Graphene Oxide Fuel Cell Materials Development and Testing

Cooperative Research and Development Final Report

CRADA Number: CRD-16-648

NREL Technical Contact: Judith Vidal

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Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5500-76720
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National Renewable Energy Laboratory
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Golden, CO 80401
303-275-3000 • www.nrel.gov

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Report Date: 2/25/20

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Garmor

CRADA Number: CRD-16-648

CRADA Title: Graphene Oxide Fuel Cell Materials Development and Testing

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$100,000.00
TOTALS	$100,000.00

Abstract of CRADA Work:

The objective of the work performed under this CRADA is to assist Garmor to quantify technical and cost payoffs of achieving a very high through-plane electrical conductivity in a composite BPP for Proton Exchange Membrane Fuel Cells (PEMFCs).

Summary of Research Results:

Task 1: Ex-situ testing of Garmor BPP materials. This may include leaching and/or corrosion studies, conductivity studies, and measurements of interfacial resistance with beginning of life and long term durability implications

Leaching/corrosion tests:

The purpose was to determine the leaching of the resin used to hold the graphitic powders into the bipolar plates (BBP). Samples consisted of graphite and graphene oxide. Company sent 1" diameter disks that were mounted to a glass slide with a small amount of silicone for mechanical support. Leaching tests were performed exposing just one side of the BPPs at a time in 1 M H_2SO_4, aerated solution with zero-air at 80°C. Because of evaporation, fresh electrolyte was replenish every hour during 6 hr of leaching test. Fig. 1 shows the corrosion test setup.

After corrosion, the samples were removed and the electrolyte was analyzed to determine expected elements leached out of resin using an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) for elemental concentration. Optically, samples did not show observable damage at the surface indicating that corrosion was not significant. Fig. 2 shows the leaching results from the

two types of samples (10-533 and 10-535) that does not appear to be discernibly different from each other, but there are differences between the samples and the control. The control runs consisted of leach testing with everything the same except no BPP sample in place. It looks like Ca, Fe, and Zn leach from the BPP samples in appreciable quantities and P, Cr, Ni, and Mn leach in detectable quantities. The measured Si, K, and Cu quantities do not appear to be significantly different from the control.

Fig. 1. Leaching/corrosion setup

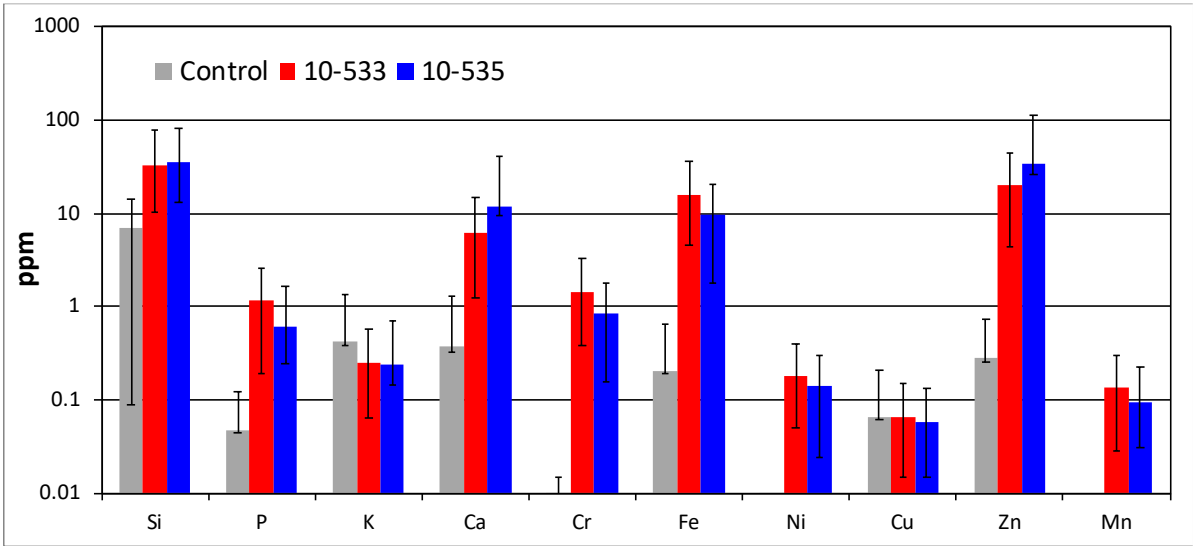


Fig. 2. Composition of elements dissolved/leached-out of BPP samples. Results from ICP-MS.

Interfacial contact resistance (ICR) tests:

Shimpo Force Gauges was employed to control pressure over the samples while an electrical set-up was used to measure the electrical resistance as a function of load. Fig. 3 shows the equipment and electrical set up used. The results shown in Fig. 4 indicate that graphite samples have less contact resistance than graphene oxide samples.

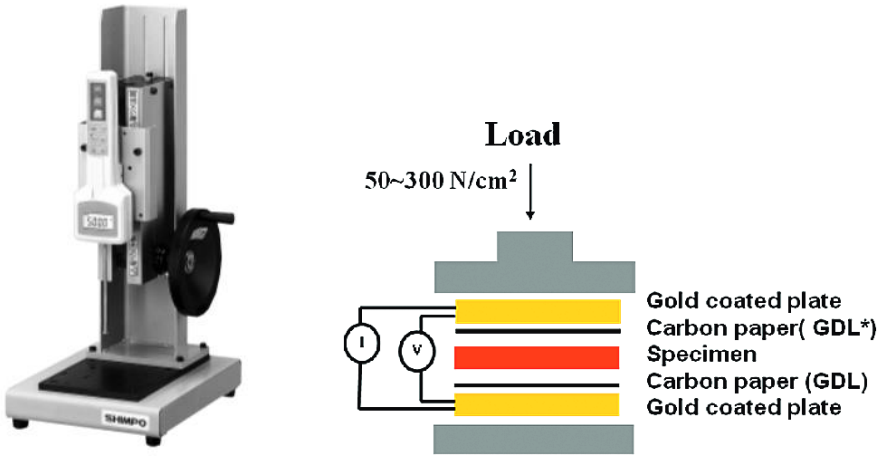


Fig. 3. Squematic diagram of electrical resistance measurement as a function of load applied by the Shimpo force gauge (left).

