



Article Metal–Organic Frameworks (MOFs) Based Electrospun Nanofiber Membrane for Passive Indoor Moisture Control

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Abstract: Metal–organic frameworks (MOFs), an emerging class of porous sorbents, have become one of the most promising functional materials for indoor moisture regulation. However, the practical application of MOFs in building environments is challenging. Common shaping forms of MOFs (e.g., pellets, tablets, monoliths, granules, coating, etc.) may lead to agglomeration of MOF particles, higher usage costs, low efficiency, and material waste. Here, we report a new MOF-based electrospun nanofiber membrane with high porosity, light weight, and a large surface-area-to-volume ratio. MOF nanoparticles distributed on the fibers can fully contact moisture in the air, thus significantly enhancing MOFs' utilization and performance. The results of the moisture adsorption test show that the improved MOF membrane has significantly higher water vapor uptake than most conventional hygroscopic materials and textiles in built environments. A building energy model was established to evaluate the MOF membrane's effect on building energy consumption under different climates worldwide. The simulation results show that the MOF membrane can efficiently moderate indoor moisture fluctuation and has excellent energy-saving potential. The latent heat load reduction rate in summer can be up to 80–90% in arid/semi-arid climates and around 50% in temperate climates in a purely passive manner.

Keywords: MOF; electrospun nanofiber membranes; moisture control; building energy conservation

1. Introduction

The demand for comfort cooling is rapidly increasing globally. By 2050, space cooling (including dehumidification) is expected to become a major contributor to building energy usage, accounting for over 16% of the world's electricity consumption [1,2]. Regulating the latent (moisture) load continues to be a critical challenge for achieving energy-efficient indoor environment control [3,4]. The traditional heating, ventilation, and air conditioning (HVAC) system simultaneously achieves refrigeration and dehumidification by cooling the process air below the dew point and then reheating it to the desired supply air conditions, which is both energy-intensive and environmentally unfriendly [5,6]. Decreasing the latent load in the HVAC system is vital for improving building energy efficiency and reducing carbon dioxide emissions. A radical transformation of dehumidification technology through the use of innovative hygroscopic materials can significantly reduce the energy demand of HVAC systems, enhance indoor hygrothermal comfort, and minimize negative effects on the environment and climate. However, the moisture adsorption capacity of conventional hygroscopic materials is limited [7,8]. Traditional sorbents such as silica gel and zeolite are unsuitable for passive indoor moisture control due to their low water uptake and high energy demand for regeneration [9,10]. Therefore, developing advanced porous sorbents and proper shaping methods for passive dehumidification approaches is a promising solution to reducing building energy consumption [11,12]. Many indoor moisture control materials and technologies have been developed over the past few decades. To improve the adsorption ability of traditional construction material (e.g., gypsum board) or desiccant material (e.g., activated carbon and silica gel), hydrophilic salts, such as LiCl and CaCl₂, are



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). added to these traditional materials. Adding hygroscopic salts can significantly improve the water vapor absorption performance of the materials. At the same time, due to the isolation of porous materials, the leakage of hygroscopic salt can be effectively attenuated [13–15]. A phase change humidity control material is a combination of a phase change material and hygroscopic material. It can adjust thermal and humidity comfort simultaneously in built environments and reduce the energy consumption of the air conditioning system [16,17]. To further reduce building energy consumption, a combination of advanced novel hygroscopic and photosensitive materials becomes a promising solution for solar-driven indoor humidity control [18]. Moreover, some recent studies focus on improving the hygroscopic properties of materials by adding functional groups [19].

Recently, metal–organic frameworks (MOFs), a new group of porous sorbents, have garnered widespread attention from researchers. MOFs, composed of metal clusters and organic ligands, feature highly tunable and homogeneous microporous structures [20,21]. It has been shown that many MOFs exhibit S-shaped water uptake isotherms, which present a much higher water vapor uptake and milder regeneration conditions compared to traditional sorbents [22,23]. Therefore, MOFs have been recognized as one of the most promising sorbent materials for indoor moisture control [24,25]. Feng et al. have proved that MIL-100(Fe), with high water uptake and a low recycle temperature, has an excellent moisture buffer ability and good application prospects for built environment control [26]. Kan et al. studied the application of a new green carboxylate-based MOF MIL-160(Al) for indoor climate control. The results show that MIL-160(Al) can be regenerated under 70 °C conditions. MIL-160(Al) shows advantages in adsorption ability and regeneration conditions compared with traditional desiccants. It has more excellent application prospects in built environments than other toxic MOFs (e.g., MOFs based on Cr) [27].

