Membrane Working Group

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Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Coordinate the research community investigating polymer electrolyte membranes for hydrogen production and conversion devices.
- Exchange research information in the polymer materials area in terms of targets, baselines, and test protocols.
- Educate the research community to accelerate technology advances.
- Prioritize research needs/areas and provide the information to the DOE program office.

Fiscal Year (FY) 2019 Objectives

- Define the mission and scope of the Membrane Working Group.
- Organize an anion exchange membrane (AEM) workshop.

Technical Barriers

- Low durability due to membrane degradation.
- High costs for high-performance membranes.
- Membrane performance under the extremes of automotive drive cycles.

Technical Targets

The Membrane Working Group will identify the highest priority issues for AEMs and AEM-based devices through an AEM workshop.

FY 2019 Accomplishments

In the one-day AEM Workshop, more than 50 industrial, academic, national laboratory, and government experts representing the needs of AEMs, membrane electrode assemblies (MEAs), and system and stack components discussed the high-priority issues for AEMs and AEM-based devices. Detailed discussion will be presented in the workshop final report.

The workshop also proposed the anion exchange membrane fuel cell (AEMFC) milestones listed below

- **2021**: Efficiency: 100 mW/cm^2 performance at 0.8 V (T ≥80°C) with 0.2 mg$_{PGM}$/cm^2, P ≤250 kPa.
- **2022**: AEM fuel cell initial performance at 0.65 V: 1,000 mA/cm^2 on H_2/O_2 (maximum pressure of 1.5 atm) in MEA with total <0.2 mg$_{PGM}$/cm^2 and <10% voltage degradation over 1,000 h at T ≥80°C.
- **2022**: CO_2 tolerance: <65 mV loss for steady state operation at 1.5 A/cm^2 in H_2/air scrubbed to 2 ppm CO_2.
- **2022**: Catalyst durability with H_2/CO_2-scrubbed air after accelerated stress test: <40 % loss after 10,000 cycles from 0.6 V to 0.95 V. Membrane durability: 1,000 h open circuit voltage hold at 70% relative humidity (RH) and ≥80°C.
- **2025**: 1 W/cm^2 at 0.65 V; H_2/CO_2-free air with total platinum group metal (PGM) loading <0.125 mg/cm^2, T ≥80°C, pressure ≤250 kPa.
- **2030**: AEMFC peak power performance >600 mW/cm^2 under H_2/air (maximum pressure of 1.5 atm) in PGM-free MEA.
- **Ultimate**: 1 W/cm^2 at rated power (~0.65 V at 95°C), PGM-free MEA, T ≥80°C, pressure ≤250 kPa.

Table 1. AEM Workshop Focus

Area of Interest	Identification of Issues
AEMs	- Baseline materials - Round robin/standardized testing protocols - Metrics/targets - Challenges with carbonate, ion exchange
AEM-based devices	- Catalyst ionomer interaction (fuel cell, electrolyzer) - Water management - CO_2 issues

INTRODUCTION

The previous High Temperature Membrane Working Group consisted of government, industry, and university researchers interested in developing high-temperature membranes for fuel cells. The working group focused on hot and dry proton exchange membrane (PEM) operation. The new Membrane Working Group has an expanded interest for any polymeric materials used in fuel cells and other energy devices.

APPROACH

The Membrane Working Group will coordinate discussion on fuel cell membrane research. Membrane materials used in fuel cells based on AEM, PEM, and high-temperature PEM are of interest in the present. In addition, ionomeric binders in the fuel cell electrodes will be discussed in the Membrane Working Group. In the future, membranes for different applications such as electrolyzers, flow batteries, water desalination, ammonia synthesis, and CO_2 reduction may be included in the scope of work. In 2019, the Membrane Working Group decided to focus on anion exchange membranes. In 2016, NREL and LANL had co-organized an AEMFC Workshop. In the workshop, experts in the relevant fields discussed research priorities of AEM materials and AEM fuel cells and proposed protocols, metrics, and targets/milestones. The progress in AEM fuel cells has been impressive since 2016. However, many challenging issues and struggles within the community remain related to testing protocols, comparisons of test results among groups, and baseline materials. Therefore, the Membrane Working Group planned a 2019 AEM Workshop to discuss the research needs, priorities, and standardized protocols, metrics, milestones, and targets. Before the AEM Workshop, the Membrane Working Group led a discussion meeting at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting (April 29–May 1, 2019, Washington, DC) and held a webinar (March 5, 2019).

