

# Approaches and technical challenges to high temperature operation of proton exchange membrane fuel cells

C. Yang<sup>a,b,\*</sup>, P. Costamagna<sup>b</sup>, S. Srinivasan<sup>b</sup>, J. Benziger<sup>c</sup>, A.B. Bocarsly<sup>d</sup>

<sup>a</sup>Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08540, USA

<sup>b</sup>Center for Energy and Environmental Studies, Princeton University, Princeton, NJ 08540, USA

<sup>c</sup>Department of Chemical Engineering, Princeton University, Princeton, NJ 08540, USA

<sup>d</sup>Department of Chemistry, Princeton University, Princeton, NJ 08540, USA

Received 9 May 2001; accepted 15 May 2001

## Abstract

Water loss and the coincident increase in membrane resistance to proton conduction are significant barriers to high performance operation of traditional proton exchange membrane fuel cells at elevated temperatures where the relative humidity may be reduced. We report here approaches to the development of high temperature membranes for proton exchange membrane fuel cells; composite perfluorinated sulfonic acid membranes were prepared to improve water retention, and non-aqueous proton conducting membranes were prepared to circumvent the loss of water. Experimental results of composite membranes of Nafion and zirconium phosphate show improved operation at elevated temperatures. Imidazole impregnated membranes poisoned the electrocatalysts. Cesium hydrogen sulfate membranes were not able to produce appreciable current. A brief analysis of temperature requirements for CO tolerance and a framework for understanding water loss from fuel cell membranes are presented. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Nafion; Zirconium phosphate; Imidazole; Cesium sulfate; Proton conductivity; Water balance

## 1. Introduction

### 1.1. Background and motivation

Proton exchange membrane fuel cells (PEMFCs, also called polymer electrolyte fuel cells) offer potential advantages of clean and efficient energy conversion systems for automobiles, portable applications, and power generation. PEMFCs function best with high purity hydrogen gas as the fuel source, but pure hydrogen is unlikely to be the fuel source in the near term due to technical and economic considerations in production and storage, especially in applications such as transportation and stationary power generation. Instead, hydrogen from reformed fuels such as natural gas, gasoline, or alcohols will likely be the fuel that is supplied to the fuel cell. These gas streams will contain small amounts of carbon monoxide (CO) which poisons the platinum anode catalyst. High temperature operation of a PEMFC (above 120°C) has been investigated [1–4] to reduce the effects of CO adsorption onto the platinum electrocatalyst. In addition to increasing the tolerable CO

concentration in the anode fuel, higher temperature operation can improve thermal management and heat utilization of the fuel cell stack, increase reaction rates at the anode and cathode, and potentially simplify fuel cell water management.

The typical membranes for these low temperature proton exchange membrane fuel cells (PEMFCs) are DuPont Nafion<sup>TM</sup> or other perfluorinated sulfonic acid polymers (e.g. Aciplex from Ashai Chemicals). These membranes have a multi-phase structure [5]: a hydrophobic region which is the continuous phase with inclusions of hydrophilic sulfonic acid groups. The continuous hydrophobic phase is essential for the structural integrity of the membrane. Water is essential for proton conductivity because it promotes dissociation of the proton from the sulfonic acid and provides highly mobile hydrated protons. For optimal performance, these membranes must be well hydrated, which swells the membranes and allows for bridging between ionic inclusions facilitating proton conductivity. To keep the membrane hydrated one or both of reactant gas streams must be humidified; integrated systems that rely on product water to maintain membrane hydration are still under development. Use of these membranes at elevated temperatures leads to evaporation of water from the membrane, and a loss

\* Corresponding author. Fax: +1-609-258-366.  
E-mail address: cyang@princeton.edu (C. Yang).

of membrane ionic conductivity. Changes in the conductivity by several orders of magnitude are correlated with water content of the membrane [6,7].

High protonic conductivity in the membrane is crucial to achieving high power density in a fuel cell. Low membrane hydration leads to large Ohmic losses which lowers operating voltage, power, and efficiency at a given current. As a result, dehydration at higher temperatures could potentially offset any performance benefits that would arise from higher CO tolerance. One of the objectives of our investigations was to prepare and operate membranes that can operate at elevated temperatures ( $\geq 120^\circ\text{C}$ ) with comparable performance to state-of-the-art low temperature ( $80^\circ\text{C}$ ) membranes. Operation of PEMFCs above  $100^\circ\text{C}$  presents technical challenges to maintaining proper hydration of these membranes. In the present paper, several approaches for high temperature membrane operation are analyzed along with experimental exploration of these approaches. This paper reviews the relevant thermodynamics for CO tolerance and for water balance in fuel cell membranes, which is important for understanding and improving fuel cell membranes and for defining the proper operating conditions for PEMFCs.

### 1.2. Possible approaches for high temperature operation

Several approaches have been attempted to prevent the loss of water from the ionic regions (pores) of the membrane thereby maintaining the conductivity of the ionomer membranes at temperatures near and above the normal boiling point of water. Hydrophilic, inorganic material may be incorporated into the perfluorinated ionomer membrane to increase the binding energy of water. The efficacy of these hydrophilic additives has been demonstrated in the case of heteropolyacids in Nafion [1]. Water molecules are strongly hydrogen bonded to the ions or dipoles in the inorganic material; additionally, the acid may increase proton conductivity by adding additional solvent and increasing proton density. Previous attempts were made by our group to evaluate some of the results of work on heteropolyacids [8]. The acid helped to maintain sufficient membrane hydration at  $115^\circ\text{C}$  to have good performance in a fuel cell; however, over time the liquid water drained from the fuel cell and leached acid from the membrane, reducing the water retention. To overcome this problem, solid materials that can be immobilized in the membrane were investigated. The materials examined in our labs include silica gel, sulfated zirconia, and zirconium phosphate.

