Improvement in high temperature proton exchange membrane fuel cells cathode performance with ammonium carbonate

Ying Song[a,b,*], Yu Wei[b], Hui Xu[b], Minkmas Williams[b], Yuxiu Liu[a,b],
Leonard J. Bonville[c], H. Russell Kunz[c], James M. Fenton[a,b]

[a] *Environmental Research Institute, University of Connecticut, 270 Middle Turnpike Unit 5210, Storrs 06269, USA*
[b] *Department of Chemical Engineering, University of Connecticut, 191 Auditorium Road, Storrs 06269, USA*
[c] *Ionomem Corporation, University of Connecticut, 270 Middle Turnpike Unit 5210, Storrs 06269, USA*

Abstract

Proton exchange membrane (PEM) fuel cells with optimized cathode structures can provide high performance at higher temperature (120 °C). A "pore-forming" material, ammonium carbonate, applied in the unsupported Pt cathode catalyst layer of a high temperature membrane electrode assembly enhanced the catalyst activity and minimized the mass-transport limitations. The ammonium carbonate amount and Nafion® loading in the cathode were optimized for performance at two conditions: 80 °C cell temperature with 100% anode/75% cathode R.H. and 120 °C cell temperature with 35% anode/35% cathode R.H., both under ambient pressure. A cell with 20 wt.% ammonium carbonate and 20 wt.% Nafion® operating at 80 °C and 120 °C presented the maximum cell performance. Hydrogen/air cell voltages at a current density of 400 mA cm^{-2} using the Ionomem/UConn membrane as the electrolyte with a cathode platinum loading of 0.5 mg cm^{-2} were 0.70 V and 0.57 V at the two conditions, respectively. This was a 19% cell voltage increase over a cathode without the "pore-forming" ammonium carbonate at the 120 °C operating condition.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Proton exchange membrane (PEM) fuel cells are one of the most promising types of fuel cells because of their non-mobile solid polymer electrolyte and relatively lower operating temperature. The PEM fuel cell allows better vehicular fuel economy and meets more stringent emission standards than internal combustion engines. Usually, PEM fuel cells are operated at low temperatures (<80 °C). However, PEM fuel cells operated at elevated temperatures (>100 °C and atmospheric pressure) have significant advantages over low temperature PEM fuel cells. High-temperature (~120 °C) operation reduces system weight, volume and complexity, which increases power density, specific power, and functionality through system and component simplification. High temperature enhances carbon monoxide tolerance and eliminates the need for a selective oxidizer. High-quality waste heat increases system efficiency through cogeneration, and simplifies water management. When operated at atmosphere pressure, the under-saturated operating environment alleviates mechanical stress imparted by water expansion upon freezing and facilitates rapid start-up in freezing conditions, because melting ice becomes unnecessary. Enhanced freeze tolerance, and reduced system complexity make the system more durable. Therefore, a significant economic incentive exists to develop and commercialize PEM fuel cells that operate at high temperatures.

Unfortunately, the currently most common membrane, for example, the perfluorosulfonic acid based on Nafion® mem-

* Corresponding author. Tel.: +1 860 486 6675; fax: +1 860 486 5488.
E-mail address: yingsong@eri.uconn.edu (Y. Song).

brane, as a proton electrolyte medium loses ionic conductivity at temperatures above 100 °C due to membrane dehydration at atmospheric pressure [1,2]. Ionomem Corp. and the University of Connecticut (UConn) have developed an innovative proton exchange high temperature membrane electrode assembly that provides good ionic conductivity within the membrane and the electrode structure in an under-saturated environment [3]. Solid proton conductors, such as phospho-tungstic acid mixed with Nafion® decrease polymer water vapor pressure, provide more water-independent ionic conduction, and achieve excellent performance at high temperature. With a reinforcement of PTFE this unique composite membrane fabrication technique also provides high temperature mechanical integrity. In this study, the membrane used was the Ionomem high temperature membrane, unless otherwise stated.

The catalyst layer, referred to as the active layer, is the location of the reactant reaction in a PEM fuel cell. One of optimization of an electrode design is the attempt to obtain good catalyst activity and gas diffusion properties and chemical and physical durability. There are a number of catalyst layer properties that have to be carefully optimized to achieve high utilization of the catalyst material. For example, catalyst loading, ionomer content, reactant diffusivity, and ionic and electrical conductivity etc. have been receiving a lot of attention [4,5]. The catalytic activity for oxygen reduction in the cathode is reduced as water is lost when the cell temperature is above 100 °C [6]. Mass-transport issue, which contribute to performance loss especially at high current densities are becoming an important problem, too [7]. High performance can be achieved with well-dispersed platinum catalysts if the cathode catalyst layer is designed to maximize catalyst utilization.

In the past, earlier preparation methods of membrane electrode assemblies (MEAs) used platinum black bonded directly to the polymeric membrane, but the limited dispersion and low utilization in the catalyst mixture required a high platinum loading, typically 4 mg cm^{-2}, to obtain satisfactory performance [8]. Other approaches for the application of unsupported Pt catalyst to the electrodes, such as the direct deposition of platinum onto the membrane surface or a two-step deposition process, had also been explored [9–11]. However, these approaches yielded relatively large platinum agglomerates, lower electrochemical surface area and poor access of gas, electrons, and protons to the platinum catalysts. The application of Pt black to the cathode side of the electrode using a simple, rapid and reproducible technique for fabrication of MEAs with unsupported Pt black catalyst was developed by the first author of this paper [12,13].

To further improve PEM fuel cell performance at 120 °C, a study to optimize the electrode structure was done to minimize all transport resistances within the electrode structure. One method to reduce gas diffusion transport resistance, especially at the cathode side, is to apply "pore-forming" materials into the catalyst layer to allow better oxygen transport to the catalyst surface. Although other research groups have used various additives in the catalyst layers for modification of the electrode structure, no performance increase was demonstrated and no data has been reported on performance of high temperature PEM fuel cells [14–22]. The following paragraphs describe work using "pore-forming" materials or other additives to improve performance at low temperatures.

