Compressive Creep of Polymer Electrolyte Membranes: A Case Study for Electrolyzers

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Abstract

For proton-exchange membrane (PEM) water electrolyzers to be commercially feasible, PEMs must perform over long lifetimes in liquid environments under compression while maintaining mechanical stability. Hydrated environment, while inherent for operation and conductivity, undermines PEM stability. Mechanical stability of PEMs is commonly characterized in tension, which is not applicable to electrolyzers, wherein PEMs could undergo high pressures. In this study, a compression creep procedure is developed using a custom-designed setup to monitor creep response of hydrated PEMs. Our results show PEMs exhibit continuous creep response under compression over 24 hours, with a dependence on the applied pressure and hydration state.

Keywords: compression, electrolyzer, creep, ionomer, mechanics, hydration

Proton-exchange membrane (PEM) water electrolyzers (PEMWEs) are a promising clean energy technology for electrochemical generation of hydrogen by splitting water. PEMWEs use an ion-conductive polymer, or ionomer, membrane to conduct protons from the anode to cathode while inhibiting crossover of electrons and product gases (O_2, H_2). PEMWEs

offer a variety of end-uses in industry and power generation because hydrogen is essential to many industrial applications, such as turbine blanketing gas, semiconductors, heat treating, and submarines for O_2, and industrial gas applications. Hydrogen's energy capacity can be directly used in PEM fuel cells (PEMFCs).

Electrolyzers provide decarbonized hydrogen unlike methane reforming, currently the most common method of industrial hydrogen gas production.[1] For electrolyzers to compete with methane reforming, capital cost of these devices must be reduced.[1,2] To achieve cost reduction, thinner, more durable membranes are needed.[2–5] Improved durability of thinner PEMs is important for cost reduction of PEM electrolyzers[3,4,6] because PEMs must perform over 80,000 hours in electrolyzers in liquid environments according to the Department of Energy's hydrogen program goals.[7] Currently, most PEMWEs are operated at 1.5 - 3.0 MPa (15 - 30 bar) differential pressure and 30 - 50 °C.[3] However, higher pressure (> 35 MPa or 350 bar) and high temperature (>50 °C) operation is desirable for PEM electrolysis.[2,4,5,8] Higher pressure allows electrolyzers to deliver hydrogen at a high pressure to the end user thus reducing the additional compressor cost and energy needed to compress and store the gas.[2,4,8] High pressure operation also allows for design flexibility for optimizing product gas removal.[2,4,9] However, operating at high differential pressure across the active area increases the required sealing pressures to prevent off-board leaks, thus further increasing the internal compressive stresses experienced by the active area of the electrolyte.[8] High pressure acting on the active area in PEMWE makes compressive creep a great concern which could impact the interfacial resistance between the membrane and the electrodes.[2,10] From a PEM perspective, high pressure deteriorates efficiency by increasing gas crossover (product loss) and induces larger stresses in the membrane which may compromise their mechanical stability.[2,4,5,9] For this reason, industry has favored thicker membranes in PEMWEs, however, this increases the capital and operating cost since the electrical expense increases due to higher voltages resulting from the increase in ohmic resistance. Therefore, to overcome the challenges of improving PEMWE performance and durability, one must develop an accurate

way of assessing PEM mechanical stability by accounting for the effect of compression.

The prototypical PEM in acid-based low-temperature electrolyzers is perfluorosulfonic acid (PFSA) due to its mechanical and chemical stability and high ionic conductivity.[11] Most previous studies on the mechanical stability of PFSAs investigated its mechanical properties only in tension.[11] However, in electrochemical devices, membranes undergo compression loads arising from a combination of assembly loads (pressures) and hydration-driven expansion within the constraints of the device geometry and edge effects, as discussed to a large extent in the fuel-cell literature.[12,13] Compression behavior, however, is even more critical for understanding membrane behavior and durability in electrolyzers, where the PEM experiences a high-pressure, hot liquid environment during longer operating times. Furthermore, creep failure has been observed in Nafion-type membranes, especially at elevated temperature such as 80 °C.[2,10] Thus, for electrolyzers, it is even more imperative that creep be studied in a compressive mode, especially in water, as this is more relevant to device operation and will inform device lifetime.