While MOFs possess exceptional moisture adsorption capabilities, their practical application for built environment control is challenging. Many studies in the past have attempted to use MOF powder [28,29], MOF granules, and MOF coatings [30] for indoor moisture control. Qin et al. synthesized a new MOF-PHCM material that precisely controls indoor humidity. The practical moisture buffer value (MBV) of MOF-PHCM, in the form of a brick, is much higher than the conventional porous material. Numerical simulation results show that the MOF-PHCM material can moderate indoor moisture levels within the range of 40–65% in most climates [31]. Hou et al. developed a novel humidity pump using MIL-100(Fe). MIL-100(Fe) was coated on the surface of the fins by a silica sol water-borne binder. The result shows that the dehumidification performance of the MOFbased humidity pump is much better than the silica-gel-based one [32]. However, these existing practical shaping forms of MOFs have low material utilization and may lead to agglomeration of MOF particles, higher usage costs, and material waste. Especially in built environments, a higher usage ratio and lower price are critical for the large-scale application of MOFs. Furthermore, for the separation and purification process, it is also crucial to fix MOF particles and have good transportation kinetics through these particles. One of the methods under consideration is electrospinning technology [33].

Electrospinning is an excellent way to acquire flexible, self-support, and high-porosity MOF-based nanofiber membranes (MOF NFMs). MOF particles are fixed on nanofibers, and then these fibers can form thin non-woven membranes. Recently, the technology of electrospinning of MOFs has been widely used in energy and environmental applications [34]. Zhang et al. developed various MOF/PAN NFMs to remove fine particles in the air. Compared with pure PAN NFMs, MOF/PAN NFMs can remove PM2.5 and PM10 more efficiently and selectively because of some specific functional groups in MOF structures [35]. Efome et al. used MOF NFMs to remove lead and mercury ions in aqueous solutions. Insoluble Fe (III)- and Zr (IV)-MOF were embedded into PAN and polyvinylidene fluoride polymer. Experimental results show that water produced by the Fe-MOF/PAN can meet drinking water requirements [36]. The MOF has been used for gas storage and separation because of its tunable high porosity structure. Many recent studies proved that a MOF/polymer nanofiber combination can improve the performance of pure MOF

or pure membrane in gas storage and separation. Ren et al. embedded Uio-66 and MIL-101 into a PAN polymer matrix for H_2 storage. Even if the MOF mass fraction of the membrane is only 20%, the H_2 uptake can achieve 60% of pure MOF nanocrystals [37]. Moreover, electrospinning is also a promising technology in atmosphere water harvesting or energy-efficient dehumidification. Kim et al. demonstrated that a super water adsorbing hydrogel nanofibrous membrane could turn airborne water vapor into potable water, even in low-humidity environments [38]. Li et al. made an MIL-101(Cr)-based photothermal composite membrane. It produced 15.9 L kg^{-1} of water from air per day by a multicycle procedure [39]. Zhang et al. reported a super hygroscopic nanofibrous composite membrane for solar-driven indoor dehumidification. The desiccant layer PAN/MIL-101(Cr) LiCl exhibits a large moisture capacity and can reduce indoor humidity to a comfort zone under one-sun illumination [40]. However, a chromium MOF may cause potential health issues when it is used indoors [25]. Electrospinning can combine the advantages of the MOF and polymer nanofiber, resulting in MOF NFMs with high porosity and large surface area-to-volume ratios. MOF NFMs have low agglomeration rates, are well suited in size, and are compatible [34]. These desirable characteristics of MOF NFMs can potentially address the challenges faced with the practical application of MOF powder in indoor environments. However, little related research has been reported yet.

Herein, we fabricated a new type of MOF NFM with electrospinning technology and the impregnation method. In previous studies, MIL-100(Fe) has been proven to have outstanding moisture-regulating performance within 30–65% RH [26,41]. Additionally, its vapor adsorption performance can be further improved by impregnating LiCl solution without deteriorating the long-term stability performance [42]. PAN, the precursor of the traditional micro carbon fibers, has been widely used as the carrier for nanoparticles in electrospinning technology because of its good mechanical stability and insoluble in water. We tested the micromorphology, adsorption isotherm, and XRD to show the material characteristic of MIL-100(Fe) NFMs. The moisture adsorption capacity of this MOF NFM was also tested and compared with other common porous materials in the indoor environment. Then, we synthesized MOF@LiCl NFM by impregnating LiCl solution in MIL-100(Fe) crystals to improve the hygroscopic performance of the membrane further. Finally, a building energy consumption simulation model was built to evaluate the energy-saving potential of this MOF@LiCl NFM in different climates.

2. Materials

2.1. Preparation of MIL-100(Fe)

The synthetic procedure of MIL-100(Fe) was adopted from previous research [43,44]. In this work, MIL-100(Fe) samples were prepared without mineralizing. Firstly, the reactants $Fe(NO_3)_3 \cdot 9H_2O$ (36 mmol) and H_3BTC (24 mmol), with a molar ratio of 1:0.67, were dissolved in 36 mL of Milli-Q water. Secondly, the mixture was stirred at room temperature for 1 h and then put in an oven at 160 °C for 12 h. Thirdly, the orange solid could be gathered by centrifugation after cooling the mixture to room temperature. Fourthly, the product had to be washed with hot deionized water and hot ethanol for 3 h to remove the unreacted H_3BTC and then centrifugated. Finally, the product was put in the oven at 90 °C overnight to be dried. A picture of the synthesized MIL-100(Fe) powder is shown in Figure 1.