A second approach investigated is the use of a non-aqueous, low volatility solvent to replace water as the proton acceptor within the perfluorinated ionomer membrane. Replacing water as the primary proton carrier has been demonstrated in membranes with phosphoric acid, imidazole, butyl methyl imidazolium triflate, and butyl methyl imidazolium tetrafluoroborate [4,9,10]. The rationale is that other liquid solvents can perform the function of water in

proton conduction but with improved physical characteristics (i.e. low volatility). Water is an excellent solvent for use in the fuel cell membrane because of its ability to act as a Bronsted base, its high dielectric constant, and because it is a product of the fuel cell reaction. In order for another solvent to serve as a replacement for water, it is important that it fulfill the first two characteristics. We extended the work of Kreuer et al. and examined composite Nafion membranes saturated with imidazole in hydrogen fuel cells [9].

The third approach we explored was the use of a solid state protonic conductor whose conduction mechanism occurs in the absence of water. Whereas the first two approaches relied on an acidic membrane such as Nafion and a liquid solvent for proton transport, this approach is based on a solid state material that conducts protons in the absence of a liquid solvent. Solid oxide conductors have been employed for many years in high temperature fuel cells but work is beginning on low temperature solid state proton conductors for fuel cells [11]. Cesium hydrogen sulfate, a low temperature proton conductor, was immobilized in a porous support and incorporated in a hydrogen fuel cell.

Our results account for the improved performance of composite membranes and identify the technical challenges in finding water-dependent proton conducting membranes for PEMFCs operating at elevated temperatures. We present a thermodynamic analysis of CO tolerance and the water balance in perfluorinated membranes. This analysis relates the minimum operating temperature for CO tolerance and the required relative humidity and operating pressure for adequate membrane hydration.

## 2. Experimental methods

### 2.1. Composite membranes and methods of preparation

Nafion 115 membranes were purchased from E.I. du Pont de Nemours and Company (DuPont) and prepared as follows: (i) immersing in a boiling 3%  $\text{H}_2\text{O}_2$  solution for 1 h to remove any organic impurities; (ii) rinsing in boiling  $\text{H}_2\text{O}$ ; (iii) removing any metallic impurities from the membrane by boiling in 1 M  $\text{H}_2\text{SO}_4$  for 1 h, and (iv) then rinsing again in boiling  $\text{H}_2\text{O}$ . The membranes were dried at  $80^\circ\text{C}$  for 1 h to prepare for impregnation. Recast Nafion membranes were prepared from a DuPont Nafion Solution (5% in water and lower alcohols) as follows: Nafion solution and isopropanol were mixed in a 1:2 volume ratio and then set in an  $80^\circ\text{C}$  oven overnight until all solvent evaporated. Then the film was heat-treated by placing into a  $170^\circ\text{C}$  oven for 30 min. The membrane was weighed and its thickness measured. The pre-treatment cleaning process was applied, following same procedure as for Nafion 115.

Composite Nafion/zirconium hydrogen phosphate ( $\text{Zr}(\text{HPO}_4)_2$ ) membranes were prepared by swelling pre-treated Nafion 115 in a 1:1 volume mixture of methanol and water at  $80^\circ\text{C}$  and placing the swollen membranes in 1 M

ZrOCl<sub>2</sub> (Aldrich) for 2 h at 80°C to introduce the zirconium into the membrane (ion exchange of Zr<sup>4+</sup> ions for H<sup>+</sup> ions) and then immersed in 1 M H<sub>3</sub>PO<sub>4</sub> (80°C) overnight [12]. The membrane was rinsed in boiling water for several hours, dried, weighed, and its thickness measured. The form of zirconium phosphate in the membrane is believed to be one of the crystalline forms of  $\alpha$ -zirconium phosphate (Zr(HPO<sub>4</sub>)<sub>2</sub>) [13]. These membranes increase in weight by approximately 25% and in thickness by about 30% from 5 mil (125  $\mu$ m) to 6.5 mil (165  $\mu$ m) as compared with the Nafion 115.

Solid sulfated zirconia was prepared in the following manner: dry zirconium hydroxide was sulfated by reaction with boiling 0.5 M H<sub>2</sub>SO<sub>4</sub> for 1 h. The material was filtered at 110°C and calcined at 700°C to promote the acidic surface. This solid material was crushed into a fine powder ( $\sim$ 20  $\mu$ m) and added to the Nafion solution to recast into a membrane, as described above. Membranes were formed in this manner with varying amounts of the sulfated zirconia added.

Imidazole/Nafion membrane were prepared by three different methods. The first method involved dipping a dried Nafion 115 membrane into molten imidazole (90°C) and allowing the imidazole to recrystallize inside the nanopores of Nafion. In the second method, a Nafion 115 membrane was soaked in a solution of imidazole dissolved in methanol. The methanol solvent was then evaporated from the membrane at 80°C. In the third method, imidazole was added to the solubilized Nafion. The solution was introduced onto porous glass paper (i.e. filter paper) and the solvent evaporated to produce a supported Nafion/imidazole recast membrane.

