Solar Desalination

Osmotic Pumping and Salt Rejection by Polyelectrolyte Hydrogel for Continuous Solar Desalination

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Efficient mass transport and selective salt rejection are highly desirable for solar or thermally driven seawater desalination, but its realization is challenging. Here a new liquid supply mechanism is proposed, i.e., ionic pumping effect, using a polyelectrolyte hydrogel foam (PHF), demonstrated with poly(sodium acrylate) [P(SA)] embedded in a microporous carbon foam (CF). The PHF simultaneously possesses high osmotic pressure for liquid transport and a strong salt-rejection effect. The PHF is able to sustain high flux of \approx 24 L per m² per hour (LMH), comparable to the evaporative flux under 15 suns, and a salt rejection ratio over 80%. Compared to the porous carbon foam without the polyelectrolyte hydrogel, i.e., with only the capillary pumping effect, the PHF yields a 42.4% higher evaporative flux, at ≈1.6 LMH with DI water and ≈1.3 LMH with simulated seawater under one-sun condition due to the more efficient ionic liquid pumping. More importantly, thanks to the strong salt-rejection effect, the PHF shows a continuous and stable solar-driven desalination flux of ≈1.3 LMH under one-sun over 72 h, which has not been achieved before. The successful demonstration of both efficient ionic pumping and strong salt rejection effects makes the PHF an attractive platform for sustainable solar-driven desalination.

1. Introduction

Efficient harnessing of solar energy attracts wide-spread interest in the context of water-energy nexus. Recently, solar steam generation has become an attractive research area due to the promising application for water purification and desalination^[1–4] assisted by the conceptual and technological breakthroughs in the fields of nanophotonics and nanomaterials that enabled the high solar-thermal energy efficiency. It is estimated that up to 325 GW of solar power is potentially available in

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the United State and the power density of natural evaporation is comparable to the current wind and solar technologies.^[5] While the solar-thermal energy conversion efficiency was intrinsically limited by the performance of the absorber, which already reached $\approx 94\%$,^[6,7] the overall performance of the solar-thermal desalination system would be compromised without sufficient water supply and the ability to resist salt contamination. To solve this problem, several studies explored the capillary pumping effect as a passive liquid supply mechanism where liquid was driven by the capillary pressure in the micropores,^[8,9] microgrooves,^[10] fibrous meshes.^[11,12] and carbon foam.^[13,14] etc. Although the capillary pumping is able to provide high liquid flux, there are two challenges associated with the capillary-driven desalination. First, there is an inherent tradeoff between capillary pumping pressure and flow resistance, as the former scales inversely with the pore

size (i.e., 1/d) and the latter as d^2 for the same flow rate. As a result, the pore diameter cannot be too small in order to ensure a certain flow rate. This tradeoff is even more prominent in solar desalination, as the thickness of the capillary pumping layer has to be large enough to minimize the dissipation of solar heat to the underlying seawater, a major contributor to the total heat loss.^[11] which in term limits the overall flow rate due to the flow resistance. Typically, a thick thermally insulating layer was used to separate the absorber and seawater.^[15,16] We calculated the maximum achievable flow rate for various foam thickness and thermal conductivity in a capillary pumping layer when the heat loss to the bulk seawater is less than 10% of the incident solar energy under the 1 and 3-sun condition (Sections S2.1 and S3, Supporting Information). These optimal flow rates are far lower than the theoretical flow rate of solar evaporation due to the solar heat if the thick foam is used. Second, the capillary pumping pressure is inversely proportional to pore size, so small pores, often at micron scale, are usually used for liquid pumping. The fine porous structures as liquid pathways were inherently prone to the clogging by contamination^[6,17,18] during the evaporation, which undermined the liquid flux and stability in the long term. The salt sediment on the top of the absorber would reduce the solar absorbance^[17] as well as the effective area for evaporation. Therefore, the absorber needed to be taken out for cleaning periodically,^[6] which may impact the durability of the absorber and stability



of the entire system even though antiscratching carbon-based absorber was developed for periodic salt-removal.^[19] Although salt-dissoluble fabric^[20] and Janus membrane^[21] were developed to allow the salt crystal to diffuse back to the sea at night and thus systems were stable on the daily basis, it was still unclear if these systems would sustain when operated under concentrated sun light or working with more concentrated brine water where the salt sediment rate could exceed the rate of salt back diffusion. Therefore, despite the great improvement in the material/structural designs with increasing efficiency over the years, interfacial solar desalination is still not ready for practical application due to the lack of efficient salt-rejection strategies.^[22] The problem of membrane fouling is also a critical concern in many other applications, including forward-osmosis (FO) and reverse-osmosis (RO) separations.

In this work, instead of capillary pumping, we proposed a new ionic pumping effect utilizing common highly ionic polyelectrolyte hydrogel for simultaneous high liquid flux and salt rejection. The high water flux is achieved through the osmotic pressure provided by the polyelectrolyte, e.g., the 14 wt% poly(sodium acrylate), or P(SA) had a high osmotic pressure of ≈ 90 atm,^[23] which was a factor of 10^5 higher than the capillary pressure in microgroove/pores (e.g., 360 Pa for micropore of 400 µm in diameter in the completely wetting state given by the Young-Laplace equation Equation S3-1, Supporting Information). Due to the high osmotic pressure, the ionic hydrogels (e.g., P(SA),^[23] poly(sodium styrene-4-sulfonate),^[24] and poly(acrylate acid^[25,26]), showed a high FO flux of >10 LMH. The swelling ratio of P(SA), defined as the weight ratio of hydrogel at the fully swollen state to that at the dry state, could reach ≈ 100 .^[27] The ionic hydrogel also showed promise for humid vapor absorption due to the favorable hygroscopic effect.^[28] More importantly, the ionic hydrogel was able to resist ≈35% of the salt molecules going through it^[29,30] due to its high ionic strength. Although some salt molecules could enter the hydrogel, they were trapped inside the crosslinking network owing to electroneutrality.^[29] And thus, there would be zero salt-sediment on the top of the solar evaporator if ionic hydrogel is used as the path for water pumping.

