Fabrication and Characterization of Polyaniline Monolithic Actuators Based on a Novel Configuration: Integrally Skinned Asymmetric Membrane

Hsing-Lin Wang,* Junbo Gao, Jose-Maria Sansiñena, and Patrick McCarthy

MSJ 586, Bioscience Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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We report the synthesis and characterization of polyaniline integrally skinned asymmetric membranes (PANI ISAMs) and their use as chemical and electrochemical actuators. SEM characterization of a PANI ISAM cross section showed a thin dense skin and a microporous substructure with a PANI density gradient. The deformation mechanism of chemical monolithic PANI ISAM actuation was found to result mainly from asymmetric volume expansion/contraction because of the presence/absence of counterions during PANI doping/dedoping cycles. Actuator performance was affected by acid concentration and film thickness. Our results also show that the deformation mechanism in electrochemical PANI ISAM actuation involves mainly changes in polymer conformation with changes in oxidation state. Because these PANI ISAM actuators are monolithic, that is, they are fabricated without any additional layer (tape, polymer, or gold), their structural stability is expected to be superior to bimorph actuators.

Introduction

There has been growing interest in the development of conducting polymer (CP) actuators because they are lightweight, have low operating potential (typically <2 V), have high mechanical strength, and have potential applications in advanced robotics, microactuators, and artificial muscles.[1] Most prototype conducting polymer actuators have been constructed by laminating CPs onto inert flexible substrates that are not subject to volume changes upon exposure to external stimuli. Typical inert substrates include adhesive tape,[2] polymer films,[3] or sputtered thin metal layers.[4] Because two materials are used, these actuators are referred to as bimorph actuators. Previous studies suggest that during electrochemical oxidation of the CP film, counterions are incorporated as dopants in the CP matrix, leading to volume expansion. Meanwhile, the inert flexible substrate volume remains constant, resulting in a bending movement toward the inert substrate side. Electrochemical reduction releases counterions from the CP matrix and causes contraction of the CP film, resulting in bending in the opposite direction.[5] A bimorph electrochemical actuator containing two different conducting polymers was demonstrated by Morita et al.[6] Pei and Inganas[7] constructed a bimorph (polypyrrole/polyethylene) chemical actuator that generated deflection upon exposure to ammonia gas. Regardless of the origin of the driving force (chemical or electrochemical), actuators constructed from a single homogeneous film (without substrate) do not exhibit bending motion because volume changes are symmetric; that is, they occur in all directions. When one or both ends of a symmetric membrane are firmly fixed, however, volume change generated during the oxidation/reduction or doping/dedoping process is observed as linear strain. Linear actuators have been constructed by encapsulating conducting polymer films[8] and fibers[9] in a polyelectrolyte matrix. Recently, Irvin et al. fabricated a novel linear actuator made with a porous polythiophene-based conducting polymer gel, allowing facile diffusion of electrolyte and solvent in and out of the actuator.[10]

By design, bimorph conducting polymer actuators have limitations. Bimorph actuators undergo delamination during long working cycles.[11] The stress gener-

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ated at the CP/substrate interface not only breaks down adhesion between the two materials but also consumes input energy, making the device less efficient. The bimorph design also results in reduced conversion efficiency because the inert substrate increases device weight. The aim of our work is to overcome these limitations through construction of a monolithic chemical and a monolithic electrochemical actuator based on a novel membrane configuration "polyaniline integrally skinned asymmetric membranes (PANI ISAMs)" (see Figure 2). This unimorph actuator has potential advantages over bimorph actuators including longer life cycles by eliminating the possibility of delamination and better energy conversion efficiency. ISAMs were originally developed for gas separations.[12] They consist of a thin dense skin layer of submicrometer thickness and a porous substructure. To date, there have been no reports of their use as actuators. The thin dense skin layer of ISAMs allows for faster diffusion of ionic species, leading to faster response time. We believe this is the first time that monolithic chemical and electrochemical CP actuators have been constructed based on the same material. Finally, we have concluded a simplified operational mechanism for both PANI ISAM chemical and electrochemical actuation by comparing performance under varying experimental conditions.

Experimental Section

Polyaniline emeraldine base (EB) powder was obtained from Neste Oy. *N*-Methyl-2-pyrrolidone (99% Aldrich) and heptamethyleneimine (98% Acros) were used without further purification.

A typical example of preparing highly concentrated polyaniline solution follows: 4.14 g of *N*-methyl-2-pyrrolidinone (NMP) was mixed with 0.747 g of heptamethyleneimine (HPMI). This mixture was placed inside a 10-mL Teflon vial. Then, 1.15 g of EB powder was added to this solution slowly (over a 5-s time period) and while stirring. The solution was transferred to an oven set at 60 °C and was allowed to heat for 20 min. The resulting solution became homogeneous and flowed freely. The mass content of EB powder in this solution was 20% w/w. On the basis of the above procedure, we can prepare concentrated EB solution up to 35 wt %.

