FUNDAMENTAL RESEARCH AND DEVELOPMENT CHALLENGES IN POLYMER ELECTROLYTE FUEL CELL TECHNOLOGY

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ABSTRACT
The purpose of this paper is to define needs for improved membrane and catalyst materials that would accelerate commercialization of Polymer Electrolyte Fuel Cells (PEFCs) in automobiles. Starting with system and cost considerations, we define targets for membrane operating temperature, conductivity vs. relative humidity, gas permeability, and water uptake. To consider the catalysts needs, we examine the polarization losses in state-of-the-art membrane electrode assemblies (MEAs) and demonstrate that approximately 2-3 fold improvement in electrocatalyst activity is needed to enable achievement of automotive Pt targets of <0.2 gPt/kW.

INTRODUCTION
Many companies are diligently working to bring hydrogen, reformate, and methanol fed polymer electrolyte fuel cell (PEFC) products to a variety of markets. It appears that currently available fuel cell materials and designs will be adequate for near-term markets with the highest cost ($/kW) entry points. In these cases, challenges in engineering, manufacturing, and marketing must be overcome prior to successful market penetration. However, there are also more technically demanding and lower-cost markets (e.g., automotive) for which current materials and designs may not be sufficient. In this paper, we attempt to identify key automotive system and cost issues and show how they lead to specific materials development challenges.

Current PEFCs systems run at a maximum of 80°C because operation above that temperature requires too much system support of the membrane as will be explored further below. Also, current membranes have glass transition temperatures in the range of 80-120°C and are thus subject to creep and hole-formation at temperatures in that range. Unfortunately, it turns out that the heat rejection rate of automotive radiators is insufficient to reject continuous full power waste heat loads with the 80°C source temperature. Although fuel cell vehicles are inherently more efficient than the internal combustion engine (ICE), the ICE has a thermal system packaging advantage. This is because the ICE rejects approximately one-third of its waste heat in the exhaust stream (vs. <10% for the PEFC), and the ICE-system coolant temperature reach approximately 120°C (vs. 80°C for the PEFC) (1). This system problem has given rise to a need for development of a “high-temperature membrane”. In this paper, we will begin with
system considerations and define targets for membrane operating temperature, conductivity vs. relative humidity, gas permeability, and water uptake.

State-of-the-art catalysts comprise Pt-containing metals or alloys supported on carbon. We will consider Pt-containing catalyst cost in automotive applications for both state-of-the-art and projected performance. This is a particularly critical question in light of the probable upward pressure on Pt price, a limited natural resource, as volume increases; this is in contrast to the membrane material cost which would be expected to benefit from economies of scale. To do this analysis, we examine the polarization losses in state-of-the-art MEAs and demonstrate the degree of improvement in electrocatalysts needed to achieve automotive Pt targets of <0.2 gPt/kW.

HIGH-TEMPERATURE POLYMER ELECTROLYTE NEEDS

The High-Temperature Target:
GM automotive system analysis suggests a reasonable target for high-temperature membrane operation is between 110-120°C for H2-fueled fuel cell vehicles (2). At this temperature, heat rejection with conventional packaging becomes feasible. Furthermore, CO tolerance improves to approximately 50 ppmv CO without air bleed at low anode catalyst loading (0.1-0.2 mg active metal/cm²) (3), thereby reducing the purity requirement for on-board stored H2. For stationary systems with reduced dynamic load-following requirements and operating with hydrocarbon-based H2-reformate, system operation at ca. 140-160°C would offer an increase of the CO-tolerance level to ca. 0.1-0.5%, thereby allowing for a simpler Preferential Oxidation (PROX) reactor, or even PROX elimination. Whereas some gains in oxygen reduction activity would be realized at 160°C, these would probably have small impact on system size and mass since they would be counteracted by a loss in equilibrium voltage. (Equil ca. 70±5 mV lower at 160°C compared to 80°C, i.e., approximately one Tafel-slope (4)). At temperatures >160°C, carbon-support material stability becomes problematic (5). For H2-fueled automotive fuel cell systems, the focus of this paper, we conclude that 120°C is the best target temperature to guide high-temperature membrane development efforts.

Proton Conductivity Requirements:
In this section, we define targets relevant to high-temperature ionomer development. In order to provide material property targets that can be directly measured in *ex-situ* tests, we assume electrode and membrane structures similar to what we have today. Specifically, we assume membranes in the neighborhood of 20-50 μm and electrode structures with thickness of 10-20 μm in which 15-25 volume percent ionomer (εionomer) is incorporated to provide proton conductivity (6). The ionomer requirements are different for membrane vs. electrode application, and we consider this in setting targets. Of course, more radical departures from current MEA architectures are welcome, and the targets we provide here can readily be generalized to evaluate alternative MEA constructions.

Conductivity of Ionomer in Membrane – The operating conditions of current PEFC technology are dictated by the properties of the perfluorosulfonic acid (PFSA) ionomers that are used in the membrane and the catalyst layers. Figure 1 shows the proton conductivity (σH+) vs. relative humidity for 1100 EW Nafion® as measured by Alberti (7, 2 Electrochemical Society Proceedings Volume 2002-31
through-plane), a relationship he found to be roughly independent of temperature in the 80-120°C temperature range. The conductivity is above 0.1 S/cm for relative humidity (RH) values greater than 90%, but drops to 0.01 S/cm at 40% RH. Also represented on the right-hand axis of the plot is the ohmic loss for a 25 μm membrane at 1 A/cm². At 0.1 S/cm, the loss is 25 mV, a voltage efficiency penalty of about 2%. Whereas this loss appears relatively small, overall voltage efficiency is a critical issue due to sluggish cathode kinetics. Thus, assuming a membrane thickness, $\delta_{\text{membrane}}$, in the neighborhood of 20-25 μm we suggest a 0.1 S/cm target be adopted for ionomer development directed at membrane application. Alternatively, one could target an overall membrane sheet resistance, $R_{\text{sheet}}$, of less than 25 mΩ cm² (i.e., $R_{\text{sheet}} = \frac{\delta_{\text{membrane}}}{\sigma} + \frac{1}{\sigma_H}$).

![Graph](image)

Figure 1: Relationship between proton conductivity and adjoining gas stream relative humidity at various temperatures for perfluorosulfonic acid (1100 EW) (7) and phosphoric-acid-doped polybenzimidazole (8). Curves are also shown for materials that would enable and be ideal for system simplification.

Conductivity of Ionomer in Electrode – In current PEFC electrode configurations, ionomer dispersed throughout the electrodes also contributes a resistance. The voltage-loss ratio between the electrolyte phase in the electrode and the membrane can be estimated using simple geometric arguments and typical values for state-of-the-art electrodes based on optimal cathode performance, assuming the membrane ionomer has the same intrinsic conductivity in both phases.

$$\frac{\Delta V_{\text{ionomer,electrode}}}{\Delta V_{\text{membrane}}} = \frac{\delta_{\text{electrode}}}{\delta_{\text{membrane}}} \frac{\tau}{2 \cdot \varepsilon_{\text{ionomer}}} = \frac{15 \mu m}{25 \mu m} \cdot \frac{1}{2 \cdot 0.20} = 1.5$$  [1]

The factor of 2 in the denominator accounts for conduction of protons halfway, on average, through the catalyst layer thickness. The tortuosity, $\tau$, is not well known but

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was assumed to be unity to provide a lower-limit estimate of the voltage-loss ratio. We assumed electrode and membrane thickness of 15 and 25 μm, respectively, and ionomer volume fraction in the electrode of 0.2. Thus, the total electrolyte phase voltage losses in a single electrode are approximated to be at least 1.5 times those in the membrane.

