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Risks in the Implementation of Hydrocarbon Replacements for Fluoropolymer Ionomers – Chemours™ July 2023 (A. Plymill et al.)

EXECUTIVE SUMMARY

Purpose

- A restriction proposal has been submitted requesting the broad removal of per- and polyfluoroalkyl materials as a group.
- This proposal suggested that there is strong evidence for hydrocarbon replacements for these materials in hydrogen applications.
- Aside from their ubiquitous application throughout hydrogen applications, we intend to refute this claim with regard to membranes and electrode binders for fuel cells and electrolyzers.

Key Findings

- Hydrocarbon membrane alternatives fail prematurely due to a combination of mechanical and chemical degradation modes.
- Hydrocarbon membranes are innately vulnerable to hydroxide attack as only the carbon-fluorine bond is resilient to the prevalent radical.
- Hydrocarbon ionomers necessitate drastically higher water uptake to achieve similar conductivity leading to higher swelling and decreased toughness.
- Hydrocarbon ionomers rely on a structure built off of a stiff aromatic backbone, leading to brittle behavior, particularly under dry conditions.
- Hydrocarbon binders have a worse property set that innately harms electrode performance. Lack of reactant and product permeability, excessive swelling, insufficient conductivity, poor electrode dispersity, catalyst poisoning, and detachment tendencies lead to poor performance and durability.
- Alkaline versions of hydrocarbon membranes face a host of additional challenges while simultaneously failing to demonstrate durable benefits of their purported platinum group metal free catalyst compatibility.

Solutions

- Technologies to implement a hydrogen economy will be hamstrung if not completely halted without the capacity to use fluoropolymers of low concern.
- As an alternative to banning these materials, we need to look towards practices of product stewardship to ensure that these materials can be made, used, and recycled or discarded in a safe and environmentally friendly manner.

Risks in the Implementation of Hydrocarbon Replacements for Fluoropolymer Ionomers

Abstract

Technology critical to enabling hydrogen production and usage targets set by national governments heavily rely on fluoropolymers to enable their function in a competitive fashion. Their mechanical, ionic, electronic, structural, durability, thermal, and wetting properties lead to their ubiquitous application in hydrogen technologies that must withstand challenging thermodynamic environments while maintaining superior functional properties. Hydrocarbon alternatives have been proposed to supplant the ionically conducting fluoropolymers currently enabling fuel cell and water electrolysis technologies. These materials suffer from mechanical brittleness, insufficient chemo-mechanical durability, excessive water uptake, catalyst poisoning, and electrode diffusion limitations to the extent that commercially relevant implementation is challenging. Instead of banning a materials class critical to the function of hydrogen technology applications irrespective of the actualized health and environmental risk profile, this moment serves as an opportunity to demonstrate product stewardship where materials should be appropriately managed throughout their life cycle of production, implementation, and end of life.

Introduction

Five European countries have submitted a restriction proposal that seeks a broad ban of per- and polyfluoroalkyl materials as a group. This proposal explicitly calls for not considering the method of manufacturing, material properties themselves of concern criteria, the possibility of harmful exposure in use of application, or material end of life considerations[1]. Without the capacity to delineate between materials for their actualized health and environmental impact, this indiscriminate grouping would jeopardize water electrolysis and fuel cell technologies which rely on a host of fluoropolymer materials for effective, durable use including in membranes, reinforcements for membranes, electrode binders, gas diffusion layers, coating materials, sealants, and gaskets.

The currently proposed approach which chooses to disregard specific hazard profiles of materials and availability of readily available alternatives risks causing socioeconomic, industrial, energy security, and environmental damage. This proposal suggests that the worst impacts of this restriction on hydrogen for the energy sector might be potentially mitigated by the availability of non-fluoropolymer alternatives. Herein, we look to assess the claim of the dossier that there is "sufficiently strong evidence" for material alternatives for use in membranes and reinforcements [1]. Hydrocarbon materials will be evaluated as they have been the sole material class that has been proposed as a replacement.

Ion Exchange Membranes for Fuel Cells

The namesake critical component for polymer electrolyte membrane fuel cells (PEMFCs) is the ion exchange membrane. This membrane must maintain a broad set of properties to enable the critical function requirements of this component including high ionic conductivity, high electrical resistivity, low gas permeability, and high durability. Durability is a particular challenge for this application as a relatively thin polymer membrane (<20 μm to ensure adequate ion conduction[2]) must withstand an aggressive hygrothermal and chemical environment under a range of operating potentials with transient operation. Significant levels of pressure and swelling will place significant mechanical stressors on the membrane. This component needs to survive under these conditions for greater than 10 years of operation and greater than 8,000 hours of operation which probe this range of environmental survivability including transient operating modes, startup and shutdown activity, and freeze/thaw cycling[3].