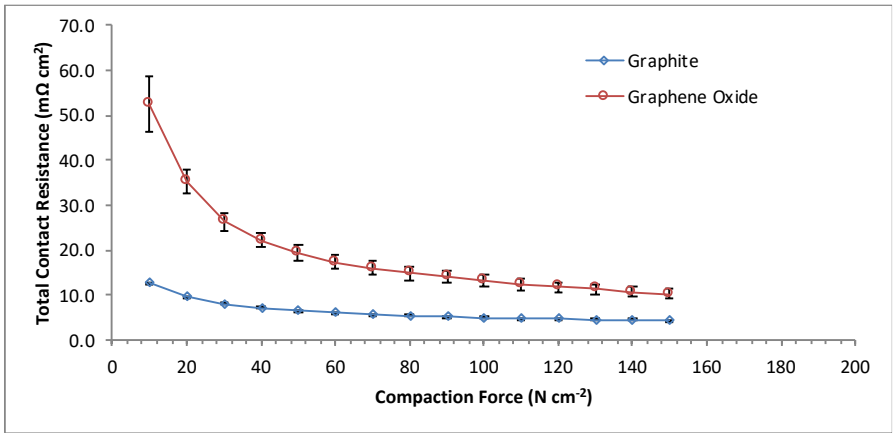
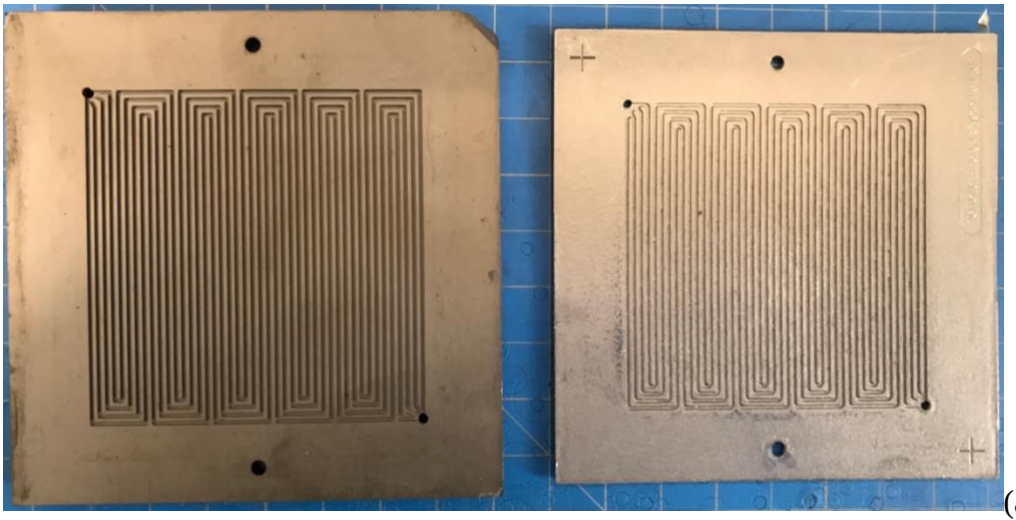


Fig. 4. Interfacial contact resistance (ICR) tests as a function of compaction force for graphite and graphene oxide samples

Task 2: In-situ testing of Garmor BPP materials in single cell and/or stack configurations and comparison to other materials

Graphite BPP were constructed and sent to NREL for in-situ testing in a single cell configuration. NREL conducted in-situ tests on new flow-field materials. Graphite BPP were compared to commercial Poco-graphite materials. Flow-fields were fabricated using a molding process. Flow-fields were significantly thinner than NREL standard single cell lab flow-fields. Metric were polarization and other in-situ experiments using 3M fuel cell materials.

Hardware configuration adjustments were necessary because received graphite plates were significantly thinner than reference Poco Graphite material (0.5” thick) (see Fig. 5). Alignment through tubes into flow-field were not feasible. Sealing area around inlet and outlet were reasonably flat. Regular alignment pins were extended through thin graphite plate and current collector plate was placed into the end plate. Seal strategy was still using viton o-ring

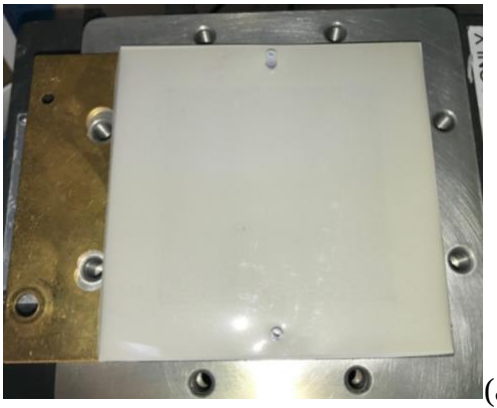


(a)

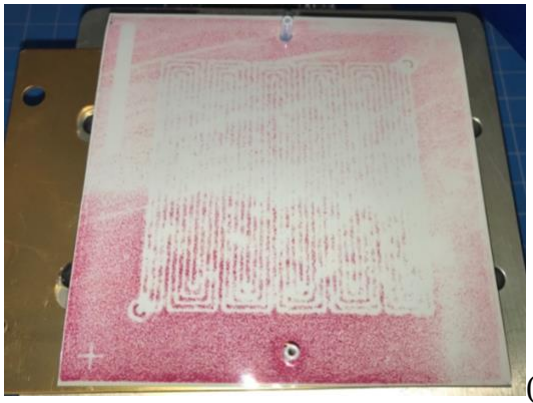
(b)

Fig. 5. Commercial Poco-graphite BPP (left) and graphene/graphite blends BPP (right) top view (a) and angular view (b) showing differences in thicknesses between samples.

A compression test using Fuji paper was used. For this test the assembly only used pressure paper in hardware. Eight bolts and four pairs of Belleville washers were employed. 40 inch*lbs was applied in three steps. Results indicate that pressure was applied on all areas of the cell. Terella signature stamped in sealing area may impact sealing of cell. Otherwise no compression gaps or voids indicated (see Fig. 6).



(a)



(b)

Fig. 6. (a) Compression test assembly. (b) Fuji pressure paper after test.

The compression at O-Ring showed no depressions at o-ring locations, sealing material seems appropriate (see Fig. 7)

Fig. 7. Compression at O-Ring test.

The hardware sealing/leak test was performed with an assembly of two SGL BC29 units. The PTFE gasket thickness was calculated for 20% GDL compression assuming 6% gasket compression. Eight bolts and four pairs of Belleville washers were used. 40 inch*lbs was applied in three steps. Initial pressure was at 30 psi, loosing 3 psi over 10 min, which is an acceptable pressure loss indicating that flow field was ready for testing.

DOE protocol used with two kinds of humidification for polarization curve experiments is shown in Fig. 8. The electrochemical procedure followed for polarization curve is shown in Fig. 9.

