Experimental Study on Energy Dissipation of Electrolytes in Nanopores

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When a nonwetting fluid is forced to infiltrate a hydrophobic nanoporous solid, the external mechanical work is partially dissipated into thermal energy and partially converted to the liquid–solid interface energy to increase its enthalpy, resulting in a system with a superior energy absorption performance. To clarify the energy dissipation and conversion mechanisms, experimental infiltration and defiltration tests of liquid/ion solutions into nanopores of a hydrophobic ZSM-5 zeolite were conducted. The characteristics of energy dissipation were quantified by measuring the temperature variation of the immersed liquid environment and compared against that estimated from pressure–infiltration volume isotherms during infiltration and defiltration stages of the test. Both stages were observed to be endothermic, with the temperature of the liquid phase showing a steady increase with changes in liquid saturation. The confinement of the molecular-sized pore space causes the liquid molecules/ions to transit between statuses of orderly and disorderly motions, resulting in dissipation behaviors that vary with liquid infiltration/defiltration rates and the types and concentrations of additive electrolytes in the liquid—both factors of which alter the characteristics of the nanofluidic transport behavior.

1. Introduction

As a subset of nanostructured materials, nanoporous crystals have uniform void spaces with dimensions on the order of nanometers, which enable them to interact closely with foreign atoms, ions, and molecules. Because of the very large pore surface area of nanoporous crystals, unique nanofluidic behaviors are generated when fluids move through the nanopores. As a result, studies of nanofluidic behavior in nanoporous systems are contributing to advances in nanoscience and nanotechnology, including selective ion absorption and adsorption, separation, catalysis, sensing, biological molecular isolation, purifications, and hydrogen storage.^{1,2}

Recent attention on nanofluidic behavior in nanoporous materials has been focused on the potential contribution to next-generation energy-absorption, protection, and/or damping systems, or nanoporous energy absorption systems (NEAS), which utilize the principal that as a nanoporous material is immersed in a nonwetting liquid or liquid solution, the liquid can be forced to infiltrate the otherwise energetically unfavorable nanopore when an external mechanical pressure (or other driving force) exceeds a critical threshold.^{3–9} During the infiltration process, part of the work done by the external mechanical load is reversibly converted into the interfacial energy (“the reversible

energy conversion”) between the invading liquid and the interstitial fluid (e.g., air that initially occupies the nanopores), with the excessive part being irreversibly dissipated via the extensive solid–liquid interface friction (in the form of thermal energy) as the invaded liquid transporting along the nanopore (“the irreversible energy dissipation”). The interfacial energy is proportional to the product of $\bar{\gamma} \cdot \tilde{A}$, where $\tilde{A}$ is the specific nanopore surface area ($\sim 1000 \text{ m}^2/\text{g}$ for typical nanoporous materials),³ $\bar{\gamma}$ the effective liquid–gas interfacial tension and can be estimated as $\bar{\gamma} = -\gamma_{1a} \cdot \cos \alpha$, where γ_{1a} is used in the sense of enthalpic part of the interfacial energy,¹⁰ and α the contact angle ($\alpha > \pi/2$).

As the external mechanical load is progressively decreased, in some NEAS systems, the liquid is retained in the nanopores and the unloading process is essentially “elastic”.¹¹ In this case, the total “energy absorption” of NEAS is the summation of “energy conversion” and “energy dissipation” that occurred during the infiltration process. In some other cases, the liquid that invaded the nanopores will be expelled from the pore spaces by the stored interfacial energy; during this process, the interfacial energy will be primarily dissipated into thermal energy via a similar “frictional effect”. [Although the variation of system thermal energy is primarily caused by the “frictional” dissipation process due to the close interaction between confined liquid molecules and solid pore, we note that according to the first law of thermodynamics, the change of interfacial area during infiltration and defiltration processes could also contribute to part of the system thermal energy variation (which may be termed as the “reversible heat”). However this part is difficult to quantify during experiment and therefore in the present work, the thermal energy variation is mainly attributed to the solid surface resistance, and more a sophisticated experiment will be carried out in future.] In this case, the total “energy absorption” of NEAS is primarily attributed to the “energy dissipation” effect during the loading/unloading

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cycle, similar to the behavior of a dashpot. Under such a scenario (which is the material system employed in the present study), the “intermediate” stage of energy conversion, or wetting energetics, matters less in the final energy absorption performance (after unloading) although it is still important during the infiltration process (during loading) and critical for nanofluidic behavior. The nanoscopic mechanism that distinguishes defiltration vs nondefiltration behavior upon unloading was discussed elsewhere.¹²

In view of the enormous specific surface area possessed by nanoporous materials, the resulting absorption density could be orders of magnitude larger than that of conventional energy-absorption materials (e.g., foams and shape memory alloys that absorb energy only by deformation).³ By adjusting solid phase, pore size, liquid phase, liquid concentration, and other working conditions (e.g., temperature, loading rate), the NEAS energy absorption performance can be varied over large ranges and thus be attractive for a number of civilian, military, and national security applications.^{3–7,13} [NEAS also has advantages over nanocomposite based systems: the liquid “filler” in NEAS is flexible and can maximize the accessible surface area of nanoporous particles. This overcomes the intrinsic difficulty with nanocomposites because, in such systems, the filler–matrix interaction not well controlled and the nanocomposite often becomes less ductile with the addition of the nanofiller, which leads to catastrophic cracking and lower energy absorption performance.]

