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Carbide-derived carbon and poly-3,4-ethylenedioxythiphene composite laminate: linear and bending actuation

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ABSTRACT

Carbide-derived carbon is a well-known material for ionic electroactive systems like sensors and actuators. Typically, a gold foil or other current collector is applied on top of either side to enhance the conductivity of such laminates. Here, metal foil is replaced by an electrochemically deposited layer of poly-3,4-ethylenedioxythiophene (PEDOT). While lower in conductivity, PEDOT has the advantages of lowered risk of delamination and being electro-chemo-mechanically active itself. Such laminates were tested in both linear actuation mode in lithium bis(trifluoromethane) sulfonamide propylene carbonate solution (LiTFSI-PC) under isotonic and isometric electro-chemo-mechanical deformation measurements (ECMD), and in bending mode in air using a room-temperature ionic liquid as the electrolyte. The exchanged charge as well as the actuation response of the laminate was dominated by the PEDOT layer, overriding even the actuation direction of the carbon-based layers. The stress of all investigated samples was found in similar range of 30 kPa. The materials were characterized by scanning electron microscopy (SEM), FTIR and energy-dispersive X-Ray spectroscopy (EDX).

1. Introduction

Conducting polymers (CP) in combination with carbon based materials have been investigated in view of applications such as electrochemical capacitors [1,2] electrodes for batteries [3], energy storage [4], sensors [5] and actuators [6,7]. The main reason to combine conducting polymers with carbon particles relies on the beneficial properties of the carbon material such as enhanced charging/discharging capacitance [8] and electronic conductivity (especially in case of carbon nanotubes [9]). Carbide-derived carbon (CDC) based materials have shown linear actuation properties as free-standing films in an electrolyte [10] or bending actuation in trilayer design [11], caused by the volume effects accompanying the charging of the electric double layer (Non-Faradaic actuators) [12]. There are two possible procedures for making composites of CDC materials with conducting polymers: the simplest is to electrodeposit conducting polymers on a layer of CDC, either freestanding or coated on another material [10], alternatively CDC particles can be embedded into the film from the electrolyte solution [6,13]. The strain achievable for CDC free-standing films consisting of CDC particles and a polymer binder in electrolyte is rather small, in range of 0.5% [10]. A main drawback of CDC based actuators especially in bending displacement of trilayers is the back relaxation that takes place at low frequencies [14] and is influenced by high humidity [15]. The main reason to combine CDC and conducting polymer material in trilayer design relates to the rather brittle and inherently asymmetric properties of free standing CP films in general, which leads in most cases to creep effects [16,17]. Recent research of CP deposited on CDC material showed no creep after 100 cycles, while polypyrrole (PPy) free-standing films themselves showed creep [10].

While PPy composites with CDC have been shown to possess several advantageous properties, little work has been done on PEDOT – CDC composites. In this work, we electropolymerize PEDOT on CDC-trilayers (CDC with binder on fiber glass reinforced PVdF (HFP) membrane) and investigate their combined linear and bending actuation properties. PEDOT free standing films and CDC-trilayers without PEDOT were used as reference systems.

PEDOT has some advantages over PPy, namely higher electrochemical stability and higher electronic conductivity [18]. There have been few studies of actuators based on PEDOT free-standing films, maximum strain of 3% in organic electrolyte with mainly cation-driven actuation [19] has been demonstrated.

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2. Material and methods

2.1. Materials

1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMImTFS, ≥98%) and *N,N*-dimethylacetamide (DMAc, ≥99.5%), 4-methyl-2-pentanone (MP, 99%) were obtained from Fluka and used as received. Bis (trifluoromethane) sulfonamide lithium salt (LiTFSI, 99%), propylene carbonate (PC, 99%), tetrabutylammonium trifluoromethanesulfonate ($TBACF_3SO_3$, 99%), were obtained from Sigma-Aldrich and used as supplied. Ethylene dioxythiophene (EDOT, 99%) was distilled and stored under nitrogen at −20 °C prior to use. Amorphous titanium carbide (TiC) derived carbon (CDC TiC-800) was made by Skeleton Technologies Ltd from TiC precursor powder by chlorination at 800 °C. Poly(vinylidene-fluoride-co-hexafluoropropene) (PVdF-HFP) Kynar Flex TRM 2801 from Arkema Chemicals Inc. was used as received. Glass-fiber fabric (18 g m^{-2}) was purchased from Storm RC World.