RESULTS

The AEM Workshop started with opening remarks by Donna Ho (Fuel Cell Technologies Office) and Grigorii Soloveichik (Advanced Research Projects Agency–Energy [ARPA-E]). In the morning session, Bryan Pivovar (NREL) presented an overview of the 2019 AEM Workshop and a summary of the current AEM development status. The morning breakout sessions covered standardized protocols and membrane metrics/targets after two invited talks by Mark Pouy (ARPA-E) and Mike Yandrasits (3M). The afternoon breakout sessions covered electrode performance, water/CO_2 management, and device performance/durability milestones, metrics, and targets after two invited talks by Bill Mustain (University of South Carolina) and Yu Seung Kim (LANL).

The key results from the breakout sessions are listed below.

Morning Breakout Session 1: Standardized Protocols—Conductivity and CO_2.

- Need a good methodology to measure in-plane and through-plane conductivity. Bekktech for in-plane conductivity and MTS (Scribner Membrane Test System) for through-plane conductivity measurement.

- Anisotropic membranes require both in-plane and through-plane measurements.

- DC vs. AC measurements: AC measurements work well. DC measurements may need verification by area specific resistance (ASR) measurements in operating cells.
- Need wet thickness dimensions for an accurate measurement of conductivity.
- Thickness target is 10–80 µm, but maybe as thin as 5 µm depending on the applications.
- Cl^- and HCO_3 form of AEMs can be used for quick screening conductivity. Decreased water is critical for hydroxide conductivity.
- 30°C and 80°C may be proper measurement temperatures. 50% RH is a lower bound for conductivity. Hysteresis is essential to evaluate.

Morning Breakout Session 2: Standardized Protocols—Mechanical Properties, Water Uptake, and AEM Stability

- Mechanical properties of AEMs should be evaluated with consideration for particular applications.
- Measurement of stress-strain behavior is the most commonly practiced method. Once an AEM achieves the level of sufficient stress-energy, ca. >20 MPa, elastic behavior is more important than stress.
- Not only elongation at break but also maximum recoverable elastic strength should be considered.
- For fuel cell applications, water uptake measurements should be done at different RH. For electrolyzer applications, water uptake measurements should be done after submerging the membrane in water for a certain period of time. Swelling ratios need to be evaluated as well.
- The most commonly practiced alkaline stability test is conducted by immersing membrane into 1 M KOH/NaOH at 80°C for a certain period of time to measure the change in ion exchange capacity and conductivity. Electrochemical stability tests that mimic real cell conditions may also need to be performed.

Morning Breakout Session 3: Membrane Metrics/Targets

- AEM chemical stability: ≥1,000 h with ≤5% loss in ion exchange capacity and conductivity
- AEM ASR (hydroxide form, 80°C in liquid water): ≤0.04 $\Omega\ cm^2$
- AEM ASR (80°C, ≤50% RH under air [400 ppm CO_2] exposure): ≤0.08 $\Omega\ cm^2$
- Electronic ASR: ≥1,000 $\Omega\ cm^2$, humidity stability factor: >5; swelling in liquid water at 25°C: <50%; H_2 crossover: <5 mA/cm^2; H_2O transport: >4 $\Omega mol/cm^2$-s
- Membrane cost: ≤\$20/m^2

Afternoon Breakout Session 1: Electrode Performance

- Alkaline stability of ionomer and ionomer interaction with catalysts play a key role in device performance. Specific cationic functional groups may be required for different purposes (membrane, anode ionomer, and cathode ionomer)
- PGM-free oxygen reduction reaction (ORR) catalysts: three different potential PGM-free ORR classes (M-N-C, transition metal oxides, and silver-based materials) have been developed. Need further research to implement those catalysts in MEAs.
- PGM-free hydrogen oxidation reaction (HOR) catalysts: significant effort is required in this field to bring high performance and durability to the level of PGM.

