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Paper

Development of solid super desiccants based on polymeric superabsorbent hydrogel composite

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A solid super desiccant was developed based on the concept of impregnating a super liquid hygroscopic agent in a superabsorbent polymer to take advantage of the vast vapour absorption capacity of the hygroscopic agent and the liquid withholding capacity of the superabsorbent polymer. The maximum hygroscopic salt loading was determined based on different salt concentrations in sodium polyacrylate. The newly developed desiccant showed a vapor absorption capacity of 276±20%, which is superior in comparison to that of conventional solid desiccants such as silica gel, activated alumina and molecular sieves. Thus they have great potential in applications requiring solid desiccants such as desiccant cooling, air conditioning, storage of moisture sensitive materials, and dehydration of natural gas.

1. Introduction

Desiccants are a group of hygroscopic substances that can attract water-vapor molecules via adsorption or absorption. Desiccants have numerous industrial applications, for example, in oilfields (natural gas dehydration), heating, ventilation, the air conditioning (HVAC) industry (energy-saving desiccant-aided cooling systems and desiccant dehumidification wheel), and in electronics, pharmaceutical formulations, diagnostic reagents storage and delivery, etc. Based on the physical state, there are two types of desiccants, liquid desiccant and solid desiccant. Examples of typical liquid desiccants are concentrated aqueous solutions of hydroscopic salts (i.e. calcium chloride or lithium chloride solutions) and glycols, etc. The vapor pressure of a liquid desiccant solution is proportional to the temperature and is inversely proportional to the desiccant concentration. Liquid desiccants, in general, have a much higher capacity than solid desiccants. For instance, a lithium chloride solution is a popular choice for liquid desiccant air conditioning because of its great humidity capture capacity. As an illustrative example, aqueous LiCl solution can still absorb water vapour at a concentration of 10% (w/w) at 30 °C and 90% relative humidity (RH), implying a water vapour absorption capacity of 10 g water/g LiCl.[1, 2] Liquid desiccants have found numerous applications.[3, 4] One of the liquid desiccant systems is the Advantix Systems (Sunrise, FL), which uses a 40% lithium chloride solution as the desiccant. It has been proven to be an energy-saving, air quality improving, low maintenance cooling and dehumidification method.

Nevertheless, liquid desiccants, mostly lithium chloride solutions, are not applicable in many scenarios. For instance, desiccant cooling is designed for personal heat mitigation. A safer desiccant is required, specifically toxic-free. Therefore, solid desiccants are preferred due to their dryness, and simplicity of their structure.[5] Solid desiccants are favoured in many other scenarios over liquid ones for their ease of operation, simplicity of device, and chemical inertness.[6] In contrast, liquid desiccants are usually corrosive, difficult to handle, and require complicated systems.

Most commonly encountered conventional solid desiccants are silica gel, activated alumina, molecular sieves, and activated carbon. Further, certain synthetic polymers have also been recognized as great desiccant options. For instance, various polymers and proteins were studied in terms of water vapor adsorption at a temperature of 25 °C, and the carboxyl groups presented a strong affinity with the adsorbed water.[7, 8]

Unlike liquid desiccants, which absorb water molecules into the entire volume of the solution, solid desiccant relies on the adsorption of vapor molecules onto their surface to retain moisture. As a result, solid desiccants are inherently of low vapor adsorption capacity in comparison to liquid desiccants.

In the 1960's, researchers developed cross-linked polyacrylamide which can absorb liquid water up to 15-75 times its own weight and retained the water under pressure at about 2.5 psi. In the 1970's, the Agricultural Research Administration of US (Northern Regional Res. Lab. (NRRL), Bureau of Agricultural and Industrial Chemistry, Peoria, IL) developed a new material that can absorb more than 10^3 times its weight in water and was called a super absorbent polymer (SAP). Since then, this type of polymer, which has great water retention ability, has been widely used in disposable diapers and in agriculture industries.

We hypothesized that the superb liquid holding capacity of SAP, could be exploited in combination with superior vapour absorption capacity of liquid desiccants to create a super solid desiccant. Since sodium polyacrylate has been proven to be a great water retention agent, and also a decent moisture absorption material, further optimization in order to develop a super solid desiccant seems feasible theoretically. With the motivation of developing a super solid desiccant that is highly efficient, non-corrosive and easy to regenerate, we have proposed the use of a superabsorbent hydrogel composite (SHC), a material that is based on sodium polyacrylate, with the impregnation of a hydroscopic agent (lithium chloride), as a novel solid desiccant material. SHC takes advantages of both, the great absorption capacity of lithium chloride and the large liquid-holding property of SAP. Moreover, commercial sodium polyacrylate is available at around $10 per kilogram, which is comparable in price to the commercial silica gel. This newly developed desiccant has shown big potential in applications in oilfields, HVAC industries, etc.

