

Electroplastic Elastomers

by

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A series of composite materials comprising a polyelectrolyte hydrogel, a porous scaffold and exchangeable multivalent metal ions was prepared and studied with the goal of identifying formulations that would allow for an electrochemically stimulated change in modulus. Composites based on poly[(styrene sulfonate)-*co*-acrylate] hydrogels exhibited the best combination of properties. When prepared as an interpenetrating network in a porous polyurethane scaffold and subjected to exchange with Fe^{3+} ions, these materials exhibit compressive moduli in the 1-3 MPa range. Comparable samples prepared with Fe^{2+} ions exhibit smaller moduli (0.1-0.13 MPa). Chemical oxidation of samples prepared with Fe^{2+} results in a concomitant increase in the modulus.

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ABBREVIATIONS

CEPs	Conducting electroactive polymers
PAn	Polyaniline
PPy	Polypyrrole
EIS	Electrochemical impedance spectroscopy
EPE	Electroplastic elastomer
HEMA	Hydroxyethyl methacrylate
EDMA	3,4-Ethylenedioxy-N-methylamphetamine
LCST	Lower critical solution temperature
PSS	Poly(styrene sulfonate)
SS	<i>p</i> -Styrene sulfonate sodium salt
PA	Poly(acrylate)
A	Acrylate sodium salt
PAA	Poly(acrylamide)
AA	Acrylamide
PEG	Polyethylene glycol

PREFACE

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1.0 INTRODUCTION

1.1 OVERVIEW

The goal of this project is to design and prepare a new class of materials with mechanical properties that can be controlled by the application of electricity (Figure 1).

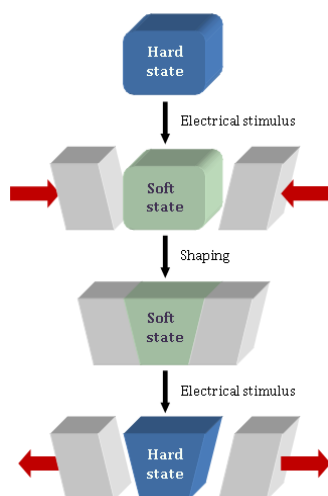


Figure 1. Targeted behavior for ideal electroplastic elastomer

Not many materials exist that have the ability to exhibit reversible property changes and those that do exist do not use electricity to control the transformation. Prior work in the area includes the study of an electroconductive blended copolymer¹ and an organic hydrogel that responds to oxidation and reduction.² Electroconductive hydrogels are blends or co-networks of inherently conducting electroactive polymers (CEPs) and highly hydrated hydrogels. These

polymeric networks offer the promise of engineered biocompatibility associated with the hydrogel component and the low electrical interfacial impedance, both ionic and electronic, associated with the inherently conductive polymer component. Moreover, the electrochemical behavior of composites of conducting electroactive polyaniline (PAn) and polypyrrole (PPy) formulated within cross-linked hydrogel networks was investigated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS)³. Redox process can be achieved in these hydrogel materials. However, none of these materials used metal ions coupled with the practical mechanism of electrical control.

The electroplastic elastomeric materials that we are developing have the potential to be used in many applications. For example, these materials could be used as robotic manipulators, the creation of variable mating surfaces, and as materials for drug delivery, etc. The fact that the properties of the materials can be changed from elastically flexible to stiff and that the changes can be stimulated reversibly by electrical control make them suitable for many applications.

The electroplastic elastomers (EPE) described herein exploit transition metal coordination chemistry to generate a reversible mechanism for controlling the degree of crosslinking and thus, the mechanical properties.

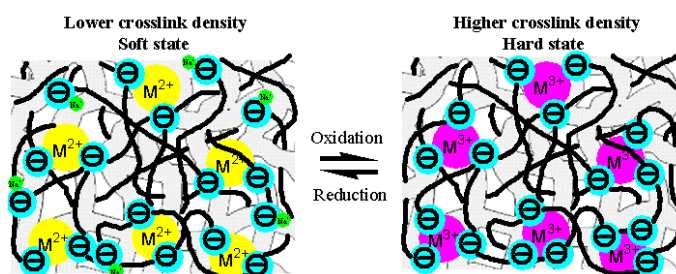


Figure 2. Design of electroplastic elastomer and effect of oxidation or reduction

In Figure 2 the fundamental design of the material is illustrated. A polyelectrolyte polymer in a scaffold bears high oxidation metal ion. In this state, the mechanical properties are

maximized (hard state) due to the attraction of the metal ion for the anionic hydrogel ligands. Electrochemical reduction of the metal should decrease the metal oxidation state and decrease the interaction strength and/or coordination number of the metals to the anionic hydrogel ligands. The overall effect is a decrease in crosslink density which should also affect the mechanical properties (soft state).

Electrical stimulation is a convenient mode for this change because the stimulation is reversible and easy to generate from variable sources. We can apply the electricity in the safe range and the process can be controlled by either on or off potential reversals.

1.2 HYDROGELS

Since our electroplastic elastomers are hydrogel-based, it is important to examine the design and inherent properties of these materials. Hydrogels, water swollen materials that have a three dimensional structure, can be classified by the type of crosslinking, nature of network, or the source.⁴ Due to the high water content in the hydrogel, most hydrogels exhibit excellent biocompatibility. The amount of water in the equilibrium-swollen state is balanced by both the thermodynamic force of mixing (hydration) and the retractive force of the three-dimensional network. The mixing force depends mainly on the hydrophilicity of the polymer backbone (characterized by the polymer-solvent interaction parameter, χ) while the retractive force depends on the crosslinks that create the three-dimensional network. By varying these factors it is possible to prepare hydrogels of different structures and properties.

Hydrogels can be responsive to a variety of conditions. There are, for example, many stimuli-sensitive hydrogels that respond to minor changes in pH⁵, temperature, ionic strength,⁶ or quality of solvent.⁷ Introduction of ionogenic groups into HEMA hydrogels (crosslinked with EDMA) allowed for control of the permeability and specific resistance as a function of pH. Transitions in temperature-sensitive hydrogels usually depend on the exhibition of a lower critical solution temperature (LCST), i.e., the gels collapse as temperature increases; water molecules form hydrogen bonds with polar groups and organize around hydrophobic groups when below the LCST. Above the LCST, bound water molecules are released to the bulk with a large gain in entropy resulting in collapse of the polymer network.

The mechanical properties of hydrogels can also be affected by changing the crosslink density or by copolymerization. For example, crosslinked gels with freely movable crosslinks gave outstanding mechanical properties—a high degree of swelling in water and a high stretching ratio without fracture (Figure 3).⁸

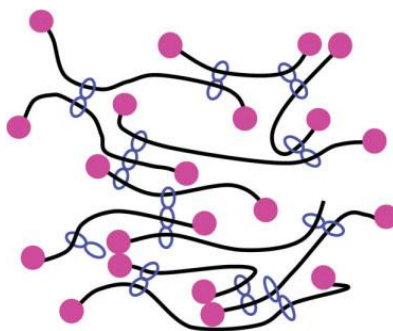


Figure 3. Mechanically improved hydrogel.⁸

1.3 POLYELECTROLYTES

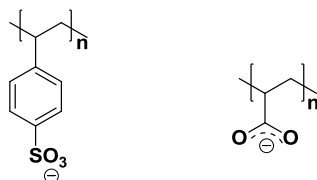


Figure 4. Structure of common polyelectrolytes

Polyelectrolytes are polymers whose repeating units bear electrolyte groups (Figure 4). A very limited numbers of precedents exist for reversible coordination in polymers and/or electrolyte gels that are controlled by the changing metal oxidation state. Chujo's group prepared polymer gels by the addition of cobalt ions to polymers bearing bipyridine-based side chains and observed reversible oxidation state dependent behavior. In the +3 oxidation state, the cobalt ions acted as crosslinks and a water-swellaible gel resulted. The conversion to the more labile +2 oxidation state using a chemical reductant gave a water soluble material.⁹ A related system was also described in general terms in a patent by Gaub.¹⁰ Chujo et al. also produced a non-metal redox switchable polymeric system based on sulfide crosslinks.¹¹ Other thiol-based systems have been reported.¹²⁻¹⁴ Most polyelectrolytes can generate water swellaible hydrogels under certain conditions, especially if chemical crosslinks are also present. The tendency of hydrogels to swell in water has been related to the degree of crosslinking promoted by metals of differing oxidation states. Allcock and coworkers conducted a study of the swelling behavior of a polyphosphazene bearing carboxylate side groups and found that the higher oxidation state metals exhibited less swelling.¹⁵ Although the materials proposed herein will undoubtedly experience potential driven swelling of the type described above during electrolysis, this is not the phenomenon that

we are proposing to exploit to generate the differences in materials properties. The response of our materials will depend on changes in crosslink density.

1.4 COORDINATION AND OXIDATION STATE

If we consider polyelectrolytes as ligands, we would expect that their degree of coordination will depend both on the identity of the metal and on its oxidation state. If these coordination events represent crosslinks in an hydrogel, it should be expected then that the materials properties will depend on the metal and/or oxidation state. In the case where a hydrogel is prepared with a metal that has the potential to vary its degree of coordination by an electrochemically stimulated change in oxidation state, it should be possible to use electrochemical redox events to control the crosslink-density dependent properties of the materials.

