Salinity Gradient Energy from Expansion and Contraction of Poly(allylamine hydrochloride) Hydrogels

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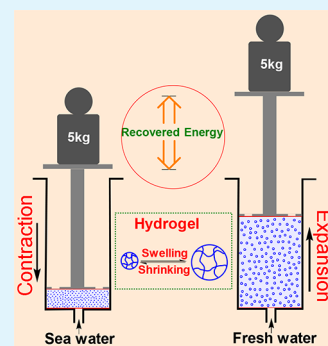
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ABSTRACT: Salinity gradients exhibit a great potential for production of renewable energy. Several techniques such as pressure-retarded osmosis and reverse electrodialysis have been employed to extract this energy. Unfortunately, these techniques are restricted by the high costs of membranes and problems with membrane fouling. However, the expansion and contraction of hydrogels can be a new and cheaper way to harvest energy from salinity gradients since the hydrogels swell in freshwater and shrink in saltwater. We have examined the effect of cross-linker concentration and different external loads on the energy recovered for this type of energy-producing systems. Poly(allylamine hydrochloride) hydrogels were cross-linked with glutaraldehyde to produce hydrogels with excellent expansion and contraction properties. Increasing the cross-linker concentration markedly improved the energy that could be recovered from the hydrogels, especially at high external loads. A swollen hydrogel of 60 g could recover more than 1800 mJ when utilizing a high cross-linker concentration, and the maximum amount of energy produced per gram of polymer was 3.4 J/ g. Although more energy is recovered at high cross-linking densities, the maximum amount of energy produced per gram of polymer is highest at an intermediate cross-linking concentration. Energy recovery was reduced when the salt concentration was increased for the low-concentration saline solution. The results illustrate that hydrogels are promising for salinity gradient energy recovery, and that optimizing the systems significantly increases the amount of energy that can be recovered.

KEYWORDS: *hydrogel, salinity gradient, energy, swelling, poly(allylamine hydrochloride)*

INTRODUCTION

Energy from fossil fuels are causing a number of environmental issues, such as emissions of greenhouse gases, depletion of finite sources, and dependence on a few oil-exporting regions in the world. The demand for green, clean, and sustainable energy are therefore high. Current renewable energy sources such as solar, wind, ocean, biomass, and hydro energy are considered as successful substitutes.[1] However, to facilitate a complete replacement of fossil fuel, efforts in optimizing new sources of renewable energy are needed. Salinity power is completely renewable and subject to less periodic fluctuations than wind and solar energy.[2] Since storage of huge amounts of electric energy is challenging, renewable energy sources that can produce electricity independently of the weather is a valuable part of an environmentally friendly energy supply. Large amounts of potential energy are released when water with different levels of salinity is mixed. This has recently emerged as a viable source of renewable power.[3−5] The potential energy from the salinity difference when river water is mixed with seawater is estimated to be >1 TW, enough to supply a significant percentage of the global energy demand.[6−8]

Known techniques for energy conversion from salinity gradients are utilizing membranes. These are pressure-retard

osmosis (PRO),[9−12] and reverse electrodialysis (RED).[13−16] In PRO, osmotic pressure drives water from a low-salinity solution to a high-salinity solution across a semipermeable membrane. This generates a pressure, which is used to generate electricity utilizing a hydroturbine. In RED, the membranes are permeable to either positive or negative ions. The ion diffusion through the membranes results in potential difference (membrane potential). The main drawback of these membrane-based techniques is the high price of membranes. Additionally, the large surface areas of the membranes are compromised by fouling over time, and they are difficult to clean effectively.[1,17]

A new approach based on low-priced hydrogel materials was initially suggested by Zhu et al.[17] The swelling and shrinking of poly(acrylic acid)-based hydrogels due to exposure to alternating high- and low-salinity solutions were employed in a piston-type process utilizing a modified syringe. When the high-salinity solution flows through the hydrogel, the charged acid groups on the polymer are screened out. This diminishes

the electrostatic repulsion between the polymer chains, which causes the hydrogel to shrink. In addition, the salt causes a salting-out effect of the polymer network, further reducing the size of the hydrogel. In freshwater, the hydrogels absorb a large amount of water because of electrostatic repulsion between the charged groups, resulting in a swollen hydrogel. Energy is produced by the expansion of the hydrogels.

