# IMPROVED ELECTROCHEMICAL AND MECHANICAL PROPERTIES OF POLY(VINYLPYRROLIDONE)/NAFION® MEMBRANE FOR FUEL CELL APPLICATIONS

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**Abstract -** These instructions give you guidelines for preparing papers for the International conference ICCSE). Use this document as a template if you are using Microsoft Office Word 6.0 or later. Otherwise, use this document as an instruction set. The electronic file of your paper will be formatted further at International Journal of Computer Theory and Engineering. Define all symbols used in the abstract. Do not cite references in the abstract. Do not delete the blank line immediately above the abstract; it sets the footnote at the bottom of this column. A novel blend of membranes made of Nafion®, and poly(vinylpyrrolidone) (PVP) was prepared and characterized to investigate its applicability in proton exchange membrane fuel cells (PEMFCs). In addition to being effectively proton conductive, the membranes exhibited better mechanical strength, chemical stability, and adequate water retention ability, as well as ion exchange capacity comparable to that of cast Nafion® membrane. The data obtained from an electrochemical impedance spectroscopy (EIS) fitting of the fuel cells revealed the membrane electrode assemblies (MEAs) made of 0.5 wt. % PVP/Nafion® had lower ohmic, and charge transfer resistance compared with that of the Nafion® membrane. The intermolecular interactions and morphology of these membranes were assessed using Fourier-transform infrared spectroscopy and field-emission scanning electron microscopy. The results of the performance curve indicate that the introduction of PVP as a modifier played a vital role in improving membrane performance. Accordingly, this solution-casted polymer electrolyte membrane with suitable PVP content offers a simple way to improve electrochemical, mechanical, and chemical properties, and thereby promises the prospect of use in low-temperature PEMFCs.

**Index Terms -** Durability, Mechanical Properties, Nafion, Pemfc, Proton Conductivity, Pvp.

## I. INTRODUCTION

Proton exchange membranes (PEMs) have been studied extensively in recent years because of their superior proton conductivity, chemical and mechanical stability at moderate temperatures [1]. However, with the objective of minimizing performance loss in Nafion® membranes,as PEMs, improvement in durability [2] during long-term operation and proton conductivity under low relative humidity [3] are considered key requirements. In order to address these issues, one approach is to make polymer blends with Nafion® and hygroscopic materials [4]. The interest in new structures and the characteristics of the blends is associated with the requirement for materials with distinctive features that are not found in homopolymers and copolymers [5]–[6]. Nafion® has been observed to form homogeneous, one-phase blends with heterocyclic nitrogen compounds [7]–[8]. Though a few studies in this field were reported with poly(vinylpyrrolidone) (PVP) [9], to date no one has introduced this hygroscopic material as a physical modifier of Nafion® for application in PEMFCs. Among the broad range of substitute membranes investigated for PEMFCs, cyclic amide-based membranes such as PVP are considered to be a potential candidate on account of their strong polarity, amphiphilic character, film forming property, ease of processing, complexing ability, toughness, and other unique physico-chemical features [10]. Though PVP is a proton acceptor polymer [11], the proton conductivity of this membrane is low in comparison with Nafion®. This is because the numerous dead-end ion conducting channels possessed by PVP limit the proton transport across the membrane, whereas the ionic domains in Nafion® are well interconnected. For enhanced proton conductivity, it is essential to open these dead-end channels to interconnect them, and to modify the PVP membranes by sulfonation. However, with an increased degree of sulfonation, the mechanical properties of the PVP membrane tend to deteriorate due to dimensional instability caused by higher water uptake. This phenomenon becomes more severe when the fuel cell operates for an extended time at higher humidity and temperatures. An alternative approach to improving the physicochemical [12]–[14] and electrochemical [15] properties is to form a blend of PVP directly with Nafion® as a primary polymer, which refines the ionic domains of PVP. The polar PVPs, if used in small ratio, act as physical chain cross-linkers in the Nafion® matrix and make the blend resistant to water-rich media, thus enhancing membrane durability, and thermal stability.

In this study, we report a novel strategy for the preparation of PEMs with a simple solution casting

method by blending PVP, and Nafion® solutions in order to improve $H^+$ conductivity, mechanical strength, oxidative and thermal stability. To the best of our knowledge, the application of PVP as a physical cross-linker of the Nafion® membrane for proton exchange membrane fuel cells (PEMFCs) has not been investigated yet.Procedure for Paper Submission and the form should accompany your final submission.

