ABSTRACT

Title of Document: SOFT HYDROGEL BATTERIES: THE DANIELL CELL
                       CONCEPTUALIZED IN HYBRID HYDROGELS

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Energy storage devices such as batteries are important elements in many electronic devices. Currently, researchers are seeking to create new electronic devices that are "soft", i.e., bendable and stretchable. However, the batteries that power such devices are still mostly hard structures. In the current thesis, we have attempted to develop a "soft" battery out of hydrogels. Specifically, we have made a soft version of the Daniell Cell, which is a classic electrochemical cell. Our design involves a hybrid gel composed of three distinct layers. The top and bottom layers are gels swollen with a zinc salt and a copper salt, respectively, while the middle layer is akin to a "salt bridge" between the two. The hybrid gel is made by a polymerization technique developed in our laboratory and it retains good mechanical integrity (i.e., the individual layers do not delaminate). Zinc and copper foils are then attached to the hydrogel, thus creating an overall battery, and its discharge performance is reported. One unique aspect of these gel batteries is that they can be dehydrated and stored in a dry form, whereupon they are no longer batteries. In this inactive state, the materials are safe and light to transport. Upon rehydration, the gels revert to being functional batteries. This concept could be useful for military or other applications where an emergency energy storage is needed.

Soft Hydrogel Batteries: The Daniell Cell Conceptualized in Hybrid Hydrogels

By

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Dedication

This thesis is dedicated to my parents for their continuous love and support

during my good and bad times.

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I of course must thank and acknowledge my family. I am grateful to my father for instilling in me a love of nature, science, and history, and for his willingness to drop everything else if one of us needed him to. I am thankful to my mother for her continuous love and support. Without her inspiration it would not have been possible for me to stay confident even during my bad times.

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List of Abbreviations

AAm   Acrylamide

DMAA   N,N dimethylacrylamide

KPS   Potassium Persulfate

BIS   N,N'-methyleneBIS acrylamide

TEMED   N,N,N',N' tetramethylethylenediamine

PEGDA   Poly (ethylene glycol) diacrylate

SS   Stainless Steel

GE   Gel Electrolyte

EIS   Electrochemical Impedance Spectroscopy

CHAPTER 1: INTRODUCTION AND OVERVIEW

Batteries are an integral part of our daily lives for energy requirements. Almost all electronic devices require a battery to power them. Various types of batteries with different electrochemistries such as nickel-cadmium, lead-acid and lithium-ion are available in the market. While these batteries can have various shapes and sizes, they are all hard structures. In comparison, there is significant research currently into "soft" electronics, i.e., electronic components or devices that are bendable or stretchable.[1-4] These include stretchable displays, devices that can be implanted into the body[5] or that can be in contact with skin,[6] and electronics that can be integrated into clothing.[7] Figure 1.1 shows examples of devices with such unique properties. Various research groups and companies like PARC and Samsung have been working in this area.
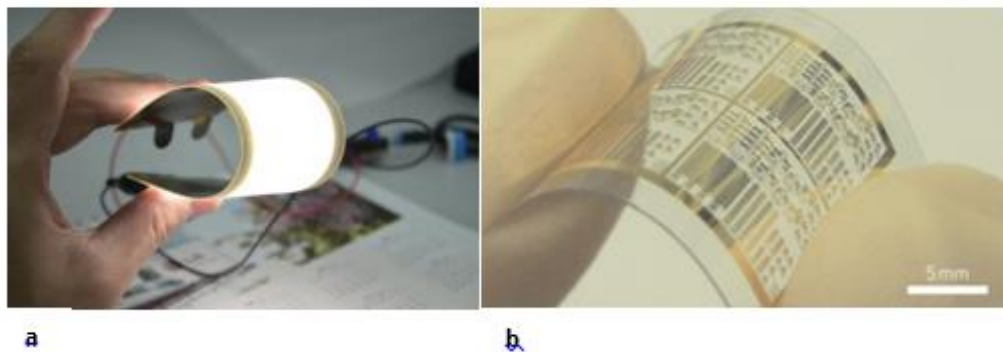
Figure 1.1 a) A bendable Organic Light Emitting Diode (OLED). b) Bendable thin film transistors.

To power these electronic devices, it is imperative to develop new kinds of power sources. Current battery designs are limited by their rigid structure and cannot integrate easily with these devices However, progress in the field of soft batteries or other power

sources has been relatively slow. There have been a few reports of bendable fuel cells,[8] stretchable supercapacitors,[9] soft photovoltaic devices,[10] and stretchable batteries.[11] Figure 1.2 shows a stretchable battery based on the electrochemistry of a dry cell. This were designed using commercially available acrylic elastomer as the substrate. Zinc, carbon and xanthan gum were used as the cathode. For the anode, pastes of manganese dioxide and carbon were used.[12] A gel of xanthan gum with ammonium chloride and zinc chloride salts were used as the electrolyte.
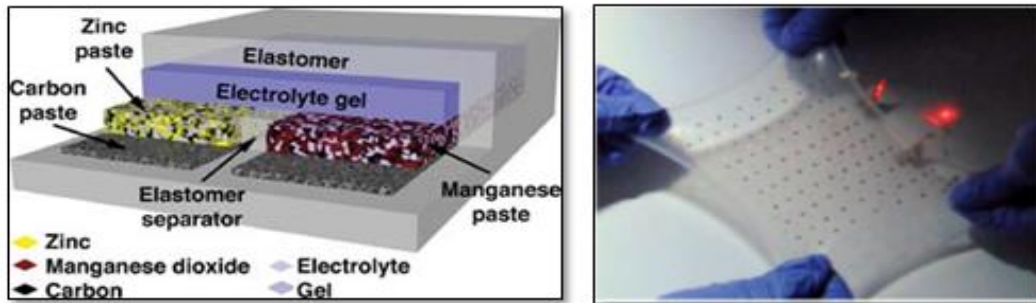
Figure 1.2 Stretchable batteries based on dry cell chemistries reported by Kaltenbrummer.et.al[12] (left). On the right is a stretchable battery made by interconnecting small Li ion batteries. The whole assembly is developed on stretchable silicone elastomer and flexible inter connects.[11]

Hydrogels have also been exploited for the fabrication of energy and electronic devices. As the name suggests, hydrogels are are interconnected polymer networks that absorb water. Their remarkable properties such as stimuli responsiveness, high water uptake capacity and biocompatibility have made them attractive candidates for various applications such as drug delivery,[13] medical implants, contact lenses and several others. The application of hydrogels in the fields of energy and electronics is relatively new. One such example is transparent loud speakers developed by Keplinger et al.[14] Soft photovoltaic

cells based on hydrogels have been reported by Velev et al.[10] The design in this case consisted of an agarose gel embedded with a photosensitive dye. To the best of our knowledge, the above are the only examples of energy storage devices fabricated using hydrogels.

In this thesis, we have exploited the properties of hydrogels to develop a soft, portable, energy storage device. To realize our goal, we have incorporated the electrochemistry of the Daniell Cell in hydrogels. Three electrolyte components of the conventional Daniell Cell, namely: zinc sulfate electrolyte, copper sulfate electrolyte and salt bridge have been incorporated into three distinct hydrogel layers, which are sandwiched using a hybridization technique developed in our laboratory. These are then integrated together with copper and zinc foils to produce an overall battery. We have characterized the performance of the resulting battery as a function of typical variables like the swelling ratio of the hydrogels. One important feature of our hydrogel battery is that it can be dehydrated and stored in a dry form, whereupon it is no longer a battery. In this inactive state, there is no liquid in the battery and hence no concerns with leakage etc, i.e., the material can be safely transported and stored. In addition, the absence of liquid also makes the material much lighter to transport. Upon rehydration, the hydrogel increases in weight by a factor of 2 and reverts to being a functional battery. The performance of the battery before and after rehydration is comparable. This concept could be useful for military or other applications where emergency energy supply (battery power) is needed.

CHAPTER 2: BACKGROUND

Hydrogels are critical component in the design of our battery. In this section, we will discuss various types of hydrogels and the principles involved in their synthesis. Swelling of hydrogels will also be reviewed. We will also review various battery electrochemistries. Fundamental principles behind the characterization techniques used in this work will also be discussed.
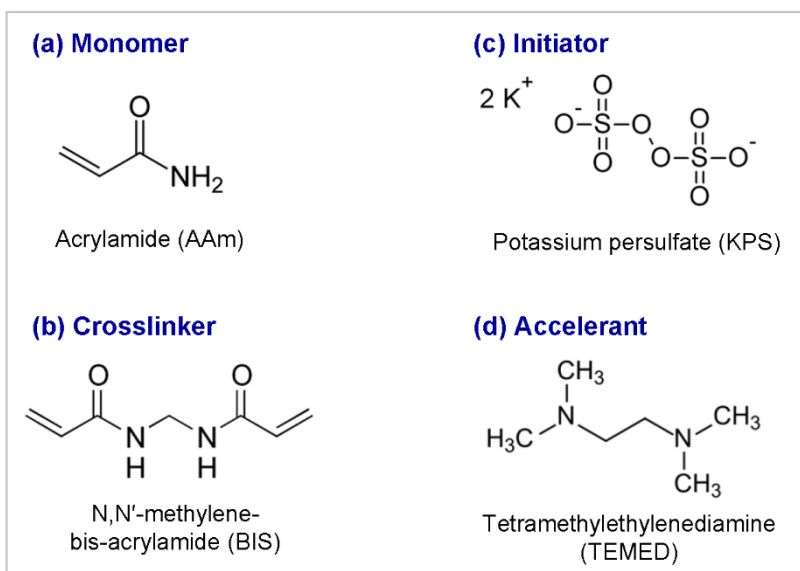

Figure 2.1 Components required for the synthesis of an AAm hydrogel.

