

Design and Preparation of a Novel Temperature-Responsive Ionic Gel. 1. A Fast and Reversible Temperature Response in the Charge Density

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We propose a novel temperature-responsive ionic gel (*T*-responsive ionic gel) that can control the transport modes of specific ions by changing its charge density in response to the temperature. We also describe the design and preparation of the *T*-responsive ionic gel that has a fast and reversible temperature response in the charge density. The gel consists of an interpenetrating network of two kinds of modified poly(vinyl alcohol): a polymer with sulfonic acid groups and a polymer on which poly(*N*-isopropylacrylamide) [poly(NIPAAm)] chains were grafted. Phase separation in the gel at temperatures above the lower critical solution temperature (LCST) of poly(NIPAAm) gives steep decrease in the water content of the gel at temperatures around the LCST, while the ion-exchange capacity does not change with temperature. The charge density, which is defined as the division of the ion-exchange capacity by the water content, increases with increasing temperature. The measurements of the charge density change over stepwise changes of temperature between 10 and 50 °C indicate that the value of the charge density changes from 0.07 to 0.24 mol dm⁻³ within a period of 1 min and the temperature response of the charge density is reversible in all the temperature changing steps. Permeation experiments in a dialysis system consisting of the gel membrane and mixed KCl and CaCl₂ solutions show that the membrane can control the transport modes of Ca²⁺ ions by changing the temperature in two ways: downhill transport (transport along their own concentration gradient in a system) at temperatures below the LCST of poly(NIPAAm) and uphill transport (transport against their concentration gradient) at temperatures above the LCST.

Introduction

There are many studies on stimuli-responsive hydrogels that undergo abrupt changes in volume in response to external stimuli, such as pH,^{1–4} temperature,^{5–13} electric fields,^{14–16} light,^{17–19} antigens,²⁰ and saccharides.^{21–25} The gels have potential applications in medicine, biotechnology, industry, and in solving environmental problems because the permeability of solutes through the gels can be controlled by these stimuli. For some applications, it would be very useful to have a hydrogel that could control not only the permeability but also the transport modes (downhill and uphill) of specific ions in response to external stimuli. In this study, downhill is transport of ions along their own concentration gradient in a system and uphill is that against their own concentration gradient.

Let us consider a diffusion dialysis system where an ionic gel membrane separates two cells. The two cells contain both the *m* species M_kA₂ electrolytes ($1 \leq k \leq m$) and the *n* species M_jA electrolytes ($1 \leq j \leq n$) where M_k²⁺, M_j⁺, and A[–] denote a bivalent cation, univalent cation, and univalent anion, respectively. Initially, the composition of the M_kA₂ and M_jA electrolytes in the two cells is identical, and the concentrations of the electrolyte solution in one cell is higher than that of the other cell. Higa et al.^{26,27} have simulated that in such a case, and the bivalent ions, M_k²⁺, are transported against their concentration gradients due to the diffusion of the driving electrolyte, M_kA, under suitable conditions. This transport is referred to as uphill transport or counter transport. The simulations show that the

transport modes of the ions will be controlled by changing membrane charge density: the uphill transport of bivalent ions occurs when the charge density is much higher than the ionic concentration of the external solution; the downhill transport occurs when the charge density is lower than the ionic concentration. Hence, an ionic gel whose charge density changes in response to external stimuli will control the transport modes of the specific ions by the stimuli. However, to our knowledge, there have been no studies on such an ionic gel.

The aim of this study is to propose a novel concept of a temperature-responsive ionic gel that can control the transport modes of ions by changing its charge density in response to the temperature. Our strategy for preparing such a gel is to use reversible phase separation in a temperature-responsive (*T*-responsive) ionic gel consisting of an interpenetrating network (IPN) of a polyanion and a polymer on which *T*-responsive polymer chains are grafted as shown in Figure 1. Aqueous solutions of poly(*N*-isopropylacrylamide) (polyNIPAAm) exhibit a lower critical solution temperature (LCST) at around 32 °C. Hence, the graft polymers on the poly(vinyl alcohol) (PVA) network are soluble in the water phase of the networks at temperatures below the LCST. At temperatures above the LCST, phase separation occurs; the graft copolymers form insoluble aggregates, with the charged groups on the ionic network concentrating in the water phases. Hence, the charge density of the gel will increase with increasing temperature. The ionic gel having a temperature response in the charge density will control the transport modes of ions in response to temperature changes. We prepare a *T*-responsive ionic gel that has a fast and reversible temperature response in the charge density from two kinds of