For fuel cell systems with pure H₂-feed, the electrode ionomer-phase loss is expected to be present mainly in the cathode and could be reduced by designing thinner cathode electrode structures (note that it is unlikely to achieve electrodes with good gas-diffusion properties using significantly larger values of ε_{ionomer}). Thinner cathode structures are enabled by the development of either (i) higher-loaded Pt-catalysts (> 50%wt. Pt/carbon) without compromising Pt-dispersion and/or (ii) more active cathode catalysts which would allow operation at significantly reduced catalyst loading resulting in thinner electrodes. In the case of fuel cell system operation with CO-contaminated reformate, the very much reduced anode kinetics would produce similar comparable voltage losses on the anode and the same development goals as stated for cathode catalysts would apply. In summary, it is reasonable to set an ionomer conductivity target of 0.1 S/cm at 120°C for high-temperature ionomers that are developed for use in electrodes, i.e., identical to the membrane conductivity target.

**System-Imposed RH Requirements:**

Because of the rapid drop-off in conductivity with decreasing relative humidity for PFSA ionomers, they are typically operated in the high-RH window as shown in Figure 1. The role of the system built around such a membrane is to provide the 100% RH environment so that the membrane/electrode can efficiently conduct protons with minimum voltage loss. However, maintaining 100% RH in the gas streams is problematic from the system point-of-view. The membrane RH requirement drives high-pressure operation (resulting in higher compressor auxiliary loads), low temperature operation (resulting in lower system heat-rejection rates), and increased RH in inlet streams (resulting in higher complexity and cost due to humidification/condensation requirements). Although Figure 1 indicates that PFSA conductivity at 120°C for current ionomers is above 0.1 S/cm at 100%RH, we will next show that this is an impractical operating region from a system point-of-view. We will also seek to define a suitable target RH at 120°C at which the 0.1 S/cm target developed above should be applied.

To define a target RH-value at 120°C, we will assume a dead-ended H₂ system running at air stoichiometry of 2 as shown in Figure 2:

![Figure 2: Dead-ended H₂/air fuel cell system with air stoichiometry of 2 on a one-mole H₂ basis.](image)

**Figure 2:** Dead-ended H₂/air fuel cell system with air stoichiometry of 2 on a one-mole H₂ basis.
A state-of-the-art system using conventional PFSA membranes is indicated in Table 1 as System 1. For such a low pressure system (ca. 150kPa$_{abs}$) at 80°C, fuel and air streams must be (nearly) fully humidified to achieve high conductivity in the membrane and in the catalyst layers. Since the water vapor pressure at 80°C is ca. 50kPa, the effective gas pressure (fuel and air) is ca. 100kPa. To fully humidify the fuel and air inlet streams at 100%RH at 80°C and 150kPa$_{abs}$, 0.5 and 2.4 moles of H$_2$O per moles of H$_2$ consumed, respectively, must be added, and this total water-flux of 2.9 molesH$_2$O/moleH$_2$-consumed (last column in Table 1) must be recirculated to avoid net consumption of water on the vehicle.

For a high-temperature system to be feasible, we can set the following system guidelines:

- No more humidification water-recirculation, i.e., (m+n)H$_2$O (Table 1), to the fuel cell stack than for 80°C/150 kPa$_{abs}$ system, with 100% RH requirement (current systems are already too complex and costly).
- Operation near 150kPa$_{abs}$, otherwise parasitic compressor power is excessive.
- Retain fuel/air partial pressures of ≥100kPa$_{gas}$ (dry-basis) to avoid performance losses compared to current systems. This is particularly critical to avoid excessive cathode kinetics losses.

Table 1: Four potential system operating conditions based on Figure 2 (dead-ended H$_2$, air stoichiometry of 2), illustrating the effect of membrane RH requirement on system pressure and water supply requirements. System 1 is feasible with conventional PFSA membranes, Systems 3 and 4 are target high-temperature membrane systems with membrane conductivity requirements as shown in Figure 1 (lines labeled "Desired" and "Ideal").

| System | System Description | RH$_{in}$ | RH$_{out}$ | P$_{total}$ | P$_{air}$, P$_{H_2}$ | P$_{H_2O}$ | n$_{H_2O,an}$ | n$_{H_2O,ca}$ | (m+n)H$_2$O |
|-------|-------------------|----------|----------|------------|-------------------|----------|-------------|-------------|----------|
| 1     | Current 80°C-System | 100      | 135      | 150        | 100               | 50       | 0.5         | 2.4         | 2.9      |
| 2     | 120°C-System, Current Membrane | 100      | 135      | 300        | 100               | 200      | 2           | 9.6         | 11.6     |
| 3     | 120°C-System, Desired Membrane | 50       | 67       | 200        | 100               | 100      | 1           | 4.8         | 5.8      |
| 4     | 120°C-System, Ideal Membrane | 25       | 33       | 150        | 100               | 50       | 0.5         | 2.4         | 2.9      |

We now consider a future system running at 120°C, System 2 in Table 1. Membranes which require 100%RH for optimal operation would require 300kPa$_{abs}$ total system pressure to maintain 100kPa fuel/air pressure, since the water vapor pressure at 120°C is ca. 200kPa. In addition, the amount of water to be recirculated would be four times (!) that of the currently used systems at 80°C, i.e., (m+n)H$_2$O = 11.6. We conclude that a 120°C system with current membranes is not feasible due to undesirably high system pressure and water recirculation requirements.

System 3 in Table 1 represents a 120°C system if one had a membrane maintaining ca. 0.1 S/cm at 50%RH (see Figure 1). The water partial pressure of 100 kPa in addition to the reactant partial pressure of 100 kPa results in a total system pressure requirement of
200 kPa$_{abs}$, higher than the target of 150 kPa$_{abs}$. Furthermore, the required water recirculation rate would be approximately twice the requirement for 80°C systems, i.e., $(m+n)\text{H}_2\text{O} = 5.8$. System 4 represents the ideal case, enabled by a 120°C membrane requiring 25% RH to provide a conductivity of 0.1 S/cm (see Figure 1). The system pressure (50 kPa water plus 100 kPa fuel/air) and the water recirculation rate are equivalent to those of the baseline 80°C system, i.e., $(m+n)\text{H}_2\text{O} = 2.9$.

We conclude that demonstration of ca. 0.1 S/cm at 25%RH (80-120°C), is a necessary condition for a high-temperature membrane which would operate in a 120°C system. Long term, the system would obviously benefit from membranes that required no external humidification. Membranes can be screened for this necessary condition without fuel cell testing and MEA preparation.

