



## Polypyrrole/carbide-derived carbon composite in organic electrolyte: Characterization as a linear actuator

Zane Zondaka<sup>a</sup>, Madis Harjo<sup>a</sup>, Mahdi Safaei Khorram<sup>b</sup>, Pejman Rasti<sup>c</sup>, Tarmo Tamm<sup>a</sup>, Rudolf Kiefer<sup>d,\*</sup>

<sup>a</sup> Intelligent Materials and Systems Lab, Institute of Technology, University of Tartu, Nooruse 1, 50411 Tartu, Estonia

<sup>b</sup> State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehuajie, Guangzhou 510640, China

<sup>c</sup> INRA, UMR 1345 Institute de Recherche en Horticulture et Semences (IRHS), Université d'Angers, F49071 Beaucauzé, France

<sup>d</sup> Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam

### ARTICLE INFO

#### Keywords:

PPy/CDC  
Phosphotungstic acid  
Linear actuators  
Organic electrolyte  
FTIR

### ABSTRACT

Polypyrrole (PPy) doped with dodecylbenzenesulphonate (DBS) (PPy/DBS) was polymerized with the addition of phosphotungstic acid (PTA), thus, incorporating multicharged phosphotungstate anions (PT) to give PPy/DBS-PT films. With carbide-derived carbon (CDC) particles included, the obtained films contained CDC-PT, DBS and PT anions forming PPy/DBS-CDC-PT (PPy/CDC). Our goal was to test the applicability of the material for actuation in an organic electrolyte. The material properties of PPy/CDC films, such as conductivity, charging/discharging and actuation as strain and strain rate were significantly changed in comparison to PPy/DBS-PT films. FTIR (Fourier transform infrared) and EDX (energy dispersive X-ray) spectroscopy revealed that CDC-PT is incorporated in the PPy films and the SEM (scanning electron microscopy) images showed a more porous film with CDC particles packed into PPy. Electro-chemo-mechanical deformation studies (ECMD) revealed that PPy/CDC films had anion-dominated actuation resulting in nearly 6 times higher strain, 2 times higher force, higher strain rates, and 7 times higher conductivity than PPy/DBS-PT films, which had mixed ion transport and rather poor strain and stress behavior. Thus, only one of the two materials - PPy/CDC – could have some practical use in this type of electrolyte solutions.

### 1. Introduction

During the last decades, a lot of research has been dedicated to find suitable applications for conducting polymer actuators including micro-machining [1,2], soft robots [3], pumps [4] and biomedical applications [5], including tissue engineering [6]. Conducting polymers (CP) have been of great interest due to their low-voltage operation and high strain and stress, reaching 20–30% [7] and 20 MPa [8], respectively. Besides the optimization of strain and stress in recent years, research has been focused on creating conducting CP including those with nanoparticles [9], carbon aerogels [10], carbon nanotubes [11] and carbide derived carbon (CDC) [12,13] with the goal to achieve novel properties for actuators [13] or super capacitors [14], increased stability, and many more. Perhaps the most common linear conducting polymer actuator is the electropolymerized PPy/DBS, where the counter-anion DBS<sup>-</sup> is virtually immobile, leading to cation (C<sup>+</sup>) and solvent (S) incorporation during reduction [15]. As a consequence, the polymer swells upon reduction and contracts upon oxidation. Such

actuators are called cation-driven.

Recent research [13] of CDC solubilized by multicharged phosphotungstate anions (PT in combination with PPy/DBS) has revealed that in aqueous electrolyte the elastic modulus of the material changed, and therefore, the strain increased in comparison to pristine PPy/DBS. The addition of PTA in PPy/DBS did show that the resulting PPy/DBS-PT film [16] exhibited higher charging/discharging properties, and with a more compact film, 3 times higher strain in aqueous electrolyte as compared to pristine PPy/DBS was demonstrated. Additionally it was shown that a typical cation-driven actuator (PPy/DBS) can be “trained” to become anion active, which is an effect from the electrolyte and the solvent [17]. However, the mechanical properties of the films in aqueous solution left room for improvement, as PT incorporation tends to make the films rather brittle. Overall, the performance as well as the stability of CP actuators depends on and can be controlled via many different parameters, including polymerization techniques [18], electrolyte [19], temperature [20], overoxidation [21] and over-reduction [22].

\* Corresponding author.

E-mail address: [rudolf.kiefer@tdt.edu.vn](mailto:rudolf.kiefer@tdt.edu.vn) (R. Kiefer).

<https://doi.org/10.1016/j.reactfunctpolym.2018.08.020>

Received 26 September 2017; Received in revised form 21 August 2018; Accepted 30 August 2018

Available online 31 August 2018

1381-5148/ © 2018 Elsevier B.V. All rights reserved.