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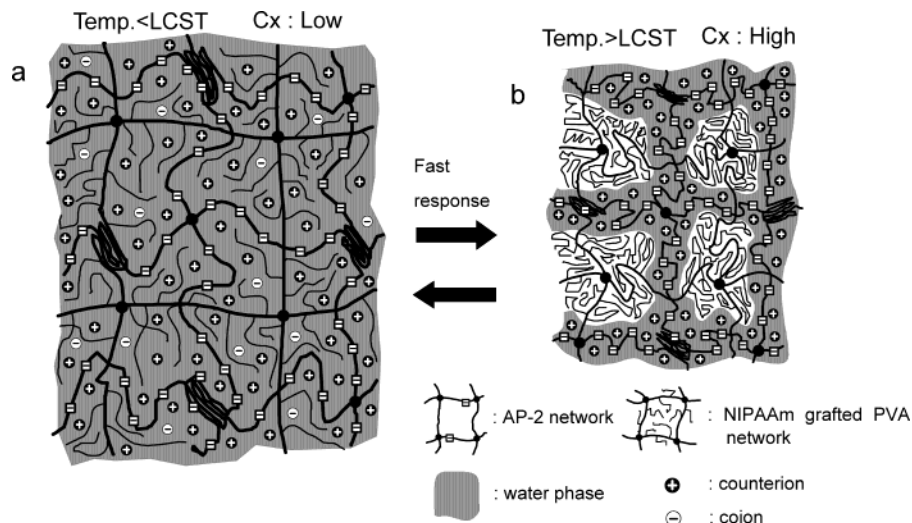


Figure 1. Diagrams of a suggested mechanism for the temperature dependence of the charge densities of *T*-responsive ionic gels: (a) at a temperature below the LCST and (b) at a temperature above the LCST.

modified poly(vinyl alcohol): a polymer with sulfonic acid groups and a polymer on which poly(*N*-isopropylacrylamide) [poly(NIPAAm)] chains were grafted. A permeation experiment in a diffusion dialysis system consisting of the gel membrane and mixed KCl–CaCl₂ solutions will be carried out in order to examine whether the gel can control the transport modes of just Ca²⁺ ions in response to the temperature.

Experimental Section

Synthesis of Graft Polymer. A temperature-responsive polymer was prepared by in situ polymerization of *N*-isopropylacrylamide in a poly(vinyl alcohol) (PVA) solution as follows: PVA (Aldrich) (1.0 g), NIPAAm (Wako Pure Chemical Industries, Ltd.) (11.0 g), and potassium persulfate (0.06 g) as an initiator were dissolved in 80 mL of dimethyl sulfoxide (DMSO). The glass tube containing the solution was sealed by conventional methods and immersed in an oil bath held at 40 °C for 20 h. The reactant was poured into acetone to precipitate the *T*-responsive polymer.

Preparation of Gel Membrane. The polymer obtained (1.54 g), a polyanion AP-2 (Kuraray Co. Ltd.) (0.32 g), and PVA (0.66 g) were dissolved in 34 mL of DMSO. AP-2 is a kind of PVA that contains 2 mol % of 2-acrylamido-2-methylpropane-sulfonic acid groups as a copolymer and hence provided negatively charged sites. After casting the solution on a glass plate and drying it at 50 °C with a hot stage (NISSIN, NHP-45N), a self-standing membrane (its thickness is 0.1 mm) was obtained. The membrane was annealed for 20 min at 160 °C with an electric drying oven (ADVANTEC, FS-320) and after this was cross-linked in an aqueous solution of a mixture of 0.025 vol % glutaraldehyde, 0.1 mol dm^{−3} HCl, and 2 mol dm^{−3} NaCl at 25 °C for 24 h.

Measurement of Water Content. The gel, weighed in the dry state, was immersed in an ion-exchanged water at the desired temperature for 3 days. The gel was removed from the water, tapped with filter paper to remove excess water on the gel surface, and then weighed in the wet state. The water content, *H*, is derived from weights in the wet state, *W_w*, and in the dry state, *W_d*, as

$$H = \frac{(W_w - W_d)/1.0}{(W_w - W_d)/1.0 + W_d/1.3} \quad (1)$$

where 1.0 and 1.3 are the densities of water and PVA, respectively.

