Materials Chemistry and Physics 143 (2014) 1191–1198

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

# Photovoltaic performance of dye-sensitized solar cells fabricated with polyvinylidene fluoride–polyacrylonitrile–silicondioxide hybrid composite membrane

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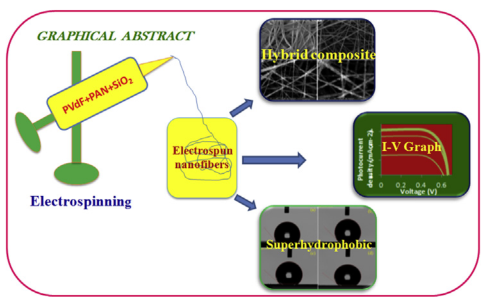
## HIGHLIGHTS

- Electrospun poly (vinylidine–acrylonitrile) silicon dioxide membrane was prepared.
- This membrane has good conductivity, porosity and electrolyte uptake.
- It has higher hydrophobicity and interconnected network with plenty of cavities.
- DSSCs fabricated with polymer electrolyte exhibited good photovoltaic efficiency.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 29 June 2013
Received in revised form 15 October 2013
Accepted 11 November 2013

*Keywords:*
Polymers
Electron microscopy (SEM)
Thin films
Electrical conductivity

## ABSTRACT

Electrospun fibrous membranes of hybrid composites of polyvinylidene fluoride (PVdF), polyacrylonitrile (PAN) and silicon dioxide ($SiO_2$) (PVdF–PAN–$SiO_2$) are prepared with different proportions of $SiO_2$ (3, 5 and 7% w/w). The field emission scanning electron microscopy (FE-SEM) reveals that these membranes have three-dimensional, fully interconnected network structures, which are combined with micropores of fine $SiO_2$ distribution. The surface roughness of the membranes increases with increasing the $SiO_2$ content. It is found that 7 wt% $SiO_2$/PVdF–PAN electrolyte membrane has the highest ionic conductivity ($6.96 \times 10^{-2}$ S $cm^{-1}$) due to the large liquid electrolyte uptake (about 570%). As the concentration of $SiO_2$ nanoparticles increase, the contact angle value also increases, ranging from 135.70° to 140.60° which indicates that the membrane has higher hydrophobicity. The dye sensitized solar cells (DSSCs) are fabricated using the hybrid composite membrane with PVdF–PAN with 7 wt % $SiO_2$. Its photovoltaic performance exhibits an open circuit voltage ($V_{oc}$) of 0.79 V and a short circuit current 11.6 mA $cm^{-2}$ at an incident light intensity of 100 mW $cm^{-2}$, producing an efficiency of 5.61%. DSSC, using the hybrid composite electrospun membrane which shows more stable photovoltaic performance than other assembled DSSCs.



## 1. Introduction

Dye-sensitized solar cells (DSSCs) attracted extensive attention in the academic as well as industrial field because of their high power conversion efficiency, low cost, easy handling and as an alternative source to a conventional silicon solar cell since Gratzel's result reported in 1991 [1,2]. Initially, the liquid electrolyte based solar cell was in use but its success was limited due to long practical

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http://dx.doi.org/10.1016/j.matchemphys.2013.11.020

operation, electrolyte leakage, evaporation, high temperature instability and flammability, possible desorption and photo-degradation of the attached dye on $TiO_2$, at large-scale production. The corrosion of counter electrode with such electrolytes also affects the cell fabrication and limits the long-term performance of these DSSCs [3]. To overcome these troubles, many researchers reported ionic liquids [4], inorganic or organic hole conductors [5], polymer [6] and gel electrolytes [7] as an alternative in the place of liquid electrolytes. However, different kinds of gel-polymer electrolytes were introduced to increase the photovoltaic conversion efficiency. Polymer gel electrolytes are largely used in lithium batteries, fuel cells, smart windows and dye-sensitized solar cells [8,9]. They have several advantages like limited internal shorting, low vapor pressure, excellent contacting and filling properties between the nano structured electrodes and counter electrode, higher ionic conductivities compared to the solid electrolytes and excellent thermal stability [10,11]. Thus, various kinds of polymers or co-polymers, such as polyacrylonitrile [12], polyethyleneglycol [13], polymethyl methacrylate [14], polyethylene oxide [15], poly-vinylideneflouride [16], polyoligoethylenegylcol methacylate, poly (vinylidenefluoride–co-hexafluoropropylene [17], etc., have been used to prepare gel polymer electrolytes for DSSC applications. Among them, the fluorinated polymers poly-vinylideneflouride (PVdF) and poly-acrylonitrile (PAN) are selected as polymer electrolyte because PVdF exhibited higher conductivity, higher degree of crystallinity and photochemically stability even in the presence of working electrode ($TiO_2$) and counter electrode (Pt) [18], while PAN is having some attractive individuality such as thermal constancy, high-quality ionic conductivity and excellent morphology for electrolyte uptake and good compatibility with liquid electrolyte [19]. The –CN groups that easily make bond with –C=O groups in the presence of propylene carbonate (PC) or ethylene carbonate (EC) [20]. Thus, the polymers are still the main components of membrane technology with good characteristics as membrane forming ability, flexibility and low cost but individually they have certain limitations like chemical, mechanical and thermal resistance [18,21]. The nanocomposites are a new class of materials and they can be combined with basic properties of both organic and inorganic materials and proposed specific characteristics for the preparation of synthetic membranes by means of the flexibility, good mold ability of the organic part, excellent separation performances, and heat stability, high strength, and chemical resistance of the inorganic part and adaptability to the harsh environments, as well as membrane forming ability [22,23]. Thus, these organic and inorganic nanocomposites are found to be potential materials for membranes and attracted more attentions [24].

