

# Ion-Conducting Polymer Gels of Polyacrylamide Embedded with $K_2CO_3$

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**ABSTRACT:** A highly ionic conductive solid-gel membrane based on polyacrylamide hydrogels with a  $K_2CO_3$  additive was investigated. The polymer-based gel was prepared by adding ionic species  $K_2CO_3$  to a monomer solution followed by polymerization. After polymerization, the ionic species was embedded in the polymer-based gel, where it remained. The ionic species behaved like a liquid electrolyte, whereas the polymer-based solid-gel membrane provided a smooth impenetrable surface that allowed for the exchange of ions. The gel membranes were obtained in the form of thin films of reasonable mechanical strength. Their ambient

temperature conductivities were in the range  $10^{-2}$  to  $10^{-1}$  S/cm. The effect of  $K_2CO_3$  concentration on the conductivity of the gels prepared was examined in the temperature range from 0 to 100°C. The microstructure and chemical composition of the gels studied were characterized by environmental scanning electron microscopy and FTIR, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2076–2081, 2004

**Key words:** conducting polymers; gels; electrochemistry; microstructure; infrared spectroscopy

## INTRODUCTION

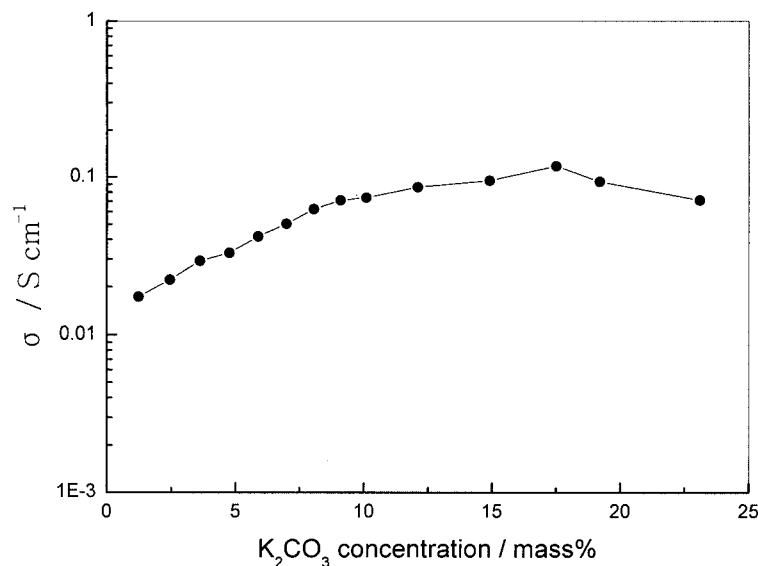
Electrochemical devices, such as metal/air, Zn/MnO<sub>2</sub>, Ni/Cd, smart windows, flat panel displays, and fuel cells, generally incorporate an electrolyte source to provide the anions or cations necessary to produce an electrochemical reaction. Thus the development of novel ionic-conducting polymeric electrolytes for various electrochemical applications is attracting considerable interest. It is industrially important to increase the ionic conductivity of electrolytes up to  $>10^{-3}$  S/cm at ambient temperature. So far, many literature reports have been focused on the complexes of polyacrylamide (PAAM) gels with strong inorganic acids, such as  $H_3PO_4$  or  $H_2SO_4$ . According to some indications in the literature,<sup>1–5</sup> electrolytes based on polyacrylamide hydrogels with  $H_3PO_4$  or  $H_2SO_4$  as additives exhibit ambient temperature conductivities in the range  $10^{-3}$  to  $10^{-2}$  S/cm, and conductivity increases with temperature to  $>10^{-2}$  S/cm at 100°C. Although the acid electrolytes have very high ionic conductivity, electrochemical reaction mainly depends on characteristics of electrode reactants and catalysts in the media. For the oxidation of small organic molecules as fuels

in fuel cells, Pt seems to be the only sufficiently active catalyst in acid media.<sup>6</sup> However, the expense of Pt may increase the cost of the fuel cell. Accordingly, it is very important to research other electrolyte media suitable for the cheaper materials with sufficient activity as catalysts.

