

## Electronic Supplementary Information (ESI)

### Designing Membrane Electrode Assembly for Weakly Humidity- Dependent Proton Exchange Membrane Fuel Cells

Kangwei Qiao<sup>a</sup>, Huibing Liu<sup>a</sup>, Kui Ren<sup>b</sup>, Panpan Sun<sup>a</sup>, Liu Yang<sup>a</sup>, Shitao Wang<sup>a,\*</sup>, Dapeng Cao<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

<sup>b</sup> Research Institute of Petroleum Processing, Sinopec, Beijing 100029, People's Republic of China

\*Corresponding Authors. Email: [stwang@buct.edu.cn](mailto:stwang@buct.edu.cn); [caodp@mail.buct.edu.cn](mailto:caodp@mail.buct.edu.cn)

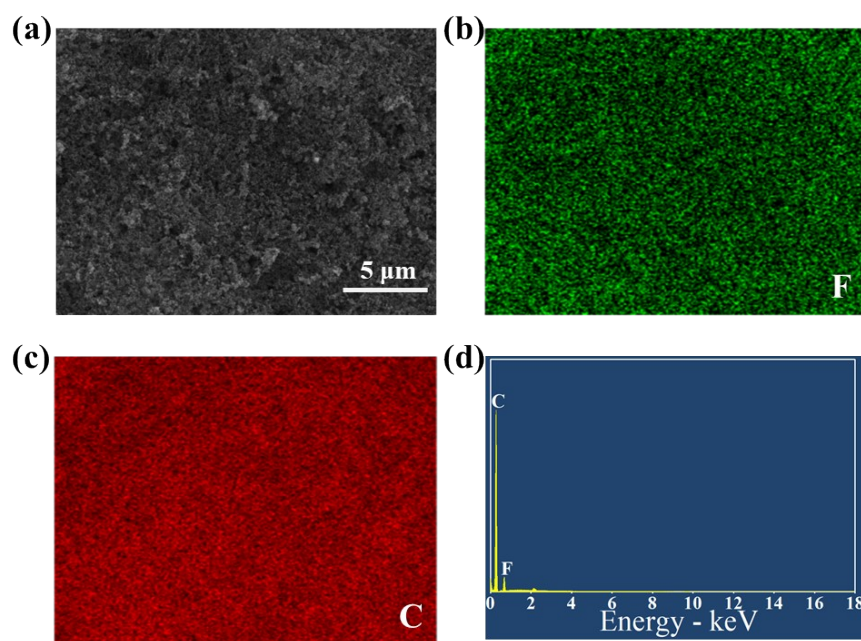


Fig. S1. (a)SEM image (15.00 kV) of microporous layer, (b-d)EDS of the microporous layer.

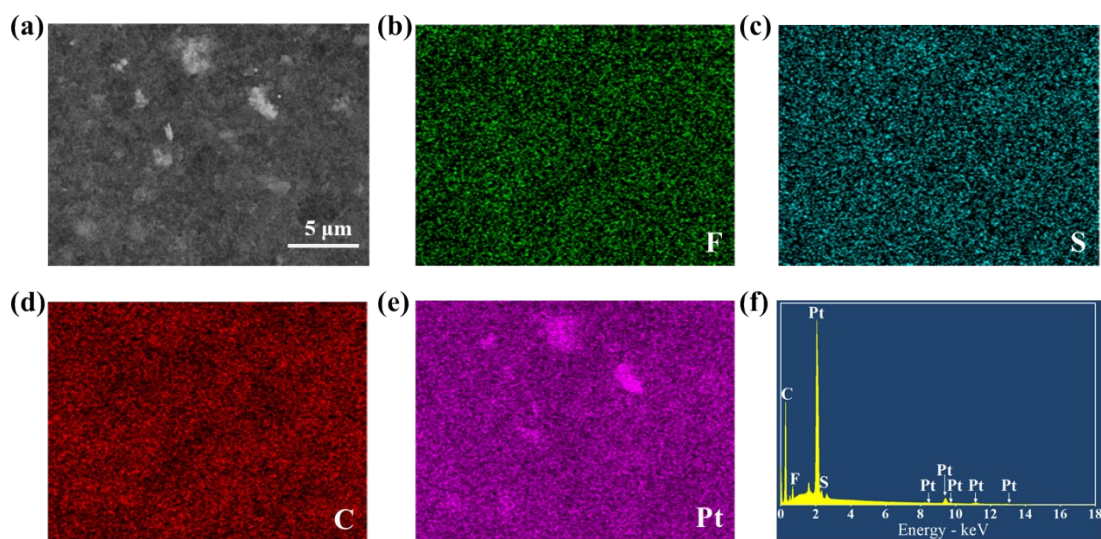


Fig. S2. (a) SEM image (15.00 kV) of catalyst layer, (b-f)EDS of the catalyst layer.

