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Self-Oscillatory Actuation at Constant DC Voltage with pH-Sensitive Chitosan/Polyaniline Hydrogel Blend

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Hydrogels constructed from semi-interpenetrating polymer networks (semi-IPNs) of chitosan and polyaniline (CP) were prepared and the effect of various pH (1, 4, 7, 10) levels on the equilibrium water content (EWC) and electromechanical response were investigated. In swelling experiments, the freeze-dried membranes exhibited a high EWC value in acidic conditions. The electromechanical behavior of the CP membranes was also measured in a direct current electric field in pH buffer solutions. The electric potential induced bending actuation in the membrane, with the direction of bending being reversed in acidic and basic solutions. A novel oscillatory bending was observed in neutral electrolyte, which may ultimately prove useful as a simple propulsion mechanism in fishlike swimming robots or for simple pumps.

1. Introduction

Bending actuation from hydrogels in electric fields has been known for some decades[1−3] and has been used to generate fish or eel-like propulsion.[1] In these previous studies, a switching electric field has been used to generate oscillatory bending in the hydrogel. In the present paper, we report a self-oscillatory behavior in a novel hydrogel/conducting polymer blend under a constant DC electric field. Although currently a small response, further development may allow a simple propulsion mechanism for fishlike swimming robots. This communication reports the initial observations and focuses on possible mechanisms for the oscillatory behavior.

The unique combination of a pH-sensitive hydrogel (chitosan) and a redox-active conducting polymer (polyaniline) is believed to be responsible for the unusual actuation behavior. We are interested in developing hydrogel actuators that operate by redox-induced pH switching. Ultimately, we aim to prepare an electronically conductive network (composed of polyaniline) that may be stimulated electrochemically to alter its surrounding pH, and so induce large-scale phase changes in the neighboring hydrogel network. The molecular distances involved should shorten the time required for the actuation response. In our previous work, we have shown that chitosan/polyaniline (CP) blends show separate actuation responses due to pH and electrochemical stimuli.[4]

Polyaniline (PANi) is one of the most useful conducting polymers and has been chosen for this study because of its solution processability and unique pH-switching capability. PANi's versatility is demonstrated by its use in a wide range of applications,[5] including actuators, electrochromic devices, batteries, sensors, and others. The starting material for redox reactions involving PANi is usually the emeraldine salt (ES), as this is the only conductive form of PANi. As shown in Scheme 1, oxidation or reduction of the ES produces the pernigraniline base (PB) and the leucoemeraldine base (LB), respectively.[6] Both the leucoemeraldine salt and pernigraniline salts are only stable at pH below 1 or 0 so that they do not occur in common electrolytes.[7−10] Of interest in the present study is the fact that reduction and oxidation of the polyaniline could induce a change in the local pH.[11] This local pH change may then trigger a response from the neighboring hydrogel polymer.

Chitosan has been chosen as the hydrogel phase in the present study because of its high swellability at low pH and its general usefulness in biomedical applications. Chitosan is a high-molecular-weight carbohydrate polymer manufactured from chitin[12,13] by conferring a cationic nature to the free amino groups left by the partial removal of the acetyl

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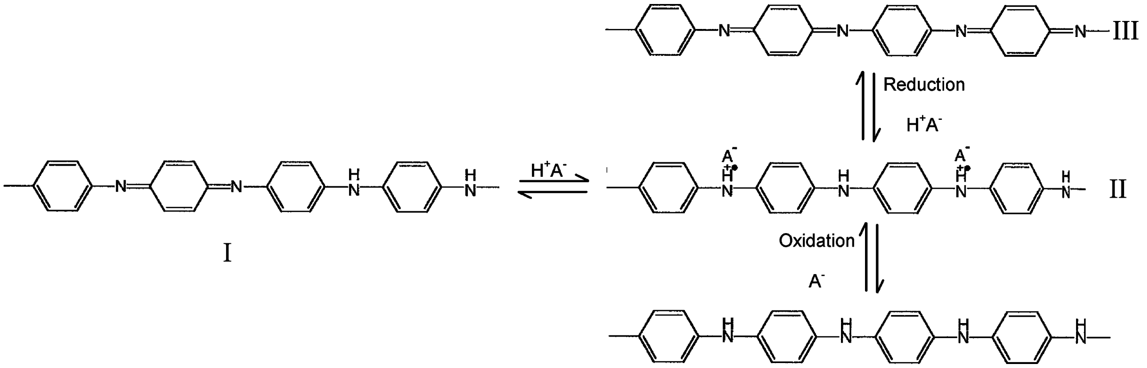
Scheme 1 Common Forms of Polyaniline[a]