To date, there have been a reasonable number of studies on the oxidation of small organic molecules in alkaline media and alkaline media have several distinct advantages.<sup>6</sup> The most notable advantage is that other metals are as active as Pt in alkaline media. However, the use of alkaline media is not without drawbacks, the most serious of which is that KOH or NaOH will be consumed as fuel because the solution picks up CO<sub>2</sub>. Thus KOH or NaOH must be added in proportion to the fuel. However, alkaline carbonate such as  $K_2CO_3$  or  $Na_2CO_3$  should be more resistant to further CO<sub>2</sub> uptake in alkaline media. To this end the polymer gel electrolytes based on PAAM hydrogels with a  $K_2CO_3$  additive were investigated. The polymer-based gel was prepared by adding ionic species, such as  $K_2CO_3$ , to a monomer solution followed by polymerization. After polymerization, the ionic species was embedded in the polymer-based gel, where it remained. The ionic species behaved like a liquid electrolyte, and the polymer-based solid-gel membrane provided a smooth impenetrable surface that allowed for the exchange of ions. The effects of  $K_2CO_3$  concentration of the gels obtained on the conductivity, microstructure, and chemical composition were also examined.

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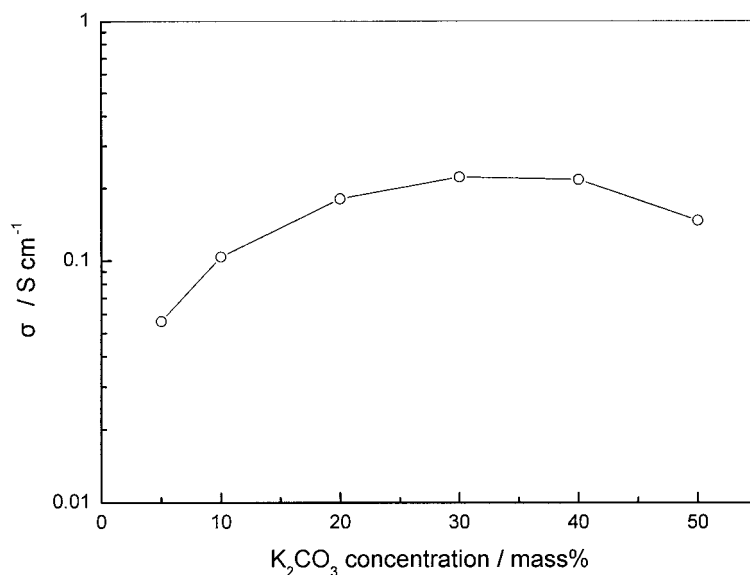
**Figure 1** Room-temperature ionic conductivity versus concentration of  $\text{K}_2\text{CO}_3$  in PAAM solid-gel electrolyte (AAM : MBAA :  $\text{H}_2\text{O}$  mass ratio = 11.5 : 1 : 100) at 25°C.