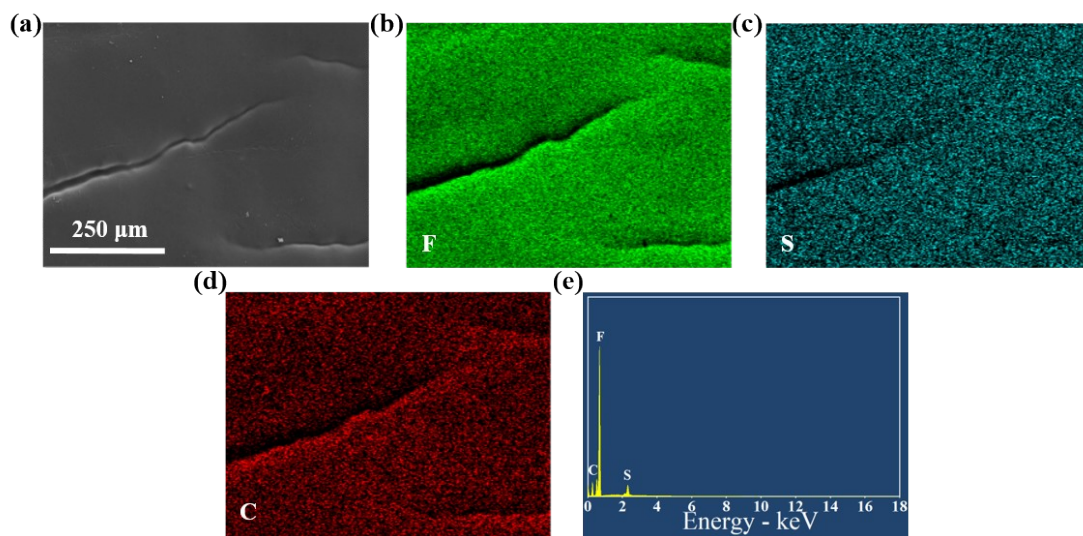


Fig. S3. (a) SEM image (15.00 kV) of membrane formed by ionomer in i-MEA, (b-e)EDS of the membrane of i-MEA.

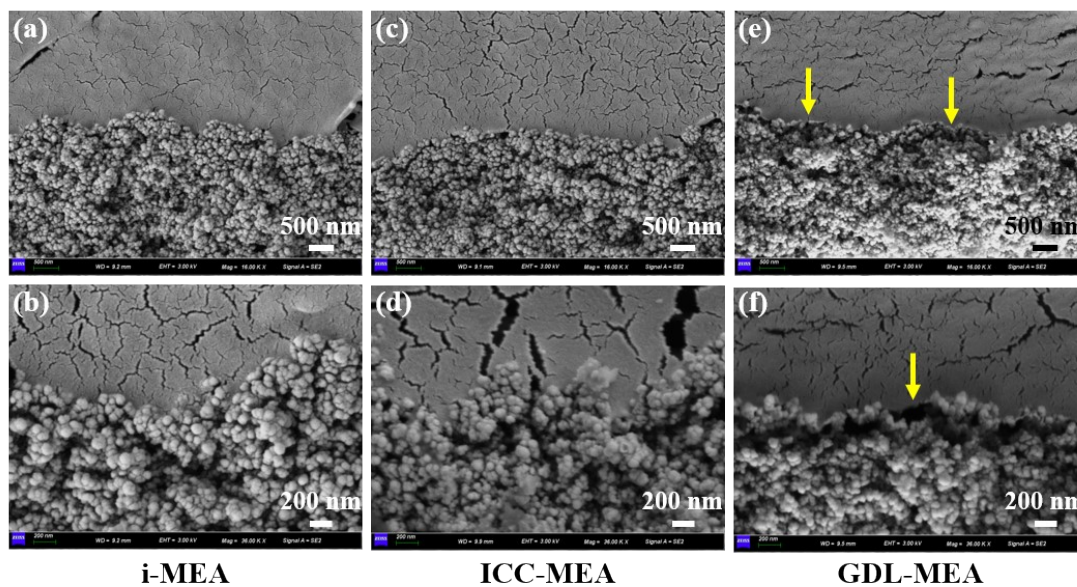


Fig. S4. SEM images of (3.00 kV) Cross-section of PEM/CL interface: (a, b) i-MEA, (c, d) ICC-MEA, (e, f) GDL-MEA.

