

Direct Air-Water Capture and Hydrogen Generation via Flowing Hygroscopic Solvents

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Abstract: *Extracting water directly from the air to produce hydrogen holds significant potential for sustainable and environmentally friendly energy production. This approach eliminates the need for water resources and reduces environmental pollution associated with traditional hydrogen production methods. It is particularly well-suited for humid environments. Currently, direct hydrogen production from air involves first capturing water using hygroscopic materials, followed by regeneration processes such as light or heat to obtain high-purity water. However, commonly used solid hygroscopic gels, despite their excellent moisture absorption properties, are limited by their inherent volume and water-holding capacity, making continuous water extraction from air and subsequent hydrogen production challenging. Here, we propose a straightforward method using a continuously flowing hygroscopic solution to achieve continuous water extraction from air for hydrogen production. We used a highly concentrated LiCl solution to capture moisture from the air, resulting in a water-enriched, lower-concentration LiCl solution. This water-enriched LiCl solution was then subjected to low-temperature membrane distillation (<333K), where water was transferred through a porous polytetrafluoroethylene (PTFE) membrane to an electrolytic cell and*

subsequently split into hydrogen and oxygen, effectively converting moisture from the air into hydrogen energy. We demonstrated and validated the method's ability to continuously extract moisture from the air and produce hydrogen for 100 hours in both alkaline electrolytic cells and proton exchange membrane (PEM) electrolytic cells. This work offers new insights into direct hydrogen production from air. Future advancements could pave the way for greener and more efficient energy production methods.

Hydrogen is a clean energy carrier with the potential to significantly reduce global dependence on fossil fuels (1). Traditional hydrogen production methods, such as natural gas reforming, are energy-intensive and result in greenhouse gas emissions (2). Producing hydrogen through water electrolysis using renewable electricity is considered a green energy production method (3-5). However, these methods require substantial amounts of purified water. A promising solution is to extract water directly from the atmosphere, eliminating the need for purified water and reducing environmental impact. This approach is particularly advantageous in humid regions rich in atmospheric water vapor, such as coastal or lakeside areas. Capturing water directly from the air for hydrogen production offers a more sustainable and environmentally friendly alternative, potentially transforming current hydrogen production practices (6). Current methods for extracting water from the air typically involve using hygroscopic materials to absorb moisture from the air (7-8). These materials are then regenerated through heating, releasing the absorbed pure water for hydrogen production. Solid hygroscopic gel materials are widely used due to their high moisture absorption capacity. Examples include poly-pyrrole chloride composite gels

(7), nanostructured hygroscopic gels (9), starch-derived hygroscopic gels (10), and chloride-based gels (11). However, the economic viability and long-term effectiveness of these hygroscopic gels in large-scale applications need further evaluation. In particular, for hydrogen production from atmospheric water, these gels must overcome challenges of continuous stability and high Faradaic efficiency during electrolysis to achieve higher water absorption and faster release, thereby improving overall system efficiency. Using liquid-based hygroscopic electrolytes, such as concentrated H_2SO_4 or KOH solutions, is a potential effective strategy for capturing moisture from the air (9). However, direct electrolysis of these electrolytes for hydrogen production poses risks like low conductivity and CO_2 absorption, making long-term stable hydrogen production a challenge (6).

Here, we propose a method to capture atmospheric water using a flow hygroscopic solvent for hydrogen production via electrolysis (Figure 1a). First, a concentrated LiCl solution captures water from the air, transforming into a water-rich, dilute LiCl solution. Next, the water-rich, dilute LiCl solution is fed into a low-temperature membrane distillation device (12-15). This device contains a porous polytetrafluoroethylene (PTFE) membrane, which blocks liquid water but allows vapor to pass through. On the opposite side of the membrane, a 7mol/L KOH solution is introduced for water electrolysis. By applying heat on the LiCl side, water is distilled from the water-rich LiCl solution into the KOH electrolyte, diluting it. Subsequently, the temperature of the LiCl solution is lowered through heat exchange, preparing it for further atmospheric water capture. During hydrogen production via electrolysis, water in the electrolyte is

consumed, and the electrolyte concentration eventually reaches equilibrium. The ability of various concentrations of lithium chloride (LiCl) solutions to absorb water from the air was tested (Figure 1b). The rate is defined as the percentage of water absorbed relative to the mass of salt. When air with 80% relative humidity is slowly bubbled into a LiCl solution, the water vapor immediately liquefies and is absorbed by the solution. As the concentration of the LiCl solution increases, the total amount of water absorbed over the same period also increases.

