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Development of Solid-in-Hollow Electrochemical Linear Actuators Using Highly Conductive Polyaniline

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In this paper, we report the use of highly electrically conductive (400−1000 S/cm) polyaniline fibers for the development of electrochemical linear actuators. The high conductivity of the fibers ensures well-defined electroactivity and actuation without a metal backing. In propylene carbonate (PC), the electrochemical and actuation behavior of the fibers was influenced by the dopants' solubility and size: solubility in the electrolyte ensured easy expulsion from the polymer, thus facilitating ion transport and resulting in high electroactivity and strain in the fibers. Actuation of fibers was also affected by electrolyte anions. Small anions led to anion-exchange dominated actuation, and large anions led to cation-exchange dominated actuation. Electrochemical linear actuators with a unique solid-in-hollow configuration were developed using a polyaniline solid fiber in a polyaniline hollow fiber with a gel electrolyte. These actuators were simple to construct and allowed two-electrode operation. Isotonic strains of 0.9% and isometric stresses of 0.9 MPa were realized.

1. Introduction

Conducting polymers have attracted attention around the world as new electrochemical actuator materials.[1−10] They have attractive properties, such as being lightweight and having low cost, high stress generation, and low operating voltages. Polyanilines, polypyrroles, and polythiophenes are typically used. Actuation is achieved by utilizing an electrochemical reaction to generate mechanical motion. Volume change of a conducting polymer during its redox process is thought to be achieved by electrolyte ion transport into/out of the polymer, solvent transport into/out of the polymer, polymer chain configuration changes, and electrostatic expulsion between polymer chains.

The conductivity of the polymer plays an important role in determining polymer electroactivity and actuation. If the polymer is resistive, then the applied potential decreases with distance from the electrical contact. Unfortunately, applying a higher potential at the electrode to achieve a desired oxidation level further from the electrode damages the material closer to the electrode. Moreover, oxygen reduction reactions further limit the electrochemical potentials in a resistive film.[11] If the material is not highly conductive, therefore, a metal contact is required along the length of the polymer. The conductivity of conducting polymers used in electrochemical devices is typically 100 S/cm or less, with 300 S/cm the highest used in an actuator.[12] These materials need a metal layer,[4−7,13] however, which poses some problems. For example, the metal may corrode, react in the electrolyte, delaminate, or crack. In addition, it adds processing steps and expense to the production of actuators.

Most research on conducting polymer actuators to date has been carried out in aqueous electrolytes, which have a narrow electrochemical window. Furthermore, some conducting polymers degrade in aqueous media.[14,15] The use, instead, of a nonaqueous electrolyte with a wide electrochemical window, a high boiling point, and a high ionic conductivity can thus be advantageous.

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An actuator working in air is expected to have an even wider range of practical applications. In current quasi-solid actuators, a polymer or a gel containing a liquid electrolyte is sandwiched between two conducting polymer electrodes.[10,16−18] One is the working electrode and the other is the counter electrode; no reference electrode is needed. These were initially bending actuators, but linear actuators have recently been reported.[3,19]

We use a highly conductive polymer, namely, polyaniline doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (PANI·AMPSA), to fabricate electrochemical actuators. In prior work, we fabricated bending and linear actuators using both films and fibers.[20] In this paper, we focus on the use of fibers to fabricate linear actuators. We first demonstrate that high conductivity allows the elimination of a metal backing. We next report the electrochemical behavior and actuation of PANI·AMPSA fibers in propylene carbonate electrolytes. Finally, we describe the successful fabrication of novel linear actuators using PANI·AMPSA solid and hollow fibers with a gel electrolyte. Advantages of the unique configuration of solid-in-hollow fiber actuators are discussed. Because of the absence of a liquid electrolyte, these actuators can operate in air and would find applications in the development of some practical devices such as life-like robots, artificial limbs, and other biomimetic devices in the future.

2. Experimental Section

Reagents. All reagents were analytic grade. Aqueous acid solutions were prepared with deionized water. Propylene carbonate (PC, Aldrich) was dried over molecular sieves (3 Å, beads, 8−12 mesh) prior to use. Ethylene carbonate (EC, Aldrich) and poly(methyl methacrylate) (PMMA, MW = 990000, Scientific Polymer Products) were used without further purification. Polyaniline was synthesized as described elsewhere.[20]

Preparation of PANI·AMPSA Materials. For the preparation of films, polyaniline emeraldine base (0.19 g) and AMPSA (0.26 g) were ground together for 5 min with a mortar and pestle. The gray powder was dissolved in a solvent mixture of dichloroacetic acid (DCA, 5.9 g) and formic acid (23.6 g). The mixture was homogenized for 5 min at ∼15000 rpm using an Ultra-Turrax T25 homogenizer to give a green solution of emeraldine salt. A portion of the homogenized solution, weighing 5.3 g, was placed on a glass microscope slide (5 × 7 cm) in an oven at 55 °C. After 2 h, the slide was removed, allowed to cool to ambient temperature, and soaked in acetone for 15 min. The polymer film was then removed from the glass substrate and cut into strips measuring approximately 0.2 × 7 cm.