Despite over half a century of research investigating alternative polymer electrolyte membranes, fluorinated ionomers continue to serve as the prevailing membrane of choice due to their high ionic conductance coupled with its chemically and mechanically robust structure that is highly electrically insulative and inhibits significant cross-diffusion of gaseous species[4]. This unique combination of a highly resilient material that also possesses a high ionic conductivity lies in the coupling

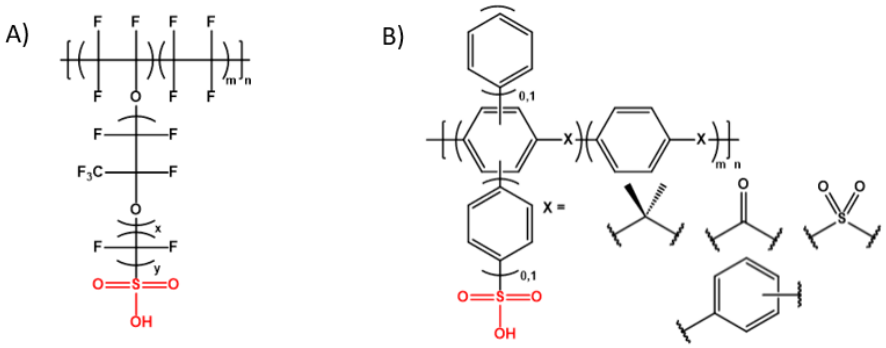

Figure 1. Prototypical structures of acidic polymer electrolytes. A) Shows the fluorinated PEM employing a hydrophobic PTFE backbone with a distinct hydrophilic side chain ending with a sulphonic group while B) shows the general structural model for hydrocarbon-based model for PEMs relying on a network of rigid aromatic groups with a degree of sulphonic groups attached at some ends.

of the highly robust, inert polytetrafluoroethylene (PTFE) in the form of a semicrystalline backbone paired with a fixed sidechain ending with a sulfonic pendant ionic group associated with an acidic counterion, as shown in Fig. 1a. The disparate nature of this highly hydrophobic backbone and hydrophilic sidechain naturally lends itself towards a phase segregated structure where the backbone offers the polymer resilience while not impeding rapid ion conduction through solvated sulfonic channels. Carboxylic acid end groups on the polymer backbone are preferred chemical attack vectors leading to commercial membranes being fluorinated to the extent that most of these end groups are replaced with inert C-F bonds[5]. Modern fuel cell membranes are further made mechanically rugged through the incorporation of expanded polytetrafluoroethylene (ePTFE) and resilient to hydroxide radical attack through the incorporation of radical scavengers (e. g. manganese or cerium).

Hydrocarbon-based membranes for fuel cells have been long-sought as an alternative material class as they exhibit lower gas permeability[6] and higher glass transition temperatures[7] dating back to General Electric's development of fuel cells implementing solid hydrocarbon cation exchange membranes in the late 1950's[8]. Many modern hydrocarbon ionomers have structures stemming from the development of a bisphenol-A-derived polyethersulfone[9] in which the ionomer tends to consist of a chain of aromatic units that can be linked by an array of potential functional groups (see Fig. 1b). Despite their desirable lower gas permeability and higher glass transition temperature, hydrocarbon membranes have not been adopted due to the excessive ion exchange capacity required to achieve sufficient ionic conductivity (and ramifications thereof) in addition to insufficient chemical and mechanical durability. Additionally, while higher glass transition might suggest possible higher operating temperature windows, it can also lead to challenges in synthesis, such as needing prohibitively high temperatures for MEA fabrication. Many catalyst-coated membranes involving fluorinated membranes rely on decal transferring electrodes above the glass transition temperature of the membrane allowing for excellent membrane to catalyst interfaces[10].

The origin of higher required ion exchange capacity lies innately lies in the materials and structure properties of hydrocarbon-based ionomers. As hydrocarbon ionomers typically consist of conductive sulfonic groups directly attached to the rigid aromatic backbone, their structure tends to not phase separate into highly conductive regions. This leads to lower proton mobility at the same water volume fraction, which in turn necessitates higher water uptake to achieve comparable ionic conductivity[11-12]. Further exacerbating the issue, decreased dielectric screening[13] and decreasing degree of dissociation in the sulfonic group in hydrocarbon-based ionomers, excess protons will tend to be more strongly bound to the local vicinity of the acidic functional group, further decreasing the proton mobility[11]. This higher water uptake dependence makes conductivity fall off significantly at low relative humidity (where dry and not just wet conditions must be operable for the fuel cell application), leads to hydrocarbon ionomers being structurally brittle under dry conditions and gelatinous

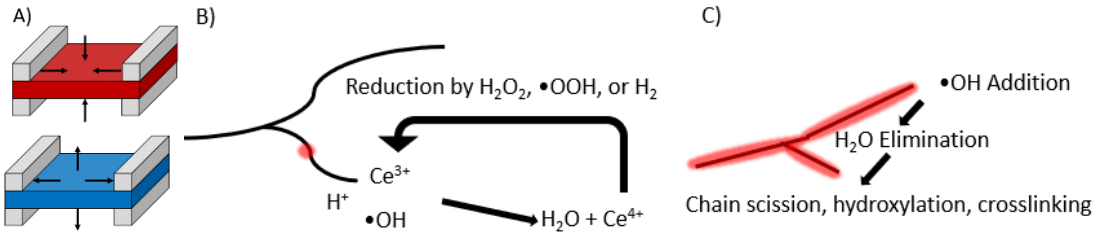

Figure 2. Typical degradative stressors experienced in PEMFC membranes. A) shows in-plane and out-of-plane stresses experienced during shrinkage from drying (with red membrane on top) and swelling from hydration (with blue membrane on bottom). B) shows hydroxide attack on a fluorinated ionomer. As there are few vulnerable sites example highlighted in red for demonstrative purposes), reasonable site density of ceria can easily react with the presence of protons to convert the radical to water and the ceria can be subsequently reduced again. C) The abundance of available fast reacting sites for hydroxide radicals to attack on a hydrocarbon ionomer lead to degradation that is too rapid for a radical scavenger to sufficiently shield against.