Step #	Step Name	Descriptor	Details	Comments
1	Cell Assembly	Assemble MEA in 50cm2 hardware	3M MEAs, PTFE gaskets, SGL29 BC GDL, 50cm^2 cell, quad/quad flow-field, 40 in*lbs/bolt	
2	Leak Test	Perform NREL standard hardware leak test	30psig, delta p of ~2psi over 10 min acceptable	
3	Hook up	connect cell to test station, leak test	at ambient pressure flow 500/500 sccm N2/N2, switch to H2/N2, perform test with manual H2 detector	
4	electrical short/H2Xover	Test integrity of the cell for holes and electrical shorts	room temp, ambient pressure, 200/200 sccm H2/N2, 0.1 mV/sec scanrate, OCV to 0.5V, 100% RH at 25C	Determines Area Specific Resistance and Hydrogen Crossover Limiting Current
5	Warm up	Bring cell to operating temperature	1. Set 800/1800 sccm H2/N2, 12/12 psi ambient Denver pressure 2. Increase RH temperatures to 70/70C while trailing cell temperature to 70C 3. Set cell to 0.65V and activate load 4. Switch gas to H2/Air 5. Wait until current does not change any more	
6	Conditioning	Perform 3M standard procedure	a) Perform **PDS** (Alternate Polarization Scan) (duration 4min 10sec) 1. Set V to 0.9V and hold for 10sec 2. Step V down 0.05V and hold for 10 sec 3. Repeat step 2. until 0.3V is reached. 4. Step V up 0.05V and hold for 10 sec 5. Repeat step 4. until 0.9V is reached	
			b) Perform **PSS** (Static High Current Hold) (duration 5 min) 1. Set V to 0.4V and hold for 5 min	
			c) Repeat 20x cycles of d) (PDS) and e) (PSS) (duration ~3 hours)	
			d) Switch to thermal cycle 1. Switch load off 2. Switch gas flows to 0/0 sccm H2/Air 3. Flow DI/DI water through cell	+ Manual switching, we need to be there in person + Needle valve to regulate water flow + 2-way valves for on/off
			e) Perform thermal cycle 4. Wait for cell to reach room temp but no longer than 30 min	
			f) Switch to PDS 1. Switch DI/DI water off 2. Run Warmup (see above)	
			g) Run **PDS** (step a) and **PSS** (step b)) for one hour (=7 cycles)	
			h) repeat d)-g)	
7	Cool Down	Prepare cell for integrity test		
8	electrical short/H2Xover	Test integrity of the cell for holes and electrical shorts	room temp, ambient pressure, 200/200 sccm H2/N2, 0.1 mV/sec scanrate, OCV to 0.5V, 100% RH at 25C	
9	store overnight			
10	Warm up		H2/N2 => reduce all oxides => V<0.1 V	
		Load Warm up at 40/40% RH	20 min Equilibrium step 0.6 A/cm2, 1.5/1.8 stoich, H2/air, 80C, 150/150 kPa, 59/59 C dew points	NREL stations are calibrated to run stoichmetrics of 1.5/2
		OCV measurement at 40/40% RH	1 min, OCV point, 0 A/cm2, EQLF for 0.2 A/cm2 with 1.5/1.8 stoich, H2/air, 80C, 150/150 kPa, 59/59 C dew points	
	Pt reduction step	clean Pt surface from Pt-Ox, H2 take over at 40/40% RH	Until V < 0.1V, 0 A/cm2, EQLF for 0.2 A/cm2 with 1.5/1.8 stoich, H2/N2, 80C, 150/150 kPa, 59/59 C dew points	
11	VI curve, Low RH	Run VI curve DOE protocol with EIS at 40/40% RH	3 min steps, start at 80C, 59/59 C dew points, 0.2 A/cm2, stoich 1.5/1.8, H2/Air, 150/150 kPa 0.2/0.40.6/0.8/1/1.2/1.4/1.6/1.8/2/1.8/1.6/1.4/1.2/1/0.8/0.6/0.4/0.2/0.1/0.05/0.02/0.05/0.1/0.2	
	switch RH settings	switch RH to 100/100%RH	wait until temps are reached, 20 min minimum Equilibrium step 0.6 A/cm2, 1.5/1.8 stoich, H2/air, 80C, 150/150 kPa, 59/59 C dew points	
12	Pt reduction step	clean Pt surface from Pt-Ox, H2 take over at 100/100% RH	Until V < 0.1V, 0 A/cm2, EQLF for 0.2 A/cm2 with 1.5/1.8 stoich, H2/N2, 80C, 150/150 kPa, 59/59 C dew points	
13	VI curve, High RH	Run VI curve DOE protocol with EIS at 100/100% RH	3 min steps, start at 80C, 80/80 C dew points, 0.2 A/cm2, stoich 1.5/1.8, H2/Air, 150/150 kPa 0.2/0.40.6/0.8/1/1.2/1.4/1.6/1.8/2/1.8/1.6/1.4/1.2/1/0.8/0.6/0.4/0.2/0.1/0.05/0.02/0.05/0.1/0.2	

Fig. 8. DOE protocol used with two humidifications for polarization curve experiments.

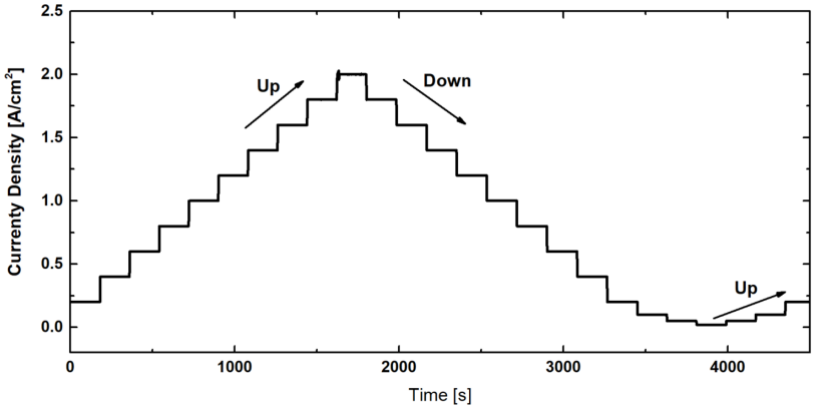


Fig. 9. Electrochemical procedure followed for polarization curve

Experimental results shown in Figs. 10 to 17 determined that the current density increased at the beginning and became stable after about 100 min and the HFR was stable during the first 3hr conditioning step (Fig.10). In the voltage control conditioning step (Fig. 11), the current density was highly reproduceable. Since the cell was stable after the 1st step, a shorter conditioning time was suggested.

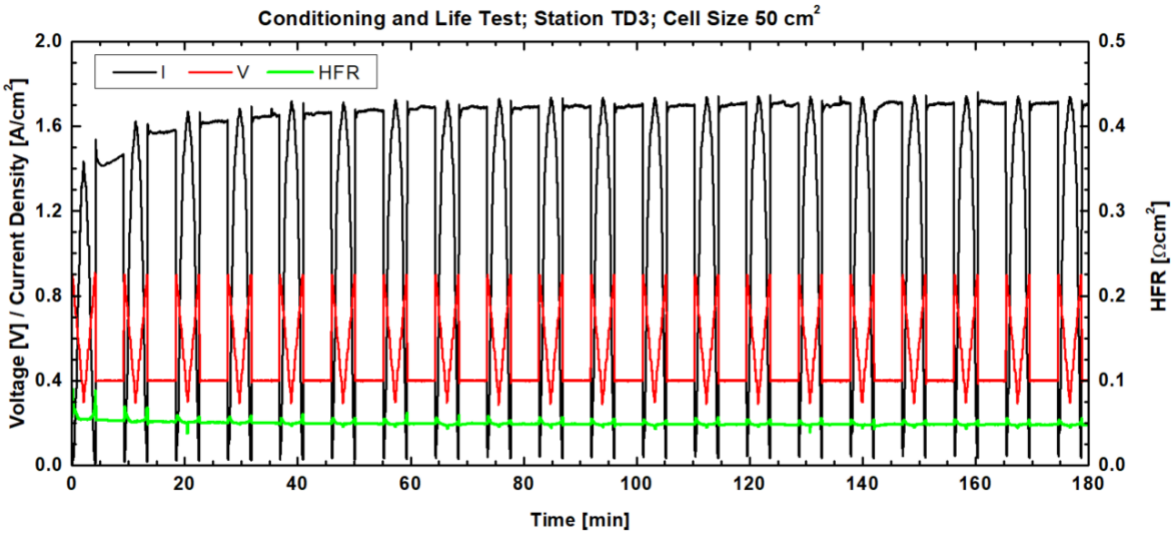


Fig. 10. Conditioning steps for in-situ testing.

