doi:10.1246/cl.2011.1152

Electrochemical Control of Threshold Value of Molecular Valve Consisting of Poly(acrylic acid) Gel

Kazutake Takada,* Tetsuya Ohara, Kouki Takeue, Natsumi Ishikura, Chie Kato, and Akio Yuchi
Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya, Aichi 466-8555

(Received July 13, 2011; CL-110600; E-mail: takada.kazutake@nitech.ac.jp)

A molecular valve, consisting of a poly(acrylic acid) gel-coated Au mesh and a Au mesh working electrode, allowed electrochemically control of a concentration where the valve opens. At open circuit and when +0.9 V vs. Ag/AgCl was applied to the Au mesh electrode, the valve opened at concentration higher than 3–4 × 10^{-4} M. At −0.7 V it increased to 9 × 10^{-4} M. On the other hand, it remained virtually constant for Ca^{2+} at those potentials.

There has been a great deal of attention devoted to molecular valves due to the miniaturization required for flow control in nano- and microfluidic systems. Molecular valves consisting of polymer gels are capable of self-regulating flow control without external power supply on the basis of volume change responding to various stimuli such as temperature,[1,2] pH,[3–5] cation concentration,[6] and solvent composition.[2] In most valves a threshold value of stimuli to open/close the molecular valve is fixed. In order to vary it, a composition of polymers/gels needs to be altered. That is, by copolymerizing with another monomer with different characteristics or by introducing a functional group, intensity of stimuli which gives rise to phase transition of polymer or volume change of gels can be modulated. For example, the temperature to open a thermosensitive valve consisting of poly(*N*-isopropylacrylamide) was adjusted by introducing azidophenyl groups.[1] In these cases a variety of valves with suitable composition could be prepared to accommodate different valve-opening thresholds. Therefore, there has been interest in varying threshold values of a single molecular valve for practical applications. However, to the best of our knowledge, there has been no report on such a molecular valve.

We have recently reported a reversible molecular valve consisting of a Au mesh covered with poly(acrylic acid) gel, which is responsive to cations including H^+, Na^+, K^+, Ca^{2+}, Cu^{2+}, and Al^{3+}.[6] The valve closes at lower cation concentration as the gel expands to block the mesh, whereas the valve opens at higher concentration as the gel contracts to make spaces in the mesh. In the present report, we attempted to control a concentration where a valve opens by applying a potential to an additional Au mesh serving as a working electrode. In this study Cu^{2+} was chosen as a stimulating ion since it is expected that its concentration can be electrochemically varied. That is, reduction to Cu^0 results in decrease in Cu^{2+} concentration in solution, whereas oxidation of Cu^0 leads to increase in the concentration. In addition, Cu^{2+} causes sharp valve operation as it induces sharp volume change in poly(acrylic acid) gel, which simplifies data analyses and interpretation.[6]

Acrylic acid (reagent grade, Wako Pure Chemical Industries, Ltd.) was distilled prior to use. Calcium nitrate was dried over P_2O_5 under vacuum. All other reagents were of at least reagent grade and were used without further purification. Aqueous solutions were prepared with distilled-deionized water.

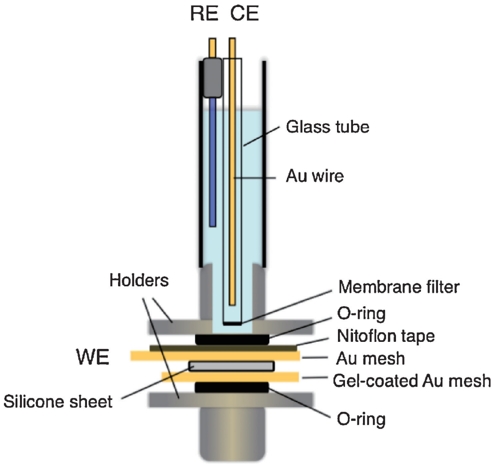

Figure 1. Schematic illustration of electrode-separated molecular valve.

Poly(acrylic acid) gels were prepared on a Au mesh (10 × 20 mm^2, ca. 0.1 mm thick, 100 mesh, Nilaco Co.) following a previously reported method.[6] The gel was coated twice to make the film thicker. Another Au mesh (the same size, without gel film), which serves as a working electrode, was set above the gel-modified Au mesh separated by a silicone sheet (0.5 mm thick) with a 4.5-mm diameter hole. Those Au meshes were set in between homemade holders (polycarbonate, 5.0 mm i.d.) via an O-ring (fluoro rubber, 4.8 mm i.d.) on the lower side and another O-ring and Nitoflon tape (0.08 mm thick, Nitto Denko Co.) on the upper side (Figure 1).

