Novel actuators based on polypyrrole/carbide-derived carbon hybrid materials

Janno Torop, Alvo Aabloo and Edwin Jager

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Janno Torop, Alvo Aabloo and Edwin Jager, Novel actuators based on polypyrrole/carbide-derived carbon hybrid materials, 2014, Carbon, (80), 387-395.

<http://dx.doi.org/10.1016/j.carbon.2014.08.078>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-112604>

Novel actuators based on polypyrrole/carbide-derived carbon hybrid materials

Janno Torop¹, Alvo Aabloo², Edwin W.H. Jager^{1,*}

¹ Linköping University, Dept. of Physics, Chemistry and Biology, Biosensors and Bioelectronics Centre, 58183 Linköping, Sweden

² University of Tartu, Institute of Technology, Intelligent Materials and Systems Lab, Nooruse 1, 50411, Tartu, Estonia

Abstract

Polypyrrole (PPy) hybrid films incorporated with porous carbide-derived carbon (CDC) particles are synthesized through a novel one-step electrochemical synthesis process that provides a simple and efficient alternative for current tape-casting and inkjet printing technologies to make conducting polymer-CDC-based electroactive composites. The resulting porous, robust and electrically conductive hybrid layer was used to fabricate electroactive polymer actuators both as perpendicularly expanding actuators and as bending trilayer actuators. Raman and FTIR spectroscopy confirm successful incorporation of CDC in the PPy matrix. Cyclic voltammograms confirm slightly higher charging/discharging currents of the PPyCDC hybrid. This indicates the successful coupling of CDC in order to increase electric double-layer capacitance in the hybrid films. The maximum steady state electromechanical diametrical strain is 13% for hybrid material which is in the same order of magnitude as for PPy and 10x more than previously reported CDC films made with non-conducting polymer binders. Furthermore, the expanding actuators made from hybrid material are more efficient than non-modified PPy actuators, having doubled the amount of swelling per injected charge.

* Corresponding author. Phone: +46 13 281246 E-mail: edwin.jager@liu.se

This improvement is very important since the low energy efficiency is a major shortcoming for ionic electroactive polymers. The high pseudocapacitance makes these new hybrid materials also interesting for energy storage applications.

1. Introduction

Materials that can transform electrical energy into a mechanical force are extremely useful as actuators for a wide span of applications ranging from robotics to manipulation of single cells [1–4]. So called ionic electroactive polymers (EAPs), comprising conducting polymers (CPs), ionic polymer-metal composites (IPMCs), responsive gels, and carbonaceous materials such as carbon nanotubes, are specifically interesting due to their low driving potentials, but their low energy efficiency is still a major shortcoming. CPs such as polyaniline, polypyrrole, and poly(3,4-ethylene-dioxythiophene) have been widely studied as active material for actuators especially for use in biomedical applications [5–8]. The volume change of CPs is caused by insertion and extraction of ions and solvent from the electrolyte the when material is electrochemically switched between the oxidized and reduced states [5,9].

The volume change of EAPs based on porous carbons such as CDC on the other hand is caused by the intercalation of ions due to the electric double layer charging of the electrodes [10,11]. Generally it is understood that high electric double-layer capacitance of porous carbon is related to high surface area and precise pore size distribution according to electrolyte used [12,13]. CDC synthesis allows formation of highly porous carbon materials with good mechanical properties. Microstructure, pore size, pore shape, and surface termination of nanoporous CDC can be precisely controlled by changing the synthesis parameters and the composition and structure of the initial carbide precursor [13]. As such, the process allows optimization of nanoporous CDC for various applications [11,14].

Charging of electrical double-layers in polymer-supported carbon matrixes made of highly porous CDC is highly efficient and could potentially be used to boost the CP charge injection. Here we describe hybrid materials combined with highly porous carbon and CPs as the actuating material to acquire stable and efficient actuation and to enhance the performance of ionic EAPs. We expect the addition of CDC nanoparticles having a large specific surface area in the CP matrix to lead to an increased charge injection as well as to an enhanced overall stability and energy efficiency of CP actuators.

