Reinforced perflurosulfonic acid membrane with improved water holding capacity in low humidity polymer electrolyte fuel cells: Its future significance in unitized regenerative fuel cells

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Abstract:

The performance of polymer electrolyte fuel cells (PEFCs) is significantly influenced by the membrane's ability to maintain optimal hydration levels. This study focuses on enhancing fuel cell performance through the optimization of humidity levels using a reinforced perfluorosulfonic acid (PFSA) membrane with improved water-holding capacity. The research investigates the impact of varying humidity conditions on the efficiency and durability of PEFCs, particularly under demanding operational environments. Reinforced PFSA membrane (Nafion-HP) to enhance water retention, was considered and tested under different humidity regimes to assess its effectiveness in maintaining stable hydration. The results demonstrate a marked improvement in fuel cell performance, with enhanced proton conductivity and reduced degradation rates observed in the optimized membrane. The findings have significant implications for the future development of unitized regenerative fuel cells (URFCs), where maintaining precise humidity control is crucial for efficient energy conversion and storage. This study contributes to the advancement of high-performance fuel cell technology by providing insights into the role of membrane hydration in optimizing fuel cell efficiency and longevity

Keywords: *PEFCs; PFSA; URFCs; MEA; EL; ORR*

Introduction

Unitized regenerative fuel cells (URFCs) represent a promising technology for energy storage and conversion, offering the potential for seamless transition between electrolysis and fuel cell operation. Integrating self-humidified membranes into URFCs enhances their performance, durability, and practicality, making them a compelling solution for various applications. An URFC consists of a membrane electrode assembly (MEA) that includes an ion-conducting membrane, typically a H^+-conducting perfluorosulfonic-acid membrane, which separates the electrodes responsible for electrocatalysis (catalyst layer) and gas or liquid transport (gas diffusion or porous transport layers) [1]. During charging (EL mode), the oxygen-evolution reaction (OER) occurs at the anode, and the hydrogen-evolution reaction (HER) occurs at the cathode. During discharging (FC mode), the hydrogen-oxidation reaction (HOR) occurs at the anode, and the oxygen-reduction reaction (ORR) occurs at the cathode. An URFC requires each electrode to be bifunctional to support both modes of operation. This bifunctionality can be achieved through two configurations: constant-gas (CG) or constant-electrode (CE). In the CG configuration, the URFC consists of an oxygen electrode (ORR/OER) and a hydrogen electrode (HOR/HER) [2]. In the CE configuration, the URFC consists of an anode (HOR/OER) and a cathode (ORR/HER), with gases at the anode and cathode being switched between EL and FC modes [3].

The relevance of URFCs with self-humidified membranes lie in their ability to address key challenges associated with membrane dehydration in URFC operation and conventional fuel cell systems along with energy storage technologies while unlocking new opportunities for renewable energy integration and sustainable development [4]. Self-humidified membranes play a critical role in maintaining optimal hydration levels within the fuel cell, thereby improving proton conductivity and electrochemical kinetics. By effectively managing water distribution and retention, these membranes minimize mass transport losses and ensure efficient proton transport across the electrolyte. This results in enhanced fuel cell performance, higher power density, and improved overall energy conversion efficiency in URFCs, making them more competitive with other energy storage technologies [5].

The integration of self-humidified membranes enhances the durability and reliability of URFCs by mitigating issues related to membrane dehydration, water flooding, and chemical degradation. The self-humidified membranes offer superior water management, maintaining stable hydration levels under varying operating conditions and reducing the risk of performance degradation over time [6]. As a result, URFCs with self-humidified membranes exhibit prolonged service life, increased operational reliability, and reduced maintenance requirements compared to traditional fuel cell systems. Self-humidified membranes streamline the design and integration of URFCs by eliminating the need for external humidification systems and complex water management components. This simplification not only reduces system complexity and manufacturing costs but also enhances system compactness and portability, making URFCs more suitable for diverse applications, including automotive, stationary power generation, and off-grid energy storage [7].

Additionally, the integration of self-humidified membranes facilitates the development of plug-and-play URFC systems that are easier to install, operate, and maintain in real-world applications. URFCs with self-humidified membranes offer a versatile platform for integrating renewable energy sources, such as solar and wind power, into the energy infrastructure. By converting excess renewable energy into hydrogen through electrolysis during periods of low demand, URFCs enable efficient energy storage and grid balancing, thereby enhancing the stability and reliability of renewable energy systems. Moreover, the reversible operation of URFCs allows for the generation of clean electricity from stored hydrogen during peak demand periods, supporting grid stability and reducing reliance on fossil fuels [8].

