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DVS & MPA Case Study 626

Investigations into Nafion hydration and its influence on water and oxygen transmission rates

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The hydration-dependent transport behavior of Nafion was investigated using combined dynamic vapor sorption (DVS) and membrane permeability analysis techniques. Water uptake was measured as a function of relative humidity and temperature, revealing kinetically limited hydration at low humidity and non-linear sorption consistent with microstructural reorganization of ionic domains. The sorption data directly linked to measurements of water vapor transmission rate (WVTR) and oxygen transmission rate (OTR), both of which increase strongly with humidity and temperature. Time-resolved oxygen permeation experiments were analyzed using the long-time solution of Fickian diffusion, allowing effective oxygen diffusion coefficients to be extracted and correlated with the membrane hydration state. Together, the results demonstrate how slow initial hydration and humidity-dependent transport govern mass transfer in Nafion, providing insight into water management, gas cross-over, and performance in real-world electrochemical devices.

Introduction

Proton-exchange membranes based on perfluoro sulfonic acid polymers, most notably Nafion, are central to a wide range of electrochemical and separation technologies, including polymer electrolyte fuel cells and electrolyzers. In these applications, membrane performance is governed not only by ionic conductivity but also, critically, by interactions with water and by the transport of small molecules such as oxygen. Understanding how Nafion hydrates and how this hydration state influences mass transport is therefore essential for predicting performance, durability, and efficiency under realistic operating conditions[1].

Nafion is a phase-separated material comprising a hydrophobic fluoropolymer backbone and hydrophilic sulfonic acid side chains[2]. Upon exposure to water vapor, the sulfonic acid groups adsorb water and form interconnected ionic domains whose size, connectivity, and dynamics depend strongly on relative humidity and temperature. This hydration process controls membrane swelling, mechanical properties, proton conductivity, and the permeability of gases and vapors. Because practical devices rarely operate under fully saturated conditions, quantitative characterization of hydration behavior across a wide humidity range is required.

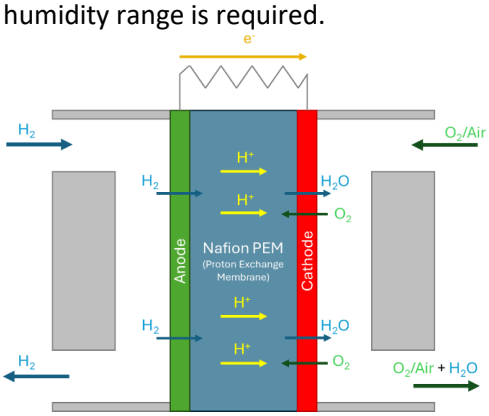

Figure 1: Simplified hydrogen fuel cell schematic[3]

Dynamic vapor sorption (DVS) provides a sensitive and reproducible means of probing water uptake in Nafion as a function of relative humidity and

temperature. By directly measuring mass changes during controlled humidity ramps, DVS enables the construction of sorption isotherms that reflect the non-linear uptake of water associated with ionic cluster formation and swelling. These hydration data form a critical foundation for interpreting transport measurements, as water content directly influences both diffusivity and solubility of permeating species.

In parallel, water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) measurements offer practical metrics of membrane permeability that are directly relevant to real-world operation. WVTR governs membrane dehydration, water management, and cross-over losses, while OTR is linked to parasitic losses, and degradation pathways in electrochemical systems.

This application note brings together DVS-based hydration measurements with WVTR and OTR permeability studies using a novel multicomponent permeability analyzer (MPA Horizon) to provide a coherent picture of how water uptake controls mass transport in Nafion. By linking fundamental hydration behavior to practical transmission rates, the work aims to support more informed membrane selection, modelling, and optimization for demanding real-world applications.

Methods

The material of study was the commercial proton-exchange membrane (PEM) Nafion (N-112) (50 µm thickness), HPLC-grade water was used to generate humidity, Oxygen (>99.98%), and dry N_2 was used in both the membrane permeation analyzer (MPA) and DVS experiments.

Water uptake measurements under controlled humidity and temperature were performed in situ using a DVS Resolution instrument. Approximately 30 ± 5 mg of sample material was placed in the sample pan for each experiment. Relative humidity was incrementally adjusted between 0 and 95 % RH and maintained until mass equilibrium was achieved at each step. Measurements were conducted at 25 and 60 °C to simulate ambient and elevated fuel-cell operating conditions. The recorded data were analyzed to yield water uptake as a percentage of the initial dry mass.