The composition of the hydrogels plays a crucial role in this method. Hydrogels are three-dimensional, cross-linked polymer networks that swell in water. A swollen hydrogel consists mostly of water. In fact, swollen hydrogels can constitute more than 99 wt % of the hydrogel mass.[18] Hydrogels can swell or shrink in response to different stimuli such as temperature, light, pH, or ionic strength.[19−22] To facilitate a high-energy recovery, the hydrogels should exhibit high swelling ratios. Polyelectrolytes are polymers carrying multiple positive or negative charges along their chains, and are therefore promising candidates for highly swollen hydrogel materials. Polyelectrolyte-based hydrogels are called superabsorbent hydrogels, and may absorb up to 400 times their weight in water.[23] The total swelling capacity of superabsorbent hydrogels is affected by the type and degree of cross-linkers.[24−26]

Poly(allylamine hydrochloride), PAH, is a water-soluble cationic polyelectrolyte with pendant primary amino groups (NH_2)[27] that can be chemically cross-linked to produce highly swollen hydrogels. In this work, poly(allylmine hydrochloride) hydrogels were synthesized by cross-linking with glutaraldehyde,[28] at different cross-linker degrees. The swelling/shrinking behavior and recovered energy were examined after alternating exposure to saltwater versus freshwater.
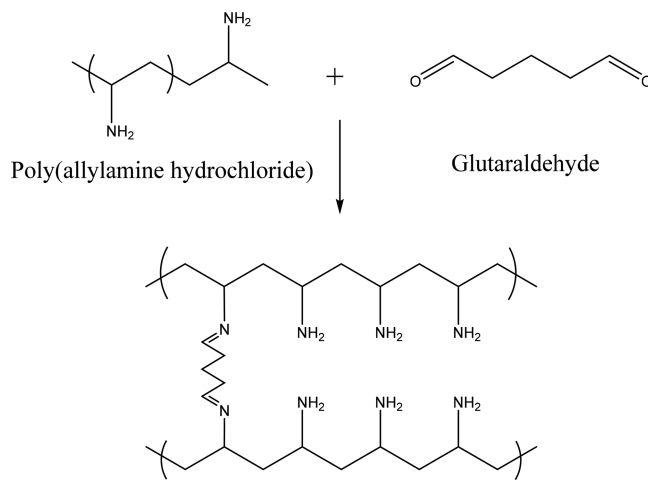
■ MATERIALS AND METHOD

Materials. Poly(allylamine hydrochloride) (PAH) was purchased from VWR; glutaraldehyde and sodium chloride were obtained from Sigma-Aldrich. The reagents were of analytical grade, and used without further purification.

Peristatic pumps (Reglo ICC, Ismatec, Cole-Parmer GmbH) were used to flush the freshwater and saltwater through the hydrogels at pump rates of 3 mL/min for saltwater and 5 mL/min for deionized water. The excess water that was flushed through the hydrogels was pumped out with a pump setting of 25 mL/min to ensure removal of all the excess water during the shrinking process.

Synthesis of Poly(allylamine hydrochloride)-Based Hydrogels. A series of hydrogels were synthesized from PAH utilizing different concentrations of the cross-linker (glutaraldehyde). The cross-linking reaction is illustrated in Scheme 1. The polymer stock solution was prepared by dissolving 0.5 g of PAH in 2 mL of deionized water. The resulting polymer solution has a pH of 2.0. Although the reaction between glutaraldehyde and amino compounds consume more amino groups at higher pH values,[29] the cross-linker reaction still proceeds satisfactorily in this pH range. Various amounts of glutaraldehyde (1.5, 2.0, 2.5, 3.0, and 5.0 mol %) were added to the polymer solutions. The mol % is calculated as $100 \cdot mol_{GA}/mol_{PAH}$, where mol_{GA} is the number of moles of glutaraldehyde in the samples and mol_{PAH} is the number of moles of repeating units of the PAH in the samples. The mixtures were homogenized by a magnetic stirrer. The hydrogels formed within a few minutes, and were stabilized for 15 min before they were immersed in 800 mL of deionized water to remove excess cross-linker. The water was changed every day for 1 week to ensure complete removal of unreacted glutaraldehyde.

Salinity Gradient Setup. Salinity gradient energy recovery was tested utilizing a modified plastic syringe and plunger. The syringe had a diameter of 35 cm and a volume of 100 mL. The syringe was placed vertically, allowing low and high salt concentration solutions to

Scheme 1. Synthesis of PAH Hydrogels

be pumped from the bottom to the top. Holes were drilled at the bottom of the plunger to allow water to flow through. The holes were covered by two small cloths to prevent the hydrogel from being pressed through the holes when heavy weights were applied. The aqueous solutions were pumped from the bottom of the syringe through the hydrogel. High-concentration (HC) and low-concentration (LC) NaCl aqueous solutions were alternately pumped through the hydrogel. The high concentration was kept constant at 35 g/L, while the low concentration was varied (0, 0.1, 0.3, and 0.5 g/L).

Operation. The syringe was filled with 60 g of gel fully swollen in deionized water. Weight loads were placed on top of the plunger. The applied weights were calculated as the combined weight of the plunger (15 g) and the external load (500−1300 g), and varied between 515 and 1315 g. The flow-out solution was pumped out from the top through the holes. The swollen gel was initially fully swollen in deionized water for 1 week and then placed in the syringe. The external load was placed on the top of the plunger (Figure 1), and the high-concentration solution was pumped through at a rate of 3 mL/min. After the gel shrunk to the minimum swelling volume, the system was switched to pumping the low concentration through the syringe at a rate of 5 mL/min. The hydrogel expanded and lifted the load system to maximum level. Each cycle, including shrinking and swelling, lasted for 1 h. This shrinking−swelling cycle was repeated four times, and the average of the last three cycles was used. It was observed that if the hydrogels were allowed to shrink to a very compact structure, they were not able to reswell to their full potential afterward. Therefore, 10 mL of shrunk hydrogel volume was chosen as a safe value to prevent the extremely compact structure. The experiments were conducted at ambient temperature (25 °C).