The tensile stress-strain response of PFSA membranes is widely-studied and known to be highly sensitive to the surrounding environment, particularly, temperature and hydration.[11,14–19] However, as shown in Figure 1b, the monotonic stress-strain response of PFSA is very different between tension and compression. In tension, the membrane exhibits a stress-strain response typical of semi-crystalline polymers; a linear elastic region followed by strain hardening after the onset of yielding, ending with failure. In compression, a monotonic, nonlinear increase in stress is observed. For a given strain, the membrane experiences much higher stress under compression than in tension. These findings indicate that creep behavior will also be disparate between the two stress-states.

It should be noted that this comparison between tension and compression is performed on Nafion 212, a dispersion-cast membrane, which is more commonly used in fuel-cell studies, whereas electrolyzer studies predominantly use the thicker Nafion membranes (N11x series, where x=5, 7, 10).[2,3,11] Extruded membranes exhibit anisotropy in their mechani-

cal properties, primarily between the extruded "machine" direction and the transverse direction.[11,14,18,20,21] This anisotropy in mechanical properties could be linked to the intrinsic structural anisotropy in membranes observed via x-ray scattering studies.[12,13,21] Cast membranes, on the other hand, have been shown to be less anisotropic in the plane, both structurally and mechanically.[12,21,22] Moreover, morphological domain-alignment occurring in Nafion membranes, whether induced intrinsically through manufacturing (cast vs. extruded) or externally through (pre/post)stretching, is related to anisotropy observed for transport properties, such as diffusion and conductivity.[11–13,22–24] However, it was also shown that, any intrinsic morphological anisotropy in Nafion membranes, especially in an extruded one, can be reduced upon boiling in water, which serves as part of a pretreatment procedure commonly employed in Nafion membrane studies.[11,12,21] Therefore, a dispersion-cast Nafion is selected to clearly demonstrate the disparity between tension and compression, but in the following, for the purposes of investigating the compression creep relevant to electrolyzer conditions, extruded Nafion 11x series will be employed in pretreated form (see supporting information (SI) for details on sample preparation).

In this study, we have developed a novel technique to study the creep compression of PEMs *in-situ* with controlled temperature and hydration, from ambient (referred to as dry, 40-55% RH, 25-30 °C) to hydrated fully with liquid water (referred to as wet). The set-up, inspired from a design by Budinski et al.[25] and prior works of Kusoglu et al.,[12,13,26] is shown in Figure 1a and the experimental procedure explained in the SI.

Creep occurs when a material held under a constant stress over time generates a strain response. For a perfectly elastic material with no time-dependent response, no creep would occur. Creep deformation in polymers is governed by the time-dependent changes in their morphology due to segmental mobility of polymer chains or relaxation of the network in response to constant load. In ionomers, creep response is also dependent on the hydration-driven dynamic changes in the structure, as previously shown for PFSAs under tension.[11,15,27–29]

*During a wet compression test, the membrane is in a bath of liquid DI water whereas in wet tension, the membrane was fully hydrated just prior to the experiment