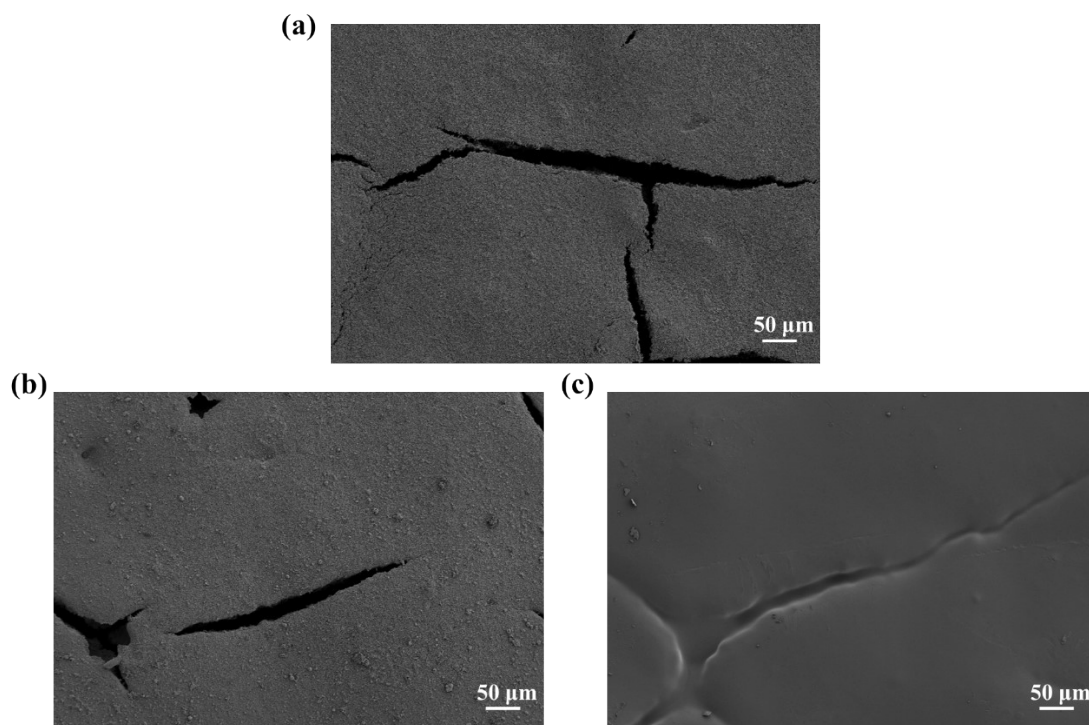


Fig. S5. SEM images (3.00 kV) of surface of (a) microporous layer, (b) catalyst layer on the microporous layer, (c) ionomer covering the catalyst layer. Cracks are eventually filled with ionomer.

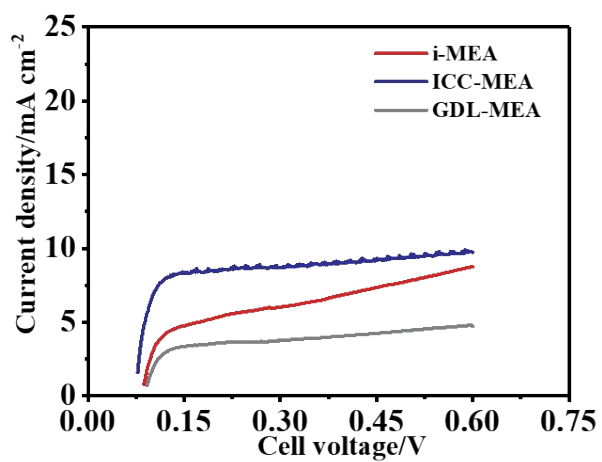


Fig. S6. Linear sweep voltammetry measurements for these MEAs. Cell conditions: 80 °C, 100% RH, no backpressure, and 0.2/0.2 splm for H<sub>2</sub>/N<sub>2</sub>.

