

Research Article

Electrical and Magnetic Properties of Polymer Electrolyte (PVA:LiOH) Containing *In Situ* Dispersed Fe₃O₄ Nanoparticles

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Nanocomposite magnetic polymer electrolytes based on poly(vinyl alcohol) (PVA) complexed with lithium hydroxide (LiOH) and containing magnetite (Fe₃O₄) nanoparticles were prepared using an *in situ* method, in which the nanoparticles were grown in the host polymer electrolyte. Ion carriers were formed during nanoparticle growth from the previously added LiOH precursor. If a high concentration of LiOH was added, the remaining unreacted LiOH was distributed in the form of an amorphous complex around the Fe₃O₄ nanoparticles, thus preventing agglomeration of the nanoparticles by the host polymer. By addition of Fe₃O₄ the composite polymer electrolytes improved the ionic conductivity, resulting in a maximum conductivity of $1.81 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$. The magnetic properties of the polymer electrolyte were investigated through magnetic susceptibility studies, and the material was predominantly ferromagnetic.

1. Introduction

The normal role of inorganic particle fillers in polymer electrolytes is to influence the recrystallization kinetics of the polymer chain and promote localized amorphous regions, thus enhancing cation transport. Examples of inorganic particles used in polymer composites include SiO₂, Al₂O₃, TiO₂, CdO, and ZnO [1–9]. Inorganic particles are also used to enhance the mechanical properties of polymer electrolytes [10]. Most authors agree that the role of nanoparticle fillers is very important and must be present in the host polymer for proper function.

Magnetic nanoparticles such as magnetite (Fe₃O₄) have a unique response to magnetic fields and a saturation magnetization much lower than that of the corresponding bulk materials. The saturation magnetization decreases with particle size [11, 12]. One interesting point is that dispersion of Fe₃O₄ nanoparticles in polymer electrolytes may also assist in ionic transport. We sought to produce a magnetic polymer electrolyte containing Fe₃O₄ nanoparticles as magnetic centers. This class of materials has considerable potential for producing devices that simultaneously interact with both electrical and magnetic fields, such as magnetic electrochemical cells and sensors.

The Fe₃O₄ nanoparticles were produced using a coprecipitation method. Two typical synthetic approaches are coprecipitation of partly oxidized Fe²⁺ to Fe³⁺ in oxidizing solutions and direct coprecipitation of Fe²⁺ and Fe³⁺ in alkaline media [13, 14]. This approach ensures facile dispersion of the nanoparticles in the host polymer without requiring intensive mixing. Since the LiOH solution contained lithium ions, the insertion of lithium ion carriers in the composite occurred during growth of the Fe₃O₄ nanoparticles. Since the Fe₃O₄ displays magnetic behavior, we obtain a new class of polymer electrolytes known as nanocomposite magnetic polymer electrolytes.

2. Experimental

2.1. Materials. The poly(vinyl) alcohol (PVA, MW 22,000 g/mol) host polymer was obtained from Bratachem, Indonesia. Lithium hydroxide (LiOH) was obtained from Kanto Chemical, Japan. The magnetite (Fe₃O₄) nanoparticles were prepared from precursor solutions containing iron nitrate (Fe(NO₃)₃) as a source of Fe³⁺ ion and iron sulfate (FeSO₄) as a source of Fe²⁺ ions, which was obtained from Merck, Germany.

2.2. Preparation of the Charge Membranes. PVA.LiOH mixtures were prepared containing 0–10 wt%. The PVA and LiOH were dissolved in separate solutions. The solutions were mixed at 50°C for 2 h and evaporated under ambient condition for 5 days to obtain a thin sheet of polymer electrolyte. The polymer composition exhibiting the highest electrical conductivity was used to prepare the magnetic material containing dispersed Fe₃O₄ nanoparticles. The nanoparticles were prepared using an *in situ* coprecipitation method in the host PVA.LiOH. Between volume fraction 0–0.35 v% of Fe₃O₄ nanoparticles were dispersed in the host polymer electrolyte.

