

Capillary-Condensation-Dominated Moisture Sorption in Triple-Ion Cross-Linked Composite Gels for Reusable and High-Capacity Humidity Regulation

Jialin Liu

Yuqian Chen

Xiaowang Lu

Haicun Yang

yhcbobo@cczu.edu.cn

Changzhou University - Wujin Campus: Changzhou University <https://orcid.org/0000-0002-5222-9195>

Junfeng Cheng

Dong Wang

Chunlin Liu

Zheng Cao

Research Article

Keywords: Composite gel, Triple-ion synergy, Moisture absorption capacity, Cycling stability, Environmental adaptability

Posted Date: September 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10948527/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

**Capillary-Condensation-Dominated Moisture Sorption in Triple-Ion Cross-Linked Composite
Gels for Reusable and High-Capacity Humidity Regulation**

Jialin Liu^{1,3}, Yuqian Chen¹, Xiaowang Lu², Haicun Yang^{1*}, Junfeng Cheng¹, Dong Wang¹, Chunlin Liu^{1*}, Zheng Cao^{1*}

1. *Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P. R. China*

2. *School of Material Science and Engineering, Yancheng Institute of Technology, Yancheng, 224051, P. R. China*

3. *Changzhou Xingyu Automotive Lighting Systems Co., Ltd., Changzhou 213022, Jiangsu, P. R. China*

*Corresponding author: yhcobo@cczu.edu.cn; chunlin301@hotmail.com; zcao@cczu.edu.cn

ABSTRACT: A series of P(AM-co-AANa)/CaCl₂/LiCl composite gels were successfully prepared via a one-pot free radical copolymerization strategy, realizing a triple-ion synergistic moisture absorption and conduction system. FT-IR, SEM, and TG results confirmed the successful construction of a cross-linked porous network with excellent thermal stability. The integrated Ca²⁺, Li⁺, and Na⁺ ions endow the gel with distinct functional advantages: Na⁺ provides sufficient fundamental absorption sites, Li⁺ optimizes low-humidity adsorption kinetics, and Ca²⁺ strengthens network rigidity through coordination cross-linking and effectively restricts excessive gel swelling. The composite gel exhibits a typical Type III adsorption isotherm, and its moisture absorption behavior is predominantly governed by capillary condensation. The PANA30-Ca160 gel demonstrates excellent regenerability and cyclic stability, achieving complete regeneration within 24 h at 60 °C and maintaining 98.2% of its initial absorption capacity after five cycles. The optimized PANA30-Ca130-Li30 gel presents outstanding comprehensive humidity-control performance, delivering a high equilibrium absorption capacity of 2.61 g·g⁻¹ at 30 °C and 90% RH (4.7 times that of pure PAM), while retaining 0.16 g·g⁻¹ absorption capacity even under 30% low RH. The gel dehydration behavior follows non-Fickian diffusion kinetics, and the water release rate constant *k* increases significantly from 1.318 × 10⁻³ to 4.879 × 10⁻³ with increasing temperature from 30 to 70 °C. Benefiting from multi-ion synergistic regulation and structural optimization, the proposed composite gel effectively overcomes the inherent trade-offs among high absorption capacity, anti-deliqescence performance, adsorption kinetics, and cyclic stability of traditional desiccants. This work provides a promising high-performance material for advanced humidity regulation applications.

Keywords: Composite gel; Triple-ion synergy; Moisture absorption capacity; Cycling stability; Environmental adaptability

1. INTRODUCTION

Desiccants are functional materials that can selectively adsorb water vapor from ambient environments. They have been widely adopted in traditional scenarios including pharmaceutical moisture protection [1,2], food preservation [3], and industrial humidity regulation [4], and have recently been extended to emerging frontier fields such as heat exchanger dehumidification and atmospheric water harvesting [5-7]. Moisture absorption capacity, adsorption kinetics, environmental adaptability, and cycling stability serve as the core indicators for evaluating the comprehensive performance of desiccants [8]. Nevertheless, traditional desiccants suffer from inherent and irreconcilable performance trade-offs in practical applications, which severely restrict their large-scale engineering deployment. These limitations are mainly reflected in three aspects. Firstly, there exists a capacity-rate imbalance. Physically adsorbed desiccants (e.g., activated carbon, silica gel, and molecular sieves) function via micropore adsorption, with a typical moisture absorption capacity of only 30-40% of their own weight and a slow adsorption kinetic rate [9-13]. In contrast, chemically adsorbed desiccants (e.g., CaCl_2) can achieve a moisture absorption capacity close to 100% through deliquescence reactions. However, the deliquescence process tends to cause liquid leakage and subsequent equipment contamination [14,15]. Secondly, the environmental robustness is insufficient. Traditional desiccants exhibit poor environmental adaptability and significant performance degradation under extreme working conditions. At low temperatures (below $-10\text{ }^\circ\text{C}$), the microporous channels of silica gel are susceptible to freezing and structural failure, while CaCl_2 tends to crystallize and deactivate. Under low relative humidity ($\text{RH} < 30\%$), organic resin desiccants show drastically weakened moisture absorption capability and even spontaneous moisture desorption, making it impossible to sustain stable dehumidification performance [16]. Finally, the sustainability of regeneration is poor. The regeneration energy consumption of porous desiccants (e.g., molecular sieves) is extremely high. Meanwhile, inorganic desiccants based on

reversible hydration reactions (e.g., $\text{Mg}(\text{ClO}_4)_2$) require temperatures above 300 °C for effective desorption [17]. The aforementioned performance bottlenecks essentially stem from the inherent limitations of the adsorption mechanisms of different desiccants. Physical adsorption is constrained by the specific surface area and pore structure of materials, resulting in a theoretical upper limit on moisture uptake. Chemical adsorption usually involves irreversible phase transformation, which readily causes structural deterioration and poor cycling stability. Traditional polymer gels rely primarily on osmotic pressure-driven liquid water transport, exhibiting weak capture capability and low adsorption efficiency toward gaseous water vapor. Therefore, the development of novel desiccants integrating high moisture absorption capacity, fast adsorption kinetics, superior temperature-humidity tolerance, and low regeneration energy consumption can effectively address the defects of conventional materials. Such advanced desiccants hold great theoretical significance and engineering application value for precise humidity regulation in high-end scenarios, including precision medical cold-chain storage and lithium battery microenvironment management.

To overcome the performance limitations of traditional desiccants, current research efforts are mainly focused on physical composite fabrication, organic/inorganic hybrid modification, and innovative processing techniques. Despite the preliminary progress achieved, these approaches still suffer from evident drawbacks. In terms of physical composite modification, a composite desiccant fabricated by impregnating lithium chloride and silica gel into activated carbon pores delivers a water vapor adsorption capacity of $0.81 \text{ kg} \cdot \text{kg}^{-1}$ at 60% RH, which is 4.5 times that of pure activated carbon [18]. This composite design is also applicable to liquid desiccant systems [19]. Nevertheless, these composites still exhibit insufficient moisture absorption capacity and slow adsorption rates under high-humidity conditions, restricting their overall dehumidification performance. In the field of organic/inorganic hybrid gels, gas-foamed super-porous hydrogel composites exhibit prominent high-humidity adsorption performance. At 25 °C and 90% RH, pure P(AA-co-AM) porous

hydrogels and modified composites achieve maximum moisture absorption capacities of 1.03 gw/gads and 1.24 gw/gads, respectively. However, their adsorption performance deteriorates drastically under low relative humidity (20%–50% RH), limiting their applicability in low-humidity dehumidification scenarios [20]. Alternatively, a PAM/PVA/TA/(Gly/NaCl) gel system has been fabricated via acrylamide pre-polymerization and glycerol/sodium chloride solution modification. This tailored composite reduces the freezing point below $-80\text{ }^{\circ}\text{C}$, offering a feasible strategy for enhancing the low-temperature environmental adaptability of desiccants [21]. In terms of advanced preparation technologies, electrospun polyvinyl alcohol/lithium chloride composite membranes possess unique nanoarchitectures and shortened vapor diffusion pathways, endowing the materials with rapid adsorption-desorption kinetics. Desorption isotherm tests demonstrate that over 90% of the adsorbed water can be removed at mild temperatures of $40\text{--}60\text{ }^{\circ}\text{C}$, which significantly lowers regeneration energy consumption and improves recyclability [22]. Overall, although existing modification methods can separately optimize the moisture absorption capacity, low-temperature stability, or regeneration performance of desiccants, they fail to realize the coordinated and dynamic regulation of the full water vapor “capture-transport-desorption” process. Consequently, these materials cannot satisfy multi-condition and full-dimensional dehumidification requirements. In contrast, the material design strategy based on ion synergistic conduction and dynamic crosslinking networks can effectively break the one-sided performance limitations of current modification technologies, providing a promising and innovative avenue for the development of next-generation high-performance multifunctional desiccants.

To address the aforementioned inherent drawbacks of conventional desiccants, this study proposes a poly(acrylamide-sodium acrylate)/ $\text{CaCl}_2/\text{LiCl}$ composite gel ($\text{P(AM-co-AANa)/Ca}^{2+}/\text{Li}^{+}$) with a rationally designed triple synergistic mechanism. (1) Dual-network topological reinforcement via multi-scale crosslinking. The P(AM-co-AANa) copolymer constructs a covalently crosslinked rigid main network, while

Ca²⁺ ions coordinate with carboxyl groups to form a dynamic secondary network with a typical “egg-box” structure. This hierarchical topology significantly enhances the mechanical strength and effectively improves the anti-swelling and anti-collapse performance of the gel. Previous studies have demonstrated that coordination networks constructed by multivalent metal ions (e.g., Al³⁺ and Ca²⁺) can prominently strengthen the structural stability of polymer materials, verifying the feasibility and universality of metal coordination strategies for network topology optimization [23,24]. (2) Multi-ion synergistic activation realizes complementary functional advantages under diverse humidity and temperature conditions. Under low-humidity conditions (30% RH), Na⁺ acts as the primary hydration center, endowing the composite with reliable initial moisture absorption capacity. Benefiting from its low hydration entropy, Li⁺ disrupts the hydrogen-bonded ice crystal network and imparts favorable flexibility to the material at −20 °C. Meanwhile, Ca²⁺ maintains stable moisture absorption performance under high-humidity environments through competitive ion shielding effects. Existing literature has confirmed that Li⁺/Ca²⁺ binary salt systems exhibit excellent synergistic effects in regulating hydration structures and improving low-temperature tolerance, further validating the great potential of multi-ion synergistic strategies for optimizing environmental adaptability [25,26]. (3) Active gaseous water capture mechanism. The synergistic coupling of ionic hydration and moderate polymer swelling reduces the adsorption energy barrier, thereby achieving efficient capture and high-capacity adsorption of gaseous water molecules. This study systematically investigates the moisture absorption kinetics, cycling stability, and extreme environmental adaptability (high humidity and low temperature) of the composite gel [27,28]. This work aims to provide a novel strategy for the development of intelligent responsive desiccants that transcend the limitations of traditional passive adsorption materials.

