tafel slope prevented accurate determination of the exchange current density.

2. TP-WS Capabilities of MEAs in this work.

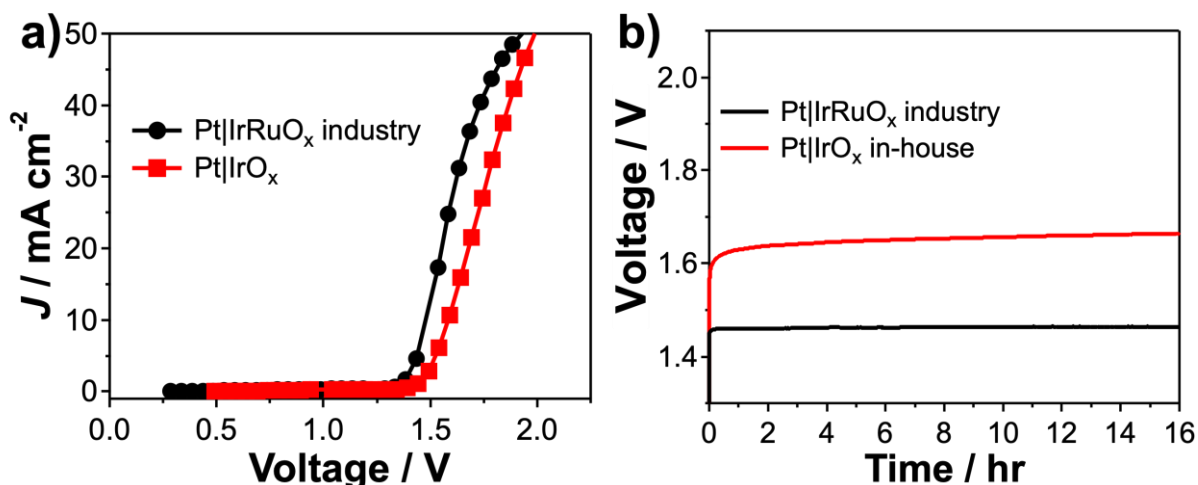


Figure S3. Comparison of the TP-WS performance in a two-electrode configuration under humid-N₂(g) flow at room temperature of a commercially available Pt|IrRuO_x sample (black trace) with that of an in-house Pt|IrO_x MEA used in this work (red trace). a) Steady-state polarization data and b) constant-current electrolysis at 10 mA cm⁻². Catalyst loadings were 3 mg cm⁻².

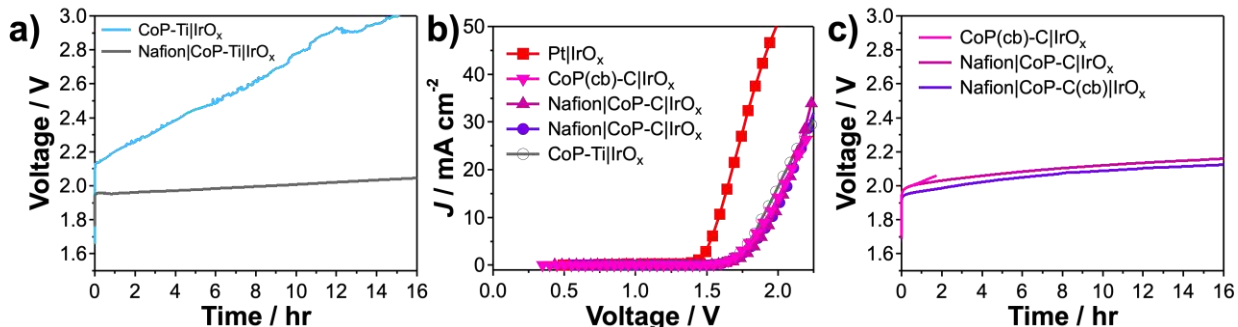


Figure S4. a) Constant-current electrolysis (10 mA cm^{-2}) data for CoP-Ti|IrO_x MEAs performing TP-WS under humid-N₂(g) flow at room temperature in the absence (blue trace) and presence (grey trace) of a Nafion overcoat. b) Steady-state polarization and c) constant-current electrolysis (10 mA cm^{-2}) data for CoP-C|IrO_x MEAs performing TP-WS under humid-N₂(g) flow at room temperature with and without C black (cb) incorporated into the CoP side or a Nafion overcoat. Nafion-based Pt/C|IrO_x MEA (red squares) shown for comparison. CoP loading of 2 mg cm^{-2} for C-paper-based cathodes. IrO_x loading of 3 mg cm^{-2} on C-paper for the anode.

