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Letter

4D sequential actuation: combining ionoprinting and redox chemistry in hydrogels

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Abstract

The programmable sequential actuation of two-dimensional hydrogel membranes into three-dimensional folded architectures has been achieved by combining ionoprinting and redox chemistry; this methodology permits the programmed evolution of complex architectures triggered through localized out-of-plane deformations. In our study we describe a soft actuator which utilizes ionoprinting of iron and vanadium, with the selective reduction of iron through a mild reducing agent, to achieve chemically controlled sequential folding. Through the optimization of solvent polarity and ionoprinting variables (voltage, duration and anode composition), we have shown how the actuation pathways, rate-of-movement and magnitude of angular rotation can be controlled for the design of a 4D sequential actuator.

 Online supplementary data available from stacks.iop.org/SMS/25/10LT02/mmedia

Keywords: hydrogels, ionoprinting, actuators, sequential actuation, selective redox


(Some figures may appear in colour only in the online journal)

1. Introduction

Hydrogels, three-dimensional hydrophilic polymer networks, can have high (~99%) water content and the ability to reversibly respond to a range of stimuli, including pH, temperature, light and ionic strength [1]. These unique properties permit hydrogels to be used as novel devices in the fields of biomedical engineering, soft-robotics, waste management and agriculture [2]. The stimuli responsive volume change of hydrogel have been used to make artificial muscles

(actuators), self-folding origami and enviro-intelligent sensors [3–6].

Non-sequential actuation of hydrogels, i.e. the transformation from one shape to another, has been demonstrated increasingly over the past few decades, with non-homogenous shape change of non-homogenous hydrogels proving to be the most interesting and complex. The most common motions created using non-homogenous hydrogel actuators are twisting, bending and coiling [1], created through the introduction of material non-homogeneity or through an external stimuli applied. Generally, non-homogeneity is built into the hydrogel during manufacture or synthesis producing a hydrogel actuator with fixed shape change. These materials and structures are adding another dimension to the material, namely four-dimensional (4D) material, with their response to stimuli.

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The term 4D printing was introduced by Tibbitts to describe the 3D printing of active materials [7]. The fourth dimension in 4D printing comes from the ability of the prints to transform over time or the ability to change from one shape to another in response to a stimuli. The 3D printing of a stimuli-responsive hydrogel to produce a 4D printed structure has only been recently demonstrated in the last few years. Examples included the work by Bakarich *et al* where the researchers use extrusion printing of an ionic covalent entangled double network hydrogel to create a heat responsive material; when combined as part of a multi-material print can be used to create a thermally responsive hydrogel valve [8]. Another example is the work by Gladman *et al* who utilize extrusion printing of an anisotropic composite hydrogel to generate restricted swelling in the print direction. The printing of the hydrogel allows the creation of an extensive range of shape changes included positive, negative and varying Gaussian curvatures, twisting, coiling and ruffling and combinations of all, within a single print by varying the print path [9].

While two-dimensional polymeric materials are relatively inexpensive and easy to manufacture, store, pack and ship, their transformation into three-dimensional forms adds both value and functionality [10]. The addition of sequential actuation of hinges allows for another level of complexity to be achieved, extending the field of out-of-plane polymeric actuation and the sophistication of shape changes achievable. Chronological actuation in polymeric materials can be created through the localized application of stimuli, as illustrated in the work of Felton *et al* where sequentially heated shape memory composite hinges are triggered to achieve ordered folding. Liu *et al* and Laflin *et al* used pre-stained polymer sheets, locally heated with a laser to create sequential folding [11–13]. Sequential actuation by applying a bulk stimuli has been shown by Mao *et al* and Lee *et al* using pre-stained shape memory polymers (SMPs) with the active hinges being respectively created with SMP with variable glass transition temperatures (T_g) and variable infrared transparency [14, 15]. Mao *et al* progressively heats their structures above the T_g of all the hinges to trigger sequential actuation, with the hinges folding in order of increasing T_g of the SMPs [14]. Lee *et al* use the positive relationship between opacity and light absorbance to create hinge fold, controlled through the time differential for the hinges to be heated above the polymer's T_g [15]. Liu *et al* and Laflin *et al* created an ordering of the folding by incorporating a gradient to the actuation speed of the hinges; work by Liu *et al* has created sequential actuation where the ordering is not known *a priori* determined by the external stimuli [16]. By using different colored inks on pre-stained SMP, active hinges are created which are triggered through different colored light sources. The order in which the hinges fold is determined by the light source used and the efficiency of the hinge to absorb the wavelengths of light emitted. Stoychev *et al* have also achieved hierarchical multi-step folding of hydrogel bilayers, where coordinated folding is achieved by using the progression of the diffusion front through the hydrogel [17]. Their work presents rules for predicting the folding sequence based on the shape of the star-

like bilayers however has no way of programming the desired pathway of shape change.

