

Influence of nanoscale NiO on magnetic and electrochemical behavior of PVDF-based polymer nanocomposites

Aarti Sripathi Bhatt · Denthaje Krishna Bhat

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Abstract New poly(vinylidene fluoride) (PVDF)/NiO-based polymer nanocomposites were prepared by phase inversion method, using dimethyl formamide as solvent and deionized water as non-solvent. The structure and porous morphology of the membranes were studied by field emission scanning electron microscopy. The presence of NiO resulted in overall decrease in porosity and crystallinity of the nanocomposite membranes. Using electrochemical impedance spectroscopy, a maximum ionic conductivity of $1.08 \times 10^{-3} \text{ S cm}^{-1}$ was obtained for PVDF membrane with 1 wt% content of NiO. The good efficiency of conductivity observed in the membrane was explained on the basis of decrease in crystallinity and movement of charge carriers in NiO structure. The magnetization of nanocomposite membranes gradually increased with increase in NiO content.

Keywords PVDF · NiO · Porosity · Crystallinity · Conductivity · Magnetic measurements

Introduction

Inorganic polymer nanocomposites are promising materials for electrochemical devices and recently also as electrolyte membranes. For more than a decade, commercially available Nafion[®] has been widely used as proton conducting membrane due to its high conductivity. However, these membranes suffer from major drawbacks like low thermal stability and low methanol selectivity [1]. Hence

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A. S. Bhatt · D. K. Bhat (✉)
Department of Chemistry, National Institute of Technology Karnataka, Srinivasnagar,
Surathkal 575025, India
e-mail: denthajekb@gmail.com

research has been directed toward finding better alternatives. Many polymers, such as polyethylene oxide [2], polymethylmethacrylate [3], polyacrylonitrile [4], have been used as host polymer matrices for proton conducting membranes. Among these, PVDF has attracted the scientific community for its versatility. Compared to other fluoropolymers, PVDF has high purity, good strength, excellent chemical resistance, low melt process temperature, and low cost. Moreover, it can be easily dissolved in variety of solvents, and porous PVDF membranes can be easily produced by phase inversion techniques [5, 6]. PVDF as such is being used for lithium ion batteries [7–9]. However, incorporating PVDF matrix with inorganic nanofillers improves its overall conductivity. Cao et al. [10] showed that a high ionic conductivity can be obtained on using polyvinylpyrrolidone as additive in PVDF-HFP polymer membrane. Additives like salt [11] and polyethylene glycol (PEG) [12] were also used in PVDF and their various properties were studied. Consequently, it was observed that addition of inorganic materials along with these additives helped in improving the conductivity of PVDF. Croce et al. [1] reported the conductivity and current–voltage studies of PVDF-CTFE copolymer with dispersed ceramic fillers. The ionic conductivity of PVDF-HFP membranes treated with PEG increased on adding Al_2O_3 particles [13].

With the advent of nanomaterials, study on the effect of nano sized particles on PVDF matrix has gained interest. It has been suggested that transition metal oxides with poor conductivity are capable of storing high charge when they are highly dispersed and nanosized [14]. NiO has a wide band gap energy range from 3.6 to 4.0 eV and hence is considered as a p-type semiconductor [15]. Hence, one can assume that incorporation of NiO nanoparticles will definitely affect the conductivity of the host polymer. Qureshi et al. [16] have employed Li- and Ti-codoped NiO/PVDF films as electric and gas sensors.

In this study, PVDF/NiO nanocomposites were prepared by phase inversion technique and with different contents of NiO filler. The main focus of the study is to investigate the influence of NiO nanoparticles on conductivity and saturation magnetization of the membrane.

Experimental

PVDF ($M_w = 275,000$) was purchased from Sigma Aldrich and was used in pellet form. Dimethyl formamide (DMF) (Merck) of purity 99.5% was used as solvent. Distilled water was used throughout the experiment.

Preparation of PVDF/NiO nanocomposite films

NiO nanoparticles of average diameter 10 nm were synthesized by hydrothermal method [17]. Since the phase inversion process requires the polymer solution to remain in a uniform and stable state, measures were taken to obtain a homogeneous polymer solution. Desired amounts of PVDF polymer pellets were added to DMF and were subjected to vigorous shaking to insure thorough wetting of the polymer pellets. The dissolution was done by keeping the mixture in a sonicator maintained

at 60 °C. After the complete dissolution of the polymer pellets, required amount of NiO nanoparticles were added (wherever applicable) and sonication was continued till the nanoparticles dispersed homogeneously in the polymer solution. The solutions were then spin coated (Spin-Coater ACE-1020 Series) on a glass substrate at 500, 1000, and 2000 rpm for 60 s sequentially. The polymer films were precipitated out by immersing the glass substrate in deionized water. The films were retained in water for 24 h to insure complete removal of residual solvent. The films were labeled as PVDF, PNH1, PNH2, PNH3, and PNH4 for NiO content of 0, 0.3, 0.5, 0.7, and 1 wt. %, respectively.