Water vapor and oxygen permeation measurements were conducted using a Membrane Permeation Analyzer (MPA Horizon), Figure 2.

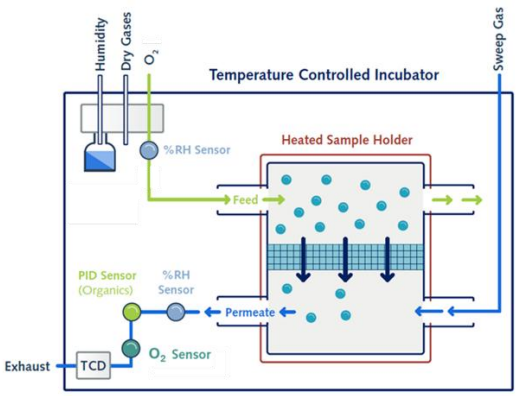

Figure 2. MPA Horizon schematic

In this cross-flow configuration, humidified oxygen was introduced on the feed side of the membrane, while dry nitrogen was used as a sweep gas on the permeate side to transport permeating species to the outlet gas-specific sensors. WVTR and OTR measurements were performed at 25 and 60 °C using a flow rate of 20 sccm on both sides of the membrane.

The time-resolved oxygen permeation data was analysed using the long-time solution of Fick's law for diffusion through a flat sheet, subject to a step change in oxygen partial pressure[6]. In this regime, the permeation signal $S_{(t)}$ approaches its steady-state value S_∞ according to a first-order exponential relationship, Equation 1.

$$S_{(t)} = S_\infty \left(1 - e^{(-t/\tau)}\right) \quad (1)$$

Where τ is the characteristic permeation time constant and t is the time. For a membrane of thickness l, the time constant is directly related to the effective oxygen diffusion coefficient D via Equation 2.

$$\tau = {}^{l^2}/_{\pi^2 D} \quad (2)$$

Which corresponds to the diffusion-limiting step in the long-time regime through a slab. Effective diffusion coefficients were therefore obtained by linearising the permeation curves, Equation 3.

$$\ln\left(1 - {}^{S_{(t)}}/_{S_{(\infty)}}\right) = -{}^{t}/_{\tau} \quad (3)$$

Therefore, a plot of $\ln\left(1 - {}^{S_{(t)}}/_{S_{(\infty)}}\right)$ against t, time, yields the characteristic permeation time from the slope, allowing the determination of the effective diffusion coefficient D. The model is widely used in membrane transport studies where permeation curves exhibit a single, monotonic approach to steady state after the initial gas-switching and provides an effective diffusion coefficient that captures the combined influence of membrane hydration, temperature, and microstructural connectivity on oxygen transport.

Results

Water sorption isotherms

Measurements of water sorption in the Nafion membrane were first undertaken at 25 and 60 °C to investigate temperature-dependent changes in water vapor uptake.

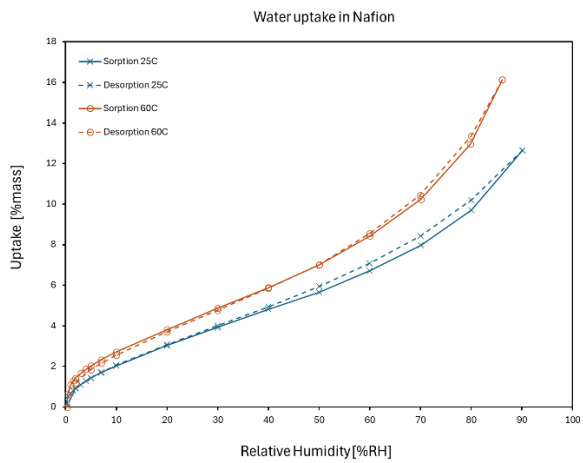

Figure 3. Water sorption isotherms of Nafion (25 and 60 °C)

Figure 3 shows the water sorption isotherms of Nafion at 25 and 60 °C, with increased humidity uptake observed at elevated temperature. This unclassical adsorption behavior is observed at all partial pressures, indicating that increased uptake is a result of increased molecular mobility and therefore water vapor diffusion with temperature (as discussed in application note 49).