To demonstrate the ionic pumping effect as a new liquid supply mechanism for simultaneous high flux and salt-rejection, we developed a polyelectrolyte hydrogel foam (PHF) with P(SA) embedded in the microporous matrix. The PHF could provide high flux of ≈24 LMH, equivalent to the evaporative flux under 15 suns condition with DI water and >80% saltrejection ratio for 3.6 wt% NaCl solution. To demonstrate the practical application of the PHF, we applied the PHF for solardriven desalination. Due to the efficient liquid supply, a thick (≈5 mm) PHF could be used, which reduced the heat loss and thus yielded a high evaporative flux (≈1.6 LMH under one sun condition with DI water). The strong salt-rejection ability of the PHF helped maintained a high evaporative flux of ≈1.3 LMH (i.e., a high energy efficiency of \approx 79%) in the long-term test, i.e., 72 h consecutively in the lab and 6 d outdoor using a 3.6 wt% NaCl solution. The successful demonstration of PHF for solardriven desalination could be extended to a broader range of application in chemical processing and separation where both high flux and salt-rejection are required.

2. Results and Discussions

2.1. Operational Principle of Ionic Pumping and Characterization of PHF

To demonstrate the high flux and salt-rejection performance of the ionic pumping effect, we tested the PHF for solardriven desalination using 3.6 wt% NaCl solution mimicking the seawater. As shown in Figure 1a,b, the CF or PHF floated on the 3.6 wt% NaCl solution in a glass beaker. The incident light (varying from 1 to 3 suns, i.e., 1 to 3 kW m⁻²) was absorbed by the carbon foam which heated up the thin laver of the foam close to the surface as well as the liquid trapped therein. It should be noted that water was driven by different pumping mechanisms between the CF and the PHF. In the CF, the seawater was driven upward from the bulk to the top surface due to the capillary force provided by the micropores, which was heated up and evaporated when transported close to the top surface. Due to the thick foam design (5 mm), little heat was dissipated to the bulk seawater. However, to sustain the high liquid flux through the thick foam, the micropores in the CF were small (≈400 µm) and thus were intrinsically prone to the clogging of salt and contamination during evaporation due to the lack of salt-resistance (see Section S8.1, Supporting Information). In addition, the salt sediment on the top of the CF reflected some of the incident solar power, which also degraded the performance of the CF absorber in the long term. The trade-off of pore size and thickness is resolved by the ionic pumping effect. The PHF avoided the clogging and sediment of salt while maintaining high liquid flux due to the ionic pumping effect of the P(SA) embedded in the micropores of the foam. As shown in Figure 1c, the PHF was filled with 20 wt% P(SA) hydrogel, which had a high osmotic pressure (>100 atm^[23]) to provide high liquid flux. The osmotic pressure of 20 wt% P(SA) was measured to be 230 atm (see Section 2.2) while that for the 3.6 wt% NaCl solution was 27.6 atm. After absorbing water, the osmotic pressure of P(SA) close to the seawater decreased due to the reduced concentration while the top layer maintained a high concentration due to the continuous evaporation, and thus there was an osmotic pressure gradient established inside the hydrogel, which pumped water from the bottom to the top. The salt-rejection at the brine/foam interface was realized by the high ionic strength difference between the polyelectrolyte hydrogel and seawater. Although some ions (<20%) might penetrate into the P(SA), they were trapped by the charged group in the P(SA) chains (e.g., negatively charged CH2=CHCOO⁻ acrylate groups and mobile Na⁺) during the water transport in the micropores, and thus, there was little salt sediment on surface of the PHF absorber, which ensured the long-term stability of PHF. If polyelectrolyte hydrogels with higher ionic strength are used, we could obtain higher flux and better salt-rejection effect, e.g., the osmotic pressure doubles and the ionic strength quadruples if poly(magnesium acrylate) [P(MA)] is used because of the doubly charged Mg²⁺.

As shown in Figure 1c, the PHF was synthesized by copolymerizing the P(SA) hydrogel with SA monomers in the micropores of the porous carbon foam (CF). It should be noted that the CF was chosen for the demonstration of the solar-driven desalination due to its high solar absorbance, i.e., 97.8%

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Figure 1. Experimental setup and schematics of dual ionic pumping and salt rejection effects offered by polyelectrolyte hydrogel poly(sodium-acrylate) [P(SA)]. a) Bench-scale evaporation test with 3.6 wt% NaCl solution mimicking the seawater. CF or PHF with the thickness of 5 mm floated on the bulk solution to receive solar radiation varying from 1 to 3 suns. b) Polyelectrolyte hydrogel foam (PHF) absorber with its micropores filled with P(SA). Liquid flow is pumped by the osmotic pressure gradient between the bulk seawater ($\Pi \approx 27.6$ atm) and P(SA) hydrogel ($\Pi \approx 230$ atm). Salt ions are rejected at the PHF-seawater interface due to the high ionic strength of P(SA), and thus there is no salt clogging and sediment in the PHF. Liquid water is heated up close to the top of the PHF and evaporates. The surface temperature rises with increasing input solar flux. c) Composition and microstructures of the PHF. The micropores with the diameter of \approx 400 µm are filled with P(SA) hydrogels after the copolymerization. d) High absorbance of PHF and CF in the solar spectrum. e) FTIR characterization of P(SA) hydrogel.