The adoption of URFCs with self-humidified membranes contributes to the advancement of sustainable development goals by promoting clean energy production, reducing greenhouse gas emissions, and fostering energy independence and security. By harnessing renewable energy sources and enabling efficient energy conversion and storage, URFCs play a crucial role in transitioning towards a low-carbon economy and mitigating the impacts of climate change. Furthermore, the scalability and versatility of URFC technology make it adaptable to various socioeconomic contexts and geographic regions, empowering communities to achieve energy access, resilience, and economic prosperity.

Nafion HP membranes represent a significant advancement in proton exchange membrane (PEM) technology for polymer electrolyte membrane fuel cells (PEMFCs). These membranes offer high proton conductivity, excellent mechanical strength, low methanol permeability and increased water management capabilities [9,10], making them particularly suitable for enhancing the performance and durability of PEFCs. However, optimizing the humidity levels and water balance in operating PEMFCs is a critical challenge to enable high performance URFCs. In this study, we explore the optimization of humidity levels in operating PEMFCs using reinforced Nafion HP membranes, focusing on their benefits and applications and its further relevance to unitized regenerative fuel cells.

Hence, in the present study, the entire focus was on optimizing the humidity levels in operating PEMFCs with the self-humidified Nafion HP-based reinforced membrane electrode assemblies (MEAs) and analyzing the chemical stability of the membranes at lower humidity and high temperature (30 %RH and 80 ^{o}C for longer duration @ OCV hold). The presence of silica in the reinforced membrane is an added advantage since it holds water even at low relative humidity as we envisage retention in cell performance even at low RH.

2.Experimental

2.1. Membrane electrode assembly fabrication

The MEA is fabricated using a Nafion HP membrane (reinforced perflurosulfonic acid membrane with silica nanoparticles, 0.8 mil thick, designed for lower relative humidity environments and high operating temperature, procured from Ion Power®), carbon-supported platinum catalyst (50 wt.% Pt/Vulcan XC72, BASF®) and Toray (Toray-060, 5% PTFE wet proofing) carbon gas diffusion layers (GDLs). In brief, a 5 cm × 5 cm area of Toray® carbon (TGP-H-060, 5 wt. % wet proofing) is cut and weighed. For slurry preparation, Pt/C (100 mg) is dispersed in 6 mL of water and to that mixture, 3.06 mL of iso-propyl alcohol (IPA) is added. 0.807 mL Nafion ionomer is added to the above dispersion to achieve a Nafion/Carbon mass ratio of 0.75. This is sonicated for 90 min to have a uniform dispersion. The above slurry is spray coated onto the Nafion membrane to achieve a loading of 0.3 mg Pt/cm^2. The membrane is dried to remove excess solvent. Two 5 cm^2 electrodes are cut from the larger 25 cm^2 electrode, one to be used as the anode and the other to be used as the cathode. The

schematic of the fabrication of catalyst coated membrane (CCM) and MEA is represented in **Figure 1.**

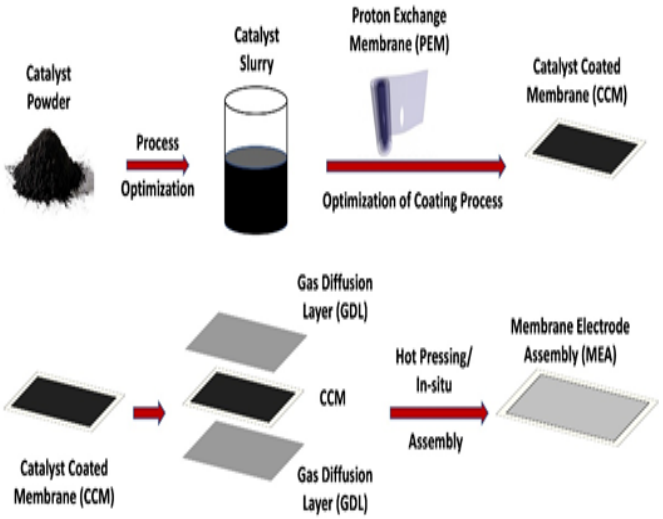


Fig. 1. Schematic illustration of catalyst coated membrane via spray coating and membrane electrode assembly fabrication

The electrodes are pressed with the catalyst coated membrane (integrated between 6 mil PTFE gaskets on either side) using a hot press (Karver). The hot press temperature was 130 °C and 3.79 MPa of pressure was applied at this temperature for 3 min to form the MEA. Next, the MEA is integrated into a Scribner fuel cell fixture comprised of graphite plates with a single channel serpentine flow field along with other components (current collector and endplate with nuts and bolts). The cell was bolted together with 30 in.lb torque.

