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Low pH-range control of McKibben polymeric artificial muscles

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ABSTRACT

Reversible swelling and de-swelling of pH reactive polymers are mainly made using strong bases and strong acids, typically with pH equal to 0 or 1 and 14 or 13. As a consequence, pH-artificial muscles are triggered at pH values too extreme to be in contact with living tissues. This report analyses the possibility of using weak base–weak acid buffers to generate the ion circulation necessary for swelling/de-swelling phenomena with a limited pH-range. Further, we describe experiments with ion-exchange resins swelling and de-swelling in response to standard $NaHCO_3/CH_3COOH + CH_3COONa$ weak base–weak acid solutions. The ion-exchange resin is placed inside the inner tube of a McKibben-braided structure whose functioning we have discussed elsewhere in connection with its reliability to define a chemo-mechanical artificial muscle with static and dynamic behaviour close to human skeletal muscle. We experimentally show that a 0.25 M buffer solution leads to a maximum isometric force and a contraction time response similar to that obtained with 0.1 M NaOH/HCl strong base–strong acid. As a consequence, our McKibben polymeric artificial muscle is now controlled within a lower pH-range with muscle contraction triggered at about 8.3 pH, and muscle relaxation at about 4.5 pH. Finally, we report the dynamic performance of an artificial muscle that is 170 mm long/7 mm diameter in an isotonic mode with loads between 0.25 and 10 kg.

1. Introduction

Activation of artificial muscles by pH variations is a promising approach in the present-day search for "new motors" based on artificial polymer muscle technologies [1] due to its chemical simplicity and the rapid generation of pH steps in comparison with control by temperature variations. This purely chemical activation mode also appears as an alternative to electrical activation modes by current or tension control. All pH-muscles are based on the use of pH-sensitive polymers swelling either in basic pH by means of acidic groups such as $-COOH$ or $-SO_3H$, or in acidic pH by means of basic groups such as $-NH_2$. From Kachalski and Kühn's historical experiments [2,3], to more recent attempts at using thin strips of PVA-PAA [4], PAN (nano)fibres [5–8], or chitosan-based fibres [9], pH-muscle activation is performed with 1 M acid–base solutions, corresponding to a [0–14] pH-range. These extreme pH values are motivated by the maximum protonation and deprotonation of the ionizable reactive polymer functional groups. In a previous work we showed how to employ the McKibben-braided structure to construct a compact pH-muscle producing a reversible contraction force with 0.1 M, and even 0.05 M acid–base solutions [10]. However, when lower concentrations ranging from 0.01 to 0.001 M were used, the force generated by the artificial muscle dramatically decreases and approaches zero at 0.0001 M concentrations. Other studies also emphasize the limitations of pH-muscles to very acidic or very basic ranges: for example, PAAM hydrogel actuators have recently appeared to be effective for pH < 3 or pH > 12 [11]. Without going into the ultra-sensitive issue of integrating active elements into the human body, such pH values are no longer adapted for future medical applications in which the artificial muscle could be used as an external support. We wish to demonstrate in this paper how the use of standard weak acid–weak basic buffer solutions can be a very simple way of triggering an ion-exchange resin pH-muscle with a limited pH-range. The following section explains the application of buffer solutions to the control of ion-exchange resin pH-muscles and the next section reports the experimental results obtained with our McKibben-type braided structure both in isometric and isotonic conditions.

1.1. Buffer solutions as a simple way of controlling a pH-muscle at low pH-ranges

Artificial muscles utilizing pH changes are generally controlled using strong acid HCl–strong base NaOH. In the case of a pH-sensitive polymer containing acid groups such as ion-exchange resins with COOH functional groups, resin-swelling in basic pH is

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obtained by the exchange of Na^+ ions (from NaOH) with H^+ ions (from COOH functions) inside the aqueous medium, and the de-swelling in acid pH by the exchange of H^+ ions (from HCl) with Na^+ ions (from the $RCOO^-Na^+$ functions). When the pH varies, the concentration of Na^+ and H^+ ions also vary. Although the term pH-muscle has been adopted for designating this kind of artificial muscle, it appears that the pH-sensitivity is essentially an ion-sensitivity. This means that the true control variable of these artificial muscles is the concentration of reactive ions inside the aqueous medium and the pH, in terms of control, is a dependent control variable. As a consequence, the possibility of generating a high concentration of reactive ions in the reactive medium while maintaining a moderate pH, can be postulated. The standard use of buffer solutions can thus be considered as a very simple and efficient method of making real this possibility. Consequently, we substitute the weak acid buffer and weak base buffers for the strong acid HCl and strong base NaOH. Two potentials candidates are $NaHCO_3$–$CH_3COOH + CH_3COONa$. Subsequently, we substitute a strong basic ion-exchange equation responsible for the polymer swelling:

$$RCOOH + Na^+OH^- \rightarrow RCOO^-Na^+ + H_2O \tag{1}$$

with the following reaction in which it is assumed that the weak basic buffer is in excess, *i.e.* $a \gg 1$:

$$RCOOH + \underbrace{aNa^+ + aHCO_3^-}_{\text{weak basic buffer in excess}} \rightarrow RCOO^-Na^+ + (a-1)HCO_3^- + (a-1)Na^+ + aH_2CO_3 \tag{2}$$

and the strong acid ion-exchange reaction responsible for the polymer de-swelling:

$$RCOO^-Na^+ + H^+Cl^- \rightarrow RCOOH + Na^+Cl^- \tag{3}$$

with the following reaction:

$$RCO_2^-Na^+ + \underbrace{aCH_3CO_2H + aCH_3CO_2^- + aNa^+}_{\text{weak acid buffer in excess}} \rightarrow RCO_2H + (a-1)CH_3CO_2H + (a+1)Na^+ + (a+1)CH_3CO_2^- \tag{4}$$