To fulfill the promise of nanoporous materials in the NEAS application, the fundamental infiltration and transport behaviors of liquids inside the nanopore, as well as the related energy conversion/dissipation mechanisms, must be sufficiently understood. The bottom-up knowledge of the confined liquid molecules could make important contributions to chemical and materials science. Ideally, this understanding should be based on a synergy between experiment and atomistic simulation.^{12,14–16} From molecular dynamics (MD) simulations, new nanofluidic transport mechanisms have been reported, including the dramatically enhanced flow in a very small nanotube (diameter D is smaller than about 1–2 nm)^{17–20} inside which the water molecules/ions form a quasi-one-dimensional chain-like structure^{8,9} and can rapidly transport along the axial direction,^{21,22} while for a medium or larger sized nanochannel, the confined liquid molecules may exhibit layered structural characteristics, depending on the liquid and solid phases as well as the boundary conditions.^{23–25}

Despite these useful insights, most of the previous MD simulations were based on overly simplified systems with either a constant temperature or constant energy and thus may not

represent realistic situations. Note that in a nanoenvironment, the variation of temperature could lead to fundamentally different system properties, e.g., the change in fluid wetting ability.^{26,27} Therefore, the investigation of temperature variation during nanofluidic transport is of fundamental importance. Moreover, in the aforementioned NEAS, by exploring the system’s temperature variation one could deduce the relative contributions of energy conversion (from mechanical work to interface energy) and dissipation (through interfacial friction between liquid and solid) in the confined nanoenvironment. An improved understanding of this fundamental subject can not only provide information to validate or improve numerical models but also shed some light on the fundamental energy absorption behavior of NEAS, which will benefit the design and optimization of NEAS function and performance.²⁸

In this paper, we carry out an experimental investigation on the fundamental nanofluidic energy dissipation behavior as the liquid infiltrates and then defiltrates from a nanoporous crystal with molecular-sized nanopores under external mechanical loadings. The energy dissipation is primarily characterized by a careful measurement of system temperature variation as well as that estimated from the pressure–infiltration volume sorption isotherm, which is related to the unique behaviors of liquid molecules in a confined nanoenvironment. The mechanical loading rate and liquid solutions are also varied to explore their effects on system behavior, which is also consistent with previous numerical studies.^{9,22,29} The findings could contribute to improved understanding of nanoscale energetics.

2. Experimental Section

A ZSM-5 zeolite was used as an example nanoporous material. The surface of the zeolite particles was chemically treated following the similar procedure outlined by Han et al.²⁸ The modal values of the pore size (which is essentially uniform in the zeolite crystal), according to gas absorption tests, were determined to be $D_{\text{ZSM-5}} \approx 0.81$ nm and the specific pore volume is about 280 mm³/g, from which the accessible specific pore area to liquid phase ($\bar{A}$) is estimated as about 1500 m²/g. The surface coverage was 10–12% mol/m², which led to a high degree of hydrophobicity, and the particle size was in the range of 15–35 μm . Prior to the infiltration tests, a thermal anneal process was performed to get rid of any undesirable impurities.³⁰

In each experiment, 3.0 g of surface treated ZSM-5 zeolite was mixed with 5.0 g of a liquid solution (pure deionized (DI) water or electrolyte–DI water solution). The liquid–nanoporous solid mixture was placed under a high vacuum condition (<0.05 bar) to get rid of easily dissolved air bubbles and then sealed in the testing cell (chamber), which is a stainless steel cylinder that was seamlessly mounted on a flange base, as illustrated in Figure 1. The gap between the pressure chamber and piston was tightly sealed by an O-ring. Surrounding the external surface of the cylinder, a polyisoprene insulating layer was wrapped to prevent rapid heat loss. On top of the cylinder, a modified Tee connector was used to directly connect a type-E thermal couple and a pressure transducer with the cylinder, to measure the temperature and pressure variations inside the cylinder during loading/unloading (infiltration/defiltration) cycles. The piston (a linear shaft) was driven by a servo motor to compress the mixture of

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Figure 1. Schematic setup of the high pressure cylinder (up to 9000 psi $\approx$ 60 MPa) fabricated in stainless steel that was used as the apparatus for the experiment. The cylinder was mounted firmly on a steel base and wired with a National Instrument Data Acquisition (NI DAQ) system.

Figure 2. Calibration of the thermocouple to determine the dependency of output voltage on the loading pressure and environment temperature. Temperature has been varied to make sure there is only a linear relationship between output voltages with loading pressure.

nanoporous powders and liquid solution sealed in the cylinder. A linear voltage differential transformer (LVDT) was attached to the piston to record piston displacement. The real-time signals were analyzed by a NI LabVIEW data acquisition system.

During the infiltration test, the piston moved forward at a constant velocity to impose pressure on the mixture inside the chamber. After the pressure reached 50 MPa, the piston retracted (at the same velocity), and when the pressure was reduced to a certain preset value, such as 0.1 MPa, to avoid excessive system compliance, the piston was driven forward again and the loading–unloading cycles were repeated for a few times to observe the repeatability of the loading cycle. The loading rate (forward/reverse motion speed of piston) is adjustable and was varied in the range between 0.2 and 5.0 mm/min, allowing the investigation of the dynamic system response. To explore the effect of additive electrolyte as well as its concentration, both KCl and NaCl solutions with variable concentration were tested and the results were compared with that obtained using pure deionized (DI) water. For all of the reported infiltration isotherms in the current paper, system compliances, including deformation of the steel cylinder and the compressibility of the liquid phase, have been subtracted from the recorded data to accurately reflect the true infiltration characteristics of the nanoporous zeolite.

Figure 3. Calibration of the thermocouple probe in a relative long range of time to make sure there was no self-heating effect included in the output voltage from the thermocouple.

