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Materials Today: Proceedings 3 (2016) 1409–1414

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Recent Advances In Nano Science And Technology 2015 (RAINSAT2015)

Perchloric acid doped fluorinated polymer membranes for fuel cell applications

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Abstract

Solid proton conducting polymer electrolytes of high ionic conductivity were prepared using Poly (vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP) and Perchloric acid ($HClO_4$) by solvent casting technique. PVdF-co-HFP has high dielectric constant and possesses good mechanical strength. Perchloric acid is an interesting supporting electrolyte for methanol oxidation and gives perfect plasticizing effect for polymer electrolytes. These films were dry, free standing and dimensionally stable. The prepared electrolytes were characterized by X-ray diffraction (XRD), Infra-red spectroscopy (FTIR), Ac impedance spectroscopy and contact angle measurements .The X-ray diffraction analysis confirms the polymer - $HClO_4$ complex formation. FTIR spectra analysis reveals the interaction between the proton and the polymer matrix. The Contact angle measurement explains that hydrophobic or hydrophilic and super hydrophobic nature of the polymer electrolyte membranes. Conductivity study of these polymer electrolytes systems were carried out in the temperature range 308-373K. The log vs. 1/T plot shows Arrhenius behaviour.

Keywords: *Pvdf-hfp; $HClO_4$; proton conductivity;hydrophobicity;Arrhenius behavior*

1. Introduction

In recent years solid polymer electrolyte membranes (SPE) are promising materials that can be utilized in electrochemical power sources such as hydrogen sensors, steam electrolyzers, fuel cells, proton battery as well as

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super capacitors [1]. From the application point of view a polymer electrolyte membrane with good physical, electrochemical property, high mechanical strength and ionic conductivity would be useful [2]. Previously commercial Nafion-based perflourinated backbone for use in fuelcells. The major disadvantages of this type of fuel cells are higher initial cost and an unwieldy fabrication process. Therefore, a great effort is in progress to develop fuel cells that consist of more easily processed and low-cost membrane materials. A lot of work on ammonium salt doped proton conducting polymer electrolyte based on PVA, PEO, PEI, and PVDF has been found in literature[3-6], very few studies on synthesis and characterization of acid-doped proton conducting polymer electrolyte based PVdF-co-HFP has been reported [7-8]. PVdF-co-HFP is a particularly well known for its hydrophobic polymer, higher chemical resistance and thermal stability [9], Perchloric acid is an interesting supporting electrolyte for methanol oxidation and is a perfect plasticizing material [10]. So these two materials are compatible in the polymer electrolyte system. Hence, an attempt has been made to develop and characterize a new proton conducting polymer electrolyte based on PVdF-co-HFP doped with HClO4.

2. Experimental details

The polymer PVdF-co-HFP (Molecular weight=4, 00,000 Sigma Aldrich) and the acid HClO4 (Merck) were used as the raw material in this study. Acetone was used as the solvent. The polymer electrolytes PVdF-co-HFP doped with HClO4 in different compositions such as 95:05, 90:10, 85:15, 80:20, and 75:25 have been prepared by solution casting method.

3. Result and discussion

3.1. XRD Analysis

XRD Analysis is used to analyze the complexation behavior of conducting polymer electrolyte films. The XRD measurements for polymer electrolyte based on PVdF-co-HFP and their doped with $HClO_4$ complexes are shown in fig 3.1.The peaks at 17.5°, 18.5^0,20.2^0 and 37^0 corresponds to the α(100),(α+γ)(020),(α+γ)(110) and α(021) corresponds to semi crystalline nature of pure PVdF-co-HFP [11]. In complexes the broad peak observed at 20^0, which suggests that the addition of $HClO_4$ into the polymer matrix increases with the addition of Perchloric acid into the polymer matrix increases with the addition of acid concentration. This result can be explained by Hodge et.al [12].In the fig 1(a-e) for the concentration of acid ranging from 5 to 25 mol%. No sharp peaks corresponding to Perchloric acid have been observed in the pattern. This indicates that, increment of crystalline phase to amorphous phase and thus results in the improvement of conductivity.

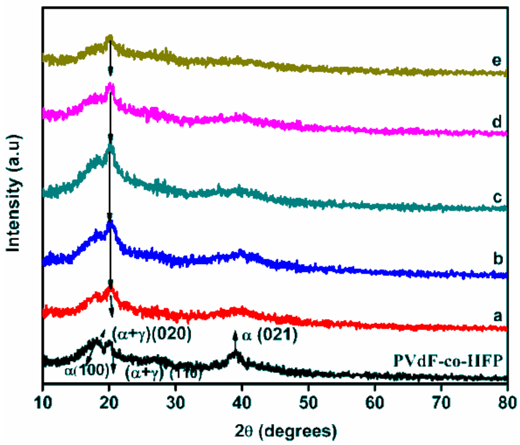

Fig. 3.1. XRD pattern of PVdF-co-HFP and HClO4 doped PVdF-co-HFP Concentrations.

3.2. FTIR analysis

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs and contaminants. FTIR is perhaps the most powerful tool for the identifying types of chemical bonds or functional groups [13]. FTIR spectra