Aqueous polytetrafluoroethylene (PTFE) and a pore-former material (zinc oxide) were used to co-agglomerate with the catalyst and applied to a gas diffusion substrate to form an electrode structure [14,15]. This method required high temperature, near the melting point of PTFE (335 °C), to sinter the PTFE particles. The high sintering temperature exceeds the allowable temperature of most proton exchange membranes and thus precludes the use of this technique to form an electrode structure directly on the membrane. Hartmut et al. described a membrane-electrode unit for PEM fuel cells with a high porosity that improved electrochemical performance [16]. The high porosity of the electrode, 40% < porosity < 75%, was achieved by using pore-formers in combination with a special spray process. Unfortunately, the pore-former poisoned the electrode and additional steps were needed to remove the pore-former from the membrane-electrode unit. US Patent 5,211,984 [17] describes how to make the electrode layers more robust by having the dissolved ionomer present in a thermoplastic form in the suspension of catalyst and ionomer solution used to produce the electrode layer. US Patent 4,469,579 [18] used this approach to produced porous electrodes on solid electrolyte membranes for use in sodium chloride electrolysis cells by dispersing pore-forming materials with the electrocatalyst and ionomer. The pore-former was dissolved out of the electrodes after removal of the solvent by drying the electrodes. Fisher and his co-workers [19,20] disclosed a method for the preparation of gas diffusion electrodes for fuel cells. A finely divided electrocatalyst was mixed with pore-forming materials in a solution of an ion-conducing polymer. After the drying (130–170 °C) of the non-acidic, temperature-stable electrode coating, the ionomeric material of the gas diffusion electrode/membrane/gas diffusion electrode was converted to the proton-conducting form by treatment with acid. Kong et al. [21] reported the microstructure of the diffusion layer could be modified by a pore-former, Li_2CO_3, to improve the performance. Unfortunately, the reported performance at 400 mA cm^{-2} was only 0.37 V even at a low temperature of 75 °C. In this method, the diffusion layer was heat-treated at 350 °C or acid-treated for pore-forming, which means this method cannot be used directly on the Nafion® membrane. Recently Gamburzev and Appleby [22] reported performance improvement in a PEM fuel cell by introducing a pore-former into the electrode. He showed that the current density at 0.7 V increased from 200 to 600 mA cm^{-2} at 50 °C.

In this paper, ammonium carbonate, as low temperature decomposable pore-forming material, was added in the cathode Pt black catalyst layer [23]. The quantity of ammonium

carbonate and Nafion® in the active catalyst layer was examined to further optimize the characteristics of the reaction layer and to improve the cell performance at higher temperatures and low relative humidities under atmosphere pressure.

2. Experiment

2.1. Thermal stability of ammonium carbonate

Thermogravimetric analysis (TGA) measures weight loss of a sample as a function of temperature, thereby providing thermal stability of materials. A HI-RES TGA2950 Thermogravimetric Analyzer (TA Instruments, New Castle, DE) was used to study the thermal stability of ammonium carbonate. The sample of ammonium carbonate was tested from 30 to 300 °C using an air atmosphere with a 5 °C min^{-1} heating rate.

2.2. Morphological characteristics of the catalyst layers

The morphological characteristics of the catalyst layers were measured using mercury-intrusion porosimetry (Pore-Master33, Quantachrome Corp., Boynton Beach, FL). Information on the internal structure of the catalyst layers can be obtained by measuring the amount of mercury penetration as a function of the applied pressure.

2.3. Preparation of the membrane-electrode assembly

Platinum black (supplied by Alfa Aesar Corp., Word Hill, MA) with surface area of 21.45 m^2 g^{-1} Pt mixed with solubilized Nafion® (5 wt.%, EW1100, supplied by Solution Technology Inc.) was used in the cathode catalyst layer. The catalyst layer was uniformly applied onto the membrane by spraying catalyst inks consisting of Pt black, Nafion®, and solvents with/without the pore-forming additive, ammonium carbonate (reagent ACS, supplied by Acros Organics, Pittsburgh, PA). The catalyst coated membrane was then hotpressed for 5 min at 130 °C and 517 × 10^3 Pa (75 psig) between two 25 μm PTFE sheets. Another thin layer of Pt/C (40% Pt on Vulcan XC-72, supplied by Alfa Aesar Corp., Word Hill, MA) with surface area of 61.04 m^2 g^{-1} Pt mixed with Nafion® was applied onto the first layer of Pt black to insure good current collection from the thin Pt black layer and provide good contact with the gas diffusion layer. It also provided some additional catalytic activity. Total Pt loading was controlled at 0.5 mg cm^{-2} on the cathode side and 0.4 mg cm^{-2} on the anode side. The ratio of Pt loading in the Pt black layer and Pt/C layer was controlled at 95:5. The amount of the ammonium carbonate in the Pt black catalyst layer was varied in the range of 10 to 40%. The Nafion® loading in the electrodes was optimized to further improve the cell performance at higher temperatures. Ionon-

mem/UConns Nafion®–Teflon®–phosphotungstic acid high temperature membrane which was about 25 μm thick was used in this study. The gas diffusion layers (GDLs) prepared in-house (210–225 μm thick) comprised carbon Vulcan XC-72R (Supplied by Cabot Corp., Boston, MA) and PTFE (60 wt.% solution, supplied by Aldrich, St. Louis, MO) on Toray paper (TPGH 120, supplied by E-TEK Corp., Somerset, NJ) [24]. The average thickness was about 365 μm. The active area of all MEAs in this study was 25 cm^2.