Ionoprinting, the technique of patterning metal cations into hydrogels using electric potential, has been previously used to create localized ionic crosslinking and actuating hydrogels [18]. Ionoprinting, in its simplest form, can be described as electrolysis through a hydrogel instead of a solution. It is the presence of the polymer network, more specifically the functionality of the side groups within it, which causes the cations produced to remain proximal to the anode. These regional cations cause localized ionic crosslinking, deswelling and stiffening of the hydrogel resulting in the creation of a foldline along the ionoprinted hinge. Functionality of side groups that have been previously used within ionoprinted hydrogels include acrylic acid, catechol and phosphate [18–21]. Ionoprinting has been successfully used to print cations of copper, iron, zinc, vanadium, calcium, aluminum and titanium [18–22].

The ionoprinting of iron has been explored in the open literature, with iron being oxidized to iron(III) cations (Fe^{3+}) [21–24]. The presence of adjacent, relatively stable oxidation states of iron (+2/+3), that can switch between ‘hard’ and ‘soft’ cations, has resulted in their use in polymeric systems for shape-memory, self-healing and sol–gel transition [25–29]. The oxidation state of Fe^{3+} and iron(II) (Fe^{2+}) are separated by a reduction potential of +0.77 V, allowing for Fe^{3+} to be reduced by weak reducing agents and Fe^{2+} aerobically oxidized [29].

In this study, we present a hydrogel actuator that can perform controlled sequential actuation through the combination of ionoprinting with selective redox reactions. Sequential actuation is demonstrated through the application of ionoprinted vanadium and iron hinge lines, where the iron hinge is triggered to selectively unfold through the selective reduction of Fe^{3+} by a mild reducing agent, ascorbic acid, in the similar manner as demonstrated by the authors’ previous proof-of-concept work on the same cruciform-cube geometry [21]. Here we present the first study to show controlled sequential actuation of hydrogels, with control over the initial and final angle created and the rate and order of unfolding. The initial angle created is determined by voltage input, the printing duration and metal used for ionoprinting. While the final angle achieved, rate of change and ordering of unfolding is controlled by the cation created by ionoprinting and the reducing potential or hydrophilicity of the solution medium used. Investigations into the processing variables affecting the initial and final fold angles have been characterized enabling the creation of a design matrix for the preferred actuation pathway to be repeatedly achieved; this methodology allows for programming of the initial and final shape formation independently of the material manufacture. Sequential actuation of hydrogel with controllable shape change has not been demonstrated previously. In a similar fashion to the addition of sequential actuation to SMP materials, our chemical approach for programming of the regional chemistry allows another level of shape change complexity to be achieved with existing hydrogel systems: thereby extending

