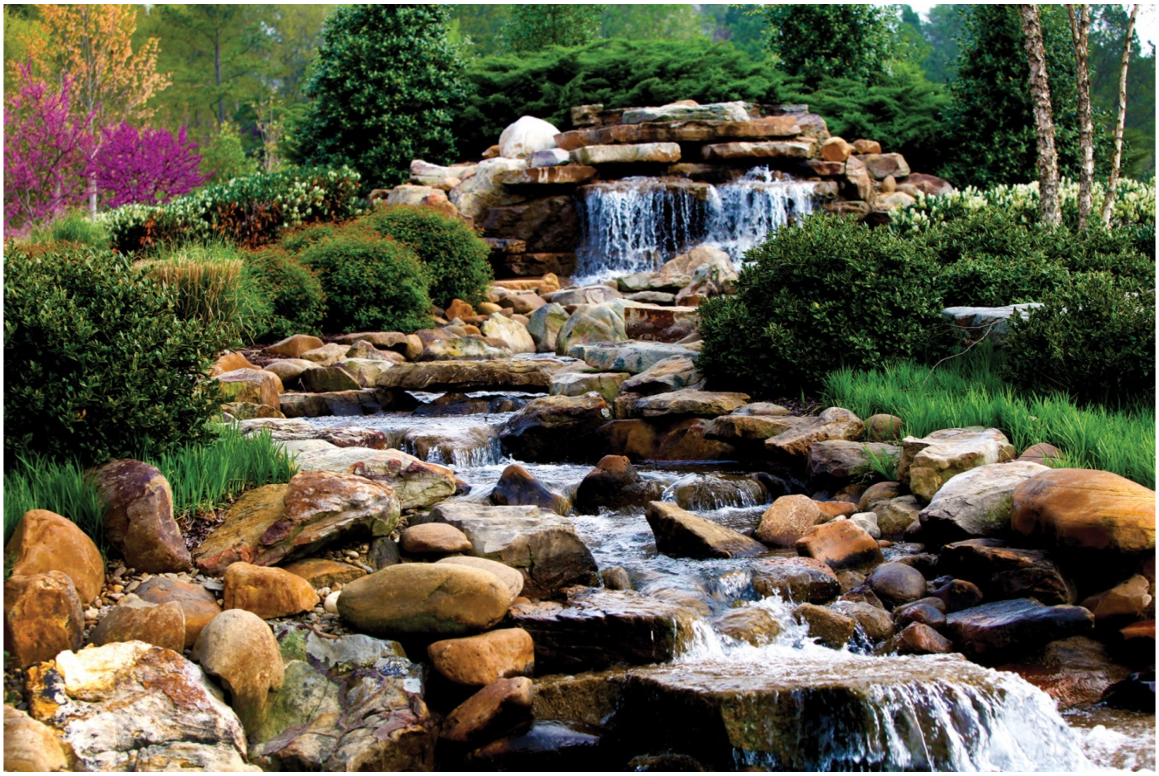
ORNL/SPR-2021/1875

Innovative Proton-Conductive Membranes Based on Two-Dimensional Materials



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April 2022

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Electrification and Energy Infrastructure Division

INNOVATIVE PROTON-CONDUCTIVE MEMBRANES BASED ON TWO-DIMENSIONAL MATERIALS

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FINAL SCIENTIFIC/TECHNICAL REPORT

Innovative Proton-Conductive Membranes Based on Two-Dimensional Materials

Award:	DE-AR0000986
Sponsoring Agency:	US Department of Energy, Advanced Research Project Agency–Energy (ARPA-E)
Lead Recipient:	Oak Ridge National Laboratory
Prime Recipient:	General Graphene
Project Team Members:	General Graphene, New Mexico State University, Oak Ridge National Laboratory
Project Title:	Innovative proton-conducting membranes based on two dimensional materials
Program Director:	Dr. Grigorii Soloveichik
Principal Investigator:	Dr. Georgios Polyzos
Contract Administrator:	Dr. Claus Daniel
Date of Report:	December 26, 2020
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This report contains no protected data.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

The team of Oak Ridge National Laboratory, New Mexico State University, and General Graphene Corporation staff will develop and commercialize paradigm-shifting low-cost, high-performing, proton-conductive membranes made from abundant and durable 2D materials. Proposed membranes are expected to be an order of magnitude better in performance and cost compared with the current state-of-the-art formulation, Nafion, and thus are expected to eliminate huge roadblocks in proliferation of fuel cells and flow batteries. The major goal for this work is to develop a fundamentally new learning curve for novel proton exchange membranes needed for various applications. The new technology will overcome the shortcomings of the current state-of-the-art membranes that are based upon Nafion polymer by offering higher proton conductivities, the ability to operate at much lower external humidity levels and higher temperatures (>120°C), and negligible fuel and oxidant crossover through the membrane.

ACKNOWLEDGMENTS

This work was supported by the US Department of Energy (DOE), Advanced Research Projects Agency-Energy (ARPA-E DE-AR0000986). The portion of this project involving the sample fabrication effort including lithography, scanning electron microscopy, scanning transmission electron microscopy, Raman spectroscopy, and focused ion beam and He^+ and Ne^+ beams were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility at DOE's Oak Ridge National Laboratory. Research scholars Dr. Pavan Chaturvedi and Dr. Dhanraj B. Shinde (New Mexico State University) contributed to the project. X-ray photoelectron spectroscopy analysis was performed by Dr. Harry Meyer (Oak Ridge National Laboratory). Dr. Ilia Ivanov (Oak Ridge National Laboratory) helped with obtaining Raman spectra.

ABBREVIATIONS

ARPA-E	Advanced Research Projects Agency-Energy
ASR	area specific resistance
CVD	chemical vapor deposited
DMFC	direct methanol fuel cell
DOE	US Department of Energy
FIB	Focused Ion Beam
hBN	hexagonal boron nitride
IP	intellectual property
N 212	Nafion 212
N 117	Nafion 117
NMSU	New Mexico State University
PVP	polyvinylpyrrolidone
SBIR	Small Business Innovation Research
SEM	scanning electron microscope
STEM	scanning transmission electron microscope
T2M	tech-to-market
TEA	techno-economic analysis
VFB	vanadium flow battery

1. INTRODUCTION

Sustainable green energy based on renewable resources is a huge world challenge, and its realization in electrochemical storage can have different forms, many of which rely on special selective membranes. For example, proton exchange membranes have a broad range of applications including fuel cells, electrolyzers, flow batteries, and others. The most commonly used membranes are based on perfluorosulfonic acid (PFSA or Nafion), which are actually cation exchange membranes that effectively reject only anions. It makes them vulnerable to crossover of molecular and cationic species and requires the presence of water for hydration of sulfonic groups to achieve effective transport of protons, making water management a challenging engineering task.

