Gas Separation at the Solid-Solid Interface of a Piezoelectric Bimorph Using an Electric Field

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A new system for controlling gas separation through the solid-solid interface of a piezoelectric bimorph and using an applied electric field was made. By applying vapor deposition of metal (aluminum) to a surface of the bimorph, we created a field-induced aperture at the interface of nanometer dimensions. The device provided separation of H_2 and CO_2 slightly higher than theoretical Knudsen values. The permeation rates were significantly affected by imposed electric fields.

In gas separation and catalysis it is important to control a small space for diffusion of gas molecules.[1-3] We devised new systems that use external electric fields to control the size of nano-scale apertures used for gas permeation. These were the solid-solid interfaces of ferroelectrics with aperture size controlled by piezoelectric effects[4] and elecrostatic force.[5] Further, we reduced the aperture size as close as possible to molecular dimensions, because we expect that this will allow efficient, real-time, controlled separation and catalysis. We recently made a new device based on the effect of a piezoelecric bimorph. The most effective field-affected aperture for permeation was attained at the fine solid-solid "mold" interface of a piezoelectric bimorph and a metal film deposited onto the bimorph. In this letter, we report the design and performance of this system.

Piezoelectric bimorph consists of two ferroelectric materials attached to each other so that polarization of the two ferroelectric materials is opposite each other. By imposing electric fields between the two surfaces of the bimorph it becomes warped, and near its end a displacement normal to the surface is generated.

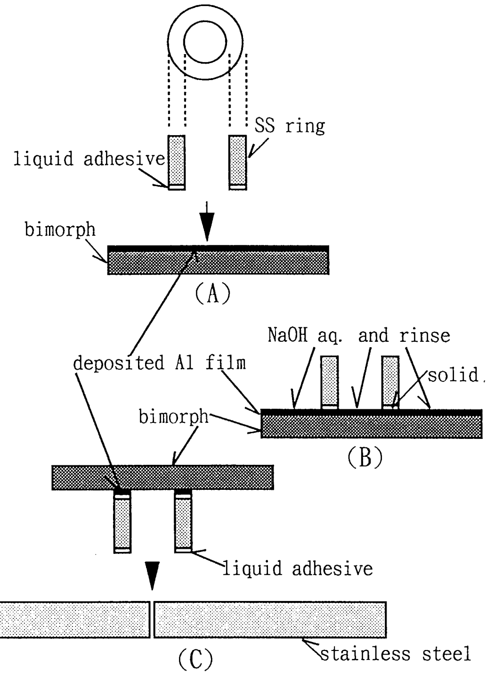

Figure 1. Process for making the solid-solid interface.

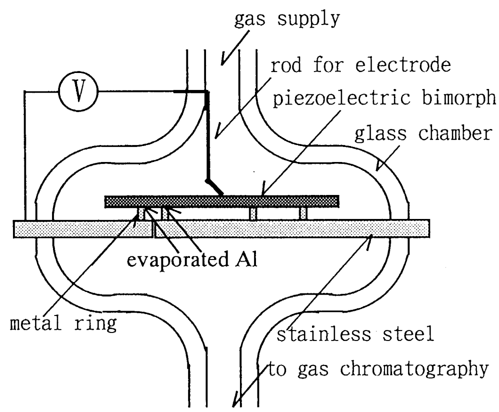

Figure 2. Schematic diagram of piezoelectric bimorph system.

Figure 1 shows the process of making the solid-solid interface. At a pressure of about 1×10^{-3} Pa, aluminum was deposited onto the PZT bimorph to a thickness of about 400 nm. An SS ring with a diameter of 8 mm, a thickness of 0.5 mm, and ends polished with number 800 abrasive to achieve sufficient flatness, were attached to the surface of an Al/bimorph using liquid adhesive (α -cyanoacrylate adhesive, Toagosei Co.). Then, 10 wt% of NaOH aq. was added to the free regions of the Al thin film to completely dissolve it, but the region hidden by the end of the ring was protected and therefore not dissolved. Therefore, after rinsing and drying, we obtained a system of ring/Al/bimorph in which the Al exists only in the form of a thin loop at the interface between the bimorph and the ring, as shown in Figure 1(C). Then, by using the adhesive, the system was attached to the SS plate with a small hole so that the hole of the SS plate would be inside the SS ring, as shown in Figure 1(C). This entire system was put in a glass chamber.

Figure 2 shows the apparatus for permeation with the electric field. Two lead zirconate titanate (PZT; thickness: 300 μ m; dimensions: 23 mm $\times$ 10 mm; relative dielectric constant: 550; and surface roughness, Ra= 6.6 nm) plates were attached to each other so that their directions of polarization were rotated 180° to each other. The bimorph was attached to the two stainless steel (SS) plate on the right side with two rods. The key interface is on the left side of the bimorph. The method of imposing an electric field and introducing gases was the same as described in our previous paper.[5] When the electric field was imposed onto the PZT bimorph, a strain normal to the loop-interface of deposited Al and bimorph was generated, and a small aperture at the interface was generated, strongly influencing the gas permeation. We observed the interface using atomic force microscopy (AFM). The permeation rate of the gas mixture of H_2 and CO_2 (1:1) was measured with a diaphragm vacuum gauge and a gas chromatograph (column: Gaskuropack, GL Sciences Co.; carrier gas: N_2).