**Available High-Temperature Membrane** – Phosphoric-acid doped polybenzimidazole (PBI), first identified by Case Western Reserve University and now under development by Celanese, is a high-temperature membrane that does allow operation at temperatures up to approximately 200°C (8). Available data for PBI membrane conductivity vs. RH and temperature are included in Figure 1. At 200°C, its conductivity is 0.06-0.08 S/cm with an RH of 5-10%. Whereas this is interesting performance, the reported conductivity drops rapidly as a function of temperature reaching 0.01-0.02 S/cm at 15-30% RH and 80°C. This is problematic from an automotive system start-up point-of-view. However, recently presented data indicate significant improvements in low temperature conductivity with this material (9). Additional issues with PBI have been stability in the presence of liquid water and inefficient cathode structures resulting in low areal power density. Whereas the material is not yet suitable for use in automotive systems, its potential for high proton conductivity at low RH is attractive. Hopefully, further development will overcome these shortcomings and enable its use in automotive applications.

**Hydrogen/Oxygen Permeability Requirement:**

In addition to proton conductivity, other critical ionomer properties include the H$_2$ and O$_2$ permeability. The membrane material must not be too permeable to the reactive gases to avoid excessive gas crossover and resulting fuel efficiency loss. On the other extreme, the ionomer in the electrode must have sufficient gas permeability so that the reactant transport through it occurs without significant concentration gradients and associated mass transfer losses. In this section, we present simple calculations to roughly estimate the maximum and minimum H$_2$ and O$_2$ permeability requirements.

**Gas Permeability through the Membrane** – PFSA-based membranes allow permeation of gases at a rate proportional to the product of a permeability coefficient (dependent on temperature and RH, normalized by membrane thickness) multiplied by a partial pressure driving force and divided by the membrane thickness. This permeation leads to a fuel cell crossover efficiency loss with two components: direct reaction at the anode determined by the O$_2$ crossover rate and direct reaction at the cathode determined by the H$_2$ crossover rate. This crossover loss can be expressed in terms of an equivalent current that would be observed externally if the H$_2$ consumed by crossover had been reacted electrochemically:
\[ i_{\text{Fuel Loss}} [A/cm^2] = \frac{2F \cdot k_{H_2}(T,P) \cdot \Delta p_{H_2}}{\delta_{\text{membrane}}} + \frac{4F \cdot k_{O_2}(T,P) \cdot \Delta p_{O_2}}{\delta_{\text{membrane}}} \]  

where \( k_i \) indicates the \( H_2 \) or \( O_2 \) permeability coefficient, \( \Delta p_i \) is the partial pressure difference driving force of \( H_2 \) or \( O_2 \) from one face of the membrane to the other, and \( \delta_{\text{membrane}} \) is the membrane thickness. Knowing this “crossover current density” one can calculate the fuel efficiency loss from the following

\[ \eta_{\text{Loss, Crossover}} = \frac{i_{\text{Fuel Loss}}}{i_{\text{External}}} \times 100\% \]  

where \( i_{\text{External}} \) is the current observed in the external circuit divided by the electrode active area.

Rather than conduct a more complicated analysis involving a drive cycle and transients in the stack load/temperature/pressure profile, we will set criteria at the low and high current density points on the load curve and calculate the permeability requirements at those two extremes. The assumptions are listed in Table 2. The fuel cell stack temperature is assumed to instantaneously vary with load: 60°C at 0.05 A/cm\(^2\) and 120°C at 2 A/cm\(^2\) (high-temperature stack at high-current-density rating point). The gas partial pressures reflect average conditions of Systems 1 and 4 in Table 1.

Table 2: Basic assumptions for the determination of the permeability requirements for high-temperature ionomers to be used in the membrane and in the electrodes.

| Quantity                          | Units    | Low Load | High Load |
|-----------------------------------|----------|----------|-----------|
| Current Density                   | A/cm\(^2\) | 0.05     | 2         |
| Temperature                       | C        | 60       | 120       |
| Avg. \( H_2 \) Partial Press. (Absolute/Anode to Cath. Difference) | kPa abs | 100 |
| Avg. \( O_2 \) Partial Press. (Absolute/Anode to Cath. Difference) | kPa abs | 15 |
| Membrane Thickness                | micron   | 25       |           |
| Fuel Efficiency Loss due to Crossover (a) | % | <10     | <1       |
| Electrode Permeability            |          |          |           |
| Ionomer Film Thickness            | nm       |          | 2         |
| Roughness Factor                  | cm\(^2\)/(Pt/cm\(^2\)) | 100 |
| \( H_2 \) Tafel Slope (Ref. 10)  | V/decade | 0.03     |           |
| \( O_2 \) Tafel Slope (Ref. 6)   | V/decade | 0.065    |           |
| Efficiency Loss Due to Film (a)   | %        | <1.6 (20 mV) |           |

(a) criterion applied separately to \( O_2 \) and \( H_2 \), so total crossover loss can be twice these values

The calculated membrane-permeability limits based on Table 2 and calculated using Eq. [2] are shown as endpoints of the solid lines in Figure 3 for \( H_2 \) and Figure 4 for \( O_2 \). Permeability values above the lines would be unacceptably high based on the criteria. Measured permeability values from a variety of sources are also shown in the figures. The data extend to lower temperatures than assumed to be present in the system operating...
Figure 3: $\text{H}_2$ Permeability as a function of temperature and RH. Upper limit (solid line) defined by crossover losses (assuming no contribution from $\text{O}_2$ crossover), lower limit (dotted line) defined by electrode ionomer film transport requirements, and data is for wet and dry Nafion 1100 EW based membranes (11,12,13).

Figure 4: $\text{O}_2$ Permeability as a function of temperature and RH. Upper limit (solid line) defined by crossover losses (assuming no contribution from $\text{H}_2$ crossover), lower limit (dotted line) defined by electrode ionomer film transport requirements, and data is for wet and dry Nafion 1100 EW based membranes (11,12,14).
at steady state. In the 60-90°C region, the H₂ data approach the limit, suggesting that a high-temperature membrane, if implemented at 25 μm, cannot be any more permeable than a conventional PFSA-based membrane. The data show that the permeability of wet PFSA membranes is as much as an order of magnitude higher than dry membranes at a given temperature.

**Gas Permeability through the Ionomer in the Electrode** — Although the architecture of state-of-the-art electrode layers is still a matter of debate, one can reasonably postulate a structure like that shown in Figure 5. The average thickness of the ionomer film can be estimated by assuming that the ionomer volume is spread uniformly over the Pt and carbon surface area:

\[
\delta_{\text{film}} = \frac{m_C \left( \frac{m_{\text{ionomer}}}{m_C} \right)}{(m_{\text{Pt}} \cdot A_{\text{Pt}} + m_C \cdot A_C) \cdot \rho_{\text{ionomer}}}
\]  

where \( \frac{m_{\text{ionomer}}}{m_C} \) is the weight ratio of dry ionomer to dry carbon (values from 0.8/1.0 (6) to 1.7/1.0 (15), \( m_{\text{Pt}} \) is the Pt-loading in \([\text{gPt/cm}^2]\) of the catalyst characterized by a Pt-specific surface area \( A_{\text{Pt}} \) (typically \( 5 \times 10^5 - 1 \times 10^6 \text{ cm}^2/\text{gPt} \) (16), \( m_C \) is the carbon-loading in \([\text{gc/cm}^2]\) of a catalyst characterized by a carbon-specific surface area \( A_C \) (typically \( 2.5 \times 10^6 - 8 \times 10^6 \text{ cm}^2/\text{gPt} \) (17), and \( \rho_{\text{ionomer}} \) is the ionomer density (=2 g/cm³). For state-of-the-art catalysts, the Pt-loading is typically on the order of 50%wt Pt/(carbon+Pt) (generally ranging from 40-60%wt Pt/(carbon+Pt), in which case Equation 4a reduces to:

\[
\delta_{\text{film}} = \frac{m_{\text{ionomer}}}{(A_{\text{Pt}} + A_C) \cdot \rho_{\text{ionomer}}}
\]

This yields a range of values for the film thickness between 0.5 and 3 nm. Experimental support for this electrode structure comes from double layer capacitance measurements using cyclic voltammetry and AC impedance techniques. We have observed values on the order of 20 μF/cm² total surface area independent of \( m_{\text{ionomer}}/m_{\text{carbon}} \) between 0.4/1.0 and 0.8/1.0 for Vulcan XC-72 (18). This capacitance is characteristic of Pt and carbon interfaces with electrolyte and implies that the entire solid surface was in contact with electrolyte for these electrodes.