## II. EXPERIMENTAL

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### A. Synthesis of PVP/Nafion® Blend Membranes

PVP (source: Sigma-Aldrich) of molecular weight of 160000 [16], and 5 wt. % Nafion® (Source: D521, DuPont South Korea) were used without any further purification. The blend membrane was fabricated using the solution casting method [17]. A fixed amount of PVP was dissolved in distilled water by stirring at 60°C for 30 min. Various prepared concentrations of PVP (0.5, 1, 2, 4, and 5 wt. %) were then added to 8 g of a 5 wt. % Nafion® solution, and mixed together by sonication for 30 min. Addition of more than 5 wt. % of PVP to the Nafion® renders the membrane too brittle, causing cracks to form during its handling. For this reason, the addition of PVP is limited to 5 wt. % in this study. The resulting mixture was then transferred to a polytetrafluoroethylene (PTFE) dish and placed in a vacuum oven at 60°C for 15 h. In order to compare the properties of these membranes, pure Nafion® membrane was also prepared with same solution casting method under identical conditions. Again, all the membranes were annealed at 130 °C for 2 h. The thickness of all fabricated membranes is 50 μm on average.

### B. Mechanical Properties

Mechanical strength was tested using a universal testing machine (Instron, model 4465) with an operating head load of 100 N at 25 °C, and 50 % RH. The sample membranes were vacuum dried at 80 °C for 12 h prior to the analysis. The tensile strength (N $mm^{-2}$) was calculated as follows:

Tensile strength = max load/cross-sectional area (1)

### C. Chemical Durability Test

Fenton's test was exercised as a well-known ex-situ accelerated test for predicting the oxidative stability of membranes. Membrane samples (3 cm × 3 cm) were immersed in Fenton's reagents (30 wt% $H_2O_2$ solution, and 20 ppm $Fe^{2+}$) at 80 °C and kept in the dark. In order to maintain a constant concentration, the Fenton's solutions were replaced every 3 h. The weight loss of membranes was calculated by this equation:

$$\text{Weight loss} = (W_i - W_f) / W_i \times 100\% \quad (2)$$

Where, $W_i$, and $W_f$ are the dry weights of the membranes prior to and following the treatment in Fenton's reagent, respectively.

### D. Proton Conductivity

Conductivities were measured at room temperature with 100% RH using a two-probe impedance measurement method between 0.1 kHz and 1 MHz using AC impedance spectroscopy (Versastat 3, Ametek). The proton conductivity (σ) was calculated via the following equation:

$$\sigma = L / (R \times A) \quad (5)$$

Where, L (m) is the thickness of the conducting membranes, R (Ω) is the ohmic resistance, and A ($cm^2$) is the surface area of the membranes [19].

### E. Performance Test

A single cell was tested using a PEMFC test station (HTS-125, Shanghai Hephas Energy Co. Ltd.) operated at 100% RH under ambient pressure to obtain the polarization curves. At a cell temperature of 100 °C, pure $H_2$ and $O_2$ gases were fed at stoichiometries of 1.5/2 ($H_2/O_2$) to anode and cathode, respectively. The cell was conditioned at a current density of 1 A $cm^{-2}$ for 2 h prior to the recording of the polarization curves [20].

### F. Characterization

FT-IR spectra of the membranes were acquired using a PerkinElmer (Spectrum GX AutoIMAGE™) instrument at 50% relative humidity (RH), and 25 °C. Morphology of the blend membrane was determined using FE-SEM (Hitachi, JSM-6701F, JEOL). Thermogravimetric analysis (TGA; TGA-2050, TA Instruments) was performed under a nitrogen atmosphere from 25 °C to 700 °C at a heating rate of 102 °C $min^{-1}$. The water uptake and IEC were determined following Kabir et al. [18].

## III. RESULTS AND DISCUSSION

### A. Molecular Structure

In the FT-IR spectrum (Fig. 1) of the PVP/Nafion® blend, the C–N bond stretching peak from PVP [21]–[22] was suppressed because of the intensified symmetric stretching vibrations of $–CF_2$ groups and $SO^{3–}$ groups in Nafion®. Broad bands in the 3000-3600 $cm^{-1}$ range, which correspond to the hydrogen bonding network [23], appeared due to the hygroscopic nature of membranes and the humid operating conditions (50 % RH). The peak shift in this

band from 3460 $cm^{-1}$ in the cast Nafion® membrane to 3444 $cm^{-1}$ in the PVP/Nafion® blend signified hydrogen bond network proliferation [24]. The absence of chemical binding between the two polymers was lucidly indicated by the lack of any other major peak shifting, i.e., the PVP/Nafion® blend is a simple blend of both polymers.

