Stabilized composite membranes and membrane electrode assemblies for elevated temperature/low relative humidity PEFC operation

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Abstract

An approach is presented to combine existing heteropolyacid (HPA) additive and membrane electrode assembly (MEA) stabilization techniques to yield a stabilized MEA for operation at 120 °C and 35% relative humidity (RH). MEAs were prepared using Nafion®/phosphotungstic acid composite membranes with a phosphotungstic acid (PTA) particle size of 30–50 nm. The PTA additive was stabilized by substituting its protons with cesium counter ions. The Nafion® in the membrane and electrodes was simultaneously converted to the Cs^+ form by an ion-exchange process. The melt processability of the Nafion® in the Cs^+ form permitted the MEA to be heat treated at 200 °C and 30 atm, promoting the development of a durable membrane/electrode interface. The prior stabilization of the PTA permitted MEA re-protonation with minimal additive loss. FTIR spectroscopy and thermogravimetric analysis (TGA) were employed to present evidence of ion-exchange and protonation. In situ electrochemical impedance measurements (EIS) and cyclic voltammetry (CV) measurements confirmed ion-exchange and protonation within the active portion of the stabilized MEA. The stabilization process did not affect the integrity of the MEA, with the hydrogen crossover currents through the membrane remaining unchanged at $2\,mA\,cm^{-2}$. The MEA was evaluated at 120 °C and 35% relative humidity in an operating fuel cell environment and yielded respectable performance under these conditions.
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1. Introduction

Several advantages, such as more efficient heat rejection, improved impurities tolerance and more useful waste heat, result by operating a polymer electrolyte fuel cell (PEFC) at elevated temperatures (above 100 °C). However, operating a fuel cell above the boiling point of water necessitates either pressurized operation at high relative humidities (RHs) or lower RH operation at atmospheric pressure. Many approaches have been adopted to extend the operating temperature of the polymer electrolyte membrane (PEM) from the traditional 60–80 °C to temperatures around 120 °C, as detailed in two recent reviews [1,2]. With few exceptions, the studies were conducted under fully saturated environments, necessitating elevated operating pressures at temperatures above 100 °C. From a systems viewpoint, operation close to atmospheric pressure is desired to avoid work associated with air compression [3]. Therefore, a need exists to develop PEMs that are functional at low operating RHs.

Nafion® based organic/inorganic composite membranes with different heteropolyacid (HPA) additives have been investigated as alternate materials for low humidity PEMFC operation [4–8]. We have recently developed [9,10] stabilization techniques to limit the solubility and leaching of the HPA additive by ion exchanging the protons in the HPA with large cations and by forming a in situ generated metal oxide linkage between the HPA and the clusters of Nafion®. The lack of improvement of conductivity of the stabilized composite mem-

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branes thus developed has been attributed [8,9] to the large HPA particle size that, according to the proposed hypothesis, could not effectively bridge the gap between shrunken clusters at low RH. We have independently presented an approach to reduce the heteropolyacid additive particle size within the Nafion® matrix, which has resulted in an improvement in composite membrane conductivity [11]. However, largely because of additive solubility concerns, the membrane electrode assembly (MEAs) prepared using the composite membranes with small particle sizes were not subjected to the advanced heat treatments recommended in the literature [12] to promote durability. This paper describes the results of a study directed towards developing a hybrid strategy that permits simultaneous additive and membrane–electrode interface stabilization in MEAs prepared using composite membranes containing small phosphotungstic acid (PTA) particles. In situ additive stabilization was achieved by an ion-exchange process that replaces the protons in the PTA with Cs⁺ ions, while the membrane was simultaneously converted to a melt processible form by exchanging the protons in Nafion® to the same cation. By subjecting the entire MEA (with Nafion® based electrodes) to this ion-exchange process, the Nafion® in the electrode was simultaneously converted to a melt processible form, readily permitting heat treatment at 200 °C and 30 atm [12] and greatly simplifying the manufacturing process. The MEA was re-protonated in sulfuric acid after the heat treatment, with minimal loss of the stabilized PTA additive during this operation. In this manner, the benefits of having small PTA particles were retained, while the concern about PTA solubility in aqueous media was eliminated. The successful implementation of this strategy along with experimental evidence of ion-exchange and additive stability are discussed below.

