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A Low Temperature Unitized Regenerative Fuel Cell Realizing 60% Round Trip Efficiency and 10,000 Cycles of Durability for Energy Storage Applications

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Table S1. *Membrane electrode assembly builds parameters*

Catalyst	Pt- and Ir-black	Pt/C
Ionomer weight % (wrt catalyst)	11.6[1]	-
Ionomer:carbon (weight ratio)	-	0.6[2]
Solid weight % in the ink	0.28	0.28
Solvent volume ratio	H_2O:EtOH:NPA = 25:25:50	H_2O:NPA = 50:50
Sonicator	Probe (ice water)	Bath (10-12 °C)
Sonication time (min)	30	30-60
Catalyst loading (mg/cm^2 metal)	1.0	0.3
Spray rate (mL/min)	0.2	0.2
Spray temperature (°C)	90	90
Shaping Air (psi N_2)	1.0	1.0

Table S2. Efficiencies at various current densities without iR corrections.

Device	Memb/Cath-feed/An ff	Eff (%) 0.5 A/cm^2	Eff (%) 1.0 A/cm^2	Eff (%) 1.5 A/cm^2	Eff (%) 2.0 A/cm^2
EL (discrete)	N117 / N_2 / Ti	89	81	74	68
EL (URFC)	N212 / N_2 / Ti	100	99	96	94
FC (discrete)	N212 / Air / Graphite	65	58	51	40

FC (URFC)	N212 / Air / Ti	65	58	48	33
FC (URFC)	N212 / O_2 / Ti	66	62	58	53
URFC	N212 /Air (FC) N_2 (EL) / Ti	64	57	46	30
URFC	N212 / O_2 (FC) N_2 (EL) / Ti	64	60	54	49

Notes: 1. EL – electrolyzer, FC – fuel cell, URFC – unitized regenerative fuel cell, discrete – the membrane electrode assembly (MEA) is manufactured to run in only one mode, Cath – cathode, An – anode, ff – flowfield, Eff – efficiency (%),.

Efficiency Calculation:

Round trip efficiency calculation. The overall reaction is

$$H_2O_{liquid} \leftrightarrow H_2 + \frac{1}{2}O_2$$

The reversible potential is governed by temperature and activity of the species:

$$E_{rev,(T,P)} = E_{rev}^{0} + \frac{RT}{2F} ln[\frac{a(H_2)\cdot\sqrt{a(O_2)}}{a(H_2O)}]$$

At a temperature of 80 °C, the saturation pressure of H_2O is 0.47 bar_a. For liquid water, the activity of water is $a(H_2O)$ is one, while the activity of the gaseous species is represented by the ratio of their partial pressure to the standard pressure of 1 bar. The temperature dependent standard reversible potential, E_{rev}^{0}, can be obtained from the literature.[3]

$$E_{rev}^{0} = 1.2291\,V - 0.0008456\,V\cdot(T - 298.15K)$$

Therefore, the fuel cell efficiency at each current density is given by:

$$FC_{effi} = \frac{V_{measured}}{E_{rev,(T,P)}} * 100\%$$

Under the electrolyzer testing condition, the $E_{rev,(T,P)}$ is calculated to be 1.168 V. Since the energy that is required for splitting of a mole of liquid water to produce a mole of H_2 at 25 °C is not only from electricity but also heat[4], which adds an extra of 0.252 V of cell voltage on top of the calculated $E_{rev,\ (T,P)}$.

Then, the electrolyzer efficiency at each current density is given by:

$$EC_{effi} = \frac{1.42}{V_{measured}} * 100\%$$

And the related RTEs is give by:

$$RTE = FC_{effi} * EC_{effi}$$

Table S3. Efficiencies of various PEM based URFCs using comparable membrane thicknesses.

Temp (°C) EL/FC	I (A/cm²) EL/FC	RTE (%)	Membrane	Remark/Reference
80/80	0.5	50.3	N212	Both EL and FC RTEs used HHV[4]
NA/NA	0.1	37.5	N212	Both electrodes with 0.25 mg Pt/C.[5]
65/65	0.5	40.6	N212	Discrete mode.[6]
80/80	0.5	46	N212	Oxygen catalyst on carbon paper.[7]
75/75	0.5	49	N212	Oxygen as the cathode feed.[8]
80/80	0.4	42	N212	Oxygen catalyst is Pt-Ru/IrO_2[9]
75/70	1.0	43.8	N112	Oxygen catalyst is Pt and Ir-black.[10]
80/75	0.5	50.3	N112	RTE is 42.2% at 1 A/cm².[11]

Table S4. Concentrations of Pt and Ir post electrolyzer tests.

