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A Redox Gel. Electrochemically Controllable Phase Transition and Thermally Controllable Electrochemistry

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Some gels in a solvent are known to undergo volume phase transition upon changes in temperature, solvent composition, concentrations of ions, and so forth.[1] Further functionalization of gels is also envisaged by introducing functional groups to a polymer chain of the gel. Suzuki and Tanaka[2] demonstrated that a copolymer gel of *N*-isopropylacrylamide (NIPA) and a porphyrin derivative undergoes volume phase transition induced by visible light. In the present report we modify poly(*N*-isopropylacrylamide) gel, which shows thermally induced volume phase transition in aqueous media, with an electrochemically active group, envisaging electrochemical control of the phase transition and thermal control of the electrochemistry of the gel. Materials having these properties could be used for a gel actuator, a drug-release membrane, a permeability-controlled film, a thermal switch, and so forth. Though Yoshino et al.[3] have reported on a conducting polymer gel, its electrochemical properties have not yet been studied.

Irie et al.[4] polymerized NIPA and vinylferrocene (VF) to yield a redox-active copolymer (poly(NIPA/VF)). They found that an aqueous solution of the polymer shows thermally induced phase separation and that the phase separation temperature depends on the redox state of the ferrocene site. We[5] prepared a cast film of poly(NIPA/VF) on an electrode surface and demonstrated that the film possesses two very interesting properties: electrochemically controlled phase transition temperature and a strong dependence of electrochemistry on temperature. Further, poly(NIPA/VF) can be used for enzyme electrode fabrication because it functions as an enzyme support and as an electron mediator between a redox enzyme and electrode.[6] However, the poly(NIPA/VF) film was rather soluble in water in the swollen state, so that the film was not suitable for a practical use. Then, in the present work, we synthesized a hydrogel from NIPA, VF, and *N,N'*-methylenebisacrylamide (BIS) (Figure 1A). Thus obtained redox gel is not soluble in water. Here we show that the volume phase transition of the gel is electrochemically controllable and that the electrochemistry of the gel is thermally controllable.

Preparation of the Redox Gel. Prior to the preparation of the poly(NIPA/VF) gel-coated electrode, base electrodes (Au or indium tin oxide (ITO)) were treated with a 10% toluene solution of methoxydimethylvinylsilane to introduce the vinyl group onto the electrode surface. The electrode was partially immersed in a dimethyl sulfoxide solution of NIPA (9.4 M), VF (0.31 M), BIS (0.094 M), and 2,2'-azobis(isobutyronitrile) (0.34 M, polymerization initiator) and left for 8 h at 60 °C under nitrogen. The resulting gel was cut off from the electrode except for the vicinity of the electrode surface (1–3 μm thick in a dry state, unless otherwise noted) to obtain the poly(NIPA/VF) gel-coated electrode. A bulk gel was obtained similarly in the absence of the electrode. The gel film was thoroughly washed with dimethyl sulfoxide and cold water (below 10 °C).

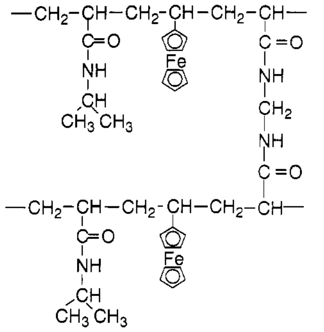

Figure 1. Structure of poly(NIPA/VF) gel.

Electrochemically Controllable Phase Transition. First, the temperature dependence of a volume of the bulk poly(NIPA/VF) gel (0.027 cm^3 in the shrunken state) was measured in water. A change in the volume proceeded between 15 and 30 °C, and the volume below 15 °C was about 8-fold larger than that above 30 °C. Similar behavior was observed for the gel film (ca. 1 mm thick in the shrunken state) on the electrode; the film thickness of the swollen film was about 7-fold larger than the shrunken film. At low temperature, the gel is swollen owing to hydrogen bonding between water molecules and the amine or carbonyl group and to hydrophobic hydration of the hydrophobic groups. At higher temperature, this hydrophobic hydration becomes weaker because of thermal movement of water, and further, hydrophobic interaction between the hydrophobic groups becomes stronger. As a result, the gel is shrunken.[7]