The cesium hydrogen sulfate was synthesized by reacting a solution of Cs<sub>2</sub>CO<sub>3</sub> with pure H<sub>2</sub>SO<sub>4</sub> at room temperature under a nitrogen atmosphere. The CsHSO<sub>4</sub> precipitate was filtered from the solution and dissolved in H<sub>2</sub>O. The solution was incorporated onto a porous glass (Millipore<sup>®</sup> glass filter paper) support and left at 80°C to remove the water and crystallize in the 0.7  $\mu$ m pores of the support. Overall thickness of the supported membrane was 200  $\mu$ m.

Each of these membranes was used to prepare the membrane–electrode assemblies (MEAs) with commercial ELAT 5 cm<sup>2</sup> electrodes (20% Pt on carbon, 0.4 mg Pt/cm<sup>2</sup> from E-TEK), impregnated with 0.6 mg/cm<sup>2</sup> of Nafion (dry weight). For this purpose, two electrodes were hot-pressed onto both sides of the membranes for 2 min at 130°C and 1000 kgf.

## 2.2. Conductivity measurements

Conductivity measurements were made external to the fuel cell environment, rather than on the membrane–electrode assembly [14,15]. The membrane was held in the transverse or longitudinal position between small graphite electrodes and this assembly kept at 100% relative humidity at temperatures between 50 and 100°C. For non-aqueous samples, the samples were maintained in a dry atmosphere

as temperature was varied between 50 and 200°C. The measurements were made using a two probe method on a Princeton Applied Research potentiostat/galvanostat Model 273A and Princeton Applied Research lock-in amplifier Model 5210, connected to a PC running electrochemical impedance software (EIS). These conductivities are compared to that of fully-hydrated Nafion ( $\sim$ 0.1 S/cm).

## 2.3. Performance evaluation in PEMFC

Membrane–electrode assemblies were tested in a single cell under typical fuel cell operating conditions and high temperature conditions. The MEAs were placed in 5 cm<sup>2</sup> single cell test fixture and the gas pressure, flow rate, temperature, humidification and single cell temperature were controlled using a Globetech<sup>™</sup> fuel cell humidification system. Pure H<sub>2</sub> and O<sub>2</sub> were used at the anode and cathode, respectively. The humidity of the anode and cathode reactant gases was varied by bubbling the gas streams through bottles of water at controlled temperature. The temperature, pressure and humidification conditions in the fuel cell were varied and current–potential (*I*–*V*) curves were generated using an Amrel Fuel Cell Electronic Load (FEL-60). For water-dependent membranes, the fuel cell conditions that were most often used were a total pressure of 3 atm and several temperatures between 80 and 140°C.

## 3. Experimental results and analysis

### 3.1. Analysis of results on water-dependent membranes

Fig. 1 shows the typical current–voltage response of a PEMFC with an unmodified Nafion 115 when operated at 3 atm total pressure over a range of temperatures and humidification conditions. The water vapor pressure varied with the temperature in the humidification bottles, and the

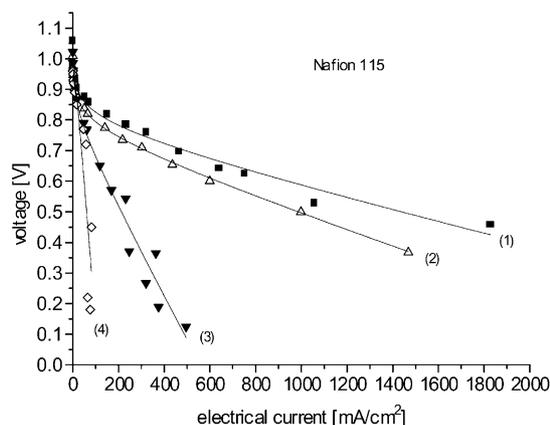


Fig. 1. Nafion 115 control sample at 3 atm operating pressure under different temperature and humidification conditions: (1) (■) anode: 99°C; cell: 80°C; cathode: 88°C; (2) (Δ) 130/120/130; (3) (▼) 130/130/130; (4) (◆) 130/140/130.

hydrogen and oxygen pressures made up the difference. Direct measurement of the relative humidity was not possible in the fuel cell; we estimate the vapor pressure to be around 90% of the saturation vapor pressure at the bottle temperature. When the humidification bottle temperatures were higher than the single cell temperature, the membrane performance was good (i.e. modest Ohmic losses  $\sim 0.25 \Omega \text{ cm}^2$ ) as characterized by the low slope of the linear region. The performance was slightly better at the temperature conditions of 99/80/88 (anode humidification/cell/cathode humidification temperatures, respectively) than at 130/120/130. The reactant gas partial pressure at both the anode and cathode and relative humidity in the cell were higher at lower temperatures, which would improve cell performance.

However, when the humidification temperature was equal to that of the single cell or lower (i.e. at 130/130/130 or 130/140/130) resulting in reduced relative humidity conditions, the PEMFC performance decreased considerably with Ohmic losses increasing dramatically to greater than  $2.5 \Omega \text{ cm}^2$ . Increasing the cell temperature while keeping humidification bottles fixed, reduced the relative humidity in the cell. Under these conditions, reduced relative humidity of the vapor phase leads to greater evaporation of water from the membrane and the increase in the slope of the linear (Ohmic) region. Even under these high temperature conditions, the fuel cell performance was reasonably stable over several hours of testing. There was no significant difference between the performance of the MEA with a recast Nafion membrane including sulfated zirconia ( $20 \mu\text{m}$  particle size) and the control MEA with unmodified recast Nafion. The lack of improvement in performance from the sulfated zirconia for both the membrane conductivity and fuel cell behavior can most likely be explained by the uneven and discontinuous distribution of the sulfated zirconium particles in the recast Nafion matrix. Further optimization of this membrane, incorporating a more even distribution of finer particles needs to be carried out.