Scanning Electron Microscopy. The morphology of freeze-dried hydrogels was observed using scanning electron microscopy (Zeiss SUPRA 55-VP, Germany). Freeze-dried samples of swollen and shrunk hydrogels with a cross-linker concentration of 3% and 5% were cut to expose their inner structure. Porous hydrogels were coated with gold nanoparticles for 1 min under vacuum.

Oscillatory Shear Rheology. The rheological properties of the hydrogels were investigated utilizing an Anton Paar MCR 302 rheometer with a 50 mm plate−plate system. Swollen hydrogel circular sheets for the rheological measurements were prepared by mixing 3 mL polymer solutions (25 wt %/v) with a cross-linker concentration of 2%, 3%, and 5% under magnetic stirring. The mixture was rapidly added into a 40 mm diameter circular mold on a plastic film. The hydrogels were left to stabilize for 20 min, after which the hydrogel sheets were transferred to a water bath for swelling in deionized water for 40 min. The resulting swollen hydrogel sheets had a diameter of 60−80 mm and thickness of 4−6 mm depending on the cross-linker concentration, and were carefully transferred to the rheometer.
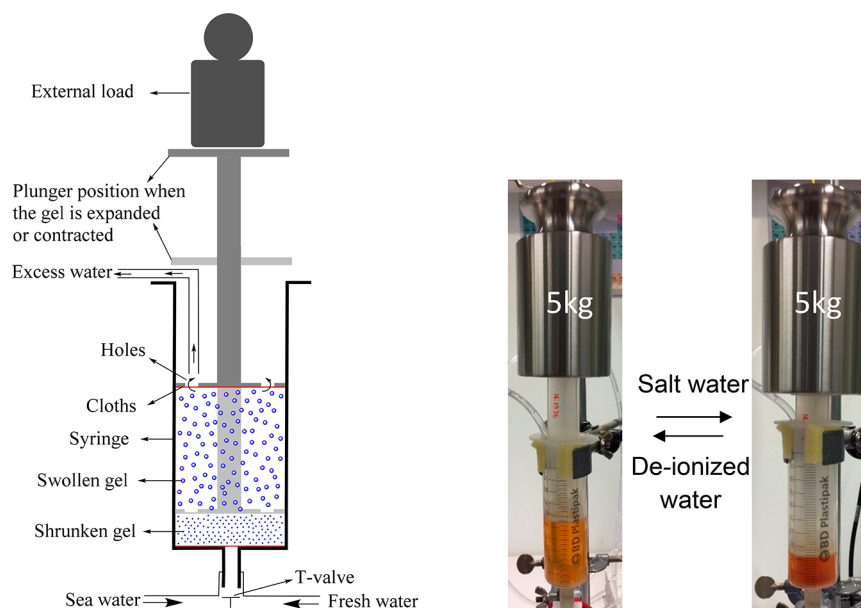
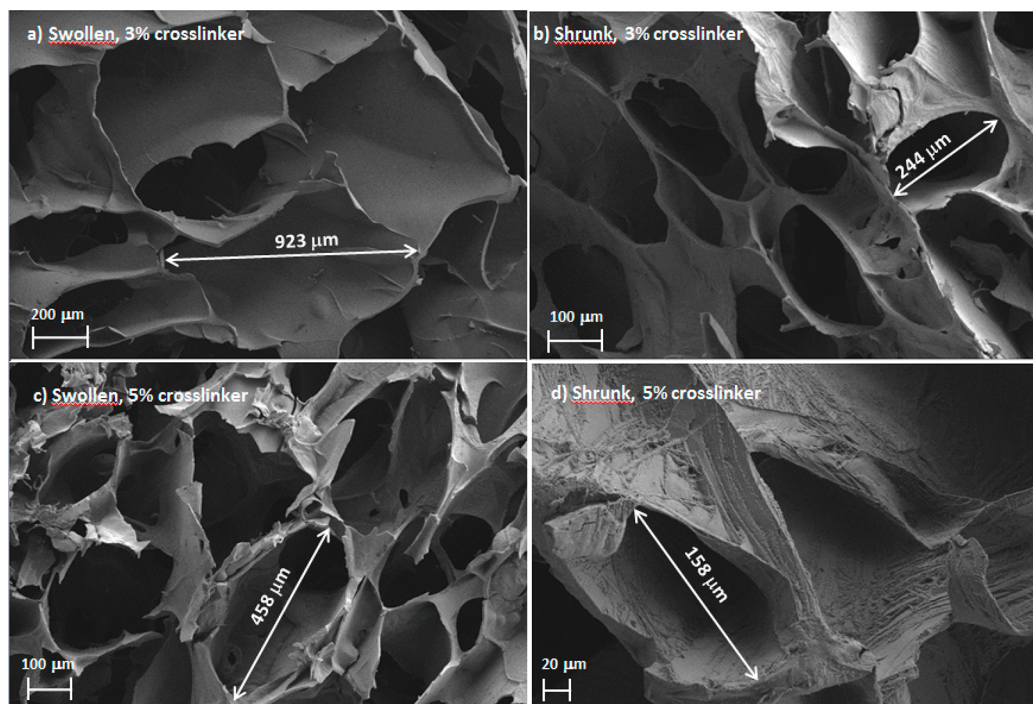**Figure 1.** Schematic diagram and pictures of the experimental setup.

