Polyvinyl Chloride Composite Membranes Made with Nafion and Polysiloxanes for Use in Electrochemical Breath Alcohol Sensors

Jesse T. S. Allan and E. Bradley Easton*

*Electrochemical Society Member.

E-mail: Brad.Easton@uoit.ca

Polyvinyl chloride (PVC) is widely used in industry, and has found a use as a proton exchange membrane (PEM) for fuel cell devices.1,2 Specifically, PVC is used as the membrane of choice for fuel cell breathalyzers, or breath alcohol sensors (BrAS). PVC is used for its durability, chemical robustness, cost and stiffness.3 The PVC used in these devices are of a porous free standing nature with 10 μm spheres and pores of the same diameter. While the PVC itself does not produce the ionic conductivity required for proton conduction, the porous film is usually filled with ca. 4 M H₂SO₄ to impart ionic conductivity to the membrane.2 This creates a material that has superior ionic conductivity and water-uptake to the more commonly used Nafion and has excellent ionic conductivity properties.6–8 Nafion is highly dependent on water, however, and performance begins to suffer in drier environments.9 By casting the Nafion into a porous PVC material, the performance begins to suffer in drier environments.9 By casting the Nafion into a porous PVC material, the membrane for power generating PEM fuel cells. A more detailed analysis of the PVC used in BrASs can be found in our previous studies.1,2

Our previous studies have highlighted that the hydration state of the membrane electrode assembly (MEA) can greatly affect the performance of these BrASs.1,2 The hydration state of the MEA is mainly influenced by the relative humidity (RH) of the environment in which it is operated. Higher humidity conditions will reduce ionic resistance within the MEA, while lower RH conditions will increase ionic resistance.3 If the device is not calibrated for the humidity conditions it will operate in, the reliability and accuracy of the device will be greatly reduced.

Improving water management and retention within the BrAS should reduce the performance variation caused by variable RH. We have recently demonstrated that chemical modification of the porous PVC will not only increase ionic conductivity, but also improve the overall uptake of water within the membrane.2 With a greater content of water within the membrane, performance in lower humidity is expected to increase.

We have synthesized composites of PVC with various other materials to investigate their potential for improved membrane performance. The first composite will be composed of the PVC with Nafion imbued into the PVC. Nafion is commonly used in power generating devices, and has excellent ionic conductivity properties.5–7 Nafion is highly dependent on water, however, and performance begins to suffer in drier environments.5 By casting the Nafion into a porous PVC material, the water-content within the PVC is hypothesized to ensure the Nafion remains hydrated to allow for adequate ionic conductivity.

We have also investigated a second composite that used sulfonated silicates (SS). These materials have been found to impart excellent ionic conductivity and water-uptake in both freestanding films and within catalyst layers for fuel cells.6–10–12 In particular, Nafion films that incorporated sulfonated silica showed improved ionic conductivity and water-uptake performance.6 By incorporating SSs into the PVC membrane, the same performance enhancements should be expected.

In this report, composites of PVC with Nafion (PVC-Nafion) and PVC with sulfonated silica (PVC-SS) have been prepared and evaluated for their ionic conductivity and water-uptake. As well, the performance of these materials in a sensor application has been investigated to determine their viability within a sensor application role using our state-of-the-art testing station and cell that has been described in detail in our previous work.1

Materials and Methods

Materials.—Free standing PVC membranes were donated by Alcohol Countermeasure Systems (ACS) in 15 cm × 15 cm sheets with a thickness of 1 mm. The PVC used for experiments were cut to size as needed. The PVC was used as-received with preparatory work required. Figure 1 shows the PVC and an SEM image of the PVC membrane, highlighting the pressed spheres diameter of approximately 10 μm, with pore sizes of similar diameter.

Sulfuric Acid and the 5% Nafion solution were obtained from Sigma Aldrich. Tetraethylorthosilicate (TEOS) and 3-(triethoxysilyl)-1-propanesulfonic acid (TPS) were obtained from Gelest. 95% ethanol was obtained from Commercial Alcohols Inc. Johnson Matthey HiSpec 1000 100% Pt black was purchased from Alfa Aesar and is hereafter referred to as JM100.