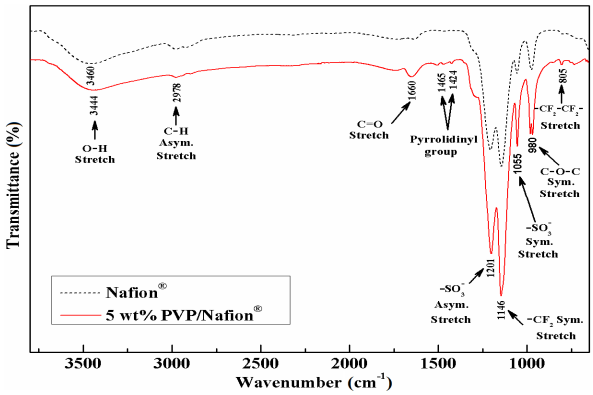



**Fig. 1: FT-IR spectra of cast Nafion® and 5 wt. % PVP/Nafion® blend membranes.**

## B. Morphology

Owing to strong polarity and miscibility, the PVP is well mixed and evenly distributed in the Nafion® matrix. It was previously established that a miscible ionic polymer blend membrane exhibits greater proton conductivity and IEC values than immiscible ionic blend membranes [25]. A clear transition from the dense and void-free [26]–[27] structure of the pure cast Nafion® to a porous PVP/Nafion® blend is apparent in the FE-SEM image (Fig. 2). These pores (with an average diameter of approximately 0.3 µm) are created by the incorporation of PVP in the Nafion® matrix due to the interactions among the functional groups of components.

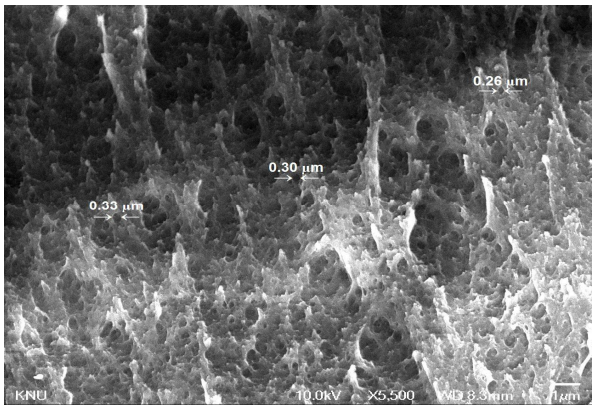



**Fig. 2. FE-SEM micrograph of cross-section of 5 wt. % PVP/Nafion® blend membrane revealing its macro-porous structure.**

## C. Mechanical Properties

The addition of PVP as a reinforcing agent was expected to enhance the mechanical properties of the membrane [14]. From Fig. 3, it is clear that an increase in the PVP percentage made the blend membrane harder and more brittle compared with the ductile and tough membrane of cast Nafion®. PVP is mechanically strong because of the intrinsic dipole-dipole interaction between PVP carbonyl groups. Additional interfacial hydrogen bonding among PVP and Nafion® molecules gives the PVP/Nafion® membrane significantly improved tensile strength compared with that of the unmodified cast Nafion® membrane. However, the elongation of the blend membranes decreases compared with that of pure cast Nafion® (Table I), owing to the presence of the inflexible backbone of PVP, which may affect the resilience of the blend.

## D. Oxidative stability

Fenton's reagent leads to the generation of hydroxyl radicals in the solution via the reaction $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-}$ [28]. The loss of membrane weight due to the release of fluoride in Fenton's solution is used here to quantify the degree of degradation. These results (Fig. 4) imply that PVP/Nafion® blends exhibit more chemical durability with an increase in PVP content than the pure cast Nafion® membrane. Fig. 6 exhibits the surface morphology of the unmodified cast Nafion® and 5 wt. % PVP/Nafion® blend membranes at various sampling times during the oxidative stability test. It is apparent that few pinholes appeared on the pure Nafion® membrane surface after treatment in Fenton's solution for 6 h, but gradually evolved with increased immersion time, causing a major rupture in the Nafion® membrane texture at 18 h. These pinholes are the reasons for gas crossover, and they consequently lead to structural failure of the membranes. In contrast, the chemical degradation trend is slower in 5 wt% PVP/Nafion® blend membranes.

