Protocol
An encapsulation protocol of salt-based composite sorbents for atmospheric water harvesting

Sorption-based atmospheric water harvesting (SAWH) is a feasible and sustainable approach to address water scarcity issues. Featuring the high affinity of hygroscopic salts with water vapor, salt-based composite sorbents have been widely used. However, the risk of salt solution leakage is still challenging. In this protocol, we introduce a porous waterproof and moisture-permeable membrane encapsulation technique to develop salt-based sorbents. The high salt content composites (HSCC-Ex) exhibit remarkably high salt content of 80 wt % without the risk of leakage.

Highlights
Protocol for preparation of membrane-encapsulated ultrahigh-salt-content sorbents
A universal porous moisture-permeable membrane encapsulation technique
A salt solution confinement strategy to prevent solution leakage
Water harvesting via salt-based sorbents with ultrahigh salt content of 80 wt %

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Protocol
An encapsulation protocol of salt-based composite sorbents for atmospheric water harvesting

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SUMMARY
Sorption-based atmospheric water harvesting (SAWH) is a feasible and sustainable approach to address water scarcity issues. Featuring the high affinity of hygroscopic salts with water vapor, salt-based composite sorbents have been widely used. However, the risk of salt solution leakage is still challenging. In this protocol, we introduce a porous waterproof and moisture-permeable membrane encapsulation technique to develop salt-based sorbents. The high salt content composites (HSCC-Ex) exhibit remarkably high salt content of 80 wt% without the risk of leakage. For complete details on the use and execution of this protocol, please refer to Shan et al. (2021).

BEFORE YOU BEGIN
The protocol below describes the specific steps and typical characterizations of a salt-based composite sorbent HSCC-Ex with the ultra-high salt content of 80 wt%. The developed sorbent HSCC-E10 shows high vapor sorption capacity of 3.75 g/g, 2.83 g/g, and 1.47 g/g for 90%, 70%, and 30% RH, respectively. The sorbents are suitable for any ambient conditions to realize water harvesting in anytime and anywhere. Furthermore, scale-up and practical application potential of developed sorbents are also reported.

The protocol takes the active carbon fiber felt (ACFF) matrix, 30 wt% lithium chloride solution, and porous PTFE membrane as examples. But more importantly, a porous waterproof and moisture permeable membrane encapsulation method is developed and can be applied to any salt-based sorbents to prevent the risk of solution leakage. For example, other matrixes for salt-based sorbents, such as PAM-CNT (Li et al., 2018) and rGO-SA (Xu et al., 2021), other hygroscopic salts, such as LiCl and CaCl2, even different waterproof and moisture permeable membranes, such as PVDF membrane or omniphobic fabric (Li et al., 2021), can be used for synthesizing membrane encapsulated salt-based sorbents according to this protocols. Here lithium chloride (LiCl), as a kind of salt with the highest AWH capacity, was selected as an example, which produces the maximum amount of salt solution and the largest volume expansion during the sorption process. Other salts will produce less volume expansion than lithium chloride. The applicability of the encapsulation method could pave the road for future middle- or large- scale SAWH applications.

Lithium chloride solution preparation

© Timing: 40 min

The preparation of the sorbents requires a large amount of lithium chloride solution with different concentration (from 10 wt% to 30 wt%). The total quantity varies according to the size and weight...
of the prepared sorbents. The following procedures takes the preparation of 800 g 30 wt% lithium chloride solution as an example.

1. Weight out 240.0 g of anhydrous lithium chloride (Figure 1A) by using precision balance (Figure 1B) and transfer to a 1 L beaker.

△ CRITICAL: The weighting and transfer process must be as quick as possible to minimize water vapor sorption by anhydrous lithium chloride.

2. Add 560.0 g of deionized water to the beaker (Figure 1C) and magnetic stir (Dragon Lab, MS7-H550-Pro, details see the key resources table) to totally dissolve until the solution become transparent (Figure 1D).

△ CRITICAL: The solution is initially turbid (Figure 1E) and then gradually turn transparent. A large amount of heat will release during the dissolving process.

3. Transfer the solution to a 1 L reagent bottle, seal it tightly with a bottle cap, and label it (Figure 1F).

△ CRITICAL: To seal the solution is critical, otherwise the hygroscopic salt solution can absorb moisture and cannot be reused.
Optional: The reagent bottle is not the only choice to seal and store the lithium chloride solution. The solution can also be stored in the breaker and sealed by Parafilm containing in a breaker.