in the solar spectrum (320–2600 nm) as shown in Figure 1d. Different types of microporous foam or membrane could be used based on the requirements for particular application. As shown in the SEM image in Figure 1c, the micropores in the CF matrix have a diameter of ~400 μ m and are interconnected as liquid pathway for capillary pumping. The chemical residual on the carbon fibers is adhesive for fiber connection. After copolymerization, the micropores were filled with P(SA) hydrogels, indicating the successful synthesis of PHF. The average absorbance value of the PHF is 97.7%, which indicates that the P(SA) does not changes the high absorbance of the active carbon foam. The Fourier-transform infrared spectroscopy (FTIR) spectrum of the P(SA) is displayed in Figure 1e. The peaks at the 1650 and 1559 cm⁻¹ represent the C=O groups in the >C=O…H–N< species (amide bands I and II, respectively)

and MBA (N,N'-methylenebisacrylamide) repeated units.^[31–35] The 1386 cm⁻¹ peak refers to the C–H vibrations of CH(CH₃)₂ repeated units.^[35] The peak at 1455 cm⁻¹ is attributed to the stretching vibration of the $-CH_2$.^[36] In addition, the peak at 1705 cm⁻¹ is due to the carboxylate anion of SA units.^[35] The polyelectrolyte hydrogel, i.e., 20 wt% P(SA), has two functions:

- i) the high osmotic pressure (Π), which is measured to be ≈ 230 atm, drives the water from the bulk solution upwards to the top of the foam. The osmotic pressure of P(SA) is a factor of 10^5 higher than the capillary pressure in the micropores (e.g., 360 Pa for pore of $\approx 400 \ \mu m$ in diameter assuming the completely wetted state).
- ii) The P(SA) resists the ions at the brine–foam interface due to the high ionic strength and entraps the ions, which penetrate

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into the hydrogel by the charged groups (i.e., negatively charged $CH_2=CHCOO^-$). Therefore, the PHF is expected to possess good antifouling capability. It is noted that we just used a common porous activated-carbon foam and P(SA) hydrogel, which could be easily replaced by other materials in different application scenarios.

2.2. Characterization of Ionic Pumping and Design of Evaporator

Instead of the surface tension in the capillary pumping mechanism, in the ionic pumping mechanism, the liquid is pumped by the osmotic pressure difference between the polyelectrolyte hydrogel and seawater. Therefore, we first determined the osmotic pressure of the 20 wt% PSA by comparing it to the NaCl solution of equivalent concentration as shown in **Figure 2**a. The average absorption flux in the first 5 min, defined by Equation (4), decreased linearly from 2.3 LMH to 0.25 LMH as the osmotic pressure of the NaCl solution increased from 27.6 atm (equivalent to 3.6 wt%) to 230 atm (equivalent to 30 wt%), which was in line with the theory of diffusion. The diffusion-govern water transport in the hydrogel was also observed in literatures^[27,37] and could be proven by the analysis of diffusive permeability in Section S3.2 (Supporting Information). The diffusivity of water molecules in 20 wt% P(SA) was measured to be 2.92 $\times 10^{-10}$ m² s⁻¹, which was close to that reported for various types of hydrogels, such as GMA, TEGDMA, and HEMA hydrogels.^[37] Since this value was smaller than the self-diffusion coefficient of water $(2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})$,^[38] it was evident that water was transported in the form of diffusion in ionic pumping instead of viscous flow^[39] for capillary. It could be estimated from Figure 2a that the osmotic pressure of 20 wt% PSA was ≈240 atm although we did not further increase the NaCl concentration due to the dissolution limit, which was a factor of 10⁵ higher than the capillary pressure of the CF with ≈400 µm micropores assuming the completely wetting state (≈360 Pa), and would still be ≈ 1000 times higher than the capillary pressure of $\approx 1 \, \mu m$ pores. More importantly, the osmotic pumping pressure is independent of the pore size and hence is independent of the flow resistance, and thus it can still be very high even with large pore size. The high osmotic pressure of P(SA) was attributed to the ionic SA monomers. By reducing the weight ratio of SA from 100 wt% [pure P(SA)] to 50 wt% [P(NIPAAm-co-SA)] and 0 wt% [P(NIPAAm)], the equivalent osmotic pressure of hydrogels decreased to ≈200 atm and <30 atm, respectively.

To evaluate the liquid flux sustained by the PHF, we measured the absorption flux for hydrogels with different osmotic



Figure 2. Ionic pumping mechanism for high flux and salt-rejection. a) Average water absorption flux in 5 min of 20 wt% P(SA), P(NIPAAm-co-SA) and P(NIPAAm) hydrogels with variation of osmotic pressure of NaCl solution. The osmotic pressure of solution at the flux of zero indicates the equivalent osmotic pressure for the hydrogels. b) Instantaneous water absorption flux of hydrogels with different osmotic pressures and CF. The inset shows the contact angle on the surface of CF. c) Salt-rejection ratio for hydrogels and CF using 3.6 wt% NaCl solution, which is defined by the weight ratio between the NaCl salt rejected by hydrogels when it absorbs water from the 3.6 wt% NaCl solution and that contained in the 3.6 wt% NaCl solution of equivalent mass to the absorbed water (see Section S1, Supporting Information). d) Heat transfer modeling of the solar desalination system.