2. Experimental

2.1. Membrane preparation

The membrane preparation methodology previously described [8] was modified according to the procedure of Gebel et al. [13] to yield membranes with small (∼30 nm) HPA particle size. These membranes were abbreviated as Nafion®–phosphotungstic acid—small particle size (NPTA-S). The amount of DMF added to the Nafion®/HPA precursor solution was maintained between zero and five times the mass of the Nafion® present in solution. The resultant dispersion was mixed on a stirring plate for 1 h and then cast on a glass plate. The solvent was evaporated at room temperature over a period of 8–10 h, following which the film was annealed under vacuum at 150 °C for several hours. The high boiling solvent addition and annealing steps were omitted in some of the membranes prepared to yield samples with large additive particle sizes for the FTIR study discussed in this paper. These membranes were abbreviated as Nafion®–phosphotungstic acid—large particle size (NPTA-L).

2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) studies were performed on selected membranes and additives using a thermogravimetric analyzer (TA instruments; Model no. 2950, Newcastle, DE). A scan rate of 10 °C min⁻¹ was applied over the temperature range 40–800 °C. Sample weights of approximately 15 mg were used. The studies were performed in a nitrogen atmosphere.

2.3. Fourier transform infrared (FTIR) spectroscopy

The IR spectra of membranes were obtained directly on membrane samples using a Vector 22 FTIR spectrometer (Bruker Analytic GmbH, Bremen, Germany).

2.4. MEA preparation

MEAs were prepared using Nafion®/modified PTA membranes containing 15% w/w of additive. The catalysts used were 46.5% (w/w) Pt/C on the cathode and 30.1% Pt–23.4% Ru/C on the anode. Both anode and cathode catalysts were obtained from Tanaka Kikinzoku Kogyo K.K., Japan. Details about catalyst ink and MEA preparation and MEA assembly are provided in a previous publication [8].

The MEAs were used only to demonstrate applicability of the composite membranes in a fuel cell environment at elevated temperatures and low humidities; no efforts were expended to maximize performance.

2.5. MEA stabilization

Stabilized MEAs were prepared by immersing the entire MEA 0.1 M Cs₂CO₃ solution overnight. The protons in the Nafion® (both in the membrane and in the electrode) and the PTA were exchanged to Cs⁺ during this process. The MEA, in this melt processible form, was then subjected to heat treatment at 200 °C and 30 atm for up to 10 min, followed by re-protonation for 3 h in 1 M H₂SO₄ at 85 °C and rinsing for 1 h in deionized water at 85 °C to remove excess acid.

2.6. Linear sweep voltammetry

Linear sweep voltammetry (LSV) experiments were performed at room temperature (∼25 °C) to evaluate and monitor fuel crossover and to check for the presence of electronic shorts. The experiments were done using a Solartron electrochemical interface (Model no. SI 1287) with a flow rate of 200 cm³ min⁻¹ of H₂ on the anode and 200 cm³ min⁻¹ of N₂ on the cathode. The gases were humidified at room temperature. A scan rate of 4 mV s⁻¹ was used in the potential range of 0–800 mV with higher working electrode potentials being avoided to prevent platinum oxidation. Further details about the experiment are provided in an earlier publication [8].

2.7. Cyclic voltammetry

Cyclic voltammetry (CV) experiments were performed using a Solartron electrochemical interface (model no. SI 1287) with a flow rate of $200\,cm^3\,min^{-1}$ of H_2 on the anode and $200\,cm^3\,min^{-1}$ of N_2 on the cathode. A scan rate of $30\,mV\,s^{-1}$ was used in the potential range of 0–800 mV. The electrochemical redox activity of hydrogen on the cathode catalyst surface was thereby monitored.