Pause point: Lithium chloride solution can be stored at ambient conditions (25°C) with carefully sealed. We still recommend a maximum storage time of 2 weeks due to its strong hygroscopicity.

### KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Lithium chloride    | Ark Pharm / Sigma-Aldrich | CAS:7447-41-8 Product Number for Ark Pharm: AK323906-500g Product Number for Sigma-Aldrich: 31046 8, ACS reagent, ≥ 99% |
| Deionized water     | N/A    | 18 MΩ      |
| Porous PTFE membrane| Jinchun Environmental Protection Tech. Co., Ltd. Changzhou, China | 0.22-10 μm, [https://detail.1688.com/offer/608912374556.html](https://detail.1688.com/offer/608912374556.html) |
| Active carbon fiber felt; 1 mm thickness | Kejing Carbon Fiber Co., Ltd. | KJF1800 |

Other

| Equipment            | Source          | Identifier |
|----------------------|-----------------|------------|
| Precision Electronic Balance (Range: 600 g / Precision 0.01 g) | ZOGGI Co., Ltd. | N/A |
| Electric Blast Drying Oven | LICHER Co., Ltd. | 101-00BS |
| Vacuum Drying Oven   | KUNTIAN Co., Ltd. | DZF-6020A |
| Magnetic Stirrer      | Dragon LAB Co., Ltd. | MS7-H550-Pro |
| 1L Beaker            | N/A             | N/A        |
| 500 mL Beaker        | N/A             | N/A        |

### STEP-BY-STEP METHOD DETAILS

**Removing the water content and the volatile impurities of ACFF matrix**

© Timing: 8–9 h

The original active carbon fiber felt (ACFF) matrix is cut and the contained impurity is removed via following steps.

1. Cut the active carbon fiber felt (ACFF) matrix with the thickness of 1 mm into 5 × 5 cm² squares and weight (Figure 2A).

   **Optional:** Any shapes and sizes are available and can be chose according to the requirements of SAWH devices (Figure 2B).

2. Place the above ACFF matrix in a clean culture dish with the diameter of 10 cm and transfer them inside an oven at 120°C (Figure 2C). The heating process need keep for 8 h to totally remove water content and impurities.

3. Take out the heated ACFF matrix and seal it inside a new 2# self-sealing bag (Figure 2D).

Pause point: These ACFF matrices can directly proceed next operation without the need to re-remove water content and impurities. To store them for a long time, matrixes with self-sealing bags need to place inside a desiccator (Figure 2E).
Immersing in the lithium chloride solution to load hygroscopic salt

**Timing:** 8–9 h

By performing the following steps, the salt solution is fully filled inside the matrix, which is a key step to reach high salt contents.

4. Place the ACFF matrix that has been removed the impurities in a 500 mL beaker containing 300 mL 30 wt% lithium chloride solution (Figures 3A and 3B). The salt solution can quickly wet the matrix within 10 s (Figure 3C).

OPTICAL: The concentration of lithium chloride solution can be varied from 10 wt% to 30 wt%, which would result in developed sorbents with different salt contents. To obtain the best performance, 30 wt% lithium chloride solution is needed to reach the maximum salt content of 80 wt%. The discussion about the effect of various salt contents can be found in (Shan et al., 2021).

**Critical:** There must be at least 3 cm height of salt solution above the ACFF matrix in order to have sufficient static pressure to drive the salt solution into the matrix.

5. Place the above beaker in a vacuum drying oven at room temperature (10°C–30°C) with the vacuum of -0.06 MPa for 8 h to remove the air trapped inside the matrix. (Figure 3D).

Optional: It is not always necessary to place them in the environment with the vacuum of -0.06 MPa for 8 h. The timing and pressure depend on the thickness and amount of the ACFF matrix. This process is to ensure the internal trapped air escaped; therefore, it is necessary to observe whether the bubble is still in the process of escaping before removing the samples out of the vacuum. The time and pressure we have demonstrated above are sufficient for the bubbles to escape when the thickness is less than 4 mm.