Here we investigate two types of proton conductive graphene-based membranes to overcome current-state-of-the art membrane crossover limitation. The first type is based on nacre-like composite membranes prepared by reduction of graphene oxide (GO)/polymer thin films can work as a very selective barrier with exclusively high proton conductance. A combination of finely tuned properties allows achieving performance in most aspects superior to those of PFSA. We illustrate that the best results are obtained with HI as a reducing reagent and polyvinylpyrrolidone (PVP) polymer, where rGO, produced by reduction of GO, serves as a stabilizing barrier, and PVP with well-coordinated triiodide serves as an efficient proton conductive media. In the second membrane type, we study ionic conductance across graphene prepared by chemical vapor deposition (CVD) before and after introduction of defects with the goal of answering the question whether CVD graphene can be utilized as proton selective membranes with conductivity relevant for various applications. Defects in graphene were introduced via ion-beam irradiation (Ga+, He+), different types of plasma (N_2, H_2), and during synthesis. To address the change in conductance, solutions with different pH and electrolyte concentrations were evaluated. It was found that treatment with He+-ion beam and N_2 or H_2 plasma have the best outcome and need further study in a larger setting for evaluation in applications that are based on proton/cation selective membranes.

2. ACCOMPLISHMENTS AND OBJECTIVES

2.1 CONTINUOUS CHEMICAL VAPOR DEPOSITION GROWTH OF GRAPHENE ON COPPER

Continuous chemical vapor deposition (CVD) growth of Gr on Cu was shown using a Gen 2.0 CVD–Gr synthesis system, with >2.54 cm/min speeds and >25.4 × 50.8 cm sheet sizes. Synthesis of 12.7 cm^2 hexagonal boron nitride (hBN) films on Cu was shown in a batch mode CVD reactor. Researchers presented the description of inventions and the initial intellectual property (IP) landscape to the Program Director on March 25, 2019. A Gr/hBN production cost analysis was performed. Sensitivity analysis suggests that major cost parameters are the rate of Gr/hBN growth front and the number of times Cu foil can be recycled.

Table 1. A summary of progress for FY 2019 milestone metrics (by task)

Milestone (Due Date)	Milestone Metric	Progress to Date
Task 2: Manufacturing development		
Milestone 2.1.1 (03/31/2019)	**2D continuous equipment commissioned:** Develop batch system that delivers hBN samples with >12.7 cm^2 size. Develop a ontinuous Gr system yields 25.4 × 50.8 cm Gr sheets on Cu using a custom conveyer belt furnace with moving speed >2.54 cm/min.	The Gen 2.0 continuous synthesis system was demonstrated during 03/25/2019 ARPA-E visit. The system has the following metrics: >25.4 × 50.8 cm Gr sheets on Cu with moving speeds >2.54 cm/min. Gen 2.5 is scheduled to be finished by June 30, 2019. Batch synthesis setup for synthesis of ~12.7 cm^2 hBN on Cu is completed. Milestone is complete.
Task 3: Technology-to-market		
Milestone 3.2.2 (03/31/2019)	**Initial description of inventions**: Describe all possible inventions. Complete an initial IP landscape position paper and present summary of IP landscape to Program Director and tech-to-market adviser. Rank threats and hypothesize paths toward resolution.	A description of inventions/initial IP landscape was presented to ARPA-E on March 25, 2019. A presentation file will be provided upon request. Milestone is complete.
Milestone 3.3.1 (03/31/2019)	**Initial TEA:** Provide a framework for techno-analysis of various manufacturing options. Include an initial sensitivity analysis. Set and adjust product and research priorities based on this analysis.	A Gr/hBN production cost analysis was performed. Excel scripts/macros can be demonstrated upon request. Milestone is complete.

Milestone 2.1.1: 2D continuous equipment commissioned (03/31/19)

The batch system delivers hBN membrane samples with >5 × 5 cm^2 size. The continuous Gr system yields 25.4 × 50.8 cm Gr sheets on Cu using a custom conveyer belt furnace. The moving speed was >2.54 cm/min. Figure 1 shows a batch system for hBN synthesis capable of producing ~13.97 hBN on

Cu. While Figure 2 shows optical characterization of prepared hBN samples. The samples were characterized “as grown” on copper foil and transferred from copper to a SiO_2/Si wafer.

Figure 1. Batch hBN CVD synthesis system.

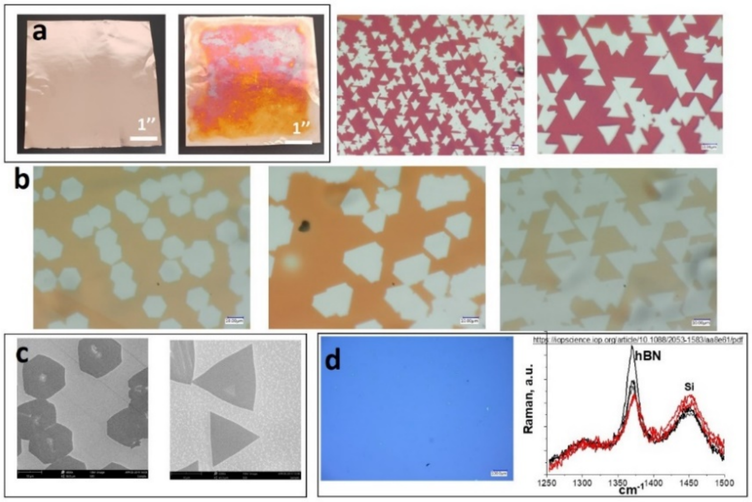


Figure 2. Characterization of hBN synthesized using batch CVD system shown in Figure 1. (a) Photographs of (left) top and (right) bottom sides of Cu foils with hBN overlayer. The hBN protects the top side of the Cu from oxidation, whereas bottom is easily oxidized. (b) Optical microscope images of separated hBN domains. (c) SEM images of separated hBN domains. (d) (left) Optical image of transferred hBN on SiO_2/Si substrate and (right) Raman spectra showing hBN band at ~1,368 cm^{-1}.

2.2 GRAPHENE TRANSFER FROM COPPER SUBSTRATE

A Nafion 212 (N 212) film was used to transfer Gr single layers that were grown on Cu substrates using CVD. The N 212 film was sandwiched between Cu-Gr substrates, and the Cu-Gr–N 212–Gr-Cu substrate configuration was hot-pressed under different conditions. Oxidized and non-oxidized Cu substrates were used. The N 212 film was peeled off after hot-pressing. The optical images and Raman spectra of the Cu substrate are shown in Figure 3. The characteristic Raman peaks for the single-layer Gr crystal are present on the non-oxidized Cu substrate only. There is no evidence of Gr on the oxidized Cu after peeling the N 212 film, indicating that the Gr was successfully transferred from the Cu using the hot-press method.

A similar configuration of Cu-Gr-N 212 was sandwiched between Teflon films and then hot-pressed. The Gr was again successfully transferred from the oxidized Cu substrate (Figure 4).