2. EXPERIMENTAL SECTION

2.1. Materials

N,N'-Methylenebisacrylamide (MBA, 98%) was purchased from J&K Scientific Co., Ltd. (Beijing, China). Acrylamide (AM, AR, $\geq 99\%$), sodium acrylate (AANA, 95%) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), AR) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. Ammonium persulfate (APS, CP) was obtained from Sinopharm Group Chemical Reagent Co., Ltd. Lithium chloride (LiCl , $\geq 99\%$) was provided by Shanghai Adamas Reagent Co., Ltd.

2.2. Preparation of P(AM-co-AANA)/CaCl₂/LiCl composite hydrogel

Figure 1 illustrates the fabrication procedure of the composite gel, and **Table 1** summarizes the detailed formulations of all hydrogel samples. First, AM and AANA powders were dissolved in a certain amount of distilled water at a predetermined ratio, and the mixture was stirred at room temperature for 30 min to achieve full dissolution. Subsequently, anhydrous calcium chloride, anhydrous lithium chloride, and N,N'-methylene bisacrylamide crosslinker solution were sequentially added to the above system, followed by continuous stirring for 60 min to ensure uniform dispersion and thorough mixing of all components. Afterward, APS initiator solution was introduced, and the mixture was stirred for another 30 min to form a homogeneous prepolymer solution. The obtained prepolymer solution was quantitatively transferred into customized plastic molds using a pipette, sealed, and heated in an oven at 70 °C for 3 h to complete polymerization. The synthesized composite gels were pre-frozen at -40 °C for 48 h and then freeze-dried for 72 h in a vacuum freeze dryer. Finally, the porous P(AM-co-AANA)/CaCl₂/LiCl composite gel desiccant was successfully fabricated.

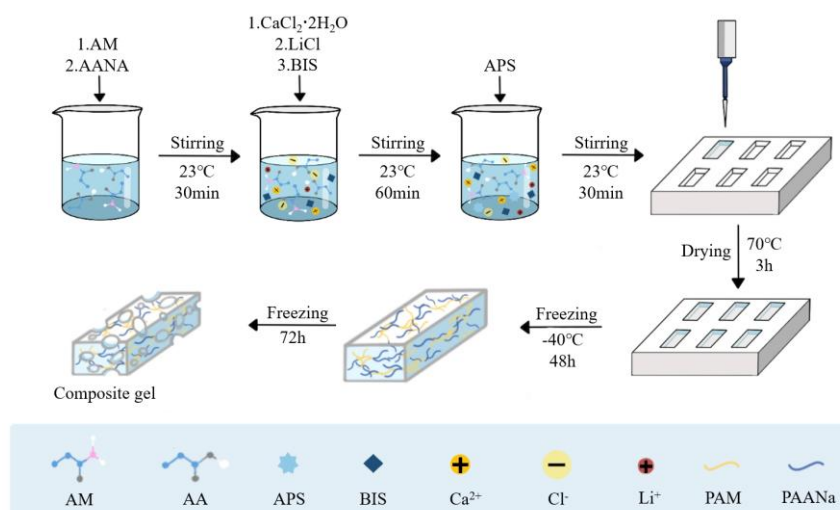


Fig. 1. Schematic diagram of preparation process of gel desiccant

Table 1 Formulation of different gel desiccants

Sample	AM (wt%)	AANa (wt%)	CaCl ₂ ·2H ₂ O (wt%)	LiCl (wt%)	MBA (wt%)	APS (wt%)
PAM	100	0	0	0	0.2	2.2
PANA10	90	10	0	0	0.2	2.2
PANA30	70	30	0	0	0.2	2.2
PANA50	50	50	0	0	0.2	2.2
PANA70	30	70	0	0	0.2	2.2
PANA10-Ca20	90	10	20	0	0.2	2.2
PANA10-Ca40	90	10	40	0	0.2	2.2
PANA10-Ca80	90	10	80	0	0.2	2.2
PANA30-Ca20	70	30	20	0	0.2	2.2
PANA30-Ca40	70	30	40	0	0.2	2.2
PANA30-Ca80	70	30	80	0	0.2	2.2
PANA30-Ca120	70	30	120	0	0.2	2.2
PANA30-Ca160	70	30	160	0	0.2	2.2
PANA50-Ca20	50	50	20	0	0.2	2.2
PANA70-Ca20	30	70	20	0	0.2	2.2
PANA70-Ca80	30	70	80	0	0.2	2.2
PANA30-Ca150-Li10	70	30	150	10	0.2	2.2
PANA30-Ca140-Li20	70	30	140	20	0.2	2.2
PANA30-Ca130-Li30	70	30	130	30	0.2	2.2

2.3. Material characterization

Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27, Germany) was employed to analyze the chemical composition of the prepared composite gels. The surface morphology, elemental distribution, and internal microstructure of the samples were characterized via scanning electron microscopy (SEM, JSM-6360LA, JEOL, Japan). A programmable constant temperature and humidity test chamber (C7-1500Pro, Weiss-Voetsch, Germany) was utilized to evaluate the moisture absorption performance under various temperature and humidity conditions. An electrothermal drying oven (TMJ-9713E35, TEMAK, China) was used to investigate the water loss behavior of the samples. Furthermore, the thermal stability of the composite gels was measured using a thermogravimetric analyzer (TG 209 F3, Netzsch, Germany).

2.4 Determine of moisture rate

The P(AM-co-AANa)/CaCl₂/LiCl composite gel desiccant was adopted for water vapor adsorption tests to determine the moisture rate (*MR*). Experiments were carried out at temperatures of 10–50 °C and relative humidity (RH) of 15%–90%. A given mass of dried desiccant sample (W_0) was weighed and placed either in an airtight glass bottle for static moisture absorption or in a ventilated constant temperature and humidity chamber for dynamic moisture absorption. After exposure to environments with different relative humidity for preset durations, the sample mass (W_t) was recorded. The moisture absorption capacity was calculated according to the following formula (1).

$$MR = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

2.5 Determine of water loss rate

The water desorption performance of moisture-saturated P(AM-co-AANa)/CaCl₂/LiCl composite gel desiccant was investigated at temperatures ranging from 30 to 70 °C. In the experiment, a pre-moistened and saturated desiccant sample with an initial mass of W_0 was weighed and placed in a constant-temperature drying oven. After heat treatment at different temperatures for various durations, the residual mass of the

sample (W_t) was recorded. The water loss rate (WLR) was calculated based on the following formula (2).

$$WLR = \frac{W_t - W_0}{W_0} \times 100\% \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Characterization of composite gel

Figure 2 displays the FTIR spectra of AM and AANa monomers, as well as PAM, PANA10, PANA30, PANA50, and PANA70 copolymers. Spectral analysis showed that both acrylamide (AM) and sodium acrylate (AANa) monomers exhibited a characteristic absorption peak at 1640 cm^{-1} , which was assigned to the stretching vibration of C=C double bonds. This peak significantly weakened or even disappeared in the spectra of the copolymer samples, confirming that the C=C double bonds of the monomers were fully involved in the polymerization and that the monomers were completely converted. The pure AM monomer presented a characteristic double peak at approximately 3400 cm^{-1} originating from the N–H stretching vibration. This characteristic signal was clearly retained in the copolymer spectra, verifying the successful incorporation of AM structural units into the copolymer molecular chains. Moreover, the intensity of the N–H stretching double peaks gradually decreased with the increasing AANa content in the copolymers. In addition, two new distinct absorption peaks appeared at 1560 and 1405 cm^{-1} in the copolymer spectra, corresponding to the antisymmetric and symmetric stretching vibrations of carboxylate groups (COO), respectively. The intensities of these two peaks increased progressively with the rise in AANa dosage, which further demonstrated the successful introduction of AANa moieties and the gradual enrichment of COO groups in the copolymer networks. Compared with the pure AANa monomer, an obvious red shift of the symmetric COO stretching vibration to 1405 cm^{-1} was observed for the copolymers. This wavenumber shift was primarily attributed to the formation of intensive intra- and intermolecular hydrogen bonding between amide groups of AM units and carboxylate groups of AANa units, which was further strengthened by

intermolecular electrostatic interactions. Overall, the above spectral variations strongly confirm the successful copolymerization of AM and AANa monomers, validating the synthesis of targeted binary copolymers.

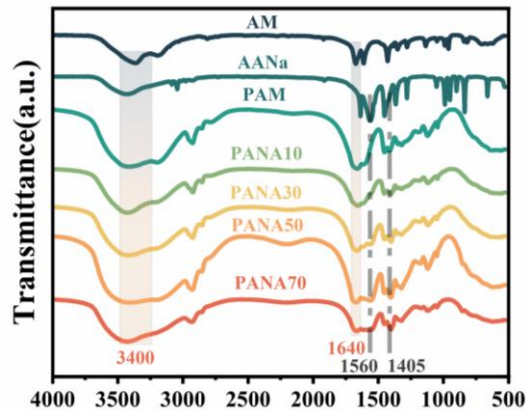


Fig. 2. FTIR spectra of AM, AANa monomers and PAM, PANA10, PANA30, PANA50 and PANA70.

Figure 3 displays the SEM micrographs of P(AM-co-AANa)/CaCl₂ composite gel desiccants with different component ratios, illustrating the evolutionary behavior of the gel microstructure. **Fig. 3(a)–(c)** present the gel micromorphology with a fixed AANa content of 30 wt% and varying CaCl₂ dosages. As the CaCl₂ dosage increases from 40 wt% to 160 wt%, the average surface pore size of the gel decreases significantly from 50 μm to 12 μm. This structural variation is governed by two synergistic mechanisms. First, the increased Ca²⁺ concentration enhances the crosslinking density between Ca²⁺ and carboxylate groups on the polymer chains, which induces the shrinkage of the polymer network and compresses the internal pore space. Second, the high-concentration CaCl₂ generates a prominent salting-out effect, which reduces the hydrophilicity of polymer chains and facilitates their aggregation in solution. This process accelerates phase separation and ultimately yields a refined and compact porous structure. **Figure 3(d)–(e)** show the micromorphological changes of gels with a constant CaCl₂ content of 80 wt% and gradiently increased AANa content. When the AANa dosage rises from 30 wt% to 70 wt%, the surface pore size is further reduced from 20 μm to 10 μm. The abundant carboxylate groups introduced by high-content AANa

provide sufficient ionic crosslinking sites, which effectively strengthen the shrinkage of the polymer network and achieve the fine modulation of porous structures. **Figure 3(f)** depicts the cross-sectional morphology of the PANA70-Ca80 gel. The gel interior exhibits a uniform layered network structure with pore sizes at the 10 μm scale, which is highly consistent with the surface pore characteristics. This confirms that the phase separation behavior regulated by ionic crosslinking density occurs uniformly throughout the three-dimensional polymer network. Overall, these results demonstrate that the precise and directional design of porous gel microstructures can be achieved by rationally tuning the component ratios of polymeric monomers and inorganic salts.