2.2. Preparation of MIL-100(Fe) NFM

Electrospinning technology is used to fix MOF nanoparticles on nanofibers, forming a membrane with a fluffy porous structure inside. Before electrospinning, the MOF powder should be milled to minimize particle aggregation. Secondly, 8% PAN was dissolved in Dimethylacetamide (DMAC), and then MIL-100(Fe) was added to the solution with a MOF to PAN weight ratio of 1:1, 1.25:1, 1.5:1, 1.75:1, and 2:1. The mixture was magnetically stirred at 50 °C for 48 h. The MIL-100(Fe) NFM was prepared by using the electrospinning apparatus from Linar Nanotech. The mixture was transferred into two 10 mL plastic syringes connected to a metal needle with a diameter of 0.8 mm. The flow rate of the

mixture was 0.5 mL h⁻¹, and the stable voltage was 10 kV. The plastic syringe mixture was fed into the metal needle, and then the nanofiber with MOF particles was sprayed onto a glossy paper roller. The distance between the needle and the roller was 15 cm. The ambient temperature and relative humidity were kept at 23 ± 1 °C and $46 \pm 3\%$, respectively. The membrane with a MOF/PAN ratio of 1.5:1 was selected for this study because it makes the membrane have certain mechanical properties while maximizing the MOF loading. Finally, the MIL-100(Fe) NFM with a MOF/PAN ratio of 1.5:1 was put at 50 °C under vacuum conditions and used for the following experiments. The schematic diagram of the electrospinning process is shown in Figure 2a. Figure 2b shows a simplified three-dimensional (3D) illustration of the self-assembly process of MOF nanoparticles (the orange crystals) and PAN nanofibers (the white fibers). The electrospinning apparatus is shown in Figure 2c.



Figure 1. Powder of MIL-100(Fe).



Figure 2. (a) Schematic diagram of electrospinning process; (b) 3D Illustration of the self-assembly mechanism of MOF nanoparticles and PAN nanofibers; (c) electrospinning apparatus.

2.3. Preparation of MIL-100(Fe)@LiCl NFM

To further improve the moisture adsorption sensitivity and capacity of the MOF NFM, a moisture-sensitive material such as LiCl was impregnated into MIL-100(Fe). MIL-100(Fe) was first put in LiCl solution with concentrations 0.1 mol L⁻¹, 0.15 mol L⁻¹, 0.2 mol L⁻¹, 0.25 mol L⁻¹, and 0.3 mol L⁻¹. After 30 min, the LiCl-impregnated MIL-100(Fe) was put in an oven at 105 °C for 3 h to be dried. After the moisture uptake tests and the deliquescence test, MIL-100(Fe) impregnated with 0.25 mol L⁻¹ LiCl was selected in this study. It is the optimal concentration for significantly enhancing the moisture adsorption capacity while

not causing salt deliquescence and changing the morphology of the membrane. Finally, the MIL-100(Fe)@LiCl nanofiber membrane was fabricated by electrospinning.

3. Characterization

3.1. Micromorphology and Chemical Characterization

The morphology of MIL-100(Fe) and the MOF membranes was characterized by a scanning electronic microscope (SEM, FEI Quanta 200 ESEM FEG microscope). Figure 3 shows the microstructure of MIL-100(Fe) crystals. The as-synthesized MIL-100(Fe) mainly consists of irregular cubic or stick-shaped particles. The Brunauer–Emmett–Teller (BET)-specific surface area and pore structure parameters of MIL-100(Fe) powder were measured by an Autosorb iQ-MP/XR analyzer. The surface area of MIL-100(Fe) is 1321 m² g⁻¹, the micro-pore volume is 0.63 cm³ g⁻¹, and the pore size is around 2.5–2.9 nm.



Figure 3. SEM image of MIL-100(Fe).

The SEM images of the MOF-based electrospun nanofiber membrane are shown in Figure 4. The figures show that MIL-100(Fe) nanoparticles were distributed throughout the PAN nanofibers. The nanofiber membrane has a highly nanoporous structure, which is beneficial for moisture adsorption and vapor diffusion. The BET surface area of the MIL-100(Fe) membrane is 583 m² g⁻¹, and the micro-pore volume is 0.258 cm³ g⁻¹. Moreover, the SEM images show that LiCl loading does not substantially affect the micromorphology and mechanical properties of the MOF membrane. The MIL-100(Fe)@LiCl NFM retained a similar hierarchical roughness and nanotextures as MIL-100(Fe) NFM, which fits the findings from some previous studies [40]. The BET surface area of the MIL-100(Fe)@LiCl membrane is 384.104 m² g⁻¹, and the micro-pore volume is 0.138 cm³ g⁻¹, which implies that the LiCl loading to the MOF crystals blocked some of the pores.



Figure 4. SEM images of the MOF membranes: MOF NFM (left) and MOF@LiCl NFM (right).