2.8. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance measurements were performed on MEAs using a Solartron 1260 frequency response analyzer (Solartron Analytical) with a frequency range of 10 MHz–0.1 Hz in conjunction with a Solartron 1287 Electrochemical Interface (Solartron Analytical). H_2 was used at the anode and N_2 was used at the cathode. The impedance spectra were recorded at open circuit.

2.9. In situ resistance and conductivity measurements

The membrane resistance was obtained using the current interrupt technique built into the cell testing system. Further details of the system used and testing conditions adopted are provided in a previous publication [8].

2.10. Cell performance

The performance of the cell was evaluated by obtaining polarization curves at 120 °C and 35% RH (both anode and cathode gases saturated at 90 °C). H_2 was used at the anode and air at the cathode. The cell was started by increasing the cell temperature set point to the desired value and raising the saturator temperatures (dew points) to their respective values. The fuel and oxidant line temperatures were maintained at least 10 °C higher than the saturator dew points to avoid condensation in the lines. Performance data were obtained with oxygen and air. All data were obtained at a pressure of 1 atm. Further details about the test system are provided in a previous publication [8].

3. Results and discussion

3.1. TGA

TGA analysis was performed on recast Nafion® membranes in the H^+, Na^+ and Cs^+ forms. The onset of decomposition was shifted to higher temperatures when the H^+ was replaced by the alkali metal cations (Fig. 1). Though the rate of decomposition of the Nafion® membrane in the Cs^+ form was higher than that of the membrane in the Na^+ form *after* the onset of decomposition, there was no significant change in the actual onset of decomposition between the different alkali metal cations, with both cations displaying a 100–120 °C
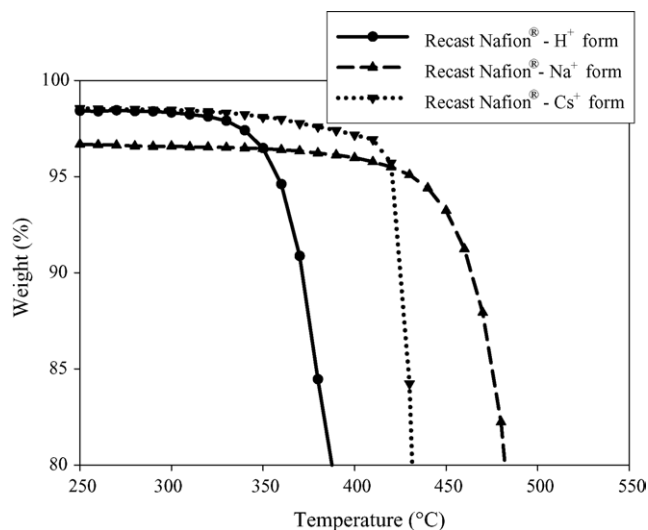

Fig. 1. Thermograms of Nafion® with different counter ions.

advantage over recast Nafion®. It was assumed based on this evidence that Nafion® in the Cs^+ form would be as melt processible as in the Na^+ form and that the MEA heat treatment described in the literature [12] could be successfully employed if the Nafion® in the membrane and electrode are in the Cs^+ form.

Fig. 2 shows the thermograms of recast Nafion® and NPTA-S after conversion to the Cs^+ form, and of a NPTA-S membrane after re-protonation. The samples were obtained from the extended edges of an MEA prepared for testing. The ion-exchange process (overnight immersion) was efficacious (increase in decomposition onset) and the protonation treatment was equally effective (return of decomposition onset towards original value). The residue in the NPTA-S sample after protonation was very close to the initial 15% PTA loading, evidencing success of the stabilization technique. Finally,
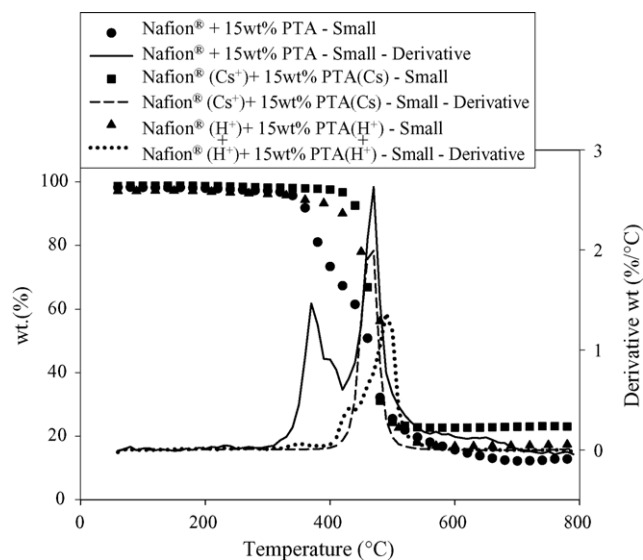