Measurement of Ion-Exchange Capacity. The gel, weighed in the dry state, was immersed in an ion-exchanged water for 3 days and immersed in 1 N potassium chloride solution for 2 h, in 0.001 N potassium chloride solution for 6 h, and then in 50 mL of 0.1 N hydrochloride solution for 3 h. The potassium ion concentration in the hydrochloride solution, *C_K*, was measured by an ion chromatograph (Hitachi Co. L-3710). The ion-exchange capacity, *Q*, defined as the division of the molar of the fixed charged sites in the gel by its dry weight, is given as:

$$Q = \frac{50}{1000} \frac{C_K}{W_d} \quad (2)$$

Determination of the Charge Density. The charge density was estimated from membrane potential data.²⁶ The potential was measured at various temperatures by using an acrylic plastic cell of two parts separated by the *T*-responsive gel membrane. One chamber of the cell was filled with KCl solutions of various concentrations (0.01, 0.03, 0.1 M), *C_o*. The other chamber was filled with KCl solutions whose concentration was 5 times higher than those in the first chamber (*r* = 5). From the measured membrane potentials, Δφ, the charge density, *C_x*, was calculated in terms of^{28,29}

$$\Delta\phi = -\frac{RT}{F} \ln \left(r \cdot \frac{\sqrt{C_x^2 + (2C_o)^2} - C_x}{\sqrt{C_x^2 + (2rC_o)^2} - C_x} \right) - \frac{RT}{F} W \ln \left(\frac{\sqrt{C_x^2 + (2rC_o)^2} - C_x W}{\sqrt{C_x^2 + (2C_o)^2} - C_x W} \right) \quad (3)$$

where *W* = (*ω_K* − *ω_{Cl}*)/(*ω_K* + *ω_{Cl}*), and *ω_K* and *ω_{Cl}* are the K⁺ and Cl[−] mobilities in a gel membrane, respectively, and *F*, *R*, and *T* are the Faraday constant, the gas constant, and the absolute temperature, respectively. Parameters *W* and *C_x* were adjusted so that the left-hand side of eq 3 fits the experimental data of Δφ at various KCl concentrations.

Permeation Experiments. Permeation experiments were performed by using an acrylic plastic cell of two parts separated by the *T*-responsive gel membrane. One chamber of the cell was filled with a mixed salt solution of 3.0 × 10^{−3} M KCl and

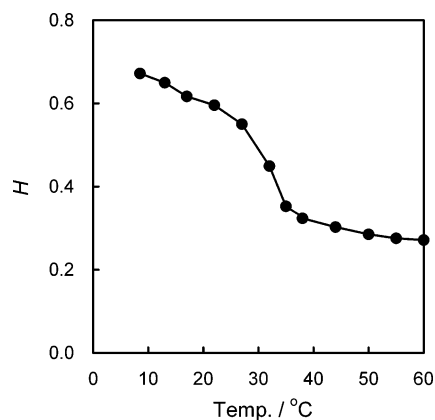


Figure 2. Water content of the *T*-responsive ionic gel vs temperature.

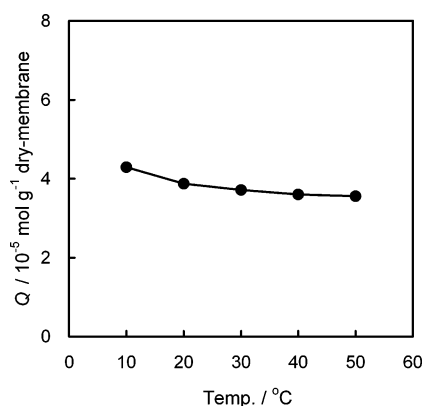


Figure 3. Ion-exchange capacity of the *T*-responsive ionic gel vs temperature.

5.0×10^{-4} M CaCl_2 , and the other chamber a mixed salt solution of 3.0×10^{-2} M KCl and 5.0×10^{-3} M CaCl_2 . The volumes of the chambers at the low- and the high-concentration sides were 120 and 400 cm^3 , respectively. The effective membrane area of the cell was 7.07 cm^2 . The solution in the chamber at the low-concentration side was sampled to measure the concentration of K^+ and Ca^{2+} ions using an ion chromatograph (Hitachi Co. L-3710).

