Final Report - Fuel Cell Membrane Electrode Assemblies with Ultra-Low Pt Nanofiber Electrodes

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Executive Summary

H_2/air fuel cell membrane-electrode-assemblies (MEAs) were fabricated with electrospun particle/polymer nanofiber mat cathodes (0.1 mg_{Pt}/cm^2 or 0.2 mg_{Pt}/cm^2 Pt/C, PtCo/C or PtNi/C) and anodes (0.1 mg/cm^2 Pt/C), where the binder was a mixture of acid-form perfluorosulfonic acid ionomer (e.g., Nafion™) and poly(acrylic acid) (PAA) carrier polymer or sodium-form PFSA with a carrier polymer of either PAA or polyethylene oxide (PEO). For the latter two cases, the water-soluble carrier was removed from the fibers after electrospinning. MEAs with Pt/C anode/cathode catalyst loadings of 0.1 mg_{Pt}/cm^2 each, an 1100 EW PFSA binder (Nafion™ dispersion), and a Nafion 211 membrane produced high power at both high and low relative humidity (RH) conditions, e.g., a maximum power density of 919 mW/cm^2 at 100% RH and 832 mW/cm^2 at 40% RH for a test at 80 °C and 200 kPa_{abs}. The high power at low RH was attributed to nm-size pores within the fibers that trap water via capillary condensation thus maintaining a high proton conductivity of the PFSA binder in the cathode and especially the anode while minimizing/eliminating ionic isolation of catalyst particles in low water content, poorly conductive binder. At the same time, micro-porosity between fibers in the cathode allows for fast removal of electrogenerated water, thus minimizing cathode flooding. Nanofiber MEAs with Pt-alloy catalyst cathodes also performed well, where a fibrous PtCo/C catalyst cathode at a loading of 0.1 mg/cm^2 produced 20% more power than a conventional powder cathode MEA, e.g., a maximum power density of 1,045 mW/cm^2 vs. 869 mW/cm^2at 80 °C, 100% RH, and 200 kPa_{abs}, and a PtNi/C fiber cathode MEAs prepared with Na^+-form Nafion + PEO generated a maximum power of 820 mW/cm^2 at 40% RH. Fiber electrode MEAs with a neat Nafion binder (prepared from Na+-form Nafion + PEO or PAA) where the cathode Pt loading was ~0.1 mg/cm2 exhibited a 25% loss in maximum power at 30,000 metal dissolution cycles, as compared to a 12% loss when the cathode binder was H+-form Nafion + PAA. The performance of a fiber mat electrode MEA with Pt/C catalyst (0.2 mg/cm^2 cathode loading and 0.1 mg/cm^2 anode loading) was excellent. At 80 oC and 200 kPa_{abs} the maximum power density was 1104 mW/cm2. The maximum power was independent of feed gas humidity for $40 < RH < 100\%$. The power loss after a metal dissolution AST (30,000 voltage cycles) was only 13%.

Overall Objectives

- Fabricate, characterize, and evaluate membrane-electrode-assemblies (MEAs) with nanofiber mat cathodes containing highly active oxygen reduction reaction (ORR) catalysts for H_2/air fuel cells.
- Generate useful correlations and insightful understandings regarding nanofiber electrode electrospinning.
- Develop collaborations with researchers at National Laboratories that are part of the Fuel Cell Consortium for Performance and Durability (FC-PAD).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability (aging and degradation of fuel cell electrodes).

(B) Cost (lowering the material and manufacturing costs of high-performance electrodes and MEAs).

(C) Performance (fabricating MEAs that generate higher power at lower precious metal loading, with special emphasis on the cathode).

Technical Targets

Table 1. Progress towards Meeting Technical Targets for Electrocatalysts and MEAs for Transportation Applications

Characteristic	**Units**	**DOE 2020 Electrocatalyst and MEA Targets**	**Project Status**
Mass activity	$A/mg_{PGM}@0.90\ V_{IR\text{-}free}$	0.44	0.464[a]
PGM total loading (both electrodes)	$mg\text{-}PGM/cm^2_{geo}$	0.125	0.117
Loss in performance at 0.80 A/cm^2 after a load cycling AST (30,000 voltage cycles)	mV	<30	30[b]
Loss in performance at 1.5 A/cm^2 after a load cycling AST (30,000 voltage cycles)	mV	<30	32[b]
MEA performance @ 0.80 V	mA/cm^2_{geo}	300	424[c]
MEA performance @ rated power (150 kPa_{abs})	mW/cm^2_{geo}	1000	803[d] 702[e]

[a] Measured at Los Alamos National Laboratory; Nafion-PAA cathode with PtCo/C at 0.2 mg_{Pt}/cm^2 total loading.
[b] 5 cm^2 MEA, TKK Pt/C cathode catalyst (0.12 mg_{Pt}/cm^2), Pt/C anode catalyst (0.1 mg_{Pt}/cm^2), Nafion binder, Nafion 211 membrane, T=80°C, 200 kPa_{abs}, 100% RH.
[c] 5cm² MEA, TKK PtCo/C cathode catalyst (0.1 mg_{Pt}/cm^2), Pt/C anode catalyst (0.1 mg_{Pt}/cm^2), Nafion + PEO binder, Nafion 211 membrane, T= 80 °C, 200 kPa_{abs}, 100% RH.
[d] 10 cm^2 MEA, TKK PtCo/C cathode catalyst (0.1 mg_{Pt}/cm^2), TKK Pt/C anode catalyst (0.1 mg_{Pt}/cm^2), Nafion + PEO binder, Nafion 211 membrane, T=95°C, 150 kPa_{abs}, 100% RH
[e] 10 cm^2 MEA, TKK PtCo/C cathode catalyst (0.11 mg_{Pt}/cm^2), TKK Pt/C anode catalyst (0.013 mg_{Pt}/cm^2), Nafion binder, Nafion 211 membrane, T=95°C, 150 kPa_{abs}100% RH

Project Accomplishments

- MEAs were fabricated with electrospun particle/polymer nanofiber mat cathodes (0.1 mg_{Pt}/cm^2 Pt/C, PtCo/C or PtNi/C) and anodes (0.1 mg/cm^2 Pt/C), where the binder was a mixture of acid-form Nafion and poly(acrylic acid) (PAA) carrier polymer or sodium-form Nafion with a carrier polymer of either PAA or polyethylene oxide (PEO). For the latter two cases, the carrier was removed from the fibers after electrospinning.

- Electrospun electrodes were prepared with Pt/C catalyst and Na^+-form Nafion and PEO carrier polymer using the multi-spinneret industrial electrospinning equipment at eSpin Technologies. The electrodes were then evaluated in a hydrogen/air fuel cell at Vanderbilt University. MEAs using eSpin electrodes performed well at beginning-of-life, with power densities comparable to Vanderbilt fiber electrodes, but the maximum power decreased by 45% after 30,000 metal dissolution voltage cycles, versus a 25% power loss for a Vanderbilt electrode MEA.
- Fiber electrodes were prepared with Pt/C catalyst, Na^+-form Nafion, and either PAA or PEO as the carrier polymer. MEAs performed similarly, exhibiting a marked improvement in power density, especially at low RH, as compared to a nanofiber cathode MEA with a binder of H^+-form Nafion and PAA (PAA cannot be extracted from the cathode fiber mat and lowers the proton conductivity of the binder; its presence in fibers does not trap water).
- Water content in Pt/C fiber electrode MEAs was compared to that in a conventional spray electrode MEAs during fuel cell operation via operando neutron imaging experiments at NIST. Under fully humidified conditions and high current density operation, there was less water within fiber electrode MEAs when the binder was H^+-form Nafion + PAA.
- Fiber electrode MEAs with a neat Nafion binder (prepared from Na^+-form Nafion + PEO or PAA) where the cathode Pt loading was ~0.1 mg/cm^2 exhibited a 25% loss in maximum power at 30,000 metal dissolution cycles, as compared to a 12% loss when the cathode binder was H^+-form Nafion + PAA.
- STEM-EDX imaging of electrospun fiber cross sections at ORNL and Vanderbilt revealed that fiber electrodes (using a Pt/C or PtCo/C catalyst) prepared with Nafion/PAA or Nafion/PEO binder showed an ionomer-rich surface and a catalyst-rich fiber interior.
- PtNi/C fiber cathode MEAs prepared with either H+-form Nafion + PAA or Na+-form Nafion + PEO generated a high maximum power at low RH (40%), 750 mW/cm^2 and 820 mW/cm^2, respectively.
- An all-electrospun MEA was prepared using 725 EW PFSA (provided by 3M Co.) for the membrane and electrode binder and Pt/C catalyst at the anode and cathode. The 725 EW MEA generated high and near-constant power over a wide range of feed gas relative humidity (20-100%). At 20% RH, the 725 EW MEA generated a maximum power of 815 mW/cm^2.
- Rated power targets, as set forth by the DOE, were achieved for a low Pt loaded MEA (0.117 mg$_{Pt}$/cm^2 total for the anode + cathode) using a PtCo/C-Nafion cathode and a Pt/C-Nafion anode.
- Fiber electrode MEAs prepared with salt-form Nafion binder worked exceptionally well at low humidity (a max power density of ~800 mW/cm^2 at 40% RH, 80^{o}C, and 200 kPa$_{abs}$) due to a high intrafiber porosity and an increased number of pores sufficiently small to condense water at low humidity.
- Pre-compaction of fiber mats was required to achieve high power for cathodes with a loading of ~0.20 mg$_{Pt}$/cm^2. Increased cathode catalyst loading improved power density and metal dissolution durability.

- The performance of a fiber mat electrode MEA with Pt/C catalyst (0.2 mg/cm^2 cathode loading and 0.1 mg/cm^2 anode loading) was excellent. At 80 °C and 200 kPa_{abs} the maximum power density was 1104 mW/cm^2. The maximum power was independent of feed gas humidity for 40% < RH < 100%. The power loss after a metal dissolution AST (30,000 voltage cycles) was only 13%.

1. Introduction

Despite widespread literature demonstrations of excellent O_2 reduction reaction activity of some new catalysts in rotating disk electrode experiments, almost none of them have shown promising performance in fuel cell membrane-electrode-assemblies (MEAs). This is because MEA fabrication remains centered on decal, catalyst-coated membrane, and/or catalyst coated gas diffusion electrode methodologies, with little or no control over the macro-scale organization of catalyst particles and polymer binder. Features such as electrode macroporosity, microporosity, and particle and binder interconnectivity become more critical when high-performance nanomaterials are used in electrodes. Consequently, new electrode fabrication techniques are needed for next-generation MEAs, which accommodate and control the multi-scale arrangement of catalyst and binder for improved power output and durability.

Building from strong initial data showing electrospinning as a viable approach to the design and fabrication of fuel cell electrodes [1-4], this project sought to fabricate and evaluate MEAs with electrospun nanofiber electrodes containing Pt and Pt-alloy catalyst powders and selected perfluorosulfonic acid ionomer binders, with the goal of meeting the DOE 2020 performance and durability targets for MEAs and catalyst layers.

2. Approach

The research approach for this project directly addresses three critical issues: (1) the use of high-activity Pt/C, PtNi/C, and PtCo/C catalysts in hydrogen/air fuel cell MEA cathodes, (2) the organization of Pt-alloy catalytic nanoparticles into intelligently designed nanofiber mat electrodes via particle/polymer electrospinning, where the fiber volume fraction, nanoparticle loading, binder type, fiber diameter, and mat thickness are independently controlled, and (3) the identification of the optimum composition and structure of nanofiber electrode MEAs which meet the DOE 2020 performance, Pt-loading, and durability targets.