![Figure 5: Schematic of carbon primary particle supporting a Pt particle. These electronically conducting phases are considered to be uniformly coated by an ionomer film.](image-url)
One can estimate the mass transport overpotential associated with transport loss in the ionomer film adjacent to the Pt catalyst. We derive below the relationship for the O\textsubscript{2} transport losses through the ionomer film; the losses due to hydrogen transport are directly analogous. The IR-free cell voltage (E\textsubscript{IR-Free}) is related to the ionomer-film O\textsubscript{2} concentration at the Pt surface (c\textsubscript{O\textsubscript{2}}\textsuperscript{o}) at constant current density (i), surface H\textsubscript{2} concentration on the anode (c\textsubscript{H\textsubscript{2}}\textsuperscript{o}), and temperature (T) as

\[
\frac{\partial E_{\text{IR-Free}}}{\partial \log(c_{O_2}^o)} = m \cdot b
\]  

[5]

where m is the O\textsubscript{2} reaction order at constant IR-free cell voltage (approximately 1) and b is the Tafel slope (V/decade) observed in the kinetically controlled region (6). Integrating Eq. [5] and taking m=1 gives the following equation for the transport overpotential due to dissolved gas transport through the ionomer (\(\eta_{O_2,ionomer}\))

\[
\eta_{O_2,ionomer} = -b \cdot \log \left( \frac{c_{O_2}^o}{c_{O_2}^\delta} \right)
\]

[6]

where concentrations at the Pt/ionomer interface and the ionomer/gas interface are designated with superscript o and \(\delta\), respectively. The flux through the film adjacent to the Pt surfaces is proportional to the average current density based on the active area (i) divided by Pt roughness factor (f\textsubscript{rough} with units of cm\textsuperscript{2} Pt/(cm\textsuperscript{2} active area)). This flux is proportional to the diffusion coefficient and the concentration driving force across the film

\[
N_{O_2} = \frac{i}{nFf_{\text{rough}}} = \frac{D_{O_2} (c_{O_2}^\delta - c_{O_2}^o)}{\delta_{\text{film}}}
\]  

[7]

Combining Eqs. [6] and [7] to eliminate the unknown surface concentration, we arrive at

\[
\eta_{O_2,ionomer} = -b \cdot \log \left( 1 - \frac{i \cdot \delta_{\text{film}}}{nF \cdot f_{\text{rough}} \cdot D_{O_2} \cdot c_{O_2}^\delta} \right)
\]

[8]

We assume that the O\textsubscript{2} concentration in the ionomer phase is related to the O\textsubscript{2} partial pressure (p\textsubscript{O_2}) through Henry's law

\[
c_{O_2}^\delta = H_{O_2} p_{O_2}
\]

[9]

where \(H_{O_2}\) is the Henry's law constant. The permeability coefficient, introduced in Eq. [2], is related to the diffusion coefficient as

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\[ k_{\text{O}_2} = \text{H}_2 \text{O}_2 \text{D}_2 \]  \hspace{1cm} [10]

Combining Eqs. [8], [9], and [10], we find

\[ \eta_{\text{O}_2, \text{ionomer}} = -b \cdot \log \left( \frac{i \cdot \delta_{\text{film}}}{nF \cdot f_{\text{rough}} \cdot k_{\text{O}_2} \cdot P_{\text{O}_2}} \right) \]  \hspace{1cm} [11]

the relationship that predicts the voltage loss as a function of operating conditions and film properties. An analogous relationship applies for the H\textsubscript{2} transport on the anode side. The value of n is 2 and 4 for H\textsubscript{2} and O\textsubscript{2}, respectively.

To estimate the lower permeability limit, we assume the values shown in Table 2: a 2 nm thick film and an electrode roughness factor, \( f_{\text{rough}} \), of 100 cm\textsuperscript{2}Pt/cm\textsuperscript{2}MEA (ca. 0.15 mgPt/cm\textsuperscript{2}electrode with 65 m\textsuperscript{2}/gPt). Based on a criterion of no more than 20 mV loss due to ionomer phase gas transport, we calculate the low permeability limits shown in Figures 3 and 4. The permeability window is approximately 3 to 4 orders of magnitude for both H\textsubscript{2} and O\textsubscript{2}. PFSA materials represented by Nafion 1100 are orders of magnitude higher than the limit defined here, so we conclude that losses due to ionomer-phase reactant transport are negligible with current materials and structures, consistent with the literature (13).

For initial screening purposes, we suggest measurements at 80°C and use of the following criteria taken from Figures 3 and 4 (note: permeability, \( k_{\text{gas}} \), in units of (mole cm)/(cm\textsuperscript{2} sec kPa)):

i) \( \text{H}_2 \) permeability of \( k_{\text{H}_2} < 1 \cdot 10^{-12} \) for the ionomer used in the membrane and \( k_{\text{H}_2} > 1 \cdot 10^{-17} \) for the ionomer used in the electrode;

ii) \( \text{O}_2 \) permeability of \( k_{\text{O}_2} < 3 \cdot 10^{-12} \) for the ionomer used in the membrane and \( k_{\text{O}_2} > 1 \cdot 10^{-16} \) for the ionomer used in the electrode.

**Water Interaction Requirements:**

**Solubility** – Many new materials are being considered as next generation ionomers. Even for systems that run at low RH, we anticipate that ionomers could come in contact with liquid water during automotive system start-up and shutdowns. Therefore, we require insolubility of the ionomer in the liquid water. One could try to avoid liquid water formation with an engineering solution, but this would add undesirable system complexity. A reasonable screening test is <1% ionomer loss when held in liquid water at 150°C in an autoclave for 24 hours.

**Swelling** – PFSA materials uptake about 50% of their dry weight when boiled in liquid water, and some alternative ionomers take up even more. For example, versions of sulfonated poly ether ketone (PEEK) membranes can exhibit over 100% (i.e., 100% m\text{H}_2O/m\text{dry-polymer}) water uptake (19). One can estimate the wet thickness relative to the dry thickness of a membrane as a function of water uptake by assuming conservation of volume and zero in-plane expansion for MEAs sandwiched between diffusion media under relatively high compressive forces.
\[
\frac{\delta_{\text{wet}}}{\delta_{\text{dry}}} = 1 + \frac{\rho_{\text{dry}}}{\rho_{\text{H}_2\text{O}}} \left( \frac{m_{\text{H}_2\text{O}}}{m_{\text{dry polymer}}} \right)
\]

where the \( m_{\text{H}_2\text{O}}/m_{\text{dry polymer}} \) is the water uptake (wt/wt). For PEEK (\( \rho_{\text{dry}} = 1.5 \text{ gm/cc} \)) and 100\% water uptake the membrane would swell by a factor of 2.5. This creates a practical issue in that, assuming state-of-the-art PEFC construction, the diffusion media would compress in response to the membrane swelling. Assuming constant total thickness for the components before and after swelling, a scenario like that shown in Table 3 could occur. In this case, each diffusion media is forced to compress by 22 \( \mu \text{m} \) to accommodate the swollen membrane.