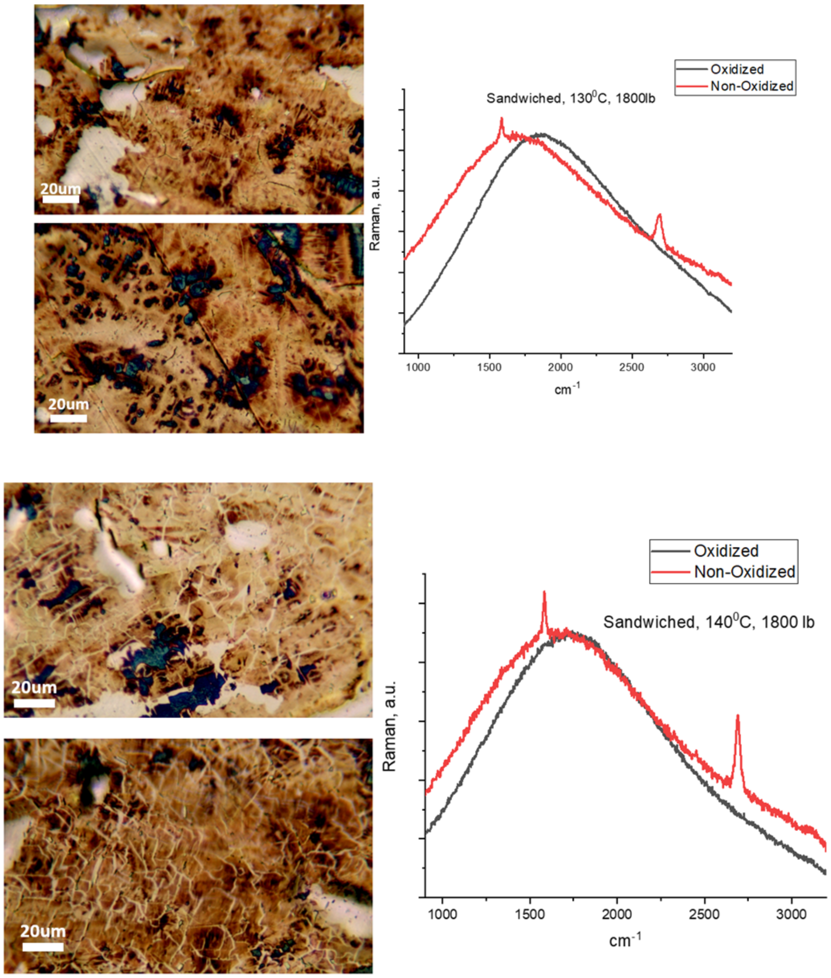


Figure 3. The Cu-Gr–N 212–Gr-Cu substrates were sandwiched and then hot-pressed at 130°C and 140°C under 1,800 lb force. Oxidized and non-oxidized Cu substrates were used. The optical images (left) and Raman spectra (right) of the Cu after peeling off the N 212 film are presented.

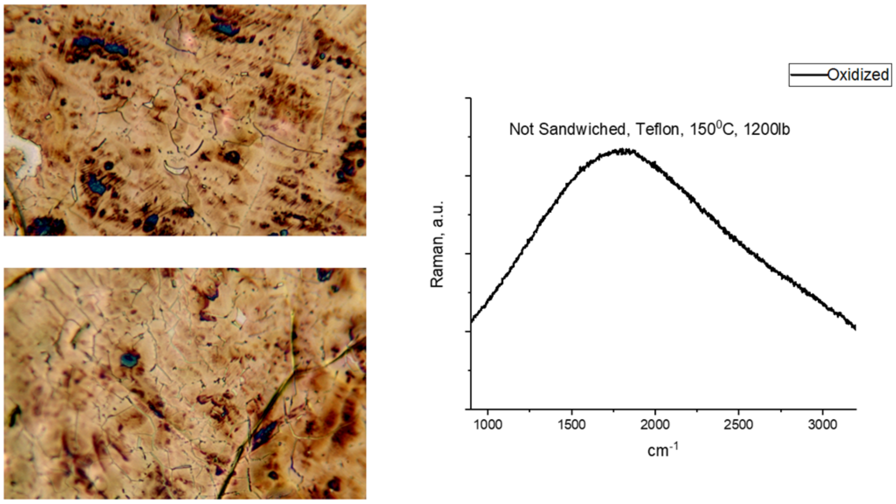


Figure 4. The Cu-Gr-N 212 substrates were sandwiched between Teflon films (200 µm thick) and were hot-pressed at 150°C for 3 min under 1,200 lb force. An oxidized Cu substrate was used. The (left) optical images and (right) Raman spectra of the Cu after peeling the N 212 film are presented.

Milestone 1.1.1: Intermediate membrane performance (09/30/19)

The prepared multilayer membrane on porous support has a proton area specific resistance (ASR) <2 omh-cm^2, V^{4+} permeability <1E-9 cm^2/s, and electronic ASR >1E3 ohm-cm^2, when compressed between carbon paper electrodes. Mechanical properties were assessed when the membrane had been soaked in a V/H_2SO_4 solution. Membrane soaked in a solution with V^{5+} and H_2SO_4 (1.5 M V^{5+} and 3 M H_2SO_4, or as discussed with and approved by the Program Director) for >200 h showed a <10% change in proton ASR, permeability, and stress–strain curves.

Crossover summary

The membrane performance has been improved. To minimize project risks, two different membrane geometries were pursued—both showed great promise (Table 2). Possible geometries for two membranes types assembly are shown in Figure 5.

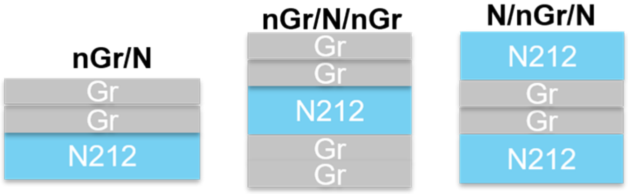


Figure 5. Possible geometries for membrane assemblies. n: the number of Gr layers; N: Nafion.

Table 2. Performance of developed membranes comparison to N 212 and N 117.