2.1 HYDROGEL SYNTHESIS

Hydrogels are interconnected polymeric networks swollen in water. The polymer chains can be physically or covalently crosslinked using various crosslinkers. Various components involved in the synthesis of hydrogels are monomers, crosslinkers and

initiators. Numerous monomers have been investigated for hydrogel synthesis. Hydrogels are formed by free-radical polymerization of monomers. We will illustrate the process with the example of polyacrylamide (AAm). The starting materials for the polymerization reaction are shown in Figure 2.1. These include acrylamide (AAm), which has a single carbon-carbon double bond; another monomer called bis-acrylamide (BIS) which has two acrylamide moieties and acts as a crosslinker; an initiator, in this case potassium persulfate (KPS), and an accelerant, tetramethyl-ethylenediamine (TEMED) that speeds up the reaction.
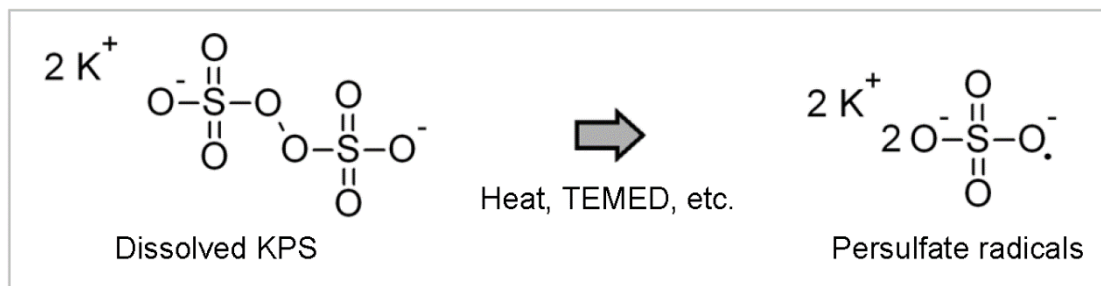
Figure 2.2 The initiation step of free radical polymerization. Potassium persulfate (KPS) dissociates to give free radicals in the presence of an accelerant like TEMED or heat.

The first step of this process is the generation of free radicals from KPS (Figure 2.2). This can be achieved in a number of ways but the most common way is by heat. Alternately, chemical accelerants such as TEMED can be employed and the polymerization can be conducted at room temperature. Polymerization begins with the attack of the free radical on the carbon-carbon double bond (i.e., vinyl bond) of AAm, which is then converted into a radical. This reactive monomer can then attack another monomer making it reactive and can attach to it. The process continues generating a polymer chain. In the

meantime, radicals also attack unsaturated carbon-carbon moieties of BIS making it reactive also. Since BIS has two carbon-carbon moieties it can react with two acrylamide chains simultaneously, thus forming a branched interconnected network (Figure 2.3). Since the concentration of BIS is much less than AAm, the latter grows into long polymer chains before it meets the crosslinkers. Polymerization will stop when the supply of monomers is exhausted; in this case, two reactive chains combine to give a terminated or unreactive chain.
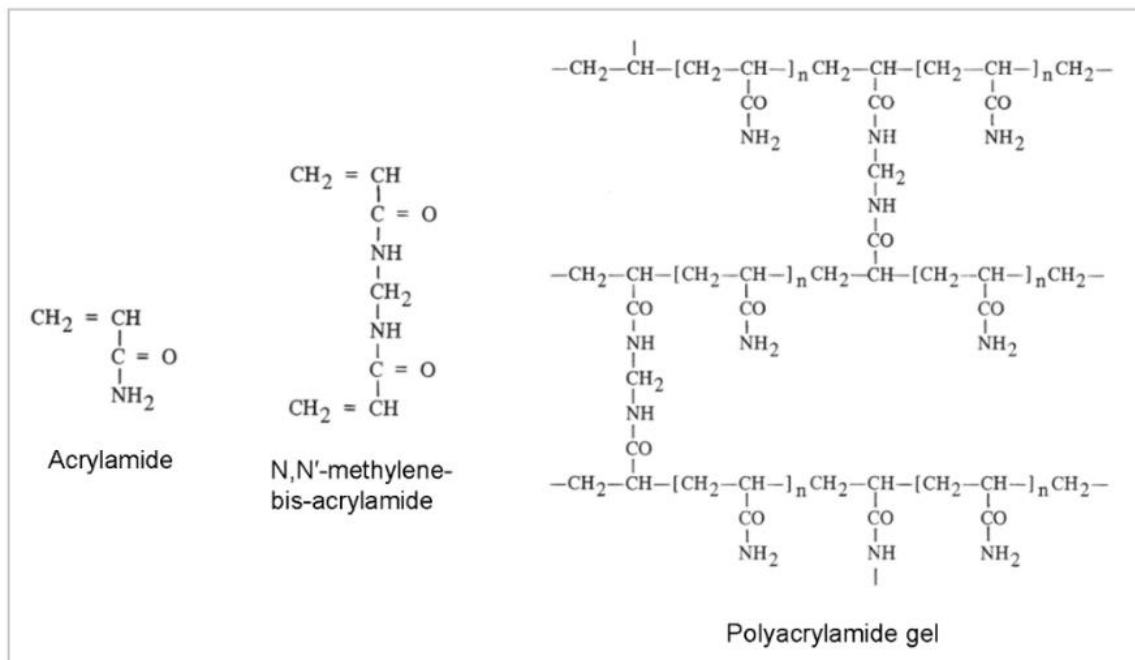

Figure 2.3. AAm and BIS monomers react and form an interconnected network of polymeric chains, which is swollen in water to give a hydrogel.
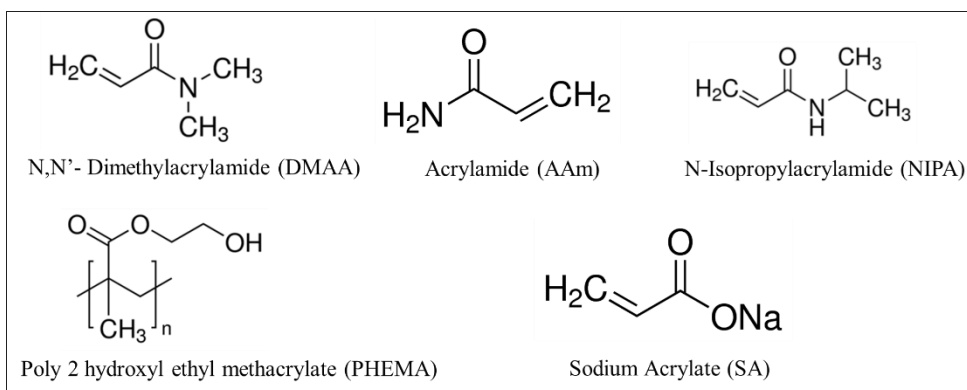
Figure 2.4. Common monomers used for the fabrication of hydrogels. Each monomer has a vinyl group, which is the reactive site for the polymerization.

Various water-soluble monomers can be used to form hydrogels, including 2-hydroxyethyl-methacrylate (HEMA), acrylamide (AAm), N-isopropyl acrylamide (NIPA), dimethyl acrylamide (DMAA) and others (Figure 2.4). [15] Also, in addition to BIS, other molecules such as polyethylene-glycol-diacrylate (PEGDA) can also be employed as crosslinkers for the formation of hydrogels (Figure 2.5). One further example of a crosslinker that is not a small molecule is a type of nanoparticle called laponite. Laponite is a layered silicate that exists in the form of nanoscale discs, with each disc approximately 25 nm in diameter and 1 nm in thickness (Figure 2.5). The faces of the particles are negatively charged.[16] It has been shown that laponite particles can serve as crosslinkers during free-radical polymerization of monomers such as AAm and NIPA (one still needs to use monomer, initiator, and accelerant). Laponite-crosslinked hydrogels tend to swell more and are mechanically stronger than hydrogels made with crosslinkers like BIS. However, these particles are not suitable as crosslinkers when the monomer solution contains salt, since salt can lead to the flocculation of the particles.[17]
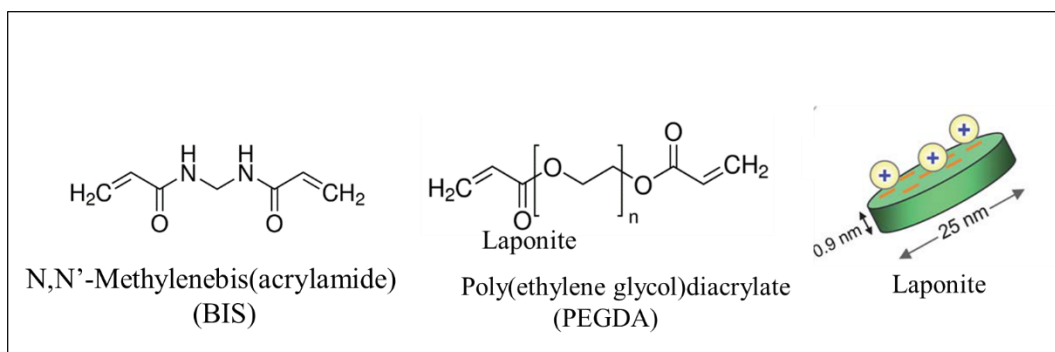
Figure 2.5 Various cross linkers used for hydrogel synthesis. BIS-acrylamide and polyethylene-glycol-diacrylate are small-molecules that serve as crosslinkers. Laponite is a type of clay nanoparticle that also acts as a crosslinker during free-radical polymerization.