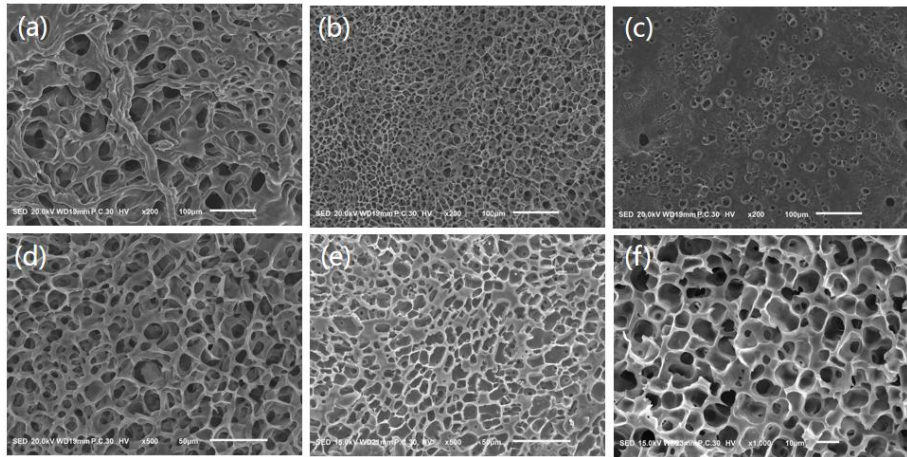


Fig. 3. Surface SEM images of (a) PANA30-Ca40, (b) PANA30-Ca80, (c) PANA30-Ca160, (d) PANA30-Ca80 and (e) PANA70-Ca80; (f) Section SEM image of PANA70-Ca80.

Figure 4(a) shows the typical surface SEM morphology of the PANA10-Ca20 composite gel, while **Fig. 4(b)** presents the corresponding EDS spectrum acquired from the selected surface microarea to characterize the elemental composition of the sample. The EDS elemental mapping in **v** demonstrates that the characteristic elements (C, N, O, Na, Cl, and Ca) are continuously and homogeneously distributed over the sample surface, without noticeable local enrichment or agglomeration. Several structural implications can be drawn from the elemental distribution results. First, the uniform dispersion of Na and Cl matches the introduction of AANa monomers and CaCl_2 salts, verifying the successful incorporation of each component

within the gel system. Second, the homogeneous distribution of Ca^{2+} directly confirms the uniform dispersion of crosslinking sites throughout the polymer network, which provides solid evidence for the formation of a well-crosslinked and homogeneous gel structure. Third, the continuous distribution of the skeleton elements (C, N, and O) is highly consistent with the uniform micromorphology of the gel at the microscale. Overall, the micrometer-scale EDS characterization confirms that all components of the PANA10-Ca20 composite gel are evenly dispersed, and no obvious macroscopic phase separation occurs, indicative of excellent structural homogeneity of the prepared gel.

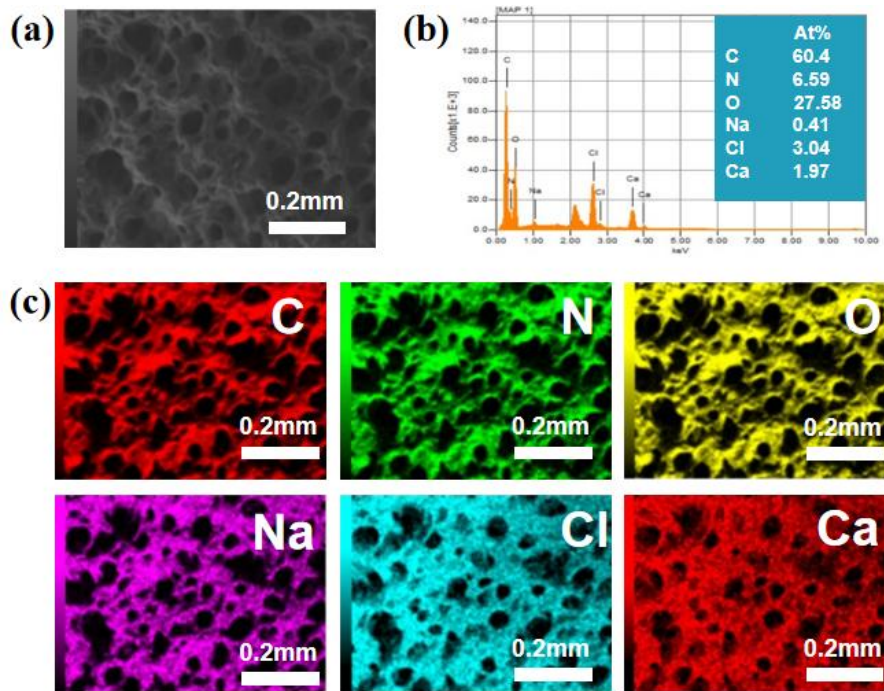


Fig. 4 (a) SEM surface morphology of the PANA10-Ca20 composite gel; (b) corresponding EDS spectrum; (c) EDS elemental distribution mappings.

3.2. Adsorption properties of composite gel system

3.2.1. Water, salt and static moisture adsorption performances of *P(AM-co-AANa)* series gels

Figure 5 presents the adsorption performance of *P(AM-co-AANa)* series gels tested at 23 °C. **Fig. 5(a)–(c)** display the dynamic adsorption curves of the gels in pure water, 5 wt% NaCl saline solution, and a 90% relative humidity (RH) atmosphere, respectively, while **Fig. 5(d)** compares the adsorption behavior of the

PANA30 gel under the three aforementioned environments. The results demonstrate that the incorporation of sodium acrylate (AANa) into polyacrylamide (PAM) hydrogels induces distinct medium-dependent adsorption behaviors, which are synergistically regulated by the dissociation degree of hydrophilic groups, polymer network stability, and environmental ionic strength. In pure water, gel swelling is predominantly driven by the osmotic pressure gradient across the gel network. As the AANa content increases from 0% to 70%, the 72 h water absorption ratio drastically rises from 27 to 575 times, confirming that anionic hydrophilic groups effectively improve the water uptake capacity of the hydrogels. Notably, polymer network stability serves as a critical limiting factor for highly hydrophilic hydrogels. The 10% AANa gel fails to maintain structural integrity and dissolves after 24 h of swelling due to insufficient crosslinking strength. By contrast, 50% and 70% AANa gels achieve a maximum swelling ratio of up to 746 times. However, after reaching the swelling peak, continuous dilution of internal Na^+ by external pure water sharply intensifies the electrostatic repulsion between carboxylate ($-\text{COO}^-$) groups, eventually destroying the three-dimensional network structure and causing structural collapse after 48 h. In comparison, pure PAM and 30% AANa gels maintain a favorable balance between osmotic driving force and network rigidity, thereby achieving stable and sustained water absorption. In the 5 wt% NaCl saline solution, high ionic strength significantly suppresses gel swelling, with the 50% AANa gel exhibiting a low 72 h salt absorption ratio of only 41 times. Such suppression originates from the dual effects of external Na^+ ions. The reduced osmotic gradient weakens the swelling driving force, and the charge shielding effect screens the electrostatic repulsion between internal $-\text{COO}^-$ groups. For the high-content 70% AANa gel, ionic shielding completely eliminates interchain electrostatic repulsion after 24 h. Consequently, hydrogen bonding and hydrophobic interactions dominate the network behavior, triggering polymer chain rearrangement and deswelling, with the absorption ratio slightly decreasing from 31 to 28 times and exhibiting typical salt-induced shrinkage characteristics. In

a 90% RH gaseous environment, water adsorption merely depends on surface hydrogen bonding without the dominant osmotic driving force required for liquid-phase swelling. Accordingly, all gels exhibit low moisture absorption ratios ranging from 0.6 to 1.6 times, with slowly and steadily increasing adsorption curves. Taking the optimal PANA30 gel as an example, its pure water absorption ratio reaches 235 times, its saline absorption ratio is 31 times, while its vapor moisture absorption ratio is merely 1.1 times, demonstrating a dramatic discrepancy in adsorption capacity across different media. In conclusion, the P(AM-co-AA_{Na}) gels exhibit distinct medium-responsive adsorption behaviors. Liquid water absorption is governed by osmotic pressure and restricted by network structural stability. Saline absorption is inhibited by ionic charge shielding, which suppresses swelling and induces network contraction. In contrast, gas-phase moisture adsorption is limited by surface adsorption and vapor diffusion kinetics, leading to a much lower adsorption capacity than that of liquid-phase swelling.

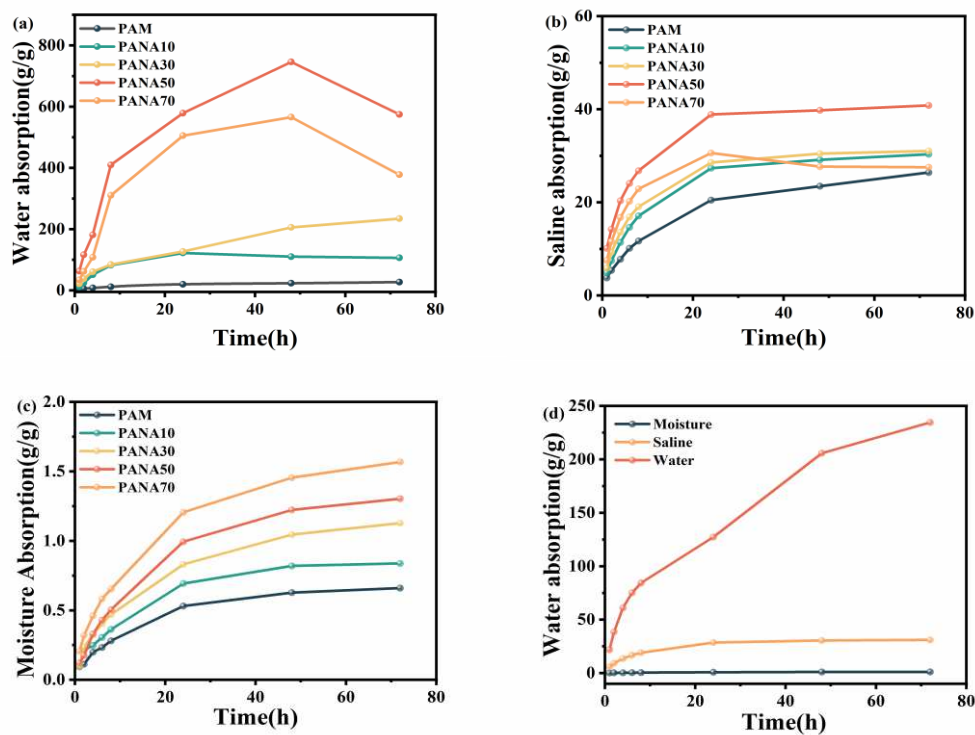


Fig. 5. (a) Water uptake curves, (b) salt uptake in 5 wt% NaCl, (c) static moisture uptake at 90% RH for P(AM-co-AA_{Na}) gels; (d) performance comparison of PANA30 under three test conditions.