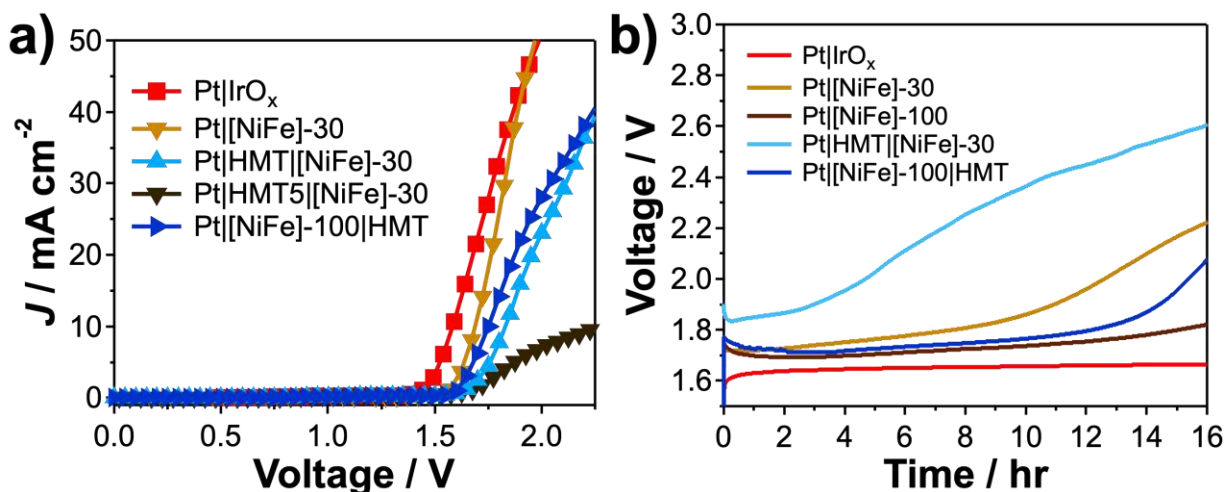


Figure S5. a) Steady-state polarization and b) constant-current electrolysis (10 mA cm^{-2}) data for [NiFe]-LDH samples performing TP-WS under humid-N₂(g) flow at room temperature with a HMT-PMBI overlayer (light blue, brown traces) and a HMT-PMBI backlayer (dark blue trace). A Nafion-based Pt/C|IrO_x MEA (red) is shown for comparison. [NiFe]-LDH loading of 0.6 mg cm^{-2} on the anode; Pt/C loading of 3 mg cm^{-2} on C-paper for the cathode.

