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Novel conducting polymer structures for electrochemical actuators

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NOVEL CONDUCTING POLYMER STRUCTURES FOR ELECTROCHEMICAL ACTUATORS

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To my parents for their endless love and encouragement.

To my husband Hongbin Ren and my daughter Silvia Ren for their support and patience.

CERTIFICATION

I, Binbin Xi, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Binbin Xi

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PUBLICATIONS

1. Spinks, G. M., Xi, B, Zhou, D., Truong, V-T., Wallace, G. G., "Enhanced control and stability of polypyrrole electromechanical actuators**",** *Synthetic Metals,* volume **140**, 2004, p 273-280.

2. Spinks, G. M., Xi, B, Truong, V-T., Wallace, G. G., "Actuation behaviour of layered composites of polyaniline, carbon nanotubes and polypyrrole", *Synthetic Metals,* volume **151**, 2005, p 85-91.

3. Xi, B., Truong, V-T., Whitten, P., Ding, J., Spinks, G. M., Wallace, G. G., "Poly(3-methylthiophene) electrochemical actuators showing increased strain and work per cycle at higher operating stresses", *Advanced materials*, Submitted.

4. Xi, B., Truong, V.-T., Mattaghitalab, V., Whitten, P., Spinks, G. M., Wallace, G. G., "Actuation behaviour of polyaniline films and tubes prepared by the phase inversion technique", *Smart Materials and Structures,* Submitted.

5. Xi, B., Truong, V.-T., Whitten, P., Ding, J., Spinks, G. M., Wallace, G. G., "Poly(3-methylthiophene) based Electrochemical Actuators", *Proceeding of SPIE, The International Society for Optical Engineering Smart Structures, Devices and Systems II*, volume **5649**, 2005, part 1, p. 137-144.

6. Xi, B., Truong, V.-T., Mattaghitalab, V., Whitten, P., Spinks, G. M., Wallace, G. G., "Actuation Behaviour of Polyaniline Films and Tubes Prepared from Phase Inversion Technique", *Proceeding of SPIE, The International Society for Optical Engineering Smart Structures, Devices and Systems II*, volume **5649**, 2005, part 2, p. 436-444.

7. Spinks, G. M., Xi, B., Campbell, T., Whitten, P., Mattaghitalab, V., Samani, M. B., Wallace, G. G., "In Pursuit of High-Force/High-Stroke Conducting Polymer Actuators", *Proceeding of SPIE, Smart Structures and Materials*, volume **5759**, 2005, p. 314-321.

ABSTRACT

Electrochemical actuators based on conducting polymers and conducting polymer/carbon nanotube composites have been constructed and characterised. The actuation performance was optimised in terms of the actuation strain, cycle life, stability and work-per-cycle.

Different conducting polymers, such as polypyrrole, polythiophene, and polyaniline were investigated as actuator materials. More reproducible and stable strain response from polypyrrole actuators has been achieved by the combination of current pulsing control for electrochemical stimulation and ionic liquid for the electrolyte. Current pulsing ensures that the oxidation and reduction processes are equal in their magnitude and prevents the slow net oxidation (or reduction) that typically occurs during symmetrical voltage cycling. Ionic liquid electrolytes permit higher current densities to be applied to the polymer because the polymer can endure a wider potential window in ionic liquids. Also, operation of polypyrrole actuators in ionic liquids produces much smaller changes in elastic modulus, thus resulting in a more stable isotonic strain with increasing applied loads and a higher work-per-cycle. The effect of dopants, potential scan rate and electrolyte temperature on actuation performance is also investigated for polypyrrole actuators. For polythiophene actuators, an increasing strain response was observed under increasing applied loads when operated in ionic liquids as electrolytes. This is the first time that conducting polymer actuators have been reported to exhibit an increasing strain with increasing applied loads. Using the phase inversion technique, polyaniline actuators were prepared in different geometrical configurations such as films, tubes and tubes with a platinum wire as helix. The actuation strain of the polyaniline actuator was

significantly increased by incorporating a platinum wire as helix configuration into the polymer in acid solution electrolyte. However, the porous nature and subsequent brittleness of the polyaniline actuators prepared using the phase inversion technique has restricted their actuation performance and limited practical application.