Fig. 2 shows the performance of the PEMFC with a Nafion/zirconium phosphate composite membrane. Compared to the performance of the PEMFC with an unmodified Nafion membrane shown in Fig. 1 or the sulfated zirconia membrane (not shown), the Ohmic resistance of the zirconium phosphate membrane under conditions of reduced relative humidity at 130 and  $140^\circ\text{C}$  was substantially less than for the Nafion or the Nafion/sulfated zirconia membranes. The difference between the Nafion/ZP membrane and the Nafion/sulfated zirconia membrane is most likely due to the distribution of the inorganic phase within the membranes. The zirconium phosphate was prepared by impregnation to promote a continuous structure which both occupies and connects the ion-cluster domains of the Nafion. The particulate sulfated zirconia is not evenly distributed throughout the recast Nafion membrane so that any improved hydration effect is limited to the immediate region where the particles are situated and are not able to enhance the conductivity of the entire membrane. This improved fuel

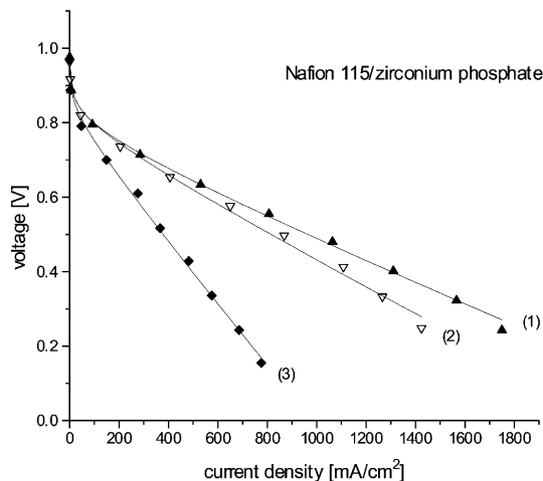


Fig. 2. Nafion 115/zirconium phosphate membrane (22 wt.%) at 3 atm under different temperature and operating conditions: (1) ( $\blacktriangle$ ) 130/120/130; (2) ( $\nabla$ ) 130/130/130; (3) ( $\blacklozenge$ ) 130/140/130.

cell operation with the Nafion<sup>TM</sup>/zirconium phosphate composite membranes has also been observed with silica/Nafion composite membranes with well dispersed silica [16].

Composites of Nafion with polymeric silicon oxide, sulfated zirconia, zirconium phosphate and proton conducting glasses were investigated in our laboratory. In each of these composites, the second component added to the Nafion was hydrophilic. In addition, some inorganic compounds have surface acidity which may increase proton conductivity of the membrane [17,18]. However, as shown in Fig. 3, the specific conductivity of the Nafion/zirconium phosphate composite membranes as a function of temperature were approximately the same or slightly lower as for the control Nafion samples. The results of the conductivity measurement are consistent with their respective performances in proton exchange membrane fuel cells under well-hydrated conditions, at  $80^\circ\text{C}$ . However, at temperatures above  $100^\circ\text{C}$ , the PEMFCs with the composite membranes including silicon oxide and zirconium phosphate showed higher current density at fixed voltage than obtained with Nafion. The

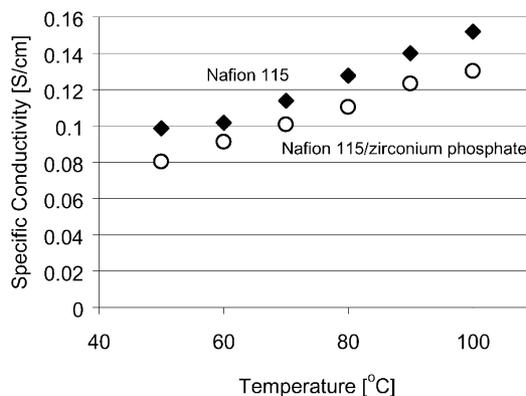


Fig. 3. Membrane conductivity for Nafion and Nafion/zirconium phosphate membrane measured by two probe ac impedance.

Table 1  
Comments of performances of composite membranes

Composite membrane material	Comments about high temperature performance
<b>Water-dependent membranes</b>	
Sulfated zirconia/recast Nafion	Large particles: no improvements
Zirconium phosphate/Nafion 115	Crystalline precipitate: large improvement
Zirconium phosphate/recast Nafion	Particulate oxide: large improvement
Silicon oxide/Nafion 115	Particulate oxide: large improvement
Silicon oxide/recast Nafion	Particulate oxide: large improvement
Proton conduction glasses/recast Nafion	No improvement
Heteropolyacids/Nafion	Temporary improvement but loss of HPA over time
<b>Non-aqueous membranes</b>	
Imidazole/Nafion 115	Low conductivity
Imidazole/recast Nafion	Good conductivity: poisoned Pt electrodes
Cesium sulfate/porous glass support	Low conductivity: poor stability in fuel cell

performances of PEMFCs with composite membranes are summarized in Table 1. Our studies suggest that composite membranes incorporating silicon oxide and zirconium phosphate are the most promising for operation of the PEMFCs above 100°C (Fig. 4).