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**Figure 2. Pretreatment of ACFF matrix**
(A) Photo of original commercial ACFF matrix.
(B) Photo of cut-out ACFF matrix with different shapes and sizes.
(C) Placing the cut-out square ACFF matrix in the culture dish.
(D) Sealing the ACFF matrix after being heated inside a 2# self-sealing bag.
(E) Storing the ACFF matrix inside a desiccator.
Timing: 8–9 h

The following steps show the detail activation and encapsulation methods of the sorbents.

6. Cut the porous PTFE membrane with the average pore size of 10 μm into 11 × 6.5 cm² and weight (Figure 4A)

OPTICAL: Waterproof and moisture permeable PTFE membranes with different pore sizes (0.22, 0.45, 1, 3, 5, 10 μm) can also prevent the risk of solution leakage, but the membranes with pore size of 10 μm are the best choice known to the authors for obtaining the best kinetic performance among these mentioned membranes. However, for engineering applications, the membranes with pore size of 3 μm may be a better choice because of its tradeoff robustness, stability and moisture permeability.

7. Place the wetted ACFF matrix on the surface of the cut-out PTFE membrane (Figure 4B) and fold to wrap the both upper and bottom sides of the matrix (Figure 4C).

△ CRITICAL: There may be air gap between the surface of matrix and the membrane that needs to be expelled. Any gaps can adversely affect the sorption kinetics of sorbents.

Figure 3. Impregnation process
(A) The 500 mL beaker containing 300 mL 30 wt% LiCl solution.
(B) Placing the ACFF matrix into the LiCl solution.
(C) The surface of ACFF matrix is wetted after contacting the solution around 10 s.
(D) Transfer the beaker into a vacuum drying oven, and keep it lasted 8 h to make the solution completely filled with the matrix.
Optional: The steps 6 and 7 can be skipped to obtain sorbents without membrane encapsulation, named HSCC. HSCC can be used to evaluate the effect of encapsulation on the sorption performance.

8. Hang the wrapped sorbent in the oven at ambient temperature with a clamp (Figure 4D).

   △ CRITICAL: Hanging the sorbent to dry is necessary. If the composite is placed on a solid surface drying, it would result in ununiform salt distribution due to the surface contact.

   Note: Because the strong hygroscopic salts are highly corrosive, the clamps and ovens used in the drying process need the anti-corrosion treatment. A convenient method is to wrap the contact areas with Kapton high temperature tapes (Figure 4E).

9. Turn on the oven power and set the temperature at 120°C. The temperature inside the oven gradually raises from ambient temperature to 120°C.

   △ CRITICAL: The initial temperature increase process takes about 1 h. Excessive heating or placing the composite directly in the oven at 120°C will adversely affect the uniform distribution of salt, thus affecting the sorption kinetics.

10. Take down the dried composite after 8-h heating and weight the composite.
11. Seal the edges of the membrane by Kapton high temperature tape (Figure 4F).
12. Obtain HSCC-E10 and store in the desiccator (Figure 4G).

**Note:** The obtained sorbent needs to be placed inside a new 2# self-sealing bag and a desiccator to prevent sorb water vapor from air.

**EXPECTED OUTCOMES**

This protocol allows for the synthesis of HSCC-E10 with ultra-high salt content of 80 wt%. More importantly, this protocol shows a membrane encapsulation method, which is suitable for salt-based composite sorbents to prevent the risk of solution leakage. The expected results will be consistent with our previous paper on Cell Reports Physical Science (Shan et al., 2021), and some criteria lists below.

**Expected visual outcomes**
The selected ACFF matrix consists of many entangled fibers (Figure 5A), and the PTFE membranes are therefore composed of a large number of nodes and fibers (Figure 5B). The gap sizes of the selected membranes were determined by the density of nodes. After impregnation, nanoscale crystallization of LiCl particles occupy the micropores on the surface of each fiber, although there were small amounts of agglomeration due to the ultra-high salt content (Figures 5C and 5D).
Expected masses of original matrices and prepared sorbents

The impregnation process is to fully fill the matrix with lithium chloride solution, so that after drying, the water in lithium chloride solution will be lost, only leaving lithium chloride salts as the hygroscopicity component. The most critical parameter in the whole process is how much hygroscopic salt is left after drying, as the salt content is critical to the water harvesting performance. Therefore, we do not record how much salt solution enters the matrix, instead of caring about how much hygroscopic salt ends up in the composite sorbents. Table 1 shows the weights of original ACFF and ACFF loaded salts after drying. The weight of membrane is not accounted here, so the salt content is higher than ~80% (ave. 84.37%). The areas of these matrices are 25 x 25 cm², and the concentration of lithium chloride solution is 30 wt%. As expected, the sorbents show nearly the same salt content in 10 repeated experiments, because each matrix has a similar capillary force to contain a basically same weight of salt solution before drying. Thus, the final difference in salt content (max. 2.16 wt %) is very small.

