Infiltration pressure of a nanoporous liquid spring modified by an electrolyte

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In a hydrophobic zeolite, the infiltration and defiltration of water can be controlled by adjusting external pressure, and therefore the system behaves as a "liquid spring." Since the hysteresis of sorption isotherm is negligible and the working pressure is thermally controllable, volume memory devices can be developed based on this phenomenon. With the addition of sodium chloride, both infiltration and defiltration pressures increase, which should be attributed to the cation exchange. The temperature sensitivity of the system increases with the electrolyte concentration, beneficial to improving the output energy density.

I. INTRODUCTION

In general, any materials or structures that change their dimensions or configurations as temperature varies can be potentially used to develop thermally controllable intelligent systems. For instance, titanium-nickel (Ti–Ni) alloys can undergo thermoelastic phase transformations, and they have been widely used for actuation or damping.¹ Their deformability is typically 5–8%, and the energy density is around 50 mJ/g.² While their properties are better than those of many other smart materials, very often they still cannot meet the increasingly high functional requirements of displacement and output force in structural and mechanical system design.

Recently, Kong and Qiao developed an electrically controllable nanofluidic system,³ in which the solid–liquid interfacial tension was adjusted by an external electric field. In a nanoporous alloy soaked by a conductive liquid, as the applied voltage varied, the relative wettability changed considerably, leading to the liquid motion. The system deformability is dominated by the nanopore volume fraction, which is in the range of 30–70%, and the output energy density is

$$U = \Delta \sigma \cdot A \quad , \tag{1}$$

where $\Delta \sigma$ is the variation in solid–liquid interfacial tension and *A* is the specific nanopore surface area. Because in a nanoporous material *A* is orders of magnitude higher than in bulk phases, *U* can be ultrahigh.

Under a few conditions, especially when the nanoporous network is electro-nonconductive and di-

rectly applying external electric fields is difficult, it is desirable to control the system by thermal methods. According to a discussion on energy transfer processes in heating, shrinking, cooling, and expansion cycles, Laouir et al.⁴ proved that such a device does not violate any thermodynamic laws. Inspired by a study on nanoporous liquid spring,⁵ this concept was recently validated by Qiao et al.⁶ using a hydrophobic zeolite of nonhysteretic sorption isotherm, as depicted in Fig. 1. In this system, the effective solid-liquid interfacial tension decreases as temperature increases, and therefore at a reduced temperature the zeolite becomes effectively more hydrophobic. Under the working pressure, the confined liquid would defiltrate out of the nanopores, leading to the system expansion. If the temperature is increased, the zeolite would become less hydrophobic, and the liquid would infiltrate into the nanopores, resulting in the system shrinkage. Because this process is reversible, the system exhibits a volume memory characteristic. The output energy density, which can be calculated using Eq. (1), is at the level of a few Joules per gram, much higher than that of conventional smart solids.

In the current investigation, we analyzed the effect of addition of an electrolyte on the system performance. In previous studies on nanoporous silicas,^{7,8} it was discovered that the infiltration pressure increased slightly with the electrolyte concentration. It is envisioned that, if the electrolyte can also increase the infiltration and defiltration pressures of zeolite, it might have a beneficial effect on its temperature sensitivity, which helps to increase the output energy density. Note that a key factor dominating the nanoporous system performance is the hysteresis of sorption isotherm. For reasons that are still inadequately understood, in many nanoporous materials, defiltration of confined liquids is difficult.^{9–12} Therefore, even when

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FIG. 1. Schematic diagram of the thermally controllable nanoporous liquid spring consisting of a hydrophobic nanoporous solid immersed in water. (a) At a high temperature, the nanoporous solid is less hydrophobic and the liquid infiltrates into the nanopores under the working pressure, leading to the decrease in system volume and (b) as the temperature is reduced, the nanoporous material becomes more hydrophobic and the liquid defiltrates out of the nanopores, leading to the increase in system volume.

the temperature changes and the nanoenvironment becomes nominally energetically unfavorable, the liquid still remains in the nanopores, and the system volume does not vary.