2.2. Actuator fabrication

A solution containing PVdF(HFP) and EMImTFS in propylene carbonate: 4-methyl-2-pentanone (1:10) mixture was brushed on the glass-fiber fabric to make a membrane for the actuator. Using an airbrush, the formed membrane was covered on both sides with a suspension that included solution of PVdF(HFP) in DMAc mixed together with suspension of TiC-CDC and EMImTFS in DMAc. The CDC layer deposited on each side of the glass fiber reinforced membrane had a thickness 39 µm (weight of CDC material: 2.38 mg). Glass fiber-CDC-TL (CDC-TL) was applied as the working electrode for the electropolymerization (Scheme 1), with PEDOT deposited galvanostatically (0.1 mA cm^{-2}. 40,000 s, −20 °C) from a solution containing 0.1 M EDOT, 0.1 M $TBACF_3SO_3$, in propylene carbonate using a two-electrode cell with a stainless steel mesh as the counter electrode. The CDC-PEDOT-TL had a total thickness of 158 ± 12 µm with PEDOT layers on each side in range of 25 ± 2 µm. Under the same conditions, but using stainless steel working electrode, PEDOT free standing films (PEDOT-fs) were deposited. The thickness of freestanding PEDOT films was in range of 38 ± 1.5 µm. From each trilayer system and PEDOT-fs films, 3 samples were fabricated and measured separately. The actuators were stored in 0.1 M $TBACF_3SO_3$ PC solution.

2.3. ECMD linear actuation

The PEDOT-fs, CDC-TL and CDC-PEDOT-TL samples were fixed on the holder connected over gold wires from both sides as working electrode while the other end was connected over a clamp that was connected with the force sensor (TRI202PAD, Panlab) of the in-house linear muscle analyzer set up [20] (Scheme S1). The actuation solution was 0.2 M LiTFSI in PC solution. Different electrochemical programs (controlled by PG 581 potentiostat) were applied to measure the strain (isotonic ECMD, constant force of 4.4 mN) and stress change (isometric ECMD, constant length of 1 mm) of the samples: cyclic voltammetry (scan rate 5 mV s^{-1}), square wave potential step measurements at applied frequencies 0.0025 Hz to 0.1 Hz in potential range 1 V to −0.8 V. To calculate the diffusion coefficients Equations (1) and (2) were applied [21]:

$$\ln\left[1-\frac{Q}{Q_t}\right] = -bt \tag{1}$$

$$D = \frac{b * h^2}{2} \tag{2}$$

where the total charge Q_t during the time t was determined from the chronoamperometric measurements, and Q is the charge consumed at time t. The values for Q, Q_t can be obtained by integration from the current density - time curves. Plotting $\ln[1-Q/Q_t]$ against time t allows to determine the slope b. From Eq. (2), the diffusion coefficient D can be calculated using the slope b and the thickness h of the samples.

2.4. Bending displacement

CDC-TL and CDC-PEDOT-TL with dimensions of 4 cm × 1 cm were immersed in EMImTFSI. Strain measurements were carried out using an in-house setup consisting of a National Instruments PCI-6036E analogue input DAQ and a laser displacement meter LK-G82/LK-G3001 P (Keyence). The actuators were mounted side-ways between flat gold contacts before a mirrored logarithmic sweep sine signal (0.0025–0.1 Hz, 1 V to −0.8 V) was applied to obtain the frequency response. Strain measurements were carried out at the applied frequencies ranging from 0.0025 Hz to 0.1 Hz in a potential range of 1 V to −0.8 V. The displacement was measured at a 1.5 cm distance from the contacts. The strain difference between the electrodes was calculated from the displacement signal using Eq. (3) [22]:

$$\varepsilon = \frac{2 * d * h}{L^2 + d^2} * 100\% \tag{3}$$

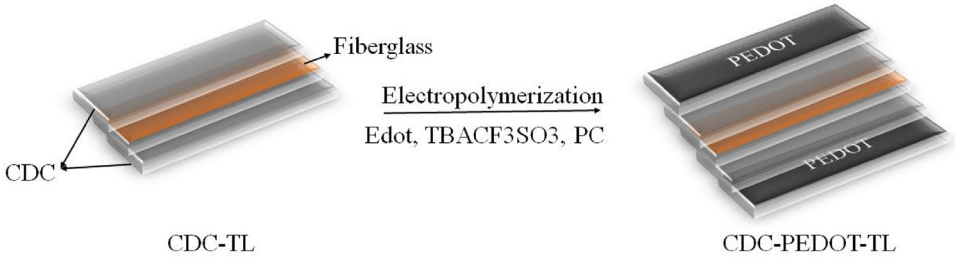
where ε is the strain difference, d is half of the peak-to-peak displacement, h is the thickness of the actuator, and L is the measurement distance from the fixed input contacts.

2.5. Characterization

The samples were characterized with Fourier transform infrared (FTIR) spectroscopy (2500–500 cm^{-1}, Bruker Alpha with Platinum ATR), Scanning electron microscopy coupled with energy dispersive X-ray (EDX) spectrometry (Helios NanoLab 600, FEI). The conductivity of the samples was determined by four-point probe method with a surface resistivity meter (Guardian SRM) measuring the sheet conductivity σ_S following Eq. (4):

$$\sigma_S = \frac{1}{R_s * h} \tag{4}$$

where R_S is the sheet resistance, and h is the thickness of the electrode.



Scheme 1. CDC-TL as working electrode is applied in electropolymerization forming CDC-PEDOT-TL devices.