Preparation of PANI ISAMs was carried out using the phase inversion technique pioneered by Loeb and Sourirajan.[12] A typical example of preparing PANI ISAMs is described as follows: The as-prepared concentrated PANI solution was poured onto a glass substrate and a homogeneous thin solution layer was made using a Gardner blade. Substrate and film were immersed in a nonsolvent (e.g., water) bath. Rapid solvent−nonsolvent exchange led to polymer precipitation and subsequent thin skin layer formation above a porous substructure. Once the membrane was made, it was left in the water bath for more than 3 days. Water was replaced every 24 h to ensure complete removal of the NMP and HPMI through a solvent−nonsolvent exchange process. After 72 h the membrane was removed from the water bath, tap dried with a Kimwipe, and air-dried for 24 h. Finally, it was placed inside a vacuum oven under a dynamic pump for 24 h.

Preparation of thermally cured dense films was achieved as follows: The as-prepared concentrated PANI solution was poured onto a glass substrate and a homogeneous thin solution layer was made using a Gardner blade. The film was transferred to an oven set at 110 °C and was allowed to heat for 2 h, evaporating the solvent and resulting in a thermally cured dense film.

The cross section of the PANI ISAM membrane was prepared by breaking the membrane samples in liquid nitrogen. Membrane freeze fracturing keeps the cross-section structure of the membrane intact. The surface of the membrane was coated with a thin layer of carbon prior to SEM measurements.

Mechanical properties of the membranes were measured using Shimadzu EZ-TEST equipment controlled by a Pentium III DELL computer using WinAGS Lite software. All measurements were performed using 50.0-mm-length × 5.0-mm-width strips cut from the PANI membranes. Both strip ends were held by the instrument grips. The membrane was stretched at a constant displacement rate of 1 mm/min and the stress−strain curve was obtained. Typically, three tests were performed on each membrane. The reported values are an average of three measurements.

UV−Vis−NIR spectra of thin films and solution were obtained using a Perkin-Elmer Lambda 19 spectrometer. Standard four-point probe conductivity measurements were made using an Agilent model 34401A digital multimeter in connection with a Signatone mounting stand model S-301-4 and a four-point probe head model SP4-40-45-0 (R = 5 mm).

Chemical actuators were fabricated simply by cutting 50.0 mm × 5.0 mm strips from PANI ISAM membranes. The strips were fixed at one end, leaving the other end free. The strip was then immersed in HCl aqueous solution at room temperature. Bending began almost immediately. A simple homemade device (see Figure 4) where an angular plot was placed behind the actuator was used to monitor the chemical actuator bending angle. The experiment was recorded using a Panasonic Digital Video Camcorder (model PV-DV800). The camera was connected to a Pentium III DELL computer through an ATI DV-Wonder PCI card and controlled using ULEAD VideoStudio-5 software (Version 5.00.0006). This enabled us to measure the chemical actuator bending rate.

Electrochemical characterization of all PANI films was carried out using a CHI660 electrochemical workstation controlled from a Pentium II DELL computer using the CHI660 software (Version 2.06) in 1.0 M hydrochloric acid (HCl) aqueous solution.

Results and Discussion

Characterization of Concentrated EB Solution and PANI Membranes. PANI ISAMs were prepared from concentrated polyaniline EB solution through a gel inhibitor assisted dissolution route.[13] In this paper, heptamethylenimine (HPMI) was used as a gel inhibitor in NMP to prepare highly concentrated EB solutions. A previous study by Han and co-workers indicated that when EB powder was processed by and only by amines, concurrent reduction and nucleophilic substitution resulted in substituted leucoemeraldine base.[14] Reduction of EB chains caused deterioration of the mechanical and electrical properties of the cast film.[15] UV−Vis of substituted leucoemeraldine base showed only one peak at ≈330 nm. Because our procedure involved usage of the secondary amine HPMI (gel inhibitor), it is crucial to know that the molecular structure of EB in the concentrated solution and thin film was not impacted by the presence of gel inhibitor; that is, the EB was not reduced. The UV−Vis−NIR spectra of an ultrathin EB film prepared from concentrated EB/HPMI solution (Figure 1b) showed absorption peaks at 331 nm ($\pi-\pi^*$) and 630 nm (exciton peak), which are consistent with

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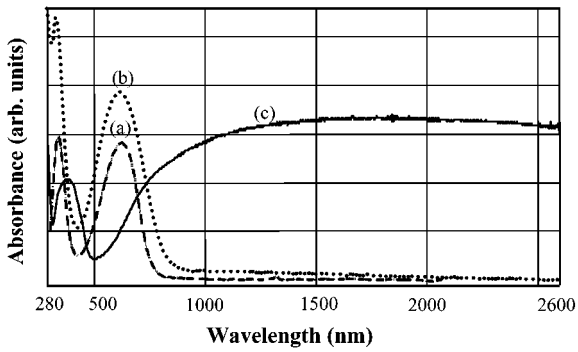

