Supporting Information

Bidirectional Energy & Fuel Production Using RTO-Supported-Pt-IrO₂ Loaded Fixed Polarity Unitized Regenerative Fuel Cells

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# Equal Contribution

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Physicochemical Characterization of RTO, IrO$_2$/RTO and Pt-IrO$_2$/RTO. Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDX) using FEI Nova Nano 230 Field Emission SEM is used to determine the particle size, elemental composition and mapping (distribution) of RTO, IrO$_2$/RTO and Pt-IrO$_2$/RTO. X-ray diffraction (XRD) is performed with Bruker d8 advance x-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA to determine the phases of the above materials. The scanning is done by sweeping from 20-80° (2θ) at a rate of 0.02° per step with 0.5 sec per step. To determine the surface elemental composition and oxidation states of the elements x-ray photoelectron spectroscopy (XPS) is performed on RTO, IrO$_2$/RTO and Pt-IrO$_2$/RTO using 5000 VersaProbe II Scanning ESCA Microprobe with Al K-alpha x-ray source. Work function of the materials is determined via ultra-violet photoelectron spectroscopy (UPS) using 5000 VersaProbe II Scanning ESCA Microprobe with He I (21.2 eV) source. For UPS measurements, the catalysts are sonicated in iso-propanol solution followed by deposition onto an Au-sputtered silicon wafer. Transmission electron microscopy (TEM) (FEI Tecnai G2 Spirit) is performed to determine the particle size of RTO, IrO$_2$/RTO and Pt-IrO$_2$/RTO, Pt dispersion and distribution on IrO$_2$/RTO.

Electrochemical Characterization using Rotating Disk Electrode (RDE). For OER activity measurement, an aqueous suspension of the catalyst is obtained by dispersing 11 mg of catalyst (IrO$_2$-RTO) in 10 ml of isopropanol and 7.5 ml of DI water. 70 µl of Nafion solution (5 wt% Nafion; 1100 EW) is added as the binder. Catalyst inks are prepared by ultrasonication (QSonica; Q700 sonicator) of the mixture (sonication ON = 1 min. and sonication OFF = 30 sec.) for 5 min. Then 7.4 µl of the ink is deposited onto a freshly polished glassy carbon (GC) disk electrode (area = 0.196 cm^2) using the inverted RDE method.[1] The inverted electrode is rotated at 400 rpm and dried at room temperature to achieve a uniform thin catalyst layer on the GC electrode. This procedure results in a loading of 20 µg PGM (platinum group metal) oxide catalyst (RuO$_2$, IrO$_2$ or IrO$_2$+RuO$_2$) cm^{-2} disk on the GC electrode as those are the OER active catalysts. The procedure differs slightly for different catalysts to achieve similar PGM oxide catalyst loading.

For HOR, the catalyst ink is prepared according to the following recipe: 30 mg of Pt-IrO$_2$/RTO, 2.5 ml of deionized water, 5 ml of isopropanol, and 220 µL of Nafion solution (5 wt% Nafion; 1100 EW). Similarly, the mixture is ultrasonicated followed by drop-casting of 9 µL of the solution onto the GC electrode to achieve Pt (HOR active) loading of 20 µg cm^{-2}.

The loadings of different elements in the catalyst using SEM/EDX and the mass-loading of PGMs for Pt-IrO$_2$/RTO, IrO$_2$/RTO, RTO and Pt/C in RDE setup are as follows (Table S1),

Table S1a. The loadings of different elements in the catalyst using SEM/EDX and the mass-loading of PGMs for Pt-IrO$_2$/RTO, IrO$_2$/RTO, RTO and Pt/C in RDE setup.