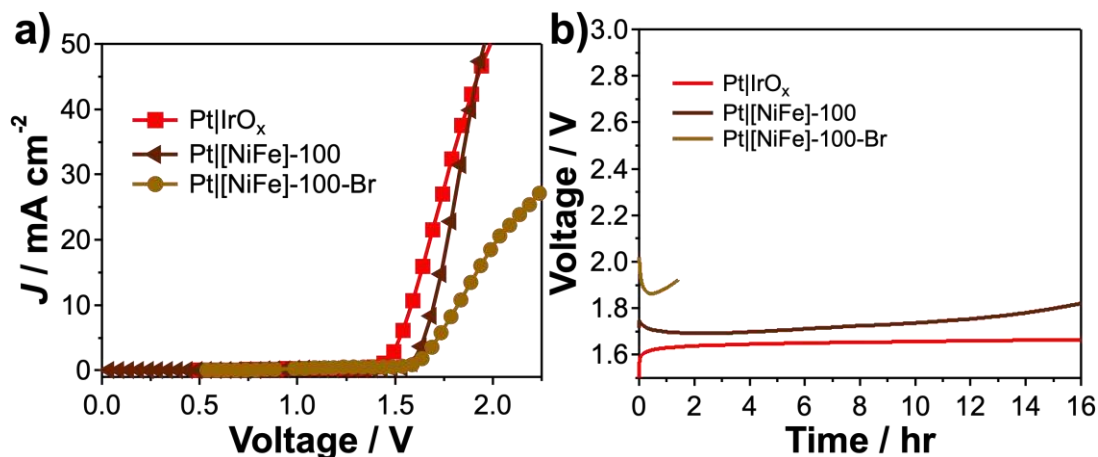


Figure S6. a) Steady-state polarization and b) constant-current electrolysis (10 mA cm^{-2}) data for [NiFe]-LDH samples performing TP-WS under humid- $\text{N}_2(\text{g})$ flow at room temperature with HMT-PMBI-Br (gold) or HMT-PMBI-OH (brown) as the ionomer binder. Nafion-based Pt/C|IrO_x MEA (red) shown for comparison. [NiFe]-LDH loading of 0.6 mg cm^{-2} on the anode; Pt/C loading of 3 mg cm^{-2} on C-paper for the cathode.

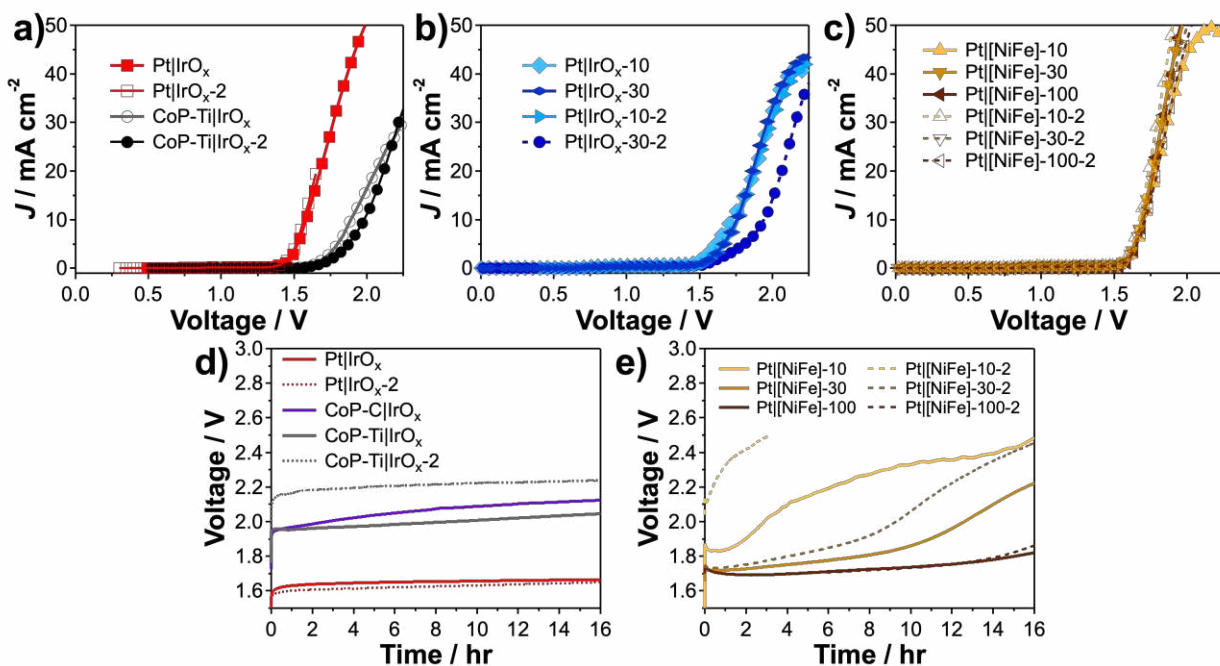


Figure S7. a-c) Steady-state polarization and d-e) constant-current electrolysis (10 mA cm^{-2}) data for multiple samples of a,d) Nafion-based Pt|IrO_x and CoP-Ti|IrO_x MEAs, b) Pt|IrO_x BPM-based MEAs, c,e) Pt|[NiFe] BPM-based MEAs performing TP-WS under humid- $\text{N}_2(\text{g})$ flow at room temperature. CoP loading of 2.5 mg cm^{-2} on Ti-paper or C-paper for the cathode; IrO_x loading of 3 mg cm^{-2} on C-paper for the anode; [NiFe]-LDH loading of 0.6 mg cm^{-2} on C-paper for the anode; Pt/C loading of 3 mg cm^{-2} on C-paper for the cathode.

