Pressurized Flow in a Mesostructured Silica Modified by Silane Groups

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By applying a quasi-hydrostatic pressure, water or electrolyte solution can be compressed into a surface treated MSU-H mesoporous silica. Based on the pressure-volume curves, thermodynamic and kinetic characteristics of the pressurized flow are analyzed. For pure water based system, continuum theory explains the testing data quite well but fails to capture the rate effect. For electrolyte solution based system, the classic interface theory breaks down, probably due to the unique ion behaviors in the nanoenvironment. [DOI: 10.1115/1.3089542]

1 Introduction

Liquid behavior in nanoenvironment has been an important research topic for more than a decade [1,2], which shed much light on fundamental mechanisms governing solid-liquid interactions at small length and time scales. The studies in this area have been immensely useful to developing better techniques for drug delivery, micro-/nanotransportation, micro-/nanofabrication, biosensing, etc.

Over the years, energy dissipation associated with nanofluidic behaviors has drawn considerable attention [3,4]. The initial idea was based on the assumption that, as a liquid flows innanopores and the internal friction takes place across the large pore surface, the energy dissipation capacity can be ultrahigh. Such a system may have great applicability in advanced dampers, bumpers, and armors. For instance, in an experiment performed by Li [5], bending moments were applied on a hydrophilic nanoporous silica block soaked by water. As water flowed from compressive parts to tensile parts, there was a detectable damping effect. However, the energy dissipation efficiency was lower than the expected level.

Recently, an improved concept has been investigated by a few research teams [6–11], including the authors of this paper, who replaced the hydrophilic nanoporous solids by hydrophobic ones. Due to the capillary effect, as a hydrophobic nanoporous material is immersed in water, the nanopores remain empty. Once a high pressure is applied on the liquid phase, pressure induced infiltration (PPI) would occur, accompanied by conversion of a significant amount of external work to excess solid-liquid interfacial energy. In a number of nanoporous systems, the excess solid-liquid interfacial energy cannot be converted back to the hydrostatic pressure as the external loading is removed; that is, the sorption isotherm curves are hysteretic, which results in ultrahigh energy dissipation efficiency larger than a few J/g, much better than many conventional protective materials [12]. A similar design concept can be extended to nonpolar liquids using lyophobic nanoporous materials, which has led to an even higher energy density [13,14]. In these investigations, it has been noticed that increasing degree of hydrophobicity, decreasing pore size, and adding electrolytes can be of beneficial effects to improving system performance.

2 Experimental Procedure

In the current study, we investigated a MSU-H type nanoporous silica that was commonly used as adsorbent and catalyst support. It was of a hexagonal framework, small pore size, and relative large specific pore volume, ideal for energy absorption applications. The network material was obtained from Sigma-Aldrich (St. Louis, MO) (CAT No. 643637). The as-received material was in powder form. The particle size was 20–80 μm. According to a gas absorption analysis using a Tristar-3000 analyzer, the average pore size was 7.1 nm, the specific pore volume was 0.9 cm³/g, and the specific pore surface area was 510 m²/g. Figure 1 shows the Barrett–Joyner–Halenda (BJH) analysis result of nanopore volume distribution. Its pore surface was hydrophilic, and therefore could not be directly used for PPI testing. In order to modify the pore surface structure, the silica particles were first dried at 100°C in a vacuum oven for 24 h and then refluxed in a silicone agent solution in a hot mantle. The solution was prepared by injecting 1 part of chlorotrimethylsilane into 40 parts of dry toluene. Prior to the refluxing, the mixture had been gently stirred at room temperature for 10 min. The refluxing time ranged from 3 h to 24 h. During this process, the chlorotrimethylsilane molecules diffused into the nanopores and formed hydrophobic O—Si(CH₃)_3 groups at nanopore walls, changing the surface wettability [15]. The treated sample was vacuum filtered, washed with dry toluene, and dried at 100°C for 24 h in vacuum.