under humidified conditions, dilutes local proton concentration at high hydration, and causes an increase in gas permeability as the net permeability will be a mixture between the dry polymer permeability and the significantly higher permeability of pure water [6, 14]. Furthermore, the dimensional swelling from excessive water uptake is challenging from a processing perspective due to the need for reliable dimensional stability, increasing delamination forces in membrane electrode assemblies as well as causing issues from the stresses imbued in assembled stacks[15]. Research from General Motors has suggested that over 100% volumetric swelling of a membrane (in boiling water for one hour) vs. the dry condition is prohibitive from the standpoint of managing internal stack forces on the membrane[16]. Additionally, accumulated stress within the membrane needs to be considered as a function of this dimensional change. In the case that a membrane is clamped, there will be a restriction towards how a material is allowed to expand and contract and this restriction can lead up to the build-up of residual stress[17-18].

Mechanical durability issues that arise particularly for hydrocarbon membranes are highlighted by the ubiquitous failure mode in fuel cell operation experienced by humidity cycling. Constrained membranes will experience in-plane compression while swelling in the wet state and compressing while shrinking dry state as depicted in Fig. 2a. This then drives a fatigue-based failure from the cumulative generated stress eventually leading to pinholes or catastrophic fracture[16]. The capacity of a membrane to withstand these stresses depends both on the toughness of the membrane itself as well as the magnitude of the stresses, which also is dictated by membrane properties. The stress profile is dictated by both steady-state magnitudes of stress-strain related parameters (such as the expansion and modulus of the membrane under different humidity, temperature conditions), but also by the transient state between humidity conditions which is affected by the wetting and drying rate of the polymer as well as the time spent in each of the humidity conditions[19]. Several aspects of hydrocarbon membranes exacerbate these stressors and their impact. The tendency of hydrocarbon-based membrane to experience drastic water uptake with the associated dimensional strain increases the magnitude of experienced stress and the degree of softening. While the high stiffness of hydrocarbon membranes is often lauded as a mechanical performance benefit[20], this higher modulus leads to greater stresses being imparted upon the membrane[2], and additionally the loading can lead to the accumulation of more residual stress[18]. Additionally, the aromatic-based hydrocarbons have a significantly more brittle character than the fluorinated membranes, particularly in the dry state. This inherent brittleness makes hydrocarbon membranes more susceptible to fracture under mechanical stress[21]. Fluorinated ionomers are uniquely enabled to achieve high toughness, fracture energy, and flexibility through the incorporation of the PTFE backbone.

Chemical degradation for PEMFCs has largely stemmed from the from the formation of reactive oxygen species (•OH, •H, and •OOH) that form in appreciable concentrations within the fuel cell environment given the availability of hydrogen, oxygen, and active catalysts[22-23]. The strength of fluorine-bonded groups in PSFA-based ionomers are particularly resilient to most chemical radical attack to

all but the most aggressive reacting species. Among these, it has been found that the hydroxyl radical is particularly destructive due to its high oxidizing potential coupled with the appreciable concentrations of the radical that are formed under fuel cell conditions, though the rate is relatively sluggish (with hydroxyl radicals existing with a half-life on the order of a microsecond)[22-24]. Antioxidant radical scavengers (Cerium and Manganese ions) have been found to be effective at rapidly neutralizing these radical species at low exchange concentrations enabling drastic chemical durability increases with minimal performance impact. Critically, these ions effectively regenerate after eliminating hydroxide ions with species present in the fuel cell environment, enabling the continuous, effective durability enhancement over the fuel cell membrane lifetime[25]. Figure 2b. demonstrates the limited area of attack for oxidizing radicals, coupled with the capacity of a radical scavenger to mitigate and regenerate hydroxyl attack. The chemical durability challenge with hydrocarbon membranes is that the rate of hydroxyl radical attack is vastly more rapid with hydrogen-carbon bonds. Due to the more facile reaction and availability of reaction sites (as depicted in Fig. 2c), hydroxyl radicals attack aromatic groups at a rate of around three orders of magnitude greater than their fluorinated counterparts[26]. Even employing the most effective regenerating scavengers at high concentrations would be insufficient to provide meaningful lifetime extensions due to the nanosecond-scale lifetime of hydroxyl radicals in hydrocarbon membranes[2].