Figure 1. UV−Vis NIR spectra of 1 wt % EB solution (a), thin film prepared from concentrated EB solution (b), and thin film doped by 1.0 M HCl aqueous solution (c).

the UV−Vis−NIR spectra of a 1% EB/NMP solution in the absence of HPMI (Figure 1a). The thin film described above was obtained by spin casting concentrated EB/HPMI solution on a quartz plate and immersing it in a water bath for 2 h to remove the NMP and amine residue. Figure 1c shows the UV−Vis−NIR spectra of a doped EB thin film cast from EB/HPMI. HCl-doped EB membrane cast from EB/HPMI has a conductivity of ≈1.5 S/cm. A free-carrier tail extends into the near-infrared region, indicating formation of a highly delocalized polaron. These results are all consistent with properties of solution and thin film prepared from EB powder in the absence of an amine gel inhibitor. Therefore, we are confident that our processing route does not cause reduction of EB.

Mechanical Properties. The mechanical strength of PANI ISAMs correlated directly with maximum actuator work force. We have measured the mechanical properties of doped and undoped PANI ISAMs with varying thickness. Typically, we carried out three measurements on each membrane and reported values as the average. Example measurements are shown in Figure 2a. The mechanical strength (Young's Modulus) of undoped membranes is represented by the slope of the initial linear component of the stress−strain curve. Mechanical strength varied from 0.40 GPa (51-μm membrane) to 0.26 GPa (160-μm membrane). Elongation of these membranes ranged from 2 to 5%. As the membrane thickness was increased, mechanical strength decreased and strain at break increased. This result is consistent with our previous observation that mechanical strength of fibers spun from highly concentrated EB solutions decreased as fiber diameter increased.[16]

To examine the mechanical properties of doped PANI ISAMs, we cut three 1 × 3 cm pieces from a 185-μm membrane. We doped one with hydrochloric acid (inorganic acid) and one with camphorsulfonic acid (organic acid) and one was left undoped. Conductivity for the HCl- and CSA-doped membranes were 1.5 and 1.0 S/cm, respectively, suggesting both membranes were fully doped. The mechanical strength of the above membranes was measured (Figure 2b). After the PANI ISAM membrane was doped with HCl, we observed an increase in membrane thickness (from 185 to 195 μm) and Young's Modulus (from 0.27 to 0.42 GPa). The HCl-doped membrane strain at break, however, was only

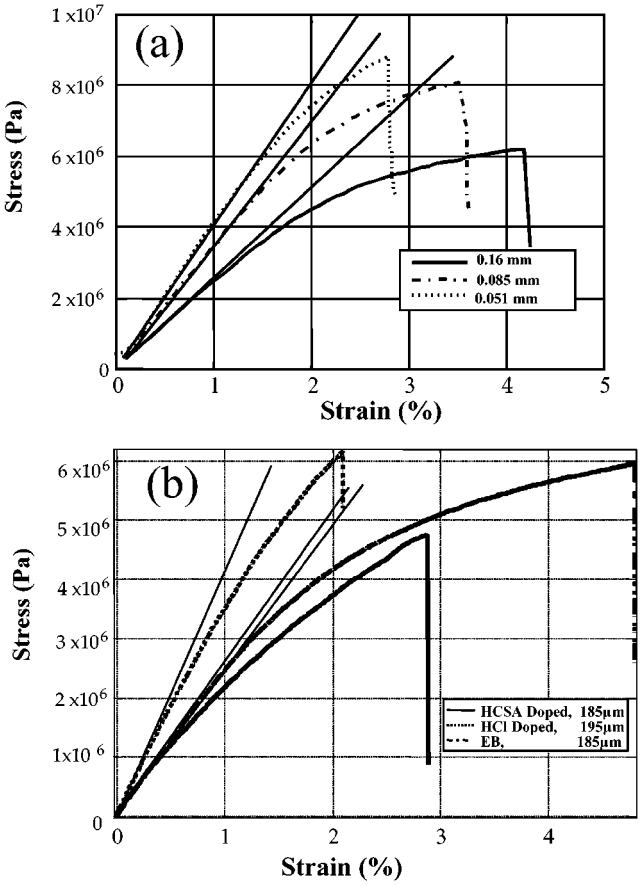

Figure 2. Stress−strain curves of PANI ISAMs with various thicknesses (a) and doped with various acids (b).