Figure 2. SEM pictures of PAH hydrogels: (a) swollen 3% cross-linker, (b) shrunk 3% cross-linker, (c) swollen 5% cross-linker, and (d) shrunk 5% cross-linker.

Oscillatory shear measurements were conducted at angular frequencies of 100 to 0.1 rad/s, with an amplitude of 0.1% (which was found to be within the linear viscoelastic region of these samples).

Swelling Ratio. The swelling ratio is expressed as the ratio between the hydrogel mass before and after drying.[30] After the hydrogels were allowed to fully swell in deionized water at 25 °C for 1 week, the mass (m_s) of the swollen hydrogel was weighed (approximately 60 g). The hydrogels were completely dried by freeze-drying, and the mass (m_d) of the dried samples was measured. The swelling ratio (Q) was determined as

$$Q = m_s/m_d \tag{1}$$

At least three repetitions were carried out, utilizing at least two separate batches of hydrogels.

Recovered Energy. The recovered energy (E) was calculated from the work conducted by lifting the external load W_1 and the work related to the upward movement of the gravity center of the hydrogel W_2:[17,31]

$$E = W_1 + W_2 = m_1 g_0 h_1 + m_2 g_0 h_2 \tag{2}$$

where g_0 (9.81 m/s²) is the gravitational constant, h_1 is the displacement of the plunger calculated based on the expanding volume and the diameter of the syringe (D), h_2 ($=h_1/2$) is the displacement of the center of gravity of the hydrogel, m_1 is the external load, and m_2 is the average weight of the swollen and

deswollen hydrogels calculated according to volumes, assuming a hydrogel density (d) in water of 1000 kg/m^3.

Energy Efficiency. The energy efficiency (η_E) was calculated as the ratio of the recovered energy relative to the energy consumed by the system

$$\eta_E = \frac{E}{X^{in} - X^{out}} \times 100 \tag{3}$$

where X^{in} is the total energy provided to the system and X^{out} is the total energy leaving the system. The energies were calculated from the change in the free energy due to a complete mixing of the HC and LC solutions.[17,32,33]

$$X^{in} = RT \sum_i \left(V_{HC} c_{i,HC}^{in} \ln \frac{a_{i,HC}^{in}}{\alpha_{i,M}} + V_{LC} c_{i,LC}^{in} \ln \frac{a_{i,LC}^{in}}{\alpha_{i,M}} \right) \tag{4}$$

where R (8.314 J mol^{-1} K^{-1}) is the gas constant, T (298 K) the absolute temperature, V the volume of the solution, c_i the molar concentration of the ionic species i in the solution, and α the activity of the ionic species i in the solution. The subscript M indicates the mixed solution, while subscripts LC and HC indicate the low and high concentrations of NaCl, respectively. The aqueous solutions are mixed with each other after leaving the system, and accordingly $X^{out} = 0$.

■ RESULTS AND DISCUSSION

Morphology of the Hydrogels. Typical SEM micrographs of cross-section surfaces of freeze-dried swollen and shrunk hydrogels containing 3% and 5% cross-linker are shown in Figure 2. As expected, the pore size of the hydrogels is larger for the swollen hydrogels than for the shrunk counterparts. When the cross-linker concentration is raised, the distance between the cross-linker points becomes shorter, leading to a tighter network with a smaller pore size.[20]

Swelling Ratio. The swelling ratio is one of the important factors to evaluate the ability of the hydrogels to recover energy. The equilibrium swelling ratios of the PAH hydrogels prepared at different cross-linking concentrations are shown in Figure 3. A profound decrease of the swelling ratios was
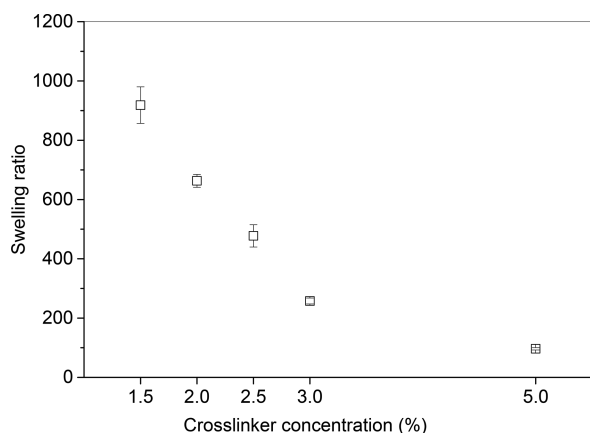

Figure 3. Swelling ratio as a function of cross-linker concentration.

observed when the cross-linking concentration was increased from 1.5 to 3.0 mol %. A higher cross-linker concentration increases the number of cross-linking points, and accordingly the distance between the cross-linking points becomes shorter (as is evident from the smaller pore sizes in Figure 2). A shorter distance between the cross-linker points restricts the swelling of the hydrogels, thereby reducing the swelling ratios.