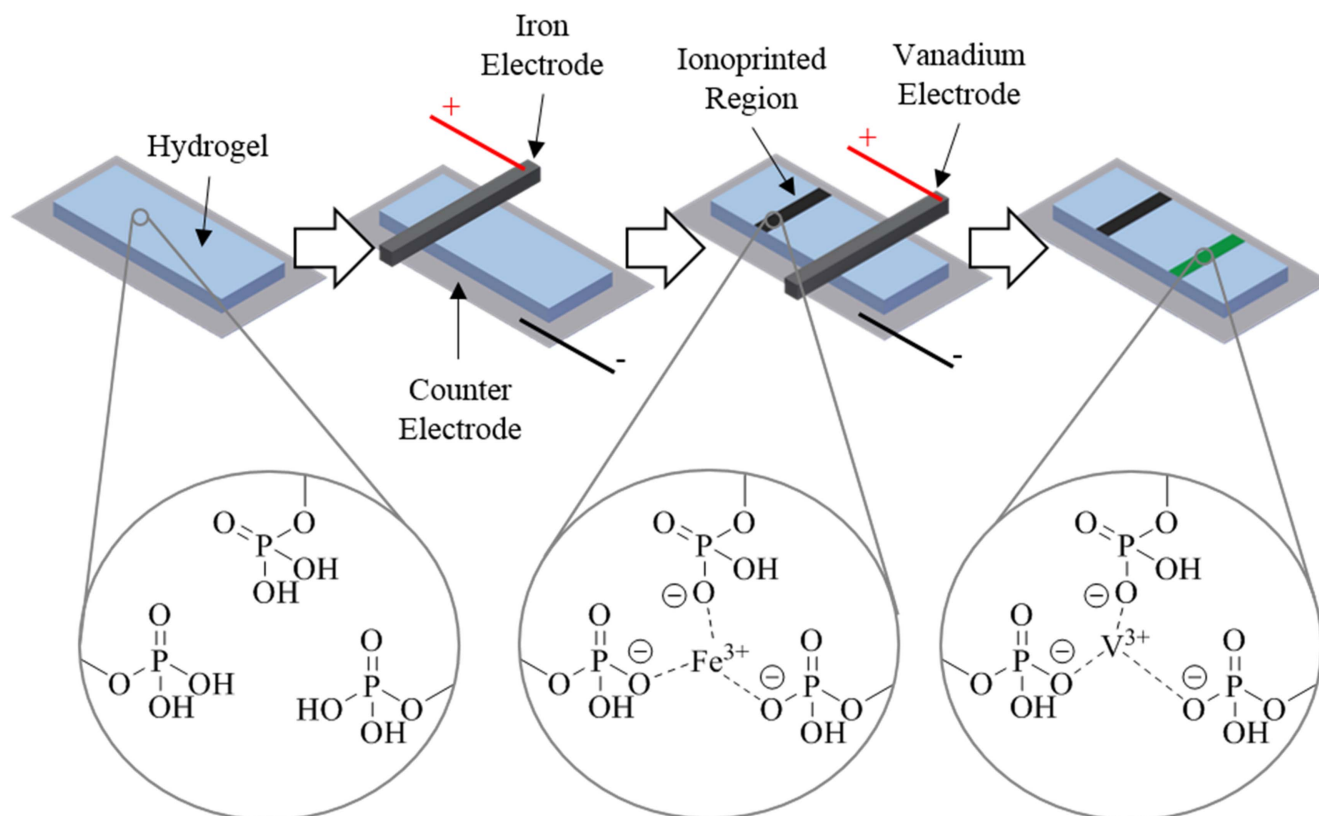


Figure 1. Ionoprinting of multiple metal anodes (iron and vanadium). Highlighting the change in ionic crosslinking caused by ionoprinting. (See supplementary information for video of ionoprinting.)

the potential applications of hydrogel actuations beyond what has been currently achieved.

2. Results and discussion

Ionoprinting produces a redox reaction within a hydrogel with oxidation of an anode material occurring at the interface between the anode and the hydrogel with the cations produced diffusing in the hydrogel and becoming bound proximal to this interface. The binding of the cations produced is dependant on the composition of the hydrogel, i.e. the binding affinity of the side groups contained within the hydrogels; within this work, the acrylic hydrogel employed contains both phosphate and hydroxyl functional side groups (see supplementary information 2) [20]. The simultaneous reduction of protons to gaseous hydrogen occurs at the interface between an aluminum foil cathode and underside of the hydrogel (figure 1). Multi metal ionoprinting can create areas with different cations present and therefore offer unique ionic crosslinking environments with different susceptibility to stimulus. In this way, ionoprinting allows programming of regional chemistry into an initially homogenous hydrogel.

2.1. Sequential actuation of a cube

The concept of combining ionoprinting of multiple metals and selective redox chemistry is demonstrated by the sequential

actuation of a cube formed from a cruciform hydrogel. The sequential actuation of the cube (figure 2) is achieved by ionoprinting the hinges with vanadium and iron. The four base hinges of the cube are ionoprinted with vanadium, while the 'lid' hingeline is ionoprinted with iron. The first stage of actuation is the opening and closing of the lid, by the selective reduction (opening) and oxidation (closing) of the iron hinge. The second stage of actuation is the complete un-folding and re-folding of the cube, through the deswelling (un-folding) and reswelling (folding) of the bulk of the hydrogel, i.e. the non-ionoprinted regions.

The cube demonstration (figure 2(a)) requires only five conditions to achieve cyclic and reversible sequential actuation; these are ionoprinting and solutions of a selective reducing agent, chelating agent, as well as polar and non-polar solvents. To demonstrate the first stage of actuation, ascorbic acid reducing agent was used; this is a weak reducing agent able to reduce ions with a standard reduction potential above +0.06 V [30]. The second stage of actuation was achieved with a relatively non-polar solvent of ethanol and polar solvent of deionized water. The resetting to a virgin hydrogel is achieved with the chelating agent ethylenediaminetetraacetic acid (EDTA) (figure 2(b)).