Figure 1. A) Optical image of the PVC and B) SEM of the PVC used in BrASs.
Membranes.—PVC-sulfonated silica composite.—The PVC-sulfonated silica composite was synthesized by first establishing the sol-gel reaction: 30 mL of TEOS, 9.3 mL of TPS, 31 mL of 95% ethanol, and 38 mL of DI water were added to a 125 mL three-necked round bottom flask and heated to 60 °C. Once at temperature, 4 drops of concentrated HCl (Sigma Aldrich) was added to catalyze the reaction. The reaction was allowed to proceed for 2 hours, yielding a sol-gel material with a 95:5 atomic ratio of TEOS:TPS. Afterwards, the solution was cooled and various PVC samples were immersed into this solution for 15 minutes. The samples were then removed from the sol-gel solution and allowed to dry in a vacuum oven at 60 °C to evaporate excess solvent and complete the sol-gel reaction within the PVC pores. Once dry, the PVC-sulfonated silica composites were introduced into a 4 M sulfuric acid solution and were ready to be used. The PVC-sulfonated silica will be referred to hereon after as PVC-SS.

PVC-Nafion composite.—The PVC membranes were immersed into a 5% solution of Nafion for 15 minutes. After immersion, the membranes were removed and allowed to dry at 60 °C in a vacuum oven under vacuum for 24 hours. The dry membranes were then immersed into 4 M sulfuric acid before use.

Electrode synthesis.—The JM100 electrode was prepared from a JM100 catalyst ink, which was composed of a mixture of the JM100 catalyst powder, PTFE solution (Sigma Aldrich, 15 wt%), and water. While Pt supported carbon does show good performance compared to Pt-black,1,15 Pt-black was used here to mimic the electrode of the commercial material. The ink was mixed thoroughly for several hours and spray deposited onto a gas diffusion layer (Toray TGP-H-090, 10% wet-proofing) using an airbrush.1,10 The electrodes were dried for 30 mins at room temperature, and a further 30 mins at 130 °C. The electrode had a loading of 30 wt% PTFE for all cases. The platinum loading of these electrodes was 1.13 mg/cm².

TG and IR analysis.—Thermogravimetric analysis (TGA) was performed using a TA Instruments Q600 SDT thermal analyzer. Samples were dried in an oven under vacuum at 60 °C before testing. The samples were initially held at 80 °C for 15 minutes to ensure they were fully dried and the mass at this point was defined as the 100% value (the “dry mass”).2,12 The analysis was performed under flowing argon with a heating rate of 20 °C/min from 80 °C to 1000 °C.

FT-IR was performed using a PerkinElmer Spectrum 100 instrument. The samples were also dried before use similar to the conditions described for TGA measurements. The analysis was performed using an attenuated total reflectance (ATR) germanium crystal with a scan between 4000 cm⁻¹ to 700 cm⁻¹ with a resolution of 2 cm⁻¹ for 10 scans. The samples were pressed with a force between 30–50 N onto the ATR crystal.

Ion exchange capacity (IEC).—The washed PVCs membranes were removed from their DI solution and dried in a vacuum oven at 60 °C for 24 hours to remove excess water from the pores. The dried PVCs was then weighed to obtain the dry mass (m dry). The PVCs membranes were then placed into a known volume of 3 M NaCl solution for 24 hours. The solution was then titrated with a 3 mM solution of NaOH to determine the IEC of the materials. A Nafion 115 membrane was used as a control to ensure accuracy in this technique. The obtained 0.91 mmol/g IEC of Nafion agrees with literature (0.9 mmol/g).14

Solvent uptake and conductivity.—Membranes were imbibed with 4 M sulfuric acid at room temperature for 1 hour to ensure the pores were full, which are the conditions normally used for deployment in fuel cell BrAs. The membranes were placed into an ESPEC SH-241 humidity chamber. The temperature was held constant at 25 °C for these tests. The humidity was ramped from 95% down to 45%, with 10% interval holds for 30 minutes each. At the end of each hold, the weight of the membrane was obtained (m wet). Once the measurements were complete, the membranes were washed of the electrolyte in a similar fashion to the IEC procedure and weighed to obtain the dry mass. The water uptake of these membranes were obtained with the following formula:2,6

$$ \text{Water Uptake (Mass %)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\% \quad [1] $$

where m_wet is the mass of the membrane wet, and m_dry is the dry membrane weight.