### 3.2. Analysis of results of non-aqueous membranes

The proton conductivity of Nafion/imidazole samples depended on their preparation. Introduction of imidazole via a methanol solution produced a membrane with low conductivity ( $<10^{-3}$  S/cm) over the range of temperatures tested (40–200°C). The membrane impregnated with molten imidazole had a conductivity around  $10^{-5}$  S/cm below 90°C; the conductivity increased to  $10^{-2}$  S/cm above 90°C. This increased in conductivity is attributed to the melting of the imidazole. At room temperature, the membranes became brittle and easily broke after impregnation with imidazole. The recast Nafion and imidazole membrane (~10 wt.%) had the highest conductivity. At high temperatures (160–180°C),

its conductivity ( $\sim 0.1$  S/cm) was comparable to hydrated Nafion at low temperatures and over an order of magnitude higher than pure imidazole ( $5 \times 10^{-3}$  S/cm at 130°C) [9].

The imidazole impregnated recast Nafion membrane was tested in a fuel cell but was not able to generate any current. Cyclic voltammetry indicated that the imidazole poisoned the platinum electrocatalyst in the potential region for electro-oxidation of hydrogen and it was oxidized in the potential region of oxygen reduction. Although the imidazole-based membrane was promising with respect to its proton conductivity at elevated temperatures, its chemical incompatibility with the platinum catalyst makes it necessary to search for new materials with the desired electrochemical properties.

CsHSO<sub>4</sub> is a solid state proton conductor with reasonably high conductivity in the temperature range 150–350°C [3,11,19,20]. At temperatures below 140°C, the conductivity is fairly low ( $\sim 10^{-6}$  S/cm) and at a temperature of around 140°C, the material undergoes a super-protonic transition; above 140°C, the conductivity increases dramatically and at 200°C has a value of 0.04 S/cm. In our experiments, the cesium sulfate membrane produced no current in the fuel cell. The reasons for this behavior were not extensively studied although the membrane is soluble in water which could lead to stability problems. Haile et al. report that they are able to produce small currents with the solid electrolyte fuel cell ( $\sim 44$  mA/cm<sup>2</sup> at short-circuit) though this performance is significantly lower than that of fuel cells operating with typical Nafion membranes [11]. Improved electrodes, higher conductivity and thinner membranes could greatly increase the performance of this type of fuel cell.

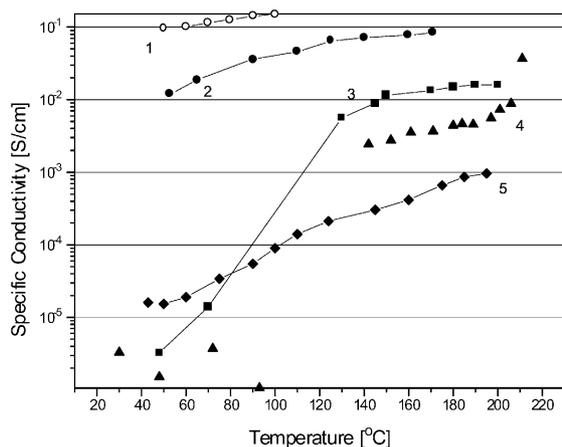


Fig. 4. Membrane conductivity for water-independent membranes: (1) (○) fully-hydrated Nafion membrane at 100% RH; (2) (●) recast Nafion/imidazole membrane; (3) (■) Nafion 115 membrane swollen with molten imidazole; (4) (▲) cesium hydrogen sulfate membrane; (5) (◆) Nafion 115 membrane swollen with methanol/imidazole solution.

## 4. Theoretical analysis

### 4.1. CO tolerance and operating temperature

Higher temperature operation of fuel cells has been shown to increase the tolerance of fuel cells to CO poisoning. This increased tolerance is related to the thermodynamics of

adsorption of CO and H<sub>2</sub> on the Pt electrocatalyst. Competitive adsorption of CO and H<sub>2</sub> on the Pt surface may be described by Langmuir adsorption isotherms. The CO molecule adsorbs associatively on Pt below 500 K, whereas H<sub>2</sub> is dissociatively adsorbed.



The fractional coverage ( $\theta$ ) of CO and H on the surface of the catalyst are given by Eqs. (3) and (4)

$$\theta_{\text{CO}} = \frac{K_{\text{CO}}P_{\text{CO}}}{1 + K_{\text{CO}}P_{\text{CO}} + K_{\text{H}}^{1/2}P_{\text{H}_2}^{1/2}} \quad (3)$$

$$\theta_{\text{H}} = \frac{K_{\text{H}}^{1/2}P_{\text{H}_2}^{1/2}}{1 + K_{\text{CO}}P_{\text{CO}} + K_{\text{H}}^{1/2}P_{\text{H}_2}^{1/2}} \quad (4)$$

where  $K_{\text{CO}}$  and  $K_{\text{H}}$  are the equilibrium constants for adsorption and  $P_{\text{CO}}$  and  $P_{\text{H}_2}$  the partial pressures of the carbon monoxide and hydrogen in the gas phase, respectively. Because hydrogen adsorption is less exothermic than CO and hydrogen adsorption requires two adsorption sites, increased temperature leads to a beneficial shift towards lower CO coverage and higher H coverage. It must be noted that there are other effects that can influence the CO coverage and promote non-equilibrium fractional coverage besides these reactions, namely CO<sub>2</sub> reduction and CO oxidation [21], but these are small compared to the active CO adsorption.