Table 3: Component thicknesses before and after swelling with liquid water (\( \rho_{\text{dry polymer}} = 1.5 \text{ g/cm}^3 \), 100\% water uptake, initial membrane thickness of 30 \( \mu \text{m} \)). Based on stress-strain data of Toray paper shown in Figure 6.

| Layer                                      | Initial -Dry [\( \mu \text{m} \)] | Final -Wet [\( \mu \text{m} \)] |
|--------------------------------------------|------------------------------------|----------------------------------|
| Anode Diffusion Media Thickness [\( \mu \text{m} \)] | 170                                | 148                              |
| Anode Catalyst Layer Thickness [\( \mu \text{m} \)] | 15                                 | 15                               |
| Membrane Thickness [\( \mu \text{m} \)]     | 30                                 | 75                               |
| Cathode Catalyst Layer Thickness [\( \mu \text{m} \)] | 15                                 | 15                               |
| Cathode Diffusion Media Thickness [\( \mu \text{m} \)] | 170                                | 148                              |
| Total Thickness [\( \mu \text{m} \)]       | 400                                | 400                              |

This membrane expansion will apply pressure on the diffusion media which can be estimated using the stress-strain data for carbon fiber paper (Toray TGPH-060) in Figure 6. We assume an initial uncompressed thickness of 200 \( \mu \text{m} \). Each diffusion media compresses to 170 \( \mu \text{m} \) in the cell build, resulting in 30 \( \mu \text{m} \) of strain and a stress of about 180 psi. Upon further strain of an additional 22 \( \mu \text{m} \), the stress more than doubles.

![Stress-strain data for Toray TGPH-060 taken at Southwest Research Institute. Effect of membrane swelling in this scenario (Table 3) is to more than double the compressive force on diffusion media.](image)

Figure 6: Stress-strain data for Toray TGPH-060 taken at Southwest Research Institute. Effect of membrane swelling in this scenario (Table 3) is to more than double the compressive force on diffusion media.
It is possible to handle this issue using a more compressive element in the stack. However, to avoid impractical requirements for that material, we set a criterion of less than 100% water uptake for the membrane ionomer when boiled in water. This criterion does not apply to the electrode ionomer (since it is embedded in a highly porous structure), although we project that water uptake of >200% for that material would be impractical from the point-of-view of long-term electrode stability.

Chemical Stability of Membranes/Ionomers:
Chemical degradation of current PFSA materials is believed to proceed via peroxide radical attack, whereby fluoride ions and low-molecular-weight perfluorosulfonic acid species are the major decomposition products which can be found in the water exiting fuel cell stacks (20). Peroxide radicals are mainly produced by the permeation of oxygen through the membrane followed by partial electrochemical reduction to H₂O₂ on the anode catalyst (21); the presence of adsorbed CO (from CO-contaminated H₂-reformate) further increases the yield of H₂O₂ under these conditions (22).

Accelerated chemical stability tests of candidate ionomer/membrane materials have been conducted by exposing membranes to an aqueous solution of 3%wt H₂O₂ and 4 ppm of Fe²⁺ at 68°C (Fenton’s reagent). Ionomer degradation is determined from fluoride analysis of the solution, assuming that the major degradation product is HF; the percent degradation represents that amount of fluoride released relative to that in the original membrane. Under these conditions, the degradation of current PFSA membranes is ca. 0.5% in an 8 hour period compared to a value of ca. 5% in the case of cross-linked polyphosphazene membranes and ca. 50% in the case of cross-linked sulfonated polystyrene (20). In general it has been found that ionomers which contain hydrogen bonded to aliphatic carbon atoms are not sufficiently stable in the PEFC environment (e.g., sulfonated polystyrene).

Based on our current understanding, this accelerated degradation test is a reasonable predictive method to determine whether certain ionomeric materials may be stable in the fuel cell environment. Nevertheless, there is a small but finite chance that ionomeric materials which fail this test may still be suitable fuel cell materials and consequently this criterion is less stringent than the above presented requirements on conductivity, permeability, solubility, and swelling in the presence of water.

Mechanical Stability of Membranes/Ionomers:
In addition to the requirements described above, there are requirements on ionomer mechanical properties. However, we are not yet able to suggest screening criteria for these properties since the mechanical stresses experienced by the membrane in operating fuel cells are still poorly understood. We have set up such equipment at Giner Electrochemical Systems, LLC (Newton, Massachusetts) where we regularly screen high-temperature membrane candidates for the all of these properties.
Summary of the Requirements for High-Temperature Ionomers/Membranes:

In the above analysis we have attempted to describe the required physical-chemical properties of high-temperature membranes/ionomers, all of which can be determined in *ex-situ* tests so that no fuel cell testing (and MEA preparation) is necessary for the screening of candidate materials. Even though our analysis has been based on simplified assumptions on the design of fuel cell systems, the numerical values of the required properties should be largely independent of the specific fuel cell system design based on our premise that a fuel cell system be as simple as possible in order to be reliable, economical, and efficient.

For a better overview, the physical-chemical and mechanical requirements on high-temperature membranes/ionomers are listed together in Table 4, starting with the most clearly specified requirements on the top and the least well-defined requirements toward the bottom to the table. It should be mentioned that these requirements are necessary but not sufficient conditions for high-temperature membranes/ionomers and we do believe that MEA preparation and fuel cell testing are of limited use unless at least conductivity and permeability of candidate materials fall within the required ranges.

Table 4: Summary of physical-chemical and mechanical property requirements of high-temperature membranes/ionomers and possible testing methods. All properties can be measured *ex-situ* and do not require fuel cell testing.

| Property                  | Membrane | Electrode<sup>a</sup> | Methods                           |
|---------------------------|----------|----------------------|-----------------------------------|
| Conductivity at 25%RH     | >0.1 S/cm at 120°C | >0.1 S/cm at 120°C | 2- or 4-point methods (e.g., (7)) |
| (see Figure 1)            | >0.03 S/cm at 25°C | >0.03 S/cm at 25°C | via GC methods (e.g., (12))       |
| H<sub>2</sub>-Permeability| below solid black line in Figure 3 | above dashed black line in Figure 3 | via GC methods (e.g., (12))       |
| O<sub>2</sub>-Permeability| below solid black line in Figure 4 | above dashed black line in Figure 4 | via GC methods (e.g., (12))       |
| Solubility in H<sub>2</sub>O| <1% at 150°C for 24h | <1% at 150°C for 24h | Autoclave in H<sub>2</sub>O        |
| Swelling in H<sub>2</sub>O| <100% H<sub>2</sub>O uptake in boiling water | <200% H<sub>2</sub>O uptake in boiling water | weight-gain meas. (e.g., (23))    |
| Chemical Stability        | stable in presence of peroxy species | stable in presence of peroxy species | test with Fenton's reagent (e.g., (20)) |
| Mechanical Stability      | critical | less critical | specifications and requirements not yet determined |

<sup>a</sup> note that the ionomer in the membrane may be different from the ionomer used in the electrodes.
CATALYST DEVELOPMENT NEEDS

Over the past decades, volumetric (kW/liter) and gravimetric (kW/kg) power densities have been the most commonly used indicators for tracking the progress of PEFC development, particularly in industry. Having exceeded the initially defined automotive stack power density requirements of 1 kW/liter and 1 kW/kg (e.g., 1.7 kW/liter and 1.2 kW/kg published by GM/Opel (24)), the focus of PEFC R&D in the automotive industry is now shifting toward both an increase in stack operating temperature (see above discussion) and a reduction of the platinum-specific stack-power density (gpt/kW). The latter significantly impacts the final cost of the membrane electrode assembly (MEA) and, equally important, determines the feasibility of a large-scale automotive PEFC market in view of platinum supply constraints.