The above-mentioned valve was set horizontally and filled with water. It was left for at least 15.5 h to remove unreacted reagents and to allow the gel to reach equilibrium volume. When the mesh working electrode was not set to allow the gel to freely expand, the average of thickness of the gel film after immersion in water for 15.5 h was 1.6 ± 0.5 mm ($n = 4$, average of 5 points on each sample). However, in the actual set up, expansion to upper direction was restricted to 0.5 mm which is the distance between the two Au meshes. For monitoring the valve operation, the holders were set vertically and a glass tube (75 mm length × 7.2 mm i.d.) was attached to the upper holder. To check leakage of the gel film, fluid level of 2 mL of water was monitored for 2 h. After this test, the water was replaced with 2 mL of various electrolyte solutions. A no-leak Ag/AgCl reference electrode (EE009, Cypress Systems) and a coiled Pt counter electrode which was set in a glass tube (4.0 mm diameter) shield with a Omnipore membrane filter (pore size: 10 µm) at one end were set in the glass tube (Figure 1). A desired potential was then applied to the upper Au mesh electrode by a potentiostat (HA-301, Hokuto Denko or HZ-5000, Hokuto Denko) within 30 s after the sample electrolyte solution was introduced. The volume of solution passed through the gel film (valve) was measured for 2 h. All measurements were performed at room temperature (25 ± 2 °C).

Dependency of solution volume passing the poly(acrylic acid) gel valve on concentration of $Cu(NO_3)_2$ at open circuit is shown in

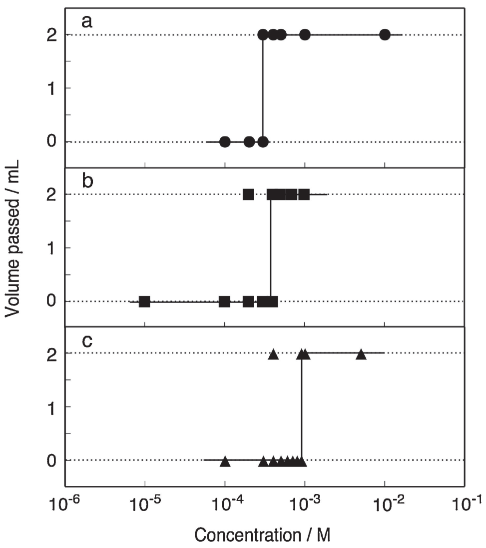

Figure 2. Dependencies of solution volume passing the valve on concentration of aqueous $Cu(NO_3)_2$ solution at (a) open circuit, (b) +0.9 V vs. Ag/AgCl, and (c) −0.7 V.

Figure 2a. At lower concentration the valve remained closed, whereas at higher concentration all solution (2 mL) passed. The concentration where the valve opens was found to be ca. 3×10^{-4} M. At +0.9 V vs. Ag/AgCl the concentration to open valve remained nearly the same at ca. 4×10^{-4} M (Figure 2b). This is rationalized by taking into account the fact that copper exists as its oxidized form (Cu^{2+}) at open circuit and +0.9 V. At −0.7 V the concentration shifted to 9×10^{-4} M (Figure 2c). The positive shift is ascribed to decrease in an apparent concentration of Cu^{2+} ion in the vicinity of the working electrode (upper Au mesh) due to its reduction to Cu^0. Cyclic voltammetry of the mesh working electrode in contact with 3×10^{-4} M $Cu(NO_3)_2$ solution at a scan rate of 100 mV s^{-1} showed a cathodic peak corresponding to reduction of Cu^{2+} to Cu^0 at ca. −0.7 V and a stripping anodic peak corresponding to its oxidation at ca. +0.45 V. Further, when −0.7 V was applied to the electrode in the same condition, a steady-state cathodic current of ca. −10 μA passed and resulted in deposition of Cu on the electrode. Despite a lack of supporting electrolyte, these results clearly demonstrated that reduction of Cu^{2+} takes place, which gives rise to decrease in Cu^{2+} concentration in a solution.