Conductivity was performed with a Bekktech BT-110 conductivity clamp attached to a Schlumberger Solatron SI 1286 Potentiostat. This 4-probe technique has been used for other membrane conductivity measurements.2,15,16 The membranes were prepared in the proper size for the clamp (2 cm × 1 cm) and placed into the clamp. The clamp with membranes was then placed into the humidity chamber to investigate conductivity at various relative humidities. The measurements were taken directly inside the humidity chamber, after a 30 minute equilibration time. A cyclic voltammetry (CV) sweep was performed to determine the resistance. A sweep rate of 30 mV s⁻¹ was chosen and was ramped between 0 V to 0.3 V vs. reference. The conductivity (σ) was determined using Equation 2:

$$ \sigma_H^+ = \frac{L}{R + A} \quad [2] $$

where L is the length between the working and counter electrode, R is the resistance, and A is the cross-sectional area.

MEA fabrication.—The two modified PVC-MEAs, as well as an unmodified PVC control had two 2.25 cm² electrodes placed across the acid loaded PVC membranes. They were hot pressed for 180s at 80 °C at a pressure of 355 kg cm⁻². Before sensor testing, they were placed into a 4 M H₂SO₄ solution to reload the membrane with acid.

Measurements in UOIT sensor cell.—Full details and validation of our sensor cell and test station is reported elsewhere.4 Briefly, the fuel cell (which will be denoted as the UOIT cell) used had an electrode area of ca. 2.25 cm². The test MEA was placed inside the cell and held in place with a clamp force of 4520 N. The working electrode compartment was connected to an ethanol feed that used nitrogen to carry gas from the breath simulator at a flow rate of 145 mL/min. The breath simulator was maintained at 34 °C. The device operated in air breathing mode with a load of 200 Ω was placed across the cell. A Solartron SI-1287 was used for the sensor mode measurements. A Solartron 1470E Multichannel Potentiostat and a Solartron 1260 frequency response analyzer controlled using Multistat software (Scribner Associates) were used to measure cyclic voltammograms (CVs) and electrochemical impedance (EIS) during the diagnostic testing.

Sensor mode measurements.—The UOIT cell was placed into an ESPEC SH-241 humidity chamber to allow precise control of humidity. The cathode was left open to expose the MEA to the ambient environment. The cell was conditioned at 95% RH, 25 °C for 24 hours before testing. The working electrode (WE) was interfaced to the breath simulator. An injection of 10 s via an electronic timer was used to simulate a breath injection. A current trainset was recorded before testing. The working electrode (WE) was interfaced to the breath simulator. An injection of 10 s via an electronic timer was used to simulate a breath injection. A current trainset was recorded and this process was repeated every 5 minutes at each BAC for 4 measurements. The BAC measured ranged between 0 to 0.18 BAC. After the 95% RH sensing, the humidity was reduced to 45% RH, with a conditioning of 24 hours. The sensor testing was repeated the following day.

Diagnostic mode measurements.—The diagnostic mode was measured after the 95% RH and 45% RH sensor tests. For diagnostic mode, the WE was connected to a humidified N₂ gas feed. The counter electrode (CE) was exposed to a flow of humidified H₂ and served as both the counter and reference electrode (RE). CV measurements were made in a potential range of 0.0 and 1.4 V vs. the reversible hydrogen electrode (RHE). A minimum of 20 cycles were performed before
collecting a stable CV for determination of the electrochemically active surface area (ECSA). EIS spectra were acquired for each catalyst layer over a frequency range of 100 kHz–0.1 Hz using a DC biased potential of 0.425 V (double layer region). The uncompensated resistance was used to find the interfacial resistance of the electrode to the MEA, and the uncompensated resistance was subtracted from the impedance spectra to measure the catalyst layer ionic conductivity, as well as the capacitance of the catalyst layer.