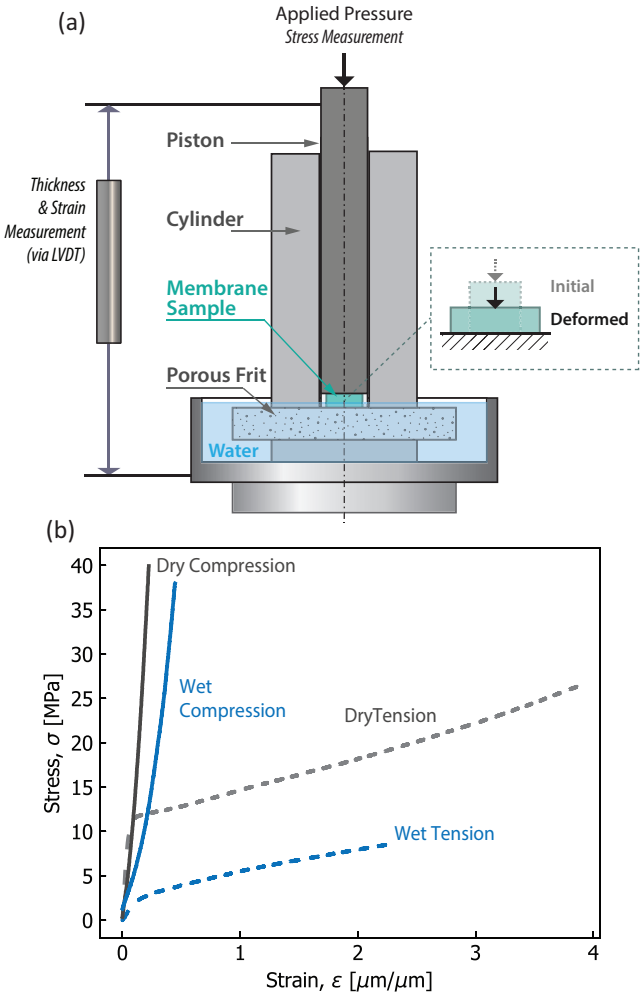

Figure 1: (a) Custom experimental compression setup with liquid water chamber. (b) Monotonic compression and tension of Nafion 212 in dry (ambient RH) and wet (fully hydrated) states. In tension, dry Nafion 212 exhibits a characteristic elastic-plastic response with an onset of non-linearity at 10 MPa, followed by strain hardening. In compression, however, the response is stiffer and nonlinear without a discernible yield point. Hydration of the membrane reduces its stiffness in both compression and tension mode while still preserving the characteristic response for each mode.*

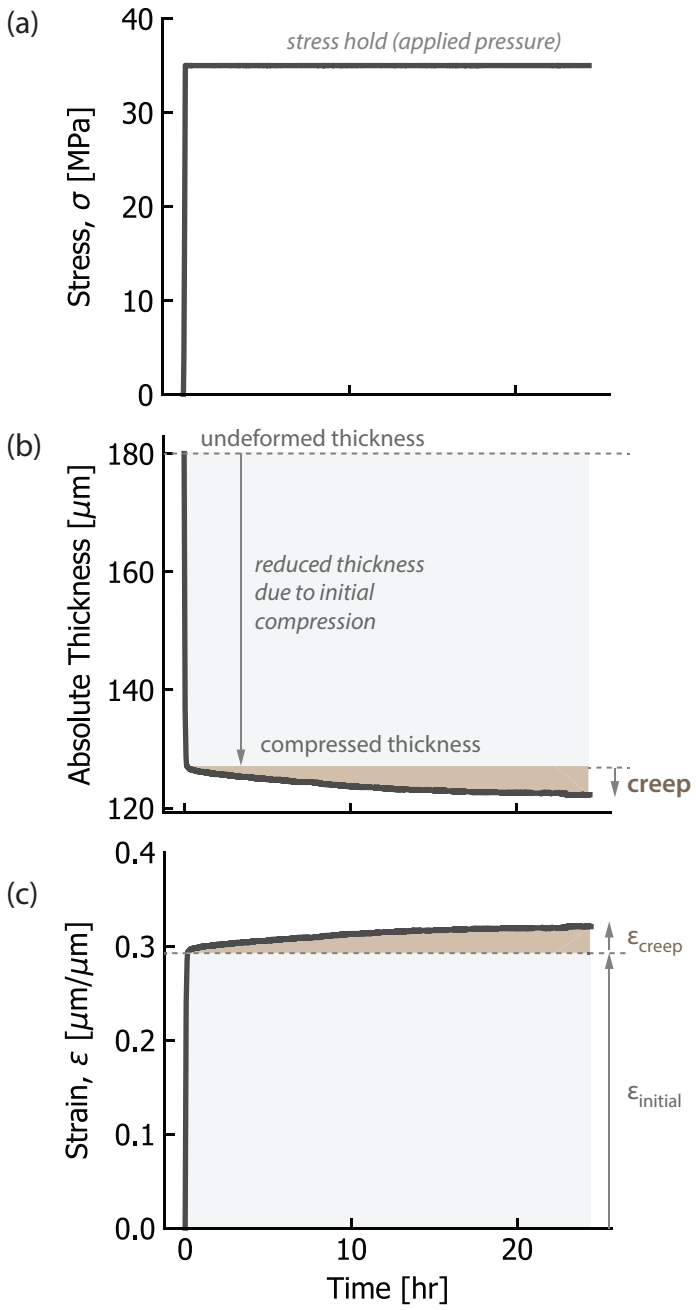

Figure 2: Compressive creep response of Nafion 117 PB for 24 hours at 35 MPa (350 bar). (a) The applied stress over time as the controlled input into the system. A quick ramp is applied followed by a constant load at 35 MPa (held for creep). (b) The measured output as the reduced membrane thickness over time due to compression (ramp) and then creep (hold). (c) The resulting compressive strain in the sample, which is defined positive. The ramp generates an initial strain, and then as the load is held, the thickness reduces over time corresponding to a positive increase in the strain, which is the creep strain.