	Pt (Wt%)	Ir (Wt%)	Ru (Wt%)	Ti (Wt%)	RDE loading (mg cm^{-2})
Pt-IrO$_2$/RTO	4.8	9.2	45.2	10.1	0.02 (of Pt+Ru+Ir)
IrO$_2$/RTO	-	9.4	44	9.6	0.02 (of Ir+Ru)
RTO	-	-	57	12	0.02 (of Ru)

Table S1b. The elemental composition determined in the electrocatalysts using ICP-MS for Pt-IrO$_2$/RTO, IrO$_2$/RTO and RTO.

	Pt (Wt%)	Ir (Wt%)	Ru (Wt%)	Ti (Wt%)
Pt-IrO$_2$/RTO	4.2	9.7	44.3	8.5
IrO$_2$/RTO	-	11.3	42.2	8.8
RTO	-	-	58.1	10.2

Electrochemical characterization is performed in a jacketed glass cell at room temperature with a three-electrode setup (catalyst deposited GC – working electrode, Pt mesh - counter electrode and saturated calomel electrode (SCE) - reference electrode). The electrolyte used is 0.1 M perchloric acid (HClO$_4$) that is saturated by bubbling appropriate gases for at least 45 minutes prior to the experiments (OER – O$_2$, HOR – H$_2$ and background – N$_2$). The cyclic voltammetry (CV) is employed to determine the electrochemical active surface area (ECSA) of Pt-IrO$_2$/RTO and Pt/C by scanning the potential between 0.06 V - 1.2 V vs RHE under a scan rate of 20 mV s^{-1}. ECSA is measured using the total charge transfer (Q$_{Hads}$) associated with hydrogen adsorption and desorption (from CV) and the amount of charge (Q$_{0,Hads}$) transferred with monolayer adsorption (210 µC cm^{-2}).[2] The double layer capacitance (C$_{dl}$) (surrogate of ECSA) of the other catalysts without Pt is measured by using CVs at different scan rates (υ = 5, 10, 20 and 50 mV/s) by scanning from 0.5 – 1.2 V vs RHE. C$_{dl}$ is determined using the following equation,[1, 3]

$$i = C_{dl} \times \upsilon \qquad (S1)$$

Linear sweep voltammetry (LSV) is employed to measure the activity of the catalysts towards OER at 1600 rpm by sweeping the potential from 1.2 V - 2.05 V vs RHE under oxygen purging. Different rotation rates are not used for OER due to the absence of mass transfer limitation. For HOR the electrode is rotated with 400, 900, 1600 and 2500 rpm by scanning the potential from -0.35 to 0.38 V vs SCE under H$_2$ purging to show the effect of diffusion limitation.

OER stability is performed on the catalysts by applying a constant potential of 1.7 V vs RHE for 2 hours in 0.1 M HClO$_4$ under oxygen purging at 1600 rpm. Chrono-amperometry is also performed only on Pt-IrO$_2$/RTO by applying 0.3 V vs RHE for 2 hours in 0.1 M HClO$_4$ under hydrogen purging at 1600 rpm to show the effect of HOR on the stability of the catalyst. The activity of the catalysts is also measured before and after the stability test by performing LSVs.

All the experiments are done in triplicates.

Efficiency Calculation. Round-trip efficiency (RTE) is calculated using the following equation:[4]

$$RTE(\%) = WE_{efficiency} \times FC_{efficiency} \qquad (S2)$$

Where, $WE_{efficiency}$ is the water electrolyzer efficiency, and $FC_{efficiency}$ is fuel cell efficiency. The fuel cell efficiency at a given current density is calculated according to the following equation:

$$FC_{efficiency} = \frac{V_{observed}}{E_{reversible}(T,P)} \times 100\% \qquad (S3)$$

Where, $E_{reversible}(T, P)$ is determined as 1.168 V and $V_{observed}$ is measured cell potential at a given current density.[5]

An extra 0.252 V needs to be added to $E_{reversible}(T, P)$ as energy requirement for a mole of H_2 production via a mole of liquid water splitting to produce at 25 °C is supplied by electricity as well as heat.