Test	[Ir] (ppb)	[Pt] (ppb)
CE-AST	0.086	0.051
CG-AST	0.026	0.101
Daily cycle day 1	0.109	0.119
Daily cycle day 2	0.034	0.075
Daily cycle day 3	0.048	0.072
DI water	0.044	0.051

Notes: 1. Starting volume of electrolyzer tests was 800-900 mL. 2. AST tests were conducted with the same water samples throughout the 10000 AST cycles. 3. Daily cycle tests were conducted on fresh batch of water samples for each day.

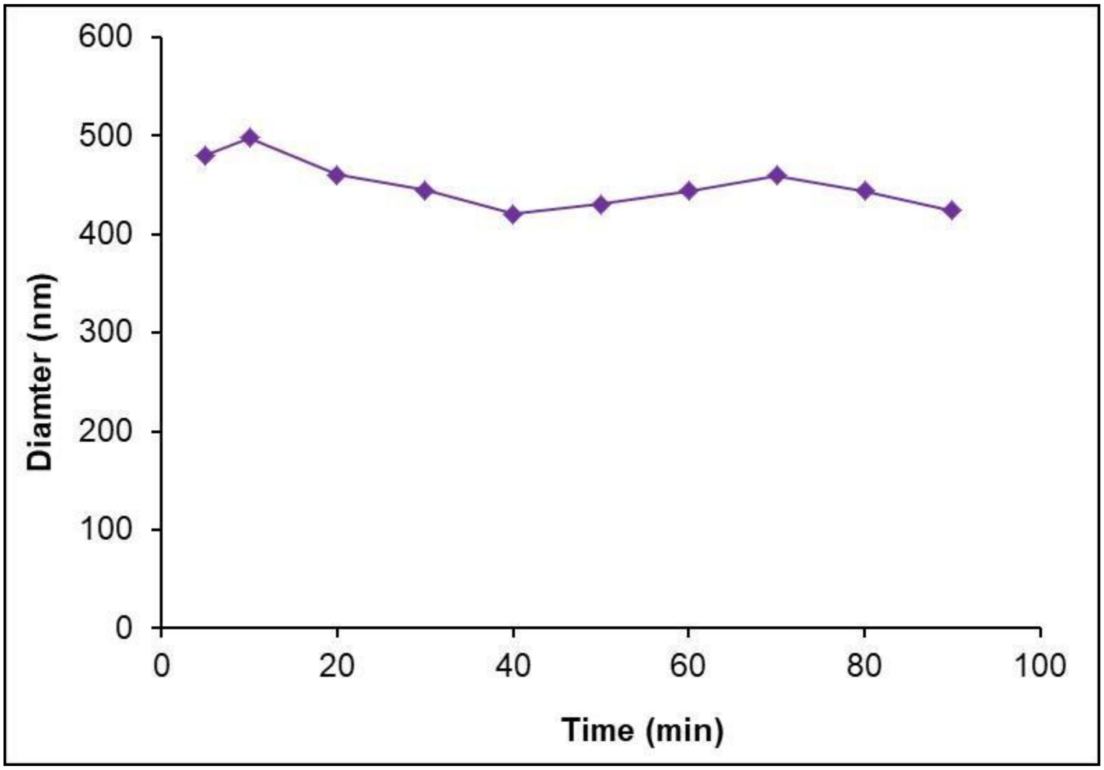
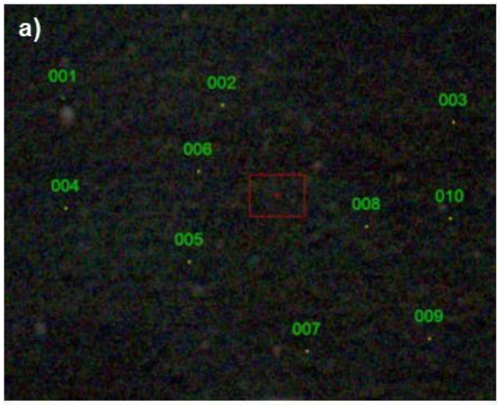
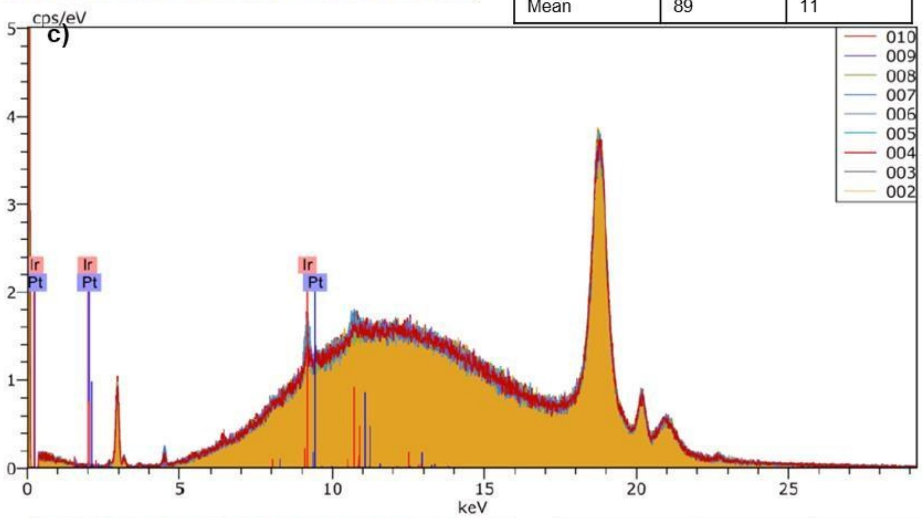


