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b. *Award Number*	DE-EE0011328	
c. *Project Title*	Advanced PEM Electrolyzer Membrane for Hydrogen Crossover Mitigation	
d. *Recipient Organization*	Plug Power Inc. (Plug)	
e. *Project Period*	*Start*: 09/01/2024	*End*: 08/31/2025
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2. Disclaimer:

3. Executive Summary:

An unintended reaction in the electrochemical conversion of water to hydrogen in proton exchange membrane (PEM) electrolyzers is the crossover of hydrogen from the anode to the oxygen-containing cathode through the membrane, creating hydrogen losses and safety concerns. Efforts to date have focused on embedding platinum catalysts in perfluorosulfonic (PFSA) membranes to convert H_2 to protons. The objective of this project is to design and develop hydrocarbon (HC) proton exchange membranes (PEMs) that can help overcome the risk of high H_2 crossover in current PEM electrolyzer (ELX) stacks by designing and optimizing the gas recombination catalyst (GRC) within the membrane and membrane electrode assembly (MEA) structure.

Due to the high permeability of H_2 through PFSA membrane, crossover is always a critical safety concern that prohibits high-pressure operation of PEM ELXs. Common practices to minimize crossover in PEM ELX applications and research include using thick PFSA membrane (5-mil or 7-mil) at ambient pressure. Thick membranes introduce significant ohmic losses, which adversely impact ELX efficiency. And pressurized H_2 is preferred over ambient by end users because the efficiency of electrochemical compression is much higher than mechanical compressors at low pressure. Targeting high efficiency and operation pressure in next-generation membranes, Plug has been working to develop a thin membrane with improved crossover mitigation to achieve DOE’s cell voltage target of 1.8 V at 3 A/cm^2 with low crossover goal (<6% LEL at 580 psi) in this project. To achieve this goal, we developed

nanoscale recombination catalyst and incorporated it into the MEA. Significant efficiency and crossover mitigation have been demonstrated.

Sulfonated aromatic polymer PEMs that are free of heteroatom linkages should afford better oxidative stability in PEM working environments, but they are difficult to synthesize. We applied BP-S and mTP-S (Pagels, 2020) recently developed by RPI and applied it to electrolyzer applications. These polymers (with one CF3-group) have a >95% reduction of fluorinated carbon in repeating units compared to PFSA.

Fluorinated membranes are only a tiny fraction of our current generation of HC PEMs, we also developed zero-fluorine HC PEMs by replacing the -CF3 moiety to a zero-fluorine moiety in this project. This will help the whole industry to reach PFAS-free systems.

4. Table of Contents:

5. Background:

As the demand for green hydrogen (H_2) grows, so does the demand for electrolyzers (ELXs). Yet, one of the significant challenges faced by proton exchange membrane (PEM) ELXs is H_2 crossover through the PEM during operation which poses a severe safety hazard due to the mixing of H_2 with oxygen (O_2). The PEM ELX industry is currently seeking to increase the differential pressure on the H_2 side for direct high pressure H_2 delivery. Meanwhile, high efficiency is driving the whole industry in the direction of adopting thinner PEMs, to decrease cell resistance and help to reduce electricity consumption. However, higher H_2 differential pressure on the cathode side plus thinner PEMs will make the H_2 crossover more severe. Without proper design of the thin membrane to sufficiently mitigate the crossover, it will be unsafe to operate the ELX. Hence, mitigating membrane crossover would be one of central topics for PEM research. Another challenge is the increase in regulations around fluorinated materials, such as the perfluorinated sulfonic acid (PFSA) membranes used in electrolyzers, and replacing them with robust, hydrocarbon (HC) membranes. The long-term trend is clearly away from PFSA based membranes, but more information is needed on how they operate under pressure and with mitigation catalysts. Hydrocarbon based materials, which are more environmentally friendly, have gained more attention recently aiming to replace PFSA and convert the green hydrogen to a per- and polyfluoroalkyl substances (PFAS) free industry.

Plug Power (“Plug” or the “Applicant”) was founded in 1997 to build out the green hydrogen ecosystem with the ultimate goal of enabling a Green Hydrogen Highway. Plug has broken ground and is building a domestic network of green hydrogen plants that will exceed 500 tons of daily production by 2025 and 800 tons by 2028 to serve multiple industries. As the world leader in the hydrogen space, with multi-gigawatt PEM ELX and fuel cell manufacturing capabilities, as well as the infrastructure to deliver to end users across the US economy, Plug is well positioned to offer H_2 at cost-competitive rates in every region of the US. Plug has developed end-to-end, vertically integrated capabilities to commercialize the hydrogen economy, and it is currently scaling its electrolyzer technology from lab-scale stacks (1 kg/day) to 1 MW stacks and 5 MW arrays that can be assembled to create H_2 plants capable of generating thousands of tons of H_2 (or derivative fuels) per day.

6. Project Objectives:

One of the significant challenges faced by PEM water electrolyzers is H_2 crossover through the PEM during operation which poses a severe safety hazard due to the mixing of H_2 with O_2. The PEM ELX industry is currently seeking to increase the differential pressure on the H_2 side for direct high pressure H_2 delivery. Meanwhile, high efficiency is driving the whole industry in the direction of adopting thinner PEMs to decrease cell resistance and help to reduce electricity consumption. However, higher H_2 differential pressure on the cathode side plus thinner PEMs will make the H_2 crossover more severe. With the membrane developed in this proposed work, the safe operation of a PEM electrolyzer will be possible with high efficiency.

The overall objective of the proposed project is to design a HC proton exchange membrane (PEM) that can mitigate the high H_2 gas crossover issue in electrolyzer

(ELX) applications which aim to use thinner membranes to improve the PEM ELX efficiency and reduce/eliminate fluorine in PEMs.

Only the first year or budget period (BP) of this 3-year project was funded. During this 1-year period, we focused on the synthesis of support-less GRCs, development of low and zero-fluorine HC ionomer/membranes, and optimization of the PFSA-based ionomer/membrane platinization process. The results of this 1-year effort are included below.

