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Electrospun nanofibers composed of poly(vinylidene fluoride-co-hexafluoropropylene) and poly(oxyethylene)-imide imidazolium tetrafluoroborate as electrolytes for solid-state electrochromic devices☆

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ABSTRACT

In this work, a novel electrochromic device (ECD), consisting of phenyl viologen (PV) as the cathodically coloring material and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the stable radical provider for charge balance, was proposed. Nanofibers (NFs) obtained by electrospinning, using poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and poly(oxyethylene)-imide imidazolium tetrafluoroborate (POEI-IBF_4), were introduced into the electrolyte to absorb tetrabutylammonium tetrafluoroborate and propylene carbonate, so as to form a solid-state electrolyte for the ECD. The NFs were characterized by distribution of their diameters, or histograms, based on the scanning electron microscope (SEM) images; their physical properties, including electrolyte uptake, ionic conductivity, and porosity were studied. The proposed ECDs were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), UV–visible spectra, and dynamic transmittance curves. The pertinent N15P10-ECD exhibited a high transmittance change (ΔT) of 68.7% at 590 nm, while maintaining a good cycling stability (95.5% of its original ΔT) after continuous 1000 switching cycles of operation at room temperature.

1. Introduction

Electrochromic devices (ECDs) offer color change through the electrochemical variation of redox states by their electrochromic (EC) materials [1–3]. ECDs have been studied for several years; they endow many commercially viable applications, including smart windows [4,5], automatic rear view mirrors [6], safety helmets [7], and displays [8]. Since the discovery of the phenomenon of electrochromism by Deb in 1969 [9], its research has been focused essentially on three parts of the ECD, namely (1) EC material, (2) electrolyte, and (3) ion-storage layer (at the counter electrode). The electrolyte plays an important role in an ECD. Numerous papers dealing with electrolytes have been published in the past decade [10–12]. Efforts have been consistently made to identify electrolytes for longer life; including polymer electrolytes [13,14], ionic liquids [15], polymeric ionic liquids (PIL) [16], and biomaterial-based electrolytes [17].

Phenyl viologen (PV) is a well-known electrochromic material in solution state. The disadvantage of rendering a high transmittance to its ECD is attributed to its unwanted aggregation on the working electrode surface during electrochemical operation. This type of aggregation leads the colored viologen radical cations difficult to bleach and thereby to poor long-term stability of the device. We used 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in this research as the stable radical provider for the ECD. The polar copolymer poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) [18] was used with an ionic liquid to solve the leakage problem in an electrochemical cell. Chemically cross-linked ultrathin electrospinning poly(vinylidene fluoride) (PVDF) nanofibrous mats, with excellent mechanical properties and high ionic conductivities, were used as an ionic liquid host in an ECD [19]. Electrospinning is a relatively new technique for use in the area of electrochromism [20,21]. This technique has been used in other electrochemical devices, including fuel cells [22], lithium-ion batteries [23], supercapacitors [24], and dye-sensitized solar cells [25,26]. The electrospinning technique was used to obtain either an electrochromic

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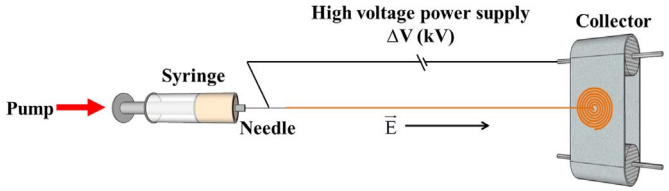

Scheme 1. Operational principle of the electrospinning technique.

material [27,28] or an electrolyte [29–33] for an ECD. Electrospinning technique has the advantage of obtaining the diameter of electrospinning material in nanoscale; the pore size of such material is tunable through this technique.

In this work, we fabricated a novel type of ECD, consisting of PV as the cathodically coloring material and TEMPO as the stable radical provider. Composite nanofibers (NFs) of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and poly(oxyethylene)-imide imidazolium tetrafluoroborate (POEI-IBF_4, PIL) were used to adsorb tetrabutylammonium tetrafluoroborate and propylene carbonate to form the solid-state electrolyte. The device was operated after the addition of PV, TEMPO, and the supporting electrolyte tetrabutylammonium tetrafluoroborate in propylene carbonate. The nanofibers were characterized by scanning electron microscope (SEM) images and histograms of fiber diameter distributions. The electrolyte uptake and porosity of the nanofibers were determined. The ionic conductivity, diffusion behavior, and electrochromic properties of the ECD were studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Cyclic voltammetry and in-situ potential-UV–vis absorption spectra were utilized to find the operation voltage of the device. The electrochromic behavior, including the dynamic transmittance responses and stability of the ECD, was also studied by potential-UV–vis absorption spectra.