For the preparation of fibers, emeraldine base (4.22 g) and AMPSA (5.78 g) were ground together for 5 min with a mortar and pestle. The gray powder was then placed inside a glovebag together with DCA (190 g), and the bag was filled with nitrogen gas. The powder was added gradually to the DCA solvent and homogenized as described above. The thick solution was then sealed and transferred to a fiber spin line. A nitrogen pressure of 100 psi was applied to one end of the dope pot. The other end of the dope pot was attached to a gear pump. The spin solution was passed through 240- and 140-μm filters before being extruded, for a solid fiber, through a 250-μm-diameter spinneret into a 2-butanone coagulation bath. For the hollow fiber, a spinneret with an outer diameter of 4 mm, stem outer diameter of 2 mm, and stem inner diameter of 1.5 mm was used. The nascent fibers were removed after 10 min and allowed to dry overnight.

The PANI·AMPSA films and fibers were stretched approximately 200% by gripping the ends and pulling slowly at 90 °C over a heat source (a soldering iron whose tip was wrapped with a thin section of PTFE plastic). This has the effect of aligning the polymer chains approximately parallel to the stretch direction, thereby increasing the tensile strength, Young's modulus, and electrical conductivity along the alignment axis.[21−23] The stretched PANI·AMPSA films had a thickness of ∼20 μm and an electrical conductivity of ∼400 S/cm. The stretched solid fibers had a diameter of ∼80 μm and an electrical conductivity of ∼1000 S/cm, and the stretched hollow fibers had an outside diameter of 1.5 mm, an inside diameter of 1 mm, a wall thickness of 250 μm, and an electrical conductivity of ∼400 S/cm.

Dopant Exchange for PANI·AMPSA. In aqueous 1 M HCl, the as-spun PANI·AMPSA materials were used directly without any pretreatment. However, for nonaqueous work, PANI·AMPSA materials were subjected to dopant exchange followed by drying. To do this, PANI·AMPSA materials were electrochemically redoped by potential cycling between −0.2 and 0.6 V (vs Ag/AgCl) in 1 M CF_3SO_3H until stable cyclic voltammograms were obtained and then held at 0.6 V for 5 min. The resulting PANI·CF_3SO_3 samples were then dried under dynamic vacuum for 24 h. After this, they were ready for use in 1 M $LiClO_4$/PC (or other salt-containing PC solutions) or in the fabrication of actuators with gel electrolytes.

Electrochemical and Electromechanical Measurements. Electrochemical measurements of polymer samples were performed with a three-electrode electrochemical cell using an EcoChemie pgstat30 potentiostat. In aqueous HCl, this system consisted of a polymer sample as the working electrode, a 1.5-mm-diameter platinum wire as the counter electrode, and an Ag/AgCl (3 M NaCl) reference electrode. In PC electrolytes, a 1.0-mm-diameter silver wire was utilized as a quasi-reference electrode.

To perform linear actuation measurements, the polymer sample was partially immersed in the electrolytes in the above electrochemical cell. One end of the sample was clamped to the bottom of the cell, and inside the clamp it was electrically contacted by a platinum plate. This contact was connected to the working electrode of the potentiostat. The other end of the sample was fixed with epoxy resin onto the tip of the arm of a lever arm system (Aurora Scientific, model 300B). The upper portion of the sample, approximately 2 cm in length, was in the air, and only the lower portion, approximately 1 cm, was immersed in the electrolyte. A small load (usually 1 g) was applied through the arm of the lever arm system to the sample to keep it straight and slightly taut.

Upon electrochemical stimulation from the potentiostat, two mechanical actuation measurements, isotonic length change and isometric force change, were performed on the polymer samples. In isotonic measurements, a fixed force was applied to the polymer sample, and the position change of the arm of the lever arm system, corresponding to length change of the polymer sample upon its redox reactions, was recorded. In isometric measurements, the arm position and thus the length of polymer sample was fixed, and the generated force of the polymer sample upon its redox reactions was recorded.