2. Experimental

Materials

The cross-linked sodium polyacrylate, sodium salt of poly(acrylic acid) with partial sodium salt-*graft*-poly(ethylene oxide), powder (granular) was purchased from Sigma-Aldrich Inc., with a particle size reported to be 90-850 µm. The chemical structure of cross-linked sodium polyacrylate is shown in Fig. 1. The anhydrous lithium chloride (99% purity) was purchased from the same source. All the above mentioned chemicals were used without any further treatment.

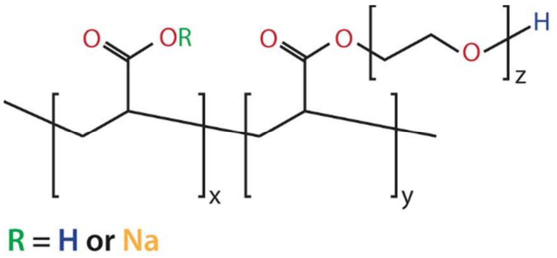

Fig. 1. The chemical structure of cross-linked sodium polyacrylate.

Preparation of superabsorbent hydrogel composite desiccant

The superabsorbent hydrogel composite (SHC) is formed by soaking sodium polyacrylate powder with a pre-determined lithium chloride solution, and then rinsed with distilled water. The resulting gel was dried in the oven to form the final desiccant. Different concentrations of lithium chloride solutions were prepared. These are 1, 2, 2.5, 3, 4, 5 mol/l. 3 grams of sodium polyacrylate powder were weighed and added slowly into a flask with a magnetic stirrer, which contained 100 ml of the solution. The mixture was stirred for another 5 minutes before being transferred into a programmable shaker (180 rpm, 25 °C) to incubate for 1 h. Excess liquid was filtered out with mesh fabric and then, the flask was refilled with a fresh LiCl solution. This step in the shaker was repeated as needed for a complete ion exchange. At the end of the ion exchange process, the resulting gel mixture was again filtered out. A volume of 300 ml of deionized water was added into the flask to rinse the LiCl impregnated polymers. The mixture was kept in the shaker for 1 h and this step was repeated one more time to ensure complete rinsing. The final gel was filtered out and transferred onto a piece of glass plate to form a thin layer of gel film. The plate together with the gel film was placed inside a gravity convection oven (Model 18EG, Precision Scientific Inc., Buffalo, NY) at 80 °C to dry for 24 h.

Methods of characterization

Vapor absorption performance

Vapor absorption tests were performed inside a programmable water bath (Model 1225, VMR Int., Radnor, PA) with a cover, shown in Fig. 2. The water bath was preheated to allow the water temperature to be stabilized at 26 °C. The air temperature inside the water bath is maintained at 25±0.2 °C and the relative humidity is stabilized at 99%. 0.5 grams of the sample was put into a pre-weighed petri-dish, and then the loaded dish weight was recorded. The loaded dish was kept on a rack which was half-immersed under water within the water bath. The total dish weight was recorded every hour from the 1st h to the 4th h, along with the 24 h final dish weight. The absorption capacities were defined as the absorbed vapor amount per unit mass of dry desiccant sample, which can be calculated by the following formula:

$$\text{Absorption Capacity}\left(\frac{\text{g}}{\text{g}}\right) = \frac{(W_f - W_i)}{W_d}$$

Where W_f is the dish weight at a specific time interval (1-h, 2-h, etc.), W_i is the initial dish weight with the dry sample loaded, W_d is the dry sample weight.

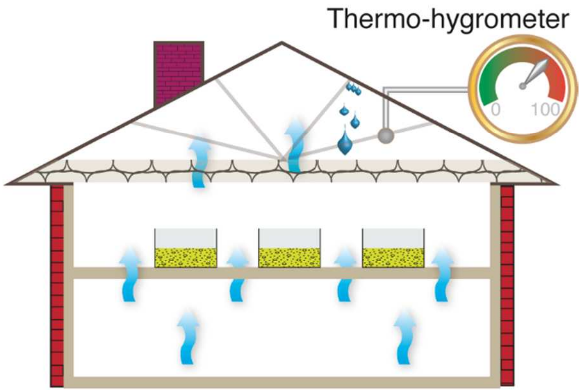

Fig. 2. Schematic diagram for vapor absorption test within water bath.