[a] (I) Emeraldine base (EB); (II) emeraldine salt (ES); (III) pernigraniline base (PB); (IV) leucoemeraldine base (LB).

groups of the chitin. Chitosan appears to be more useful for biomedical applications and in the dehydration of aqueous solutions than does chitin, because it has both hydroxyl and amino groups that can be easily modified.[14,15] Chitosan has many useful features, such as hydrophilicity, biocompatibility, and antibacterial properties.[14]

Recent studies have shown that chitosan IPN structures with polyvinylalcohol show strong swelling in acidic media because of the protonation of the amino groups. Thus, chitosan is a suitable candidate for swelling induced by the reduction of PANi ES.

In this work, a freeze-drying method was applied to fabricate CP membranes with a highly porous structure. Freeze-drying has been shown to modify the inner structure of the gel producing a very open layered structure so as to improve the diffusion of mobile ions and water.[16] As a result, the freeze-dried CP membranes should show improved electromechanical properties. Our main objective was to investigate these electromechanical properties of the CP membrane under different pH and electric field conditions.

2. Experimental

2.1. Materials. The chitosan was obtained from the Jakwang Co., Korea, and had an average molecular weight of 2.0×10^5, with a 76% degree of deacetylation. Glutaraldehyde (25 wt % solution in water; GA), hydrochloric acid (HCl), 1-methyl-2-pyrrolidone (NMP), pH buffer solutions (pH 1, 4, 7, and 10), acetic acid, and methanol were purchased from the Aldrich Chemical Co., USA. The polyaniline emeraldine base (PANi EB Aldrich Chem. Co., USA) used had an average molecular weight of 6.5×10^4 (undoped form, minimum assay 99.5%).

2.2. Preparation of Chitosan/Polyaniline Membranes. The chitosan was allowed to dissolve in a 2 wt % acetic acid solution (solid content in solution = 2 wt %) over a period of 24 h, and the PANi EB was dissolved in NMP (0.5 wt %). The chitosan/PANi mixed solutions were formed by mixing the chitosan and PANi-EB precursor solutions. The pH of the mixed solutions were adjusted to pH <1 using HCl, and the solutions were then mechanically stirred for a period of 24 h[13]. The resulting solutions were then poured into petri dishes and dried in a vacuum oven at 50 °C for 48 h. The dried blended films were either used as they were or crosslinked to form semi-IPNs. Crosslinking of the samples was carried out by immersing the film in a 1:1 methanol:glutaraldehyde solution containing 6 wt % chitosan in deionized water at room temperature. The pH of the resulting GA solution was also adjusted to pH <1. The residual NMP in the films and any residual material was then extracted by washing the samples using a 1:1 methanol: deionized water solution at pH <1 and dried under vacuum for 24 h.

Freeze-drying was employed to obtain a more porous CP membrane structure, as shown previously.[16] After drying, the CP membrane was fully swollen by immersing in deionized water for 24 h. The fully swollen CP membrane was then frozen in a freezer (Forma Scientific InC, Marietta, USA) at −70 °C. The frozen samples were dried in freeze dryer (OPERON, Korea) under a vacuum of 1×10^{-5} Torr for 24 h.