## EXPERIMENTAL

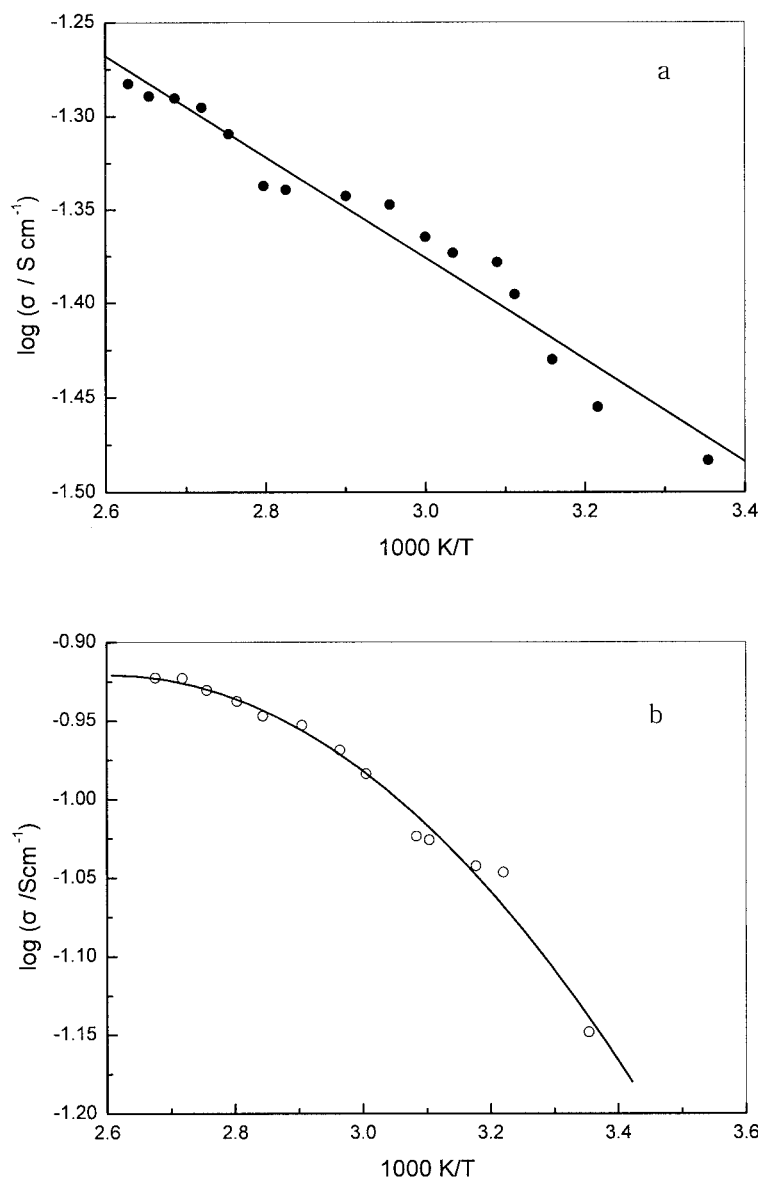
### Sample preparation

Aqueous ion-conducting gel electrolytes were prepared according to the following procedure. Acrylamide (AAM),  $N,N'$ -methylenebisacrylamide (MBAA), and  $\text{K}_2\text{CO}_3$  were mixed together in a glass flask and dissolved in a specific amount of deionized water. The solution was mixed using a magnetic stirrer until visible dissolution of the solid components. After about 0.5 h of mixing, to the solution were added a few drops of 10 mass %

$(\text{NH}_4)_2\text{S}_2\text{O}_8$  (acting as an initiator for the polymerization reaction) solution and a few microliters of tetramethyl-ethylene-diamine (TEMED) (acting as a catalyst for the polymerization reaction). All monomers and reagents were from local sources and of analytical grade. The reaction mixture was subsequently transferred to a glass mold. The glass mold was sealed and placed in an oven at 60°C for 6–8 h, and a gelation process could be observed during the course. The gels obtained were stored in an airtight container with constant humidity for future use.



**Figure 2** Room-temperature ionic conductivity versus concentration of  $\text{K}_2\text{CO}_3$  in  $\text{K}_2\text{CO}_3$  water solution at 25°C.



**Figure 3** Ionic conductivity versus reciprocal temperature for PAAM solid-gel electrolyte membranes based on mass ratio AAM:MBAA:H<sub>2</sub>O = 11.5:1:100. (a) K<sub>2</sub>CO<sub>3</sub> concentration = 4.26 mass %; (b) K<sub>2</sub>CO<sub>3</sub> concentration = 8.16 mass %.

### Conductivity measurements

Ionic conductivity was determined using a complex impedance method. The samples were sandwiched between two stainless-steel blocking electrodes, sealed in a quartz tube, and placed in a temperature-controlled furnace. The impedance measurement was carried out on a computer-interfaced AUT980583 (Eco Chemie B.V., The Netherlands) impedance analyzer over the frequency range of 1 Hz to 40 kHz.

