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High-performance polymer actuators based on an iridium oxide and vapor-grown carbon nanofibers combining electrostatic double-layer and faradaic capacitor mechanisms

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ABSTRACT

The electrochemical and electromechanical properties of polymer actuators that leverage the synergistic effect from combining a noble metal oxide (iridium oxide dihydrate ($IrO_2{\cdot}2H_2O$)), vapor-grown carbon nanofibers (VGCFs) and an ionic liquid (IL) in the electrode were compared with those of actuators prepared using VGCFs or single-walled carbon nanotubes (SWCNTs) without IrO_2, or with an $IrO_2{\cdot}2H_2O$/carbon black (CB)/IL composition. The electrode in this actuator system is equivalent to an electrochemical capacitor, and exhibits behavior similar to that of both an electrostatic double-layer capacitor (EDLC) and a faradaic capacitor (FC). The mechanism underlying the functioning of the $IrO_2{\cdot}2H_2O$/VGCF/IL actuators which exhibit from both EDLC and FC mechanisms was found to be different from that for devices produced using VGCFs or SWCNTs alone (which exhibit only the EDLC mechanism) and using $IrO_2{\cdot}2H_2O$/CB/IL, which exhibit from both EDLC and FC mechanisms, with the FC mechanism providing the largest contribution. An $IrO_2{\cdot}2H_2O$/VGCF/EMI[BF_4] actuator exhibited a maximum strain of 0.75%, a value approximately 1.8 times that obtained from a SWCNT-only actuator. This device also generated a maximum blocking force stress of 2.58 MPa (1.3 times that of a SWCNT-only actuator) and a maximum calculated stress of 0.66 MPa (2.2 times that of a $IrO_2{\cdot}2H_2O$/CB/EMI[BF_4] actuator).

Although the frequency dependence of the displacement responses of an $IrO_2{\cdot}2H_2O$/CB/IL polymer actuator was not successfully simulated using a double-layer charging kinetic model in previous work, this was found to be possible for the $IrO_2{\cdot}2H_2O$/VGCF/IL actuators in the present study. Simulations of the electromechanical response of the $IrO_2{\cdot}2H_2O$/VGCF/IL actuators correctly predicted strains at low frequencies as well as the associated time constants, confirming that the model is applicable to both EDLC-based actuator systems and the newly fabricated EDLC/FC system. These results suggest that flexible, robust films enabled by the synergistic effect obtained by combining noble metal oxides and VGCFs can have significant potential as actuator materials for wearable and energy-conversion devices.

1. Introduction

Soft materials that are capable of directly transforming electrical energy into mechanical work have been the subject of many recent studies, since they have a large number of potential applications [1]. Low-voltage electroactive polymer actuators with fast response times are highly promising as artificial muscle-like actuators for biomedical devices [2,3]. We previously reported [4–6] a dry actuator based on a gelatinous, room-temperature ionic liquid (IL) containing single-walled carbon nanotubes (SWCNTs), known as a "bucky gel" [7]. The device consists of a polymer-supported IL electrolyte layer held between two polymer-supported bucky gel electrode layers. As a result, it is capable of rapid operation and has a significant useable lifespan when operated in air at low applied voltages. However, we found that the specific IL, nanocarbon, and polymer in such devices can affect the electromechanical and electrochemical characteristics of the actuator [6,8–11].

Electrochemical capacitors (ECs) can be divided into two broad categories. The first is the faradaic capacitor (FC), which employs electrochemically active compounds, such as metal oxides, as electrodes. FCs can directly store charge throughout the charging and discharging processes [12–14]. Electrostatic double-layer capacitors (EDLCs), which employ electrochemically inactive substances,

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such as carbon particles, as electrode materials comprise the second type.

Thus, it is evident that FCs, also known as pseudo-capacitors, differ from EDLCs. The application of a potential to an FC generates rapid, reversible faradaic (or redox) reactions on the electrode surface. Conductive polymers and various metal oxides, including RuO_2, MnO_2, and Co_3O_4, are known to enable these redox reactions [12,15–17]. During this process, charge moves across the double layer in a manner that mimics battery charging and discharging. In this way, a faradaic current passes through the capacitor cell.

Hydrous metal oxides are particularly promising for ECs because they offer good energy-storage capabilities [14,18]. Capacitors based on metal oxides have also been found to have optimal specific peak power generation values. The best transition metal conductor is IrO_2, which has been used as both an anode and a cathode material because it exhibits metallic conductivity at room temperature, in addition to catalytic activity and superior chemical stability, especially in acids. Although IrO_2 is less active than RuO_2 during oxygen evolution reactions [19], it generates hydrogen at lower overpotentials than RuO_2 when employed as a cathode [20]. IrO_2 as an anode material is also more stable than RuO_2; moreover, it lowers the hydrogen evolution rate of this oxide when the two are combined [21].

SWCNTs are specially prepared compounds that are very expensive. In contrast, MWCNTs are relatively inexpensive and so are commonly used in battery electrodes. Vapor grown carbon fibers (VGCFs), a type of MWCNT, are specially designed to enhance the electrical and thermal properties of high performance materials. A further disadvantage of SWCNTs is their poor dispersibility. Thus, because VGCFs disperse much more readily than SWCNTs, and because they also exhibit good electrical conductivity and mechanical strength, they have been applied to the fabrication of actuators.