CPs have been combined with different carbon materials prior to, but either synthesized onto or into the carbon electrodes or *vice versa* as CP electrodes with carbonaceous coatings, and not as a single hybrid material. They have been characterized for electromechanical actuator applications, [15–18] as well as electrode materials for electrochemical capacitors specially due to the high electrical conductivity, high pseudocapacitance, and relatively low cost [19,20]. However, the considerable volume change of the electrode films caused by the intercalation and depletion of ions during the reversible charge and discharge process resulted in a poor mechanical stability in advanced battery and supercapacitor applications [18,21,22]. Aforementioned works do not describe an *in situ* co-polymerization methodology of conducting polymer and highly porous CDC. Here, we present for the first time a hybrid PPyCDC material, where the CDC particles are embedded in the conducting polymer matrix. We describe a novel direct co-electropolymerization method of polypyrrole and carbide-derived carbon composite materials in presence of dodecylbenzenesulphonate dopant on plain gold films and onto Au wire working electrodes in order to develop energy efficient and electromechanically active hybrid layers. The hybrid composite films are expected to bridge highly porous carbide-derived carbon materials and polypyrrole. CDC store electric energy physically and efficiently by ion adsorption, while

PPy has attracted intense interest due to significantly higher electromechanical strain and higher specific capacitance (pseudocapacitance) than carbon materials.

2. Experimental section and methods

2.1. Preparation of PPy(DBS)CDC hybrid films

Pyrrole was acquired from Sigma Aldrich and vacuum-distilled prior to use. Sodium dodecylbenzenesulfonate (NaDBS) was received from TCI Europe (Purity > 95%), and CDC was received from Skeleton Technologies Ltd [23]. PPyCDC hybrid films were prepared from a CDC/Pyrrole precursor suspension using electrochemical synthesis routes. Gold coated silicon wafers were used as working electrodes and Au coated Si wafers or Pt wire were selected as counter electrode. For the diametrical strain measurements a Au wire working electrode (AuWE) was made using high purity gold wire (0.5 mm diameter) obtained from Goodfellow (Figure 1A and 1B).

Figure 1. Illustration of experimental set-up for hybrid material synthesis (A), diametrical strain measurement with a laser scanning micrometer (LSM) (B), and strain measurement of triple layer actuator device in the bending mode (C).

Electrochemical synthesis of electroactive PPy(DBS) and PPy(DBS)CDC composite films were carried out in the three electrode configuration containing dispersed CDC particles ($\sim 1 \text{ gL}^{-1}$), Py (0.1 M) and NaDBS (0.1 M) dissolved in MilliQ filtered water ($18.2 \text{ M}\Omega$). Chronoamperometric synthesis routes at constant potentials and with cyclic voltammetry (CV) pulses were employed to generate the PPy(DBS) and PPy(DBS)CDC hybrid films using an Ivium Compact.e potentiostat.

For bending the beam measurements, we fabricated so-called trilayer actuators that can operate in air. First, a 20–30 nm layer of Au was sputtered on both sides of a dry Millipore Immobilon-P PVDF membrane (pore size $0.45 \text{ }\mu\text{m}$, area $5 \times 5 \text{ cm}^2$) using a Vacutec PlasmaSystems sputter at a pressure of 4.6 mTorr, $36.6 \text{ cm}^3/\text{min}$ Ar flow and a sputter rate of 10 nm/min. Thereafter, PPy or PPyCDC hybrid material was electrosynthesized simultaneously on the on both sides of the Au coated PVDF film at a constant potential of 0.7 V for 5 h in a solution of 0.1 M LiTFSI, 0.1 M Pyrrole in propylene carbonate (PC) with 1% H_2O . In order to prepare the PPy(TFSI)CDC hybrids a CDC powder with concentration 1

mg/ml was added to the electropolymerization solution before polymerization. Electropolymerized actuators were then rinsed with small amount of PC and stabilized in 0.1 M LiTFSI for 12 h. Finally, 0.5 x 2.5 cm² sized films were sliced with scalpel for bending beam experiments. All potentials presented are given vs. a Ag/AgCl (3 M KCl) reference electrode.