3.2.1. Water, salt and static moisture adsorption performances of P(AM-co-AANa)/CaCl₂ series gels

Figure 6 presents the comprehensive performance test results of the P(AM-co-AANa)/CaCl₂ gel system. Specifically, **Figure 6(a)**, **6(b)**, and **6(c)** display the water and moisture absorption curves of the gel under pure water, 5% NaCl saline solution, and 90% relative humidity (RH) conditions, respectively. **Figure 6(d)** further compares the performance of the optimized PANA10-Ca80 system in these three different environments. As demonstrated, the pristine PANA10 hydrogel exhibits two critical limitations due to its low sodium acrylate content. First, the insufficient number of hydrophilic groups results in a low 72 h moisture absorption rate of only 0.83. Second, the fragile polymer network lacks structural stability, leading to complete dissolution of the hydrogel after 24 h of immersion in pure water. To address these drawbacks, CaCl₂ was introduced as a modifier to optimize the gel system. The experimental results confirm that CaCl₂ significantly enhances the overall performance of the gel via multiple synergistic mechanisms. On the one hand, Ca²⁺ replaces the native Na⁺ within the gel matrix and forms a stable “egg-box” ionic crosslinking structure with the –COO[–] groups on the polymer chains. This strategy constructs a dense, high-strength ionic network that effectively remedies the structural deficiencies of the original hydrogel. The reinforced ionic network greatly suppresses water-induced dissolution; no dissolution behavior is observed for all modified gels with CaCl₂ contents ranging from 20% to 80% within 24 h. Furthermore, the crosslinked network restricts excessive swelling caused by osmotic pressure differences. As the CaCl₂ dosage increases, the pure-water swelling ratio decreases sharply from 106 (20% CaCl₂) to 11 (80% CaCl₂), demonstrating greatly improved swelling controllability. On the other hand, the densely crosslinked ionic network endows the gel with superior environmental stability in high-salt conditions. The introduced crosslinking effectively buffers the intense anti-polyelectrolyte effect and stabilizes the water absorption behavior in saline media, with the saline absorption rate decreasing from 30.3 to 9.3. Notably, the optimized PANA10-Ca80 system exhibits

similar 72 h absorption values in pure water (10.9) and saline solution (9.3). This negligible difference directly verifies that the ionic crosslinking network effectively mitigates the salt sensitivity of conventional hydrogels and improves their salt tolerance. In terms of moisture absorption performance, CaCl_2 imparts a unique dynamic moisture-absorbing behavior to the gel. In the initial stage (within 24 h), ionic crosslinking induces network shrinkage and pore densification, which temporarily reduces the moisture absorption rate and capacity. In the later stage, however, the strong hydration capability of Ca^{2+} becomes dominant. Combined with the capillary force generated by the refined porous structure of the crosslinked network, the modified gel efficiently captures gaseous water molecules. Consequently, the 72 h moisture absorption rate is drastically increased from 0.83 to 2.01, corresponding to a 142% enhancement in moisture absorption performance. In summary, the ionic crosslinking network constructed by CaCl_2 not only stabilizes the polymer skeleton and improves structural durability but also optimizes moisture absorption behavior through the superior hydration ability of Ca^{2+} . This modification strategy effectively addresses the inherent defects of low-sodium-acrylate hydrogels, including poor water resistance, weak moisture absorption capacity, and high salt sensitivity. Through synergistic multiple effects, the modified gel achieves simultaneous improvements in anti-dissolution ability, moisture absorption performance, and salt tolerance, realizing a comprehensive optimization of overall application performance.

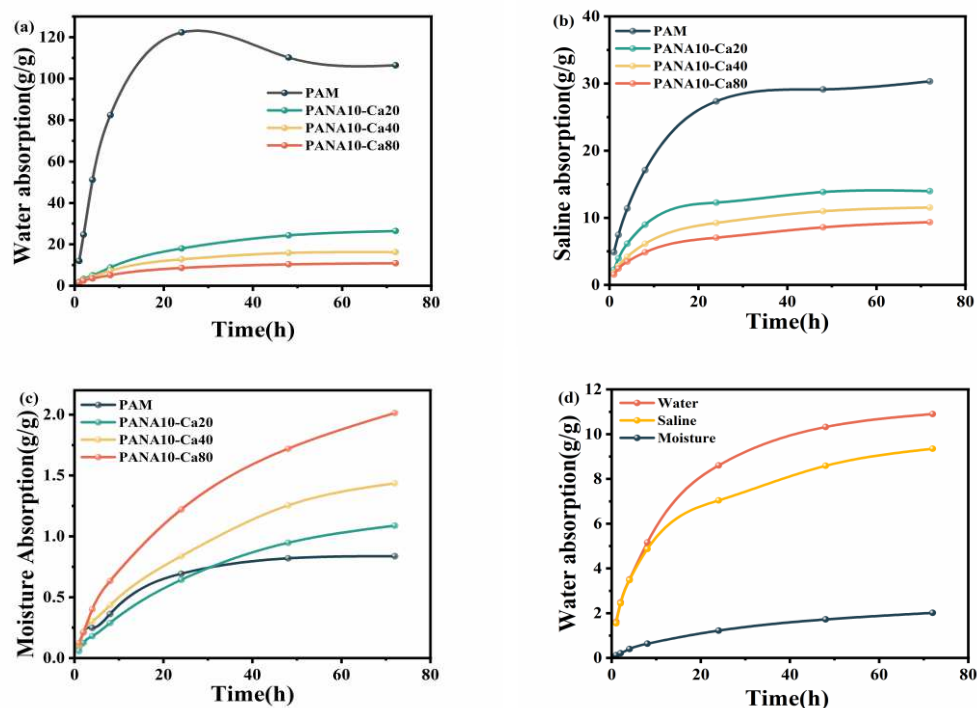


Fig. 6. (a) Water absorption, (b) saline absorption (5% NaCl), and (c) static moisture absorption (90% RH) curves of P(AM-co-AANa)/CaCl₂ gels; (d) Performance comparison of PANA10-Ca80 under the above three conditions.

Figure 7 illustrates the dynamic moisture absorption behavior of polyacrylamide/sodium polyacrylate (PAM/P AANa) composite gels with different component ratios under the conditions of 10 °C, 90% RH, and continuous air circulation. The curves exhibit complex non-monotonic variations, indicating that the moisture absorption performance of the gels is synergistically governed by the density of hydrophilic groups, the configuration of the ionic crosslinking network, and the capillary adsorption effect. With the CaCl₂ dosage fixed at 20%, **Figure 7(a)** shows that the moisture absorption capacity first increases and then declines with increasing PAANa content, rather than rising monotonically with the addition of hydrophilic components. Specifically, pure PAM presents low moisture absorption of only 0.28. As the PAANa fraction increases to 50%, the moisture absorption reaches a maximum of 1.23, whereas a further increase of PAANa to 70% reduces the value to 0.91. This tendency originates from the structural evolution of the polymer network. Appropriate PAANa content provides abundant carboxylate groups ($-\text{COO}^-$) that effectively promote water molecule adsorption. In contrast, excessive PAANa induces severe polymer chain entanglement and strong

intermolecular electrostatic repulsion, which compresses the internal porous structure and reduces the number of effective moisture-absorbing pores, ultimately deteriorating the hygroscopic capacity. **Figure 7(b)** presents the moisture absorption performance of gels with varying CaCl_2 contents (20%-160%) at a fixed PAANa fraction of 30%. The results reveal a distinct monotonic increase in moisture absorption from 0.72 to 1.71 with increasing CaCl_2 concentration. The enhancement becomes particularly prominent when the CaCl_2 dosage exceeds 80%. Such improvement is mainly attributed to the formation of interconnected dynamic Ca^{2+} ion cluster networks within the gel matrix at high salt concentrations. These ion clusters possess strong hydration capability to efficiently capture gaseous water molecules. Meanwhile, the nano-porous architecture generated by ionic crosslinking produces a capillary condensation effect, which cooperates with the ion hydration behavior to significantly enhance the dynamic moisture absorption performance. Comparative analysis of **Figure 7(a)** and **7(b)** demonstrates a synergistic optimization relationship between Ca^{2+} and P AANa contents, where their ratio plays a decisive role in regulating gel hygroscopicity. For low CaCl_2 dosages (20%-40%), the ionic crosslinking degree is limited and hydrophilic sites are insufficient. Accordingly, a relatively high P AANa proportion (50%) is required to supply adequate hydrophilic groups and compensate for the active sites consumed during crosslinking, thereby shifting the optimal moisture absorption toward a high P AANa content. In comparison, for high CaCl_2 dosages ($\geq 80\%$), the hydration effect of Ca^{2+} clusters dominates the moisture absorption process. In this case, a lower PAANa content (30%) effectively alleviates polymer chain entanglement and pore blockage, maximizing the hydration-driven hygroscopic performance and moving the optimal condition toward a low PAANa ratio. Furthermore, the gel with 40% CaCl_2 and 50% P AANa exhibits a slightly higher moisture absorption (1.09) than the 20% CaCl_2 counterpart (1.08), confirming that a moderate crosslinking density can optimize pore distribution and facilitate water molecule adsorption and transportation. Among all formulations, the PAM/30%

PAANa/160% CaCl_2 gel achieves the optimal comprehensive moisture absorption performance with a maximum value of 1.71. This superior performance benefits from a well-balanced structural design. The 30% PAANa provides sufficient hydrophilic sites while avoiding excessive chain entanglement and microchannel blockage, whereas the high-dose CaCl_2 constructs a robust and highly hydratable ionic network. This unique structure efficiently captures and immobilizes water molecules under flowing humid conditions, achieving a significant improvement in dynamic hygroscopic performance.