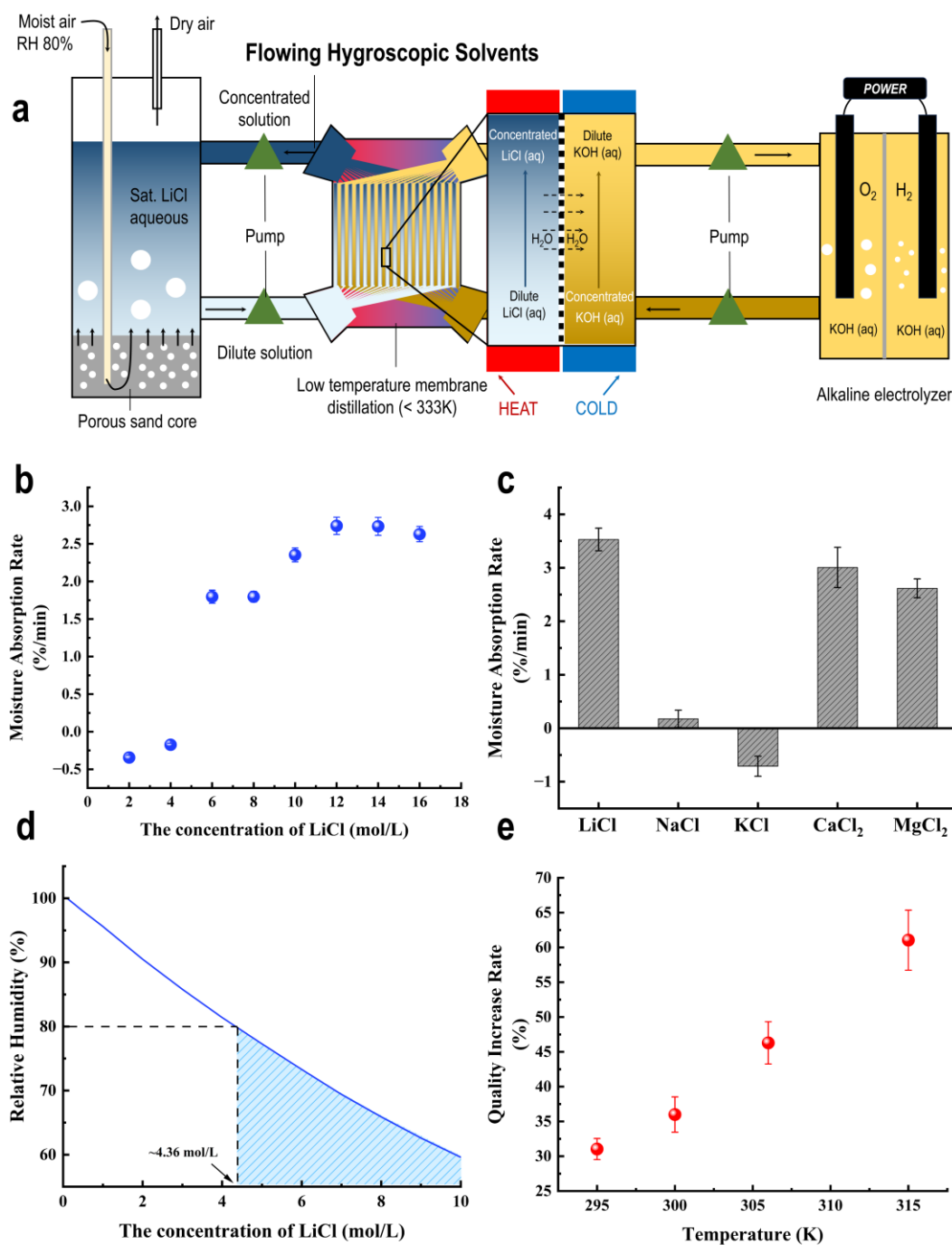


Figure 1 a. Process flow for hydrogen production by capturing moisture from air using a flowing absorbent solvent; **b.** Moisture absorption rates of different concentrations of LiCl solutions; **c.** Moisture absorption rates of different saturated chloride salts; **d.** Relative humidity of different LiCl solutions at 298K; **e.** Change in moisture absorption rate of saturated lithium salts with temperature.