While it has not been measured previously, creep is expected to occur in a compressed PFSA as well.[2,10] PFSA ionomers have a phase-separated nanostructure resulting from the molecular hydration of their ionic groups forming hydrophilic nano-domains separated by the hydrophobic fluorocarbon backbone. While the hydrophilic domains impact PEM's ion and water transport functionality across time and length-scales, the overall phase-separated structure governs mechanical properties.[11] This dynamic, chemically-heterogeneous structure of PFSA also makes its mechanical behavior dependent on time, temperature, and hydration.[11,14–19,28,29] Thus, to better mimic the environment an ionomer undergoes in an electrolyzer, creep response of PFSA is monitored under compression, as shown in Figure 2. Under a compression-type load, a compressive strain, or initial strain ($\varepsilon_{initial}$), develops in the membrane. When the applied stress is held constant, the membrane thickness decreases further over time, indicating creep response. The change in strain over time represents the creep strain (ε_{creep}). The total strain can therefore be decomposed into the initial and the creep strain as:

$$\varepsilon_{total} = \varepsilon_{initial} + \varepsilon_{creep}. \tag{1}$$

Building upon the compelling evidence for compressive creep in PFSA, in the following, we investigate the effect of hydration, applied pressure, and thickness.

Figure 3a shows compression creep of Nafion 117 at two pressure levels in dry and wet states at 25 °C. It is relevant to note that strain is normalized with respect to initial thickness of the membrane in the equilibrium condition (either wet or at ambient conditions). In the wet state, there is a highly transient primary creep stage for the first hour, where approximately 80% of the creep strain develops (Figure 3b). Then, a period of slower creep ensues. Whereas, for the dry case, creep strain develops more linearly over time. Table 1 shows the creep strain and displacement rate over the whole length of the experiments. By splitting the creep into two stages, 0-1 hr and 1-24 hr, additional comparison can be made. In the secondary state, the dry membrane under 35 MPa exhibits the highest creep strain rate, $\dot{\varepsilon}_{creep} = 1.30 \times 10^{-3}$ hr^{-1}, whereas the wet membrane at 35 MPa exhibits the

lowest creep strain rate, $\dot{\varepsilon}_{creep} = 0.484 \times 10^{-3}$ hr^{-1}. At the high and low creep strain rate, this corresponds to approximately a 7.4 and 2.2 μm change in thickness over 23 hours, respectively. Therefore, a wet membrane exhibits a higher creep resistance, after the first hour, than the dry membrane. Additionally, the total creep decreases with increasing stress when the membrane is wet. Thus, increasing hydration reduces the magnitude of creep occurring in PFSAs under compression: the higher the pressure, the lower the thickness change due to creep. This is an important outcome for PEM mechanical stability in high-pressure electrolyzers as the membranes undergo higher stresses in hydrated conditions.

Table 1: Creep strain and displacement rates for the experiments on Nafion 117.

Hydration State	Applied Pressure [MPa]	Length of Experiment [hr]	Creep Strain Rate $\times 10^3$ [(μm/μm)/hr]	Creep Displacement Rate [μm/hr]
Dry	5	120	0.634	0.096
Dry	5	24	0.979	0.148
Dry	35	24	1.72	0.219
Wet	5	24	2.81	0.473
Wet	10	24	3.83	0.646
Wet	15	24	3.20	0.402
Wet	35	24	2.32	0.257

Figure 4a shows the effect of the applied compression load (pressure level) on the creep response of hydrated Nafion membranes at 25 °C. With increasing stress, the initial and total strain increase monotonically, as expected (Figure 4b). However, the creep strain decreases with increasing stress. This could be attributed to the hindered mobility of ionomer aggregates and backbone chains under higher pressures in a phase-separated morphology wherein less compressible water domains are trapped. When the hydrated ionomer is held compressed, the ability of the polymer chains to accommodate the deformation by changing their conformation is suppressed. It has been observed that membrane domain spacing becomes smaller in the direction of applied pressure and elongate in the plane of the membrane to accommodate the nanostructural orientation effects.[12] In addition, resistance to nanoscale deformation caused by the load-bearing hydrophobic domains is exacerbated further by the additional restrictions imposed by the hydrophilic domains filled with incompressible water.