2.1% compared to 4.9% for the undoped membrane. These results show that PANI ISAMs doped with HCl are stronger but more brittle than undoped PANI ISAMs. Interestingly, CSA-doped PANI ISAMs exhibited mechanical strength (0.25 GPa) similar to the undoped membrane, but the strain at break was 2.9%. This suggests that the kind of acid used to dope the EB membrane significantly impacts its mechanical properties. The benchmark number for the mechanical strength of an EB membrane came from a thermally cured dense (nonporous) film prepared from EB/HPMI solution. The thermally cured films had an average mechanical strength of 2.34 GPa, making them ≈10 times stronger than porous EB membranes. The strain at break of the thermally cured membrane was ≈17%. We speculate that the improved mechanical properties of thermally cured dense films are due to their dense structure.

Chemical Actuator. PANI density within PANI ISAMs varied from the skin side (dense) to the porous side (Figure 3a). SEM of a PANI ISAM cross section showed a porous (density) gradient. The density gradient was crucial for good chemical actuator performance. Immersing PANI ISAM into acidic solution caused doping of polyaniline chains, which draws dopants (counterions) into the polymer network (Scheme 1). Inserting counterions into the membrane causes density-dependent volume expansion within the membrane (Figure 4, left). As a simple demonstration of a chemically powered actuator, a 200-μm undoped PANI ISAM was immersed in 1.0 M HCl aqueous solution. Acid doping of the ISAM led to bending toward the porous side (Figure 4a). On the other hand, base de-doping (4

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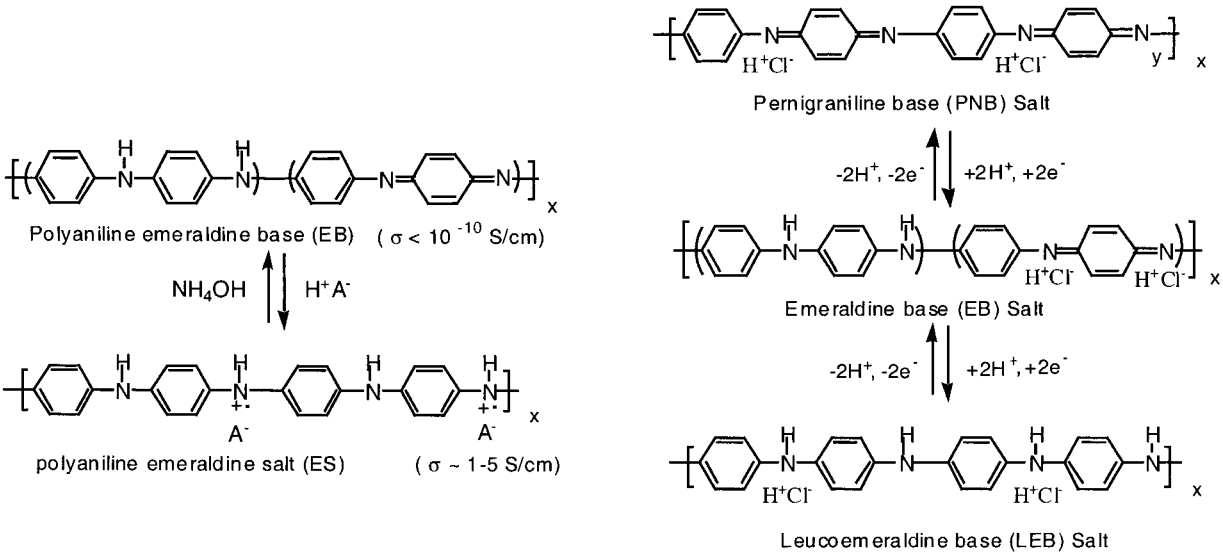
Scheme 1. Molecular Structure of Doped and Undoped Polyaniline (left) and Three Distinct Polyaniline Oxidation States (right) in 1.0 M HCl Aqueous Solution



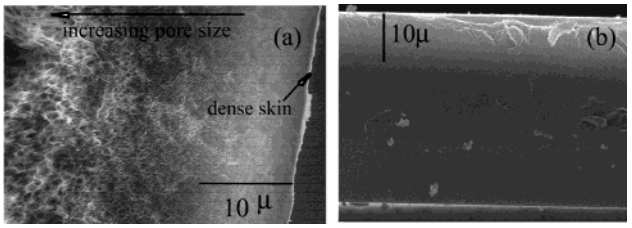


Figure 3. SEM of a cross section of the PANI ISAM (a) and thermally cured dense film (b).

M NH_4OH) released counterions from the PANI ISAM and led to bending toward the skin side (Figure 4b). In this example, the membrane went through angle changes of 180° in <5 s. This relatively fast response is likely due to rapid diffusion of dopants in to and out of the porous membrane structure and the submicrometer dense skin layer. A detailed study of the effect of HCl concentration on chemical actuators prepared from 20 wt % EB solution is shown in Figure 5a. In this study, we found the bending rate (angle per time period) increased as the HCl concentration increased. Higher HCl concentration caused faster diffusion of dopants into the membrane observed as faster bending rates. This is consistent with our hypothesis that the deformation mechanism of the chemical actuator is governed by protonic doping. Similarly, addition of LiCl salt into the HCl solution resulted in faster bending rates. This can be explained by the Donnan phenomenon. LiCl and HCl have a common ion, chloride. The common ion amplifies the ion concentration difference at the polymer−water interface, thereby shifting the equilibrium and allowing more efficient protonic doping.[17] In a direct comparison, a thermally cured homogeneous dense film exhibits no bending motion regardless of the solution pH and time of exposure.