II. EXPERIMENTAL

In the current study, we investigated a Zeolyst ZSM-5 zeolite (Valley Forge, PA). It was previously noticed that its sorption isotherm was nearly nonhysteretic.⁶ The zeolite was of a high silicon content, with the SiO_2/Al_2O_3 ratio of 280. Along the [100] direction, the nanopores were zigzag and the effective nanopore size was 0.51 nm $\times 0.55$ nm; along the [010] direction, the nanopores were straight and the effective nanopore size was $0.53 \text{ nm} \times$ 0.56 nm.¹³ The zeolite sample was dried in air at 350 °C for 12 h and then immersed in aqueous solution of sodium chloride and sealed in a steel cylinder by a piston, as shown in Fig. 1. The zeolite to liquid ratio was 1:14 in weight. In the liquid phase, the sodium chloride concentration c was in the range of 0–26 wt%. To determine the temperature sensitivity of working pressure as a function of c, pressure induced infiltration experiments were performed at different temperatures T in the range of 22 to 85 °C. The system temperature was controlled by an Aldrich DigiTrol II Z28 water bath (St. Louis, MO). At rest, the piston was compressed into the container at a constant rate of 0.5 mm/min using an Instron machine (Norwood, MA). Once the infiltration was completed, the piston was moved out at the same speed. For each set of $\{T, c\}$, a reference pressure-volume curve was obtained by testing a similar reference system containing no zeolite, compared with which the excess part of the measured sorption isotherm curve reflected the infiltration volume. The specific infiltration volume was defined as the infiltration volume normalized by the mass of zeolite. The pressure was calculated as the applied load divided by the cross-sectional area of the container. Figure 2 shows typically sorption isotherm curves. At each temperature, for each electrolyte concentration, 2–4 samples were tested, and the average infiltration pressure values are shown in Fig. 3. For self-comparison purpose, the infiltration pressure was taken as the pressure at the middle point of the infiltration plateau, and the infiltration plateau was defined as the portion of the sorption isotherm curve between the two points where the slopes equal one-half that of the initial linear compression section.

The zeolite samples were analyzed in a Micromeritics TriStar-3000 Physisorption Analyzer (Norcross, GA) before and after the infiltration experiment. The samples after infiltration experiment had been dried at 350 °C for



FIG. 2. Typical sorption isotherm curves of the system based on 26 wt% aqueous solution of sodium chloride. The dashed reference lines indicate the behaviors of a pure water based system. The curves have been shifted along the horizontal axis.



FIG. 3. Infiltration pressure as a function of the electrolyte concentration and the temperature.

2 h prior to the porosimetry test. The average Brunauer– Emmett–Teller (BET) areas were measured to be 399.2 (before) and 382.1 m²/g (after), respectively, based on the N₂ sorption data at 77 K. The average pore volumes were 0.15 (before) and 0.17 (after) cm³/g, respectively.

III. RESULTS AND DISCUSSION

The high silica/alumina ratio of the zeolite leads to a high degree of hydrophobicity. Therefore, when the external pressure is low, water does not enter the nanopores due to the well-known capillary effect. As the pressure increases, water molecules would diffuse into the nanopores more easily, resulting in a limited infiltration volume, as shown by the initial linear sections of sorption isotherm curves in Fig. 2. When the pressure is relatively high, it becomes energetically favorable for the liquid molecules to enter the nanopores, and pronounced pressure-induced infiltration occurs. As a result, an infiltration plateau is formed in the sorption isotherm curve. The width of the infiltration plateau, which reflects the specific nanopore volume involved in pressurized liquid infiltration, is around 0.1 cm³/g at all the temperatures and electrolyte concentrations, smaller than but close to the total nanopore volume in the zeolite. When all the accessible nanopore surfaces are exposed to the liquid molecules, the pressure-induced infiltration ends and the slope of sorption isotherm increases rapidly.

As the pressure is lowered, the confined liquid defiltrates out of the nanopores quite smoothly. Consequently, the unloading path of sorption isotherm curve is about the same as the loading path. The nonhysteretic characteristic is probably related to the reversible process of diffusion of liquid molecules and the low energy barrier of gas phase nucleation and growth. Under a reduced pressure, the gas nano-bubbles that exist in the nanopores can grow and eventually occupy the entire space, repelling the liquid molecules into the bulk phase.¹⁴ Since, according to the gas absorption analysis, the changes in pore area and pore volume are negligible after the infiltration test, the external pressure has little influence on the porous structure.