Characterization techniques

A Zeiss SUPRA 40VP Gemini field emission scanning electron microscope (FESEM) was used for morphology and microstructure studies of the composite films. The magnetic properties were assessed with a Vibration Sample Magnetometer (ADE-DMS EV-7 VSM).

The porosity of polymer electrolyte membranes was measured by immersing the membrane into *n*-butanol for 2 h after which the membrane surface was dried with a filter paper. The membranes were weighed before and after the absorption of *n*-butanol. The porosity was calculated using the following equation:

$$P\% = \frac{M_b/\rho_b}{(M_p/\rho_p) + (M_b/\rho_b)} \quad (1)$$

where *P*% is porosity of the membranes, *M_p* is mass of membrane, *M_b* is mass of the absorbed *n*-butanol, ρ_p is density of the membrane, and ρ_b is density of *n*-butanol.

Differential Scanning Calorimetry (DSC) data was obtained in the temperature range of 35–250 °C (DSC-60, Shimadzu, Japan). The samples, sealed in an aluminum pan, were heated at a rate of 10 °C per min under nitrogen atmosphere. An empty pan was used as reference.

Electrochemical impedance measurements were carried out using an electrochemical work station, AUTOLAB 30. The films were placed in between two stainless steel electrodes. The whole set up was held tightly with a plastic clamp. 1 M KOH solution was used as electrolyte. Measurements were carried out using a small amplitude AC signal of 10 mV over a frequency range of 100 kHz to 0.01 Hz. To avoid ambiguity, the measurements were taken thrice for each trial.

Results and discussions

Morphology

The porous morphology of the polymer is necessary to understand the transport of ions, thereby providing information on its conductivity. The FESEM images of PVDF/NiO films are shown in Fig. 1. In the first step of synthesis, the solvent evaporation occurred during the spin coating process. The boiling point of DMF is

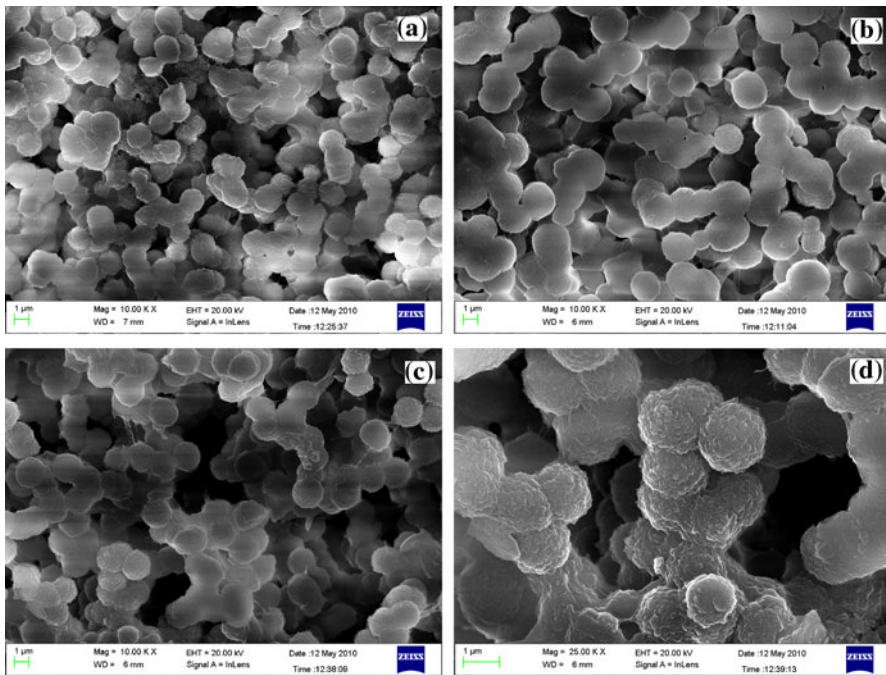


Fig. 1 FESEM images for **a** PNH1, **b** PNH2, **c** PNH3, and **d** PNH4

153 °C, so theoretically it can remain in the membranes. However, during the high speed spinning, the probability of DMF evaporation is also high. In the extraction stage, the residual DMF, if any, gets exchanged with water. Since DMF has high viscosity, the rate of exchange between DMF and water is slow. As a result, the contraction of the membrane would be homogeneous leading to better uniformity. Also, DMF is a low molecular weight compound. Hence, after extraction, a homogeneous nanoporous membrane is obtained. The surface of these pores gets occupied by the NiO additive and there are chances that the inside of the pores also get agglomerated by these nanoparticles. It is assumed that addition of larger content of nanoparticles leads to more aggregation which in turn affects the porosity of films.