The bending rate of a chemically driven PANI ISAM actuator can be fine-tuned by varying the membrane thickness. Membranes prepared from the same concentrated solution show increased bending rate with decreased membrane thickness (Figure 5b). For example, it took more than 600 s for a 206-μm membrane in 0.1 M HCl aqueous solution to bend 90° and only 20 s for a 62-μm membrane to bend the same amount.

All of the above results strongly support that chemical actuators are driven by the doping−dedoping process and that the bending movement is governed by the rate of counterion diffusion into and out of the membrane. It appears that the deformation mechanism of PANI chemical actuators is similar to electrochemical actuators on the basis of polypyrrole and polythiophene where doping is induced by electrochemical oxidation.

Electrochemical Actuators. A voltammetric study of PANI ISAMs, thermally cured PANI dense films, and thin PANI films coated on platinum sheets was performed (Figure 6). The cyclic voltammograms for both PANI ISAM (Figure 6a) and thermally cured PANI dense film (Figure 6b) were obtained by attaching a platinum electrode to the end of the membrane/film while keeping the platinum electrode above the aqueous solution (Figure 7, top). PANI ISAM and dense film show only one oxidation peak and its corresponding reduction peak, compared to two peaks observed for PANI film deposited on a platinum sheet (Figure 6c). This can be explained by the nonuniform potential distribution along PANI ISAM and higher resistance in the thermally cured PANI dense film. PANI thin film (<5 μm) deposited on a platinum sheet has a uniform potential distribution and the substrate has a much lower resistance. Nonuniform potential distribution with PANI ISAMs leads to a potential drop that promotes a nonuniform oxidation state along the length direction during the applied cyclic voltammetry. This causes the two independent peaks observed for PANI film deposited on a platinum sheet to collapse into one single peak.

Higher current and redox potential for thermally cured PANI dense films is related to higher EB mass and higher energy necessary to draw counterions into a dense film, respectively. The density of the thermally cured dense film and the PANI ISAM is 1.3 and 0.51 g/cm^3, respectively. We believe that the electrochemical

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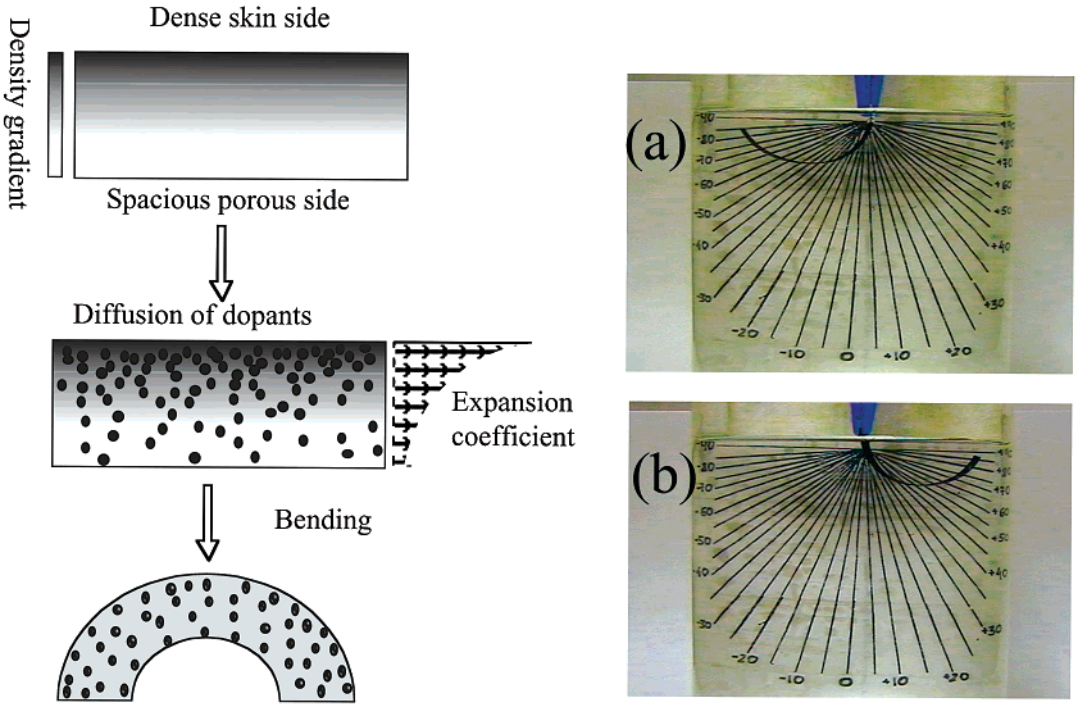

Figure 4. Left: bending mechanism of PANI ISAM through chemical doping. Right: PANI ISAM immersed in (a) 1.0 M HCl aqueous solution and (b) 4.0 M NH_4OH aqueous solution.