Objectives of Budget Period 1 (BP1):

1. Develop a highly active and high surface area (electrochemical active surface area > 60 m^2/g) H_2 GRC.
2. Deliver a low/zero fluorine HC ionomer and membrane.

Summary of tasks and Milestones in Budget Period 1:

Task 1. Design and synthesis of Pt-based recombination catalyst.
Subtask 1.1: Design and synthesis of Pt nanocatalysts with high active surface area. **(Q1-Q4)**
Subtask Summary: WUSTL team will develop ethylene glycol-assisted reduction and organic solution colloidal approaches for the synthesis of high-surface area Pt nanoparticles. The particle size can be controlled by reaction time, temperature, and the presence of surfactant. Surface area/porosity, and chemical activity/stability for H_2 recombination will be characterized.
Go/No-Go 1.1: Synthesize Pt-based materials with electrochemical surface area > 40 m^2g^{-1}Pt. **(Completed)**

Task 2. Synthesis and scale up of HC ionomer and membrane.
Subtask 2.1: Synthesize HC sulfonated polymers (**Q1-Q4**)
Subtask Summary: RPI will conduct synthesis and characterization of sulfonated copolymers with different backbone compositions made of biphenyl (BP) and terphenyl (TP) and down-select optimized polymer for membrane and ionomer.
Go/No-Go 1.2: Deliver ten letter-size HC membranes with a thickness of 2 mils, >100 mS/cm proton conductivity, <60 % water uptake, <20 % in-plane swelling ratio in water, N_2 permeability at 30 bar <0.02 mL/min/cm^2 at room temperature with no more than 60% N_2 permeability increase in ex-situ test under 30 bar, 80 ^oC for 500 hrs. Membrane will also be provided to H2NEW labs for conductivity and N_2 permeability cross check in MEAs. **(Completed)**

Subtask 2.2. Supply of zero-fluorine PEM prototypes from Ionomr (IMR). (**Q1-Q4**)
Subtask Summary: Ionomr will manufacture & supply various zero-fluorine PEM samples across a range of thicknesses and equivalent weights (EW) based on first-generation Pemion® ionomer and standard mechanical reinforcements. These baseline PEMs will be evaluated for water uptake/swelling, proton conductivity, and gas crossover to understand fundamental behavior across the parameter space and identify critical pathways for further refinement and optimization in subsequent tasks.

Milestone 2.2: Deliver four 8.5”x11” (letter-size) fluorine-free membranes to Plug for initial evaluations comprising 2 thickness variations and 2 EW variations. **(Completed)**

Task 3: Chemically platinize and fabricate ionomer and crossover mitigated membrane.
Subtask 3.1: Construct an ex-situ membrane crossover test stand. **(Q1-Q2)**
Subtask summary: Plug will design and build a membrane H_2 crossover test stand to accurately measure the H_2 crossover rate through the membrane under a range of temperature and pressure without testing the membrane in real stacks. This will help to increase the throughput of the screening process.
Milestone 3.1: Complete the construction of crossover test stand. **(Completed)**

Subtask 3.2: Synthesize and test platinized PFSA ionomer via ion exchange process. **(Q1-Q4)**
Subtask Summary: Plug will focus on platinization of PFSA dispersion via wet chemistry process. The characterization and MEA tests of the synthesized ionomer will also be conducted. The results will be used for optimization of the platinization process of HC-based ionomer.

Subtask 3.2.1: Introduce Pt into the PFSA ionomer dispersion via ion exchange. **(Q1-Q4)**
Subtask Summary: PFSA ionomer dispersion will be used for the platinization process optimization which includes Pt precursor selection and reaction condition controls.

Subtask 3.2.2: Ex-situ characterization of synthesized platinized ionomers. **(Q2-Q4)**
Subtask Summary: Ex-situ characterization will be carried out to support the development of platinized ionomers. Characterization will include TEM analysis for the platinum particles formed in the platinized ionomer, thermal gravity analysis (TGA) to determine the Pt loading in the dispersion and ex-situ membrane crossover test using the test stand built in subtask 1.3. H2NEW resources will be heavily leveraged for advanced and comprehensive characterization.

Subtask 3.2.3: Test the MEAs made of the platinized ionomer from subtask 3.2.1. **(Q3-Q4)**
Subtask Summary: MEAs will be made by applying the platinized ionomer directly onto the regular NR212 Nafion membrane as a recombination layer. The mitigation efficiency of H_2 crossover will be evaluated under the field operation conditions in PEMI (Plug’s 40cm2 electrolyzer stack platform) stacks (4-cell PEMI stack, 38.5 cm^2/cell active area, tested at 70 ^oC, 30 bar and 3 A/cm^2 condition). MEAs will also be sent to H2NEW for evaluation.
Go/No-Go 1.3: Achieve beginning of life (BOL) MEA performance of 1.9V at $3A/cm^2$, 70^oC, 30bars, and < 6 %LEL (3 A/cm^2) and < 20 %LEL (1 A/cm^2) H_2 in O_2 at 30 bar using platinized PFSA ionomer after 500 h of operation at 3 A/cm^2. **(Completed)**

Task 8: Project management
Subtask 8.1: Finish and submit the hydrogen safety plan. **(Q1)**
Subtask Summary: The hydrogen safety plan will be finished and submitted to the DOE according to the FOA requirements.

Milestone 8.1: Finish and submit the hydrogen safety plan. **(Completed)**

Subtask 8.2: Project kick-off **(Q1)**.
Subtask Summary: A project kick-off meeting will be hosted with the whole project team and DOE program manager to brief the plan of the project.
Milestone 8.2: Host the project kick-off meeting with team members. **(Completed)**

Subtask 8.3.1: Attend the DOE annual merit review and present the work in the first budget period. **(Q2)**
Subtask Summary: The team will attend the DOE annual merit review and present the work in the first budget period.
Milestone 8.3.1: Attend and present at the DOE AMR. **(AMR 2025 cancelled)**

7. Project Results and Discussion:

Task 1: Design and synthesis of Pt nanocatalysts with high active surface area

Washington University at Saint Louis (WUSTL) systematically studied the specific surface area and electrochemical performance of two commercial Pt-black catalysts as benchmarks. Next, they focused on the synthesis, characterization, and electrochemical measurements of Pt nanoparticle (NP) and nanowire (NW) catalysts.