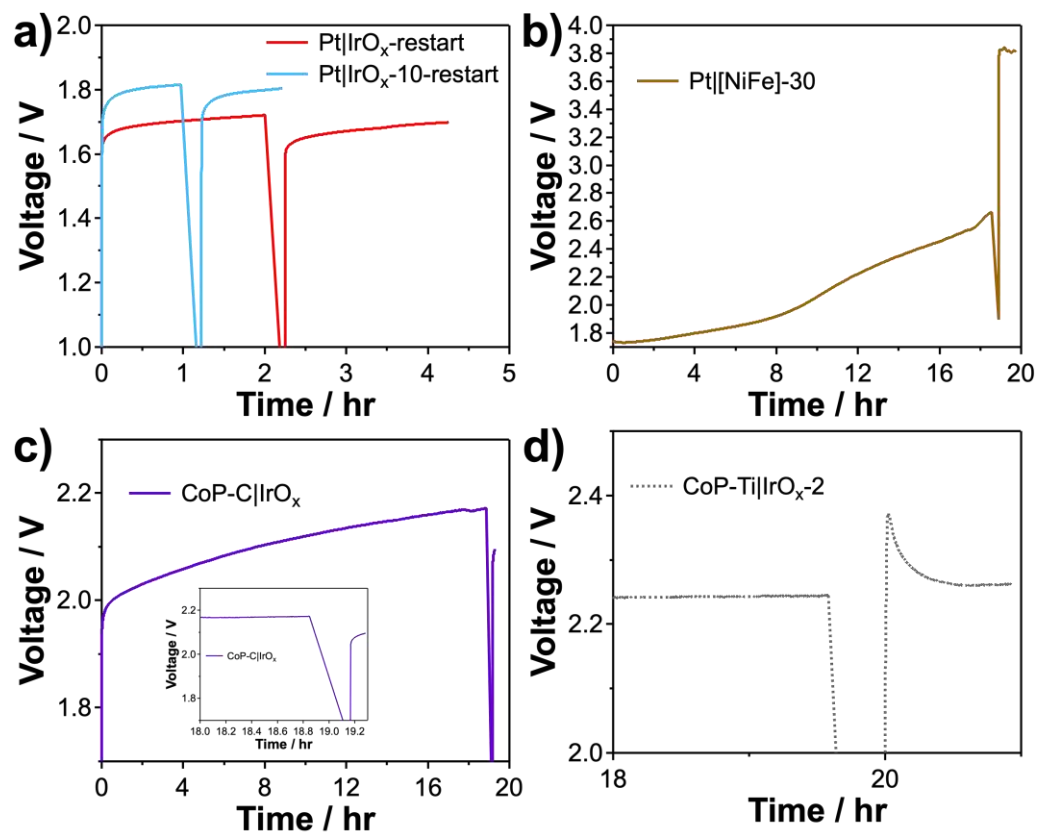


Figure S8. Constant-current electrolysis (10 mA cm^{-2}) data for a) Nafion-based (red) and BPM-based (blue) Pt|IrO_x MEAs; b) Pt|[NiFe] BPM-based MEA; c) CoP-C|IrO_x Nafion-based MEA; and d) CoP-Ti|IrO_x Nafion-based MEA before and after rehydration of the MEA under open-circuit voltage conditions. CoP loading of 2.5 mg cm^{-2} on Ti-paper or C-paper for the cathode; IrO_x loading of 3 mg cm^{-2} on C-paper for the anode; [NiFe]-LDH loading of 0.6 mg cm^{-2} on C-paper for the anode; Pt/C loading of 3 mg cm^{-2} on C-paper for the cathode.