The project has five major tasks: (1) prepare and evaluate MEAs with commercial Pt-alloy cathodes at ultra-low Pt loading with various perfluorinated ionomer-based binders, (2) synthesize Pt-alloy octahedra catalysts with high oxygen reduction activity (the octahedra catalysts did not as well as commercial materials and this parr of the project was discontinued), (3) incorporate the octahedra Pt-alloy catalysts into nanofiber and sprayed electrode MEAs, (4) optimize the nanofiber cathode mat composition and mat morphology to maximize fuel cell performance and durability at high and low relative humidity conditions, and (5) provide catalyst powder, electrospun cathode mats, MEAs, experimental skills, and the team's electrospinning knowledgebase to our FC-PAD collaborators.

3. Results

3.1 Fiber Morphology

Solutions for electrospinning were prepared with Pt/C, PtCo/C, or PtNi/C catalyst powder from Tanaka Kikinzoku Kogyo Group, 1100 EW Nafion ionomer dispersion, and either poly(acrylic acid) (450 kDa) or poly(ethylene oxide) (600 kDa). The resulting particle/polymer nanofibers were characterized by SEM and STEM. Top-down SEMs of fiber mats and STEM/EDX elemental maps of Pt and F in electrospun fiber cross sections with Pt/C catalyst and different binders are shown in Figure 1. There is a high concentration of Nafion at the fiber surface, for poly(acrylic acid) (PAA) and polyethylene oxide (PEO) carriers. Additionally, it is presumed that the fiber coating is hydrophobic with a high concentration of CF_2 groups from the PTFE backbone of Nafion, due to the electrospinning conditions, where fibers were spun into low dielectric constant air at low relative humidity. This hydrophobic coating assists in expelling product water from a fiber mat cathode during fuel cell operation. The low water content in electrospun electrode MEAs was confirmed by in-operando neutron scattering experiments (see Kavitha Chintam *et al* 2019 *ECS Trans.* **92** 125). Fibers made with Na^+-form Nafion had an internal porosity of 15-17%, with a large number of nm-size pores to trap water via capillary condensation (see Figure 2). The condensed water enabled the fiber mat electrode MEAs to operate at high power when the RH of the feed gases was low.

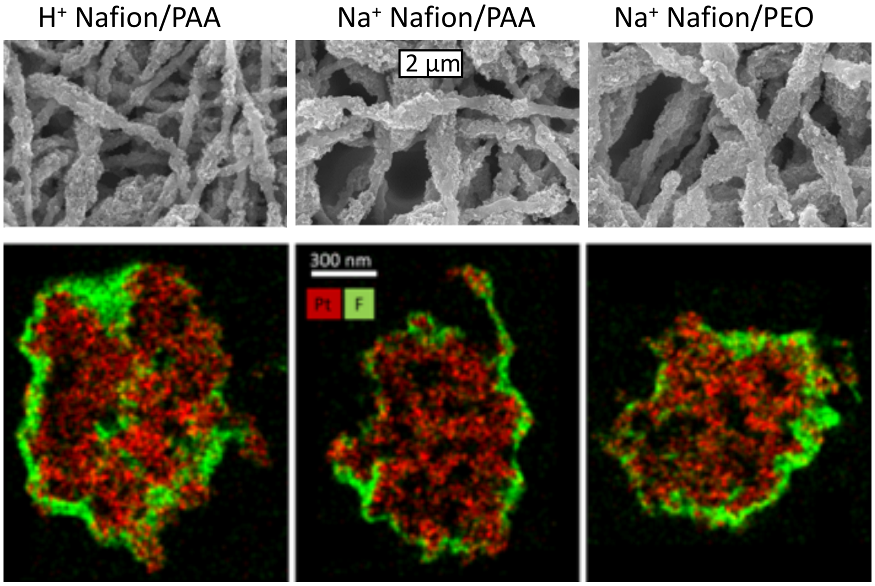

Figure 1. SEM images of fiber mats and elemental mapping of Pt and F in STEM/EDX fiber cross-sections, with Pt/C catalyst particles.

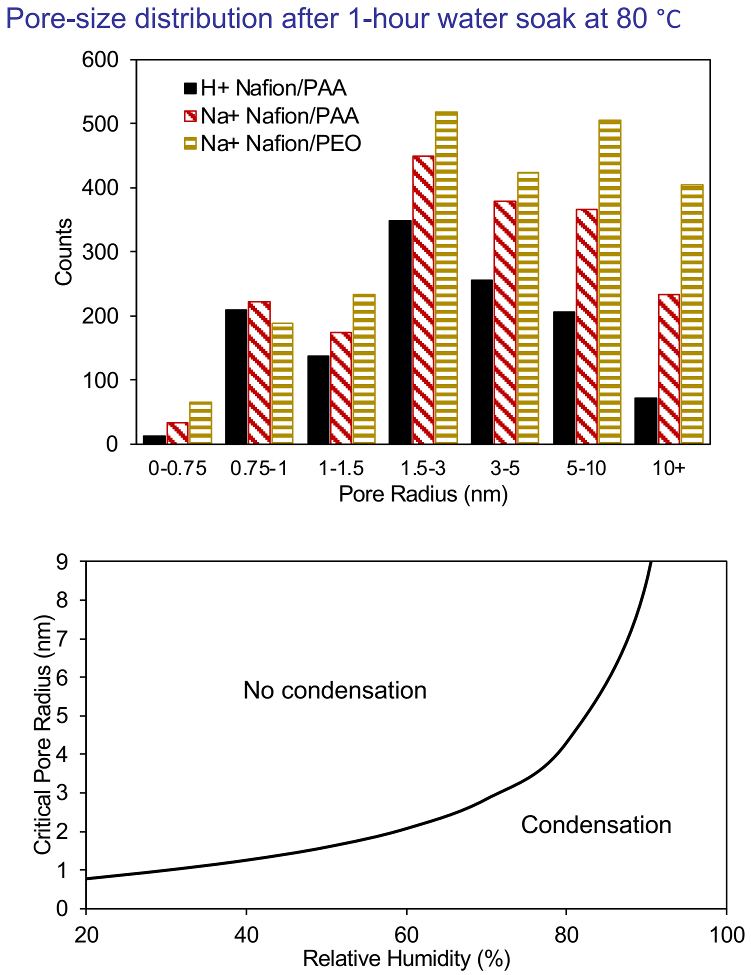

Figure 2. Pore size distribution in electrospun fibers (from STEM images) and the required power radius for capillary condensation of water at 80 °C

3.2 Fuel Cell Performance of Nanofiber Cathode MEAs with Nafion/PAA Binder

H_2/air fuel cell tests were carried out at 80°C, 200 kPa, and 100% RH. Figure 3 compares the performance of nanofiber MEAs with a PtCo/C cathode and a Johnson Matthey Pt/C cathode (from reference 1). Measured current-voltage data and IR-corrected polarization plots are shown. The lower performance of the Pt/C catalyst is due to its lower ORR activity, as compared to PtCo/C. The PtCo/C catalyst generated more than 30% more power as compared to Pt/C. The ECSA of PtCo/C and Pt/C nanofiber cathodes were nearly identical (48 vs. 45 m^2/g). The high-power output with PtCo/C was associated with its significantly higher ORR mass activity; 270 mA/mg_{Pt} for PtCo/C which is ~70% greater than that of a Pt/C fiber cathode (160 mA/mg_{Pt}) and 2.5-times greater than that of a Pt/C spray electrode with Nafion (110 mA/mg_{Pt}, from reference 1).

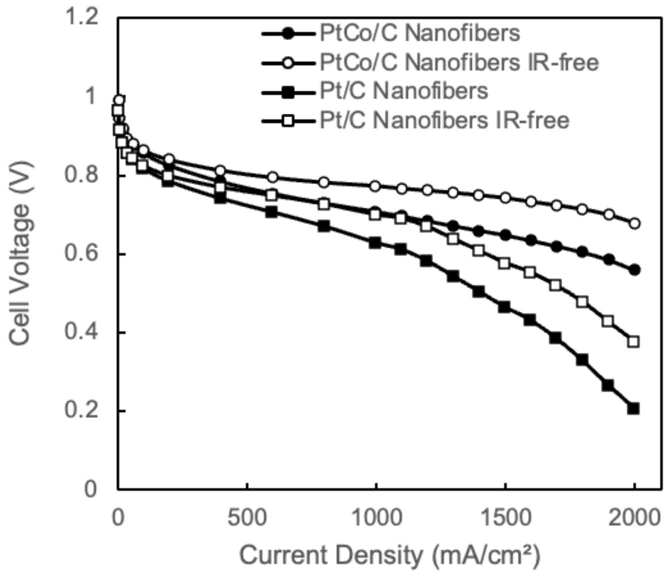

Figure 3. H_2/air fuel cell polarization data (IR-corrected and uncorrected) comparing two types of catalysts in nanofiber cathode MEAs (TKK PtCo/C and JM Pt/C) at 100% RH, 80°C and 200 kPa absolute pressure.

Polarization data from PtCo/C cathode MEAs with a sprayed or nanofiber electrode morphology are shown in Figure 4 at beginning-of-life (BOL) and end-of-test (EOT), where the latter refers to MEA performance after 30,000 voltage cycles in a metal dissolution accelerated stress test (AST). The results in this figure were reproducible to within ± 5% using duplicate MEAs and the data represent averages from multiple repeated experiments. It should be noted here that the sprayed MEA utilized neat Nafion as the binder (no PAA was needed, whereas PAA is critical for fiber formation via electrospinning) and the sprayed anode loading in the sprayed cathode MEA was higher than the nanofiber anode (0.4 vs. 0.1 mg/cm^2). Despite these differences, important findings can be drawn from Figure 4 and the associated measurements of ECSA, mass activity, ionomer resistance, and GTR, as listed in Table 1. The improved power densities of the nanofiber electrode MEA (1045 vs. 869 mW/cm^2 for a maximum power density and 751 vs. 715 mW/cm^2 for the power density at 0.65 V) are associated with the combined effects of a higher mass activity and a lower GTR, a consequence of the high inter-fiber and intra-fiber porosity of the nanofiber cathode with little or no catalyst or binder agglomeration. The larger ECSA for nanofiber MEA cathodes results in a higher Pt roughness factor (the product of ECSA and platinum loading), which has been shown to correlate inversely with gas transport resistance. It is well established in the literature that gas transport resistance leads to significant voltage loss in the high current density region of the polarization curve, especially for low Pt loading cathodes. Thus, the lower GTR in nanofiber cathodes is consistent with the higher power densities at high current densities shown in Figure 4.

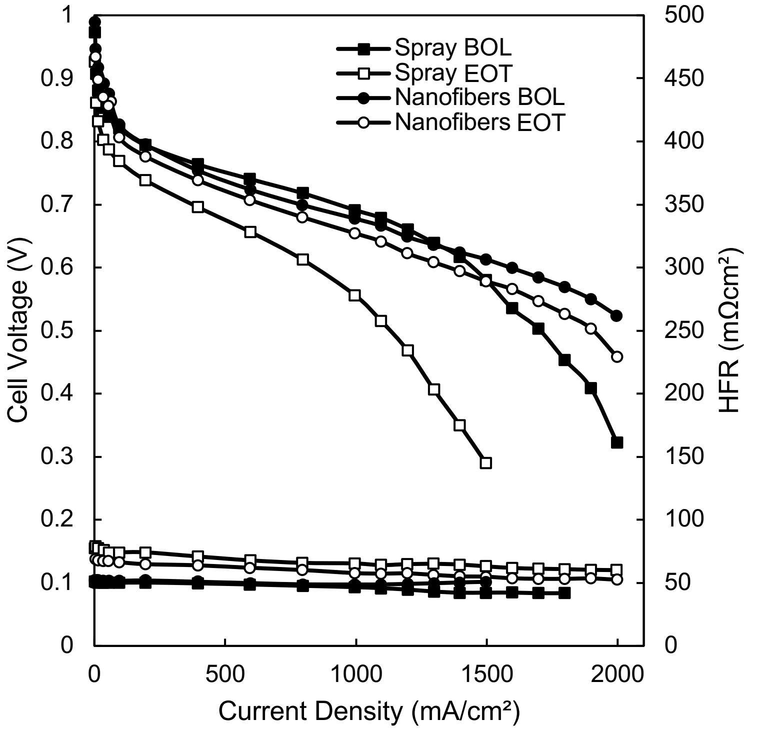

Figure 4. H_2/air fuel cell polarization data for nanofiber and sprayed electrode MEAs using PtCo/C cathodes and Pt/C anodes at 80 °C, 100% RH, and 200 kPa absolute with feed gas flow rates of 4000/8000 sccm H_2/air. BOL data were collected after break-in. EOT data was collected after 30,000 square-wave voltage cycles, 0.60 V to 0.95 V.