Fabrication of All-Polymer Solid-in-Hollow Fiber Actuators. Solid and hollow PANI·AMPSA fibers underwent dopant exchange prior to their use in the fabrication of linear

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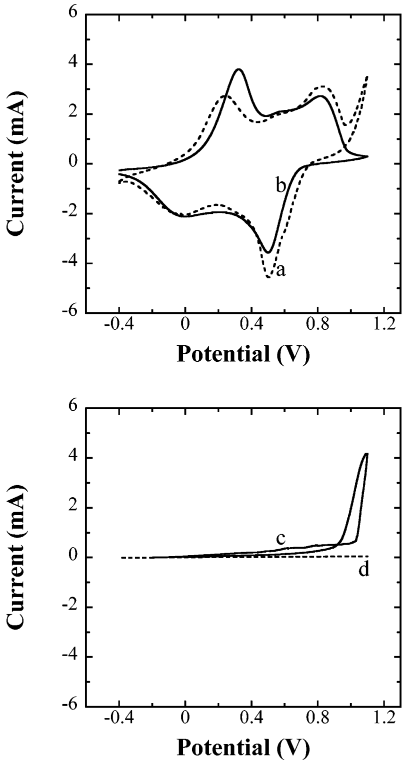

Figure 1. Cyclic voltammograms in 1 M HCl of a gilded PANI·AMPSA film (curve a), an ungilded PANI·AMPSA film (curve b), a gold film (curve c), and an ungilded low-conductivity PANI film (curve d). Scan rate: 50 mV/s.

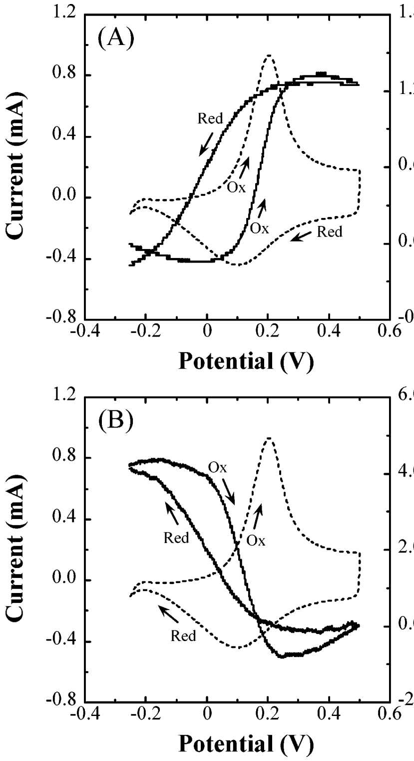

Figure 2. Cyclic voltammogram (dashed line), length change (A, solid line), and force change (B, solid line) of a PANI·AMPSA film in 1 M HCl. Scan rate: 5 mV/s.

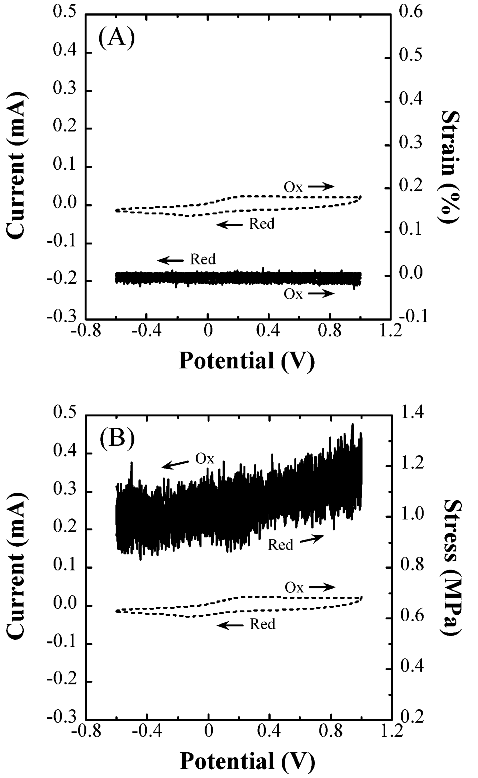

Figure 3. Cyclic voltammogram (dashed line), length change (A, solid line), and force change (B, solid line) of a PANI·AMPSA film in 1 M LiClO$_4$/PC. Scan rate: 5 mV/s.

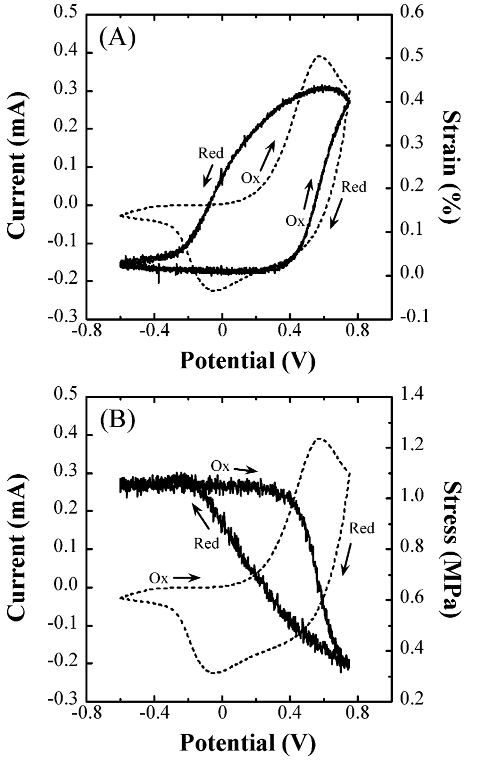

Figure 4. Cyclic voltammogram (dashed line), length change (A, solid line), and force change (B, solid line) of a PANI·CF$_3$SO$_3$ film in 1 M LiClO$_4$/PC. Scan rate: 5 mV/s. The PANI·CF$_3$SO$_3$ film was prepared by dopant exchange from a PANI·AMPSA film.