The electrolyzer efficiency is determined according to the following equation:

$$WE_{efficiency} = \frac{1.42}{V_{observed}} \times 100\% \qquad (S4)$$
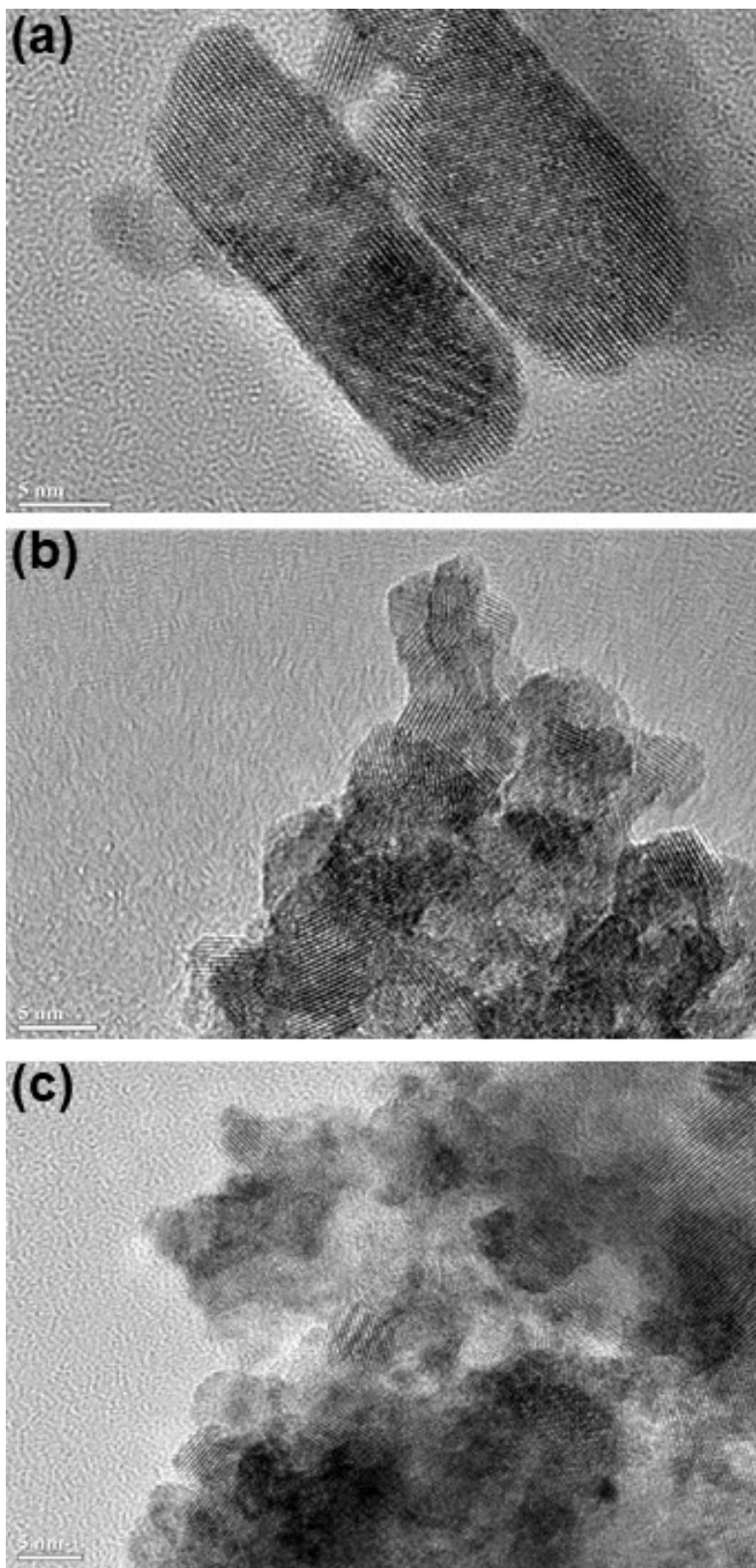