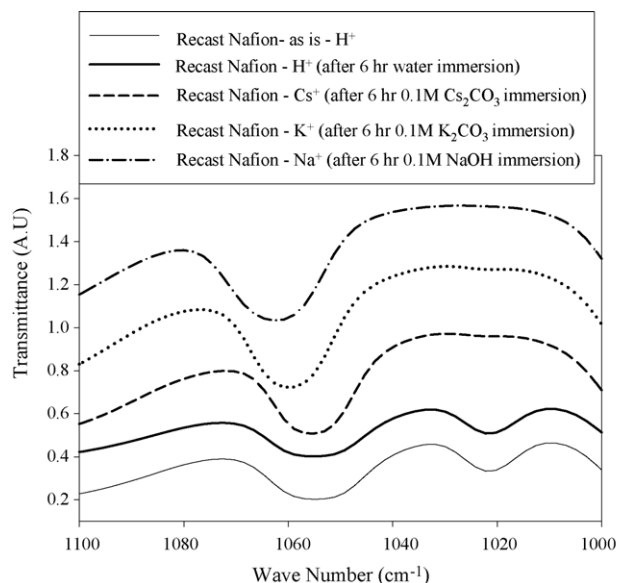Fig. 2. TGA evidence for ion-exchange and reprotonation.

Fig. 3. FTIR spectra of recast Nafion® with different counter ions.

Fig. 4. Influence of annealing on FTIR spectra of Nafion® and NPTA membranes. The spectrum of Nafion® 112 is provided for comparison.

the residue of the NPTA-S membrane after ion-exchange was slightly higher, which was explained by the conversion of the Nafion® and PTA to the Cs$^+$ form. Therefore, the TGA analysis proved that the stabilization (both additive and MEA stabilization) technique adapted was effective.