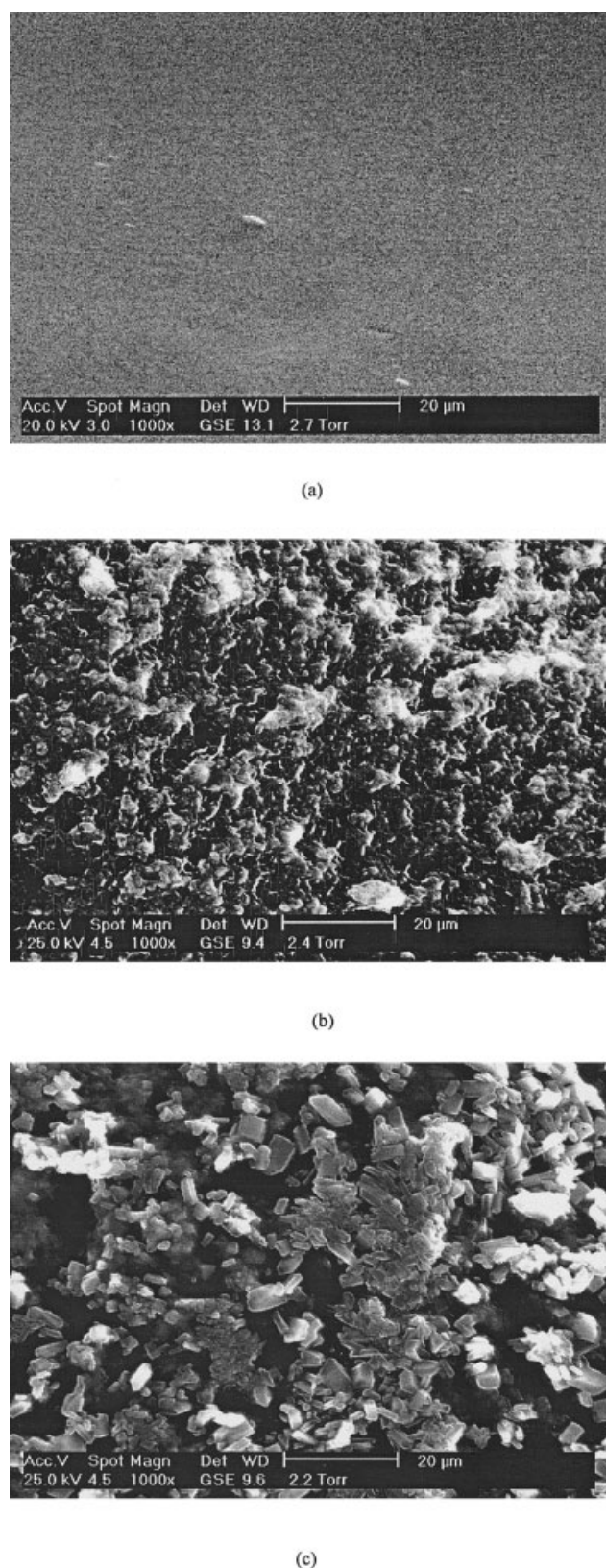
### Environmental scanning electron microscopy

Investigation of the samples' microstructure was carried out with an environmental scanning electron mi-

croscope (ESEM; Philips XL30 ESEM, The Netherlands).

### FTIR

Infrared spectra were recorded on a computer-interfaced Bio-Rad FTS3000 instrument (Bio-Rad, Hercules, CA) with a wavenumber resolution of  $2 \text{ cm}^{-1}$  in the range  $4000\text{--}400 \text{ cm}^{-1}$ . Before the measurement, the gels were repeatedly washed with deionized water to remove small molecule impurities, and then dried in a furnace at  $100^\circ\text{C}$  until complete removal of water. The dried samples were shattered and mixed with KBr to prepare the measured plates. No interaction was observed between the dried samples and KBr.



**Figure 4** ESEM photomicrographs of  $\text{K}_2\text{CO}_3$ -doped PAAM solid-gel electrolyte membranes based on mass ratio AAM : MBAA :  $\text{H}_2\text{O}$  = 11.5 : 1 : 100 ( $\times 1000$ ): (a)  $\text{K}_2\text{CO}_3$  concentration 0 mass %; (b)  $\text{K}_2\text{CO}_3$  concentration 15.9 mass %; (c)  $\text{K}_2\text{CO}_3$  concentration 21.1 mass %.