We now briefly discuss the effect of metal ions on hydrogel synthesis. Abramov et al.[18] describe the effect of copper salts on radical polymerization of acrylamide. They showed that the cations in these salts retard the polymerization. As described earlier, polymerization begins with the attack of free radicals on the monomers. In the presence of Cu^{2+} ions, these radicals will react with the ions instead. This slows down the overall polymerization process. Similar retardation is also seen with some other metal ions like Fe^{2+}, but it is not seen with Zn^{2+}. This aspect will be relevant for our studies in Chapter 3.

2.2 HYDROGEL SWELLING

Swelling of hydrogels in various solutions has been investigated extensively. Charge, crosslinking density and polymer concentration are the three main governing factors in hydrogel swelling.[19,20] When a gel swells, the polymer chains are stretched, leading to an increase in elastic energy. Water uptake by the gel leads to a decrease in free energy of mixing. Also in the case of gels based on ionic monomers like sodium acrylate, there are additional energy considerations. Mobile ions will not separate far from the

polymer chains to maintain electroneutrality. The difference in ion concentration between solvent and gel will lead to inflow of solvent. Equilibrium in swelling is attained when there is a balance between the forces that drive and oppose swelling. In the case of gels based on ionic monomers, if salt is present in the solvent, the overall driving force for swelling is reduced. Typically, divalent ions have a stronger effect in this context than monovalent ions. [21,22]

2.3 BATTERY ELECTROCHEMISTRIES

The first battery was the Voltaic cell, invented in 1800, which consisted of two dissimilar metals, copper and zinc separated by an electrolyte solution. [23] This cell suffers from the problem of polarization due to evolution of hydrogen gas at the copper electrode. To overcome this problem, the Daniell cell was developed by John Fredric Daniell, a British chemist, in 1836. This has the same set of electrodes as the Voltaic cell. It has two electrolytes in two chambers, copper sulfate and zinc sulfate, connected by a salt bridge (Figure 2.6). An open circuit potential of 1.1 V is observed in a Daniell cell. The redox reactions at the anode and cathode are listed below:

At anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (2.1)

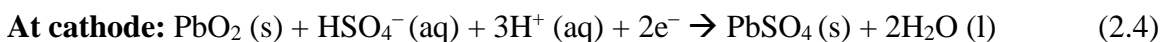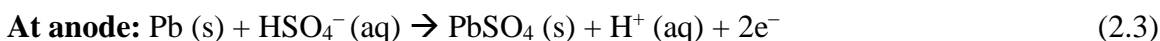**At cathode:** $Cu^{2+} + 2e^- \rightarrow Cu$ (2.2)

The salt bridge is an important component of the Daniell Cell. It is generally a gel made from agar that contains potassium chloride or sodium sulfate salts. In the absence of the salt bridge, excess positive charge will build up in the chamber on the left due to excess Zn^{2+} ions produced during oxidation of Zn atoms. Similarly there will be a build up of

excess negative charge in the chamber on the right due to the reduction of Cu^{2+} ions. The salt bridge helps in maintaining electroneutrality by balancing the excess ions with their counterions in the salt bridge.
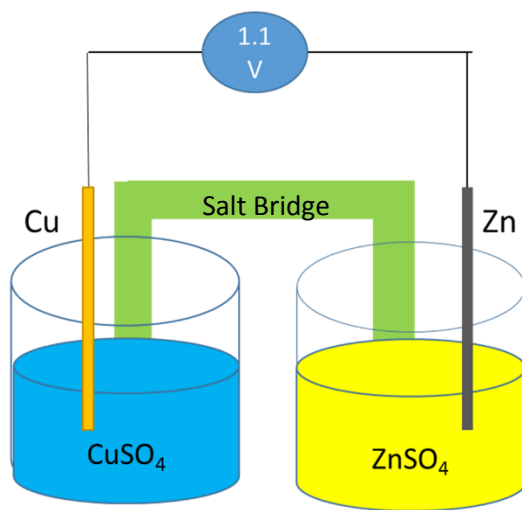
Figure 2.6 Schematic of a Daniell Cell. It consists of two chambers, one with copper sulfate ($CuSO_4$) as the electrolyte and with a copper (Cu) rod as the elecrode, and a second chamber with zinc sulfate ($ZnSO_4$) as the electrolyte and with a zinc (Zn) rod as the electrode. The two chambers are connected by a salt bridge,

Batteries like the Daniell cell are not rechargeable and hence can only be used one time. To overcome this drawback, rechargeable cells were developed, such as the lead-acid battery, which has the following half-cell reactions: [24]

At anode: Pb (s) + HSO_4^- (aq) $\rightarrow$ $PbSO_4$ (s) + H^+ (aq) + $2e^-$ (2.3)

At cathode: PbO_2 (s) + HSO_4^- (aq) + $3H^+$ (aq) + $2e^-$ $\rightarrow$ $PbSO_4$ (s) + $2H_2O$ (l)   (2.4)

The open circuit potential of this battery is 2.1 V. Lead-acid batteries are bulky and have highly corrosive sulfuric acid as the electrolyte. Nickel-cadmium batteries are another kind of rechargeable batteries that are an improvement over lead acid batteries with respect to

energy densities. It employs cadmium as the anode and nickel oxide hydroxide as the cathode. Potassium hydroxide is the electrolyte. [24] Typical half-cell reactions are:

At anode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$ (2.5)

At cathode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$ (2.6)
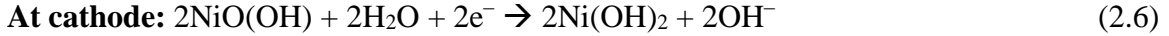
New battery electrochemistries have been developed more recently, such as the lithium-ion and sodium-ion batteries, which are based on ion insertion chemistries. Aqueous rechargeable lithium-ion batteries have also been developed. These employ $LiFePO_4$, $LiNiPO_4$, and $LiMnPO_4$ as cathodes and VO_2, MoO_3 covered with polypyrrole as anodes.[25] Redox flow batteries have been developed in which solid anode and cathodes have been replaced with liquid anolyte and catholyte. [26] A common aqueous redox flow battery is the all-vanadium redox flow battery, and in this case, the reactions at anode and cathode are: [27]

At anode: $VO^+ + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$ (2.7)

At cathode: $V^{+3} + e^- \rightarrow V^{2+}$ (2.8)

2.4 CHARACTERIZATION TECHNIQUES

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance is measured by applying an alternating (AC) potential $E = E_0 \exp(j\omega t)$ on an electrochemical cell. [28]The response is in the form of an alternating current, $I = I_0 \exp(j\omega t - \varphi)$. The impedance Z of the cell then can be expressed as:

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\varphi) = Z_0 (\cos\varphi + j\sin\varphi) \tag{2.9}$$

The above equation consists of real and imaginary parts. Nyquist plots are obtained by plotting the real part on the x-axis and the imaginary part on the y-axis. An equivalent circuit comprising combinations of resistors, capacitors and inductors can be related to the Nyquist curve. This can give us an idea about the various impedances associated with the electrochemical system.

Rheology

Rheology is the study of the flow and deformation of materials. Information about the elastic and viscous characteristics of a sample can be obtained by subjecting the material to an oscillatory strain and recording the oscillatory stress. [29] From this, we can back out the elastic modulus G' and the viscous modulus G'' of the material as functions of frequency. Gels will show an elastic response, i.e., the viscous component will be much smaller than the elastic one. The elastic modulus of a gel (i.e., the gel modulus) strongly depends on the extent of crosslinking of the gel. A more crosslinked gel will have a higher G', i.e., it will be more stiff.

CHAPTER 3:

A HYDROGEL BATTERY BASED ON THE DANIELL CELL

3.1 Introduction

In this chapter, we will discuss our attempt at constructing a hydrogel-based battery. As mentioned in the Introduction, there is a need for designing soft power sources that could be compatible with the next generation of soft electronic devices. Thus far, very few energy storage devices have been made from soft materials. Examples include bendable fuel cells[8] and stretchable super capacitors.[9] Recently, a stretchable dry-cell battery was reported,[12] and it used a xanthan-gum-based hydrogel as the electrolyte. Another example of a hydrogel-based device is a soft photovoltaic cell developed by Velev et al.[10]

In our work, we focus on the Daniell cell, which was invented by John Frederic Daniell in 1836. This is among the oldest batteries known and it was the first battery suitable for practical use. The design of the Daniell cell was discussed in Chapter 2. In the current work, we have transformed the components of the Daniell cell into a design involving hydrogels. In doing so, we have used a method for building hybrid gels that was previously developed in our laboratory. [30,31] This method is used to combine different gels into one whole while retaining good mechanical and interfacial properties.

3.2 EXPERIMENTAL

Materials. The monomers N-N dimethyl acrylamide (DMAA) and acrylamide (AAm) were obtained from TCI America while sodium acrylate was purchased from Sigma Aldrich. Accelerant N,N,N',N'-tetramethylethylene diamine (TEMED) was purchased from TCI America. The initiator potassium persulfate (KPS) and cross linkers polyethylene glycol diacrylate (PEGDA; molecular weight 575 Da) and N,N'-methylene-bis(acrylamide) (BIS) were obtained from Sigma Aldrich. Zinc sulfate and copper sulfate salts were also purchased from Sigma Aldrich. Zinc foil of thickness 0.25 mm was purchased from Sigma Aldrich while copper foil was obtained from SAFT Inc.