If −0.7 V was directly applied to the gel-coated Au mesh (lower side), the valve turned to open even for water. After the valve opening the gel appeared to peel off from the Au mesh. The fact that cathodic current passed during the potential application indicates that oxygen reduction takes place. The resulting formation of H_2O, H_2O_2, and/or OH^- at the Au mesh electrode surface where the gel is also immobilized likely causes the peeling. This result indicates an advantage of use of an independent electrode to which potential is applied apart from a Au mesh supporting the gel.

Time to open the valve, which was defined as the time when solution level started to drop, upon loading of an electrolyte solution was found to be scattered in the range from less than 1 to 40 min but relatively slow at lower concentrations and to become shorter as the concentration increases. It was also virtually independent of potential applied. This is reasonable because collapse of the gel is anticipated to be faster at higher concentration.

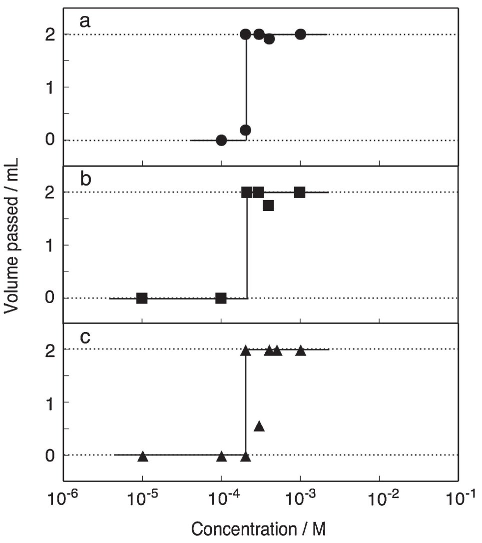

Figure 3. Dependencies of solution volume passing the valve on concentration of aqueous $Ca(NO_3)_2$ solution at (a) open circuit, (b) +0.9 V vs. Ag/AgCl, and (c) −0.7 V.

The valve reclosed upon loading of pure water. The length of time to reclose took at least 1 h when the valve was opened by a 9×10^{-4} M Cu^{2+} solution at open circuit. This relatively long period was ascribed to a strong interaction between Cu^{2+} and carboxylate groups, which prevents gel from re-expanding.[6]

If the above-mentioned mechanism for the changes in the cation concentration where the valve opens is true, it should remain constant when Ca^{2+} ion, which is electrochemically inactive over the potential range employed, is used. Figure 3 shows the solution volume passing the valve vs. concentration of $Ca(NO_3)_2$ at the same potentials as in the case of Cu^{2+} (open circuit, +0.9, and −0.7 V). At all potentials the concentration where the valve opens appeared to be the same at ca. 2×10^{-4} M. This result strongly supports the adequacy of the mechanism mentioned above. In the case of Ca^{2+} ion, the time required to open the valve was also scattered but typically in the range from less than 1 to 30 min. The variation in the opening time would reflect slight variance in film thickness of the gel, as the rate of swelling/shrinking is known to be proportional to the square of thickness of gels.[7]

These results clearly demonstrated that concentration where the valve opens can be controlled by simply switching applied potential for redox-active species such as Cu^{2+}. This is one of the advantages of the present valve over others because threshold concentration could be controlled without altering kinds and/or composition of molecular valve material, resulting in saving cost, time, and effort to prepare such a valve. Toward practical use of the valve, response to other redox-active species and durability of the valve upon repeated use will be studied and will be reported in the future.

This work was partially supported by the Japan Chemical Innovation Institute.

References

1 Y. S. Park, Y. Ito, Y. Imanishi, *Langmuir* **1998**, *14*, 910.
2 K.-F. Arndt, D. Kuckling, A. Richter, *Polym. Adv. Technol.* **2000**, *11*, 496.
3 S. Nishi, T. Kotaka, *Macromolecules* **1986**, *19*, 978.
4 D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss, B.-H. Jo, *Nature* **2000**, *404*, 588.
5 A. M. Mika, R. F. Childs, J. M. Dickson, *J. Membr. Sci.* **2002**, *206*, 19.
6 K. Takada, K. Ito, A. Yuchi, *Sens. Actuators, B* **2009**, *142*, 377.
7 Y. Li, T. Tanaka, *J. Chem. Phys.* **1990**, *92*, 1365.