Results and Discussion

Membrane physical properties.— As both silica and Nafion are transparent, no obvious color changes occurred. The wt% of sulfonated silica in the PVC-SS membrane was found to be ca. 10.1% and the wt% of Nafion in the PVC-Nafion composite was ca. 3.6%.

Ex-situ characteristics.—FTIR spectroscopy.— The FTIR spectra for the composites vs. an unmodified control can be found in Figure 2. The IR spectrum for PVC displayed peaks at 2950 cm$^{-1}$, 1425 cm$^{-1}$, 1340 cm$^{-1}$, 1200 cm$^{-1}$, 1050 cm$^{-1}$, and 950 cm$^{-1}$, which correspond to various C-C and C-H vibrational modes within the polymer. The large peaks at 700 cm$^{-1}$ and 650 cm$^{-1}$ correspond to the C-Cl stretches. There is a small, wide peak present above 3000 cm$^{-1}$ which corresponds to absorbed water by the extremely hygroscopic KBr used in the press pellet. The PVC-Nafion can be classified as follows: a large –OH stretch above 3000 cm$^{-1}$ is observed in this case due to the KBr absorbing water, which the Nafion can now interact with to form –OH bonds. The very broad peak present at approximately 1100 cm$^{-1}$, which dominates this spectra compared to the PVC is the –CF$_2$ stretching, which corresponds to the Nafion backbone. Finally, the O=S=O stretches are present at 1220 cm$^{-1}$. Therefore, from the observations described, the Nafion has been incorporated into the PVC matrix.

The PVC-SS can be classified as follows: above 3000 cm$^{-1}$, –OH stretching is observed, which corresponds to water absorbed by the KBr, as well as by the sulfonated silicate itself, allowing for hydrogen bonding to occur with the sulfonic acid groups present within the polymer. The spectra for this composite also has a very large, broad dominate peak at 1090 cm$^{-1}$, which would correspond to the Si-O-Si stretches, as well as SO$_2$ stretching that cannot be resolved due to the overlap of the two vibrations. With this information, it can be conclusively stated that a silicate network has been synthesized within the pores of the PVC matrix.

TGA and IEC.—The TGA/DTG curves obtained for the three membranes can be found in Figure 3. PVC has two main degradation peaks. The first occurred at ca. 230°C which is due to the loss of pendant chloride as HCl gas, leaving residual polyethylene and/or cross-linked hydrocarbon backbone. The second occurred at 425°C and is attributed to the backbone degradation of PVC, resulting in volatile aromatic compounds.

The PVC-Nafion composite can be analyzed as if the PVC and Nafion spectra were overlaid with one another. The Nafion degradation analysis was explained in detail in Chapter 4. The DTG does show two peaks occurring between 225°C and 375°C. The first of the two peaks corresponds to the Nafion side chain degradation, leading to SO$_2$ by-products and species that exhibit C-F stretching, and the second is the loss of the HCl in the PVC backbone. The residual mass of the PVC and PVC-Nafion are very similar, with only a slight increase in weight for the PVC-Nafion due to the incorporation of the Nafion.

The PVC-SS shows a trend similar to the PVC-Nafion, but with a larger peak at a lower temperature, and the reduction in size of the second peak below 375°C. The degradation of the sulfonated silica side chain would occur at this temperature, and it appears the...
Figure 3. A.) DTG and B.) TGA of PVC, PVC-Nafion, and PVC-SS. Measurement was performed under Ar with a ramp rate of 10°C/min up to 1000°C.

degradation of the silica side chains affects the stability of the PVC chloride group. This would mean that as the silica begins to degrade, it catalyzes the degradation of the HCl resulting in a PVC backbone of crosslinked polymers and polyethylene. The second degradation peak at 425°C remains unchanged, indicating backbone degradation of the PVC. The residual mass of the PVC-SS composite is higher than the unmodified PVC due to the incorporation of the sulfonated silica.