Membrane	**Thickness**	**Area proton resistance (ohm-cm^2)**	**VO^{2+} crossover(10^{-7}cm^2/min)**	**MeOH crossover (10^{-7}cm^2/s)**	**Water crossover (10^{-8}cm^2/min)**
N 212	50 µm	0.75 ± 0.3	1.2 ± 0.1	1.4 ± 0.1	6.9 ± 0.2
N 117	183 µm	2.2 ± 0.3	2.2 ± 0.2	2.2 ± 0.2	7.8 ± 0.3
Gr grown on Cu					
Gr/N*	~1 nm	1	0.19 (>6 times smaller vs. N 212)	0.025 (>5 times smaller vs. N 212)	N/A
Gr/N/Gr	~1 nm	1.1	0.05 (>22 times smaller vs. N 212)	0.045 (>31 times smaller vs. N 212)	N/A
3Gr/N/3Gr (sample 22)	~2 nm	1.5	5e-4(>2,000 times smaller vs. N 212)	N/A	N/A
3Gr/N/3Gr (sample 41), Gr was cross-linked	~2 nm	2.7	0	N/A	N/A
N/Gr/N	Possibly, Gr was ruptured during hot-pressing procedure.				
Gr grown on Cu-Ni alloy (multilayer)					
Gr(15)/N/Gr(15) (sample 42) 15% Ni in Cu	~2 nm	1.2	0	N/A	N/A
Gr(23)/N/Gr(23) (sample 43) 23% Ni in Cu	~4 nm	3	0	N/A	N/A
Gr(23)/N (sample 44) 23% Ni in Cu Gr was peeled off	~2 nm	0.7	0	N/A	N/A
Type 2 membranes prepared from GO					
r(PVP/GO)	11 ± 1 µm	0.65 ± 0.15	0	0	0

*N: Nafion.

As shown in Table 2,Gr synthesis/transfer and membrane geometry were tuned to reach targeted milestones—namely, prepared membranes have ASR <2 ohm-cm^2 and virtually zero V^{4+} crossover, which is well below the targeted value of 1E-9 cm^2/s.

Crossover measurement

One example of crossover calculation is provided here. Thorough details are provided in the supporting information in the recent publication by the New Mexico State University (NMSU) team: https://doi.org/10.1021/acsnano.9b05979.

The VO^{2+} permeability of a membrane was measured using a glass U-tube cell/diffusion cell, filled with 1.5 M $VOSO_4$ solution (V_A = 4 mL) in one compartment and 1.5 M $MgSO_4$ solution (V_B = 4 mL) in the other compartment. As shown in Figure 6, only r(PVP/GO) membrane has no crossover of vanadium.

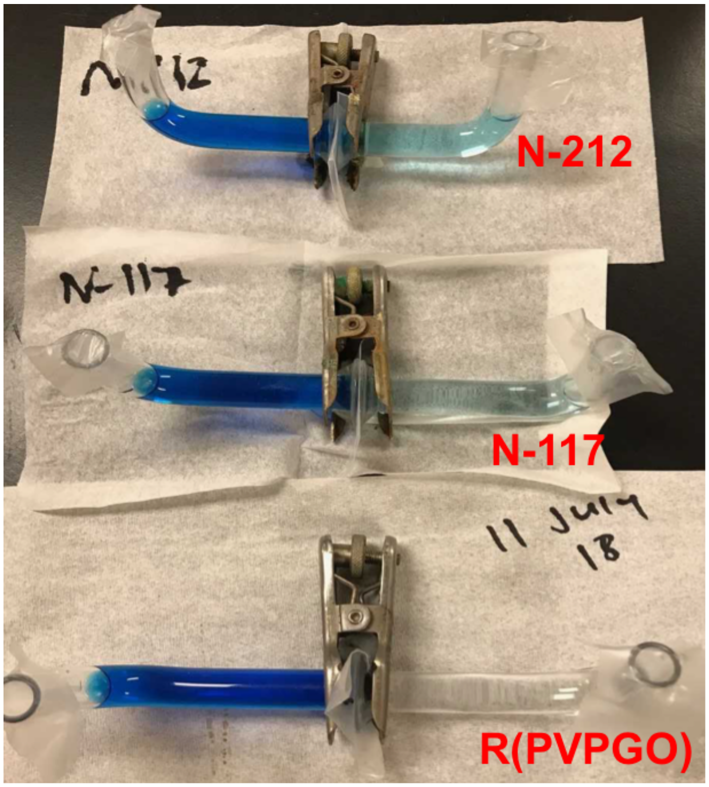


Figure 6. Illustration of the vanadium crossover experiments with U-tubes filled with 1.5 M $VOSO_4$ in one compartment and 1.5 M $MgSO_4$ in the other. Blue-colored VO^{2+} ion most effectively passes through the N 212 membrane, whereas no coloration was detected for the r(PVP/GO) membrane. Additionally, the same setup still does not show any coloration after 10 months.

Since ions, cations, and anions do not move through the membrane, water crossover experiments can be carried out also using a similar U-tube cell with 1 M NaCl solution in one compartment and the same volume (4 mL) of water in the other. Water movement through the membranes is virtually nonexistent; however, water does move through Nafion. In the MeOH/water mixture, crossover of water through Nafion is significantly suppressed, so MeOH crossover experiments can be carried out in a similar manner for both using a similar U-tube cell with a 1:1 water:MeOH solution (12.5 M) in one compartment and the same volume of water in the other.

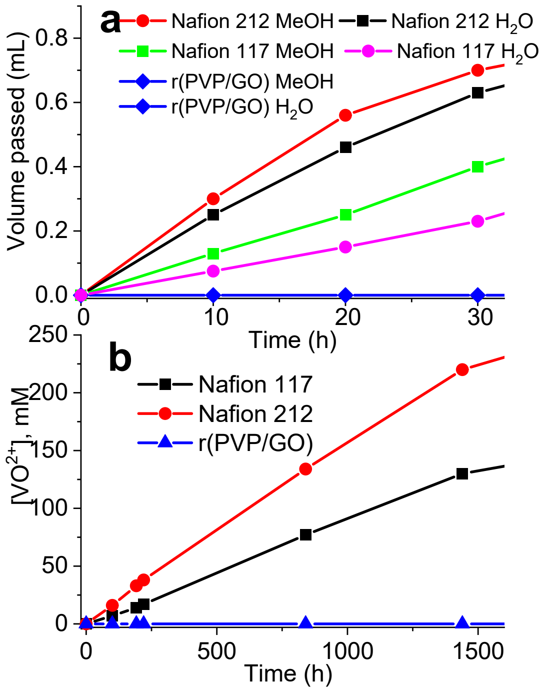


Figure 7. a. Crossover of MeOH from 50/50 aqueous solution into water through 0.3 cm^2 of N 212 and r(PVP/GO) membranes. There is no detectable crossover of MeOH through r(PVP/GO) after 3 days. **b.** Crossover of VO^{2+} through 0.3 cm^2 of N 212, N 117, and r(PVP/GO) membranes between isotonic solutions of 1.5 M $VOSO_4$ + 3 M H_2SO_4 and 1.5 M $MgSO_4$ + 3 M H_2SO_4. There is no detectable crossover of vanadium through r(PVP/GO) even after 10 months. Low MW PVP (3.5 kDa) was used in all cases.

The crossover was calculated using the equation

$$V_B \frac{dc_B}{dt} = A \frac{P}{L}(c_A - c_B) \ ,$$

where A and B denote left and right compartments of the U-tube ($V_A = V_B = 4$ mL), A is the membrane area, P is the permeability, and L is the membrane thickness. The *dc/dt* for V^{4+} (slope in Figure 7b) were measured by absorbance at 760 nm = 20.2 $M^{-1}cm^{-1}$.