2.2. Characterisation

All electrochemical characterisations of the EAP films also all expanding mode measurements were performed using a three-electrode system consisting of a KCl saturated Ag/AgCl reference electrode, a Pt wire or Au evaporated Si counter electrode. Depending on the experiment chosen, Au evaporated on Si (for electrochemical characterization) or Au-wire electrodes (for electromechanical characterization), were coated in advance with PPy(DBS) or PPy(DBS)CDC films. Charge induced swelling of the films was recorded by Mitutoyo LSM-501H contactless Laser Scan Micrometer (LSM), controlled by a display unit (Mitutoyo LSM-6100) and the output signal was fed to the potentiostat. Schema of LSM for *in situ* thickness measurements is given in Figure 1A and 1B, and detailed description of the measurement procedure can be found in Melling *et al.* [24]. Electrochemical impedance spectroscopy (EIS) characterization was performed with an Ivium CompactStat.e electrochemical workstation. The impedance spectra were recorded at 0V bias potentials in the frequency range of 10 mHz–10 kHz, using an ac voltage of 5 mV amplitude. Particle size distribution and zeta potential in electropolymerization mixtures were analyzed with a Malvern Zetasizer. Fourier transform infrared (FTIR) spectroscopic measurements were performed on a PerkinElmer Spectrum GX FTIR. Raman measurements were carried out with Renishaw inVia microRaman using 514 nm laser excitation line. The Scanning Electron Microscopy (SEM) micrographs were taken using a Leo 1550 Gemini SEM operating at 5.02 keV. The bending of trilayer actuators was measured by a laser displacement sensor using a

control unit (LK-KD500, Keyence) with a 30 mm-range laser head (LK-G82, Keyence), and Simulink (The MathWorks, Inc) software was used to compile and run the controllers (Figure 1C) [25].

3. Results and Discussion

3.1 Synthesis

The electrochemical deposition of PPy(DBS) and PPy(DBS)CDC hybrids and their dual actuation modes are illustrated in Figure 1. Depending on the geometry used, the electrodeposited films demonstrate the ability to act as swelling cylinders (Figure 1B) or as electroactive bending beams (Figure 1C). Before the electrodeposition the synthesis solutions for PPy(DBS) and PPy(DBS)CDC films were analyzed by the Zetasizer instrument to measure particle size distribution and zeta potentials in solution. Figure 2 shows the size distribution of the two different synthesis solutions containing pyrrole monomers and NaDBS with or without the CDC particles. The peak around 200 nm refers to the pyrrole micelles.[26] The size distribution analysis of pyrrole, NaDBS and CDC mixture clearly shows the presence of the CDC particles in the solution with a size distribution of 0.5 to 1.5 μm and having a peak at 0.8 μm . The disappearance of first peak (~ 4 nm) which is present in pyrrole NaDBS solution is due to agglomeration of the small pyrrole-DBS micelles to CDC particles to form larger micelle structures. The zeta potentials of pyrrole, NaDBS and pyrrole, NaDBS, CDC were -24 mV and -37 mV, respectively, confirming the increased stability of pyrrole-DBS-CDC micelles [27]. The electrolyte solution containing the CDC particles was optically opaque and therefore direct film growth monitoring from solution via LSM method was not possible. The thickness of PPy(DBS)CDC layers was measured directly after electropolymerization.

Figure 2. Size distributions of 0.1M Py, 0.1 M NaDBS (aq) (PPy(DBS)) and 0.1 M Py, 0.1 M NaDBS, 1 mg/mL CDC (aq) (PPy(DBS)CDC) measured by the Malvern Zetasizer.

The amperometric graphs of the potentiodynamic synthesis of both materials are shown in Figure 3A. The radical polycondensation reaction of PPy(DBS) starts at the usual oxidation potential of $\sim 0.5\text{V}$, [28] however the oxidation potential of the CDC comprising solution is shifted to higher potentials. The same tendency can be seen for potentiostatic synthesis (Figure 3B). The current density, thus the reaction rate, is lower for the hybrid material compared to the pure PPy(DBS) when using the same synthesis potential of 0.7 V .

Figure 3. (A): Cyclic voltammetry electrodeposition of pure PPy(DBS) (dashed red line) and PPy(DBS)CDC hybrid composite (black solid line). Scan rate: 10 mV/s . (B) shows potentiostatic electropolymerization curves of PPy(DBS) and PPy(DBS)CDC material at $E=0.7\text{ V}$. All potential are given vs. Ag/AgCl/3 M KCl.