The IEC values (Table I) are quite low and do not relate to other common solid polymer electrolytes (SPEs) such as Nafion, which generally have IEC values of ca. 0.9 meq/g. However, due to the low overall loading of both the Nafion and SS, it is not expected that a large IEC would be obtained. It is important to note is that both composites do have a measureable IEC value, indicating that a sulfonated group has been incorporated into the PVC matrix.

Water-uptake and ionic conductivity.—The water-uptake measurements for the membranes can be found in Figure 4. The unmodified PVC showed the highest uptake over the range of humidities tested. This can be explained by the fact since there are no other components within the pores, there is more space within the pores for electrolyte, and hence is able to more readily hold electrolyte compared to the composites. Nafion and the silicates do occupy volume within the pores, and hence would reduce the overall water content. PVC-SS showed higher uptake compared to that of the PVC-Nafion. The backbone of the silicate (Si-O-Si), as well as the sulfuric acid group, are both hydrophilic. Due to the hydrophilic nature of these groups, they are more likely to retain water they come into contact with, and will not repel the liquid water. In comparison, PVC-Nafion has a much lower water uptake. The only hydrophilic region within the Nafion is the sulfonic acid region at the end of the side chain. The backbone and majority of the side chain are all hydrophobic, and would repel water that it would come into contact with. This would have the overall effect of lowering the water-uptake of the composite material.

The variation in ionic conductivity with relative humidity for each membrane is shown in Figure 5. The trend of ionic conductivity is similar to that of water-content: as RH decreases, as does the ionic conductivity. The PVC has the highest overall conductivity. This can be attributed to the greater volume of water (and electrolyte) within the pores compared to the other two materials. This significantly aids in proton conduction across all RHs. PVC does, however, show a significant decrease in performance below an RH of 65%, decreasing by more than a factor of two at 45% RH compared to its initial 95% RH conductivity. This indicates that PVC requires a large volume of electrolyte to obtain the high conductivities. If the water-uptake decreases to a value of 80%, as it does at a RH of 45%, than ionic

Table I. IEC Analysis for the membranes synthesized for this work.

| Membrane   | Equivalent weight (g) | IEC (meq/g) |
|------------|------------------------|-------------|
| PVC        | N/A                    | 0           |
| PVC-SS     | 49000 ± 8%             | 0.033 ± 0.003 |
| PVC-Nafion | 146000 ± 31%           | 0.006 ± 0.002 |

Figure 5. Ionic conductivity for PVC, PVC-SS, and PVC-Nafion. The temperature of the humidity holds was 25°C.
conductivity drops off quite significantly. Requiring such a higher water content with a very hydrophobic material in a dry environment would be extremely difficult to maintain.

The composites also follow a similar trend in ionic conductivity: as RH decreases, as does ionic conductivity. The PVC-Nafion does have an edge in performance over the PVC-SS. This can be associated with the fact the Nafion is sufficiently loaded with water to aid in the proton conduction within the membrane. Nafion does show higher performance on its own compared to comparable silicate membrane materials, and thus a composite composed of Nafion and PVC should have higher performance compared to that of a PVC-SS hybrid. While performance does decay as RH decreases, the decrease in performance is not as significant compared to that of PVC. This would mean the composites would be better adapted to environments with large fluctuations in humidity as they have better stability over the RH range tested compared to the unmodified PVC.

Sensor performance.— Sensor testing.— Figure 6 shows the calibration curves for PVC, PVC-Nafion, PVC-SS, and a Dräger MEA in the UOIT cell, as well as the 0.09 BAC transients for mentioned MEAs. Measurements taken at 25°C.

Figure 6. A.) and C.) Calibration Curve for a PVC MEAs, as well as the Dräger MEA in the UOIT cell for comparison and B.) and D.) transients at 0.09 BAC for mentioned MEAs. Measurements taken at 25°C.

are in-fact shorter and wider than the 45% RH transients, which are narrower and peak at a higher current.