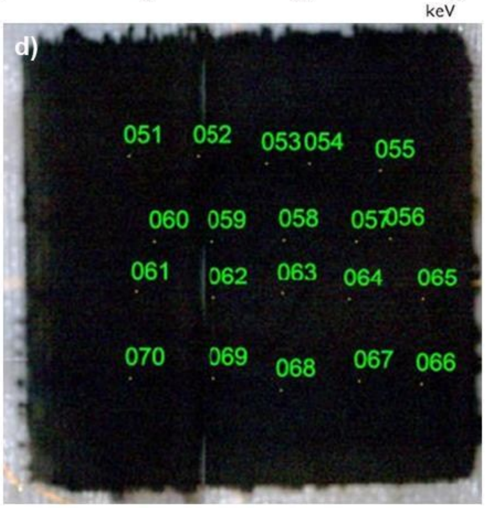
Figure S1. *Particle size analysis of a cathode catalyst layer Pt/C ink. Particle sizes were monitored to correspond with the time it took to spray coat 3 cathode catalyst layers using the same batch of Pt/C ink. Weighted averages of viscosity and refractive indexes were used to calculate average particle size.*



b)

Spectrum	Ir at%	Pt at%
1	88	12
2	81	19
3	90	10
4	89	11
5	79	21
6	97	3
7	96	4
8	95	5
9	89	11
10	88	12
Mean	89	11





e)

Spectrum	Ir at%	Pt at%
51	73	27
52	73	27
53	73	27
54	72	28
55	73	27
56	73	27
57	72	28
58	72	28
59	72	28
60	73	27
61	72	28
62	73	27
63	72	28
64	72	28
65	73	27
66	72	28
67	73	27
68	74	26
69	72	28
70	72	28
Mean	73	27