Swelling measurements for different concentrations of LiCl solution

The pre-weighed 0.1 grams of dry SAP was put into a teabag, where the opening of the teabag was closed with staples. The loaded teabag was weighed before immersion in large amount of LiCl solution (100 ml). After allowing 24 h to reach its equilibrium swelling state, the swollen SHC within the wet teabag was taken out of the solution and hung up for 1 h to remove the excess water[9]. The teabag was finally dried by using a paper towel before measuring the final weight and the resulted swollen gel weight is repeatable. The equilibrium solution absorption amount was calculated by using the following equation:

$$\text{Q}_{eq} = \frac{W_2 - W_1}{W_1}$$

Where Q_{eq} is the swelling capacity, defined as grams of solution per gram of dry SAP, W_1 and W_2 are the mass of sample before and after swelling, respectively.

Surface morphology of the SHC desiccant

The dry SAP was measured by X-ray diffraction (XRD) and the surface morphologies of dry SHC samples with different loadings were examined by scanning electron microscopy (SEM) with a Vega-II XMU with Oxford Inca Energy (Tescan Inc., Warrendale, PA) at 20 kV. Prior to taking images, graphite was used to sputter-coat the samples and the images were taken at magnifications ranging from 60× to 5000×. The qualitative surface elemental information was analysed by the SEM coupled energy dispersive X-ray (EDX) spectroscopy.

Surface area measurement

The specific surface areas of dry sodium polyacrylate powder and dry SHC samples were determined by nitrogen adsorption and desorption at 77 K using a physisorption analyzer (Model ASAP 2020, Micromeritics Instrument Corp., Norcross, GA). The surface area was calculated using the Brunauer-Emmett-Teller (BET) method that was applied to the adsorption data in the relative pressure (P/P_o) range of 0.05−0.20.

Lithium and sodium ion concentration measurement in SHC gel mixture leachates

Lithium and sodium ion concentration in the leachates from each round of gel / solution mixing steps were measured by Varian (Agilent Technologies Inc., Santa Clara, CA) Vista Pro Inductively Coupled Plasma Emission Spectrometry (ICP-ES). This information can reveal ion exchange rates at each stage and the total ion exchange capacity of the sodium polyacrylate being studied. The 1st sample was taken from the leachate of 1 h gel preparation and then, 100 ml of fresh 2.5 M LiCl solution was used to replace the previous batch of leachate. The flask containing new gel mixtures were put into the shaker at the same condition for another hour of preparation. The 2nd equilibrium ion concentration sample was then taken from this batch of leachate and samples were collected until the 5th equilibrium. The measured sodium ion amounts from the 5 samples were added up as the total sodium ion exchange capacity of the sodium polyacrylate used in this study. Ion exchange efficiency is defined as amount of sodium ion in the leachate divided by the total sodium ion exchange capacity. The data analysis was based on results of 3 replicates.

3. Results and discussion

Effect of LiCl solution concentration on SAP swelling capacity

The swelling capacity (g of weight gain / g of dry SAP) of SAP and LiCl loading (mmol of LiCl / g of dry SAP) were plotted vs LiCl concentration in Fig. 3. Results showed that the SAP swelled less when the concentration of LiCl solution increased. This is reasonable because the Na^+ density on the matrices of the SAP was constant. As a result, when the concentration of the LiCl solution increases, the osmotic pressure difference between the liquid phase inside the SAP and that outside of it would decrease, resulting in reduced swelling of SAP.

Fig. 3 also shows that a 2.5 M LiCl soluiton led to the largest LiCl retention in SAP, which can be potentially benificial because of the larger moisture retention for the resulting SHC desiccant. The existence of a LiCl concentration at which a maximum LiCl retention was obtained was due to the fact that the amount of LiCl retained in the gel, which equals the amount of solution absorbed at equilibrium multiplies the solution concentration. When low concentrations of LiCl solution was used for swelling, little LiCl was contained in the relatively large volume of solution absorbed. On the other hand, when the LiCl concentration was high (i.e., 3 M or higher in this study), the reduced volume of solution absorbed by the SAP led to less LiCl rentation despite of the relatively high LiCl concentration.

The swelling behaviour of ionic hydrogel such as SAP is a result of a balance between the elastic energy of the SAP network and the osmotic pressure difference between the liquid phase inside the gel matrices and that outside of it. The elastic term is described by the Flory expression derived from an assumption of Gaussian chain distributions, and in an electrolytic solution, the osmotic pressure is associated with the molarity of the solution and temperature.