2.0 RESULTS AND DISCUSSION

2.1 SYNTHESIS OVERVIEW

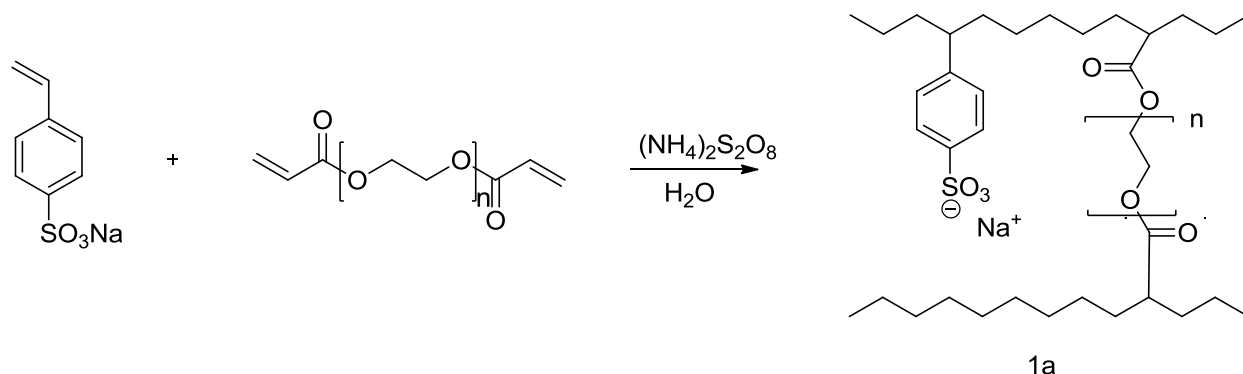
The general preparation of the EPE composite samples involves the free radical copolymerization of 2-3 monomers dissolved in aqueous solution and absorbed into a pre-cut piece of polyurethane foam scaffold. Samples without scaffolding are prepared analogously. The hydrogels produced are transparent and have a semi-solid gel consistency. The initial hardness of hydrogel is adjusted by controlling the identity and ratio of monofunctional to difunctional monomers. After polymerization, Na^+ counterions are exchanged for multivalent ions by immersion into and repeated injections of a solution of the multivalent ion.

Although samples of any dimension can be prepared, the studies herein focus on three sample sizes. Size A samples are cubic and have dimensions of 1" x 1" x 1". Size B samples are cubic and have dimensions of 1 cm x 1 cm x 1 cm. Size C samples are prepared in a 16-well reactor (vide infra) and have dimensions of 1" x 1" x 0.2". The Size A samples are particularly suitable for compression modulus testing using a standard load frame set up. The Size B samples are used for qualitative studies to determine initial conditions. The Size C samples are used for optimization experiments and are mechanically tested using a lab-built indenter apparatus.

2.2 HYDROGEL PREPARATION

2.2.1 Poly(styrene sulfonate) hydrogel (PSS)

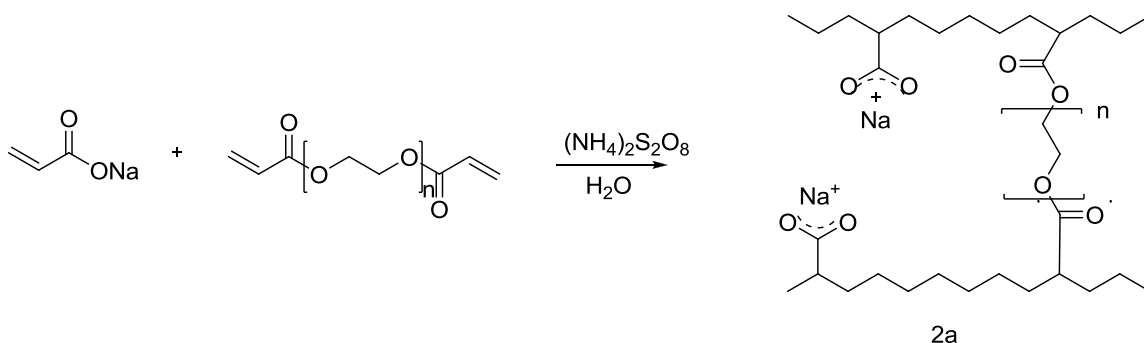
Poly(styrene sulfonate) hydrogels were prepared by the free radical polymerization of mixtures sodium *p*-styrene sulfonate and a 7% by wt. PEG-diacrylate ($M_n = 575$) in aqueous solution (Scheme I). Standard free radical polymerization conditions were employed ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator, 80 °C, N_2).



Scheme I. PSS hydrogel synthesis

Although the target reversible crosslinking of these materials is ultimately metal-based, there is an initial level of non-reversible crosslinking introduced by the copolymerization with PEG-diacrylate ($M_n = 575$). The degree of irreversible crosslinking was optimized so that the hydrogels would have some integrity yet remain responsive to the reversible metal crosslinking upon exchange. To determine the ideal conditions, PSS hydrogels with 5-10% by weight PEG-diacrylate were prepared. Optimal properties were obtained when a 7% PEG diacrylate was combined with the PSS monomer.

2.2.2 Poly(acrylate) hydrogel (PA)

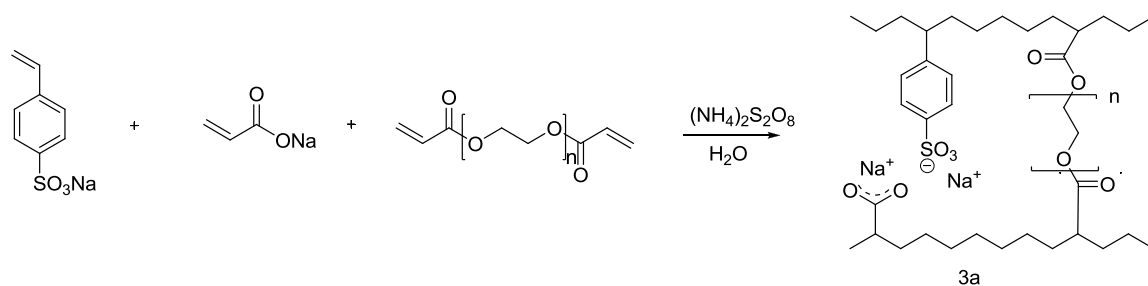


Scheme II. PA hydrogel synthesis

To improve the coordination ability of the hydrogel, we explored the use of a polyacrylate (PA) hydrogel (Scheme II). Preparation of PA with PEG-diacrylate crosslinking (7% by weight PEG-diacrylate) produced hydrogels with acceptable pre-exchange properties.

2.2.3 Poly[(styrene sulfonate)-*co*-acrylate] hydrogel (PSS/PA)

In order to fine-tune the composites behavior a copolymer of sodium acrylate and *p*-styrene sulfonate monomers was prepared. After screening several combinations, it was determined that a weight ratio of 8:12:1 of the SS, A and PEG diacrylate crosslinker gave a hydrogel that exhibited both stable pre-metal exchange shape (vide infra for metal exchange) and a significantly harder but still flexible post-exchange shape (Scheme III).

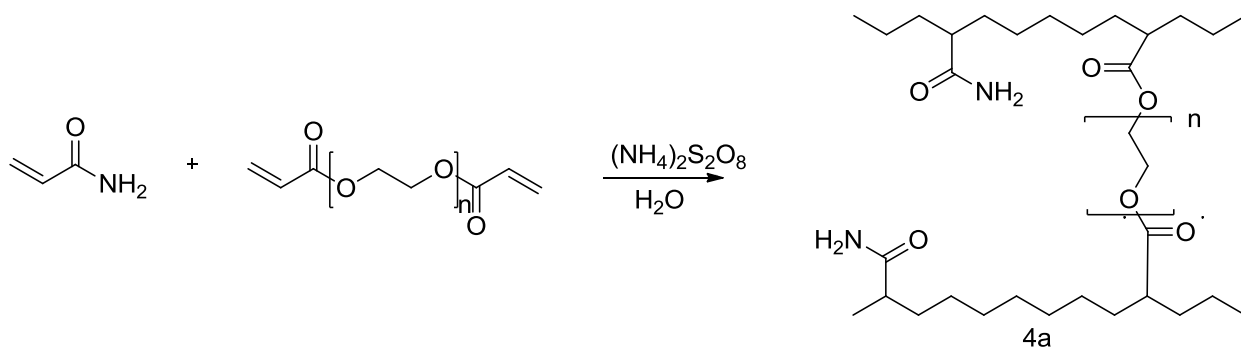


Scheme III. PSS/PA hydrogel synthesis.

Although reactivity ratios for the two monomers under these conditions are known, we did observe that initially the sodium *p*-styrene sulfonate was consumed faster than the sodium acrylate monomer. After the reaction was complete, however, IR spectroscopy showed that the absorptions for the acrylate and sulfonate groups were roughly equivalent.