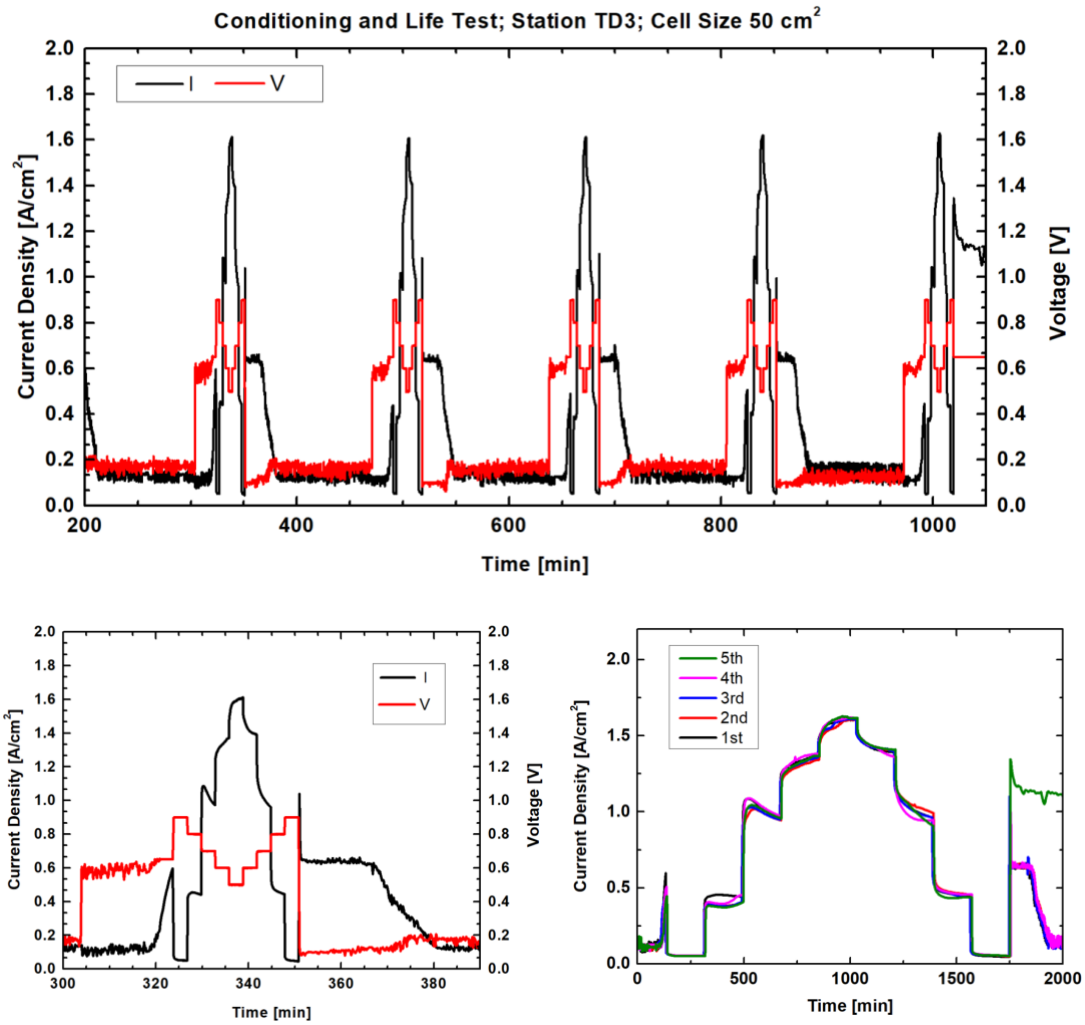


Fig. 11. Conditioning for voltage control for in-situ testing.

Results for the thin graphite 1 flow field (1.16mm thick) are shown in Fig. 12. Results for the thin graphite 1 plate compared for relative humidity (RH) in Fig. 13 shows that in the low RH condition, the HFR dropped first, and then slightly increased due to the anode dryout. In the high RH condition, the HFR was relatively stable. The thin graphite cell in the low RH outperformed the one in the high RH at low current density. The up polarization curve in the high RH was wiggled at around 1 A/cm2, and this was checked with a repetition thin graphite 2 cell.

The thick graphite flow field (Poco-graphite, 12.7mm) and the thick graphite plate compared with RH are shown in Figs. 14 and 15, respectively. According to the polarization curve, the cell in the high RH condition outperformed that in the low RH. In the low RH condition, the HFR dropped first, and then slightly increased due to the anode dryout. In the high RH condition, the HFR was stable.

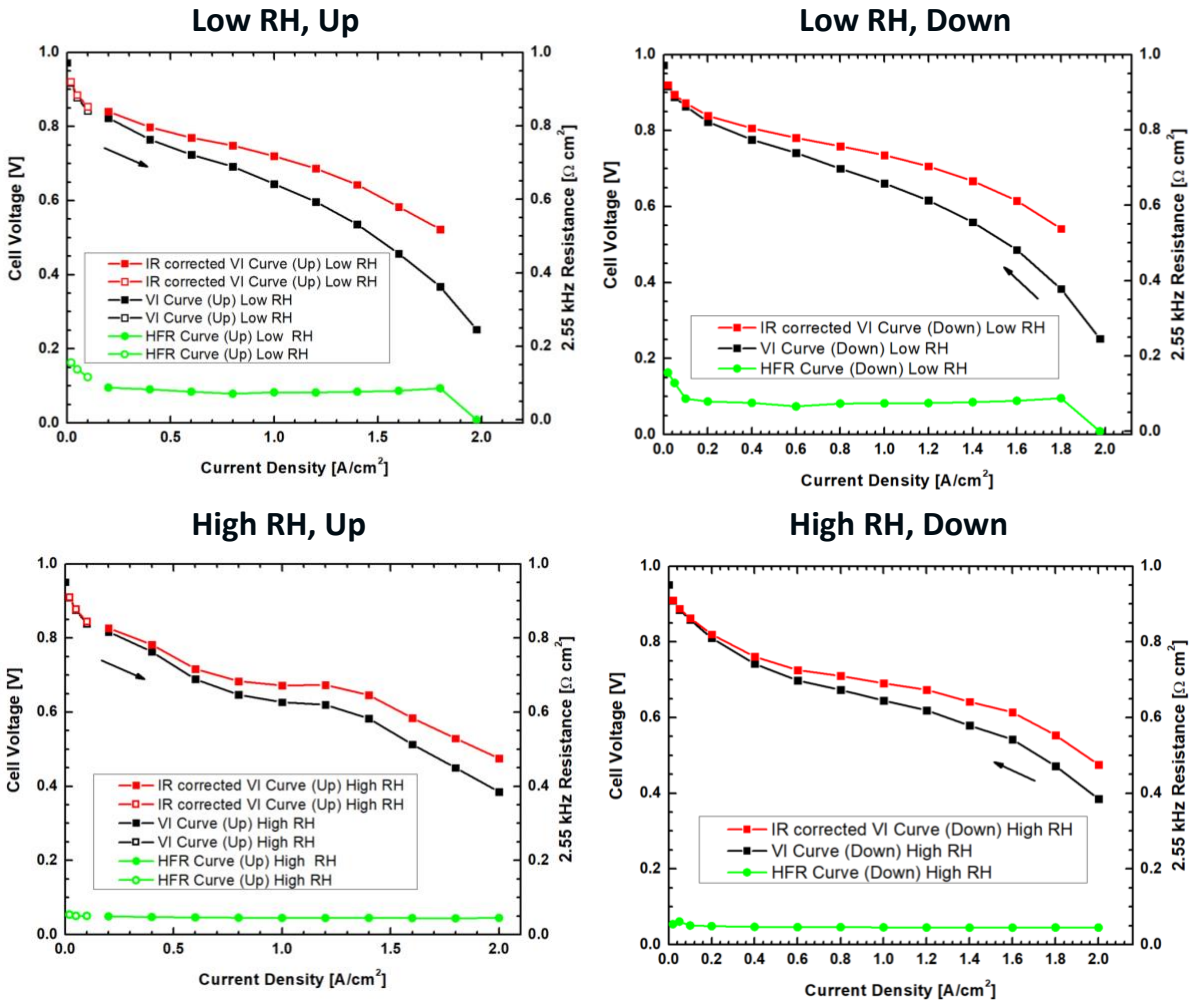


Fig. 12. Results for the thin Graphite 1 Flow Field (1.16mm thick).