X-ray diffraction (XRD) patterns of as-synthesized MIL-100(Fe) are shown in Figure 5. The diffraction peaks are consistent with the reported ones [45,46]. These peaks correspond to diffraction planes that intersect the main pore window perimeter and the super cage of the MOF structure. The XRD patterns of both MOF membranes are also presented in Figure 5, which show the same characteristics peaks as synthesized MIL-100(Fe), for example, around $2\theta = 11^{\circ}$, 14.2° , and 20° . That means well-defined MOF crystals exist in both membranes. The diffraction patterns of the MIL-100(Fe) NFM and MIL-100(Fe)@LiCl NFM are closely matched to each other, revealing the amorphous structure of LiCl in MIL-100(Fe)@LiCl NFM.



Figure 5. XRD patterns of MIL-100(Fe), MIL-100(Fe) NFM, MIL-100(Fe)@LiCl NFM, and simulated MIL-100(Fe).

3.2. Hygric Properties

3.2.1. Water Vapor Sorption Isotherms

A water vapor sorption isotherm is one of the most important hygric properties of humidity control materials. The water sorption isotherms of MIL-100(Fe), MIL-100(Fe) NFM, and MIL-100(Fe)@LiCl NFM were measured by a dynamic vapor sorption instrument (DVS, Surface Measurement Systems DVS Adventure). The test results are shown in Figures 6–8, respectively. Figure 6 shows the water vapor adsorption isotherm of MIL-100(Fe). It is an S-shape isotherm (type V [47]), which rises significantly from 20% to 50% and then increases slowly over the relative humidity. Two steep adsorptions occur at RH = 25% and 40% because MIL-100(Fe) has a polymodal pore size distribution from both 2.5 nm and 2.9 nm mesopores. Figure 7 shows that the MIL-100(Fe) NFM keeps the advantage of high moisture adsorption uptake ability and the S-shape isotherm of MIL-100(Fe). Steep adsorption occurs at 30% RH, and steep desorption occurs at 45% RH. Figure 8 shows the adsorption and desorption isotherm of the MIL-100(Fe)@LiCl NFM. By loading LiCl to MIL-100(Fe), the moisture adsorption ability of the MOF membrane has been significantly improved, and the isotherm type has changed from type V to type III. The higher the relative humidity, the steeper the adsorption isotherm becomes. LiCl can significantly improve the moisture adsorption capacity of MOFs under high humidity conditions, which is beneficial for moisture control in humid climates.



Figure 6. Sorption isotherm of the MIL-100(Fe) powder.



Figure 7. Sorption isotherms of MIL-100(Fe) NFM.



Figure 8. Sorption isotherms of MIL-100(Fe)@LiCl NFM.

The equilibrium moisture content (EMC) at 85% RH of different samples was also measured. EMC₈₅ is a straightforward indicator to show and compare the moisture adsorption ability of different porous materials under high-humidity conditions. The indoor relative humidity rarely exceeds 85% for a long period of time. Before the test, the specimen was put in an oven at 105 °C until the weight no longer changed. Then, the specimen was placed at 20 $^{\circ}$ C and 85% RH until equilibrium. The EMC₈₅ was calculated as the ratio of the maximum moisture adsorption weight to the dry weight of the sample. The test results for the MIL-100(Fe), MIL-100(Fe) NFM, and MIL-100(Fe)@LiCl NFM are shown in the first part of Table 1. The EMC data of some traditional building materials (under the same test conditions: 20 °C and 85% RH) and other MOF-based materials or recent humidity control materials gathered from previous research [28,48–50] are shown in the second and third part of Table 1. The moisture adsorption ability of MOF NFMs is much higher than that of traditional hygroscopic building materials and other MOF-based materials or recent desiccant materials. In particular, the EMC $_{85}$ of the MOF@LiCl NFM reached 1.726 g g⁻¹, which is one order of magnitude larger than most conventional hygroscopic building materials, which indicates that the MOF@LiCl NFM has an excellent moisture control capacity.

Material	EMC ₈₅ (g g ⁻¹)	Ref.
MIL-100(Fe)@LiCl NFM	1.726	this work
MIL-100(Fe) powder	0.539	this work
MIL-100(Fe) NFM	0.356	this work
MIL-100(Fe)/MicroPCM	0.25	[27]
70% diatomite + 20% zeolite + 10% MIL-100 (Fe)	0.06	[48]
UiO-67-4Me-NH ₂ -38%	0.576	[49]
Plywood	0.179	[50]
Spruce	0.17	[50]
Gypsum Board	0.099	[50]
Filter paper	0.092	[50]
Cotton	0.079	[50]
Cement	0.069	[50]
Cellular concrete	0.02	[50]
Brick	0.0036	[50]

Table 1. Comparison of EMC₈₅ for different hygroscopic materials.