While the previous comparisons well describe the challenges of implementing acidic hydrocarbon membranes vs. their fluorocarbon analogs, alkaline exchanged membrane fuel cells (AEMFCs) based on hydrocarbons have also been attempted with the promise that they might enable compatibility with more earth-abundant catalysts. To date, such fuel cell membranes have had even greater durability concerns than their acidic counterparts due to adding a host of new challenges in addition to the innate challenges with hydrocarbon membranes in general. The predominant challenge lies in the lower stability of organic cations under alkaline conditions versus organic anions in acidic conditions as well as the lower backbone stability at high pH. Significant work has been made to improve the stability of such ionomers as it was recognized that traditional ammonium cation groups were inherently unstable[27] and that ether linkages were primary weak points to alkaline stability[28-29]. This led to the development of more alkaline stable ether-free backbones paired with more stable cationic functional groups such as imidazolium or piperidinium. Despite this advancement in alkaline stability, AEMFCs have failed to demonstrate effective operation over 1,000 hours[30].

One critical yet innate challenge with AEMFCs lies in the instability of the hydroxide anion with atmospheric carbon dioxide. Upon exposure to carbon dioxide (<5 ppm), the hydroxide initially can form the bicarbonate and can further react to form the carbonate. Not only do the ionic resistance losses mount from the lower mobility of carbonate anions, but also there is a dramatic drop in the electrochemical equilibrium potential arising from the drop in pH in addition to an increasing resistance from a lack of available hydroxide ions since the carbonate anion is unable to facilitate the hydrogen oxidation reaction at the anode[31]. This is a large barrier to overcome for AEMFCs as fuel cells in commercial applications are fed with atmospheric air as an oxidant.

Another significant challenge that AEMFCs have faced lies in water management. Part of this issue arises from the fundamental nature of the alkaline electrochemical reaction versus its acidic counterpart. For the proton-mediated hydrogen fuel cell reaction, hydrogen directly generates the ionic charged species in the hydrogen oxidation reaction (HOR) as shown in Eq. 1 and then two water molecules are generated at the cathode in the oxygen reduction reaction (ORR) as shown in Eq. 2 due to the stoichiometrically requirement per the diatomic oxygen reactant.

(1) $2H_2 \rightarrow 4H^+ + 4e^-$

(2) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

For the hydroxide-mediated case, water is generated during the HOR side of the net reaction where twice as much water is produced per charge species (and per reactant species in general) since the ionic species has twice as much oxygen as the final product of water as shown in Eq. 3. Furthermore, the hydroxide species needs to be first generated from water, thus water is consumed at the cathode in the ORR as shown in Eq. 4. This necessarily entails a stoichiometric water difference from the reaction that is three times higher than in the acidic case.

(3) $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

(4) $O_2 + 2H_2O + +4e^- \rightarrow 4OH^-$

Higher electroosmotic drag can further exacerbate this issue (drag coefficient of ~8 water molecules per ion compared to ~1-2 for fluorinated[32-33]) as ions carry significant amount of water towards the side of the cell that is already generating water. This leads to flooding in the case that there is excess water leading to blocking of gas access. In the case of areas with insufficient water the ionomer is dried out lowering stability and the availability of reacting water becomes a limiting factor[34-36]. While promising performance has been demonstrated if humidification of side of the cell can be carefully balanced[37], maintaining this profile in practical fuel cell applications is not feasible, particularly when considering high operating current densities and temperatures[30]. As the dry state of these polymers accelerates chemical degradation, even minor membrane dehydration can lead to a self-reinforcing degradation propagation mechanism[38].

Ion Exchange Membranes for Water Electrolyzers

The water electrolyzer case necessitates many of the same ionomer properties including high ionic conductivity, high strength, low electronic conductivity, and low gas permeability while maintaining chemical and mechanical durability in a relatively harsh environment, leading to hydrocarbon membranes experiencing similar challenges that are faced in the fuel cell application[39]. Many of the operating environmental conditions are distinct in the electolyzer case as shown in Table 1. Significantly altering degradation promoting factors meriting unique consideration as will be reviewed here.

The electrolyzer is typically operated in a flooded state as opposed to the potential dynamic hydration states experienced in fuel cells. This hydrated leaves the membrane more susceptible to creep (as opposed to fatigue in the fuel cell case) as the strength is greatly reduced with maximal water uptake in addition to the swelling susceptibility, which also worsens as increased temperature is sought to improve conductivity and reduce electrocatalytic overpotentials. For this reason, reinforcements are still introduced in the water electrolyzer case as they can vastly improve the lifetime of membranes from a mechanical perspective[40]. Membrane-based electrolyzers are sought to be operated with differential pressure (cathode-side pressurized from 30-50 bar) to benefit from the much higher efficiency of electrochemical compression compared to mechanical compression, to benefit from the added purity to the produced hydrogen, and to lower the amount of drying required on the produced hydrogen[41]. This adds a significant, unique hydraulic pressure stressor to the water electrolysis case. Stress can accumulate at the edge of the electrode and the gasket, potentially leading to tearing suggesting that tear resistance is also an important aspect of mechanical robustness[42-43]. Additional stressors can arise from uneven swelling due to localized water activity dropping from insufficient evolved gas removal or local thermal hot spots. Differences in pressure distribution applied onto the membrane further exacerbate durability issues, reflecting the importance of considering membrane electrode interfaces mechanically[44-45]. Considering not only that the conductivity is highly hydration dependent, but also that the water is also the main cooling action enacted in the electrolyzer, thermally accelerated degradation can also be initiated by across cell uniformity challenges[39].