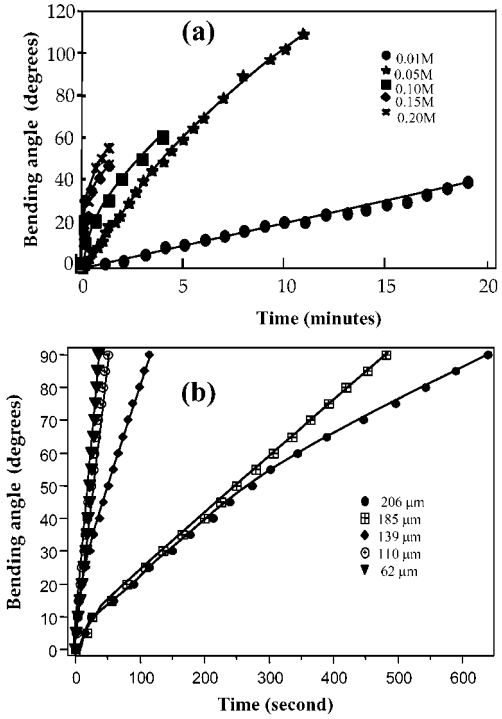

Figure 5. PANI ISAMs chemical actuators tested under different acid concentrations (a) and with various thicknesses (b).

behavior of the thermally cured PANI dense film and PANI ISAM is basically identical. Electrochemical cycling of the potential across PANI ISAMs resulted in membrane bending. The same electrochemical cycling applied to thermally cured PANI dense films did not show any movement. This suggests that deformation of the electrochemical actuators is based on membrane asymmetrical configuration. A density-dependent volume change during electrochemical polarization creates a stress gradient along the cross section of the membrane that promotes bending movement (Figure 7, bottom).

Our preliminary results show that a monolithic actuator based on 60-μm PANI ISAM was able to operate in 1.0 M HCl aqueous solution for at least several hundred cycles. Figure 8 shows electrochemical behavior during the first 35 cycles of a monolithic actuator based on PANI ISAM. During this study we applied a square wave potential with a frequency of 0.25 Hz (from -1 V (2 s) to 1.5 V (2 s) vs SCE) in 1.0 M HCl aqueous solution. Although the bending angle decreased gradually with the number of cycles (from $\pm 30°$ to $\pm 15°$), the electrochemical behavior of the PANI membrane remained intact. This result shows a very stable electrochemical response of PANI ISAM that can allow a monolithic actuator to operate over long periods of time. However, the maximum bending angle (45°) of this electrochemical PANI ISAM monolithic actuator did not reach the same level as the chemical PANI ISAM monolithic actuator or the bimorph actuator based on the thermally cured PANI dense film (90°). We think the lack of electrochemical PANI ISAM monolithic actuator response is due to a nonoptimal spatially dependent stress gradient (internal). We are currently working on optimizing PANI ISAM membrane configuration to achieve electrochemical monolithic actuators with higher bending angles.

Differences in the PANI ISAM's performance as a monolithic chemical and electrochemical actuator can be explained from the perspective of underlying deformation mechanisms (Scheme 1). When PANI emeraldine base (EB) is immersed in acidic media (Scheme 1, left), protonation of imine nitrogens (doping) gives rise to radical cations along the polymer chains. Counterions (anions) enter the polymer matrix to maintain charge neutrality. Therefore, acid doping promotes volumetric