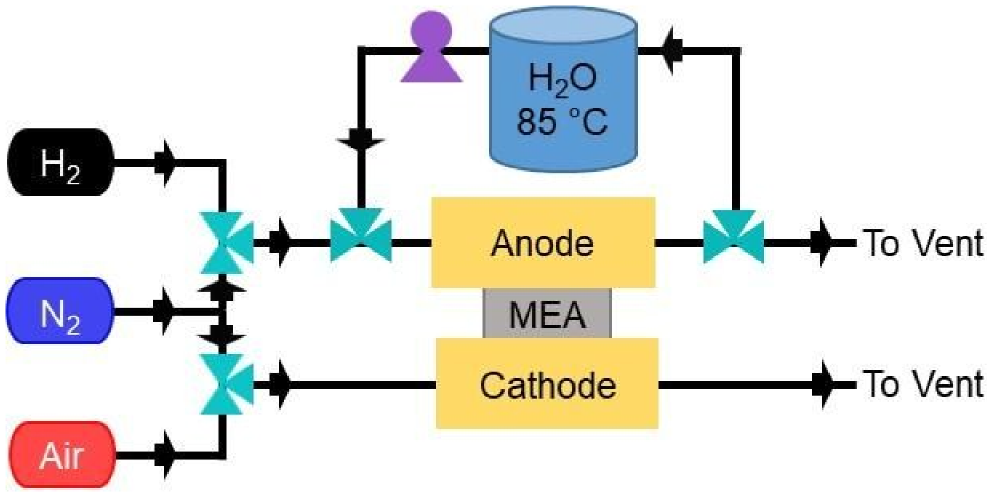


Figure S3. *Test Stand Schematic.*

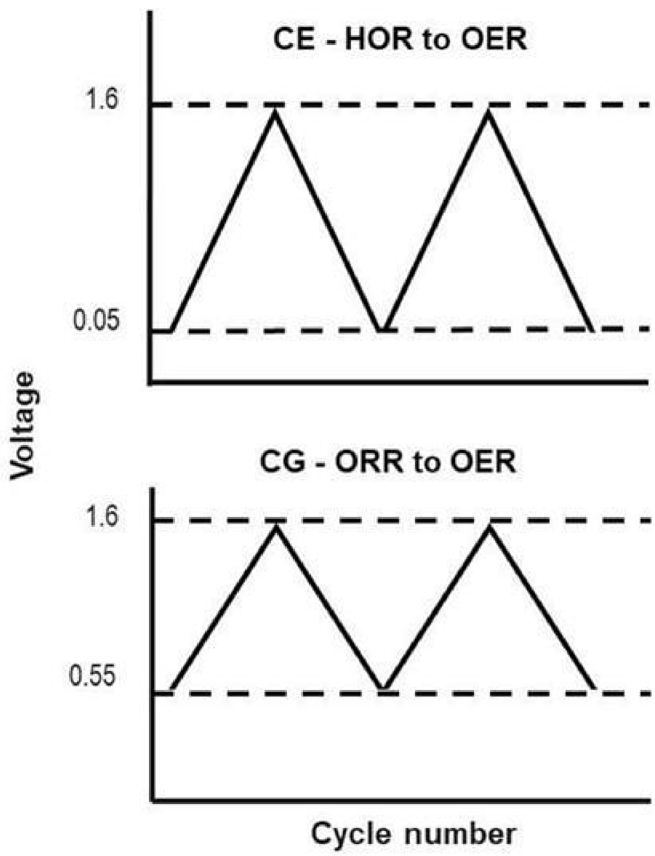


Figure S4. *Saw tooth profile of the AST performed on the URFC electrode with Pt-black and Ir-black mixed metal catalyst layer. During the AST, H_2 flow rate is 0.17 Pa at 100 RH on cathode and liquid water (80 °C) flow rate is 100 mL/min on anode. The scan rate is 300 mV/s.*