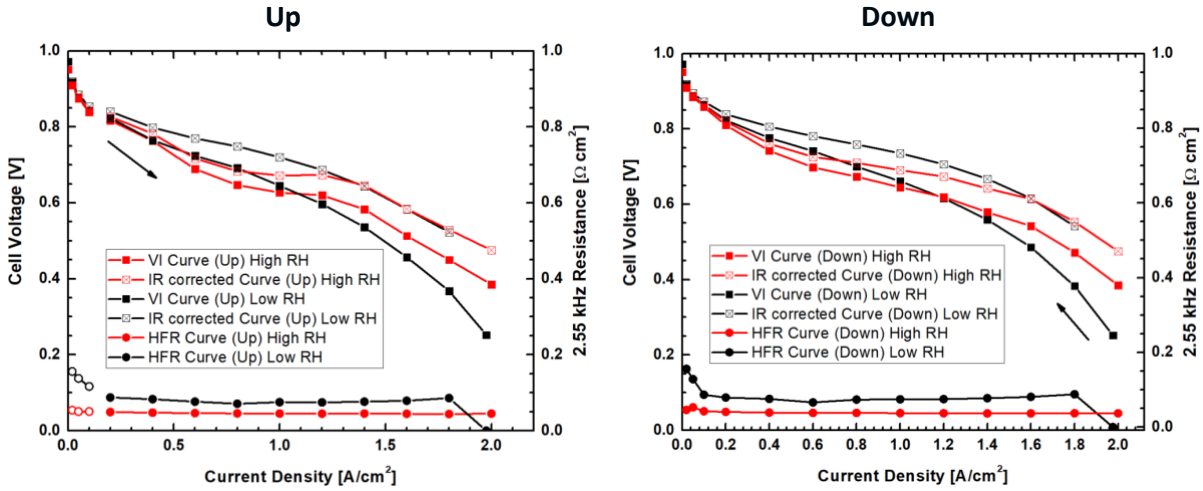


Fig. 13. Results for the thin Graphite 1 Plate: Comparison of RH.

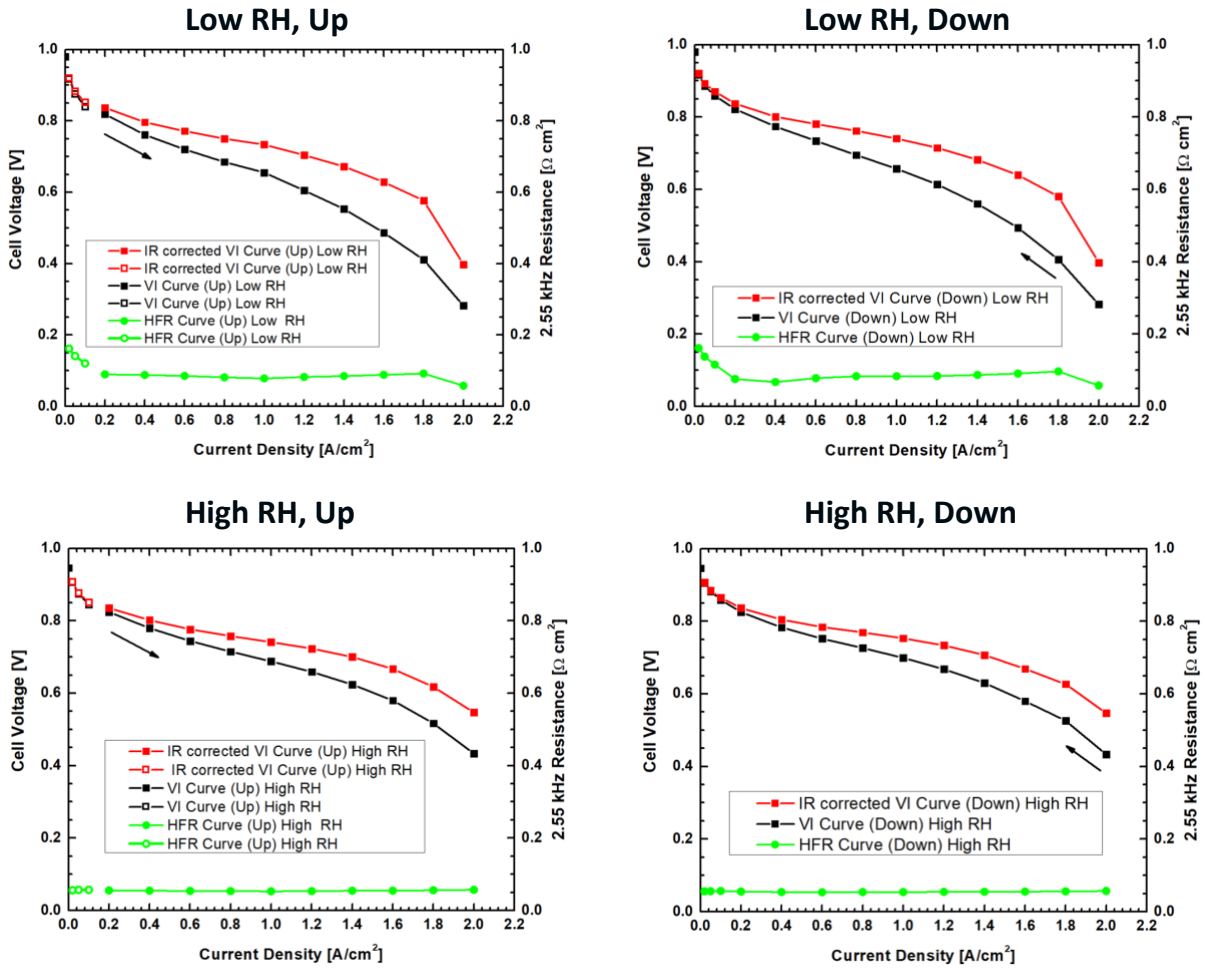


Fig. 14. Results for thick Graphite Flow Field (Poco-Graphite, 12.7mm).

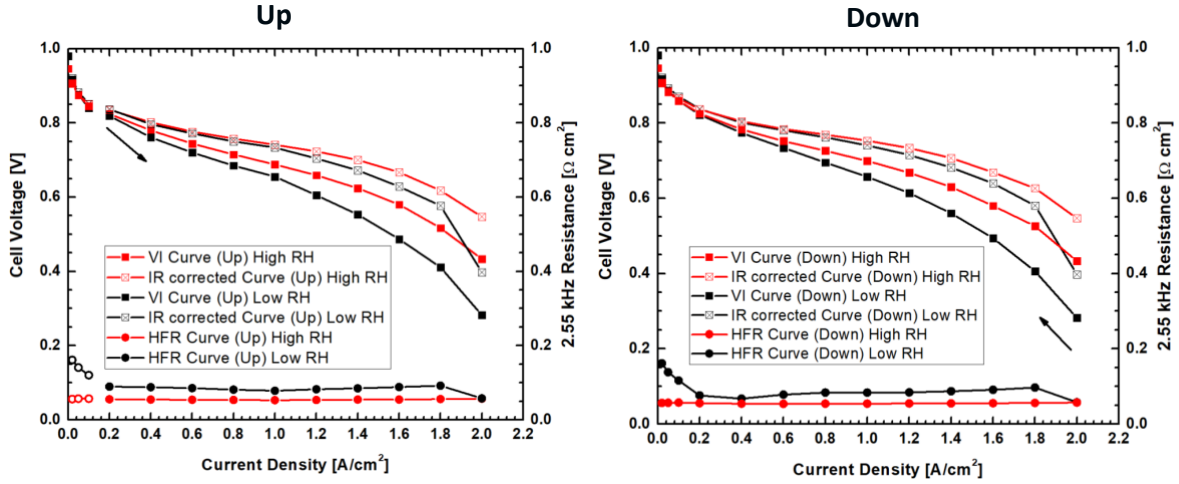


Fig. 15. Results for thick Graphite Plate: Comparison of RH

The BPP hardware comparison for low and high RH are shown in Figs. 16 and 17. In the low RH condition, the thick graphite cell had a higher HFR than the thin graphite 1 cell. The overall performance of the thick graphite cell was a little bit better. In the high RH condition

(Fig. 17), the thick graphite cell had a higher HFR than the thin graphite 1 cell. The overall performance of the thick graphite cell was much better than the thin one. The high RH condition demonstrated the importance of the flow field thickness.