Liquid absorption by polymer can be described by the Flory theory for an ionic network.[10]

$$Q^{5/3} = \left(\frac{1}{2} * \frac{i}{V_u} * \frac{1}{2S}\right) + \left(\frac{X_1}{2V_1} * \frac{V_0}{v}\right)$$

Where Q is the maximum swelling ratio of SAP, i is the electronic charge on the polymer structure per polymer unit, V_u is the polymer repeating unit volume, S is the ionic strength of solution, X_1 is the thermodynamic parameter of polymer with solvent (expressed by Flory-Huggins parameter), V_1 is the molar volume of solvent, in a real network, V_0 is the unswollen polymer volume, and v is the effective number of chains. These parameters in the equation formed a balance of the swelling which can be further defined as follows: the first term in the equation represents the ionic strength on both polymer structures and in the solution, the second term is the affinity of network with solvent and $\frac{V_0}{v}$ is the cross-linking density. This equation shows that the water absorption power results mainly from the osmotic pressure, the polymer's affinity of water, and the cross-linking density of the network. [10]

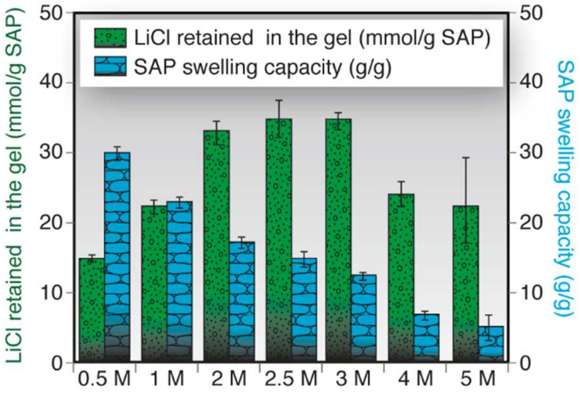

Fig. 3. SAP swelling capacities and LiCl retained amount with respect to the molarity of LiCl solution.

The osmotic pressure dependency is through *i* / *S*, which is the electronic charge on the polymer structure per polymer unit versus ionic strength of solution. When the solution is more concentrated or solution contains ion with more charges, the swelling capacity of the particular polymer decreased due to raised ionic strength of the solution. The affinity of water and polymer in this case is referring to the water affinity of the hydrophilic group on the polymer chain, more specifically carboxylate and carboxylic acid groups in this system (as shown in Fig. 1).

By recognizing the mechanism of hydrogel swelling, based on the same polymer structure, the affinity of the water and the polymer and cross-linking density of the network remain the same. The swelling capacity is directly affected by the osmotic pressure. Thus, decreasing the ionic strength, more specifically, decreasing the concentration of the LiCl solution for this system, can increase the polymer swelling capacity (liquid retention). We can see that there is a trade-off for an higher amount of liquid retention which requires a low solution concentration and more LiCl amount trapped inside of SAP which generally prefers a higher soultion concentration. Fig. 3 has shown the optimum solution concentration for the maximum LiCl retention within SHC.

Effect of lithium chloride content on SHC vapor absorption performance

Lithium and sodium are both alkali metals, and have the same electric charge, +1. The cation radius of lithium is smaller than that of sodium as lithium is from period 2 and sodium is from period 3. Lithium ion therefore has a greater charge density, and can attract water molecules more effectively than sodium ions. Thus, theoretically, both lithium ions on the polymer chain, which were part of the SAP matrices after ion exchange with Na^+, and lithium chloride crystals, which were impregnated inside the SAP matrices, will benefit from the moisture absorption of SHC.

Vapor absorption experiments on the different loading of SHC were tested with a sample preparation based on a 1 time of solution / SAP equilibrium. As shown in Fig. 4, 2.5 M SHC has the largest 24 h moisture absorption capacity compared to the other loading of SHC. The results followed the same trend as the LiCl solution retained in the SAP gel in Fig. 4, meaning that the larger the amount of LiCl absorbed on the polymer, the greater the moisture absorption ability of the final SHC. The retained LiCl solution in the gel became a salt crystal after drying and staying on the SHC surface. The crystal acts like the separate moisture absorbent on the polymer, which further increases the capacity.

It is worth noting that more LiCl salt outside of the polymer did not always positively affect the SHC performance. When large amounts of free lithium chloride crystals absorb moisture, a layer of concentrated LiCl solution film is slowly formed around the SHC, and this is hardly absorbed by the SHC due to its high osmotic pressure. This layer of free LiCl solution becomes more and more diluted and corrosive, and is harmful to the equipment. Therefore a rinsing step as the last step of SHC preparation is important to ensure that the resulting desiccant is non-corrosive and therefore ease of operation.

