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Experimental investigation on pressurized liquid in confining nanoenvironment

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In this letter, the authors report the experimental observations of pressure induced liquid motions in a confining nanoporous gel. As the pressure is sufficiently high, water molecules can move out of the initially energetically favorable gel matrix and enter the hydrophobic nanopores. As the pressure is lowered, this process is irreversible, leading to the pronounced hysteresis of sorption isotherm. This phenomenon is essential to developing advanced energy absorption systems. A first-order thermodynamics analysis is presented. © *2006 American Institute of Physics*.
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Over the years, the behavior of confined liquid in nanoenvironment has been an active research area, which led to solid progress in selective absorption and adsorption, programmable catalysis, micro-/nanotransportation, etc.[1,2] Recently, the motion of pressurized nanofluids has drawn increasing attention of a few research teams.[3–5] For instance, as the pressure is increased, a liquid can be compressed into a lyophobic nanoporous material by overcoming the capillary effect, but when the pressure is lowered, depending on the factors that have not been fully understood, the confined liquid may remain in the nanopores, and therefore the work applied to force the liquid into the nanopores is dissipated. This phenomenon can be employed to develop advanced protective and/or damping systems, for which the preliminary experimental study has shown encouraging results.[6–9]

However, currently, the study in this area is focused on the pressure induced infiltration of free water, which cannot be directly applied in engineering practice. The required sealing and handling processes would significantly increase the system complexity. Prior to the infiltration, it is desirable that the water molecules can be confined, e.g., in a gel, so that the system can be of a certain resistance to shear stresses. To activate the liquid motions in such a structure, the water molecules must be forced to move away from the energetically favorable gel matrix and enter the energetically unfavorable nanopores, preferably by using only mechanical methods, particularly, by applying a nominally hydrostatic pressure. In this letter, we report the experimental results on a nanoporous gel system and a first-order thermodynamics analysis. We intend to answer the following two questions: (1) whether the desired liquid motions in the confining nanoenvironment can be achieved and (2) if yes, what would be its influences on the system parameters, such as the infiltration pressure and the accessible nanopore volume.

Figure 1 depicts the structure of the testing sample. Initially, 0.5 g of Fluka 100 C_8 reversed phase end-capped nanoporous silica particles were immersed in 7 g of distilled water. The nanopore size was in the range of 5–11 nm, with the average pore size of 7.8 nm and the standard deviation of 2.4 nm. The specific pore surface was 287 m^2/g and the specific pore volume was 0.55 cm^3/g. The particle size was 15–35 μm. The pore surface was covered by a layer of silane groups, with the surface coverage of 10%–12%, making the nanopores nonwettable to water.[10,11]

In order to confine the free water outside the nanoporous silica particles, 2 wt % of Aldrich 535141 poly(isobutylene-co-maleic acid) sodium salt (PIMA-Na) was added. Figure 2 shows its molecular structure.[12] The PIMA-Na macromolecules formed unified networks with high cross-link densities.[13] The water molecules would be attracted by the functional groups and be confined in the network cells, and thus became a gel and could no longer flow. The gel, with the nanoporous silica particles being embedded, was then placed into a steel cylinder and compressed by a piston. The piston was driven by a type-5569 Instron machine; the speed of the piston was set to 0.5 mm/min. Such a loading rate could be regarded as quasistatic.[7] As the pressure in the gel, which was calculated as the load applied on the piston divided by its cross-sectional area A_{cs}, reached about 50 MPa, the piston was moved back at the same rate. The loading-unloading