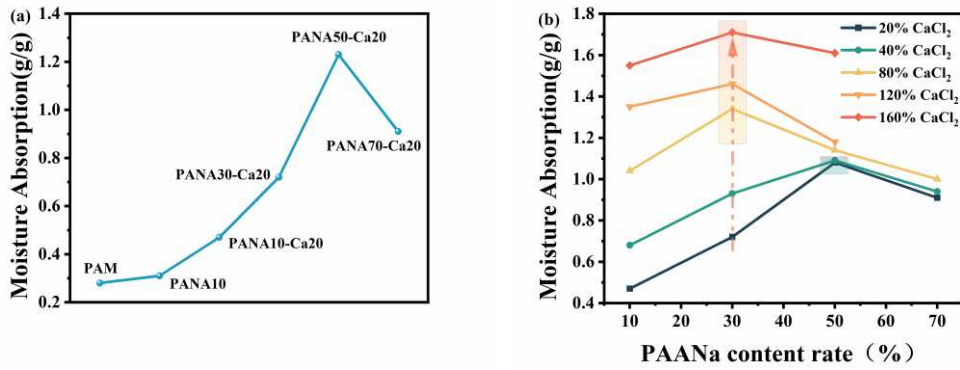


Fig. 7. (a) Effect of sodium acrylate content (0–70 wt%) on the moisture absorption of P(AM-co-AA)Na gels at a fixed CaCl_2 dosage of 20 wt% under 90% RH; (b) Dual-variable effects of sodium acrylate and CaCl_2 contents on the moisture absorption performance of P(AM-co-AA)Na/ CaCl_2 composite gels.

3.2.3. Moisture absorption and desorption behavior of P(AM-co-AA)Na/ CaCl_2 /LiCl gels

Figure 8 systematically investigates the temperature-dependent dynamic moisture absorption behavior of the PAM/30%NaPAA/160% CaCl_2 composite gel under constant temperature and humidity conditions. The hygroscopic kinetic curves in **Figure 8(a)** indicate that ambient temperature exerts a significant regulatory effect on the gel's moisture absorption performance. Within the temperature range of 10–50 °C, the 48 h moisture absorption capacity does not increase monotonically with temperature but presents a non-monotonic trend of first increasing and then decreasing. Specifically, the moisture absorption value increases from 1.71 at 10 °C to a peak of 2.21 at 30 °C, and subsequently decreases to 2.03 at 50 °C. This unique temperature response originates from the competitive and synergistic effects between the diffusion kinetics of

water molecules and the thermodynamic entropy variation of ionic hydration. During the initial stage of moisture absorption (0–4 h), a higher temperature (e.g., 50 °C) accelerates the thermal motion of water molecules and improves the initial diffusion rate of moisture. However, sustained high temperatures disrupt the stable hydrated ionic clusters constructed by Ca^{2+} within the gel matrix and weaken the dominant hydration effect, thereby impairing long-term moisture absorption stability. In comparison, 30 °C is identified as the optimal temperature for this system. At this temperature, water molecules possess sufficient kinetic energy to ensure rapid mass transfer, while favorable thermodynamic conditions are provided for the formation of stable Ca^{2+} hydration structures, enabling efficient and durable moisture absorption. Furthermore, the cyclic test results in **Figure 8(b)** verify the excellent reversible hygroscopicity and regenerability of the composite gel. After drying at 60 °C for 24 h, the adsorbed moisture is completely removed, and the gel mass fully recovers to its initial state, achieving reversible moisture absorption–desorption cycling. After five consecutive absorption–drying cycles, the gel retains 98.2% of its original hygroscopic capacity, demonstrating outstanding cyclic stability. Such excellent recyclability is attributed to the physical nature of the moisture absorption mechanism. The hygroscopic behavior is primarily governed by Ca^{2+} hydration and capillary physical adsorption, without chemical bond breaking or reconstruction. Consequently, no irreversible structural damage occurs in the polymer network, enabling the material to maintain stable and reusable hygroscopic performance.

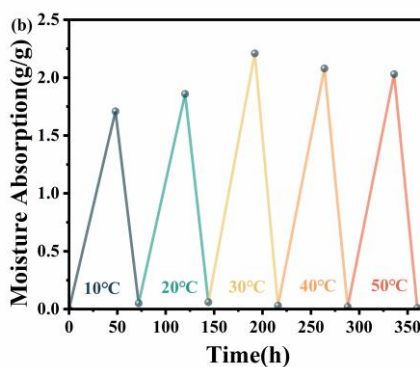
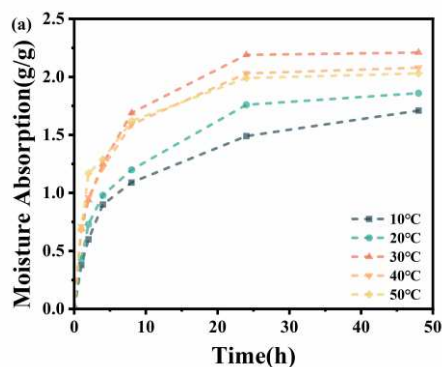


Fig. 8. (a) 48 h moisture absorption curves of PANA30-Ca160 at different temperatures; (b) Repeated moisture absorption curves of PANA30-Ca160 after drying at 60 °C for 24 h.

Figure 9 systematically investigates the dynamic moisture absorption behavior of high-salt-loaded PAM/PAANa composite desiccant gels (total salt content: 160 wt%), with a focus on the humidity responsiveness and the regulatory effect of binary $\text{CaCl}_2/\text{LiCl}$ composite salts. To further break the moisture absorption limit of single calcium-salt-modified gels, LiCl was adopted to partially substitute CaCl_2 to construct a calcium-lithium composite ionic system, thereby synergistically improving the hygroscopic performance. **Figure 9(a)** presents the macroscopic morphology of the PANA30-Ca130-Li30 composite gel before and after freeze-drying, visually demonstrating the structural changes caused by lyophilization pretreatment. **Figure 9(b)** shows the 144 h dynamic moisture absorption curves of gels with different Li^+ substitution ratios at 30 °C and 90% RH. The equilibrium moisture absorption continuously increases with increasing Li^+ content, reaching a maximum value of $2.61 \text{ g} \cdot \text{g}^{-1}$. This prominent enhancement originates from the superior intrinsic hydration capability of Li^+ , which forms a compact hydrated configuration of $[\text{Li}(\text{H}_2\text{O})_4]^+$ with an average hydration number of approximately 4.8. Such a structure enables the binding of abundant gaseous water molecules per unit volume and greatly improves the moisture absorption density [29]. In addition, all curves reach equilibrium at approximately 72 h, reflecting the high migration energy barrier of hydrated Li^+ and the prolonged dynamic equilibrium process. Benefiting from the synergistic regulation of ion species, temperature, and thermodynamic conditions, the binary $\text{Ca}^{2+}/\text{Li}^+$ system effectively overcomes the moisture absorption bottleneck of single CaCl_2 -modified gels. **Figure 9(c)** further illustrates the humidity sensitivity and critical hygroscopic threshold of the composite gels. At 30 °C, the moisture absorption capacity of all samples increases significantly as the relative humidity rises from 15% to 90% RH. Specifically, the pure CaCl_2 gel exhibits a remarkable increase in moisture uptake from $-0.13 \text{ g} \cdot \text{g}^{-1}$ to 2.21

$\text{g}\cdot\text{g}^{-1}$. A critical transition occurs at 30% RH: the pure CaCl_2 gel still undergoes slight moisture release (-0.06
 $\text{g}\cdot\text{g}^{-1}$), whereas the 30% LiCl-doped gel transitions from desorption to absorption with a positive moisture
uptake of $0.16 \text{ g}\cdot\text{g}^{-1}$. This comparison confirms that Li^+ incorporation effectively lowers the critical
hygroscopic threshold and enables efficient moisture capture under low-humidity conditions. Under high-
humidity conditions above 45% RH, the moisture absorption capacity is positively correlated with the LiCl
dosage. For instance, the moisture uptake increases from $0.42 \text{ g}\cdot\text{g}^{-1}$ for the pure CaCl_2 system to $0.70 \text{ g}\cdot\text{g}^{-1}$
for the 30% LiCl system at 60% RH. The improved low-humidity water-capturing ability of Li^+ , together
with the synergistic adsorption effect of Cl^- at high humidity, jointly enhances the hygroscopic capacity,
which conforms to the typical characteristics of Type III adsorption isotherms [30]. **Figure 9(d)** compares the
dynamic desorption behavior of fully saturated gels at 23°C and 50% RH. Distinct desorption kinetics are
observed among different ionic formulations. The pure CaCl_2 -modified gel exhibits the fastest desorption rate
and the largest water loss within 48 h, owing to the relatively weak hydration bonding of Ca^{2+} and the facile
detachment of bound water. In contrast, increasing the LiCl dosage from 10% to 30% remarkably slows the
desorption process. The strong hydration energy of Li^+ constructs dense and stable hydration layers with high
desorption energy barriers. Meanwhile, Li^+ migration rearranges the internal hydrogen-bond network of the
gel, further hindering the outward diffusion of water molecules. Notably, all groups achieve a consistent final
water loss ratio of approximately 60% after 48 h, indicating that the ambient humidity (50% RH) dominates
the thermodynamic equilibrium state of absorption–desorption cycling, while ion compositions primarily
govern the kinetic rate and equilibrium pathway. In summary, precise regulation of the $\text{CaCl}_2/\text{LiCl}$ ratio
enables synergistic optimization of the hygroscopic threshold, maximum moisture absorption capacity, and
desorption kinetics. The optimized system simultaneously achieves improved low-humidity responsiveness,
high moisture storage capacity, and controllable desorption behavior. This binary ionic modification strategy

provides a feasible and versatile route for the design of high-performance, humidity-tunable polymer desiccants for multi-scene intelligent humidity regulation.

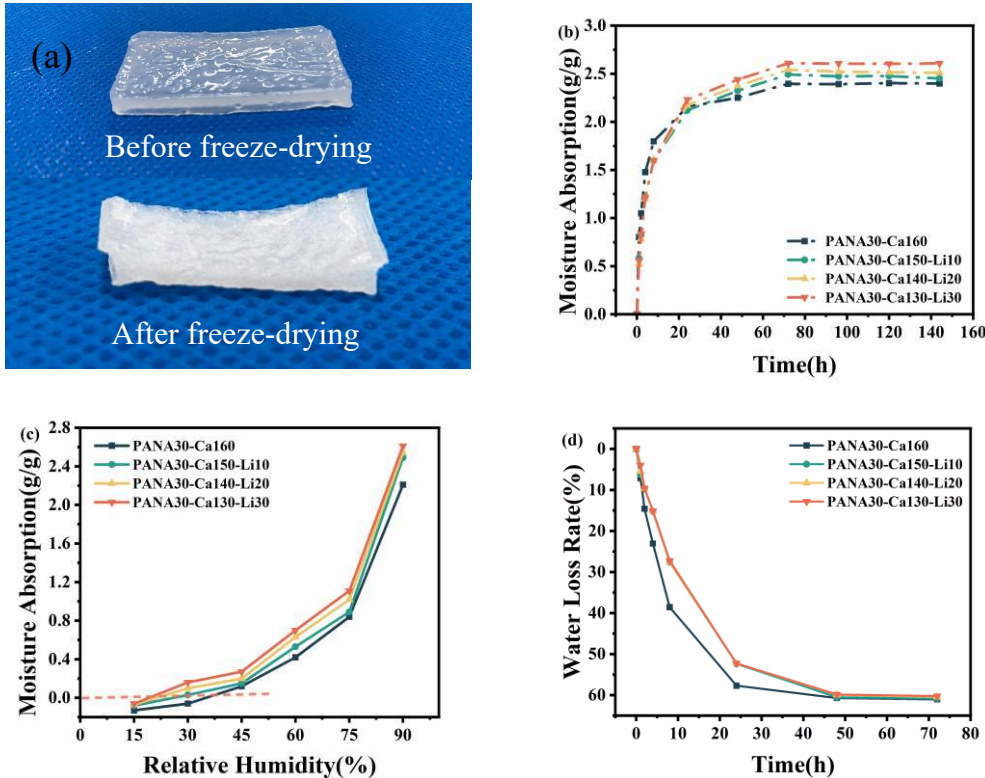


Fig. 9. (a) Digital images of the composite gel before and after lyophilization; (b) 144 h hygroscopicity at 30 °C, 90% RH; (c) 72 h hygroscopicity under different RH at 30 °C; (d) Moisture desorption profiles at 23 °C and 50% RH (gels with varied LiCl loadings).