Figure S1. HRTEM images of (a) RTO, (b) IrO$_2$/RTO and (c) Pt-IrO$_2$/RTO samples.
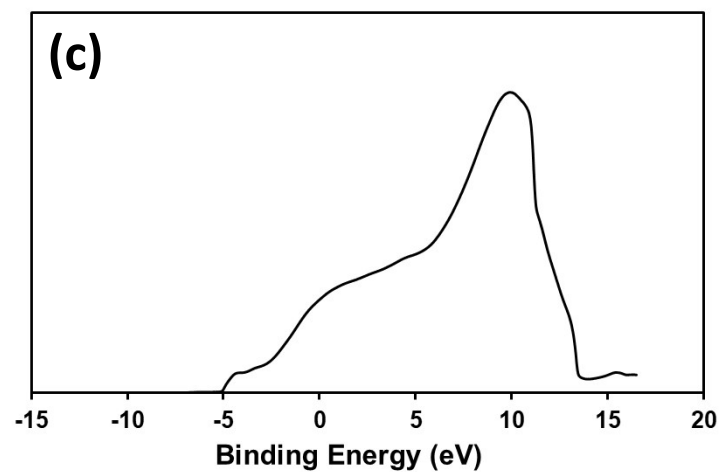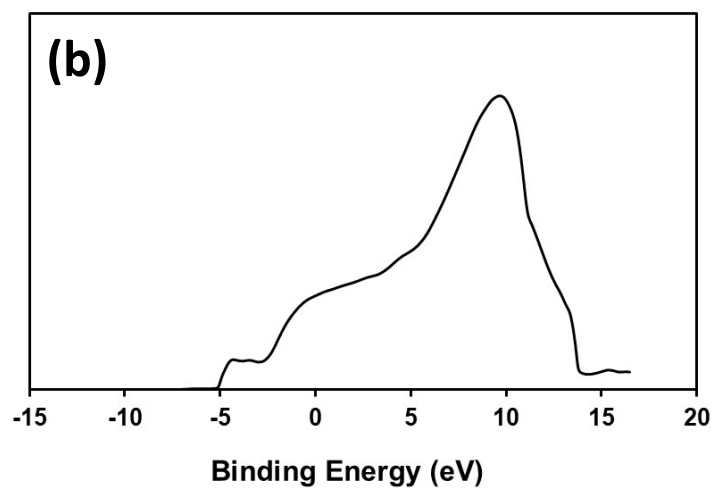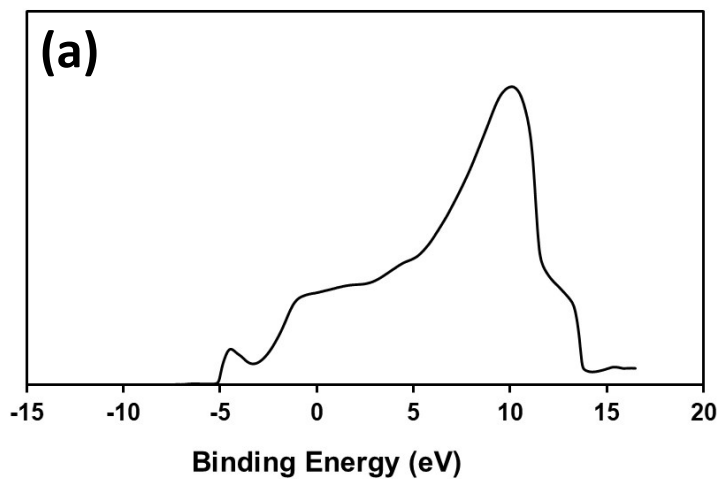