Assuming a stack peak-power requirement of ca. 75 kW for an average automotive fuel cell vehicle (see reference 1), a Pt-specific stack-power-density of 0.2 gpt/kW would translate into a consumption of 15 gpt/vehicle, a value which may be compared to the Pt-metals loading of catalytic-converters in current vehicles of ca. 3-5 g. The production of 10 million vehicles/year would therefore require 150 tonspt/year, which at a current platinum mining rate of 170 tonspt/year (25) is obviously only feasible if the rate of platinum mining can be increased significantly. According to Jaffray and Hards (25), the latter can be accomplished if the platinum requirements can be forecast reliably 3 to 4 years into the future, an argument based on the time required for a significant expansion of current platinum mines. In conclusion, if Pt-specific stack-power-densities of 0.2 gpt/kW can be achieved, both platinum cost (ca. <$5/kW at <$25/gpt (i.e., <$780/troy-ounce of Pt)) and platinum supply requirements can be met for a large-scale penetration of the automotive market (currently 52 million vehicles/year (25)) with PEFC-based vehicles.

In the following we will outline the three principal approaches toward increasing the Pt-specific power density: i) reduction of the mass-transport losses observed at high current densities in order to maximize the MEA power density; ii) reduction of anode and cathode catalyst loadings at minimized voltage losses (i.e., Pt-thrifting); iii) implementation of improved cathode catalysts. Based on the analysis of 50 cm² active-area MEA fuel cell measurements, it will be shown that the above stated requirement of 0.2 gpt/kW can be met if Pt-alloy cathode catalysts with a claimed 2-3 times improved Pt-mass-activity ((16, 22, 26) or other yet-to-be-developed catalysts can be implemented successfully into PEFCs.

Experimental Details/Procedures:

MEA Preparation – 50 cm² active-area catalyst-coated membranes (CCM) were prepared in-house (6). Carbon-supported 47%wt Pt/carbon (Tanaka, Japan) and organic-solvent based ionomer solutions (ca. 900 EW (equivalent weight)) were used to fabricate thin-layer electrodes which were transferred via a decal method onto ca. 25 μm thick low- EW membranes (ca. 900 EW). An ionomer/carbon ratio of approximately 0.8/1 (weight ratio) was maintained in the electrodes of all prepared CCMs using ionomers identical to the ones used in the membrane. CCMs with various catalyst loadings were produced and loadings are referred to as anode-loading/cathode-loading (e.g., 0.05/0.4 mgpt/cm² refers to a 0.05 mgpt/cm² anode and a 0.4 mgpt/cm² cathode loading). Gas-diffusion media (DM) were treated in-house and are based on carbon-fiber-paper
substrates (Toray Inc., Japan). Both anode and cathode DMs were teflonated and additionally processed using a proprietary surface treatment. Single cells (50 cm²) were assembled by sandwiching CCMs between the appropriate DMs and applying an average compressive load of ca. 1500 kPa_{abs} to the active-area.

**Fuel Cell Testing** – Fuel cell stations from Fuel Cell Technology (Los Alamos, NM) were used to test 50 cm² active-area MEAs. Pure oxygen or air were used as cathode reactants and pure H₂ as anode reactant (all gases of 99.99% purity). Stoichiometric flow rates were used for current densities ≥0.2 A/cm², while at lower current densities constant flows based on the stoichiometric flows at 0.2 A/cm² were used. Reactant humidification was achieved by water-bubblers, the temperature of which was calibrated to yield the quoted relative humidity (RH) values. Cell resistances as a function of current density (i.e., the sum of the proton-conduction resistance in the membrane and the various electronic resistances (bulk and contact resistances)) were determined using an AC perturbation of 1 kHz. For each data point, the cell voltage was stabilized over 15 minutes and data were averaged over the last 5 minutes; it should be noted at this point that measurement times of this order are imperative if one desires to obtain meaningful steady-state fuel cell performance and kinetic data. Kinetic analysis was conducted on the basis of H₂-crossover-corrected effective current densities, i_{eff}=i+i_{x}, whereby the value of the H₂-crossover current density, i_{x}, was measured according to reference (13).

Multiple-path serpentine flow-fields (2 and 3 parallel channels for the anode and cathode, respectively) machined into sealed graphite blocks (Poco) were used. The flow-field channel width was approximately 0.8 mm with a channel/land width ratio of 1.3/1.

**Analysis of Voltage-Loss Terms in State-of-the-Art MEAs:**

*H₂/O₂ performance* – Figure 7 shows the resistance-corrected cell voltage versus the logarithm of the effective current density with fully humidified pure H₂/O₂ (stoichiometric flows of s=2.0/9.5) at 150 kPa_{abs} and 80°C. The fact that a straight Tafel-line with a constant slope of 70 mV/decade is obtained for current densities ranging from ca. 0.02 to 2 A/cm², suggests pure kinetic control by the oxygen reduction reaction (ORR). The overpotential of the ORR, η_{orr}, can therefore be modeled by a simple Tafel-relation

\[ η_{orr} = 70 \text{ mV/decade} \cdot \log(i_{eff}) \]  

Analysis of the H₂/O₂ data in Figure 7 in combination with the *in-situ* determined accessible platinum surface area of ca. 60 m²Pt/gPt (measured in the so-called driven cell mode (see reference 13)) results in a value for the exchange-current density of 1.7×10⁻⁸ A/cm²Pt (normalized to P_{O₂}=100 kPa_{abs} and assuming an equilibrium voltage of E_{eq}=1.184 V (4); for details see reference 6). This is slightly larger than the exchange-current densities at 80°C published in the literature, ranging from 0.2–10⁻⁸ A/cm²Pt to 0.9×10⁻⁸ A/cm²Pt (6, 27, 28, 29), a discrepancy which we associate with the large error in extrapolating the H₂/O₂-Tafel-line over many orders of magnitude in current density. Consequently, much better consistency is found by comparing the intrinsic activity at 0.90 V which is obtained directly from Figure 7 without extrapolation. Clearly, the value of i_{x,0V}=44 mA/cm²=0.18 mA/cm²Pt (at 100 kPa O₂) extracted from Figure 7 falls now within the rather narrow range of 0.14 to 0.32 mA/cm²Pt reported in the literature (6, 27, 28, 29). Therefore, the evaluation and benchmarking of new or modified catalysts is
achieved most precisely via evaluating values of \( i_{0.9V} \) rather than the exchange-current density; however, it is critical to use steady-state data (>5 mins./point) rather than voltammetric sweep data as the latter would result in much higher non-steady-state values.