2.2.4 Poly(acrylamide) hydrogel (PAA)

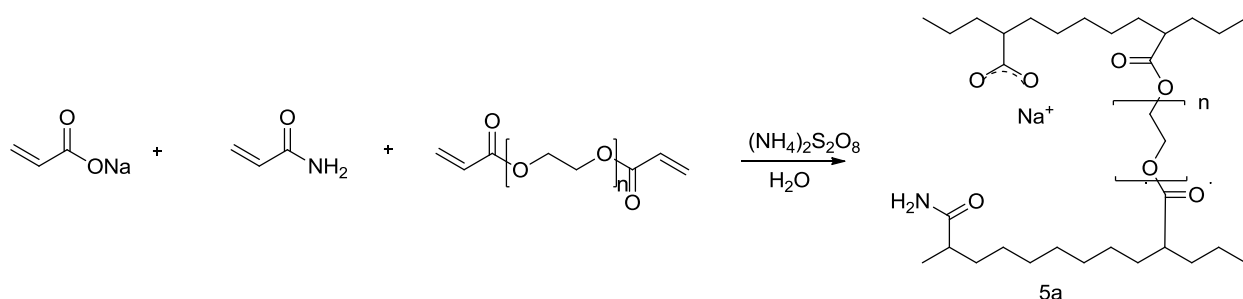
Hydrogels based on an acrylamide monomer (AA) were also prepared.¹⁶ PAA hydrogels with a 5% PEG diacrylate crosslinking were prepared using standard conditions (Scheme IV). These colorless hydrogels exhibited a much larger initial stiffness than either the PSS or PSS/PA hydrogels but were unacceptably brittle.



Scheme IV. PAA hydrogel synthesis.

2.2.5 Poly [acrylate-*co*-acrylamide)] hydrogel (PA/PAA)

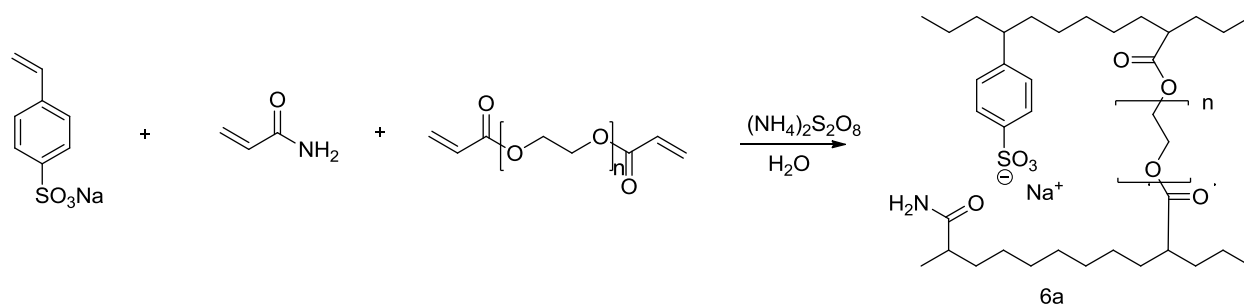
To further explore the properties hydrogels bearing acrylamide groups a copolymer with the acrylate monomer was prepared using a weight ratio of 8:12:1 of the sodium acrylate, acrylamide and PEG diacrylate monomers¹⁷ (Scheme V). The PA/PAA hydrogel as prepared was stiffer than the PSS/PA hydrogels and softer than PAA hydrogels. These hydrogels have a slightly yellow color as prepared.



Scheme V. PA/PAA hydrogel synthesis.

2.2.6 Poly[(styrene sulfonate)-*co*-acrylamide)] hydrogel (PSS/PA)

To tune the properties of the PAA-based hydrogel a PSS copolymer was prepared using a weight ratio of 8:12:1 of the SS, AA and PEG diacrylate monomers (Scheme VI). The PSS/PAA hydrogel as prepared was again stiffer than the PSS/PA hydrogels but did not exhibit the brittleness that was problematic for the PAA-only hydrogels. These hydrogels have a slightly yellow color as prepared. The true ratio of the monomers in the copolymer was not determined.



Scheme VI. PAA/PSS hydrogel synthesis.

2.2.7 Metal Exchange

As the ultimate goal of the project is to change crosslinking density by reversible reduction/oxidation of a metal crosslinking agent, multivalent metal ions were introduced into the hydrogels after synthesis. In all but the pure PAA samples, this introduction involves an exchange for the Na^+ cation already present in the sample. A variety of metal ions were explored and it was found that hydrogel coloration was determined by the exchanged metal ion (Figure 5). Multivalent ions also had the effect of increasing the stiffness of the hydrogel.



Figure 5. Representative samples of PA/PSS hydrogels with Cu(II), Ba(II), Fe(III), Co(II), and Na(I) (left to right).

In order to affect the exchange of the multivalent metal ions into the samples, the hydrogel was immersed for defined periods in saturated aqueous solutions of the metal ion. After soaking for a period of time (1-12 h) the samples were removed and injected using a syringe with the same saturated metal ion solution multiple times in multiple locations. These

injections were necessary in order to produce samples with homogeneous distributions of the metal ions within the bulk samples. After injection the samples were rinsed with DI water. The soak, inject, rinse cycle was repeated multiple times.

Iron (III) chloride was exchanged into each of the hydrogels and was used generally to test the suitability of specific hydrogel formulations (Table 1). All samples treated with Fe^{3+} became orange to dark orange in color. PSS hydrogels did not exhibit a significant change when treated with Fe^{3+} solutions. As the sulfonate moiety would not be expected to bind strongly to the iron ions, this behavior is not surprising. PA-based hydrogels, in contrast, became extremely hard and exhibited significant shrinkage (Figure 6).

Table 1. Qualitative behavior exhibited by hydrogels upon Fe^{3+} exchange.

Hydrogel composition	Initial hardness	Shrinkage	Change in hardness upon Fe^{3+} exchange (or addition)
PSS	Medium stiff +	None	Modestly stiffer
PA	Least stiff	> 50%	Much stiffer
PSS/PA	Medium stiff	20%	Stiffer
PAA	Very stiff	< 10%	Modestly stiffer
PA/PAA	Stiff	< 10 %	Modestly stiffer
PSS/PAA	Stiff	< 10 %	Modestly stiffer



Figure 6. Significant shrinkage of sample observed during $\text{Na}^+/\text{Fe}^{3+}$ metal exchange for the PA-based hydrogels: (left) PA hydrogel; (middle) PA hydrogel after 1h in FeCl_3 soln.; (right) PA hydrogel after 9h in FeCl_3 soln. Note: images are blurred due to magnification of a low resolution image.

The random copolymer of PSS/PA produced a sample with an intermediate response to iron substitution. In the 8:12:1 ratio of SS to A to PEG diacrylate, the exchanged hydrogel

samples exhibited a significant increase in qualitative hardness but did not contract more than about 20% in volume. Pure PAA hydrogel had an extremely high initial hardness and did not appear to change much upon addition of Fe^{3+} . The copolymers, PSS/PAA and PA/PAA, were less hard initially but also only change to a modest level upon addition of Fe^{3+} .

Fe^{2+} , in the form of FeCl_2 , was also introduced into the hydrogels. The lower solubility of FeCl_2 complicated the exchange. Hydrogels thus treated were pale green in color and were not as hard as samples prepared with Fe^{3+} .

Samples bearing other multivalent ions were also prepared. Neither Cu^{2+} nor Cu^+ bound well to the PA/PSS hydrogel. Although the color change indicated that some of the ion had been absorbed, the hydrogel samples did not become noticeably harder. Better results for copper ions were observed for the PSS/PAA hydrogels as was evidenced by the increase in hardness after the introduction of the metal ions. Other ions were also introduced (Co^{2+} and Ba^{2+}) but the properties of these hydrogels were not studied in any detail.

2.2.8 Quantitative analysis of Fe (III) in hydrogel

To understand the coordination degree of metal ions and organic ligands, the relative ratio of Fe^{3+} to carboxylate ions in a typical PSS/PA hydrogel sample was quantified. The overall procedure involved using UV-Vis spectroscopy to measure the concentration of FeCl_3 in solution after release by treatment of the hydrogel with concentrated HCl. Three hydrogel samples of the same dimension were prepared in parallel. Sample 1 was dried in an oven and weighed in order to determine the total mass of polyelectrolyte polymer per sample. Samples 2 and 3 were subjected to the Fe^{3+} exchange conditions as described. After extensive rinsing to remove excess FeCl_3 , the Fe^{3+} remaining in each sample was released by treatment with 12M HCl. The

concentration of FeCl_3 was then measured using UV-Vis spectroscopy (Figure 7). Each sample contained approximately 0.4 millimoles of Fe^{3+} (Table 2).