Additionally, we tested different types of chloride salts. The solubility of these salts in water varies, determining their maximum dissolution limits. We compared the moisture absorption performance of different types of salts in their saturated solutions. As shown in Figure 1c, under the same airflow, temperature, relative humidity, and concentration, the LiCl solution exhibited superior hygroscopic capacity. This is due to the interaction between ions and water molecules. The hydration of ions affects the freedom of water molecules, reflecting differences in their activity coefficients and, consequently, impacting vapor pressure. Ions with smaller radii and higher charge densities interact more strongly with water, leading to reduced activity and thus lower saturation vapor pressure. Na^+ and K^+ ions have larger radii and lower charge densities, resulting in weaker interactions with water molecules. This leads to higher water activity and, consequently, higher vapor pressure, making them less effective at absorbing moisture. In contrast, Li^+ ions have smaller radii, and Ca^{2+} and Mg^{2+} ions have higher charge densities, resulting in stronger interactions with water molecules. This decreases water activity and lowers the saturation vapor pressure. This enhances the mass transfer driving force with atmospheric water vapor, demonstrating excellent water-capturing capabilities. Additionally, we observed that saturated potassium chloride solutions lose water during air purging due to their high saturation vapor pressure. We calculated the saturation vapor pressure of different concentrations of LiCl solutions at 25°C and converted it to relative humidity, as shown in Figure 1d. After absorbing water vapor from the air, the relative humidity of the outlet gas depends on the concentration of the absorbent solution. Theoretically, LiCl solutions with

concentrations greater than 4.36 mol/L are considered feasible. Higher concentrations enhance the mass transfer driving force, highlighting the superiority of using LiCl as a flowing absorbent solvent due to its high solubility. However, one points need to be clarified here: In high-concentration salt solutions, the ideal solution model under Raoult's law significantly deviates from reality. Additionally, we investigated the water absorption of sat. LiCl solution over 1 hour across varying environmental temperatures (295-315 K, typical daytime temperatures in India), as shown in Figure 1e. An increase in temperature helps raise the saturation vapor pressure of air moisture, thereby enhancing the mass transfer capability of water.

When moisture in the air is captured by LiCl, the concentration of the LiCl solution decreases. Using a low-temperature membrane distillation device, water is evaporated from the LiCl solution while the LiCl salt is retained by the membrane, leading to concentration. The operating temperature for this device is typically below 333K, achievable through heat exchange. Here, we compared three different membrane materials: porous polyvinylidene fluoride (PVDF), porous polytetrafluoroethylene (PTFE), and porous polypropylene (PP). These materials have low surface energy, making them highly hydrophobic and suitable for commercial low-temperature membrane distillation devices. Figures 2a-c present data on the distillation rates of these membranes at various temperatures and LiCl concentrations, all showing satisfactory performance. Using direct contact membrane distillation (DCMD) operations. As the concentration of LiCl increases, the water flux decreases. This is because high-concentration salt solutions have lower saturation vapor pressure, reducing the mass

transfer driving force. With increasing temperature, the water flux increases. High-temperature operations enhance water flux but also involve higher heat consumption. When absorbing air with 80% relative humidity using high-concentration LiCl solutions, the equilibrium concentration of LiCl should exceed 4 mol/L. Higher relative humidity corresponds to a lower equilibrium concentration. Under the same conditions, low-temperature membrane distillation achieves greater flux. We emphasize that the advantage of using LiCl solutions lies in their superior moisture absorption capacity and higher solubility, preventing membrane pore blockage due to salt crystallization during membrane distillation. Due to the excellent chemical and thermal stability of PTFE, subsequent experiments used PTFE membranes.