3.2.2. Deliquescence Test

Deliquescence is an essential factor that hinders the use of hygroscopic salts in built environments. Salt deliquescence produces salt solutions that will damage the building envelope materials. The main advantage of loading LiCl into MOFs is using the pores of MOF crystals to encapsulate hygroscopic salt, which can solve the problem of deliquescence. LiCl is dispersed in MIL-100(Fe) pores. At the beginning of water adsorption, it exists in the form of a solid crystalline hydrate, and after further adsorption of water vapor, it will form an aqueous salt solution and fill the pores of the MOF. The moisture leakage test of the MOF@LiCl NFM was carried out. The test results show that no salt solution leaks out of the MOF@LiCl NFM (when the concentration of LiCl solution is 0.25 mol/L). The leakage test confirms that it is safe to integrate the current MOF@LiCl NFM into building envelope structures.

3.2.3. Water Vapor Transfer Coefficient

The water vapor transfer coefficient is another essential property of a humidity control material. Moisture movement will be less hindered if the water vapor transfer coefficient is high. The membrane with a significant vapor transfer coefficient can rapidly adsorb and release moisture, more effectively control the ambient humidity within a relative comfort range, reduce latent heat compliance, and thus reduce the energy consumption of the air conditioning system. The water vapor transfer coefficient was measured by using the cup

method [51]. The saturated salt solution (NaCl, sodium chloride) was used to provide a constant relative humidity of 75.3 \pm 0.12% at 20 °C. The cup was placed in a climate chamber with 33% RH and 23 °C temperature. The vapor pressure difference between the inside and outside of the cup drives moisture transfer. The schematic of the cup method is shown in Figure 9.



Figure 9. Schematic diagram of the cup method.

The weight of the cup was measured regularly until the mass loss reached a steady state. The vapor transfer coefficient can be expressed as:

$$\delta = \frac{g_v \cdot d}{\Delta R H} \tag{1}$$

where g_v (kg m⁻² s⁻¹) is the moisture flow, d (m) is the thickness of the sample, and ΔRH is the relative humidity difference between two sides of the sample.

After repeated experiments, the average water vapor transfer coefficient of the membrane was obtained. It is 1.88×10^{-7} kg m⁻¹s⁻¹, which shows that the MOF NFM has a good vapor transfer ability. According to previous research, the vapor transfer coefficient of some other traditional materials and MOF materials, such as plywood, particle board, and MIL-100(Fe) are 3.92×10^{-8} kg m⁻¹s⁻¹, 3.92×10^{-8} kg m⁻¹s⁻¹, and 1.26×10^{-7} kg m⁻¹s⁻¹, respectively [31,52]. Compared with traditional materials, the MOF-based NFM's vapor transfer coefficient is an order of magnitude higher. MOF-based NFMs have a high vapor transfer ability, which is beneficial for indoor moisture control.

3.3. Cycling Performance of MOF NFM

Cycling performance is vital for using MIL-100(Fe)@LiCl NFM in built environments. Ten adsorption-desorption cycles of the MIL-100(Fe) NFM and MIL-100(Fe)@LiCl NFM were measured and are shown in Figure 10. Before the test, the MIL-100(Fe)@LiCl NFM sample was put in an oven at 105 °C until the weight no longer changed. Every time in the adsorption period, the sample was placed at 20 °C and 85% RH for 24 h and weighed. Every time in the desorption period, the sample was put in an oven at 105 °C until the weight no longer changed. The results show that after ten continuous adsorption/desorption cycles, the loss in adsorption capacity was less than 5%.



Figure 10. Cycling stability of moisture adsorption–desorption of MIL-100(Fe) NFM and MIL-100(Fe)@LiCl NFM.

4. Energy-Saving Potential

4.1. Indoor Moisture and Building Energy Simulation

The test results in Section 3 show that the MOF NFM has both high water vapor uptake and a high vapor transfer ability, which makes it promising for passive indoor moisture management. In this section, the effect of the MOF@LiCl NFM on passive indoor moisture control and its building energy-saving potential in different climates will be investigated by numerical simulations. The scientific program used for the simulation is WUFI[®] Plus. WUFI[®] Plus, a holistic model based on the hygrothermal envelope calculation model, was developed by the Fraunhofer Institute for Building Physics (IBP). In this model, sources and sinks of moisture inside a component, liquid water transport, diffusion, vapor adsorption, desorption, and thermal parameters are considered. It has been widely used in building hygrothermal analysis, and WUFI simulation accuracy for this case has been proven in our previous research. Qin et al. compared the experimental data from a series of experiments to validate moisture buffer models from the International Energy Agency (IEA) Annex 41 project [53] with the WUFI simulation result. Good agreement was found between predicted and measured values. Therefore, it is shown that the WUFI model can simulate indoor moisture buffering [31].

The following assumptions and limitations are considered in the WUFI hygrothermal building simulation:

- The air temperature is constant within each zone: the temperature and humidity are the same throughout the room, and the air is thoroughly mixed.
- Heat and moisture transfer processes through components are considered to be onedimensional. Consequently, the entire surface of each component has a constant temperature. Due to the one-dimensional approach to the component, direct interactions over the components' boundaries or inhomogeneous components in between the different materials are not considered.
- Physical material properties are not time-dependent.