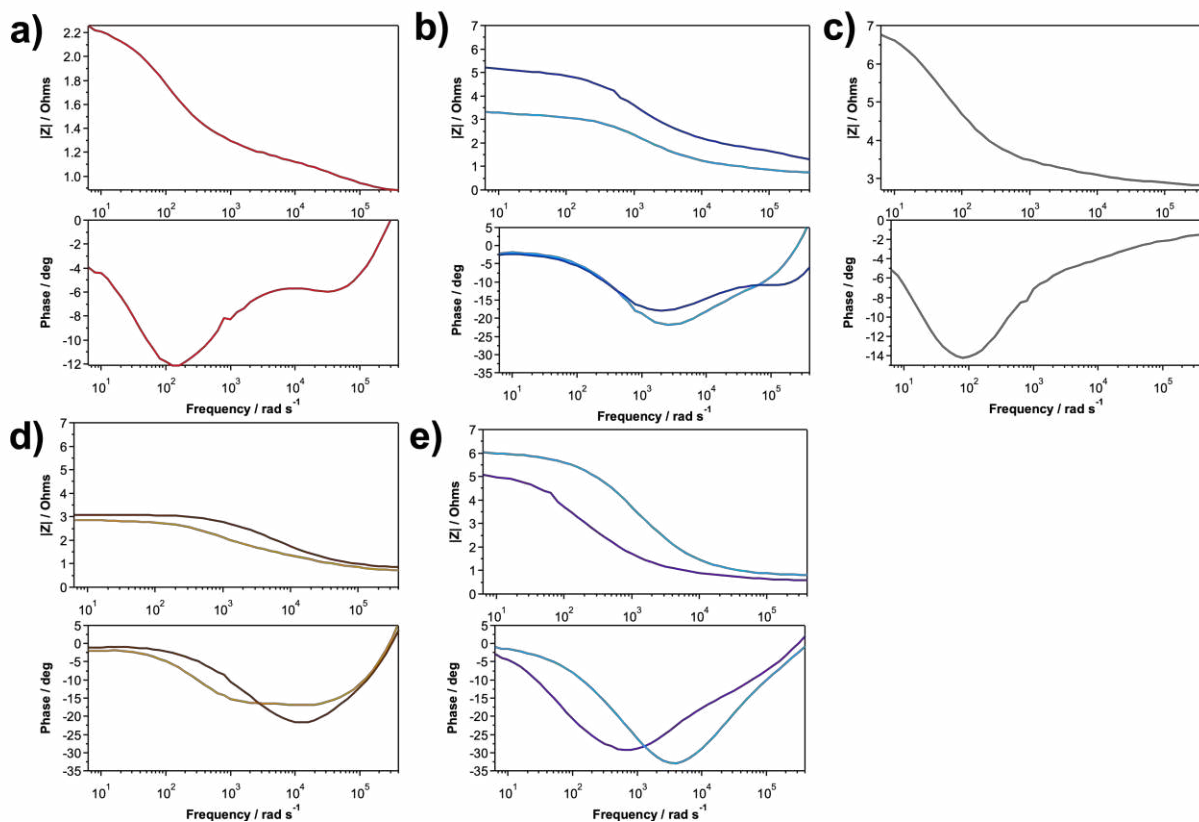


Figure S9. Bode Plots for representative MEAs at the operating voltage $V_{10 \text{ mA cm}^{-2}}$ for TP-WS in this work: a) Pt|IrO_x Nafion-based MEA; b) Pt|IrO_x BPM-based MEAs (Pt|IrO_x-10 light blue; Pt|IrO_x-30 dark blue); c) CoP-Ti|IrO_x MEA; d) Pt|[NiFe]-30 (gold) and Pt|[NiFe]-100 (brown) BPM-based MEAs; e) CoP-C|IrO_x MEA before (purple) and after (blue) constant-current electrolysis at 10 mA cm⁻².