To avoid the coverage of active sites by surfactants and create a synthetic path that is favorable to subsequent scale-up, WUSTL employed a surfactant-free one-step liquid-phase synthesis method to prepare Pt NPs. Specifically, a certain amount of chloroplatinic acid hydrate (precursor salts), ethylene glycol (EG, solvent, and reducing agents), and water (solvent) were mixed in a glass vial, subsequently placed in an oil bath at 130 °C for 4 hours to obtain the target sample. By adjusting the ratio of EG and water, the amount of salts, and the addition of extra reducing agents (ascorbic acid (AA)), WUSTL synthesized a series of Pt NPs, named sample 1 (only EG), sample 2 (V_{EG}:V_{water}=1:1, standardized procedure), sample 3 (V_{EG}:V_{water}=1:3), sample 4 (2-times salts), sample 5 (1/2-times salts), and sample 6 (adding 30 mg AA). Figure 1 shows the corresponding transmission electron microscopy (TEM) images and particle sizes of these new Pt NPs. With the increase of water, the size of the NPs becomes progressively smaller from sample 1 to sample 3, indicating that the nucleation rate is lower than the growth rate during the NP growth process in the reaction system. Although the size of the individual NP for sample 3 is smaller, noticeable aggregation is observed. Increasing (sample 4) or decreasing (sample 5) the amount of precursor salt can also lead to a decrease in NP size compared to sample 2; however, this decrease tends to result in NP aggregation. Meanwhile, adding AA obviously caused the agglomeration of NPs, aligning with the trend of samples 1-3.

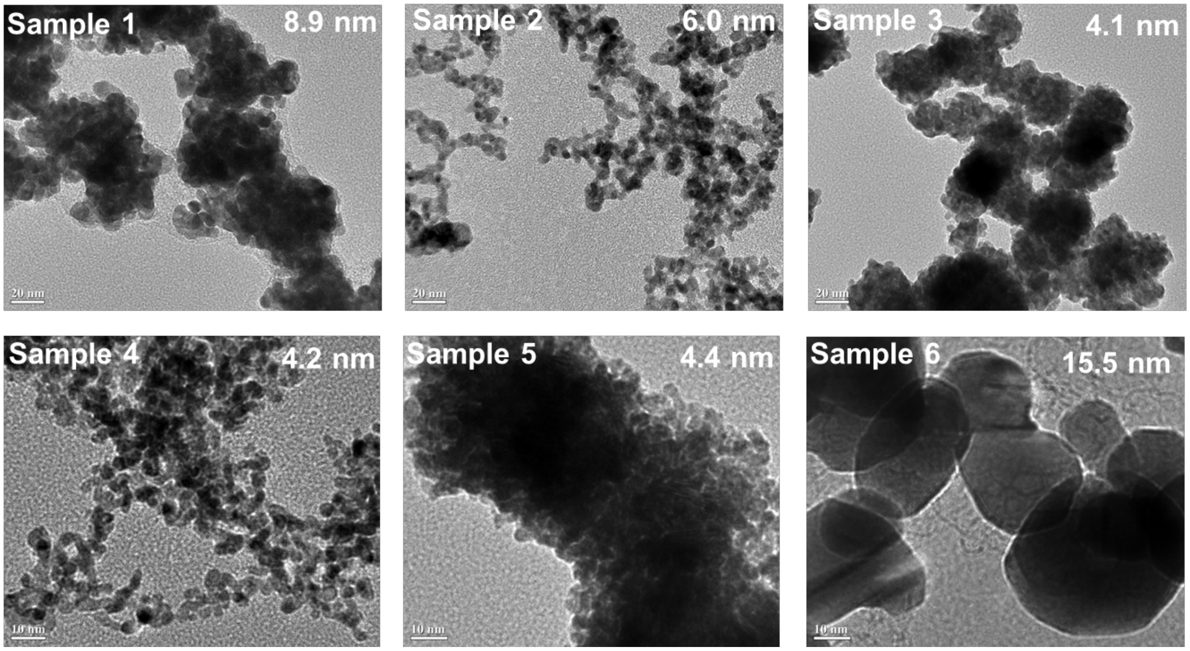


Figure 1: Transmission electron microscope images of developed Pt NPs.

Figure 2 shows cyclic voltammetry (CVs) of the Pt NP catalysts recorded at room temperature in an N_2-saturated 0.1 M $HClO_4$ solution at a sweep rate of 50 mV s^{-1}. The electrochemical surface area (ECSA) of the catalysts is calculated from the charge of hydrogen underpotential adsorption within the potential range of 0.05-0.42 V_{RHE}. The ECSA reflects the number of active sites on the catalyst. For all these platinum-black (unsupported) catalysts, sample 4 achieved the largest ECSA of 18.8 $m^2 g^{-1}$, consistent with the conclusions made from the TEM imaging provided in Figure 1. The accelerated stress test (AST) CV results provided in Figure 3 show that the loss of ECSA of the sample 4 Pt NP is slightly less than the loss of ECSA observed for Plug's baseline Pt black catalyst (20.7% vs. 23.6%, respectively). This result suggests good stability for the developed sample 4 Pt NP.

To further increase the ECSA of the Pt, WUSTL employed a simple one-pot wet chemical synthesis to fabricate citric acid-modified multihole Pt NPs (CA-Pt NPs). Specifically, a certain amount of chloroplatinic acid hydrate (precursor salts), water (solvent), and CA (as a capping agent) were mixed in a glass vial, and subsequently incubated for 10 min under vigorous stirring. $NaBH_4$ was quickly added under continuous stirring. The mixture was incubated for 30 min and centrifuged (13 000 rpm, 25 min) to precipitate the CA-Pt NPs. By adjusting the ratio of CA and Pt salts, WUSTL synthesized a series of Pt NPs, named CA-Pt-0 NPs (m_{CA}:m_{Pt}=0:1), CA-Pt-1 NPs (m_{CA}:m_{Pt}=1:1), CA-Pt-2 NPs (m_{CA}:m_{Pt}=2:1), and CA-Pt-4 NPs (m_{CA}:m_{Pt}=4:1). CV of the different catalysts were recorded at room temperature in an N_2-saturated 0.1 M $HClO_4$ solution at a sweep rate of 50 mV s^{-1} (Figure 4a). WUSTL found that the ECSA of the CA-Pt-1 NP catalyst (27.2 m^2 g^{-1}) was the largest among the CA-PT NP catalysts, but lower than the milestone target (40.0 m^2 g^{-1}).

