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An electrically controllable nanoporous smart system

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The major problems of conventional intelligent materials include the small output forces and the poor deformability. In this article, we show that by directly utilizing the large specific surface area of a nanoporous material, a high-performance shape memory system can be developed based on the electrocapillary effect. As voltage varies, the pressure in the system can be controlled reversibly. The output energy density and the displacement are much higher than that of piezoelectrics and magnetostrictives. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2185832]

I. INTRODUCTION

The conventional electrically controllable intelligent materials include piezoelectrics and magnetostrictives, which, when external voltages are applied, can undergo reversible deformations. The major challenges for these materials are the relatively small output forces and displacements. The output energy density and maximum strain of piezoelectrics, for instance, are only about 0.3 mJ/g and 0.4%, respectively.[1] In order to meet the increasingly high functional requirements, high-energy-density and large-displacement shape memory mechanisms must be discovered.

Since the era of Faraday and Franklin, it has long been noticed that once a potential difference is applied across a solid-liquid interface, the interfacial energy can be changed considerably.[2] This phenomenon, known as the electrocapillary effect, has been applied in chemical and bioscience fields for advanced filtration,[3] supercapacitors,[4] etc. However, the studies on using it in electromechanical devices, particularly for intelligent systems, are rare. With the rapid progress in processing techniques of nanoporous materials of pores smaller than 1000 nm,[5] it is now feasible to develop high-performance intelligent systems based on the electrocapillary effect. Due to the ultrahigh specific surface area that is typically in the range of $1-10^3$ m^2/g, the nanoporous material can be an ideal platform for energy exchange.

II. EXPERIMENT

In the current study, we investigate a Chand Eisenmann nanoporous monel rod produced by sintering monel nanoparticles at near-melting-point temperature. The average pore size $r=480$ nm and the specific surface area is about 1.3 m^2/g. The diameter of the rod is 9.5 mm and the length is 19.1 mm. The monel rod was tightly inserted in a metal cylinder, as depicted in Fig. 1. The metal cylinder was connected to two polymethyl methacrylate (PMMA) cylinders, forming a container. A 15 wt. % aqueous solution of calcium chloride was added in the container from end "B" and sealed by a metal piston with gasket. From the other end ("A"), a Sigma M2047 methyl salilylate oil was added and sealed. Then, piston A was compressed into the container so that the oil-water interface was within the nanoporous monel rod and close to the end toward B. By using a Proteck 6030 dc power supply, a voltage was applied between the monel electrode and piston B. With the piston position being fixed, the pressure variation in the oil phase δp was measured by an embedded Honeywell model-s pressure sensor, and the results are shown in Fig. 2.

III. RESULTS AND DISCUSSION

It can be seen clearly that the pressure increases monotonically with the magnitude of potential difference, which can be attributed to the difference in voltage dependence of wettability of the oil and the aqueous solution (see Fig. 3). When a potential difference presents across the solid-liquid interface, both sides are electrified.[6] The electrified layer in the liquid phase is often referred to as the outer Helmholtz

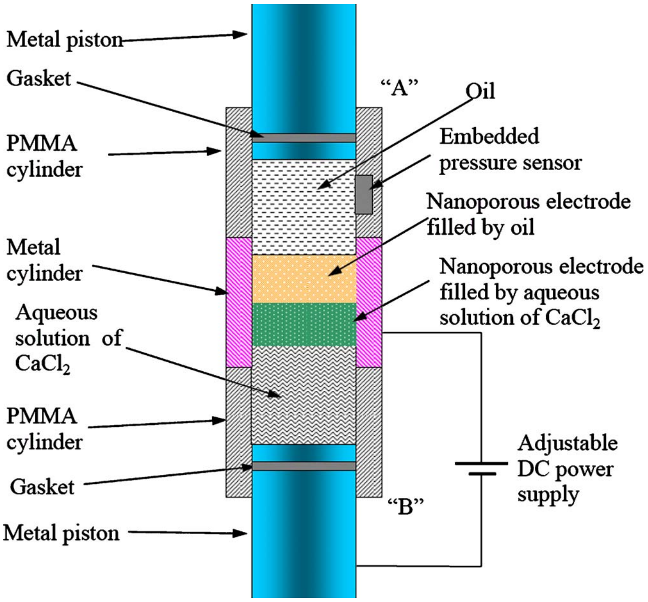

FIG. 1. (Color online) A schematic diagram of the nanoporous intelligent system. By applying a voltage on the nanoporous electrode, due to the electrocapillary effect, the equilibrium at the interface of the two liquids is disrupted; that is, one liquid becomes more wetting to the solid than the other. Consequently, the liquid-liquid interface tends to move. Since this process is reversible, the system exhibits a shape memory characteristic.

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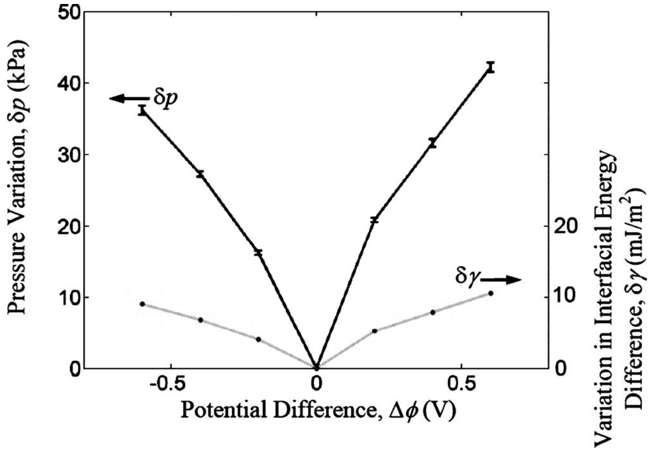