Figure 7 shows the analyzed calibration data for the PVC, PVC-Nafion, and PVC-SS MEAs with the Dräger MEA in the UOIT cell as well. The PVC material shows a small drop in sensitivity from 95% RH to 45% RH. This was attributed to the drier environment, which allowed water to evaporate from the membrane and CL to reduce performance. The Dräger MEA in the UOIT cell also shows this drop in performance for the same reason. The normalized mass performance of the PVC is higher than the Dräger MEA due to the better platinum utilization compared to the commercial MEA.

The PVC and Dräger MEA also have similar stability. Due to the small pores of the Pt electrode, the ability of water to exit the membrane is significantly reduced. This ensures the membrane remains adequately hydrated to ensure good performance at both 95% RH and 45% RH.

The PVC-SS membrane shows an improvement in sensitivity at 95% RH compared to the PVC MEA, with a drop in sensitivity at 45% RH that is slightly lower than the unmodified PVC. While this factor is significant, what makes this remarkable is the amount of water required to obtain this performance. PVC had a water content of ca. 100 w/w% and ca. 80 w/w% for 95% RH and 45% RH respectively. The PVC-SS on the other hand had a water content of ca. 25 w/w% at 95% RH and ca. 18 w/w% at 45% RH. Therefore, PVC-SS is able
to match the performance of the PVC material with significantly less water and ionic conductivity. This has profound advantages. With less water, less acid is also present. This not only reduces the hygroscopic absorption of water by the sulfuric acid which causes flooding, but it also reduces the amount of corrosion that will inevitably occur using the sulfuric acid.

PVC-Nafion shows a similar decrease in performance from 95% RH to 45% RH, but the overall sensitivity is significantly lower compared to PVC. Even with ca. 4% Nafion by weight in this composite, the performance is extremely poor. The initial thought was that PVC acted as an electrolyte reservoir for the Nafion, allowing for sufficient ionic transport by the Nafion alone, allowing for more stable performance. However, this is not the case since Nafion is also somewhat hydrophobic. Nafion is peculiar in that it has both hydrophilic and hydrophobic properties. Thick Nafion membranes (as used as PEMs) are very hydrophilic. Thin films of Nafion, however, tend to be quite hydrophobic (thicknesses < 250 nm), and thus can act as barriers to water.8 The Nafion may have cast within the pores of the PVC in very thin films on the surface of the PVC pressed spheres. If this is the case, the hydrophobic properties of the Nafion would be dominant, and repel water and electrolyte. The Nafion also may have agglomerated within the pores of the PVC which would also block the transport of protons through the membrane. This would also cause a significant reduction in performance. Therefore, during sensing, the amount of available water for ion transport would be significantly reduced, significantly affecting performance, and this is what is observed. Similarly, the Nafion blocks pores that were accessible to water movement in the unmodified membrane. Since the Nafion also repels water, the amount of water within the membrane would be very low, and this will greatly reduce performance.

Diagnostic testing.—Figure 8 shows the CV’s for the PVC and PVC-SS during diagnostic testing after the 95% RH sensing. CVs could not be obtained after testing at 45% RH due to the highly resistive nature of the dried PVC and PVC-SS. The CVs after 95% RH and 45% RH sensing for PVC-Nafion are not shown at all as the material was extremely resistive at both humidities.

The unmodified PVC shows a slightly increased ECSA (ca. 75 m²/gPt) compared to the PVC-SS material (ca. 67 m²/gPt). The silicate within the PVC is effecting the surface area of platinum exposed to the electrolyte, which is not unexpected. However, as the change is not significantly large, this would indicate that the silicates form deeper within the pores of the PVC rather than concentrating at the surface of the PVC.
directly exposed to the liquid electrolyte, allowing for direct access of the catalyst to the electrolyte. This would benefit ionic transport, as well as water management within the catalyst layer. PVC also has the advantage that no material is in the pores that could potentially block catalytic sites, increasing the interfacial resistance.

