Data Article

Data on a temperature-dependent thermic and electrical properties of a novel blend polymeric system based on poly(vinyl alcohol), chitosan and phosphoric acid

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\textbf{A B S T R A C T}

In this work, data on a temperature-dependent thermic and electrical properties in a novel blend polymer electrolyte membranes based on poly(vinyl alcohol) (PVA) and chitosan (CS) doped with H\textsubscript{3}PO\textsubscript{4} at different concentrations were prepared by solution casting method. Their phase behavior and ionic conductivity were studied by DSC, TGA and IS. These membranes exhibit good proton conductivity of the order of \(10^{-2} \text{ Scm}^{-1}\) at \(200 \text{ C}\) and the understanding of the H\textsubscript{3}PO\textsubscript{4} at different concentrations effect in the polymer electrolyte membranes is crucial for possible applications in fuel cells. The data have not been reported nor discussed in the research paper to be submitting.

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1. Data

The DC conductivity, $\sigma_0$, can be determined from the resistance of the volume of the sample obtained from the impedance graphs, Nyquist plots ($-\text{Im}Z$ vs $\text{Re}Z$), by extrapolating the circular part of the spectrum to the real axis $Z''$, using $\sigma_0 = \frac{d}{AR}$, where $R$ is the intercept with the $Z''$ axis, $d$ is the thickness of the membrane and $A$ the contact area of the sample with the electrodes. It is also possible to determine $\sigma_0$ from the adjustment of the experimental data to the Jonscher model [4],

$$\sigma'(\omega) = \sigma_0 + A\omega^n$$

where $\sigma_0$ is the DC conductivity (independent of the frequency), $A$ is a pre-exponential factor related to the frequency of regime change, $\omega_p$, as $A = \frac{\sigma_0}{(\omega_p)^n}$ and $n$ is a value between 0 and 1, where the values of $n$ close to zero indicate that the correlation between the ions is greater than for the values close to 1, which would be the case where the ionic jumps are random (Debye model). From the impedance data, $Z'(\omega)$ and $Z''(\omega)$, the values of the real conductivity, $\sigma'$ were obtained using the relation,

$$\sigma'(\omega) = \frac{Z''}{Z'^2 + Z''^2}$$

The experimental data (TGA, DSC and IS) are reported in Tables 1–6.

- The Table 1 shows the weight percent loss in three different temperature regions for all the membranes.
Table 1
Weight percent loss in three different temperature regions.

| Solution                | (30–170) °C | (170–450) °C | (310–450) °C |
|-------------------------|-------------|---------------|---------------|
| PVA                     | 4.89%       | 68.22%        | 8.82%         |
| CS                      | 10.88%      | 33.69%        | 15.94%        |
| (PVA:CS) (80:20)        | 8.34%       | 52.13%        | 21.81%        |
| (PVA:CS) + 10% H₃PO₄  | 21.69%      | 14.74%        | 10.19%        |
| (PVA:CS) + 20% H₃PO₄  | 9.78%       | 32.03%        | 10.01%        |
| (PVA:CS) + 30% H₃PO₄  | 10.58%      | 27.74%        | 9.31%         |
| (PVA:CS) + 40% H₃PO₄  | 13.31%      | 23.97%        | 11.07%        |

Table 2
Characteristic values of the membranes using the DSC.

| Solution                | T_g (°C) | T_m (°C) | ΔH (J/g) | T_d (°C) | ΔH (J/g) |
|-------------------------|----------|----------|----------|----------|----------|
| PVA                     | 67       | 203      | 62.43    | 273      | 791.30   |
| CS                      | 67       | 203      | 62.43    | 273      | 791.30   |
| (PVA:CS) (80:20)        | 53       | 194      | 38.66    | 288      | 532.80   |
| (PVA:CS) + 10% H₃PO₄  | 56       | 190      | 79.24    | 217      | 300.00   |
| (PVA:CS) + 20% H₃PO₄  | 41       | 156      | 25.11    | 199      | 113.00   |
| (PVA:CS) + 30% H₃PO₄  | 37       | 153      | 13.09    | 185      | 83.63    |
| (PVA:CS) + 40% H₃PO₄  | 20       | 152      | 57.14    | 202      | 12.74    |