A critical issue that needed to be addressed was the calibration of the thermocouple. Because of the ultra high pressure environment under which the thermocouple was placed, there was a concern that the variation in the electrical conductance of the thermocouple probe with pressure would lead to pseudotemperature readings. To isolate such effects, calibrations of the thermocouple were performed under cyclic loading, with the thermal couple inserted into the cylinder filled with only electrolyte aqueous solution. The fluid temperature within the cylinder was changed from 20 °C (room temperature) to 60 °C to make sure there was no temperature dependency. As shown in Figure 2, the calibration results clearly indicate that even if there is no zeolite inside the cylinder, the output voltage from the thermocouple linearly increases with loading pressure, and the correlativity between output temperature and confining pressure could be approximated as $\Delta T \propto 0.01 \cdot \Delta P \pm 0.1$ (MPa). During the calibration process, the time history of recorded thermocouple output signals, shown in Figure 3, suggests that the output from the thermal couple was relatively invariant with advancing time. Hence, any thermocouple self-heating effect is believed to be negligible.

3. Results and Discussion

3.1. General Trend of Energy Dissipation and Temperature Variation. **3.1.1. Sorption Isotherms.** The surface treated zeolite is hydrophobic to aqueous based liquids and thus an external pressure is required to induce infiltration of an aqueous based liquid. As shown in the MD simulations in Figure 4, at normal (ambient) conditions, only a few water molecules can diffuse into the zeolite pore spaces [the equilibrium state of water molecules surrounding a ZSM-5 zeolite crystal (MFI type), in a simulation cell with dimensions of $100 \times 100 \times 160 \text{ \AA}^3$, was estimated by molecular dynamics (MD) simulation, employing the COMPASS forcefield and *NVT* ensemble ($T = 293.5 \text{ K}$)]. Hence, the bulk of the water molecules remain outside. However, with applied pressure, more water molecules can invade the nanopore space. Owing to the molecular-sized nanopore of zeolite used in our tests, following liquid invasion, a quasi-one-dimensional chain of liquid molecules (and ions when electrolyte solution is used) forms inside the nanopore space.^{8,29} Figure 5 shows a typical infiltration and defiltration isotherm obtained for a system of ZSM-5 zeolite with saturated NaCl/DI-water solution under the loading rate of 0.2 mm/min. It is important to note that in the present case shown in Figure 5, the loading rate (0.2 mm/min) is sufficiently slow such that the process can be regarded as quasistatic, that further reduction of the loading rate did not

Figure 4. Snapshot of MD simulation of the diffusion of water molecules into ZSM-5 sample (MFI type) zeolite at ambient pressure. The molecular simulation was conducted by employing the COMPASS force field and canonical ensemble NVT with temperature T fixed at room temperature, 293.5 K.

change the characteristics of sorption and thermal variation. The deductive system properties obtained at this loading rate, e.g., the effective aqueous solution surface tension γ or the stored interfacial energy ΔE^S , could be used as a benchmark. In the early stages of loading when the pressure was low, the observed pressure–volume relationship was almost linear (“A” $\rightarrow$ “B”), with a slope that was believed to be close to the compressibility of the nanoporous particles. The critical pressure for infiltration to occur was determined at point “B” as $P_{IN} \approx 16.1$ MPa; from this value, the effective surface tension $\bar{\gamma}$ can be obtained from the Young’s equation as $P_{IN} = 4\bar{\gamma}/d$, with the calculated value of $\bar{\gamma} \sim 3.36$ mJ/m². [As mentioned in the introduction, $\bar{\gamma} = \gamma_{la} \cdot \cos \alpha$ is the effective liquid–vapor interface tension, where γ_{la} is the liquid–vapor interfacial tension and α the contact angle between liquid and solid phase, d is the effective (accessible) nanopore diameter defined as $d = D_{ZSM-5} - 2h$, where $h \approx 0.14$ nm from Mattia et al. (ref 7) and D_{ZSM-5} the modal value of the zeolite pore size.]

After the initial liquid invasion, driven by the further increase in pressure, a larger volume of liquid overcame the resistance from the solid wall of nanopores and invaded the nanopore spaces, forming the infiltration stage “B” $\rightarrow$ “C”. Finally, when the nanopores were filled, the system underwent linear compression again (“C” $\rightarrow$ “D”), with a slope close to the bulk modulus of the liquid filled solid phase.

As the unloading phase started, the column (or chain) of liquid molecules began to be forced out of the invaded nanopores by the system’s interfacial energy. However, because of the resistance and confinement of the solid wall, the confined liquid did not move outward until a critical defiltration pressure (point “E”, ~ 15.9 MPa) had been reached. At point E, the loading pressure is close to the infiltration pressure and lower than that at point C (~ 27.1 MPa), so that enough pressure difference could be built up to overcome the resistance to liquid defiltration (drainage). After point E had been passed, a defiltration plateau formed (“E” $\rightarrow$ “F”) and the interfacial energy was dissipated. When the external pressure was reduced back to 0.1 MPa, the isotherm curve did not completely return to its origin, “A”, which indicates that there does exist an irrecoverable system deformation, possibly due to some liquid becoming permanently trapped within the pore space. However, this irrecoverable deformation is not very significant. Such a defiltration behavior also indicates that the area of the hysteresis enclosed by the sorption curve, which equals to the total energy absorbed by the NEAS under investigation, is essentially due to the “energy dissipation” behavior during loading and unloading and will be elucidated below. During the

Figure 5. Graph of loading and unloading sorption isotherms expressed in normal (black solid line) and log scale (red solid line). Also included on this graph are the 2nd and 3rd periods of a cyclic loading test. The dots in orange stand for pivot points used to interpret the loading cycle.

second loading cycle, the sorption curve started from point “G”, repeated the above stages and returned almost completely to its origin, completing an “outflow” hysteresis, which suggests that the current NEAS could work well under cyclic loadings. In what follows, only the first few loading and unloading cycles will be focused on.