The high frequency resistance ($\text{R}_{HF}$) for PVC increases from as the relative humidity decreases. Since the CV for the PVC MEA at 45% RH was highly resistive, it would indicate that while the catalyst layer may be drying out, the membrane is still sufficiently hydrated to allow for adequate ionic transport. In fact, the change in resistance for $\text{R}_{HF}$ is lower than the change in resistance measured during the ex situ conductivity. This may indicate that the PVC is not only reabsorbing a small amount of water during the diagnostic testing, but that water is moving from the CL into the membrane when exposed to a drier atmosphere.

The PVC-Nafion system showed extremely poor sensor performance, and the diagnostic testing also confirms the poor nature of this MEA. Since meaningful CV’s could not be obtained, it would indicate that both ionic transport through the MEA, as well as the hydration of the CL is significantly hindered. EIS measurements confirmed this. The total resistance of the PVC-Nafion MEA is significantly higher than the unmodified PVC. Since the PVC-Nafion MEA contained very little water as a whole, the CL would also remain significantly dry. This greatly increases the interfacial resistance, as well as increasing ionic resistance in both the CL and membrane. This explains the poor sensor performance at both 95% RH and 45% RH for this material.

The PVC-SS shows a slightly increased interfacial resistance compared to the PVC MEA. This is due to the fact the hydrophilic silicates within the pores are blocking interfacial sites, increasing the ionic resistance at those locations. Nevertheless, the increase is not sufficiently large to cause major performance losses.

Comparing $\text{R}_{HF}$ at 95% RH and $\text{R}_{HF}$ at 45% for the PVC-SS, there is a slight increase in the resistance. This is again expected as drier conditions would remove water from the PVC-SS membrane.

Conclusions

The purpose of this study was to explore modifications to the commercially used PVC that is used in commercial BrAs. It was found that a PVC-Nafion composite actually greatly reduces performance of the membrane. The water available for proton conductivity is significantly reduced, which is due to Nafion blocking the pores of the PVC, and also acting as a hydrophobic barrier. This greatly effects all properties of the MEA, including interfacial contact, conductivity, and sensor performance.

The PVC-SS on the other hand not only shows a slight improvement in sensor performance at 95% RH, but is able to do so whilst requiring only 20% of the water content the PVC uses. This reduction in the amount of electrolyte required will not only avoid flooding that can occur at very high humidities, but also prolong the life of the sensor as the amount of acid present is reduced, which will reduce the amount of corrosion that can occur over time.

Acknowledgments

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation and UOIT. JA acknowledges NSERC for scholarship support.