The electrosynthesis resulted in black polypyrrole films. In the case of pure PPy, the films were glossier, while the hybrid PPyCDC films had a more matte appearance. The surface morphology is an important parameter as the hybrid films will be used in electromechanical applications. If the relatively large CDC particles were present in hybrid films, the SEM images could easily verify presence of carbon particles in the hybrid film. Figure 4 shows a high magnification SEM images taken, demonstrating the difference in surface morphology of PPy(DBS) and PPy(DBS)CDC films. Figures 4A and 4B show the typical cauliflower-like nodular structure of PPy(DBS) films. As can be seen in Figures 4C and 4D, the PPy(DBS)CDC films had a distinctly different structure, clearly showing the embedded CDC particles in the film layer. However the nodular structure of PPy(DBS) is preserved as well, covering the embedded CDC particles. This indicates that the addition of the CDC does not have a negative effect on the PPy morphology.

Figure 4. SEM pictures of a pure PPy(DBS) film surface (A, B), and a modified PPy(DBS)CDC surface showing the carbide-derived carbon particles embedded in PPy (C, D).

The interaction between PPy and CDC in the composite was investigated using Raman spectrometry. It is known from literature that typical disordered carbons as CDC hold disorder-induced D-band associated with a double-resonance Raman process located at 1340 cm^{-1} [29,30]. The position of this band may vary, depending on the structure of the disordered carbon and the presence of impurities or functional groups. TiC-derived carbons also have G-band, located at 1590 cm^{-1} and corresponding to graphite in-plane vibrations. Figure 5A shows the Raman spectra of PPy(DBS) and PPy(DBS)CDC films. The Raman spectrum obtained for PPy(DBS) film prepared in the absence of any CDC particles is in good

agreement with literature spectra. The observed three bands at 933, 1248 and 1596 cm^{-1} indicate the presence of bipolarons, which are characteristic of highly conductive doped polypyrrole chains [31]. These spectral features are also clearly observed for the PPyCDC hybrids. As seen in Figure 5A the spectra of PPy(DBS) and PPy(DBS)CDC were almost identical and the CDC G-band is drowned in the PPy signal. However, a significantly, broad band located between 1247 cm^{-1} and 1394 cm^{-1} can be seen in PPy(DBS)CDC spectrum, including distinct peak at 1334 cm^{-1} which is contributed to the CDC D-band thus confirming the incorporation of CDC in the hybrid material. The small difference between the hybrid material and PPy spectra obtained by Raman spectroscopy can be explained by the fact that this method is a surface sensitive. The small difference in intensity of electrodeposited thin films with and without CDC is due to the fact that the carbon material is shielded by the conjugated polymer. This effect has been described for instance in PPy/graphene blends as well [32].

Figure 5. Raman (A) and FTIR (B) spectra of PPy(DBS)/CDC hybrid and PPy(DBS).

The infrared spectra (Figure 5B) provide further proof that the CDC is embedded in the PPy matrix. Compared with the pure PPy(DBS) spectrum, it is clearly observed that most

of the present peaks are shifted to the higher wavenumbers when the CDC was introduced. The shifting is probably related to interactions such as π - π stacking between PPy backbone and CDC particles. Strong peaks near 1044 cm^{-1} and 887 cm^{-1} indicate the doping state of polypyrrole and these peaks are not so acutely seen at PPy(DBS)CDC spectrum [33].

3.2 Electrochemical characterisation

The cyclic voltammetric response of PPy(DBS) and PPy(DBS)CDC films is shown in Figure 6. PPy(DBS)CDC composite electrode displayed more distorted rectangular CV, indicating an uncompensated resistance in the system due to the poor electrical conductivity. This has also been noticed in graphene-oxide/PPy [34,35]. For the PPy(DBS)CDC, the current measured during the CV is a mixture of the charging of the electrical double layer in CDC and of the redox nature of PPy(DBS). At fast scan rates ($>100\text{ mVs}^{-1}$), each of the two sets of voltammograms has a similar, distorted rectangular shape. This deviation from ideal behaviour is indicative of an uncompensated resistance in the system. At higher scan rates, the currents are correspondingly higher as well, leading to a more pronounced iR loss. At the lower scan rates the redox peaks of PPy(DBS) are clearly expressed, although they are relatively smaller in the hybrid films. The PPy(DBS) redox behaviour characteristic peaks are at their normal positions. However, in the case of PPyCDC composite the redox peaks are shifted anodically, which indicates that these films can be more easily oxidised and reduced, most probably due to the fact that the CDC incorporation results in more porous films resulting in easier ion transport and less compressed films [36]. Table 1 shows the specific capacitance, C_m (Fg⁻¹) which was calculated the basis of the mass of deposited PPy(DBS) and PPy(DBS)CDC and evaluated from the cyclic voltammetry data shown in Figure 6 using the equation $C_m = I/m(dE/dt)$, where I is the average current, dE/dt is the potential scan rate and m is the mass of electrochemically deposited active material layer.

