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# High-performance graphene oxide/vapor-grown carbon fiber composite polymer actuator

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ABSTRACT

The electrochemical and electromechanical properties of poly(vinylidene fluoride-*co*-hexafluoropropylene)-based actuators using graphene oxide (GO) or graphene (G)/vapor grown carbon fiber (VGCF)/ionic liquid (IL) composite gel electrodes formed are compared with those of actuators using only GO, only G, and only SWCNT.

We compare the results with previous results on actuators with electrodes based on single-wall carbon nano-tubes (SWCNTs). In the frequency range 0.005–10 Hz, the GO/VGCF/IL and G/VGCF/IL actuators exhibit higher strains than actuators fabricated without VGCF. For the GO/VGCF/IL actuators, the maximum strain is greater than for actuators made with only GO or only VGCF. The maximum strain for the GO/VGCF/EMI[$BF_4$] actuators is 56% greater than that for an SWCNT-based actuator (GO:VGCF ratio of 7:1)—sufficient for possible practical applications. The maximum generated stress obtained for the GO/VGCF/EMI[TFSI] actuators is 10% greater than that for an SWCNT-based actuator. The maximum generated stresses for GO/VGCF/IL and G/VGCF/IL actuators are greater than those for actuators made with only GO or only G. For a limited number of GO:VGCF and G:VGCF ratios, an electrochemical kinetic model, similar to that used for SWCNT-based actuators, successfully predicts the frequency dependence of the displacement response for GO/VGCF and G/VGCF actuators.

These results suggest that flexible, robust films enabled by the synergistic effect obtained by combining graphene and VGCFs can have significant potential as actuator materials for wearable and energy-conversion devices.



## 1. Introduction

The recent discovery of nanoscale carbonaceous materials such as graphene, carbon nanotubes (CNT), carbon nanofibers (CNF), and fullerenes and their remarkable mechanical, electrochemical, piezoresistive and other physical properties has opened the possibility for developing a new class of "smart nanomaterials." Graphene (G), the basic building block of most carbonaceous nanomaterials, is an intriguing 2D flat material of monolayer carbon atoms whose distinct properties make it very promising for applications such as lithium ion batteries, hydrogen storage [1], sensors [2], and a reinforcing filler in high-performance polymer composites [3–5].

Graphene oxide (GO) is an oxidized form of graphene in which oxygen or oxygen-containing groups are bonded to the graphene sheet. It is generally obtained by exfoliation of graphite oxide and contains a wide range of oxygen functional groups, such as hydroxyl and epoxy groups, on the basal plane and carboxylic acid groups at the edges, which make the GO hydrophilic [6,7]. "Paper-like" materials composed of stacked GO platelets, produced by simple filtration of an aqueous GO suspension, have exhibited good mechanical properties, with a modulus of approximately 40 GPa and a fracture strength of approximately 130 MPa [8]. Chemical modification of this GO paper with divalent ions can enhance its mechanical properties beyond these values [9].

For producing mechanical actuators, the use of two different building blocks to fabricate asymmetric materials has proved to be a useful approach [10]. For example, bilayer "paper" samples comprising a layer of crisscrossed multiwalled CNTs (MWCNTs) and then a layer of GO platelets have been created. CNTs, important in many actuator designs, have been intensively studied for their potential use in micro/nanoelectromechanical systems (MEMS/NEMS), sensors, composites, and actuators [11–14]. Both G and CNTs are composed of the same basic structure, extended

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aromatic $sp^2$ carbon networks. This structural compatibility may provide for a stable interface between these two layers, and it seems appropriate to combine these materials as building blocks in a composite.

SWCNTs, which have been used to fabricate electrodes for actuators, are highly expensive, specially prepared compounds. In contrast, MWCNTs are relatively inexpensive and thus 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 the composite materials in which they are included. A further disadvantage of SWCNTs is their poor dispersibility. Thus, because VGCFs disperse much more readily than SWCNTs, and because they exhibit good electrical conductivity and mechanical strength, they have been applied to the fabrication of actuators. In the present study, we focus our attention on actuators fabricated with electrostatic double-layer capacitors (EDLCs), which employ electrochemically inactive substances, such as carbon particles, as electrode materials.

Therefore, a GO/VGCF/ionic liquid (IL) or G/VGCF/IL polymer actuator is expected to achieve high performance (high strain and high maximum generated stress), high capacitance (G or GO), and high Young's modulus (VGCF).