Expected nitrogen adsorption and desorption isotherms of ACFF and HSCC

Because of the fibers and the interstices formed by their windings, ACFF matrix shows large Brunauer-Emmett-Teller (BET) surface area (1901.95 m²/g). The texture grooves on the surface of each fiber provides pores and channels for enhancing the mass transfer of salt solution and the attachment of LiCl salt particles. As shown in Figure 6, the porous structure can be confirmed by the high nitrogen adsorption amount on the ACFF, and the type I adsorption-desorption isotherm indicated the domination of micropores. After the salt loading, these nanoscale LiCl crystals adhere on the surface of each fiber and occupied the micropores, thus, the absorbed quantity decreases much.

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Table 1. The weights of original ACFF and ACFF loaded salts after drying

| No | Mass of original ACFF (g) | Mass of dried ACFF that loaded LiCl salt without the membrane (g) | Calculated salt content (%) |
|----|--------------------------|----------------------------------------------------------|-----------------------------|
| 1  | 7.10                     | 45.76                                                   | 84.48                       |
| 2  | 7.18                     | 42.99                                                   | 83.30                       |
| 3  | 7.18                     | 43.30                                                   | 83.42                       |
| 4  | 7.01                     | 46.78                                                   | 85.01                       |
| 5  | 7.01                     | 48.22                                                   | 85.46                       |
| 6  | 6.66                     | 41.75                                                   | 84.05                       |
| 7  | 6.18                     | 40.17                                                   | 84.62                       |
| 8  | 7.05                     | 42.95                                                   | 83.59                       |
| 9  | 6.72                     | 43.85                                                   | 84.68                       |
| 10 | 6.64                     | 44.64                                                   | 85.13                       |

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Figure 6. Nitrogen adsorption and desorption isotherms of ACFF and HSCC

The low nitrogen adsorption capacity proves that LiCl crystals successfully occupied the micropores of matrix, leading to a uniform distribution of these strong hygroscopic salts. Reprinted from Cell Reports Physical Science, Volume 2, He Shan et al., High-yield solar-driven atmospheric water harvesting with ultra-high salt content composites encapsulated in porous membrane with permission from Elsevier.
**Expected dynamic water uptake performance under various relative humidity**

Due to the ultra-high salt content, HSCC-E10 shows excellent water uptake performance. The hygroscopic salt shows strong environment adaptability because of its high affinity with water vapor. To evaluate the sorption performance in different regions with various climates, three humidity conditions are selected as the simulated working conditions: 30% RH to represent the relative humidity at nighttime in arid areas, 70% RH for the typical environmental conditions in semi-humid region, and 90% RH to conform to humid regions. It shows that HSCC-E10 could harvest 3.75 g/g, 2.83 g/g and 1.47 g/g water at the RHs of 90%, 70% and 30%, respectively (Figure 7).

**Expected dynamic solar water release performance under various sunlight irradiation**

As shown in Figure 8, under practical conditions with limited heat and mass transfer, the weight variation of desorption process demonstrated water release weights of 1.69 g/g, 2.00 g/g, and 2.27 g/g under 0.6, 0.8, and 1 kW/m², respectively. Hence, most of the sorbed water can be released under natural sunlight within 6 h. Even under a weakened sunlight (0.6 kW/m²), 59 wt% of the sorbed water can be released.

**Expected cyclic sorption-desorption performance**

To demonstrate cycling stability of the sorbents, the sorption-desorption cycle of HSCC-E10 was repeated 20 times with no sign of degradation in performance shown (Figure 9), demonstrating its excellent stability and reusability. Conversely, the membrane-free composite HSCC reached its maximum sorption capacity in the first cycle. After the first cycle, the water uptake of HSCC was ~30% lower than that of HSCC-E10 due to its low salt content after the occurrence of salt solution leakage.