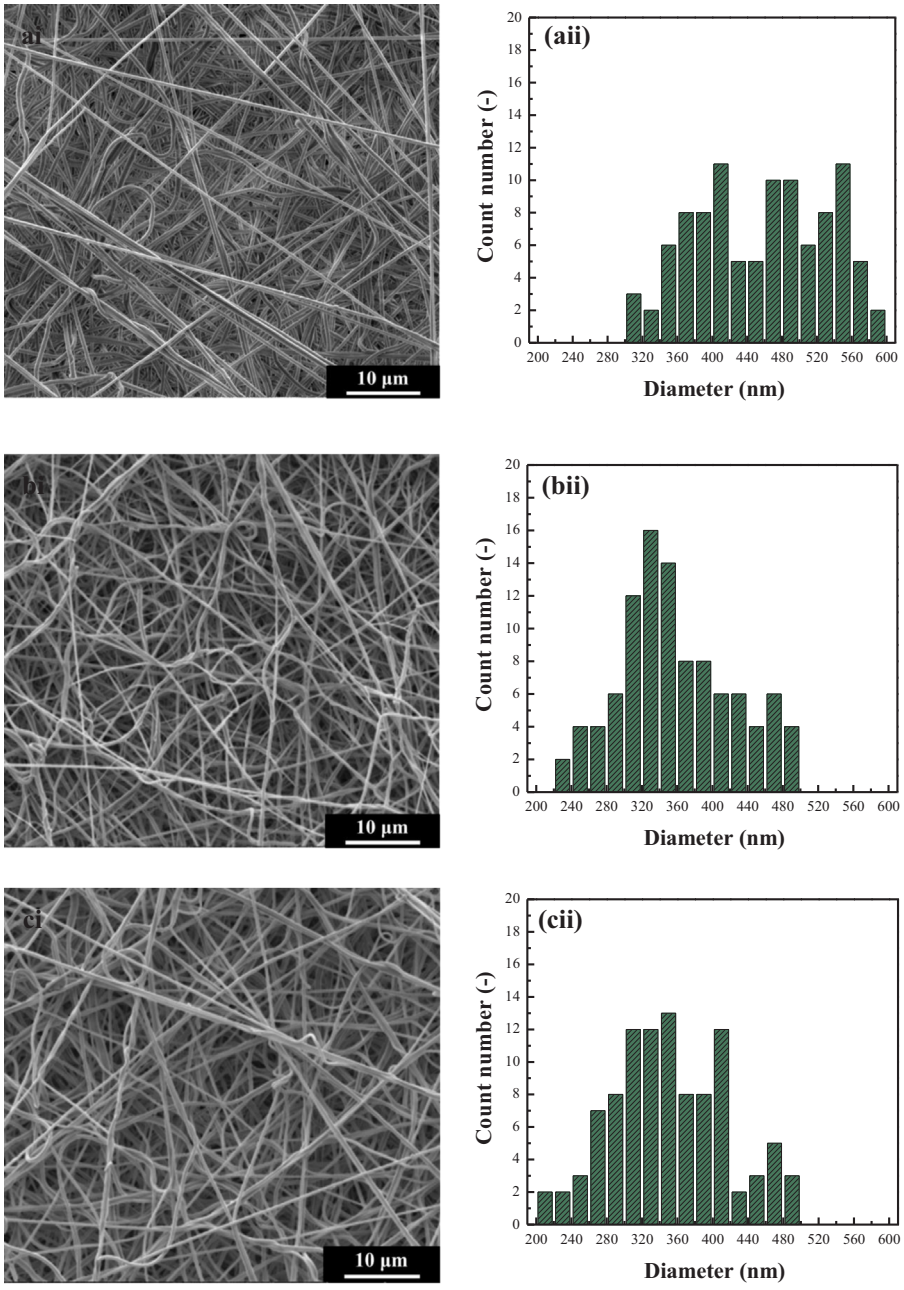

Fig. 1. SEM image shows the nanofibers (x wt% PVDF-HFP, Nx) of (ai) N15, and the composite nanofibers (15 wt% PVDF-HFP and y wt% PIL, NxPy) of (bi) N15P5 and (ci) N15P10; (aii–cii) histograms of distributions of their diameters.