actuators. The basic configuration of a solid-in-hollow fiber linear actuator is shown in Figure 7. The solid fiber was kept centered in the hollow fiber to avoid electrical shorting. A gel electrolyte consisting of 29% PMMA, 48% EC, 19% PC, and 4% LiClO$_4$ (by weight) was then filled into the space between the solid and hollow fibers with a syringe. During the operation of the actuator, voltage was applied between the solid fiber (as the working electrode) and the hollow fiber (as the counter electrode). No reference electrode was included.

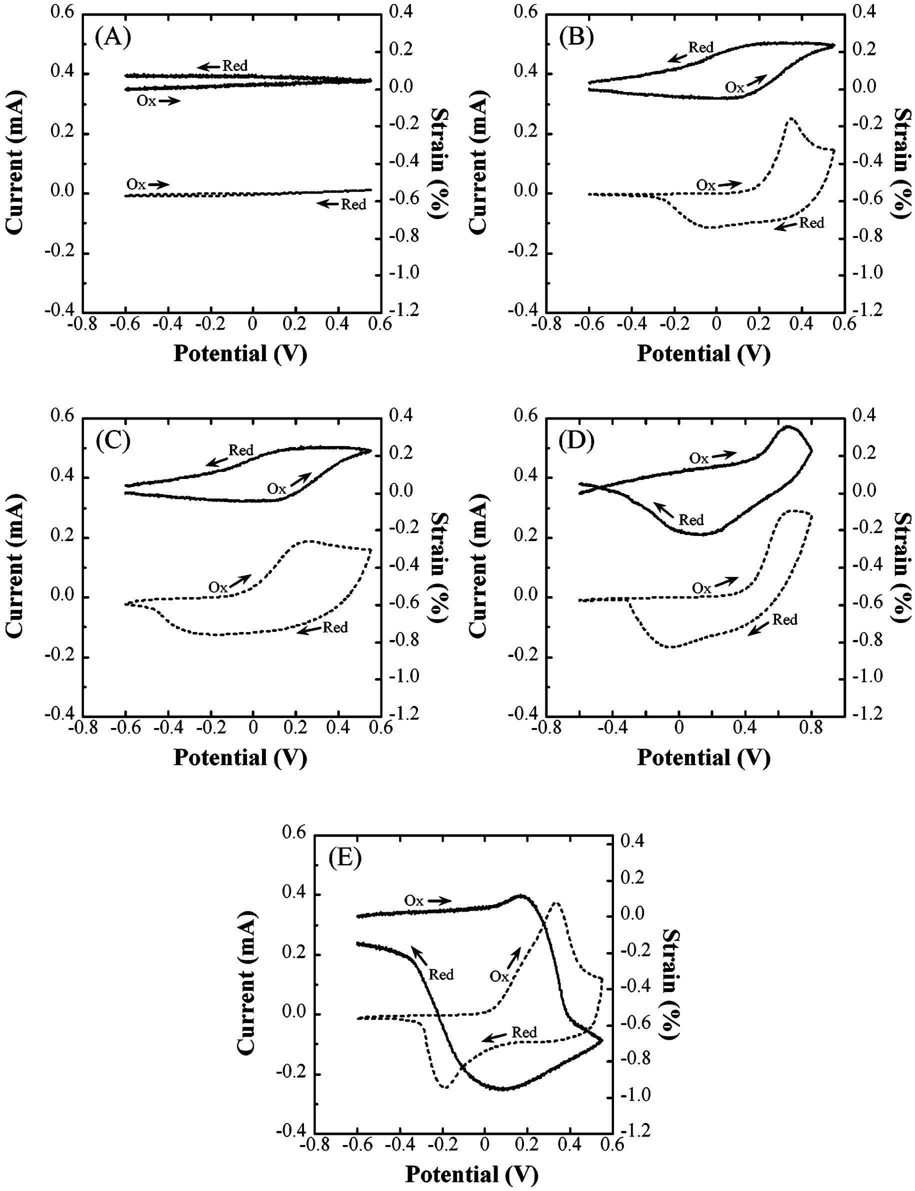

Figure 5. Cyclic voltammograms (dashed lines) and length changes (solid lines) of PANI·CF_3SO_3 fibers in 1 M $LiCF_3COO$/PC (A), 1 M $LiClO_4$/PC (B), 1 M $LiBF_4$/PC (C), 1 M $LiCF_3SO_3$/PC (D), and 1 M $LiN(CF_3SO_2)_2$/PC (E). Scan rate: 5 mV/s.