Figure S2. UPS of (a) RTO, (b) IrO_2/RTO and (c) Pt-IrO_2/RTO. The work function is determined as, *work function= He-photon energy (21.2 eV) – (Cut-off energy- Fermi level).*
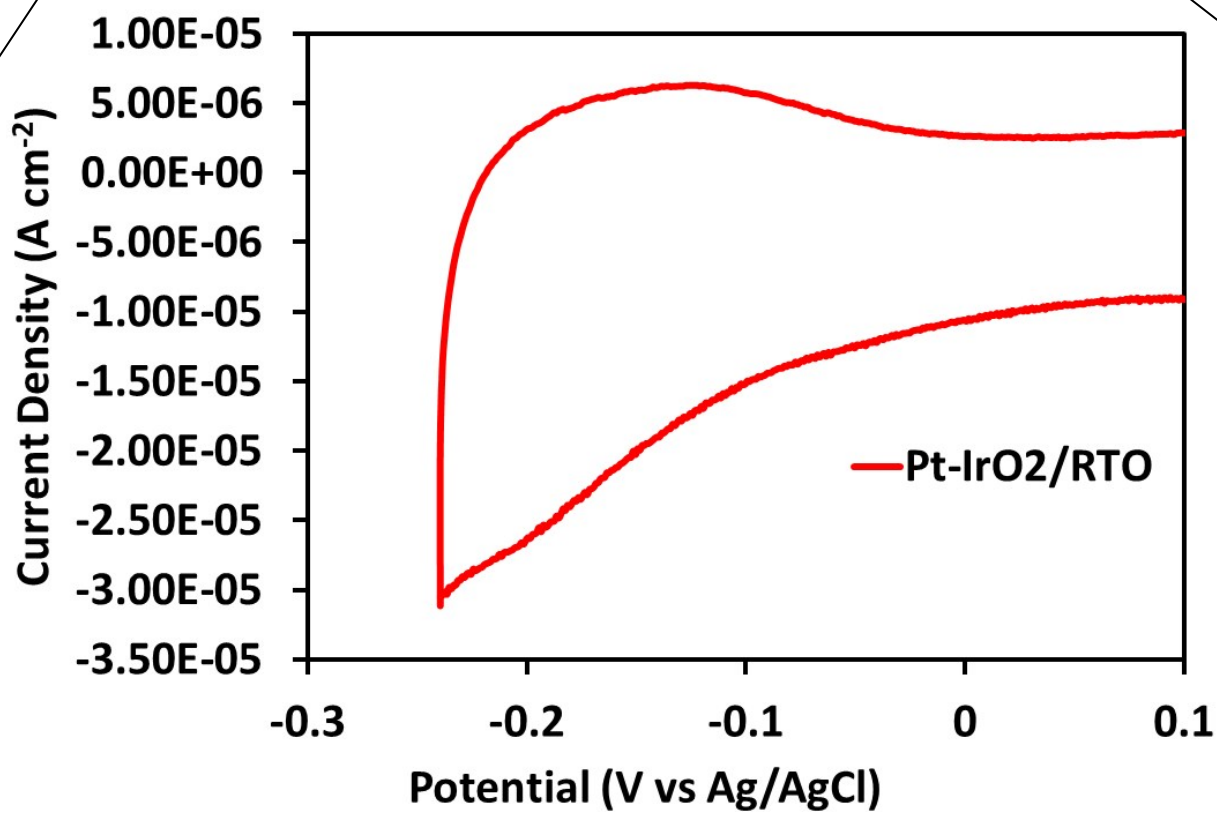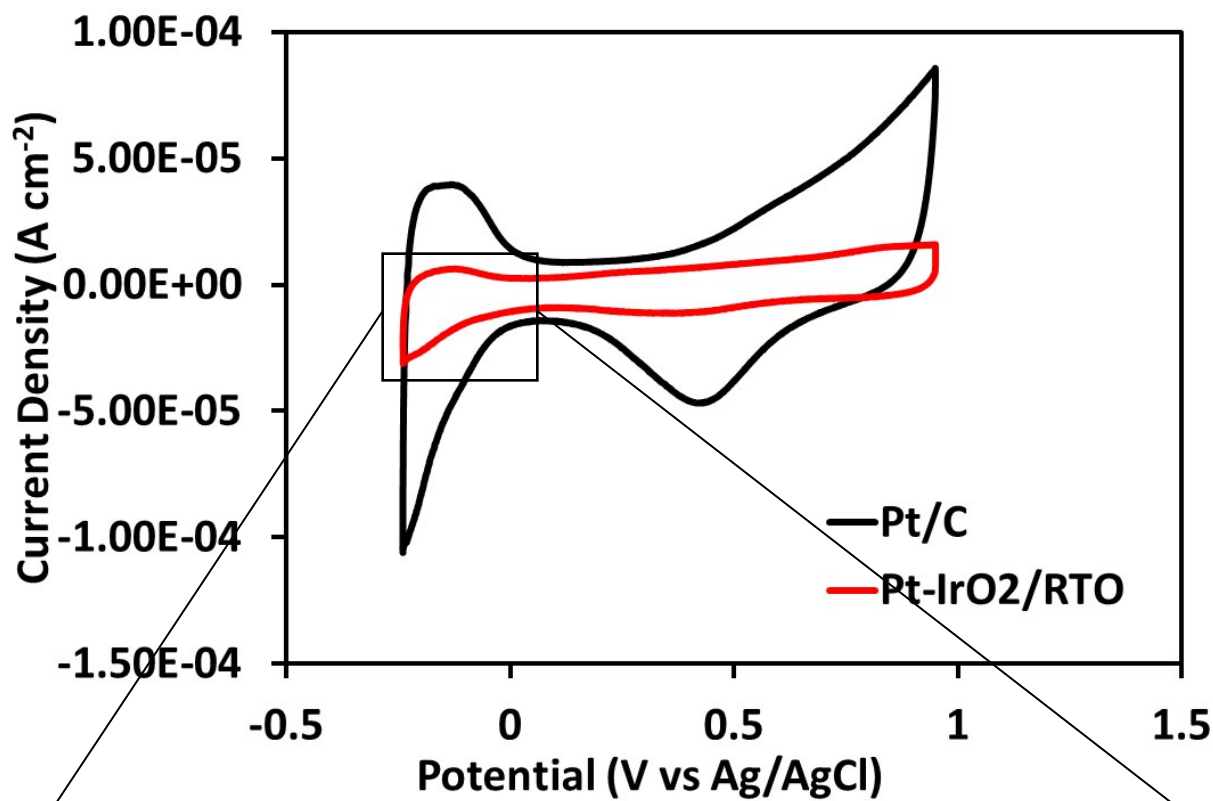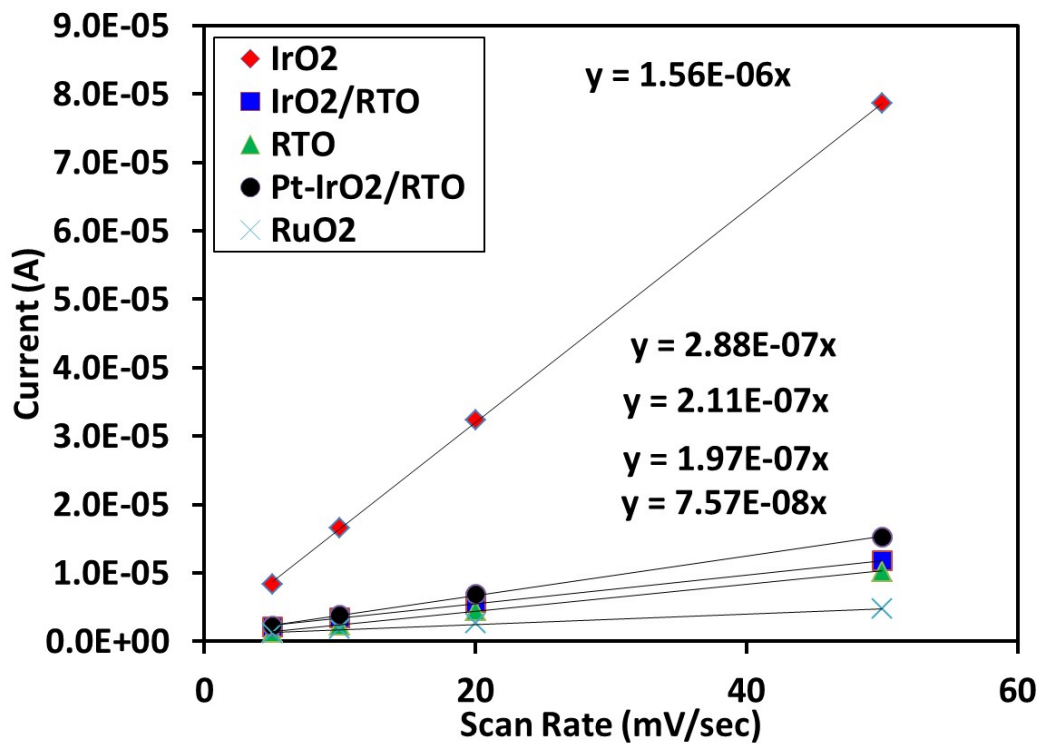
Figure S3. CV of Pt/C and Pt-IrO$_2$/RTO for ECSA measurement through H-UPD.