3.3. Application of P(AM-co-AANa)/CaCl₂/LiCl gel desiccants

3.3.1 Moisture absorption and desorption properties of P(AM-co-AANa)/CaCl₂/LiCl composite gel desiccants

Figure 10(a) compares the moisture absorption performance of the self-developed composite gel desiccant and a commercial magnesium chloride-based desiccant in a sealed glass bottle environment at 30 °C and 90% RH. The commercial desiccant exhibits rapid absorption kinetics, reaching moisture absorption equilibrium within 10 d with a saturated capacity of 1.89 g·g⁻¹. In comparison, the PANA30-Ca130-Li30 composite gel presents a relatively slow hygroscopic response and requires 30 d to achieve

equilibrium. This slow kinetic behavior is attributed to its multi-level porous network structure and the long diffusion pathway of composite ions within the gel matrix. Nevertheless, benefiting from abundant hydrophilic groups on the polymer skeleton and the synergistic hydration effect of Ca^{2+} and Li^+ ions, the composite gel delivers a higher saturated moisture absorption capacity of $2.32 \text{ g} \cdot \text{g}^{-1}$, which is significantly superior to that of the commercial desiccant. **Figure 10(b)** illustrates the moisture desorption performance of the two desiccants under constant-temperature drying at 60°C . The desorption rate of both materials decreases obviously after 24 h of treatment. After 72 h of desorption, the commercial desiccant only achieves a cumulative desorption ratio of 44.53%, while the PANA30-Ca130-Li30 gel reaches a much higher desorption efficiency of 73.42%. The excellent moisture regeneration performance of the gel originates from its well-organized three-dimensional crosslinked network and uniformly distributed pore channels, which provide efficient transport pathways for water vapor diffusion and outward migration. Accordingly, the gel can rapidly release adsorbed moisture and nearly recover its initial state after desorption. These results demonstrate that the fabricated composite gel possesses superior reversible dehumidification capability and cyclic stability, showing great application potential as a reusable and intelligent humidity-control desiccant material.

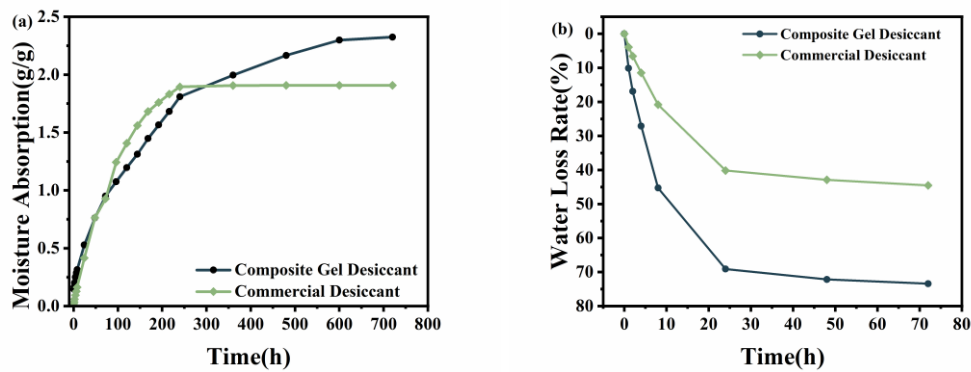


Fig. 10. (a) Moisture absorption curves of the composite gel and commercial desiccant; (b) Moisture desorption curves of the composite gel and commercial desiccant.

3.3.2. Thermal weightlessness behavior of $P(\text{AM-co-AA}^{\text{Na}})/\text{CaCl}_2/\text{LiCl}$ composite gel desiccants

TGA was performed to compare the thermal behaviors of commercial magnesium chloride desiccant and self-prepared PANA30-Ca130-Li30 composite gel desiccant. As illustrated in **Figure 11(a)**, the commercial MgCl_2 sample exhibits multiple weight loss peaks at 56.6, 93.9, 120.5, and 192.3 °C. The initial weight loss at 56.6 °C is primarily attributed to the evaporation of surface adsorbed water and the preliminary dissociation of hydrated structures. The subsequent multistage weight loss corresponds to the stepwise removal of strongly bound crystal water, accompanied by the thermal hydrolysis reaction of magnesium chloride ($\text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + 2\text{HCl}\uparrow$). In comparison, the self-prepared composite gel presents a more regular thermal decomposition profile (Figure 11(b)). The weight loss peak at 56.5 °C originates from the evaporation of physically adsorbed free water and weakly hydrogen-bonded water within the three-dimensional porous gel network. The peaks at 167.0 and 212.5 °C are assigned to the desorption of strongly bound water and the thermal degradation of the polymer backbone, respectively. When the temperature exceeds 350 °C, significant differences in residual mass are observed between the two samples. The commercial desiccant maintains a high residual rate of 52.36%, mainly consisting of thermally stable MgO and incompletely decomposed $\text{Mg}(\text{OH})_2$. In contrast, the composite gel shows a lower residual rate of 46.23%, which results from the thorough thermal decomposition of its organic–inorganic hybrid network at high temperatures. The TGA results are highly consistent with the aforementioned low-temperature desorption performance at 60 °C. In the self-made gel, most water molecules exist in the form of physical adsorption and weak hydrogen bonding with low binding energy, enabling efficient and thorough water removal under mild heating conditions and thus endowing the material with excellent regeneration and cyclic stability. However, the commercial magnesium chloride desiccant contains abundant crystal water with high binding energy. Meanwhile, thermal hydrolysis and solidification effects further hinder water desorption, resulting in low desorption efficiency and poor regenerability. The distinct thermal behaviors fundamentally

reveal the microscopic mechanism behind the superior reversible moisture absorption–desorption performance of the composite gel desiccant.

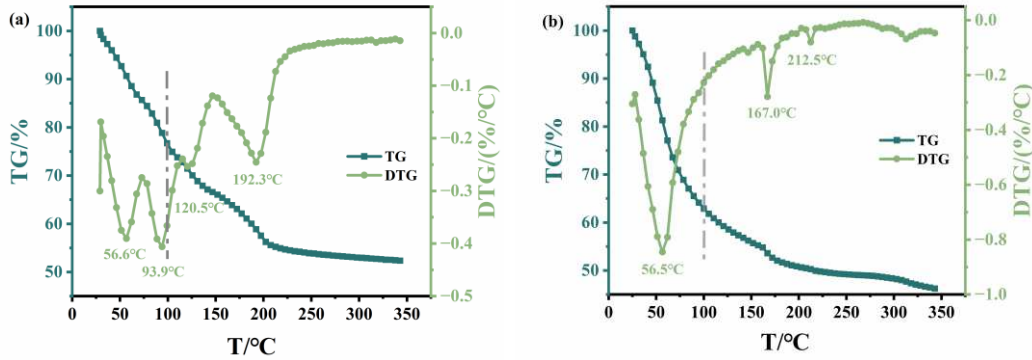


Fig. 11. (a) Thermogravimetric curve of the (a) commercial desiccant and (b) composite gel desiccant.

3.3.3. Dehumidification dynamics of $P(AM-co-AANa)/CaCl_2/LiCl$ composite gel desiccants

Figure 12(a) systematically illustrates the water release dynamics of the composite gel desiccant under different temperature conditions. In this work, the normalized mass ratio m_t/m_0 is defined as the vertical coordinate and time t as the horizontal coordinate, where m denotes the real-time mass of the gel at time t , and m_0 represents the initial saturated mass when the gel reaches moisture absorption equilibrium. The curve variations indicate that ambient temperature exerts a significant regulatory effect on the water release behavior of the gel. Specifically, increasing temperature markedly accelerates the water release rate within the first 24 h, while the water release rate gradually declines after 24 h, leading to a stabilized water release process. Combined with the existing kinetic models of gel moisture absorption and the water release kinetic characteristics presented in **Fig. 12(a)**, an empirical kinetic model tailored to describe the water release behavior of this composite gel system is established, as shown in Equation (3) [31]. In this equation, k refers to the water release rate constant, and n is the water release diffusion index, which characterizes the diffusion and transport mechanism of water molecules within the gel matrix. To obtain the kinetic parameters via linear fitting, Equation (3) is logarithmically transformed twice to derive the linear correlation expressed in

Equation (4). This transformation provides a theoretical basis for the quantitative analysis of water release kinetics and the mechanistic investigation of temperature-dependent water molecule diffusion behavior.