3. Results and Discussion

3.1. Importance of High Conductivity for Eliminating the Metal Backing. In our previous studies, we found that with low-conductivity polyaniline, a metal backing was necessary to ensure a uniform potential distribution along the length of polymer.[13] To overcome this problem, we have developed highly conductive polyaniline PANI·AMPSA for the fabrication of electrochemical actuators.[20] A comparison of the electroactivity of these highly conductive PANI·AMPSA films in HCl with and without a gold backing (prepared by gilding[13]) is shown in Figure 1. In both cases, two pairs of peaks were obtained, corresponding to the two redox processes of polyaniline,[24] that is, leucoemeraldine ↔ emeraldine in the lower and emeraldine ↔ pernigraniline in the upper potential ranges. The identical electroactivity shows that this material can be used directly without a metal backing for at least 1-cm lengths due to its high conductivity. In contrast, no apparent electroactivity is observed for low-conductivity polyanilines (conductivity: ~1 S/cm) without gilding,[13] which can be confirmed by a flat CV curve (Figure 1d). Furthermore, the oxidation peak at $E > 1.0$ V observed for the gilded PANI·AMPSA film (Figure 1a) due to the oxidation of the attached gold layer (Figure 1c) was eliminated (Figure 1b).

3.2. Electroactivity and Actuation of PANI·AMPSA Films in HCl. We investigated the electrochemical linear actuation of free-standing PANI·AMPSA films (without metal backing) in aqueous 1 M HCl. To avoid polyaniline degradation in this electrolyte,[25,26] the potential range was kept below 0.5 V, covering only the first redox process of polyaniline. Typical cyclic voltammograms, length change, and force change upon potential cycling are shown in Figure 2. Expansion/contraction (Figure 2A) and decrease/increase in force

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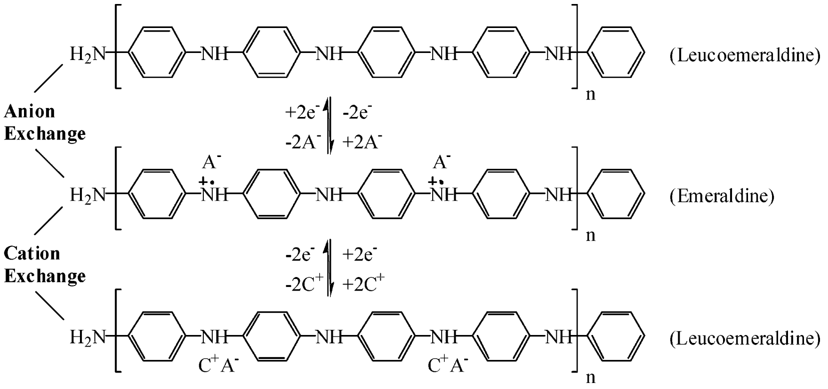
Scheme 1. Redox Reaction Scheme of Polyaniline between a Fully Reduced (Leucoemeraldine) and a Partially Oxidized (Emeraldine) States in Nonaqueous Electrolytes[a]



[a] A^- and C^+ present the anion and cation of the electrolyte, respectively. Anion exchange is obtained in the small anion (ClO_4^- or BF_4^-) containing electrolyte. Cation exchange is obtained in the large anion ($N(CF_3SO_2)_2^-$) containing electrolyte. Mixed anion–cation exchange is obtained in a medium-sized anion ($CF_3SO_3^-$) containing electrolyte.

Table 1. Volumes of Various Anions and Conductivity of the Corresponding Li Salts

anion	volume ($Å^3$)[a]	conductivity of Li salt at 0.1 M in PC (S/cm)
CF_3COO^-	60	1.74×10^{-4}
ClO_4^-	52	2.04×10^{-3}
BF_4^-	48	1.69×10^{-3}
$CF_3SO_3^-$	80	1.11×10^{-3}
$N(CF_3SO_2)_2^-$	143	1.17×10^{-3}

[a] Calculated using Hyperchem software.

(Figure 2B) were obtained. Presumably, this actuation behavior is predominantly due to anion insertion upon oxidation and deinsertion upon reduction of polyaniline in aqueous acidic electrolytes.[7,24,27,28] Similar results were also obtained for fibers (not shown). This hypothesis is supported by our recent observation that electroactivity and electrochemical actuation of PANI·AMPSA are strongly influenced by anion size in a range of aqueous acidic electrolytes (this result will be published elsewhere).

3.3. Electroactivity and Actuation of PANI·AMPSA Films in PC. Poor electroactivity and no actuation were initially encountered for PANI·AMPSA in PC as shown in Figure 3. (This was also observed in acetonitrile.) On the basis of our previous study of the effect of the polyaniline dopant on polymer electroactivity and actuation,[29] we believe this to be due to the insolubility of $AMPS^-$ in PC, and thus the difficult transport of the anion into the polymer.