References

1. M. R. Rahman, J. T. S. Allan, M. Z. Ghavidel, L. E. Prest, F. S. Saleh, and E. B. Easton, “The application of power-generating fuel cell electrode materials and monitoring methods to breath alcohol sensors,” Sensors Actuators B Chem. 228, 448 (2016).
2. J. T. S. Allan, L. E. Prest, and E. B. Easton, “The sulfonation of polyvinyl chloride: Synthesis and characterization for proton conducting membrane applications,” J. Membr. Sci., 175, 175 (2015).
3. S. Mei, C. Xiao, and X. Hu, “Preparation of porous PVC membrane via a phase inversion method from PVC/DMAc/water/additives,” J. Appl. Polym. Sci., 120, 557 (2011).
4. A. Modjtahedi, M. R. Rahman, and E. B. Easton, “The influence of relative humidity on the performance of fuel cell catalyst layers in ethanol sensors,” Sensors Actuators B Chem. 239, 120 (2017).
5. L. Prest, Fundamental Investigation of Fuel Cell-based Breath Alcohol Sensors and the Cause of Sensor Degradation in Low-Humidity Conditions, Thesis, UOIT. 2011.
6. K. M. Yarrow, N. E. De Almeida, and E. B. Easton, “The impact of pre-swelling on the conductivity and stability of Nafion/sulfonated silica composite membranes,” J. Therm. Anal. Calorim., 119, 807 (2013).
7. S. Feng and G. A. Voth, “Proton solvation and transport in hydrated Nafion,” J. Phys. Chem. B., 115, 5905 (2011).
8. A. A. Khan, S. Sridhar, and A. A. Khan, “Solid polymer electrolyte membranes for fuel cell applications—a review,” J. Membr. Sci., 259, 10 (2005).
9. J. I. Eastcott, K. M. Yarrow, A. W. Pedersen, and E. B. Easton, “Fuel cell electrode structures containing sulfonated organosilane-based proton conductors,” J. Power Sources, 197, 102 (2012).
10. N. E. De Almeida and E. B. Easton, “Nafion/Sulfonated Silica Composite Membranes for PEM Fuel Cells,” ECS Trans., 28, 29 (2010).
11. J. I. Eastcott and E. B. Easton, “Electrochemical studies of ceramic carbon electrodes for fuel cell systems: A catalyst layer without sulfonic acid groups,” Electrochim. Acta., 54, 3460 (2009).
12. A. Modjtahedi, A. Amirfazli, and S. Farhad, “Low Catalyst Loaded Ethanol Gas Fuel Cell Sensor,” Sensors Actuators B Chem., 234, 70 (2016).
13. S. Lyov, E. Chalkova, G. Ryba, M. Fedkin, D. Wosinslow, and M. Roelofs, “Nafion/TiO2 Composite Membranes for PEM Fuel Cells Operating at Elevated Temperature and Reduced Relative Humidity,” ECS Trans., 3, 73 (2006).
14. M. Eldin, H. A. El Enshasy, M. E. Hassan, B. Haroun, and E. A. Hassan, “Covalent immobilization of penicillin G acylase onto amine-functionalized PVC membranes for 6-APA production from penicillin hydrolysis process. II. Enzyme immobilization and characterization,” J. Appl. Polym. Sci., 125, 3820 (2012).
15. Y. Soudais, L. Moga, J. Blazek, and F. Lemott, “Coupled DTA–TG–FT-IR investigation of pyrolytic decomposition of EVA, PVC and cellulose,” J. Anal. Pyrolysis, 78, 46 (2007).
17. E. B. Easton, T. D. Astill, and S. Holdcroft, “Properties of gas diffusion electrodes containing sulfonated poly (ether ether ketone),” J. Electrochem. Soc., 152, A752 (2005).
18. M. C. Lefebvre, R. B. Martin, and P. G. Pickup, “Characterization of ionic conductivity profiles within proton exchange membrane fuel cell gas diffusion electrodes by impedance spectroscopy,” Electrochem. Solid-State Lett., 2, 259 (1999).
19. F. S. Saleh and E. B. Easton, “Determining electrochemically active surface area in PEM fuel cell electrodes with electrochemical impedance spectroscopy and its application to catalyst durability,” Electrochim. Acta, 114, 278 (2013).
20. F. S. Saleh and E. B. Easton, “Assessment of the ethanol oxidation activity and durability of Pt catalysts with or without a carbon support using Electrochemical Impedance Spectroscopy,” J. Power Sources, 246, 392 (2014).
21. D. L. Tabb and J. L. Koenig, “Fourier transform infrared study of plasticized and unplasticized poly (vinyl chloride),” Macromolecules, 8, 929 (1975).
22. R. R. Stromberg, S. Straus, and B. G. Achhammer, “Infrared spectra of thermally degraded poly (vinyl chloride),” J. Res. Natl. Bur. Stand., 60, 147 (1958).
23. L. Grosmaire, S. Castagnoni, P. Huguet, P. Sistat, M. Boucher, P. Bouchard et al., “Probing proton dissociation in ionic polymers by means of in situ ATR-FTIR spectroscopy,” Phys. Chem. Chem. Phys., 10, 1577 (2008).
24. Q. Deng, C. A. Wilkie, R. B. Moore, and K. A. Mauritz, “TGA-FTIR investigation of the thermal degradation of Nafion and Nafion/silicon oxide-based nanocomposites,” Polymer (Guildf), 39, 5961 (1998).