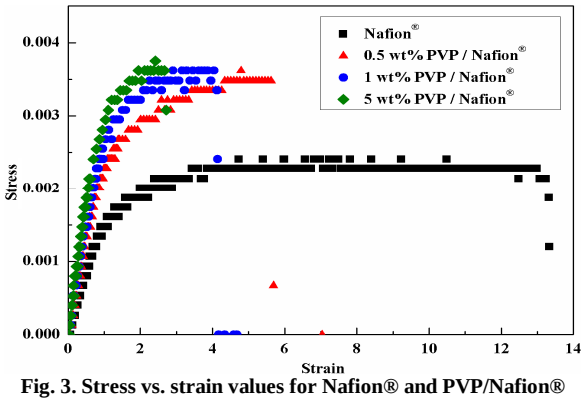



**Fig. 3. Stress vs. strain values for Nafion® and PVP/Nafion® blend membranes.**

**Table I. Comparison of tensile strength and elongation percentage of cast Nafion® and PVP/Nafion® blend membranes.**

| Membranes | Tensile strength (MPa) | Elongation (%) |
|---|---|---|
| Cast Nafion® | 15.8±0.3 | 29.2±0.4 |
| 0.5 wt. % PVP/Nafion® | 17.5±0.1 | 27.4±0.2 |
| 1 wt. % PVP/Nafion® | 21.4±0.2 | 23.8±0.3 |
| 5 wt. % PVP/Nafion® | 23.9±0.4 | 13.3±0.3 |

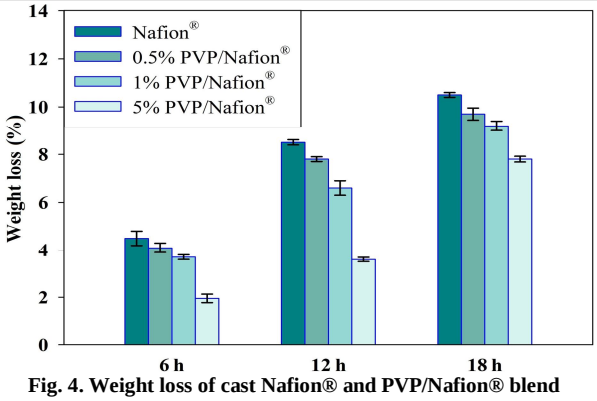



**Fig. 4. Weight loss of cast Nafion® and PVP/Nafion® blend membranes as a function of Fenton's reagent reaction time**

## E. Thermal stability

The decomposition behavior of cast Nafion® and PVP/Nafion® blend membranes by TGA is displayed in Fig. 7 In the case of all membrane samples, elimination of $H_2O$ molecules accounts for the initial weight loss in their thermogravimetric profiles, which ended at temperatures above 300 °C. Whereas impurities can safely be ignored here owing to the controlled fabrication process for all membranes, the lower weight loss percentage in the PVP/Nafion® blend membranes indicates that there are not as many $H_2O$ molecules absorbed in these blend membranes as in the pure Nafion® membrane. The higher thermal stability of PVP [29] compared with Nafion® provides these blends an extra thermal resistance capacity of up to almost 300 °C and therefore, with the increase in PVP loading, their thermal stability increases.

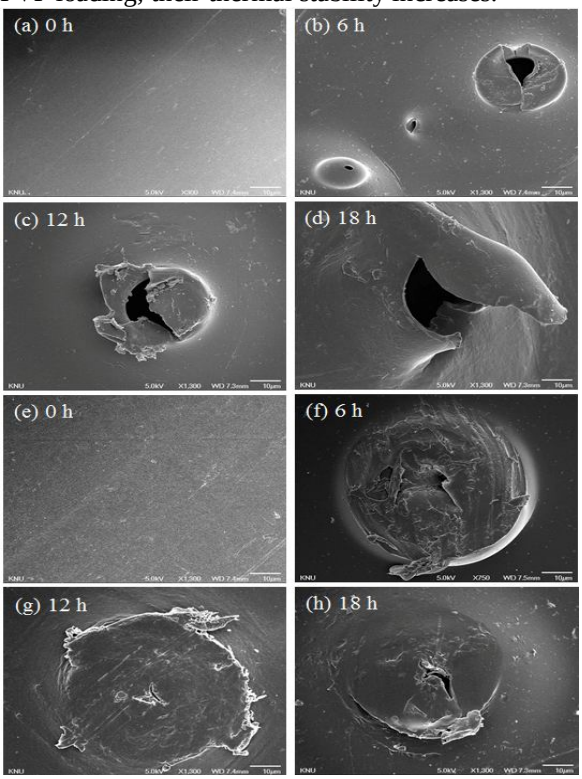



**Fig. 6. FE-SEM images of the cast Nafion® [from (a) to (d)] and PVP/Nafion® membranes [from (e) to (h)] at different Fenton's reagent reaction time. Scale: 10 µm.**