2.3. Characterization. To measure the equilibrium water content (EWC), preweighed dry membranes were immersed in pH buffer solutions at 27 °C until they swelled to an equilibrium value. A period of 3 h was found to be sufficient for each membrane to reach equilibrium. The equilibrium water content (EWC) was calculated using the following equation[17]

$$\mathrm{EWC}\ (\%) = ((W_e - W_d)/W_e) \times 100 \qquad (2)$$

where W_e denotes the weight of the swollen state at equilibrium and W_d is the dry weight of the membrane. The swelling experiments were repeated three times until no further weight increase was observed.

Before electromechanical measurements were performed, the CP membranes were immersed in each pH buffer solution for 30 min. After the membranes were soaked, the bending experiments were carried out by applying a various contact DC voltage in each pH buffer solution. An electrical connection was made directly to both sides and at one end of the CP membrane using platinum contacts (insulated from the electrolyte), so that one side of the membrane acted as the anode and the other side the cathode. The bending deformation of the CP membranes with porous structures were measured using a CCD camera.[18] At least 20 different samples were evaluated at each pH, and the average degree of bending was determined from the multiple samples when the DC potential was applied.

For CV measurements, the sample was immersed in an electrochemical cell containing 1.0 M HCl and a CV-27 potentiostat (Biolab) and Maclab (AD Instruments) were employed using a scan rate of 50mV/sec. For conductivity measurements, the fully swollen

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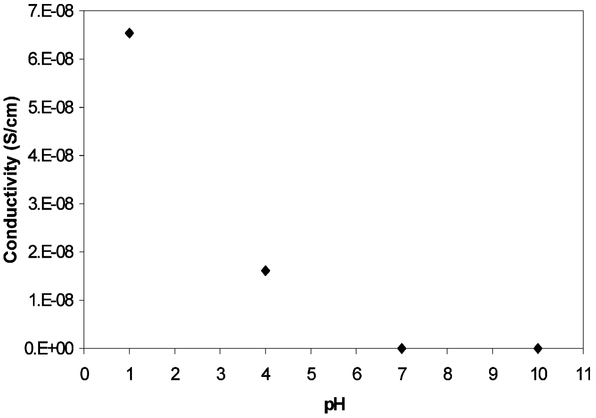

Figure 1. Conductivity of CP membranes after conditioning for 30 min in buffer solutions of different pH.

samples (dimension: length = 20 mm, width = 5 mm, and thickness = 2 mm) were sandwiched between two ITO glass plates wrapped with copper foil at the tip of one end to form a two-electrode system. Impedance resistance analysis was conducted using a model 1260 frequency response analyzer (Solartron) driven by Solartron impedance measurement software version 3.2.0 over a frequency range of 1 MHz to 1 Hz with a perturbation ac voltage of 0.1 V. The bulk resistance (R) was the average value of impedance taken from the platen resistance in the high-frequency region from 10 kHz to 1 MHz and was assumed to be dominated by electronic rather than ionic processes. Conductivity was calculated from

$$\sigma = \frac{d}{RA} \tag{3}$$

where d is the sample thickness, A is the area, and R is the measured resistance.

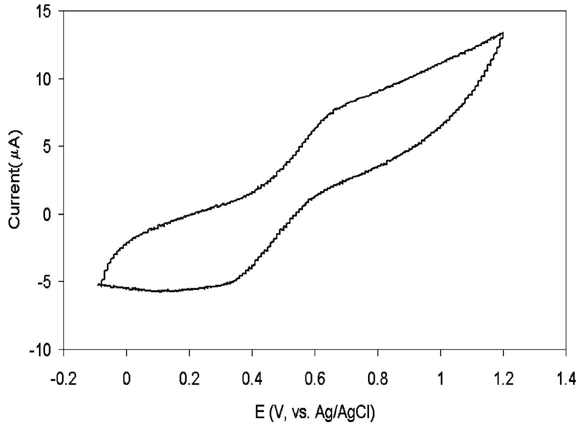

Figure 2. Cyclic voltammogram of CP membrane in 1 M HCl.