2.3. Characterization. Structural studies were carried out on the PVA.LiOH and (PVA.LiOH): Fe₃O₄ membranes using X-ray diffraction (XRD) analysis (Philips Analytical-Diffractometer PW1710, using Cu-K_α radiation). The sample was scanned in the 2θ ranging from 10° to 80° for 2 s in the step mode. Electrical conductivity measurements were obtained using electrochemical impedance spectroscopy (EIS) at frequencies from 20 Hz to 2 MHz (Agilent E4980A Precision LCR meter). The surface morphology of the polymer electrolyte membranes was examined using a scanning electron microscope (SEM JEOL JSM-6360LA). The magnetic properties were measured using a Bartington MS2B susceptibility meter.

3. Results and Discussion

Figure 1 is the complex membrane impedance spectrum (Nyquist Plot) of pure PVA and several PVA.LiOH mixtures. The squares represent experimental data and the curve is an approximation from the equivalent circuit used to determine the bulk resistance (R_b). The ionic conductivity of polymer electrolytes was calculated using the relationship:

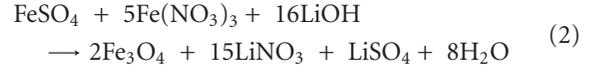
$$\sigma = \frac{1}{R_b} \frac{\ell}{A}, \quad (1)$$

where ℓ is the thickness and A is the cross-section of the membrane.

The room-temperature ionic conductivity of the membranes as a function of LiOH concentration is plotted in Figure 2. The ionic conductivity increased with increasing LiOH concentration in the host polymer to a maximum at 9 wt%.

The increase in ionic conductivity with LiOH concentration is due to an increase in the number of mobile charge carriers and a decrease in the crystallinity of the host polymer similar to that previously reported for other polymer electrolyte systems [15–17]. The decrease in ionic conductivity at concentrations greater than 9 wt% may be explained by the aggregation of ions. An excess of ions in the host polymer can result in ionic interactions with the polymer chains, leading to restriction of the segmental relaxation of the polymer chain (Figure 3).

In order to further improve the ionic conductivity, inorganic fillers were added to the host polymer. Fe₃O₄ nanoparticles were dispersed *in situ* in the host polymer electrolyte containing 9 wt% LiOH using a coprecipitation technique:



The reaction produced black-colored particles indicating the formation of Fe₃O₄ nanoparticles in the polymer electrolyte matrix (Figure 4). Synthesis of Fe₃O₄ nanoparticles in a polymer electrolyte matrix results in smaller particles with excellent dispersion, while synthesis of Fe₃O₄ nanoparticles outside the polymer matrix results in formation of particle aggregates. Sensitivity to an external magnetic field was used as simple proof of the formation of magnetic nanoparticles, and the results were supported by XRD and magnetic measurements.

Dispersion of Fe₃O₄ nanoparticles in the host polymer enhanced the ionic conductivity. The nanoparticles assist ionic transport by increasing segmental mobility and interaction between Li⁺ ions and the polymer chains. In addition, the presence of Fe₃O₄ nanoparticles in the polymer electrolyte alters the electrical potential distribution around the particle surface, which induces a space charge layer at the interface between the particles and the electrolyte. The typical room temperature complex impedance spectrum of the polymer electrolyte PVA.LiOH containing dispersed Fe₃O₄ nanoparticles exhibiting maximum conductivity is shown Figure 5. The conductivity of the prepared samples at room temperature is found to be $\sim 10^{-3} \text{ S} \cdot \text{cm}^{-1}$.

In order to explain the effect of Fe₃O₄ nanoparticles on ionic conductivity, we used the effective medium approximation (EMA) to calculate the effective ionic conductivity. The model was developed by considering that a polymer electrolyte is composed of amorphous and crystalline phases, as illustrated in Figure 6.