Figure S4. Current vs scan rate of the electrocatalysts at different scan rates (double layer capacitance) at 0.75 V vs RHE.
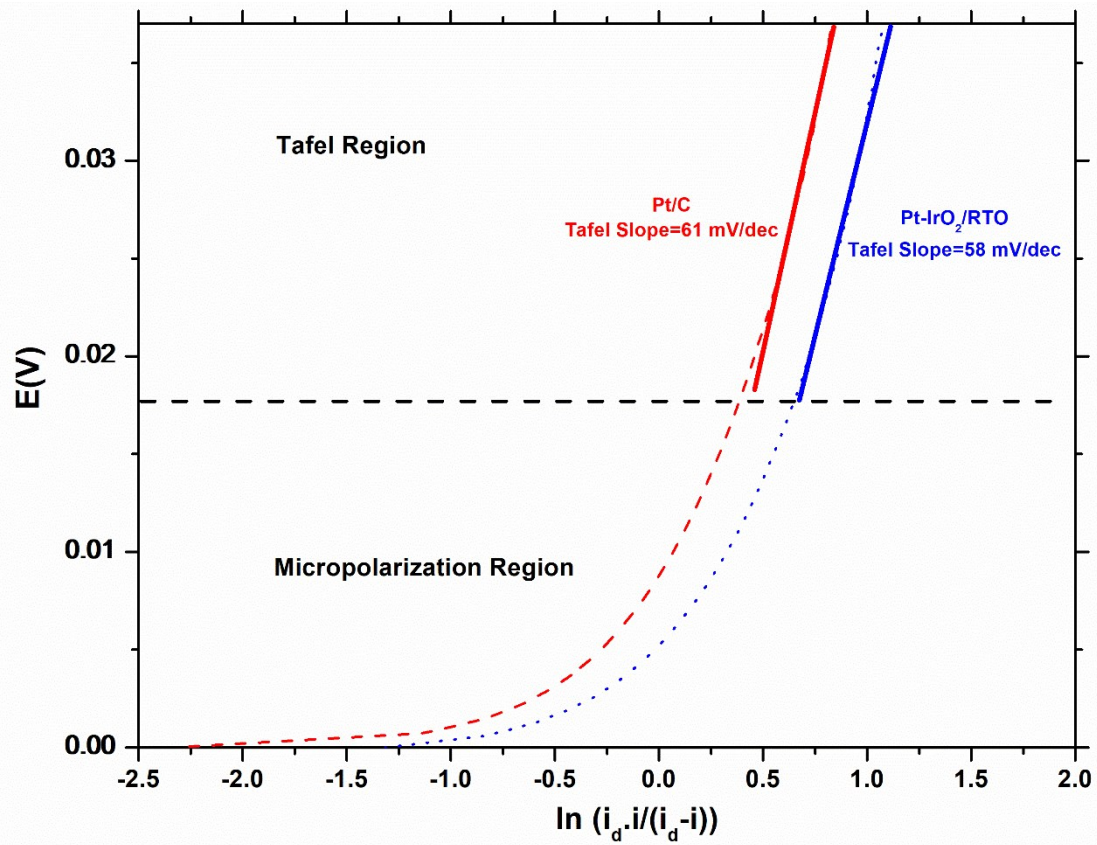
Figure S5. Tafel HOR analysis of Pt/C and Pt-IrO$_2$/RTO.