Phase transition of a thin gel film was monitored using a quartz crystal resonator. The resonator used here (5 MHz) is an AT-cut quartz crystal plate coated with two gold electrodes (sputtered on both sides of the quartz plate). Poly(NIPA/VF) gel was prepared on one side of the resonator. The gel-coated side of the resonator was in contact with a 0.1 M $NaClO_4$ aqueous solution, and the other side was kept in air. Since the redox potential of the gel was +180 and +235 mV vs SSCE in the swollen and shrunken states, respectively, a dc potential of +480 or −50 mV vs SSCE was applied to the gel-coated electrode to keep the ferrocene site oxidized or reduced, respectively.

Electromechanical impedance of the gel-coated resonator was measured at various temperatures, and parameters R_1, C_1, L_1, and C_0 in the electrical equivalent circuit for a quartz crystal resonator (inset in Figure 2) were evaluated from this measured impedance.[8] Among the parameters, R_1 measures losses of the oscillation energy. Therefore, its value changes upon phase transition of the film on the resonator,[5,9–11] because the energy loss depends on the film thickness and viscosity.[5,8–12]

Figure 2 shows temperature dependencies of the parameter R_1 for the reduced and oxidized poly(NIPA/VF) gel films. The temperature was scanned from 10 °C up to 45 °C and then scanned back to 10 °C (ca. 1 °C min^{-1}). Large changes in the parameter R_1 caused by the phase transition were observed at 23–32 °C (heating process) or 19–33 °C (cooling process) for the reduced film and at 27–38 °C (heating process) or 23–43 °C (cooling process) for the oxidized film. The difference in the phase transition temperature between the bulk gel (reduced state) and the reduced thin film may have resulted from a slight difference in gel structure. The observed difference in the phase transition temperature between reduced and oxidized films can be explained as follows: As described

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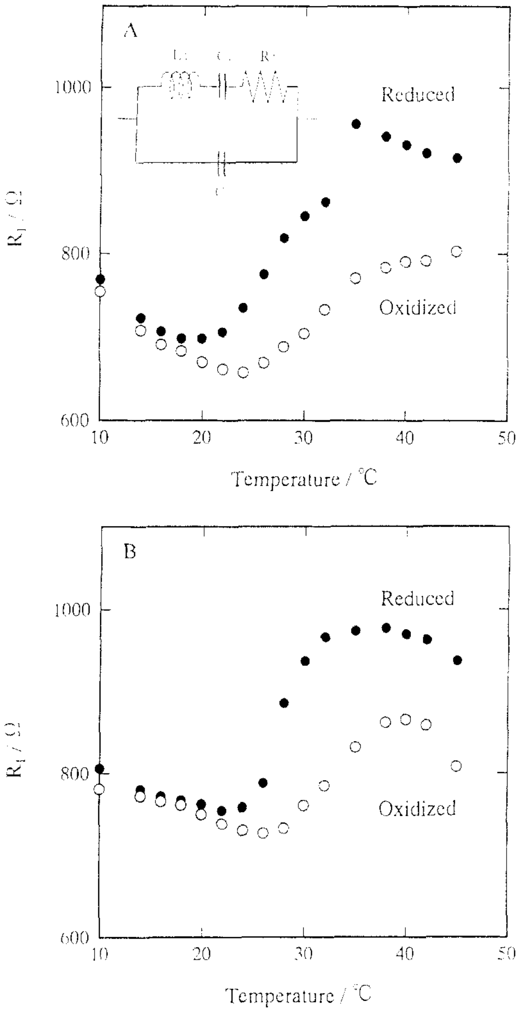

Figure 2. Changes in the parameter R_1 in the electrical equivalent circuit (inset) for the poly(NIPA/VF) gel-coated quartz crystal resonator in the heating (A) and cooling (B) processes.

above, a balance of the hydrophilic domain and the hydrophobic domain of a gel determines the phase transition temperature. Indeed, the phase transition temperature of poly(*N*-alkylacrylamide) gels is known to depend on the hydrophobicity of the alkyl group.[7] Ferrocene is electrically neutral but the oxidized form (ferricinium ion) is cationic. Therefore, increased hydrophilicity of the oxidized ferrocene must be responsible for the higher transition temperature of the oxidized gel.