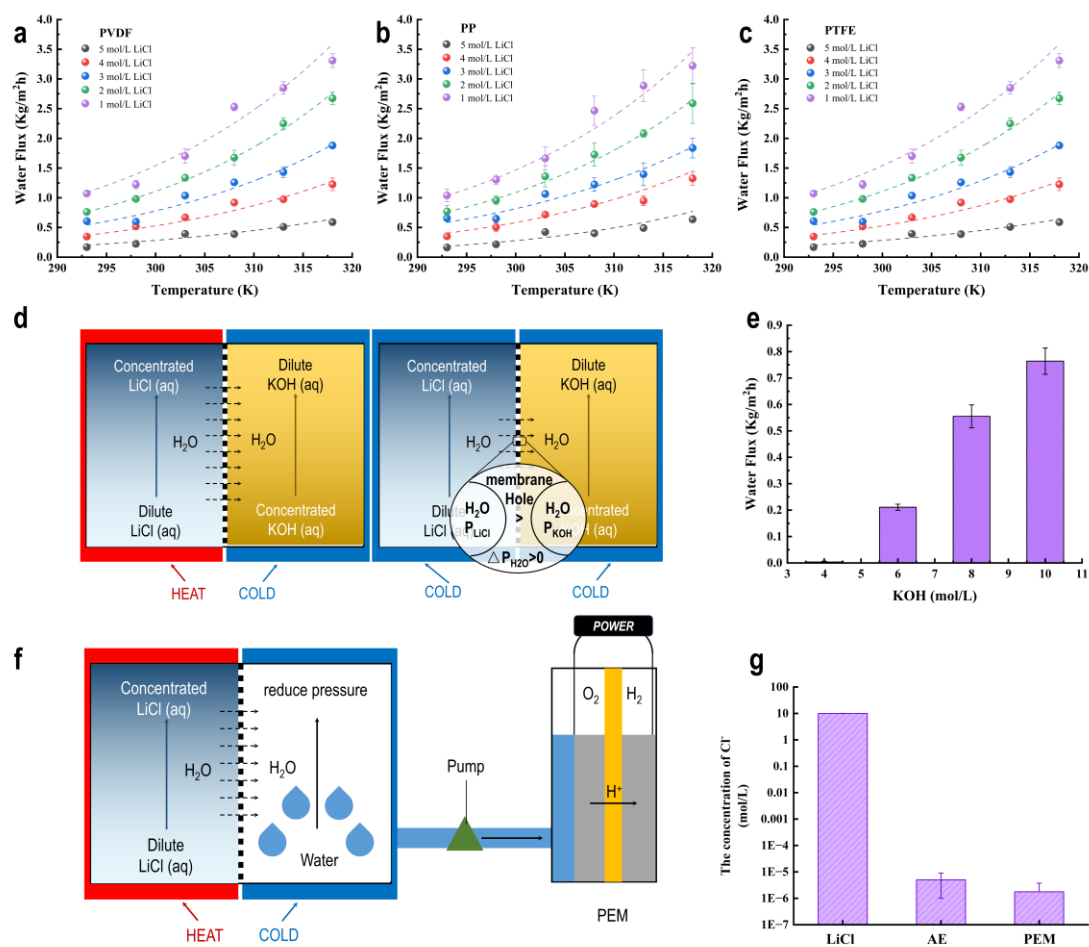


Figure 2 a-c. Water flux versus temperature curves for direct contact membrane distillation using three different membrane materials (a: PVDF, b: PP, c: PTFE); d. Direct contact membrane distillation; e. Water flux versus different KOH concentrations at 298K; f. Vacuum membrane distillation for PEM; g. Cl⁻ content in different solutions.

Different electrolytic structures require distinct membrane distillation methods. For alkaline electrolyzers, which typically use a 7 mol/L KOH solution as the electrolyte, direct contact membrane distillation (DCMD) is utilized. In this method, LiCl and KOH solutions are placed on opposite sides of a porous membrane. Due to the difference in saturated vapor pressures between the two solutions at the membrane surface, water from the LiCl solution transfers to the KOH electrolyte side under ambient temperature and vapor pressure difference, as illustrated in Figure 2d. This pressure difference persists even at 298K. As water is absorbed by the KOH solution, its concentration decreases until thermodynamic equilibrium is reached and water transfer ceases. The equilibrium can shift forward through thermal driving or the concentration of KOH resulting from hydrogen production via electrolysis. We tested water transfer performance at various initial KOH concentrations (Figure 2e) to validate this concept. For proton exchange membrane (PEM) electrolyzers, vacuum membrane distillation (VMD) can be employed to obtain pure water for hydrogen production, as shown in Figure 2f. This setup requires reduce pressure to produce pure water for the electrolyte. This method offers high water flux We also tested the Cl⁻ content in the electrolyte under different conditions, demonstrating excellent desalination capability Figure 2g. It is important to note that low-temperature membrane distillation is

primarily used because direct electrolysis of LiCl solution results in chlorine evolution, rather than oxygen evolution from water splitting.