FIG. 2. The pressure variation, δp, and the change in interfacial energy difference, $\delta\gamma$, as functions of the applied potential difference.

plane (OHP). Beyond the OHP the charge diffusion is dependent on the thermal motion. This structure is sometimes simplified as an electrical double layer with the thickness $d_1 \approx 1-5$ nm. Due to the small thickness, even a low potential difference can cause a large electric field.[7] As the voltage $\Delta\phi$ varies, the charge density at the interface, σ_M, changes accordingly, which in turn affects the interfacial energy. The total potential difference can be decomposed as $\Delta\phi = {}^M\Delta^S\psi + {}^M\Delta^S\chi$, where ${}^M\Delta^S\psi = \psi_M - \psi_S$ is the Volta potential, with ψ_M and ψ_S being the potentials of isolated solid and liquid phases, respectively, and ${}^M\Delta^S\chi$ is the Chi potential accounting for the dipole contribution. At constant temperature and pressure, the thermodynamic equilibrium condition is reduced to the Lippmann equation, $\partial\gamma_{1s}/\partial\Delta\phi = -\sigma_M$.[8] Note that $\partial\sigma_M/\partial\Delta\phi = C_e$, with C_e being the capacity. If C_e is constant, γ_{1s} follows the Helmholtz-Perrin theory,

$$\gamma_{1s} = \gamma_{\max} - \hat{\varepsilon}\hat{\varepsilon}_0\Delta\phi^2/2d_1, \tag{1}$$

with $\gamma_{\max}$ being the maximum interfacial energy, $\hat{\varepsilon}$ the dielectric constant, and $\hat{\varepsilon}_0$ the permittivity of free space. If the $\Delta\phi$ dependence of C_e must be taken into account, the effect of the "charge cloud" should be considered.[9]

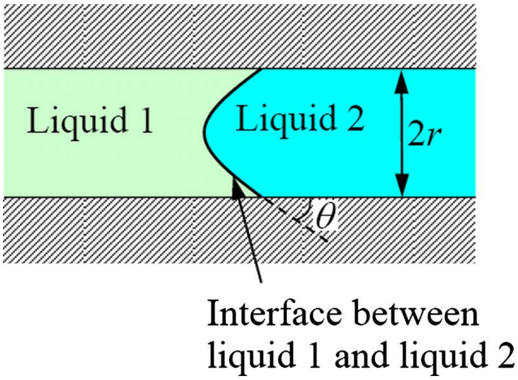

FIG. 3. (Color online) A schematic diagram of the liquid interface in a nanopore. As the voltage changes, due to the difference in variation in wettability, with a constant pressure difference, the liquid-liquid interface tends to move from the high-free-energy environment toward the low-free-energy environment

The measured $\delta p - \Delta\phi$ curve shown in Fig. 2 fits well with the parabolic $\gamma_{1s} - \Delta\phi$ relation (1). As $\Delta\phi = 0$, the equilibrium condition at the water-oil interface can be stated as

$$\Delta\gamma = \gamma_0 \cos\theta = \frac{\Delta p r}{2} \tag{2}$$

where $\Delta\gamma$ is the difference in solid-liquid interfacial energies of the oil and the aqueous solution, γ_0 is the liquid-liquid interfacial energy, θ is the effective contact angle, and Δp is the pressure difference across the oil-water interface. Since the oil-solid and the water-solid interfacial energies change with $\Delta\phi$ at different rates, the contact angle is a function of $\Delta\phi$. In the system under investigation, the water-monel interfacial energy decreases with $\Delta\phi$ slower than the oil-monel interfacial energy, and thus the aqueous solution becomes effectively more wetting to the solid under the applied pressure, which must be balanced by the pressure change, δp. Similar to Eq. (2), we have

$$\delta\gamma = \frac{\delta p r}{2}, \tag{3}$$

where $\delta\gamma$ is the variation in $\Delta\gamma$ caused by $\Delta\phi$, which is also shown in Fig. 2. The result is in consistent with the literature data that, with a 0.5 V potential difference, the interfacial energy can vary by 10%–30%.[7]

If the pistons are subjected to constant external loadings, the pressure variation would result in a large displacement $d = V_0/A_0$ of 7.8 mm, equivalent to a strain of nearly 40%, with $V_0 = 2.8 \times 10^3$ mm^3 being the volume of the pores initially filled by the oil and $A_0 = 283$ mm^2 the cross-sectional area of the container. This effective strain is larger than that of conventional shape memory ceramics and magnetostrictives by orders of magnitude. The output energy can be calculated as $\delta p A_0 d = 92$ mJ. The mass of the functional components of the intelligent system, including the nanoporous electrode and the liquid, is 20.5 g. Thus, the output energy density is 4.6 mJ/g, much higher than that of piezoelectrics.

The concept discussed above can be extended to a large number of liquids and nanoporous solids. In fact, one of the liquid phases can be air, which would further simplify the system structure. Note that since the compressability of air is much larger than that of liquids, the working pressure of an air-based system can be relatively low. For a multiple-liquid system, a key factor affecting the system performance is the stability of the liquid-liquid interface in nanopores. Depending on the porous structure, as the liquid-liquid contact line moves, a creaming interface layer can be formed. While this phenomenon should not affect the pressure variation since δp is determined by the net interfacial tension, deemulsification is preferred so as to avoid additional complexity. This technique has important relevance to programmable actuators, smart structures, intelligent platforms, among others, which, when incorporated with electrohydraulic devices or microelectromechanical systems, will provide simple yet powerful actuation mechanisms.

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