The real distinction between a sprayed and nanofiber electrode MEA and the benefits of the nanofiber electrode morphology are seen at EOT. The spray electrode lost 32% of its maximum power after the metal dissolution AST, as compared to an 8% power loss for the nanofiber electrode MEA, with smaller losses in both ECSA and mass activity. In a previous study, Brodt et al. [1] showed that sprayed and nanofiber MEAs with Pt/C cathode catalyst exhibited similar durability after 10,000 metal dissolution voltage cycles. The present results show that the two MEA morphologies diverge after extended voltage cycling. At EOT, the GTR of nanofiber cathodes was lower than that of a sprayed cathode at BOL. Thus, nanofiber cathodes exhibit a low initial resistance to oxygen transport and retain this low resistance after a voltage cycling AST durability experiment. The low transport resistance is due to the unique mat morphology, with high inter and intra-fiber porosity, more accessible Pt sites (evident from the high ECSA), and a thinner (more uniform) ionomer coating on catalyst particles (with no/few agglomerates), as compared to sprayed/conventional MEAs.

The effect of a cathode recovery protocol on MEA power output is illustrated in Figure 5 where the performance in both the kinetic and mass transport regions of a pol curve improves significantly. Four repeated recovery cycles were sufficient to reach maximum initial MEA performance; for example, the peak power at BOL increases from 1050 to 1140 mW/cm^2 at 200 kPa. After the recovery process, the mass activity of the nanofiber cathode MEA (based on the initial weight of catalyst) reaches a maximum of 464 mA/mg$_{pt}$ while the sprayed electrode reaches 431 mA/mg$_{Pt}$ (see Table 2). The recovery process also improves the GTR at every stage of the AST with the recovered amount decreasing with catalyst ageing. The recovery protocol decreases the BOL nanofiber cathode GTR to 21 s/m (Table 2) vs. 35 s/m shown in Table 1. After 15,000 voltage cycles of a metal dissolution AST, the recovery protocol decreases the GTR from 35 to 28 s/m. After 30,000 metal dissolution voltage cycles and 4 recovery cycles, the GTR of the nanofiber cathode was 35 s/m while the spray cathode was 52 s/m, showing much better retention of gas transport properties. These results illustrate the importance of the recovery protocol in evaluating the maximum performance achievable with any MEA. It should also be noted that the recovered performance (polarization and mass activity) of the nanofiber cathode MEA after 15,000 AST cycles is actually better than its BOL performance (mass activity of 496 mA/mg$_{Pt}$) illustrating that the initial loss in performance is due to processes that are reversible. However, after 30,000 cycles, the performance (polarization, mass activity, and GTR) is degraded from those observed at BOL due to irrecoverable voltage losses.

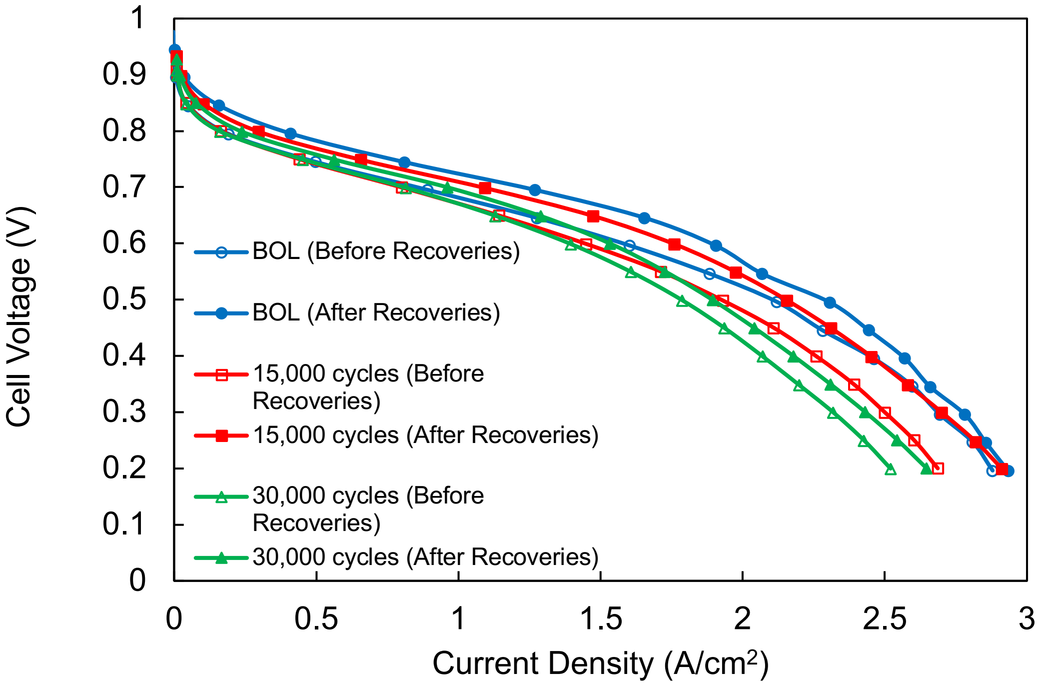

Figure 5. Polarization data for a 5 cm^2 nanofiber MEA with a PtCo/C cathode at 80°C, 100% RH, 200 kPa, with feed gas flow rates of 500 sccm H_2 at the anode and 2000 sccm at the cathode.

Table 1. Electrochemically active surface area and mass activity of nanofiber and spray electrode MEAs at beginning and end of life (after 30,000 metal dissolution cycles).

	ECSA (m^2/g_{Pt})		**Mass Activity (mA/mg_{Pt})**		**Gas Transport Resistance (GTR) (s/m)**		**Ionomer Resistance (Ω-cm^2)**	
	BOL	**EOT**	**BOL**	**EOT**	**BOL**	**EOT**	**BOL**	**EOT**
PtCo/C Spray	44	33	190	144	52	68	0.19	0.29
PtCo/C Nanofibers	48	41	270	219	35	37	0.14	0.19

Table 2. Mass activity and gas transport resistance (GTR) changes during a square wave accelerated stress test after either 15,000 or 30,000 voltage cycles (0.60 – 0.95 V) with and without recovery (measurements were carried out at LANL).

	Nanofiber MEA Mass Activity (mA/mg_{Pt})	**Nanofiber MEA GTR (s/m)**	**Spray MEA Mass activity (mA/mg_{Pt})**	**Spray MEA GTR (s/m)**
BOL	270	35	N/A	N/A
BOL + 4 Recovery cycles	464	21	431	29
15k voltage cycles	236	35	121	41
15k voltage cycles + 4 Recovery cycles	496	28	231	37
30k voltage cycles	202	37	147	59
30k voltage cycles + 4 Recovery cycles	296	35	189	52

3.3 Fuel Cell Performance of Nanofiber Cathode MEAs with Nafion/PEO Binder

H_2/air fuel cell polarization curves for nanofiber electrode mats made with Nafion (in the Na^+ counterion form)/PEO binder or H^+-Nafion/PAA binder are shown in Figure 6, where the cathode catalyst was either Pt/C (Johnson Matthey HiSpec 4000) or PtCo/C (Tanaka Kikinzoku Kogyo: TKK TEC36E52). For the salt-form Nafion MEAs, the cathode fiber mats were pre-treated in hot water to remove PEO but there was no attempt to exchange Na^+ counter-ions with H^+ in the cathode and anode Nafion binders. The catalyst/binder ratio in both Nafion nanofiber cathodes was 52/48 on a weight basis, which corresponds to an I/C ratio of 1.15. From Figure 6, it can be seen that nanofiber cathode MEAs with a Nafion binder, i.e., those made with a Nafion/PEO ink, with the extraction of PEO after electrospinning, produced more power than a slurry electrode of the same loading and binder, e.g., after PEO removal, the maximum power density for the slurry cathode MEA with a Pt/C cathode was 590 mW/cm^2 versus 779 mW/cm^2 for a fiber cathode MEA. Also, higher power was observed for both binder types when the Pt/C cathode catalyst was replaced by PtCo/C. A summary of the nanofiber MEA fuel tests is presented in Table 3 (two different cathode catalysts and two different binders). The ORR mass activity and ECSA are higher for nanofiber cathodes that employ neat Nafion as the binder.

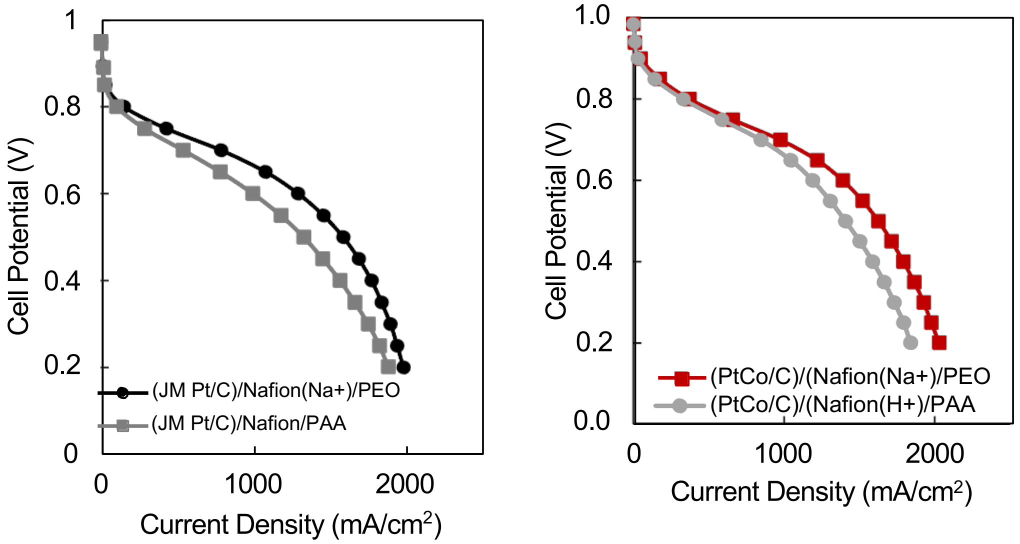

Figure 6. Polarization data for Johnson Matthey Pt/C cathode (left) and TKK PtCo/C cathode (right). The loading of the cathodes is 0.1 mg/cm2 in both cases. The anode for both MEAs is a nanofiber Johnson Matthey Pt/C anode at 0.1 mg/cm2 with the same binder as the cathode. The operating conditions are 80 °C, 200 kPa (absolute), 125/500 sccm H2/air, and 100% RH.

Table 3. Summary of Power Density, ORR Mass Activity, and electrochemical surface area for nanofiber electrode MEAs with Pt/C and PtCo/C using the Nafion/PAA or Nafion/PEO as the cathode fiber binder with a Nafion/PAA nanofiber anode.