Inorganic metal oxide nanoparticles like alumina ($Al_2O_3$), zirconium dioxide ($ZrO_2$), titanium dioxide ($TiO_2$), silica ($SiO_2$) and some small molecule of lithium salts [25–29] have been used in preparation of composite polymer electrolytes. These inorganic nanoparticles improve the mechanical properties, interfacial stability between polymer electrolytes and also enhance the ionic conductivity by dropping the crystallinity nature of the host polymer and introducing Lewis acid–base interaction between the polar groups of the metal oxide nanoparticles and the electrolyte ionic species [30]. Amongst all metal oxide, $SiO_2$ is the most suitable and widely used one for preparing composite polymer electrolytes because its mild reactivity, well-known chemical properties and its starburst shape supports the ionic mobility [31]. Earlier reported literatures revealed that a direct blending method of the pre-equipped nanoparticles with polymers give asymmetric membranes [23,32]. Therefore, there is lack of reproducibility, poor stability and the nanoparticles are aggregated on the membrane surfaces. A new simple method is introduced to obtain an organic–inorganic hybrid by mixing of organic polymer with a metal alkoxide, sol–gel process involving hydrolysis and poly-condensation [33]. Thus the development of sol–gel techniques has provided new opportunities for the preparation of nanosols materials, which allows the formation of inorganic scaffold under mild condition and amalgamation of metal oxide into polymers, improving the chemical, mechanical and thermal compatibility of inorganic organic materials without disturbing the polymer properties [18,34].

Now-a-days, the widely employed method for the preparation of nanofiber matrices is the electrospinning technique which has a large number of applications in the biomedical field, such as wound therapeutics, drug delivery systems and tissue engineering scaffolds as well as in industrial sector also [35]. Recently an electrospinning tool was used to prepare polymer composite membranes that are composed of ultrafine fibers with micron and sub-micron diameters. They have high porosities in the form of nonwoven membranes possessing high surface area. They are characterized by a large electrolyte uptake due to interconnected porosity that enhanced ionic conductivity also [36–38]. However, electrospun fibers, prepared from pure polymers, have limited capability in stabilizing the efficiency of DSSCs due to polymer degradation and the leakage of organic liquid. Electrospun nanofibers include both synthetic and natural polymers both, but recently hybrid fibers of metal and ceramic nanofiber like silica ($SiO_2$) and titanium ($TiO_2$) nanofibers have been reported [39,40]. In this study, $SiO_2$ as particulate filler has been used as electrospun composite polymer electrolyte because it enhances the electrochemical performance by providing large surface area and high conductivity. The good dispersion of $SiO_2$ particles decides the morphology of membrane and electrochemical property. In this work, two polymer electrolytes, PVdF and PAN, blended with hydrophobic $SiO_2$ nanoparticles, were electrospun to get PVdF–PAN–$SiO_2$ composite nanofiber membranes. Electrospinning process and the addition of hydrophobic silica nanoparticles within the PVdF–PAN matrix are two main key factors in enhancing the electrochemical performance. Furthermore, $SiO_2$ as the filler acts as a supporter to sustain tunneling structures and to bind the liquid electrolyte. The $SiO_2$ fillers improve the mechanical properties of the polymer composite electrolytes and give better cation transference and interfacial stability between the electrolyte and electrode [29,41].

The electrochemical performance and morphological characteristics of the membrane were evaluated. The porosity, conductivity and interfacial stability of polymer composite electrolyte were found out.

## 2. Experiments

### 2.1. Materials

Poly(vinylidene fluoride) (PVdF), Polyacrylonitrile (PAN), silica ($SiO_2$), acetone, *N*, *N*-dimethylacetamide, lithium iodide, iodine, ethylene carbonate (EC), and propylene carbonate (PC), 1-Hexyl-2,3-dimethylimidazolium iodide were purchased from Aldrich Chemicals and 4-*tert*-butylpyridine from TCI Chemicals. All reagents were used without further purification and all other reagents and solvents were commercially available and were used as received. The particle size of the $SiO_2$ used is 10–15 nm.

### 2.2. Preparation of electrospun nanofiber composite membrane PVdF–PAN–$SiO_2$

Mixture of PVdF–PAN solution was prepared by mixing PVdF and PAN in the 3:1 weight ratio and the mixture was dissolved in acetone:DMF (7:3, v/v). Then nano size $SiO_2$ was mixed with