Figure 6. CVs recorded in 0.1 M NaDBS for PPy(DBS) and PPy(CDC)DBS electrodes cycled between 0.7 V...-1 V at 10 mV/s, 20 mV/s and 100 mV scan rates. Potentials are given vs. Ag/AgCl/3 M KCl.

Table 1. Specific capacitance of PPy(DBS) and PPy(CDC)DBS electrodes calculated at different scan rate values.

Scan rate (mVs^{-1})	$C_m(\text{PPy}(\text{DBS}))$ (Fg^{-1})	$C_m(\text{PPy}(\text{DBS})\text{CDC})$ (Fg^{-1})
---------------------------------	--	--

10	125	132
20	116	122
100	94	38

Figure 7. Electrochemical impedance spectra of pure conducting polymer (PPyDBS) and hybrid material (PPy(DBS)CDC). Inset show impedance response at higher frequency range.

Figure 7 shows the Nyquist plot of both materials. The two impedance spectra lines are featured by a vertical trend at low frequencies, indicating capacitive behaviour according to the equivalent circuit theory. The inset of Figure 7 presents data collected at higher frequencies. It is seen that PPy(DBS)CDC material revealed a knee frequency, beyond which the capacitive behaviour was replaced by more inclined diffusion line, and the higher resistance due the lower conductivity of CDC particles, thus increasing the total film resistance.

3.3 Electromechanical characterisation

Using the LSM we measured the diametrical strain of PPy(DBS) and PPy(DBS)CDC hybrid material electrodeposited on Au wire (Figure 8). For both materials the expansion occurred during the cathodic wave indicating that the cation motion (including solvent) is indeed the main driving mechanism in these materials [37]. The unmodified PPy showed the typical large perpendicular volume change of PPy(DBS) reaching up to ~25 %, similar rate as showed previously in ref. [24,38]. The PPy(DBS)CDC hybrid material had a diametrical strain of 13%, which is 10 times higher than that of pure carbide-derived carbon films made with non-conducting polymer binders [39,40]. Therefore, the conducting polymer is mainly responsible for increased expansion through PPy redox behaviour. Although, the absolute displacement of the hybrid material was lower compared to the PPy(DBS), the displacement per charge was actually doubled meaning that the hybrid material based actuators were more efficient. PPy(DBS)CDC showed 1.17% volume change per 1 mC inserted charge compared to 0.6% per mC of PPy(DBS). This improvement is very important since the low energy efficiency is a major drawback for ionic EAPs [41].

Figure 8. Diametrical strain measurements describe relative dimensional change together with current and charge profiles during charging and discharging of PPy(DBS) electrode (thickness=14 μm) between 0 V and -1 V for 200s (a, b, c). Displacement, current, and charge profiles for PPy(DBS)CDC electrode (thickness= 13 μm) (c, d, e). Cylindrical film electrodes were deposited on Au wire.

Having demonstrated that the hybrid materials do have a large volume change, we constructed trilayer actuators in order to demonstrate a bending actuator. The electrolyte, 0.1 M LiTFSI in PC, was stored in the PVDF intermediate layer to allow operation in air. The PVDF, a commercial membrane used for instance in protein blotting applications, was used as passive electrolyte storage layer only and chosen for its electrolyte storage properties only. The PVDF was not poled thus it did not have any piezoelectricity. The deflection of trilayer bending actuator was reduced from 200 μm for PPy(TFSI) to 8 μm for the PPy(TFSI)CDC hybrid (Figure 9). Also, bending signal had more noise, which is mostly related to two important factors that are specific for this experimental set-up. Firstly, the bending response