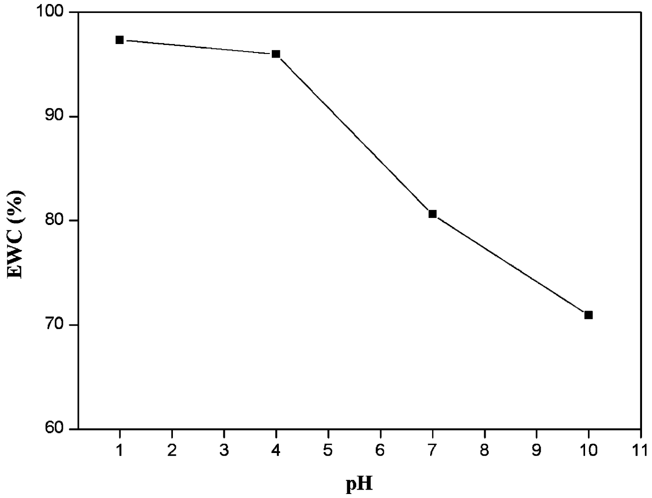

Figure 3. pH-dependent EWC values of CP ion-exchange membrane at 27 °C

Results and Discussion

The electrical and electrochemical properties of the CP membrane were characterized through conductivity testing and cyclic voltammetry. As shown in Figure 1, the electrical conductivity of the membranes was quite low (~10^{-8} S/cm) in acidic conditions, which is indicative of poorly connected PANi islands within the chitosan matrix. The conductivity becomes immeasurably small at pH >4. This observation is explained by the fact that PANi exists in the protonated and conductive emeraldine salt form (Scheme 1, II) at pH ≤ 4 and is in the non-protonated and nonconductive emeraldine base form (Scheme 1, I) at pH >4.[6] Despite the low conductivity of the membranes, reasonable electroactivity was observed in acid (Figure 2). Clear evidence of reversible oxidation and reduction of the PANi can be seen from the voltammogram, although the redox peaks are not well-defined because of the low electronic conductivity of the CP samples.

Figure 3 shows the EWC obtained from each pH buffer solution. These measurements were made to determine how the CP membranes responded to the pH of the surrounding electrolyte. The highest EWC occurred at pH 1 as a result of the protonation of the amino NH_2 groups in chitosan and NH groups in PANi-EB to form PANi-ES. In acidic solutions, the protonation of the amino groups in the CP membrane and the dissociation of the hydrogen bonds develops an internal ion osmotic pressure. On the other hand, in basic solutions, hydrogen bonds tend to associate because NH_3^+ and NH^+ groups are deprotonated to NH_2 and NH, respectively. These results may help to explain the bending behavior of the CP membranes when a voltage is applied, because redox reactions may change the pH of the surrounding electrolyte.

When the CP membranes were subjected to an applied electric field at pH 1, they bent toward the anode. Figure 4 shows the bending degree of the samples under various DC voltages in the pH 1 buffer solution, showing that the degree of bending increased as the magnitude of the applied voltage increased. The degree of bending also increased with time and reached the maximum value for $t = 15-25$ s in all cases. The results are the average of 20 different samples with the variation between samples being less than 2−3°.

Bending toward the anode is believed to result from the locally high ionic strength that develops near the positively charged anode because of the migration of mobile anions. These anions include the Cl^- counterions introduced into the membrane during protonation with HCl. Other anions from the buffer solution may also enter the gel and participate in the electric-field driven ion migration. Although the mass transport of anions (and solvent) to the anode side should produce swelling at the anode and bending toward the cathode, a different mechanism must dominate in the CP membranes in acidic electrolyte. Previous reports have attributed the bending of anionic gels toward the cathode as