Nanofiber cathode catalyst & binder.	**Max Power (mW/cm^2)**	**Power at 0.65V (mW/cm^2)**	**Cathode Mass Activity (mA/mg$_{Pt}$)**	**Cathode ECSA (m^2/g)**
PtCo/C Binder: Nafion(H$^+$)/PAA	718	679	298	62
PtCo/C Binder: Nafion(Na$^+$)/PEO	840	793	350	69
Pt/C Binder: Nafion(H$^+$)/PAA	650	510	160	59
Pt/C Binder: Nafion(Na$^+$)/PEO	779	703	191	67

Durability studies with nanofiber cathode MEAs containing Nafion binder (spun from a Nafion/PEO ink) were carried out. After a metal dissolution AST (30,000 square wave voltage cycles from 0.6 V to 0.95 V vs SHE), the Nafion nanofiber electrode MEA lost a larger percentage of power, vs. a Nafion/PAA binder; but the actual measured power at both BOL and EOT were higher for a Nafion binder vs. a Nafion/PAA binder as is shown in Figure 7 and Table 4 (when the binder for a nanofiber electrode is labeled as Nafion, it means the that fibers were spun with salt-form Nafion and the PEO or PAA was removed from a fiber mat by a hot water soak). The Nafion binder nanofiber electrode MEA produced more power at BOL than a Nafion/PAA cathode, but it also lost more power after the AST (a 21% drop in maximum power for a Nafion binder vs. a 9% drop for a Nafion/PAA binder). The better durability for Nafion/PAA nanofibers is due presumably to a decrease in the Nafion binder's ion exchange capacity, a consequence of the presence of PAA. With fewer mobile protons in the binder of a Nafion/PAA electrode, the dissolution of catalyst metal species is lowered. The nanofiber mat electrospun from a Nafion/PEO ink (with removal of PEO) has a higher IEC and more mobile protons; it is expected that the EOT/BOL power density ratio will be lower than a Nafion/PAA binder cathode.

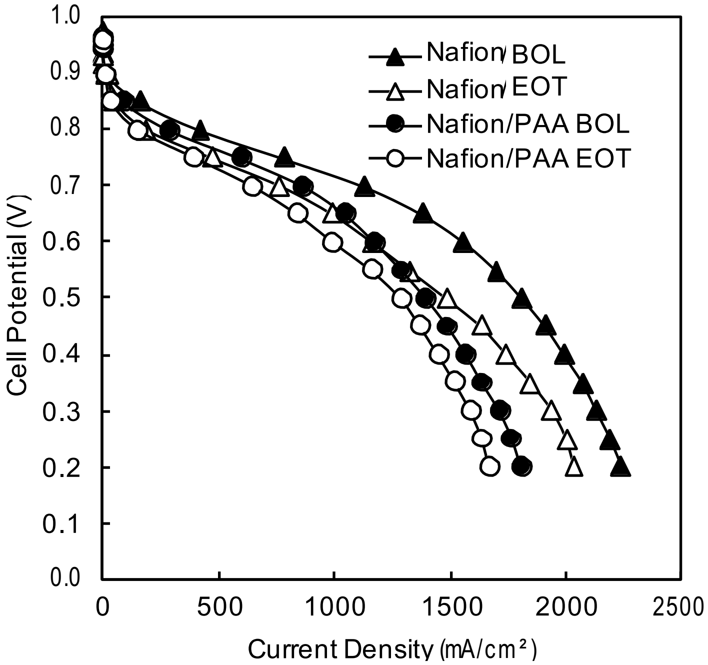

Figure 7. Metal Dissolution AST for 30,000 cycles using a TKK PtCo/C catalyst. The loading on both MEAs is 0.1 mg/cm^2 on the cathode and 0.1 mg/cm^2 on the anode. Polarization conditions are: 125/500 sccm H_2/air, 80 °C, 200 kPa absolute.

Table 4. Power density comparison between MEAs with cathode/anode binders of either Nafion or Nafion/PAA before and after metal dissolution AST.

Nanofiber electrode binder (for cathode and anode)	**80°C, 100% RH, 200 kPa (abs)**	
	Max Power (mW/cm^2)	**Power at 0.65 V (mW/cm^2)**
Nafion/PEO fibers – BOL/EOL	935/741	897/643
Nafion/PAA fibers– BOL/EOL	711/645	679/546

The use of salt-form Nafion as the electrode binder was further studied by comparing H_2/air fuel cell polarization curves for nanofiber electrode mats made with Nafion(Na^+)/PEO binder, Nafion(Na^+)/PAA binder or H^+-Nafion/PAA binder. When salt-form Nafion is used, the carrier polymer (either PEO or PAA) can be removed from the electrode by a water soaking step. The results are shown in Figure 8, where the cathode catalyst was either Pt/C (Johnson Matthey HiSpec 4000) or a PtCo/C (Tanaka Kikinzoku Kogyo: TKK TEC36E52). The catalyst/binder ratio in both Nafion nanofiber cathodes was 52/48 on a weight basis, which corresponds to an I/C ratio of 1.15. Higher power was observed for both carriers when Nafion(Na^+) was used to electrospin fibers, due to a higher ORR mass activity and ECSA.

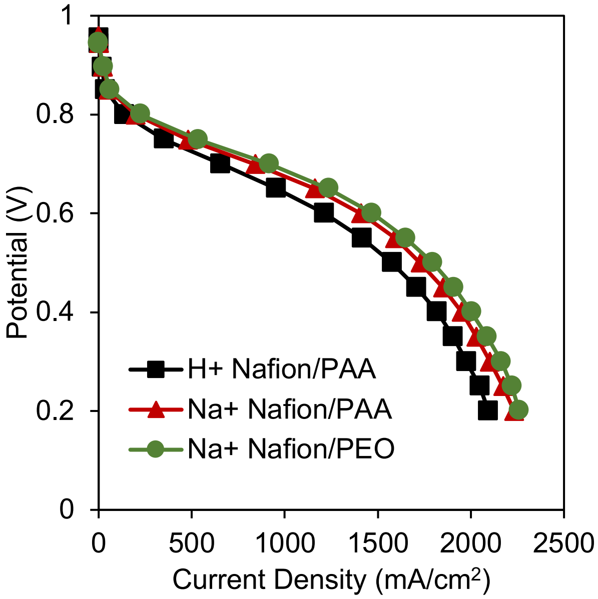

Figure 8. Polarization curves for fiber electrode MEAs using Pt/C (TKK) with binders of (black squares) H^+-Nafion/PAA, (red triangles) Na^+-Nafion/PAA, and (green circles) Na^+-Nafion/PEO. Data were collected at 80 °C, 200 kPa_{abs}, 100% RH, with hydrogen and air flowrates of 125 and 500 sccm, respectively.

Whereas the results in Figure 8 show some improvement in using a salt-form Nafion binder, the effect of the binder on performance was more pronounced when the feed gas RH was lowered. Polarization data at 40% RH (Figure 9a) show that the H^+-form Nafion/PAA fiber electrode MEA suffered a significant power loss with decreasing RH, as compared to MEAs prepared with Na^+-form Nafion and either PEO or PAA. The discrepancy between binder types was most prominent in the ohmic region (0.4-0.65 V), where the HFR was 194, 85, and 86 $m\Omega\cdot cm^2$ at 0.65 V for H^+-Nafion/PAA, Na^+-Nafion/PAA, and Na^+-Nafion/PEO fibers, respectively. Since HFR is a measurement of membrane and membrane/electrode contact resistance and the ionic resistance of Nafion rises significantly at low RH, it is concluded that fiber electrodes prepared with Na^+-Nafion allow the electrodes and membrane to retain more water at low humidity. The removal of PEO or PAA from the electrode fibers also helps to improve power, since these carrier polymers dilute Nafion and their presence lowers the overall conductivity of the binder at both high and low RH. As shown in Figure 9b, the maximum power was nearly constant between 40% and 100% RH for the two nanofiber electrode MEAs prepared using Na^+-form Nafion. For MEAs with H^+-Nafion/PAA fiber electrodes, there was a modest but discernable optimum in maximum power vs. relative humidity at ~80% RH; at higher humidification, there was some electrode flooding (the PAA carrier polymer added to the hydrophilicity of the cathode) while at lower RH there was ionomer dehydration and a drop in proton conductivity. There was no indication of cathode flooding with salt-form Nafion binder at high current densities.

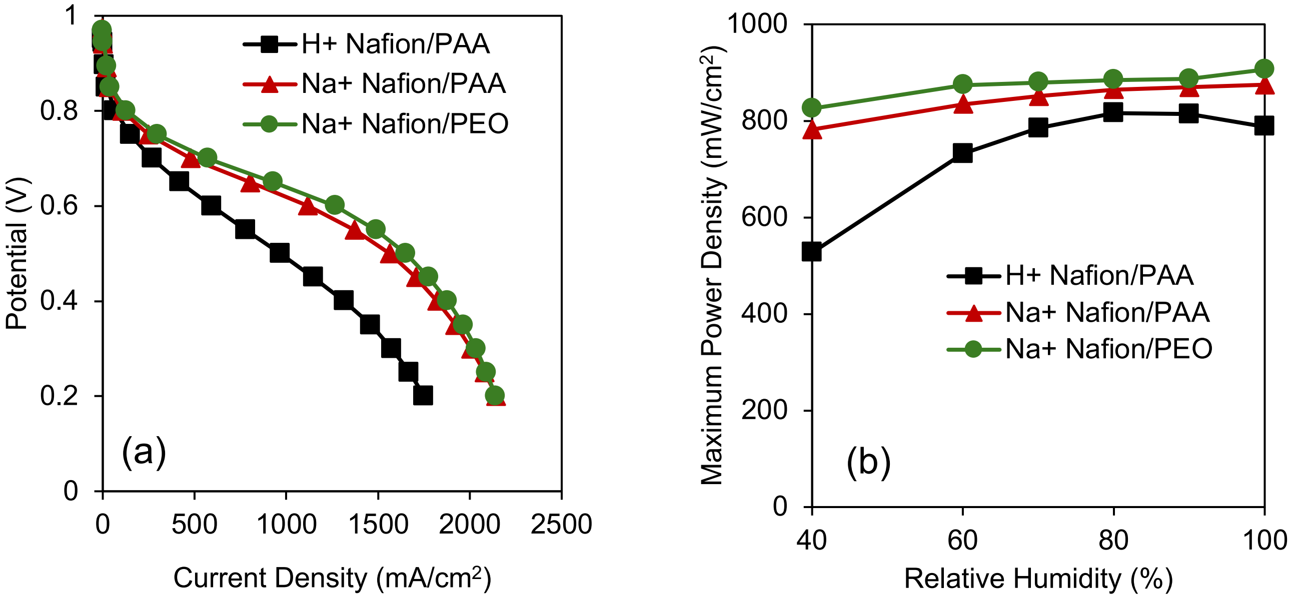

Figure 9. (a) H_2/air polarization data at 40% RH and (b) maximum power density vs. relative humidity for fiber electrode MEAs using Pt/C (TKK) with binders of (black squares) H^+-Nafion/PAA, (red triangles) Na^+-Nafion/PAA, and (green circles) Na^+-Nafion/PEO. Data were collected at 80 °C, and 200 kPa_{abs}, with hydrogen and air flowrates of 125 and 500 sccm, respectively.

The ratio of power densities at 40% RH and 100% RH as a function of operating voltage and backpressure was examined. The resulting data are plotted for Na$^+$-Nafion/PEO and H$^+$-Nafion/PAA fiber electrode MEAs in Figure 10. It is expected that higher operating voltages would result in poor power retention at low humidity due to less water production. For both binders, the power ratio decreased with increasing potential and decreasing backpressure, but fiber electrode MEAs prepared with Na$^+$-Nafion binder were less sensitive to these operating conditions and retained more power overall than the H$^+$-Nafion/PAA MEA. Thus, for a fiber mat MEA made with Na$^+$-Nafion/PEO binder, the power densities at 40% RH and 100% RH are essentially the same for operating voltages between 0.2 and 0.55 V. It should be noted that the voltage window for a power ratio of 1.0 could be extended to higher voltages than those shown in Figure 10a if a thinner membrane were used for the fiber MEAs (25 μm was used for all MEAs in the present study). Similarly, a nanofiber electrode MEA with a thinner membrane will give higher power a feed gas humidities < 40%.