2.2. Conditioning of the fuel cell and cell polarization

To begin cell testing, the cell is connected to the fuel cell test station (Scribner 850e). It is ensured that the fuel cell test station has enough water, as well as proper amounts of N_2, H_2 and O_2 gas in the connected gas cylinders. These gases will be supplied to the humidifiers and cells throughout the testing.

2.2.1. Cathode starvation break-in for the cell before the testing

To initiate cell break-in, humidifier temperature (dew points) of 80 °C and Cell temperature of 80 °C was maintained. H_2 and O_2/air are supplied to the anode and cathode sides of the cell, respectively. A hydrogen backpressure of 0.5 bar is applied; the backpressure on the anode is increased from ambient to 1.5 bar total pressure to aid the crossover of H_2 from the anode to cathode during break-in. The current is increased in steps until the cell voltage is decreased 0.3 V. The voltage is held at 0.3 V for 2-5 min for the current response to stabilize. The current density is then reduced to 200 mA/cm^2. Oxygen/air supply is stopped while maintaining the current at 200 mA/cm^2. The voltage of the cell is observed to drop since there is no supply of oxygen to the cathode. When the voltage drops to 0.2 V, oxygen/air is re-supplied to the cathode quickly. The process is repeated until the voltage difference between the two cycles is < 5 mV. At the end of the conditioning procedure, the back pressure was reverted to ambient [10].

2.2.2. Conditioning of the cell after the break in and cell testing

The cell was purged with Nitrogen initially at the rate of 0.4 lpm through both the anode and cathode of the cell. Both humidifier temperatures are raised from 30 to 80 °C, followed by the cell temperature (80 °C). When the cell temperature reaches 80 °C, the cell is stabilized for 1 h and then the H_2 and O_2/air fuel is supplied at the required stoichiometry (0.2 lpm for H_2 and 0.1 lpm for O_2 and 0.47 lpm for air). After stabilization of the OCV, the current is applied (200 mA/cm^2) and the cell can stabilize for 2 h. After this, the polarization curve is recorded at regular time intervals, stepping the current in set amounts until a lower cutoff voltage of 0.1 V is achieved. After recording the polarization, the cell is cooled down by turning off the heaters and passing humidified nitrogen.

2.2.3. Cell polarization at different relative humidities and stability test

The cells are polarized at different relative humidities to see the effect of the relative humidity (30 to 100 %RH on both anode and cathode) on fuel cell performance. Further, chemical stability for the membrane is analyzed by monitoring the OCV in relation to time at 30 % RH @ 80 °C.

3. Results and Discussion

The unique structure of the Nafion HP membrane facilitates efficient proton transport while effectively managing water content within the membrane, critical for maintaining high fuel cell performance. This reinforced

membrane offers several advantages for humidity control in PEFCs with respect to improved water retention properties to help maintain adequate hydration levels even under low humidity conditions. This feature is particularly beneficial for mitigating dehydration effects and ensuring continuous proton conduction within the membrane. In addition, with reduced water flooding, reinforced membranes exhibit superior water management capabilities, effectively preventing water flooding under high humidity conditions. By regulating water uptake and distribution, these membranes minimize the risk of flooding-induced performance degradation and enhance overall cell efficiency and enhanced durability. The mechanical robustness and chemical stability of Nafion HP membranes contribute to their long-term durability in fuel cell operation. These membranes are less prone to swelling, degradation, and pinhole formation, even in harsh operating environments with fluctuating humidity levels. The presence of silica in the Nafion HP membrane provides water holding capacity for the membrane to work at various relative humidity. The uniform distribution of silica is seen in membrane morphology from Scanning electron microscopy as represented in **Figure 2**.