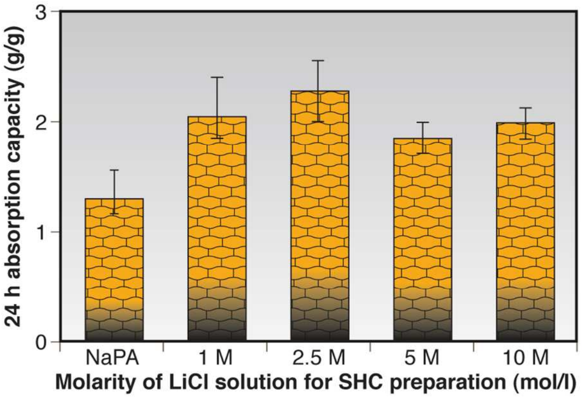

Fig. 4. 24 h absorption capacity versus molarity of LiCl solution for SHC preparation (1-h equilibrium duration).

From Fig. 4, it can also be observed that the absorption capacity increased slightly from 5 M SHC to 10 M SHC. This could imply that the ion exchange degree also affected moisture absorption ability. A 10 M LiCl solution, which is an almost saturated LiCl solution, can exchange the largest amount of Li^+ onto the polymer chain at equilibrium conditions compared to a lower concentration solution. However, for 10 M SHC, it retained the least amount of LiCl solution within the polymer structure during SHC formation. Overall, the active lithium ions or lithium chloride salts on the 10 M SHC is still less compared to the others (especially 2.5 M SHC). For similar reasons, the 1 and 5 M SHC, either have a lesser degree of ion exchange or they retained less amounts of LiCl crystal on the polymer, resulting in a less moisture absorption performance.

The 2.5 M SHC shows the best performance with Fig. 4 revealing the impact of ion exchange degree on the moisture absorption capacity. This led to the concerns about ion exchange rate limiting factors, with these two factors being studied. One is equilibrium duration and the other is number of equilibrium.

Effects of equilibrium duration on the ion exchange degree

Equilibrium duration is referred to as the step where the solution / SAP was stirred inside the shaker. This stirring duration can affect the ion exchange degree depending on the ion exchange rate. Thus, the effects of equilibrium duration were tested based on the vapor absorption tests for 2.5 M SHC. This stirring period was extended from 1 to 4 h for the sample preparation. The vapor absorption capacities for the SHC prepared, were done using both 1 h equilibrium and 4 h equilibrium, and were compared with the results shown in Fig. 5. No significant differences were observed between the two, since the rinsing step was performed following the same procedure and the freest LiCl salts were removed. Therefore, the similarity of vapor absorption results shows the similarity of the ion exchange degree on the polymer chain. We further concluded that 1 h preparation of SAP soaking with LiCl solution would be sufficient for ion exchange to reach equilibrium. As such, 4 h preparation was not necessary.

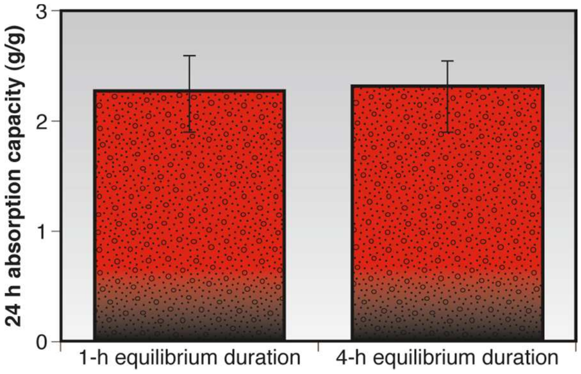

Fig. 5. 24 h absorption capacity comparisons for 1-h and 4-h equilibrium durations.

The effects of the number of equilibrium steps on vapor absorption performance

Repeating the solution/gel equilibrium step with fresh LiCl solution can further push the completion of ion exchange. By replacing the leachate from the previous step, the sodium ion has been removed out of the system. As a result, more lithium ion is transferred onto the polymer. This should benefit the vapor absorption capacity of SHC, since the lithium ion has a higher hydration power due to its high charge density compared to sodium ion. SHC with different numbers of equilibrium were prepared, i.e., 1 - equilibrium, 2 - equilibrium, 3 - equilibrium, 5 - equilibrium, vapor absorption tests were performed and the absorption data is listed in Fig. 6.