The controlled actuation achieved by ionoprinting of multiple metals and selective redox chemistry is dependent on the redox potential of the metal cations created through ionoprinting. Here, we demonstrate the unfolding order (figure 2(b)) is dependent on the ability of iron and vanadium

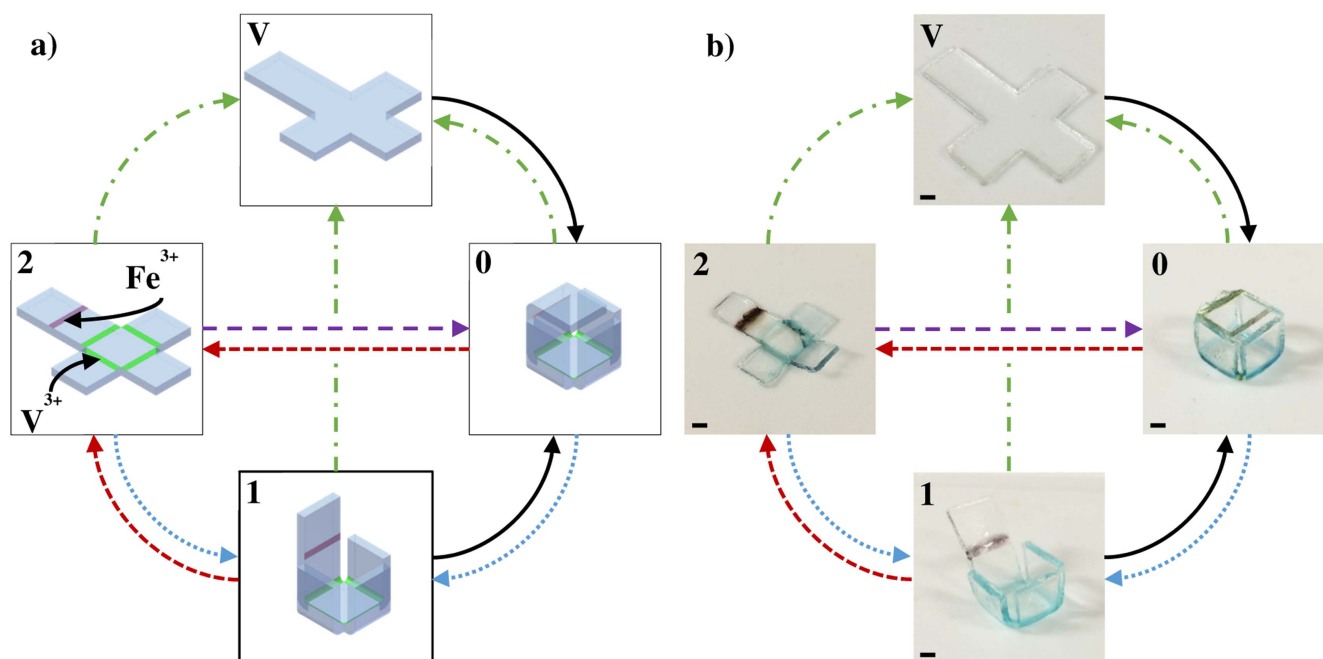
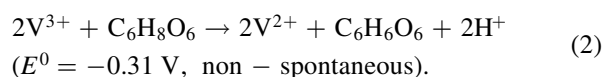
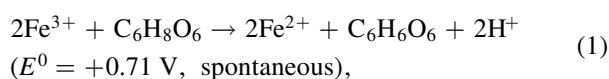


Figure 2. Sequential actuation of a cube from a cruciform hydrogel ionoprinted with iron (lid hinge) and vanadium (base hinges). V: virgin cruciform hydrogel. 0: ionoprinted cube. 1: first stage of the sequential actuation, lid opening. 2: second stage of the sequential actuation, complete opening. (a) Diagram of sequential unfolding. (b) Photographs of sequential actuation Key: ionoprinting (solid black line), selective reducing agent (dotted blue line), non-polar solvent (close dashed red line), polar solvent (and re-ionoprinting if coming through 1) (spaced dashed purple line) and chelating agent (dotted-dashed green line). Scale bar = 2 mm. Reprinted with permission from [21], Copyright 2016 Materials Research Society.

cations to be reduced from oxidation state +3 to +2. These reduction potentials, relative to a hydrogen electrode at 25 °C, are +0.77 V and −0.26 V, respectively [31]. The cations formed by ionoprinting with iron are highly susceptible to reduction, while the cations formed by ionoprinting vanadium are not. By using a weak reducing agent, with intermediate reduction potential, the ability to selectively reduce the cations in one ionoprinted region while leaving the remaining regions unchanged can be achieved. In the case of iron and vanadium trivalent cations the weak reducing agent of ascorbic acid can be used to selectively reduce iron cations from oxidation state +3 to +2, as indicated in equations (1) and (2). The intermediate oxidation potential of −0.06 V allows the selective reduction of the iron cations. This reduction results in a decrease in strength of ionic crosslinking, due to the change from ‘hard’ to ‘soft’ cations, permitting the re-swelling of the ionoprinting region and thus unfolding of the hinge



Refolding of the reduced hinge, i.e. the iron ionoprinted hinge, cannot be achieved by an oxidising agent as the reduced cations do not remain bonded to the hydrogel, or at their original ionoprinted location. This is due to the reduced binding affinity between the Fe^{2+} and the phosphate functional groups in the hydrogel. It is a combination of the

reduction in ionic crosslinking strength and the diffusion of the reduced cation away from the hinge that results in the unfolding and destruction of the hinge.