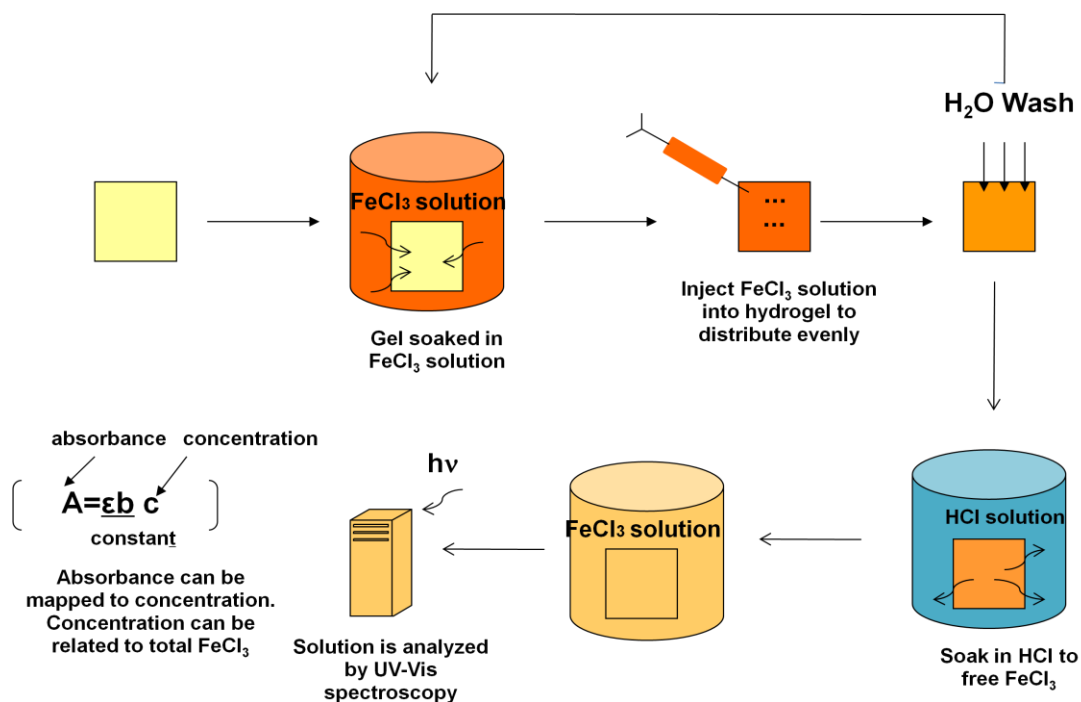


Figure 7. Fe^{3+} quantitative analysis procedure.

Table 2. Quantitation of Fe^{3+} in a typical PA/PSS hydrogel sample.

Sample ^a	Fe^{3+} (mmol)
2	0.352
3	0.408
average	0.38

^aSample 1 was a control used to measure electrolyte present

Comparing the absolute quantity of iron measured per sample to the number of carboxylate ions present in the hydrogel gives a ratio of 10.8 Fe ions per 100 carboxylate groups. As the theoretical maximum would be approximately 33 Fe ions per 100 carboxylate groups, if it is assumed that each iron can ligate to three carboxylates, the sample is not saturated with iron.

To verify the accuracy of the method, two other controls were analyzed. The first control sample involved the injection of a known amount of FeCl₃ (0.2 mL x 1M) directly into a solution of HCl. The sample was diluted using the same sequence of dilutions as used for the unknowns to make a 0.0800 M solution of FeCl₃. The second control was prepared by injecting a known amount of FeCl₃ (0.2 mL x 1 M) into a hydrogel (no soaking, just a single injection). After 3 h the gel sample was treated with HCl and diluted in an analogous manner to the unknown samples. All samples were determined to contain approximately the same amount of Fe³⁺ as expected (Table 3).

Table 3. Control samples for quantitative analysis of iron.

	0.0800 mM FeCl ₃	FeCl ₃ soln. + HCl	Hydrogel injected with FeCl ₃ Trial 1	Hydrogel injected with FeCl ₃ Trial 2
Absorbance (315 nm)	0.39204	0.38421	0.33972	0.39845
Concentration (mM)	0.080	0.079	0.070	0.083

2.2.9 Preparation of composites with polyurethane scaffolding

Composite EPE materials were prepared by incorporation of a scaffold. The polyurethane scaffold used is an open cell material and its inclusion improves the minimum mechanical properties of the materials. In particular, the scaffold decreases the tendency of the hydrogels to fracture when subjected to stress. Two types of foams, regular density foam and high density foam, were pretested by a mechanical compression test. Because of its more durable and elastic properties, the high density scaffold was selected. To prepare the scaffold-containing materials,

the scaffold was first submerged in the solution and purged with N₂. The scaffold was compressed and released several times to ensure a homogenous distribution. The initiator was then added and the polymerization was carried out as before. Ion exchange was conducted as described above for the non-scaffolded hydrogels. The composite product is similar in shape but tougher than the hydrogel sample with same crosslink density. Figure 8 shows a series samples at different stages.



Figure 8. PSS/PA composites components and products: (left to right): PSS/PA hydrogel; PSS/PA hydrogel in polyurethane foam scaffold; PSS/PA hydrogel after FeCl₃ exchange; PSS/PA hydrogel in polyurethane foam scaffold after FeCl₃ exchange.

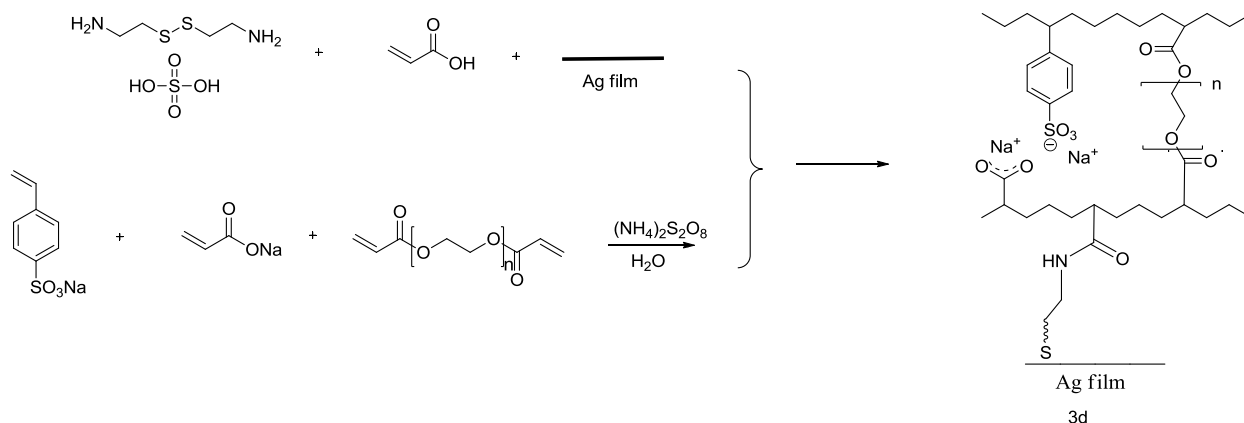
2.3 MEDIUM THROUGHPUT EXPERIMENTS

Samples of hydrogels both with and without scaffolding were also prepared in a 16-well plate (Figure 9). These “Size C” arrays were meant to facilitate optimization by allowing the parallel preparation, mechanical testing and electrochemical evaluation of multiple samples with different compositions.

With the long term goal of being able to measure the electrochemical behavior of these samples *in situ*, the chemical bonding of the hydrogel to a silver plate (later to become the working electrode) was explored as well¹⁸ (Scheme VII).



Figure 9. Teflon 16-well plate designed for medium throughput experiments. Six of the sixteen wells contain hydrogel samples.



Scheme VII. Preparation of a hydrogel sample with chemical attachment to Ag electrode.

2.4 SCAFFOLD COATING WITH CONDUCTING POLYMERS.

In order to increase the conductivity of the EPE composites and thereby facilitate electrochemical oxidation and reduction, we prepared modified scaffolds comprising the original PU foam coated with two different conducting polymers: polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT). Using the methodology reported by Lau and coworkers, the monomers were polymerized in the presence of the foam.¹⁹ Although the coated foams became very dark in color (nearly black in the case of the PPy) they retained the necessary flexibility and

porosity (Figure 10). Sectioning of the coated scaffolds established that the coating was homogeneous on a macroscopic scale. Composites of these coated scaffolds with hydrogels were prepared analogously to those with the non-coated scaffolds.

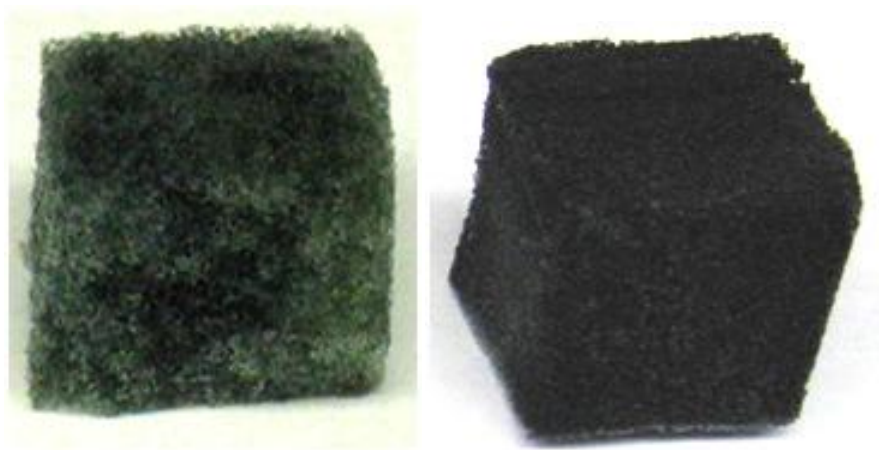


Figure 10. Conducting foams: (left) PU-PEDOT foam (right) PU-PPy foam.