Accordingly, to improve the electroactivity and actuation for PANI·AMPSA materials in nonaqueous electrolytes, we developed dopant exchange procedures to replace $AMPS^-$ with anions that are soluble in PC. Three methods were investigated: direct redoping, dedoping–redoping, and electrochemical redoping. Electrochemical redoping (as described in the Experimental Section) was found to be the most effective. The resulting PANI·CF_3SO_3 film showed 17 times stronger electroactivity defined by redox peak currents (Figure 4) than the PANI·AMPSA (Figure 3) in the same 1 M $LiClO_4$/PC electrolyte. They also had significant stress and strain, although the strain was substantially smaller than that in HCl. Thus, dopant exchange of AMPSA with anions soluble in PC is critically important to ensure polymer electroactivity and actuation.

3.4. Effect of Supporting Electrolyte on Actuation of PANI·AMPSA Fibers in PC. To better understand the actuation mechanism of polyaniline fibers in PC, a range of salts was employed. PANI·AMPSA fibers were converted to PANI·CF_3SO_3 fibers prior to use. Cyclic voltammograms and length changes are shown in Figure 5.

The electroactivity of PANI·CF_3SO_3 fibers in $LiCF_3COO$/PC (Figure 5A) was much lower than that in other electrolytes: a smaller current and no clear redox peaks were observed. This phenomenon may be explained by the low ionic conductivity of $LiCF_3COO$/PC compared to that of the other electrolytes (Table 1), indicating a low dissociation of $LiCF_3COO$ in PC. Reduced ion concentration results in high electrolyte resistance and thus low polymer electroactivity. Consequently, there was no actuation.

In electrolytes with small anions, $LiClO_4$/PC (Figure 5B) and $LiBF_4$/PC (Figure 5C), the fibers expanded upon oxidation and contracted upon reduction as observed for the films (Figure 4A), indicating anion exchange. In the electrolyte with a large anion, $LiN(CF_3SO_2)_2$/PC, PANI·CF_3SO_3 fibers contracted upon oxidation through deinsertion of cations (Figure 5E). This has been observed previously.[30,31]

When medium-size anions were used (i.e., $CF_3SO_3^-$), the actuation behavior was more complex (Figure 5D), as has been previously reported,[30,31] because of mixed anion and cation transport. The fibers first expanded upon oxidation at potentials below 0.65 V (anion insertion), but then contracted (cation expulsion). During the reverse scan, the fibers contracted upon reduction from 0.8 to 0.2 V, which might be due to the deinsertion of anions, while they expanded upon further reduction below 0.2 V, presumably due to the reinsertion of cations. Electrochemical actuation of polyaniline fibers observed in these different size anion-containing electrolytes can be presented by polyaniline redox mechanisms as proposed in Scheme 1.

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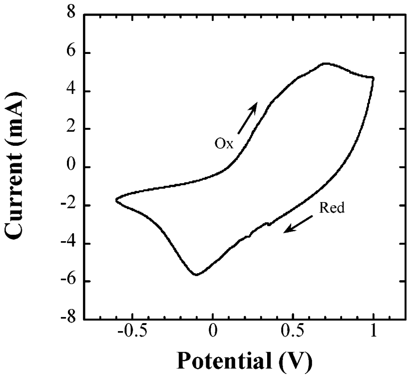

Figure 6. Cyclic voltammogram of a PANI·CF_3SO_3 hollow fiber in 1 M $LiClO_4$/PC. Scan rate: 5 mV/s.

3.5. Fabrication of All-Polymer Solid-in-Hollow Fiber Actuators. Solid PANI·CF_3SO_3 fibers showed well-defined electroactivity and actuation in $LiClO_4$/PC, as shown in Figure 5B, ensuring their use as actuation electrodes in all-polymer actuators. Due to its thickness, hollow fibers did not show movement upon electrochemical stimulation. Nevertheless, these fibers did have well-defined electroactivity (Figure 6), which enabled their use as counter electrodes in all-polymer actuators.

A PMMA/PC/EC/$LiClO_4$ gel electrolyte was used, which has an ionic conductivity of 1×10^{-3} S/cm and has been demonstrated to be useful for the fabrication of conducting polymer bending actuators in our previous studies.[29] A photograph and an SEM close-up image of the actuator are shown in Figure 7. This actuator configuration has some advantages. First, the space in the hollow fiber serves as an electrolyte storage chamber for either liquid or solid electrolytes. Second, evaporation of the electrolyte is minimized by the small area exposed to air, extending the lifetime of the device. Third, since the same material is used to make both solid and hollow fibers, the same redox processes take place at both electrodes. Current and strain upon voltage cycling are shown in Figure 8. In a comparison of the cyclic voltammograms of a single solid fiber in a liquid electrolyte (Figure 5B) and a solid-in-hollow actuator (Figure 8), the most significant difference was the slower redox process for the encapsulated gel actuator, evidenced by the broader peaks and larger peak separation at the same scan rate. This indicates slower ion movement in the solid electrolyte, and possibly also slower transport of electrolyte ions between the electrolyte and the polymer. Accordingly, for a slower scan rate of 1 mV/s (Figure 9A), the hysteresis in actuation was reduced from 1 to 0.6 V and a more typical actuation profile of expansion upon oxidation and contraction upon reduction for an anion-exchange conducting polymer actuator was obtained (compare with Figure 5B). To speed up the redox reaction and thus actuation, we are currently working on spinning thinner fibers.