Carrier accumulation near the particle surfaces locally enhances the ionic conductivity due to the increased carrier concentration, leading to a high-conductivity region. In areas far from any nanoparticles, the carrier concentration is approximately equal to that in the pure electrolyte (when insulator particles are absent). These areas are known as medium-conductivity regions. When two particles make contact, the electrolyte medium between the particles is removed and ion transport does not occur. The conductivity of this region is reduced to nearly zero (approximately equal to that of insulator particles), and these are known as low-conductivity regions. The effective ionic conductivity satisfies the equation:

$$\left(\frac{\nu}{f}\right)^2 \frac{\sigma_l - \sigma_e}{\sigma_l + (z/2 - 1)\sigma_e} + \left(\frac{1 - \nu}{f}\right)^2 \frac{\sigma_m - \sigma_e}{\sigma_m + (z/2 - 1)\sigma_e} + 2\left(\frac{\nu}{f}\right)\left(\frac{1 - \nu}{f}\right) \frac{\sigma_h - \sigma_e}{\sigma_h + (z/2 - 1)\sigma_e} = 0 \quad (3)$$

in which ν , f , z , σ_l , σ_m , and σ_h are the volume fraction of the particle, the packing fraction, the coordination number, and the conductivity of the low, medium, and high conductivity regions.

