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Thermal effects on infiltration of a solubility-sensitive volume-memory liquid

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As the ion density at a solid–liquid interface changes, the interfacial tension varies accordingly, which can lead to a large energy density output, particularly when amplified by the high specific surface area of a nanoporous material. This concept is validated by the results of a controlled-temperature infiltration experiment on a hydrophobic zeolite immersed in a saturated aqueous solution of sodium acetate. As the temperature changes, the sodium acetate concentration varies significantly, which in turn causes a variation in infiltration pressure. Since the infiltration and defiltration are reversible, under the working pressure, this system exhibits a volume memory characteristic, with a non-monotonic temperature–volume relationship.

1. Introduction

Developing smart materials, which can provide large displacements and output forces as their temperature is varied, has long been an active area of research [1]. Conventional smart materials are solids, such as titanium–nickel alloys, iron/copper based alloys, shape-memory polymers, etc. [2]. When the temperature changes across a critical range, reversible phase transformations or glass transitions can take place and, as a result, the shape and/or dimension of the smart material can vary considerably. Such materials have been widely applied for advanced control, active damping, smart structures, etc.

Recently, Qiao *et al.* [3, 4] developed liquid-like smart materials, namely nanoporous material functionalized (NMF) liquids. A NMF liquid consists of nanoporous particles immersed in a liquid matrix. As the temperature changes, the solid–liquid interfacial tension in the nanopores varies, which, under a working pressure, results in liquid motions, causing the NMF liquid to expand or shrink at the macroscopic level. Such a system can be regarded as a thermal machine working between two different temperatures. Through a thermodynamics analysis of the Carnot cycle [5], the net output energy is

$$W_{\text{out}} = \delta\gamma \cdot A \tag{1}$$

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where $\delta\gamma$ is the change in solid–liquid interfacial tension due to temperature variation, and A is the nanopore surface area. Since typically in a nanoporous material A ranges from 100 to 2000 m^2/g, even if $\delta\gamma$ is only at the level of 10 mJ/m^2, W_{out} can be 1–10 J/g, which, compared with the energy density of a Ti–Ni alloy around 50 mJ/g, is nearly two orders of magnitude higher. The system deformability is determined by the nanopore volume fraction, which is usually about 30–70%, also much larger than that of ordinary smart solids. In the above NMF liquids, the solid–liquid interfacial tensions are directly controlled by temperature via the thermocapillary effect. At a large solid surface exposed to an electrolyte solution, it is well known that the interface tension is highly dependent on the ion concentration, particularly the ion density in the interface double layer. The classic Van Oss–Chaudhury–Good (VCG) equation [6],

$$(1+\cos\theta)\cdot\gamma_{\text{L}} = 2\left(\sqrt{\gamma_{\text{S}}^{\text{LW}}\gamma_{\text{L}}^{\text{LW}}}+\sqrt{\gamma_{\text{S}}^{+}\gamma_{\text{L}}^{-}}+\sqrt{\gamma_{\text{S}}^{-}\gamma_{\text{L}}^{+}}\right) \tag{2}$$

can be used to determine the contact angle, θ, the surface free energy, γ_{S}, and its components that are indicated by the superscripts 'LW', '+' and '−', based on the liquid parameters that are indicated by the subscript 'L'. However, in a nanopore, especially in a micropore of the zeolite analyzed in the current study with a diameter of only about 0.5 nm, there are only a few liquid molecules across the cross-section in the liquid phase and, therefore, no contact angle can be defined. Moreover, many continuum concepts that are the basis of the VCG equation, such as the Debye distance, are no longer valid at small length scales. Nevertheless, it is generally accepted that the effective solid–liquid interfacial energy in a nanopore is a function of the absorbed species. Hence, if an NMF liquid is based on an electrolyte solution and the electrolyte concentration changes with temperature, a new degree of freedom is provided for system design.

In this article, we report the results of a controlled-temperature infiltration experiment on a hydrophobic zeolite. It is shown that, as the NMF liquid is modified by an electrolyte with a temperature-sensitive solubility, the pressure–temperature relationship can be non-monotonic and the output energy density can be very large.

2. Experimental

The NMF liquid analyzed in the current study was based on a well-crystallized, hydrophobic Zeolyst ZSM-5 zeolite with a high silicon content. The silica/alumina ratio was 280. The nanopore size was about 0.56 nm and the specific nanopore surface area was 930 m^2/g [7]. The experimental system was produced by sealing 0.5 g of the zeolite crystals and 7 g of liquid in a stainless-steel cylinder using a steel piston equipped with a gasket. The zeolite crystals were dried in air for 12 h before testing. The piston could slide into or out of the cylinder as an external load was applied, with the friction force being less than 2% of the peak load. The details of the system have been described elsewhere [8].

