A Novel LiCl/H-STI Zeolite Guest/Host Assembly Material with Superior Humidity Sensitivity: Fabrication and Characterization

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A thermal dispersion method was used for assembling LiCl (the guest) into H-STI zeolite (the host) with a two-dimensional channel system of appropriate pore sizes to develop a novel guest/host material with excellent sensitivity, linearity and fast response to humidity change. The assembly process was investigated by the methods of XRD and ^{7}Li MAS-NMR.

Nowadays, humidity sensors have received extensive attention for its technological importance in different applications.[1–5] Conventionally, the sensors are fabricated based on ceramics, polymers and solid electrolytes.[1] However, the need for humidity sensors with superior performance has rarely been met. High fabrication cost, difficult preparing condition of high purity samples make the ceramics no so ideal for practical application.[6] The application in condition of high temperature and high humidity is limited for the polymers.[2] Thus, the solid electrolytes[2] such as LiCl[7, 8] are of growing interest. LiCl possesses a strong tendency to adsorb water vapor and form solutions with different concentrations, whose electrical conductivity is correlative with the ambient humidity. Nevertheless, the quantitative relationship is frequently destroyed due to the losing of LiCl after moistening, which makes the stabilization of LiCl a critical problem for its practical application.

In our attempt, H-form stilbite (H-STI) zeolite with a unique two-dimensional channel system[9] is employed as the host to fit the guest, LiCl. The 10-ring channel of H-STI zeolite in [100] direction, with the pore size (0.49 × 0.62 nm) close to the size of LiCl (~ 0.48 nm), is proper for the guest settled in. More interestingly, the 8-ring channel (0.27 × 0.56 nm) in [101] direction intersecting with the 10-ring one is a suitable and easy access for H_2O molecule (~ 0.26 nm) to the humidity sensitive guest tightly trapped in the zeolite. In this way, the entire humidity sensing process can be performed inside the microstructure of the novel guest/host assembly, LiCl/H-STI.

Pure parent STI zeolite was ion exchanged with a solution of 1 M NH_4Cl, and then calcined to get the host of the assembly, H-STI zeolite, according to Li et al.[10] H-STI was mixed with certain amounts of $LiCl{\cdot}H_2O$ and deionized water, stirred, dried at 100 °C, then calcined at 250 °C for 16 h. After that, a series of samples with various LiCl loading prepared by thermal dispersion (TD) method[11] were obtained. The sample with LiCl loading of 0.00 g/g, 0.08 g/g, 0.14 g/g, 0.17 g/g, 0.20 g/g or 0.45 g/g in H-STI, respectively, was denoted as sample A, B, C, D, E, or F. All powder samples for impedance measurement were pressed into uniform cylinders of $\phi\ 20 \times 1.4$ mm.

In Figure 1, the XRD patterns of samples B and C are close to that of sample A (host) without any diffraction peak assigned to the crystalline guest (LiCl and $LiCl{\cdot}H_2O$). This indicates that LiCl in samples B and C ($\leq$ 0.14 g/g of guest loading) exists in a highly dispersive phase inside the zeolite channels. With increasing the loading, the diffraction peaks of the guest appear and their intensities enhance gradually in the XRD patterns of sample D, E and F (> 0.14 g/g of guest loading). The fact implies that there does exist a threshold for the guest assembled in the host during the TD process, based on the microstructure of the zeolite. The threshold is about 0.14 g/g (sample C) estimated from the characterization of XRD pattern. Beyond that amount, the residual guest agglomerates in crystalline phase outside the host crystallites instead of dispersing into the zeolite channels. A contrastive experiment is carried out on both the uncalcined sample C and the sample with 0.14 g/g of the LiCl loading prepared by mechanical grind method. The results prove that strong stirring and thermal treatment by calcination are essential for the maintenance of the host structure and the successful dispersion of the guest into the host.

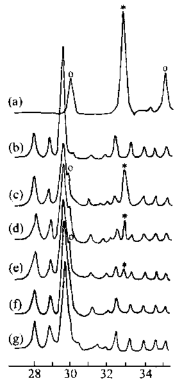

Figure 1. The XRD patterns of assembly samples a, LiCl (o) + $LiCl{\cdot}H_2O$(*); b, sample A (H-STI, 0.00g/g); c, sample F (0.45g/g); d, sample E (0.20g/g); e, sampleD (0.17g/g); f, sample C (0.14g/g); g, sample B(0.08g/g).

EDX analysis was carried out to clarify whether LiCl salt was dispersed into H-STI zeolite after thermal treatment by comparing the content of chloride in LiCl crystal, ion-exchanged Li-STI zeolite (sample G) and LiCl/H-STI. It was clearly found that the chlorine signals identical to that of the LiCl crystal appear in the EDX spectrum of LiCl/H-STI sample. However, no chlorine signal was observed in the spectrum of Li-STI sample (not shown here). It is concluded that LiCl salts in the LiCl/H-STI assembly have dispersed into the host zeolite rather than just experience solid-state ion-exchange reaction.