Liu et al. [22] demonstrated the fabrication of compact, flexible and mechanically robust films based on interpenetrative nanocomposites composed of graphene/MnO_2, as well as CNTs with superior electrochemical characteristics that are meant for use in supercapacitor electrodes. This approach differed from earlier work by leveraging the synergistic effects obtained from the combination of graphene and nanotubes.

Tailoring the concentrations of both IrO_2 and VGCFs in IrO_2/VGCF/IL polymer actuators is a crucial aspect of optimizing performance. Numerous characteristics of an IrO_2/VGCF/IL polymer electrode, including its electrical conductivity, capacitance and Young's modulus, all play a vital role in determining its performance, particularly its ability to achieve high strain values, and these characteristics are in turn affected by the levels of both IrO_2 and VGCFs.

Our group previously applied a triangular waveform voltage at various frequencies to a bucky gel actuator as a means of assessing its voltage–current and voltage–displacement characteristics [6,23]. We also developed polymer actuators that contained VGCFs in conjunction with either $MnO_2{\cdot}nH_2O$ or $NiO_2{\cdot}nH_2O$, and examined the mechanism underlying the functioning of the $MnO_2{\cdot}nH_2O$ or $NiO_2{\cdot}nH_2O$/VGCF/IL actuators, which exhibited both EDLC and FC mechanisms [24,25]. More recently, we developed polymer actuators that contained VGCFs in conjunction with the noble metal oxide RuO_2 [26]. However, it is not still examined that the variations of displacement with frequency for the noble metal oxide/VGCF/IL actuators were successfully predicted during the present work by employing a double-layer charging kinetic model.

In our previous work [27], we also anticipated the possibility of quantitatively modelling the frequency dependence of the $IrO_2{\cdot}2H_2O$/CB/IL polymer actuator strain using an electrochemical equivalent circuit model based on the lumped resistance and capacitance of the electrode layer and the lumped resistance of the electrolyte layer. However, we were not able to successfully predict the variations in the displacement with frequency of these devices when a double-layer charging kinetic model was employed.

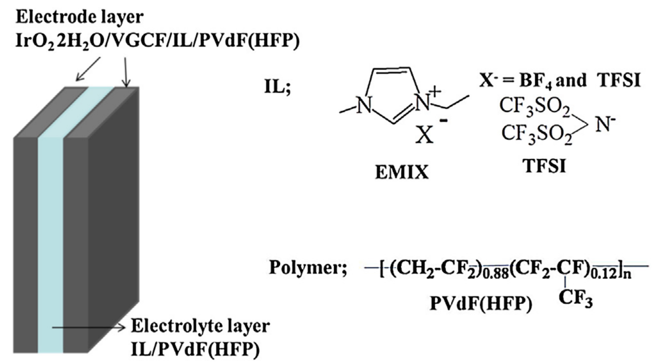

Fig. 1. Configuration of the polymer-supported $IrO_2{\cdot}2H_2O$/VGCF/IL gel actuator and the molecular structures of the ILs and polymer used.

The study reported herein produced a hybrid EDLC/FC polymer actuator that takes advantage of the synergistic effects obtained by combining VGCFs and $IrO_2{\cdot}2H_2O$. In contrast to our previous work, IrO_2 was used instead of RuO_2 as both the anode and cathode material because IrO_2 exhibits metallic conductivity at room temperature, is more stable than RuO_2, and exhibits catalytic activity and superior chemical stability, especially in acid. The electrochemical and electromechanical characteristics of this device were subsequently compared with those of polymer actuators made using only SWCNTs or VGCFs and $IrO_2{\cdot}2H_2O$/carbon black (CB)/IL. (Fig. 1). In the present work, because the Young's moduli of polymer-supported VGCF/IL actuators are higher than those of polymer-supported CB/IL actuators [24,27], it was anticipated that the performance of actuators containing VGCFs and $IrO_2{\cdot}2H_2O$ would surpass that of SWCNT-containing actuators in terms of the strain and maximum generated stress. This work also examined the mechanism underlying the functioning of $IrO_2{\cdot}2H_2O$/VGCF/IL actuators that exhibit both EDLC and FC characteristics, and this mechanism was found to be different from that of devices produced using $IrO_2{\cdot}2H_2O$/CB/IL.

2. Experimental

2.1. Materials

The specifications of the materials used in this work are as follows. The $IrO_2{\cdot}2H_2O$ material was obtained from Alfa Aesar. The vapor grown carbon nanofibre (VGCF-X, Showa Denko Co. Ltd.) had an average diameter of 10–15 nm, an average length of 3 μm, and a surface area of 270 m^2/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 μm, and a surface area of 400–1000 m^2/g. The ionic liquids (ILs) employed were 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI[BF_4], Fluka) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI[TFSI], Merck), which were used as received. The chemical structures of these compounds 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 of which were used as received.

2.2. Preparation of the actuator films [8]

The configuration of the $IrO_2{\cdot}2H_2O$/VGCF actuator is illustrated in Fig. 1. The $IrO_2{\cdot}2H_2O$/VGCF electrode layer was composed