of PPy(TFSI)CDC actuators is close to the detection limit of laser displacement sensor ($2\text{ }\mu\text{m}$ in this configuration). Secondly, the bending signal is affected by the roughness of PPy(TFSI)CDC actuator surface. Compared to relatively flat PPy(TFSI) samples the PPy(TFSI)CDC samples include CDC particles with peak size distribution of $0.8\text{ }\mu\text{m}$ as shown in Fig. 2, making the surface more rough resulting in an added noise on the displacement signal. We attribute the decreased displacement to the increased stiffness (Young's modulus) of the hybrid material due to the incorporation of the CDC particles and lower conductivity when the $\pm 1\text{ V}$ sinusoidal signal with 1 Hz was applied to the bending actuator. Interestingly the deflection of the hybrid trilayer actuator is similar to the deflection of corresponding pure CDC based actuators illustrating that the mechanical and electrical properties of CDC might be dominating in hybrid material based actuator and advantages of PPy are more suppressed [10].

Figure 9. Bending displacement of PPy(TFSI) and PPy(TFSI)CDC trilayer actuators, and corresponding voltage and current profiles.

The PPy(DBS)CDC hybrid material showed a slightly increased oxidative synthesis potential (Figure 3) as well as slightly reduced redox currents (Figure 6). We contribute this to the increased resistance of the hybrid material due to the insertion of the CDC nanoparticles that have lower conductivity, thus increasing the total film resistance as can be seen in Figure 7. The bending displacement (Figure 9) was reduced compared to PPy(DBS), when the CDC particles were added, being in the same range as pure CDC bending actuators. We contribute this to the dominating effect of the stiffer CDC particles compared to the low Young's modulus of the polypyrrole polymer, increasing the total actuator stiffness thus reducing the displacement. However, the volume change per inserted charge (calculated from Figure 8) nearly doubled in the hybrid material compared the unmodified PPy, which we believe is caused by the synergetic behaviour of the CDC double layer charging and the PPy redox properties.

4. Conclusion

Here we have demonstrated for the first time the synthesis and characterisation of ionic EAP hybrid materials comprising conducting polymers and nanoporous carbon. PPy(DBS)CDC composites were prepared by an in-situ synthesis of nanoporous carbide-derived carbon powder and pyrrole monomers using electrochemical polymerization. This one-step electrochemical synthesis method provides a novel, simple and efficient alternative for current tape-casting and inkjet printing technologies to make CDC-based electroactive composites. The PPy assisted as highly conductive and as electromechanically active binder increasing the maximum diametrical strain of the hybrid from 1.5% to 13 %, as compared to CDC with nonconductive polymer binders. The strain is the same order of magnitude as for

PPy(DBS). Although, the overall thickness change of hybrid material was somewhat lower compared to PPy(DBS), the PPy(DBS)CDC films demonstrated more efficient swelling per charge inserted, 1.17% volume change per mC inserted charge compared to 0.6% per mC of PPy(DBS). This improvement is very important as the low energy efficiency is still a shortcoming for ionic EAPs. In addition the hybrid layer might increase the durability, or life time, of the actuator, because electric double-layer capacitance of the new electrode is increased. Morphology analysis of hybrid films showed effective incorporation of PPy and CDC and clarified a remarkable increase in porosity. The increased surface roughness may be of interest for bioelectronics applications such as the interaction with cells and bacteria as well as for energy storage applications.

Acknowledgements

This study was supported by COST Action MP1003 ESNAM - “European Scientific Network for Artificial Muscles”, COST-STSM-MP1003-10794 & -12937 and the Carl Trygger Foundation (Grant CTS 12:206) and Linköping University. The authors also expresses their gratitude to Prof Anthony Turner (LiU), Dr Amy Gelmi (LiU), Dr Wing-Cheung Mak (LiU), Dr Chun-Xia Du (LiU), and Dr Tavo Romann (UT) for their support.

REFERENCES

- [1] Lu W, Fadeev AG, Qi B, Smela E, Mattes BR, Ding J, et al. Use of ionic liquids for pi-conjugated polymer electrochemical devices. *Science* 2002;297:983–7.
- [2] Bauer S, Bauer-Gogonea S, Graz I, Kaltenbrunner M, Keplinger C, Schwödiauer R. 25th anniversary article: a soft future: from robots and sensor skin to energy harvesters. *Adv Mater* 2014;26:149–62.

