Conversion of mechanical work to interfacial tension in a nanoporous silica gel

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A calometric measurement is performed to analyze energy exchange in a nanoporous material functionalized (NMF) liquid. As an external pressure is applied, the hydrophobic nanopore surfaces can be exposed to the liquid phase. When the pressure is removed, the system does not return to its initial configuration. Unlike ordinary energy absorption systems, no significant temperature variation can be detected during the infiltration of pressurized liquid water, indicating that the sorption process is nonexothermic. This is attributed to the conversion of mechanical work to excess solid-liquid interfacial tension. © 2008 American Institute of Physics. [DOI: 10.1063/1.2844884]

With the development of processing techniques of nanostructured materials, understanding the behavior of nanofluidics has been an increasingly active research area. For instance, in a liquid phase, with the formation of small-sized bubbles, the shock wave structure can be considerably changed. In a recent research on liquid based energy absorption systems, we used nanoporous materials to create nanometer-scale gas phases. As hydrophobic nanoporous particles are suspended in a liquid, the gas phase in the nanopores can be dispersed quite uniformly, forming a nanoporous material functionalized (NMF) liquid. Since the inner surfaces of nanopores are nonwettable, the gas phase is stable. Only when a high quasistatic pressure is applied on the liquid medium can the gas phase be dissolved in the liquid. Associated with the exposure of the nanopore surfaces to the liquid phase, the system free energy increases. Due to the large specific surface area of the nanoporous material, the energy density of such a system is high. For many nanoporous materials, the confined liquid does not diffract even when the external pressure is fully removed. The sorption curves of these systems are hysteretic and they can be utilized for energy absorption applications, e.g., liquid bumpers, liquid armors, etc.

Conventionally, infiltration experiments of NMF liquids have been performed at constant temperatures, and the sorption and desorption processes were assumed to be isothermal. As the external pressure is applied, a certain amount of mechanical work needs to be done to force the liquid into the nanopores, associated with the decrease in overall volume. As the external load is reduced, since the confined liquid remains being “locked” inside the nanopores, the liquid volume does not recover. In an ordinary energy absorption material, usually, the dissipated mechanical work is converted to heat, such as in a dashpot or a reinforced polymer. In a nanopore, as the nanopore diameter approaches but is still larger than the molecular size, since the effective viscosity tends to be smaller than that of bulk liquid phase, when the loading rate is relatively low, the interactions among liquid molecules may be negligible. Moreover, at such a small length scale, the solid-liquid boundary condition is still inadequately understood. As a result, it is quite unclear how the external work is dissipated.

In order to understand the energy exchange process, we investigated a nanoporous silica gel. The material was obtained from Sigma-Aldrich. By using a Tristar-3000 gas absorption analyzer, its average nanopore size was determined to be 16.1 nm; its specific surface area was 305 m²/g; and its specific nanopore volume was 1.07 cm³/g. The particle size was 200–500 μm. The as-received material was hydrophilic, and thus, when it was immersed in water, it would be soaked up spontaneously. To produce an energy absorption system, it must be surface treated. After the silica gel had been dried in vacuum at 100 °C for 24 h, it was treated at 90 °C for 24 h in a round-bottom flask in 40 ml of dry toluene and 1 ml of chlorotrimethylsilane, with the mixture being stirred at the rate of about 30 rpm. Then, the silica gel was collected by vacuum filtering, washed by dry toluene and warm water repeatedly, and vacuum dried. During the surface treatment, the hydroxyl groups at nanopore surfaces were deactivated.

Figure 1 depicts the setup of infiltration experiment, which consisted of a double-layer cylinder. The outer layer was made of stainless steel and the inner layer was made of Teflon. The thickness of the inner layer was 12.6 mm. The cylinder contained 1.0 g of surface treated silica gel and 5 g of de-ionized water. According to a differential scanning calorimetry measurement, the specific heat of the mixture of de-ionized water.
silica gel and water was 3.4 J/g K. A quasihydrostatic pressure was applied on the liquid phase through a stainless steel piston. The piston was insulated from the liquid phase by a 12.6 mm thick Teflon layer. The average temperature in the central part of the cylinder was measured by a type E thermocouple, with the accuracy of 0.05 °C. By using warm water to calibrate the system, it was confirmed that the insulation property was quite good. The temperature decrease was smaller than 0.1 °C within 20 s.

By using a type 5569 Instron machine, the piston was intruded into the cylinder at a constant rate of 7.5 mm/min. As the inner pressure reached 10 MPa, it was moved out at the same rate. The loading-unloading cycle took 10–15 s. The set point of 10 MPa was chosen so that the nanopores would not be fully filled, as will be discussed shortly. Figure 2 shows typical sorption curves. If the loading rate was changed to 1 mm/min, no detectable variation in sorption curves could be observed, indicating that such a loading rate could be regarded as quasistatic. During the infiltration experiment, the temperature inside the cylinder was measured continuously. For comparison purpose, a similar testing procedure was repeated on a reference system which contained only 5 g of de-ionized water but no silica gel. Table I shows the measurement results.