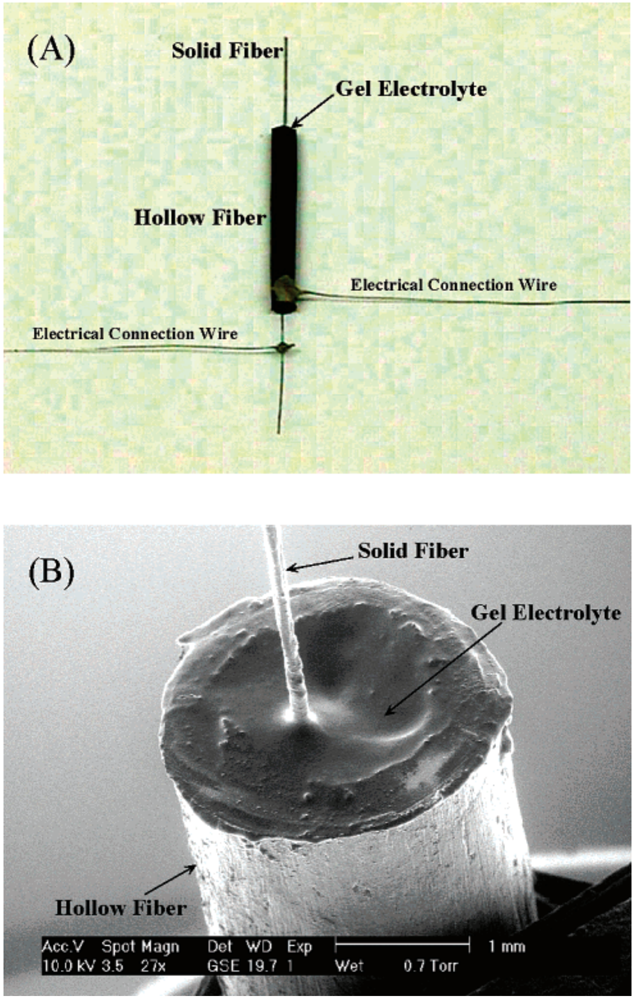

Figure 7. Photograph (A) and SEM close-up (B) of a PANI·CF_3SO_3 solid-in-hollow fiber linear actuator.

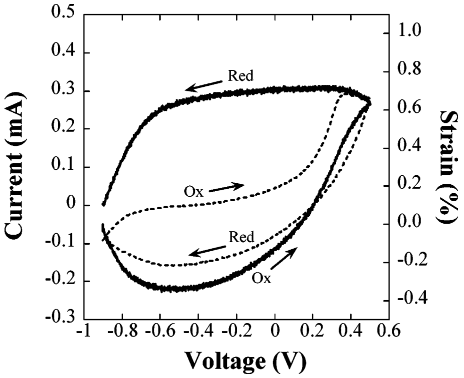

Figure 8. Cyclic voltammogram (dashed line) and length change (solid line) of a solid-in-hollow fiber actuator. Scan rate: 5 mV/s. Effective length of solid fiber: 1 cm.

Due to the fairly small current passed through the actuator (Figure 8), IR drops related to the resistance of the whole device (~30 Ω) should be negligibly small compared to the voltage applied. Therefore, the applied voltage would be mainly used to control the difference in potentials between solid and hollow fibers. If the hollow fiber can serve as a reference electrode (i.e., its potential remains approximately constant), then the potential of the solid fiber would be determined by the applied voltage. Because of its much greater volume, the oxidation level of the hollow fiber does not change significantly as a result of the charge passed in oxidizing/reducing the solid fiber. Therefore, its use as a quasi-reference is justified. This ensures that, in the configuration of a solid-in-hollow fiber actuator, the potential and thus actuation of the solid fiber can be controlled by adjusting the voltage applied.

The strain and stress generation of the actuator upon voltage cycling and pulsing are shown in Figure 9, and the actuation performance is summarized in Table 2.