An example calculation for V^{4+} crossover of N 212 membrane is

$$P = V_B \frac{1}{A} \frac{dc_B}{dt} \frac{1}{C_A} L \ .$$

From Figure 7b, we get

$$\frac{1}{A} \frac{dc_B}{dt} = \frac{55 mM}{100h * cm^2} \ .$$

Thus,

$$P = 4 \text{ cm}^3 \frac{55 \text{ mM}}{100 \text{ h} * \text{cm}^2} \frac{1}{1.5 \text{ M}} 50 * 10^{-4} \text{ cm} = 1.2 * 10^{-7} \text{cm}^2/\text{min} \ .$$

Calculation example for MeOH crossover of N 212 membrane:

dc/dt = 0.03 mL/h * 25 M = 7.5E-4 mol/h/3.2 mL = 0.23 M/h

Thus,

P = 3.2 cm^3/0.3 cm^2 * 0.23 M/h * 50E-4 cm/25 M = 1.4E-7 cm^2/s (see Table 2)

Electronic ASR

Decoupling electronic and proton conductivity is difficult. The best way to minimize proton conductivity is to perform measurements on dry membranes. Measured impedance of Gr/Nafion/Gr membranes pressed against two carbon electrodes coincides with bare Nafion membranes showing ASR >1E3 ohm-cm^2, which still primarily corresponds to proton ASR.

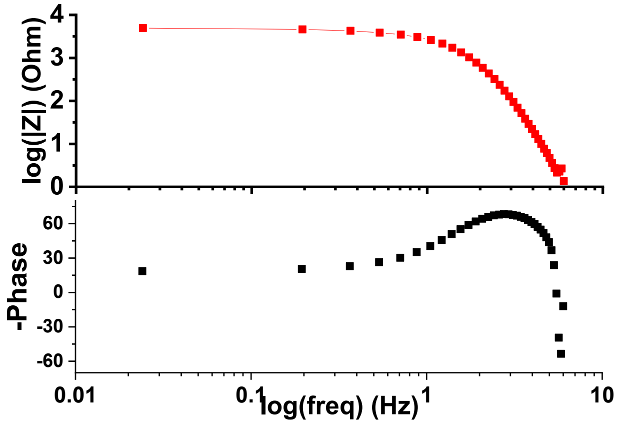


Figure 8. Impedance of dry Gr/Nafion/Gr in the Scribner cell. Impedance exceeds 1E3 ohm-cm^2.

Preliminary tests in vanadium flow battery (VFB) application

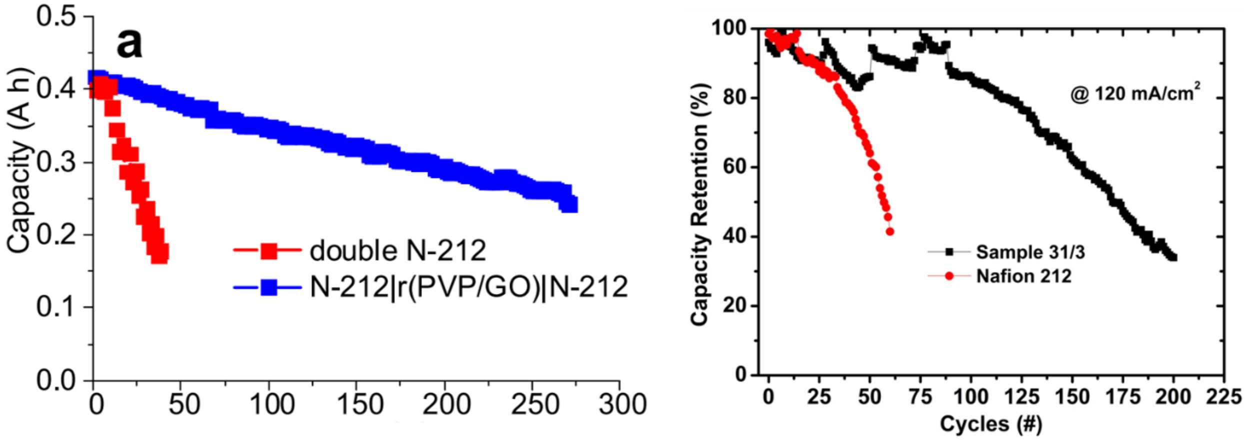


Figure 9. Preliminary tests in VFB. Capacity fading at (a) 40 mA/cm^2 for Type 2 r(PVP/GO) membrane and (b) 120 mA/cm^2 Type 1 Gr/N/Gr membrane. In both cases, suppressed crossover results in slower capacity fading.

Mechanical strength

Mechanical properties after testing membrane VFB are still being measured; however, most of the membranes are based upon N 212 membranes and, as a result, have very similar mechanical characteristics to N 212. Figure 10 shows examples of N 212 (left), reduced GO film (middle), and reduced GO with PVP (right).

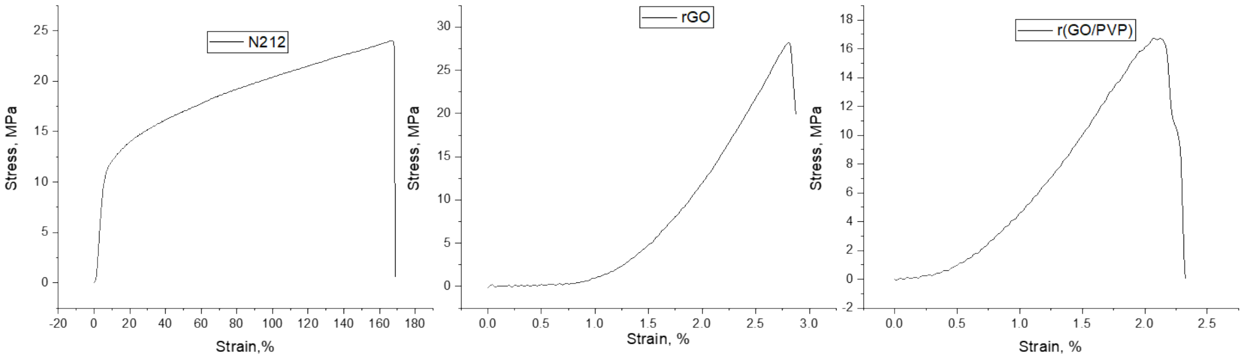


Figure 10. Example stress–strain curves for (left) N 212, (middle) reduced GO, and (right) reduced GO with PVP. Most of the membranes are based on N 212 and, as a result, have very similar characteristics.