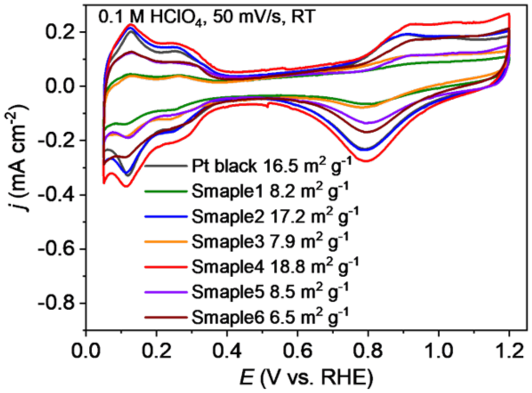


Figure 2: CV of Pt NP catalysts in 0.1 M $HClO_4$.

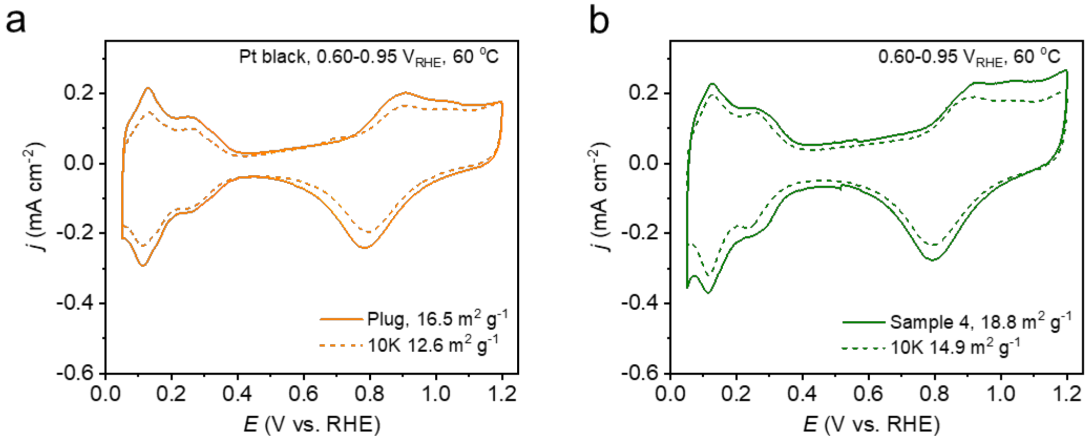


Figure 3: Before and after AST CV at 60 °C of (a): Pt black (Provided by Plug Power Inc.) and (b): sample 4 Pt NP catalyst.

WUSTL further replaced CA with ascorbic acid (AA) and glucose (Glu) to synthesize Pt NPs named AA-Pt-1 NPs and Glu-Pt-1 NPs. Figure 4b shows the resulting CV for the Pt NP catalysts developed with different capping agents recorded at room temperature in an N_2-saturated 0.1 M $HClO_4$ solution at a sweep rate of 50 mV s^{-1}. These results showed that varying the capping agent did not further increase the catalyst ECSA.

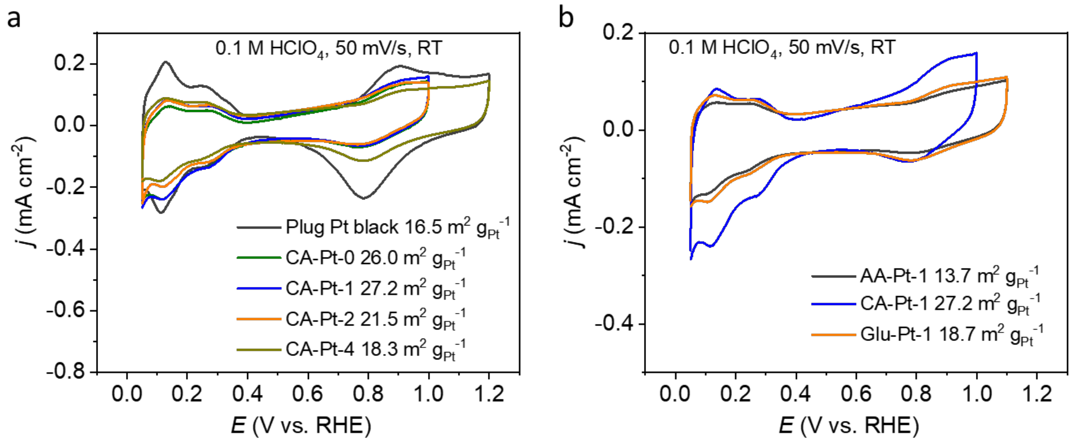


Figure 4: Room temperature CV of (a): developed CA-Pt NP catalysts and (b): alternative capping agent Pt NP catalysts.

To meet the 40.0 m^2 g^{-1} ECSA milestone, the controlled synthesis of one-dimensional materials at atomic-scale dimensions represented a potential solution. As such, WUSTL used a simple one-step hydrothermal method to synthesize ultrathin Pt NWs. Specifically, a certain amount of chloroplatinic acid hydrate (precursor salts), ethylene glycol (EG), N,N-Dimethylmethanamide (DMF), and potassium hydroxide (KOH) were mixed in a 100-mL Teflon-line autoclave. The autoclave was sealed, heated to 150 °C for 6 h, and then cooled to room temperature. The resulting suspended black products were dispersed in ethanol or water (solvent) and ultrasonicated for 1 hour to obtain a black solution, which was collected by centrifugation. By adjusting the solvent and ultrasonication time, WUSTL were able to regulate the morphology of the NWs. Figure 5aS shows the corresponding TEM images of cable-like Pt NW (CL-Pt NWs) bundles with diameters of ~20 nm and individual NWs measuring ~2 nm in diameter (ethanol wash for 5 min). The products were further washed three times with deionized water, with ultrasonication for 30 minutes between each of the washes, to obtain a single ultrathin Pt NW (U-Pt NWs) (Figure 5b).