2.4. Electrochemical measurements

MEA performance was evaluated using a conventional 25 cm^2 fuel cell fixture with single serpentine flow-fields machined on graphite plates. After wet-up conditions, all of the single-cells were tested at cell temperatures of 80 °C and 120 °C with pure hydrogen and oxygen or air at atmospheric pressure, respectively. Both fuel/air were externally humidified and the relative humidities were 100% at the anode/75% at the cathode at a cell temperature of 80 °C and 35% at the anode/35% at the cathode at a cell temperature of 120 °C, respectively. The gas stoichiometry was kept constant at 3.4 for hydrogen and 4.0 for oxygen in air at all cell current densities. Cell voltage versus current density was obtained with a computer-controlled fuel cell test load (Series 890B, Scribner Associates Inc., Southern Pines, NC), which has the ability to measure the cell internal resistance. This internal resistance is primarily due to the cell membrane. The IR-free cell voltage is almost completely controlled by the cathode polarization because the hydrogen anode polarization is small. In measuring polarization curves, current was stepped up from zero to the maximum test current density with an increment between 10 and 100 mA cm^{-2}. Time spent at each current density was 5 min.

Cyclic voltammetry measurements were conducted at 25 °C to determine the electrochemically active surface area using a potentiostat (Solartron SI1287, Solartron Analytical, Hampshire, England). The reference and counter electrode leads were attached to the cell anode and the working electrode lead was connected to the cell cathode. Hydrogen and nitrogen were fed to the anode and cathode, respectively. The potential was scanned from 0.01 V to 0.8 V at a sweep rate of 20 mV s^{-1}.

The electrochemical surface area (ECA) of all the cathode electrode was calculated based on the relationship between the surface area and the hydrogen adsorption charge on the electrode determined from the cyclic voltammetry measurement, hydrogen adsorption charge on a smooth Pt electrode of 210 mC cm^{-2} Pt, and the Pt loading in the catalyst layer. The electrochemical surface area of the Pt catalyst was calculated by Eq. (1) [25]:

$$\text{ECA (cm}^2 \text{ Pt/g Pt)} = \text{Charge (μC cm}^{-2})/[210(\text{μC cm}^{-2} \text{ Pt})$$
$$\times \text{ Electrode loading (g Pt cm}^{-2})] \quad (1)$$

3. Results and discussion

Ammonium carbonate was chosen as the pore-former since it completely decomposes to ammonia, water and carbon dioxide above 59 °C. Ammonia present as an impurity in oxidant streams has been reported to react with the electrolyte to form ammonium ions leading to a lower oxygen reduction rate at the cathode side and phosphoric acid fuel cell performance losses [26]. Uribe et al. [27,28] found that traces of ammonia in the anode feedstream of a proton exchange membrane fuel cell caused a decrease in cell current. They also reported that high trace levels and long time exposure caused severe and irreversible decreases in performance. In our study ammonium carbonate was used as a pore-forming material in the electrodes. The electrode with ammonium carbonate was heat-treated at 130 °C for 3 min to allow the ammonium carbonate to decompose and so that it would not react with the Nafion® in the electrode and influence cell performance. A thermal analysis was carried out to verify that the ammonium carbonate decomposed during the thermal treatment applied to the catalyst during MEA preparation. Fig. 1 shows the thermogravimetric analysis (TGA) from room temperature to 300 °C at a heating rate of 5 °C min⁻¹ in air. Ammonium carbonate begins to decompose at about 47 °C and is totally lost at about 125 °C. Therefore, if the electrode is heat-treated at 130 °C, a loss of 100% of ammonium carbonate should occur. This easy decomposition of ammonium carbonate makes MEA fabrication and cell assembling simple and rapid since no other treatment was needed to remove ammonium carbonate out of the electrode.

The pore-size distributions in the catalyst layers without ammonium carbonate ("the standard electrode") and with 10 wt.% ammonium carbonate are shown in Fig. 2. Nafion® loading was kept at 10 wt.% for both MEAs. The pore size distribution was changed after removing ammonium carbonate in the catalyst layer. Fig. 2a shows that the pore volume increased in two different pore size ranges, 0.005–0.015 μm, 0.02–0.07 μm. Fig. 2b show that there was also an increase in the amount of 7 μm diameter pores. The total porosity
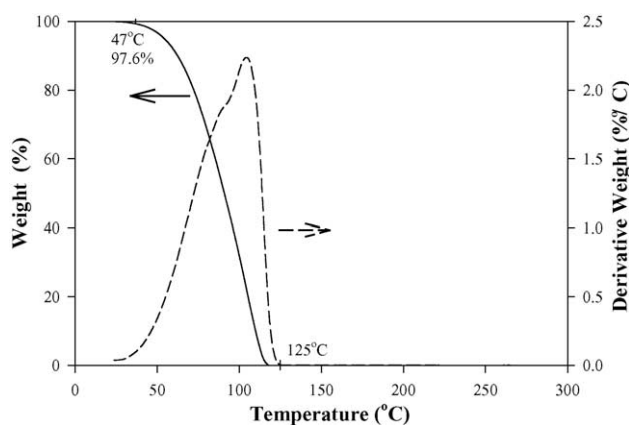

Fig. 1. Thermogravimetric analysis for ammonium carbonate. Heating rate: 5 °C min⁻¹ in air from room temperature to 300 °C.