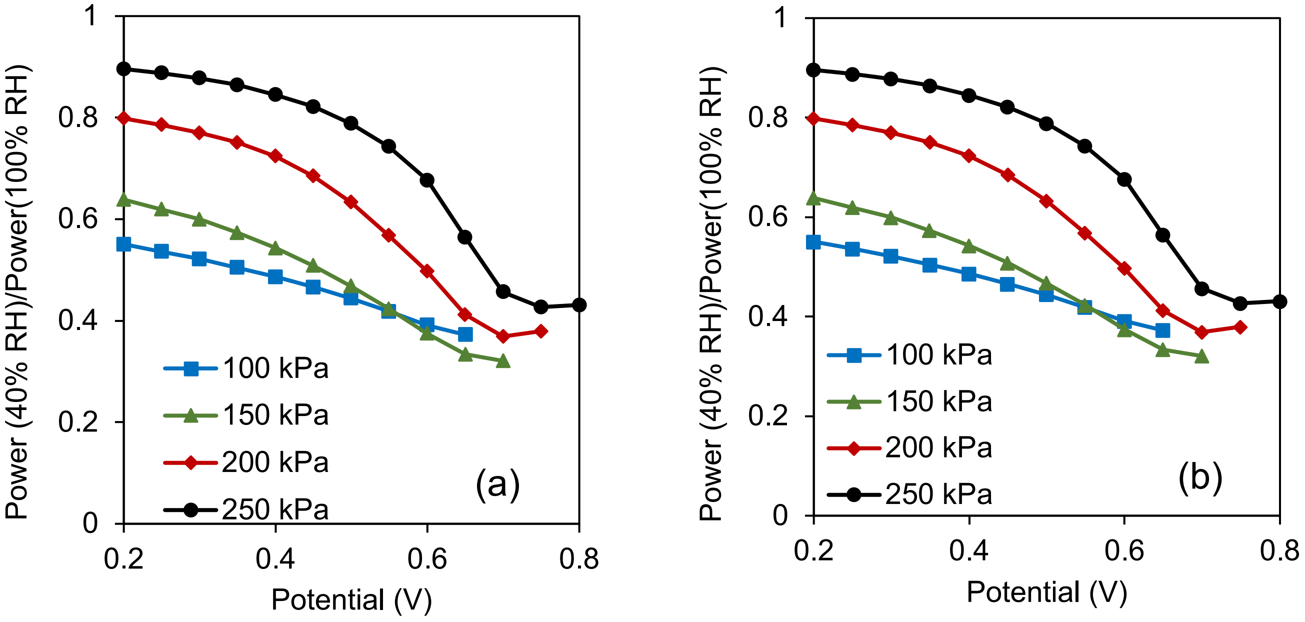

Figure 10. The ratio of power at 40% RH and 100% RH vs. potential at varied pressures for fiber electrode MEAs prepared with a binder of a) Na$^+$-Nafion/PEO and b) H$^+$-Nafion/PAA. Data were collected at 80 °C with hydrogen/air flowrates of 125/500 sccm.

As another example of low humidity operation of a fiber mat electrode MEA, a fully electrospun nanofiber MEA was created using 725 EW PFSA as the membrane and electrode binder, where PEO was employed as the electrode fiber carrier polymer. The membrane was a dual fiber electrospun nanofiber composite film with a composition of 80/20 PFSA/PVDF with a thickness of ~20 μm. The cathode was electrospun from an ink that contained PtCo/C, Nafion, and PEO. The anode was electrospun from an ink that contained Pt/C, 725 EW PFSA, and PEO. H_2/air polarization curves at 40% and 20% RH are compared to those collected for a MEA with Nafion/PEO nanofibers and a Nafion 211 membrane in Figure 11(a,b). The variation in maximum power density as a function of RH for the two MEAs is shown in Figure 11c.

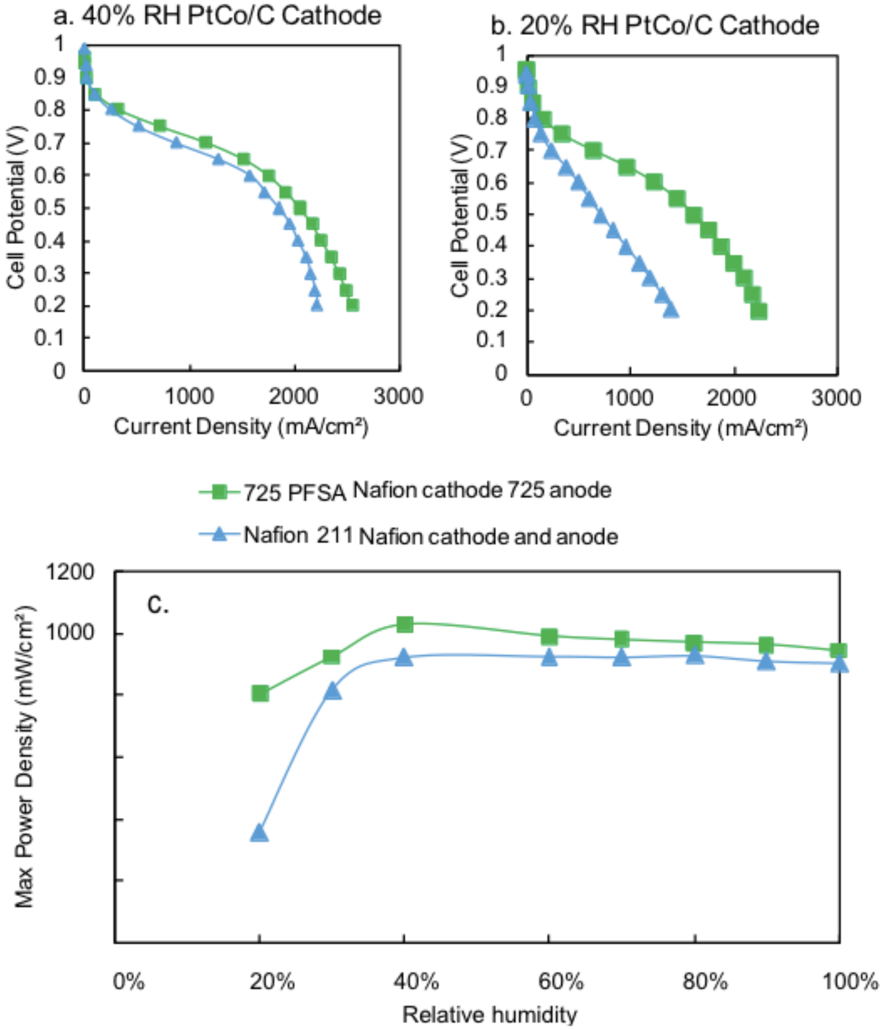

Figure 11. Performance of a fully electrospun MEA containing Nafion as the cathode binder and 725 EW PFSA as the anode binder. A PVDF fiber-reinforced Membrane was used (80/20 725EW PFSA/ PVDF; 20 μm membrane thickness). The cathode catalyst was PtCo/C, and the anode catalyst was Pt/C. Operating conditions: 200 kPa (abs), 125/500 sccm H_2/air, 80 °C, anode/cathode loading at 0.1 mg/cm² ± 0.005 each. Square symbols are for the fully electrospun MEA with 725 EW PFSA. Triangular symbols are for a nanofiber anode/cathode MEA with a Nafion 211 membrane.

3.4 Fiber Mat Electrode MEAs with a High Pt-Loading Cathode

The processing of sprayed and nanofiber cathode MEAs with a catalyst content of ~0.2 mg_{Pt}/cm^2 was studied. At 0.2 mg_{Pt}/cm^2, fiber electrode MEAs produced higher power when cathode mats were pre-compacted at high pressure. When the same pre-compaction conditions were applied to a 0.2 mg_{Pt}/cm^2 sprayed electrode MEA, the power decreased. The pre-compaction step was necessary to decrease the overall thickness of a 0.2 mg/cm^2 nanofiber mat cathode. For the sprayed cathode, the pre-compaction step may have overly compressed the electrode, with an unacceptable decrease in cathode porosity and/or the impregnation of some catalyst particles into the membrane (such particles would be isolated from O_2 reactant).

An MEA was fabricated with a cathode loading of 0.2 mg_{Pt}/cm^2, a Xergy Xion™ composite membrane, and a nanofiber anode at 0.1 mg_{Pt}/cm^2. The fiber-reinforced Xion™ composite PEM-Aquivion-830-10 was purchased from the Fuel Cell Store. The film is 10 µm thick and uses Aquivion PFSA ionomer with an equivalent weight of 830. Particle/polymer inks for electrospinning were prepared using Pt/C catalyst powder (TEC10F50E) from the Tanaka Kikinzoku Kogyo Group (TKK). Electrospinning inks were prepared by dispersing catalyst, Na^+-form Nafion, and PEO in a water/alcohol solvent. Inks were electrospun at a flowrate of 0.75 ml/h, 20% RH, 20 cm tip-to-collector distance, and ~9 kV. The dry fiber mat composition was 52:37:11 by weight of catalyst:Nafion:PEO. Two electrospun fiber mats (each at 0.10 mg_{Pt}/cm^2) were stacked and pressed together at 20,000 lb_f and 140 °C for 5 minutes during MEA fabrication to achieve a total cathode catalyst loading of 0.2 mg_{Pt}/cm^2. Next a 0.1 mg_{Pt}/cm^2 anode was hot-pressing to the opposite side of the membrane at 1000 lb_f and 140 °C for 5 minutes. The anode and cathode used the same binder and catalyst. After hot-pressing, MEAs were soaked in 80 °C water for 1 hour to remove PEO and then vacuum dried. Post drying, MEAs were fitted with incompressible gaskets and Sigracet 29BC gas diffusion layers. MEAs were evaluated in a Scribner Inc. 850e test station, using a Fuel Cell Technologies 5 cm^2 test fixture with single serpentine anode and cathode gas channels.

H_2/air fuel cell polarization data for the Xion-Aquivion 830 membrane MEA were collected at 40% and 100% RH, 80 °C, 200 kPa_{abs}, and 125/500 sccm of H_2/air. The results were compared to a Nafion 211 membrane MEA with the same nanofiber electrodes. Polarization curves at 40% and 100% RH are shown in Figure 12 and relevant MEA performance metrics are summarized in Table 5. Both the Xion-Aquivion 830 membrane and Nafion 211 membrane MEAs showed similar values of ORR mass activity and ESCA and the Xion-Aquivion 830 membrane MEA produced slightly higher power than the Nafion 211 membrane MEA at both 100% and 40% RH for voltages < 0.65 V. It should be noted that the Xion-Aquivion 830 membrane MEA exhibited an improvement in power at low voltages (high current densities) when the feed gas RH was reduced from 100% to 40%. This improvement in performance is presumably due to the reduced thickness of the membrane and increased hydrophilicity of the low EW PFSA ionomer. The use of a low EW ionomer improves proton conductivity at low RH and a thinner membrane increases the rate of water back-diffusion from the cathode to the anode. The present results are encouraging; fiber mat MEAs at a high Pt loading can be made with an ultrathin membrane (the fiber mats do not appear to damage the membrane) and high power is achievable at low RH gas feed conditions. Further studies are needed to optimize the hot pressing conditions for the Xergy membrane and to examine the durability of fiber electrode

MEAs with this ultrathin film. AST voltage cycling durability tests a 100% and 40% RH are planned for next quarter.