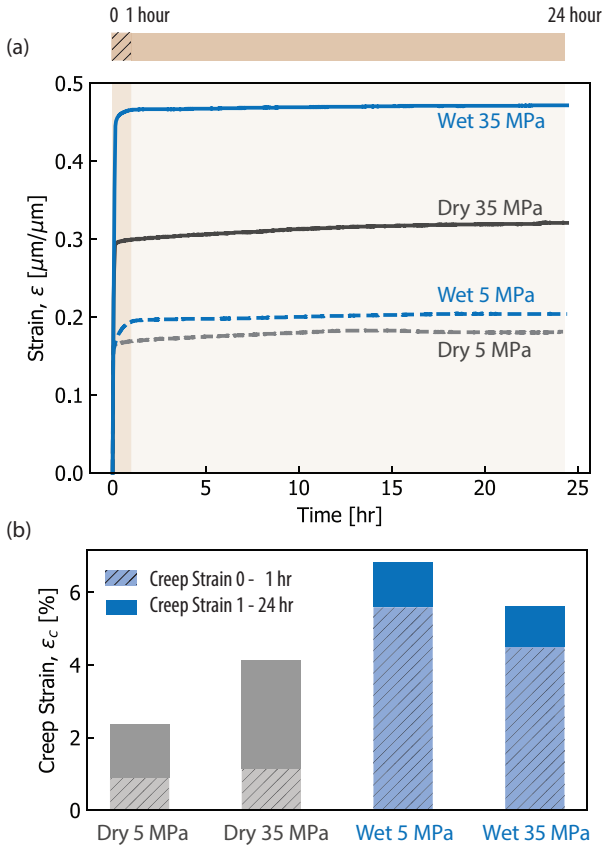

Figure 3: (a) Compression creep of pretreated Nafion 117 at 5 and 35 MPa and in dry and wet conditions. (b) Creep strain of these tests with the creep strain of the first hour in blue and the creep strain after the first hour in orange.

These hydrophilic domains act, mechanically, as occlusions, thereby increasing the creep stiffness of the structure, and reducing creep strain.

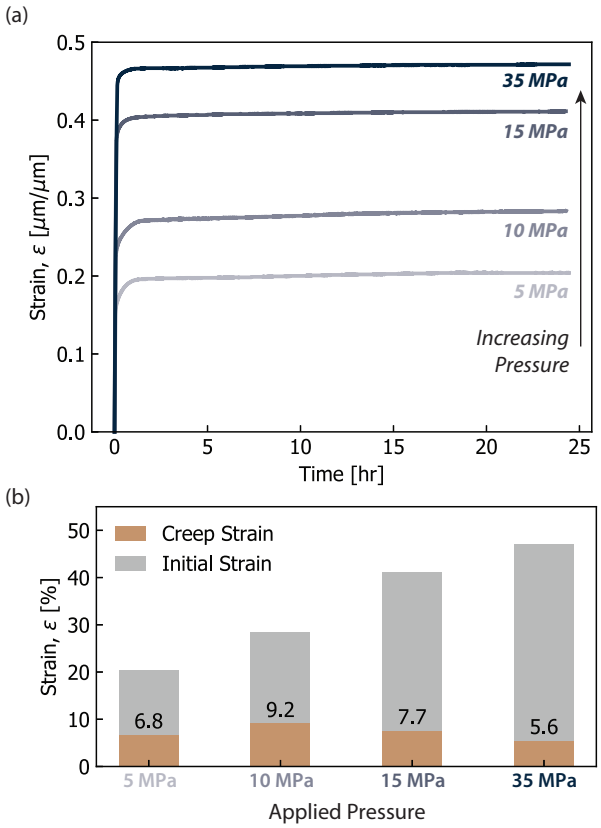

Figure 4: (a) Compression creep of wet preboiled Nafion 117 at 5, 10, 15, and 35 MPa of applied stress. The 5 MPa and 35 MPa curves are also shown in Figure 3. (b) The total strain decomposed into creep strain and initial strain as a function of applied stress. With increasing stress, the initial strain increases, but the creep strain decreases. The tan and gray color for creep and initial strain correspond to the colors used in Figure 2.

