Available online at www.sciencedirect.com
SCIENCE DIRECT®
Synthetic Metals 152 (2005) 53–56
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Factors Influencing Electrochemical Actuation of Polyaniline Fibers in Ionic Liquids

Wen Lu, Benjamin R. Mattes*

Santa Fe Science and Technology, Inc., 3216 Richards Lane, Santa Fe, New Mexico, 87507, U.S.A.

Abstract

Room-temperature ionic liquids have been demonstrated to be advantageous in the development of conducting polymer electrochemical devices. In this paper, we fabricated electrochemical actuators using polyaniline fibers and ionic liquid electrolytes and investigated factors that influence their actuation performance in the ionic liquid [BMIM][BF_4], such as the dopant anion, conductive and mechanical properties of the polyaniline fibers, external load, and operational potentials. Long-term testing was also performed on these ionic liquid/polyaniline fiber actuators and the actuators showed an excellent lifetime of over one million redox cycles.

Keywords: Ionic liquids; Conducting polymers; Polyaniline fibers; Electrochemical actuators

1. Introduction

Conducting polymers represent a unique class of materials that can be fabricated into electrochemical actuators that possess the unique combination of high stress generation, being lightweight, and low operational voltages [1]. During the operation of a conducting polymer electrochemical actuator, the electrolyte is an essential component to ensure good electroactivity and thus actuation for the polymer. Ideal electrolytes should have high ionic conductivity, large electrochemical windows, excellent thermal and electrochemical stability, and negligible evaporation. These electrolyte properties will enable conducting polymer based electrochemical actuators to have high actuation performance over an extended period of time (> one million redox cycles). Room-temperature ionic liquids meet all of these requirements. Using ionic liquids as electrolytes, we and others have previously demonstrated stable and strong performance conducting polymer electrochemical actuators [2 - 5], electrochromic devices [2, 3, 6 - 8], and electrochemical capacitors [9].

In the present work, we investigated additional factors that affect the electrochemical actuation of polyaniline fibers in ionic liquid electrolytes, including the dopant anion, conductive and mechanical properties of the polyaniline fibers, external load, and operational potentials. Finally, we successfully demonstrated an excellent lifetime of over one million redox cycles for polyaniline fiber actuators in an ionic liquid electrolyte.

2. Experimental

The ionic liquid 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]) was synthesized according to methods described elsewhere [10]. The polyaniline fiber used in this study was prepared according to the procedure published by Pomfret et al [11]. The polyaniline fibers were then stretched at different ratios by slowly passing the fiber over a 90° heat source (a soldering iron whose tip was wrapped with a thin PTFE film). The diameters of these fibers were on the order of 40 ~ 70 μm. Prior to use in ionic liquids, polyaniline fibers were subjected to dopant exchange with desired dopants using the procedure as described previously [12].

Electrochemical actuation measurements of the polyaniline fibers were carried out using an EcoChemie PGSTAT30 potentiostat with a 3-electrode electrochemical cell consisting of the polymer fiber as the working electrode, a platinum wire counter electrode, and a silver wire quasi-reference electrode. Linear actuation measurements were carried out by partially immersing the polyaniline fiber in the ionic liquid electrolyte. One end of the fiber was clamped to the bottom of the electrochemical cell, and inside the clamp, electrical contact was made to the polyaniline fiber using a platinum plate. The other end of the fiber was fixed with epoxy resin onto the arm of an Aurora Scientific dual-mode lever arm system (Model 300B). In these experiments, approx. 3 cm length of fiber was used, but only 1 cm length of the fiber was immersed in the ionic liquid

* Corresponding author. Tel: +1-505-474-3500; fax: +1-505-474-9489;
E-mail: mattes@sfst.net

0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2005.07.122

electrolyte. A small load (0.5 g) was applied to the fiber to keep it straight and slightly taught.

3. Results and Discussion

We have previously shown that the electrochemical actuation of polyaniline fibers was strongly affected by their dopants [2]. For the polyaniline fibers doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), the PANI.AMPSA fibers showed negligible electroactivity and actuation (Fig. 1) in the [BMIM][BF_4] electrolyte. However, by doping the fiber instead with triflic acid (CF_3SO_3H), good electroactivity and actuation in the [BMIM][BF_4] electrolyte were obtained (Fig. 2). According to the cation exchange redox mechanism of polyaniline fibers in ionic liquid electrolytes which we previously proposed [2], this may suggest a strong interaction between the $CF_3SO_3^-$ dopant of the fiber polymer and the $[BMIM]^+$ cation of the ionic liquid.