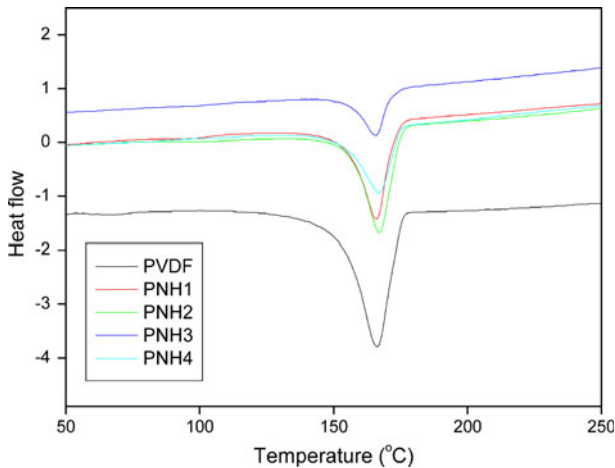
The impact of the presence of NiO nanoparticles on porosity of polymer matrix was estimated by porosity measurements. The porosity values are given in Table 1. It can be seen that with increase in the content of NiO, there is a decline in porosity of the films. This can be possibly due to the occupation of NiO nanoparticles on surface as well as inside of the pores.

DSC analysis

Knowledge of a polymer's crystallinity is important as a basis for understanding its conductivity. The DSC thermograms of PVDF/NiO nanocomposite films are

Table 1 Porosity, enthalpy, and % crystallinity values of PVDF/NiO films

Sample	Porosity (%)	Enthalpy (J g^{-1})	Crystallinity (%)
PVDF	62.39	71.54	100.00
PNH1	56.78	58.84	56.20
PNH2	54.93	55.47	52.98
PNH3	54.12	48.12	45.96
PNH4	51.70	40.75	38.92

**Fig. 2** DSC thermograms of PVDF/NiO composite films

displayed in Fig. 2. By assuming that pure PVDF is 100% crystalline, the relative percentage of crystallinity was calculated based on the following equation

$$\% \text{ Crystallinity} = \frac{\Delta H}{\Delta H^0} \times 100\% \quad (2)$$

where ΔH^0 is the heat of fusion of pure PVDF (104.7 J g^{-1}) [18] and ΔH is the heat of fusion of PVDF/NiO electrolyte membrane. The latter is obtained by the DSC data. The enthalpy obtained and the calculated crystallinity of films are listed in Table 1. The crystallinity of NiO filled PVDF membranes were lower than that of blank PVDF film. This shows that the amorphous domain of membranes increased after the incorporation of NiO nanoparticles. This is the reason that the porosity also showed a gradual decrease. A possible explanation for the observed decrease in crystallinity is that the polymer undergoes some significant structural reorganization after the addition of NiO nanoparticles. There may be some complicated interactions between nickel and oxygen of NiO and fluorine of PVDF which restricts the crystal formation and promotes amorphicity.

Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy is a well-established technique to deduce number of material properties like conductivity, dielectric constant, relaxation frequency, and other interfacial properties. The Nyquist plots for the blank PVDF film and the sample PNH4 is given in Fig. 3. It is obvious from the plots that the resistance of the polymer film decreased after the incorporation of NiO nanoparticles. By fitting the curves, the charge transfer resistance value for PNH4 was found to be 2.3713×10^2 ohms. This value is comparatively lower than that obtained for PVDF film (3.154×10^3 ohms). From the impedance plots, the ionic conductivity of the polymer electrolytes was estimated by the equation $\sigma = L/RA$, where L , A , and R are thickness, area, and bulk resistance of the composite films, respectively. The bulk resistance was calculated from the high frequency intercept on the real impedance axis of the Nyquist plot [19]. The conductivity of the blank PVDF film is $4.77 \times 10^{-4} \text{ S cm}^{-1}$. The value increased to $1.08 \times 10^{-3} \text{ S cm}^{-1}$ with the presence of 1 wt% NiO. On careful observation it can be seen that the impedance of blank PVDF is a quasi-vertical line whereas after the incorporation of NiO, the impedance curve tends to be semi-circular in shape. A pure NiO generally gives a semi-circular curve [20] which implies that the conduction is mainly under charge transfer control. It is known that ionic conductivity is governed by the content of carrier ions and their mobility. Also, the semi-circle nature of the impedance plot suggests that there is a major contribution of NiO to the conductivity of the membrane. Conductivity in NiO is attributed to the large number of Ni^{2+} vacancies [21]. A single Ni^{2+} vacancy leads to the transformation of two adjacent Ni^{2+} ions into Ni^{3+} to attain charge neutrality [22]. The size of NiO here being nano, the density of Ni^{2+} vacancies is expected to be high. Thus, the presence of NiO nanoparticles increases the conductivity of PVDF membrane. Moreover, as discussed in previous sections, NiO also restricts the crystallinity of the polymer segment. This further enhances the conductivity.