Results and Discussion

Water Content as a Function of Temperature. Figure 2 shows the water content of the gel as a function of temperature. The water content decreases with increasing temperature. A steep decrease of the water content is observed at temperatures around 32 °C. The steep decrease of the water content is due to poly(NIPAAm) chains grafted on PVA network becoming hydrophobic at temperatures above the LCST of poly(NIPAAm) so that phase separation occurs in the gel, as shown in Figure 1. The gel was clear at temperatures below the LCST but cloudy at temperatures above the LCST. This phenomenon supports that the phase separation occurs at temperatures above the LCST.

Ion-Exchange Capacity as a Function of Temperature. Figure 3 shows the ion-exchange capacity of the gel membrane as a function of temperature. The value of the ion-exchange capacity was about 4.0×10^{-5} mol/g of dry membrane and did not change with temperature. This means that when phase separation occurs at temperatures above the LCST, almost all of the hydrophilic phases in the gel will connect each other and almost all of the ion-exchange groups will concentrate to the inter-connected hydrophilic phase. In other words, few charged sites in the gel remain in the hydrophobic phases and/

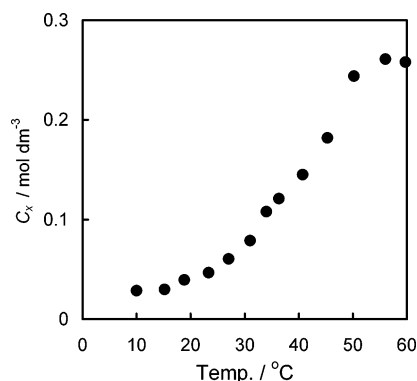


Figure 4. The charge density of the gel as a function of temperature.

or in hydrophilic phases that are isolated from the inter-connected hydrophilic phase.

Charge Density as a Function of Temperature. Figure 4 shows the charge density of the gel as a function of temperature. The charge density increases with temperature. The charge density is defined as the division of the ion-exchange capacity by the water content. The water content decreases with increasing temperature, while the ion-exchange capacity does not change with temperature. Hence, the increase of the charge density is partly due to the decrease of the water content. The charge density at 50 °C, however, is more than 7 times larger than that at 10 °C, while the water content just decreases to half values. When the phase separation occurs at temperatures above the LCST, the charged groups concentrate to the interconnected hydrophilic phase. The heterogeneous distribution of the charged groups in the gel facilitated the increase of the charge density, because Figure 1 shows that the charge density calculated as the division of the ion-exchange capacity by the volume of the inter-connected hydrophilic phase is larger than that calculated as the division of the capacity by the volume of the gel.

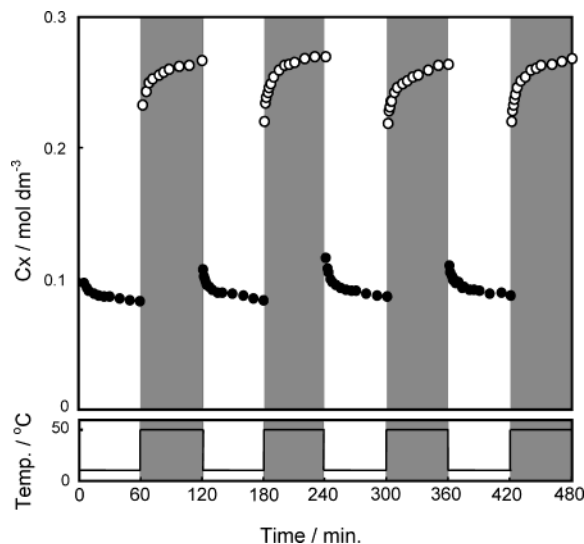
We used PVA as the main chain of the IPN structure because an IPN gel consisting of hydrophilic main chains such as PVA will have larger charge density differences with temperature changes than one consisting of hydrophobic polymer chains such as styrene using as many commercially available ion-exchange resins and ion-exchange membranes. This is because at temperatures below the LCST both the graft polymers and the main chain of the former gel are hydrophilic; hence, the fixed charge groups distribute homogeneously in the gel, as shown in Figure 1.

The charge density does not change abruptly at temperatures around the LCST but increases gradually with increasing temperature. This property of the charge density will facilitate the application of the gel to a polymer device for controlling the transport modes of specific ions in response to temperature changes.