Membrane thickness is a key design parameter that directly contributes to the Ohmic resistance in the cell. Thus, it is of interest to understand how reducing thickness for improved ohmic losses would impact creep behavior. Table 2 shows the results from the creep compression on three hydrated membranes with different thicknesses: Nafion 1110 (250 μm), 117 (175 μm), and 115 (125 μm). Thickness should not affect intrinsic response of a polymer but it could affect the creep compliance because of geometric factors. In a hydrated state, the thinnest membrane creeps the least with 5.58% creep strain over 24 hours.

The findings in this study demonstrate that mechanical response of PEM during mono-

Table 2: Creep strain, creep strain rates, and creep displacement rates for preboiled Nafion 1110, 117, and 115. The conditions of the experiments are wet, 35 MPa, at 25 °C, and held for 24 hours

Material Name	Nominal Thickness [μm]	Creep Strain [%]	Creep Strain Rate $\times 10^3$ [(μm/μm)/hr]	Creep Displacement Rate [μm/hr]
Nafion 1110	250	5.67	2.36	0.392
Nafion 117	175	5.60	2.32	0.257
Nafion 115	125	5.58	2.22	0.127

tonic loading changes dramatically from tension to compression, a mode that is not widely studied despite its relevance to energy devices. Using a custom-designed *in situ* compression setup, creep response of PEMs is demonstrated using PFSA membranes in both dry and hydrated states. Creep is observed to occur over 24 hours and beyond (at least five days as shown in Table 1) and exhibits dependence on hydration, membrane thickness, and applied pressure levels. In hydrated state, Nafion membranes exhibit a creep strain rate of 0.2-0.3% change in thickness per hour, depending on the pressure level. During creep compression, a hydrated PFSA is more resistant to creep but exhibits a stronger dependence on stress level. These findings translate into suppressed thickness reduction in the membrane under high-compression regions, and possibly a non-uniform thickness change over time during cell operation. Considering that membranes in electrolyzers must be optimized for thickness, cost, performance, and mechanical stability over long times, these results show operating parameters, such as pressure and hydration, could have significant impact on membrane durability, with key implications also for membrane conductive resistance.

For example, Kaddouri et al.[30] have studied the effects of static compressive stress on an extruded Nafion membrane's water self-diffusion and have demonstrated a reduced diffusion in the direction of applied compression (up to 10 MPa), particularly at higher humidities ($\geq$ 95% RH). This anisotropy in diffusion is attributed to the structural changes within the membrane, which is expected to increase further at higher pressures accessed in this study. At higher pressures, the deformation may be irreversible and thus, a plastic deformation of the membrane would exhibit a permanent reduction in water sorption. Kusoglu et al.[12]

have demonstrated that as the membrane is compressed, its water content decreased and its hydrophilic domain spacing inferred from SAXS studies decreases in the direction of the applied load, thereby affecting the proton conductivity within the membrane. The conductivity decreases with increasing pressure especially at higher humidities and in liquid water, in agreement with the nanostructural orientation observed under those conditions.

In summary, mechanical compression creates a unique environment for PEMs, especially under high-compression loads and in hydrated state, as is the case in electrolyzer devices. On one hand, continuous creep reported in this work reduces the membrane thickness, thereby possibly altering the membrane-electrode interface and overall Ohmic resistance over time. On the other hand, based on prior studies denoting a strong morphological link between transport properties and morphological changes, such as intrinsic orientation and domain-alignment due to deformation, one would also anticipate changes in water content and transport properties under compression load. These affects altogether impact membrane performance and stability in an electrolyzer device. Hence, this study has shown that mechanical stability for electrolyzer membranes could be characterized using compression loads and creep, which would have implications not only for longevity of PEMs, but also for their properties relevant to operation.