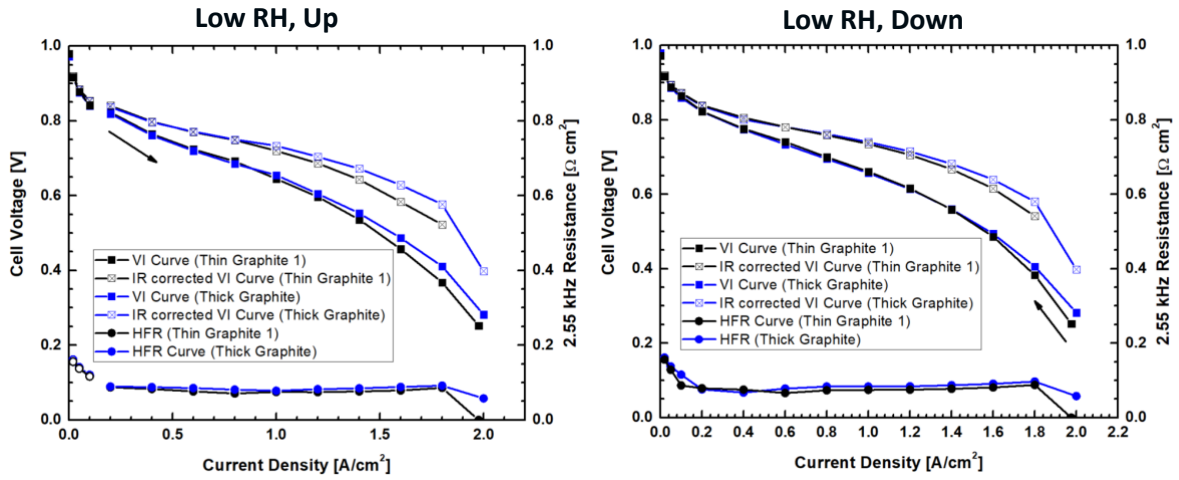


Fig. 16. BPP hardware comparisons for low RH.

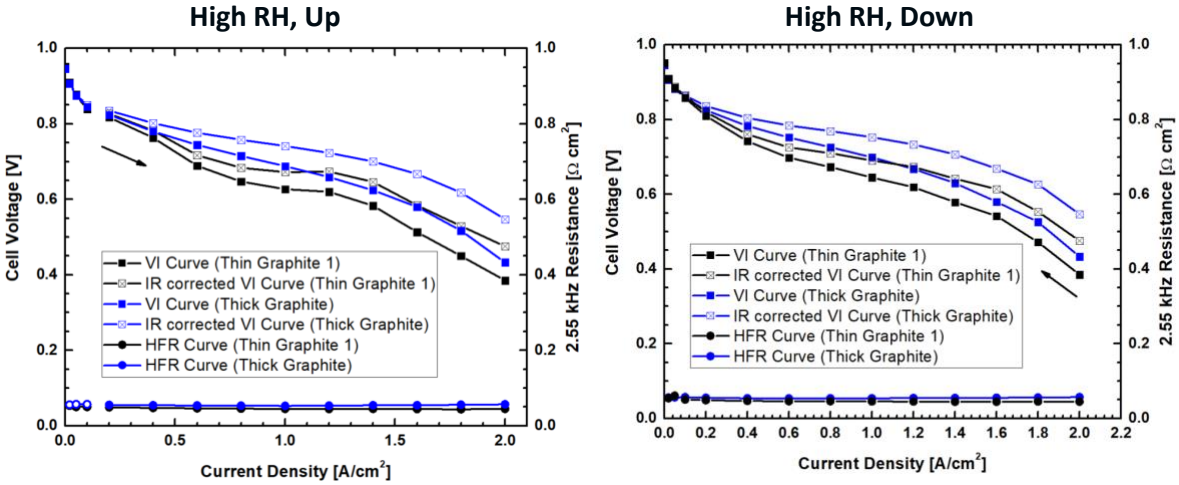


Fig. 17. BPP hardware comparisons for high RH.

After these results we modified the testing protocols. We used the same MEA and a new thin graphite flow field (thin graphite 2) for the test with a thickness of about 1.16mm. We modified the polarization curve protocols for thin graphite 2. The i-t curve of the current control process is shown in Fig. 18. All the other test condition were the same as previous protocol.

Experimental results of thin graphite 2 flow field (1.16mm thick) and the thin graphite 2 plate compared with RH are shown in Figs. 19 and 20, respectively. In the low RH condition, the HFR dropped first, and then slightly increased due to the anode dryout. In the high RH condition, the HFR was quite stable. The thin graphite 2 in the high RH outperformed the one in the low RH. It is the same trend with thick graphite flow field.

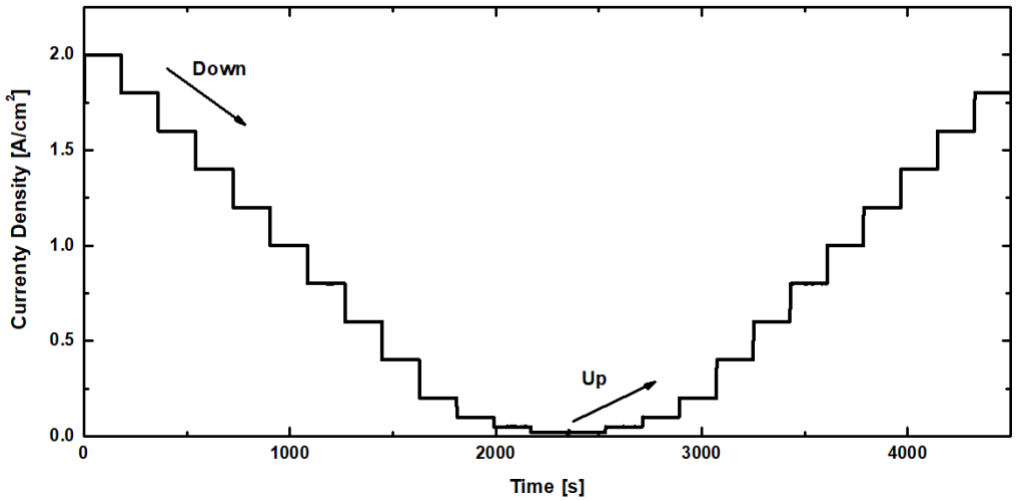


Fig. 18. Modified testing protocol.