Figures 3(A) and 3(B) show the AFM images of the PZT bimorph surface and the inverse view of the surface of the Al thin film which contacted the PZT bimorph. The irregular surface structure of the PZT bimorph was cast onto the surface of the Al as a mold pattern. The nanometer-sized patterns observed on the mold indicate that the solid-solid interface of the PZT bimorph and Al fit together on a nanometer-size level. The statistical roughness of many PZT and Al surfaces were compared. The PZT surface had Ra=6.6 nm, and an average tilt angle of asperities of θ a=4.1°. The Al surface contacting the PZT had similar values of Ra=6.1 nm and θ a=3.6°.

Figure 4 shows the result of separation of H_2 and CO_2 at 30 mmHg in steady state under an electric field with a downward polarity. Here, a relative permeability means a quantity of gas permeating per time per difference of pressure at inlet and outlet (arbitary unit). Relative permeability=100 corresponds to permeation quantity per time=1.90 $\times 10^{-9}$ mol s^{-1}. The permeabilities of H_2 and CO_2 increased with increasing electric voltage. The increase of the permeabilities was proportional to the electric voltage. The separation factors were 6 ~ 7, higher than the theoretical Knudsen value of 4.7. On the other hand, under an electric field with an upward polarity, the permeabilities changed irregularly and only to a small extent. A displacement, Δz, vertical to bimorph at the end follows $\Delta z = K d_{31} (L/D)^2 V$,[6] where K, d_{31}, V, L, and D are constant, piezoelectric strain constant, electric voltage, the length of the bimorph, and the thickness, respectively. The displacement is proportional to electric voltage. The electric field with a downward polarity induces an upward displacement of the left side of the bimorph (see Figure 2). Further, the permeability of CO_2 was clearly constant against the pressure of introduced CO_2 in the range of 0-150 mmHg. The non-Poiseuille permeation suggests the aperture narrower than that of the previous device.[5]

Our result that the increase in permeation rate is proportional to V is consistent with the bimorph effect-based concept, which states that the increase in the aperture size is proportional to V. The result that the separation factors exceed the theoretical Knudsen values must be explained by a mechanism other than Darcy-law flow. We can exclude many potential effects as follows. First, it can not result from surface diffusion, where CO_2, more adsorbable than H_2,[7-9] would increase its permeation rate more than H_2. Second, the result is not due to a complete capillary condensation, because a condensed phase of CO_2 would block the permeation of H_2.[11-14] Both mechanisms would resut in separation factors smaller than the theoretical Knudsen value. Third, it can not be attributed to a mechanism of complete molecular sieving, the difference in the molecular size is only 0.1-0.2 nm,[10] smaller than the estimated nanometer dimensions of our system. Finally, we may attribute it, in part, to configurational diffusion induced by partial capillary condensation. When an aperture near molecular dimensions is decreased by condensed layers of adsorbable gas (e.g., CO_2), the narrowed aperture may discriminate based on gas diffusion, in part, because of its small size.

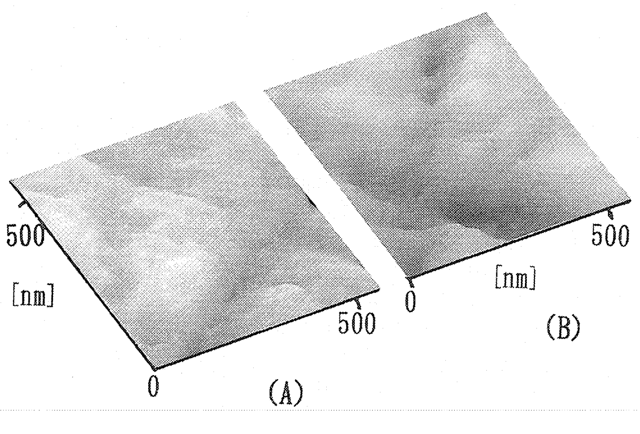

Figure 3. AFM images. (A) the surface of the PZT bimorph. (B) the inverse view of the surface of the Al thin film which contacted the PZT bimorph. The height from the darkest place to the lightest place is 20 nm in (A) and (B).

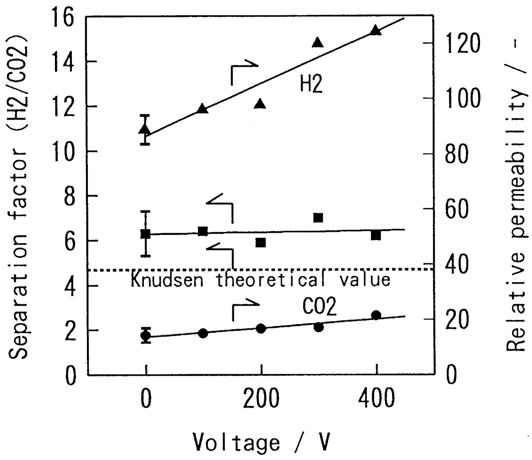

Figure 4. Separation of H_2 and CO_2.

Using an electric voltage up to 400 V, we obtained a relatively small change of the permeation rate of 40%, compared with the device using the effect of electrostatic forces.[5] Here, our new device based on the effect of the piezoelectric bimorph provided the most effective separation factor in "field-induced aperture change."[4,5] Our construction technique is expected to provide further large separation factor by investigating evaporated metals.

References and Notes

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