The use of carbon nanotubes as reinforcement fillers and electrical conductors in polyaniline was investigated due to the remarkable properties of carbon nanotubes such as high tensile strength, Young's modulus, and electrical conductivity. Polyaniline/carbon nanotube composite actuators were fabricated aiming to improve the actuation behaviour. Layered composite actuators consisting of polypyrrole, polyaniline and carbon nanotubes were fabricated by coating a polyaniline/carbon nanotube solution onto the polypyrrole tube and drying on a hotplate. Polyaniline/carbon nanotube composite fibre actuators were prepared using a wet-spinning process. The presence of carbon nanotubes allowed high stresses to be applied to the composite actuators. The actuation performance of the composite actuators is enhanced by the carbon nanotubes as reinforcement fillers in conducting polymers.

ABBREVIATIONS

3MT	3-methylthiophene
A	cross-section area
A^-	doping anion
Ag/AgCl	silver/silver chloride reference electrode
Ag/Ag^+	silver/silver ion reference electrode
BS^-	benzenesulfonate
C	coulomb
°C	degree Celsius
CEP	conducting electroactive polymer(s)
cm	centimetre
CNT	carbon nanotube(s)
CV	cyclic voltammetry
D	diffusion coefficient
DBS^-	dodecylbenzene sulfonate
DMPU	*N,N'*-dimethylpropylene urea
ΔE	potential difference
E	potential
E_{app}	applied potential
$E_{p(a)}$	anodic peak potential
$E_{p(c)}$	cathodic peak potential
EB	emeraldine base
EMI.Br	1-ethyl-3-methylimidazolium bromide
EMI.TFSI	ethylmethylimidazolium bistrifluoromethanesulfonimide
ES	emeraldine salt
F	Faraday's constant
F	load
G	gram

HCSA	camphorsulfonic acid
HDBSA	dodecyl benzenesulfonic acid
$HFSI^-$	bis(heptafluorobutane-sulfonyl)imide
i	current
$i_{p,a}$	anodic peak current
$i_{p,c}$	cathodic peak current
Δl	actuator length change
IL	ionic liquid
LEB	leucoemeraldine base
LiTFSI	Lithium bistrifluoromethanesulfonimide
M	molar
mA	milliampere(s)
mC	millicoulomb
MPa	mega Pascal
MSA	methanesulfonic acid
mV	millivolt
MW	molecular weight
MWNT	multi-walled carbon nanotube(s)
n	number of electron
$NFSI^-$	bis(nonafluorobutanesulfonyl)imide
NMP	*N*-methyl-2-pyrrolidinone
ox	oxidation process
PAn	polyaniline
PC	propylene carbonate
PF_6^-	hexafluorophosphate
$PFSI^-$	bis(pentafluorobutanesulfonyl)imide
PmPV	poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene)
PPS^-	*p*-phenolsulfonic

PPy	polypyrrole
Pt	platinum
PTh	polythiophene
P3MT	poly(3-methylthiophene)
Q	charge
Q_{ox}	charge consumed during oxidation process
O_{red}	charge consumed during reduction process
R	resistance
R_T	total resistance
R_p	polymer resistance
red	reduction process
S	siemens
s	second
SEM	scanning electron microscopy
T	temperature
$TBA.BF_4$	tetrabutylammonium tetrafluoroborate
$TBA.PF_6$	tetrabutylammonium hexafluorophosphate
$TFSI^-$	bis(trifluoromethanesulfonyl)imide
μm	micrometre
V	volt
W	work-per-cycle
W_G	gravimetric work
W_V	volumetric work
Y	Young's modulus
Y_d	Young's modules at expanded state
Y_o	Young's modules at contracted state
X^+	cation

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