- [3] Jager EWH. Microrobots for Micrometer-Size Objects in Aqueous Media: Potential Tools for Single-Cell Manipulation. *Science* (80-) 2000;288:2335–8.
- [4] Svennersten K, Berggren M, Richter-Dahlfors A, Jager EWH. Mechanical stimulation of epithelial cells using polypyrrole microactuators. *Lab Chip* 2011;11:3287–93.
- [5] Smela E. Conjugated Polymer Actuators for Biomedical Applications. *Adv Mater* 2003;15:481–94.
- [6] Festin N, Plesse C, Pirim P, Chevrot C, Vidal F. Electro-active Interpenetrating Polymer Networks actuators and strain sensors: Fabrication, position control and sensing properties. *Sensors Actuators B Chem* 2014;193:82–8.
- [7] Otero TF, Cortés MT. Artificial Muscles with Tactile Sensitivity. *Adv Mater* 2003;15:279–82.
- [8] Wu Y, Alici G, Madden JDW, Spinks GM, Wallace GG. Soft Mechanical Sensors Through Reverse Actuation in Polypyrrole. *Adv Funct Mater* 2007;17:3216–22.
- [9] Wilson SA, Jourdain RPJ, Zhang Q, Dorey RA, Bowen CR, Willander M, et al. New materials for micro-scale sensors and actuators. *Mater Sci Eng R Reports* 2007;56:1–129.
- [10] Torop J, Palmre V, Arulepp M, Sugino T, Asaka K, Aabloo A. Flexible supercapacitor-like actuator with carbide-derived carbon electrodes. *Carbon N Y* 2011;49:3113–9.
- [11] Torop J, Sugino T, Asaka K, Jänes A, Lust E, Aabloo A. Nanoporous carbide-derived carbon based actuators modified with gold foil: Prospect for fast response and low voltage applications. *Sensors Actuators B Chem* 2012;161:629–34.
- [12] Arulepp M, Permann L, Leis J, Perkson A, Rumma K, Jänes A, et al. Influence of the solvent properties on the characteristics of a double layer capacitor. *J Power Sources* 2004;133:320–8.
- [13] Gogotsi Y, Nikitin A, Ye H, Zhou W, Fischer JE, Yi B, et al. Nanoporous carbide-derived carbon with tunable pore size. *Nat Mater* 2003;2:591–4.
- [14] Gao Y, Presser V, Zhang L, Niu JJ, McDonough JK, Pérez CR, et al. High power supercapacitor electrodes based on flexible TiC-CDC nano-felts. *J Power Sources* 2012;201:368–75.
- [15] Sugino T, Kiyohara K, Takeuchi I, Mukai K, Asaka K. Actuator properties of the complexes composed by carbon nanotube and ionic liquid: The effects of additives. *Sensors Actuators B Chem* 2009;141:179–86.
- [16] Biso M, Ansaldo A, Picardo E, Ricci D. Increasing the maximum strain and efficiency of bucky gel actuators by pyrrole oxidative polymerization on carbon nanotubes dispersed in an ionic liquid. *Carbon N Y* 2012;50:4506–11.

