

Effects of graphite particles on ion transport in a zeolite Y

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We report an experimental result that the effective ion transport pressure in nanopores of a zeolite Y is strongly affected by the graphite particles outside. This phenomenon may be related to the electrification of zeolite-graphite interface, which is negligible for large pores but can be greatly amplified by the small nanopore size. © 2011 American Institute of Physics.

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Ion transport behavior in nanochannels was studied intensively in the past a few decades.^{1–3} It is not only of basic scientific interest but also critical to technological development for drug delivery,⁴ catalysis,⁵ separation,⁶ energy conversion,^{7–9} etc. The molecular structures of liquids in nanoenvironment are unique.^{10,11} In a carbon nanotube, for example, water molecules can form a quasi-one-dimensional chain.¹² The solvated ions can be repelled by the nanotube wall.^{13–15} In a nanochannel, the effective gas solubility can be reduced to nearly zero,¹⁶ further increasing the complexity of the problem. The concept of solubility variation can be extended to ions.¹⁷

Many continuum theories are no longer valid at small length scales. If the nanochannel surface is nonwettable to the liquid phase, an external pressure must be applied to force the ions to enter into it. If the channel size is large, the ion transport pressure is affected by the surface tension, which can be captured by the classic Laplace–Young equation¹⁸ and the internal friction such as the pressure gradient in a Poiseuille flow.¹⁹ However, if the channel size is comparable with the Debye length, neither of the theories can explain the experimental observations.²⁰ The concept of liquid motion must be reinvestigated to take into account the reduced effective viscosity,²¹ the energy barrier,²² and the energy exchange.^{23–25}

The above analyses of liquid and ion transport are focused on the solid-liquid interactions. Few experimental data are available in open literature that can shed light on the effects of the environment outside the nanochannel, which will be the focus of the current study.

The experimental setup is depicted in Fig. 1. We investigated a zeolite Y (ZY) obtained from Zeolyst. Its crystal size was 10–50 μm . X-ray diffraction indicated that it was well crystallized with a regular nanoporous structure.^{26,27} In order to increase the degree of hydrophobicity, after being air dried at 120 °C for 10 h, the material was placed in a vertical furnace in which a slow nitrogen flow carrying saturated silicon tetrachloride vapor was maintained at 400 °C for 0.5 h. Then, the material was cooled in furnace, washed in distilled water, and thermal treated at 500 °C for 1 h in open air, followed by a hydrothermal treatment at 650 °C for 48 h

in a saturated steam flow. Finally, the material was refluxed in 7.5% ethylenediaminetetraacetic acid solution for 12 h at 80 °C and rinsed thoroughly in alcohol and distilled water. By using a Micromeritics ASAP-2000 system, the effective specific pore volume was measured as 210 mm^3/g . The treated ZY crystals were mixed with solid graphite (C) powders with a mass ratio of 1:3. The mixture was mixed at 100 rpm for 10 min and then at 10 rpm for 10 min. The mixture was placed in a steel mold and compressed at 1 MPa for 1 min, forming disks with the diameter of 13 mm and the thickness of about 1 mm.

In a stainless steel testing cell, a ZY-C disk was immersed in 24 wt % aqueous solution of potassium chloride (KCl), sealed by a piston. In a type 5580 Instron machine, the piston was compressed into the testing cell at 0.5 mm/min at room temperature. When the pressure exceeded 35 MPa, the piston was moved out. The loading-unloading cycle was repeated for five times. The measured curves are shown in Fig. 2. Because from the second loading all the subsequent cycles were nearly identical, only the first two loops are shown. The two dashed curves indicate the behaviors of reference systems based only on ZY (i.e., no graphite was added) at 20 and 40 °C, respectively.