2.5 OXIDATION AND REDUCTION OF THE EPE COMPOSITES

2.5.1 Chemical Oxidation

In order to test the hypothesis that increasing the oxidation state of a metal crosslinker would increase the stiffness of the composite, a PSS/PA composite (prepared with a standard scaffold) was subjected to chemical oxidation with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in H_2O . The sample became noticeably harder. Quantitative data can be found in section 2.6.

2.5.2 Attempted Electrochemical Reduction

In collaboration with Kathy Davis and Prof. David Waldeck, we attempted to carry out a bulk electrolysis of the EPE composite samples. The apparatus consisted of a Ag coil auxiliary electrode, separated from the bulk solution by a fritted glass disk, a Ag/AgCl reference electrode, and a working electrode composed of several stainless steel needles inserted deeply into the sample (Figure 11). The gel was placed into $\text{H}_3\text{PO}_4/\text{KH}_2\text{PO}_4$ buffer solution (pH = 4) that had been purged using Ar or N_2 gas. A CHI618B or CHI430A (CH Instruments) potentiostat was used to hold the potential at -0.5 V vs. Ag/AgCl, which is sufficient for the reduction of Fe^{3+} to Fe^{2+} . Electrolysis times varied from 1000-1500 seconds.

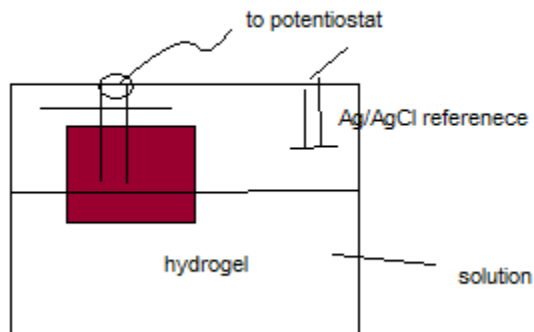
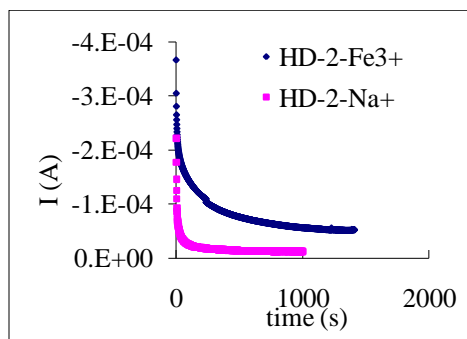
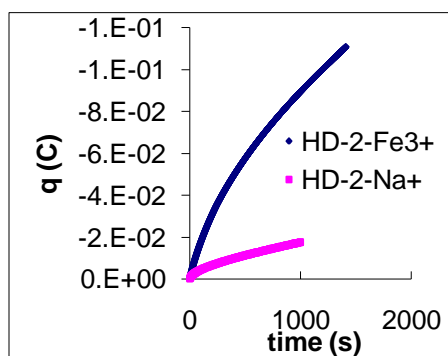


Figure 11. Bulk electrolysis cell.



(a)



(b)

Figure 12. Current and charge curves for EE composite samples. Potential held at -0.5 V (vs. Ag/AgCl electrode)

Figure 12 shows a comparison between the reduction process of an Fe^{3+} crosslinked hydrogel sample and the Na^+ hydrogel. The increased current and steepness of the current-time curves (see Figure 12a), as well as the much larger amount of charge passed (see Figure 12b), during the course of the experiment for gels containing Fe^{3+} indicates the presence of a reducible ion, presumably Fe^{3+} in the matrix. However, the current is observed to reach a plateau at >1000 s electrolysis time, and this plateau occurs at currents higher than 0 A. This result suggests that there is sufficient time for Fe^{2+} to re-oxidize in the sample, perhaps via contact with any air that had not been purged out of the gel or the solution. Regardless of mechanisms, however, it

strongly suggests that there is an insufficient transport of electricity through the sample, leading to incomplete conversion.

2.6 MECHANICAL PROPERTIES TESTING

2.6.1 Mechanical properties testing methods

The compression modulus of the hydrogels and composites were determined by Mark Delaney, a graduate student in the research group of Lisa Weiland, in the Dept. of Mechanical and Materials Engineering at the University of Pittsburgh. Two methods were employed, depending on the sample size. For samples of size A, compression tests were performed utilizing a MTI-1K (Measurement Technology Inc.) screw driven load frame equipped with 2.5 lb and 75 lb Transducer Technologies load cells in conjunction with a Messphysik ME46-450 non-contacting video extensometer (Figure 13). For samples of size C, the modulus was determined using an in-lab constructed indenting apparatus (Figure 14) (or the load frame in some cases). A more detailed description of the data collection, error analysis and procedure can be found in the M.S. thesis of Mr. Mark Delaney²⁰.

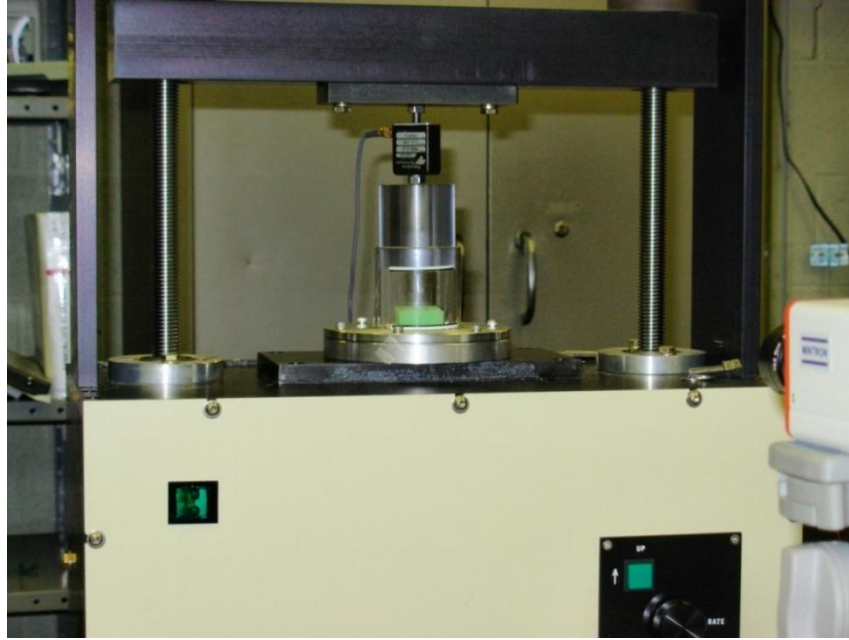


Figure 13. Instrumentation for testing the compression modulus of Size A samples.

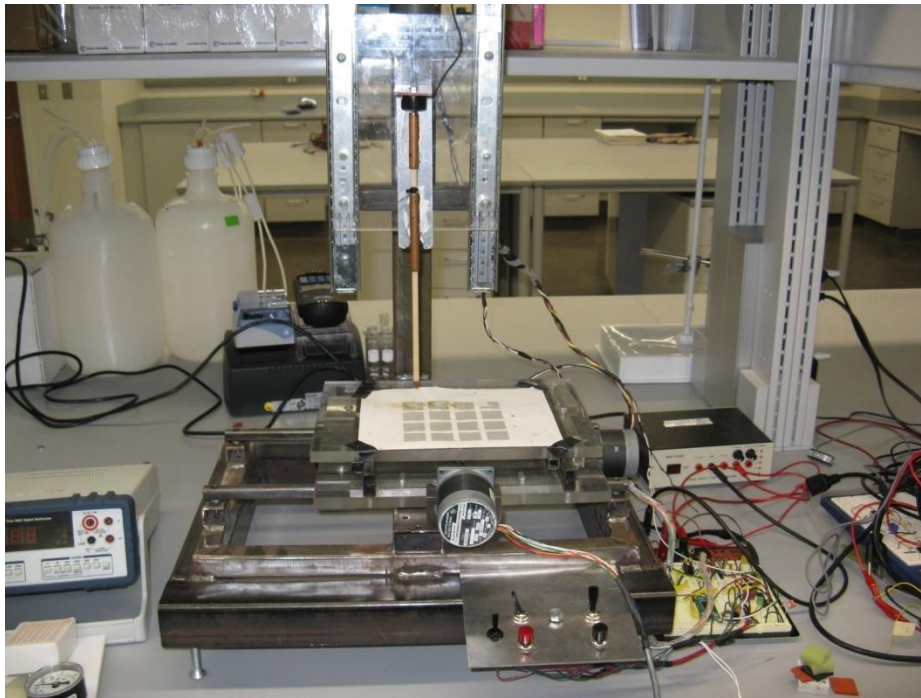


Figure 14. In-house constructed indentation apparatus for measuring the compression modulus of samples in 16-well plate (Size C samples).