The ^{7}Li MAS-NMR spectra[12] depicted in Figure 2 show that only one signal was observed in the spectra of LiCl/H-STI. It is consistent with the hypothesis that 10-ring channels are the only sites where LiCl salts can occupy owing to their compatible sizes. In addition, NMR spectrum of the LiCl/STI sample shows a small but detectable high-field shift or low-field shift respectively, compared to that in aqueous solution or in LiCl crystal (see Figure 2). The signal also presents at the higher field with a line broader than Li-STI's. (see Figure 2c). This indicates that Li cations in the assembly locate in the different chemical coordination environment with respect to the other three Li-containing species, which agrees with the results of EDX (see Table 1). Interestingly, we also note the significant variations both in the chemical shift and signal breadth of ^{7}Li signals with the change of humidity as displayed in ^{7}Li MAS-NMR spectrum of the assembly. Under 0% RH, Li cations reveal high-field chemical shift with broader line (fwhm = 188 Hz, caused by static disorder), somewhat similar to that in the spectrum of LiCl crystal. Whereas increasing the humidity to 45%, the signal becomes narrow (fwhm = 114 Hz) and shift to the low field. In this case, it is much similar to that of the Li cations in aqueous solution. This dynamic change corresponds well to humidity-sensing process of LiCl assembled in the zeolite host. One possible explanation is that, the electron clouds of Cl$^-$ anions have screening effect on the Li cations, leading to a relatively high field signal of LiCl crystal. When LiCl dispersing into the channels of the zeolite, this electrostatic force was weakened for the cation partly interacted with the O^{2-} on the framework. With the lowered shielding, the resonance of ^{7}Li cations consequently shifts to the low field. After adsorbing water, Li cations in the channels are surrounded by water molecules. This therefore results in both the further weakening of the interaction between Li$^+$ and Cl$^-$ relative to down-field shift, and the increasing of the mobility of Li cation associated with the more narrow line shape. The result of NMR provides a direct proof of the humidity sensitivity of the assembly material.

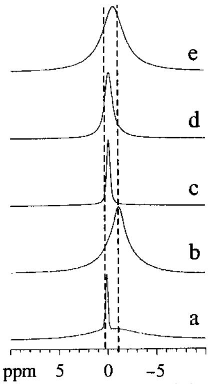

Figure 2. ^{7}Li MAS NMR spectra of Li-containing samples a.1M LiCl solution; b. LiCl crystal; c. Li-STI; d. LiCl/H-STI under 45%RH; e. LiCl/H-STI under 0%RH.

Table 1. Chemical shifts of ^{7}Li cations on various samples

Sample	RH	δ/ppm	$\Delta\delta_{\lvert x\text{-soln}\rvert}$/ppm^a	$\Delta\delta_{\lvert x\text{-cryst}\rvert}$/ppm^b	fwhm/Hz
LiCl (Soln)	-	0.09	-	1.18	20
LiCl (Cryst)	-	–1.09	1.18	-	250
Li-STI	-	–0.078	0.17	1.01	50
LiCl/H-STI	0%	–0.37	0.46	0.72	188
	45%	–0.12	0.21	0.97	114

$^a\Delta\delta_{\lvert x\text{-soln}\rvert}$: the difference between $\Delta\delta_x$, the chemical shift of ^{7}Li in certain sample, and $\Delta\delta_{soln}$, the chemical shift of ^{7}Li in aqueous solution of LiCl. $^b\Delta\delta_{\lvert x\text{-cryst}\rvert}$: the difference between $\Delta\delta_x$, the chemical shift of ^{7}Li in certain sample, and $\Delta\delta_{cryst}$, the chemical shift of ^{7}Li in crystal of LiCl.

The humidity–impedance characteristics on some typical samples are exhibited in Figure 3 (the impedance was measured by EG&G AC-impedance instrument). It seems that the conductivity, which is inversely proportional to the impedance of humidity sensitive material, was affected by its composition. Under the humid isolation ambient, the conductivity of the host measured is less than 10^{-12} s·cm^{-1} before assembly. With increasing the guest loading, the conductivity of the samples obviously grows, reaches the maximum of 3.7×10^{-8} s·cm^{-1} on the threshold sample, which is 4 orders of magnitude higher than that on the guest, then decreases on the samples with excessive loading. In fact, the excessive loading of LiCl in the host results in the agglomeration of the residual LiCl crystal, which hinders the current continuity of the guest/host material. After exposed to the moist atmosphere, the assembly material begins to adsorb the moisture in air. Although showing certain hydroscopicity, the host and the ion-exchanged Li-STI zeolite are restricted their application by the high bulk impedance and the poor humidity sensitive linearity. The higher impedance on sample B with low loading and the poorer linearity on sample F with exceeding loading show the disadvantage of them as well. Only the sample C with the threshold loading possesses the excellent humidity sensitivity, Log R/Ω = 3.9–7.4, in humidity range of 0–95% RH, and the best linearity, confirming its potential for humidity sensitivity material. The time response characteristics of the threshold sample were recorded at rapid humidity changes from 0% to 80% RH (adsorption process) and then back to 0% (desorption process). (It is measured by CHI660 electrochemical workstation, not shown here.) The results indicate that the material exhibits a quick response to the humidity change. The respond time for adsorption and for desorption relevant to a 63.2% change in ΔRH are within 26.5s and 38.6s, respectively.

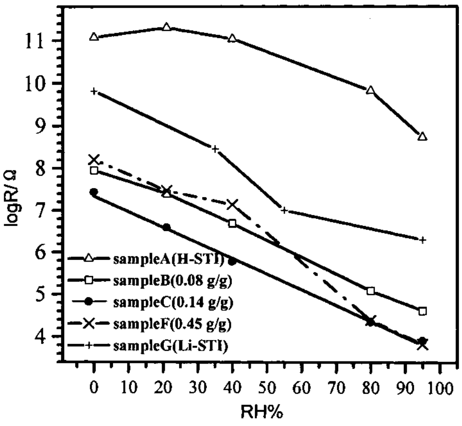

Figure 3. Humidity-sensitivity plot of samples.

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