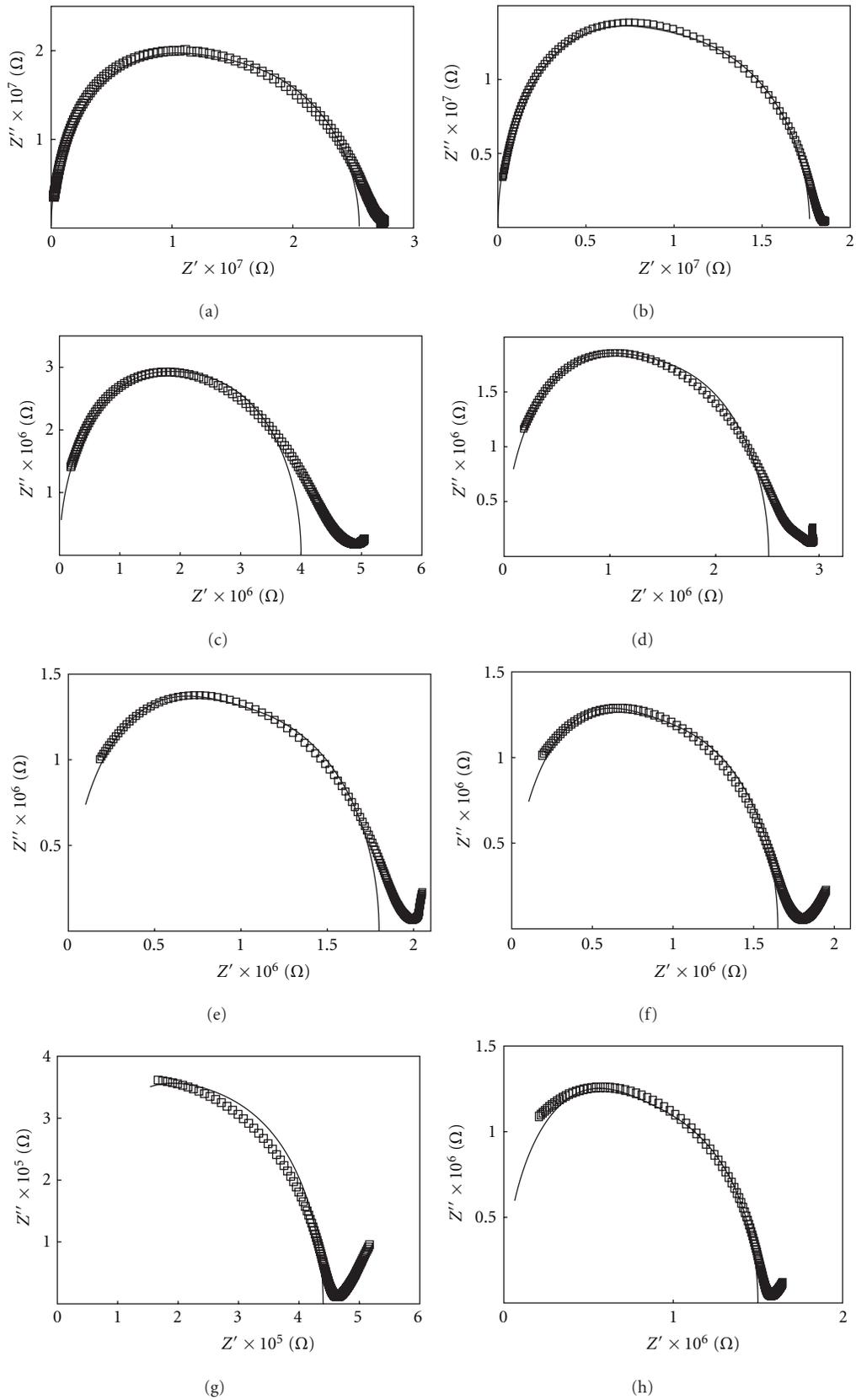


FIGURE 1: Impedance spectrum and fitting curve for PVA.LiOH complex membrane polymer electrolyte at room temperature (a) 0 wt% LiOH, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 7 wt%, (f) 8 wt%, (g) 9 wt%, and (h) 10 wt%.

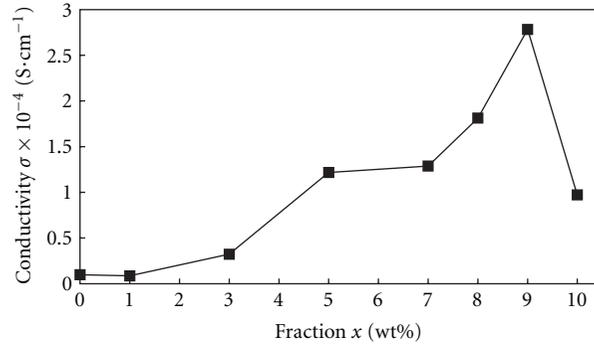


FIGURE 2: Ionic conductivity of PVA.LiOH polymer electrolyte as function of LiOH weight fraction. Measurements were performed at room temperature.

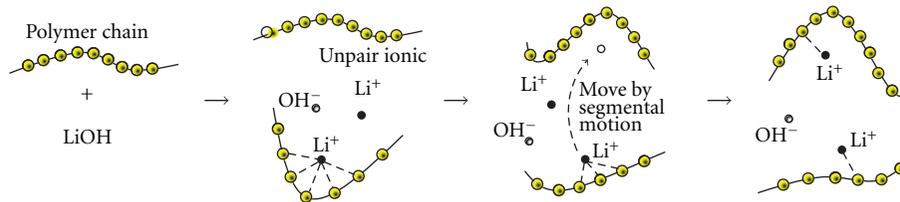


FIGURE 3: Schematic of ionic transport by relaxation segmental motion of polymer chains.