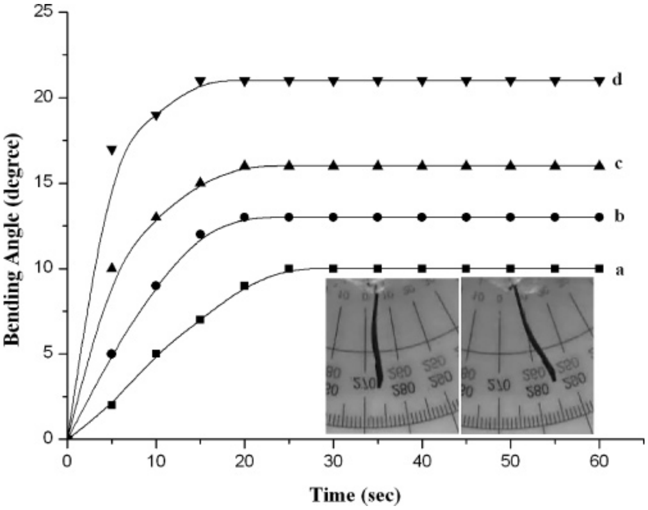

Figure 4. Bending degree of CP freeze-dried membrane at pH 1 when various potentials were applied ((a) 3, (b) 5, (c) 7, and (d) 10 V). Photographs show neutral position (left) and maximum bending at 5 V (right). Bending is toward the anode.

being due to the electrostatic shielding induced by locally high ionic strength near the cathode[19] resulting from the migration of free cations. In the positively charged CP membrane used in the present study, a high concentration of anions will occur at the anode, causing shrinking at the anode and bending toward the anode (as observed). The high ion concentration can shield the fixed positive charges on the polymer backbones, reducing electrostatic repulsion between neighboring charged sites and allowing the polymer to relax to a less-extended conformation. Deswelling of chitosan gels by increasing the ionic strength of the surrounding electrolyte has been reported previously.[20]

Electrochemical reactions of PANi and/or the electrolyte may also contribute to the bending actuation. PANi oxidation at the anode leads to volume contraction due to expulsion of both protons and counterions to the surrounding electrolyte[6]

$$\text{Anode: } \mathrm{ES^+{\cdot}A^- \rightarrow PB + H^+ + A^- + e^-} \text{ in acid} \qquad (6)$$

$$\text{Cathode: } \mathrm{ES^+{\cdot}A^- + e^- \rightarrow LB + A^-} \text{ in acid} \qquad (7)$$

This volume contraction at the anode also contributes to the bending toward the anode.[21] However, the reduction of PANi at the cathode side in acid also likely produces a contraction at the cathode[6,21] and so limits the bending toward the anode.

Finally, the high DC potentials applied may induce changes in pH near the electrodes according to the following reactions

$$\text{Anode: } \mathrm{2H_2O \rightarrow 4\,H^+ + O_2 + 4e^-} \qquad (4)$$

$$\text{Cathode: } \mathrm{2H^+ + 2e^- \rightarrow H_2} \qquad (5)$$

These pH changes would lead to swelling at the anode (decrease in pH), contraction at the cathode (increase in pH), and bending toward the cathode. Because bending was observed to occur toward the anode, these processes must be less significant in the pH 1 buffer than those mechanisms described above.

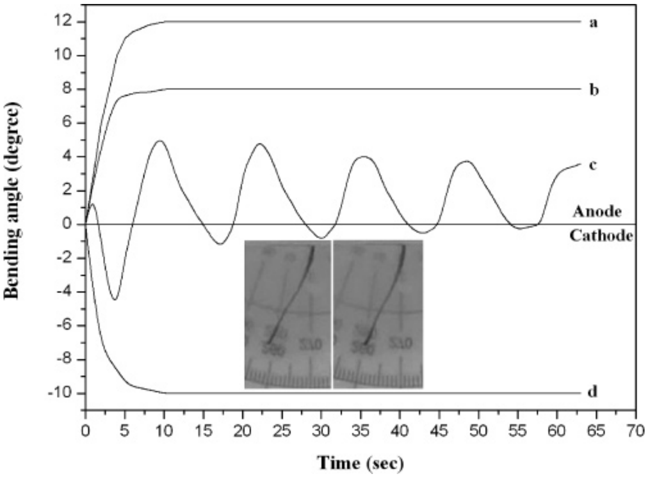

Figure 5. Bending degree at different pH when 5 V was applied ((a) pH 1, (b) pH 4;, (c) pH 7, (d) pH 10). Photographs show limits of small oscillatory motion at pH 7.