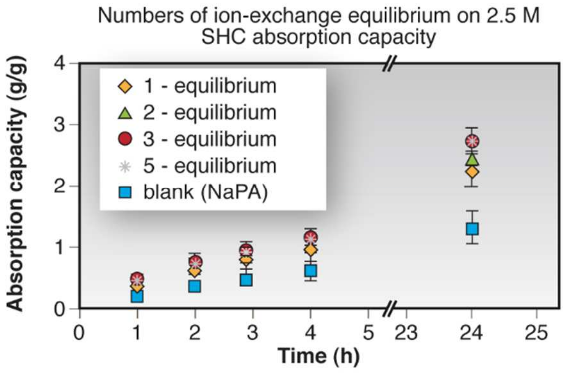

Fig. 6. Vapor absorption performance with 2.5 M SHC prepared by different numbers of ion-exchange equilibrium.

SAP vapor absorption data was also plotted as a baseline for comparison. The 24 h absorption for SAP without further treatment is measured as 1.31 g of vapor per gram of SAP. For different numbers of equilibrium preparation, the higher the equilibrium number, the higher the vapor absorption capacity. The slope for each type of SHC increases as well when a higher number of equilibrium is achieved. It is interesting to note that the 3-equilibrium SHC has a similar vapor absorption curve to that for 5-equilibrium SHC, meaning that the ion exchange might be completed by the end of 3-equilibrium. This hypothesis needs to be further proven by ICP-ES results.

The relative ion exchange degree is calculated based on the ICP-ES results. The sodium ion amount from the leachates of different equilibrium runs was summarized to calculate the total ion exchange capacity for sodium polyacrylate.

$$\text{Total exchangeable sodium ion on SAP} = \frac{\sum_1^5 sodium\ ion\ amount_i \frac{mg}{23\left(\frac{g}{mol}\right)}}{amount\ of\ treated\ SAP\ (g)} = 0.86\,\frac{mmol}{g\ of\ SAP}$$

The relative ion exchange degrees were then calculated by using the sodium ion amount from each batch of equilibrium divided with the total ion exchange capacity. The calculation is summarized in the following equation:

$$Relative\ ion\ exchange\ degree_i = \frac{sodium\ ion\ amount_i}{\sum_1^5 sodium\ ion\ amount_i}$$

From the grey curve shown in Fig. 7, we can see that the ion exchange degree reaches a plateau after the 3rd equilibrium, reaching 97.2% of ion exchange degree at the 3rd equilibrium. This trend is maintained for the 24 h moisture absorption tests from different equilibrium degrees of SHC samples. The 5th equilibrium showed the same 24 h moisture absorption capacity as that of the 3rd equilibrium SHC, and these are the largest results of all 5 tests. The sodium polyacrylate sample was tested at the same condition as the control. The reason for this is because more numbers of equilibrium pushed the ion exchange to the Li^+ favour direction on the polymer, and more Li^+ on the polymer chain can help attract more vapor, resulting in a better desiccant performance.

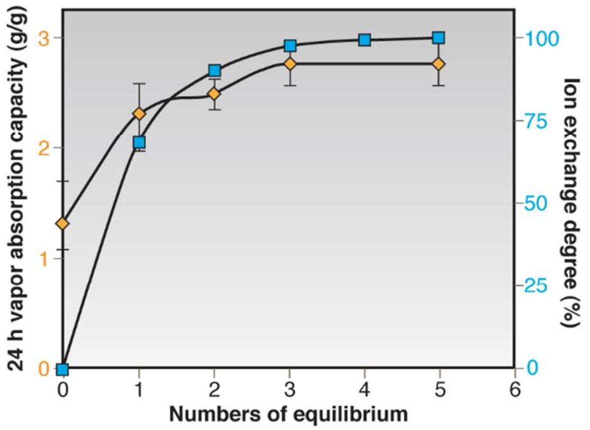

Fig. 7. 24 h vapor absorption capacity and ion exchange degree with respective to the numbers of equilibrium.

The morphologies of the SHC under different equilibrium conditions were measured by SEM-EDX. Fig. 8 lists the SEM images for 2.5 M 1-equilibrium, 2.5 M 3-equilibrium and 2.5 M 5-equilibrium SHC at a magnification of 60×. These images clearly showed that the amount of salt crystals (white dots) on the polymer surface decreased when the number of equilibrium increased. To better understand this phenomenon, an elemental analysis was performed by EDX to confirm the crystal content. The EDX results are listed in Fig. 9.

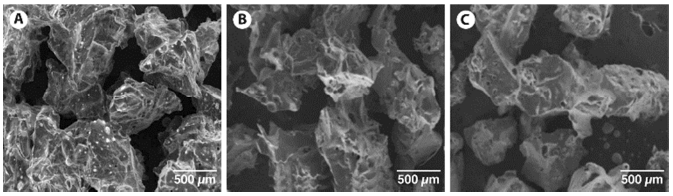

Fig. 8. SEM images for (A) 2.5 M 1-eq), (B) 2.5 M 3-eq SHC and (C) 2.5 M 5-eq SHC (magnification 60×).