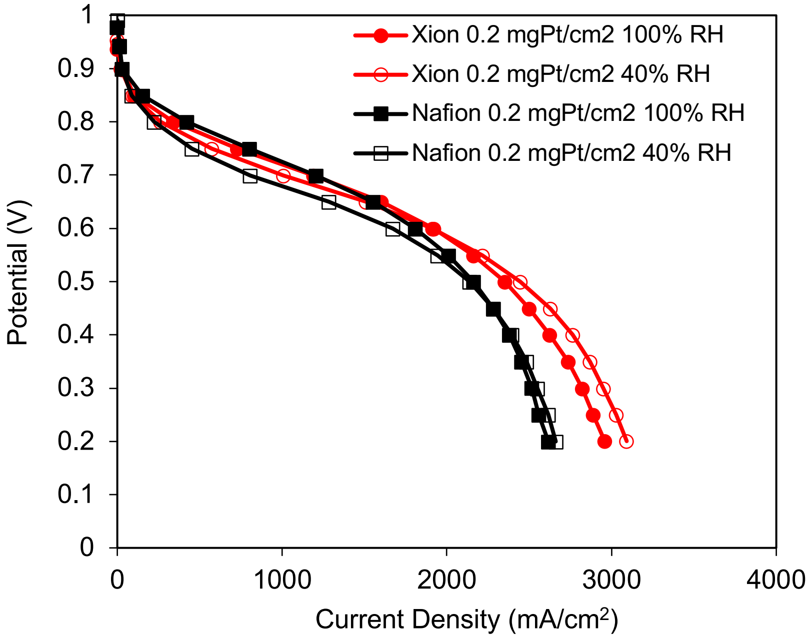

Figure 12. Polarization curves for fiber MEAs with a Xion-Aquivion 830 membrane (red circles) and a Nafion 211 membrane (black squares) at 100% RH (filled) and 40% RH (unfilled). Data were collected at 80 °C, 200 kPa_{abs}, and 125/500 sccm H_2/air.

Table 5. Summary of mass activity, ECSA, and power density at 100% RH and 40% RH for fiber cathode MEAs with a Nafion 211 or a Xion-Aquivion 830 membrane.

Membrane	**Mass Activity (mA/mg_{Pt})**	**ECSA (m^2/g_{Pt})**	**Max. Power (mW/cm^2)**		**Power at 0.65 V (mW/cm^2)**	
			100% RH	**40% RH**	**100% RH**	**40% RH**
Nafion 211	179	67	1104	1069	1008	833
Xion-Aquivion 830	191	74	1187	1222	1042	979

A high cathode loading MEA was further tested for its durability in a metal dissolution voltage cycling AST (30,000 voltage cycles from 0.60 to 0.95 V). This MEA had a Nafion 211 membrane MEA, Pt/C anode and a cathode loading of 0.21 mg_{Pt}/cm^2. H_2/air fuel cell polarization curves at BOL and EOT are shown in Figure 13. The drop in power density (maximum power and power at 0.65 V) and the changes in ORR mass activity and ECSA after the AST are listed in Table 6. This MEA exhibited excellent durability, with a decrease of only 13% in power density.

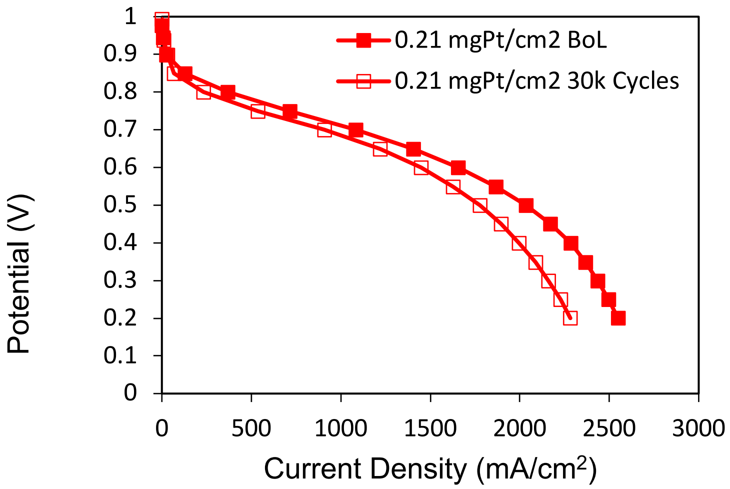

Figure 13. BOL and EOT H_2/air polarization curves for nanofiber electrode MEA (5 cm^2 area) with TKK Pt/C catalyst and Nafion binder. The membrane was Nafion 211. The anode loading was 0.1 mg$_{Pt}$/cm^2 and the cathode loading was 0.21 mg$_{Pt}$/cm^2. Polarization data collected at 80°C, 200 kPa$_{abs}$, H_2/air at 125/500 sccm

Table 6. Changes in mass activity, ECSA, and power density after a 30,000 voltage cycle metal dissolution AST. Fuel cell operating conditions: 80°C, 200 kPa$_{abs}$, H_2/air at 125/500 sccm.

	0.21 mg/cm^2 Pt/C fiber cathode MEA (EOT after 30000 voltage cycles)
Mass Activity EoT/BoL (mA/mg$_{Pt}$)	93/173
ECSA EoT/BoL(m^2/g$_{Pt}$)	32/67
EoT/BoL Power at 0.65 V (%)	87
EoT/BoL Maximum Power (%)	87

3.5 Pt/C-Nafion/PAA Fibers Made with the Inovenso Pilot-Scale Spinner

Initial scale-up studies for nanofiber mat electrodes were carried out using an Inovenso Model PE-300 pilot-scale NanoSpinner. Fiber mats were made using Pt/C catalyst and Nafion/PAA binder. The PE-300 NanoSpinner has the capability of producing fiber mats using 18 individual spinneret orifices. In the present test, fibers were made using only one orifice. A photograph of the PE-300 NanoSpinner is shown in Figure 14.

Figure 14. The Inovenso PE-300 pilot-scale electrospinning apparatus.

Catalyst/Nafion/PAA solutions for the Inovenso Spinner were made using Pt/C catalyst (TEC10F50E) from the Tanaka Kikinzoku Kogyo Group (TKK) and D2021 Nafion dispersion from Chemours. The PAA content in the solution was fixed at 10 wt.% with a mixture of water and IPA as the solvent. Solutions were electrospun at a flowrate of 1 ml/h, 20% RH, 15 cm tip-to-collector distance, and 25 kV. The dry fiber mat composition was 58:28:14 catalyst:Nafion:PAA by weight. A comparison of the electrospinning parameters for a single needle lab-scale electrospinner and the Inovenso Spinner is shown in Table 7.

Table 7. Comparation between Inovenso spinner and normal electrospinner for fibers composed of Pt/C, Nafion, and PAA

	single needle lab-scale spinning	**Inovenso spinning**
ink composition (Pt/C: Nafion: PAA)	58:28:14	58:28:14
voltage	9 KV	25 KV
distance	10 cm	15 cm
RH	20%	20%
flow rate	1 mL/h	1 mL/h (one needle)

Fibers made on the Inovenso Spinner were used in an MEA with a Nafion 211 membrane and a sprayed anode with Pt/C powder and neat Nafion binder. The anode and cathode loadings were each 0.1 mg_{Pt}/cm^2. Beginning-of-life (BOL) fuel cell data were collected using a Scribner Inc. 850e test station and a Fuel Cell Technologies 5 cm^2 test fixture with single serpentine anode and cathode gas channels. Polarization data were collected at 80°C, 100% RH, and 200 kPa_{abs} backpressure, where the H_2/air flow rates were 125/500 sccm.

Figure 15(a) shows fuel cell polarization plots for two nanofiber cathode MEAs. For one MEA, the fibers were made on the single needle lab-scale electrospinner (denoted as regular PAA coated fibers in the figure) and for the second MEA, the fiber were made using the Inovenso Spinner. As can be seen, the two MEA performed equally well at voltages > 0.6 V. At lower voltages (high current density) the Inovenso fibers performed somewhat better. A summary comparison of the maximum power density and the power density at 0.65 V is presented in Figure 15(b). Within the reproducibility limits of making MEAs, the Inovenso fiber ink cathode MEA and the lab-scale fiber ink cathode MEA worked equally well, with power densities much higher than those collected on a sprayed anode/cathode MEA.

Top-down SEM images of as-spun fiber mats made using the Inovenso Spinner and the single needle lab-scale electrospinning apparatus are shown in Figure 16. The Inovenso fibers appear to have more bead-on-fiber defects, as compared to fibers made on the lab-scale single needle apparatus. Further experimentation is needed (and will be carried out) to identify the preferred/optimum ink composition and electrospinning conditions for the Inovenso Spinner, with a focus on making mats using multiple orifices.

A metal dissolution AST was performed on the Inovenso fiber mat MEA with H_2 (anode) and N_2 (cathode) feed gases at 80ºC, 100 % RH and 100 kPa_{abs}, where the voltage was cycled between 0.6 V and 0.95 V for 15000 cycles. After cycling, a H_2/air polarization curve was generated at 80 ºC, 100% RH, 200 kPa_{abs}, and gas flow rates of 125/500 sccm for H_2/air. Polarization curves at BOL and EOT are shown for two MEAs in figure 17; one made with Inovenso fibers (identified as coated fibers) and on made with a lab-scale single-needle electrospinning apparatus. At BOL the two MEAs performed equally well, with slightly higher power from the Inovenso fiber MEA. At EOT, however, the Inovenso fiber electrode exhibited a greater power loss (36% at 0.65 V), as compared to the MEA where the cathode was made with lab-scale electrospinner fibers (17% power loss at 0.65 V). These results are summarized in Table 8. We associate the poor durability of the Inovenso fibers with the bead-on-fiber defects. We have seen previously that poor quality fiber mats (i.e., those with droplets or numerous bead-on-fiber defects) perform reasonably well in a fuel cell MEA at BOL, but do not show the same durability in an AST, as compared to well-formed fibers of near uniform diameter (with no binder or catalyst agglomerates).

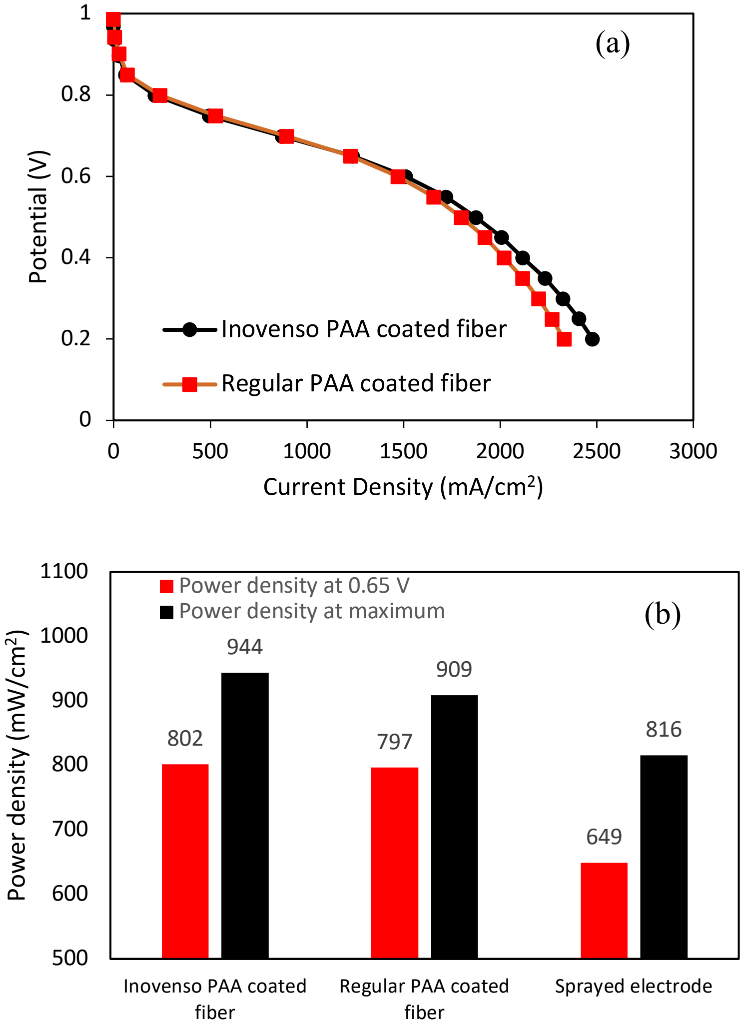

Figure 15. (a) H_2/air fuel cell polarization data for MEAs with a cathode made by coating a GDL with an ink containing pre-formed fibers, where the fibers were made using either a lab-scale single needle electrospinning apparatus or the pilot-scale Inovenso Spinner. (b) Summary of power output at maximum power and power at 0.65 for MEAs with three different cathodes. Data were collected at 80°C, 100% RH, 200 kPa_{abs}, with H_2/air flowrates of 125/500 sccm. The anode and cathode loadings for all MEAs were each 0.1 mg_{Pt}/cm^2.