3.2. FTIR

The FTIR spectra of recast Nafion® with different counter ions are shown in Fig. 3. The change in counter ion caused a slight shift in the stretching vibrations of the SO$_3$ group (1056 cm^{-1}), which have been attributed interactions between the cation and the sulfonic acid group [14]. The Cs$^+$ form was closest to the H$^+$ form in terms of vibrational spectra. The difference in the extent of the shift seen for different cations could be explained by the differences in cation size and hydration enthalpy. Unlike Na$^+$ and K$^+$, when Cs$^+$ was used, it was difficult to conclude from the shift in this band whether successful ion-exchange (and protonation) had occurred. Fig. 3 also shows that no change was seen in the vibrational spectrum as the Nafion® was immersed in deionized water, which further confirmed that the ion-exchange is the key cause for the band shift. It was observed that a different feature in the vibrational spectra of Nafion® could be used to detect the degree of conversion of Nafion® in the protonic form to its counter ionic form (though not vice versa). Fig. 4 shows the spectra of Nafion® and NPTA-S membranes with and without annealing treatments. The spectrum of Nafion® 112 is also included. The samples that were annealed had an added feature in the spectrum at 1022 cm^{-1}. This feature was absent in the samples that were not annealed. The feature was reproducible, and was only seen if the films were annealed at high temperatures. This suggested that the feature was associated with induced crystallinity or similar restructuring of the polymer chains during the annealing process. Note in Fig. 3
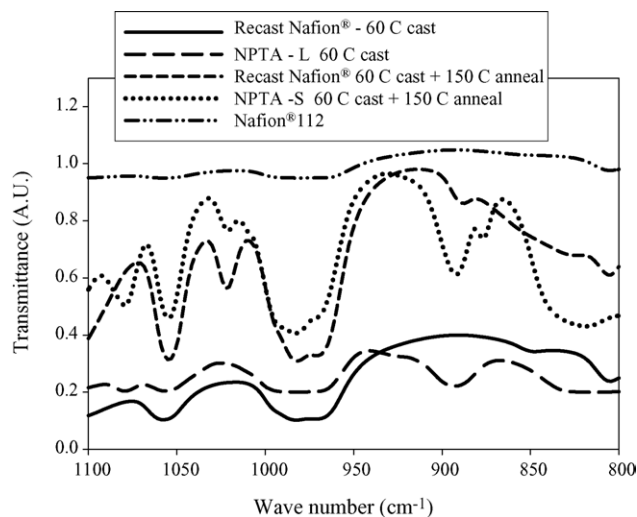
that the feature at 1022 cm^{-1} vanished when the counter ion was changed but remained stable when the membrane was merely immersed in water (in which case there was no possibility of ion-exchange). It was interesting to note (Fig. 5) that the feature at 1022 cm^{-1}, which was present even after boiling in deionized water for 1 h, disappeared if the sample was placed in H$_2$SO$_4$ even at room temperature. This suggested that the feature was associated with the ionic clusters, and disappeared upon any form of ion-exchange. A preliminary explanation for this phenomenon could be that an interaction induced by thermal treatment exists between the polymer backbones and the counter-ions (H$^+$) in the clusters, and this interaction is weakened if ion-exchange occurs. The immersion in liquid media during ion-exchange may destroy the arrangement of the polymer chains, thereby precluding re-formation of this interaction even if H$^+$ is present in the clusters. This reproducible phenomenon was used to study
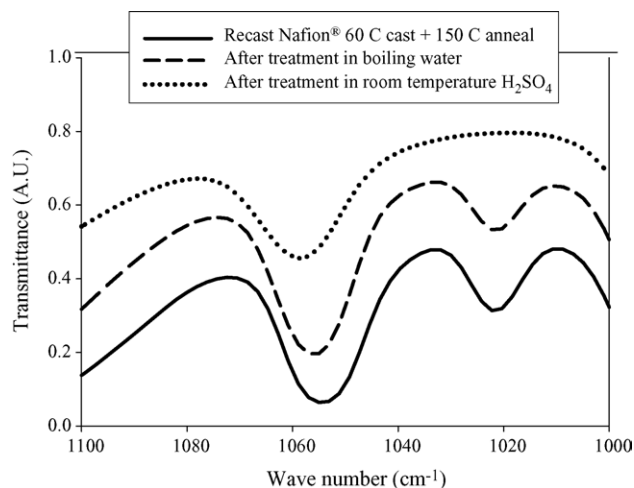

Fig. 5. Effect of H$_2$O and H$_2$SO$_4$ treatment on the FTIR spectra of Nafion®.
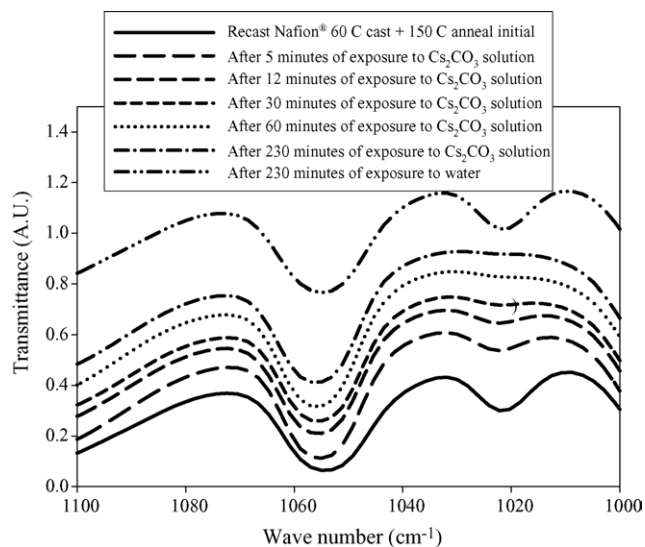
Fig. 6. FTIR spectra of Nafion® upon immersion in Cs_2CO_3 solution for different amounts of time.

the extent of conversion of the protonic form of the membrane to its counter ionic (Cs^+) form.