Fig. 5 shows the equilibrium coverage of CO on the platinum electrocatalyst at concentrations of CO ranging from 1 to 100 ppm with a hydrogen pressure of 0.5 bar. The enthalpies of adsorption are those determined for a Pt(1 1 1) surface, and the adsorption entropies are determined from desorption kinetics as described by Benziger [22]. It is clear that operation at higher temperatures will increase the ability

of the fuel cell anode to perform in the presence of small amounts of CO by decreasing the coverage of CO on the catalyst surface, thereby increasing hydrogen coverage. CO tolerance is defined as operation of a fuel cell in the presence of CO where the significant polarization at the hydrogen electrode does not occur (i.e. the voltage loss is less than 10–20 mV). This implies enough Pt sites for adequate H<sub>2</sub> oxidation. According to the theoretical studies of Bellows et al.  $\theta_{\text{CO}}$  should be less than 0.9 (i.e.  $\theta_{\text{H}} \geq 0.1$ ) for tolerance [21].

The quantitative behavior illustrated in Fig. 5 can be modified slightly by electrode preparation. The colloidal Pt nanoparticles that are typically used on the active layer of the electrodes will expose a range of crystal surface planes. The adsorption enthalpies of CO depend on crystal orientation ranging from –110 to 150 kJ/mol. The enthalpies of H<sub>2</sub> adsorption are less dependent on crystal orientation varying between –55 and 65 kJ/mol of H<sub>2</sub>. Therefore, the temperature for CO tolerance as predicted by Fig. 5 can be adjusted over the range of about  $\pm 20^\circ\text{C}$  depending on catalyst preparation and what crystalline surfaces are exposed on the electrocatalyst.

A simple means of approximating the operating conditions for a polymer membrane fuel cell to be CO tolerant, is to determine conditions where the CO coverage is less than 90%. Fig. 6 shows a set of curves for the CO tolerance temperature as a function of difference in adsorption enthalpy for H<sub>2</sub> and CO on the catalyst surface for different CO concentrations. It is evident that the smaller the difference in adsorption enthalpies of CO and H<sub>2</sub>, the less susceptible the fuel cell anode is to CO poisoning. Alloy catalysts help improve CO tolerance by altering the adsorption enthalpies of CO and H<sub>2</sub>, as well as their oxidation rates. Thus, a combination of increasing operating temperature of the PEMFC and modified electrocatalysts can reduce performance losses of a PEMFC in the presence of CO [23,24].

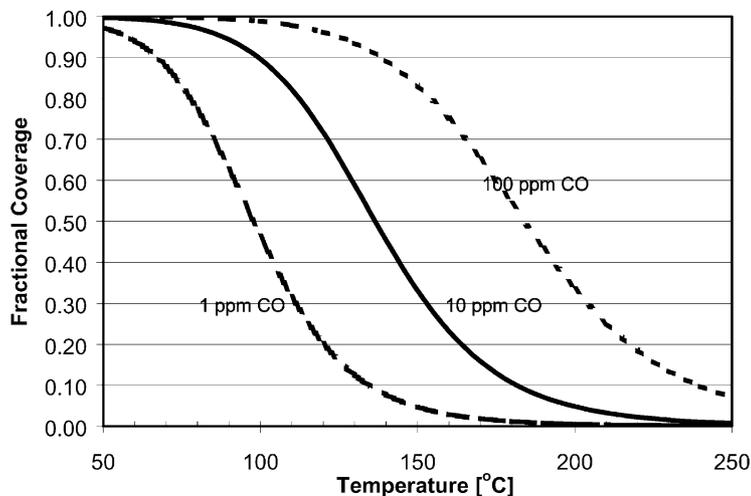


Fig. 5. CO coverage on a platinum surface as a function of temperature and CO concentration. H<sub>2</sub> partial pressure is 0.5 bar.

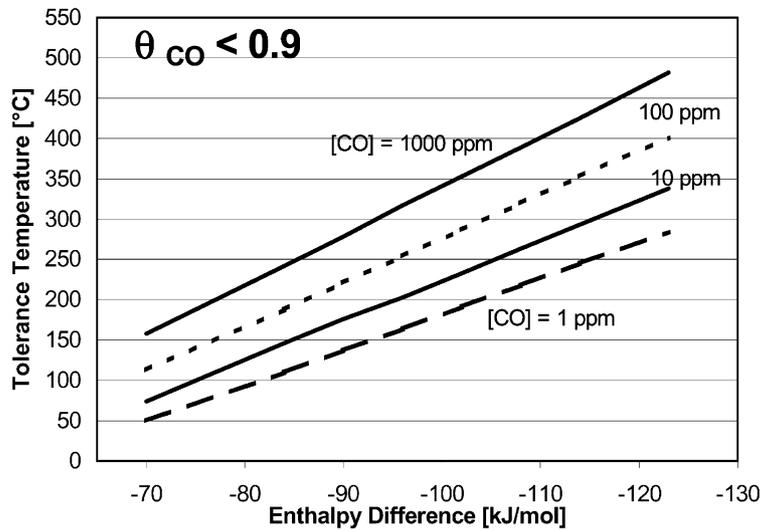


Fig. 6. CO tolerance temperature as a function of CO concentration and enthalpy difference for adsorption of CO and H onto platinum. Tolerance is approximated as the temperature where the coverages are equal. Enthalpy difference is calculated as  $\Delta H_{\text{ads,CO}} - 1/2\Delta H_{\text{ads,H}}$ .