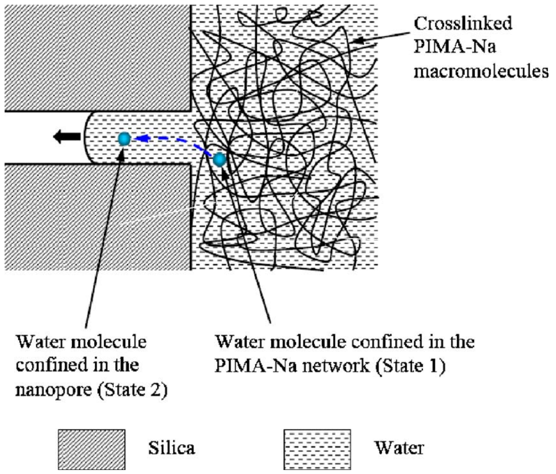

FIG. 1. (Color online) Schematic diagram of the pressure induced liquid infiltration in a nanopore.

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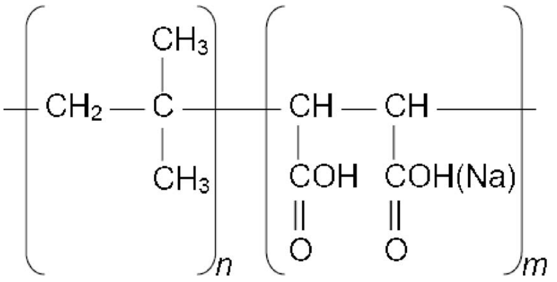

FIG. 2. Molecular structure of PIMA-Na, where *n* and *m* are the numbers of repeated units.

cycle was repeated for four times. Since the sorption isotherm curves in the second, the third, and the fourth cycles were almost identical, only the data of the first two loadings are shown in Fig. 3. The specific volume change was calculated as $A_{cs}d_p/m_s$, where d_p is the piston displacement and m_s is the mass of the nanoporous silica. For comparison purpose, similar experiment was also carried out on a pure water based system without PIMA-Na and the results are shown as the dashed lines.

The sorption isotherm curves shown in Fig. 3 indicate clearly that the pressure induced infiltration was achieved. As the pressure is lower than 17 MPa, water molecules cannot enter the nonwettable nanopores and the system volume changes nearly linearly with the pressure. In the pressure range of 17–26 MPa, the system volume decreases rapidly, forming the infiltration plateau. This should be attributed to that the liquid is forced to be released from the PIMA-Na network and enter into the nanoporous particles, starting with the relatively large nanopores. The width of the infiltration plateau, which can be regarded as the volume of the nanopores being filled, is around 0.5 cm^3/g, close to the specific pore volume measured by the gas absorption technique,[6] as it should be. When all the nanopores are occupied by the water molecules, the infiltration ends and the system becomes rigid again. Upon unloading, the water molecules are "locked" in the nanopores and therefore the infiltration-defiltration loop is highly hysteretic. The "nonoutflow" might be related to the "ink bottle" structure of the nanopores or the insufficient driving force of liquid motion,[14,15] the detailed mechanisms of which are still under investigation. The area enclosed by the hysteretic loop indicates the absorbed solid-liquid interfacial energy, which is about 12 J/g.

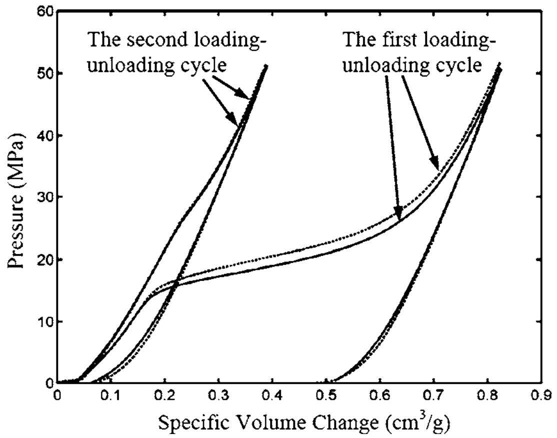

FIG. 3. Sorption isotherm curves. The dashed lines are for the pure water based system and the solid lines are for the PIMA-Na modified system. The curves have been shifted along the horizontal axis.