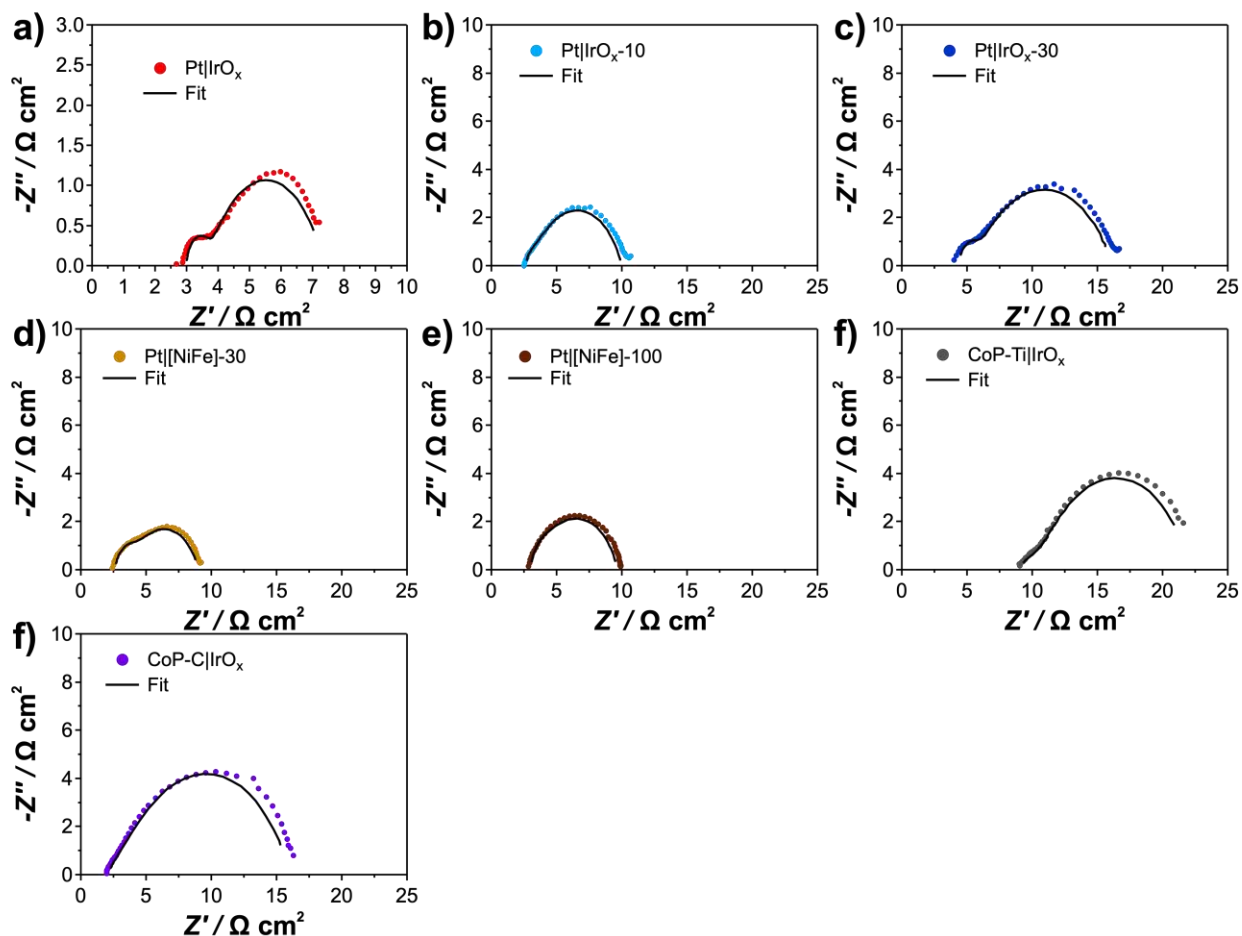


Figure S10. Equivalent circuit model fits to EIS spectra at the operating voltage $V_{10 \text{ mA cm}^{-2}}$ for representative MEAs in this work.

Table S2. Series, polarization, mass-transport and activation overvoltages determined from EIS data at $V_{10 \text{ mA cm}^{-2}}$ for representative MEAs studied in this work.

MEA	$\Delta V_{\text{iR}} \text{ (V)}^{\text{a}}$	$\Delta V_{\text{polarization}} \text{ (V)}^{\text{b}}$	$\Delta V_{\text{mxt}} \text{ (V)}^{\text{c}}$	$\Delta V_{\text{act}} \text{ (V)}^{\text{d}}$
Pt IrO _x	0.03	0.05	0.005	0.38
Pt IrO _x -10	0.02	0.08	0.009	0.56
Pt IrO _x -30	0.04	0.12	0.010	0.54
CoP-Ti IrO _x	0.09	0.13	0.012	0.60
CoP-C IrO _x	0.02	0.14	0.010	0.75
CoP-C IrO _x after	0.02	0.17	-	-
Pt [NiFe]-30	0.02	0.07	0.005	0.48
Pt [NiFe]-30 after	0.02	0.32	-	-
Pt [NiFe]-100	0.02	0.08	0.005	0.50
Pt [NiFe]-100 after	0.02	0.28	-	-