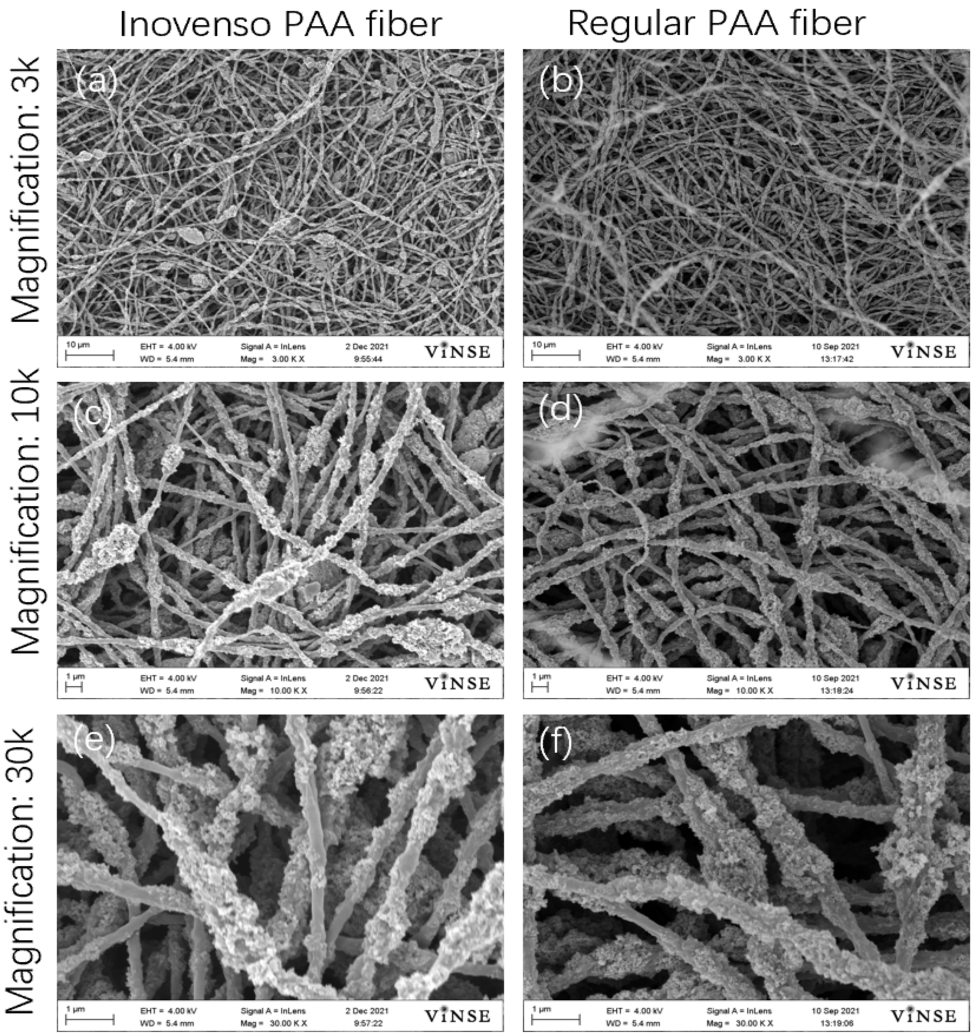

Figure 16. Top-down SEM images of a fiber mat made using either the Inovenso Spinner or the lab-scale single needle electrospinning apparatus.

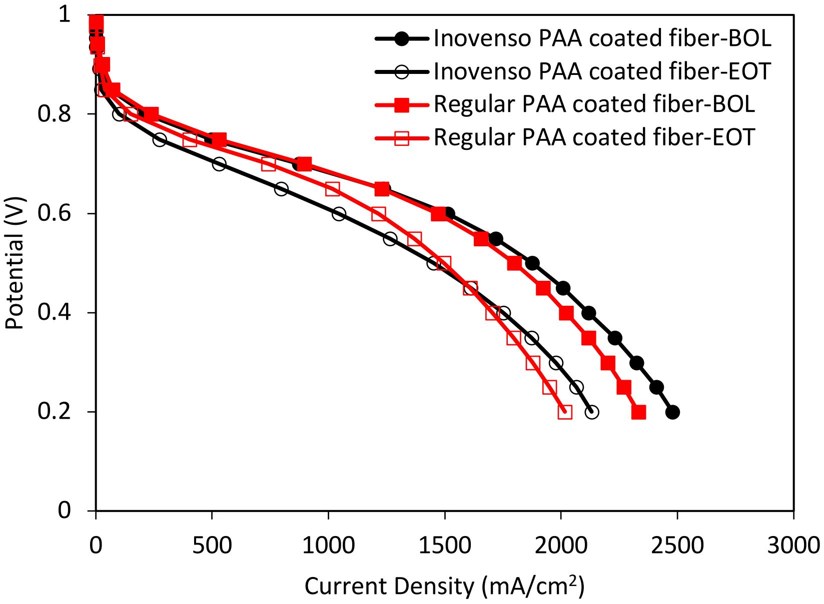

Figure 17. Polarization data for Inovenso PAA coated fiber electrode (black circles) and a regular PAA coated fiber cathode (red squares) at BoL (filled) and after 15,000 metal dissolution cycles (open). Data were collected at 80 °C, 100% RH, 200 kPa_{abs}, with H_2/air flowrates of 125/500 sccm.

Table 8. Summary of the metal dissolution AST results for Inovenso PAA coated fiber and regular PAA coated fiber electrode.

MEA (15000 cycles)	Power density at 0.65 V mW/cm^2 (EOT/BOL)	Power density at maximum mW/cm^2 (EOT/BOL)
Inovenso PAA coated fiber	517/802 (64%)	725/944 (77%)
Regular PAA coated fiber	660/797 (83%)	751/909 (83%)

3.6 Water Management of Electrospun Nanofiber MEAS, as Measured by *Operando* Neutron Radiography Experiments

One attractive characteristic of nanofiber mat electrode MEAs is their ability to expel product water from the cathode, with little or no flooding at high current densities. This was investigated further by viewing directly the water profile in an operating fuel cell MEA via neutron imaging. Data was collected on a nanofiber electrode MEA (0.10 mg/cm^2 Pt/C anode and cathode with an acid-form Nafion + PAA binder) and a sprayed electrode MEA (Pt/C and a neat Nafion binder). Water profiles are shown in Figure 18 for various operating current densities during H_2/air fuel cell operation at 80 °C, 200 kPa_{abs}, and 100% RH. As can be seen, there is less water in the nanofiber electrode MEA (more water in the outer portions of the anode and cathode GDLs) as compared to the sprayed electrode MEA, due to intra and interfiber porosity of the fiber mat cathode.

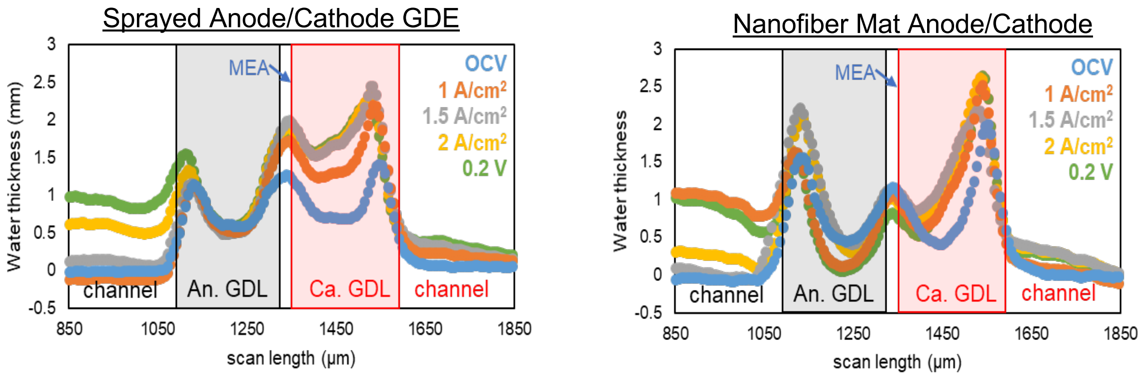

Figure 18. Water profiles in a sprayed electrode MEA and a nanofiber MEA at 100% different H_2/air fuel cell operating conditions. Pt/C anode and cathodes at 0.1 mg_{Pt}/cm^2, Nafion 211 membrane, Neat Nafion binder for sprayed GDEs; H^+-form Nafion + PAA binder for the nanofiber MEA. Data were collected at 80 °C, 200 kPa_{abs}, and 100% RH.

3.7 Determining Rated Power

The rated power of a hypothetical 90 kW fuel cell stack with nanofiber electrode MEAs and a Nafion 211 membrane was determined using Equation 1 with Q/ΔT equal to 1.45 kW/°C.

$$Q/\Delta T = \frac{\left[Stack\ Power\ (kW) \times {}^{(1.25 - V\ @\ rated\ power)}\!\big/\!{}_{V\ @\ rated\ power} \right]}{Cell\ Operating\ Temperature\ (^{o}C) - Ambient\ \ Temperature\ (^{o}C)} \qquad \text{[Equation 1]}$$

Rated power results at 95°C (0.663 V) and 100% RH are summarized in Table 9 for nanofiber MEAs at two total anode + cathode loadings and three different backpressures. The MEAs had a total Pt loading of 0.2 mg/cm^2 (0.1 mg_{Pt}/cm^2 anode and 0.1 mg_{Pt}/cm^2 cathode) or 0.017 mg/cm^2 (0.095 mg_{Pt}/cm^2 at the cathodes 0.022 mg_{Pt}/cm^2 at the anode). Hydrogen and air flow rates of 4 L/min and 8 L/min were used at the anode and cathode, respectively (these experiments were carried out at Nissan Technical Center North America, where they typically use high gas flow rate conditions). TKK PCo/C catalyst was used in the cathode and TKK Pt/C was used in the anode. The membrane was Nafion® 211. At an elevated backpressure of 250 kPa, both nanofiber MEAs met the 2020 DOE performance target. Values of rated power for an MEA with a Pt/C fiber mat cathode at a loading of 0.2 mg/cm^2 and a fiber mat Pt/C anode at 0.1 mg/cm^2 are listed in Table 10. A rated power near/above 1.0 W/cm^2 was achieved at the higher MEA Pt loading, using a less active Pt/C catalyst (versus PtCo/C) at a pressure of 250-300 kPa (abs).

Table 9. Summary of rated power results for electrospun anode/cathode MEAs with a PtCo/C cathode (electrodes electrospun with PEO carrier) at 95°C.

Total nanofiber MEA loading	**Rated Power at 150 kPa$_{abs}$ (mW/cm^2)**	**Rated Power at 200 kPa$_{abs}$ (mW/cm^2)**	**Rated Power at 250 kPa$_{abs}$ (mW/cm^2)**
0.2 mg$_{Pt}$/cm^2	803	961	1033
0.117mg$_{Pt}$/cm^2	702	945	1018

Table 10. Summary of rated power densities for electrospun anode/cathode MEAs with a Pt/C cathode (electrodes electrospun with PEO carrier) at a total (anode + cathode) Pt loading of 0.3 mg/cm^2.