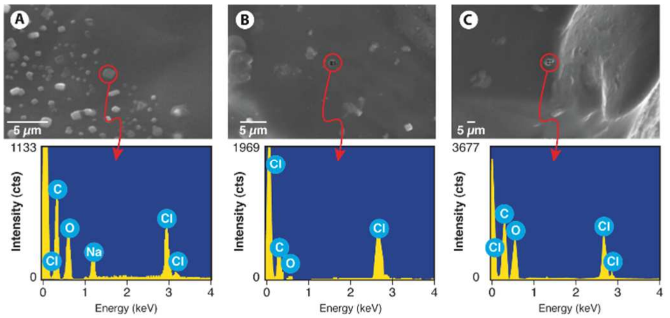

Fig. 9. SEM-EDX elemental analysis results for (A) 2.5 M 1-eq, (B) 2.5 M 3-eq and (C) 2.5 M 5-eq.

The top images of Fig. 9 are the SEM images for the corresponding SHC at a magnification of 5000X. The actual detecting spots are highlighted in the images, and the bottom images are the EDX peaks showing elements detected from the selected spot. It was found that most of the crystal shown in Fig. 9A was made of sodium chloride, which had a perfect cubic crystal shape. The crystals found on Figs. 9B and 9C are mainly made of lithium chloride. It is noted that lithium is not detectable by EDX due to its small atomic size. However, the peaks show high levels of chlorine and zero cation. Based on the fact that only lithium and sodium ion exist in the system, it is therefore concluded that the crystal is made of lithium chloride.

Another interesting fact from the SEM images shown in Fig. 9, is that the shape of the crystals found on the surface of 3-equilbirium (Fig. 9B) and 5-equilibrium (Fig. 9C) SHC are not the perfect cubic shape as those found in 1-equilibrium (Fig. 9A). These deformed crystals are all detected as lithium chloride while those cubic shaped crystals found in the Fig. 9A are sodium chloride. The deformation of lithium chloride crystals may be due to the hygroscopic nature of lithium chloride salt. It has a higher affinity for moisture compared with sodium chloride. Therefore, under the same sample preparation period before the SEM measurement, the lithium chloride attracted slight amount of moisture and slowly deformed. This also explains another observation from Fig. 9, that it seems to have more crystals on Fig. 9B comparing to Fig. 9C, this doesn't means that 3-equilibrium has more lithium chloride crystals than 5-equlibrium, it is again due to the trace amount of sodium chloride on the surface of Fig. 9B (cubic shaped crystals found on the bottom right of Fig. 9B). The observed less crystals on Fig. 9C surface is due to the fast moisture capture from the lithium chloride crystal during sample preparation, the ICP-ES results have confirmed that 5-equilibrium has more completed sodium removal comparing to 3-equilibium, and therefore Fig. 9C should contain slightly more lithium chloride crystal comparing to Fig. 9B. This phenomenon also leads to another conclusion that by performing more equilibrium steps, less sodium ion exists within the system. This leaves more space for lithium chloride crystals to be attached on the polymer surface, thus further improving the vapor absorption capacity.

Performance comparison with common solid desiccant

Bakass et al. measured the vapour absorption capacity of different polymers and concluded that SAPs have weak surfaces (lower than 10 m^2/g) and are nonporous.[11] The surface area measured in this study is by BET for SAP is 3.5±0.06 m^2/g, and the 3-equilibrium SHC has 4.6±0.08 m^2/g of surface area. These results confirm that the SAP has a small surface area compared to other common solid desiccants, and by impregnating lithium chloride salts on SAP, the resulting SHC surface area has increased due to salt crystal formation on the polymer surface. The adsorption isotherms of water vapor on a SAP surface follows type III isotherms at an ambient temperature with hysteresis phenomena. The absorption capacity of sodium polyacrylate has been tested by Zhang et al.,[12] and the monomer concentration, dosage of initiator and reaction temperature effects on the moisture absorption capacity have been systematically investigated. Moisture absorbing capacities of sodium polyacrylate have shown a better performance compared to conventional solid desiccants, such as silica gel and molecular sieve. The optimum moisture capacity of sodium polyacrylate from Zhang's research group reached 1.01 g/g.

