

Enhanced Fuel Cell Performance with Modified Nafion[®] Membranes

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ABSTRACT

The interaction of a carbocyclic fuel, decalin, with a commercial proton exchange membrane, Nafion[®] 212 (N212) was studied. Treatment of N212 with decalin showed higher water uptake at low relative humidity and membrane electrode assemblies fabricated with these membranes exhibited lower hydrogen crossover and internal resistance compared to the untreated membranes. This resulted in a significant increase in peak power in a H₂/Air fuel cell at 60% relative humidity. Small angle X-ray scattering was used to understand the morphological and dynamic effects in the membrane due to the fuel treatment. The effect of decalin incorporation in the catalyst layer was also studied.

Keywords: organic liquids, decalin, fuel cell, Nafion[®], SAXS

1 INTRODUCTION

The direct use of energy dense liquid fuel in a PEM fuel cell is the focus of Energy Frontier Research Center for Electrocatalysis, Transport Phenomena and Materials (CETM). The absence of safe and economical methods of hydrogen storage and transportation hampers wider deployment of hydrogen-based proton exchange membrane fuel cells (PEMFCs). The direct use of organic fuels in PEMFCs as virtual hydrogen carriers, generating stable organic molecules, protons and electrons without the use or production of gaseous hydrogen, could provide an attractive alternative [1]. Recent advances in the reversible dehydrogenation/hydrogenation of carbocyclic and heterocyclic hydrocarbons provided motivation to re-evaluate these organic liquids as potential direct and regenerable fuels [2,3]. Previous evaluation of hydrocarbon fuels in PEMFCs with Pt catalyst and fluoropolymer-based PEMs [4] demonstrated low power densities. These results show that more research is needed to both develop dehydrogenation catalysts for these fuels and also to study the impact of such fuels on PEM morphology and performance. An understanding of fuel-PEM interactions and their impact on proton conductivity, water uptake, polymer morphology and fuel cell performance was viewed by our group as critical to the development of direct regenerative hydrocarbon fuel cells and motivated this study.

2 EXPERIMENTAL SECTION

Decalin (anhydrous, Sigma-Aldrich) and commercial N212 (IonPower Inc.) were used as received. The modified membrane was prepared by immersing the membrane in decalin at room temperature for 24 hours. Fuel uptake was determined gravimetrically after removal of excess fuel. Proton conductivity of the untreated and fuel treated membranes was determined using a MTS740 membrane test system (Scribner Inc.). The cell setup and experimental details are explained in detail elsewhere [5]. Water sorption and desorption measurements were conducted using Dynamic Gravimetric Vapor Sorption (DVS) (DVS-Advantage, Surface Measurement Systems. Small Angle X-ray Scattering (SAXS) measurements were performed in beamline 7.3.3. of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. To fabricate membrane electrode assemblies (MEA) commercial electrodes purchased from Fuel Cell Earth with 40% Pt/C and 0.5 mg/cm² Pt loading were used for both anode and cathode. No additional ionomer was painted to the catalyst layer prior to MEA fabrication. MEAs were constructed by hot pressing the anode and cathode with the fuel treated N212 and untreated N212 at 125 °C and 350 psi for 3 minutes. The active area of the MEAs was 5 cm² in all cases. MEAs were also fabricated with decalin treated electrodes under the same conditions. Neat decalin was painted on the catalyst layer of both anode and cathode to the amount of 10% by weight of the catalyst and MEAs were fabricated as described above. The polarization curve was performed at constant current mode from 0-1 A/cm² with a 2 minute dwell time at each current density. Incubation and polarization curves were performed at 1.2 H₂ and 5.0 Air stoichiometric flow rates. For low RH measurements, the fuel cell was held at 75 °C while the anode and cathode humidifier temperatures were reduced to achieve desired RH. Hydrogen crossover current density and catalyst active area was measured according to methods reported in literature [6].

3 RESULTS AND DISCUSSION

Fuel uptake, determined gravimetrically, after removal of excess fuel was 2.6% after immersion in neat decalin and remained unchanged after 24 hours. DVS was used to determine changes in λ , which represents the moles of H₂O/moles of sulfonic acid, at 50°C as a function of relative humidity (RH). The observed isotherm for untreated membrane is qualitatively consistent with known models of Nafion® sorption [7] and the decalin treated N212 exhibited up to a 20% increase in λ compared to the untreated membrane.