In the WUFI model, the balance equation of the moisture content in the room air is defined as:

$$\frac{dC_i}{dt} = \sum_j W_{comp,j} + W_{in} + W_{Vent} + W_{HVAC}$$
(2)

where C_i is the overall moisture content of the air in the *i*th zone (kg); *t* is the time (s); $W_{comp,j}$ is the moisture flow between the inner wall surface *j* and room air (kg); W_{in} is the moisture source in the room (kg s⁻¹); W_{Vent} is the moisture flow due to ventilation (kg s⁻¹); and W_{HVAC} is the moisture flow due to the HVAC systems (kg s⁻¹).

Moisture flow is calculated with the equation:

$$W_{comp,i} = A_{\rm C} \cdot \beta \cdot \left(P_{pi} - P_{psi} \right) \tag{3}$$

where β is the water vapor transfer coefficient (kg m⁻²s⁻¹Pa⁻¹); P_{pi} is the partial water vapor pressure in the zone (Pa); and P_{psi} is the partial water vapor pressure on the component surface (Pa).

Since hygroscopic materials only affect indoor air humidity and their effect on indoor temperature can be ignored, we focus more on moisture buffering and balance in the simulations. Therefore, we will first evaluate indoor humidity fluctuations and then compare the latent load of the cases with and without the MOF@LiCl NFM. Suppose the building cases with the MOF@LiCl NFM have a lower latent heat load and minor indoor humidity fluctuations. In that case, we expect the MOF membrane to reduce energy consumption and improve indoor thermal comfort.

4.2. Test Building

The BESTEST (Building Energy Simulation Test) base case building from the IEA (International Energy Agency) ECBCS (Energy Conservation in Buildings and Community System) Annex 21 and Annex 41 was selected as the test building [11]. It is an $8 \text{ m} \times 6 \text{ m} \times 2.7 \text{ m}$ single zone room (see Figure 11). The structure layer of this building is shown in Table 2. The current study only uses the characteristics of the BESTEST case in terms of volume and surface area to calculate the moisture buffering effect of interior hygroscopic materials on the indoor relative humidity variation and the latent heat load. There are no windows on the walls. The building, only occupied from 9:00 a.m. to 5:00 p.m., is assumed to be a typical office room. We assume that three people work in the office, so the internal moisture gain during the occupied period is 300 g h^{-1} . The internal heat gain is 300 W during the occupied time. During the unoccupied period, there is no internal moisture gain. The building has a ventilation rate of 0.5 ACH (air changes per hour) throughout the occupied period. The ventilation rate during the unoccupied period depends on the climate. The indoor temperature is maintained at 25 °C during the occupied period. The permissible maximum indoor relative humidity is 65% during the occupied period. If the indoor RH is higher than 65%, the latent load will be removed by an independent dehumidification system. There is no temperature and humidity control during the unoccupied period.

Figure 11. A single office room model from the BESTEST test case.

Position (Outside to Inside)	Material	Density (kg m ⁻³)	Specific Heat Capacity (J kg ⁻¹ K ⁻¹)	$\lambda \ (W\ m^{-1}\ K^{-1})$	Thickness (m)
	Roofdeck	530	900	0.14	0.019
Roof	Fiberglass	12	840	0.04	0.112
	Plasterboard	950	840	0.16	0.01
Floor	Insulation	1	1	0.04	1.003
	Timber flooring	650	1200	0.14	0.025
Wall	Wood siding	530	900	0.14	9.00×10^{-3}
	Fiberglass	12	840	0.04	0.066
	Plasterboard	950	840	0.16	0.012

Table 2. The structure layer of the building case.

Since well-insulated modern buildings are often equipped with vapor barriers and are virtually impervious to water, vapor diffusion through building envelopes is ignored in the simulation. All internal and external wall surfaces are assumed to be covered with steel sheets where no vapor diffusion/transfer is possible. For the cases with humidity control materials, a 16.2 m² wall curtain/tapestry made by MOF@LiCl NFM (thickness of 0.015 m) is hung on the west internal wall, which is the only moisture buffer material indoors.

The numerical simulation aims to evaluate the performance of the MOF curtain/tapestry on the passive regulation of internal humidity conditions, which means there is no mechanical system to regenerate the MOF@LiCl NFM. Three typical climates/cities worldwide were selected for the simulation cases. They are Phoenix (hot desert climate), Madrid (Mediterranean climate), and Paris (temperate maritime climate). For dry and semi-arid climates, the ventilation rate during the unoccupied period is 1 ACH. The MOF NFM can be regenerated or partly regenerated by night ventilation. For temperate and mild humid climates, the ventilation rate during the unoccupied period is reduced to 0.35 ACH to prevent the MOF NFM from adsorbing moisture from the humid outdoor air in the evening. The time step for the simulation is 1 h. The latent heat load in summer and the whole year are compared.