$$\frac{m_t}{m_0} = \exp^{-kt^n} \quad (3)$$

$$\log\left[-\ln \frac{m_t}{m_0}\right] = \log k + n \log t \quad (4)$$

The fitting curve plotted with $\log[-\ln(m_t/m_0)]$ versus $\log t$ is displayed in **Fig. 12(b)**. The excellent linear correlation obtained from linear fitting confirms that the proposed kinetic model can precisely describe the water release behavior of the composite gel. The corresponding kinetic parameters are summarized in **Table 2**. Within the temperature range of 30–70 °C, the fitted diffusion index n ranges from 0.742 to 0.813. Such values fall between 0.5 and 1.0, demonstrating that the gel dehydration process is governed by a typical non-Fickian diffusion mechanism, corresponding to a coupled mass transfer behavior involving simultaneous water diffusion and polymer chain relaxation. The non-Fickian diffusion behavior originates from the competitive coupling effect between water diffusion and polymer network relaxation inside the gel system, and the underlying mechanism is elaborated as follows. On the one hand, a mutual restriction exists between the rigid cross-linked skeleton and the dynamic relaxation of polymer chains. The “egg-box” structure formed by the complexation of Ca^{2+} and PAA_{Na} chains constructs a rigid and stable cross-linked network, which restricts water migration and network deformation, thereby tending to reduce the n value. Nevertheless, the PAM/P AANa copolymer possesses intrinsically flexible chain segments with microscale reversible motion capability. During drying, the capillary pressure generated by continuous water loss drives persistent shrinkage and structural reconstruction of the polymer network, exhibiting time-dependent chain relaxation behavior and providing a structural foundation for macromolecule-dominated relaxation mass transfer. On the other hand, the plasticizing effect of LiCl plays a critical role in regulating the mass transfer

mechanism. The incorporation of 30% LiCl endows the gel with prominent plasticizing modification. Specifically, LiCl forms continuous hydration layers among polymer chains via strong hydration interactions, which effectively decreases the glass transition temperature (T_g) of the polymer network and alleviates network vitrification induced by severe water loss in the late drying stage. This effect activates the segmental motion suppressed by dense cross-linking and remarkably enhances the contribution of polymer chain relaxation to the overall water release kinetics. Consequently, the typical non-Fickian feature ($0.5 < n < 1$) observed in this system results from the dynamic equilibrium of two competing mechanisms [32]. The rigid cross-linked network favors classical Fickian diffusion, whereas the LiCl-induced plasticization strengthens polymer chain relaxation and shifts the mass transfer toward relaxation-controlled behavior. The synergistic competition between these two mechanisms ultimately dominates the water release kinetics of the composite gel. The water release rate constant k increases significantly with rising temperature, increasing from 1.318×10^{-3} at 30 °C to 4.879×10^{-3} at 70 °C. This variation highly conforms to the classic Arrhenius law, verifying that elevated temperature effectively accelerates the gel dehydration process. The underlying dual promotion mechanism is explained as follows. Higher temperature increases the thermal kinetic energy of water molecules, facilitating their diffusion and migration within the hydrated gel network. Meanwhile, additional thermal energy activates polymer segmental motion, promotes chain relaxation and network reconstruction, and further accelerates the dehydration process. Furthermore, the diffusion index n slightly increases from 0.742 to 0.813 with increasing temperature. This trend indicates that high temperature exerts a more pronounced enhancement on polymer chain relaxation than on water diffusion. Consequently, the weight of chain relaxation in the diffusion-relaxation coupling competition increases, slightly shifting the water release behavior toward the relaxation-controlled limit ($n=1$). Nevertheless, the overall diffusion behavior remains within the typical non-Fickian regime. The systematic variation of kinetic parameters

demonstrates that the dehydration of the PANA30-Ca130-Li30 composite gel is a sophisticated dynamic process co-regulated by water diffusion and polymer network relaxation. Temperature manipulates gel dehydration kinetics through two synergistic pathways: it accelerates water release by enhancing molecular thermal diffusion and regulates the mass transfer mechanism by activating polymer segmental relaxation. These two effects jointly determine the overall dehydration kinetic characteristics of the composite gel.

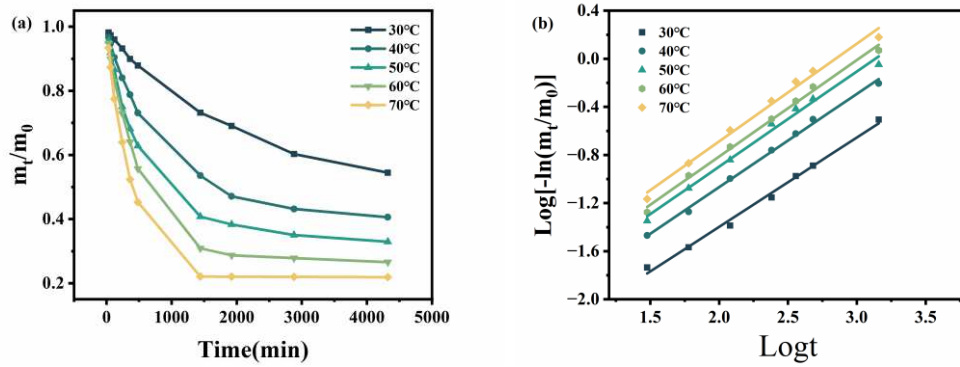


Fig. 12. (a) Water release kinetic curves of the composite gel at different temperatures; (b) kinetic fitting curves based on the established water release model at different temperatures.

Table 2 Water release kinetic parameters of the composite gel at different temperatures

NO	$T/^\circ\text{C}$	R^2	n	$\log k/\text{min}^{-1}$	$k/\times 10^{-3} \text{ min}^{-1}$
1	30	0.992	0.742	-2.881	1.318
2	40	0.996	0.775	-2.617	2.416
3	50	0.989	0.791	-2.479	3.321
4	60	0.994	0.802	-2.417	3.827
5	70	0.988	0.813	-2.312	4.879

The moisture absorption mechanism of the composite gel desiccant is illustrated in **Fig. 13**. A stable stagnant boundary layer exists between the solid surface of freeze-dried PANA30-Ca130-Li30 gel desiccant and the bulk gas phase. Water vapor in the bulk gas firstly penetrates through the boundary layer via interfacial mass transfer and diffuses onto the desiccant surface. The calcium chloride and lithium chloride loaded on the gel surface exhibit excellent hydrophilicity, which can spontaneously adsorb water vapor to form crystalline hydrates. Partial hydrates further dissolve and generate a high-concentration salt solution on

the gel surface. Driven by the osmotic pressure originating from the concentration gradient, the hydrated salt components continuously migrate and diffuse inward into the gel matrix. Meanwhile, partial water vapor achieves internal pore diffusion through the interconnected porous structure of the desiccant and penetrates deep into the material interior. These water molecules form hydrogen bonds with polar hydrophilic groups (e.g., carboxyl and hydroxyl groups) on the PAM and PAANa polymer networks, realizing the gradual inward transfer of moisture from the material surface. As the moisture absorption capacity increases, the gel matrix continuously absorbs water and swells, leading to a remarkable increase in macroscopic volume. In this process, the three-dimensional network skeleton of polymer macromolecules and the ionic cross-linking structure between calcium ions and carboxyl groups effectively restrict excessive gel swelling and prevent unlimited structural deformation. Ultimately, the gel system reaches a stable swelling equilibrium state and achieves dynamic moisture absorption balance.

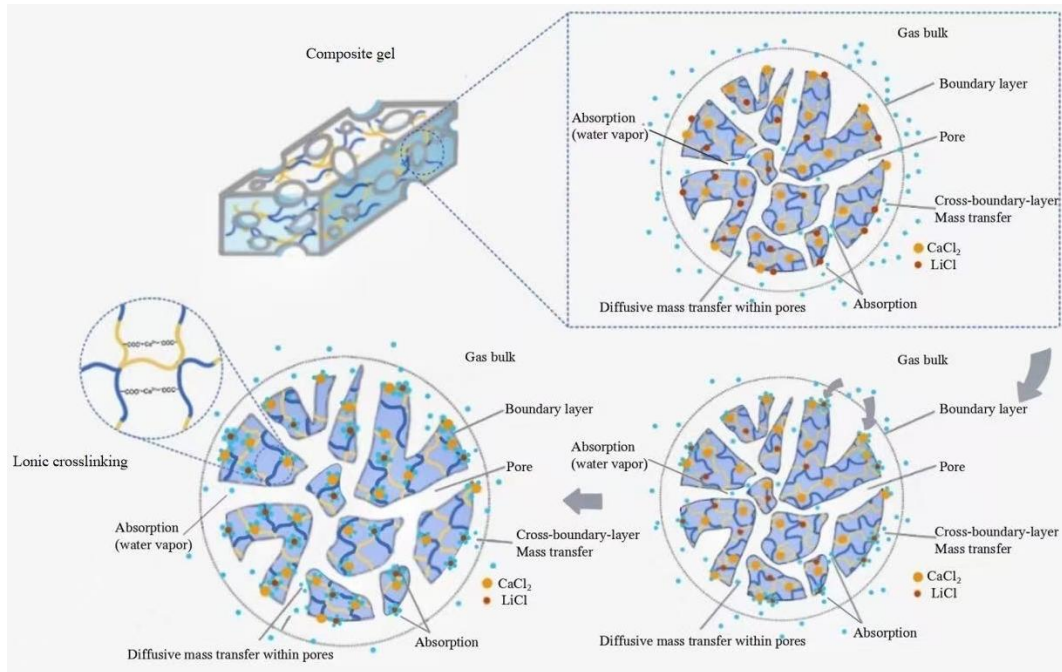


Fig. 13. Schematic diagram of moisture absorption mechanism of the gel desiccant

4. CONCLUSIONS

In this study, a P(AM-co-AANa)/CaCl₂/LiCl composite gel desiccant with synergistic sodium/lithium/calcium ion conduction and moisture absorption functions was successfully fabricated via a one-pot free radical copolymerization method. The optimal component ratio was determined through systematic formula optimization. Structural characterization verified the successful construction of a cross-linked copolymer network with interconnected porous structures and excellent thermal stability. A triple-ion synergistic mechanism was clarified: Na⁺ provides fundamental moisture absorption sites, LiCl improves the adsorption kinetics under low-humidity conditions, and Ca²⁺ enhances network rigidity and suppresses excessive swelling via coordination cross-linking. The gel follows a Type III isotherm, and its moisture absorption behavior is dominated by capillary condensation. Performance tests demonstrated the distinct advantages of different gel formulations. The PANA30-Ca160 sample exhibits outstanding structural stability, achieving full regeneration within 24 h at 60 °C and retaining 98.2% of its initial absorption capacity after five adsorption–desorption cycles. The optimized PANA30-Ca130-Li30 gel delivers excellent humidity adaptability, with a high equilibrium moisture absorption capacity of 2.61 g·g⁻¹ at 30 °C and 90% RH (4.7 times that of pure PAM), and maintains a valid absorption capacity of 0.16 g·g⁻¹ even under 30% low RH. In practical application tests, although the porous structure and long ion transport pathway extend its equilibrium time to 30 days, the PANA30-Ca130-Li30 gel achieves a high saturated absorption capacity of 2.32 g·g⁻¹, which is superior to commercial magnesium chloride desiccant (1.89 g·g⁻¹, 10 days to equilibrium) under identical conditions. Water release kinetic results confirm that the gel dehydration follows a typical non-Fickian diffusion mechanism, controlled by the coupling of water molecular diffusion and polymer chain relaxation. As the temperature increases from 30 to 70 °C, the water release rate constant *k* increases significantly from 1.318×10⁻³ to 4.879×10⁻³, indicating that elevated temperature accelerates water diffusion and network reconstruction to promote dehydration. In summary, the synergistic multi-ion design and

structural optimization effectively improve the gel's moisture absorption capacity, humidity adaptability, deliquescence resistance, and cycling stability. This work provides a feasible experimental basis and technical strategy for the development of high-performance gel-based humidity-control materials.