This is also further evidenced by the decreasing hysteresis observed with increasing temperature, with hysteresis typically arising from diffusion restricted mobility within a material.

At 60 °C, a comparison between the equilibrium water uptake results, and results obtained from humidity ramps yielded insights into the hydration mechanisms within the polymer. For comparison against equilibrium data, three ramps, one slow, medium, and fast (300, 200, and 100 minutes), shown in Figure 4.

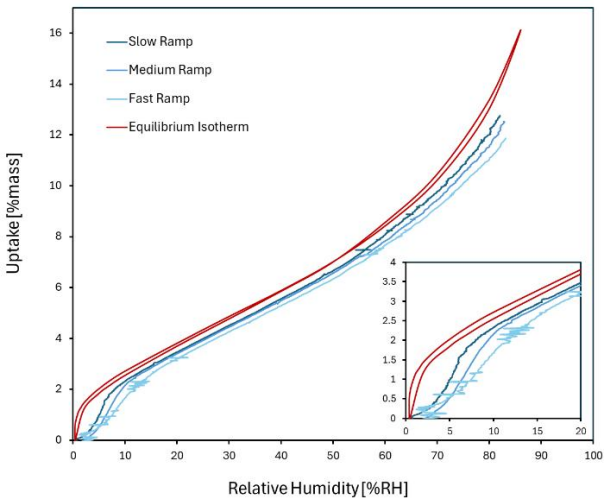

Figure 4. Comparison between kinetic and equilibrium sorption isotherms at 60 °C

As shown in Figure 4, for much of the sorption uptake the ramp and equilibrium isotherm are consistent. At low relative humidity, ramp-derived uptake values fall well below equilibrium values, indicating that even at elevated temperature it is the initial hydration of Nafion which remains kinetically limited. Initial hydration involves water sorption at sulfonic acid sites followed by redistribution into ionic clusters and channels.[2,7] At low water content, these domains are small, poorly connected, and embedded within a rigid fluoropolymer matrix, resulting in slow bulk water diffusion.[8]

Water and oxygen transmission rates

The transmission rates of water vapor and oxygen through Nafion were measured at 25 and 60 °C, shown in Figure 5a and 5b. Process relevant measurements were obtained concerning material hydration and water transport, and oxygen cross-over as a function of relative humidity. At 25 °C, the initial hydration of the polymer at low %RH results in a negligible WVTR. The WVTR at 25 °C increases with exposure relative humidity, but never matches the values achieved at 60 °C. This higher WVTR at 60 °C likely arises from a swelling of the channels due to water clustering. The WVTR values at 1-8 g m^{-2} day^{-1} are consistent with those found in literature[4] at 25 °C. Additionally, the values for 60 °C between 19-55 g m^{-2} day^{-1} are also consistent with literature for similar materials. The water vapor flux values for Nafion-115 reported in Motupally *et al.*[4] were between 0.1–1 x10^{-5} mol/cm^2 s, a similar order of magnitude to those in this study for Nafion 112 between 0.2–3.4 x10^{-5} mol/cm^2 s.

At 60 °C, WVTR is measurable even at the lower 10 %RH, and increases approximately linearly with humidity up to 60% where the increase in WVTR appears to level off. This plateau of the WVTR above 60 %RH is attributed to hydration saturation, where the mobility in the channels is no longer significantly affected the exposure relative humidity[9]. Indeed from the sorption isotherm, above 60 %RH the water uptake behavior changes from linear uptake to channel swelling.