This work demonstrates that characterizing the mechanical response of polymer-electrolyte membranes under conditions relevant to device operation, such as compressive creep rate, is important and must be accounted for in material research for energy and environmental devices. Also, state-of-the-art PEMs are being challenged to operate at higher temperatures and stresses in an effort to further improve device efficiency and reduce operating costs to address the needs of emerging energy challenges. Therefore, future investigations could explore the effects of various operating environments on the creep response and mechanical stability of electrolyte membranes, and factors related to cell assembly conditions and device design.

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Supporting Information Available

Associated Content: Full experimental methods are provided in detail in Supporting Information.

References

(1) Ayers, K. E.; Renner, J. N.; Danilovic, N.; Wang, J. X.; Zhang, Y.; Maric, R.; Yu, H. Pathways to ultra-low platinum group metal catalyst loading in proton exchange membrane electrolyzers. *Catalysis Today* **2016**, *262*, 121–132.

(2) Ayers, K. E.; Anderson, E. B.; Capuano, C.; Carter, B.; Dalton, L.; Hanlon, G.; Manco, J.; Niedzwiecki, M. Research Advances towards Low Cost, High Efficiency PEM Electrolysis. *ECS Transactions* **2010**, *33*, 3–15.

(3) Danilovic, N.; Ayers, K. E.; Capuano, C.; Renner, J. N.; Wiles, L.; Pertoso, M. (Plenary) Challenges in Going from Laboratory to Megawatt Scale PEM Electrolysis. *ECS Transactions* **2016**, *75*, 395–402.

(4) Carmo, M.; Fritz, D. L.; Mergel, J.; Stolten, D. A comprehensive review on PEM water electrolysis. *International Journal of Hydrogen Energy* **2013**, *38*, 4901–4934.

(5) Babic, U.; Suermann, M.; Büchi, F. N.; Gubler, L.; Schmidt, T. J. Critical Review—Identifying Critical Gaps for Polymer Electrolyte Water Electrolysis Development. *Journal of The Electrochemical Society* **2017**, *164*, F387–F399.

(6) Suermann, M.; Bensmann, B.; Hanke-Rauschenbach, R. Degradation of Proton Exchange Membrane (PEM) Water Electrolysis Cells: Looking Beyond the Cell Voltage Increase. *Journal of The Electrochemical Society* **2019**, *166*, F645–F652.

(7) Department of Energy, *Department of Energy Hydrogen Program Plan*; 2020; pp 1–51.

(8) Cropley, C. C.; Norman, T. J. Low-Cost High-Pressure Hydrogen Generator. **2008**, N.p.

(9) Aricò, A. S.; Siracusano, S.; Briguglio, N.; Baglio, V.; Di Blasi, A.; Antonucci, V. Polymer electrolyte membrane water electrolysis: Status of technologies and potential applications in combination with renewable power sources. *Journal of Applied Electrochemistry* **2013**, *43*, 107–118.

(10) Stucki, S.; Scherer, G. G.; Schlagowski, S.; Fischer, E. PEM water electrolysers: Evidence for membrane failure in 100 kW demonstration plants. *Journal of Applied Electrochemistry* **1998**, *28*, 1041–1049.

(11) Kusoglu, A.; Weber, A. Z. New Insights into Perfluorinated Sulfonic-Acid Ionomers. *Chemical Reviews* **2017**, *117*, 987–1104.

(12) Kusoglu, A.; Hexemer, A.; Jiang, R.; Gittleman, C. S.; Weber, A. Z. Effect of compression on PFSA-ionomer morphology and predicted conductivity changes. *Journal of Membrane Science* **2012**, *421-422*, 283–291.

(13) Kusoglu, A.; Savagatrup, S.; Clark, K. T.; Weber, A. Z. Role of Mechanical Factors in Controlling the Structure–Function Relationship of PFSA Ionomers. *Macromolecules* **2012**, *45*, 7467–7476.

(14) Kusoglu, A.; Tang, Y. L.; Lugo, M.; Karlsson, A. M.; Santare, M. H.; Cleghorn, S.; Johnson, W. B. Constitutive response and mechanical properties of PFSA membranes in liquid water. *Journal of Power Sources* **2010**, *195*, 483–492.

(15) Satterfield, M. B.; Benziger, J. B. Viscoelastic properties of nafion at elevated temperature and humidity. *Journal of Polymer Science, Part B: Polymer Physics* **2009**, *47*, 11–24.