2.6.2 Mechanical Properties Data and Analysis

A relatively small number of the samples whose preparation is described in section 2.2 were analyzed quantitatively. The results are summarized in Table 4. Entries 1-9 comprise a series of PSS/PA samples prepared with a constant composition but variable in metal ion, scaffolding, and size. Entries 10-13 represent a series of pure PAA copolymers with and without Fe^{3+} exchange. Entries 14-17 and 18-21 represent a series of composition-variable experiments designed to determine the optimum ratio of A:AA and SS:AA in copolymer hydrogels, respectively. Entries 22 & 23 present the mechanical data for samples prepared with the conducting polymer coated scaffolding.

Table 4. Mechanical testing results for hydrogel and composite materials

Entry	Composition % by weight ^a			X- link % ^b	Metal ion	Time (h) ^c	Scaff. ^d	Size ^e	Mod (MPa) ^f	Testing method ^f	Comments
	SS	A	AA								
1	40	60		5	Na ⁺		PU	A	0.136	LF	
2	40	60		5	Fe ²⁺	24	PU	A	0.22	LF	Prepared directly
3	40	60		5	Fe ³⁺	36	PU	A	3.0	LF	Prepared directly
4	40	60		5	Fe ²⁺	24	PU	A	0.119	LF	Prepared directly
5	40	60		5	Fe ³⁺	24	PU	A	1.05	LF	Chemical oxidation of entry 4
6	40	60		5	Na ⁺		no	A	0.017	LF	
7	40	60		5	Fe ³⁺	12	no	A	2.4	LF	
8	40	60		5	Na ⁺		no	C	0.57	I	
9	40	60		5	Fe ³⁺	36	no	C	0.64	I	
10			100	3	Na ⁺		no	A	0.04	LF	
11			100	3	Fe ³⁺	36	no	A	1.2	LF	
12			100	3	Na ⁺	2	no	C	0.6	I	
13			100	3	Fe ³⁺	36	no	C	0.56	I	
14		40	60	3	Na ⁺		no	C	0.031	LF	
15		55	45	3	Na ⁺		no	C	0.017	LF	Sample broke apart during testing
16		70	30	3	Na ⁺		no	C	0.027	LF	
17		85	15	3	Na ⁺		no	C	0.024	LF	
18	40		60	5	Na ⁺		no	C	0.078	LF	
19	55		45	5	Na ⁺		no	C	0.058	LF	
20	70		30	5	Na ⁺		no	C	0.036	LF	
21	85		15	5	Na ⁺		no	C	0.032	LF	
22	40	60		5	Fe ³⁺	24	PEDOT	A+	0.334	LF	1.5 in ³ cube
23	40	60		5	Fe ³⁺	24	PPy	A+	0.428	LF	1.5 in ³ cube

^a SS: sodium *p*-styrene sulfonate; A: sodium acrylate; AA: acrylamide; % by weight of PEG-diacrylate ($M_n = 575$);
^c metal ion solution soaking time; Use of polyurethane scaffold (PU); ^e Sample size: A = 1" x 1" x 1"; B = 1 cm x 1
cm x 1 cm; C = 1" x 1" x 0.2"; ^f Compression modulus; ^g Method for testing compression modulus.

The data in entries 1-9 substantiate the fundamental hypothesis behind the project i.e. that the stiffness of the composites will depend on the identity and oxidation state of the metal ion crosslinker. The Young's modulus (stiffness) values reported in Table 4 show a modest two-fold increase for the hydrogel with iron (II) relative to that with sodium mono-cation (entries 1 & 2). More significantly, a nearly 15-fold difference in stiffness was noted between samples prepared

with iron (II) vs. iron (III) (entries 2 & 3). It should be noted that the stiffness of entry 3 is higher than normally observed because the sample was allowed to soak in the FeCl_3 solution overnight pending measurement.

The most exciting result, the key preliminary result, is the observation of an order of magnitude increase in the stiffness *in the same sample* when a sample initially prepared with Fe^{2+} as the crosslinker is oxidized to Fe^{3+} under slightly acidic conditions with $\text{S}_2\text{O}_8^{2-}$. Although the Fe^{3+} sample is less stiff than the sample prepared by direct exchange of Fe^{3+} into the virgin hydrogel, an increase of almost an order of magnitude is observed.

Entries 6 & 7 represent hydrogel samples with no scaffolding. It can be seen by comparison of these entries with entries 1 & 3, that the addition of scaffolding increases the modulus for the samples significantly in the case of Na^+ and less so for Fe^{3+} . Note that entries 1-7 were all tested using the very well understood load frame apparatus described earlier. Entries 8 & 9, in contrast, are size C samples tested with the lab-built indenter. As these samples were prepared identically with 6 & 7, one would expect a correlation in modulus if the two methods of measurement were accurate. Although the trend is the same, the Na^+ sample is less stiff than the Fe^{3+} sample, the indenter does not appear to capture well the magnitude of the difference.

In the effort to determine the suitability of PAA-based polymers as electroplastic elastomers, hydrogel samples were prepared and tested with both the load frame and the indenter. The load frame data confirm our qualitative observation that the PAA samples have a higher initial hardness than the PSS/PA hydrogels but that there is less change upon addition of Fe^{3+} (entries 10 & 11). The indenter data do not correlate well in this case (entries 12 & 13).

Entries 14-17 summarize the search for an optimal composition for hydrogels based on the PA/PAA copolymer. The data show that the 40% by weight PA copolymers exhibit the highest

initial stiffness. Increasing the amount of acrylate monomer appears to decrease the stiffness. Entry 15 is anomalous because the sample broke apart during the testing. Quantitative data for the effect of Fe^{3+} substitution were not obtained.

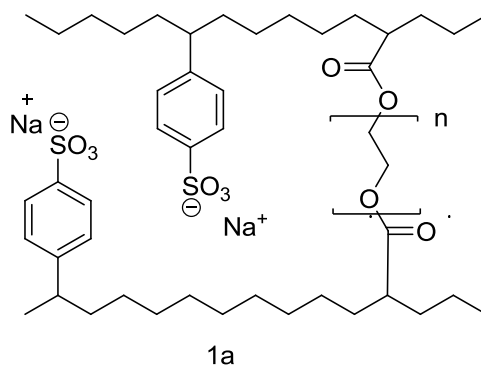
Entries 18-21 summarize the search for an optimal composition based on the PSS/PAA copolymer. Again the composition with the highest % by weight of PAA was the stiffest as prepared. Quantitative data for the effect of Fe^{3+} substitution were not obtained.

Entries 22 & 23 show the mechanical behavior of PSS/PA based hydrogels incorporating conducting polymer coated scaffolds. Interestingly, the stiffness after exchange for these samples is less than that observed for the non-coated scaffolds and the scaffold-free samples (entries 3 & 7). The origin of this difference is not completely understood but may be due to the larger size of these samples relative to the normal Size A samples (1.5 in^3 vs. 1 in^3) rather than to an intrinsic difference in the composite arising from the scaffold coating. The larger size of the sample increases the chance of an inhomogeneity in the distribution of the Fe^{3+} . These measurements must be repeated on true Size A samples before any conclusions can be made.

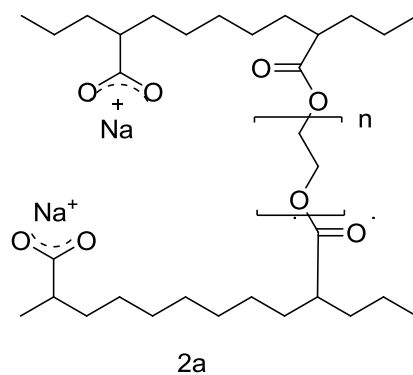
3.0 CONCLUSIONS AND FUTURE WORK

In summary, we have prepared a series of composite materials comprising polyelectrolyte based hydrogels, polyurethane scaffolding and multivalent metal ions. In the case of the PSS/PA hydrogels we have determined that the compression modulus increases with the increasing oxidation state of the iron ion crosslinking agent. Initial electrochemical testing established that the samples exhibited poor conductivity. EPE composites with conducting polymer coated scaffolds have been prepared to address this problem. Future work will focus on determining the conditions for electrochemical reduction and oxidation of the metal ions.

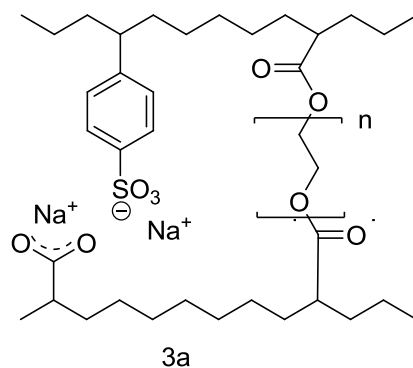
4.0 EXPERIMENTAL



Poly (styrene sulfonate) with poly (ethylene glycol) diacrylate crosslinking (1a) 4-Styrenesulfonic acid sodium salt monohydrate, (1.5 g), poly (ethylene glycol) diacrylate ($M_n = 575$, 0.07 ml), and H_2O (7 ml) were combined in a scintillation vial (20 ml). The solution was purged with N_2 for 10 min. $NH_4S_2O_8$ (40 mg) was added and the vial was sealed using a screw cap. The mixture was heated in a closed system at $85\text{ }^\circ\text{C}$ for 2 h. The resulting pale yellow hydrogel was removed from the vial and trimmed to give a $1\text{ x }1\text{ x }1\text{ cm}^3$ cube (Size B).