Hydrogel Preparation. For simplicity, we will term the hydrogel layer containing zinc salt as Gel 1, the middle layer as Gel 2 and the layer in which copper salt is imbibed by swelling as Gel 3. Hydrogels were prepared using DMAA as the monomer. For the preparation of Gel 3, DMAA was dissolved in 10 mL of deionized water at a concentration of 33 wt%. This solution was then degassed with nitrogen for 1 h. To this solution, 0.35 wt% KPS (initiator) was added and the sample was again degassed for 1 h with nitrogen. This was then poured in a petri dish and polymerization was initiated by adding 40 μL of TEMED (accelerator). Polymerization was conducted for 24 h. Note that DMAA can be crosslinked into a hydrogel without the use of a separate chemical crosslinker; this is called self-crosslinking (see next section). For Gel 2, the same procedure as for Gel 3 was used, but in the case of the monomer, DMAA (33 wt%) was mixed with sodium acrylate (4 wt%). Gel 1 was also prepared using the same procedure as for Gel 1, but additionally zinc sulfate salt (0.5 M) was added to the pre-gel solution of DMAA. Since TEMED can chelate with

Zn^{2+} ions, the pre-gel solution was heated until it started to get viscous. At this point, heating was stopped and the sample was left to polymerize for 24 h.

Table 3.1 Summary of formulations used to prepare hydrogels in our studies.

Investigated Parameters	Monomer type	Monomer concentration	Crosslinker type and concentration
Swelling ratios	AAm	3.8 wt%	2.4 wt% PEGDA
	AAm	3.8 wt%	4.8 wt% PEGDA
	AAm	3.8 wt%	9.9 wt% PEGDA
	DMAA	15 wt%	0.15 wt% PEGDA
	DMAA	15 wt%	0.5 wt% PEGDA
	DMAA	15 wt%	0.8 wt% PEGDA
	DMAA	15 wt%	1 wt% PEGDA
	DMAA	33 wt%	Self crosslinked
Ionic conductivity	AAm	3.8 wt%	0.32 wt% BIS
	AAm	7.4 wt%	0.64 wt% BIS
	AAm	13.8 wt%	1.28 wt% BIS
	DMAA	33 wt%	Self crosslinked
	DMAA	40 wt%	Self crosslinked
	DMAA	50 wt%	Self crosslinked

Besides self-cross linked DMAA hydrogels, we also investigated other hydrogels fabricated from different combinations of monomers and crosslinkers as potential

candidates for the battery (see Table 3.1). In all cases, KPS was used as the initiator, and its concentration was 0.2 wt% for the AAm-based gels and 0.35 wt% for the DMAA-based gels. Also, TEMED was used as the accelerant in all cases and its amount added was 20 µL of TEMED for AAm-based systems and 40 µL for DMAA-based ones. In all cases, polymerization was conducted for 24 h.

Hydrogel Swelling. For swelling studies, gels were cut into small rectangular pieces, 0.2 cm thick, 0.6 cm wide and 1 cm in length. The slabs were dried under vacuum for several days to remove water, and then weighed. The slabs were then immersed in 0.5 M copper sulfate solution and left to swell for 48 h. Swollen slabs were then wiped to remove excess water and reweighed. Swelling ratio Q was calculated by the following equation:

$$Q = \frac{\text{Mass of swollen gel}}{\text{Mass of dry network}} \tag{3.1}$$

Rheological Studies. Dynamic rheological studies on the gels were performed using an AR2000 stress-controlled rheometer (TA instruments). A parallel plate of 20 mm diameter was used and the gels were subjected to an oscillatory strain in the linear viscoelastic region. The moduli were recorded as a function of frequency.

Ionic Conductivity. To characterize the ionic conductivity of the gels containing salt, the gel was placed between two stainless steel (SS) electrodes to make a sandwich of SS/Gel/SS. AC impedance spectroscopy 10^6 Hz to 10^{-1} Hz using a Reference 3000 Potentiostat (Gamry Instruments). An AC signal with an amplitude of 10 mV was used.

The impedance at high frequency was used to calculate the resistance R of the gel. The resistance was converted to ionic conductivity ρ using the following relation:

$$\rho = \frac{l}{A \cdot R} \tag{3.2}$$

Here, A is the area of the electrodes and l is the distance between electrodes.

Battery Performance. Battery performance was studied using a Arbin BT2000 battery tester (Arbin Instruments). Batteries were discharged at a constant current of 1 mA. The lower limit for the discharge was kept at 0.01 V. Weight readings were taken before and after the testing and it was found that there was negligible decrease in the mass of the battery.

3.3 RESULTS AND DISCUSSION

Concept of Hybrid Hydrogels

Figure 3.1 illustrates the concept behind the formation of hybrid hydrogels, which was developed in our laboratory by Banik et al.[30] The hybrid is formed by bringing oligomer solution A and oligomer solution B in contact. Since the two solutions are viscous, there is no convective mixing at the interface. As polymerization occurs, the two hydrogels become covalently attached to each other at the interface while still retaining their individual identity.
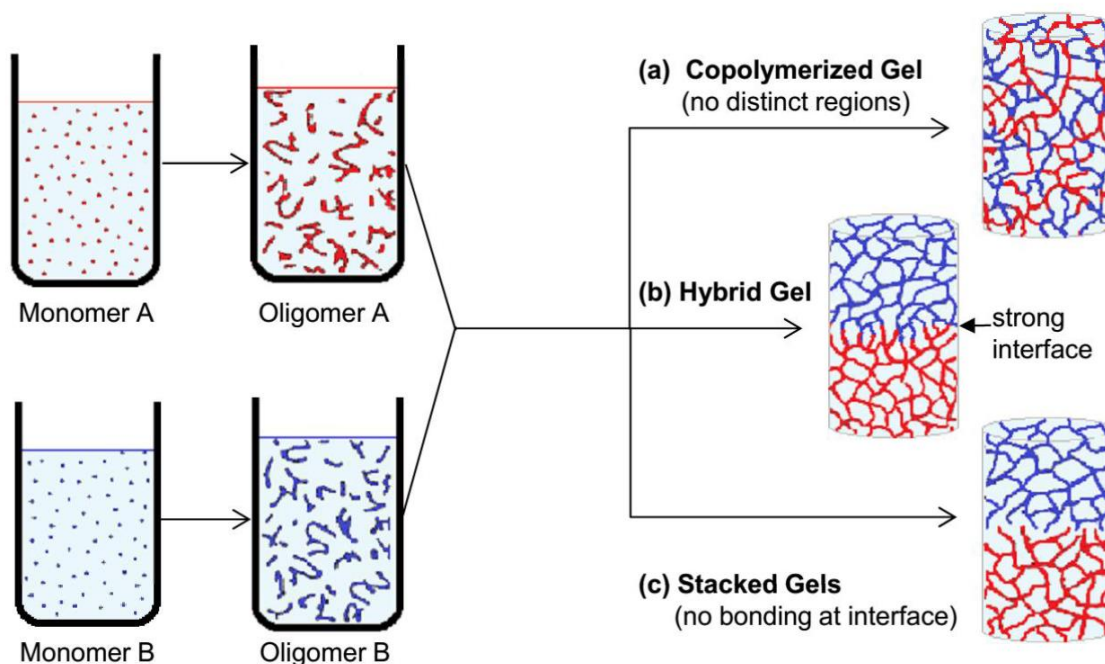
Figure 3.1 Strategy to prepare hybrid gels while each gel retains its own identity. If the two monomer solutions are co-polymerized, the result will be case A where the individual identity of each hydrogel is not retained. If the gels are stacked together after polymerization (case C), they will retain their individual identity but the mechanical strength at the interface will be poor. Case B is the hybrid gel case where the pregel solutions are brought into contact after partial polymerization. The resulting hybrid hydrogels shows good stability and mechanical integrity at the interface, while each portion of the gel retains its individual identity.
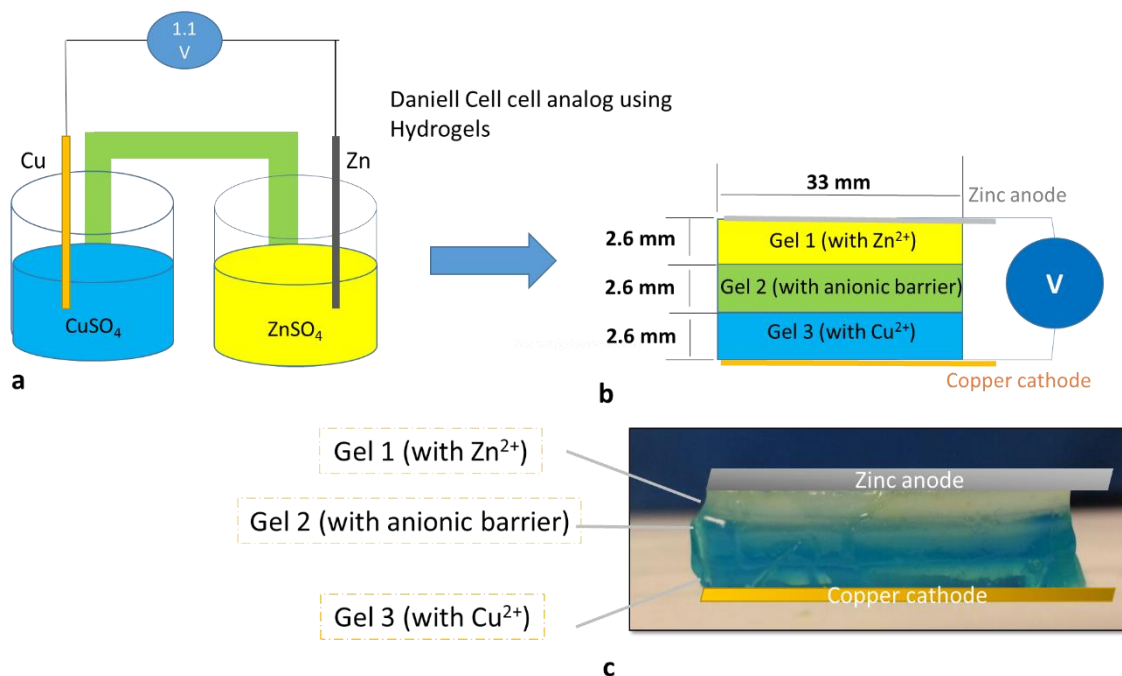
Figure 3.2 (a) Schematic of a Daniell cell. (b and c) The Daniell cell design replicated in a hybrid gel-based system. The top (b) is a schematic and the bottom (c) is a photograph of the overall battery.