Rheology. In addition to the degree of swelling, the mechanical properties of the hydrogels play an important role in recovering energy from salinity gradients. The balance between swelling and mechanical properties should be optimized to facilitate high energy recovery and high energy efficiency. In addition, the hydrogel should maintain its properties through repeated swelling/shrinking cycles. The cross-linker concentration significantly affects the swelling ratio as well as the mechanical strength of the porous structure. Hydrogels exhibit viscoelastic and poroelastic properties.[34] Raising the cross-linker density is expected to significantly increase the mechanical strength of the network.[35] This is confirmed by the rheological measurements of the swollen hydrogels (Figure 4), where both the storage modulus (G')
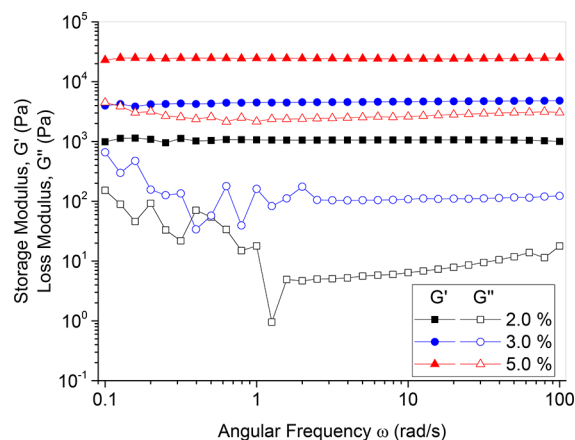

Figure 4. Storage modulus (G') and loss modulus (G'') of swollen hydrogels at three different cross-linker concentrations.

and the loss modulus (G'') becomes higher when the cross-linker concentration is raised. Figure 4 illustrates that the elastic properties of the hydrogels (G') increases when the amount of cross-linker is raised. This suggests that raising the cross-linker concentration might enable the hydrogels to lift heavier loads. The tighter network with smaller pore sizes at high cross-linker concentrations (Figure 2) is probably the reason for the improved mechanical properties.

Swelling Volume under External Loads. The swelling of the hydrogels was examined at different external loads and cross-linker concentrations. Figure 5a−e shows the swelling volume as a function of time. When the HC solution (35 g/L NaCl) was pumped through the hydrogels, the gels started to shrink because of screening of the electrostatic repulsions between the charged amine groups, combined with a salting-out effect of the polymer network. This causes the plunger to move downward. As expected, the hydrogels shrink faster at higher external loads because of the greater external pressure.

The swelling was initiated by switching the solution from HC to LC (deionized water). The plunger is raised as the hydrogel swells because of the repulsive electrostatic forces between the positively charged amine groups.[36] The maximum amount of swelling depends on the repulsive electrostatic forces between the polymer chains, the amounts of cross-links, and the weight of the external load. The maximum amount of swelling is displayed in Figure 5f.

At a low cross-linker concentration of 1.5%, the hydrogels exhibit a large swelling degree because of the high distance between the cross-linking points. However, these hydrogels
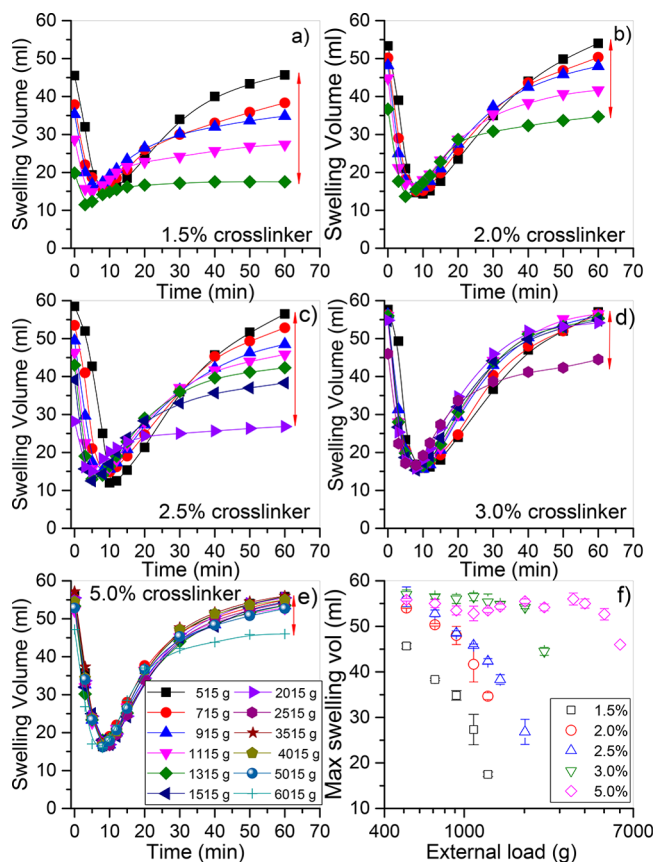
Figure 5. Average swelling volume of the three last shrinking/swelling cycles of the hydrogels as a function of time with cross-linker concentrations of (a) 1.5%, (b) 2.0%, (c) 2.5%, (d) 3.0%, and (e) 5.0%. (f) Maximum swelling volume of the hydrogels.