Poly (acrylate) with poly (ethylene glycol) diacrylate crosslinking (2a) Sodium acrylate (2.0 g), poly (ethylene glycol) diacrylate ($M_n = 575$, 0.14 ml) and H_2O (14ml) were added to a scintillation vial (20 ml). The solution was purged with N_2 for 10 min. $NH_4S_2O_8$ (40 mg) was added to the mixture and it was heated to $85\text{ }^\circ\text{C}$ for 2 h. The resulting hydrogel was cut into $1 \times 1 \times 1\text{ cm}^3$ cube (Size B).



Poly[(styrene sulfonate)-*co*-acrylate] with poly(ethylene glycol)diacrylate crosslinking (3a) 4-Styrenesulfonic acid, sodium salt hydrate (0.8 g), sodium acrylate (1.2 g), poly(ethylene glycol) diacrylate (0.1 ml) and H_2O (9 ml) were added to a scintillation vial (20 ml). The solution was purged with N_2 for 10 min. $NH_4S_2O_8$ (30 mg) was added to the mixture and it was heated to $85\text{ }^\circ\text{C}$ for 1 h. The resulting hydrogel was cut into $1 \times 1 \times 1\text{ cm}^3$ cube (Size B).

Poly[(styrene sulfonate)-*co*-acrylate] with **poly(ethylene glycol)diacrylate crosslinking + scaffold (3b)** High density polyurethane foam was cut into cylindrical cross-section $\pi \times 2.5 \times 2.5 \times 0.5 \text{ cm}^3$ to fit a custom reactor (see Figure 5 below). H₂O (90 ml) was added to the container. The foam was repeatedly compressed and allowed to expand in order to promote even wetting. The wet foam and surrounding solutions was purged with N₂ for 10 min. 4-Styrenesulfonic acid sodium salt monohydrate (8.0 g), sodium acrylate (12.0 g), poly (ethylene glycol) diacrylate (1.0 ml) were added to the reactor. The solution was purged with N₂ for 10 minutes. NH₄S₂O₈ (150 mg) was added to solution and the mixture was heated to 85 °C for 1.5 hour. The resulting hydrogel + scaffold was cut into 1" x 1" x 1" cube (Size A).



Figure 15. Reactor for the synthesis of size A and B samples.

Hydrogel Ion Exchange (Fe³⁺) (3c) Hydrogel cube **3a** was submerged in 10 ml of a saturated solution of FeCl₃ for one hour. To promote even distribution of the iron within the sample it was removed from the solution and manually injected with 3 ml of the saturated FeCl₃ at multiple sites. The sample was rinsed with deionized water. The soak, inject, rinse cycle was repeated 3x. Finally, the sample was allowed to soak for 12 more h in the saturated FeCl₃ solution.

Hydrogel + scaffold Ion Exchange (Fe^{3+}) (3d) The hydrogel + scaffold cube **3b** was submerged in 10 ml of a saturated solution of FeCl_3 for one hour. The sample was injected at multiple sites with 3 ml of the saturated FeCl_3 using a syringe. The excess FeCl_3 was removed by rinsing with deionized water. The soak, inject, rinse cycle was repeated 3x. Finally, the sample was allowed to soak for 12 more h in the FeCl_3 solution.

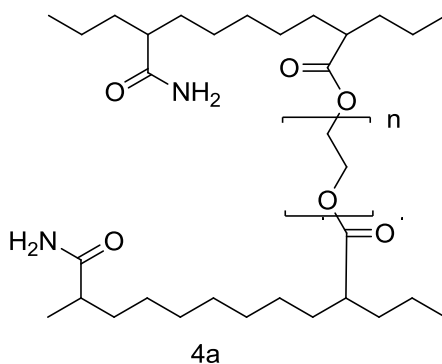
Hydrogel + scaffold Ion Exchange (Fe^{2+}) (3e) The hydrogel + scaffold cube **3b** was submerged in 10 ml of a saturated solution of FeCl_2 for one hour. The sample was injected at multiple sites with 3 ml of the saturated FeCl_2 using a syringe. The excess FeCl_2 was removed by rinsing with deionized water. The soak, inject, rinse cycle was repeated 3x. For each resubmersion a fresh solution of saturated FeCl_2 solution was used. Finally, the sample was allowed to soak for 12 more h in the FeCl_2 solution.

Poly [(styrene sulfonate)-*co*-acrylate] with poly(ethylene glycol)diacrylate crosslinking (Size C) (3f) 4-Styrenesulfonic acid, monosodium hydrate (0.4 g), sodium acrylate (0.6 g), poly(ethylene glycol) diacrylate (0.05 ml) and H_2O (4.5ml) were added into a custom-designed Teflon multi-well reactor (See figure 3.1 for a diagram). The solution was purged with N_2 for 10 min. $\text{NH}_4\text{S}_2\text{O}_8$ (8 mg) was added to the mixture and it was heated to 85 °C for 70 min. The resulting hydrogel was cut into 2.5 x 2.5 x 0.5 cm^3 shape.

Poly[(styrene sulfonate)-*co*-acrylate] with poly(ethylene glycol)diacrylate crosslinking and coordination to silver foil (Size C) (3g) Silver foil (25 x 25 x 1 mm) was roughened on one side

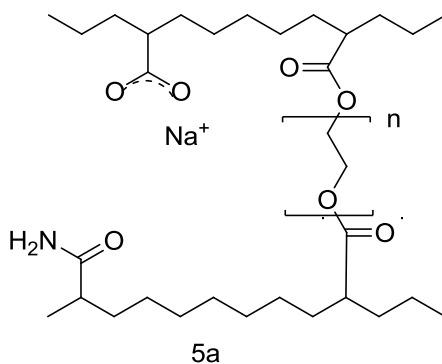
using sand paper and then immersed into a cystamine sulfate solution (10 ml x 0.01 M) for 10 min. After removal, the foil was immediately transferred into an acrylic acid solution (10 ml x 0.02 M) and soaked for 10 min. The foil then was inserted into a 1" x 1" x 1/2" square reaction well the Teflon multi-well vessel. 4-Styrenesulfonic acid, monosodium hydrate (0.4 g), sodium acrylate (0.4 g), poly (ethylene glycol) diacrylate ($M_n = 575$, 0.05 ml) and H_2O (4.5ml) were added to the well. The solution was purged with N_2 for 10 min. $NH_4S_2O_8$ (8 mg) was added to the solution and the mixture was heated to 85 °C for 70 min.

Hydrogel + scaffold Ion + Silver foil Exchange (Fe^{3+}) Size C (3h) The hydrogel sample **3g** was submerged in 10 ml of a saturated solution of $FeCl_3$ for one h. The sample was injected at multiple sites with 3 ml of the saturated $FeCl_3$ using a syringe. The excess $FeCl_3$ was removed by rinsing with deionized water. The soak, inject, rinse cycle was repeated 3x. Finally, the sample was allowed to soak for 12 more h in $FeCl_3$ solution.



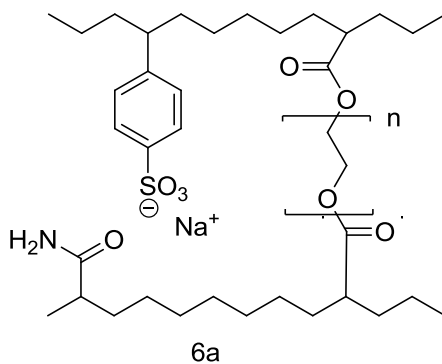
Poly (acrylamide) hydrogel with poly (ethylene glycol) diacrylate crosslinking (4a) Acrylamide, (1.4 g), poly (ethylene glycol) diacrylate ($M_n = 575$, 0.07 ml), and H_2O (9 ml) were combined in a scintillation vial (20 ml). The solution was purged with N_2 for 10 min. $NH_4S_2O_8$ (40 mg) was added and the vial was sealed using a screw cap. The mixture was heated in a

closed system at 85 °C for 2 h. The resulting transparent colorless hydrogel was removed from the vial and trimmed to give a 1 x 1 x 1 cm³ cube (Size B).



Poly[Acrylate-*co*-acrylamide] with poly(ethylene glycol)diacrylate crosslinking (5a)

Sodium acrylate (0.8 g), acrylamide (1.2 g), poly (ethylene glycol) diacrylate (0.1 ml) and H₂O (9 ml) were added to a scintillation vial (20 ml). The solution was purged with N₂ for 10 min. NH₄S₂O₈ (30 mg) was added to the mixture and it was heated to 85 °C for 1 h. The resulting hydrogel was cut into 1 x 1 x 1 cm³ cube.