## F. Water Uptake

A balanced water uptake characteristic is required for an efficient PEM, because absorbed water contributes to proton transport in the membrane. However, an excess of water leads to dimensional changes of membrane. As observed in Table II, the water uptake of the PVP/Nafion® blend membranes was much lower than that of the Nafion® membrane, and gradually decreased with an increasing weight percentage of PVP in the Nafion® matrix. This finding is evident in previous TG curves and most likely results from PVP having a lower water uptake than Nafion®. The presence of hydrophobic groups (such as the nonpolar polyvinyl chains of PVP and the PTFE backbone of Nafion®) and the inevitable steric hindrance from the bulky pyrrolidone ring [24] limit access to water in the preferred sites [30] or pores of the blend membrane.

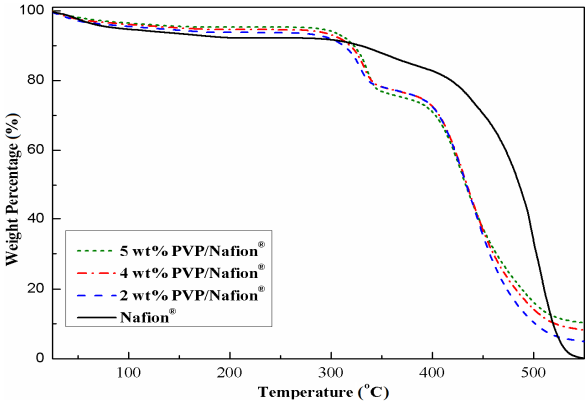



**Fig. 7. TGA thermogram of the pure cast Nafion® and PVP/Nafion® blend membranes.**

## G. Ion Exchange Capacity

The gradual decrease of the IEC values as the weight percentage of PVP incorporated into the membrane increased is apparent in Table II. The lack of cation exchange groups in PVP is responsible for this behavior [15]. This result can also be correlated to the inverse relationship between the water uptake trend and PVP content in the blend membrane. The membrane containing 0.5 wt. % PVP yielded the maximum IEC; and it is likely that a better PVP/Nafion® complex was formed in this blend membrane.

**Table II. Properties (Water uptake values, IECs, and proton conductivities) of cast Nafion® and PVP/Nafion® blend membranes.**

| Membranes | Water uptake (%) | IEC (meq. $g^{-1}$) | Proton conductivity (S $cm^{-1}$) |
|---|---|---|---|
| Cast Nafion® | 25.01 ± 0.03 | 0.97 ± 0.02 | $1.11 \times 10^{-2}$ |
| 0.5 wt. % PVP/Nafion ® | 19.98 ± 0.02 | 0.98 ± 0.01 | $1.61 \times 10^{-2}$ |
| 1 wt. % | 19.89 ± | 0.98 ± | $1.33 \times 10^{-2}$ |

| | | | |
|---|---|---|---|
| PVP/Nafion ® | 0.04 | 0.03 | |
| 2 wt. % PVP/Nafion ® | 19.17 ± 0.01 | 0.97 ± 0.02 | $1.10 \times 10^{-2}$ |
| 4 wt. % PVP/Nafion ® | 16.84 ± 0.03 | 0.95 ± 0.03 | $9.83 \times 10^{-3}$ |
| 5 wt. % PVP/Nafion ® | 14.38 ± 0.04 | 0.93 ± 0.04 | $8.62 \times 10^{-3}$ |

## H. Proton Conductivity

With lower ohmic and charge transfer resistance, the 0.5 wt. % and 1 wt. % PVP/Nafion® blends exhibited higher proton conductivities compared to that of the cast Nafion® (Fig. 8 and Table II). The polar carbonyl groups of PVP form hydrogen bonds with water molecules and thereby extend the proton passageway in the Nafion® matrix [31]. In Table II, the gradual reduction in conductivity with an increasing PVP percentage in the blend is noticeable. A similar gradual declining trend of water uptake and IEC values with increasing PVP content in the membrane may explain this behavior. In addition, the porosity of composite increases with the increasing content of PVP, and the presence of a porous PTFE structure in a composite membrane decreases its proton conductivity [32].