(a) Specific pore-size distribution
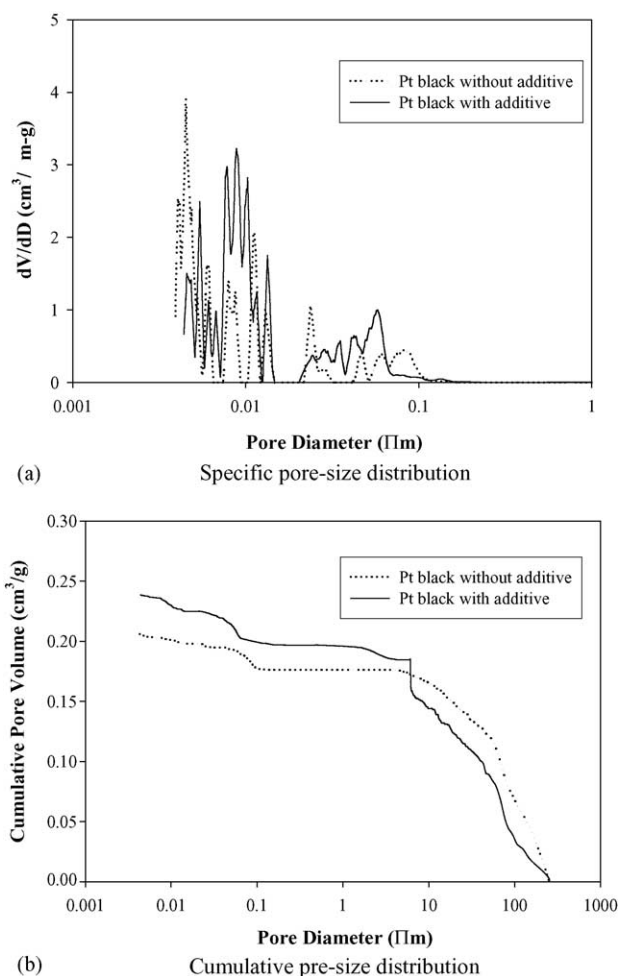

(b) Cumulative pre-size distribution

Fig. 2. Pore size distribution of Pt black catalyst layers in cathode obtained from mercury-intrusion porosimetry measurements. Total Pt loading was 0.5 mg cm⁻² and the Nafion® content was 10 wt.%. (a) Specific pore-size distribution; (b) cumulative pre-size distribution.

increased 17% in the catalyst layer prepared with 10 wt.% ammonium carbonate as a pore-forming additive.

The influence of the ammonium carbonate and its amount in the Pt black catalyst layer has been evaluated in single cells. Fig. 3 shows the ammonium carbonate content effect in the electrodes, 0 wt.%, 10 wt.%, 20 wt.% and 40 wt.%, on the cyclic voltammetry of several cells, using the same cathode Nafion® loading, 10 wt.%. The Pt black electrode without ammonium carbonate shows only one broad and weak desorption peak and no discrete H-adsorption peaks. Paulus et al. [29] in their work on the catalyst utilization of the electrode/solid polymer electrolyte interface, explained this phenomena by different facetting of the particles present in the Pt black catalyst, which results in the merging of the two H-adsorption/desorption peaks into one single peak. Compared to the electrodes without the additive (standard electrode), the electrodes with various amounts of ammonium carbonate exhibit higher electrochemical surface area and two separate H-desorption and two H-adsorption peaks can be found. One peak, located around 120 mV is hereafter referred to as
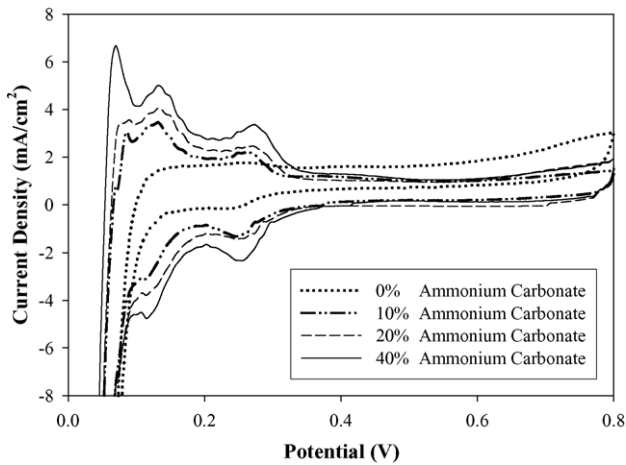
Fig. 3. Cyclic voltammetry of Pt black electrodes with different ammonium carbonate contents as an additive and 10 wt.% Nafion® as a binder mixed with Pt black catalysts. Total Pt loading was 0.5 mg cm^{-2}. Scan rates: 20 mV s^{-1}, hydrogen/nitrogen flow rates: 200 cm^3 min^{-1}, cell temperature: 25 °C and the saturator temperatures: 22 °C.

the desorption of weakly adsorbed hydrogen and other peak, around 250 mV, is referred to as the desorption of strongly adsorbed hydrogen [30].

From the hydrogen adsorption peak areas in the cyclic voltammetry curves and the Pt single crystallite hydrogen adsorption constant 210 μC cm^{-2} Pt, the electrochemical surface area (S_{ECA}) for the catalyst was calculated. The chemical surface areas (S_{CSA}) of the Pt-based catalysts are provided by the catalyst manufacturers, 21.45 m^2 g^{-1} Pt (Pt black) and 61.04 m^2 g^{-1} Pt (40% Pt/C), so the whole chemical surface area of catalysts is 23.4 m^2 g^{-1} Pt due to the ratio 95:5 of Pt black and 40% Pt/C catalyst at cathode. The Pt utilization efficiency can be calculated from Eq. (2).

$$\text{Pt utilization efficiency} = S_{ECA}/S_{CSA} \qquad (2)$$

Different ammonium carbonate content, 0%, 10%, 20% and 40%, mixed with the cathode catalyst led to significantly different electrochemical surface areas, 8.3 m^2 g^{-1}, 11.1 m^2 g^{-1}, 12.6 m^2 g^{-1}, and 17.0 m^2 g^{-1}, respectively. The Pt utilization efficiency for the catalyst with 40 wt.% ammonium carbonate was 72%, two times that of the catalyst with no additive, 35%. The larger surface area and higher Pt utilization efficiency are essential to attaining a higher reaction rate.