Figure 6 shows CV for the two Pt NW catalysts recorded at room temperature in an N_2-saturated 0.1 M $HClO_4$ solution at a sweep rate of 50 mV s^{-1}. For the two different catalysts, the U-Pt NWs achieved a larger ECSA of 49.8 m^2 g^{-1} compared to 20.5 m^2 g^{-1} for the CL-Pt NWs—this difference in ECSA is consistent with the qualitative results observed with TEM. The large ECSA is associated with extremely high atomic utilization, **meeting the milestone target (40.0 m^2 g^{-1}).**

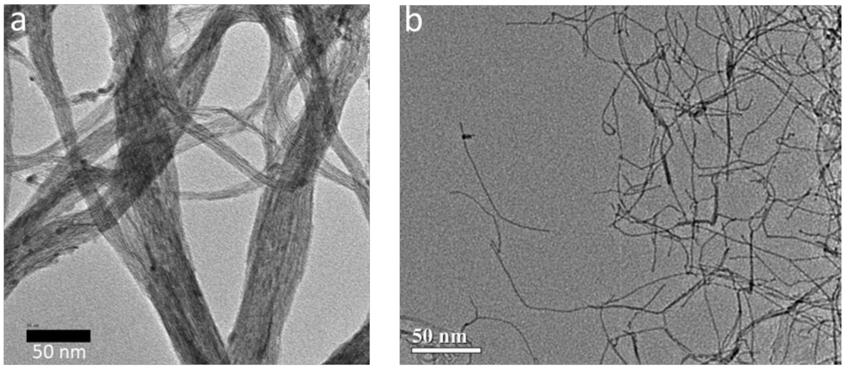


Figure 5: TEM images of (a): CL-Pt NWs and (b): U-Pt NWs.

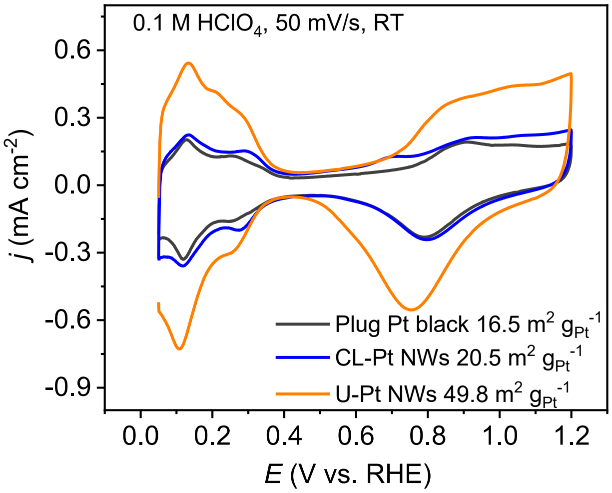


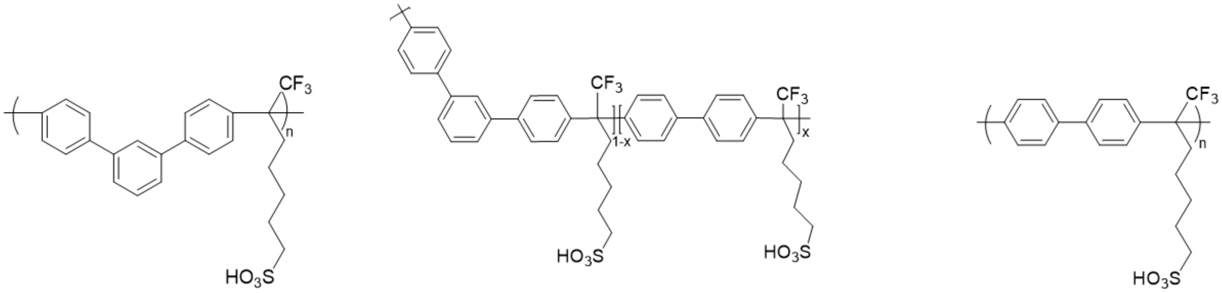
Figure 6: CV curves of (a): CL-Pt NWs and (b): U-Pt NWs.

Task 2: Synthesis and scale up of HC ionomer and membrane (RPI, IMR)

RPI fabricated a total of twelve hydrocarbon (HC) membranes from three different batches of carefully designed polymers—m-terphenylsulfonic acid (m-TPSA), biphenylsulfonic acid (BPSA), and their 65/35% copolymer - BP65-co-m-TP35SA.The tested properties of the various polymer membrane types and their chemical structures are provided in Table 1 and Figure 7, respectively. Except for the proton conductivity of the m-TPSA membrane (101 mS/cm), which had the lowest ion exchange capacity (IEC) of the developed membranes, all membranes satisfied the technical metrics of proton conductivity, water uptake, and in-plane swelling ratio. The BP65-co-m-TP35SA membrane demonstrated an excellent proton conductivity of 155 mS/cm in water at 80 °C. The water uptake of the same material was 23% at room temperature, which was significantly below the 50% limit, supporting sufficient hydration without excessive swelling. The in-plane swelling ratio was 10% at room temperature (19% @ 80°C), which is within the acceptable range for dimensional stability (≤15%). The BPSA membrane with a molecular weight of 83 kDa and IEC of 2.7 meq/g also exceeded all of the targets with a proton conductivity of 145 mS/cm, water uptake of 14%, and in-plane swelling of 8% (42% water uptake and 17% in-plane swelling @ 80°C). Furthermore, when built into an MEA the developed HC BPSA PEM demonstrated a cell performance of 1.8V at 3 A/cm² operating at 80°C under ambient pressure conditions. Scanning electron microscope (SEM) images and intrinsic viscosity/nuclear magnetic resonance (NMR) spectroscopy analyses revealed no chemical degradation of the HC BPSA PEM after operation.