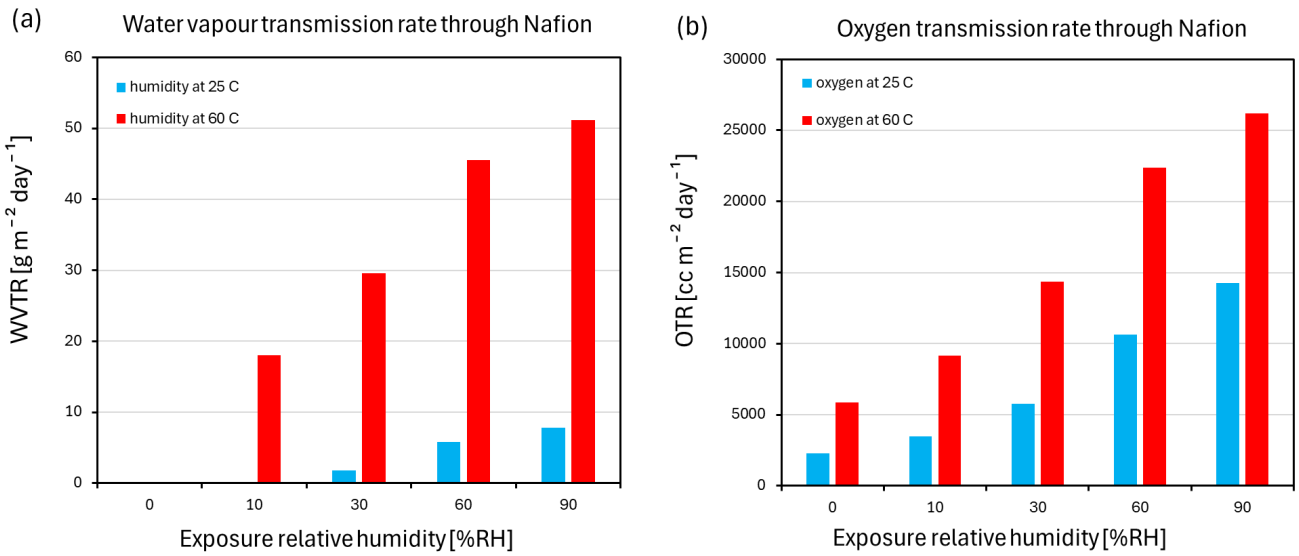

Figure 5. Nafion membrane permeation analysis data obtained for water vapor (a) and oxygen (b) at 25 and 60 °C, as a function of %RH.

As shown in Figure 5b, the oxygen transmission rate at both temperatures increases with humidity, with a higher transmission rate observed at a higher temperature. At 25 °C, the OTR increases rapidly between 30 – 60 %RH as the water vapor sorption uptake transitions from linear to non-linear behavior, which also aligns with the WVTR trend. Similarly, the OTR behavior at 60 °C broadly matches the WVTR trends at the same temperature with a somewhat linear increase until 90 %RH. Both of these data sets indicate that the oxygen transport behavior is closely linked to the hydration state of the polymer, as well as the temperature dependent diffusion[10]. The extent of diffusion limitations was measured using the time-resolved data, shown in Figure 6.