It has been discovered previously that by changing the solvent of the actuation solution of PPy/DBS linear [23] or bending [24] actuators, the actuation mechanism (and hence, direction) can be changed from cation to anion driven or *vice versa*. Moreover, due to fast evaporation and narrow electrochemical window, aqueous solutions are not always the preferred choice. For controlling CP actuators or using them as mechanical sensors, it is of paramount importance to know the mobile species under all conditions and to be able to tune the properties to establish as pure as possible cation- or anion driving. CP materials are known to behave rather differently in organic and aqueous electrolyte solutions, as shown for other systems and applications [25]. Therefore, it is important to understand the role of the electrolyte solution (including solvent) on the behavior of actuator materials.

Here we investigated the actuation properties of PPy/CDC in comparison to PPy/DBS-PT films operated in organic electrolyte. Isometric and isotonic electro-chemo-mechanical deformation (ECMD) experiments were performed under different electrochemical driving regimes (cyclic voltammetric and chronoamperometric). According to the electrochemically stimulated conformational relaxation (ESCR) model, the applied potential range was kept in the so called “steady state” (charging/discharging in balance [26]) to avoid irreversible processes. Therefore, as the charging/discharging was in balance, the obtained results of the different films can be qualitative compared, as seen previously [24]. The characterization of the PPy/CDC and PPy/DBS-PT films were made with SEM, FTIR, and EDX spectroscopy.

## 2. Material and methods

### 2.1. Materials

Amorphous titanium carbide derived carbon (TiC-800, with narrow pore size distribution, specific surface area SBET of  $1470 \text{ m}^2 \text{ g}^{-1}$ , total volume of pores  $0.71 \text{ cm}^3 \text{ g}^{-1}$ , volume of micropores  $0.59 \text{ cm}^3 \text{ g}^{-1}$ , and average pore size of  $0.97 \text{ nm}$ ) was purchased from Skeleton Technologies Ltd. Solvents: propylene carbonate (PC, 99%), ethylene glycol (EG, 99.8%) were purchased from Fluka. Pyrrole (Py,  $\geq 98\%$ , Sigma Aldrich) was vacuum-distilled prior use and stored at low temperature. The polyoxometalate (POM) used for film synthesis was phosphotungstic acid ( $\text{PW}_{12}\text{O}_{40}^{3-}$ ) hydrate (Sigma-Aldrich). Lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI, 99.95%) was bought from Solvionic. Sodium dodecylbenzene-sulfonate (NaDBS, technical grade) was acquired from Sigma Aldrich. MilliQ+ water was used for aqueous solutions.

### 2.2. Polymerization of PPy/DBS-PT and PPy/CDC

PPy/DBS-PT was polymerized galvanostatically at  $0.1 \text{ mA cm}^{-2}$  ( $40,000 \text{ s}$  at  $-20^\circ \text{C}$ ) in a 2-electrode cell with a stainless steel mesh counter electrode and stainless steel sheet working electrode ( $18 \text{ cm}^2$ ) in a  $0.1 \text{ M NaDBS}$ ,  $0.1 \text{ M Py}$ ,  $0.1 \text{ M PTA}$  in EG/Milli-Q+ (1:1) mixture. PPy/DBS-CDC-PT (in short PPy/CDC) films were made in the same way with the addition of 1% CDC. Both solutions were sonicated for 30 min in an ice bath and stored in fridge prior to the electrochemical polymerization. After polymerization, the deposited films were removed from the stainless steel electrode, washed in ethanol to remove residues of pyrrole and then in water to remove excess of NaDBS. Films were stored in  $0.2 \text{ M LiTFSI-PC}$  solution. Film thickness of PPy/DBS-PT was in range of  $19 \mu\text{m}$  and that of PPy/CDC in range of  $25 \mu\text{m}$ .

### 2.3. Isometric and isotonic ECMD measurements

PPy/DBS-PT and PPy/CDC films were cut into strips of  $1.5 \text{ cm}$  length and  $0.1$  width. The films were fixed on the force sensor (TRI202PAD, Panlab) with a fixed arm with gold contacts that served as a working electrode in the linear muscle analyzer setup [23]. Platinum sheet was used as the counter electrode in the measurements cell with