The effects of the ammonium carbonate amount on the cell performance of PEM fuel cells at 80 °C and 120 °C are shown in Figs. 4 and 5, respectively. The cathode catalyst layers in these cells were made of the same platinum loading at 0.5 mg cm^{-2} and Nafion® content at 10 wt.% in Pt black catalyst layer, but different ammonium carbonate contents for comparison. Fig. 4 shows that the performance of the cells first increases and then decreases with the ammonium carbonate content. The ammonium carbonate in the catalyst layer also increases the open circuit potential. For the cell with 10 wt.% ammonium carbonate in the catalyst layer, a 0.67 V
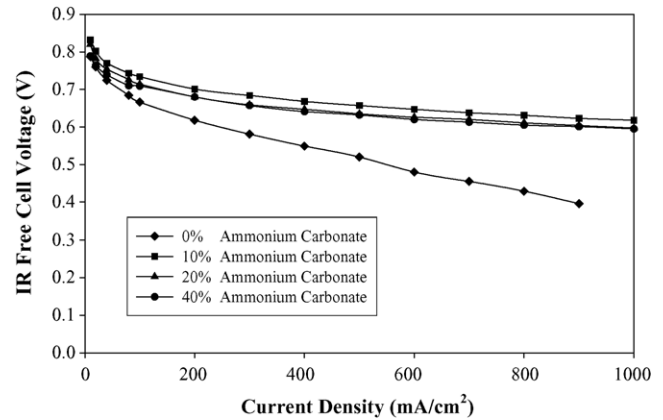

Fig. 4. Effect of ammonium carbonate content on cell performance on hydrogen/air at 80 °C with 100%/75% relative humidities under atmospheric pressure. Total Pt loading was 0.5 mg cm^{-2} and Nafion® content was 10 wt.%.

IR free cell voltage is obtained at 400 mA cm^{-2} when the cell temperature is 80 °C on H$_2$/air. When the amount of the additive further increased to 20 wt.% and 40 wt.%, the cell performance decreases, suggesting that there must exist an optimal range of ammonium carbonate in the catalyst layers.

Fig. 5 shows the influence of ammonium carbonate in the Pt black catalyst layer on the performance of the PEMFC at 120 °C. Here the best performance is achieved from the cell with 20% ammonium carbonate in the Pt black catalyst layer, a 0.60 V IR free cell voltage at 400 mA cm^{-2} on H$_2$/air. The difference in the performance for the cells with various contents of ammonium carbonate becomes much larger at higher current densities compared to the cell without the additive in the Pt black catalyst layer. The mass-transport limitation of oxygen to the cathode catalyst surface is reduced when ammonium carbonate is added into the Pt black catalyst layer. This would be expected with a pore-former [20]. A further increase in the quantity of ammonium carbonate beyond 20 wt.% does not improve cell performance at 120 °C. Since
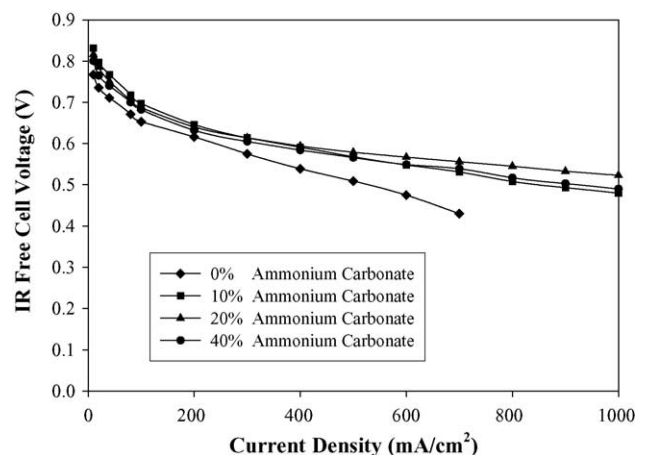

Fig. 5. Effect of ammonium carbonate content on cell performance on hydrogen/air at 120 °C with 35%/35% relative humidities under atmospheric pressure. Total Pt loading was 0.5 mg cm^{-2} and the Nafion® content was 10 wt.%.
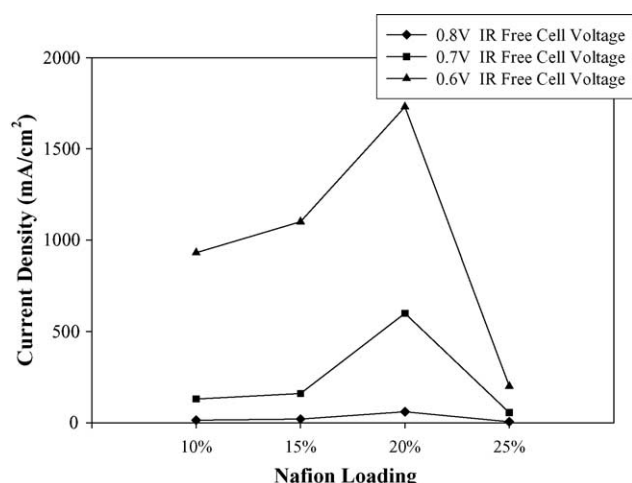
Fig. 6. Current density as a function of Nafion® loading at different IR free cell voltages at 80 °C with 100%/75% relative humidities on hydrogen/air under atmospheric pressure. Total Pt loading was 0.5 mg cm^{-2} and ammonium carbonate content was 20 wt.%.
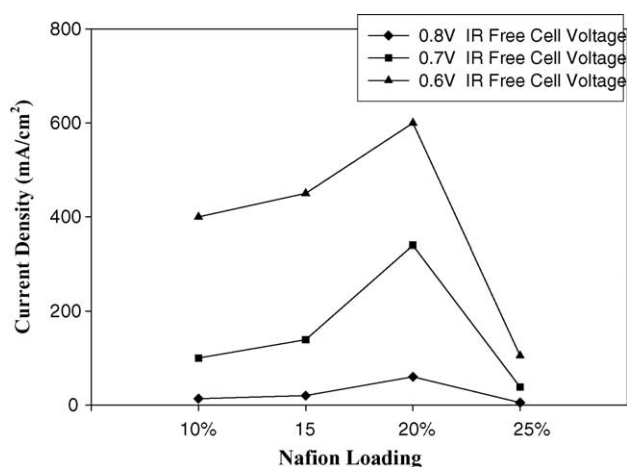