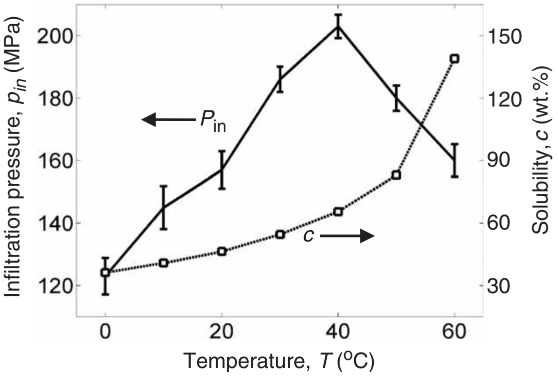

Figure 1. Electrolyte solubility and infiltration pressure as functions of temperature.

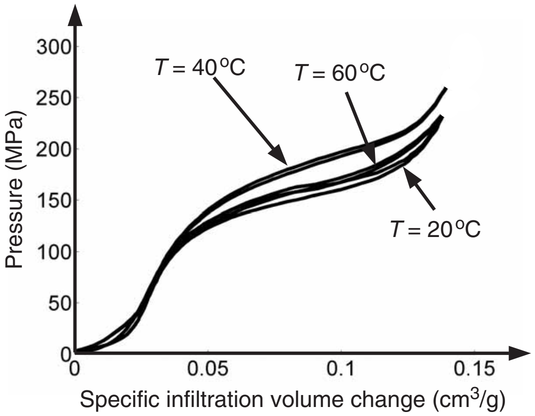

Figure 2. Typical sorption isotherm curves at different temperatures.

The liquid phase was prepared by mixing 1 part deionized water and 1.4 part Aldrich S8750 sodium acetate ($COOCH_3Na$), which was chosen as the electrolyte modifier on account of the high-temperature sensitivity of its solubility. As the temperature increased from 0 to 60°C, the solubility increased by more than three times from less than 40 wt% to nearly 140 wt%, as shown by the dashed line in figure 1. At 60°C, all the sodium acetate was dissolved in the liquid phase, forming a saturated solution. As the temperature, T, was lowered, excess sodium acetate precipitated out owing to the decrease in solubility. Thus, while the liquid was still saturated, the sodium cation and acetate anion concentrations kept decreasing; in other words, in this system, the ion content was thermally adjustable.

The infiltration pressure, p_{in}, was measured by compressing the piston into the steel cylinder using a type 5569 Instron machine. As shown in figure 2, in both low-pressure and high-pressure ranges, the system is not very compressible. At the low-pressure range, this behaviour should be attributed to the capillary effect, which prevents the liquid molecules from being compressed into the energetically unfavourable nanopores. Once the pressure is sufficiently high, the liquid molecules quickly infiltrates into the nanopores and the sorption isotherm curve then becomes quite flat. As the pressure is further increased, the nanopores are filled and the effective stiffness becomes large again. Upon unloading, the unloading path follows the loading path; that is, the sorption isotherm is non-hysteretic and the confined liquid molecules defiltrate immediately as the pressure is lowered.

The infiltration–defiltration cycles were performed at various temperatures in the range 0–60°C. Temperatures higher than room temperature were reached by using an Aldrich DigiTrol II Z28 water bath; the low temperature was controlled by ice or cold water. At each temperature, the infiltration pressure, p_{in}, was measured from the sorption isotherm curve as the pressure at the middle point of the infiltration plateau. The p_{in}–T relationship is shown by the solid line in figure 1. Based on the classic Young's equation, which may not be applicable for nanoporous materials, the infiltration pressure should be reversely proportional to the pore size. For the sake of simplicity in this article, the starting pointing of the infiltration plateau was defined as the point where the slope of sorption isotherm curve was 50% of that in the low-pressure linear section, and when the slope increased back to this value the infiltration plateau ended.

3. Results and discussion

One of the reasons that sodium acetate was chosen as the electrolyte is that the acetate ion size is quite large – comparable with the zeolite nanopore size. Thus, there is insufficient free space to permit pressure-induced infiltration [9, 10]. Therefore, only sodium cations can enter the nanopores together with water molecules, as depicted in figure 3. As the nanopore surface is exposed to the sodium cations, the solid–liquid interfacial tension varies owing to the change in atomic forces between the liquid and solid phases [11]. More importantly, as the cations diffuse into the zeolite framework, the pre-existing negatively charged surface sites, such as hydroxyl groups or other defects, can be neutralized; that is, the effective number density of surface defects decreases. As a result, the nanopore surface is less polarized and, therefore, becomes more hydrophobic, i.e. less attractive to water molecules. This phenomenon, which is often referred to as cation exchange, has been widely employed to control surface properties and/or network conductivity of zeolites or zeolite-like materials [12–14]. Consequently, as the sodium ion concentration increases with temperature, the zeolite tends to become effectively more hydrophobic, which leads to a larger infiltration pressure.

