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The effect of monomer and electrolyte concentrations during synthesis on the actuation of PPy(CF_3SO_3) films in aqueous electrolytes

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Abstract

Free-standing films of polypyrrole, PPy(CF_3SO_3), were electropolymerised galvanostatically from propylene carbonate solutions containing tetrabutylammonium trifluoromethanesulfonate of a range of pyrrole or electrolyte concentrations. The electrochemomechanical deformation (ECMD), measured in situ during cyclic voltammetry experiments, was found to increase when a higher concentration of pyrrole monomer or CF_3SO_3 electrolyte was used during the polymerisation. X-ray photoelectron spectroscopy was used to estimate the presence of different forms of carbon in the PPy(CF_3SO_3) films, including the α and β carbons of the pyrrole ring, the 'disordered carbon' and carbonyl carbon. These XPS results were correlated with the strains observed in ECMD measurements and the doping level estimated from N1s XPS spectra. The morphology of the films obtained for different growth conditions was also investigated by means of SEM.

Keywords: Polypyrrole; Actuator; Electropolymerisation; Strain

1. Introduction

The actuating performance of conducting polymers under electrochemical control has been actively investigated in recent years [1]. The extent of actuation and general performance has been related to a number of conducting polymer properties which are established during electrochemical deposition, such as the electrolyte chosen to form the dopant which in turn determines polymer conductivity and morphology [2–4]. Among the conducting polymers which have exhibited actuating properties, polypyrrole has been widely studied owing to its high conductivity and ease of synthesis [5], leading to high strain and high stress actuators which are stable [6] and biocompatible [7].

The most commonly employed dopants in preparing polypyrrole films are tetrafluoroborate (BF_4^-) [8], hexafluorophosphate (PF_6^-) [9,10], perchlorate (ClO_4^-) [11] and dodecylbenzene sulfonate (DBS^-) [12–14]. The polymerisation solvents include water [15], propylene carbonate [16,17], methyl benzoate [18,19] and acetonitrile [20].

The electrochemical strains of conventional conducting polymers have been reported to be between 1–3% [21]. Bay et al. [22] reported that PPy doped with DBS^- combined with a gold compliant electrode exhibited a 12% strain. Recently, Hara et al. [23] reported an extremely large strain for PPy films prepared from a methyl benzoate solvent containing tetrabutylammonium bis(trifluoromethylsulfonyl) imide (TBATFSI) which displayed a strain of 26% in an aqueous LiTFSI solution. The same group reported that PPy doped with bis(perfluoroalkylsulfonyl) imide $(C_nF_{2n+1}SO_2)_2N^-$ can exhibit 20–40% strain [24].

The maximum strains reported are often measured during electrochemical cycling of the film at low scan rates (i.e. $0.2\,mV\,s^{-1}$), usually with low stresses applied. Some authors have also reported that the strain produced on the first cycle is larger than in subsequent cycles [2,24,25]. For example, PPy doped with TFSI generated 26% strain in the first cycle whereas only 14% was measured in the second cycle [24]. Both low strain rate and mechanical and chemical instability of conducting polymers are the major drawbacks for practical applications. However, an approach which has produced PPy films with some of the best overall mechanical properties is that involving preparation from methyl benzoate solutions of $TBACF_3SO_3$, producing a film which exhibited an electrochemical strain of

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12.8% and a stress of 20.8 MPa [26]. This system has also shown elongation up to 100% and good flexibility suitable for use in conducting polymer-based actuator devices [19,27].

The influence of preparative conditions upon the actuation properties of PPy films doped with $CF_3SO_3^-$ is clearly important, and we have previously shown that films formed using a deposition current density of 0.05 mA cm^{-2} produce more compact films with higher actuation strains than those prepared at a higher current density of 0.2 mA cm^{-2} [28]. In this report we have studied the ECMD response of PPy films prepared from propylene carbonate solutions of $TBACF_3SO_3$ and tested in aqueous 0.5 M $NaPF_6$, as a function of monomer concentration and electrolyte concentration during electropolymerisation. The PPy films were characterised by means of electrochemical methods, scanning electron microscopy and X-ray photoelectron spectroscopy.