4.3. Simulated Indoor Relative Humidity

4.3.1. Phoenix (Hot Desert Climate)

Hot desert climate areas, usually between 20° and 33° north and south latitudes, are typically found under subtropical ridges at mid-low latitudes. Phoenix is the largest American city in the hot desert climate. Figure 12 shows the simulated indoor RH for one week in July. At the crest of the RH fluctuation curves, most show significant differences between the case with the MOF@LiCl NFM and those without moisture buffering material, meaning the MOF@LiCl NFM can passively reduce the indoor RH in most of the occupied period. During the unoccupied period, 1 ACH of night ventilation brings outside dry air into the room and lowers indoor humidity. Meanwhile, the MOF@LiCl NFM that absorbed moisture during the day begins to release water until complete regeneration. Then, it will be ready for the next cycle. However, there are a few exceptions, for example, large precipitation during the unoccupied period, which may affect the regeneration of the MOF@LiCl NFM and its performance for the next day. Generally speaking, by applying the MOF@LiCl NFM, the indoor humidity of the room can be kept in the comfortable range by a purely passive method, and extra energy for dehumidification will hardly be needed.

Figure 12. Indoor relative humidity of Phoenix with and without MOF@LiCl NFM (July).

Hygroscopic materials can save building energy by adsorbing moisture and reducing latent load demand for the HVAC system during the occupied period. Therefore, it is necessary and meaningful to analyze and compare the latent energy consumptions of cases with and without the MOF@LiCl NFM. The latent load energy consumptions of cases without moisture buffering material, with a gypsum board, and with MOF@LiCl NFM in Phoenix are shown in Table 3. The simulation results show that hanging the MOF@LiCl NFM in the room can reduce the latent load by 83.7% in summer and 80.3% for the whole year. In contrast, adding a gypsum board with the same thickness can only reduce it by 17% and 12.6% in summer and the whole year, respectively. Compared with the gypsum board, the MOF@LiCl NFM works much better for latent load reduction and energy saving in Phoenix.

Phoenix	Latent Lo	oad (kWh)	Latent Load Reduction Rate	
	Summer	Whole Year	Summer	Whole Year
Cases without moisture buffering material	27.23	37.44	-	-
Cases with MOF@LiCl NFM	4.44	7.38	83.7%	80.3%
Cases with gypsum board	22.59	32.72	17%	12.6%

Table 3. Simulated energy consumption (latent load) for building cases in Phoenix.

From the results and analysis above, we find out that the MOF@LiCl NFM works very well in Phoenix. It can reduce indoor RH levels, moderate moisture fluctuation, and improve indoor hygrothermal comfort. At the same time, it can significantly reduce latent cooling demand for the air conditioning system and shows high energy-saving potential.

4.3.2. Madrid (Mediterranean Climate)

The Mediterranean climate is mainly distributed on the west coast of the continent at 30–40° north–south latitude. It includes the Mediterranean coast, California, central Chile, the southwest corner of South Africa, southwest Australia, and other places. It is characterized by dry summers and mild and humid winters. Madrid in Spain has a typical Mediterranean climate. Figure 13 shows the simulated indoor RH for one week in July. Comparing the curves with and without the MOF@LiCl NFM, it is evident that the indoor RH of the case with the MOF@LiCl NFM has a smaller variation amplitude. That means the MOF curtain/tapestry can adsorb a significant amount of moisture and then reduce indoor humidity fluctuation during the occupied period (when there are constant moisture sources in the room).

Figure 13. Indoor relative humidity of Madrid with and without MOF@LiCl NFM (July).

The latent load energy consumptions of building cases with and without the MOF@LiCl NFM and gypsum board in Madrid are shown in Table 4. In summer, using the MOF@LiCl NFM can reduce 92.8% of the latent load, which means the MOF membrane can be entirely regenerated by night ventilation on most days in the summer period. The MOF NFM works well in the dry summer in Madrid. For the whole year, 66.2% of the latent load can be reduced based on the simulation, which is lower than that in Phoenix. The main reason is the winter in Madrid is mild and humid. The high average moisture level and small day–night humidity difference in winter may affect the regeneration of the MOF NFM and thus affect the energy-saving potential for the whole year. In contrast, hanging gypsum boards with the same thickness can only reduce the latent load by 16.7% and 10.8% in summer and the whole year, respectively. Compared with the gypsum board, the MOF NFM works much better for latent load reduction and energy saving in Madrid.

Madrid	Latent Lo	oad (kWh)	Latent Load Reduction Rate	
	Summer	Whole Year	Summer	Whole Year
Cases without moisture buffering material	13.17	39.53	-	-
Cases with MOF@LiCl NFM Cases with gypsum board	0.95 10.97	13.36 35.26	92.8% 16.7%	66.2% 10.8%

Table 4. Simulated energy consumption (latent load) for building cases in Madrid.

From the result and analysis above, we can see that the MOF@LiCl NFM can regulate indoor humidity and enhance indoor environment comfort to some extent in Madrid. Moreover, it has significant energy-saving potential, especially in summer. Furthermore, the humidity regulation and energy-saving effect of using a humidity control material in a passive dehumidification system depend on the local climate.