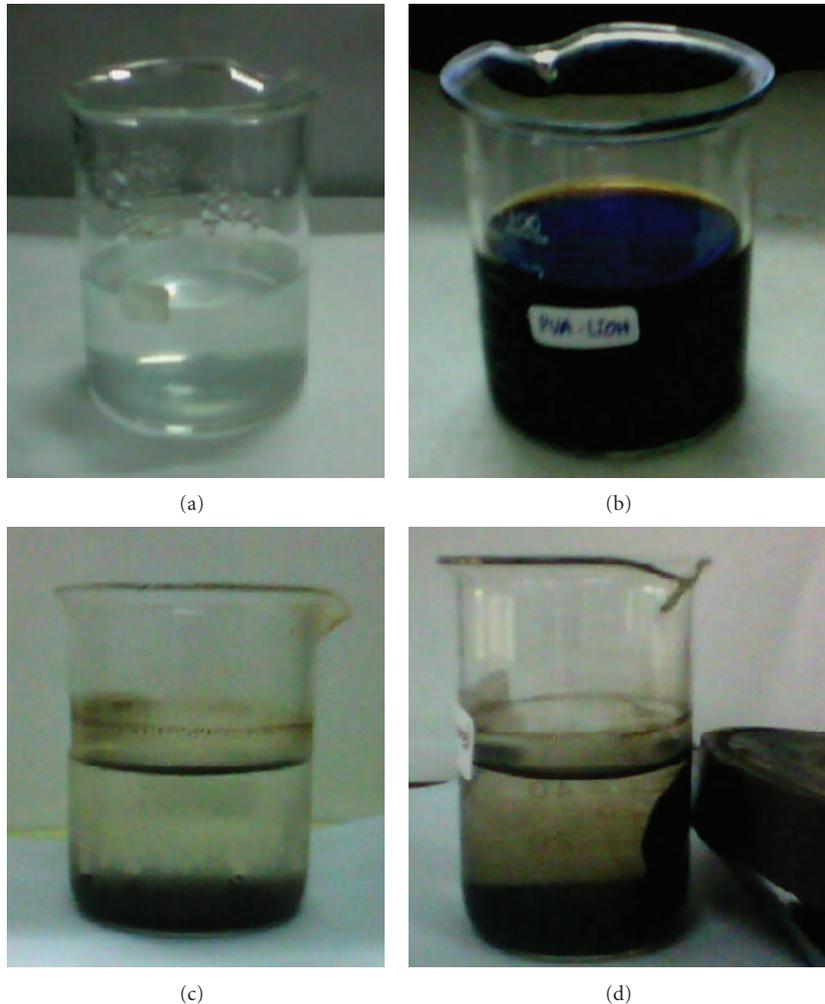


FIGURE 4: Solution of (a) PVA.LiOH polymer electrolyte, (b) polymer electrolyte containing dispersed Fe_3O_4 particles, (c) Fe_3O_4 particles in absence of polymer matrix, and (d) Response of Fe_3O_4 particles to external magnetic field.

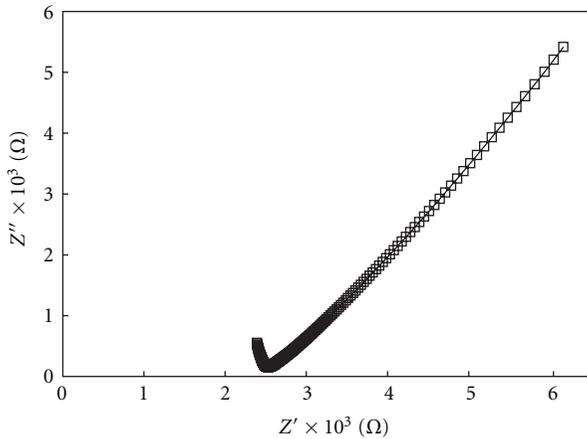


FIGURE 5: Impedance spectrum of PVA.LiOH containing dispersed Fe_3O_4 .

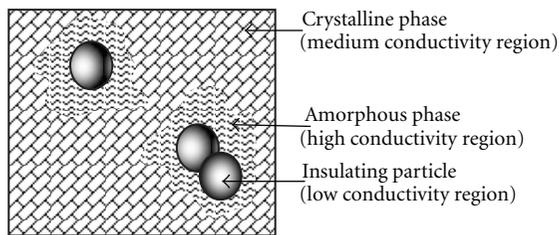


FIGURE 6: Illustration of particle arrangement in composite polymer electrolyte. Amorphous phases having high conductivity are created around the particles.

Figure 7 is a graph of the ionic conductivity of the composite polymer electrolyte as a function of Fe_3O_4 nanoparticle volume fraction. The solid line is a plot of (3) assuming simple cubic packing of filler particles in which $z = 6$ and $f = \pi/6$. The other parameters in the equation were $\sigma_l = 10^{-6} \text{ S} \cdot \text{cm}^{-1}$, $\sigma_m = 2.2 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, and $\sigma_h = 40\sigma_m$. There was consistent agreement between the predicted and experimental conductivity. The maximum conductivity occurred with an Fe_3O_4 volume fraction of approximately ≈ 0.22 .

The ionic conductivity results are supported by the X-ray diffraction patterns in PVA complexed with various amounts of LiOH and Fe_3O_4 (Figure 8). Pure PVA in the form of a powder or membrane exhibits a peak at 20° characteristic of an orthorhombic lattice, indicating the presence of a semicrystalline phase [15–17]. The intensity of the XRD peaks decreased with increasing LiOH concentration, indicating a reduction in crystallinity in the host polymer. Similar behavior was observed in membranes containing Fe_3O_4 nanoparticles.