**LIMITATIONS**

The used PTFE membranes look white and even semitransparent (depended on pore sizes), which are the poor solar absorbers. Therefore, a selective solar absorber plate with high solar-thermal efficiency can be combined with these encapsulated sorbents to convert solar energy and heat the sorbents for further water release. We also noticed that the PTFE membranes can be covered with a thin layer of carbon nanotubes to obtain the capacity of absorbing solar energy. However, these could lead to a reduced hydrophobicity.

Furthermore, to obtain a better moisture permeability, these membranes are all without support layers, therefore, the membranes with the pore sizes of 5 μm or larger should be used carefully to prevent being tore.
Problem 1
The 12 h water uptake of the sorbent is more than 10% worse than that reported above (Figure 7; step 3 in Lithium chloride solution preparation and step 5 in Immersing in the lithium chloride solution to load hygroscopic salt).

Potential solution
The ideal salt content of HSCC-E10 sorbents is 80 ± 2 wt%, and the salt content much effect the final sorption performance, so it is important to weight the different before and after impregnation and evaluate whether impregnation process is successful. If not, please check the following two points.

• Carefully check the concentration of lithium chloride solution when impregnating salt solution. If anhydrous lithium chloride is exposed in the air for too long, this hygroscopic salt can absorb a large amount of water vapor and form lithium chloride hydrate. This can lead to the weight deviation, resulting in the reduction of the actual content of lithium chloride.
• Check the impregnation process carefully. Insufficient solution height (less than 3 cm), vacuum, placing time inside the dry oven, or overlapping of ACFF matrix during impregnation can result in less solutions into the matrix, resulting in a reduced salt content.

Figure 8. Dynamic sorption and solar-driven desorption performances of HSCC-E10 under different sunlight intensities
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Figure 9. 20 sorption-desorption cycles of HSCC-E10 to demonstrate the stability of HSCC-E10
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Problem 2
SEM images show that most fibers are covered by salt particles (Figure 5; step 5 in Immersing in the lithium chloride solution to load hygroscopic salt).

Please note that a small number of fibers may be covered with salt particles due to the ultra-high salt content, especially on the surface of sorbents, but the poor sorption performance will obtain if most fibers are buried in salt particles.

Potential solution
Note that hanging to dry is essential and the slower drying speed (1–2 h from ambient temperature to 120°C) can help the salt solution to crystallize at the nanoscale on the surface channels of each fiber.

In addition, we notice that there are several types of commercial ACFF matrixes, including hydrophilic, hydrophobic, and with different specific surface areas. In this protocol, the hydrophilic ACFF matrix with high specific surface area of ~1,800 m²/g is used.

Problem 3
The lithium chloride solution remains turbid after being stirred for a long time (steps 1–3 in Lithium chloride solution preparation).

Potential solution
It is mostly caused by too many impurities in the selected lithium chloride reagent. Please change the types or providers.

Problem 4
The sorption kinetics of obtained HSCC without membrane is consistent with our reported results, however, that of HSCC-E10 is obviously slower than above results (steps 7 and 11 in Encapsulating with porous membrane and drying of HSCC-E10).

Potential solution
We notice that there are a variety of related commercial PTFE membranes, such as the PTFE-layer membranes with PE support layer that are with better strength, but it is necessary to choose a PTFE membrane only with the porous PTFE layer to minimize the impact on sorption kinetics.

Problem 5
The salt solution after sorption process is still leaked even though the membrane has encapsulated the salt-based composite sorbent (steps 7 and 11 in Encapsulating with porous membrane and drying of HSCC-E10).

Potential solution
Please carefully check that the membrane is completely sealed with sorbents and the membrane is not cracked.

RESOURCE AVAILABILITY
Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, R.Z. Wang (rzwang@sjtu.edu.cn).

Materials availability
HSCC-Ex generated in this study will be made available on request, but we may require a payment and/or a completed materials transfer agreement if there is potential for commercial application.
Data and code availability
Any additional information required to reanalyze the data reported in this article is available from the lead contact upon request.

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AUTHOR CONTRIBUTIONS
H.S. and Q.P. conceived the experiments. H.S. and C.L. designed and optimized the protocols. R.W. revised the manuscript and guided the overall project. All the authors discussed and reviewed the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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