Milestone 3.1.2:Tech-to-Market (T2M) plan update (09/30/19)

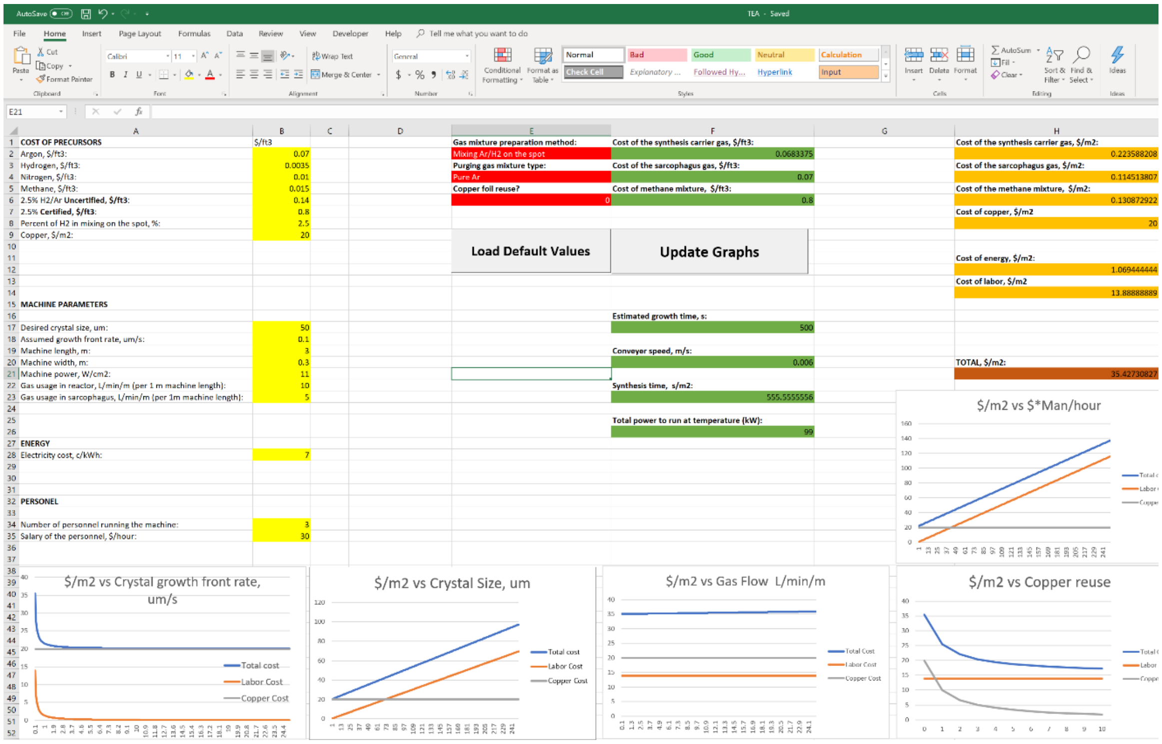
Update the T2M plan. Define supply chain and provide an analysis of opportunities; prioritize them. Include identification of specific entities. Include market assessment.

Brief techno-economic analysis of the technology

The techno-economic analysis (TEA) (the script and macros are available upon request) evaluates points at which the Gen 2.5 machine can produce Gr at the cost of ~\$50/m^2 (at a speed of ~1 m^2/20 min), excluding Cu pretreatment and Gr removal from Cu. The major cost is the Cu foil cost (\$20/m^2) and labor (~\$27/m^2), while other costs such as electricity and precursors are almost negligible. Increasing production rate and Cu reuse can drastically reduce this estimation. For example, making the machine 30 m long instead of 3 m and keeping all other parameters the same, Gr production cost is reduced to ~\$25/m^2, with \$20 being the cost of Cu. Reusing the Cu foil decreases Gr cost to <\$7/m^2 at production rates of 1 m^2/2 min.

The current largest manufacturing question is how to remove Gr from the Cu. Many approaches have been developed for Gr removal and Cu reuse; currently, however, the Cu is being dissolved, which is most universal and the simplest approach. Dissolution of Cu is performed with Fe^{3+}. The cost of FeCl$_3$ 6H$_2$O is ~ \$400/ton. Because 1 m^2 of Cu is ~10 mol, assuming 3 mm Cu thickness, ~\$2.5/m^2 of Fe^{3+} for Cu dissolution is ~10% of the cost of Cu metal. Other costs associated with the dissolution process, such as labor and chemical waste costs, are difficult to estimate at this point.

Figure 11 shows screenshot of the script written for the CVD graphene cost estimation.



COST OF PRECURSORS $/ft3
Argon, $/ft3: 0.07
Hydrogen, $/ft3: 0.0035
Nitrogen, $/ft3: 0.01
Methane, $/ft3: 0.015
2.5% H2/Ar **Uncertified, $/ft3**: 0.14
2.5% **Certified, $/ft3**: 0.8
Percent of H2 in mixing on the spot, %: 2.5
Copper, $/m2: 20

MACHINE PARAMETERS
Desired crystal size, um: 50
Assumed growth front rate, um/s: 0.1
Machine length, m: 3
Machine width, m: 0.3
Machine power, W/cm2: 11
Gas usage in reactor, L/min/m (per 1 m machine length): 10
Gas usage in sarcophagus, L/min/m (per 1m machine length): 5

ENERGY
Electricity cost, c/kWh: 7

PERSONEL
Number of personnel running the machine: 3
Salary of the personnel, $/hour: 30

Gas mixture preparation method: Mixing Ar/H2 on the spot
Purging gas mixture type: Pure Ar
Copper foil reuse? 0

Cost of the synthesis carrier gas, $/ft3: 0.0683375
Cost of the sarcophagus gas, $/ft3: 0.07
Cost of methane mixture, $/ft3: 0.8
Estimated growth time, s: 500
Conveyer speed, m/s: 0.006
Synthesis time, s/m2: 555.5555556
Total power to run at temperature (kW): 99

Cost of the synthesis carrier gas, $/m2: 0.223588208
Cost of the sarcophagus gas, $/m2: 0.114513807
Cost of the methane mixture, $/m2: 0.130872922
Cost of copper, $/m2 20
Cost of energy, $/m2: 1.069444444
Cost of labor, $/m2 13.88888889
TOTAL, $/m2: 35.42730827

Figure 11. Screenshot of TEA Excel spreadsheet. Scripts/macros can be demonstrated upon request.

Milestone 3.3.2: TEA Update (12/31/19)

Update TEA based on experimental data

The TEA has been updated based upon current experimental data. The major differences are the improved Cu reuse process (>10 times) and lower synthesis time (30 min), suggesting a current Gr cost of ~$31/m^2.

Model output includes cost of gases, Cu (dependent upon Cu recycling), energy, labor, and total cost. Sensitivity analysis suggests that the major cost parameters are (1) the rate of Gr growth front, (2) the number of times Cu foil can be used, and (3*i*) the reactor length.