Figure 2 depicts the PPI experimental setup, which consisted of 0.2 g of surface treated silica particles immersed in 7 g of liquid, a steel cylinder, and a piston. A compressive load was applied on the liquid phase through the piston by an Instron machine, forcing the piston into the cylinder at a constant rate. The liquid phase was either de-ionized water or saturated aqueous solution of sodium chloride. The compression rate, V, was 1–20 mm/min. The quasi-hydrostatic pressure in the liquid, p, was calculated as P/A₀, with P being the axial load and A₀=286 mm² being the cross-sectional area of the cylinder. The piston displacement, δ, was also measured, based on which the liquid volume change was calculated as ΔVₗ=δ·A₀. As the pressure exceeded 30–40 MPa, the piston was moved out of the cylinder at the same rate. Figures 3 and 4 show the typical sorption isotherm curves. The resolutions of load and displacement measurements were 250 N and 20 μm, respectively.

3 Results and Discussion

Without the surface treatment, the silica is hydrophilic and thus the nanoporous particles can be infiltrated by water. Under this condition, as shown by the dashed curve in Fig. 3, no infiltration can be observed in the PPI experiment. With the surface treatment, as shown by the solid curves, infiltration plateaus are formed. The infiltration plateau is defined as the middle portion of the loading part of sorption isotherm where the slope is much smaller than that of the linear compression sections. The surface treated nanoporous silica particles are initially filled by entrapped air. As the pressure is sufficiently high (4.5 MPa and 8.1 MPa for silicas surface treated for 3 h and 24 h, respectively), liquid starts to enter the largest nanopores. As a result, the system volume decreases rapidly. As the pressure rises, smaller nanopores are involved in the PPI process, during which the entrapped gas molecules are dissolved by the confined liquid. Note that the interactions among gas and liquid molecules in a nanopore can be fundamentally different from that in a bulk phase, as demonstrated by the molecular dynamics simulation in Ref. [16]. As the nanopore wall confines the molecular motion, there must be a sufficiently large “gap” between the gas molecule and the solid surface; otherwise,

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Contributed by the Fluids Engineering Division of ASME for publication in the Journal of Fluids Engineering. Manuscript received February 23, 2007; final manuscript received March 11, 2008; published online March 6, 2009. Assoc. Editor: Ali Beskok.
the liquid molecules would be blocked. When the pressure is lowered, since gas phase nucleation may be energetically unfavorable, the confined liquid does not come out of the nanopores; that is, a decrease in solid-liquid interfacial energy associated with the expansion of a nanobubble can be lower than the energy required for “evaporating” molecules from liquid phase to vapor phase, which causes a significant hysteresis in sorption isotherm. The enclosed area of the loading-unloading cycle indicates the dissipated energy (Table 1).

According to Fig. 3, the infiltration volume of the silica surface treated for 3 h, which can be measured by the width of infiltration plateau, is about 0.7 cm³/g, smaller than the BJH measurement result of nanopore volume of untreated silica. Note that the molecular size of O–Cl(CH₃)₃ is around 0.26 nm. As the nanopore surface is covered by a surface group layer, the effective pore size should be reduced from 7.1 nm to 6.6 nm, and the effective pore volume would decrease by about 15%, from 0.9 cm³/g to 0.76 cm³/g, quite close to the infiltration volume. The effective solid-liquid interfacial tension, according to the classic Young’s equation, can be calculated as $\Delta \gamma = \rho_{\text{in}} \cdot r / 2 = 13$ mJ/m², with $\rho_{\text{in}}$ being taken as 7.9 MPa and $r = 3.3$ nm.