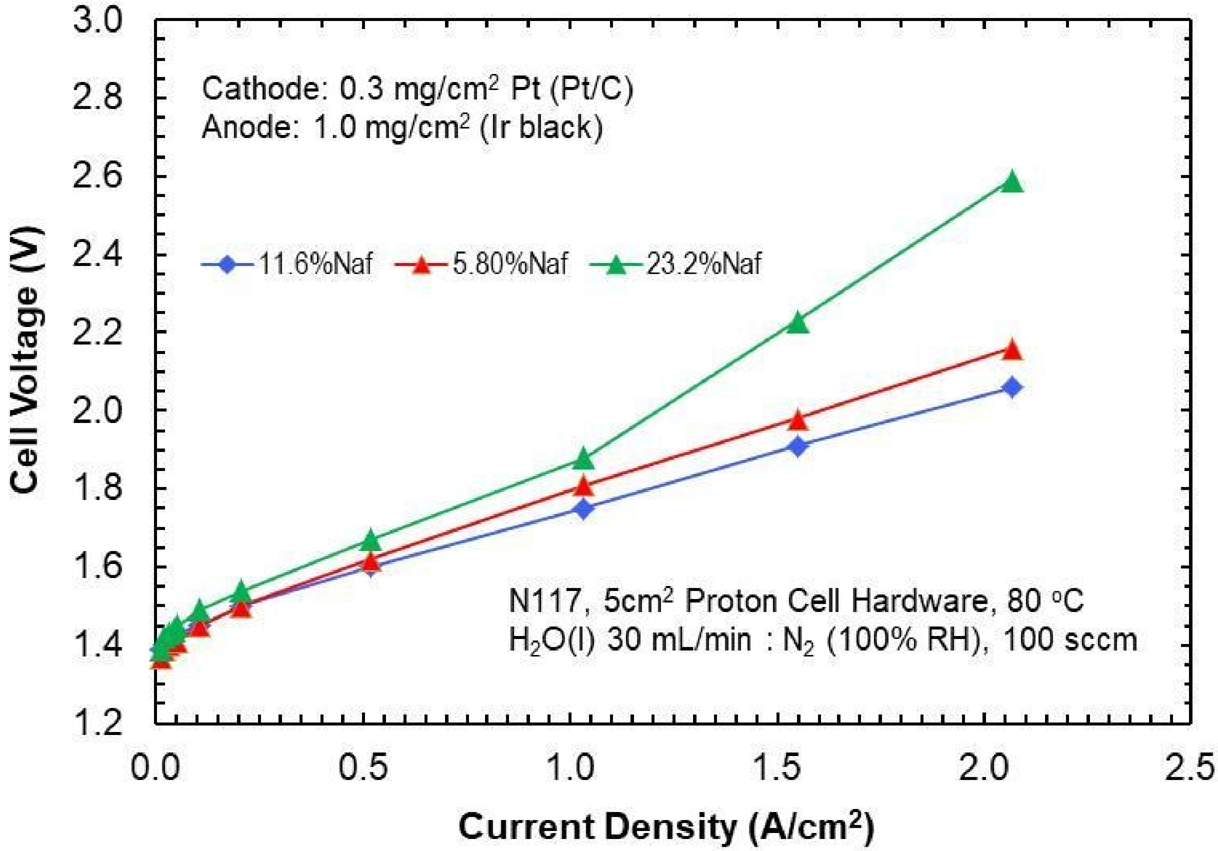


Figure S5. *Electrolyzer polarization curves for N117 CCMs with various Nafion content (weight percent of Ir-black)) on the anode. The activities are not iR corrected. Anode side contains 25 cm^2 parallel titanium flow field reduced to 5 cm^2 with gaskets and Ti PTL. Cathode side contains 25 cm^2 single serpentine graphite flow field reduced to 5 cm^2 with gaskets and 29 BC GDL.*