^aDetermined from the Z' high-frequency intercept in Nyquist plot of the EIS spectra of the MEA at $V_{10 \text{ mA cm}^{-2}}$. ^bWidth of the Nyquist plot of the EIS spectra of the MEA at $V_{10 \text{ mA cm}^{-2}}$. ^cDetermined

from application of Equation S1 to steady-state polarization data. ^dDetermined from Equation 1 in the manuscript.

Table S3. Values of the operating voltage $V_{10 \text{ mA cm}^{-2}}$ and the drift in the operating voltage during constant-current electrolysis at 10 mA cm^{-2} for individual MEAs studied in this work.

MEA	$V_{10 \text{ mA cm}^{-2}}(\text{V})^{\text{a}}$	$\Delta V_{\text{drift}}(\text{V})^{\text{b}}$	Rate (mV hr^{-1})
Pt IrRuO _x	1.45	0	0
Pt IrO _x	1.60	0.05	2.8
Pt IrO _x -2	1.59	0.05	2.8
Pt IrO _x -10	1.72	0.06	3.3
Pt IrO _x -30	1.75	0.03	1.7
CoP-Ti IrO _x	1.90	0.10	5.5
CoP-Ti IrO _x -2	2.01	0.09	5.0
CoP-C IrO _x	1.95	0.19	10.6
Pt-Ti IrO _x	1.70	0.19	10.6
Pt [NiFe]-10	1.72	0.78	43.3
Pt [NiFe]-10-2	1.74	0.76	190
Pt [NiFe]-30	1.71	0.50	27.8
Pt [NiFe]-30-2	1.75	0.70	38.9
Pt [NiFe]-100	1.70	0.15	8.3
Pt [NiFe]-100-2	1.70	0.17	9.4
Pt HMT [NiFe]-30	1.83	0.76	42.2
Pt [NiFe]-100 HMT	1.75	0.32	17.8

^aOperating voltage at 10 mA cm^{-2} as determined from steady-state polarization data. ^bDrift in $V_{10 \text{ mA cm}^{-2}}$ during constant-current electrolysis at 10 mA cm^{-2} .

Table S4. EIS equivalent circuit model values for representative MEAs in this work. Uncorrected for surface area of MEA.

MEA	$R_s(\Omega)$	$R_{\text{cath}}(\Omega)$	$Q_{\text{cath}}^{\text{a}}$	ϕ_{cath}	$R_{\text{an}}(\Omega)$	Q_{an}^{a}	ϕ_{an}
Pt IrO _x	0.8944	0.23592	0.0004818	0.88111	1.222	0.03866601	0.66835
Pt IrO _x -10*	0.81403	0.23592	0.0004818	0.88111	2.212	0.0002194	0.75934
Pt IrO _x -30	1.286	0.44631	2.4302E-05	0.98216	3.482	0.00245811	0.6883
CoP-Ti	2.741	3.528	0.01490799	0.76528	0.84837	0.02601	0.45651
CoP-C initial	0.57244	3.831	0.00631101	0.75567	0.82432	0.02221401	0.52097
CoP-C after**	0.79924	4.463	0.00140571	0.74212	0.82432	0.02221401	0.52097
Pt [NiFe]-30	0.77181	0.4936	0.0002114	0.90747	1.635	0.00380631	0.7388
Pt [NiFe]100	0.89998	0.28377	0.00013037	0.99547	1.936	0.00092538	0.77069

^aQ unit is $\Omega^{-1} \text{ s}^{\phi}$.

*Values of R_{cath} , Q_{cath} , and ϕ_{cath} were fixed to values obtained from Pt|IrO_x.

**Values of R_{an} , Q_{an} , and ϕ_{an} were kept fixed to values obtained from CoP-C initial.

Determination of the mass-transport overvoltage at 10 mA cm⁻².