structure, which is incapable of lifting heavy weights. The swelling of this sample is therefore highly dependent on the external load (Figure 5a,f), and it exhibits nearly no swelling with high external loads.

Figure 5f shows that the maximum swelling volumes are strongly dependent on both the cross-linker concentration and the external load. At low cross-linker concentrations, the swelling of the weak, loosely cross-linked networks decreases significantly when the weight of the external load is raised (Figure 5a,f). With an increase of the cross-linker density, the mechanical properties of the hydrogel are improved (Figure 4). Accordingly, the hydrogels are able to carry higher external loads. For these systems, the swelling is much less dependent on the weight of the external load, and for the highest cross-linker concentration the maximum swelling is nearly independent of the external load until it starts to decrease at very high external loads (Figure 5e,f). Since each hydrogel starts at a swollen state of 60 mL before any external load is applied, the maximum swelling volume decreases when the amount of cross-linker is reduced because of the weaker nature of networks with fewer cross-linking points (Figure 5f). A high cross-linker concentration increases the elastic properties of the hydrogels (Figure 4), resulting in high swelling volumes even with heavy external loads. Interestingly, at low external loads the hydrogels with 5% cross-linker seem to swell less than the gels with 3% cross-linker (Figure 5f). This suggests that a large cross-linker density will restrict the swelling of the hydrogel.

Recovered Energy and Energy Efficiency. Figure 6 shows the effect of recovered energy and energy efficiency as a function of external loads at various cross-linker concentrations. In Figure 6a, the recovered energy reaches a maximum when the external load is gradually increased. This maximum is shifted toward higher external loads when the cross-linker concentration is increased. The recovered energy is dependent on how much the gels swell, and how much weight they lift when they swell (eq 2). At low cross-linker concentrations, the gel networks are weak, and they are not able to lift heavy loads. Accordingly, little energy can be
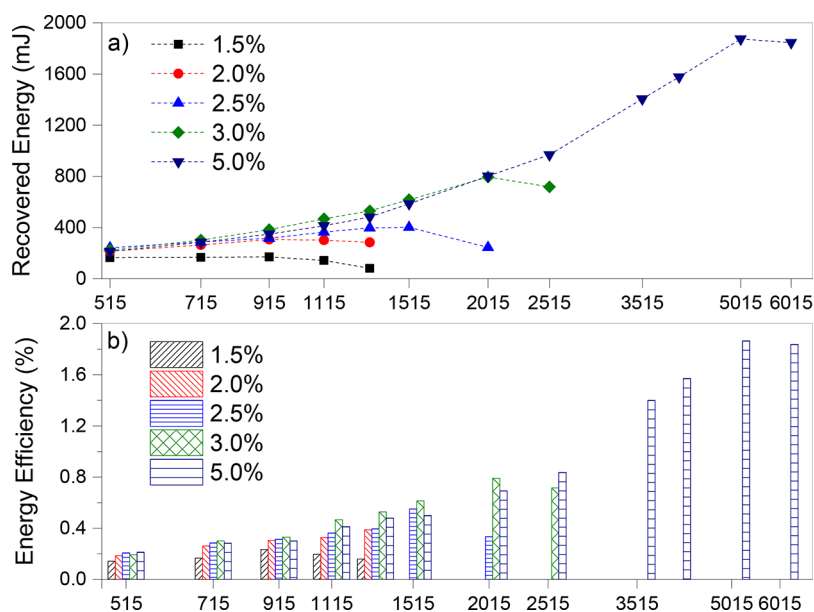
have weak mechanical strength. Accordingly, when the external load is increased, the gel structure is compressed, resulting in a reduced ability to swell. As illustrated in Figure 5a, the sample with 1.5% cross-linker has a weak and soft mechanical

Figure 6. Effect of cross-linker concentration of (a) recovered energy and (b) energy efficiency for hydrogels at different external loads.

recovered. As the cross-linker concentration is raised, the hydrogels are able to lift heavier loads, and the recovered energy becomes higher. However, at a certain point the loads become too heavy for the gels and the amount of swelling is reduced, which causes lower recovered energies. At low external loads, nearly all gels (except the weakest ones) are able to lift the loads, and there is little difference between the recovered energies. Gels with higher cross-linker concentrations are able to lift a heavier external load before the recovered energy starts to decline, because of the higher elasticity of the networks (Figure 4). Although the recovered energy generally increases when the cross-linker concentration is raised, the hydrogels with 5% cross-linker recovers less energy than the samples with 3% cross-linker at low to moderate external loads. This is related to the smaller swelling volume of the samples with 5% cross-linker at these conditions (see Figure 5f). As is evident from Figure 6a, a combination of high cross-linker concentrations and optimum external loads is needed to maximize the recovered energy.