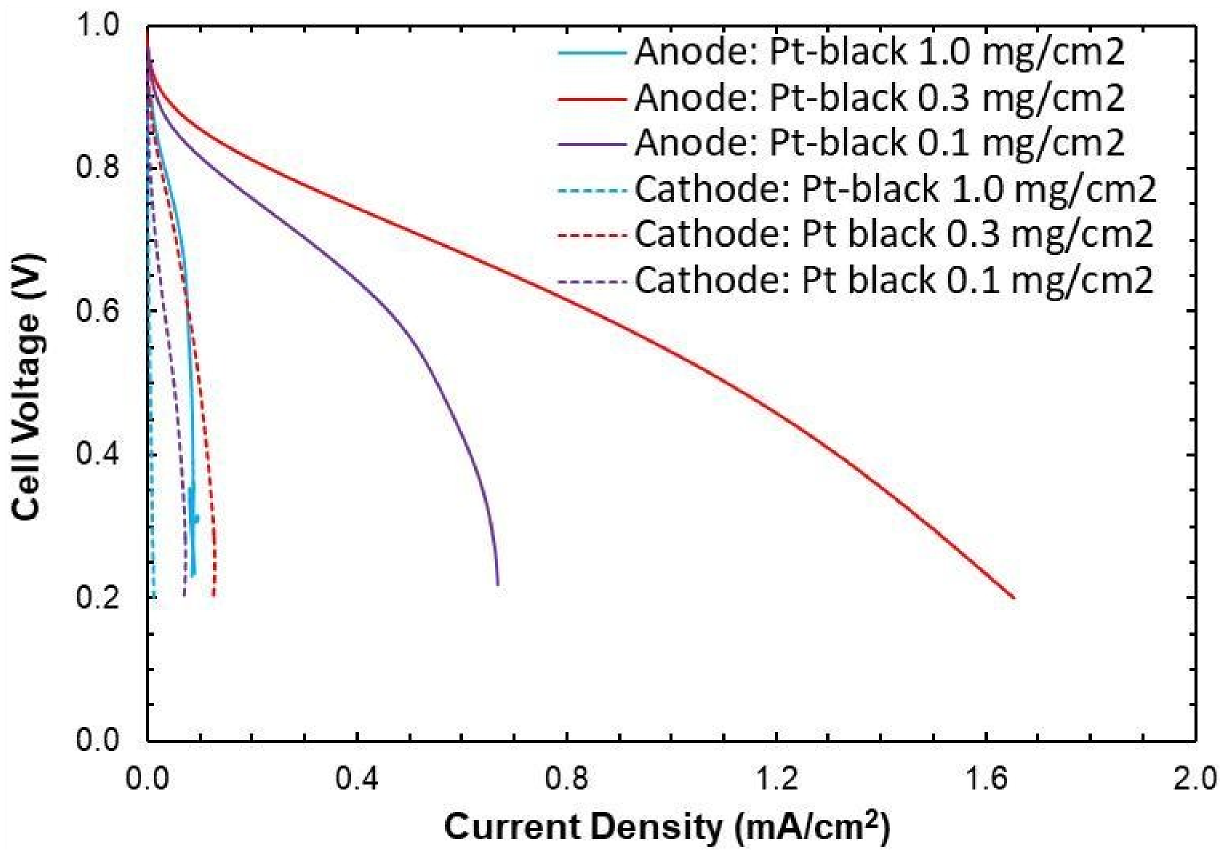


Figure S6. *Fuel cell polarization curves with electrodes fabricated with Pt-black loadings used as anodes (solids) and cathodes (dashed). Solid polarization curves represent CE configuration of URFC while dashed lines represent CG configuration. EL optimized I/C ratio is used. Note anomalous FC performance with change in Pt loading, and overall poor ORR performance.*