To better evaluate the proposed solid desiccant, the physical properties and performances of a few common solid desiccants were researched in literature. Silica gel, a generic name for a gel manufactured from sulphuric acid and sodium silicate, has a high water capacity in that it can adsorb up to 45% of its own weight in water. It is easier to regenerate and it costs less than a molecular sieve. Activated alumina, a hydrated form of aluminium oxide (Al_2O_3), is the least expensive adsorbent for gas dehydration, can produce a dew point below -105.56 °C if applied properly and less heat is required to regenerate than molecular sieves. However, molecular sieves give lower outlet water dew points. Molecular sieves are the most versatile adsorbent because they can be manufactured for a specific pore size, depending on the application and are capable of dehydration for less than 0.1 ppm water content. It is the most expensive adsorbent but offers greater dehydration and requires higher temperatures for regeneration. These are alkaline and are subject to attack by acids. Table 1 has listed the common desiccant physical properties.

Table 1 Comparisons of physical properties with common solid desiccants.

	Silica gel	Activated alumina	Molecular sieves	SAP ¶	SHC ¶
Surface area (m^2/g)⊥	600-800	200-300	600-700	3.5±0.06	4.6±0.08
Pore diameter (Å) [13]	10-90	15	3,4,5,10	Non-porous	Non-porous
Static adsorption at RH 100% [14]	38%	36-42%	23%	131±27%	276±20%
Regeneration temperature (°C) [15]	100	120-260	175-315	N/A	<80

⊥Data reported from Sigma-Aldrich; ¶data were obtained from this study.

The cost of commercial sodium polyacrylate is around $10 per kilogram, which is comparable to the commercial silica gel price, considering that the lithium chloride chemical is more expensive, a more detailed cost analysis was performed. By performing ICP-ES tests, we measured the amount of Na in the leachate solution, the total amount of Na removed from SAP is 0.85 mmole per gram of SAP, and this amount of lithium ion is expected to be on the polymer chain. The amount of LiCl obtained by the gel swelling shown in Fig. 3 (2.5 M) is 34.6 mmole per gram of SAP that is 1.5 g of LiCl per g of SAP, this amount can be considered as the amount of LiCl crystals trapped inside of SAP. The cost of the analytical grade of lithium chloride purchased from Sigma-Aldrich Inc. is $0.15 per gram ($368 per bottle of 2.5 kg), this chemical cost can be greatly reduced when approaching it to a non-analytical grade source. Therefore by this proposed modification on sodium polyacrylate, the resulted SHC has doubled the vapor absorption capacity with reasonable amount of cost during preparation.

It is noted that adding LiCl can double the vapor absorption of SAP, which is significant considering that the conventional solid desiccant has the capacity only around 40% of its own weight (shown in Table 1). Furthermore, the vapor absorption capacity reported is 24 h absorption instead of equilibrium capacity. As shown in Fig. 6, the new desiccant was still absorbing vapour after 24 h and the gap between the desiccants and the SAP would become much larger if we push the vapour absorption to equilibrium. The much larger rate of vapour absorption by the desiccant than the SAP provides another important advantage.

There is an important concern in terms of potential LiCl leaching, since this new developed solid desiccant has great potential in various health related applications, for example, life support vacuum desiccant cooling device,[16] in which three layers structures including water reservoir, spacer and solid desiccant layer are encapsulated inside of an air-tight bag, water evaporation which can be initiated through vacuuming provides cooling. LiCl solution leaching from desiccant can potentially damage the device and eventually irritates the body skin. Other applications like the compact space cooling unit, also has similar safety concern. Thus solid desiccants are required to not only be efficient but also safe to handle (non-corrosive). The rinsing step as the last step for SHC gel preparation is designed to remove all the freest LiCl outside of SHC gel so that the desiccant will stay solid (gel) with the multiple absorption-desorption cycles, and therefore is safe to the environment and equipment.

4. Conclusions

A new desiccant made from superabsorbent polymer (SAP), which was impregnated with 2.5 M LiCl solution in sodium polyacrylate, has been developed. It is clear that the impregnated SAP shows double the amount of vapor absorption capacity compared with the SAP without treatment. The 24 h absorption capacity can reach 2.76±0.2 g/g at 99% relative humidity and 25 °C air temperature. Moreover, the appropriate impregnating concentrations of 2.5 M were determined based on the equilibrium water vapor absorption performance. Polymer based solid desiccants have the potential of being regenerated below 80 °C and can maintain long-term stability through thousands of absorption-desorption cycles. The proposed modified SAP impregnated with LiCl salts, has shown a great vapor capacity and thus reveals its great potential for larger scale drying applications, such as those required in natural gas dehydration and heating, ventilation, and the air conditioning applications.

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Notes and references

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