3.1.2. Energy Dissipation. On the basis of the above analyses, the amount of energy being absorbed during the cycle of infiltration and defiltration can be determined by the magnitude of infiltration pressure, the specific volume and the resistance force encountered during the loading and unloading processes. During the infiltration stage, the work (ΔW) done by external load is converted to the interfacial energy (ΔE^S) and the energy (ΔE^D) being dissipated irreversibly via the “friction-like” interaction between solid and liquid phases; in the ideal case, they should satisfy the relationship $\Delta W = \Delta E^S + \Delta E^D$. If a horizontal line was drawn through point “B” in Figure 5, the area below the horizontal line and bordered by the infiltration curve can be regarded as the interfacial energy contribution (the reversible energy conversion) and the part over the line and bordered by the infiltration plateau is the portion of the external mechanical energy being dissipated (the irreversible energy dissipation) during infiltration. In this particular example, ΔE^S is estimated as 4.50 J/g per unit mass of the nanoporous material (or 1.69 J/g per unit mass of the mixture), and ΔE^D is about 0.73 J/g (per unit mass of the mixture). If the nanoporous material is filled up with liquid, the overall interfacial energy can also be estimated as $\bar{\gamma} \cdot \tilde{A}$, which is about 5.04 J/g (per unit mass of the nanoporous material) and agrees qualitatively with the value of ΔE^S measured in experiment.

Similarly, during the defiltration process, a portion of the interfacial energy ΔE^S is dissipated by the friction with solid surface as the invaded liquid being expelled out of the nanopore spaces, and its amount is graphically equal to the area under a horizontal line through point “E” and over the defiltration plateau. In the case shown in Figure 5, this amount is about 0.66 J/g (per unit mass of the mixture), which is qualitatively close to the ΔE^D measured during infiltration stage. The dissipated energy in defiltration is less than the stored interfacial energy so that the liquid in the nanopores has enough mechanical energy to overcome any surface resistance to motion and flow out, leading to a reusable NEAS. In some other nanopores with extremely

Figure 6. Temperature variations during the first three cycles (for a system with a liquid that is saturated NaCl and a loading rate of 0.2 mm/min), including the raw measurements from the thermocouple and the pressure-dependency-corrected net increment. The blue and orange dash-dotted lines serve as dividing markers for the loading and unloading stages. The dashed lines (in black and gray colors) indicate the general trend of temperature increments.

strong surface resistance (compared with that of the available interfacial energy as determined by the infiltration pressure), the liquid might be trapped “permanently” inside nanopores during unloading, leading to “non-outflow” hysteresis. The type of NEAS that exhibits this behavior might be used for one time only, as observed in MCM-41 silica.³¹

3.1.3. Temperature Variations. In either the infiltration or defiltration process, the dissipated external mechanical energy ΔE^D is assumed to be equal to the increased internal energy ΔU^E of the mixture. [Previous MD simulations^{8,9} revealed that after water molecules (and ions) enter a molecular-sized nanopore, they form ordered structures. This indicates that the infiltration process decreases entropy, which, along with change in interfacial area, would lead to an increase in system temperature during the energy conversion process. That is, part of the system temperature variation (which is reversible) could be related to the term of ΔE^S and that also contributes to part of the difference between the thermal energy variation during infiltration and defiltration. However, it remains difficult to experimentally quantify the magnitude of such entropy decrease, as well as the resulted temperature variation. Therefore, in the current research, we take an important assumption that the system temperature variation is roughly attributed to the interaction among solid and liquid phases, via the irreversible energy dissipation term ΔE^D . Improved experiments and MD simulations will be carried out in future to quantify the temperature variation due to ΔE^S .] Hence, the net temperature increase can be determined as $\Delta U^E = \xi \cdot m \cdot \Delta T$, where m is the mass, ΔT is the increment of net temperature, and ξ is the specific heat capacity of the mixture. [ξ could be estimated based on the weighted average of the mixture or experimentally measured using a differential scanning calorimetric test. Typically, $\xi_{\text{NaCl solution}} = 3.3 \text{ J/(g} \cdot ^\circ\text{C)}$, $\xi_{\text{water}} = 4.179 \text{ J/(g} \cdot ^\circ\text{C)}$, and $\xi_{\text{zeolite}} \approx 0.7 \text{ J/(g} \cdot ^\circ\text{C)}$.] ξ could be a function of the mass constitution of the mixture and for the zeolite-NaCl saturated solution mixture used in our tests, and ξ is estimated to be $3.136 \text{ J/(g} \cdot ^\circ\text{C)}$.³² Therefore, on the basis of the dissipated energy measured in the case shown in Figure 5, the temperature

variation is estimated to be about 0.23 and 0.21 °C during infiltration and defiltration, respectively.

On Figure 6, for the same system used in Figure 5, the actually measured temperature variations of the first three cycles are presented. The blue solid line indicates the raw data read from the thermocouple. Clearly, the linear dependency of the thermocouple output on the loading pressure is overwhelming and leads to a wavy like pattern of temperature readings. After subtracting the pressure dependence, the red solid line in Figure 6 is the net (intrinsic) temperature variation after each cyclic loading. A notable feature of Figure 6 is that the temperature of the mixture keeps increasing in both infiltration and defiltration stages, indicating that part of the external mechanical was dissipated into thermal energy via the irreversible “friction-like” interaction between solid and liquid phases, which occurred in both stages. In the case illustrated by Figure 6, the temperature variation during infiltration (0.21 °C) and defiltration (0.15 °C) is on the same order as that estimated above, further validating the proposed energy dissipation mechanism.