2.2. Controlling sequential actuation

The initial angle (see supplementary figure S1) created through ionoprinting is determined by the voltage, duration and metal used for ionoprinting, see figures 3(a) and (b). These variables determine the cations produced, their concentration and depth of penetration. The angle after 15 min here after referred to as final (see supplementary figure S1) and change of angle is determined by the submersion solution’s effect on the local ionoprinted region and the global hydrogel; either reducing the cations present, de-swelling or leaving the area relatively unchanged, see figures 3(c) and (d). Both the initial and final angle are defined as the external angle formed by the hydrogel folding i.e. a angle of 0° is a flat as synthesised hydrogel, whereas an angle of 180° is a fully folded hydrogel.

2.2.1. Ionoprinting conditions: effect on initial angle. The principle variables that control the concentration, oxidation state and species of cations produced by ionoprinting are voltage, printing duration, hydrogel conductivity and anode’s material and dimensions. This work looks at the voltage and duration of ionoprinting with anode material of vanadium and iron with fixed dimension and a hydrogel with fixed

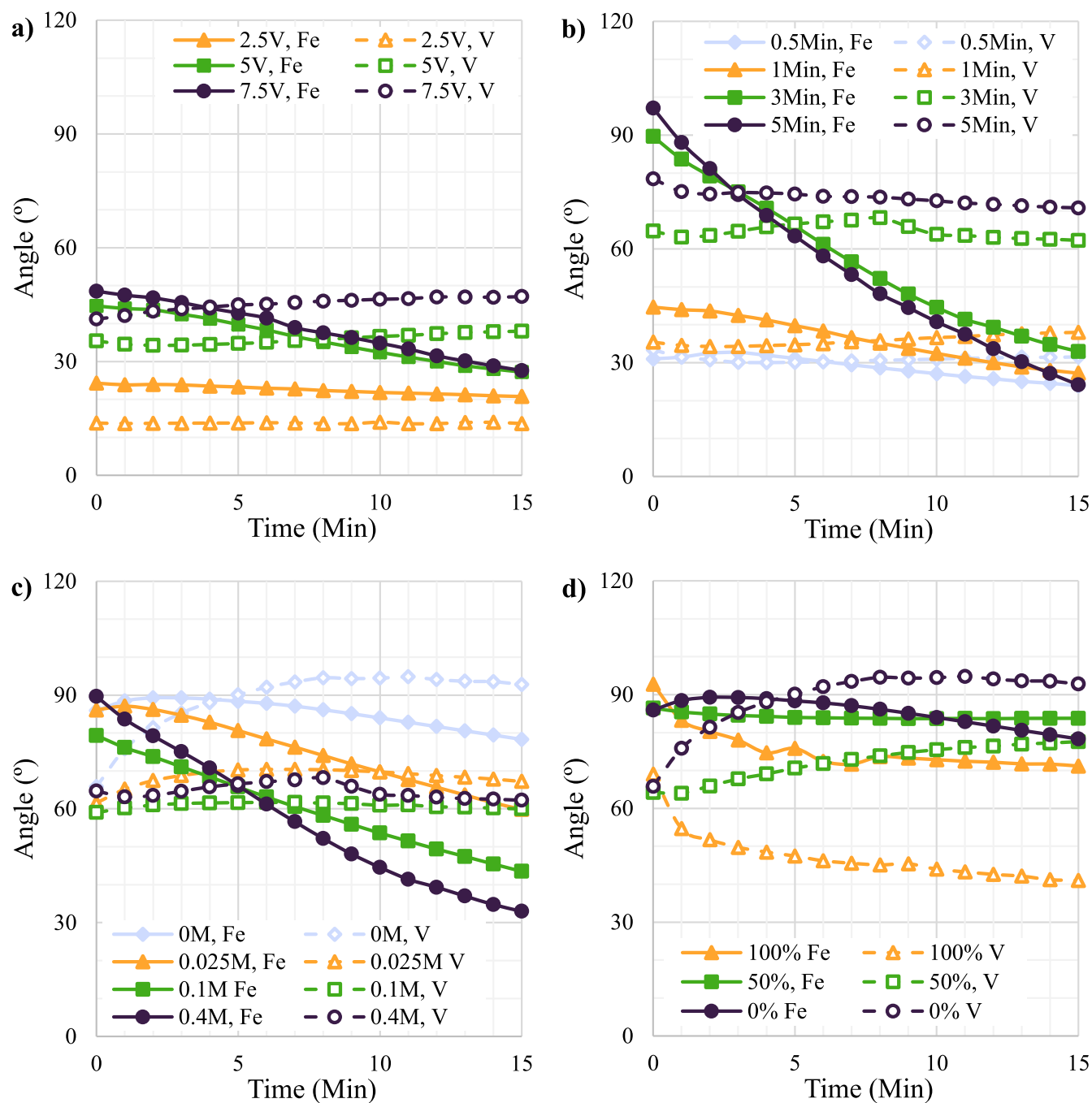


Figure 3. The variables effecting the initial angle created by ionprinting are printing duration, voltage and metal used for printing. All data points mean average of three repeats (data and standard deviation of each point in supplementary information figures 4S–7S). (a) Graph of the effect of voltage (2.5–7.5 V) of ionprinting (1 min) on the unfolding on iron and vanadium printed hinges in 0.4 M ascorbic acid. (b) Graph of the effect of duration (0.5–5 min) of ionprinting (5 V) on the unfolding on iron and vanadium printed hinges in 0.4 M ascorbic acid. The variables effecting the change in angle created by ionprinting are reducing potential and polarity of solvent hydrogel is submerged into. (c) Graph of the effect of ascorbic acid concentration (0–0.4 M) on unfolding of hinges printed with iron and vanadium (3 min at 5 V). (d) Graph of the effect of ethanol percentage (0%–100%) on unfolding of hinges printed with iron and vanadium (3 min at 5 V). (For test set up see supplementary information 5.)

conductivity (controlled by swelling in 0.1 M lithium chloride solution).

The ionprinting duration effect is captured through the fold angle magnitude at time zero, figure 3(b), with increasing ionprinting duration of both the iron and vanadium anodes yielding an increase in fold angle created. Despite the increase

in angle, the printing efficiency decreased with the fastest rate of actuation being achieved after 30 s of printing, see table 1. Ionprinting with vanadium was noted to create smaller angles and less efficient than ionprinting iron under the same experimental conditions, see table 1. It has been previously shown that as ionprinting progresses the resistance of the

Table 1. Effect of ionoprinting duration on initial angle produced and printing efficiency.