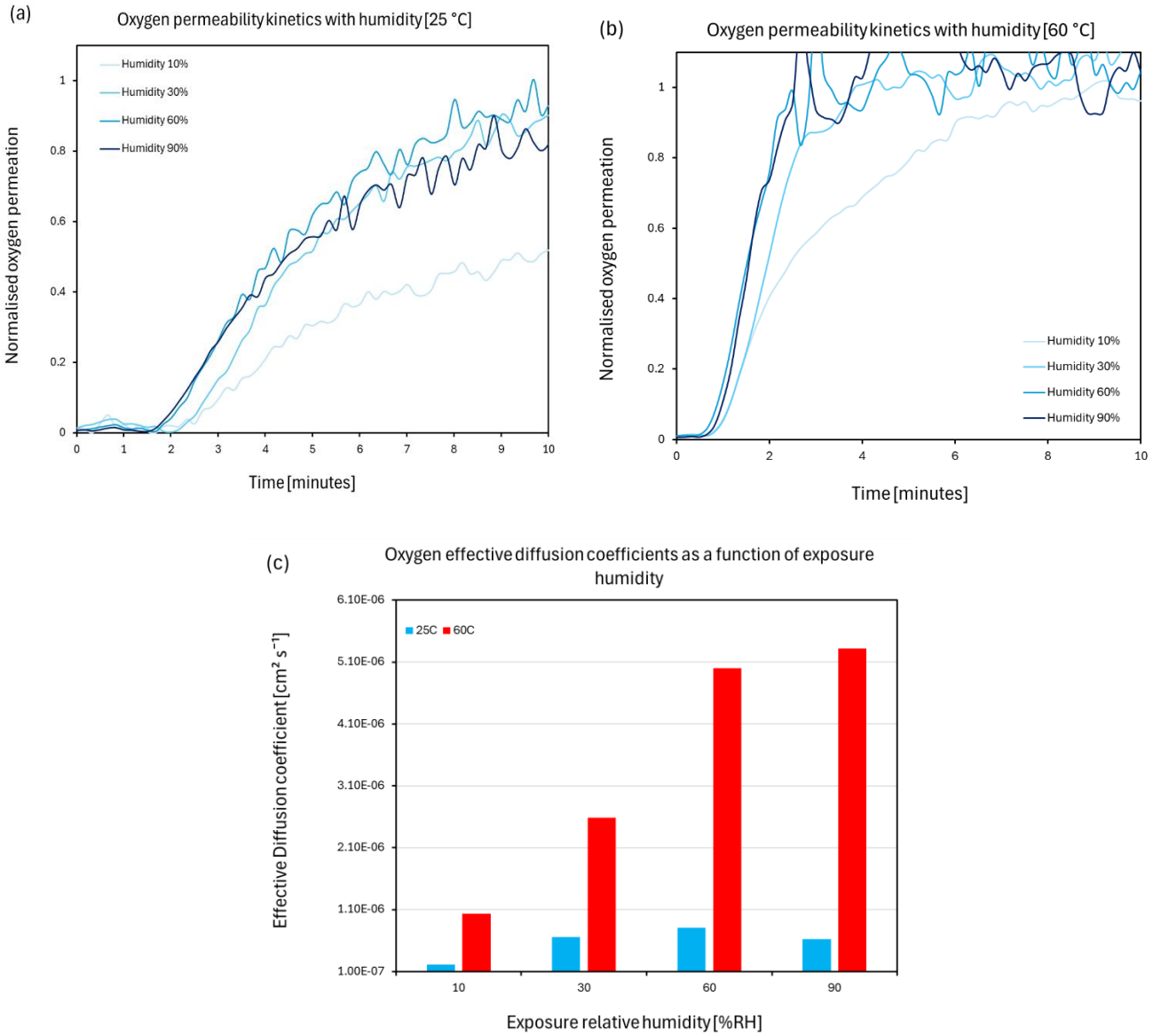

Figure 6. Nafion time resolved data obtained for oxygen, as a function of %RH at 25 °C (a) 60 °C (b) and the resulting effective diffusion coefficients (c).

From Figure 6, the oxygen permeation kinetics show a strong dependence on both humidity and temperature. At 25 °C after a 30-minute drying period, increasing relative humidity leads to a faster approach to steady state, with low humidity (10 % RH) resulting in slower kinetics indicating limited membrane hydration. At 60 °C after a 30-minute drying period, permeation occurs much more rapidly across all humidities, with the curves reaching steady state earlier and converging at high RH, reflecting accelerated diffusion and faster membrane humidity equilibration. The convergence trend at high %RH aligns with the trend in the OTR data. Analysis of the time-resolved data, via Equation 3, yields effective oxygen diffusion coefficients that increase systematically with humidity and temperature. Diffusion coefficients are an order of magnitude higher at 60 °C than at 25 °C and tend to plateau above ~60 % RH, consistent with the formation of a fully hydrated, well-connected ionic domain network in Nafion. These diffusion coefficients match well with those observed in literature.[5]

Conclusion

This application note demonstrates how the hydration state of Nafion fundamentally governs its mass-transport behavior under conditions relevant to practical electrochemical devices. DVS measurements show that water uptake is highly non-linear with relative humidity and kinetically limited at low humidity, indicating slow bulk hydration and microstructural reorganization of ionic domains. These hydration effects directly translate into membrane transport properties.

Simultaneously, as observed by the MPA Horizon membrane permeability analyzer, water vapor transmission rates increase strongly with humidity and temperature but level off at high relative humidity, particularly at 60 °C, consistent with the membrane approaching a fully hydrated, diffusion-limited regime. Oxygen transmission measurements reveal analogous behavior, with higher humidity and temperature leading to increased permeation and faster equilibration. Time-resolved oxygen permeation kinetics are well described by the long-time solution of Fickian diffusion, enabling extraction of effective oxygen diffusion coefficients. These coefficients increase by more than an order of magnitude with hydration and temperature and plateau at high relative humidity, reflecting the formation of a well-connected ionic network.

Collectively, the results highlight the strong coupling between hydration dynamics and gas and vapor transport in Nafion. Understanding these relationships is essential for predicting water management, gas crossover, and transient performance in fuel cells, electrolyzers, and related membrane-based technologies.

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