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Electrochemical properties and actuation mechanisms of polyacrylamide hydrogel for artificial muscle application

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ABSTRACT

This paper presents a comprehensive study of the electromechanical behavior of PAAM hydrogel actuators.

In this study, we developed a new method for the characterization of the pH gradient inside the gel actuator. Then we analyzed the volume variation kinetics of the gel responding to various pH stimulations and investigated the electroactivity of PAAM actuators in a fully hydrated gel. Finally we explain the bending mechanism of the hydrogel actuator based on the phenomenon of diffusion of hydroxide and hydronium ions showing the correlation between the electrical, chemical and mechanical properties of such devices.

1. Introduction

PAAM hydrogels can be defined as lightly cross-linked polymers that are insoluble but swell dramatically in the presence of water leading to a rubbery gel that can involve up to 99 wt.% water. They have the ability to absorb and retain large volume of water or biological fluids which are at the origin of their liquid-like properties. However, they also exhibit solid-like properties due to their network formed by the cross-linking reaction [1–3].

Electroactive hydrogels, like PAAM can sense the physical, chemical and biological environment and respond to external stimuli in a controllable way. They show abrupt and vast volume changes in response to various stimuli from the surrounding environment and can be driven by electric field [4–11].

On selecting PAAM for artificial muscle application, there are many advantages. First it resembles natural living tissue more than any other class of synthetic biomaterials due to their high water contents, soft consistency and their activation mode which is similar to natural tissue. Secondly it is biocompatible and not biodegradable [12–14]. Third their physical and chemical properties vary with composition and can be varied as desired [15,16]. Fourth it can take various shapes [17] and it is a low-cost material compared to other electroactive materials [3].

The problem with PAAM hydrogels resides in their time of response that is relatively slow [18] compared to the microsecond scale in human muscle, but this can be compensated by assembling a large number of small elements acting in parallel. This is a promising area for future development [19]. If this mission is accomplished, an artificial muscle with strength and speed equal to that of a human muscle may be possible.

Aiming to develop the future design of an artificial muscle made from PAAM, our work consists on providing a closer look at the PAAM hydrogel properties and giving a deeper understanding of their bending movement as well of the molecular mechanism responsible of its behavior.

The muscle is not only a material but also a system. So to ensure functional and reliable structures, there is a strong need to acquire complete understanding of the materials properties; but it is only a part of the challenge; there is a larger effort that is aimed at gaining a better understanding of the molecular mechanisms of the actuation process for making predictive models effective.

At first, a new characterization method of the pH distribution in hydrogel actuators induced by an electrical field applied across its thicknesses is presented and a justification of the molecular ion distribution inside the gel matrix is provided. This inexpensive method will contribute to the development of the theory that explains the behavior of such ionic actuators and remains until now

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incomplete [20–24]. Moreover, this method opens the door to electrochromic applications since pH changes lead to color switching in the polymer system.

After showing the pH distribution inside the gel actuator, we chemically stimulated the hydrogel in order to study the effect of these pH variations on the gel matrix. The electroactive behavior and properties of a fully hydrated gel layer are also studied and the mechanism of bending is explained.

Finally the molecular mechanism of the ion diffusion responsible of volumetric changes of the gel is discussed based on the diffusion phenomenon of hydroxide and hydronium ions.

2. Materials and methods

Acrylamide 97%, *N*,*N*′-methylenebisacrylamide ≥98%, *N*,*N*,*N*′,*N*′-tertramethylethylenediamine 99% (TEMED) and ammonium persulfate ≥98% (APS), was used. All chemicals were purchased from Aldrich and used as received without any further purification. Deionized water was used for all the dilutions, the polymerization reactions, as well as for the swelling and electrochromic studies.

Polyacrylamide gels are synthesized by the standard-free radicals copolymerization method [2,3]. An aqueous solution 29 g/100 ml of acrylamide (2 ml) with *N*,*N*′-methylenebisacrylamide 1 g/100 ml as a cross-linker (60 μl) is polymerized using 10 μl of freshly prepared solution 250 mg/ml of APS as initiator and 5 μl of TEMED as an accelerator.