For a perfectly insulated experimental set up, no heat leakage would occur and the net temperature would keep increasing if cyclic external loading was applied. However, the net temperature profiles shown in Figure 6 indicate that the rate of temperature increase drops as the loading cycles proceed, which suggests some external heat loss. Nonetheless, this external heat loss is considered trivial in comparison to the net temperature increment in a single cycle and can be neglected without causing significant error. Meanwhile, an interesting discovery is that during the unloading process, the temperature increase is smaller than that during loading process. This phenomenon can not be merely attributed to the heat loss because the impacts of heat loss on the net temperature increment in both loading and unloading processes should be approximately equal; the mechanism behind this phenomenon will be thoroughly analyzed in the following sections.

In addition to the experiment reported in Figure 5, experiments were also conducted where the loading rate, electrolyte type, and concentration were varied to explore the impact of these factors on potential NEAS performance. The details of the parameters used and comparisons of temperature increments after infiltration and defiltration for all experiments that were performed are listed in Tables 1, 2, and 3. More details of the energy dissipation mechanisms observed, including the relationship between temperature variation and infiltration/defiltration processes, are discussed below.

3.2. Relationship between Sorption, Heat and Dissipation: Loading Rate Effect.

3.2.1. Dynamic Effects on Mechanical Force Responses. The transient infiltration and defiltration performances of an aqueous liquid phase in nanopores are of importance for NEAS to work under dynamic loadings.^{22,29} In our current experimental investigations, mixtures of zeolite and saturated NaCl solutions were tested with loading rates varying from 0.2 mm/min to 5 mm/min, with the corresponding infiltration pressures as 16.1, 17.6, and 18.9 MPa, respectively (Figure 7). Prior to an infiltration process, the liquid–vapor interface at the entrance of the nanopore will first protrude into the inner space of nanopore, which increases the curvature of the interface. This, in turn, leads to a high pressure difference across the interface. Given enough time, the curvature of the interface will relax to its original position, reducing the pressure difference to its initial status. However, the faster the loading rate, the shorter the relaxation time and hence the higher the infiltration pressures.

3.2.2. Dynamic Effects on Temperature Variations. Before infiltration, the experimental observations suggest that the system

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Table 1. Comparisons of Net Temperature Increments during Infiltration and Defiltration Stages under Different Loading Rates

loading rate(mm/min)	specific heat capacity, J/(g·°C)	ΔE^{D^a} (J/g)/ ΔT (°C) measured by thermal couple probe		ΔE^{D^b} (J/g)/ ΔT (°C) based on sorption isotherms	
		after infiltration	after defiltration	after infiltration	after defiltration
0.2	3.136	0.69/0.21	0.47/0.15	0.73/0.23	0.66/0.21
1.0	3.136	0.76/0.24	0.50/0.16	0.81/0.26	0.76/0.24
5.0	3.136	0.97/0.31	0.66/0.21	1.01/0.33	0.91/0.29

^a Assuming $\Delta U^E = \xi m \Delta T = \Delta E^D$, and normalized by the total mass of the mixture (≈ 8.0 g). ^b The total dissipated energy is estimated basing on the area enclosed by the loading and unloading sorption isotherms and normalized by the total mass of the mixture.

Table 2. Comparisons of Net Temperature Increments during Infiltration and Defiltration Stages for Systems of Zeolite Mixed with Different Liquid Solutions

saturated solution type	specific heat capacity, J/(g·°C)	ΔE^{D^a} (J/g)/ ΔT (°C) measured by thermal couple probe		ΔE^{D^b} (J/g)/ ΔT (°C) based on sorption isotherms	
		after infiltration	after defiltration	after infiltration	after defiltration
pure DI-water	4.179	0.33/0.08	0.21/0.05	0.36/0.09	0.33/0.08
KCl	3.181	0.73/0.23	0.51/0.16	0.77/0.24	0.70/0.22
NaCl	3.136	0.97/0.31	0.66/0.21	1.01/0.33	0.91/0.29

^a Assuming $\Delta U^E = \xi m \Delta T = \Delta E^D$, and normalized by the total mass of the mixture (≈ 8.0 g). ^b The total dissipated energy is estimated basing on the area enclosed by the loading and unloading sorption isotherms and normalized by the total mass of the mixture.

Table 3. Comparisons of Net Temperature Increments during Infiltration and Defiltration Stages for Systems of Zeolite Mixed Electrolyte Aqueous Solution of Various Molarities

saturated solution type	specific heat capacity, J/(g·°C)	ΔE^{D^a} (J/g)/ ΔT (°C) measured by thermal couple probe		ΔE^{D^b} (J/g)/ ΔT (°C) based on sorption isotherms	
		after infiltration	after defiltration	after infiltration	after defiltration
0.0	4.179	0.33/0.08	0.21/0.05	0.36/0.09	0.33/0.08
2.0	3.356	0.71/0.21	0.47/0.14	0.77/0.23	0.73/0.22
4.0	3.279	0.89/0.27	0.59/0.18	0.93/0.29	0.86/0.26
saturated (~ 6.0 M)	3.136	0.97/0.31	0.66/0.21	1.01/0.33	0.91/0.29

^a Assuming $\Delta U^E = \xi m \Delta T = \Delta E^D$, and normalized by the total mass of the mixture (≈ 8.0 g). ^b The total dissipated energy is estimated basing on the area enclosed by the loading and unloading sorption isotherms and normalized by the total mass of the mixture.