Table 3
Resistance values of the membranes extrapolated from the Nyquist diagrams.

| Temperature (°C) | R (Ω) 80% | R (Ω) 100% | R (Ω) 200% | R (Ω) 300% | R (Ω) 400% |
|-----------------|-----------|------------|------------|------------|------------|
| 30              | 303.15    | 1.11 x 10⁶ | 5.3 x 10⁵  | 5.08 x 10⁴ | 1.47 x 10³ |
| 40              | 313.15    | 3.40 x 10⁵ | 2.78 x 10⁴ | 3.52 x 10³ | 7.93 x 10² |
| 50              | 323.15    | 6.76 x 10⁴ | 1.62 x 10³ | 2.55 x 10² | 3.81 x 10¹ |
| 60              | 333.15    | 7.92 x 10³ | 8.92 x 10² | 1.99 x 10¹ | 4.54 x 10⁰ |
| 70              | 343.15    | 1.20 x 10² | 5.79 x 10¹ | 1.66 x 10⁰ | 3.28 x 10⁰ |
| 80              | 353.15    | 1.83 x 10¹ | 1.62 x 10⁰ | 2.55 x 10⁹ | 3.81 x 10⁸ |
| 90              | 363.15    | 8.42 x 10⁹ | 4.00 x 10⁸ | 1.37 x 10⁷ | 2.61 x 10⁶ |
| 100             | 373.15    | 5.01 x 10⁸ | 2.66 x 10⁷ | 1.08 x 10⁶ | 2.01 x 10⁵ |
| 110             | 383.15    | 3.37 x 10⁷ | 2.03 x 10⁶ | 9.73 x 10⁵ | 1.56 x 10⁵ |
| 120             | 393.15    | 2.49 x 10⁶ | 1.55 x 10⁵ | 7.84 x 10⁴ | 1.17 x 10⁴ |
| 130             | 403.15    | 1.84 x 10⁵ | 1.25 x 10⁴ | 7.54 x 10⁴ | 9.54 x 10³ |
| 140             | 413.15    | 1.55 x 10⁴ | 9.61 x 10³ | 6.17 x 10³ | 6.26 x 10² |
| 150             | 423.15    | 1.30 x 10⁴ | 7.21 x 10² | 5.83 x 10² | 5.08 x 10¹ |
| 160             | 433.15    | 1.12 x 10⁴ | 5.36 x 10¹ | 4.51 x 10¹ | 2.39 x 10⁰ |
| 170             | 443.15    | 9.31 x 10³ | 3.90 x 10³ | 4.51 x 10² | 4.09 x 10¹ |
| 180             | 453.15    | 9.14 x 10³ | 4.30 x 10³ | 4.02 x 10² | 3.73 x 10¹ |
| 190             | 463.15    | 7.41 x 10³ | 3.55 x 10³ | 3.47 x 10² | 3.41 x 10¹ |

- Table 2 shows the characteristic values of the membranes using DSC.
- Tables 3 and 4 show the resistance values of the membranes extrapolated from the Nyquist diagrams in relation to the temperature and concentration of phosphoric acid.
- Table 5 shows the membrane parameters and activation energies for two temperature regions using the Arrhenius model.
- Table 6 shows the parameters obtained from Jonscher model adjustment to the membranes with (PVA:CS) + 10% H₃PO₄.
Table 4
Conductivity values of the membranes obtained from Table 3 and \( d_0 = d/AR \).