As the surface treatment time, $t_s$, is increased to 24 h, the infiltration pressure largely rises to 12.4 MPa, while the infiltration volume decreases considerably from 0.7 cm³/g to 0.4 cm³/g, even though the nanoporous structure does not change. This phenomenon may be attributed to the formation of dense layers of silane groups at nanopore surfaces. When the surface coverage is saturated, in a prolonged surface treatment process, chlorotrimethylsilane molecules would continue to diffuse into the nanopores. Consequently, the pore volume decreases. The reduction in accessible pore volume from 0.7 cm³/g to 0.4 cm³/g is equivalent to a change in effective nanopore radius from 3.3 nm to 2.5 nm. With the same solid-liquid interfacial tension of 13 mJ/m², the infiltration pressure would increase from 7.9 MPa to 10.5 MPa, which is quite close to the values shown in Fig. 3. That is, the large variation in infiltration pressure and volume associated with the increase in treatment time are caused by the decrease in empty nanopore space.

If the liquid motion in nanopores could be described by a circular Poiseuille flow, as the infiltrating liquid molecules move along the pore wall, an additional pressure must be applied to overcome the viscosity effect. For a zero-order approximation, the pressure increase can be assessed as $\Delta p = \frac{32 \mu v \cdot dz}{D^2}$ [18], where $\mu = 10^{-3}$ Pa s is the liquid viscosity, $v$ is the inflow rate, $dz$ is the pore depth, and $D = 3.6$ nm is the effective pore diameter for the silica sample that is treated for 3 h. In the current study, the cross-sectional area of the testing cylinder, $A_0$, is 286 mm², and therefore it takes about 30 s to fill the nanopores. The average silica particle size is about 50 μm. Thus, the inflow rate, $v$, is

<table>
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<tr>
<th>Experimental condition</th>
<th>Surface treatment time (h)</th>
<th>Energy absorption capacity of treated MSU-H silica (J/g)</th>
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<tbody>
<tr>
<td>$v = 1$ mm/min</td>
<td>3</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>6.8</td>
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<tr>
<td>$v = 20$ mm/min (in pure water)</td>
<td>5.2</td>
<td>5.6</td>
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around 1 \mu m/s, and the characteristic value of $dz$ is about 10 \mu m. Consequently, when the piston speed changes from 1 mm/min to 20 mm/min, the sorption isotherm curve should shift along the pressure axis by a few MPa, which was not observed in the PII experiment. When the loading rate varied in this range, the infiltration plateaus were nearly identical. Clearly, in the confining nanoevironment, the no-slip boundary condition is no longer valid, and the definition of liquid viscosity breaks down, which explains why the internal-friction-based energy dissipation mechanism did not have the expected energy density [5].

As sodium chloride is added in the liquid phase, as shown in Fig. 4, while the infiltration volume does not vary, the infiltration pressure becomes much higher. The $p_{in}$ increase is about 2.2 MPa, which corresponds to a large variation in effective solid-liquid interfacial tension of about 8.6 mJ/m$^2$, 66% of that of pure water. Note that the surface tension of saturated sodium chloride solution is larger than that of pure water by less than 10% [19]. The large increase in the effective interface tension should be related to the confinement effect of pore walls on ion distribution. In a nanopore, normal to the pore surface, there is no enough space for the formation of a double layer. The bulk phase may not exist. Therefore, the effective ion concentration is higher than that at a large solid surface; that is, the ion structure is affected by the opposite nanopore surface, causing a “squeezing” effect, which can lead to a higher liquid composition sensitivity. The details of the fundamental mechanisms are still under investigation.

4 Conclusion

To summarize, through a pressure induced infiltration experiment on a surface treated MSU-H nanoporous silica, the liquid motion in nanopores are examined. For the system under investigation, the classic capillary theory can be employed to relate the infiltration pressure to the nanopore size. However, the continuum theory does not explain the low sensitivity of sorption isotherm to loading rate. It also fails to capture the large variation in infiltration pressure caused by addition of sodium chloride.

Acknowledgment

This work was supported by the Army Research Office under Grant No. W911NF-05-1-0288, for which the authors are grateful to Dr. D.M. Stepp.

References