Figure 7. Comparisons of loading and unloading sorption isotherms (thick solid color lines) and net temperature profiles (thin dash-dotted color lines with symbols) for mixtures of zeolite with a saturated NaCl DI-water solution. Three loading rates were investigated to reveal any rate dependent effects.

mainly underwent a quasielastic compression stage where no mechanical energy would be converted to other forms of energy and dissipated. Basically, the corresponding intrinsic temperature profiles would be observed to be constant from “A” $\rightarrow$ “B”, except for some random “noise”. During the infiltration stage, “B” $\rightarrow$ “C”,

the temperature isotherms for the three investigated loading rates were almost overlapping in the early stage until a certain point between B and C, after which the net temperature profile for the highest loading rate rose much faster than the other two. From the beginning of the infiltration, the contact area between the liquid and solid phases gradually increased as more and more liquid molecules/ions entered into the nanopore space; the work dissipated by shear stress τ can thus be estimated as $\delta w = \tau \cdot \tilde{C} \cdot dx$, where $\tilde{C}$ is the equivalent wetting perimeter of the nanopore by the liquid phase and x indicates the invading distance measured from the pore entrance; so, mathematically, at a given loading rate and pore size, the amount of heat generation has a quadratic relationship with the invaded volume and its corresponding profile with infiltration volume would appear to be concave. Also, for a given nanoporous solid–liquid combination, τ is both rate-dependent and pore-size dependent; thus, at a higher loading rate, the larger τ leads to more heat generation, and such an effect is more evident when the infiltrated volume becomes large. All of these facts explain why all three loading rates resulted in similar temperature variation in the early part of the infiltration, as depicted in Figure 7, because a relatively small amount of joule heat was produced; as invasion proceeded, however, larger temperature increases were observed for the higher loading rates due to the more joule heat generation. Also note that according to a previous MD simulation,⁸ the infiltrated water molecules tend to form a quasi-one-dimensional chain and then a double-helical chain during the first-half and second-half stages of infiltration, respectively, into a zeolite nanopore. Such a structural change could suggest the entropy decreasing nature of the infiltration process and the

reversible heat generation associated with it could possibly contribute to the more apparent differences among the temperature variations of the three loading rates during the second-half-stage of infiltration.

With reference to Figure 7, the stages from “C” → “D” → “E” represent quasielastic processes in which the liquid filled nanoporous particles were under elastic compression. Under the most ideal situation, no temperature variation should be detected in these stages. In the present experiments, a finite temperature increment (although not very large) was measured during these two stages, with the ordering of the temperature magnitude of the 3 loading rates remains. The small measured increase in net temperature could be attributed to the friction among zeolite particles under high hydraulic pressure, and the internal friction between the liquid phase and solid framework in the liquid-filled particle as it undergo elastic deformation. Indeed, on the sorption curve, the slope from “C” to “D” is slightly different than that from “D” to “E”, indicating a possible occurrence of the “internal friction” energy loss. Another possible explanation could be the linear deformation of the “double-helical chain” structure of liquid molecules/ion that are formed within the nanopores above a certain critical loading pressure.⁸ Even during such quasielastic stages, some water molecules may be forced into the nanopores and contribute to the “double-helical chain” structure to alleviate the total system energy. A small portion of the system energy could then be dissipated into thermal energy, leading to a small overall increase in temperature.

By the end of stage “D” → “E”, the previously highly compressed double-helical chain of liquid molecules/ions inside the nanopore was “relaxed” due to the decreased environmental confining pressure. During the subsequent defiltration stage, “E” → “F”, for all three loading rates, an increase in temperature was observed, although its amplitude is much less significant than that during the infiltration stage. On one hand, as liquid molecules/ions moved out of the nanopores, the solid–liquid interfacial energy was dissipated into joule heat—this process is exothermic and it dominated the thermal performance of the system during defiltration; on the other hand, the decreasing pressure in the reservoir (the relatively large aqueous environment outside the nanopores) caused the molecular configuration of liquid in the nanopores to expand, which, in thermodynamics, is endothermic. As a result, the molecules inside the nanopores had to absorb a certain amount of heat so that they could overcome the resistance to motion and defiltrate (drain). Although, as stated earlier, the reversible heat due to the liquid–solid interfacial energy could also cause heat absorption during defiltration as the entropy of the invaded liquid increases and that could also contribute to the overall effect that less joule heat is generated during defiltration compared to that of infiltration;^{33,34} nevertheless, we believe that the main contribution of thermal energy variation should be resulted from the “frictional” resistance. In essence, in the present NEAS where liquid could defiltrate from the nanopores upon unloading, the energy absorbed is mainly due to the irreversible dissipation of external mechanical energy into thermal energy and that leads to a net gain in the system temperature. Meanwhile, the “intermediate” wetting energetics, i.e., the conversion of mechanical energy to interfacial energy upon infiltration, does not contribute to the final energy absorption performance (nor does it contribute to the overall gain of

system temperature after unloading) yet it is still important during the intermediate nanofluidic processes.

3.2.3. Estimations of the Dissipated Energy. As mentioned earlier, there are two ways to estimate the dissipated energy during infiltration. The first one is through the measured temperature variation using $\Delta E^D = \xi m \Delta T$, and the second one is from the area of the sorption isotherm below the infiltration stage “B” → “C” (i.e., the total external work) after removal of the contribution of ΔE^S . Similar efforts can be repeated for unloading (defiltration). It is also noted that, even in view of the observed higher infiltration pressure during the faster system loading rates, the interfacial energy density ΔE^S , determined by the properties of liquid phase and solid phase, and the geometric characteristics of nanopores, should be independent of the loading rate; and as noted in Section 3.1.1, the ΔE^S (≈ 1.69 J/g per mass of mixture) obtained at the loading rate of 0.2 mm/s is adopted as the default (reference) value in the following analyses.