| \( T(\degree C) \) | \( T(K) \) | \( \sigma(\Omega cm)^{-1} \) \( 30 \times 10^{-20} \) | \( \sigma(\Omega cm)^{-1} \) \( 10\% \) | \( \sigma(\Omega cm)^{-1} \) \( 30\% \) | \( \sigma(\Omega cm)^{-1} \) \( 40\% \) |
|-------------------|-----------|---------------------|---------------------|---------------------|---------------------|
| 30                | 303.15    | 1.12 \times 10^{-8} | 4.48 \times 10^{-6} | 1.27 \times 10^{-5} | 2.01 \times 10^{-4} |
| 40                | 313.15    | 2.20 \times 10^{-8} | 6.69 \times 10^{-6} | 1.53 \times 10^{-5} | 2.32 \times 10^{-4} |
| 50                | 323.15    | 4.21 \times 10^{-8} | 9.65 \times 10^{-6} | 2.84 \times 10^{-5} | 3.22 \times 10^{-4} |
| 60                | 333.15    | 7.24 \times 10^{-8} | 1.33 \times 10^{-5} | 4.75 \times 10^{-4} |
| 70                | 343.15    | 1.31 \times 10^{-7} | 1.71 \times 10^{-5} | 4.96 \times 10^{-4} | 1.14 \times 10^{-3} |
| 80                | 353.15    | 2.02 \times 10^{-7} | 2.05 \times 10^{-5} | 6.85 \times 10^{-4} | 8.95 \times 10^{-4} |
| 90                | 363.15    | 2.93 \times 10^{-7} | 2.48 \times 10^{-5} | 8.63 \times 10^{-4} | 1.15 \times 10^{-3} |
| 100               | 373.15    | 4.41 \times 10^{-7} | 3.15 \times 10^{-5} | 1.12 \times 10^{-4} | 1.37 \times 10^{-3} |
| 110               | 383.15    | 5.78 \times 10^{-7} | 3.50 \times 10^{-5} | 1.44 \times 10^{-4} | 1.62 \times 10^{-3} |
| 120               | 393.15    | 7.53 \times 10^{-7} | 4.34 \times 10^{-5} | 1.92 \times 10^{-4} | 2.04 \times 10^{-3} |
| 130               | 403.15    | 9.35 \times 10^{-7} | 4.51 \times 10^{-5} | 2.36 \times 10^{-4} | 2.49 \times 10^{-3} |
| 140               | 413.15    | 1.15 \times 10^{-6} | 5.08 \times 10^{-5} | 2.93 \times 10^{-4} | 2.95 \times 10^{-3} |
| 150               | 423.15    | 1.22 \times 10^{-6} | 5.51 \times 10^{-5} | 3.59 \times 10^{-4} | 3.44 \times 10^{-3} |
| 160               | 433.15    | 1.62 \times 10^{-6} | 5.84 \times 10^{-5} | 4.43 \times 10^{-4} | 4.29 \times 10^{-3} |
| 170               | 443.15    | 1.64 \times 10^{-6} | 6.35 \times 10^{-5} | 4.99 \times 10^{-4} | 5.14 \times 10^{-3} |
| 180               | 453.15    | 3.00 \times 10^{-6} | 7.54 \times 10^{-5} | 5.49 \times 10^{-4} | 6.48 \times 10^{-3} |
| 190               | 463.15    | 2.72 \times 10^{-6} | 8.47 \times 10^{-5} | 6.03 \times 10^{-4} | 7.60 \times 10^{-3} |
| 200               | 473.15    | 3.30 \times 10^{-6} | 9.79 \times 10^{-5} | 6.60 \times 10^{-4} | 9.45 \times 10^{-3} |

Table 5
Membrane parameters and activation energies for two temperature regions using the Arrhenius model.

| Solution | Area (cm²) | Thickness (cm) | \( E_a (eV) \) (30--90°C) | \( E_a (eV) \) (100--200°C) |
|----------|------------|----------------|---------------------------|---------------------------|
| PVA      |            |                |                           |                           |
| CS       |            |                |                           |                           |
| (PVA:CS) (80:20) | 1.66   | 0.03           | 0.63                      | 0.27                      |
| (PVA:CS)+ 10% H₃PO₄ | 1.71   | 0.02           | 0.24                      | 0.14                      |
| (PVA:CS)+ 20% H₃PO₄ | 1.62   | 0.06           | 0.13                      | 0.07                      |
| (PVA:CS)+ 30% H₃PO₄ | 1.78   | 0.04           | 0.14                      | 0.12                      |
| (PVA:CS)+ 40% H₃PO₄ | 1.62   | 0.02           | 0.13                      | 0.12                      |

Table 6
Parameters obtained from Jonscher model adjustment to the membranes with (PVA:CS) + 10% H₃PO₄.

