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Effect of DC-bias on electrical properties of polymer/Nafion composites

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Abstract: Ion inducted polymer composites are crucial for several applications such as fuel cell, battery electrolyte and organic electronics domain. In the present investigation Nafion a proton conducting ion mixed with polymer Polyvinylidene fluoride (PVDF)/Polyvinyl Alcohol (PVA) by solution casting. The complete electrical characterization was done by using an impedance analyzer under varying DC bias potential (0 to 25 volts) with wide band of the frequency 10 Hz to 35 MHz. The optimization of AC electrical conductivity demonstrates improved magnitude as a function of Nafion loading. The simultaneous DC bias acting as a control agency for overall electrical mechanism of Nafion based polymer systems.
Keywords: Nafion, Polyvinylidene fluoride (PVDF), Polyvinyl Alcohol (PVA), Electrical properties.

Introduction

In the recent years there has been numerous attempts made on the development of an electrical properties of polymer composites for several applications such as fuel cell, battery electrolyte and organic electronics domain[1]. Nafion, a synthetic polymer with ionic properties, called ionomers, incorporating perflurovinylether groups and terminated with sulfonated groups into a tetrafluroethylenes results as unique properties. This special property of Nafion attracts researchers towards the development of fuel cell's, electrical sensors, and biosensors[2]. The highly conductive properties also grab the attention of researchers to work with Nafion. It is also suitable for optical sensors domain. Various reports demonstrate the Nafion inducted with Polyvinylidene fluoride (PVDF) and Polyvinyl Alcohol (PVA) for various electrical applications as tabulated in Table 1. The PVDF is a pure thermoplastic fluropolymer and highly nonreactive. PVDF is ferroelectric polymer exhibiting efficient electrical properties (piezoelectric and pyroelectric properties), this make it useful for sensors and battery application domain[3,4]. However, PVA used as a copolymer, because of its excellent film forming, emulsifying and adhesive properties. PVA has flexibility and highly tensile strength, whereas these properties are dependent on humidity[5,6,7,8]. PVA is a semi crystalline polymer and has various interesting physical properties which are used for different applications[9, 10].

In the present work electrical conductivity of controlled Nafion doped with PVDF/ PVA system were studied as a function of frequency with respect to DC bias potential. The role of Nafion disclosed for the improvement of electrical properties of composites.

Table 1: Some ion inducted polymer composite.

Polymer System	Ionic Entity	Application	Effect of given optimization	References
PVA/PVDF	$LiClO_4$	Advanced lithium polymer batteries (LPB)	Temperature ↑ Conductivity ↑ Conductivity is maximum at PVA(67.5)- PVDF(22.5)- $LiClO_4$ (10) wt %	(1)
PVDF	$Nafion/AlO[OH]_n$	Direct Methanol fuelcell (DMFC)	Nafion % ↑, Methanol permeability ↑ Nafion % ↑, Conductivity ↑	(2)
PVA	$PbTiO_3$	Super capacitor film, humidity sensor	Dielectric loss decreases(ε”) ↓ Dielectric constant Increases(ε’) ↑	(3)
PVA	$CdCl_2$	Polymer Blend electrolytes, Batteries.	Frequency ↑ Conductivity ↑ $CdCl_2$ % ↑ Conductivity ↑	(4)
PVP	Cu^{2+}, Co^{2+}	Visible colour luminescent materials	Shows Intense excitation band at 419 nm. Structural properties using XRD, FTIR and Raman spectra.	(5)

Experimental

Synthesis of composite film

PVA and PVDF granules supplied by SD Fine Chem. Mumbai and Nafion (maker: E.I. Dupont de Nemours and Co.) liquid as dopant used to synthesize composite films with, controlled by weight percentage (%). PVDF dissolved in Dimethyl Formamide (DMF) at 60 °C for 2 hours. Similarly, PVA dissolves in DMF: water (9:1) at the 60 °C for 2 hours. Loading of Nafion as in above to solute and stirred magnetically for 2 hours. Then the mixed solution poured in the petrish dish, and keeps it in oven at 60 °C for 12 hours to obtain the dry composite membrane. Then use for further characterization. The schematic representation of PVDF/PVA/Nafion composites is shown in Fig. 1.

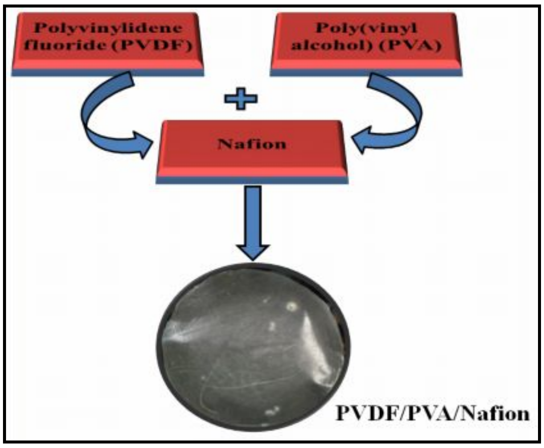

Figure 1: Flow chart of PVDF/PVA/Nafion polymer composite.