Mechanical durability issues are exacerbated when looking to employ hydrocarbon membranes in the electrolyzer application. A major source of challenges lies in the significantly higher water uptake for hydrocarbon-based membranes. Aside from the added degrees of stress from dimensional swelling and its

Table 1. Comparison of typical operating environments for PEM fuel cells and electrolyzers perturbative of stress leading to degradation.

Environmental Condition	Fuel Cell	Electrolyzer
Water Activity	Water vapor (0-100% RH)	Liquid water
Temperature (°C)	60 – 110	50 – 90
Hydraulic Pressure (bar)	1-3 (symmetric)	1-50 (differential)
Operating Voltage (V)	0.7 - 1.1	1.6 - 2
Load Profile	Dynamic	Static*
Mass-transport limiting product	Liquid Water	Hydrogen/Oxygen Bubbles
Anode Diffusion Media	Compressible Carbon-based	Rigid Titanium-based

*Load following applications are investigating dynamic electrolyzer performance

associated challenges in production and assembly, the volumetrically normalized properties of the material change as they incorporate higher fractions of water into their structure. Properties such as strength, toughness and gas permeation begin to drop towards the values of water with these increasing fractions. This difference in fraction can be drastic with hydrocarbons routinely incorporating over 100 wt% increases upon liquid water introduction resulting in high water volume fractions (e.g. 70% for sulfonated poly(phenylene sulfone with an ion-exchange capacitity of 2.8 meq/g vs. 40% for Nafion™ N115)[46]. Higher water uptake will tend to reduce the gas permeation advantage of hydrocarbons as the gas permeability of water is much higher than that of through the dry polymer. Additionally, due to this increased uptake, the relative drop-off in toughness for hydrocarbon membranes is significantly higher and have absolute values multiples lower than their fluorinated counterparts[47]. Other mechanical issues can be exacerbated from innate hydrocarbon properties from chemo-mechanical feedback mechanisms as will be discussed below or by connection to the catalyst layer interface as will be discussed in the next section.

Chemical degradation is still of prominent concern in the electrolyzer application. While the higher electron withdrawing potential at the anode makes more oxidation prone species vulnerable, fluorinated ionomers remain redox susceptible and are still mainly vulnerable to hydroxide radicals. Under the electrolyzer environment, hydrogen peroxide and its derivative oxidizing radicals are generated at varying fractions that are highly dependent on the temperature and current density (as the current here is positively correlated with the local hydrogen and oxygen partial pressures)[48-49]. Radical formation has been demonstrated near the cathode where formation is maximized at low-to-moderate current densities from reactions with permeated oxygen[39, 43]. At low current densities, hydroperoxyl formation leads to consuming the hydroxide radicals at a rate that is higher than membrane attack, while at high current densities the decrease in oxygen partial pressure at the cathode limits radical formation[48]. As there is a partial pressure dependence on the oxidizing species formation, the degree of formation is directly impacted by the degree of permeated gas and is thus dependent on membrane thickness[43]. The increase of radical formation under dry conditions further stresses the need to ensure uniform, constant hydration across the membrane. For instance, it has been demonstrated that internal blisters form on areas that can experience local dry out that concentrate radicals, where evidence of concentrated chemical degradation was demonstrated through the detection of local fluoride ions[39, 43]. Here it should be noted that the employment of gas recombination catalysts in electrolyzer membranes has been found to be an effective way to mitigate product gas diffusion on thin membranes[50] (by the thermocatalytic reaction on the catalyst surface to form water) and resultingly reduces radical attack which is dependent on crossover gas[51]. Radical scavengers can also be employed for fluorinated ionomers to reduce radical prevalence as the main challenge still lies in the hydroxyl radical.

Though hydrocarbon-based membranes benefit from lower gas crossover, the rapid nature of hydroxyl attack more offsets this with significantly higher levels of chemical degradation experienced in water electrolysis[46-47, 52-53]. While one can try to seek to mitigate this degradation with radical scavengers, which help to slow down degradation to some degree[54], the attack is still too rapid to the extent that material loss is experienced and required electrolyzer lifetimes cannot be reached. Furthermore, at the higher oxidizing potentials found in electrolyzers, the electrochemical oxidation susceptibility of employed phenyl groups needs to be considered.

Anion-exchange hydrocarbons carry forward the same challenges as cation-exchange hydrocarbons in electrolysis as well but have fared much better than their AEMFC counterparts in recent years. Applying the same membrane and ionomer in an alkaline exchange membrane water electrolyzer (AEMWE) can result in an increase in lifetime from hundreds to thousands of hours versus the AEMFC case[28, 55]. Several factors make the electrolyzer case less challenging than the fuel cell case for hydroxide conducting materials. For one, there is not the challenge of trying to eliminate carbon dioxide from reacting air as a closed liquid circulating loop is not constantly adding carbon dioxide to the system. Since the system is operated in a flooded state, balancing water hydration is not as significant a challenge. Typically, the electrochemical oxidation of phenyl groups is critically challenging as not only is the structure being degraded upon oxidation, but the acidic product phenol neutralizes the local basic hydroxide sites but operating in concentrated KOH offers a readily available neutralization source. Finally, the capacity to operate with recirculating potassium hydroxide offers significant performance

advantages over hydrating with pure water. KOH's inherent ionic conductivity not only improves the performance from an ohmic resistance perspective, but also serve to mediate ionic transfer covering potential conductivity loss of the membrane itself over time. Furthermore, the broadening of ionic site availability in the electrodes vastly increases the catalyst site availability from poorly dispersed ionically conducting binder[56], whose effect is illustrated in Fig. 3. Despite this, AEMWEs have failed to demonstrate on par performance and durability with identical complementary MEA components, much less with the supposed advantage of potentially being compatible with cheaper materials. We will briefly describe the varying degradation mechanisms for AEMWEs found in a range of operating parameters being trialed in parallel currently.