The evolution of the ion-exchange process with time is shown in Fig. 6. The extent of conversion to the Cs^+ form increased with time of immersion, as evidenced by the gradual decrease in the feature at 1022 cm^{-1}. The area under the peak of this feature has been correlated to the temperature of decomposition of the resultant membrane sample as determined by TGA (Fig. 7). As the area under the peak decreased (greater extent of ion-exchange), the decomposition temperature increased. Since the temperature plotted was the *onset* of decomposition, even a small fraction of unconverted ions would lead to early decomposition onset, and only complete conversion would permit onset at much higher temperatures than recast Nafion®. This is consistent with Fig. 7, where the final onset temperature was much higher than the penultimate one, even though the change in area under the curve
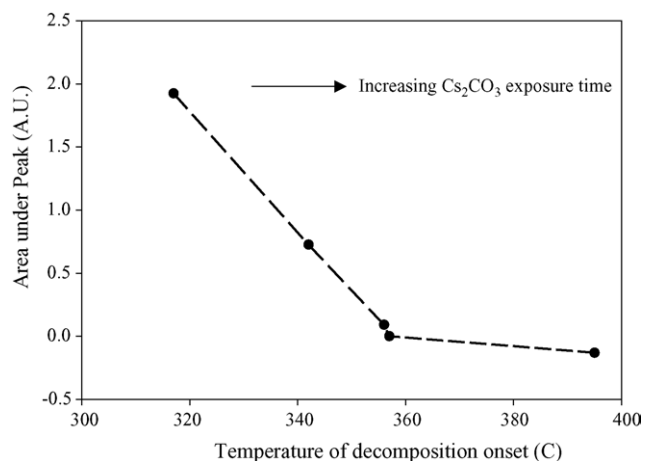

Fig. 7. Correlation between decomposition onset temperature and area under peak at 1022 cm^{-1}.
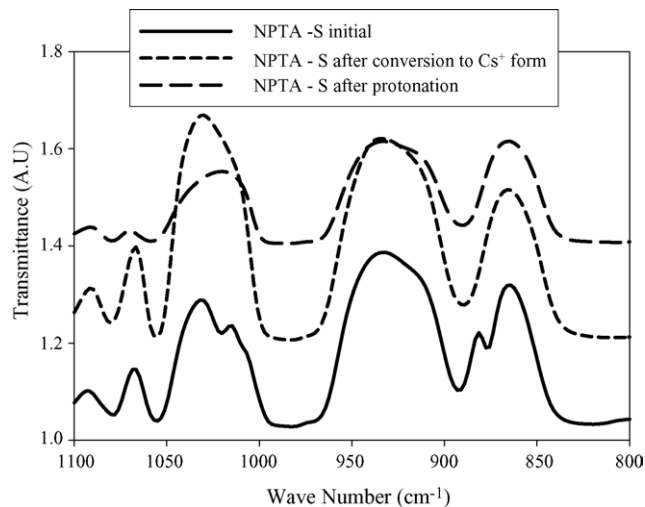

Fig. 8. FTIR spectra of an NPTA-S membrane (baseline) and the same membrane after ion-exchange and subsequent to protonation.

was not very large. This correlation between the FTIR and TGA results implied that the progress of ion-exchange could be readily monitored spectroscopically, minimizing the need for lengthy thermal analysis experiments. Fig. 8 shows spectra of an NPTA-S membrane (from the edges of an MEA) before ion-exchange, after ion-exchange and after protonation. The complete conversion of the membrane to the Cs^+ form is clearly seen, as is the retention of the PTA additive upon protonation. This study offered added experimental evidence of the successful implementation of the proposed stabilization strategy.

