



Superior performance of PEDOT:Poly(4-styrenesulfonate)/vapor-grown carbon fibre/ionic liquid actuators exhibiting synergistic effects

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ABSTRACT

This paper describes new actuators with poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate)/vapor-grown carbon fibre/ionic liquid (PEDOT:PSS/VGCF/IL) structures, as an alternative to those incorporating single-walled carbon nanotubes (SWCNTs). These devices show superior strain performance compared to those using SWCNTs in place of VGCFs or poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF(HFP)) instead of PEDOT:PSS. These improvements are attributed to be obtained from simultaneous electrostatic double-layer (EDLC) and faradaic capacitor (FC) mechanisms. The electrode in the new actuator system represents an electrochemical capacitor composed of an EDLC and an FC, since PEDOT:PSS (used as a substitute for PVdF(HFP)) acts as both an FC and a base polymer. In addition, the VGCF skeleton increases the electroconductivity of the device and provides an EDLC effect. The functioning mechanism of this device therefore differs from those of conventional actuators, which act solely as EDLC units. The PEDOT:PSS polymer helps to increase the specific capacitance, strain, and maximum generated stress values compared to those obtained with a conventional actuator. Surprisingly, the synergistic effect from the combination of the PEDOT:PSS and VGCFs is much greater than the enhancement achieved by combining PEDOT:PSS and SWCNTs. For this reason, these new, flexible and robust films may have significant potential as actuator materials for wearable energy conversion devices. A double-layer charging kinetic model was developed to account for the oxidation and reduction reactions of PEDOT:PSS, and this model is similar to that previously proposed for PEDOT:PSS/SWCNT/IL actuators. The model was successfully applied to simulate the frequency-dependent displacement response of the actuators.

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1. Introduction

Conductive polymers (CPs) are well suited for applications in electrochemical capacitors (ECs) because of their many advantages, including low cost, low environmental impact, highly conductive doped states, wide voltage windows, high storage capacities/porosities/reversibilities, and adjustable redox activities through chemical modification [1–5]. In addition, CPs can exhibit capacitive behaviour as the result of redox processes, because ions transferred to the polymer backbone during oxidation are subsequently released back into the electrolyte during reduction. These redox reactions occur not just on the surface but also through-

out the bulk CP [6]. Since no structural alterations such as phase changes are involved, the process is highly reversible [7].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a polythiophene derivative that is believed to be the best CP currently available, in terms of electrical conductivity, processability, and stability [8]. Thus, it is commercially produced on a large scale and used for many applications, such as solid electrolyte capacitors, light-emitting diodes, antistatic coatings, organic solar cells, and organic field-effect transistors [8]. PEDOT doped with poly(4-styrenesulfonate) (PEDOT:PSS) is one of the most important CPs, as it can be dispersed in water in the form of colloidal particles. This material also exhibits superior mechanical properties, thermal stability, and a tuneable conductivity from 0.1 to 3000 S cm⁻¹ [9,10], and therefore has been used in a number of organic or plastic electronic/optical devices [11–14]. Because it is highly stable, PEDOT [15,16] has been considered for applications in ECs, and recent publications have reported the deposition of this material on a gold plate as an amorphous layer

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having significant porosity, via an electrochemical method. In other work, electrodes based on PEDOT:PSS have been assessed [17–19], and the conversion of electrical to mechanical energy has been demonstrated with these devices [20,21]. In addition, the application of PEDOT:PSS as a highly conductive coating on multi-walled carbon nanotubes (MWCNTs) has been found to allow the fabrication of polycarbonate nanocomposites with improved electrical conductivity [22].

Recently, there has been significant research regarding soft materials that can directly transform electrical energy into mechanical work. These materials have a wide range of applications in robotics, tactile and optical displays, prosthetic devices, medical devices, and microelectromechanical systems [23]. Low-voltage electroactive polymer (EAP)-based actuators capable of rapid response are particularly useful in this regard, because they can be used as artificial muscle-like actuators for various biomedical and human-affinity applications [24,25]. We have previously reported [26–28] the first dry actuator fabricated with a “bucky-gel” [29], which at room temperature is a gelatinous ionic liquid (IL) containing single-walled carbon nanotubes (SWCNTs). This actuator has a bimorph configuration, in which a polymer-supported IL electrolyte layer is sandwiched between two polymer-supported bucky-gel electrode layers. This design allows rapid device operation and ensures a long lifespan in air at low applied voltages. Furthermore, the advantages of ILs, such as intrinsically low volatilities, high ionic conductivities, and wide potential windows, make them suitable for applications in quick-response actuators and devices that require high electrochemical stability [30]. Our group also determined that the electromechanical and electrochemical properties of these actuators depend on the specific IL, nanocarbon, and polymer materials used [28,31–34].