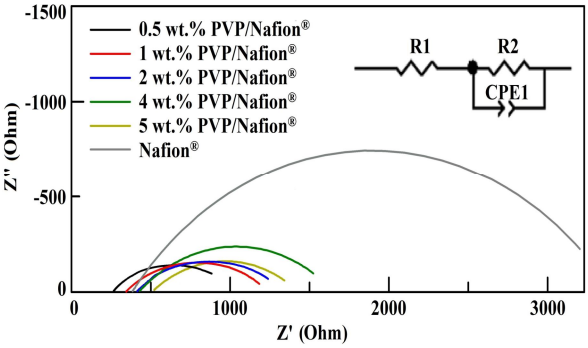



**Fig. 8. Nyquist plot of Nafion® and PVP/Nafion® blend membranes along with their equivalent circuit.**

## I. Cell Performance

Table III shows the measured voltages and peak power densities of different membranes. Other PVP/Nafion® membranes, which are not shown here, exhibited very low performance compared with the cast Nafion® membrane under the same conditions. The polarization curve in Fig. 9 clearly demonstrates the superior performance of the PVP/Nafion® membranes as compared with the cast Nafion® membrane. Table III indicates that compared to pure Nafion®, 0.5 wt. % PVP/Nafion® membranes achieved a 26% improvement in fuel cell performance due to proper hydrophilic-hydrophobic domain ratio in its structure.

**Table III. Fuel cell performance at 0.875 A $cm^{-2}$ and peak power densities of cast Nafion® and PVP/Nafion® blend membranes under 100 % RH.**

| Membranes | Open circuit voltage (mV) | Peak power density (mW $cm^{-2}$) |
|---|---|---|
| Cast Nafion® | 927 | 335.87 |
| 0.5 wt. % PVP/Nafion® | 925 | 423.09 |

## J. Mechanism of Proton Conduction

As our proton conductivity experiment was carried out in 100% RH, it is possible that the proton transfer is dominated by the Grotthuss mechanism [33]. In this case, as shown in the Scheme 1, presumable hydrogen-bonding networks related to proton conduction are extended among the polar carbonyl groups of the pyrrolidone ring, water molecules, and sulphonate groups present in the blend membrane.

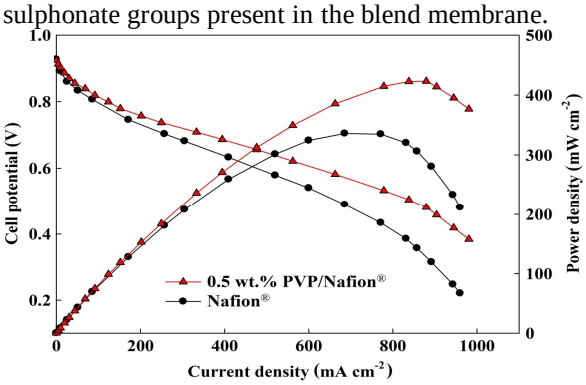
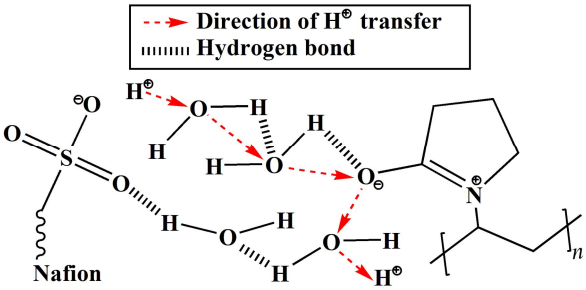



**Fig. 9. Polarization and power density curves of cast Nafion® and PVP/Nafion® at 100 °C, and 100% RH.**




**Scheme 1. Schematic presentation of proton transfer mechanism in the PVP/Nafion® blend membrane at high humidity.**

## CONCLUSION

The key motivation to this study is to investigate the effects of PVP in modifying the characteristics of PVP/Nafion® blend membranes for fuel cell applications. Incorporation of PVP successfully tuned the Nafion® matrix and served three functions: (1) the interfacial hydrogen bonds between PVP and Nafion® reinforce the membranes to yield higher oxidative and thermal stability, (2) the increasing hydrophobicity of the blend membrane with higher PVP content affected the water uptake capacity inversely, but gave the membrane higher mechanical strength and

dimensional stability, and (3) certain blends (0.5 and 1 wt. % PVP/Nafion®) exhibited higher IEC values and proton conductivity compared to unmodified cast Nafion®. Therefore, these durable polymer electrolyte membranes with appropriate PVP content show potential for use in low-temperature PEMFCs.

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