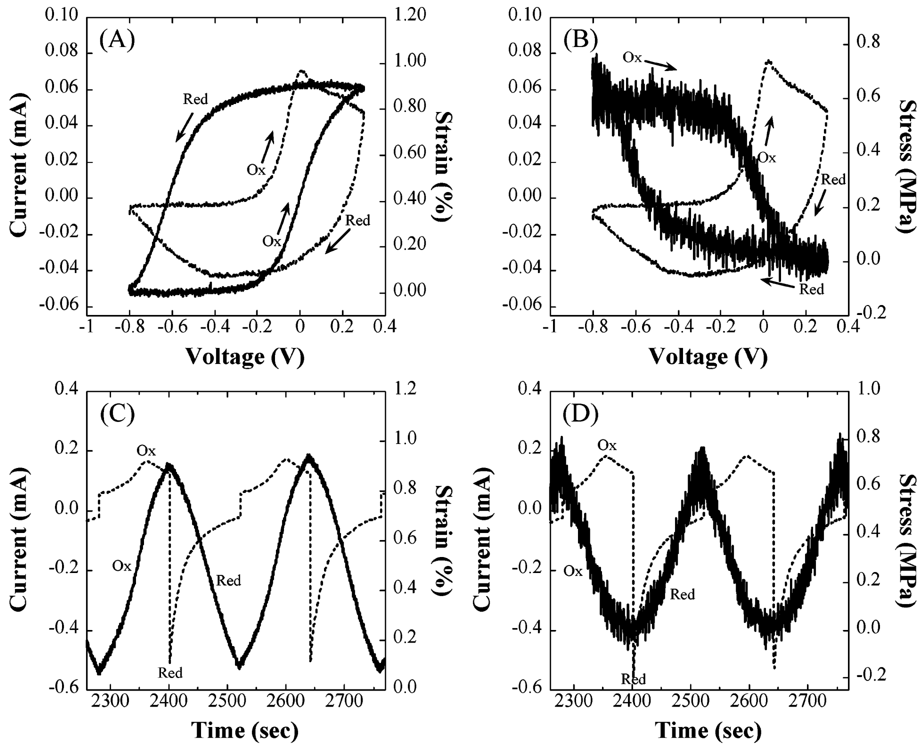

Figure 9. Actuation profile of the solid-in-hollow fiber linear actuator in Figure 8 upon voltage cycling (A, B) and voltage pulsing (C, D). Scan rate for cyclic voltammetry (dashed line): 1 mV/s. Pulse width for chronoamperometry: 120 s for each step of −0.8 and 0.3 V.

Table 2. Actuation Performance of an All-Polymer Solid-in-Hollow Fiber Linear Actuator Obtained upon Electrochemical Stimulation

	stimulation type	
actuation performance	voltage cycling[a]	voltage pulsing[a]
strain (%)	0.91	0.85
stress (force/cross-section area) (MPa)	0.69	0.93
mass lifted/mass of sample (ratio)	4000	5385
work density (kJ/m^3)	12.1	11.1
power density (kW/m^3)	0.11	0.93

[a] Experimental conditions are the same as those in Figure 9.

The weight of the actuator was 0.00013 g and the force generated by the actuator upon electrochemical stimulation was around 0.6 g, indicating that the actuator can lift an object more than 4500 times heavier than its own weight. The minimum force density required for a pseudo-muscular actuator is considered to be 0.1−0.5 MPa, which is generated by skeletal muscle;[2] thus, these all-polymer linear actuators satisfy this requirement.

A lifetime test was carried out with voltage pulsing as shown in Figure 9C. For the first 150 cycles (10 h), stable actuation (0.85% strain) was obtained. However, continuous pulsing resulted in decreased electroactivity and actuation. After ∼24 h, the gel electrolyte became almost solid, and the strain decreased to 0.17%, which has been confirmed to be due to the evaporation of PC from the gel electrolyte. Obviously, solvent evaporation is a fatal disadvantage, limiting the lifetime of the solid-in-hollow fiber actuator with its open configuration. This problem could probably be overcome, however, with the use of ionic liquids, nonvolatile room-temperature molten salts that do not evaporate and which confer excellent actuator lifetime.[32]

4. Conclusions

We used highly conductive PANI·AMPSA to fabricate electrochemical actuators. Owing to their high conductivity, and thus uniform potential distribution along the length of the material, these polymers can be used without a metal backing and show well-defined electroactivity and electrochemical actuation. While the as-made PANI·AMPSA can be used directly in aqueous electrolytes, the material needed to be dopant-exchanged with soluble anions prior to use in propylene carbonate.

Electrochemical actuation of polyaniline was affected by the composition of the electrolyte. Anion or cation exchange was achieved by using electrolytes with small or large anions, respectively. Mixed exchange was observed for medium-sized anions.

When solid and hollow PANI·AMPSA fibers were used, gel-encapsulated linear actuators were developed. These actuators possessed some advantages, including simple construction and use of the hollow fiber as a quasi-reference electrode during operation. In terms of stress generation, these actuators behaved better than skeletal muscle.

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