| \( T(\degree C) \) | \( n \)   | A           | \( \alpha_0 [\text{Scm}^{-1}] \) |
|-------------------|-----------|-------------|--------------------------|
| 30                | 0.5655    | 2.62E-11    | 1.62E-08                  |
| 40                | 0.5316    | 5.71E-11    | 3.18E-08                  |
| 50                | 0.5616    | 5.24E-11    | 6.20E-08                  |
| 60                | 0.5406    | 8.43E-11    | 1.05E-07                  |
| 70                | 0.6119    | 3.88E-11    | 1.91E-07                  |
| 80                | 0.6602    | 2.12E-11    | 2.96E-07                  |
| 90                | 0.6469    | 2.95E-11    | 4.18E-07                  |
| 100               | 0.6293    | 4.25E-11    | 6.19E-07                  |
| 110               | 0.6555    | 3.05E-11    | 8.14E-07                  |
| 120               | 0.7031    | 1.58E-11    | 1.06E-06                  |
| 130               | 0.7519    | 5.46E-12    | 1.42E-06                  |
| 140               | 0.4840    | 3.51E-10    | 1.68E-06                  |
| 150               |           |             |                           |
| 160               | 1.1209    | 2.24E-14    | 2.38E-06                  |
| 170               |           |             |                           |
| 180               | 0.9956    | 2.21E-13    | 3.86E-06                  |
| 190               | 0.3864    | 2.44E-09    | 3.99E-06                  |
| 200               | 0.1956    | 6.49E-08    | 4.46E-06                  |
2. Experimental design, materials, and methods

Hydrolyzed poly(vinyl alcohol) (PVA, Mw: 31,000–50,000 g/mol), Chitosan (CS) and phosphoric acid (H₃PO₄, Mw: 98g/mol) were obtained from Sigma Aldrich, and used as received without any further purification. A solution of acetic acid at 2% by volume of distilled and deionized water was prepared. Then, a solution of PVA and CS was established at the weight ratio of 80:20. Thus, PVA:CS (80:20) and phosphoric acid at concentrations from 10% to 40% was defined in the mixture of acetic acid and distilled and deionized water.

TGA (Q500, TA Instruments) was used to investigate sample weight changes as a function of time and temperature under a N₂ atmosphere at a flow rate of 50 ml/min. DSC (Q100, TA Instruments) was used to measure the enthalpies, and temperatures of the various thermal events that might occur in the membranes when they are thermally treated. The electrical characterization of the membranes was done by impedance spectroscopy (IS) using a Wayner Kerr impedance analyzer at an excitation signal of 100 mV and 20 Hz–5 MHz frequency range. The dc conductivity, \( \sigma \), was calculated from the Nyquist plots (\(-\text{Im}Z \) vs \( \text{Re}Z \)). The bulk resistance, \( R_{\text{bulk}} \), was obtained from the intercept of the circular arc of the spectra with the real axis, and using the formula \( \sigma = d/AR \), where \( d \) is the thickness and \( A \) the contact area of the sample.

2.1. Impedance spectroscopy results

Fig. 1 shows the Nyquist diagrams for (PVA:CS) + 30% H₃PO₄ to isotherms between 30 °C and 200 °C, where a semicircle is observed at high frequencies, and which is associated with the electrical response in the volume of the sample. At low frequency regime there is a linear tendency associated with the effects of the interface with the electrodes. The resistance and conductivity values of all membranes is show in Tables 3 and 4.

Fig. 2a shows the logarithm of the real part of the AC conductivities obtained from ec (2) as a function of the logarithm of the frequency (20 Hz–5 MHz) at several isotherms for (PVA:CS) + 10% H₃PO₄. In solid line the fit for typical curves obtained from ec (1) (Fig. 2b) and the parameters are show in Table 6. The DC conductivity (\( \sigma_0 \)) values are in agreement with those calculated from Nyquist plots (see Table 4). On the other hand, the n-exponent parameter, except for 160 °C, takes values between 0 and 1; values greater than 1 could be associated with high values of energy storage in the collective movements of the short-range ions and which cannot be explained by Jonscher model.
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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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