3.3. Electrochemical impedance spectroscopy

The above discussions pertained largely to independent membrane samples and samples taken from the fringes of the MEA. It was not possible to directly sample by either TGA or FTIR spectroscopy the active area of the membrane (i.e., area sandwiched between the electrodes). Therefore, to confirm that ion-exchange had occurred even in this area, EIS spectra were obtained at 80 °C and 75% RH of an MEA after ion-exchange and advanced heat treatment (but no protonation) and of the same MEA subsequent to protonation. These data are presented in Fig. 9. The impedance of the MEA was very large on ion-exchange to the Cs^+ form (a typical MEA would have an area specific resistance of approximately 0.1–0.2 Ω cm^2), and reduced to the specified normal range after protonation. This experimental evidence confirmed the efficacy of ion-exchange and protonation of the *membrane* within the active area of the MEA.

3.4. Cyclic voltammetry

The final experimental evidence required to confirm efficacious ion-exchange and protonation within the active area of the MEA (i.e., evidence for ion-exchange and protona-
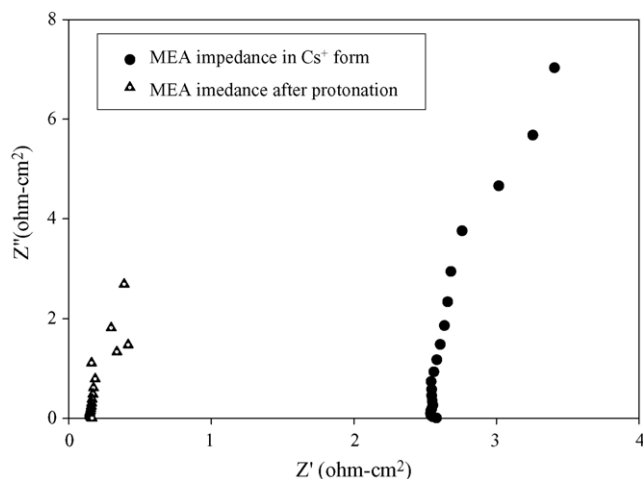
Fig. 9. Impedance spectra obtained at 80 °C and 75% RH of an MEA after ion-exchange and subsequent protonation.

tion of the Nafion® in the electrode layer) was obtained by cyclic voltammetry. CVs of the same MEA after ion-exchange before and after protonation are shown in Fig. 10. The lack of activity of the Pt electrode was very evident in the ion-exchanged form, indicating the lack of formation of the three-phase interface between ionomer, active catalyst sites and reactant protons. The poor activity was attributed to the poor proton conductivity of the Nafion® in the Cs+ form. The familiar CV of an active Pt electrode was regained upon protonation, yielding confirmation that the ion-exchange/protonation processes occurred effectively within the electrodes as well.

3.5. Linear sweep voltammetry

LSV experiments were preformed to confirm that the aggressive protonation treatment did not increase the crossover of the membrane through pin-hole formation and did not induce electronic shorting. Fig. 11 presents LSVs of an MEA prepared by the standard technique [8] (no stabilization) with
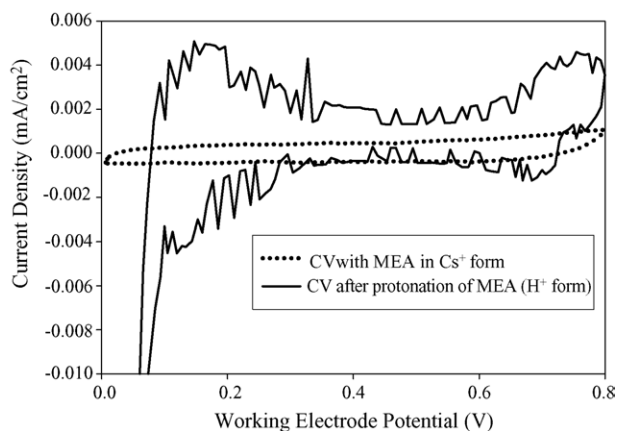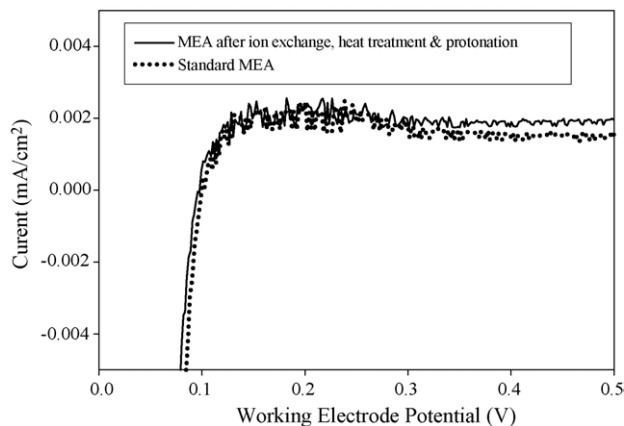