Fig. 7. Current density as a function of Nafion® loading at different IR free cell voltages at 120 °C with 35%/35% relative humidities on hydrogen/air under atmospheric pressure. Total Pt loading was 0.5 mg cm^{-2} and ammonium carbonate content was 20 wt.%.

the IR free cell voltage decrease is uniform with current density as the additive content increases above 20 wt.%, as seen in Fig. 4, the voltage decrease appears to be due to a reduction in cathode catalyst activity. This is surprising since Fig. 3 shows an increase in catalyst surface area when the amount of ammonium carbonate increases from 20 to 40 wt.%. The decrease in catalyst activity might be due to a loss of effective Pt area during cell testing (much higher current density than that used in the ECA measurement) due to the excessive porosity at additive contents above 20 wt.%. The cells in Figs. 4 and 5 only contain 10 wt.% Nafion. Data shown later in this paper indicates that a higher Nafion® content is beneficial when using 20 wt.% ammonium carbonate.

The performance can be further improved by optimizing both the content of the ammonium carbonate and of Nafion® in the Pt black catalyst layer. Nafion® has been shown to play a role in improving proton conduction or impairing mass transfer to the electrodes [31–35]. Small quantities of Nafion® coat the catalyst, larger amounts of Nafion® fill the pores of the catalyst layer and subsequent additions of Nafion® results in the formation of films on the surface of the electrode. At low Nafion® loading, the electrodes have poor ionic conductivity, which accounts for the poor electrode performance, but the conductivity increases with increasing Nafion® content. Since the study on the ammonium carbonate content with 10 wt.% Nafion® loading in the catalyst layers proved that the catalyst electrochemical surface area was enhanced with addition of ammonium carbonate, it is reasonable to consider that increasing the Nafion® loading in the catalyst layers with an increase in ammonium carbonate amount will help improve the cell performance. Cells with different Nafion® loading and a fixed content of ammonium carbonate at 20 wt.% have been tested at 80 °C, 100%/75% relative humidity and 120 °C, 35%/35% relative humidity under atmospheric conditions. Figs. 6 and 7 show

the cell current density as function of the Nafion® content in the catalyst layers at different cell performance at 80 °C and 120 °C, respectively. The catalyst activity becomes higher when the Nafion® loading increases from 10 to 20 wt.%. Cell performance is also further enhanced. The best IR free cell voltages, 0.73 V at 400 mA cm^{-2} at 80 °C and 0.68 V at 400 mA cm^{-2} at 120 °C on air, has been attained in the cell with Nafion® loading at 20 wt.% and ammonium carbonate content at 20 wt.%. The corresponding cell voltages are 0.70 V at 80 °C and 0.57 V at 120 °C, respectively. The optimal loading of Nafion® enhances the cell performance mostly at the higher current densities.

Plotting IR-free cell voltage against current density on a semilog scale produces a straight line with a slope called the Tafel slope. The Tafel slope indicates how fast the IR free cell voltage drops with current density. Fig. 8 shows the air Tafel slope of these electrodes with a Nafion® loading of
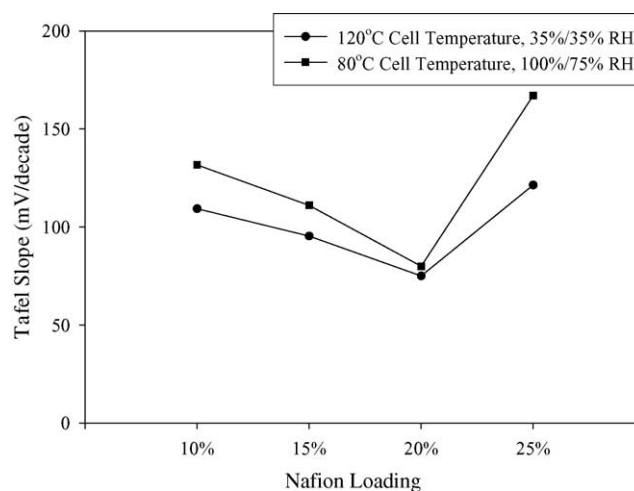

Fig. 8. Nafion® loading effects on the Tafel slope at 80 °C and 120 °C. Total Pt loading was 0.5 mg cm^{-2} and ammonium carbonate content was 20 wt.%.

20%, but different ammonium carbonate contents at $80\,^\circ$C and $120\,^\circ$C. A decrease occurs in the internal ionic resistance with increasing Nafion® loading from 10 to 20 wt.% (Tafel slope is reduced from 109 to 75 mV decade^{-1} at $80\,^\circ$C and 131 to 80 mV decade^{-1} at $120\,^\circ$C). These lower values approach the expected Tafel slope associated with the electrochemical reaction [36]. When the Nafion® loading in the catalyst layer increases to 25 wt.%, the Tafel slope increases to 121 mV decade^{-1} at $80\,^\circ$C and 167 mV decade^{-1} at $120\,^\circ$C. Cell performance with too high of a Nafion® loading becomes very poor, especially in the higher current density region. A thicker layer of Nafion® inside the pores of the electrode introduces mass transport problems by retarding the access of gas to the active sites at 80 and $120\,^\circ$C [35]. An excessive amount of Nafion® may also electronically isolate the catalysts leading to a high electronic ohmic loss in the catalyst layer. The optimal electrode with 20 wt.% Nafion® and 20 wt.% ammonium carbonate has minimal diffusional and resistive losses, so the Tafel slope is close to that of the reaction controlled values of 70 and 78 mV decade^{-1} for 80 and $120\,^\circ$C, respectively.