Thus, the phase transition temperature of the poly(NIPA/VF) gel was found to be controlled electrochemically. That is, the swelling–shrinking behavior of the gel film can be controlled electrochemically, between the phase transition temperatures of the reduced and oxidized films. Then, we measured changes in the parameter R_1 for the gel-coated quartz crystal resonator during redox reactions of the gel at 30 °C. Figure 3 shows the time course of the parameter R_1 upon potential steps between +480 and −50 mV vs SSCE. As can be seen, the gel film is swollen by oxidizing the film and shrunken by reducing the film.

Thermally Controllable Electrochemistry. Next, the electrochemical properties (thermodynamics and kinetics) of the swollen and shrunken films were examined. Thermodynamic properties were examined by means of slow cyclic voltammetry at various temperatures. A large change in the apparent formal potential of the poly(NIPA/VF) gel was observed between 15 and 30 °C, at which the phase transition occurs. The apparent formal potentials of the swollen and shrunken films were about +180 and +235 mV vs SSCE, respectively (scan rate = 0.1 mV s^{-1}). This means that the oxidized ferrocene is more stable in the swollen film and the reduced one is more stable in the shrunken film. It is reasonable because the oxidized ferrocene having a positive charge is hydrophilic; a hydrophilic group is more stable in a hydrophilic environment, such as a swollen gel. To the contrary, the reduced ferrocene is more hydrophobic so that it is more stable in a hydrophobic environment, such as a shrunken gel.

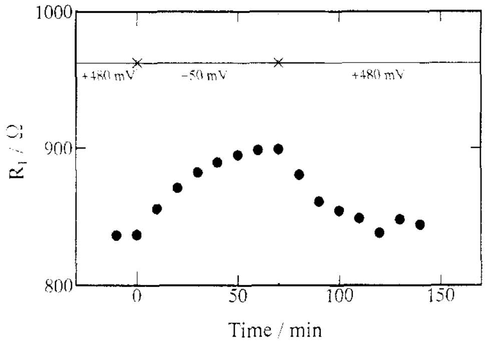

Figure 3. Time course of the parameter R_1 for the poly(NIPA/VF) gel-coated quartz crystal resonator upon potential steps between +480 and −50 mV vs SSCE at 30 °C.

Table 1. Evaluated D_{app} Values in the Swollen (10 °C) and Shrunken (35 °C) Gels

method	process	D_{app}, cm^2 s^{-1} at 10 °C	D_{app}, cm^2 s^{-1} at 35 °C
chronoamperometry	oxidation	2×10^{-9}	7×10^{-12}
	reduction	1×10^{-9}	1×10^{-11}
chronocoulometry	oxidation	2×10^{-9}	6×10^{-12}
	reduction	1×10^{-9}	2×10^{-11}

Apparent diffusion coefficients for the charge propagation (D_{app}) within the swollen and shrunken gel films were determined by means of potential-step chronoamperometry and chronocoulometry (Table 1). Concentration of the ferrocene site in the gel was determined as follows: the bulk gel (0.68 cm^3 at 10 °C) was burned in a glass tube; then the residue was dissolved in an aqueous HCl solution, and the iron content in the solution was measured by means of atomic absorption spectroscopy. As can be seen in the table, the D_{app} value for the swollen gel was larger than the shrunken gel by about 2 orders of magnitude. The D_{app} value for a polymer film is known to depend on the rates of electron hopping, motion of polymer chains, and motion of a counterion. In the absence of the phase transition, lower temperature is not favorable to all these factors. The larger D_{app} value of the gel at lower temperature is caused probably by a higher mobility of the polymer chain and/or a counterion due to the swollen structure of the gel.

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