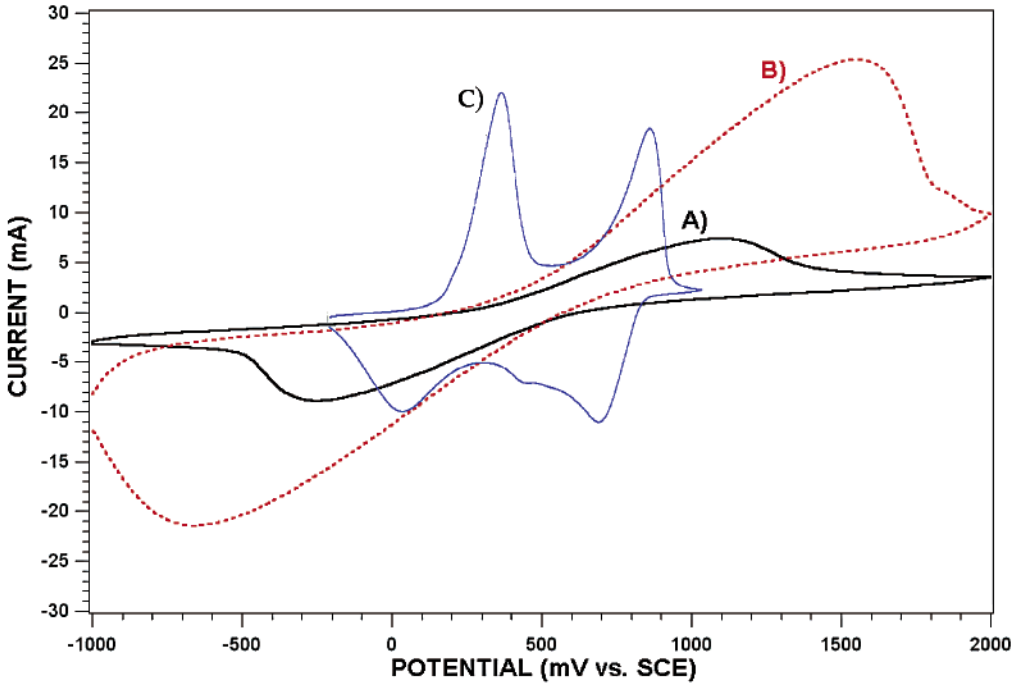

Figure 6. Cyclic voltammograms performed at a scan rate of 100 mV/s between −1000 and 2000 mV (vs SCE) in a 1.0 M HCl aqueous solution at room temperature: (A) 60-μm polyaniline membrane; (B) 60-μm polyaniline dense film; (C) 5-μm thin film coated on a platium sheet.

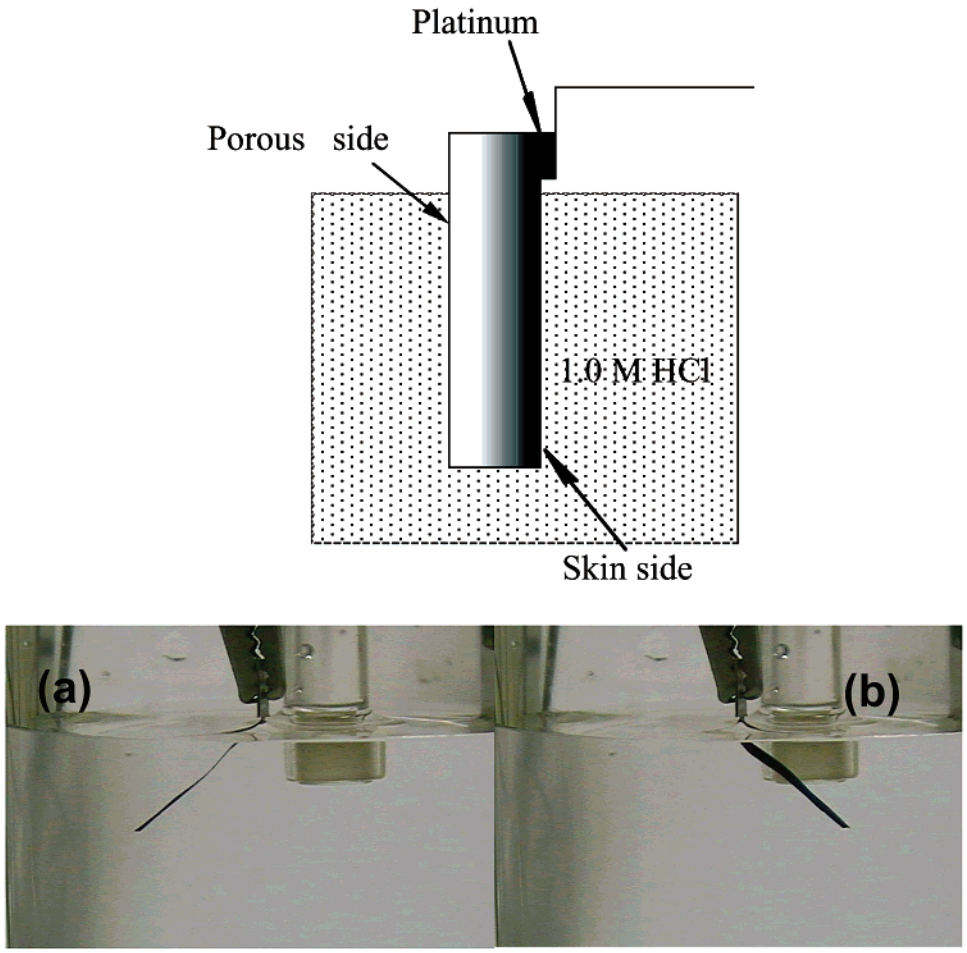

Figure 7. Top: Schematic representation of a PANI ISAM monolithic electrochemical actuator. Bottom: oxidation of PANI ISAM (a) and reduction of PANI ISAM (b).