Fig. 9 shows the electrochemically active surface area (ECA), as a function of Nafion® content in the catalyst layer. 20 wt.% Nafion® content in the electrode provides the largest surface area when the ammonium carbonate content is 20 wt.%. Since the ECA reflects the electrochemical active surface area of the electrode for adsorption or desorption processes of hydrogen on the Pt catalyst, this same condition is optimal for high performance. Increasing the active area of Pt covered with Nafion® provides easier migration of protons through the electrolyte retained inside the pores of the catalyst layer. When the Nafion® loading increases from 20 wt.% to 25 wt.%, the thicker Nafion® layer coated on the catalyst agglomerate isolates some catalysts. Therefore, the electrochemical surface area of the electrode with 25 wt.% Nafion® decreases.
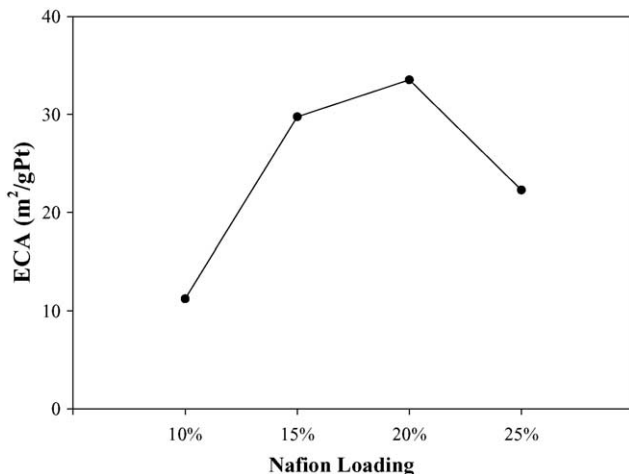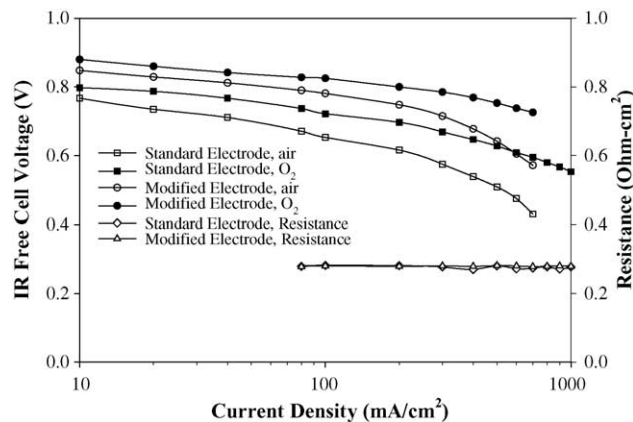

Fig. 10. Cell performance improvement with the modified electrode compared to the standard electrode at $120\,^\circ$C with 35%/35% relative humidities on hydrogen/air under atmospheric pressure. Standard electrode: 10 wt.% Nafion® and no ammonium carbonate and modified electrode: 20 wt.% Nafion® and 20 wt.% ammonium carbonate. Total Pt loading was 0.5 mg cm^{-2}.

The best performance curves of the cell with optimal ammonium carbonate and Nafion® loading are selected and compared in Fig. 10 with the standard cell without ammonium carbonate in the catalyst layers. The standard electrode included 10 wt.% Nafion® in the Pt black catalyst layer, which provides the best performance when no additive is applied. The cell with the "modified electrode" includes 20 wt.% Nafion® and 20 wt.% ammonium carbonate in the Pt black catalyst layer. Fig. 10 shows performance for the two MEAs with reactants of hydrogen and both air and oxygen at $120\,^\circ$C with 35%/35% relative humidity under ambient pressure. In this case the polarization is controlled by three factors—the ionic resistance in the catalyst layer, the diffusional resistance in the catalyst layer, and the catalytic activity. The modified electrode has a much higher cathode catalytic activity because the current at 0.8 V on oxygen is much higher than that of the standard electrode (200 mA cm^{-2} versus 10 mA cm^{-2}). This enhanced activity is due to both the optimized Nafion® loading and ammonium carbonate content. The current ratios of the standard and modified electrodes between air and oxygen at a given IR free cell voltage are very similar, 4.2 versus 4.0 and 2.8 versus 2.6 at 20 mA cm^{-2} and 200 mA cm^{-2}, respectively. The polarization curves of both the modified electrode and the standard electrode on air and oxygen are not parallel at higher current densities, indicating that there still exists diffusion loss in the cathode of the modified electrode. The polarization curves for the modified electrode are slightly flatter than that of the standard electrode, the Tafel slope 80 mV decade^{-1} of the modified electrode compared to 97 mV decade^{-1} of the standard electrode, showing that the modified electrode has less diffusional or resistive loss. Enhancement of the cell performance of the modified electrode comes from both improvement in the catalyst activity through optimization of ammonium carbonate pore-forming material and Nafion® loadings and increased gas transport. The cell voltage at 400 mA cm^{-2}

Fig. 9. Electrochemically active surface area as a function of Nafion® content. Cyclic voltammetry measurement: scan rate 20 mV s^{-1} at room temperature; ECA calculation based on Eq. (1) and ammonium carbonate content at 20 wt.%.

has been improved by use of the ammonium carbonate from 0.48 V to 0.57 V (hydrogen/air at 120 °C with 35% relative humidity under atmospheric pressure), resulting in a 19% increase in performance.

4. Conclusion

PEM fuel cells operating at elevated temperature provide significant advantages over low temperature PEM fuel cells. Introducing a pore-forming material and optimizing both the pore-former and Nafion® content in the electrode led to higher performance at higher temperatures and lower relative humidities under ambient pressure.