As temperature changes, because of the variation in effective solid–liquid interfacial tension, the energy barrier that must be overcome for liquid molecules to enter a nanopore becomes different, which is reflected by the fact that the infiltration pressure is a thermally control-lable variable. For instance, in the zeolite-water system at 85 °C subjected to a constant working pressure of 56 MPa, according to Figs. 2 and 3, the external pressure is high enough to overcome the capillary effect and the water would be forced into the nanopores. If the temperature is reduced to 22 °C, the working pressure is insufficient to keep the liquid being confined in the energetically unfavorable zeolite, and defiltration would

occur, causing the system volume increase. The equilibrium pressure at 22 °C is 82 MPa, and thus the output energy density can be estimated as $U = \Delta P \cdot \Delta V \approx 2.6 \text{ J/g}$, where $\Delta P = 26$ MPa and $\Delta V = 0.1$ cm³/g are the pressure and the volume changes, respectively. If the temperature increases back to 85 °C, the infiltration pressure would be reduced; once it is lower than the working pressure, the liquid would be compressed into the nanopores again and the piston would move back. Thus, the system is essentially a thermal machine working between two temperatures, with its volume and configuration being controlled reversibly. This is in agreement with computer simulation results of nanofluidic behaviors in zeolite nanochannels. $^{15-21}$ For instance, in a Grand Canonical Monte Carlo (GCMC) simulation,¹⁸ it was shown that water motions in a silicalite-1 zeolite is of a stepwise characteristic.

As sodium chloride is added in the liquid phase, at each temperature the infiltration pressure increases significantly. At 22 °C, when the sodium chloride concentration rises from 0 to 26 wt%, the infiltration pressure $p_{\rm in}$ increases from 82 to 112 MPa by 30 MPa. Note that in a previous infiltration experiment on a nanoporous silica,²² it was noticed that addition of sodium chloride caused only a slight change in p_{in} by 3–5 MPa, smaller by nearly an order of magnitude. The pronounced electrolyte concentration dependence of the infiltration pressure of the zeolite should be attributed to the cation exchange in the nanopores, as depicted in Fig. 4. Zeolites are stabilized by the strong electrostatic interactions between the charged zeolite wall and the protonated adsorbate.^{23,24} In the zeolite under investigation, the framework is formed by aluminum and silicon atoms. At the nanopore surface, the aluminum atoms are linked to hydroxyl groups or other negatively charged defects. As the



FIG. 4. Schematic diagram of the pressure-induced infiltration of electrolyte solution in a nanopore. The anions are not shown.

number density of the defects changes, the effective solid–liquid interfacial tension varies and so does the infiltration pressure. In fact, controlling silica/alumina ratio is a powerful way to adjust the degree of hydrophobility or hydrophilicity of zeolites and zeolite-like materials.²⁵ As the positively charged sodium cations enter the nanopores together with water molecules, they can diffuse into the framework and effectively deactivate the negatively charged defect sites, causing the variation in infiltration pressure as if the silica/alumina ratio were increased.²⁶

Note that as temperature increases, the c dependence of p_{in} is reduced. At 85 °C, as c rises from 0 to 26 wt%, $p_{\rm in}$ increases from 56 to 68 MPa by only 12 MPa, less than one half of that at room temperature, which is in agreement with the fact that at an elevated temperature the thermally aided sodium cation diffusion in nanopores is easier; therefore they distribute more uniformly, and less negatively charged defects are deactivated. This phenomenon can also be related to the decrease in solidliquid interfacial tension as temperature increases; that is, even if the cation exchange effect did not vary, because the value of p_{in} is lowered, the change in p_{in} is also reduced. However, because the temperature effect on p_{in} is less pronounced than the combined effect of temperature and electrolyte concentration, the former mechanism must be taken into consideration.

Because the infiltration pressure depends on both the temperature and the electrolyte concentration, the temperature sensitivity of p_{in} of the zeolite based system ξ is a function of c. The ξ -c relationship is quite linear. As shown in Fig. 3, the values of ξ , which is defined as $\Delta p_{\rm in}/\Delta T$ (with $\Delta p_{\rm in}$ being the change in infiltration pressure when temperature varies by ΔT) increase with the electrolyte concentration. As c increases from 0 to 26 wt%, ξ rises by more than 50% from 0.48 to 0.74 MPa/°C. Because $\Delta p_{in} = \xi \cdot \Delta T$, according to Eq. (1), the output energy density is also considerably improved. That is, addition of sodium chloride has a beneficial effect on the performance of the nanoporous liquid thermal machine. Another interesting effect of addition of sodium chloride is that, as c increases, the difference in infiltration pressure and defiltration pressure is reduced from about 3 MPa to about 0.5 MPa (see Fig. 2), which is compatible with the previous experimental observation that addition of electrolyte can increase system recoverability by promoting defiltration.²²

IV. CONCLUSIONS

In summary, through a controlled-temperature infiltration-defiltration experiment, it is found that addition of sodium chloride can lead to a significant increase in temperature sensitivity of infiltration pressure of a zeolite based liquid spring, which is beneficial to improving its output energy density. This effect should be related to the thermally aided cation exchange in nanopores. Increasing sodium chloride concentration also helps to reduce the already small extent of hysteresis of sorption isotherm.

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