changes because of electrostatic interactions among newly generated radical cations, conformational changes between undoped and doped PANI, and incorporation of counterions into the polymer matrix. Conversely, base

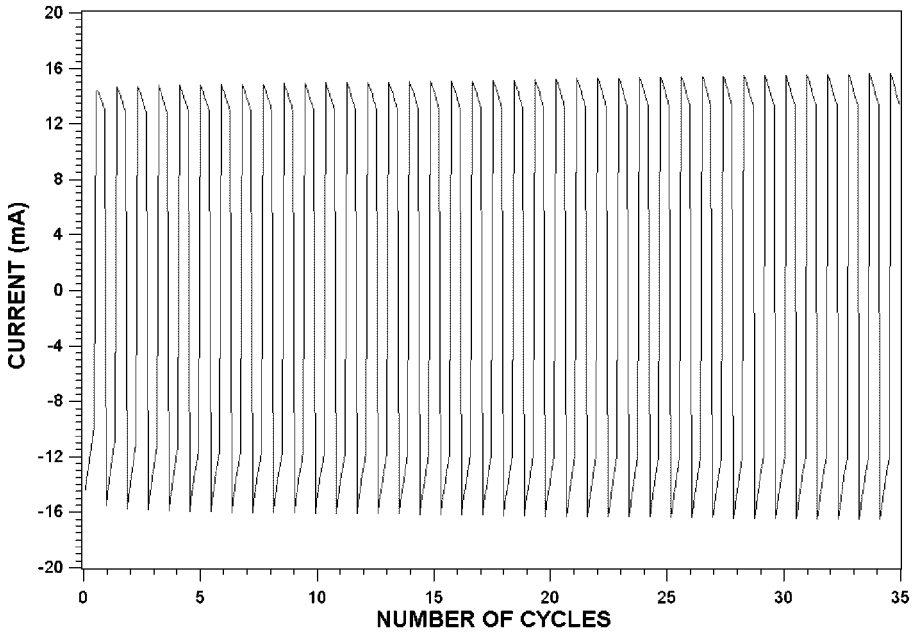

Figure 8. Plot of current vs time under a square wave of potential with a frequency of 0.25 Hz (from −1 V (2 s) to 1.5 V (2 s) vs SCE) in a 1.0 M HCl aqueous solution.

de-doping of the doped membrane removes positive charges from the polymer chains and expelled counterions from the membrane, leading to contraction of PANI ISAMs.

By comparison, electrochemical PANI ISAM actuators operate in 1.0 M HCl aqueous solution. During the redox cycle, polyaniline undergoes changes in oxidation states from pernigraniline base (PNB) and emeraldine base (EB) to leucoemeraldine base (LEB). Regardless of the oxidation state, PANI contains either secondary amines or tertiary amines or a combination of secondary and tertiary amines (Scheme 1). All of these amines are subject to protonation in acidic media. Therefore, there is little or no change in the total number of positive charges on the PANI backbone or counterions associated with PANI with changes in oxidation state. Neither the electrostatic interaction among positive charges nor the diffusion of counterions into and out of the membrane is responsible for the volumetric deformation of the electrochemical PANI ISAM actuator. We can only attribute membrane bending to changes in PANI conformation from LEB and EB to PNB. Because of this, volume change associated with electrochemical oxidation/reduction is less than that of chemical doping/de-doping. The fact that PANI ISAM exhibits good chemical actuation does not guarantee that it will also have good electrochemical actuation.

We believe that a more efficient PANI ISAM electrochemical actuator can be fabricated from a membrane with a more dense structure (>0.53 g/cm^3) and a tuned density gradient because conversion of changes in polymer conformation into actuator bending movement requires intimate contact between polymer chains. We are currently fabricating such membranes to further improve the performance of electrochemical PANI ISAM monolithic actuators.

Conclusion

In summary, various PANI ISAMs were prepared from highly concentrated EB solutions. These membranes were used as chemical and electrochemical monolithic actuators. A density gradient within the membrane generated spatially dependent expansion/contraction upon chemical doping/de-doping or electrochemical oxidation/reduction and caused membrane bending. These monolithic actuators are superior to bimorph actuators in terms of their structural stability because the possibility of delamination is avoided. The deformation mechanism of chemical actuators is mainly governed by the diffusion of dopants into and out of the membrane. The bending rate of the chemical actuator can be fine-tuned by varying the acid concentration and membrane thickness. On the other hand, the concomitant change in oxidation state and polymer conformation is likely to be responsible for the volumetric deformation of PANI ISAM electrochemical actuators. Our work highlights the potential advantage of using PANI ISAM to construct monolithic chemical and electrochemical actuators. Although this work focused on polyaniline, we believe that other conducting polymers such as polypyrrole and polythiophene and their derivatives may be used to construct ISAM configuration based actuators.

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