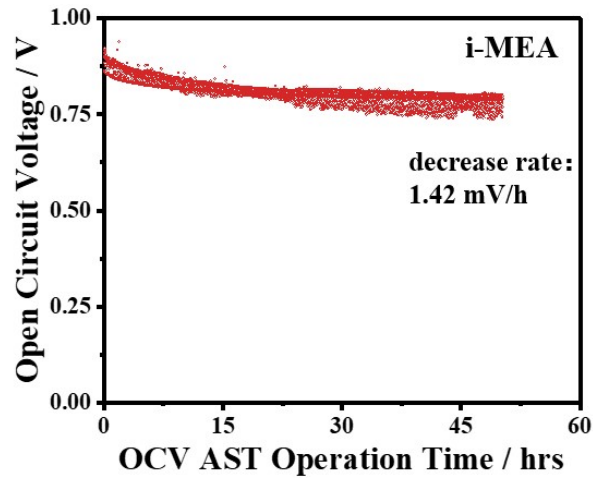


Fig. S7. OCV changes during the durability test of the i-MEA.

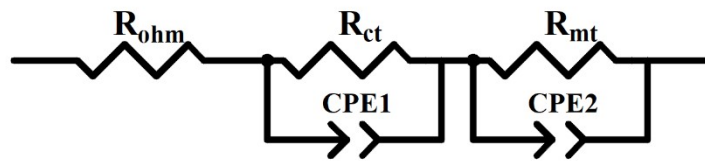


Fig. S8. Equivalent circuit diagram model of PEMFC.