The bending deformation was found to be highly dependent on the electrolyte pH. As can be seen in Figure 5, the CP membrane bent toward the anode in acid solutions (Figure 5, curves a and b) and toward the cathode side in basic solutions (Figure 5, curve d). Of particular note is curve c in Figure 5, which shows an oscillation in bending toward the anode and cathode alternately at pH 7.

To understand the oscillation behavior, it is first necessary to consider the process that causes bending toward the cathode in basic electrolytes. Under these alkaline conditions, both the chitosan and polyaniline are uncharged and the polyaniline is in the nonconductive emeraldine base state and is electrochemically inactive. The actuation due to redox processes in PANi (eqs 6 and 7) is expected to be negligible, as is the bending due to ion migration, because the CP membrane is uncharged and contains few free ions. The main actuation mechanism is likely to be due to the pH gradient induced by water hydrolysis when a DC potential is applied

$$\text{Anode: } \mathrm{4OH^- \rightarrow 2H_2O + O_2 + 4e^-} \qquad (8)$$

$$\text{Cathode: } \mathrm{2H_2O + 2e^- \rightarrow H_2 + 2OH^-} \qquad (9)$$

The lowering of the pH near the anode (eq 8) would cause protonation of the chitosan and polyaniline at the anode side leading to swelling and bending toward the cathode.

The oscillation seen in neutral electrolyte represents a cyclic shift in bending actuation between the behavior observed in acid electrolytes and that observed in basic electrolytes. At pH 7, the CP blend is partially charged with a small amount of protonation in the chitosan. Careful examination of the data in Figure 5 shows that the bending is initially toward the anode at pH 7, which is due to the movement of mobile cations to the anode, leading to high local ionic strength, shielding, and shrinkage at the anode. These processes are the same that dominate in acidic electrolyte, where the membrane is highly charged. At pH 7, however, the PANi is initially in the nonactive emeraldine base state, so the

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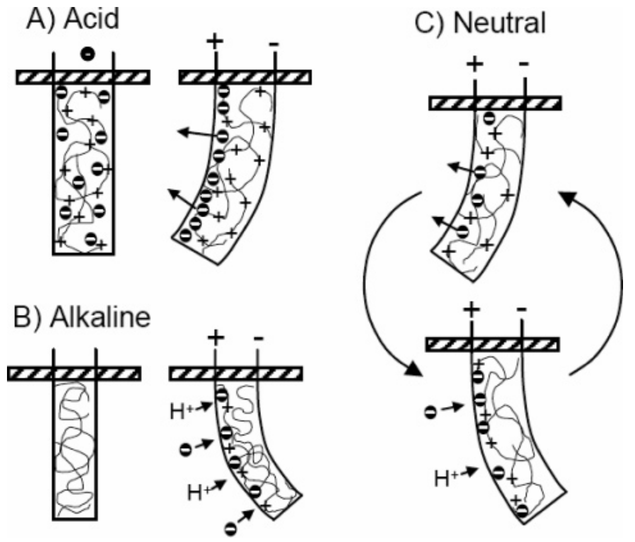