| Iron | | | Vanadium | | |
|-------------------------|---------------------------------|---|-------------------------|---------------------------------|---|
| Printing duration (Min) | Angle produced (°) ^a | Printing efficiency (° min ⁻¹) ^b | Printing duration (Min) | Angle produced (°) ^a | Printing efficiency (° min ⁻¹) ^b |
| 0.5 | 31 | 62 | 0.5 | 33 | 67 |
| 1 | 45 | 45 | 1 | 35 | 35 |
| 3 | 90 | 30 | 3 | 65 | 22 |
| 5 | 97 | 19 | 5 | 79 | 16 |

^a Nearest degrees.^b Nearest degree per minute.

hydrogel increases with the cation build-up in the ionoprinted region; resulting in a reduction in current and rate of cation production [18]. Exposing the ionoprinted hinges to the weak reducing agent of ascorbic acid resulted in selective unfolding of iron printed hinges all to below 30°, while leaving the vanadium hinges unchanged and maintaining its fold angle (see figures 3(a) and (b)). This demonstrates that sequential actuation can be achieved over a range of angles and cation concentrations.

The effect of voltage on ionoprinting is shown in figure 3(a), increasing printing voltage increased the folding angle created with both the iron and vanadium anode. The rate of actuation was increased by increasing printing voltage, however the efficiency for input voltage was decreased from 9.7 to 6.5° V⁻¹ for the iron anode, while for the vanadium anode the lower and higher voltages achieved the same efficiency of 5.5° V⁻¹, with maximum efficiency of the variables tested being achieved at 5 V printing of 7.1° V⁻¹. Previous work has shown that a threshold voltage for penetrating ionoprinting to occur is required; the threshold being determined by the sum of the activation potential of the redox reactions occurring at the hydrogel–electrode interface and an overpotential [18].

2.2.2. Actuation conditions: effect on angle change. The iron ionoprinted hinge can be selectively unfolded with ascorbic acid solution; with the rate of this unfolding being controlled with the acid concentration. As previously discussed, the ascorbic acid is only able to reduce the Fe³⁺, being too weak a reducing agent to reduce the V³⁺. Therefore, while the Fe³⁺ is being reduced the hinge unfolds, due to the weakening of ionic crosslinking and diffusion of the cations into the hydrogel. Simultaneously, the V³⁺ remains unchanged and retains the ionic crosslinking environment created through ionoprinting. This effect is shown in figure 3(c), with lower concentration of ascorbic acid reducing the speed of unfolding of the iron hinge until no un-folding of the hinge is seen in water. Water submersion resulted in an initial increase of folding angle for both the iron and vanadium hinges due to diffusion of lithium chloride from within the hydrogel into the submersion solution. This results in swelling of the hydrogel bulk (non-ionoprinted areas), increasing the differential in swelling between non- and ionoprinted areas and increasing the folding angle (see supplementary information 6). A greater increase is observed for vanadium than iron because