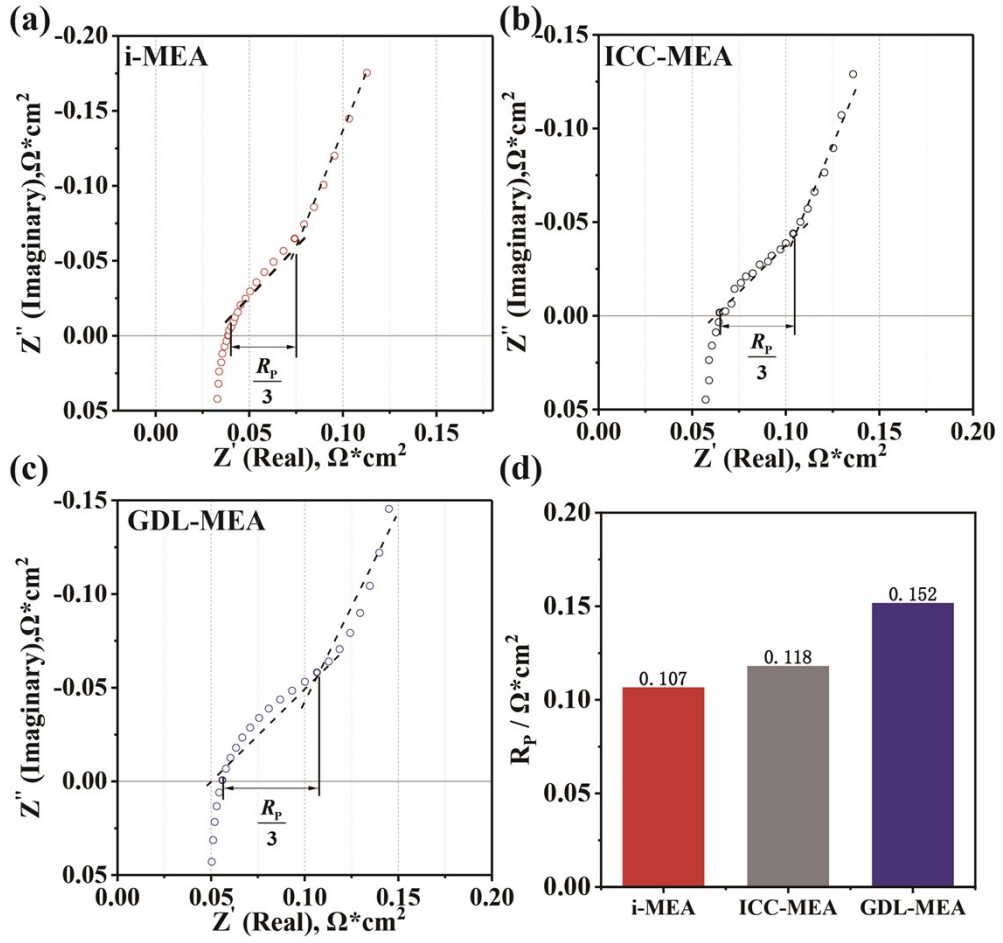


Fig. S9. Nyquist plot of PEMFC operated with  $\text{H}_2/\text{N}_2$  (0.2/0.2 L  $\text{min}^{-1}$ , 100% RH): (a) i-MEA, (b) ICC-MEA, (c) GDL-MEA; (d) the proton transport resistance of these MEA.

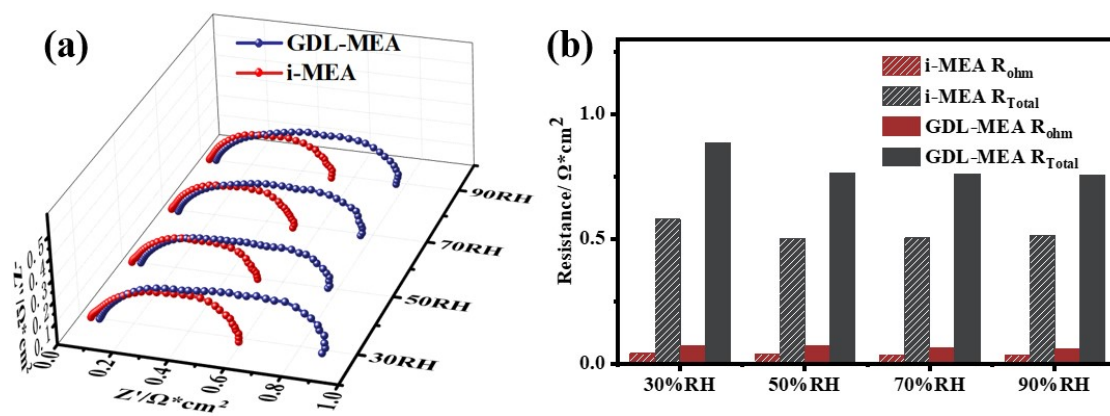


Fig. S10. (a) Electrochemical impedance spectroscopy of i-MEA and GDL-MEA at 1.2 A cm<sup>-2</sup> with different humidity. (b) Comparison of ohmic impedance and total impedance obtained by fitting from (a).