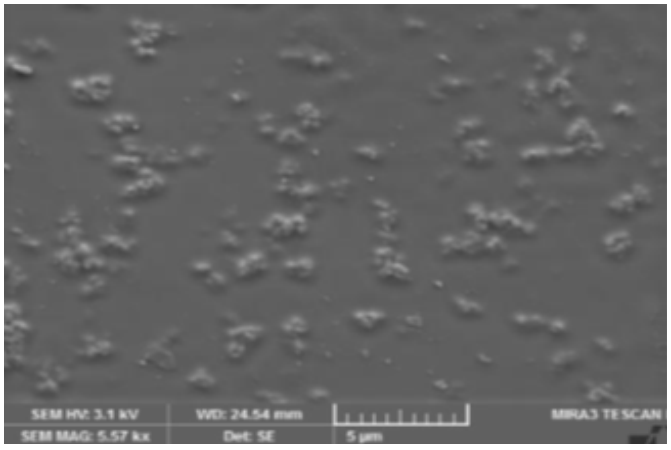


Fig. 2. SEM morphology for Nafion-HP membrane confirming the presence of silica in the membrane matrix.

In the present work, humidity levels have been optimized while using Nafion HP membranes, implementing various strategies tailored to specific operating conditions, like humidification control. Advanced humidification systems are integrated into PEFC test stations to precisely regulate the humidity of reactant gases and maintain optimal water content within the membrane. This ensures consistent proton conductivity and maximizes cell performance over a wide range of operating conditions. The humidity levels at various temperatures for the tested cells are provided in **Table 1** [11].

Table 1. Tabulation of relative humidities for the membranes with constant cell temperature in H_2-air configuration to attain the required %RH.

% RH	Cell temperature (°C)	Humidifier temperature (°C)	Cell temperature (°C)	Humidifier temperature (°C)
30	80 °C	53.0	70 °C	44.5
40		59.0		50.0
50		64.0		55.0
60		68.0		59.0
70		71.5		62.0
80		74.5		65.0
90		77.5		67.5
100		80.0		70.0

It is observed in the polarization curves, **Figure 3** that the Nafion HP membrane retains good cell performance at variable levels of humidities under H_2-Air configuration (0.2 lpm of H_2 and 0.47 lpm of Air).

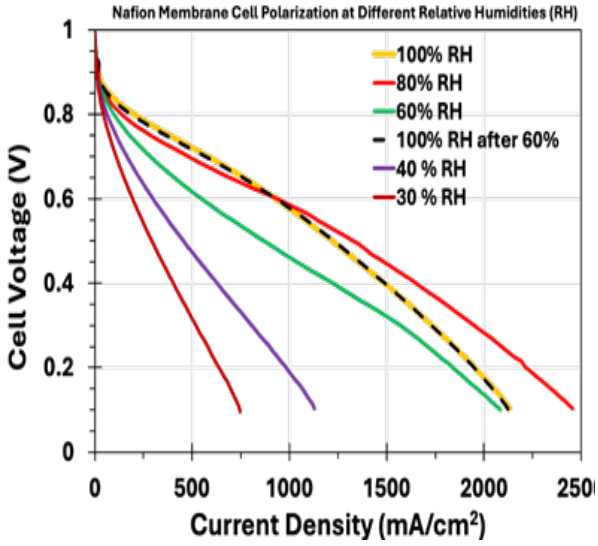


Fig. 3. Cell Voltage vs. Current density (mA/cm^2)

for the Nafion membrane at various relative humidities.

The Nafion™ HP is an ultra-thin membrane that offers high power density. The membrane is reinforced and designed for lower relative humidity environments and high operating temperature. It can be clearly seen that silica in the Nafion membrane has a very good water holding capacity and hence some reasonable cell performance retained even at 30 %RH. Maximum fuel cell performance is seen at 80 % RH along with an improvement in the mass transfer region. Cell performance is also very good at 100 %RH, but there is a drop in the mass transfer region, likely due to excess water. This clearly indicates that reinforced membrane is useful to improve the mass transfer region at slightly lower RH in comparison to 100 % saturation. In addition, the peak power density for cell using the Nafion HP