2. Experimental

2.1. Reagents and materials

Pyrrole (Aldrich) was distilled and stored under nitrogen in a refrigerator. Propylene carbonate (PC, Aldrich, anhydrous, 99.7%), tetrabutylammonium trifluoromethane sulfonate ($TBACF_3SO_3$, Aldrich, ≥99%) and sodium hexafluorophosphate ($NaPF_6$, Aldrich, 99%) were used as supplied. Deionised Milli-Q water, with a resistance of 18.2 MΩ cm^{-1}, was used to prepare aqueous electrolytes.

2.2. Electropolymerisation

The PPy films were electropolymerised in a three-electrode cell using a CH instruments electrochemical workstation (Model 440). A stainless steel substrate (purchased from NZ Fasterner Ltd., 304 grade, no. 8 finish) was employed as the working electrode. A platinum mesh was used as the counter electrode and an Ag/Ag^+ (0.001 M $AgNO_3$/0.1 M $TBAPF_6$/acetonitrile) electrode was used as the non-aqueous reference electrode.

The films were grown galvanostatically at 0.1 mA cm^{-2} from a solution of 0.06, 0.125 or 0.25 M pyrrole with 0.1 M of $TBACF_3SO_3$ in propylene carbonate (PC), and 0.05 and 0.10 M $TBACF_3SO_3$ with 0.06 M pyrrole in PC, at $-25 \pm 2\,^{\circ}C$ until the charge reached 3.0 mC cm^{-2}. The PPy films were peeled off the electrode and rinsed with PC, and then stored wet in a $TBACF_3SO_3$/PC solution.

2.3. Electrochemico mechanical deformation (ECMD) testing

The ECMD responses of the free-standing films (10 mm in length and 2 mm in width) were studied using a Dynamical Muscle Analyzer from Aurora Scientific Inc. (ASI) (Model 300B dual-mode lever arm system) during cyclic voltammetry. The top-end of the PPy strip was clamped between two PEEK plates that hung on a wire attached to the lever arm, while the bottom-end of the strip was fixed to a PEEK holder with a Pt wire as the electrical contact. A typical length of the PPy films between the clamps was 3.0–3.6 mm. A small constant force (60 mN) was applied to the film at the beginning of the measurement. The strip was immersed in the cell containing 0.5 M $NaPF_6$ (aq.) electrolyte, and a Pt sheet was used as the counter electrode and Ag/AgCl as the reference electrode. The electrolyte was purged with nitrogen prior to actuation testing.

2.4. Scanning electron microscopy

A Philips ML30S FEG scanning electron microscope was used to examine the morphology and thickness of the films. The films were sputtered with a thin layer of platinum for 150 s. The images were measured using a 5 KeV electron beam with a spot size of 3 nm.

2.5. X-ray photoelectron spectroscopy (XPS)

For XPS analysis, measurements were made on a Kratos Axis Ultra spectrometer with monochromic Al Kα radiation, at a resolution of ∼0.1 eV, voltage of 15 kV and emission current of 10 mA. The pressure was maintained at $\leq 10^{-8}$ torr. The spectra were collected with the charge neutraliser employed. To obtain narrow scans, individual peaks were recorded using a pass energy of 20 eV. The curves were fitted with Gaussian component peaks and a Shirley background using Casa XPS software 2.2.88.

2.6. Conductivity measurements

The conductivity of as grown PPy films was measured using a Jandel four point probe conductivity meter (model RM2) on several spots across the outer (solution side) surface of the films. Measurements were performed by sourcing a constant current of 1 mA between the outer electrodes and measuring the potential drop across the two inner electrodes. The thickness of the PPy films, required for the conductivity calculation, was determined using SEM images.

3. Results and discussion

3.1. Film growth

In order to investigate the effect of different pyrrole concentrations during film deposition, both the concentration of $TBACF_3SO_3$ and the deposition current density were kept constant at 0.1 M and 1.0 mA cm^{-2}, respectively, while the concentration of pyrrole was changed from 0.06 to 0.25 M. As one would expect, a higher polymerisation potential was recorded when a lower pyrrole concentration was used, as the diffusion of pyrrole is expected to be the limiting factor for the polymerisation kinetics. A decrease in the pyrrole concentration from 0.25 to 0.06 M resulted in an increase in the steady-state polymerisation potential from 0.60 to 0.67 V.

In the other series of experiments, the concentration of pyrrole was kept constant at 0.06 M, and the current density at 0.1 mA cm^{-2}, while the concentration of $TBACF_3SO_3$ was either 0.05 or 0.1 M. The chronopotentiograms recorded during