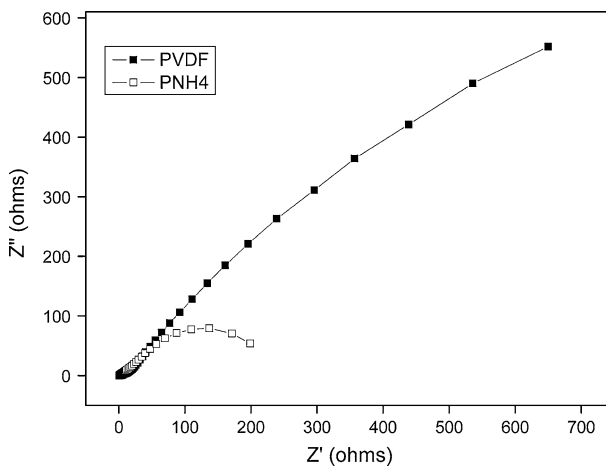


Fig. 3 Nyquist plots for PVDF and PNH4

Magnetic measurements

It is known that bulk NiO is antiferromagnetic. However, with the reduction in size, the uncompensated magnetic spins associated with the surface atoms remain no more negligible and they add up to give rise to a net magnetization. In the present case, NiO of average particle size of 10 nm, exhibited a ferromagnetic behavior [17].

Figure 4 shows the room temperature magnetization curves for PVDF films incorporated with different wt% of NiO nanoparticles. PVDF being diamagnetic [refer online resource 1], any kind of magnetization inferred to the composite films is entirely contributed by NiO. Although a slight increase in magnetization along with NiO content is observed, PVDF/NiO nanocomposite films retain diamagnetism for NiO content less than 1 wt%. However, the impact of the magnetic nanoparticles can be clearly observed for PNH4 with 1 wt% of NiO. Here, the transition from diamagnetic to ferromagnetic behavior is clearly demarcated.

Conclusion

In summary, PVDF/NiO nanocomposite membranes were successfully prepared by phase inversion method. It has been found that, mainly by porosity and crystallinity studies, NiO nanoparticles can influence the PVDF structure. Due to the presence of NiO nanoparticles, there is a possibility of some kind of structural reorganization in the polymer chain which leads to a decrease in crystallinity of the polymer. It was observed from impedance measurements that NiO also influences the conductivity to a large extent, the diameter of the Nyquist plot decreased on addition of NiO nanoparticles. Conductivity value obtained for polymer with 1 wt% NiO was $1.08 \times 10^{-3} \text{ S cm}^{-1}$. This is much smaller than that obtained for blank PVDF film.

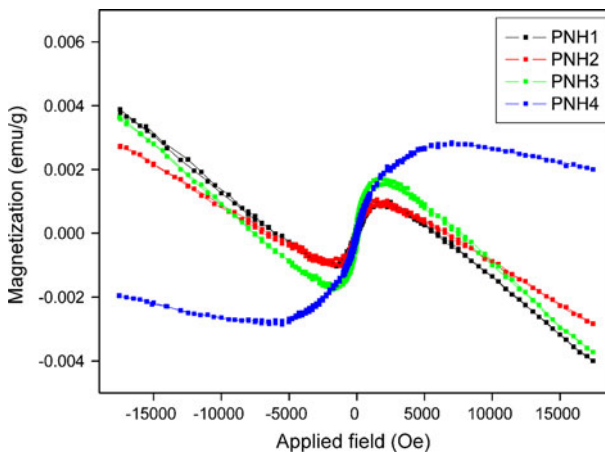


Fig. 4 Magnetization curves for PVDF/NiO composite films

The PVDF/NiO nanocomposite with 1 wt% NiO exhibited ferromagnetism. These nanocomposites can be employed as proton conducting membranes, sensors or as electrochemical devices.

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