The performance of the PEM fuel cell at higher temperatures has been improved by modifying a Pt black cathode catalyst layer structure with the optimal amounts of the "pore-former", ammonium carbonate, and Nafion®. Thermogravimetric analysis on ammonium carbonate and cell performance indicate that ammonium carbonate added into the cathode catalyst layer is not a poison when the cells are tested since the ammonium carbonate is easily decomposed before testing. Introduction of the ammonium carbonate into the Pt black catalyst layer of the high temperature membrane electrodes enhanced the total porosity of the catalyst, resulting in a higher useful surface area and higher catalyst utilization. Optimizing the Nafion® content led to a cell voltage of 0.57 V at 400 mA cm^{-2} on air at 120 °C under atmospheric pressure with low relative humidity, 35%. The cell performance improvement is mainly due to an increased catalyst activity when the pore-forming material, ammonium carbonate, and the electrolyte, Nafion®, in the cathode catalyst layer are optimized.

Acknowledgement

References

[1] T.A. Zawodzinski, J. Davey, J. Valerio, S. Gottsfeld, Electrochim. Acta 40 (1995) 297–302.
[2] Y. Song, J.M. Fenton, H.R. Russ, L.J. Bonville, M.V. Williams, J. Electrochem. Soc., in press.
[3] J.M. Fenton, H. Russell Kunz, M.B. Cutlip, J.-C. Lin, US Patent 6,465,136 (2002).
[4] Z. Qi, A. Kaufman, J. Power Sources 113 (2003) 37–43.
[5] H.A. Gasteiger, J.E. Panels, S.G. Yan, J. Power Sources 127 (2004) 162–171.
[6] H. Xu, Y. Song, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc., submitted for publication.
[7] S.S. Kocha, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells—Fundamentals, Technology and Applications, Wiley, Chichester, 2003, pp. 560–562.
[8] L.W. Niedrach, US Patent 3,297,484 (1967).
[9] R.J. Lawrence, L.D. Wood, US Patent 4,272,353 (1981).
[10] P.S. Fedkiw, W.H. Her, J. Electrochem. Soc. 136 (1989) 899–911.
[11] P. Aldebert, F. Novel-Cattin, M. Pineri, P. Millet, C. Doumain, R. Durand, Solid State Ionics 35 (1989) 3–9.
[12] Y. Song, L. Bonville, R. Kunz, J. Fenton, R. Carley, P. Farris, M. Trahiotis, Y. Wei, J. Li, The Electrochemical Society 203rd Meeting, Meeting abstract, Paris, France, Spring 2003, Abstract 1181.
[13] Y. Song, L. Bonville, R. Kunz, J. Fenton, Y. Wei, M. Trahiotis, J. Li, H. Xu, The Electrochemical Society 204th Meeting, Meeting abstract, Orlando, FL, USA, Fall 2003, Abstract 267.
[14] J.M. Baris, C.D. Iacovangelo, W.M. Vogel, US Patent 4,058,482 (1977).
[15] J.M. Baris, C.D. Iacovangelo, W.M. Vogel, US Patent 4,150,076 (1979).
[16] W. Hartmut, F. Andreas, Z. Ralf, EP 0,797,265 (1997).
[17] M.S. Wilson, US Patent 5,211,984 (1993).
[18] M.J. Covitch, D.L. DeRespiris, L.L. Benezra, E.M. Vauss, US Patent 4,469,579 (1984).
[19] A. Fischer, H. Wendt, R. Zuber, US Patent 5,861,222 (1999).
[20] A. Fischer, J. Jindra, H. Wendt, J. Appl. Electrochem. 28 (1998) 277–282.
[21] C.S. Kong, D.-Y. Kim, H.-K. Lee, Y.-G. Shul, T.-H. Lee, J. Power Sources 108 (2002) 185–191.
[22] S. Gamburzev, A.J. Appleby, J. Power Sources 107 (2002) 5–12.
[23] Y. Song, L.J. Bonville, H. Russell Kunz, J.M. Fenton, Disclosed to University of Connecticut Center for Science and Technology Commercialization, Case number 03-048.
[24] M. Vatanatham, Y. Song, L. Bonville, J.M. Fenton, H.R. Kunz, The Electrochemical Society 201th Meeting, Meeting abstract, Philadelphia, PA, USA, Spring 2002, Abstract 29.
[25] T.R. Ralph, G.A. Hards, J.E. Keating, S.A. Campbell, D.P. Wilkinson, M. Davis, J. St-Pierre, M.C. Johnson, J. Electrochem. Soc. 144 (1997) 3845–3857.
[26] S.T. Szymanski, G.A. Gruver, M. Katz, H.R. Kunz, J. Electrochem. Soc. 127 (1980) 1440–1444.
[27] F.A. Uribe, T. Zawodzinski, S. Gottesfeld, The Electrochemical Society 190th Meeting, Meeting abstract, San Antonio, TX, USA, Fall 1996, Abstract 783.
[28] F.A. Uribe, S. Gottesfeld, T.A. Zawodzinski, J. Electrochem. Soc. 149 (2002) A293–A296.
[29] U.A. Paulus, Z. Veziridis, B. Schnyder, M. Kuhnke, G.G. Scherer, A. Wokaun, J. Electroanal. Chem. 541 (2003) 77–91.
[30] W.-Y. Tu, W.-J. Liu, C.-S. Cha, B.-L. Wu, Electrochim. Acta 43 (1998) 3731–3739.
[31] S.J. Lee, S. Mukerjee, J. McBreen, Y.W. Rho, Y.T. Kho, T.H. Lee, Electrochim. Acta 43 (1998) 3693–3701.
[32] S.L. Gojkovic, T.R. Vidakovic, Electrochim. Acta 47 (2001) 633–642.
[33] E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, L. Giorgi, Electrochim. Acta 46 (2001) 799–805.
[34] M.S. McGovern, E.C. Garnett, C. Rice, R.I. Masel, A. Wieckowski, J. Power Sources 115 (2003) 35–39.
[35] E. Antolini, L. Giorgi, A. Pozio, E. Passalacqun, J. Power Sources 77 (1999) 136–142.
[36] H. Xu, Y. Song, H.R. Kunz, J.M. Fenton, The Electrochemical Society 204th Meeting, Meeting abstract, Orlando, FL, USA, Fall 2003, Abstract 172.