It is important to note that buffered solutions are often used to determine the swelling dependency of a hydrogel on pH [12–15]. However, this is generally made as if the hydrogel candidate was insensitive to the additional ions being added to the medium through the buffer solutions. This may be difficult to understand if pH-sensitivity was determined by dilution of strong acid–base solutions or by buffered solutions (for example, in [16]). In other studies, particularly with chitosan-based hydrogels known to be affected by ionic strength, the swelling performances in modifying pH by dilution or by buffered solution are emphasized. In [17], for example, it is clearly mentioned that the swelling of a modified chitosan superabsorbant hydrogel is about 50% in an on-off switching experiment from pH 10 to 3 in buffered solutions, while its swelling ability in an HCl diluted solution of pH 3 is about 300%. In the case of our artificial muscle, we make the assumption that the high ion-sensitivity of ion-exchange resins is the crucial point for preserving the high swelling ability of this material in buffered solutions.

1.2. Application to the control of a polymeric McKibben artificial muscle

We have detailed in other papers our approach to the McKibben pneumatic artificial muscle [18] and its adaptation to a chemical control approach [10]. Fig. 1 describes the experimental set-up used to test such compact pH-muscles.

In the centre we show a typical compact laboratory-developed McKibben muscle. The initial external diameter is around 7 mm and its initial active length (minus the metal tips) varies between 70 and 170 mm. The braided sheath is made of nylon and surrounds a rubber inner tube filled with 580–780 μm resin balls. The swelling of these resin balls generates a circumferential stress inside the rubber inner tube that the interwoven braided cords transform into a linear contraction force. The feeding of the artificial muscle in weak base buffer A and weak acid buffer AH, is alternatively realized by a peristatic pump. As sketched on the right-hand side of Fig. 1, the experimental set-up can be used in two modes: an isometric mode aimed at establishing static performances of the artificial muscle, and an isotonic mode for dynamic performances of the artificial muscle when a load is attached.

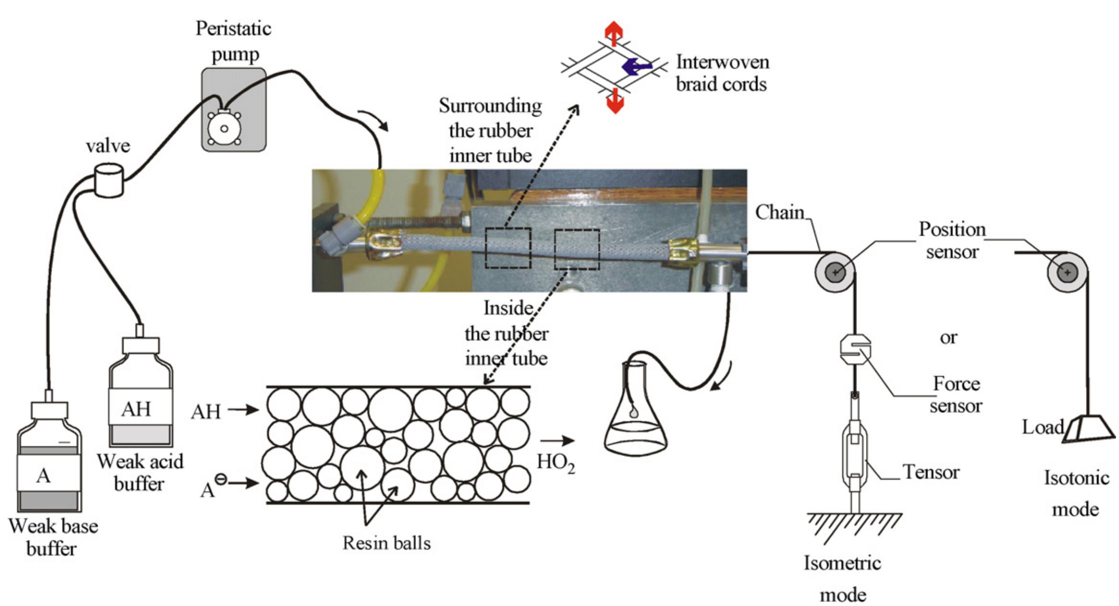

Fig. 1. Experimental set-up for determining the static and dynamic performances of a polymeric McKibben artificial muscle fed alternatively by a weak base buffer and a weak acid buffer.