(16) Tang, Y.; Karlsson, A. M.; Santare, M. H.; Gilbert, M.; Cleghorn, S.; Johnson, W. B. An experimental investigation of humidity and temperature effects on the mechanical properties of perfluorosulfonic acid membrane. *Materials Science and Engineering: A* **2006**, *425*, 297 – 304.

(17) Kawano, Y.; Wang, Y.; Palmer, R. A.; Aubuchon, S. R. Stress-Strain Curves of Nafion Membranes in Acid and Salt Forms. *Polímeros* **2002**, *12*, 96–101.

(18) Kusoglu, A.; Tang, Y.; Santare, M. H.; Karlsson, A. M.; Cleghorn, S.; Johnson, W. B. Stress-strain behavior of perfluorosulfonic acid membranes at various temperatures and humidities: Experiments and phenomenological modeling. *Journal of Fuel Cell Science and Technology* **2009**, *6*, 0110121–0110128.

(19) Silberstein, M. N.; Boyce, M. C. Constitutive modeling of the rate, temperature, and hydration dependent deformation response of Nafion to monotonic and cyclic loading. *Journal of Power Sources* **2010**, *195*, 5692 – 5706.

(20) Tang, Y.; Kusoglu, A.; Karlsson, A. M.; Santare, M. H.; Cleghorn, S.; Johnson, W. B. Mechanical properties of a reinforced composite polymer electrolyte membrane and its simulated performance in PEM fuel cells. *Journal of Power Sources* **2008**, *175*, 817–825.

(21) Elliott, J.; Hanna, S.; Newton, J.; Elliott, A.; Cooley, G. Elimination of Orientation in Perfluorinated Ionomer Membranes. *Polym Eng Sci* **2006**, *46*, 228–234.

(22) Li, J.; Wilmsmeyer, K. G.; Madsen, L. A. Anisotropic diffusion and morphology in perfluorosulfonate ionomers investigated by NMR. *Macromolecules* **2009**, *42*, 255–262.

(23) Park, J. K.; Li, J.; Divoux, G. M.; Madsen, L. A.; Moore, R. B. Oriented morphology and anisotropic transport in uniaxially stretched perfluorosulfonate ionomer membranes. *Macromolecules* **2011**, *44*, 5701–5710.

(24) Mendil-Jakani, H.; Pouget, S.; Gebel, G.; Pintauro, P. N. Insight into the multiscale structure of pre-stretched recast Nafion® membranes: Focus on the crystallinity features. *Polymer* **2015**, *63*, 99–107.

(25) Budinski, M. K.; Cook, A. Osmotic Pressure of Water in Nafion®. *Tsinghua Science and Technology* **2010**, *15*, 385–390.

(26) Kusoglu, A.; Kienitz, B. L.; Weber, A. Z. Understanding the Effects of Compression and Constraints on Water Uptake of Fuel-Cell Membranes. *Journal of The Electrochemical Society* **2011**, *158*, B1504.

(27) Majsztrik, P. W.; Bocarsly, A. B.; Benziger, J. B. Viscoelastic response of nafion. effects of temperature and hydration on tensile creep. *Macromolecules* **2008**, *41*, 9849–9862.

(28) Zhang, Z.; Tian, C.; Yuan, Z.; Li, J.; Wu, W. P.; Xia, R. Temperature and loading sensitivity investigation of nanoindentation short-term creep behavior in Nafion®. *Materials Research Express* **2019**, *6*, 055304.

(29) Satterfield, M. B.; Majsztrik, P. W.; Ota, H.; Benziger, J. B.; Bocarsly, A. B. Mechanical Properties of Nafion and Titania/Nafion Composite Membranes for Polymer Electrolyte Membrane Fuel Cells. *Journal of Polymer Science: Part B: Polymer Physics* **2006**, *44*, 2327–2345.

(30) El Kaddouri, A.; Perrin, J.-C.; Colinart, T.; Moyne, C.; Leclerc, S.; Guendouz, L.; Lottin, O. Impact of a Compressive Stress on Water Sorption and Diffusion in Ionomer

295 Membranes for Fuel Cells. A 1H NMR Study in Vapor-Equilibrated Nafion. *Macro-*
296 *molecules* **2016**, *49*, 7296–7307.

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