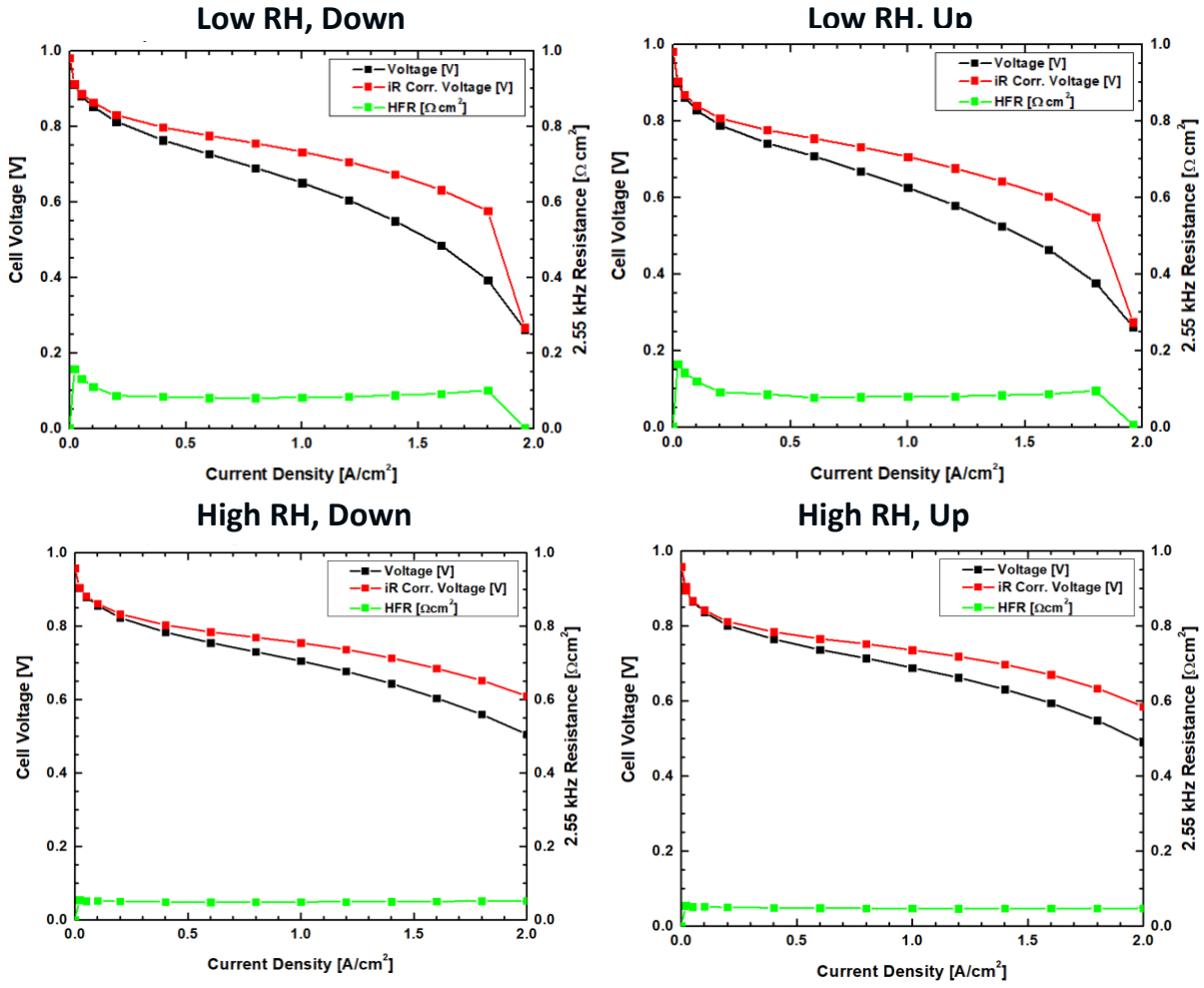


Fig. 19. Experimental results of thin graphite 2 flow field (1.16mm thick)

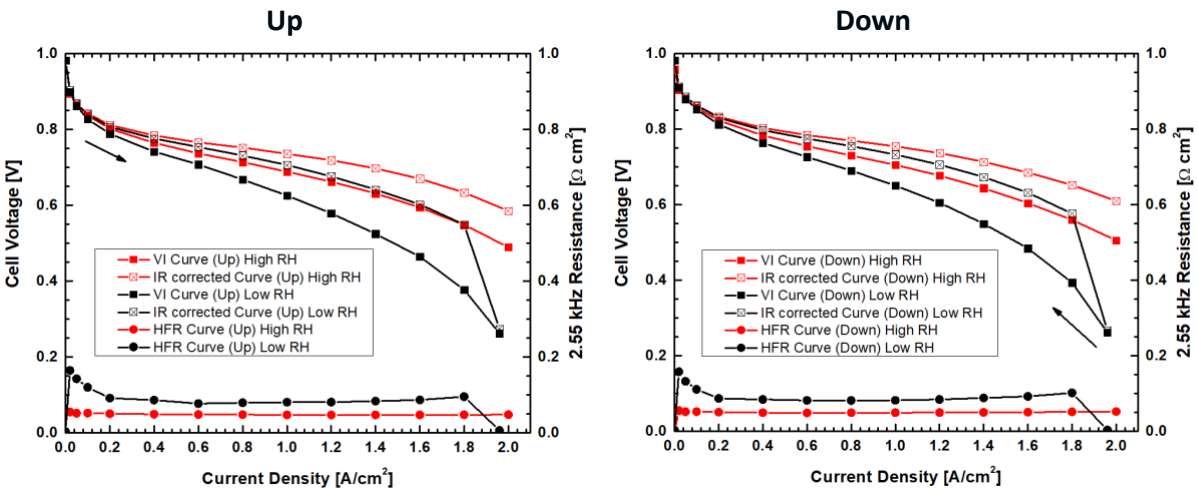


Fig. 20. Results for thin Graphite 2 Plate: Comparison of RH.

The BPP hardware comparison for low and high RH are shown in Figs. 21 and 22. In the low RH condition, the thick graphite cell had a higher HFR than the thin graphite 1 cell. The overall performance of the thick graphite cell was a little bit better. In the low RH condition (Fig. 21), the thick graphite cell had a little bit better overall performance than the thin graphite 2 cell. The thin graphite 2 and thick graphite had a similar HFR. In the high RH condition (Fig.22), the performance of thin graphite 2 cell was better at high current densities.

The BPP of thin graphite 1 and thin graphite 2 cell comparisons for low RH and high RH are shown in Figs. 23 and 24, respectively. In the low RH condition (Fig. 23), the performance of thin graphite 2 cell was comparable to that of thin graphite 1. In the high RH condition (Fig. 24), the performance of thin graphite 2 cell was much better than thin graphite 1.

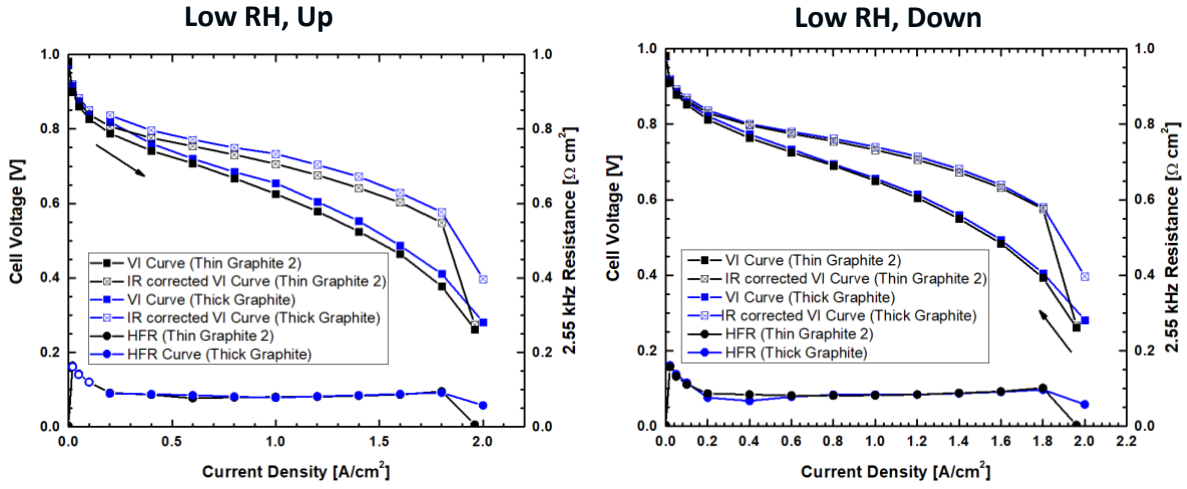


Fig. 21. BPP hardware comparisons for thin graphite 2 cell for low RH.