With increasing loading rate, the more energy contained by the even more curving meniscus at the dynamic “equilibrium” state would be dissipated via interaction with solid wall. From the sorption isotherms in Figure 7, the dissipated energy density ΔE^D during the infiltration stage were found to be 0.73, 0.81, and 1.01 J/g for the three loading rates (from lowest to highest), respectively, and correspondingly, during the defiltration stage, they were estimated as 0.66, 0.76, and 0.91 J/g, respectively. Clearly, faster loading rate dissipated more external mechanical energy during infiltration and more interfacial energy was converted into joule heat during defiltration, but still the interfacial energy dominated in all cases.

The results of the dissipated energy density (per mass of mixture) during either the infiltration or defiltration stage are listed in Table 1. Taking the 5 mm/min loading rate as an example: During the loading stage, the 0.31 °C increment in net temperature translates to ~ 0.97 J/g internal energy density increase (using $\Delta E^D = \xi m \Delta T$), which matches well with the amount of dissipated external mechanical energy density obtained from the loading isotherm, ~ 1.01 J/g. However, during the unloading stage, the 0.21 °C net temperature increment only accounts for 0.66 J/g internal energy density increase. In other words, the thermal energy absorbed by liquid molecules/ions during defiltration, as explained in the previous section, is not negligible, which in part causes the temperature increase to be less significant during defiltration than during infiltration.

Comparing the net temperature increment after infiltration for all three loading rates, it is noticeable that as the loading rate increases by 5 times, e.g., from 1.0 to 5.0 mm/min, we did not observe 25 times more joule heat being generated. This thermal discrepancy suggests a strong shear thinning dependency of the effective shear viscosity η^* on the transport rate $\bar{v}$, which echoes our previous MD simulations.^{22,29} In a nanopore, especially in a molecular-sized nanopore, there are only a small number of liquid molecules in the cross section and a chain of molecules is formed, so the effective shear viscosity, a rheological property indicating how effective the energy transition is, could be orders lower than the bulk value and also decrease with an increasing transport rate.^{22,29}

3.3. Effect of Additive Electrolyte. Influences of an additive electrolyte in liquid solution, such as LiCl, NaCl, and KCl, could greatly alter the infiltration pressure and transport behaviors of liquid molecules/ions inside nanopores and could thus lead to different energy dissipation performances.^{35–37} In our

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Figure 8. Comparisons of loading and unloading sorption isotherms (thick solid color lines) and net temperature profiles (thin dash-dotted color lines with symbols) for three systems: zeolite with KCl and NaCl saturated DI-water solution and pure DI-water, respectively. The loading rate is 5 mm/min.

tests to explore such influences, three liquid phases were used: pure DI-water, saturated NaCl DI-water solution, and saturated KCl DI-water solution, with the loading rate being fixed at 5 mm/min.

On the loading sorption curve, basic features as stated in the previous section were identified. The infiltration pressure for pure water was observed to be 11.3 MPa; while the addition of NaCl led the infiltration pressure to increase to 18.9 MPa, and KCl solution further elevated the infiltration pressure to 21.6 MPa. In a nanoenvironment, the critical infiltration P_{IN} is known to depend on the type and size of the nanopore,^{38,39} the environmental temperature,⁴⁰ and the additive electrolyte and its concentration.^{41,42} Because $P_{IN} = 4\gamma/d$, the enhanced surface tension of an electrolyte will undoubtedly increase the infiltration pressure.⁴³ In addition, the bigger size of a potassium ion (K^+ : 243 pm), in comparison with a sodium ion (Na^+ : 180 pm),⁴⁴ makes it even harder for liquid molecules/ions to enter the nanopore; both factors eventually lead to higher infiltration pressure for the electrolytic solutions and the need for more external work to induce liquid phase infiltration. However, the bigger size of a cation will also limit the specific capacity of a nanopore to accommodate more aqueous molecules/ions. From Figure 8, the infiltrated volume of saturated NaCl DI-water solution is close to that of pure DI-water (and close to the specific nanopore volume), but it reduced by ~28% in case of KCl.

Despite these differences in specific volume change, the temperature increments profile of the zeolite–KCl solution system is very close to that of the zeolite–NaCl solution system, both of which are much higher than that of the pure DI-water system. Basically, from the isotherm the amount of dissipated energy ΔE^D is proportional to the loading pressure variation ΔP and specific volume change ΔV through the infiltration process, Figure 8. In essence, ΔP is a function of the effective shear stress τ exerted by the solid wall of a nanopore on the transport of the invaded liquid

Figure 9. Comparisons of loading and unloading sorption isotherms (thick solid color lines) and net temperature profiles (thin dash-dotted color lines with symbols) for zeolite with NaCl DI-water at different molar concentrations, compared with pure DI-water system. The loading rate is 5 mm/min.

Figure 10. Qualitative comparison of the effective shear stress τ calculated from experiments with ZSM-5 zeolite and NaCl DI-water solution and molecular dynamic (MD) simulation²⁹ of comparable numerical systems.

phase. From our previous MD simulations, the effective shear stress τ is dependent on the type of cation; for example, τ of NaCl saturated solution could be ~50% higher in magnitude than that of pure water.²⁹ The experimental results reported here also verified that ΔV is a function of the electrolyte type. Among the liquids studied, the KCl solution has a higher infiltration pressure and a stronger transport shear stress, thus more joule heat dissipation should be generated for this system. However, this heat dissipation is partially counteracted by the larger specific heat capacity of the KCl aqueous solution, which makes the zeolite–KCl system appear to have a similar net temperature increment as the zeolite–NaCl system. More importantly, the deficit in specific infiltration volume due to the bigger cation size of K^+ impacts a lot on the energy dissipation performance of the zeolite–KCl system, with a ~30% deficit in the total dissipated energy as a result of this phenomenon. Overall, with additive electrolytes, there are two factors governing the energy dissipation, and the competition between these factors leads to the specific system performance.