Figure 9 contains SEM images depicting the morphology of PVA, PVA.LiOH membranes with and without Fe_3O_4 nanoparticles. The morphology of the PVA membrane was uniform, and the surface roughness increased with increasing LiOH concentration.

However, the morphology of the membrane containing Fe_3O_4 nanoparticles was fragmented. The fragments may

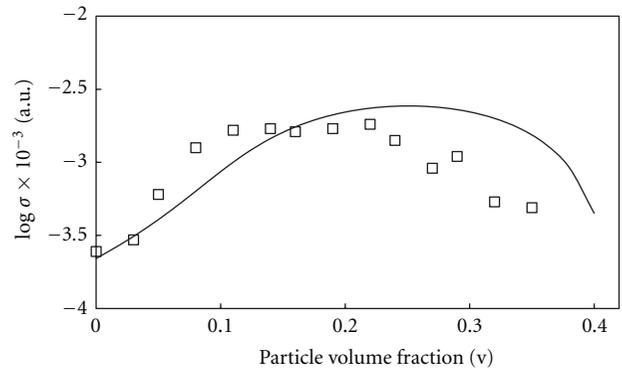


FIGURE 7: Effect of particle volume fraction on electrical conductivity of magnetic composites. Symbols represent experimental data and curve was obtained using (3) with the following parameters: $z = 6$ and $f = \pi/6$, $\sigma_l = 10^{-6} \text{ S} \cdot \text{cm}^{-1}$, $\sigma_m = 2.2 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and $\sigma_h = 40\sigma_m$.

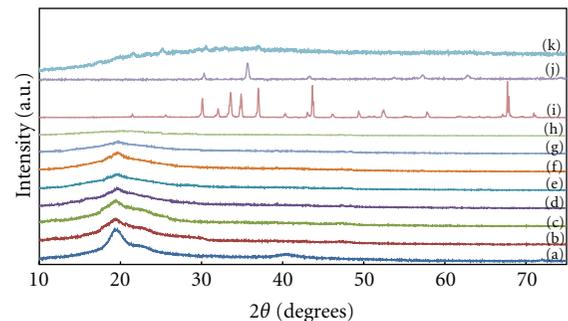


FIGURE 8: XRD patterns for (a) PVA powder, (b) PVA membrane, (c) 1 wt% PVA.LiOH, (d) 3 wt% PVA.LiOH, (e) 5 wt% PVA.LiOH, (f) 7 wt% PVA.LiOH, (g) 9 wt% PVA.LiOH, (h) 10 wt% PVA.LiOH, (i) LiOH powder, (j) Fe_3O_4 powder, and (k) composite membrane containing 9 wt% dispersed Fe_3O_4 nanoparticles.

have been formed as the Fe_3O_4 nanoparticles filled the empty spaces between polymer chains. This is supported by the results of EDS analysis indicating that the host polymer composition (C (71.02%), O (11.53%), and FeO (12.06%)) was retained in the nanoparticle-containing membranes. Fe_3O_4 particles synthesized in the absence of a polymer matrix possess an irregular morphology.

Magnetic susceptibility (χ) is a simple technique for observing the presence of magnetic particles. It is sensitive enough to detect very low concentrations of magnetic materials. PVA.LiOH membranes not containing Fe_3O_4 nanoparticles were weakly diamagnetic, with susceptibilities of $\chi = -63.14 \times 10^{-8} \text{ m}^3 \cdot \text{kg}^{-1}$. The susceptibility increased with increasing Fe_3O_4 content, although the increase was slower at higher concentrations (Table 1).

The intensity of the magnetic susceptibility was a function of the Fe_3O_4 nanoparticle concentration. However, the relationship was nonlinear, possibly due to an inhomogeneous dispersion of Fe_3O_4 nanoparticles in the polymer electrolyte.