Table S2. Comparison of the URFC performances.

URFC -mode	Bifunctional catalyst (Loading)	Membrane	Electrolyzer @ 1.8 V (mA cm^{-2})	Fuel cell @ 0.8 V (mA cm^{-2})	RTE at 1.0 A/cm^2	Ref
FG	Pt (1) (HER/HOR)- Pt-Ir (1) (OER/ORR)	N212	NA	400	60%	[4]
FG	Pt (0.35) (HER/HOR)- Pt$_{0.5}$Ir$_{0.5}$ (1.5) (OER/ORR)	N115	600	200	NA	[6]
FP	Pt (0.72) (HER/ORR)- Pt-Ir/TiC (0.72) (OER/HOR)	NE1035	1500	110	31.8	[7]
FG	Pt (0.25) (HER/HOR)- Pt (0.25) (OER/ORR)	N212	300	250	NA	[8]
FG	Pt (3) (HER/HOR)- Pt$_{85}$Ir$_{15}$ (3) (OER/ORR)	N115	NA	130	37%	[9]
FP	Pt (0.15) (HER/ORR)- Pt-IrO$_2$/RTO (1) (OER/HOR)	N212	1050	164	40.2%	This work

All the loadings are reported in mg/cm^2.

References

1. S. Jung, C. C. McCrory, I. M. Ferrer, J. C. Peters and T. F. Jaramillo, *J. Mater. Chem. A*, 2016, **4**, 3068-3076.
2. W. Li and A. M. Lane, *Electrochem. Comm.*, 2011, **13**, 913-916.
3. K. Kishor, S. Saha, S. Sivakumar and R. G. S. Pala, *ChemElectroChem*, 2016, **3**, 1899-1907.
4. Y. N. Regmi, X. Peng, J. C. Fornaciari, M. Wei, D. J. Myers, A. Z. Weber and N. Danilovic, *Energy Environ. Sci.*, 2020.
5. K. W. Harrison, R. Remick, A. Hoskin and G. Martin, National Renewable Energy Lab.(NREL), Golden, CO (United States), 2010.
6. S. Grigoriev, P. Millet, K. Dzhus, H. Middleton, T. Saetre and V. Fateev, *Int. J. Hydrogen Energy*, 2010, **35**, 5070-5076.
7. P. Kúš, A. Ostroverkh, I. Khalakhan, R. Fiala, Y. Kosto, B. Šmíd, Y. Lobko, Y. Yakovlev, J. Nováková and I. Matolínová, *Int. J. Hydrogen Energy*, 2019, **44**, 16087-16098.
8. Y.-H. Pai and C.-W. Tseng, *J. Power Sources*, 2012, **202**, 28-34.
9. T. Ioroi, T. Oku, K. Yasuda, N. Kumagai and Y. Miyazaki, *J. Power Sources*, 2003, **124**, 385-389.