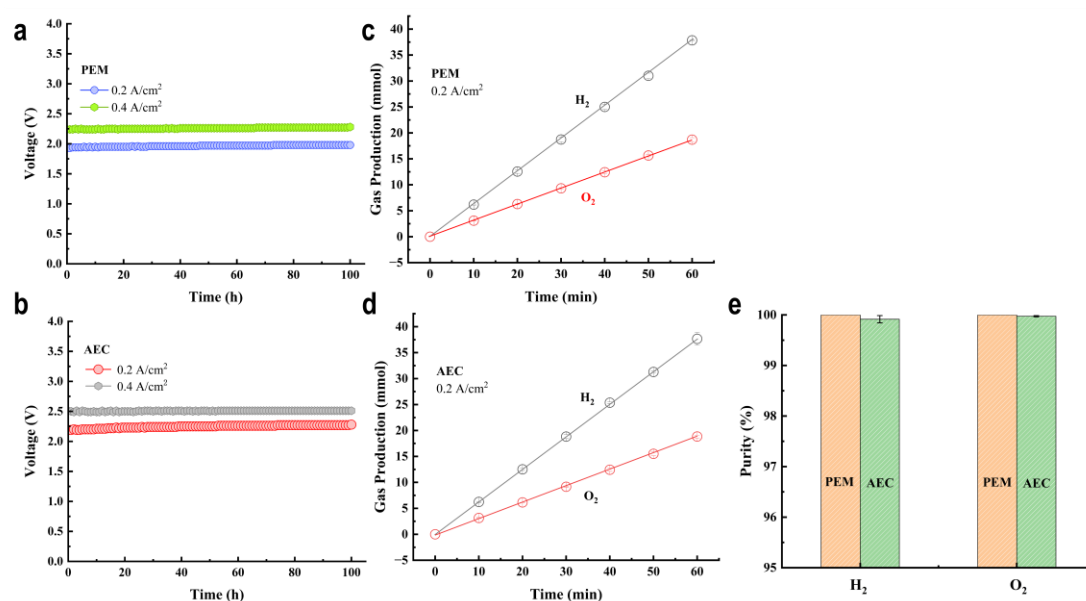


Figure 3 a. PEM electrolysis curves at different current densities; b. AEC electrolysis curves at different current densities; c. Hydrogen and oxygen production curves for PEM; d. Hydrogen and oxygen production curves for AEC; e. Purity of hydrogen and oxygen produced by PEM and AEC.

Finally, we validated the stable hydrogen production capabilities of both PEM and alkaline electrolyzers. As shown in Figures 3a and 3b, both electrolyzers demonstrated stable hydrogen production over 100 hours at various current densities. The ratio of hydrogen to oxygen produced during testing matched the stoichiometric ratio of 2:1, as illustrated in Figures 3c and 3d. Calculations indicated that the Faradaic efficiency of both electrolysis methods exceeded 99.8%. Gas chromatography was used to verify the purity of hydrogen and oxygen produced by both methods. In the PEM electrolyzer, the purity of both gases exceeded 99.9%. However, in the alkaline electrolyzer, trace

amounts of O₂, approximately 0.04-0.17%, were detected at the hydrogen outlet (Figure 3e). This reduction in hydrogen purity may be due to membrane leakage in the alkaline electrolyzer or the absorption of small amounts of oxygen from the air into the LiCl solution during membrane distillation, which then transferred dissolved oxygen into the KOH electrolyte. Nonetheless, we achieved hydrogen purity exceeding 99%. This confirms our method's excellent capability for efficiently capturing moisture from the air and producing hydrogen via electrolysis.

In this study, we propose a method that uses flow hygroscopic liquid solvents to capture water directly from the air and employ low-temperature membrane distillation to obtain pure water for electrolysis, enabling direct hydrogen production from atmospheric moisture. This method circumvents the limitations of solid gel water collection materials, which have a low absorption capacity due to their inherent volume constraints, making them unsuitable for direct hydrogen production via electrolysis. We evaluated the ability of various chloride salt solutions to capture atmospheric moisture, finding that LiCl solution demonstrated the best performance. For different types of electrolysis, namely alkaline water electrolysis and proton exchange membrane electrolysis, we proposed appropriate low-temperature membrane distillation methods, specifically DCMD and VMD. Experiments confirmed the feasibility of capturing atmospheric moisture for hydrogen production via electrolysis, demonstrating stability for up to 100 hours and achieving hydrogen purity exceeding 99%. Future advancements in electrolysis and low-temperature membrane distillation technologies promise to enhance hydrogen fuel production from air. Our work contributes to the

development of cleaner and more environmentally friendly energy production methods for the future.

Methods

All chemicals, reagents, and materials used in this study were commercially sourced. The reagents had a purity of over 99%. Three types of membrane materials were utilized: polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and polypropylene (PP). These membranes had a wall thickness of approximately 30 μm , an outer diameter of around 0.5 mm, and a length of 30 cm. The alkaline and PEM electrolyzers used in the experiments each had an effective area of 10 cm^2 . All tests were conducted with the support of laboratory facilities.

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