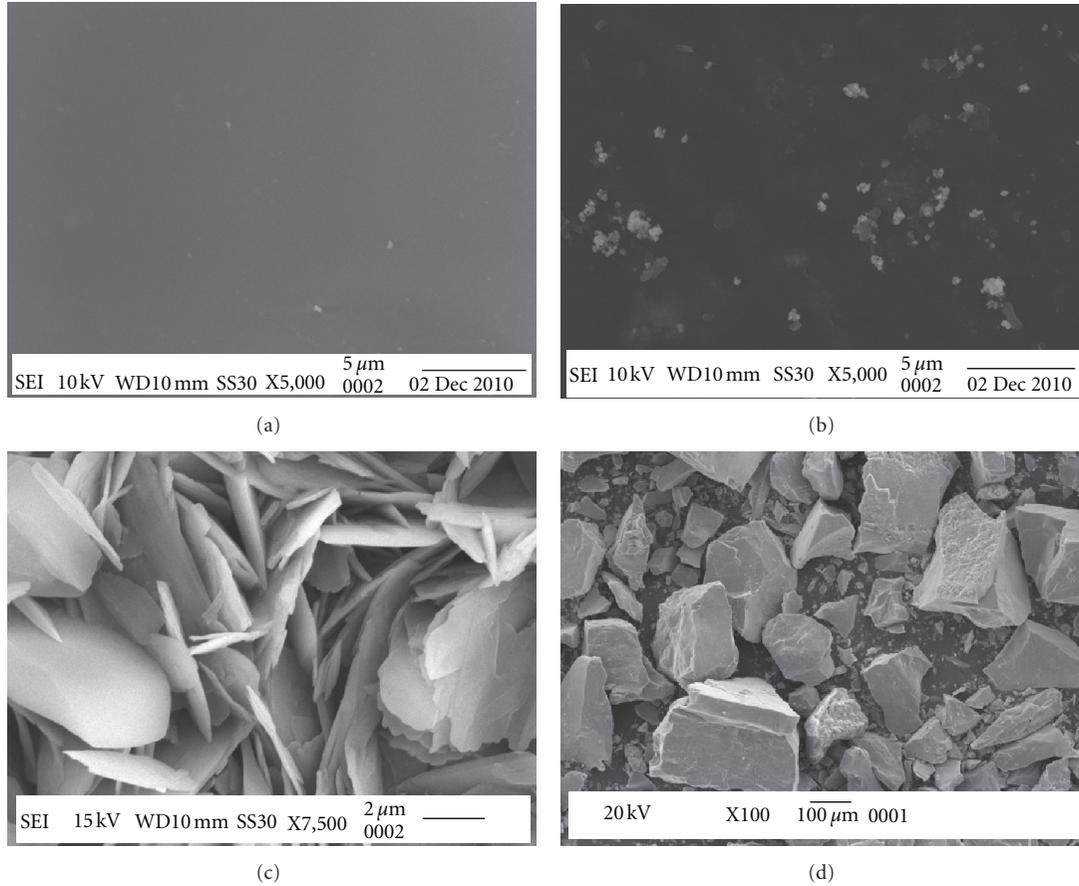


FIGURE 9: SEM images of (a) PVA membrane, (b) 9 wt% PVA.LiOH membrane, (c) 9 wt% PVA.LiOH containing Fe₃O₄ nanoparticles, and (d) Fe₃O₄ particles synthesized in absence of polymer matrix.

TABLE 1: Magnetic susceptibility of composite polymer electrolyte as a function of Fe₃O₄ nanoparticle content.

Volume fraction Fe ₃ O ₄	$\chi_m \times 10^{-8}$ (m ³ ·kg ⁻¹)
0.00	-63.14
0.03	36
0.05	112
0.08	67
0.11	468
0.14	737
0.16	227
0.19	1159
0.22	575
0.24	3300
0.27	642
0.29	1158
0.32	4134
0.35	1404

4. Conclusion

A new nanocomposite magnetic polymer electrolyte was synthesized by dispersing magnetite (Fe₃O₄) nanoparticles

in membrane composed of PVA.LiOH complex. The Fe₃O₄ nanoparticles assisted ionic transport through an increase in segment mobility and interaction between Li⁺ ions and the polymer chains. The results suggest that nanocomposite magnetic polymer electrolytes may be suitable for use in magnetic-electrochemical devices.

Acknowledgment

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