Synthesis of a Hybrid-Gel-Based Analog of the Daniell Cell

In the current work we have used the hybrid gel technique to fabricate a robust battery based on the Daniell cell. The Daniell cell (Figure 3.2a) features one container with $ZnSO_4$ as the electrolyte, and this is in contact with solid Zn as the anode. The other container has $CuSO_4$ as a second electrolyte, and it is in contact with solid Cu as the cathode. The two containers are connected by a salt bridge. To replicate this design in a gel, we have synthesized a hybrid gel composed of three distinct layers, referred to as Gel 1, Gel 2, and Gel 3, in order from top to bottom (Figure 3.2b). Gel 1 is at the top and it is a gel of the nonionic monomer, dimethylacrylamide (DMAA). This gel contains dissolved $ZnSO_4$. Gel 3 is at the bottom and it is a DMAA gel containing $CuSO_4$. Finally, Gel 2 is in the middle and it is formed from two monomers, DMAA and the anionic monomer, sodium

acrylate (SA). To complete the design, a Zn foil is attached on top of Gel 1 and a Cu foil is attached at the bottom of Gel 3. In a typical design, the thickness of each of the three gels is 2.6 mm and the overall thickness of the battery (including electrodes) is about 8 mm. Typical length and width of the battery are 33 mm and 16 mm, respectively.
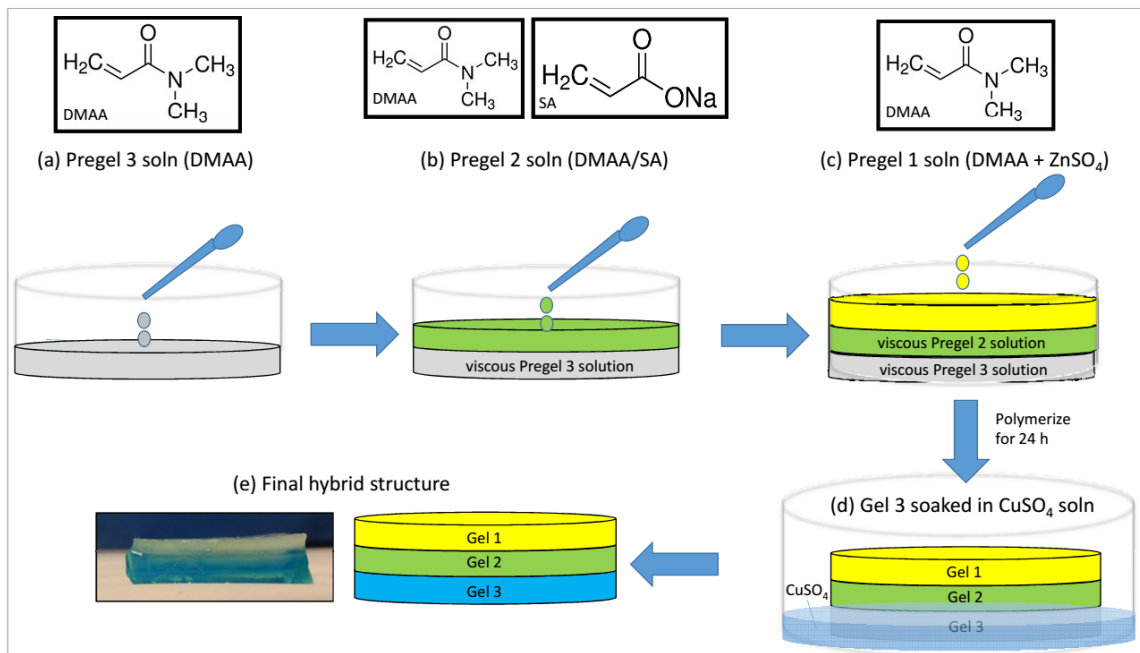

Figure 3.3 Schematic of the various steps in synthesizing a hybrid gel-based analog of the Daniell cell. (a) The pregel solution for Gel 3 is poured into a container to begin the process. (b) When this solution gets viscous due to partial polymerization, the pregel solution for Gel 2 is poured on top. (c) Once the latter gets viscous, the pregel solution for Gel 1 (this contains dissolved $ZnSO_4$) is poured on top. The three layers of the gels are left to polymerize over 24 h. (d) Next, the Gel 3 layer is soaked in 0.5 M $CuSO_4$ for 24 h. (e) This gives us the overall hybrid gel. Thereafter, the electrodes are affixed to the gel at the top and the bottom, yielding the overall battery.

We now describe in more detail the synthesis of the above hybrid (Figure 3.3). First, we synthesize Gel 3, and this involves combining 33 wt% DMAA, 0.35 wt% KPS, and 40 μL TEMED into a petri dish, as shown schematically in Figure 3.3a (the copper salt comes later; see below). As discussed in previous work from our group, DMAA undergoes "self-

crosslinking" in the presence of KPS. This means that DMAA, a bifunctional monomer, can form a network even in the absence of multifunctional crosslinkers. That is, growing linear chains of DMAA form covalent bonds between each other (branches) due to the action of persulfate radicals generated by KPS, eventually leading to a polymer network. As the DMAA polymerization proceeds towards Gel 3, the solution in the petri dish begins to get viscous. At this stage, the pregel solution for Gel 2 (33 wt% DMAA, 4 wt% SA, 0.35 wt% KPS, and 40 μL TEMED) is carefully poured on top of the polymerizing Gel 3 (Figure 3.3b). Because of the high viscosity of the partially polymerized Gel 3, there is negligble mixing of the two layers. Once the Gel 2 layer is also partially polymerized into a viscous state, the pregel solution for Gel 1 is carefully introduced on top (Figure 3.3c). This pregel contains 33 wt% DMAA, 0.35 wt% KPS, 40 μL TEMED, and 0.5 M of $ZnSO_4$. The entire system is then left to polymerize for 24 h, yielding a hybrid gel with clearly stratified layers.

The above procedure yields a Gel 1 that contains the zinc salt embedded in it. This is possible because Zn^{2+} cations do not substantially affect the free-radical polymerization of DMAA (The one issue is that the accelerant, TEMED weakly chelates with Zn^{2+} and so we had to first heat the pregel of Gel 1 to accelerate the reaction; only then did we add it to form the top layer in Figure 3.3c.) However, in contrast to Zn^{2+}, Cu^{2+} cations have a much stronger tendency to retard free-radical polymerization: in fact, we were unable to form a gel at all if the polymerizing solution contained dissolved $CuSO_4$. Therefore, we had to resort to an alternate strategy to introduce the salt into Gel 3 and this was done by soaking the Gel 3 layer alone in a petri dish containing 0.5 M $CuSO_4$ for a period of 24 h (Figure 3.3d). At this point, we have the key components: Zn^{2+} in Gel 1 and Cu^{2+} in Gel 3,

and thus the overall hybrid gel (Figure 3.3e). The final step is to affix the electrodes (Zn foil on top and Cu foil at the bottom) and that gives us the overall battery.
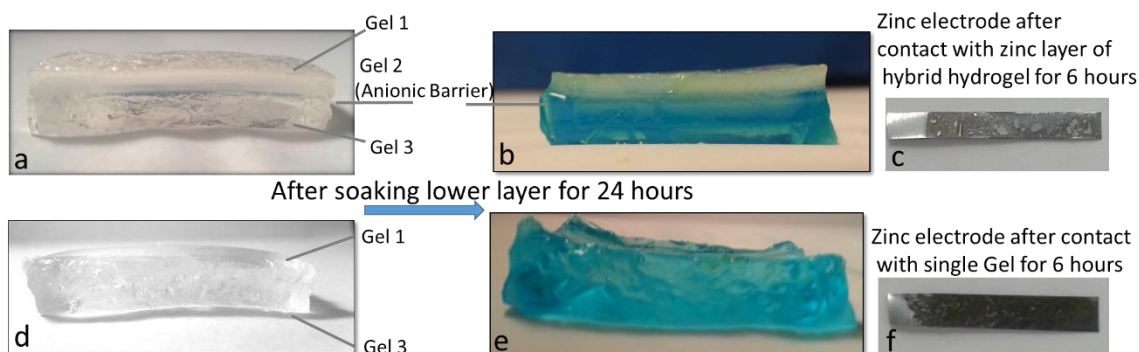

Figure 3.4 Hybrid gel with (top) and without (bottom) an anionic barrier gel (Gel 2) in the middle. Photographs are shown before and after soaking Gel 3 in $CuSO_4$ solution. If no Gel 2 is present, ions will distribute in the gel uniformly (e), but if Gel 2 is present,   the ions are confined to the bottom and middle gels (Gels 2 and 3). A Zn electrode was placed on top of Gel 1 for the two cases. Within 6 h, the electrode shows significant corrosion (due to deposition of Cu) in the case of no Gel 2 (photo f), whereas the presence of Gel 2 substantially reduces the corrosion (photo c).