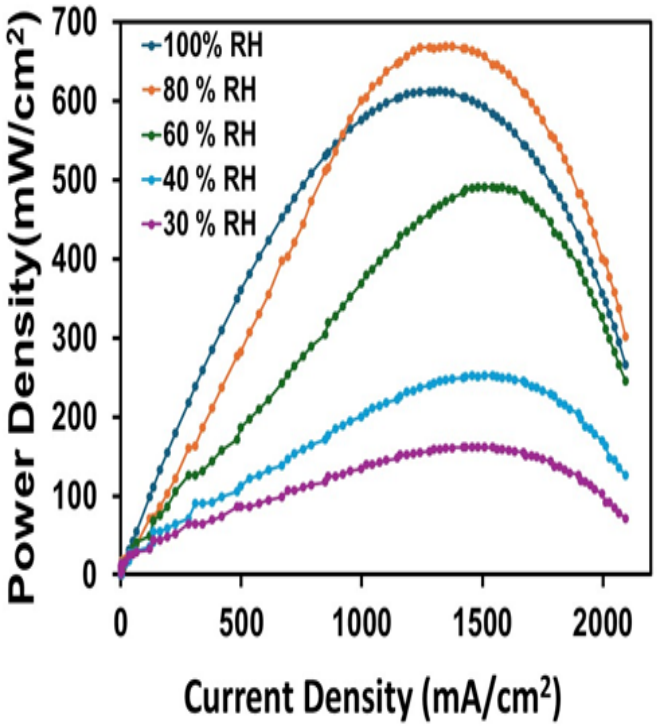


Fig. 4. Peak power densities in relation to current density for Nafion membrane at different relative humidities.

Stability data for operating cells with the reinforced Nafion HP membrane is also shown under H_2-air configuration. Cells are tested following start-stop cycle for the two days, 6 h each day, which clearly indicates that there is no drop in open circuit voltage and data while holding the open circuit voltage (OCV) at 30 %RH @ 80 °C in relation to time is stable, confirming the chemical

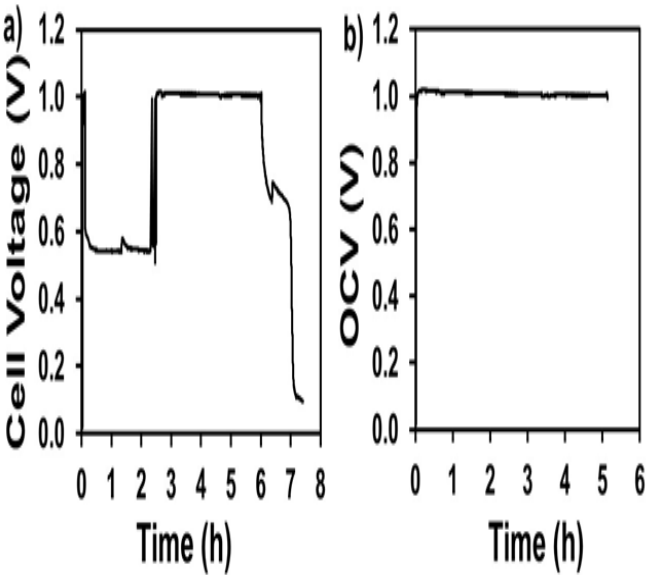


Fig. 5. (a) Change in cell voltage during cell polarization, and (b) OCV hold in relation to time for Nafion membrane at 30 %RH and cell temperature of 80 °C.

Figure 5a shows the change in OCV in relation to time during cell polarization experiments. OCV was initially recorded before the cell polarization experiments (before applying current) and then the current was applied to 1 A to analyze the change in OCV and then stabilize and the steps are repeated before the cell polarization and after the cell polarization. Stability was also analyzed at the OCV hold without any current load @ 30 %RH to see steady state as represented in **Figure 5b**. The data confirms that membrane electrolytes are stable even at lower RH during PEMFC operation.

3. Conclusions

To summarize, the optimization of humidity levels through Nafion HP membranes has significant implications for various PEFC applications, including automotive, stationary power generation, and portable electronics. It is proven that Nafion membrane in presence of silica can retain cell performance even at low RH. Cell break-in protocol and stability test are critical for these membranes which also confirms the chemical stability

of the membrane electrolytes. The current density of 1 A/cm^2 at 0.6 V at 80 % RH confirms the improved cell performance for Nafion HP membranes. By enhancing water management capabilities and ensuring reliable operation under diverse operating conditions, reinforced high performance Nafion membranes contribute to the widespread adoption of PEFC technology across different sectors. Future research directions will focus on further refining the design and properties of Nafion HP membranes to achieve improvements in URFC performance, durability, and cost-effectiveness along with preparation of bifunctional catalysts for improved round trip efficiency. Additionally, exploring novel materials and fabrication techniques could lead to the development of next-generation PEMs with enhanced humidity control and overall cell performance.

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Declaration of competing interest

There no competing financial interests to declare for the research reported in this article

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