pressure (from 240 to 30 atm as described above) and CF as a function of time as shown in Figure 2b. The maximum realtime absorption flux of carbon foam was only 16.8 LMH, which was 16.8% lower than that of the P(SA) hydrogel. The reason is that the CF foam was hydrophobic as its contact angle with DI water was $\approx 85^{\circ}$ as shown in the inset in Figure 2b, leading to a low capillary pressure of about ≈30 Pa (compared to 360 Pa if the contact angle were 0°). We calculated the contact angle of CF based on the balance of capillary pressure and viscous pressure drop in the micropore in Section S3.1 (Supporting Information), which was 89.5°. The high absorption flux was sustained by the osmotic pressure of the hydrogels. For example, the absorption flux monotonously decreased from 24 LMH [pure P(SA)] to 0.84 LMH [pure P(NIPAAm)] using DI water as the osmotic pressure decreased from 240 to 30 atm. Assuming that the evaporative flux is ≈1.6 LMH per sun, the PHF using the P(SA) will be able to provide stable liquid supply even under the 15-sun condition for DI-water and 6.6-sun for 7.2 wt% NaCl solution.

Figure 2c shows the salt-rejection ratio for the hydrogels and CF using 3.6 wt% NaCl solution. The measurement method is described in detail in Section S1 (Supporting Information). Briefly, both the 20 wt% hydrogels and CF were completely dried before the test and then put into the 3.6 wt% NaCl solution for 24 h to allow the hydrogels and CF fully absorb the liquid. Afterwards, both samples were dried again to remove all water but allow the salt to stay. We obtained the salt-rejection ratio by comparing the dried mass of hydrogels or CH before and after the test because the gained mass was only from the NaCl entrapped in the sample. The test was repeated twice for both types of samples. Due to the high ionic strength gradient at the brine/P(SA) interface, over 80% of the Na⁺ ions were rejected by the P(SA). In the P(SA) hydrogel, the Na⁺ ions are mobile while the negatively charged acrylate groups in the matrix are immobile. At the gel-brine interface, some Cl⁻ ions may still permeate through while most Na⁺ ions are rejected. As a result, the gel side of the interface is locally negatively charged while the solution side is positively charged. The unequal ion solute concentration distribution across the membrane creates the Donnan potential, which resists the ionic diffusion. We calculated the theoretical salt-rejection ratio for the 20 wt% P(SA) hydrogel against the 3.6 wt% NaCl solution based on the Donnon exclusion theory in Section S1 (Supporting Information), which was 91% and was close to the measured value (85%). Although there were still 10-20% of the Na⁺ ions that penetrated into the P(SA), they would be trapped by the charged group of the P(SA). Ali et al.^[30] confirmed that the P(SA-co-N-Isopropylacrylamide) was able to retain ≈23% of NaCl. Therefore, we believe that there will be little salt sediment on the top of the PHF in practical application due to the salt-rejection and trapping by the P(SA). The high salt-rejection ratio of P(SA) was due to the ionic strength of the SA monomers, confirmed by the decreasing salt-rejection ratio from 85% to 32% with the decreasing SA concentration from 100 wt% [pure P(SA)] to 0 wt% [pure P(NIPAAm)]. On the other hand, the CF could not reject the ions, indicated by the salt-rejection ratio of <3.6%. Due to the lack of ion-resistance, the CF would be prone to the salt crystallization and fouling of the foam in the long run.

The results from these tests clearly demonstrated the high mass flux and salt-rejection capability of the ionic pumping mechanism using the polyelectrolyte hydrogel foam. We showed the high flux of up to 24 LMH and salt-rejection ratio up to 80% using the P(SA) ionic hydrogel. The simultaneous efficient liquid supply and salt-rejection achieved by the ionic pumping effect provide us an entirely new strategy to solve the tradeoff seen in capillary assisted solar desalination. Figure 2d shows the heat transfer model of the solar desalination system. The energy efficiency of the evaporator was calculated as follows

$$\eta = \frac{q_{\rm evp}}{q_{\rm solar}} = \frac{q_{\rm solar} - q_{\rm c1} - q_{\rm r} - q_{\rm c2} - q_{\rm de}}{q_{\rm solar}}$$
(1)

where q_{solar} , q_{c1} , q_{r} , q_{c2} and q_{de} are the solar flux, convective heat loss, radiative heat loss, conductive heat loss, and additional heat loss due to insufficient liquid supply, respectively, which are calculated based on the measured surface temperature of CF/PHF (see Section S2.1 in the Supporting Information) and the thermal conductivity of the foam (Section S2.2, Supporting Information). It should be noted that although increasing the foam thickness helps reduce the conductive loss to the bulk water and increase the salt rejection ability, the energy efficiency is limited by the maximum liquid flux as shown in Figure 2b. Increasing solar power or thickness of the foam so that the sustainable liquid flux is lower than the theoretical maximum evaporative flux, the redundant solar flux will be dissipated, which leads to the q_{de} given by Equation S2-11 (Supporting Information). P(SA) was chosen to incorporate with the CF to produce the PHF to achieve the high salt-rejection ratio (85%). In the meantime, to achieve high energy efficiency >70% with the solar flux ranging from 1 to 3 suns, the thickness of the foam should be carefully chosen. Based on the absorption flux of P(SA), the foam thickness of PHF using the P(SA) was chosen to be 5 mm. The heat transfer analysis is described in detail in Section S2 (Supporting Information).