Effect of Cross-Link Conditions on the Temperature Response of the Gels. We made three types of temperature-responsive ionic gels by changing their cross-link conditions: type I, annealed for 20 min at 160 °C; type II, cross-linked in a glutaraldehyde solution at 25 °C for 1 day; type III, cross-linked in a glutaraldehyde solution after annealing. The data for the water content, H , and the charge density, C_x , at 10 and 50 °C, the difference of the water content, ΔH , and the charge density, ΔC_x , are listed in Table 1. In type I gels, the water content both at 10 and 50 °C has a high value and decreases only 9.0% at 50 °C, so that the values of both C_x and ΔC_x are low. This is because physical cross-linking by annealing is too weak to keep the water content low against the osmotic pressure

TABLE 1: Water Content, H , and the Charge Density, C_x , of the Sample Gels at 10 and 50 °C and the Difference of the Water Content, ΔH , and the Charge Density, ΔC_x

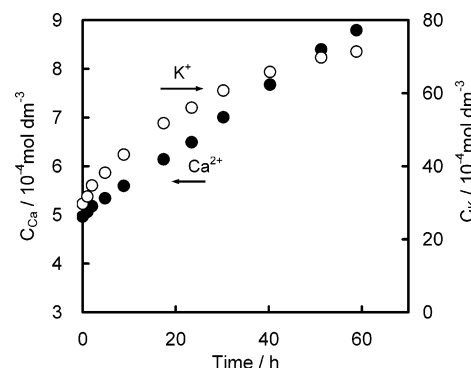
samples	H		ΔH (%)	C_x (mol dm ⁻³)		
	at 10 °C	at 50 °C		at 10 °C	at 50 °C	ΔC_x (%)
type I	0.78	0.71	-9.0	0.017	0.024	41
type II	0.29	0.20	-31	0.14	0.21	50
type III	0.67	0.26	-61	0.03	0.26	770

**Figure 5.** Time-charge density curve of the gel in response to stepwise changes in the temperature between 10 and 50 °C.

difference generated by the counterion of the polyanion in the gel. In type II gels, H has a low value and decreases 30% at 50 °C. The value of C_x is higher than that in type I gel. The value of ΔC_x of type II gel is almost the same as that in type I gel. This is because the gel is so tightly cross-linked by the chemically cross-linking that the gel has a low water content even at low temperatures. The gel is so brittle that its mechanical strength is very low. In type III gel, the change of the water content between the temperatures has the highest value in the gels. Hence, ΔC_x in type III gel also has the highest value in all the gels. This is because the crystallinity of PVA is increased by the annealing process. Hence, the chemical cross-linking after annealing will give the gel heterogeneous cross-linking. The gel has high temperature response in the charge density as well as high mechanical strength due to the heterogeneous cross-linking.

Effect of Polyanion Content on the Temperature Response of the Gels. We prepared the temperature-responsive ionic gels by changing their polyanion content and measured the charge density changes between 10 and 50 °C. The experiments, whose data are not described here, revealed that the charge density at 10 °C increases constantly with increasing polyanion content, C_p . The charge density at 50 °C increases constantly with C_p when $C_p < 20$ wt % and reaches a saturated value when $C_p > 20$ wt %, because the water content of the gels increases with increasing C_p . The difference of the charge density between two temperatures decreases with increasing polyanion content.

Temperature Response in Charge Density Changes. To apply the temperature-responsive ionic gels to ionic devices, fast and reversible temperature response in the charge density is needed. We measured the charge density changes through stepwise changes in the temperature to investigate the temperature responsibility in the charge density of the gel. Figure 5 shows the charge density change with time during stepwise

**Figure 6.** Time-concentration curves of Ca²⁺ ion, C_{Ca} , and K⁺ ion, C_K , in the low-concentration chamber at 10 °C.

changes in temperature between 10 and 50 °C. The value of the charge density changes from 0.03 mol dm⁻³ at 10 °C to 0.26 mol dm⁻³ at 50 °C within a period of 1 min. The temperature-charge density profiles are almost the same in all the steps, meaning that the charge density of the gel has a fast and reversible response to temperature changes. Yoshida et al.¹⁰ reported that a T -responsive hydrogel, in which poly(NIPAAm) chains were grafted onto cross-linked networks, collapsed in about 20 min, while similar gels lacking the grafted side chains took more than a month to undergo full deswelling. We can obtain a fast T -response of the charge density changes using poly(NIPAAm) chains grafted onto PVA.