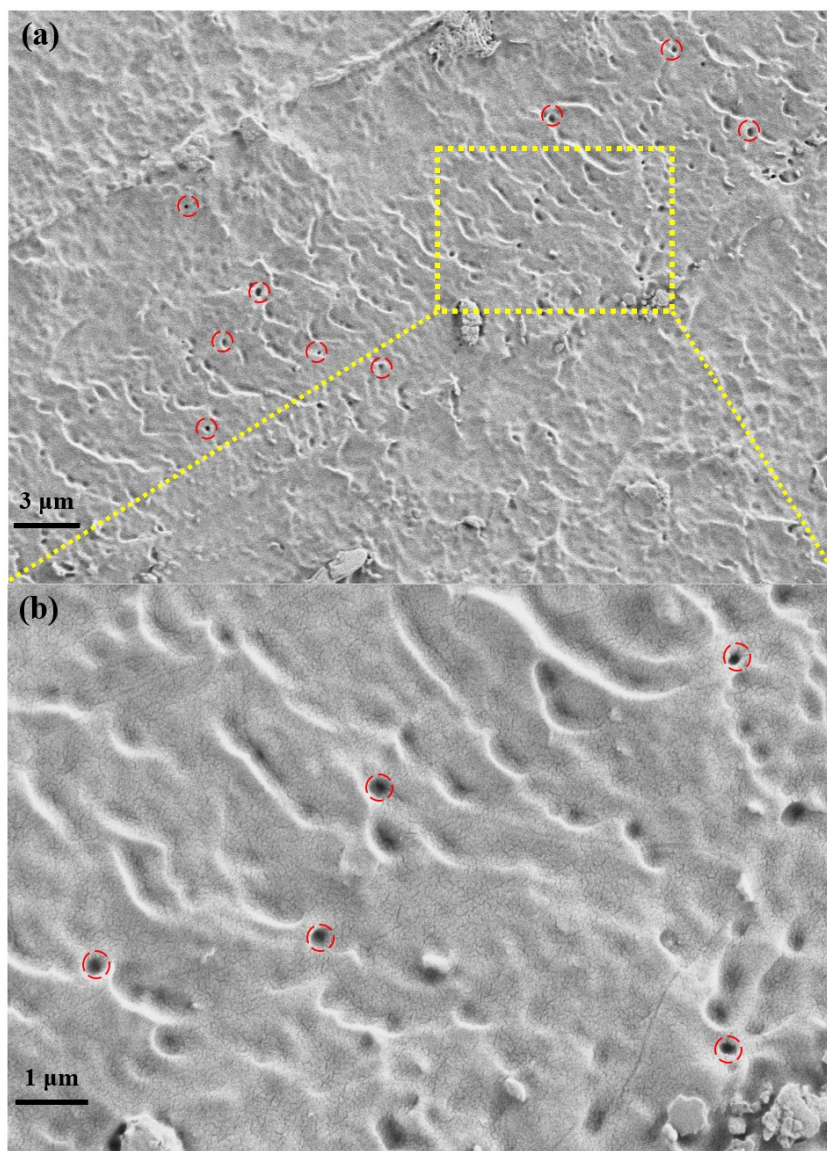


Fig. S11. (a) Tiny bubbles in the membrane (pores at the contact surface when prepared i-MEA) from i-MEA imaged at 1.00 kV. (b) magnified selected area in Figure(a).



Table S1. Element weight percent of GDL, CL and membrane in i-MEA.

Sample	wt / %				
	C	F	S	Pt	Total
GDL	92.16	7.84	-	-	100
CL	55.10	3.84	0.17	40.89	100
Membrane	30.20	66.64	3.17	-	100

Table S2. Operation conditions for linear sweep voltammetry (LSV) , proton transport resistance and open circuit voltage accelerated stress test (OCV-AST).

Characterization	Linear sweep voltammetry (LSV)	Proton transport resistance	Open circuit voltage accelerated stress test (OCV-AST)
Gas at Anode/Cathode (A/C)	H <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /air
Flow rate (A/C) (L/min)	0.2/0.2	0.2/0.2	1.0/1.0
RH (A/C)	100/100%	100/100%	Cycle from 0% RH (30 s) to 100% RH (45 s)
Back pressure (kPa)	0	0	0
Cell temperature (°C)	80	80	90
Measuring sequence	0-0.6 V, and the potential scan rate is 2 mV/s.	Potentiostatic EIS at OCV; High to low frequency (10kHz – 0.1 Hz).	2400 cycles; Total test duration 50h.

Table S3. Fitted impedance parameters for the i-MEA, GDL-MEA at different relative humidity (at 0.4 A cm<sup>-2</sup>) using the equivalent circuit diagram in Fig S8.

Sample	Relative humidity	Resistance $\Omega \text{ cm}^2$			
		$R_{\text{ohm}}$	$R_{\text{ct}}$	$R_{\text{mt}}$	$R_{\text{Total}}$
GDL-MEA	90% RH	0.062	0.307	0.046	0.415
	70% RH	0.063	0.310	0.052	0.425
	50% RH	0.077	0.376	0.104	0.557
	30% RH	0.109	0.545	0.115	0.769
i-MEA	90% RH	0.043	0.238	0.112	0.393
	70% RH	0.045	0.233	0.099	0.377
	50% RH	0.053	0.225	0.089	0.367
	30% RH	0.069	0.251	0.082	0.401

Table S4. Fitted impedance parameters for the i-MEA, GDL-MEA at different relative humidity (at 1.2 A cm<sup>-2</sup>) using the equivalent circuit diagram in Fig S8.

Sample	Relative humidity	Resistance $\Omega \text{ cm}^2$			
		$R_{\text{ohm}}$	$R_{\text{ct}}$	$R_{\text{mt}}$	$R_{\text{Total}}$
GDL-MEA	90% RH	0.061	0.609	0.085	0.755
	70% RH	0.064	0.616	0.080	0.760
	50% RH	0.070	0.627	0.071	0.768
	30% RH	0.073	0.711	0.102	0.886
i-MEA	90% RH	0.034	0.421	0.062	0.517
	70% RH	0.035	0.436	0.041	0.512
	50% RH	0.038	0.437	0.026	0.501
	30% RH	0.042	0.496	0.065	0.603