Figure 7: Resistance-corrected single-cell voltage, \( E_{R,\text{free}} \), versus \( H_2 \)-crossover corrected effective current density, \( i_{\text{eff}} \), with \( H_2/O_2 \) and \( H_2/\text{air} \) for a 50 cm\(^2\) active-area MEA using a ca. 25 \( \mu \)m low-EW membrane (ca. 900 EW) coated with electrodes consisting of ca. 50\%wt. Pt/carbon (0.4/0.4 mgPt/cm\(^2\) (anode/cathode)) and a low-EW ionomer (ca. 900 EW; ionomer/carbon ratio=0.8/1). Data were recorded at a cell temperature of 80°C with fully-humidified reactants (80°C dewpoints, i.e., 100\% RH) at a total pressure of 150 kPa\(_{\text{at}}\) and stoichiometric flows of \( s=2.0/9.5 \) (\( H_2/O_2 \)) and \( s=2.0/2.0 \) (\( H_2/\text{air} \)), respectively (controlled stoichiometric flows for \( i_{\text{eff}} < 0.2 \text{ A/cm}^2 \)). The dashed line is a parallel-shifted guide-to-the-eye, following the same Tafel-slope as for pure \( O_2 \) (solid regression line). Voltages were averaged between 10 and 15 mins, holding time at each current density (measured current densities are corrected for \( H_2 \)-crossover of 2.5 mA/cm\(^2\)).

**\( H_2/\text{air} \) performance** – Based on the above findings one would expect a similarly straight Tafel-line for fuel cell operation with air instead of \( O_2 \), but offset toward lower cell voltages due to the reduced oxygen partial pressure in air. As is shown in Figure 7, this is indeed true for very low current densities where \( H_2/O_2 \) and \( H_2/\text{air} \) Tafel-curves are parallel and offset in the expected direction. At current densities above 0.1 A/cm\(^2\), however, the \( H_2/\text{air} \) curve begins to deviate from the kinetically-controlled Tafel-line of 70 mV/decade and displays an increase in the apparent Tafel-slope with increasing current density, indicative of additional mass-transport related resistances (due to diffusion-overpotentials at the cathode and possibly potential gradients in the electrolyte phase of the electrode). Since the purely ohmic resistance losses, \( \Delta E_{\text{ohmic}} \), are measured \textit{in-situ}, the mass-transport related overpotential, \( \eta_{\text{tx}} \), can be evaluated via:

\[
\eta_{\text{tx}} = E_{\text{eq}} - E_{\text{cell}} - \eta_{\text{ORR}} - \Delta E_{\text{ohmic}}
\]  

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where the $\eta_{\text{ORR}}$-term is calculated by assuming that the resistance-free H$_2$/air cell voltage at current densities $<$0.1 A/cm$^2$ is purely controlled by the ORR kinetics with a Tafel-slope of 70 mV/decade (for details see reference 6). The mass-transport induced voltage losses may be visualized in Figure 7 by the voltage difference between the extrapolated kinetically-controlled Tafel-line (dashed line) and the resistance-corrected air-curve (circles). Overall it may be stated that the mass-transport induced voltage losses are negligible below 0.2 A/cm$^2$ and amount to ca. 65 mV at 1 A/cm$^2$. Based on comparative experiments with helox (21% O$_2$ in He), the majority of these mass-transport related losses seem to be due to flooding of the diffusion medium (6) and data in the literature (30) suggest that this can be alleviated by proper design of the flow-field/diffusion medium interface.

Figure 8 presents the polarization curve (not IR-corrected) shown in Figure 7 and indicates the various losses determined from the analysis described above, and the results reveal the various possibilities for performance improvements.

![Figure 8](image_url)

**Figure 8:** a) circular symbols: 50 cm$^2$ single-cell voltage, $E_{\text{cell}}$, versus current density, $i$, with H$_2$/air ($s=2.0/2.0$) for a 50 cm$^2$ MEA at a cell temperature of 80°C with fully-humidified reactants at a total pressure of 150 kPa abs (same experimental conditions and MEA as in Figure 7). b) triangular symbols: $E_{\text{cell}}$ vs. $i$ for the mass-transport-free $E_{\text{cell}}/i$-curve shown in a). c) square symbols: $iR$-correction of the $E_{\text{cell}}/i$-curve shown in b) using *in-situ* high-frequency resistance measurements at 1 kHz (ranging from 45 to 55 mQcm$^2$). d) diamond symbols: $E^n/i$-curve shown in a) corrected for 50% of the mass-transport losses.

The experimentally measured polarization curve achieves approx. 0.58 V at 1.5 A/cm$^2$ (circles in Figure 8), but could potentially reach 0.70 V at the same current density if one were able to reduce mass-transport related voltage losses to zero (triangles in Figure 8). Yi *et al.* have shown recently (30), that voltage losses due to "flooding" phenomena can be reduced significantly by an optimized design of the MEA/diffusion-medium/flow-field interfaces and it is not implausible to assume that at least 50% of the currently observed
mass-transport related voltage losses might be recovered (diamonds in Figure 8) by proper interface design. The ohmic resistances in the graphite hardware used in these experiments are 0.050±0.005 Ωcm² (measured in-situ), whereby the contributions from contact resistance (mainly between the flow-field and the diffusion medium) and from the proton conduction resistance in the membrane are of approximately equal value (6). Thinner or more conductive membranes and lower contact-resistance DM/flow-field configurations would reduce these losses, but the potential for improvement is clearly less than in the case of the mass-transport losses. Clearly the biggest voltage-loss is due to sluggish oxygen reduction kinetics and besides modest improvements over pure Pt reported for Pt-alloy cathode catalysts (ca. 20-40 mV at constant current density, equivalent to a factor of 2 to 3 in current density at constant cell voltage (16, 22, 26)), no other material options have ever been reported.

**Current and Projected MEA Performance and Pt-Specific Power Densities:**

We now analyze the consequence of the above deconvolution of the various voltage-loss contributions and the significance with regards to the long-term automotive requirement to obtain platinum-specific stack-power densities of ≤0.2 gPt/kW. A further consideration in defining this goal is that a cell voltage significantly above 0.60 V is required in order to both effectively harvest the higher energy conversion efficiency of fuel cell systems compared to internal combustion engines and to reduce the amount of heat which needs to be rejected by the system via the radiator (1).

The following analysis is based on the polarization curves shown in Figure 8, obtained with MEAs having a Pt-loading of 0.40/0.40 mgPt/cm² (anode/cathode). In a recent study (31) we have shown, however, that the Pt-loading of the anode electrode can be reduced to 0.05 mgPt/cm² without significant voltage loss in the case of H₂/air fuel cell operation with pure H₂ (rather than CO-contaminated reformate), a fact related to the very facile H₂ oxidation kinetics on Pt in the absence of CO (32). With this in mind, the current state-of-the-art MEA performance shown in Figure 8 (line a), circular symbols) can be analyzed in terms of Pt-specific power density vs. cell voltage, assuming a total MEA Pt-loading of 0.45 mgPt/cm² (i.e., 0.05/0.40 mgPt/cm² (anode/cathode)). This is shown by the first line from the top in Figure 9 (line a), circular symbols), clearly demonstrating the trade-off between voltage efficiency (i.e., cell voltage) and Pt-specific power density. Quite obviously, the automotive requirement of <0.2 gPt/kW at E_{cell}>0.6 V is missed by a factor of three with this MEA/cell-design technology and approaches need to be developed with which this requirement can be met.