Because most of the nanoporous space remains being occupied, from the second loading-unloading cycle, the degree of hysteresis of the sorption isotherm curve is lowered significantly. Note that in the second loading-unloading cycle, the infiltration pressure is much higher than that in the first one; i.e., the nanopores involved in the second cycle are those of relatively small sizes, suggesting that the defiltration is pore size dependent. In relatively large nanopores, the nonoutflow is more likely to occur, probably due to the lower energy barrier of gas phase nucleation and growth.[15]

Figure 3 also shows that, with the addition of PIMA-Na, compared with the pure water based system, while the width of the infiltration plateau does not vary, the infiltration pressure is decreased by about 8%. Note that the sodium ions can only cause a slight increase in the excess solid-liquid interfacial tension; as the ion concentration is only about 2%, this effect should be negligible.[6] Moreover, the water molecules must overcome the confinement effect of the PIMA-Na networks. Both of the two factors tend to increase the infiltration pressure.

For the infiltration process depicted in Fig. 1, the free energies of the two states of the liquid confined in gel network (state 1) and the liquid confined in a nanopore (state 2) can be related through

$$\xi_2 = \xi_1 + PV - \gamma A - \Delta\mu V + P^2V/2K, \tag{1}$$

where ξ_1 and ξ_2 are the free energies of state 1 and state 2, respectively, P is the applied pressure, V is the volume of the water, γ is the excess solid-liquid interfacial tension, A is the associate solid-liquid interface area, $\Delta\mu$ is the specific free energy difference, and K is the bulk modulus of the gel, which is around 0.1 GPa.[12] The second, third, fourth, and fifth terms at the right-hand side of Eq. (1) capture the external work, the solid-liquid interaction, the confinement effect of the PIMA-Na gel, and the strain energy, respectively. As the first order approximation, V can be estimated as $\pi r^2 d$, with r being the pore radius and d the effective depth of the water column in the nanopore. Similarly, $A = 2\pi r d$.

At equilibrium, $\xi_2 = \xi_1$, and thus

$$P = \frac{2\gamma}{r} + \Delta\mu - \frac{P^2}{2K}. \tag{2}$$

For the pure water based system, since the liquid matrix is nearly incompressible and free, the last two terms in Eq. (2) are negligible. Hence, since the change in γ caused by the sodium ions is small,[6] the difference in infiltration pressure between the PIMA-Na modified system and the pure water based system is

$$\delta P = \Delta\mu - \frac{P^2}{2K}. \tag{3}$$

The total nanopore volume of the system in the current study is 0.26 cm^3. At this volume variation level, according to the testing data of pressurized polyelectrolyte gels, $\Delta\mu$ is a few kilopascals.[13] Consequentely, when $P = 17$ MPa, $\delta P \approx -1.4$ MPa, which looks quite plausible.

It is clear that the above discussion is based on simplified assumptions. The details of the molecular behaviors in the gel cells and the nanopores are not taken into consideration. Nevertheless, it provides an order-of-magnitude assessment for the pressure induced infiltration of nanoporous gels. Note that the sorption isotherm curves of the second loading-unloading cycle and all the following cycles of the PIMA-Na modified system and the unmodified system are almost the same, indicating that Eq. (3) cannot be applied to analyze the smallest nanopores, probably because that, as the nanopore size becomes comparable with the size of a single water molecule, the quasicontinuum theory breaks down.

To summarize, through the infiltration experiment, it is validated that the pressure induced infiltration in hydrophobic nanoporous materials can occur even when the water molecules are confined in a gel matrix. As the pressure is high enough, the water molecules can be released from the gel network and enter the nanoproes; as the pressure is lowered, the defiltration takes place only in the smallest nanopores and most of the porous space remains being filled, resulting in the superior energy absorption characteristic. Compared with the pure water based system, the addition of PIMA-Na would not cause detectable variation in accessible nanopore volume, while the infiltration pressure is slightly lower.

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