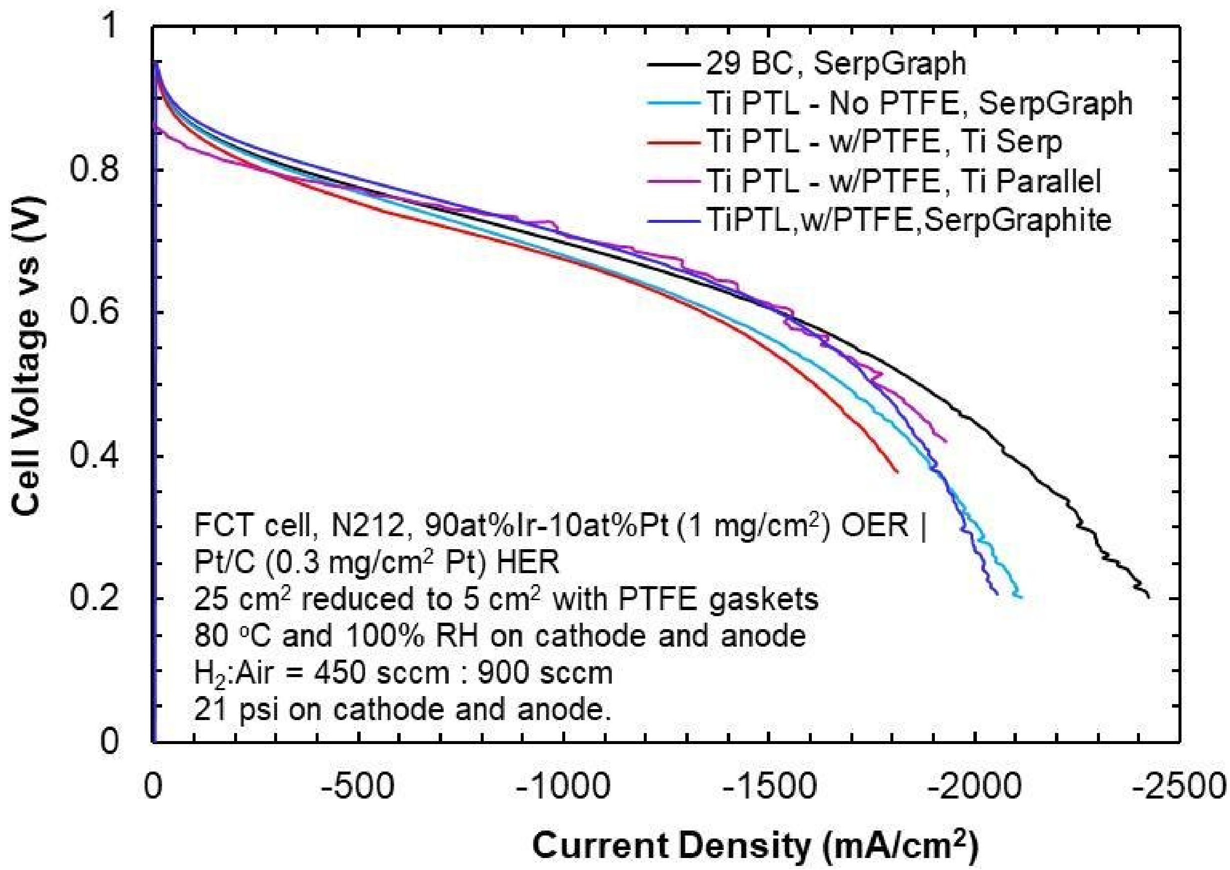


Figure S7. *FC polarization curves with various combinations of GDL/PTL and flowfields on the anode. Cathode was kept constant with 29 BC GDL and triple serpentine graphite (SerpGraph) flow field. Anode was changed to titanium PTL (Ti PTL) with or without 3 wt% PTFE and either serpentine titanium (Ti Serp) or parallel (Ti Parallel) flowfields.*