Higher Pt-specific power densities can be achieved by reducing the mass-transport related voltage-losses via improving the MEA/DM/flow-field interfaces, as was demonstrated in a recent article by Yi et al. (30). Assuming that ca. 50% of the observed mass-transport related voltage losses can be recovered by optimized design, the power density of the MEA at 0.65 V can be increased by approx. 25% (circles vs. diamonds in Figure 8), thereby increasing both the volumetric and the gravimetric power density of the fuel cell stack. This also translates to a similar improvement of the Pt-specific power density (see diamond symbols, line b) in Figure 9), but still falls short by more than a factor 2 of the desired goal of <0.2 gPt/kW.
Figure 9: Pt-specific power-density \([\text{gpt/kW}]\) vs. cell voltage, \(E_{\text{cell}}\), based on the performance data shown in Figure 8 both for the uncorrected cell voltage (see a) in Figure 8) and the performance curve projected for a 50% reduction of mass-transport losses (see d) in Figure 8). It is assumed that the cell performance can be maintained at a reduced anode loading of 0.05 mgPt/cm² (see text).

a) circular symbols: \(g_{\text{e}}/\text{kW}\) vs. \(E_{\text{cell}}\) for the uncorrected cell performance curve in Figure 8 (a).
b) diamond symbols: \(g_{\text{e}}/\text{kW}\) vs. \(E_{\text{cell}}\) for the cell performance curve in Figure 8 (d) for which the mass-transport losses were assumed to be reduced by 50%.
c) square symbols: \(g_{\text{e}}/\text{kW}\) vs. \(E_{\text{cell}}\) for the above curve (b), assuming a two-fold reduction of the Pt-cathode loading to a total loading of 0.05/0.2 mgPt/cm² (anode/cathode), accompanied by a cell voltage loss of 21 mV independent of current density (see text).
d) triangular symbols: \(g_{\text{e}}/\text{kW}\) vs. \(E_{\text{cell}}\) for the above curve (c), assuming a doubling of the Pt-specific cathode-catalyst activity without cell voltage loss, resulting in a total Pt loading of 0.05/0.1 mgPt/cm² (anode/cathode).

A more significant step toward approaching the above automotive requirements is achieved by a two-fold reduction of the platinum cathode-loading, if the associated cell voltage loss can be minimized. Considering that the PEFC performance is largely controlled by the \(O_2\) reduction reaction kinetics (see Figure 8), a reduction of the platinum cathode-loading is expected to definitely lead to a cell voltage loss. The best-case scenario, i.e., the minimum achievable voltage loss, would be the kinetic limit described by the Tafel-relation for the ORR (see reference 6 for a detailed analysis):

\[
\Delta E_{\text{loss-ORR}} = 70 \text{mV/decade} \cdot \log(L_1 / L_2)
\]

where \(\Delta E_{\text{loss-ORR}}\) describes the kinetically-limited voltage loss if the cathode Pt-loading is reduced from a value of \(L_1\) to \(L_2\). For a cathode loading reduction by a factor of two, this would translate into a minimum voltage loss of 21 mV across the entire current density range or, in other words, into a down-shift of the polarization curves in Figure 8 by 20 mV. For most available non-optimized MEAs, a cathode loading reduction from 0.40 to 0.20 mgPt/cm² leads to cell voltage losses on the order of 40 to 60 mV, i.e., far beyond the above prediction based on ORR kinetics (31). In the case of specifically optimized low-Pt-loading MEAs, however, the predicted kinetically-limited cell voltage loss of ca.
20 mV can indeed be observed over the entire current density range (31). In this case, an optimized MEA/DM/flow-field configuration with 50% improved mass-transport losses (diamond symbols in Figure 9) and a reduced MEA loading of 0.05/0.20 mgPt/cm² will produce Pt-specific power densities very closely approaching the <0.2 gpt/kW target (see square symbols, line c) in Figure 9).

Any further improvements via MEA/DM/flow-field interface optimization or Pt-thrifting are unlikely to further approach the Pt-specific power density requirement, if a cell voltage of >0.60 V is demanded. This most likely can only be achieved by an improvement of the intrinsic cathode catalyst activity by a factor of at least two, i.e., by at least doubling the mass-specific activity of platinum (in terms of A/mgPt). There are quite a few reports in the literature that this can be accomplished by the implementation of Pt-alloy cathode catalysts, e.g., PtCo, PtNi, PtCr (16, 22, 26), for which voltage gains on the order of 25 to 40 mV have been reported, consistent with a factor of two to three increase in Pt mass-specific activity. This intrinsic kinetic gain for Pt-alloys was also confirmed in our laboratory (33), and MEA implementation would allow the Pt-loading to be reduced from 0.25 mgPt/cm² (0.05/0.20 mgPt/cm² anode/cathode) to 0.15 mgPt/cm² (0.05/0.10 mgPt/cm² anode/cathode) without any loss in cell voltage. In this scenario, a Pt-specific power density of <0.2 gpt/kW could be achieved at a cell voltage of 0.65 V as is shown in Figure 9 (triangular symbols, line d)).

In summary, the very stringent automotive requirements in terms of Pt-specific power density combined with high voltage efficiency can be met only if the mass-specific activity of Pt-based cathode catalysts can be at least doubled. Initial data with Pt-alloys seem to satisfy this criterion, but significant fundamental research efforts are still required to both optimize their performance and to demonstrate the long-term durability of Pt-alloys which until now is unknown. So far, no Pt-free cathode catalysts have been demonstrated to achieve significant current densities at cell voltages comparable to what is obtained with platinum, but world-wide research efforts in cathode catalyst development have been very limited over the past twenty years and other catalysts may be found in the future if a focused effort is placed in this area.

SUMMARY AND CONCLUSIONS

As PEFC commercialization approaches, the need for product and manufacturing engineering is obviously increasing. However, the need remains for aggressive research and development focussed on new fuel cell materials, particularly if the technology is to meet demanding automotive requirements. Improved polymer electrolyte and catalyst materials will have the largest impact on PEFC commercialization. The development of these new materials will be most efficient if end-users attempt to define material requirements in terms of properties than can be measured in well-defined ex-situ characterization tests. The process of materials discovery will be most efficient if materials developers focus on making materials and obtaining ex-situ data. Once promising materials have been identified, projects involving implementation in MEAs can then be launched, ideally involving experts in MEA preparation. This approach will allow polymer scientists and electrocatalyst experts to focus their efforts on discovering materials and avoid wasting their efforts on the time consuming and potentially misleading process of MEA preparation.
We determine that an ideal automotive fuel cell polymer electrolyte would exhibit an ionic conductivity of 0.1 S/cm (at 25% relative humidity and 120°C). We identified upper (set by fuel efficiency constraints) and lower (set by electrode requirements) oxygen and hydrogen permeability limits of the electrolyte. More work is needed to identify reliable electrolyte chemical stability and mechanical property requirements. To reach automotive cost targets, cathode catalysts with mass specific activity twice that of those available today are needed. Promising approaches to achieve this include a combination of improved dispersion and improved intrinsic activities (e.g. stable Pt alloys).
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