Poly[(styrene sulfonate)-*co*-acrylamide] with poly(ethylene glycol)diacrylate crosslinking

(6a) 4-Styrenesulfonic acid, sodium salt hydrate (0.8 g), acrylamide (1.2 g), poly(ethylene glycol) diacrylate (0.1 ml) and H₂O (9 ml) were added to a scintillation vial (20 ml). The solution

was purged with N₂ for 10 min. NH₄S₂O₈ (30 mg) was added to the mixture and it was heated to 85 °C for 1 h. The resulting hydrogel was cut into 1 x 1 x 1 cm³ cube.

Chemical oxidation of Hydrogel + scaffold Ion Exchange (Fe²⁺). The Fe³⁺- crosslinked hydrogel sample **3b** was immersed in a solution of NH₄S₂O₈ (1M x 10 ml) for 10 min. The sample was also injected at multiple sites with a solution of NH₄S₂O₈ (1 M x 2 ml x 3 repetitions).

Fe (III) quantitation in a typical sample. A 6 g (measured when fully hydrated) sample of crosslinked PSS/PA hydrogel, prepared as previously reported, was divided into 3 portions of 2 g each. Water was removed from one portion (Sample 1) by thermal drying (40 °C, 24 h) to give a dry mass was 0.56 g.

Samples 2 and 3 were subjected to analysis in parallel according to the following procedure. Each 2 g sample was submerged in 10 ml of a saturated solution of FeCl₃ after 1 h the sample was removed and injected with 2 mL of the saturated FeCl₃ solution using a syringe. To prevent the formation of a crosslinked crust, excess FeCl₃ was removed from the gel surface by rinsing with deionized water. The soak, inject, rinse cycle was repeated 3x. Finally, the sample was allowed to soak for 12 more h in the FeCl₃ solution. After rinsing, the sample was submerged in a 12 M solution of concentrated HCl for 2 h. FeCl₃ rapidly diffused out of the gel as shown by the orange color of the solution and the bleaching of the hydrogel. An aliquot of the solution was removed and diluted 10x for analysis (5 mL aliquot to 50 mL) Samples 2 and 3 were analyzed spectroscopically and the concentrations were calculated from the calibration curve according to Beer's Law. **Calibration:** To create a calibration curve for UV-Vis analysis

of these samples a series of solutions of known concentration was prepared by dilution of 0.2 ml of a 1M FeCl₃ solution to 0.04 mM, 0.08 mM, 0.12 mM and 0.16 mM. The absorbance of these samples at (315nm) was used to form a standard curve. **Other Controls** Two further control samples were prepared (2 g). The first sample control involved injection of a known amount of FeCl₃ (0.2 mL x 1M) directly into a solution of HCl. The sample was diluted using the same sequence of dilutions as used for the unknowns to make a 0.08 M solution of FeCl₃. The second control was prepared by injecting a known amount of FeCl₃ (0.2 mL x 1M) into a hydrogel (no soaking, just a single injection). After 3 h the gel sample was treated with HCl and diluted in an analogous manner to the unknown samples. The expected concentration of the sample, based on the dilution was also 0.080 mM.

PU-PEDOT conducting foam (7a) The polyurethane (PU) foam was washed with soapy water and then rinsed with excess MilliQ water and dry in the air for one day. 3,4-ethylenedioxythiophene (0.8 mmol) and acetic acid (1 mmol) were dissolved into H₂O (20 ml) and CH₃CN (3 ml), the mixture was stirred in a 100 ml beaker. A piece of polyurethane (2 cm x 2 cm x 2 cm) polyurethane was soaked in the above solution for 2 h. When the foam was completely wetted with the solution, 20 ml FeCl₃ (0.04 M) was added and mixture was stirred overnight. The dark green PU-PEDOT foam was removed from container and washed with MilliQ water. Finally, the PU-PEDOT foam was dried at 40 °C in the oven overnight.

PU-PPY conducting foam (7b) The polyurethane (PU) foam was washed with soapy water and then rinsed with excess MilliQ water and dry in the air for one day. Pyrrole (0.04M) and naphthalene (NDSA, 0.5 M) were dissolved into H₂O (25 ml) and the mixture was stirred in a

100 ml beaker. A piece of PU (1.5'' x 1.5'' x 1.5'') was soaked in the above solution for 2 h. When the foam was completely wetted with the solution, 25 ml FeCl₃ (0.04 M) was added and mixture was stirred overnight. The black PU-PPY foam was removed from container and washed with MilliQ water. Finally, the PU-PPY foam was dried at 40 °C in the oven overnight.

BIBLIOGRAPHY

1. Justin, G.; Guiseppi-Elie, A.; Characterization of electroconductive blends of poly (HEMA-co-PEGMA-co-HMMA-co-SPMA) and poly(Py-co-PyBA). *Biomacromolecules* **2009**, 10, (9), 2539-2549.
2. Mano, N.; Yoo, J. E.; Tarver, J.; Loo, Y.-L.; Heller, A., An Electron-Conducting Cross-Linked Polyaniline-Based Redox Hydrogel, Formed in One Step at pH 7.2, Wires Glucose Oxidase. *J. Am. Chem. Soc.* **2007**, 129, (22), 7006-7007.
3. Brahim, S.; Wilson, A. M.; Narinesingh, D.; Iwuoha, E.; Guiseppi-Elie, A., Chemical and biological sensors based on electrochemical detection using conducting electroactive polymers. **2003**, 143, (2-3), 123-137.
4. Kopecek, J.; Yang, J., Hydrogels as smart biomaterials. *Polym. Int.* **2007**, 56, (9), 1078-1098.
5. Cao, H.; Zhu, J.; Su, H.; Fang, L.; Tan, T., Preparation a novel pH-sensitive blend hydrogel based on polyaspartic acid and ethylcellulose for controlled release of naproxen sodium. *J. Appl. Polym. Sci.* **2009**, 113, (1), 327-336.
6. Luo, R.; Li, H., Simulation analysis of effect of ionic strength on physiochemical and mechanical characteristics of glucose-sensitive hydrogels. *J. Electroanal. Chem.* **2009**, 635, (2), 83-92.

7. Bhattacharya, S.; Acharya, S. N. G., Pronounced Hydrogel Formation by the Self-Assembled Aggregates of N-Alkyl Disaccharide Amphiphiles. *Chem. Mater.* **1999**, 11, (12), 3504-3511.
8. Karino, T.; Okumura, Y.; Ito, K.; Shibayama, M., SANS studies on spatial inhomogeneities of slide-ring gels. *Macromolecules* **2004**, 37, (16), 6177-6182.
9. Chujo, Y.; Sada, K.; Saegusa, T., Cobalt(III) bipyridyl-branched polyoxazoline complex as a thermally and redox reversible hydrogel. *Macromolecules* **1993**, 26, (24), 6320-3.
10. Gaub, H.; Mittelbach, A.; Jaenker, P.; Nitschke, F.; Schubert, U. S. Reversibly switchable cross-linking of monomers. *US Pat.*, 6 469 134, 2002.
11. Chujo, Y.; Sada, K.; Naka, A.; Nomura, R.; Saegusa, T., Synthesis and redox gelation of disulfide-modified polyoxazoline. *Macromolecules* **1993**, 26, (5), 883-7.
12. Tesoro, G. C.; Sastri, V. R. Polyimide resins *US Pat.*, 5 260 411, 1993
13. Lee, H.; Parks, T. G., Reduction/oxidation induced cleavable/crosslinkable temperature-sensitive hydrogel network containing disulfide linkages. *Polymer Journal (Tokyo)* **1998**, 30, (12), 976-980.
14. Ravi, N. Hydrogel nanocomposites for ophthalmic applications. *US Pat.*, 0 269 488, 2007.
15. Fei, S.-T.; Phelps, M. V. B.; Wang, Y.; Barrett, E.; Gandhi, F.; Allcock, H. R., A redox responsive polymeric gel based on ionic crosslinking. *Soft Matter* **2006**, 2, (5), 397-401.
16. de Lumley-Woodyear T; Rocca P; Lindsay J; Dror Y; Freeman A; Heller A Polyacrylamide-based redox polymer for connecting redox centers of enzymes to electrodes. *Anal. Chem* (**1995**), 67(8), 1332-8.

17. Rodriguez, Elena; Katime, Issa. Behavior of acrylic acid-itaconic acid hydrogels in swelling, shrinking, and uptakes of some metal ions from aqueous solution. *J. Appl. Polym. Sci.* (2003), 90(2), 530-536.
18. Webster, D. C. "Combinatorial and high-throughput methods in macromolecular materials research and development" *Macromol. Chem. Phys.* 2008, 209, 237-246.
19. Inherently conducting polymer modified polyurethane smart foam for pressure sensing. Brady, Sarah; Diamond, Dermot; Lau, King-Tong. National Centre for Sensor Research, Dublin City University, Dublin, Ire. *Sens. Actuators, A* (2005), A119(2), 398-404.
20. M. Delaney. *Experimental Characterization of Electroplastic Elastomer.* 2010, M.S Thesis, University of Pittsburgh.