The energy efficiency in Figure 6b exhibits trends similar to the recovered energy in Figure 6a since the energy efficiency is directly dependent on the recovered energy (eq 3). The energy efficiency reaches about 1.9% at optimum conditions, which is higher than the energy efficiency recovered from poly(acrylic acid)-based hydrogels, which was about 0.34%.[17]

In Figure 7a, the maximum recovered energy (maximum value from Figure 6a) increases with the dry weight of the gels (the amount of polymer in the gels, Figure 3). Accordingly, larger amounts of energy can be recovered when more polymer is utilized in the gel network. The higher polymer
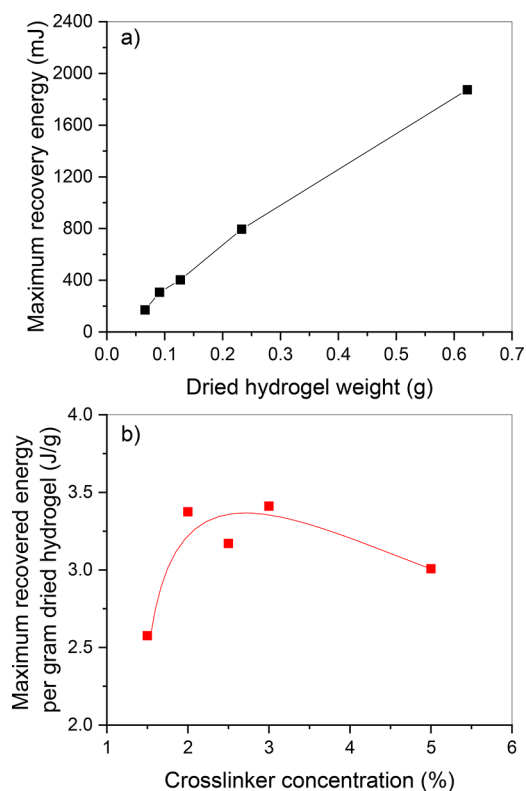
concentrations in the gel networks provide a stronger and more elastic network. They can therefore lift heavier loads to a full swelling volume and thereby recover more energy.

Figure 7b shows the maximum recovered energy per gram of dried hydrogel. Although there is some scatter in the data, it is clear that the maximum recovered energy goes through a broad maximum as the cross-linker concentration is raised. Accordingly, although more energy can be recovered at high cross-linker concentrations (Figure 6a), the energy recovered per gram of polymer has an optimum value at lower cross-linker concentrations (2−3 mol %). The maximum amount of energy produced per gram of polymer is 3.4 J/g (0.9 mW/g), which is much higher than that for previous studies on poly(acrylic acid) hydrogels utilizing the same salinity gradient (about 0.4 J/g; 0.1 mW/g).[17] However, it is important to keep in mind that details regarding the experimental setup and the differences in the utilized external loads will significantly affect these values. For practical purposes the size of the system also plays a role, and the system should be optimized both with respect to size and the amount of polymer needed.

Effect of Low-Concentration Salinity. To explore the effect of salt in the LC solution, the deionized water was substituted by low-saline solutions while the high concentration NaCl solution was kept constant at 35 g/L. For these experiments, hydrogels with 2 mol % cross-linker and an external load of 915 g was utilized. As shown in Figure 8, the salinity of the LC solution significantly affects the swelling volume as well as the recoved energy of the hydrogel. The swelling volume decreased with the increase of NaCl in the LC solution (Figure 8a). The low salt concentration partly screens
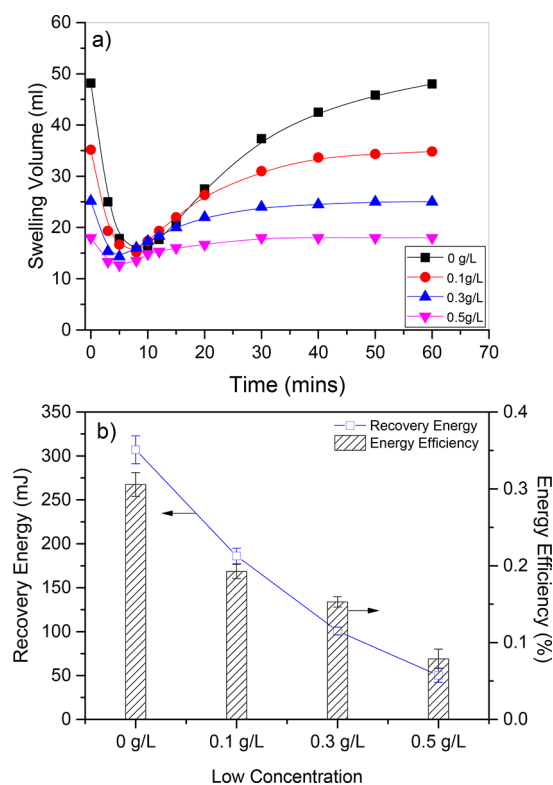

Figure 7. (a) Maximum recovered energy as a function of the dry weight of the gels. (b) Maximum recovered energy per gram of dried hydrogel as a function of cross-linker. The lines are only guides for the eye.