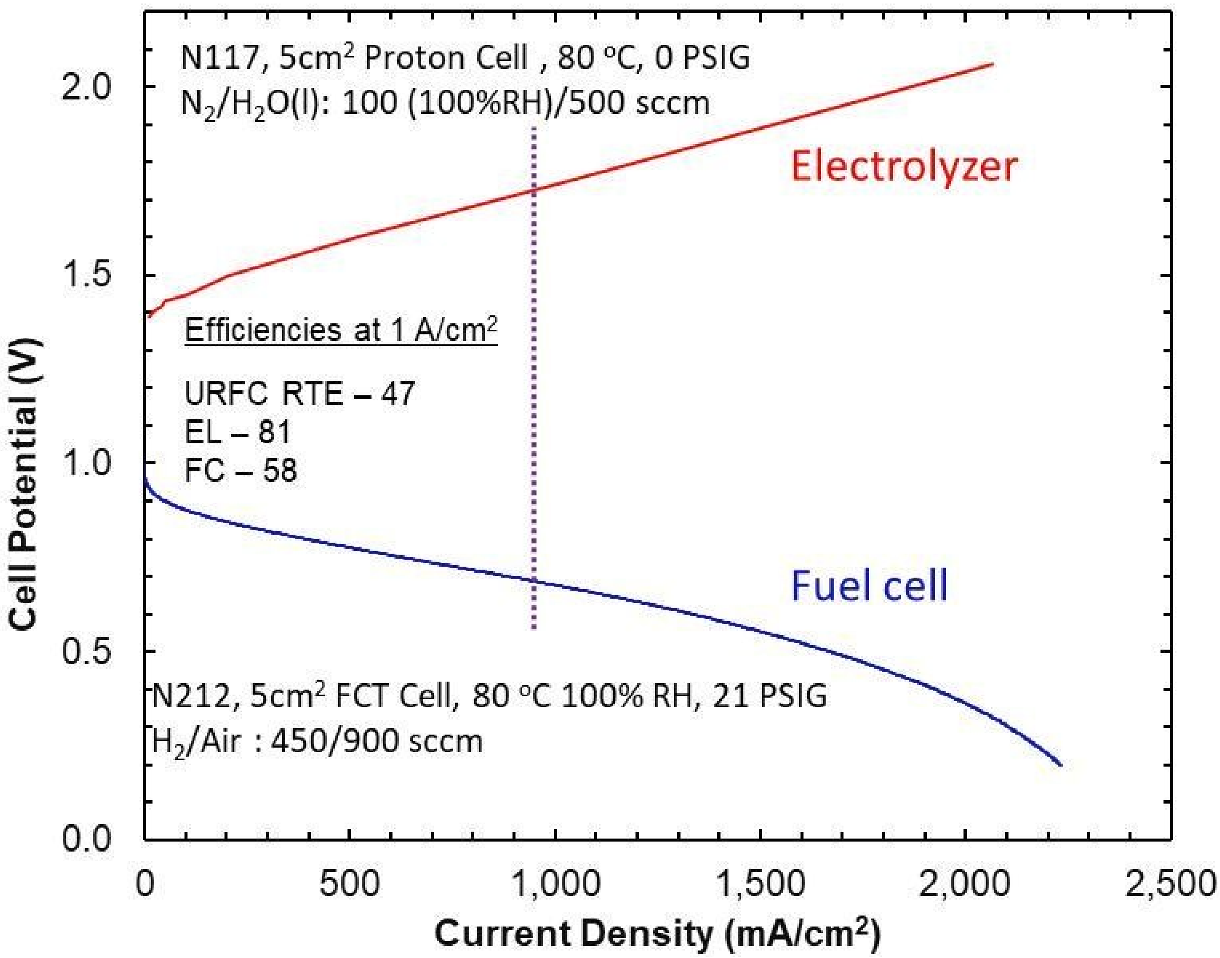


Figure S8. *Discrete FC and EC performance of the optimized URFC MEA (red) and discrete FC and EL MEA (black). The flowfields and diffusion/transport layers are the same for both discrete and URFC MEA, i.e. parallel Ti flowfield and Ti PTL on anode for EL mode and the rest serpentine graphite flowfields and 29 BC GDLs*

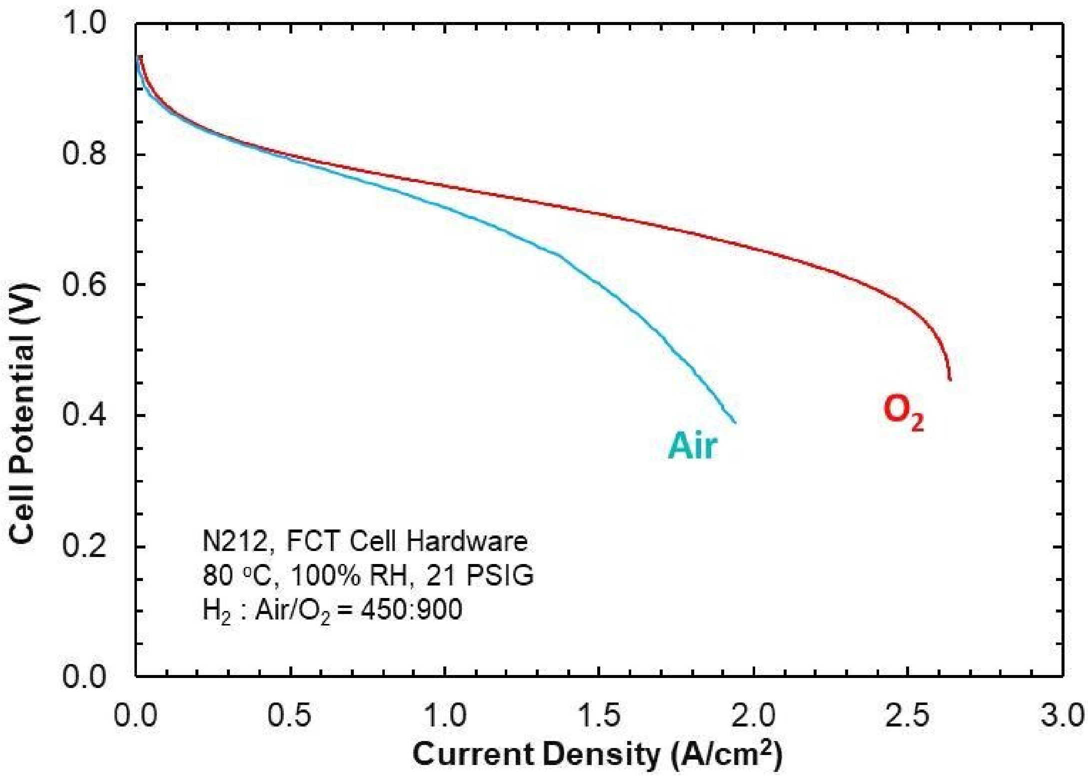


Figure S9. *FC performance of the optimized URFC MEA with air (neon) and oxygen (red) on the cathode. The flowfields are triple serpentine titanium on anode and graphite on cathode, the cathode gas diffusion layers is 29 BC, and Titanium porous transport layer on anode.*

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