Acknowledgements

This project is supported by the National Natural Science Foundation of China (Grant No. 21704008, 21644002). Further financial support for this project provided by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), and the Postgraduate Research & Practice Innovation Program of Jiangsu Province is also gratefully acknowledged (SJCX22_1329).

Authors' Contributions

Jialin Liu: Conceptualization, Formal analysis, Methodology, Investigation, Data curation, Writing-original draft. **Yuqian Chen:** Investigation, Formal analysis, Validation. **Xiaowang Lu:** Formal analysis, Validation. **Haicun Yang:** Investigation, Writing-review & editing, Data curation. **Junfeng Cheng:** Writing-review & editing. **Dong Wang:** Writing-review & editing. **Chunlin Liu:** Writing-review & editing, Resources. **Zheng cao:** Supervision, Writing-review & editing, Project fouding.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Ethical approval This article does not contain any studies involving human or animal subjects.

Consent for publication All authors agreed to publish this research article.

Competing interests The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

References

- [1] Jeong Y, Ansari JR, Sadeghi K, Seo J (2024) Applicability of polypropylene/polyethylene glycol/molecular sieve composites as desiccant pharmaceutical packaging materials. *Food Packag Shelf Life* 42, 101266. <https://doi.org/10.1016/j.fpsl.2024.101266>.
- [2] Jeong Y, Sadeghi K, Seo J (2023) Effects of molecular weight of polyethylene glycol on the moisture-absorption capacity and morphology of the channeling structure in desiccant composite. *Food Packag Shelf Life* 37, 101086. <https://doi.org/10.1016/j.fpsl.2023.101086>.
- [3] Nagaya K, Li Y, Jin Z, Fukumuro M, Ando Y, Akaishi A (2006) Low-temperature desiccant-based food drying system with airflow and temperature control. *J Food Eng* 75(1), 71-77. <https://doi.org/10.1016/j.jfoodeng.2005.03.051>.
- [4] Guan B, Liu X, Zhang Q, Zhang T (2020) Performance of a temperature and humidity independent control air-conditioning system based on liquid desiccant for industrial environments. *Energy Buildings* 214, 109869. <https://doi.org/10.1016/j.enbuild.2020.109869>.
- [5] Gado MG, Nasser M, Hassan AA, Hassan H (2022) Adsorption-based atmospheric water harvesting powered by solar energy: Comprehensive review on desiccant materials and systems. *Process Saf Environ Prot* 160, 166-183. <https://doi.org/10.1016/j.psep.2022.01.061>.
- [6] Higashi T, Yamaguchi M, Nakagawa N, Dang C, Hihara E (2018) Gravimetric method for sorption performance measurement of desiccant wheel and desiccant coated heat exchanger. *Appl Therm Eng* 144, 639-646. <https://doi.org/10.1016/j.applthermaleng.2018.05.079>.
- [7] Mulchandani A, Westerhoff P (2020) Geospatial Climatic Factors Influence Water Production of Solar Desiccant Driven Atmospheric Water Capture Devices. *Environ Sci Technol* 54(13), 8310-8322. <https://doi.org/10.1021/acs.est.0c00534>.
- [8] Kim J, Park Y, Lee S, Choi M, Lee J, Sung M, et al. (2025) Improving quality and reliability of disposable desiccant to prevent condensation in automotive headlamps. *Eng Fail Anal* 180, 109836. <https://doi.org/10.1016/j.engfailanal.2025.109836>.
- [9] A'Yuni Q, Rahmayanti A, Hartati H, Purkan P, Subagyo R, Rohmah N, et al. (2023) Synthesis and characterization of silica gel from Lapindo volcanic mud with ethanol as a cosolvent for desiccant applications. *RSC Adv* 13(4), 2692-2699. <https://doi.org/10.1039/d2ra07891k>.
- [10] Chairunnisa, Miksik F, Miyazaki T, Thu K, Miyawaki J, Nakabayashi K, et al. (2021) Development of biomass based-activated carbon for adsorption dehumidification. *Energy Reps* 7, 5871-5884. <https://doi.org/10.1016/j.egyr.2021.09.003>.
- [11] De Antonellis S, Bramanti E, Calabrese L, Campanella B, Freni A (2022) A novel desiccant compound for air humidification and dehumidification. *Appl Therm Eng* 214, 118857. <https://doi.org/10.1016/j.applthermaleng.2022.118857>.
- [12] Kempe MD, Nobles DL, Postak L, Calderon JA (2018) Moisture ingress prediction in polyisobutylene-based edge seal with molecular sieve desiccant. *Prog Photovolt* 26(2), 93-101. <https://doi.org/10.1002/pip.2947>.
- [13] Zhang Y, Liu L, Liu P, Deng L, Li J, Guo X, et al. (2025) Study on the moisture adsorption characteristics of AlPO₄-LTA and its dehumidification performance in desiccant coated dehumidifier. *Int J Refrig* 172, 158-169. <https://doi.org/10.1016/j.ijrefrig.2025.01.029>.
- [14] Wang S, Stahlbuhk A, Steiger M (2024) Hydration and deliquescence behavior of calcium chloride hydrates. *Fluid Phase Equilib* 585, 114171. <https://doi.org/10.1016/j.fluid.2024.114171>.

- [15] Vainio E, DeMartini N, Hupa L, Åmand L-E, Richards T, Hupa M (2019) Hygroscopic Properties of Calcium Chloride and Its Role on Cold-End Corrosion in Biomass Combustion. *Energy Fuels* 33(11), 11913-11922. <https://doi.org/10.1021/acs.energyfuels.9b02731>.
- [16] Lu H, Shi H, Sathasivam S, Zhang X (2022) Strong robust superhydrophobic C/silicone monolith for photothermal ice removal. *J Mater Sci* 57(13), 6963-6970. <https://doi.org/10.1007/s10853-022-07099-7>.
- [17] Yuan Y, Zhang H, Yang F, Zhang N, Cao X (2016) Inorganic composite sorbents for water vapor sorption: A research progress. *Renew Sustain Energy Rev* 54, 761-776. <https://doi.org/10.1016/j.rser.2015.10.069>.
- [18] Wang C, Yang B, Ji X, Zhang R, Wu H (2022) Study on activated carbon/silica gel/lithium chloride composite desiccant for solid dehumidification. *Energy* 251, 123874. <https://doi.org/10.1016/j.energy.2022.123874>.
- [19] Ajay PD, Arunkumar HS, Madhwesh N, Kumar S (2025) MgCl₂-silica gel mixture as a sustainable liquid desiccant for humidity control. *Energy Rep* 14, 998-1007. <https://doi.org/10.1016/j.egyr.2025.07.025>.
- [20] Mittal H, Al Alili A, Alhassan SM (2020) Solid polymer desiccants based on poly(acrylic acid-co-acrylamide) and Laponite RD: Adsorption isotherm and kinetics studies. *Colloids Surf A* 599, 124813. <https://doi.org/10.1016/j.colsurfa.2020.124813>.
- [21] Wang B, Li Y, Zhao C, Cheng J, Liao J (2025) High tensile and antifreeze polyacrylamide hydrogel strain sensor suitable for human motion monitoring under low-temperature conditions. *Sens Actuators A Phys* 387, 116467. <https://doi.org/10.1016/j.sna.2025.116467>.
- [22] Dai L, Yao Y, Jiang F, Yang X, Zhou X, Xiong P (2017) Sorption and regeneration performance of novel solid desiccant based on PVA-LiCl electrospun nanofibrous membrane. *Polym Test* 64, 242-249. <https://doi.org/10.1016/j.polymertesting.2017.10.013>.
- [23] Huang J, Zhou J, Long Y, Mu X, Zhang Z, Zhu Y, et al. (2025) A robust CMCNa-PAM salt-inhibiting double-network hydrogel for efficient solar interfacial evaporation. *J Environ Chem Eng* 13(3), 117084. <https://doi.org/10.1016/j.jece.2025.117084>.
- [24] Li X, Mu X, He F, Chen Y, Wang Y, Zhang Z, et al. (2025) Sodium Alginate/Polyacrylamide Sponge-Based Hydrogel Containing Calcium Chloride for Atmospheric Water Harvesting with High Water Release Rates. *ACS Appl Eng Mater* 3(4), 1051-1061. <https://doi.org/10.1021/acsaenm.5c00128>.
- [25] Gu X, Qiu M, Xue H, Pei X, Xiao H, Zhou L (2025) Different macroporous characteristic LiCl/CaCl₂ binary salt double network hygroscopic aerogels for atmospheric water harvesting. *J Environl Chemical Eng* 13(5), 117904. <https://doi.org/10.1016/j.jece.2025.117904>.
- [26] Lv H, Zong S, Li T, Zhao Q, Xu Z, Duan J (2023) Room Temperature Ca²⁺-Initiated Free Radical Polymerization for the Preparation of Conductive, Adhesive, Anti-freezing and UV-Blocking Hydrogels for Monitoring Human Movement. *ACS Omega* 8(10), 9434-9444. <https://doi.org/10.1021/acsomega.2c08097>.
- [27] Fu C, Zhan D, Tian G, Yu A, Yao L, Guo Z (2024) Biomimetic Aerogel Composite for Atmospheric Water Harvesting. *ACS Appl Mater Interfaces* 16(27), 35740-35751. <https://doi.org/10.1021/acsami.4c05041>.
- [28] Entezari A, Ejeian M, Wang R (2020) Super Atmospheric Water Harvesting Hydrogel with Alginate Chains Modified with Binary Salts. *ACS Mater Lett* 2(5), 471-477. <https://doi.org/10.1021/acsmaterialslett.9b00315>.
- [29] Mason PE, Ansell S, Neilson GW, Rempe SB (2015) Neutron Scattering Studies of the Hydration Structure of Li⁺. *J Phys Chem B* 119(5), 2003-2009. <https://doi.org/10.1021/jp511508n>.
- [30] Islam M, Mittal H, Al Alili A, Alhassan S, Kumar V, Islam M (2025) Activated carbon/superporous hydrogel composite-based polymer desiccants for capturing water vapor from humid air. *Powder Technol* 458, 121001. <https://doi.org/10.1016/j.powtec.2025.121001>.

- [31] Bahadoran Baghbadorani N, Behzad T, Karimi Darvanjooghi MH, Etesami N (2020) Modelling of water absorption kinetics and biocompatibility study of synthesized cellulose nanofiber-assisted starch-graft-poly(acrylic acid) hydrogel nanocomposites. *Cellulose* 27(17), 9927-9945. <https://doi.org/10.1007/s10570-020-03511-0>.
- [32] Ozdemir M, Floros JD (2001) Analysis and modeling of potassium sorbate diffusion through edible whey protein films. *J Food Eng* 47(2), 149-155. [https://doi.org/10.1016/S0260-8774\(00\)00113-8](https://doi.org/10.1016/S0260-8774(00)00113-8).