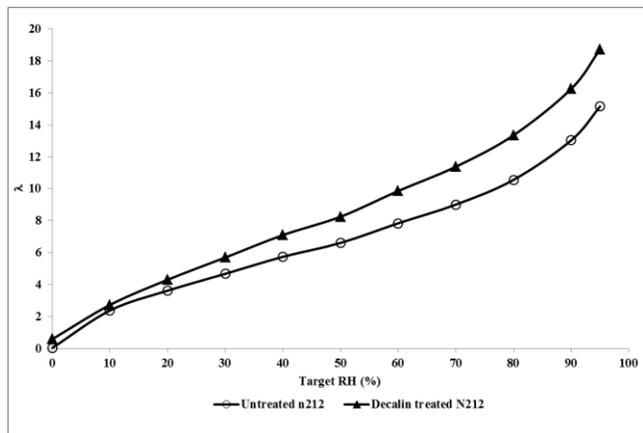


Figure 1: Vapor sorption isotherms for untreated and decalin treated N212 membranes at 50 °C as a function of RH.

Similar to vapor sorption, the untreated N212 membrane also showed an exponential increase in conductivity with RH reaching its maximum conductivity at 95% RH (not shown). However, the conductivity of decalin treated N212 remained unchanged as a function of RH. The higher water uptake of the decalin treated membranes did not translate into higher conductivity which suggests that proton conduction in these membranes does not bear a typical relationship to water activity.

MEAs fabricated with untreated and decalin treated membranes were tested in a H₂/Air fuel cell at 75 °C and the polarization curves were obtained at 60% RH. Since the proton conductivity of a Nafion® membrane depends strongly on RH, performance loss observed at 60% RH (Fig.2) is attributed to loss of water from N212, thus increasing the MEA internal resistance from 95 m Ω -cm² at 100% RH to 215 m Ω -cm² at 60% RH for the untreated N212 (Table 1). This also includes the resistance at the membrane-catalyst interface as the Nafion® in the catalyst layer is also prone to dehydration. However, under the same conditions decalin treated membranes show a profound increase in power density (86%) along with a 40 mV increase in open circuit voltage (OCV). Increase in OCV is mainly attributed to a reduction in hydrogen crossover through the membrane [6]. Molecular H₂ that permeates

through the membrane does not participate in the electrochemical reaction resulting in locally generated heat leading to membrane thinning and pinhole formation and degrades fuel cell efficiency and performance. Incorporation of decalin decreased the hydrogen crossover by 30% compared to the untreated membrane resulting in a higher OCV. Since hydrogen permeates through the hydrophobic phase, reduction of H₂ crossover by incorporation of decalin could be a result of plasticization of the hydrophobic phase, thus hindering permeation by increasing tortuosity of the diffusion pathways. The resistance for these MEAs was significantly reduced to 105 m Ω -cm² at 60% RH.

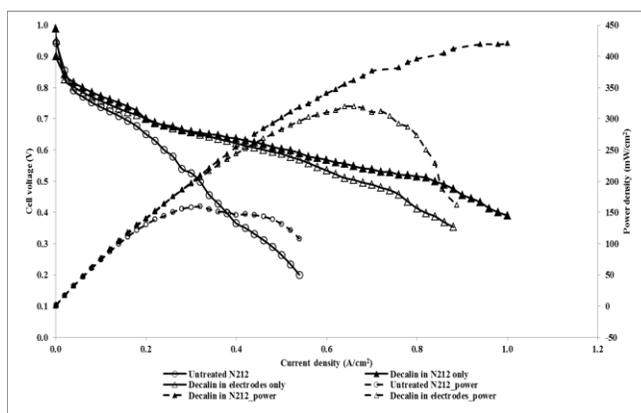


Figure 2: Fuel cell performance of decalin treated N212 (Δ) and decalin treated electrodes (\blacktriangle) at 75 °C and 60% RH. The untreated N212 (\circ) performance is also shown for comparison. Power densities are represented by dashed lines.

Fig.2 also shows the performance of decalin treated electrodes under the same conditions. Similar to the decalin treated N212, the fuel cell with decalin treated electrodes also exhibited higher performance at 60% RH but no change in OCV was observed. This further confirms that increase in OCV for the decalin treated N212 is solely due to reduction in hydrogen crossover and does not include mixed potential and oxide formation effects. A decrease in cell voltage is observed towards higher current density which is due to diffusion losses in the electrode layer due to the presence of decalin at the cathode. The observed improvement in performance with the decalin treated N212 and electrodes at low RH remained unchanged after operating the fuel cell under steady conditions for three days.

To calculate changes in platinum utilization due to decalin incorporation, cyclic voltammetry was used. These results are reported in Table 1. For the cathode containing decalin treated N212 and decalin treated electrodes, higher platinum utilization was observed compared to the untreated N212 MEA.

Table 1: Fuel cell performance of untreated, decalin treated N212 and decalin treated electrodes at 75 °C and 60% RH.