While operating in KOH has the capacity to mask many of the degradation modes in AEMWEs, the alkaline attack on even recently developed "alkaline stable" membranes will be a challenge for durable performance. Aryl ether-free polymers with wholly aromatic backbones and pendant alkyltrimethyl ammonium conducting sites were found to be vulnerable to Hoffman elimination[57]. Similarly, poly(arylene piperidium)-based AEMs were found to degrade through β-elimination on the functional group[58]. Imidazolium groups are also base vulnerable where poly(arylimidazolium) is vulnerable to dealkylation and ring opening[59] while polybenzimidazole might be the most base-stable still experienced ring opening degradation in a concentrated basic environment[60]. While the above-mentioned degradation is easily detected by changes in ion-exchange capacity, other mechanisms of degradation not detectable from this mechanism can occur in parallel. AEMs exposed to caustic solution are susceptible cross-linking and the associated gel formation. This cross-linking, when uncontrolled, reduces water uptake (and thus the capacity to conduct ions) as well as makes the more brittle and susceptible to fracture[56]. Peroxide radicals still can be formed in the AEM environment[61] and of course the hydrocarbon bonds are all susceptible to hydroxyl radical attack where such attack has been demonstrated in AEMs[62] and will proceed under basic conditions[63]. While often touted for the capacity to accommodate PGM-free catalysts as a redeeming quality, such activity and durability has not been demonstrated in practices with MEAs. Not only do the often cited as compatible 3d transition state metals (e.g. Fe, Co, Ni) and their associated hydroxides experience dissolution in alkaline conditions, but so do the precious metals (e.g. Ru, Ir, Pt) at potentially higher rates than in acidic media under electrolyzer environments[64-68]. In the same vein, while it has been proposed that cheap materials such as stainless steel and graphite might be employed AEMs, this has yet to be demonstrated successfully as stainless steel alloys suffer passivation on the surface[69] leading to high interfacial contact resistances (in addition to the contribution of the iron to the Fenton-type reactions), and graphite bipolar plates or gas diffusion layers suffer from rapid corrosion in the presence of hydroxide[70]. All such current collecting materials demonstrated so far have a tradeoff between contact resistance and stability.

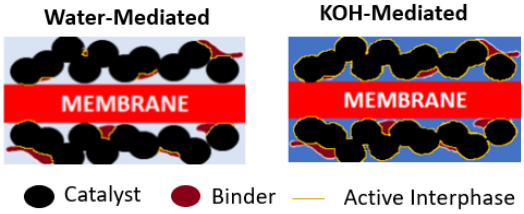

Figure 3. Illustration of how the difference of hydration medium in alkaline electrolyzers impacts the availability of active sites. This assumes the electrodes on the extent have catalysts with full electrical contact with the conductive diffusion media at the end. This illustration also assumes that the ionomer network from all displayed binder is fully connected.

One might consider that AEMs would operate more durably in a pure water medium at the sacrifice of higher performance as they are not subjected to corrosive caustic, however such operated AEMs have shown to be significantly *less* stable. One reason could be the necessarily higher oxidizing potentials (from lowered ionic conductivity) to achieve some reasonable degree of hydrogen production. Several reasons for this degradation in pure water have been proposed relating to the ionomer binder[56] and will be further discussed in the next section.

To this point, the performance and durability of alkaline-exchanged ionomers for water electrolysis have proved inferior for hydrogen production while also not demonstrating a reasonable advantage in compatibility with cheaper materials requirements. To date, the best performing and longest lasting AEMs have been enabled through operation in caustic solution. It is worth noting here that >99% caustic

solution is generated through the fluoropolymer-enabled chloro-alkali process[71]. Alternative processes to generate caustic are drastically less efficient, rely on asbestos or mercury, and are resultingly worse for safety and environmental concerns.

Ionomers for Electrode Binders

To assemble catalysts into a porous ensemble that is networked with sufficient ionic conduction, electrodes for fuel cells and electrolyzers employ ionomers as catalyst binders. While the need to effectively shuttle ions is a coincident property in what is required of ionomer in the membrane and the binder, other properties are diametrically opposed such as the electronic conductivity and the gas permeability. As there does not exist an ideal material that is ideal in all these properties, an ionomer that is at least close in composition to the membrane is employed to enable ionic conduction, and the fraction employed versus other electrode materials is optimized to mitigate a tradeoff between ionic conductivity, electronic conductivity, and mass transport.