After mixing, the solution was maintained for 24 h at room temperature for complete polymerization. The resulting gels are then hydrolyzed in a basic solution of NaOH 1 M for 2 h and then placed in deionized water for 10 days. Water was repeatedly changed to wash out most of the extractable materials and allow them to reach equilibrium volume. On reaching swelling equilibrium, gels were gently removed and used. The resulting pH of the hydrated fully swelled gel is 7.2 and the average swelling ratio is 200.

The pH indicative solution was prepared by blending red cabbage with hot deionized water at 70 °C (130 g/100 ml, approximate ratio of cabbage to water). The resulting mixture was kept for an hour to reach room temperature and then filtered through a 0.8-μm pore size filter until a solution was obtained.

3. Experimental results

In this section, we present the procedure followed in preparing the experiments. Results are presented with some explanations. In the following section detailed discussion will be presented.

3.1. Characterization of the molecular mechanism

The bending phenomenon of gel actuators is caused by the local pH gradient due to water electrolysis induced by the applied voltage. Ions produced by electrochemical reactions inside the gel matrix [3], which plays the role of electrolyte, are attracted toward their counter-electrodes to induce the pH gradient. To characterize this electrolysis phenomenon and the diffusion of ions inside the gel, a new method was developed using a natural pH indicator (red cabbage).

The color of red cabbage is due to the presence of anthocyanins. These anthocyanins are water-soluble pigments which can exist in several configurations according to the pH level [25]. One at least of these configurations is colored; it absorbs light between 400 and 800 nm. The variation of the anthocyanins structure according to the acidity of the medium is a characteristic of these molecules [26]. According to the pH, values the calibration of the indicative solution is shown in Table 1.

Table 1
Calibration of the indicative solution

Color	pH
Red	2
Purple	5
Violet	7
Blue	9
Blue-green	11
Greenish yellow	12
Yellow	13

Deionized water containing 10 vol.% of the indicative solution was used to swell a gel matrix. The swelled gel, having the dimensions of 4 cm length, 2 cm width and 1.5 cm thickness, is then submitted to an electrical field generated by a 10 V constant voltage for 2 min (Fig. 1). This external electrical stimulation induces remarkable color changes.

As electrolysis takes place on the two electrodes, the sources of the hydroxide and hydronium ions are located in the regions in contact with the electrodes. Water is oxidized at the positive electrode or anode with production of hydronium ions (Eq. (1)) and reduced at the negative electrode or cathode with production of hydroxide ions (Eq. (2)).

$$6H_2O_{(liquid)} \rightarrow O_{2(gas)} + 4H_3O^+_{(aqueous)} + 4e^- \qquad (1)$$

$$4H_2O_{(liquid)} + 4e^- \rightarrow 2H_{2(gas)} + 4OH^- \qquad (2)$$

The acidity of the area close to the positive electrode is more important than the rest of the medium, so the area close to the anode will be characterized by a red color from the indicative solution due to the hydronium ions production. The red region is shown in Fig. 1(a) in black using image processing by converting the image from RGB to CMYK then keeping only the magenta channel and deleting the other channels. In the same way, the area close to the negative electrode is more basic and the cathode will be recognized by a yellow color from the indicative solution due to the hydroxide ion production. The yellow region is shown in Fig. 1(b) in black using image processing by converting the image from RGB to CMYK, then keeping only the yellow channel and deleting the other channels. Note that between the two regions the color is blue. Thus the electromigration of hydronium and hydroxide ions toward their counter electrodes by the electro-attractive force generates a dynamic pH gradient, thus a color gradient. Based on the color variations and on the calibration given in Table 1 we plot in Fig. 1(c) the assumed pH values within the gel as function of its thicknesses.

The average diffusion rate of different types of molecules is expected to depend upon their average velocity [27]. Hydroxide ions migrate more easily in the medium due to their diffusion rate which is more important than the diffusion rate of hydronium ions [27], and the yellow color dominates in the gel matrix (Fig. 1).

3.2. Chemical stimulation

The response of the gel to a pH variation is studied. The water-saturated PAAM gel has a pH of 7.2 and is considered as the neutral gel.

Different pieces of the neutral gel are immersed in solutions of different pH levels for 1 h. The difference of pH values (ion concentration) between the gel and its surrounding liquid causes the movement of ions out of the gel matrix forcing it to contract. The volume changes of the specimens after a pH variation of the surrounding liquid was examined and the degree of shrinking is illustrated in Fig. 2.