After the compression test, the ZY-C disk was broken apart by mechanical milling and the particles were suspended in acetone. Through repeated filtering and washing, zeolite crystals and graphite powders were separated. El-

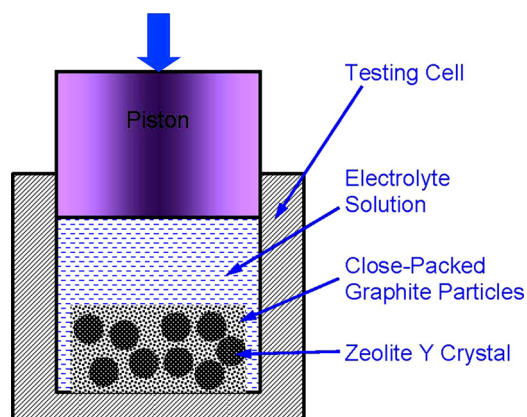


FIG. 1. (Color online) Schematic of the experimental setup.

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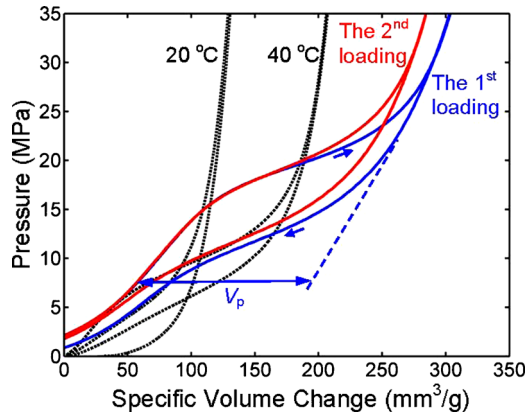


FIG. 2. (Color online) Typical sorption isotherm curves. The dashed lines are for the nonmodified system that is based on only ZY; the solid lines are for the graphite-modified system at room temperature.

elementary analysis showed that no carbon could be detected in the harvested ZY samples, indicating that no graphite phase was intruded into the nanopores.

If no graphite powders are added in the system, at 20 °C, ion transport in nanopores takes place almost immediately once an external pressure is applied, suggesting that the nanopore surface is only slightly nonwetable to the liquid phase. As the infiltration volume increases, the ion transport pressure keeps rising, which can be attributed to the “column resistance.”²⁸ When the infiltration volume reaches 90 mm³/g, the slope of the sorption isotherm curve increases abruptly, indicating that the nanopores are filled and the infiltration ceases.

The pressure induced infiltration can be employed for energy absorption. Except for the ordinary internal friction and capillary effects, energy absorption can also be achieved through “energy capture.” As the liquid that carries kinetic energy and stress energy is separated from the environment, it is “isolated” and effectively removed from the energy transmission path. The isolation is related to the small length scale of the solid walls that separate the energy-carrying confined liquid from the rest of the system, the high loading rate, and/or the large impedance mismatch.

As the temperature is increased to 40 °C, the measured sorption isotherm curve becomes different. At the low pressure range, the slope is quite large, i.e., the liquid infiltration is difficult. When the pressure exceeds about 4 MPa, a plateau region can be observed until the pressure rises to about 17 MPa. In this pressure range, ions enter into the nanopores, and similar to the phenomenon at 20 °C, the required ion transport pressure, P_t , increases with the infiltration volume. The increase in P_t may be related to the variations in surface tensions of nanopore surfaces and confined liquid as well as the effective solid-liquid interfacial tension. It may also be related to the thermal effects on the interaction between the potassium cations and the residual aluminum sites in zeolite framework, the configuration of hydration shells of solvated ions, as well as the ion exchange. The infiltration volume, $V_p \approx 120$ mm³/g, is considerably larger than that at 20 °C. The temperature dependence of V_p should be related to the variation in P_t since the spontaneous wetting becomes more difficult and a larger portion of surface area would be effectively hydrophobic.

With the addition of graphite powders, the ion transport pressure is greatly affected. When the pressure is lower than 16 MPa, little evidence of liquid infiltration can be observed. When the pressure is in the range of 16–27 MPa, a clear infiltration plateau exists in the sorption isotherm curve with the width of $V_p \approx 130$ mm³/g. The increase in ion transport pressure is similar to the thermal effect discussed above.