the differential of the swelling between water and vanadium is greater than the between water and iron (see supplementary information 6). Therefore, the diffusion of lithium cations out of the hydrogel has a more significant effect on the vanadium ionoprinted hinge than the iron ionoprinting hinge. An increase in unfolding rate with increasing ascorbic acid concentration did not reach a plateau, indicating the rate of un-folding is reaction rate dominated not diffusion rate determined. In all cases, ascorbic acid was in excess and therefore the reduction of Fe³⁺ would continue beyond the 15 min investigated and the time required for complete unfolding will be determined by the reaction rates of reduction. Similarly, samples subjected to ethanol, water and blends also exhibited some slight angular variation beyond the 15 min investigated; however, the dynamic angular rate of change had significantly decreased by this stage, and has been considered as steady-state in this investigation.

All variables investigated have shown selective actuation of the iron hinge, while the vanadium hinge has remained unchanged remaining in its initial fold angle. For sequential actuation to be achieved, un-folding and re-folding of the vanadium hinge also has to be achieved. Both hinges can be un-folded by removing the differential in swelling between non- and ionoprinted regions, this can be achieved by either deswelling the bulk of the hydrogel or removing the cations in the ionoprinted regions, through a relatively non-polar solvent or chelating agent, respectively. Using a relative non-polar solvent keeps the ionoprinted regions present allowing for re-folding, whereas a chelating agent resets the hydrogel to its virgin, pre-ionoprinted state, allowing for re-programming of the hydrogel through another cycle of ionoprinting. In figure 3(d) the effect of ethanol and water mixtures on the two hinges is shown, blends containing 50% or less ethanol were unable to induce un-folding of either hinge. Submersion of the hydrogel into pure ethanol resulted in un-folding of both hinges, creating the second stage of the sequential actuation. As shown in figure 2(b) the hinges can be re-folded by submersion in a polar solvent or the vanadium hinges selectively re-folded with a solution of mild reducing agent.

For both stages the rate is relatively quick compared to other hydrogel actuation of the same size (typically minutes instead of hours or days), this is due to actuation being surface and near surface dependent. The first stage of actuation is reaction driven, with reduction with iron cations occurring at