Table 1: Properties of HC PEMs developed and tested by RPI**.**

PEM	Conductivity (mS/cm) at 80 °C	Water Uptake (%) at 30 °C	Swelling ratio (%) at 30 °C
BP1 Target	≥130	≤50	≤15
m-TPSA	101	**16**	**10**
BP65-co-m-TP35SA	**155**	**23**	**10**
BPSA	**145**	**14**	**8**



m-TPSA (IEC = 2.2 mmol/g) **BP65-co-m-TP35SA** (IEC = 2.32 mmol/g) **BPSA** (IEC = 2.6 mmol/g)

Figure 7: Chemical structure of HC PEMs developed and tested by RPI.

Ex situ gas-permeability measurements were also carried out (Figure 8) using Plug's 40 cm² high-pressure PEM electrolysis hardware with N_2. The initial N_2 permeability, averaged over two cells and measured at room temperature under various back pressures, was 0.005 mL/min/cm², significantly below the 0.025 mL/min/cm² GO NO/GO (GNG) target at 30 bar. To simulate operational stress, the stack was held at 30 bar and 85°C for 500 hours, after which N_2 permeability less than 60% to about 0.0075 mL/min/cm². Both the beginning of life (BOL) permeability and its stability have met the GNG milestone for this task.

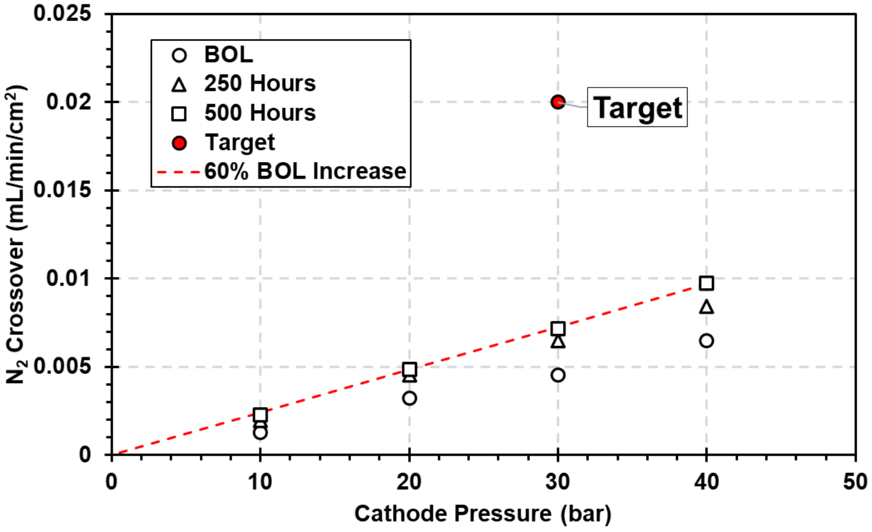


Figure 8: N_2 permeability of 50 μm mTPSA membrane at different pressure and room temperature with 250-hr and 500-hr operation time at 80 °C, 30 bar.

IMR delivered four 8.5″×11″ fluorine-free Pemion® HC PEM membranes—including two 75-μm-thick IWC8-75-X variants and two non-woven reinforced prototypes. It was demonstrated that the 75-μm IWC8-75-X matches the proton conductivity, water uptake, and in-plane swelling of a fuel-cell HLF8-15-X (15um thick IMR commercial FC membrane) variant membrane while exhibiting significantly lower through-thickness swelling. Plug optimized decal transfer conditions and found that moderate pretreatment times markedly reduced the Z-direction swelling without degrading conductivity.

A roll-to-roll non-woven reinforced candidate showed good mechanical integration and low crossover in ex-situ testing but suffered surface nonuniformity (“mottling”) attributed to coating irregularities. Plug’s 5-cm^2 cell tests of MEAs using the pilot-coated 75-μm-thick membrane achieved ~1.9 V at 4 A/cm^2—about 100-mV higher than MEAs with 50-μm-thick Nafion 212 presumably due to the increased membrane thickness. Post-mortem imaging of the tested non-woven reinforced HC membrane revealed localized degradation from uneven water distribution, prompting a shift to 50 cm^2 hardware for durability assessments. Production-scale trials of both thick (75–100 μm) and thin (30–40 μm) non-woven reinforced membranes encountered dry-spot–induced conductivity loss, mottling, and delamination issues. Due to these issues IMR prioritized higher-viscosity ionomer formulations, optimized layering, and evaluation of additional reinforcement variants for the non-woven reinforced membranes.

Meanwhile, IMR supplied Plug and H2NEW with an additional supply of eight 8.5”x11” sized pilot-coated baseline monolithic 40-μm-thick membranes, and new non-woven reinforced candidates for performance, crossover, and mechanical-stress studies. The IEC of the 40-μm monolithic membranes was modulated by thermal treatment which reduced the IEC from 2.94 meq/g (baseline value, corresponding to 340 EW) to 2.85 meq/g (350 EW) and 2.5 mmol/g (400 EW) for 1-hour and 3-hour treatment times, respectively. The 1-hour thermal treatment enabled membrane conductivity of >90 mS/cm while reducing dimensional swelling upon hydration by >50% in the X, Y and Z directions, collectively improving its suitability in a liquid water equilibrated environment of a PEM ELX device.

Task 3: Chemically platinize and fabricate ionomer and crossover mitigated membrane.

The crossover test stand (Figure 9) designed by Plug is now fully constructed and commissioned with Plug's 50 cm^2 PEM ELX stack hardware, with all mechanical, fluidic, and control subsystems in place. It supports cathode H_2 pressures up to 40 barg and anode O_2 flows to simulate electrochemical current densities from 0 to 5 A/cm^2 and includes an argon purge line downstream for safe reduced-O_2 flow operation. Additionally, the test stand can supply temperature-controlled water (up to 86 °C and 2 barg) to the anode of the cells to accurately measure membrane permeability and recombination data under real PEM ELX conditions. With the thermal conductivity detector (TCD) now installed and wired, the final commissioning phase has been successfully concluded. The stand is fully operational for non-operando in-situ crossover testing, enabling Plug to proceed immediately with high-throughput evaluations of membrane durability, hydrogen crossover rates, and recombination efficacy under realistic PEM ELX stresses.