It may be hard to understand why the presence of the graphite phase outside the ZY crystals would have a pronounced influence on the motion of confined ions. The zeolite crystals are much less compliant than the liquid phase. In the pressure range under investigation, the deformability of the zeolite crystals is negligible. Moreover, the carbon atoms may influence the configurations and motion of solvated ions around them, but once they are shielded by the nanopore walls, this effect should vanish. In a ZY crystal of the size of 10 μm, 2–3 nm away from the crystal outer surface the atomic layers of nanopore walls should be sufficient to provide a shielding effect. The volume fraction of the outer atomic layers is less than 0.1%, almost undetectable by using the current experimental setup.

As two solid materials are placed together because they often are of different polarities, their interfaces can be electrified spontaneously, generating interface electrostatics.²⁹ In an electrolyte solution, because at the solid-liquid interface the ions are subjected to different forces from both sides, a high density surface ion layer can be formed, causing the zeta potential normal to the interface.³⁰ The zeta potentials are different for different materials. When two solid surfaces are close to each other, the difference in zeta potential would result in a net electric field.

The zeta potentials of zeolite crystals and graphite particles are different.³¹ According to the measurement results of the point of zero charge of zeolite³² in a neutral electrolyte solution, the zeta potential of a dealuminated zeolite tends to be negative. Consequently, it is likely that there is an electric field along the direction from the graphite surface to the zeolite surface. Due to the confinement effect of the nanopore wall, the structure of the confined ions is chainlike. Thus, every anion must interact with the nanopore opening individually to overcome the electric field before it can enter into a nanopore. While the electric field may promote the infiltration of cations, because it is difficult to form a monopolar phase inside nanopores, the transport pressure should increase due to the high resistance to anions. Note that even if the electric field direction were opposite, while the infiltration of anions would be promoted, the infiltration of cations would be suppressed, and similar increase in transport pressure should still occur.

Compared with the system based on neat ZY at 20 °C, the increase in ion transport pressure caused by the ZY-C interface electrification is about 16 MPa. Thus, with the effective infiltration volume being taken as 130 mm³/g, the associated additional work is 2.1 J/g. In the 130 mm³/g of the infiltrated KCl solution, there are nearly 5.4×10^{20} cations. In average, each cation consumes $E_e \approx 0.4 \times 10^{-20}$ J to enter a nanopore. The zeta potential different between ZY and graphite can be estimated as $E_e/e \approx 25$ mV, which looks plausible, where e is the electron charge.

According to its crystalline structure,²⁷ in each gram of ZY the total nanopore length is around 6×10^{20} nm. If we assume that all the ZY crystals are of the same size of 10 μm, there would be about 10^{17} nanopore openings ex-

posed at the outer surfaces of ZY crystals with the effective area of $A=3.5 \times 10^{16} \text{ nm}^2$. If the effective depth of the electric field, d , is taken as the Debye length of the KCl solution, which is around 0.3 nm,³³ the capacity of the ZY-graphite interface at the order of magnitude level can be assessed as $C=\epsilon A/d=82 \text{ mF/g}$, where ϵ is the permittivity of water. The associated charge is around $1.3 \times 10^{16}e$; i.e., about 0.13e per nanopore opening or 0.1 e/nm^2 .

The second and all the subsequent infiltration-defiltration cycles of the ZY-graphite system are of similar ion transport pressure as that of the first cycle. However, the infiltration volume is slightly smaller by 10%. It may be caused by the charge exchange and surface reaction in the interior of nanopores associated with the incomplete dealumination.³⁴

To summarize, the nominal ion transport pressure of an electrolyte solution in a zeolite Y increases by about 16 MPa as the ZY crystals are mixed with fine graphite powders. This may be attributed to that each ion must interact with the nanopore opening individually. Thus, the effect of interface electrification between ZY and graphite, which is negligible if the pore size is large, can be greatly amplified.

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