2.3. Demonstration of Ionic Pumping Effect for Solar-Driven Desalination

Next, we set to demonstrate the feasibility of applying the ionicpumping effect for continuous solar-driven desalination, which is an attractive topic in recent years in the context of waterenergy nexus. Despite the abundant efforts in improving the energy efficiency of the solar absorber, the continuous solardriven desalination is yet to achieve because most previous studies employed the capillary-pumping effect for liquid supply using microporous structure, which inevitably resulted in the salt clogging and sediments under the conditions of high solar flux, high salt concentration, and long irradiation time. And thus, previous studies only achieved the stable solar-driven desalination on the daily-basis at best with self-diffusion at night.^[20,21] In the previous section, we demonstrated the high flux using the ionic pumping effect, which enabled the efficient liquid supply even under the high suns condition. More importantly, due to the strong salt-rejection ability of P(SA), the problem of salt clogging in the foam and sediment on the top of the receiver were resolved. The sufficient liquid supply www.advancedsciencenews.com

of ionic pumping was confirmed in the DI water test while the salt-rejection performance was evaluated in the test using 3.6 wt% NaCl solution.

2.3.1. Ionic-Pumping Assisted Water Supply

Figure 3a shows the mass loss of DI water in the bulk due to evaporation using the CF and PHF as absorbers under the 1-sun and 3-sun conditions, respectively. The evaporation was stable during the 1 h test indicated by the linear relation of mass loss over time. The PHF absorber yielded 1.3 g mass

change in 60 min, which was 30% greater than that of the CF under the 1-sun condition. It showed a more evident advantage over the CF under the 3-sun condition where the PHF yielded 4.1 g mass change, which was only 3.1 g for the CF. Figure 3b shows the evaporative flux for the CF and PHF under the 1 and 3 suns conditions in accordance to the mass changes shown in Figure 3a. The PHF yielded 1.65 LMH and 4.6 LMH under the 1 and 3 conditions, which were 42.2% and 79.9% higher than that for the CF, respectively. Interestingly, the surface temperatures for the PHF and CF were similar, which were \approx 43 °C and \approx 65 °C under the 1 and 3-sun conditions, respectively. This indicates that the heat loss due to radiation, convection to air, and



Figure 3. Ionic pumping effect for liquid supply and salt-rejection in solar-driven evaporation. a) Evaporation mass loss of DI water versus time under the 1 sun and 3 sun conditions, respectively. b) Evaporative flux and surface temperature using DI water under the 1 sun and 3 sun conditions, respectively. c) Evaporation mass loss of simulated seawater (3.6 wt% NaCl solution) with the solar flux varing from 1 to 3 suns. d) Evaporative flux and surface temperature using the simulated seawater under 1 to 3 suns conditions. e) Salt clogging in the micropores for the CF without salt-rejection effect. f) Infrared thermal images of PHF and CF under the 1 and 3 suns conditions using simulated seawater. The surface temperature of CF was similar to that of PHF under the 1 sun condition but it was much higher than that of PHF under the 3 suns condition, due to the salt clogging in the micropores which led to insufficient liquid supply.



convection to bulk liquid underneath the absorber were similar for the PHF and CF (refer to the Section S2.1, Supporting Information), and thus both samples had similar energy efficiency η of \approx 75% under the one-sun condition, which agreed with that of CF (72.5%) given by $\eta = \frac{n_{\rm lg}}{q_{\rm s}}$ where $q_{\rm s}$ is the solar flux and $h_{l\alpha}$ is the evaporative latent heat. Therefore, we believe that the PHF yielded a higher evaporative flux than the CF due to the more efficient liquid supply. It should be noted that the measured evaporative flux (e.g., 1.65 LMH under 1-sun) is rather high, because the water evaporation in our experiment was driven not only by the solar irradiation (which would have given a maximum theoretical flux of 1.64 LMH), but also by the ambient temperature and the wind. We modeled the evaporative flux by considering the measured surface temperature (43 °C, see Figure 3f), ambient temperature (300 K) and wind speed (about 0.5 m s⁻¹), and obtained a value of 1.56 LMH (see Section S4 in the Supporting Information), which was very close to the measured flux. Therefore, the measured flux did not contradict with the solar energy efficiency of \approx 75%, as other forms of energy (wind, ambient thermal) also contributed to the evaporation.

2.3.2. Ionic-Pumping Assisted Salt Rejection

In addition to facilitate the water supply, the P(SA) also served as the salt-rejecting agent at the seawater-PHF interface due to its high ionic strength, which helped avoid the salt clogging in the porous foam and salt sediment on the upper surface of the receiver. Figure 3c shows the mass loss of 3.6 wt% NaCl solution due to evaporation for 1 h under the 1-sun and 3-sun conditions. It was found that the PHF and CF had similar mass change rate at the 1-sun condition but the PHF yielded a higher mass change rate under the 3-sun condition. Figure 3d compares the evaporative flux for the PHF and CF from 1 to 3 suns. The PHF yielded higher evaporative flux than the CF under all conditions, e.g., at the 1-sun condition, the evaporative flux for the PHF was 1.24 LMH, which was 27.8% higher than that of the CF. This could be attributed to the relatively insufficient liquid supply for the CF compared to the PHF. As discussed in Section 2.2, the PHF yielded a higher water absorption flux than the CF due to its high osmotic pressure. More importantly, although the absorption flux for the PHF slightly decreased when using 7.2 wt% NaCl solution as shown in Figure 2b, the PHF still maintained a higher liquid flux than the CF.