#### 4.2. Thermodynamic limitations in operating temperatures for water-dependent membranes

Operation of polymer membrane fuel cells at elevated temperatures is often accompanied by poor performance due to the loss of water from the membrane. The water content in polymer membranes depends on the relative humidity. The relative humidity (RH) is representative of the relative chemical potentials of the pure liquid and vapor phases. The chemical potential,  $\mu$ , of a pure liquid is essentially constant while the chemical potential of the vapor will vary with the vapor pressure,  $P_{\text{vap}}$  according to the equation

$$\mu(\text{g}) = \mu(\text{l}) + RT \ln\left(\frac{P_{\text{vap}}}{P_{\text{sat}}}\right) \quad (5)$$

Thus, if  $\text{RH} < 100\%$ , the vapor pressure is less than the saturation vapor pressure ( $P_{\text{vap}} < P_{\text{sat}}$ ) so that the vapor phase chemical potential is lower than that of the liquid phase and net evaporation will occur until chemical potentials are equal. The greater the deviation from 100% RH, the greater the difference between the two chemical potentials and the larger the driving force towards equilibrium. This same phenomenon occurs in a fuel cell with the membrane acting as the liquid or condensed phase.

Composite membranes could be expected to improve the performance of fuel cells operating at elevated temperatures by allowing operation at reduced relative humidity. The addition of a hydrophilic inorganic phase within the membrane provides additional sites for hydrogen bonding to water molecules and also alters the microstructure of the ionic inclusions and the connection between ion clusters. The water content of the membrane is the key parameter in determining the conductivity of these membranes. Temperature, in the range from 80 to 150°C, has a relatively small effect on the conductivity. As a result, we can consider

conductivity ( $\sigma$ ) roughly to be a function of water content in the membrane.

$$\sigma_{\text{constant}} \rightarrow \mu_{\text{membrane}} = \text{constant}$$

Thus, to first order, to maintain constant conductivity, it is necessary to keep  $\mu_{\text{vapor}}$  constant, i.e. maintaining constant relative humidity. Any modifications to the membrane which reduce the chemical potential of water in the membrane will improve conductivity under conditions of reduced relative humidity. The modifications to the membrane structure by the addition of the inorganic phase that interacts strongly with water would lead to lower chemical potential of water in the membrane and could account for the improved fuel cell performance at reduced relative humidity.

Despite the performance improvements that can be achieved with these composite membranes, any membrane that relies on the presence of water for proton conductivity will have difficulties operating at elevated temperatures. The water vapor pressure will always be less than the total pressure in the cell which determines whether the feed gas stream can have enough water vapor and reactant gas to maintain membrane hydration and decrease concentration overpotential. Consequently, increasing operating temperature requires increased operating pressure to maintain 100% relative humidity and sufficient reactant gas pressure in the gas stream. Alternatively, the operating pressure of the fuel cell will, to a large extent, determine at what temperatures the fuel cell is able to operate.

Fig. 7 shows the maximum cell temperature allowable in order to have 0.5 bar partial pressure of reactants in equilibrium and completely saturated feed gases. If the temperature of the humidification bottle were to increase above this amount, the partial pressure of the water would increase, decreasing the reactant partial pressure. The decreasing slope of the curve indicates that increases in operating

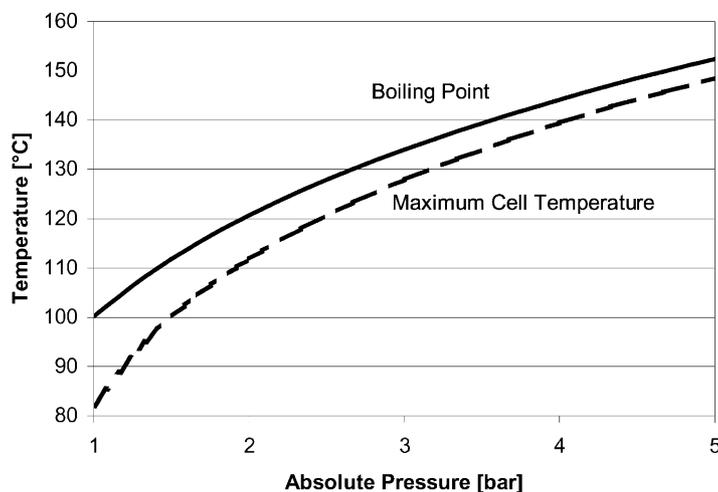


Fig. 7. Limitation on maximum fuel cell temperature based upon operating pressure, saturated reactant gas feeds and 0.5 bar reactant gas concentration.

temperature must be accompanied by larger operating pressure increases. For composite membranes, the required vapor pressure (and consequently, total pressure) can be lowered with respect to Nafion (shifting the curve to the left), though this effect is fairly small.

The experimental work in this paper has shown a reduction in the required vapor pressure for adequate hydration of the composite membrane in a PEMFC operating at elevated temperatures. However, the large reduction in performance of fuel cells operating at 140°C indicate that at or below a relative humidity of 75–80%, dehydration can have a significant impact on membrane conductivity. The ultimate limits of vapor pressure reduction with improved composite membranes and optimized chemical structure have not been reached, as further increases in composite materials can improve membrane hydration characteristics.