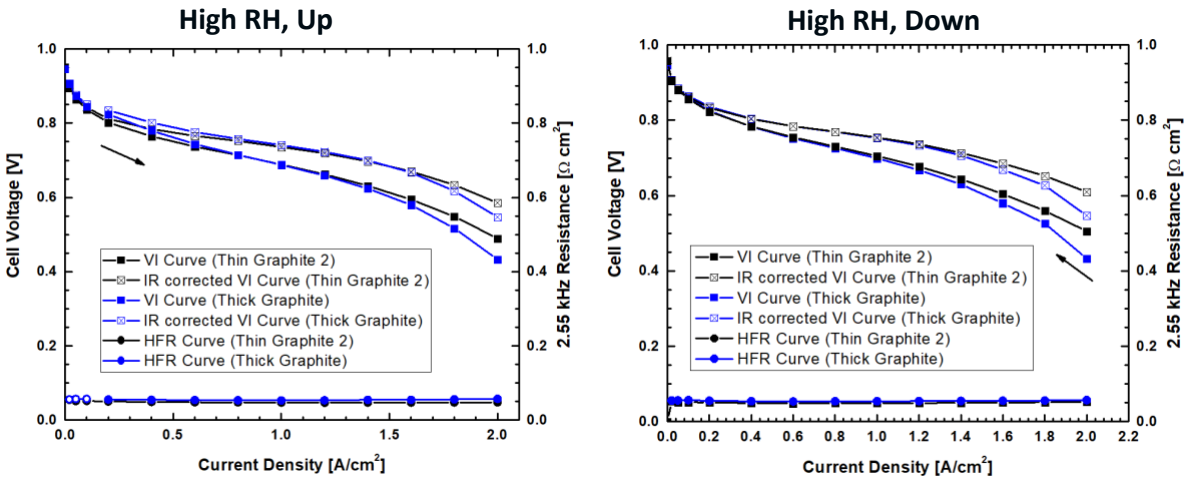


Fig. 22. BPP hardware comparisons for thin graphite 2 cell for high RH.

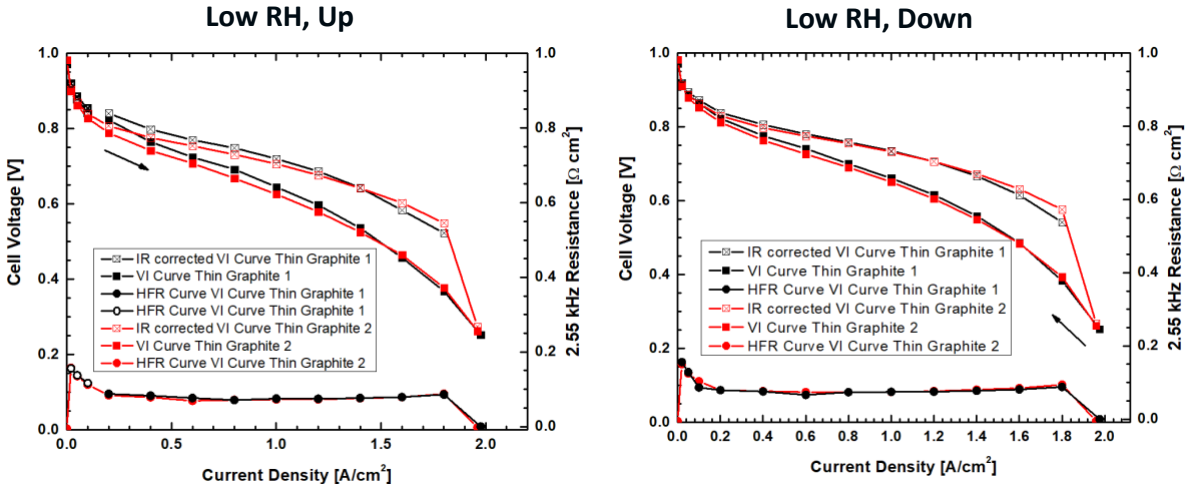


Fig. 23. BPP of thin graphite 1 and thin graphite 2 cell comparisons for low RH.

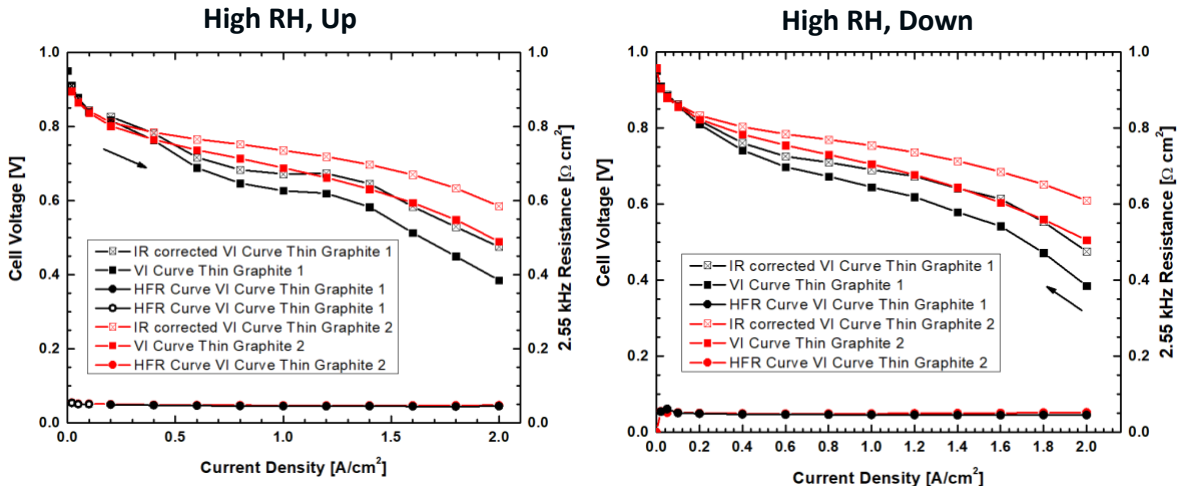


Fig. 24. BPP of thin graphite 1 and thin graphite 2 cell comparisons for high RH.

Task 3: Technical input and guidance in the area of bipolar plates and other cell materials.

Experimental results shown in Figs. 10 to 24 and their analyses discussed in previous paragraphs are compliant with this task regarding guidance for BBP and other cell materials such as the commercial Poco-graphite.

Incomplete testing of samples because samples were not provided

Graphene and Graphene/Graphite blends samples for BPP in-situ evaluations were not tested because Garmor lost connection with the company that was fabricating the samples. The funds were moved to other Hydrogen projects being performed at NREL (email from Keith Wipke, the Laboratory Program Manager of the Fuel Cell and Hydrogen Technologies Program at NREL dated February 26, 2019 informs the moved of remaining funds).

Subject Inventions Listing:

None

ROI #:

None

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DOE Program Office:

Office of Energy Efficiency and Renewable Energy (EERE) Fuel Cell Technologies Office (FCTO)