4.3.3. Paris (Temperate Climate)

A temperate (mild humid) climate is characterized by cold winters and hot summers, significant temperature differences between winter and summer, and distinct temperature changes in the four seasons. The temperate zone is the climatic zone between the subtropics and the polar circle in climatology. One of the typical temperate climate cities is Paris. Paris is quite humid with a 78% average annual RH. In winter, the mean monthly RH can be up to 85%. Moreover, its high humidity level at night may significantly affect the regeneration

of MOF materials. Figure 14 shows the simulated indoor RH for one week in July in Paris. The MOF@LiCl NFM has a significant effect on indoor moisture regulation in Paris. It can lower the peak of indoor RH and reduce RH fluctuation.

Figure 14. Indoor relative humidity of Paris with and without MOF@LiCl NFM (July).

In Paris, the high humidity levels throughout the day make it challenging to regenerate MOF materials during the unoccupied period. Therefore, its moisture adsorption capacity during the occupied period is reduced. Using a passive approach, the MOF@LiCl NFM cannot fully function in relatively humid climates. Proper mechanical regeneration systems will be needed. The energy simulation results (see Table 5) show that in summer, 47% of latent load energy consumptions can be reduced. For the whole year, the latent load energy consumption rate is around 16.8%. In contrast, hanging gypsum boards with the same thickness can only reduce it by 7.6% and 2.8% in summer and the whole year, respectively. Compared with gypsum boards, the MOF@LiCl NFM works better for latent load reduction and energy saving in Paris.

Table 5. Simulated energy consumption (latent load) for building cases in Paris.

Paris -	Latent L	oad (kWh)	Latent Load Reduction Rate	
	Summer	Whole Year	Summer	Whole Year
Cases without moisture buffering material	25.33	76.03	-	-
Cases with MOF@LiCl NFM	13.42	63.26	47.1%	16.8%
Cases with gypsum board	23.41	73.87	7.6%	2.8%

The latent load reduction rate for both summer and the whole year in three different climates is summarized in Figure 15. The MOF@LiCl NFM shows excellent energy-saving potential in Phoenix and Madrid. The latent load reduction rate for Paris is relatively lower than for the other two.

Figure 15. Energy (latent load)-saving potential in summer (S) and for the whole year (W).

It is necessary to mention that these energy savings are achieved by a purely passive approach, which means there is no mechanical system to regenerate the MOF materials. Depending on the climate, the MOF@LiCl NFM can be regenerated or partly regenerated by night ventilation. However, a conventional desiccant, such as zeolite, does not work in this purely passive method, as zeolite never releases moisture in built environments. The regeneration temperature of zeolite is usually higher than 150 °C.

5. Conclusions

Electrospinning is a low-cost and scalable technology for preparing nanofiber membranes, and it is a promising shaping method for using MOFs in built environments. Electrospinning can achieve higher utilization of MOFs and lower costs compared with the common MOF shaping methods, such as pellets, granules, and coating. In this paper, we developed a new type of MOF-based membrane by electrospinning and first used it for indoor moisture management. MOF particles are fixed on nanofibers, and the loss rate of MOFs can be meager in using the MOF membrane. Moreover, the fluffy and porous structure inside the membrane further improved the hygroscopic performance of the material. The tests of hydric properties show that the MOF NFM has a higher moisture adsorption capacity and faster vapor transfer kinetics than most traditional building materials and textiles in built environments.

Numerical simulations have been carried out to study the effect of the MOF@LiCl NFM on indoor humidity conditions and building energy consumption in different climates. The results show that the MOF@LiCl NFM can effectively moderate indoor moisture fluctuation and significantly reduce the latent cooling load in a purely passive manner in relatively dry climates with significant day-night RH differences, such as Phoenix and the summer in Madrid. In these areas, the latent load energy-saving potential in summer can be up to 83.7–92.8%, and the latent load energy-saving potential for the whole year can reach 68.9%. The situation in humid climates is complex. The high humidity level throughout the entire day will largely affect the passive regeneration of MOF materials. However, in some mild humid climates, such as Paris, the MOF@LiCl NFM can still be partially regenerated during the unoccupied period and thus has a specific energy-saving potential (the latent load energy reduction rate is around 47.1% in summer and 16.8% for the whole year). The energy-saving potential can be significantly improved if additional regeneration methods, for example, solar heating, etc., can entirely dry the MOF@LiCl NFM. It is worth mentioning that the MOF@LiCl NFM shows much higher energy-saving potential than the gypsum board, one of the most common indoor construction materials, in different kinds of climates.

Further research will be carried out to investigate the application of the MOF@LiCl NFM in hot and humid climates, where the MOF@LiCl NFM can be integrated with a proper regeneration system and/or phase change materials [17]. Since MIL-100(Fe) has a very high water vapor uptake and low regeneration temperature (around 50–60 °C [24]), it is easy for the MIL-100(Fe)@LiCl NFM to adsorb a tremendous amount of moisture and then be regenerated by using low-grade energy (e.g., solar energy, etc.) The whole MOF@LiCl NFM system is still zero-energy consumption, as the heat for regeneration is from renewable sources.

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