It is remarkable that, according to Table I, no significant temperature increase can be detected during the liquid water infiltration. As shown in Fig. 2, initially, when the pressure is relatively low, liquid water cannot enter the nanopores. Thus, the pressure increases from “A” to “B” quite linearly. The slope of the sorption curve is dominated by the liquid compressibility and the machine compliance. The specific volume change is defined as the volume occupied by the piston per unit mass of silica gel. It is clear that after the surface treatment, it is energetically unfavorable for the liquid to wet the nanopore surfaces. When the pressure is about 8.7 MPa, the liquid phase starts to enter the nanopores. The pressure induced infiltration continues to “C.” In the infiltration plateau (“BC”), the system compressibility is much larger than that in section “AB.” When the peak pressure of 10 MPa is reached, the piston is moved out of the cylinder, so that the inner pressure decreases. The unloading path, “CD,” is different from the loading path, “ABC,” which suggests that the confined liquid does not delaminate. The slope in section CD is similar to that of AB, both of which are dominated by the compressibility of liquid water as well as the machine compliance. The infiltration volume is nearly 0.3 cm³/g, only one-third of the specific nanopore volume. Note that in the infiltration process, the system volume change is quite independent of the liquid compressibility. If the peak pressure were increased, more nanopores would be involved in the pressure induced infiltration and the complicated gas dissolution may affect the testing results. The current study is focused on the solid-liquid interaction during initial stage of liquid infiltration.

When unloading is completed, at the second loading, the system compressibility is lost. Since the nanopores are filled, no more liquid infiltration can be observed, and both loading and unloading paths are linear. That is, upon the first unloading, the compressed gas phase cannot repel the confined liquid as the pressure is lowered. There are a few possible reasons of the nonoutflow phenomenon, including the nonuniform nanopore structure, e.g., the “ink-bottle” effect, the hysteresis of effective contact angle, etc., the details of which are still under investigation.

During the first loading, mechanical work is stored as compression strain energy in the liquid phase before the infiltration starts, which can be assessed as the area under section AB, Wₐ. As the liquid infiltrates into the nanopores, the external pressure must be maintained at a high level, and associated with the system volume decrease the mechanical work done by the piston can be estimated as the area under section BC, Wᵢᵣ. During unloading, since the slopes of CD and AB are close to each other, Wᵣ, is released, while Wᵢᵣ, is effectively dissipated. In the current system, Wᵢᵣ, is about 2.9 J. If Wᵢᵣ, were converted to thermal energy, since the heat capacity of the silica-water mixture is 3.4 J/g K, the system temperature should increase by 0.84 °C, which is not detected in the experiment. Table I shows that, compared with the reference system where no silica gel is added, the temperature change of the NMF liquid is nearly the same.

Figure 3 depicts the liquid motion in a nanopore. If liquid molecules slide against the solid surface, since they must overcome periodic energy barrier to move among tetrahedral sites, when they reach a metastable state excess energy can

![FIG. 3. Schematic of the confined liquid in a nanopore.](image)

TABLE I. Results of the calometric measurement (°C).

<table>
<thead>
<tr>
<th>Test</th>
<th>Onset of loading (A)</th>
<th>Onset of infiltration (B)</th>
<th>Onset of unloading (C)</th>
<th>End of unloading (D)</th>
</tr>
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<td>23.5</td>
<td>23.5</td>
<td>23.5</td>
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</tr>
<tr>
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<td>23.5</td>
<td>23.5</td>
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</tr>
<tr>
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<td>23.5</td>
<td>---</td>
<td>23.7</td>
<td>23.6</td>
</tr>
<tr>
<td>6*</td>
<td>23.4</td>
<td>---</td>
<td>23.5</td>
<td>23.6</td>
</tr>
<tr>
<td>Average</td>
<td>23.4</td>
<td>---</td>
<td>23.6</td>
<td>23.6</td>
</tr>
</tbody>
</table>

*Tests 5 and 6 are for the reference system that contains only 5 g of de-ionized water.
be transferred to the environment. Thus, the system temperature should rise. Because the temperature change is negligible, the conventional no-slip boundary condition may still be valid. One way to explain this result is to take into consideration the conversion of mechanical work to solid-liquid interfacial tension. As the nanopore surface is exposed to the liquid phase, the interfacial tension, $\gamma_{sl}$, is larger than $\gamma_s + \gamma_l$, with $\gamma_s$ and $\gamma_l$ being the surface tensions of the solid and the liquid, respectively. If the excess interfacial tension should be stored in the liquid phase, causing a variation that causes $\Delta \gamma = \gamma_{sl} - (\gamma_s + \gamma_l)$, equals to $W_{in}/A$, no work can be converted to thermal energy, where $A$ is the total pore surface area. In the current system, the mass of silica gel is 1 g, with the total surface area of 305 m$^2$. Thus, $\Delta \gamma = 9.5$ mJ/m$^2$. Since the solid structure is much more rigid than the structure of liquid molecules, the majority of the excess interfacial tension should be stored in the liquid phase, causing a variation in average molecular distance. For a first order approximation, the inner pressure inside the nanopores can be taken as the infiltration pressure, which is around 9.5 MPa. Thus, across a unit area of nanopore surface, the volume variation that causes $\Delta \gamma$ is $2 \times 10^{-9}$ m$^3$, about 50% of the corresponding nanopore volume. That is, the average distance among the confined liquid molecules varies by nearly 20%, which looks plausible. Because most of the mechanical work is consumed to overcome the capillary effect and stored as the interfacial energy, little thermal energy can be generated, so that the temperature variation is within the resolution of the testing system.

To summarize, according to a calometric measurement, during liquid water infiltration in a surface treated nanoporous silica gel, the system temperature variation is negligible; i.e., the infiltration process is nonexothermic. Since the unloading path of sorption curve is different from the loading path, the work done by the external pressure is absorbed, which should be attributed to the conversion of mechanical work to excess solid-liquid interfacial tension.

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