Figure 3e shows the SEM and EDS images of the CF after the 1 h test under the 3-sun condition. It is clearly seen that the micropores in the CF were clogged by NaCl which crystallized in the pore as water evaporated. This undermined the liquid supply through the micropores. In addition, the salt sediments on the top of the foam reduced the solar absorbance because it reflected the sun light. As shown in Figure S5a (Supporting Information), the solar absorbance of CF was reduced from 97.7% before the test (Figure 1d) to \approx 94.2% after the 1 h test. As a result of the high ionic strength of the P(SA), most salt ions were rejected at the water-foam interface while the small amount of salt that penetrated into the foam were captured by the ionic group of P(SA) (acrylate group), and thus there was little salt sediment on the top surface of the foam.

The salt-rejection effect of the PHF became more prominent under the high sun condition where the salt crystal grew faster. For example, as the solar radiation increased from 1 sun to 3 sun, the evaporative flux for the CF decreased by 45.2% while that for the PHF only decreased by 23%. Due to the insufficient liquid supply, the surface temperature of CF was higher than that of the PHF, e.g., under the 3-sun condition, the surface temperature was 79 °C for the CF and 63 °C for the PHF as shown in Figure 3f,d. According to the calculation in Section S2.1 (Supporting Information), the PHF had a 30% higher energy efficiency than the CF under the 3 suns condition using 3.6 wt% NaCl solution.

2.3.3. Demonstration of Continuous Solar-Driven Desalination

Figure 4a compares the evaporation flux of the PHF and CF under the 2-sun condition with 3.6 wt% NaCl in the bulk for 6 h. In the first hour, the PHF yielded 2.4 LMH evaporative flux which was 41.2% higher than that of the CF. The PHF maintained a stable evaporative flux ranging from 2.36 to 2.56 LMH throughout the 6 h test. However, the evaporative flux for the CF gradually decreased from 1.7 to 1.46 LMH in the first 4 h and dropped to 1.1 LMH in the fifth hours where the salt crystallization became prominent as shown in Figure 4b. The absorbance of the CF decreased to 88.92% after the 6 h test as shown in Figure S5b (Supporting Information). This test also proved that the PHF was stable for 12 h under 1 sun condition, which was equivalent to the stability on the daily basis. The stable solar-driven desalination on daily basis under the 1-sun condition was also demonstrated in Ni et al.^[20] and Xu et al.^[21] However, without the salt-rejection effect, it is difficult to further increase the equivalent sun-hours stability because the rate of salt crystallization exceeds that of the dissolution and diffusion of salt under the high sun condition. Therefore, the stable solar-driven desalination exceeding the 12 sun hours was challenging.

As shown in Figure 4c, we managed to achieve the continuous and stable solar-driven desalination exceeding the 12 sun hours using the ionic pumping effect. The PHF was placed under 1 sun condition for 72 h consecutively and its evaporative flux was measured every ≈24 h. The evaporative flux was an average value in 1 h, the same way we measured the flux shown in Figure 3b,d. The evaporative flux maintained stable between 1.2 and 1.3 LMH within 72 h. It is evident that there was no significant salt sediment on the top of the PHF (insets of Figure 4c). One may also refer to Figure S8-2 (Supporting Information) for the EDS characterization as further evidence. Therefore, in the real application, assuming the 12 h daylight, we can apply at least 6 suns onto the PHF while still maintaining the high evaporative flux of ≈1.2 LMH per sun. The PHF was also tested under the natural sun light irradiation for 6 d consecutively (24 h per day) on a rooftop without cleaning or replacing the receiver. The evaporative flux was measured at the mid day where the solar irradiation was close to 1 kW m⁻² and was averaged over 1 h. The evaporative flux maintained stable over the course of 6 d. The small fluctuation of the flux





Figure 4. Continuous and stable solar-driven desalination exceeding 12 sun hours sustained by the ionic-pumping effect. a) Mass change and evaporation flux of CF and PHF under 2 suns condition for 6 consecutive hours. b) Salt sediments (shown within the dashed circles) on the CF. c) Stable evaporation flux for the PHF throughout the 72 h test under 1 sun condition in the lab. The insets show the absence of the salt sediments on the PHF. d) Evaporation flux (left axis) and daily water production rate normalized by daily solar irradiation (right axis) over the course of 6 d of continuous operation under natural solar irradiation on a rooftop. The daily solar irradiation flux was obtained from the NASA database (Section S6, Supporting Information).

was due to the unstable ambient conditions. Similarly, due to the variation in the total solar radiation energy from day to day in the 6 d test, the production rate (in L per m² day) fluctuated as shown in Figure S6a (Supporting Information). However, after normalization with the daily solar radiation energy, which was quoted from the NASA database as shown in Figure S6b (Supporting Information), the normalized water production rate was stable ranging from 1 to 1.5 L per kWh as shown in Figure 4d. We also demonstrated the long-term stability of PHF using actual seawater (Pacific seawater provided by the Scripps Oceanography Institute, UCSD) as shown in Section S8 (Supporting Information), which proved that the PHF was also stable using the actual seawater for at least 12 d (Figure S8-1, Supporting Information) under 1 suns and 6 d under 3 suns (Figure S8-3, Supporting Information). The purified water could also be easily collected as shown in Section S8.2 (Supporting Information) and the product water was of good quality (Section S8.3, Supporting Information).