Electrical characterization

An electrical property of polymer composite films depends on the concentration of dopant[4]. The dc conductivity of Nafion inducted PVDF/PVA composite films were electrical properties characterized by using PSM-1735 impedance analyzer under varying DC bias potential (0 to 25 V) with wide band of the frequency 10 Hz to 35 MHz. Simultaneously external DC bias acting as a control agency for overall electrical mechanism.

Results and discussion

Properties of Nafion/Polymer composite films depend on the mixture of Nafion concentration and its chemical bonding. The electrical properties of Nafion/Polymer composite films play a vital role for various applications. The electrical properties of composite films depend on loading of Nafion shown in Table 2.

Table 2: Comparative electrical parameters of Nafion based PVDF/PVA composite.

Parameters	(PVDF/PVA/Nafion) (70:25:5)	(PVDF/PVA/Nafion) (65:25:10)	(PVDF/PVA/Nafion) (60:25:15)
Capacitance(Cp)	0.12µf, 15V, 10Hz	0.165µf,20V,10Hz	8.5nf,25V,10Hz
Resistance(Rp)	1kΩ, 0V, 1 kHz	1.65 kΩ, 0V,1 kHz	1.62MΩ,15V,20Hz
Conductivity (σ)	$9.5*10^{-4}$S/m,25V,10Hz	$9.2*10^{-4}$ S/m,25V,10Hz	$8.75*10^{-7}$S/m, 25V,10Hz
Dielectric constant (ε')	$12*10^{4}$, 15V,10Hz	$16*10^{4}$, 15V,10Hz	85, 25V,10Hz
Dielectric Loss (ε'')	$4.55*10^{5}$, 25V,10Hz	$4.55*10^{5}$, 25V,10Hz	450, 25V,10Hz
Impedance (Z' vs Z")	Z'=800Ω,Z"= 0.425Ω 25V	Z'=850Ω,Z"=0.45Ω, 25V	Z'=1.6MΩ,Z"=1.6Ω,15V

The electrical conductivity as function of frequency for 5, 10 and 15% inducted Nafion composite films by wt % were shown in Fig. 2(a), (b) and (c) respectively. For 5% inducted Nafion composite films the conductivity value is maximum ($9.5*10^{-4}$ S/m) for lower frequency 10 Hz at 25 V. This is due to the mobility of charge carriers increases in the composite film. The increase of conductivity also described by the fact that polymer chains in composite films are fully rearranged by increasing voltage and allows a high flowing rate of electrons. Further increase in frequency up to 100 Hz, the conductivity of Nafion/Polymer composite film decreases. For 10 and 15 wt % loading of Nafion, the electrical conductivity of polymer composite decrease it may be the saturation of ion aggregation shown in Fig. 2 (b) and (c). Overall for the all Nafion control sample DC bias is directly proportional to the electrical conductivity of polymer electrolyte. This is the unique investigation for suggesting a suitable composition for fuel cell and battery applications.

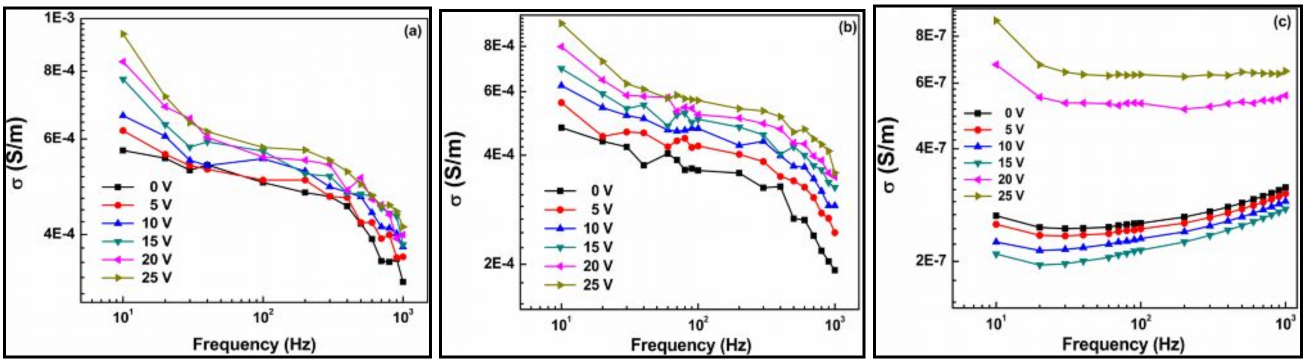

Figure 2: Electrical conductivity of PVDF/PVA/Nafion for (a) 70:25:5 (b) 65:25:10 (c) 60:25:15 loading wt %.

Conclusion

In the present investigation changes in electrical conductivity is observed due to Nafion wt%. The low amount of Nafion shows good electrical conductivity mechanism. The external DC bias is crucial for resolving the electrical properties. The conductivity demonstrated electrical properties of polymer composite films. The maximum conductivity was found to be $9.5*10^{-4}$ S/m for lower frequency 10 Hz at 25 V. An increase of the values of electrical conductivity is driven by mobility of free charges as voltage is increased. So, PVDF/PVA/Nafion membranes are one of the best choices for optical sensors, fuel cells and battery purpose applications.

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