The overvoltage associated with mass transport for TP-WS under flow can be determined by

$$\Delta V_{mxt} = \frac{RT}{nF} \left(1 + \frac{1}{\alpha}\right) \ln \left(\frac{J_{lim}}{J_{lim} - J}\right) \quad (S1)$$

Where R is the ideal gas constant, T temperature, n = 2, F Faraday's constant, charge-transfer coefficient $\alpha = 0.5$, J_{lim} the limiting current density determined from steady-state polarization data, and J the current density of interest (10 mA cm⁻²).

Determination of the longevity of co-ion current at 10 mA cm⁻² in BPM-based MEAs.

$A_{geometric} = 3 \text{ cm}^2$; $L_{nafion} = 0.0183 \text{ cm}$; $L_{cath} = 0.001 \text{ cm}$; $L_{anode} = L_{HMT-PMBI} = 0.001 \text{ cm}$
 $[M^+]_{Nafion} = 1.5 \text{ M}$; $[A^-]_{HMT-PMBI} = 1.5 \text{ M}$

Total co-ion current density time at 10 mA cm⁻²:

$$T_{total} = (n_M + n_A) * F / (0.03 \text{ A})$$

$$T_{total} = (3 \text{ cm}^2) * (0.0015 \text{ mol/cm}^3) * (0.0183 \text{ cm} + 0.002 \text{ cm}) * (96485 \text{ C/mol}) / (0.03 \text{ A})$$

$$T_{total} = 290 \text{ s}$$

Calculation of current contribution through carbonate removal.

From Ref ³:

$CO_2 = 5 \text{ ppm}$ (via GC-MS, constant value for ca. 50 h, flow rate of 0.1 L/min)

$V_{CO_2} = 5 \text{ ppm}$ (0.1 L/min)(3000 min) = 1.5 mL

$T = 323 \text{ K}$

$N_{CO_2} = PV/RT = (1 \text{ atm})(0.0015 \text{ L}) / [(0.08206 \text{ atm} * \text{L/K} * \text{mol})(323 \text{ K})] = 5.6 * 10^{-5} \text{ mol}$

Current: $I = ZNF/t = 2 * (5.6 * 10^{-5} \text{ mol}) (96485 \text{ C/mol}) / (1.8 * 10^5 \text{ s}) = 6.1 * 10^{-5} \text{ A}$

Area = 5 cm²; $J = 300 \text{ mA/cm}^2$

%Current(Carbonate removal) = $100 * 6.1 * 10^{-5} \text{ A} / (5 * 0.3 \text{ A}) = 0.004\%$

This Work: (Assume 5 ppm CO₂ being constantly generated)

Flow rate of 0.2 L/min; $V_{CO_2} = 5 \text{ ppm}$ (0.2 L/min)(960 min) = 0.96 mL

$T = 298 \text{ K}$

$N_{CO_2} = (1 \text{ atm})(0.00096 \text{ L}) / [(0.08206 \text{ atm} * \text{L/K} * \text{mol})(298 \text{ K})] = 3.9 * 10^{-5} \text{ mol}$

Current: ($Z = 4$ for this process) $I = 4 * (3.9 * 10^{-5} \text{ mol}) (96485 \text{ C/mol}) / 57600 \text{ s} = 0.26 \text{ mA}$

%Current(Carbonate removal) = $100 * 0.26 \text{ mA} / [(1.6 \text{ cm}^2)(10 \text{ mA/cm}^2)] = 1.7\%$

References

- (1) Bockris, J. O. Kinetics of Activation Controlled Consecutive Electrochemical Reactions: Anodic Evolution of Oxygen. *J. Chem. Phys.* **1956**, 24 (4), 817–827. <https://doi.org/10.1063/1.1742616>.
- (2) Shinagawa, T.; Garcia-Esparza, A. T.; Takanabe, K. Insight on Tafel Slopes from a Microkinetic Analysis of Aqueous Electrocatalysis for Energy Conversion. *Sci. Rep.* **2015**, 5, 1–21. <https://doi.org/10.1038/srep13801>.
- (3) Watanabe, S.; Fukuta, K.; Yanagi, H. Determination of Carbonate Ion in MEA during Alkaline Membrane Fuel Cell (AMFC) Operation. *ECS Trans.* **2010**, 33 (1), 1837–1845.