## 5. Conclusion

High temperature membranes offer the promise of many benefits including higher CO tolerance at the anode electrocatalyst when utilizing processed carbonaceous fuels, better water and heat management, and better prospects for waste heat utilization for fuel processing or space and water heating. This paper focused on two aspects of high temperature proton exchange membranes for PEMFCs, an experimental section detailing three different approaches to achieving higher temperature operation and a theoretical framework for understanding CO tolerance and the thermodynamics of water balance in the membrane. The experimental results showed Nafion/zirconium phosphate membranes performed better than Nafion membranes at 130°C at reduced relative humidities. Preliminary results were reported in two membrane systems which do not rely on water for proton conduction. Composite Nafion/imidazole and cesium sulfate membranes showed good conduc-

tivity at very high temperatures (180–200°C) but each had specific physical or chemical incompatibilities with the fuel cell environment.

Proton exchange membrane fuel cells that rely on water for conduction require relative humidity to be maintained above 90% to function well. High temperature operation requires increased total pressure to maintain water vapor pressure. Operation of PEMFCs at 150°C would require pressurization to about 5 bar. Composite membranes can provide some improvement in performance under given operating conditions but do not significantly change the required vapor pressure or pressure requirements for PEMFCs operating at high temperatures. Increasing operating temperature to 150–200°C without significant increases in operating pressure would require further development of non-water dependent systems.

## References

- [1] S. Malhotra, R. Datta, *J. Electrochem. Soc.* 144 (1997) L23–L26.
- [2] J.T. Wang, R.F. Savinell, J. Wainright, M. Litt, H. Yu, *Electrochim. Acta* 41 (1996) 193–197.
- [3] K.D. Kreuer, A. Fuchs, M. Ise, M. Sapeh, *J. Mater. Solid State Ionics* 97 (1997) 1–15.
- [4] R. Savinell, E. Yeager, D. Tryk, U. Landau, J. Wainright, D. Weng, K. Lux, M. Litt, C. Rogers, *J. Electrochem. Soc.* 141 (1994) L46–L48.
- [5] T.D. Gierke, W.Y. Hsu, *The Cluster-Network Model of Ion Clustering in Perfluorosulfonated Membranes* in: A. Eisenberg, H.L. Yeager (Eds.), *Perfluorinated Ionomer Membranes*, ACS, 1982, pp. 283–307.
- [6] A.V. Anantaraman, C.L. Gardner, *J. Electroanal. Chem.* 414 (1996) 115–120.
- [7] Y. Sone, P. Ekdunge, D. Simonsson, *J. Electrochem. Soc.* 143 (1996) 1254–1259.
- [8] S.J. Lee, K.T. Adjemian, A.B. Bocarsly, S. Srinivasan, in: *Proceedings of The Electrochemical Society Meeting, Toronto, Canada, 2001*.
- [9] K.D. Kreuer, A. Fuchs, M. Ise, M. Sapeh, *J. Mater. Electrochim. Acta* 43 (1998) 1281–1288.

- [10] M. Doyle, S. Choi, G. Proulx, J. Electrochem. Soc. 147 (2000) 34–37.
- [11] S.M. Haile, D.A. Boysen, C.R.I. Chisolm, R.B. Merle, Nature 410 (2001) 910–912.
- [12] W.G. Grot, G. Rajendran, United States Patent no. 5919583 (1999).
- [13] G. Alberti, U. Costantino, R. Millini, G. Perego, A.R. Vivani, J. Solid State Chem. 113 (1994) 289–295.
- [14] K. Uosaki, K. Okazaki, H. Kita, J. Electroanal. Chem. 287 (1990) 163–169.
- [15] J.J. Fontanella, M.G. McLin, M.C. Wintersgill, J.P. Calame, S.G. Greenbaum, Solid State Ionics 66 (1993) 1–4.
- [16] K.T. Adjemian, S.J. Lee, S. Srinivasan, J.M. Ogden, A.B. Bocarsly, in: Proceedings of the Electrochemical Society Meeting, Toronto, Canada, 2001.
- [17] M. Casciola, U. Constantino, Solid State Ionics 20 (1986) 69–73.
- [18] M. Casciola, F. Marmottini, A. Peraio, Solid State Ionics 61 (1993) 125–129.
- [19] A.I. Baranov, B.V. Merinov, A.V. Tregubchenko, V.P. Khiznichenko, L.A. Shuvalov, N.M. Schagina, Solid State Ionics 36 (1989) 279–282.
- [20] S.M. Haile, G. Lentz, K.-D. Kreuer, J. Mater. Solid State Ionics 77 (1995) 128–134.
- [21] R.J. Bellows, E.P. Marucchi-Soos, D.T. Buckley, Industrial Eng. Chem. Res. 35 (2000) 1235–1242.
- [22] J.B. Benziger, Thermochemical Methods for Reaction Energetics on Metal Surfaces, in: E. Shustorovich (Ed.), Metal-Surface Reaction Energetics: Theory and Applications to Heterogeneous Catalysis, Chemisorption, and Surface Diffusion, VCH, 1991, pp. 53–108.
- [23] S. Mukerjee, S.J. Lee, E.A. Ticianelli, J. McBreen, B.N. Grgur, N.M. Markovic, P.N. Ross, J.R. Giallombardo, E.S. De Castro, Electrochem. Solid State Lett. 2 (1999) 12–15.
- [24] S. Gottesfeld, T.A. Zawodzinski, Polymer Electrolyte Fuel Cells in: R.C. Alkize, H. Gerisher, D.M. Kolb, C.W. Tobias (Eds.), Advances in Electrochemical Science and Engineering, Vol. 5, Wiley, New York, 1997, pp. 197–297.