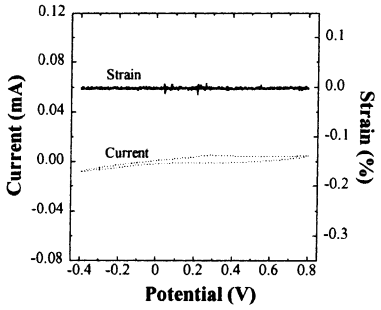

Fig. 1. Cyclic voltammograms and strain of a PANI.AMPSA fiber obtained in [BMIM][BF_4]. Scan rate: 5 mV/s.

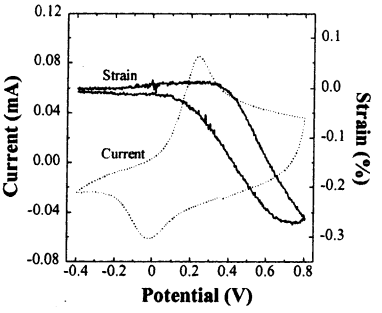

Fig. 2. Cyclic voltammograms and strain of a PANI.CF_3SO_3 fiber obtained in [BMIM][BF_4]. Scan rate: 5 mV/s.

The electrochemical actuation of polyaniline fibers in ionic liquid electrolytes was also effected by the intrinsic electrical and mechanical properties of the polyaniline fibers. By stretching the fiber at different ratios and varying the doping times in triflic acid, we were able to control the conductivity and mechanical properties of the fiber. It is imperative that the conductivity of the polyaniline fiber exceeds 260 S/cm to ensure uniform potential distribution along the fiber and thus high electroactivity and actuation. It is possible to stretch the fiber to 250% of its initial length to increase its conductivity up to 1000 S/cm and obtain better-defined electroactivity. However, this improvement in the electroactivity did not increase the strain of the actuator, but instead smaller strains upon electrical stimulation were observed.

Under the same conditions as in Fig. 2, the electrochemical behavior and actuation of a highly-stretched (250%) and highly conductive fiber, and a unstretched and less conductive fiber were compared in [BMIM][BF_4] after they were converted from PANI.AMPSA to PANI.CF_3SO_3. Although both the highly-stretched fiber (Fig. 3) and the non-stretched fiber (Fig. 2) showed the same redox peak positions and the same peak separation (ΔE_p), the former appeared much more electrochemically active defined by charge density or electrochemical efficiency (Table 1). This is believed to be due to its higher intrinsic electrical conductivity. Nevertheless, the highly-stretched fiber possessed a smaller strain and irreversible actuation. Since stretching the fiber resulted in the fiber becoming less elastic with a significant decrease by about 70% in extension at break (Table 1), this observation suggests that the electrochemical actuation of polymer fibers is determined not only by its electroactivity but also the mechanical properties of the fiber. Electroactivity should be the first requirement to ensure electrochemical actuation for the fiber. Moreover, the actuation of fibers possessing the electroactivity over a certain extent would be largely determined by their mechanical properties (more specifically the elasticity). Thus, due to the formation of more crystalline structures [13] and the loss of elasticity upon stretching during fiber preparation, the highly-stretched fiber would actuate less in spite of its higher electroactivity, i.e. slightly extended upon reduction but could not contract back upon oxidation. In contrast, the unstretched fiber was mechanically stronger and more elastic, showing stronger and reversible electrochemical actuation in spite of its smaller electroactivity.

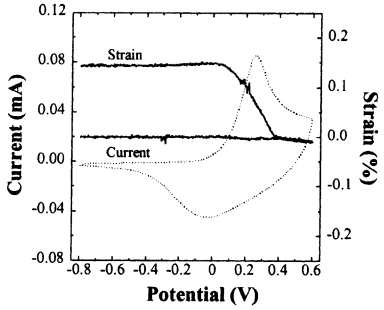

Fig. 3. Cyclic voltammograms and strain of a highly-stretched PANI.CF_3SO_3 fiber (250%) obtained in [BMIM][BF_4]. Scan rate: 5 mV/s.

The external load was another factor that was found to affect the electrochemical actuation of polyaniline fibers in ionic liquid electrolytes. Due to the fact that the work performed by the fiber actuator is proportional to the external load and the length change of the fiber, increased load and fiber length change would be beneficial to the work and thus to the energy efficiency for the conversion of electrical energy input to mechanical work of the fiber. However, based on the observation that strain of the fiber