Even though fluorinated ionomers tend to have higher gas permeability than their hydrocarbon counterparts, their resistance to gas movement still has proven to be significantly limiting to performance[72-73]. Improving the gas permeability of electrode ionomer has in fact been one of the most promising fuel cell materials developments in recent years to enable high power density and durability. By the development of fluorinated ionomers that incorporate bulky groups that increase polymer spacing and have been able to effectively increase the oxygen permeability and drastically reducing the effective oxygen transport resistance[74-77]. Additionally, as one of the predominant degradation mechanisms for fuel cells lies in the gradual loss of catalyst surface area and effective gas transport allows for the more effective use of lower catalyst surface area, the introduction of this class of high oxygen permeability ionomers (HOPIs) has enabled vast improvements in operable lifetime in high performing fuel cells[76, 78]. Hydrocarbon ionomers possessing lower gas permeabilities has proved detrimental to performance at significant levels of current density[79-81]. As all hydrocarbon ionomers already rely on bulky aromatic groups with a high free volume, the possibility of adopting the same strategy as has been used for fluorinated ionomers is moot. The difference in gas solubility lies innately with the hydrophobicity of the PTFE backbone and intrinsic low polarizability of fluorine which enable a high oxygen solubility[82-83]. This suggests that this mass transport problem of hydrocarbon materials lies endemically with the material class.

The higher required water uptake for equivalent conductivity causes a set of unique challenges when this ionomer is applied effectively as a binder. This is noted where optimal hydrocarbon ionomer contents are routinely found to be lower than their fluorinated counterparts on a weight fraction basis where on a volume fraction comparison they are similar[84]. Since hydrocarbon ionomers require higher ion exchange capacity to achieve similar conductivity, this necessitates a higher water uptake resulting in excessive water sorption, swelling, and results in flooding conditions[85-86]. This swelling action not only can block water mobility but reduced pore size leads to further reductions in oxygen gas transport.

Fluorinated ionomers are typically dispersed as colloidal aggregates in water/alcohol mixtures in which when cast with catalyst particles, will readily form a percolating network without isolating and disconnecting the electronically conductive network. Hydrocarbon ionomers on the other hand are typically not dispersible in such a way and are instead dissolved in mixtures which when incorporated in catalyst layers, tends to lead to the blocking of pores and electrical isolation[84, 87]. Furthermore, the tendency of hydrocarbon ionomers to form more dispersed and less percolating networks leads to worse ionic conduction and lower catalyst utilization[86-89]. This challenge is particularly accented at low humidity conditions where the higher water dependance of hydrocarbons leads to exacerbations of the already existing challenges of ionic conduction and network connection[90].

The incorporation of ionomer binders tends to lower the effectiveness of catalysts as well through several mechanisms. One mechanism for this can include higher degree of sulfonate poisoning due to the higher degree of sulfonate sites required to achieve comparable conductivity[91] or cation-hydroxide-water co-adsorption in the AEM case[30]. Phenyl groups have also shown to have the capacity to block catalytically active sites[92]. Lower degrees of reactant solubility also result in lower mass activity as this lowers the thermodynamic driving for the reaction, where high oxygen permeable fluorinated ionomers have demonstrated the mass activity enhancement from higher oxygen solubility[74-75].

Ionomer degradation in the form of delamination of the electrode layer is more commonly reported for hydrocarbon-based materials. Delamination clearly leads to challenges in the cell as less contact reduces conduction area, effectively increases contact resistance, resultingly increases overpotential, builds stress in the catalyst layer, and can ultimately result in loss of the catalyst layer. It has been demonstrated that a dimensional mismatch due water uptake is highly correlated with an increase in contact resistance from delamination[93]. For rigid polymers this water uptake threshold at which point delamination becomes a significant risk is much lower (~50%) than what might be possible with more flexible polymers (~100%).[30] The combination of lower catalyst and accessibility raises the potential for catalyst dislodgement in the water electrolysis case. As lower catalyst accessibility forces more significant bubble generation at the fewer available sites and the lower permeability of hydrocarbon ionomers makes the removal of bubbles more challenging, this leads to higher probabilities of binder dislodgement[56].

In the case of alkaline membrane cells, the same challenges remain with some being exacerbated while other new challenges also arise. For instance, in the delamination case, it possible that the exacerbated humidification gradient that be experienced in AEMFCs might make these MEA types more susceptible to dimensional mismatch between layers[30]. Phenyl oxidation is particularly an issue at the catalyst-ionomer interface for several factors including that the phenyl group concentration at the interface is high in concentration while being covalently bonded to the ionomer, the catalyst facilitates the oxidation to phenol, and the adsorption on the metal oxides sites for the phenyl groups is quite strong[94]. It is highly desirable to use carbon supports when possible due to their combination of cost, electronic conductivity, porosity control, and capacity to enable extremely high surface areas to improve catalyst utilization. In the alkaline case, it is more challenging to implement such carbon supports as the alkaline environments has long been establish to form carbonates and leads to significantly more corrosion particularly in the presence of a catalyst than is experienced in the acidic medium[95-97]. The alkaline stability challenge with other carbon presence also makes the implementation of graphite bipolar plates and carbon GDLs more challenging for durability concerns. While KOH-mediated AEMWEs are more challenging from a chemical durability perspective than pure-water fed systems, they mitigate some of the challenges experienced by their binders. Dislodgement, for instance, is less likely to be induced as there is a significantly higher accessibility of catalyst sites and gas permeability is increased. Water-fed AEMs do not have the benefit of quenching generated phenol groups from ionomer electrochemical oxidation that KOH-fed systems have, thus raising the probability for further ionomer degradation from the neutralization of the hydroxide exchange site. These challenges have led to water-fed alkaline membrane water electrolyzers to have orders of magnitude significantly higher voltage degradation rates[56].