Recently, much attention has been focused on soft materials that can directly transform electrical energy into mechanical work for a wide range of applications including robotics, tactile and optical displays, prosthetic devices, medical devices, and microelectromechanical systems [15]. Low-voltage electroactive polymer actuators that can respond quickly and are softly driven are particularly useful, because they can be used as artificial muscle-like actuators for various biomedical and human affinity applications [16,17]. We have previously reported a dry actuator [18–20] that can be simply fabricated by layer-by-layer casting of "bucky-gel" [21], a gelatinous room-temperature IL containing single-walled carbon nanotubes (SWCNTs)(EDLC type). The actuator has a bimorph configuration with a polymer-supported IL electrolyte layer sandwiched between polymer-supported bucky-gel electrode layers that allow quick and long-lived operation in air at low applied voltages. We have previously reported on the dependence of the electromechanical and electrochemical properties of such actuators on the type of IL, nanocarbon, and polymer used [20–25]. In addition, in recent years, several groups have developed graphene-based actuators that respond to electrical [26–28], electrochemical [29–31], and infrared [32,33] stimuli. We have also previously reported that polymer-based actuators with electrodes fabricated from a carbon black/VGCF composite exhibit higher performance than actuators with SWCNT-based electrodes [34]. However, few studies have attempted to achieve high-performance actuators by leveraging the synergistic effects obtained from the combination of nanocarbons.

In different but related work, Liu et al. [35] 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.

Optimizing the performance of the GO/VGCF/IL or G/VGCF/IL polymer actuators requires controlling the amount of GO or G and VGCF. To compete with the performance of SWCNT-based polymer actuators, GO/VGCF-based and G/VGCF-based polymer actuators must be tailored to exhibit appropriate values of capacitance, electrical conductivity, and Young's modulus, which are important factors for attaining high strain value. Therefore, we anticipate that the synergy effect arising from the GO/VGCF and G/VGCF composite electrodes may result in polymer actuators with higher performance than polymer actuators with SWCNT-based electrodes. The key difference in this paper's approach compared

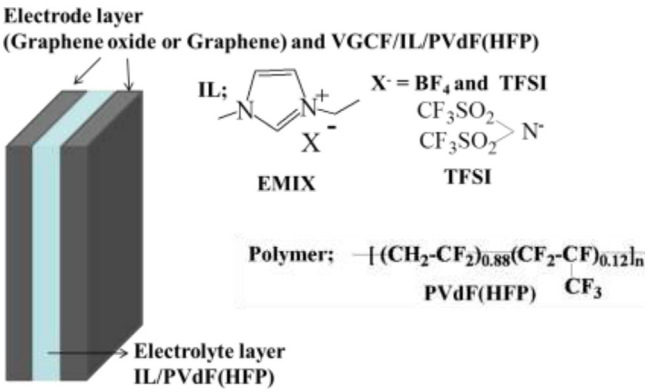


**Fig. 1.** Configuration of GO/VGCF/IL or G/VGCF/IL polymer actuator and the molecular structures of the ILs and polymer used.

to early efforts is the design to enable synergistic effects from both (G or GO) and CNTs by using graphene as a high-surface-area substrate for direct growth of CNTs to provide electron conductance and mechanical reinforcement. G or GO has been widely considered as an ideal substrate for ultrathin coating of functional materials owing to its unique structural and electrical properties, whereas the uniformly interconnected CNT network is highly conductive and porous, which is beneficial for electronic and ionic transport.

It is useful to have a model to explain the behavior of bucky-gel actuators. In a previous study [20,26,36], we investigated the voltage–current and voltage–displacement characteristics of a bucky-gel actuator by applying a triangle waveform voltage of various frequencies. To quantitatively describe the frequency dependence of the strain generated in the actuator, we proposed an electrochemical equivalent circuit model consisting of the lumped resistance and capacitance of the electrode layer and the lumped resistance of the electrolyte layer. In the present study, we discuss similar models as they apply to our fabricated actuators.

In the present work, we develop actuators that use polymer-supported GO/VGCF/IL or G/VGCF/IL composite gel electrodes (EDLC type) that exploit the synergy effects obtained by combining G or GO with VGCFs. We compare their electrochemical and electromechanical properties with those of polymer actuators that have electrodes based only on GO, G, or VGCF.

## 2. Experimental section

### 2.1. Materials

The GO (Aldrich 796034), G (STREAM STR-06-0220), and VGCF (VGCF-X, Showa Denko Co. Ltd.) were used as received. The GO was found to have 15–20 sheets and was 4–10% edge-oxidized. The G was found to have 6–8 nm thickness and 25 μm width. The VGCF had a fiber diameter of 10–15 nm, an average fiber length of 3 μm, and a surface area of 270 $m^2$/g. The ILs, 1-ethlyl-3-methylimidazolium tetrafluoroborate (EMI[$BF_4$]; Fluka) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI[TFSI]; Merck), were used as received, and their chemical structures are shown in Fig. 1. Other reagents, 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.) were used as received.

### 2.2. Preparation of the actuator film [22]

The configuration of the GO/VGCF or G/VGCF actuator is illustrated in Fig. 1. The combined GO + VGCF or G + VGCF content

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