	Rated Power (mW/cm^2)		
Pressure	**80 °C**	**90 °C**	**95 °C**
150 kPa$_{abs}$	446	705	721
200 kPa$_{abs}$	551	850	875
250 kPa$_{abs}$	629	948	983
300 kPa$_{abs}$	691	1011	1059

3.8 Impact of Polyvinylidene Fluoride on Nanofiber Cathode Structure and Durability

The impact of polyvinylidene fluoride (PVDF) as a binder component on the durability of Pt/C cathodes in a proton exchange membrane H_2/air fuel cell membrane-electrode-assembly (MEA) during a carbon corrosion voltage cycling accelerated stress test (AST) was examined using electrochemical fuel cell performance data and visual inspection/analysis of the cathode morphology (thickness and porosity) via electron microscopy. Electrospun nanofiber cathode mat MEAs with a Nafion/PVDF or Nafion/PAA binder or a slurry cathode MEA with neat Nafion or a Nafion/PVDF mixture were investigated. Both fiber mat and slurry electrode morphologies with a hydrophobic Nafion/PVDF binder exhibited the following desirable characteristics: (1) a cathode carbon loss that decreased with increasing PVDF content, as determined from CO_2 measurements in the air exhaust during an AST, (2) the retention of beginning-of-life (BOL) cathode thickness and porosity for Nafion/PVDF binders containing at least 50 wt.% PVDF, and (3) minimal/no power loss after the carbon corrosion AST for a 50/50 Nafion/PVDF weight ratio binder. The deleterious effect of PVDF in a Nafion/PVDF cathode binder (i.e., the increase in ionic/proton resistance due to the presence of uncharged PVDF polymer) is counterbalanced by the inherent advantages of the nanofiber mat electrode design, i.e., a high electrochemical surface area and a high mass activity at beginning-of-life that persists throughout the carbon corrosion AST.

The differences in MEA performance at BOL and end-of-test (EOT) for Nafion/PVDF fiber and neat Nafion sprayed cathode MEAs are best explained by combining cathode thickness and porosity data (Table 11) with electrochemical surface area (ECSA) and mass activity data in Table 12 (data from Reference 4). Thus, it can be concluded that: (1) the difference in EOT power for the Nafion slurry vs. Nafion/PVDF slurry MEAs is due to differences in cathode thickness and porosity after voltage cycling (the EOT ECSA and mas activity are nearly the same for these two MEAs), (2) the lower EOT power for the nanofiber cathode MEA with Nafion/PAA binder vs the nanofiber cathode with Nafion/PVDF binder is due to the decrease in cathode thickness and loss of porosity for the former, i.e., the structural changes to the cathode at EOT dominate over mass activity, which is higher for the Nafion/PAA fiber cathode, and (3) the higher EOT power for the nanofiber vs. slurry cathode MEA with Nafion/PVDF binder is due to a significantly higher ECSA and oxygen reduction reaction mass activity for the nanofiber cathode MEA.

Table 11. Key cathode performance metrics before and after the carbon corrosion accelerated stress test. Polarization data at ambient pressure, 80 °C, 125/500 sccm H_2/air. AST conditions: 100%RH, 80 °C, 500 mV/s triangular wave from 1.0V to 1.5V 1000 cycles in 100/100 sccm H_2/N_2.

	Power Density at 0.65 V (mW/cm²)		**Cathode thickness (EOT/BOL) %**	**Cathode Porosity (%)**	
	BOL	**EOT**		**BOL**	**EOT**
Neat Nafion Slurry	285	147	49% ± 6.0%	44%	20%
Nafion/PAA nanofibers	402	229	42% ± 8.6%	50%	28%
1/1 Nafion/PVDF Slurry	210	197	99% ± 6.0%	46%	48%
1/1 Nafion/PVDF Fibers	260	261	102% ± 4.3%	45%	52%

Table 12. Summary Electrochemical Performance of Different Cathodes at BOL and EOL (data from Reference 4)

Pt/C Cathode Type and Binder (w/w)	**Cathode ECSA (m^2/g_{Pt})**		**Cathode Mass Activity* (A/mg_{Pt})**	
	BOL	EOT	BOL	EOT
Neat Nafion slurry	36	21	0.11	0.080
Nafion/PAA nanofibers	45	28	0.16	0.14
1/1 Nafion/PVDF slurry	36	24	0.067	0.077
1/1 Nafion/PVDF nanofibers	44	30	0.093	0.11

*Measurements taken at 0.90 V in O_2 at 7 psig and 100% RH

4. Conclusions

H_2/air fuel cell membrane-electrode-assemblies (MEAs) with electrospun catalyst/binder fiber mat electrodes produced high power at high and low relative humidity conditions and exhibited excellent durability, as measured in DOE-sanctioned voltage cycling accelerated stress tests.

MEAs were made and tested with Pt/C and carbon-support Pi-alloy cathode catalyst at cathode loadings of 0.1 and 0.2 mg/cm^2. Productive collaborations with FC-PAD researchers at National Laboratories were critically important in this project, including the collection of SEM, STEM, and EDX data at Oak Ridge National Laboratory and the confirmation of MEA performance results at Los Alamos National Laboratory. A few of the highlights of this DOE-EERE-funded study are:

- The performance of a fiber mat electrode MEA with Pt/C catalyst (at 0.2 mg$_{Pt}$/cm^2 cathode loading and 0.1 mg$_{Pt}$/cm^2 anode loading) was excellent. At 80 °C and 200 kPa$_{abs}$ the maximum power density was 1104 mW/cm^2. The maximum power was independent of feed gas humidity for $40 < RH < 100\%$. The power loss after a metal dissolution AST (30,000 voltage cycles) was only 13%.
- Rated power targets, as set forth by the DOE, were achieved for a low Pt loaded MEA (0.117 mg$_{Pt}$/cm^2 total for the anode + cathode) using a PtCo/C-Nafion cathode and a Pt/C-Nafion anode. The rated power of a 10 cm^2 MEA was 803 mW/cm^2, with a TKK PtCo/C cathode (0.1 mgPt/cm2), a TKK Pt/C anode (0.1 mg$_{Pt}$/cm^2), Nafion binder for both electrodes, and a Nafion 211 membrane, at T=95°C, 150 kPaabs, 100% RH
- Water content in Pt/C fiber electrode MEAs was compared to that in a conventional spray electrode MEAs during fuel cell operation via operando neutron imaging experiments at NIST. Under fully humidified conditions and high current density operation, there was less water within fiber electrode MEAs when the binder was H$^+$-form Nafion + PAA. At the same time, nm-size pores within a fiber trap water via capillary condensation, allowing for high power density operation at low relative humidity conditions.
- STEM-EDX imaging of electrospun fiber cross sections at ORNL and Vanderbilt revealed that fiber electrodes (using a Pt/C or PtCo/C catalyst) prepared with Nafion/PAA or Nafion/PEO binder showed an ionomer rich surface and a catalyst rich fiber interior.
- An all-electrospun MEA was prepared using 725 EW PFSA (provided by 3M Co.) for the membrane and electrode binder and Pt/C catalyst at the anode and cathode. The 725 EW MEA generated high and near-constant power over a wide range of feed gas relative humidity (20-100%). At 20% RH and 80°C, the 725 EW MEA generated a maximum power of 815 mW/cm^2.
- Catalyst/binder fibers were made on an Inovenso PE-300 pilot-scale electrospinner. The resulting electrodes performed the same in a fuel cell MEA as those made using lab-scale electrospinning equipment.
- A number of useful correlations were generated from experimental data, such as the effect of operating voltage and backpressure on the measured power density at 40% RH.
- The excellent performance and durability of fiber electrode MEAs were attributed to the nanofiber mat morphology, with inter and intra fiber porosity and very few catalyst or ionomer binder agglomerates.

5. Glossary of Terms

AST – accelerated stress test
BOL – beginning of life
ECSA – electrochemical surface area
EDX – energy dispersive x-ray
EOL – end of life(used interchangeably with EOT, end of test)

EW – equivalent weight
HFR – high frequency resistance
GTR – gas transport resistance
MEA – Membrane-electrode-assembly
PAA – poly(acrylic acid)
PEO – polyethylene oxide
PFSA – perfluorosulfonic acid
PTFE – polytetrafluoroethylene
PVDF – polyvinylidene fluoride
RH – relative humidity
sccm – standard cubic centimeters per minute
SEM – scanning electron microscope
STEM – scanning transmission electron microscope

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J. Slack, C. Gumeci, N. Dale, K. S. Reeves, D. A. Cullen, K. L. More, and P. N. Pintauro, "Electrospun PtCo/C Fiber Mat Cathodes with Neat Nafion Binder for H_2/air PEM Fuel Cells."

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9. Patents

COMPOSITE FIBER ELECTRODES AND APPLICATIONS OF SAME
Publication number: 20210384493
Abstract: A composite electrode includes two or more types of fibers forming a fiber network, comprising at least a first type of fibers and a second type of fibers. The first type of fibers comprises a first polymer and a first type of particles. The second type of fibers comprises a second polymer and a second type of particles. The second polymer is same as or different from the first polymer. The second type of particles are same as or different from the first type of particles.
Type: Application; **Filed:** June 8, 2021; **Publication date:** December 9, 2021
Inventors: Peter N. Pintauro, Ryszard N. Wycisk

NANOFIBER ELECTRODES, FABRICATING METHODS AND APPLICATIONS OF SAME
Patent number: 11020939
Abstract: Nanofiber electrodes for electrochemical devices and fabricating methods of the same are disclosed. In one embodiment, the method includes forming a liquid mixture containing a catalyst, a first polymer of perfluoro sulfonic acid and a second polymer of polyethylene oxide, the first polymer of perfluoro sulfonic acid being pre-treated to remove protons in the first polymer by exchange with a cation species like Na+; and electro spinning the liquid mixture to generate electro spun fibers and deposit the generated fibers on a collector substrate to form a fiber electrode mat comprising a network of fibers, where each fiber has a plurality of particles of the catalyst distributed thereon.
Type: Grant; **Filed:** November 16, 2018; **Date of Patent:** June 1, 2021
Assignee: VANDERBILT UNIVERSITY
Inventor: Peter N. Pintauro

NANOFIBER ELECTRODES, FABRICATING METHODS AND APPLICATIONS OF SAME
Publication number: 20200353719
Abstract: Nanofiber electrodes for electrochemical devices and fabricating methods of the same are disclosed. In one embodiment, the method includes forming a liquid mixture containing a catalyst, a first polymer of perfluoro sulfonic acid and a second polymer of polyethylene oxide, the first polymer of perfluoro sulfonic acid being pre-treated to remove protons in the first polymer by exchange with a cation species like Na+; and electro spinning the liquid mixture to generate electro spun fibers and deposit the generated fibers on a collector substrate to form a fiber electrode mat comprising a network of fibers, where each fiber has a plurality of particles of the catalyst distributed thereon.
Type: Application; **Filed:** November 16, 2018; **Publication date:** November 12, 2020
Inventor: Peter N. Pintauro

INKS FOR NANOFIBER FUEL CELL ELECTRODE AND MEMBRANE-ELECTRODE-ASSEMBLIES, AND METHODS OF INK FORMULATIONS
Publication number: 20190245233
Abstract: An ink for forming nanofiber fuel cell electrodes, and methods of ink formulations, and membrane-electrode-assemblies for electrochemical devices. The ink includes a first amount of a catalyst, a second amount of an ionomer in a salt form, and a third amount of a carrier polymer dispersed in one or more solvents, where a weight ratio of the first amount to the second

and third amounts is in a range of about 1-1.5, and a weight ratio of the second amount to the third amount is in a range of about 1-3. The ink has a solids concentration in a range of about 1-30 wt %. Preferably, the solids concentration is in a range of about 10-15%.
Type: Application; **Filed:** March 21, 2019; **Publication date:** August 8, 2019
Inventors: Peter N. Pintauro, John Slack

10. Presentations

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Hong Kong University of Science and Technology, Hong Kong, China, December 2017, **Particle/Polymer Nanofiber Mat Electrode MEAs for Hydrogen/Air Fuel Cells – Recent Developments**, Peter Pintauro, John Slack, Krysta Waldrop, and Ryszard Wycisk,

University of the Western Cape, South Africa, July, 2017,
Particle/Polymer Nanofiber Mat Electrodes, Peter Pintauro

Fuel Cell Seminar, Long Beach, CA, October 2017, **Particle/Polymer Nanofiber Mat Electrode MEAs for Hydrogen/Air Fuel Cells,** Peter Pintauro, John Slack, Krysta Waldrop, and Ryszard Wycisk

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