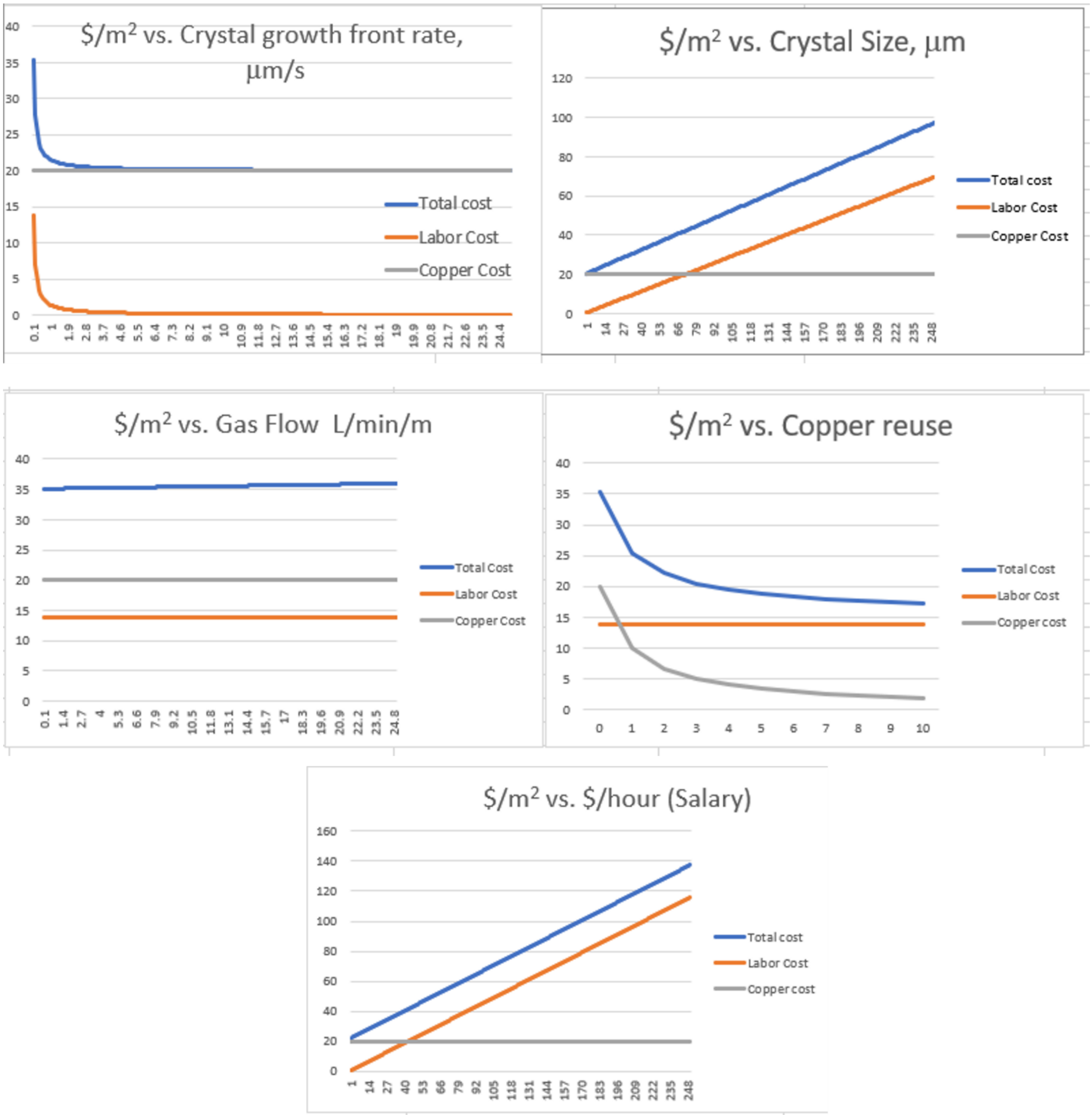


Figure 12. Cost of Gr/hBN ($/m^2) as a function of (a) crystal growth rate, (b) final crystal size, (c) gas flow, (d) number of times Cu can be reused, and (e) labor cost.

Tensile properties of Nafion/Gr membranes

The tensile properties of the N 212 and N 212/Gr membranes that were tested in a fuel cell are shown in Figure 13. The mechanical performance of the N 212/Gr membrane did not degrade compared with the N 212 membrane. Both membranes exhibited comparable performance.

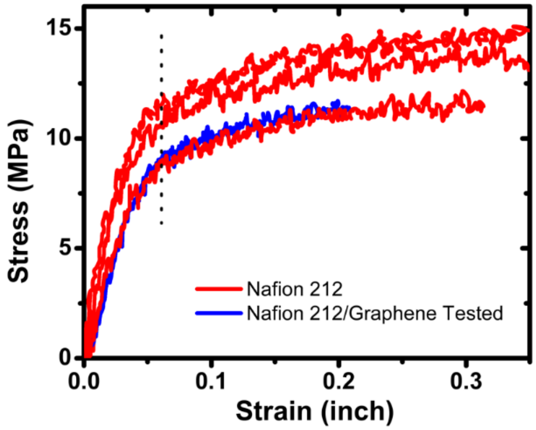


Figure 13. Tensile measurements of N 212 and N 212/Gr tested in a fuel cell.

Milestone 1.1.2: Final membrane performance (03/31/20)

The following final membrane performance tests were performed under the following conditions:

- Prepared multilayer membrane on porous support has proton ASR <0.5 omh-cm^2, V^{4+} permeability <1E-10 cm^2/s, and electronic ASR >1E3 ohm-cm^2 when compressed between carbon paper electrodes.
- Mechanical properties were assessed when the membrane had been soaked in a V/H_2SO_4 solution.
- Membrane soaked in a solution with V^{5+} and H_2SO_4 (1.5 M V^{5+} and 3 M H_2SO_4, or as discussed and approved by the Program Director) for >500 h showed a <10% change in proton ASR, permeability, and stress–strain curves.

All the metrics have been met except for 500 h stability testing. Unfortunately, the 500-h tests were interrupted by closure of NMSU labs. The experiment will be restarted as soon as possible.

Current Gr/N/Gr membrane technical data include the following:

- ASR ~0.35 ohm-cm^2
- V^{4+} permeability ~1.3E-11 cm^2/s
- Electronic ASR >1E5 ohm-cm^2
- Tensile strength ~30 MPa

A comparison of N 211 in VFB performance is shown in Table 3.

Table 3. Comparison of Gr membranes to bare N 211 in VFB

Sample	Vanadium crossover (mM/h)	Averaged ASR (ohm-cm^2)	VRFBS performance in cell (area 5 cm^2 at 120 mA/cm^2 current density) CE (%)	VE (%)	EE (%)	Capacity (% fading, no. of cycles)
Standard N 211	1.63	0.35	96	82	77	59%, 65
GR/N 211/Gr (plasma 1s, both sides)	**0.01***	0.35	98	82	81	**13%, 300**

*Values in bold indicate ___________________________.

Milestone 2.1.2: Continuous 2D material synthesis (03/31/20)

The 25-cm^2 membrane fabricated in a continuous environment meets the requirements of Milestone 1.1.2. Testing may be performed on smaller samples cut from the larger membrane; however, the total area of the smaller samples should be >30% of the original large sample.