We should discuss the role played by the middle layer, i.e., Gel 2, which we term the Anionic Barrier. It serves a role similar to the "salt bridge" in the conventional Daniell Cell. As noted earlier, if the salt bridge did not exist in a Daniell cell, no voltage would be generated. Conversely, in our case, if the Cu^{2+} ions could readily migrate from its chamber to the one containing the Zn electrode, the reaction between the ions and the metal electrode would lead to self-discharge of the battery (note that Zn^{2+} ions can also diffuse into the opposite chamber, but this is not as problematic). In the present context, ions can diffuse through the gels, and therefore between the distinct layers. To minimize diffusion of Cu^{2+} ions from Gel 3 to Gel 1 (and also of Zn^{2+} ions from Gel 1 to Gel 3), we have incorporated Gel 2 in the middle. This gel is negatively charged due to the inclusion of anionic SA as a

comonomer along with DMAA. The anionic carboxylate moieties in the DMAA/SA gel can bind the divalent Cu^{2+} and Zn^{2+} ions and thus minimize their migration. Figure 3.4 shows the importance of having such a Gel 2. The control scenario, with no Gel 2, is shown in (d). When this gel is placed in $CuSO_4$ solution, the Cu^{2+} ions diffuse through the entire gel, as indicated by the blue color throughout the gel (e). In turn, the Zn foil placed on top of Gel 1 shows a black mass with time (f), which is due to corrosion, i.e., Cu deposition on this electrode. In comparison, the three-layer hybrid with the DMAA/SA gel as the middle barrier is shown in Figure 3.4a. Here, the diffusion of Cu^{2+} occurs only up to Gel 2 (b), and this is attributed to the chelation of Cu^{2+} ions by the anionic Gel 2. Accordingly, the Zn foil in this case does not get corroded and reveals a more shiny surface (c).

To close this section, we wish to justify the choice of DMAA as the underlying monomer for the three gels in our Daniell-cell analog. As noted in the Experimental Section (see Table 3.1), we have examined a variety of other monomers for our gels. However, one clear advantage of using DMAA is that the gels have better mechanical properties. For example, if we used AAm as the monomer and BIS or PEGDA as the crosslinker, the resulting gels tend to be very brittle. This is typical of most gels made by free-radical polymerization (chemical crosslinking). Additionally, physically crosslinked gels such as gelatin, agar, and calcium-alginate also tend to be brittle and lack mechanical integrity. In comparison, DMAA gels are much more resilient and stretchable, as shown in earlier work from our laboratory (they can be stretched up to several times their original dimensions). This is shown by Figure 3.5a and b, where we stretch a three-layer hybrid (original in a, stretched state in b) and show that it holds up to the deformation. Another point is the

importance of our technique for making hybrid gels. What if we made three separate gels corresponding to layers 1, 2, and 3, and simply pressed these together to make our battery? Although this is possible (Figure 3.5c), the resulting three-layer gel will have weak interfaces between the layers. Thus, one can easily pull apart the individual layers (i.e., delaminate the gel) after preparation in this case, as shown by Figure 3.5d. In contrast, the DMAA gel does not delaminate if we try to pull apart the layers (Figure 3.5b) because the layers are chemically connected to one another, as shown by Figure 3.1.
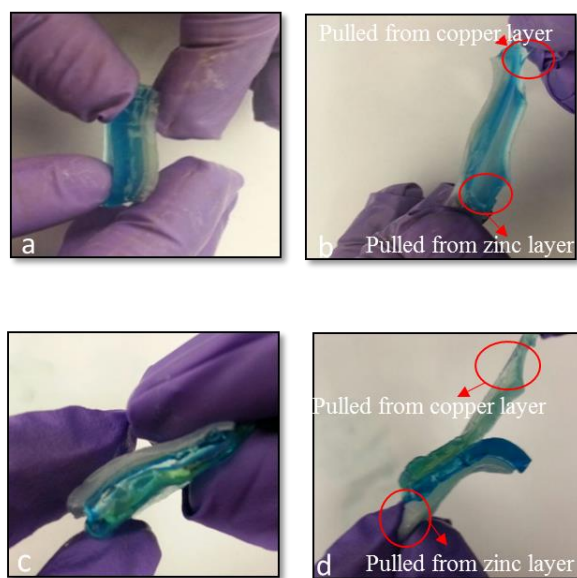

Figure 3.5 Comparison of mechanical integrity of hybrid three-layer gel (a) and a gel formed by simply stacking three gel layers (c). The hybrid, when stretched, retains its integrity and does not delaminate (b). In the case of the stacked gel, the interfaces between the layers are weak and thus the layers delaminate when stretched (d).

Performance of the Gel-Based Battery

We now proceed to discuss the electrochemical performance of our gel-based analog of the Daniell cell. First, we investigated the open-circuit potential of the battery using a multi meter. As discussed in Chapter 2, a Daniell cell involves two electrochemical half-cell reactions: oxidation to Zn^{2+} at the Zn electrode and reduction of Cu^{2+} at the Cu

electrode, which together add up to a theoretical open-circuit potential of 1.1 V. Our gel-based battery has an open-circuit potential V_{open} = 1.035 V which is close to the theoretical value (see setup in Figure 3.7a).
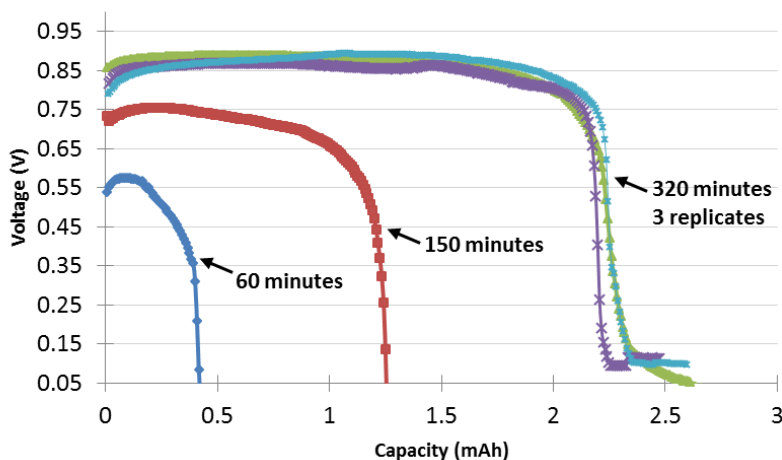
Figure 3.6. Discharge curves for gel batteries with Gel 3 swelled in 0.5 M CuSO$_4$ solution for different durations of time.

We then studied the discharge performance of our gel-based battery under different conditions. As noted, we introduce Cu^{2+} ions into Gel 3 by soaking in 0.5 M CuSO$_4$ solution. The soaking time dictates the amount of Cu^{2+} in the gel, which in turn is expected to limit the capacity of the battery (see below). To study this point, we investigated three different soaking times: 60 min, 150 min and 320 min. For these three cases, Figure 3.6 shows discharge curves of the gel-based battery under a constant current of 1 mA. We see that hybrids soaked for longer duration in CuSO$_4$ show a wider discharge plateau indicating a higher capacity. This is evidently due to the higher [Cu^{2+}] in a gel soaked for longer time. Note that, as the gel imbibes Cu^{2+} it also swells in the salt water, which is reflected as an increase in weight of the gel. Given time, the concentration of ions in the swollen gel will

equilibrate with those in the bath. However, for short durations before equilibrium has been established, the $[Cu^{2+}]$ will increase with soaking time. Note also that it is Cu^{2+} and not Zn^{2+} that limits the capacity. At the Zn electrode, Zn atoms from the metal foil are oxidized and enter the solution as Zn^{2+} ions. Since Zn atoms are available in plenty, it is not a limiting factor. Thus battery discharge time is mainly governed by the amount of copper salt in the gel. Another point to note is that the discharge curves in Figure 3.6 have different plateaus. The plateau voltage $V_{plateau}$ is about 0.9 V for the 320 min soaking time, which is slightly lower than the V_{open} of 1.035 V. For lower soaking times, $V_{plateau}$ drops further to ~ 0.7 V for 150 min and ~ 0.6 V for 60 min. This can be attributed to the lower ionic conductivities in the gels due to lower concentrations of ions. A lower ionic conductivity will increase the resistance of the battery, adding to the potential drop during discharge.
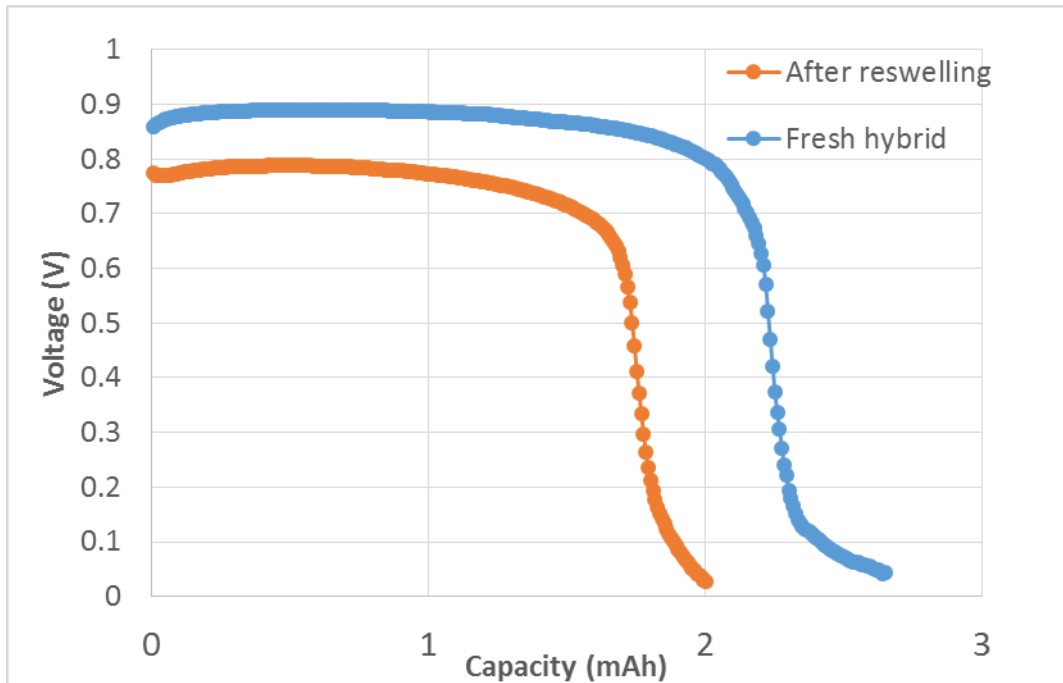
Dehydration and Rehydration of the Gel-Based Battery