- [17] Zheng W, Razal JM, Whitten PG, Ovalle-Robles R, Wallace GG, Baughman RH, et al. Artificial muscles based on polypyrrole/carbon nanotube laminates. *Adv Mater* 2011;23:2966–70.
- [18] Kaasik F, Tamm T, Hantel MM, Perre E, Aabloo A, Lust E, et al. Anisometric charge dependent swelling of porous carbon in an ionic liquid. *Electrochem Commun* 2013;34:196–9.
- [19] Li C, Shi G. Synthesis and electrochemical applications of the composites of conducting polymers and chemically converted graphene. *Electrochim Acta* 2011;56:10737–43.
- [20] Salinas-Torres D, Sieben JM, Lozano-Castelló D, Cazorla-Amorós D, Morallón E. Asymmetric hybrid capacitors based on activated carbon and activated carbon fibre–PANI electrodes. *Electrochim Acta* 2013;89:326–33.
- [21] Yoo E, Kim J, Hosono E, Zhou H, Kudo T, Honma I. Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries. *Nano Lett* 2008;8:2277–82.
- [22] Ruch PW, Hahn M, Cericola D, Menzel A, Kötz R, Wokaun A. A dilatometric and small-angle X-ray scattering study of the electrochemical activation of mesophase pitch-derived carbon in non-aqueous electrolyte solution. *Carbon N Y* 2010;48:1880–8.
- [23] Jänes A, Permann L, Arulepp M, Lust E. Electrochemical characteristics of nanoporous carbide-derived carbon materials in non-aqueous electrolyte solutions. *Electrochem Commun* 2004;6:313–8.
- [24] Melling D, Wilson S, Jager EWH. The effect of film thickness on polypyrrole actuation assessed using novel non-contact strain measurements. *Smart Mater Struct* 2013;22:104021.
- [25] Vunder V, Itik M, Põldsalu I, Punning A, Aabloo A. Inversion-based control of ionic polymer–metal composite actuators with nanoporous carbon-based electrodes. *Smart Mater Struct* 2014;23:025010.
- [26] Antony MJ, Jayakannan M. Self-assembled anionic micellar template for polypyrrole, polyaniline, and their random copolymer nanomaterials. *J Polym Sci Part B Polym Phys* 2009;47:830–46.
- [27] Jang J, Yoon H. Formation mechanism of conducting polypyrrole nanotubes in reverse micelle systems. *Langmuir* 2005;21:11484–9.
- [28] Diaz AF, Crowley J, Bargon J, Gardini GP, Torrance JB. Electrooxidation of aromatic oligomers and conducting polymers. *J Electroanal Chem* 1981;121:355–61.
- [29] Korenblit Y, Rose M, Kockrick E, Borchardt L, Kvit A, Kaskel S, et al. High-rate electrochemical capacitors based on ordered mesoporous silicon carbide-derived carbon. *ACS Nano* 2010;4:1337–44.

- [30] Ferrari AC, Robertson J. Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. *Philos Trans A Math Phys Eng Sci* 2004;362:2477–512.
- [31] Cheung K., Smith BJ., Batchelder D., Bloor D. Raman spectroscopy of conductive polypyrroles. *Synth Met* 1987;21:249–53.
- [32] Österholm A, Lindfors T, Kauppila J, Damlin P, Kvarnström C. Electrochemical incorporation of graphene oxide into conducting polymer films. *Electrochim Acta* 2012;83:463–70.
- [33] Zhang D, Zhang X, Chen Y, Yu P, Wang C, Ma Y. Enhanced capacitance and rate capability of graphene/polypyrrole composite as electrode material for supercapacitors. *J Power Sources* 2011;196:5990–6.
- [34] Zhang LL, Zhao S, Tian XN, Zhao XS. Layered graphene oxide nanostructures with sandwiched conducting polymers as supercapacitor electrodes. *Langmuir* 2010;26:17624–8.
- [35] Zhang J, Zhao XS. Conducting Polymers Directly Coated on Reduced Graphene Oxide Sheets as High-Performance Supercapacitor Electrodes. *J Phys Chem C* 2012;116:5420–6.
- [36] Peng C, Jin J, Chen GZ. A comparative study on electrochemical co-deposition and capacitance of composite films of conducting polymers and carbon nanotubes. *Electrochim Acta* 2007;53:525–37.
- [37] Pei Q, Inganaes O. Electrochemical applications of the bending beam method. 1. Mass transport and volume changes in polypyrrole during redox. *J Phys Chem* 1992;96:10507–14.
- [38] Smela E, Gadegaard N. Surprising Volume Change in PPy(DBS): An Atomic Force Microscopy Study. *Adv Mater* 1999;11:953–7.
- [39] Torop J, Arulepp M, Leis J, Punning A, Johanson U, Palmre V, et al. Nanoporous Carbide-Derived Carbon Material-Based Linear Actuators. *Materials (Basel)* 2009;3:9–25.
- [40] Hantel MM, Presser V, Kötz R, Gogotsi Y. In situ electrochemical dilatometry of carbide-derived carbons. *Electrochem Commun* 2011;13:1221–4.
- [41] Kosidlo U, Omastová M, Micusík M, Ćirić-Marjanović G, Randriamahazaka H, Wallmersperger T, et al. Nanocarbon based ionic actuators—a review. *Smart Mater Struct* 2013;22:104022.