$0.2 \text{ M LiTFSI-PC}$  electrolyte. The in-house ECMD measurement setup is different from commercial devices because it has a movable force sensor instead of a stationary one. This special set-up can determine the mass (mg) required to change the film per  $1 \mu\text{m}$  in length (k factor  $\text{mg}/\mu\text{m}$ ). The k factor is adapted in the in-house software to calculate the corresponding length changes of the films. For the PPy/DBS-PT films in LiTFSI-PC electrolyte, the k factor was  $311 \text{ mg}/\mu\text{m}$  and for PPy/CDC -  $73 \text{ mg}/\mu\text{m}$ . The initial length of the films between the clamps was  $1 \text{ mm}$ . The length changes (isotonic, constant force of  $2.5 \text{ mN}$ ) and force change (isometric, constant length  $1 \text{ mm}$ ) and the applied electrical signal were measured in real time with the in-house software. Within a voltage range of  $1 \text{ V}$  to  $-0.55 \text{ V}$  for PPy/CDC and  $0.7 \text{ V}$  to  $-0.55 \text{ V}$  for PPy/DBS-PT, steady state conditions [26] (charging/discharging in balance) were achieved. Therefore, the different potential ranges still allow comparison. The cyclic voltammetry (scan rate  $5 \text{ mV s}^{-1}$ ) and the square step measurements (frequencies  $0.0025 \text{ Hz}$ ,  $0.005 \text{ Hz}$ ,  $0.01 \text{ Hz}$ ,  $0.025 \text{ Hz}$ ,  $0.05 \text{ Hz}$  and  $0.1 \text{ Hz}$ ) were performed.

### 2.4. Characterization of the films (SEM, EDX, FTIR, and conductivity)

PPy/DBS-PT and PPy/CDC films were analyzed with ATR-FTIR (Alpha, Bruker). SEM (Helios NanoLab 600, FEI) and EDX analysis were performed on the cross-sections on the unactuated films to identify the ions inside. Liquid nitrogen fracturing was used to prepare the cross-section of films. The conductivity of the films was determined by four-point probe method with a Surface Resistivity Meter (Guardian SRM).

## 3. Results and discussions

### 3.1. Characterization of PPy/DBS-PT and PPy/CDC films

#### 3.1.1. Electrodeposition, SEM images, EDX spectroscopy and conductivities

Fig. 1a presents the polymerization curves of PPy/DBS-PT and PPy/CDC. The SEM images (surface and cross section) of PPy/DBS-PT and PPy/CDC films in oxidized state ( $0.8 \text{ V}$ ,  $5 \text{ min}$ ) after some storage time ( $10 \text{ days}$ ) in LiTFSI-PC electrolyte are shown in Fig. 1b and c respectively. The corresponding EDX spectra are presented in Fig. 1d.

It is well known that PTA functions as catalyst [27] during electropolymerization, as can be seen from the polymerization curves (Fig. 1a), where the steady state potentials for PPy/CDC and PPy/DBS-PT were at  $1.58 \text{ V}$  and in  $0.65 \text{ V}$ , respectively. The much lower potential of galvanostatic synthesis for PPy/BBS-PT led to a more compact film with smoother morphology (Fig. 1b) in comparison to PPy/CDC, where the rough surface morphology is, obviously, formed from enclosed CDC particles surrounded by PPy [12,13] (Fig. 1c). While most of the PPy-covered CDC particles are visible on the surface, the cross section also shows a porous structure. However, the material itself around the pores appears denser, in line with previous research [13]. The conductivity of PPy/CDC was in range of  $7.7 \pm 0.53 \text{ S cm}^{-1}$  and that of PPy/DBS-PT  $1.5 \pm 0.11 \text{ S cm}^{-1}$ . The EDX spectra (Fig. 1d) showed a sharp dominant tungsten peak at  $1.75 \text{ eV}$  for both PPy/DBS-PT and PPy/CDC, with a phosphorus peak at  $2.04 \text{ eV}$ , whereas the concentration of PTA in PPy/DBS was much higher. The sulfur peak at  $2.32 \text{ eV}$  and the oxygen peak at  $0.52$  were in similar range showing that about the same amount of DBS was incorporated in the two PPy films; the signal of sodium at  $1.04 \text{ eV}$  was residue from the polymerization process. The carbon peak at  $0.26 \text{ eV}$  for PPy/CDC and PPy/DBS-PT was used for normalization of intensities.

#### 3.1.2. FTIR spectra of PPy/DBS-PT and PPy/CDC films

The peaks at  $1521 \text{ cm}^{-1}$  and  $1445 \text{ cm}^{-1}$  (Fig. 2) belong to the asymmetric and symmetric  $\text{C}=\text{C}/\text{C}-\text{C}$  PPy ring breathing vibrations [28]. The peak at  $1281 \text{ cm}^{-1}$  is attributed to  $\text{C}-\text{N}$  vibrations [29]. Peaks at  $887 \text{ cm}^{-1}$  and  $968 \text{ cm}^{-1}$  ( $\text{C}-\text{H}$  out of plane vibration [30]) in both spectra describe the doping state of PPy [29]. The existence of PT ions in PPy/CDC and PPy/DBS-PT can be confirmed by the  $1074 \text{ cm}^{-1}$

Download English Version:

<https://daneshyari.com/en/article/11006447>

Download Persian Version:

<https://daneshyari.com/article/11006447>

[Daneshyari.com](https://daneshyari.com)