To introduce charged groups into a T -responsive gel, physical mixtures of T -responsive gels and polyelectrolytic chains are also a possible way; but T -responsive ionic gels obtained from this method will not show a reversible T -response, as the gels and the polymers tend to separate physically during stepwise changes in the temperature. The other way to introduce charged groups is by graft copolymerization of T -responsive and ionic monomers onto a cross-linked network. However, it will be difficult to change the charge density of a hydrogel prepared from this method because the charged groups refrain from phase separation. Thus, an interpenetrating network of T -responsive and ionic polymer networks, which has the functions of a single gel structure and does not permit physical separation, is most effective⁹ for fast and reversible responses, to temperature changes, in the charge density.

Control of the Transport Modes of Ions through the Gel Membrane by Changing the Temperature. To examine the transport properties of the gel, we performed permeation experiments in a dialysis system consisting of the gel membrane and mixed KCl and CaCl₂ electrolyte solutions. Figure 6 shows the time-concentration curves in the low-concentration chamber at 10 °C. The concentrations of both K⁺ and Ca²⁺ ions increase with time. This means that these ions transport along with their concentration gradient. Thus, downhill transport of both K⁺ and Ca²⁺ ions occur at 10 °C. On the other hand, the concentration of Ca²⁺ ions in the low-concentration chamber decreases with time at 50 °C, while the concentration of K⁺ ion increases, as shown in part a of Figure 7. This means that Ca²⁺ ions are transported against their concentration gradient (uphill transport), while the K⁺ ions diffuse from the high- to the low-concentration chamber (downhill transport). There is a possibility that the decrease of Ca²⁺ ion concentration at the low-concentration chamber occurs due to adsorption of the ion in the membrane and/or to ion exchange of Ca²⁺ ion for other ion in the membrane. However, the increase of the concentration of Ca²⁺ ions with time at the high-concentration chamber shown in part b of Figure 7 confirms that Ca²⁺ ions are transported against

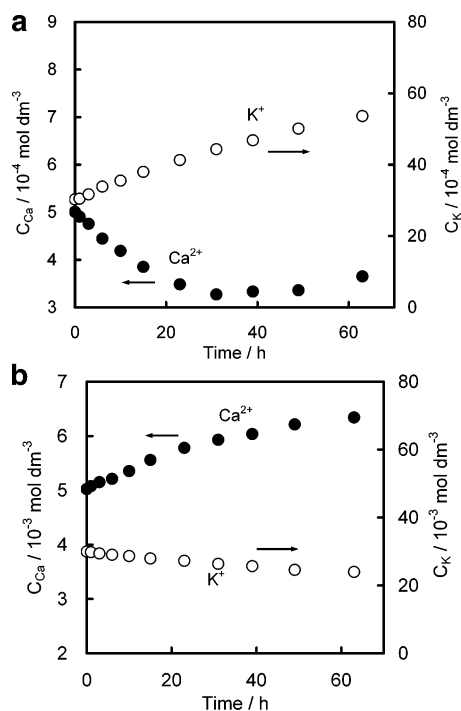


Figure 7. (a) Time–concentration curves of Ca^{2+} ion, C_{Ca} , and K^+ ion, C_{K} , in the low-concentration chamber at 50 °C. (b) Time–concentration curves of Ca^{2+} ion, C_{Ca} , and K^+ ion, C_{K} , in the high-concentration chamber at 50 °C.

their concentration gradient from the low- to the high-concentration chambers. These results indicate that the gel has enough charge density change to control the transport modes of ions. We will obtain a temperature-responsive ionic gel with much higher temperature response in the charge density than the gel in this study to optimize the preparation conditions.

Conclusions

We propose novel T -responsive ionic gels that can control the transport modes of specific ions in response to temperature. The T -response ionic gels were prepared from a modified PVA that contains 2 mol % of sulfonic acid groups and polymer on which poly(NIPAAm) chains were grafted. The charge density of the gel membrane increases with temperature. The gels have a very fast temperature response in the charge density because of the graft polymers of poly(NIPAAm) chains. The gels also have reversible temperature response in the charge density because of the IPN network of two kinds of modified poly-(vinyl alcohol) chains. Furthermore, the physical and chemical cross-link gives the charge density of the gel high temperature-

responsiveness. The permeation experiment in a diffusion dialysis system consisting of the gel and mixed KCl and CaCl_2 solutions shows that the gel can control the downhill and uphill transport modes of just Ca^{2+} ions.

Many hydrogels undergo abrupt changes in water content in response to external stimuli, and the charge density of the gels is a function of the water content. Therefore, the strategy detailed here for changing the charge density in response to temperature can be applied to other external-stimuli-responsive gels with charged groups.

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