Figure 9: Completed crossover test stand prepared for membrane non-operando in-situ testing.

Plug synthesized two platinized PFSA dispersions, which were synthesized by the reduction with H_2 for either 1 or 3 days. The platinized ionomer dispersion was cast as a recombination layer and incorporated at 120 µg Pt/cm^2 loading into Plug's standard multi-cell, 38.5 cm^2 PEM water electrolyzer stack with Nafion NR212 membranes. The H_2 reduction time was first studied to compare its effect on H_2 crossover. At the beginning of life (BOL), the 3-day reduction stack (Figure 10.1) met the 1 A/cm² crossover GNG target (15 % LEL vs. ≤20 % goal) but exceeded the 3 A/cm² target (8 % vs. ≤6 % LEL), whereas the 1-day reduction stack (Figure 10.3) achieved crossover targets at both 1 A/cm² and 3 A/cm² (8 % at 1 A/cm² and 5 % at 3 A/cm²). Durability testing at 70 °C, 3 A/cm², and 30 bar for 500 hours showed that the 3-day stack stabilized at 16% of the hydrogen in oxygen LEL at 1 A/cm² and 13% at 3 A/cm², while the 1-day stack delivered 17 % LEL at 1 A/cm² and 10 % at 3 A/cm², with minor voltage and resistance drifts attributed to in-situ decontamination and ionomer processing effects. TEM imaging confirmed that the shorter reduction times yield finer Pt particles (Figure 10.2 and Figure 10.4), which is better for high-current recombination, guiding further optimization.

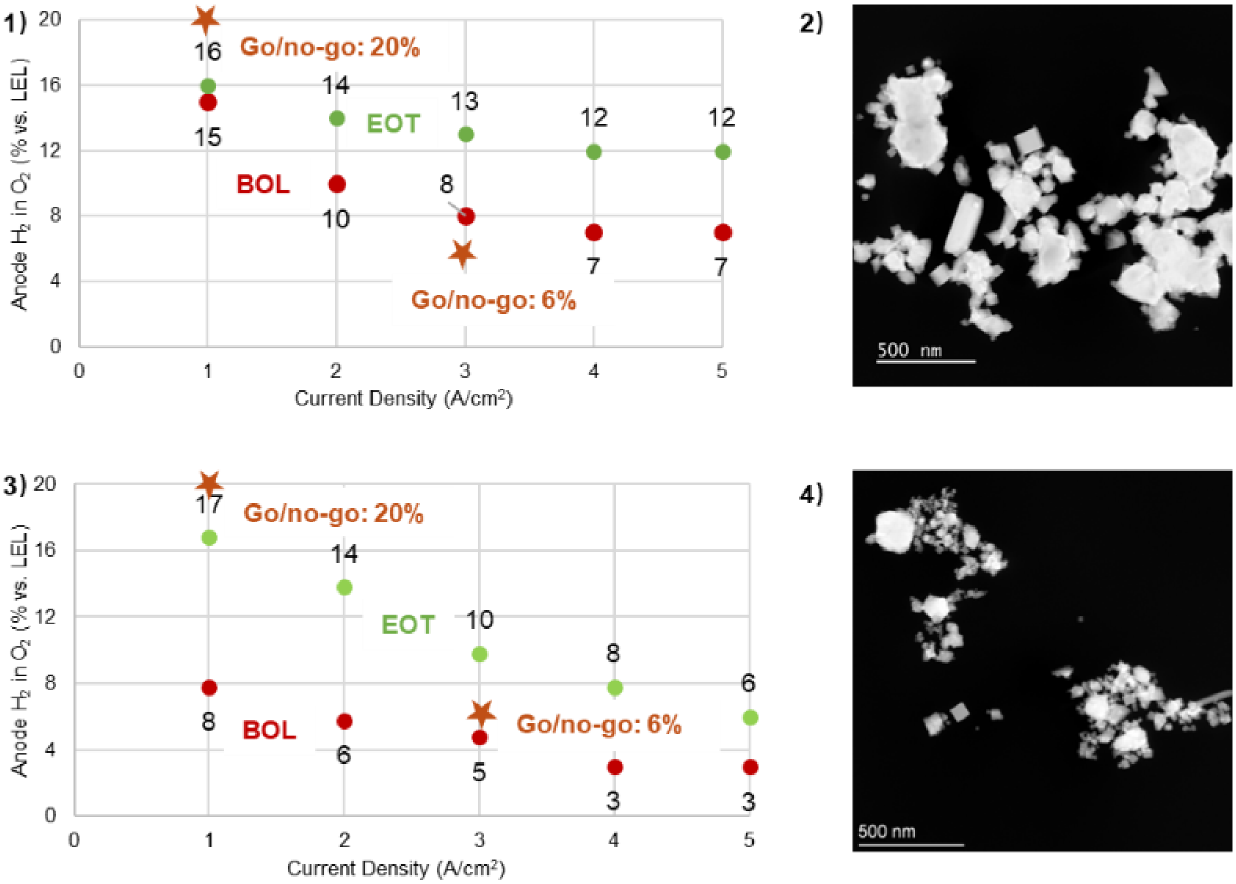


Figure 10: H_2 crossover at BOL and EOT for MEA with platinized PFSA ionomer after 3-day (1) and 1-day (3) H_2 reduction and their corresponding TEM images (2) and (4), respectively; data collected at 70°C, 30 barg; loading of platinum inside the membrane is 120 µg/cm².

A new recombination-layer dispersion method using a 16-hour H_2 reduction was prepared to achieve similar Pt particle morphology as reported above with a higher Pt loading of estimated 180 µg/cm². The test was conducted in a 10-cell stack for better statistical confidence in the resulting H_2 crossover values. Durability testing was conducted at 70°C, 3 A/cm², and 30 bar for a period of 555 hours. As shown in figure 11, the updated stack achieved the GNG targets at BOL – 3 % LEL at 1 A/cm² (vs. the goal of <20 % LEL) and 1 % LEL at 3 A/cm² (vs. the goal of <6 % LEL); and meeting or exceeding these targets at end of test (EOT) (9 % at 1 A/cm² and 3% at 3 A/cm²). The hydrogen crossover increased under constant current density operation but recovered under periodic polarization scan (Figure 12).