- PGM-based HOR catalysts: PGM catalysts with low loading (<0.1 mg/cm^2) on the anode need to be developed. Specific combinations of PGM+ionomer should be screened to obtain the highest performance and durability.
- Prioritized R&D needs for AEMFCs: (1) development of ionomers, (2) advanced HOR catalysts, and (3) high-performance PGM-free cathodes.
- Prioritized R&D needs for AEM electrolyzers: (1) stable ionomers, (2) ionomer performance metrics, (3) mass transport/water flux through membrane, (4) non-PGM oxygen evolution reaction activity, and (5) stable component development for electrolyzer operating conditions.

Afternoon Breakout Session 2: Water/CO_2 Management

- CO_2 exposure or carbonate formation has been a major issue for fuel cell operation. The ambient level of CO_2 is too high. 5 ppm of CO_2 might be acceptable.
- Possible solutions for carbonation include working with CO_2-free gases or scrubbing CO_2 from the air.
- Water management is complicated for AEMFCs. High AEMFC performance is achievable with proper water management, but advances are required if more dynamic operating conditions and further improved durability are to be achieved.
- Specific issues with electrolyzer applications were discussed in terms of carbonation, water management, porous layers, mechanical and assembly, bubble management, dry out, and liquid balance.
- Specific issues with fuel cells were discussed including humidification at the anode, low-PGM and PGM-free catalysts, humidification, flow rate robustness, electrode fabrication, conditioning protocols, operating conditions, and water transport metrics.

Afternoon Breakout Session 3: Device Performance and Durability Milestones/Metrics/Targets

- The ultimate targets of AEMFCs should be set to show advantages over proton exchange membrane fuel cells (PEMFCs).
- A PGM target of 0.05 mg_{PGM}/cm^2 was proposed. Some proposed PGM-free operation.
- AEMFCs need humidification, and it is not clear whether AEMFC system designs can be realized without external humidification.
- The power density should be determined at the rated power taking into consideration heat rejection and Q/ΔT targets rather than using peak power density. However, peak power at 0.76 V at 80°C is not realistic because current AEMs do not have the required durability.
- An ASR target equivalent to that of PEMFCs may not be necessary due to other advantages of AEMFCs such as the high kinetic activity of catalysts under high pH conditions.
- RH cycling durability tests may not be applicable for AEMFC applications as they cannot currently be operated at low RH conditions. Durability conditions of 70%–80% RH at 90°C and 60%–70% RH at T ≥80°C were proposed.
- Potential cycling tests at 10,000 cycles between 0.6 V and 0.95 V with a <40% loss may be appropriate for the catalyst durability.

- CO_2 tolerance tests may be done with 2 ppm CO_2 in H_2 steady state. Some also suggested a test in air (400 ppm CO_2) for 1,000 hours to see if any performance remains.

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2019, the Membrane Working Group has focused on alkaline AEM research. An AEM Workshop was organized on May 30, 2019, in Dallas, Texas, after the 235th Electrochemical Society Meeting. In the workshop, several high priority topics, including baseline materials, standardized testing, metrics/targets, and technical challenges of AEMs were discussed among researchers from academia, industry, national labs, and government. The Membrane Working Group plans to publish a report on the outcome of the workshop. In 2020, the Membrane Working Group will continue its efforts looking at different areas including PEMFCs, high-temperature PEMFCs, ionomeric binders, and also non-fuel-cell applications such as electrolyzers and flow batteries.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. 2019 Anion Exchange Membrane Workshop Report (in preparation).