Figure 6. Bending motion of chitosan/polyaniline membranes in different electrolyte pH solutions. (A) In acid solution, the membrane bends to the anode, as the membrane has an initial high charge density (+) and the motion of mobile anions (solid circle with white bar in center) to the anode cause charge shielding and shrinkage. Additionally, the oxidation of PANi at the anode leads to anion expulsion, causing additional shrinkage at the anode. (B) In alkaline solution, the membrane is initially uncharged, but local pH changes due to water hydrolysis generate low pH conditions near the anode, causing protonation of the chitosan and polyaniline and swelling at the anode. Net bending is toward the cathode. (C) In neutral electrolyte, the membrane is partially charged and initial movement is toward the anode because of charge shielding effects (as in A). Subsequent protonation of the polymer at the anode causes local swelling and bending back toward the cathode (as in B). The protonation renders the PANi electroactive so that oxidation may occur at the anode, causing shrinkage that promotes bending back toward the anode. A cyclic oscillation in bending results.

contribution to actuation by polyaniline redox reactions (eqs 6 and 7) is expected to be negligible.

A short time later, the direction of bending changes with the CP membrane passing back through the neutral position and then toward the cathode. As in alkaline media, the bending toward the cathode is likely to be due to the localized acidic conditions occurring at the anode (eqs 8 and 9), leading to protonation of the chitosan and PANi. These processes cause swelling at the anode and bending toward the cathode. The protonated PANi is now in the electroactive emeraldine salt state, which can be oxidized to pernigraniline base, releasing H^+ and the counterion, and producing shrinkage at the anode (eq 6). The polyaniline oxidation then results in bending toward the anode. Further reductions in pH (due to both PANi oxidation and water hydrolysis) favor the further protonation of chitosan and emeraldine base, causing oscillation back toward the cathode. The cycle of reactions can then continue to produce periodic oscillation in the bending. The process is depicted in simplified form in Figure 6. Clearly, the two competing processes occur simultaneously and the direction of bending reflects the dominance of one process over the other at a given point in time. Detailed analysis of the kinetics of both processes would be required to accurately describe the mechanism, as would micro-pH measurements to confirm changes in local pH near the electrodes.

It is interesting to note that gel oscillations have been noted previously. Most significant are the polyamphoteric gels that swell at both high and low pH. Such gels show an oscillating bending at constant DC voltage when in their neutral state.[22] The oscillation is due to competition between charge shielding and protonation/deprotonation reactions occurring because of electrochemically generated pH changes. Other gel oscillations have been driven by "chemical oscillators,"[23] where a series of chemical equilibria serve to oscillate the pH in a reaction vessel. The gel then responds to the cyclic changes in solution pH.[24]

The oscillating gel bending reported in the present study is quite different from those previously reported and appears to be critically dependent on the role of the electroactive polyaniline. Other studies of chitosan IPN gels without polyaniline have not demonstrated oscillatory behavior. In particular, IPNs formed between chitosan and poly(vinyl alcohol)[25] and poly(allyl amine)[26] both show steady-state bending toward the cathode at pH 7. In both cases, the equilibrium water content increases at low pH because of the protonation of the chitosan network, and actuation in a neutral electrolyte is most probably due to the low pH conditions produced at the anode. Neither of these systems showed oscillatory behavior, lending support to the role of polyaniline in the oscillations.

Conclusions

The electromechanical actuation of IPNs formed by chitosan and polyaniline has been investigated under DC conditions at different electrolyte pH levels. Several mechanisms were identified as probably contributing to the observed actuation. In alkaline electrolytes where the polyaniline is not electroactive, the CP membranes showed bending toward the cathode. This process was ascribed to local acidification at the anode side of the membrane causing protonation of the chitosan and polyaniline and associated swelling at the anode side. In acid electrolytes, the polyaniline electrochemistry was believed to contribute to the bending toward the anode. In addition, charge shielding due to the locally high ionic strength contributed to shrinkage at the anode. Intriguing oscillatory bending was observed in neutral electrolyte. This dynamic movement was thought to be caused by the formation of electroactive polyaniline (swelling at anode) followed by its oxidation (contraction at anode). Although the oscillation is currently small in magnitude and slow to occur, further development of this autonomous self-oscillation may ultimately be useful in actuators for propulsion or pumping.

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