The Gen 2.5 machine was upgraded to roll-to-roll (R2R). The 10 m^2 were synthesized continuously. Currently, the team produces ~40 cm^2 membranes (exceeding the milestone requirement of 25 cm^2) but can extend to 0.09 cm^2 if necessary.

Milestone 3.1.3: Final T2M plan (03/31/20)

Update T2M plan based on experimental data

The membranes were sent to four companies for performance assessment in various applications.

Table 4 details the updated performance of the membranes developed under this project.

Table 4. Updated performance of the membranes developed under this project

Membrane	Thickness (mm)	APR, ASR (Wcm^2)	VO^{2+}crossover (10^{-7}cm^2/min)	MeOH crossover (10^{-7}cm^2/s)	Water crossover (10^{-8}cm^2/min)
N 211	25	0.35 ± 0.2	2 ± 0.2	1.2 ± 0.2	N/A
N 212	50	0.8 ± 0.3	1.2 ± 0.1	1.4 ± 0.1	6.9 ± 0.2
N 117	183	1.8 ± 0.3	2.2 ± 0.2	2.2 ± 0.2	7.8 ± 0.3
Green*	25	0.35 ± 0.2	0.012	0.04	<1

*Green membrane indicates graphene-enhanced and engineered.

3. PROJECT ACTIVITIES

The project aims to create a substitute for the Nafion perfluorosulfonic acid (PFSA) membranes in various energy-related applications. Two primary applications were considered: fuel cells and flow batteries. The fuel cell industry had revenues of approximately \$2.2 billion in 2014, an increase of almost \$1 billion over revenues in 2013. In 2015, revenue is estimated to be ~\$3.5 billion; experts anticipate revenues to exceed \$25 billion by 2024, with a compound annual growth rate of 23%. Currently, the largest markets for fuel cells are stationary and portable power applications, auxiliary power units, backup power, and material handling equipment.

The current state-of-the-art PFSA membrane plays a crucial role in fuel cell technology but represents up to 45% of the cost of the fuel stack (assuming a production rate of 1000 units per year). This cost ratio drops, however, to 12% if a production rate of 500,000 units per year is assumed. The flow battery market is more challenging to evaluate, but the VFB market is estimated to be ~\$142 million in 2017 and is anticipated to expand at a compound annual growth rate of ~60% at least until 2022. Similar to fuel cells, the PFSA membrane contributes significantly to the overall cost of the flow battery, constituting ~16% in current 400 mA/cm^2 \$275/kWh systems.

In contrast to the PFSA membrane, the proposed membrane should have virtually zero crossover for any ions and molecular species (including MeOH and water), which could pave the way for the commercialization of DMFCs. Although DMFCs are appealing, the crossover problem precludes them from widespread commercial acceptance.

In the United States, PFSA membranes (marketed under the brand name Nafion) are produced by The Chemours Company (which was spun off from DuPont in 2015), a large chemical corporation with almost \$7 billion in annual revenues. Current PFSA prices are ~\$400/m^2; coupled with the uncertainty associated with ionomer costs, this cost generally represents one of the primary barriers to widespread fuel cell adoption. Indeed, some have suggested that ionomer costs could exceed ~\$500/kg even at very high-volume production, which translates to ~\$100/m^2 depending on the thickness and chemical formulation of the membrane.

4. PROJECT OUTPUTS

Journal Articles

1. Chaturvedi, P., I. V. Vlassiouk, D. A. Cullen, A. J. Rondinone, N. V. Lavrik, and S. N. Smirnov. 2019. “Ionic Conductance through Graphene: Assessing Its Applicability as a Proton Selective Membrane.” *ACS Nano* 13:12109–12119. https://pubs.acs.org/doi/10.1021/acsnano.9b06505.

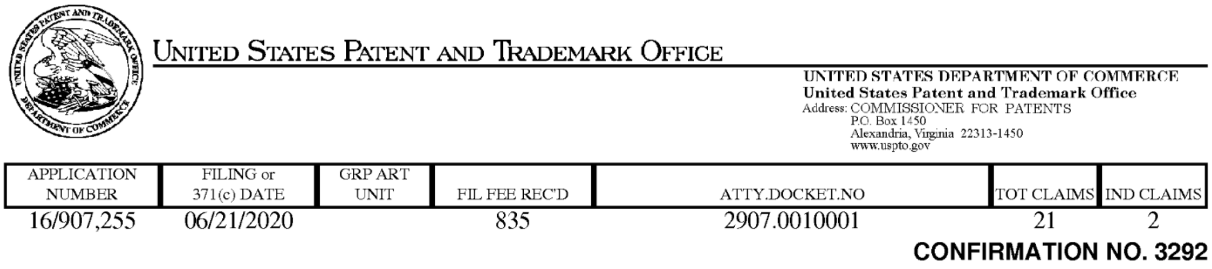
2. Shinde, D. B., I. V. Vlassiouk, M. R. Talipov, and S. N. Smirnov. 2019. “Exclusively Proton Conductive Membranes Based on Reduced Graphene Oxide Polymer Composites.” *ACS Nano* 9(13):13136–13143. https://doi.org/10.1021/acsnano.9b05979.

Invention Disclosures

1. Proton selective membranes based on two dimensional materials. iEdison Confirmation Number: 10059902-20-0002.

Patent Applications/Issued Patents

1. Proton Selective Membranes based on Two Dimensional Materials.



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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
16/907,255	06/21/2020		835	2907.0010001	21	2

CONFIRMATION NO. 3292

2. General Graphene has licensed major Oak Ridge National Laboratory patents that claim synthesis of Gr by chemical vapor deposition. These licensed patents provide General Graphene “freedom to operate,” as follows:
    - Vlassiouk, I. V., et al. US 10,023,468B2, “High Quality Large Scale Single and Multilayer Graphene Production by Chemical Vapor Deposition”. Important claims: Continues process, inductive/resistive/IR heating, annealing/growth in fluid communication chambers, gases, recipe. Limitations: $P(H_2)$ ~10–20 torr; $P(CH_4)$ ~23–100 mTorr, $P(H_2)/P(CH_4)$ >400.
    - Vlassiouk, I. V., et al. WO 2018/125591 Al, “Continuous Single Crystal Growth of Graphene.” Unique conditions to synthesize single crystal Gr.
    - Vlassiouk, I. V., et al. US10093072B2, “Graphene Reinforced Materials and Related Methods of Manufacture.”

The NMSU team is in the process of patenting a unique rGO/polymer composite proton conductive membrane discovered during the execution of this project.

5. FOLLOW-ON FUNDING

The team is waiting on receipt of the membrane assessment data for the following applications: hydrogen fuel cell, DMFC, VFB, and NH_3 fuel cell. The team is considering applying for a Phase 1 Small Business Innovation Research grant for DMFCs.