Gel-based batteries need a liquid electrolyte to function. We wanted to investigate whether these batteries could be dehydrated to a dry (inactive) state and then subsequently rehydrated back to their active state. For this, we freeze-dried our gel-based battery using a low pressure (vacuum). In this process, the water is removed by evaporation, but the salts dissolved in the water still remain in the pertinent polymeric layer. Figure 3.7 shows photographs of the initial gel (a) and the same after dehydration (b). The weight of the gel decreases from an initial weight of 3.3 g to a dehydrated weight of 1.8 g (45% decrease). In the initial state, the open-circuit potential $V_{open} = 1.035$ V. In the dry state, the material is inactive as a battery ($V_{open} \approx 0$) due to the absence of a liquid to transport ions. In this state, the material can be carried safely without problems of self-discharge, electrolyte

leakage or the growth of mold or other microorganisms. We then rehydrated the gel by adding deionized (DI) water. The gel imbibed the added water and it swelled up as a result (Figure 3.7c). The weight of the gel was monitored and when it reached the original weight of 3.3 g, we stopped adding water. (The water addition and reswelling process was conducted over about 30 min.) Thereafter, we re-tested the gel in an open circuit and found V_{open} = 1.002 V, which is within 3% of the original value. Importantly, the gel is able to regain its function as a battery.
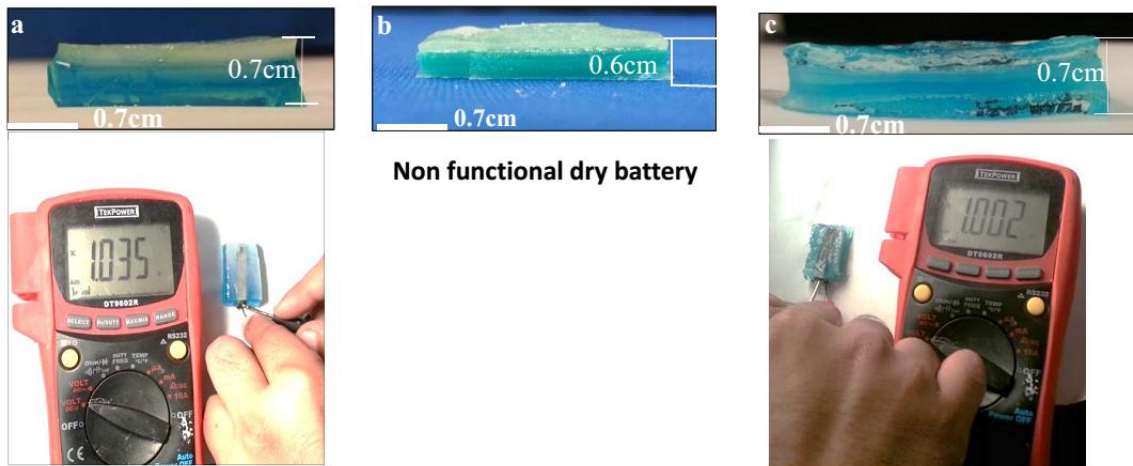

Figure 3.7 (a) A freshly made gel battery shows an open circuit potential of 1.035 V. (b) Hydrogel in (a) dried under vacuum. In this dried state, the material will be nonfunctional as a battery. (c) Dried hybrid rehydrated with water. An open circuit potential of 1.002 V is observed, indicating the restoration of a functional battery.

Figure 3.8 Discharge curves for a fresh gel battery and for a gel after rehydration from their dried state.

The discharge performance of the gel battery before after rehydration are shown in Figure 3. The fresh gel battery discharges completely in ~ 9000 s or 150 min. In comparison, the rehydrated battery discharges in ~ 7000 s or 120 min. Also, the plateau voltage $V_{plateau}$ during discharge is 0.08 V lower for the rehydrated battery compared to the fresh one. Thus, the battery regains about 80% of its original capacity as well as its voltage after rehydration. Note that we stopped the rehydration process after the weight had reverted to the original value; however, it is not clear if all the dried salt in the battery has re dissolved. If the salt is not fully re dissolved, the ionic conductivity of the electrolyte will be lower, and moreover, the total amount of ions, especially Cu^{2+} available will also be lower. This might explain the small drop in performance after rehydration. Nevertheless,

it is encouraging that the concept works, i.e., it is possible for the battery to be stored in dry form and then rehydrated as needed for use.
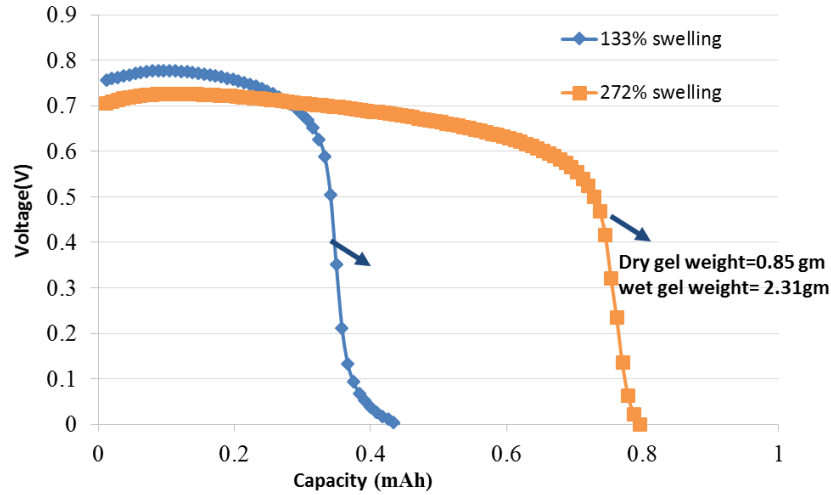

Figure 3.9. Discharge curves of gel batteries at different degrees of re swelling.

As mentioned above, during rehydration, not all the dried salt in the gels will get dissolved right away. The extent of dissolution depends both on the amount of water added, i.e., the degree of gel swelling. It also depends on the time over which rehydration is allowed to occur. Here, we have studied the effect of gel swelling on the performance of the rehydrated gel battery. Specifically, we began with two dehydrated gels that had comparable dry weights. We then added different amounts of water to them such that their swollen weights were quite different. Specifically, in one case, the gel increased in weight from 0.85 g to 2.31 g (swelling ratio $Q = 2.7$), whereas in the other case, the gel increased from 0.98 g to 1.30 g ($Q = 1.3$). The discharge curves for these two cases are compared in Figure 3.9. We note that the $Q = 2.7$ gel discharges over ~ 3500 s whereas the $Q = 1.3$ gel

discharges in ~ 1500 s, i.e., less than half the time. This difference is attributed to the fact that a Q of 1.3 may not be sufficient to dissolve all the salt, resulting in a lower discharge capacity. When Q is increased to 2.7, most of the salt is dissolved and therefore we observe a higher discharge capacity.