Treatment	OCV(mV)	Peak power (mW/cm ²)	H ₂ crossover (mA/cm ²)	Cell resistance (mohm-cm ²)	Pt utilization (%)
Untreated	950	159	6	215	28
Decalin treated N212	988	420	2	105	49
Decalin treated electrodes	950	350	6	115	47

The Pt utilization was 28% for the untreated MEA and it nearly doubled with decalin incorporation at low RH (Table 1). This suggests that the decalin on the electrode produces a similar plasticization effect on the electrode layer as that of the membrane, resulting in better water retention at the membrane electrode interface at low RH conditions. In the case of decalin treated N212, in addition to the morphological changes in the membrane, a fraction of the decalin from the membrane can be forced into the electrodes during MEA fabrication (and vice versa when using treated electrodes), thus improving catalyst utilization. The improvement at low RH was observed irrespective of the presence of decalin in the membrane as well as the electrode, which suggests that decalin is not essential to enter the membrane to produce high power density in the fuel cell. However, during MEA fabrication decalin is forced out of either the electrodes or membrane toward the membrane electrode interface forming a hydrophobic skin and affects water transport [8]. The hydrophobic skin enhances water retention at the interface resulting in high water sorption, proton conductivity consequently resulting in better fuel cell operation at low RH.

SAXS measurements were performed to understand the morphological changes due to decalin treatment. The measurements were performed at 50° C from 25-95% RH. For clarity purposes in Fig.3, SAXS profile at 95% and 60% RH is shown.

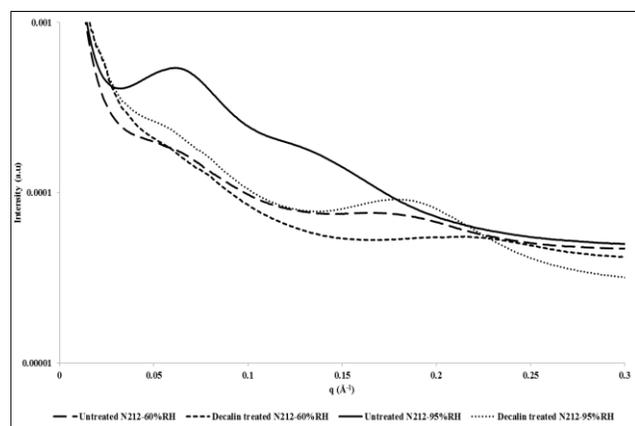


Figure 3. SAXS profile of untreated and decalin treated N212 membrane at 50 °C, 60 and 95% RH.

The profile of untreated N212 membrane reveals the existence of two maxima [9], where the maxima at low q values (ca. 0.05 \AA^{-1}) arises from lamellar crystalline domain and the second maxima at high q values (ca. 0.15 \AA^{-1}) have been attributed to ionic cluster domains containing solvated sulfonic acid residues. The untreated N212 exhibited a broadening of the ionic cluster peak and a shift to lower q ($q=0.2-0.15 \text{ \AA}^{-1}$) with increasing RH. The d-spacing ($d=2\pi/q$) of the ionic domains increases from 3.2 nm at 30% RH to 4.6 nm at 95% RH. Simultaneously, the peak assigned to lamellar crystallites increased in intensity and its maximum shifted slightly to lower q values ($0.06-0.04 \text{ \AA}^{-1}$) (larger domain sizes). The SAXS profile of a decalin treated N212 as a function of RH is different from the untreated membrane. The strong interaction of decalin with poly (tetrafluoroethylene) lamellar domains results in less pronounced crystallinity in this region and indicates that decalin treatment caused changes in membrane backbone morphology. In addition, the 3.2 nm d-spacing of the ionic domains remains unchanged from 30 to 95% RH. This indicates that the ionic domains for the decalin treated membranes are not larger than untreated N212, however, the DVS data indicates higher water sorption; therefore the ionic domains in the treated membranes must have a higher number density.

4 CONCLUSIONS

Commercial N212 membranes treated with decalin was characterized by SAXS and NMR and tested in a H₂/Air fuel cell. SAXS studies showed that treatment with decalin suppresses crystallization of the hydrophobic phase and water sorption studies revealed the greater propensity of decalin treated N212 to absorb water relative to untreated N212. Using the dependence of conductivity vs. λ found for Nafion[®] membranes, the higher λ value for decalin treated membranes is not directly translated to an increase in proton conductivity compared to untreated N212. Therefore, the proton conduction in decalin could relate to a complex interaction of hydrophobic and ionic phase microstructure as evidenced by SAXS data. In spite of modest improvement in conductivity, the combined effect of membrane treatment on fuel cell performance, at low RH, is substantial. This result is significant since the humidification required to maintaining proton conductivities of the membrane is one of major cost factors

in a fuel cell system. This work opens up the possibility of using hydrophobic additives to affect membrane morphology, conductivity and fuel cell performance.

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