2.4. Comparison between Ionic-Pumping and Capillary-Pumping Effects

Figure 5 compares the evaporative flux achieved by the PHF to that by other evaporators in literatures^[4,6–9,15,17,21,40–56] using the capillary pumping effect under equivalent solar irradiation time. It should be noted that the units in the Figure are to

facilitate the comparison of various results, and the evaporative flux and solar utilization efficiency do not necessarily scale linearly with the irradiation flux. The evaporative flux was normalized by the solar flux for the convenience of comparison. The equivalent solar irradiation hour is defined as the



Figure 5. Comparison of evaporative flux and continuous operation time of PHF to other solar evaporators in literatures.

multiplication of the concentration suns and time of test, e.g., in Zhou et al.^[50] the receiver was exposed to the 5 suns irradiation for 1 h and thus the equivalent solar radiation time was defined as 5 h. It is evident that the PHF yielded competitive evaporative flux to other evaporators. More importantly, it demonstrated a much longer continuous operational period than most of the previous evaporator, which makes it attractive in the real application. Although some studies showed higher flux than that of the PHF, they adopted the capillary wick for liquid pumping and did not demonstrate the continuous desalination, e.g., cyclic desalination with each evaporation period lasting 1-2 h and rinsing in between was demonstrated in refs. [6,7,43,47,49,57]. Ni et al.^[20] and Xu et al.^[21] demonstrated the stable evaporation on the daily-basis using salt-dissoluble foam and Janus foam, respectively, but the stability exceeding the 12 sun hours was yet to be demonstrated. Without the self-dissoluble design, the foam was completely covered by salt sediments within 5 d.^[17] Another advantage of the PHF is the cost-effectiveness because the chemicals (see Synthesis Section) and the activated carbon foam are inexpensive compared to the materials used for other studies, e.g., structured graphene,[6,7,51,55] plasmonic nanoporous membrane^[40,42] and so on, making it suitable for the large-scale production. In addition, due to the high liquid flux sustained by the PHF, it was able to maintain high energy efficiency even with a much thicker foam than that the CF, which was favorable to better salt-rejection.

3. Conclusion

In this study, to provide simultaneously high flux and saltrejection ability for chemical processing and separation, we proposed a new liquid pumping mechanism using the polyelectrolyte hydrogel, which had high osmotic pressure for liquid pumping and high ionic strength for salt rejection. Different from the conventional capillary pumping effect, the ionic pumping effect tapped the water diffusion in the polymer network instead of viscous flow in the micropores, and thus it was not prone to the fouling for the porous wick. The ions were rejected at the solution/foam interface due to the strong ionic strength of polyelectrolyte. We successfully demonstrated the feasibility of ionic pumping for chemical separation in the solar-driven desalination test. The PHF using the ionic pumping effect always yielded higher evaporative flux than that of the CF using the capillary pumping effect both using the DI water and brine water under different sun conditions due to the sufficient liquid supply and salt-rejection. For the first time, the continuous and stable solar-driven desalination with the operation period of 72 consecutive hours under 1 sun condition was reported without cleaning or replacing the absorber, or equivalent to 12 h under concentrated 6 suns condition. The high flux using the ionic pumping effect allowed us to use thicker foam to obtain better thermal insulation and foul-rejection without compromising the energy conversion coefficient. The successful application of ionic pumping effect in the solar-driven desalination showed its promise for miscellaneous chemical transport and separation processes where both high flux and good antifouling ability are required.

4. Experimental Section

Synthesis and Characterization of PHF: Highly solar-absorbing porous activated-carbon foam was used as the supporter of the P(SA) hydrogel for ionic pumping water supply and salt rejection. The sodium acrylate (SA, 99%) as monomer, ammonium persulfate (APS, 98%) as thermal initiator and N,N'-methylenebisacrylamide (MBA, 99%) as cross-linker were purchased from Sigma-Aldrich and used as-received. SA, MBA, and APS were dissolved in DI water with a fixed molar ratio of 50:1:1 to obtain a 20 wt% homogeneous solution. Before the synthesis, the carbon foam (CF) was cleaned by sonication in DI water for 30 min and then was completely dried in an oven. The dry CF was immersed in the SA solution for overnight to ensure that the pores in the foam were filled with solution, after which it was put into an oven at 70 °C for 2 h for copolymerization of SA. After the synthesis, the pores in the CF were filled with P(SA), and was named as PHF. The SEM images and EDS mapping of CF and PHF were captured with FEI Apreo SEM. The FTIR of P(SA) was conducted on a NICOLET 6700 FTIR (Thermoscientific Inc.), and the absorbance of CF before/after salt sediment and the PHF were evaluated with a UV-vis spectrophotometer (JASCO V-770).

Two sizes of samples were prepared: 5.52 cm² sample for bench-top experiment and 132 cm² (Figure S7, Supporting Information) for long-term stability test at the ambient environment. This also proved that our design could be easily applied for large-scale production.

To evaluate the contribution of ionic pumping by P(SA) to liquid supply and salt rejection, pure P(SA) hydrogel was also prepared with the same recipe described above except that the SA solution was poured into a mould to obtain P(SA) hydrogel sheet with the thickness of 2 mm. For comparison, copolymers P(N-isopropylacrylamide-co-SA) [P(NIPAAm-co-SA)] with the NIPAAm:SA ratio of 1:1 by weight and pure P(NIPAAm) were also prepared. The NIPAAm and SA monomers were dissolved in deionized water to obtain a 20 wt% homogenous solution. And then MBA and APS were added into the solution with a fixed molar ratio of monomers, crosslinker, and initiator of 50:1:1. After being fully dissolved, the homogeneous solution was degassed for 10 min before being put into the oven of 70 °C for copolymerization of P(NIPAAmco-SA). The P(NIPAAm) was made by the free-radical polymerization of NIPAAm using the UV-light initiated method with the α -ketoglutaric acid as initiator. The NIPAAm were dissolved in deionized water to produce a 20 wt% homogeneous solution. Afterwards, MBA and α -ketoglutaric acid were added into the solution with a fixed molar ratio of monomers. crosslinker and initiator of 50:1:1. The solution was degassed for 10 min and then exposed to UV-light to induce the copolymerization for 12 h. It should be noted that the NIPAAm monomers were not ionic and thus its osmotic pressure was much lower than that of the P(SA) and P(NIPAAm-co-SA). Similarly, due to the reduction of SA concentration, the osmotic pressure of P(NIPAAm-co-SA) was lower than that of the pure P(SA).