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Table 4. Contribution of Each System Factor to Variation of Energy Conversion Performance (In Terms of the Variation of the Generated Joule Heat Per Unit Mass of Nanoporous Solid Powders)^a

rate of external loading
type of electrolyte (or size of cation)
Concentration of electrolyte
	Concentration of electrolyte	type of electrolyte (or size of cation)	rate of external loading

^a The horizontal and vertical axes (shown in bold arrow-lines) point in the direction of increasing system variables; the sign of projection of the inclined arrows on the axes indicates the correlation between amount of joule heat generation and the corresponding system variable: positive means an elevated tendency with an increasing system variable, and negative means the opposite. For example, increasing either the external loading rate or the concentration of additive electrolyte would individually increase the amount of joule heat being generated, so that the arrow in element (1, 3) or (3, 1) of the above matrix points to upper right, with projections on both axes are positive.

3.4. Ionic (Cation) Concentration Effects. Finally, the influences of electrolyte aqueous solution concentration were experimentally investigated. In a nanoenvironment, the effective liquid–vapor interfacial tension has been proved to be dependent on the concentrations of ions.^{41,42,45–47} In our experimental investigations, zeolite powder was mixed with NaCl DI-water solution with molarities varying from 0.0 M (pure DI-water) up to saturation (~6.0 M). It was thus our expectation to observe a monotonic rising trend of infiltration pressure with increasing electrolyte concentration, and from Figure 9, we have $P_{\text{IN}}^{0,\text{M}} \approx 11.3$ MPa, $P_{\text{IN}}^{2.0,\text{M}} \approx 16.3$ MPa, $P_{\text{IN}}^{4.0,\text{M}} \approx 17.9$ MPa, and $P_{\text{IN}}^{\text{sat}} \approx 18.9$ MPa. Additionally, variations of the effective shear stresses²² for the different electrolyte solution concentrations could be retrieved in Figure 9, which were also found to qualitatively agree with the trend discovered in our previous MD simulations, Figure 10. Because of the strong confinement of the molecular-sized solid nanopore wall surface of zeolite, an increasing concentration of electrolyte would lead to a higher transport resistant force.²⁹ As more ions are present among the infiltrated liquid molecules, the intermolecular potential is strengthened due to an enhanced Coulombic field. As a result, to alleviate the system energy, molecules/ions would interact more closely with the electropolar nanopore, and that enhances the shear stress.

The above varying trend of shear stress, coupled with the fact that the specific heat capacity of the zeolite–NaCl solution readily decreases with increasing concentration of electrolyte aqueous solution⁴⁸ (Table 3), explains well the clearly separated thermal profiles in Figure 8. Because the dissipated energy scales with $\xi \sim m\Delta T$, for a given specific volume change, the energy dissipation increases with increased electrolyte concentration. Meanwhile, $\xi \sim$ also decreases; both factors would increase the system temperature increment as the ion concentration is increased.

4. Conclusion

In summary, the current study is focused on calorimetric experiments involving aqueous liquid infiltration and defiltration in the nanopores of a hydrophobic ZSM-5 zeolite. Both the liquid infiltration and defiltration stages are found to be exothermic, i.e., there exists an effective internal friction that generates heat during liquid motion regardless of whether the liquid is invading or leaving the zeolite's nanopores. During the liquid infiltration stage, the dissipated energy calculated from the measured temperature variations matched well with that obtained from the sorption isotherm; while during the defiltration stage, the dissipated energy density by thermal estimation was roughly 30% lower in magnitude than that of infiltration (and also that estimated from sorption curve). This phenomenon indicates a certain endothermic process happened during defiltration, with the confinement effect of nanopores and the possible change in thermodynamic status as liquid flow out of the nanopores are possible contributions to this process.

The amount of dissipated energy, as well as temperature variation, during either the loading or unloading stage, is found to closely relate to the infiltration pressure (or, equivalently, the interfacial energy between liquid–vapor phases), accessible specific volume of the nanoporous materials, and the shear resistance generated in the nanopores. During infiltration, the interfacial energy converted from mechanical work is determined by the infiltration pressure and the accessible specific volume of the nanopores. If the material is weakly hydrophobic, the infiltration pressure is low and the stored interfacial energy is not sufficiently large to allow out-flow (defiltration) during the unloading stage. Similar behavior would also occur in nanoporous materials with a strong resistance to liquid transport, and such NEAS can only be used once. If the material is more hydrophobic, then the infiltration pressure can be elevated and the invaded liquid has sufficient energy stored in interfacial surfaces to overcome the shearing dissipation (or energy barrier) to defiltration and fully come out of the nanopores upon unloading. NEAS with these properties are suitable for energy absorption applications under cyclic loadings. In other words, the strong coupling between energy

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conversion and energy dissipation during infiltration and defiltration stages may lead to distinct energy absorption characteristics.

The above findings shed important light on behavior that can be used to fine-tune the performance of NEAS. While increasing hydrophobicity could, in general, absorb or dissipate more energy and make the NEAS system reusable, an extremely hydrophobic condition could lead to a spring-like nanodevice with little energy loss.⁴⁹ Furthermore, systemic variables, such as loading rate, addition of electrolytes, and the variation of their concentration, also impact the system calometric (dissipation) performance in different ways, and the individual and combined effects of each of

these variables have been schematically summarized in Table 4. To achieve optimum energy conversion and dissipation efficiency, balancing design among these factors is crucial. Currently, we are actively working on other novel inorganic or organic nanoporous materials,⁵⁰ e.g., the covalent organic framework (COF). The COF material has been shown to possess a highly uniform pore size distribution and huge specific volume compared with traditional nanoporous zeolite and silica gel,⁵¹ which could allow more rigorous experimental studies to be conducted to verify the findings we present here.

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