Figure 8. (a) Swelling volume of various low concentrations of NaCl. (b) Recovery energy and energy efficiency as a function of the concentration of the LC NaCl solution. The cross-linker concentration is kept constant at 2.0% and the external load is 915 g.

out the electrostatic repulsions between the charged amine groups, thereby reducing the differences in swelling volume between the low and high NaCl solutions. Since the swelling volume declines when the concentration of NaCl in the LC solution is raised, the recovered energy and energy efficiency decreases (Figure 8b). This illustrates the importance of minimizing the amount of salt in the LC solution.

The LC solution of 0.3 g/L was further tested at various cross-linker concentrations. As shown in Figure 9, a trend
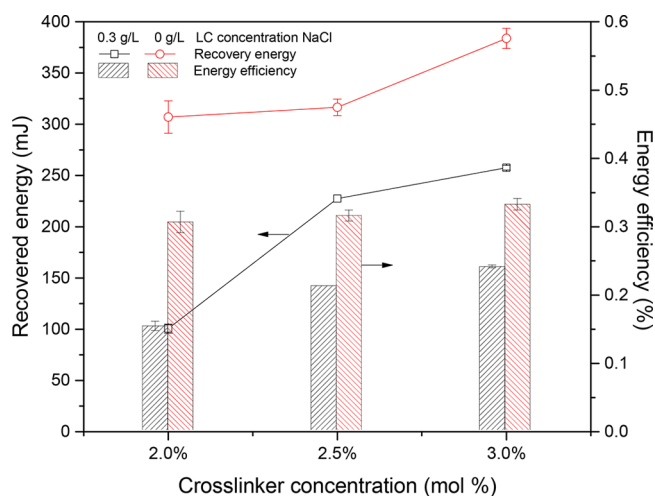

Figure 9. Recovered energy (line) and energy efficiency (bar) versus cross-linker concentrations at a low NaCl concentration of 3.0 g/L (black) and 0 g/L (red) at an external load of 915 g.

analogous to that for deionized water was observed, although the absolute values of the recovered energy and energy efficiencies is lower when 0.3 g/L NaCl is utilized as the low concentration.

CONCLUSION

Energy from salinity gradients can be recovered from the salinity-dependent swelling and shrinking of hydrogels. The swelling of poly(allyamine hydrochloride) hydrogels cross-linked with glutaraldehyde was examined at different external loads, cross-linker concentrations, and when the salinity of the low-concentration NaCl solution was varied. After cross-linking, the samples were swollen in water until they reached a steady state, and a constant amount of the fully swollen gels (60 g) were utilized in the experiments. Since a loosely cross-linked network swells more than a highly cross-linked network, the amount of polymer utilized in the experiments becomes higher when the amount of cross-linker is increased. When the cross-linker concentration is kept constant, the recovered energy goes through a maximum as the weight of the external load is raised. The external load at which the maximum occurs is shifted toward higher weights when the cross-linker concentration is increased because of a stronger and more elastic network. At low cross-linker concentrations, the gels are weak and not able to lift heavy loads while higher amounts of cross-linkers produce gels capable of lifting higher weights and thereby produce more energy. At high cross-linker concentrations, 60 g of swollen hydrogel could recover more than 1800 mJ in one cycle. The energy efficiency (compared to the change in the free energy due to a complete mixing of the high- and low-salinity solutions) reaches up to 1.9%, which is higher than previous results (0.34%) on similar systems.[17] Although

more energy is recovered at high cross-linking densities, the maximum amount of energy produced per gram of polymer (3.4 J/g) has an optimal value at a relatively low cross-linking concentration (2−3 mol %). Raising the salinity of the low-salinity solution reduces the amount of energy that can be recovered by the system. Accordingly, for energy production from rivers it is essential to avoid high salinities in the river water. This illustrates the importance of collecting the river water above the tidal water limit.

The most important factor for maximizing the recovered energy is a combination of increasing the cross-linker concentration and utilizing optimum external loads, which can increase the recovered energy more than 8.5 times compared to low external loads and/or low cross-linker concentrations. By comparison, increasing the salinity of the low-salinity solution from 0 to 0.5 g/L reduces the recovered energy to about one-sixth of the original value.

The results illustrate that hydrogels are promising for salinity gradient energy recovery. However, since this technology is still in its infancy, the produced amounts of energy are relatively low. Further studies are needed to improve this efficiency, and the scale-up of such systems needs to be investigated.

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Notes
The authors declare no competing financial interest.

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