Evaporative Flux: The evaporative flux of CF and PHF with different incident power density P_s (1–3 suns (kW m⁻²) provided by Halogen lights) and feed solution (DI water and 3.6 wt% NaCl as mimic seawater) was obtained. The absorber (CF or PHF) with an absorbing area A_s of 5.52 cm² and thickness of 5 mm, floated on the feed solution in a beaker. The beaker was thermally insulated, being wrapped by a bubble foam and then aluminum foil on the external side walls. The mass loss m_s of the setup was recorded every 10 min and the test stopped at $t_s = 1$ h. The evaporative flux \dot{m} was then calculated as follows

$$\dot{m} = \frac{m_{\rm s}}{A_{\rm s}\rho_{\rm w}t_{\rm s}} \tag{2}$$

where m_s is the mass loss, A_s is the surface area, ρ_w is the density of water, and t_s is the time of measurement. To compare the stability of the CF and PHF, both samples were exposed under 2 suns condition for 6 h using 3.6 wt% NaCl as feed solution and the mass change was recorded every hour, thus the evaporative flux accordingly. The surface condition of the CF sample was monitored and the optical absorbance after the test was measured.

The schematics of the measurement setup and the ambient conditions are shown in Figure S9 in Supporting Information. The measurement method and ambient conditions were similar to that recommended in Li et al. $^{[58]}$

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Osmotic Pressure and Absorbing Flux: The osmotic pressure Π of strong inorganic electrolytes with certain molar concentration C (i.e., NaCl solution) can be calculated with the assumption of complete hydrolysis according to

$$\Pi = iCRT \tag{3}$$

where i is the dimensionless van't Hoff index, R is the ideal gas constant and T is the temperature in K. However, it is still difficult to directly calculate the osmotic pressure of hydrogel. Instead of directly calculating the osmotic pressure of 20 wt% P(SA), it was determined by comparing the concentration of NaCl solution C_{NaCl} where the immersed P(SA) could not swell, i.e., the P(SA) and the NaCl solution reach the thermodynamic equilibrium. Since the solubility limit of NaCl solution is 26.47 wt% (≈170 atm) where the absorption flux of P(SA) was still large as shown in Figure 2a, we further increased the osmotic pressure of solution to ≈ 230 atm using 28 wt% Na₂CO₃ solution at 38 °C (only for this specific point). It is noted that the P(SA) swells when immersed in a solution of low concentration, driven by the difference in the osmotic pressures until an equilibrium of \prod between the swollen P(SA) and solution is reached. Therefore, the osmotic pressure of P(SA) was considered the same as that of the NaCl solution calculated from Equation (3).

To evaluate the capability of water supply for ionic pumping effect, the 20 wt% P(SA) with mass of m_0 and external surface area of S_0 was immersed in DI water and 7.2 wt% NaCl solution for a period of time t, and then the mass and external area of swollen P(SA) were recorded as m_1 and S_1 , respectively. We used the average value of S_0 and S_1 to represent the area (A_a). The absorption flux \dot{m}_a during this specific period of time was given according to Equation (4).

$$\dot{m}_a = \frac{m_1 - m_0}{\rho_w A_a t_a} \tag{4}$$

The absorption flux of CF immersed in DI water was also given as comparison, which was driven only by the capillary force of the micropores. The tests were conducted under the ambient condition.

Long-Term Stability: To compare the long-term stability of the PHF and CF, they were irradiated under 2 sun condition and with 3.6 wt% NaCl solution in the bulk for 6 h consecutively. The evaporative flux, which was calculated by Equation (2), was given every hour and the salt sediment on the CF was captured. The absorbance of the CF after the test was also evaluated.

To show the zero salt-sediment on the PHF due to the salt rejection by the P(SA) and the stability of PHF on hourly basis, the PHF was placed under 1 sun condition and with 3.6 wt% NaCl solution in the bulk for 72 h. The 1 h average evaporative flux was recorded every 24 h. A large PHF sample of 132 cm² (diameter of 13 cm) was placed on the rooftop of the EBU-2 building on UC San Diego campus for 6 d continuously in the summer (July, 2018). The water production rate per day was given and the evaporative flux was evaluated in the mid-day every day when the solar flux was measured to be close to 1000 W m⁻². The photo of large PHF sample for the long-term stability test at ambient condition was shown in Section S7 (Supporting Information). The 7/24 test confirmed the long-term stability of PHF not only on daily basis but also on hourly basis with zero-salt sediment during the operational lifetime.

To prove the long-term stability of PHF using actual seawater, the evaporative flux and water production rate of PHF under 1 sun condition were tested for 12 d and 24 h a day consecutively, and under 3 suns condition for 6 d and 24 h a day consecutively using actual Pacific ocean seawater, which was provided by the Scripps Oceanography Institute, UC San Diego (see Sections S8.1 and S8.2, Supporting Information). The quality of product water was also evaluated (see Section S8.3, Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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