Fig. 11. LSVs obtained at 80 °C and 75% RH of an MEA after ion-exchange and subsequent protonation.

an MEA prepared with advanced heat treatment followed by protonation. The membranes used in the two MEAs ranged in thickness from 25 to 30 μm. The similarity of the crossover currents (normalized to a 25 μm membrane thickness) and the absence of electronic shorting augured well for the stability of the latter MEA.

3.6. Single cell performance and membrane conductivity

Experiments were performed to study the MEA performance and area specific resistance using 1.3 mil (30 μm) NPTA-S membranes. Fig. 12 compares the performance and area specific resistances of an MEA prepared by standard techniques to those of a stabilized MEA. The MEAs both had similar electrode noble metal loadings ($\sim$0.35 mg cm^{-2}) and the data were obtained at 120 °C and 35% RH (1 atm operating pressure), with air as the oxidant. The performance obtained was identical, with the MEA with advanced heat treatment exhibiting a slightly lower area specific resistance. This was attributed to a lowering in contact resistance caused

Fig. 10. CVs obtained at 80 °C and 75% RH of an MEA after ion-exchange and subsequent protonation.
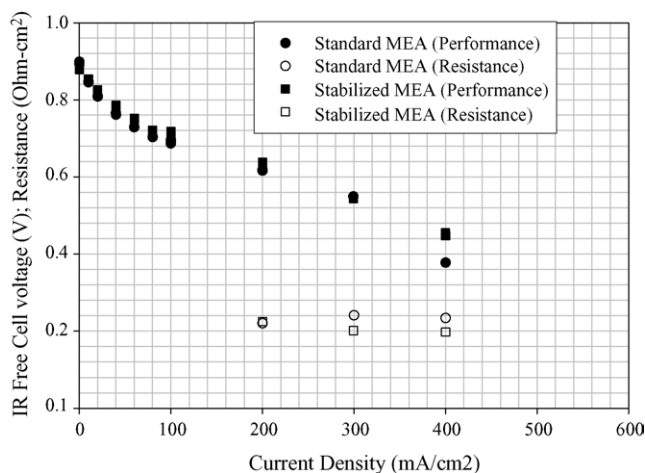

Fig. 12. Polarization curves obtained at 120 °C and 35% RH with a standard MEA and a stabilized MEA.

by better contact at the membrane electrode interface. In each case, the resistance plot showed a step change at a current density of $100\,\text{mA cm}^{-2}$ and stabilized at $200\,\text{mA cm}^{-2}$ because the instrumentation employed could only start to measure resistance above a total current of 0.5 A and could only accurately measure resistance above a total current of 1 A.

4. Conclusions and future directions

A simplified MEA preparation strategy that combines imparting advanced MEA heat treatment with stabilizing nano-sized PTA particles has been developed and demonstrated. FTIR spectroscopy and TGA analysis presented evidence of ion-exchange and protonation, with the former being used to determine when ion-exchange was complete. In situ EIS and CV measurements confirmed ion-exchange and protonation within the active portion of the MEA. Imparting an advanced heat treatment did not alter fuel cell performance at elevated temperatures and low RH, and did not hamper the integrity of the thin membrane. It is anticipated that imparting such a heat treatment will help improve the interfacial stability and promote lifetime in these MEAs, as demonstrated in the literature [12] with Nafion® based membranes.

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