Because ECs span the power and energy gaps that exist between fuel cells or batteries and standard dielectric capacitors, and due to their significant lifetimes and good power densities, these devices have lately become the focus of much research [35,36]. As a result, many publications on this subject have appeared, providing evidence of the rapid improvement in our understanding of ECs and our ability to find practical applications [37–42]. There are two main types of EC: faradaic capacitors (FCs) and electrostatic double-layer capacitors (EDLCs). EDLCs are based on electrode materials that are not electrochemically active, which may include carbon particles. Therefore, during both charging and discharging, there are no electrochemical reactions at the electrode, although the electrode/electrolyte interface accumulates a physical charge. In contrast, FCs are able to store charge during both discharge and charge operations, and employ electrochemically active substances as electrodes, including metal oxides [7,43,44]. There are basic criteria for both types, such as the incorporation of extremely conductive electrode materials (so as to ensure high capacitance), an optimal distribution of pore sizes, and a significant surface area. In addition to the above two devices, it is also possible to fabricate a unit that simultaneously exhibits both FC and EDLC characteristics, with one of the two being the primary mechanism, known as a hybrid capacitor [45].

The relatively poor capacitances of present-day actuators is a problem [33], and has led to the investigation of carbon nanotubes (CNTs) as components of electrochemical actuators that function on the double-layer electrostatic principle. This interest in CNTs results from their exceptional mechanical [46] and electrochemical [47,48] characteristics [48]. The other exceptional properties of CNTs, including good conductivity, resistance to chemical degradation, mesoporous structures, and sizes on the nanometre level, also suggest that these materials could be applied as electrode components in supercapacitors. Despite this promise, to date there appear to have been no investigations of high-performance polymeric actuators based on non-activated MWCNTs rather than SWCNTs.

Such studies would be valuable since WMCNTs are relatively inexpensive; so much so that they are presently used as electrode materials in batteries. Another challenge that restricts the practical applicability of SWCNTs is their inadequate dispersion properties in liquids. One approach to solving this problem could be to use so-called bucky-gels. In a bucky-gel, cation- π surface interactions between SWCNTs and an imidazolium ion-based IL generate fine nanotube bundles [49]. Electrode layers of this material generated ultrasonically have exhibited pronounced actuation, as a result of their significant electric double-layer capacitance. Finally, employing the WMCNTs known as vapour-grown carbon fibres (VGCFs) has the potential to improve the thermal and electrical properties of high-performance materials because VGCFs have suitable mechanical strength and conductivity values but disperse more easily than SWCNTs.

Liu et al. [50] fabricated compact, flexible, and mechanically robust films based on interpenetrating nanocomposites composed of graphene/MnO₂ and CNTs that exhibited superior electrochemical characteristics, for use as supercapacitor electrodes. This approach takes advantage of the synergistic effects arising from the combination of graphene, CNTs and MnO₂. Based on the same principle, we have previously used a film-casting method to develop a new hybrid-type PEDOT actuator that combines an EDLC and an FC [51]. These actuators (PEDOT:PSS, PEDOT:PSS/IL, and PEDOT:PSS/SWCNT/IL) were characterised electrochemically and mechanically, and showed better strain performance than the conventional PVdF(HFP)/SWCNT/IL actuator.

In the present work, we used the film-casting method to fabricate hybrid EDLC-FC PEDOT:PSS actuators that incorporated VGCFs in place of SWCNTs, in order to further exploit the synergistic effects between nanotubes and PEDOT:PSS. The resulting PEDOT:PSS/VGCF/IL actuators exhibited further improvements in strain performance compared to the PEDOT:PSS/SWCNT/IL and PVdF(HFP)/VGCF/IL actuators, due to the difference in their synergistic effects.

2. Experimental

2.1. Materials

PEDOT:PSS (poly-ion complex; 1:2.5 w/w) was obtained from Aldrich (No. 768618). The VGCFs (VGCF-X, Showa Denko Co., Ltd.) had an average diameter of 10–15 nm, an average length of 3 μ m, and a surface area of 270 m²/g. The SWCNTs (high-purity HiPco™ SWCNTs, Unidym, Inc.) had an average diameter of 0.8–1.2 nm, an average length of 0.1–1 μ m and a surface area of 400–1000 m²/g. The ILs were 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI[BF₄], Fluka) and 1-ethyl-3-methylimidazolium triflate (EMI[CF₃SO₃], Fluka), both employed as received. Their chemical structures are shown in Fig. 1. Other reagents included poly(vinylidene fluoride-co-hexafluoropropylene (PVdF(HFP)), Kynar Flex 2801, Arkema Chemicals, Inc.), methyl pentanone (MP, Aldrich), propylene carbonate (PC, Aldrich), and dimethylacetamide (DMAc, Kishida Chemical Co., Ltd.). All were used as received.

2.2. Preparation of the actuator film [51]

Fig. 1 illustrates the configuration of the PEDOT:PSS/VGCF or SWCNT/IL actuators. The PEDOT:PSS/VGCF or SWCNT/IL electrode layer typically contains 32 wt% PEDOT:PSS, 20 wt% VGCF or SWCNT, and 48 wt% IL. Each layer was prepared by first mixing 80 mg PEDOT:PSS, 50 mg VGCFs or SWCNTs, and 120 mg EMI[BF₄] or EMI[CF₃SO₃] in 9 mL H₂O, with subsequent stirring for more than 5 h. This was followed by casting 1.6 mL of the resulting gelati-

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