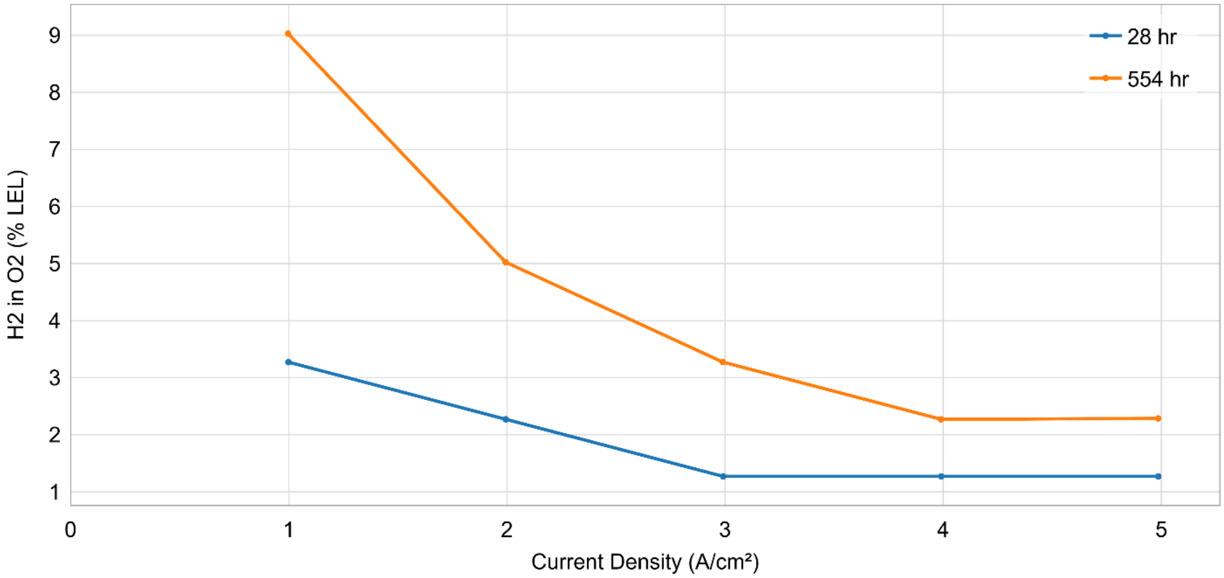


Figure 11: H_2 crossover values at BOL and EOT for MEAs with platinized PFSA ionomer after 16-hr H_2 reduction data collected at 70 °C, 30 barg; loading of platinum inside membrane is estimated to be 180 µg/cm².

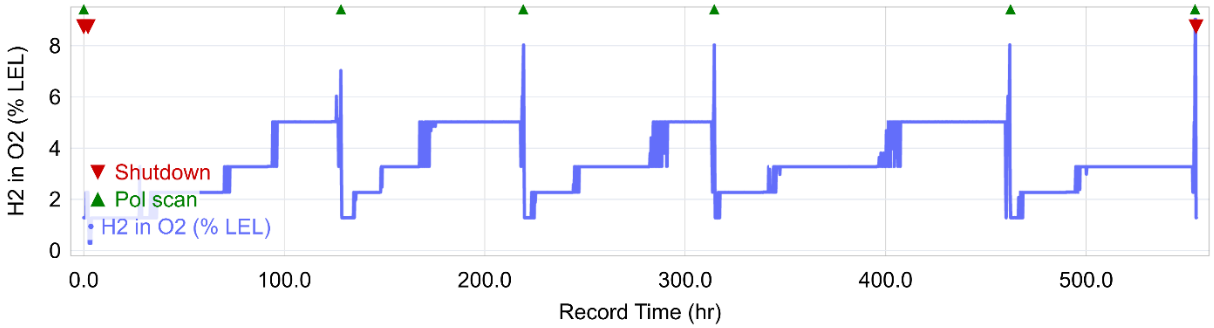


Figure 12: H_2 crossover durability data for MEAs with platinized PFSA ionomer after 16-hr reduction; data collected at 70°C, 30 barg; loading of platinum inside membrane is estimated to be 180 µg/cm².

8. Significant Accomplishments and Conclusions:

- High surface area Pt-nanowire GRCs were synthesized and characterized. This met the project goal of 60 m^2/g.
- Low-F BPSA and TPSA based membrane samples were synthesized and characterized. The results showed good mechanical stability and low gas permeability.
- Two thickness variations and 3 EW variations of F-free membrane were received and characterized.
- Crossover test stand was constructed and commissioned.
- High efficiency and low crossover were achieved in real electrolyzer stack testing with good stability.

9. Path Forward:

Next steps of R&D should include:

- Development of supported recombination catalyst.
- Improvement of mechanical properties and durability of HC-based membrane.
- Optimization of the membrane structure.
- Scale up of the membrane production.

10. Products:

Not Applicable

11. Project Team and Roles:

Dr. Fan Yang from Plug Power is the PI for this project. He is responsible for overseeing the project progress, coordinating the work among collaborators, designing the experiment and preparing technical reports.

Dr. Qiang Sun, Dr. Zhiqiao Zeng, and Connor Buek from Plug Power are participants in the project working on the membrane characterization, introduction of GRC to the membrane and electrolyzer testing.

Prof. Gang Wu is the co-PI of the project. His team from WUSTL are working on the synthesis and electrochemical characterization of Pt based nanoparticles for crossover mitigation applications.

Prof. Chulsung Bae is the co-PI of the project. His team from RPI has been working on the synthesis and characterization of low-F HC membrane.

Dr. Andrew Baker is the co-PI of the project. His team from Ionomr has been working on the synthesis of F-free membrane.

12. References:

Michael K. Pagels, Santosh Adhikari, Ramali C. Walgama, Asheesh Singh, Junyoung Han, Dongwon Shin, and Chulsung Bae, ACS Macro Letters 2020 9 (10), 1489-1493