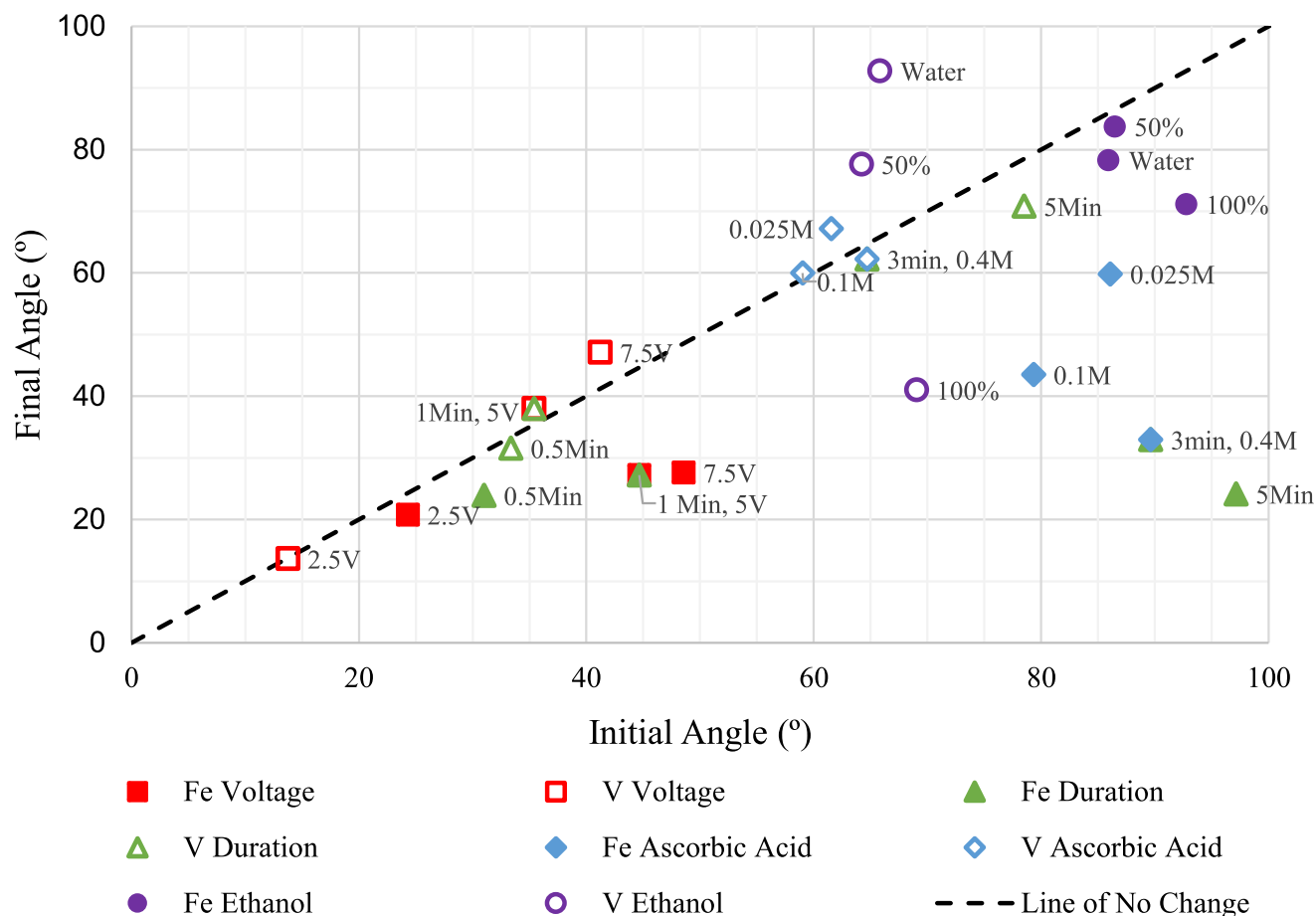


Figure 4. Graph of the initial (angle induced by ionoprinting) and final angle (angle observed after 15 min in respective conditions) created by variety of ionoprinting and actuation conditions.

the near surface ionoprinted region. Unlike the first stage, in the second stage there are no reactions occurring, the actuation is created by removing the differential in swelling; where the areas that have the largest angular effect are the areas furthest away from the neutral axis, i.e. the top and bottom surfaces. While the top surface, the area with ionoprinting, remains unchanged, the bottom surface and near surface are rapidly deswollen due to the small diffusion distances; creating the observed fast actuation. Both stages of actuation reduce the diffusion distances required for actuation to occur, which is often the rate limiting variable in other hydrogel actuators.

2.2.3. Design matrix. The experimental results generated have been collated into a design matrix shown in figure 4. The design matrix captures three distinct areas: a 'line of no change', and then regions above and below it, representing folding and un-folding, respectively. A pair of hinges printed under the same conditions is determined to create sequential actuation if they appear in different areas. For example, ionoprinting for 5 min results in the vanadium point appearing in the area along the 'line of no change', whereas the iron point appears in the area below the 'line of no change',

yielding a sequential actuation pairing. However, the submersion into 100% ethanol results in both the vanadium and iron results appearing in the area below the 'line of no change', and therefore are not a sequential actuation pair. This design matrix should be used to determine the printing variables required to achieve the initial angles required for both hinges, and the submersion conditions to create selective or complete unfolding. For example, in a two-hinge system requiring angles of 45° and 90° for the first and second hinge, respectively, and the second hinge required selective opening, the following conditions would be recommended. Printing for 1 min at 5 V with a vanadium anode and 3 min at 5 V with an iron anode would create the desired angle for the first and second hinge, respectively. Selective opening of the second hinge could then be achieved with submersion into a solution of 0.4 M ascorbic acid.

The variables explored within this work are a small fraction of the possible combinations achievable. However, our study does show how selectively varying each variable effects the initial and final folding and unfolding angle of the different ionoprinted metals. The work demonstrates two-staged sequential actuation with vanadium and iron anode materials and the selective reducing agent of ascorbic acid to

create selective reduction of Fe^{3+} to Fe^{2+} . This approach in theory could be extended to higher stages of actuation, i.e. three-stage, by ionoprinting with a wider range of metals and varying the strength of reducing agents (as introduced and discussed by Baker *et al* [21]).

3. Conclusion

Ionoprinting of multi metals is a powerful technique for creating rapid and controlled actuation of hydrogels, and by combining with redox chemistry can be used to create hydrogel systems that can be actuated sequentially. This work has demonstrated two-staged sequential actuation by combining ionoprinting with vanadium and iron, and utilizing the selective reduction of Fe^{3+} with ascorbic acid. The initial angle can be controlled by the voltage, duration and the anode material used for ionoprinting; both voltage and duration of printing showed a positive relationship with angle produced. The final angle and relative angles were controlled by submersion in solutions with a range of concentrations of reducing agent and polarity of solutions. Increasing the concentration of reducing agent resulted in an increased selective unfolding rate of the iron ionoprinted hinges. By decreasing solvent solution polarity, un-folding of all ionoprinted hinges was achieved. In our study, chemistry driven sequential actuation of hydrogels is achievable with the order of actuation being determined and controlled by the reduction potential of the cations produced.

Acknowledgments

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