One issue here is whether excessive swelling (increase in volume) would reduce the concentration of ions and therefore the ionic conductivity. However, we do not believe the ionic conductivity will be significantly lowered by gel swelling. For reference, the ionic conductivity at 25°C of a DMAA gel ($Q = 3$) containing 0.5 M $ZnSO_4$ is about 0.06 S/cm. This is a relatively high value of the ionic conductivity, and even if it is lowered by a factor of 2 or 3, the conductivity will still be sufficiently high to ensure a substantial capacity for the battery. Thus, from our experiments we conclude that incomplete dissolution of salt is a bigger problem than too much swelling of the gel, i.e., it is better to add more water than less. One further point regarding the correlation between discharge capacity and the amount of Cu^{2+}. The rehydrated gel battery in Figure 3.8 discharged over ~ 7000 s compared to ~ 3500 s for the gel battery with $Q = 2.7$ in Figure 3.9. This difference can be explained by the dry weights of the two: the former was 1.8 g whereas the latter was 0.85 g. The higher weight of the former implies a higher amount of Cu^{2+} ions, and as a result it lasts almost twice as long as the latter.
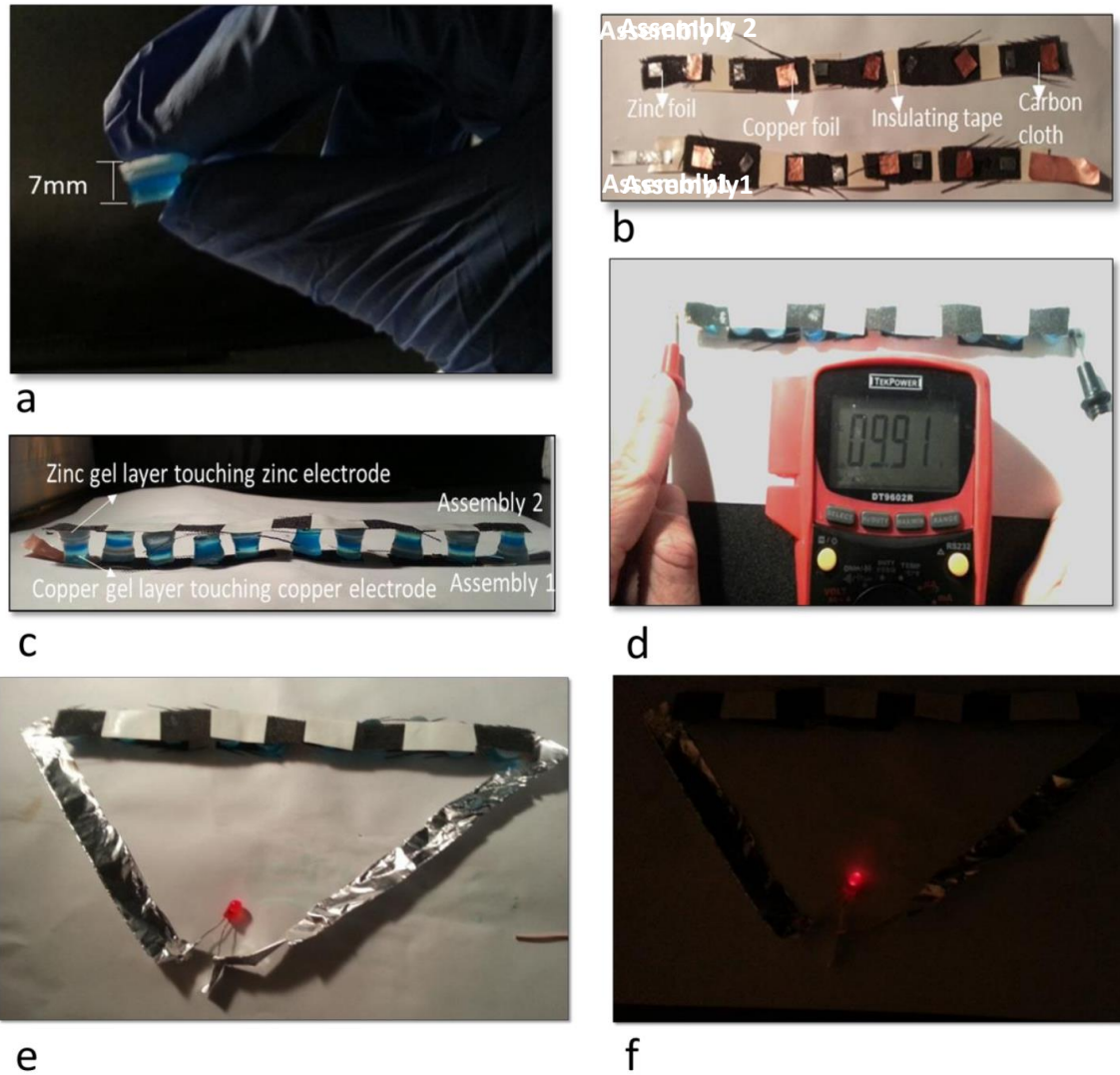
Figure 3.10.Small hydrogel batteries assembled in series. Hydrogel cylinders of thickness 0.7cm and diameter 1cm were fabricated (a) Electrode assemblies were fabricated as shown in b. Hydrogel hybrids were assembled in series (c). Voltage measurements indicate a value of 9.91V (d). (e) and (f) shows powering a 1.5V LED with the hydrogel batteries.
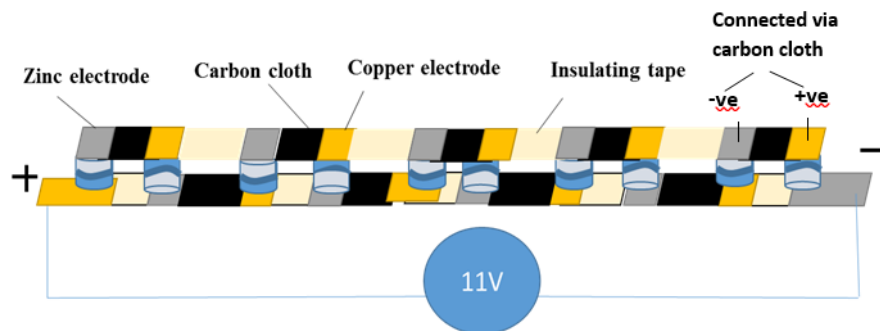
Figure 3.11 Schematic of Daniell Cells attached in series. Hydrogels are placed such that the gel containing zinc salt is in contact with the zinc electrode and gel containing copper salt is in contact with the copper electrode. Positive terminal of one battery is connected to the negative terminal of another battery via conductive carbon cloth.

The above gel batteries generate about 1 V. Generally, devices that require batteries need voltages much higher than 1 V for their operation. To access higher voltages from our gel batteries, we have assembled a series of such systems in series as shown in the Figure 3.11. The design is shown in Figure 3.10. We fabricated two assemblies of electrodes, which are termed Assembly 1 and Assembly 2 (Figure 3.10b). Each Assembly is made by gluing small pieces (~ 5 mm × 5 mm) of of Zn and Cu foil in an alternating fashion on conductive carbon cloth, with insulating tape used to connect these electrodes. In this way, we connect the positive electrode of one battery to the negative electrode of the next. Next, 10 hybrid gels (cylinders of height 7 mm and diameter 10 mm) are sandwiched between Assembly 1 and Assembly 2 in such a way that Gel 3 (which has Cu^{2+}) is in contact with the Cu electrode while Gel 1 (which has Zn^{2+}) is in contact with the Zn electrode. The result is a series arrangement of 10 gel batteries. Since each battery generates ~ 1 V under open circuit, their series assembly should generate ~ 10 V. Figure 3.10d shows a V_{open} of 9.91 V, which is close to the above value. We further tested our assembly for its ability to

power small devices such as an LED rated at 1.5 V. Figure 3.10e and f shows this LED lighting up when powered by the gel batteries in series.

3.4 CONCLUSIONS

In this chapter, we have described the construction of a hydrogel battery that incorporates the electrochemistry of a Daniell Cell. Our device is a hybrid composed of three distinct gel layers connected intimately at the interfaces by covalent bonds. The top layer (Gel 1) is prepared by polymerizing the nonionic monomer DMAA in the presence of $ZnSO_4$. The bottom layer (Gel 3) is a DMAA gel prepared without dissolved salt, with the salt ($CuSO_4$) is introduced later by immersing this layer in a salt solution. Between the two, the middle layer (Gel 3) is an anionic gel that serves as a barrier to the diffusion of Cu^{2+} ions from Gel 3 to Gel 1. We affix Zn and Cu foils as electrodes to the above hybrid gel and thereby we obtain a gel-based battery that generates about 1 V in open circuit (approximately equal to the voltage generated by a typical Daniell cell). The gel battery discharges over several hours, and the limiting factor here is the total amount of Cu^{2+} in the gel. We have shown that the gel battery can be dehydrated and stored in an inactive, dry form. Upon rehydration with water, the battery regains its activity, and the performance before and after rehydration are comparable.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

In this thesis we presented a facile and elegant way of transforming a Daniell cell in the hydrogel system. We exploited properties of hydrogels like their solid like strength and liquid like ionic conductivities to create a energy storage device. We engineered this portable device by using a 'hybrid hydrogel' concept where gels retain their individual identity while being covalently attached at the interface. We also employed a charged hydrogel as a barrier to prevent crossover of copper ions to the zinc electrodes.

We also investigated the battery performance with different copper salt contents and showed its effect on the battery performance. We have further demonstrated the ability of these hybrids to turn functional in wet state from non-functional dried state. We studied the discharge performance of the battery with different moisture contents in the hydrogel. Towards the end we extended the concept from one Daniell cell to multiple Daniell cells by attaching them in series. Thus it is easy to generate a higher voltage by simply connecting small Daniell cell in series with help of current collectors.

4.2 FUTURE DIRECTIONS

In the current work we have showed hydrogels as attractive candidates to fabricate an energy storage device. We used the Daniell Cell Electrochemistry to show the concept. This electrochemistry has limitation of low theoretical open circuit voltage. In future other electro chemistries can be exploited which has higher open circuit voltage.

In the future it will be interesting to examine the battery performance with the middle layer of the battery (gel 2) doped with Lithium Sulfate salt or replacing the middle layer with Nafion.

During the process of formation of hydrogel hybrids, there is a possibility of local intermixing between the two oligomer solutions is contact. Thus an interface comprising of polymer chains from both solutions will be formed. It will be worthwhile to examine the thickness of this interface using confocal Raman microscopy.

In future it will also be interesting to investigate hydrogels which swells faster. This will help in reducing the time required by dry hybrids to become functional as a battery. In the current work we have shown performance of the battery at discharge current of 1mA. In future it will be worthwhile to explore other monomer chemistries which can sustain higher discharge currents. It will also be interesting to explore other charged hydrogels for the middle barrier to prevent copper crossover to the zinc electrode.

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