On the other hand, if the liquid composition were constant, according to previous experimental results the zeolite–water interfacial tension would decrease as the temperature increases [3, 4], an effect that should be associated with the well-known thermocapillary effect [15–17]. As the temperature rises, the surface tensions of both the solid and the liquid decrease, usually at different rates. As a result, the excess solid-liquid interfacial tension, $\Delta\gamma$, which is the difference between the total surface free energy of the solid/liquid materials and the net solid–liquid interfacial free energy, can either increase or decrease [15]. For zeolite materials, $\Delta\gamma$ usually

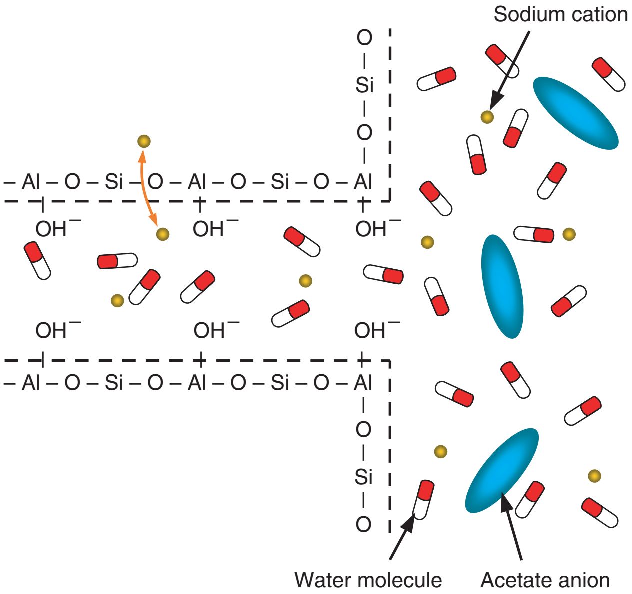

Figure 3. Schematic diagram of confined water molecules and cations in a nanopore.

decreases as temperature increases; that is, at an elevated temperature, they become less hydrophobic, or equivalently, more hydrophilic. Furthermore, the temperature sensitivity is also dependent on liquid composition. For instance, in a previous experiment, it was found that as the electrolyte concentration increased by 30 wt%, the change in infiltration pressure of the zeolite caused by the same temperature variation increased considerably [4].

Clearly, in the system under investigation, as the temperature is raised, there are two competing mechanisms: (1) the thermocapillary effect, which tends to lower the degree of hydrophobicity and the infiltration pressure; and (2) the cation exchange effect, which tend to make the zeolite more hydrophobic and thus increase the infiltration pressure. Both effects are highly non-linear with temperature. The temperature sensitivity of p_{in} caused by the thermocapillary effect, while in a fixed liquid–composite system is quite constant [3], is larger in the current study, since the ion concentration increases with temperature at an increasing rate. In other words, with more sodium cations, due to the thermocapillary effect, $\Delta\gamma$ tends to decrease faster as the temperature rises. The cation exchange effect, on the other hand, is more pronounced at a lower temperature, since it saturates as the cation density reaches about 10–100 $\mu\text{mol/m}^2$ [12], equivalent to a sodium acetate concentration of 30–50 wt%.

Therefore, as shown in both figures 1 and 2, at the low-temperature region, cation exchange is the dominant factor and the infiltration pressure increases with temperature. When the temperature exceeds 40°C, the cation concentration is higher than 60 wt% and the cation exchange rate tends to converge to the steady-state. Under this condition, as the thermocapillary effect becomes increasingly pronounced, it dominates the system behaviour and the infiltration pressure starts to decrease with increasing temperature. It is remarkable that in both the rising and descending parts of the p_{in}–T curve, the temperature sensitivity is about the same, around 2 MPa/°C. This value is much larger than that of systems without the addition of sodium acetate. For instance, the temperature sensitivity of the infiltration pressure of a pure water-based system is only 0.5 MPa/°C [3]. Note that the effective gas solubility in nanopores is also a function of temperature, which in turn affects both infiltration and defiltration behaviours [18].

As discussed in the introductory section, the NMF liquid is essentially a thermal machine, due to the high temperature sensitivity of its infiltration pressure and the low hysteresis of the sorption isotherm. If initially at 0°C, the system is subjected to a constant pressure of 125 MPa, the liquid would be confined in the nanopores as the capillary effect is overcome mechanically. As the temperature increases, the working pressure cannot prevent defiltration because the zeolite effectively becomes more hydrophobic and, thus, the system would expand. When T reaches 40°C, the change in p_{in} is around 80 MPa, which, since the specific infiltration volume associated with the infiltration plateau is about 0.1 cm^3/g, leads to a large output energy density of 8 J/g – much higher than the energy density of conventional smart solids. Owing to the non-monotonic nature of the p_{in}–T relationship, a similar system behaviour can be achieved by decreasing the temperature from a high set point to 40°C.

4. Concluding remarks

Through a controlled-temperature infiltration–defiltration experiment, it has been demonstrated that using an electrolyte with a temperature-sensitive solubility can significantly increase the output energy density of nanoporous material functionalized liquids, providing a promising way to enhance their performance. The infiltration pressure does not vary monotonically with the temperature; rather, there exists a critical temperature at which the infiltration pressure reaches a maximum value, which can be attributed to a competition between the thermocapillary effect and the cation exchange effect. The former mechanism is dominant in the high-temperature range and the latter is more pronounced in the low-temperature range.

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