Product Stewardship

The inherit properties of fluoropolymers are necessary now and for the foreseeable future to enable key hydrogen technologies. No hydrocarbon ionomer has the required combination of transport properties with sufficient mechanical and chemical robustness to bring fuel cells and water electrolyzers towards economic competitiveness. The outright ban of these fluoropolymers would in turn cripple efforts to decarbonize the most challenging parts of heavy industry at the precise moment when green hydrogen is finally seeing wide-scale deployment. Instead of banning this class of materials with an extremely low

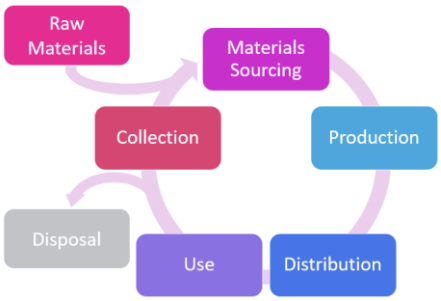

Figure 4. Circularity relationship for material lifecycle to consider for responsible manufacturing paradigms in product stewardship. Ethically sourced and safely generated materials initialize the product life cycle. After that, the conversion of a material into a product through manufacturing production needs to be considered for its health and environmental hazard level. Considerations then must be placed on generated product to how they are distributed to application and then how are they handled and contained in application. After useful life, significant effort should be placed to collect and recycle/reuse components as to minimize waste. Any waste must be disposed of safely and with low impact.

risk profile without a consideration of possible harm, it should be preferred to foster the safe and responsible manufacture, usage, and end of life of these and all materials throughout their lifecycle as depicted in Fig. 4.

The manufacturing stage of polymers has among the most challenging stage of environmental and health risk from the handling of solvents and highly reactive chemicals. To this end, Chemours is committed to responsible manufacturing of fluoropolymers and has taken industry-leading steps to reduce emissions and discharges to the environment by implementing state-of-the-art technologies and enhancing sustainability at all sites, including those in Europe. Chemours is working to establish an industry standard of non-targeted analysis to identify all byproducts and residue in fluoropolymer production processes.

Chemours is committed to reducing air and water process emissions of fluorinated organic chemicals by 99% or greater by 2030 compared vs. a 2018 baseline and share progress against this goal annually in our sustainability report. Efforts to this end include recovery projects for reuse in the chemical manufacturing process, using thermal destruction techniques that destroy over 99.99% of PFAS air emissions, and handling dilute aqueous and vapor streams through the implementation of adsorption, reverse osmosis, and thermal destruction technologies.

After these fluoropolymers are synthesized, they pose little environmental or health risks. Ionomers dispersed in solids are mixed with catalysts and cast into electrodes in a process little to no waste is generated. While material losses are experienced in transfer processes, recovery of transfer scrap is already practiced (with material waste less than 1%) since there is high value in catalyst recovery[98]. Once in the solid form, they pose an even lower risk for environmental release. Excess membrane from shaping processes is readily stable and recoverable in the solid polymer form to be handled by recycling or chemical waste.

These fluoropolymers are employed in use inside closed articles as an engineered product. This sealed product is not in direct contact with a consumer and thus poses no risk of environmental damage from the mishandling of said products from the consumer level. Such fluoropolymers demonstrate excellent thermal and chemical stability, with the thermal operation not becoming remotely close to where such materials might experience decomposition. The trace amount of degradation that occurs during operation can be handled by methods employed in-line with effluent (e.g. via ion exchange resin)[99].

At the end of life, there is already a high motivation to recover and recycle highly valuable stack materials as the catalyst materials and ionomer are expensive and of limited quantity. Two current methods to achieve this seek to either just recover the fluorine or recover the ionomer material intact. In the first method, membrane electrode assembly materials are ashed, the residual dissolved in hydrofluoric acid, and then remove the hydrofluoric acid to be used again for fluoropolymer production. Incineration of PTFE under typical conditions has been demonstrated to break down into hydrofluoric acid without the formation of any other per- or polyfluorinated alkyl substances within detectable limits[100]. This hydrofluoric acid can then be recycled into calcium fluoride, which is a critical raw material. The second method would be to simply recover the ionomer separately using solvent, to retain the valuable structure of the fluoropolymer[101].

To tackle our modern societal challenges with material solutions in a responsible manner, we must thoughtfully approach every aspect of chemicals from cradle to grave. We must determine ways of how we can implement such materials in sustainable, closed-loop circularity. We must consider what the actual risk profile of given before permanently restricting their use. Then we must consider the societal risks we run if we give up on trying to implement safe and effective materials.

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