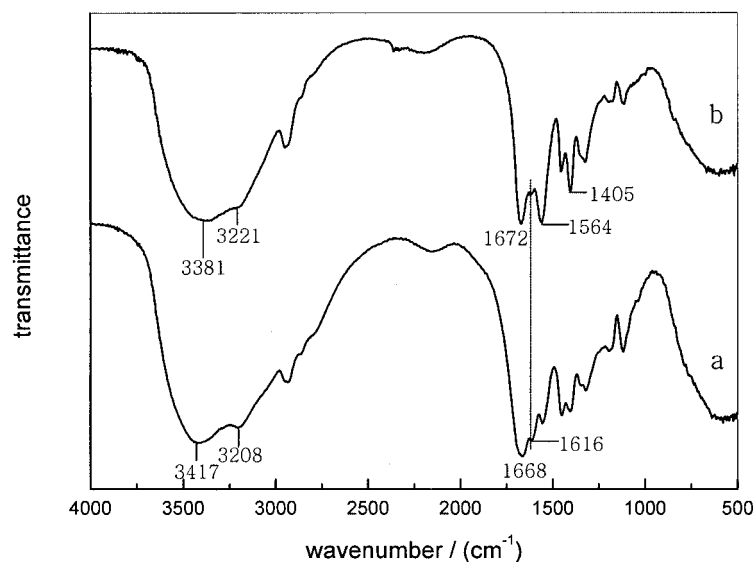
## RESULTS AND DISCUSSION

### Conductivity of PAAM gel doped with $\text{K}_2\text{CO}_3$

Figure 1 shows the variation of the ambient temperature ionic conductivity of PAAM gel doped with  $\text{K}_2\text{CO}_3$  versus concentration of  $\text{K}_2\text{CO}_3$  [denoted as concentration of  $\text{K}_2\text{CO}_3 = \text{K}_2\text{CO}_3 \text{ mass} / (\text{K}_2\text{CO}_3 \text{ mass} + \text{H}_2\text{O mass} + \text{AAM mass} + \text{MBAA mass})$ ]. The ionic conductivity increased from 0.0173 to 0.0624 S/cm with an increase in concentration of  $\text{K}_2\text{CO}_3$  up to 7.22%, and then slowly increased to 0.118 S/cm when the concentration of  $\text{K}_2\text{CO}_3$  was varied from 7.22 to 15.9%, and finally began to decrease when the concentration of  $\text{K}_2\text{CO}_3$  exceeded 15.9%. The maximal ambient temperature conductivity (0.118 S/cm) was achieved at the concentration of 15.9%  $\text{K}_2\text{CO}_3$ . A similar trend of conductivity in Figure 1 can also be observed in Figure 2, but the maximal ambient conductivity in Figure 2 is 0.22 S/cm and appears at the concentration of 30%  $\text{K}_2\text{CO}_3$ . This might be attributed to the relatively lower water content in the gel, the influence of the hydrogel network structure, and the interaction between PAAM and  $\text{H}_2\text{O}$ . The hydrogel network structure makes ion migration difficult. The interaction between PAAM and  $\text{H}_2\text{O}$  resulted in a constraint of the dissociation of  $\text{K}_2\text{CO}_3$  and of the free migration of ions. The solubility of  $\text{K}_2\text{CO}_3$  in the hydrogel is believed to be saturated at the point of the maximum conductivity achieved, which is supported by the observation of the appearance of solid  $\text{K}_2\text{CO}_3$  particles and the occurrence of opaque hydrogels. With respect to the ionic conductivities versus  $\text{K}_2\text{CO}_3$  concentration (Figs. 1 and 2), two important factors, which influence the changing trend of ionic conductivities, are ionic strength and formation of ion pairs. The ion activity coefficient is negatively correlated with the ionic strength and the concentration of ion pairs that are proportional to the  $\text{K}_2\text{CO}_3$  concentration. Thus the increase of  $\text{K}_2\text{CO}_3$  concentration led to a decrease of ion activity coefficient, which resulted in the occurrence of maximal ion activity. The ion activity increased with  $\text{K}_2\text{CO}_3$  concentration before the maximum was obtained and then decreased after that. Ionic conductivity is proportional to ion activity; therefore the ionic conductivities show similar changing trends as indicated in Figures 1 and 2.

In Figure 3(a) and (b) changes of conductivity versus reciprocal temperature are shown for samples containing  $\text{K}_2\text{CO}_3$  at 4.26 and 8.16% (AAM : MBAA :  $\text{H}_2\text{O}$  mass ratio = 11.5 : 1 : 100), respectively. For a  $\text{K}_2\text{CO}_3$  concentration  $< 7.22\%$ , for samples with higher water content, the temperature dependency of conductivity is the Arrhenius type [ $\sim \exp(-E_a/k_B T)$ ], that is  $\sigma = \sigma_0 \exp(-E_a/k_B T)$ . Here,  $E_a$  is an activation energy for ionic conduction,  $\sigma_0$  is a preexponential factor, and  $k_B$  is the Boltzmann constant. In our opinion, this results from the fact that, for higher water content, ionic





**Figure 5** IR spectra of samples: (a) pure dried gel sample in the production process of gel without adding  $K_2CO_3$ ; (b) pure dried gel sample in the production process of gel with adding 21.1 mass % of  $K_2CO_3$ . Samples based on AAM : MBAA :  $H_2O$  mass ratio = 11.5 : 1 : 100.

conductivity occurs by interstitial water pathways present in the polymer matrix. For  $K_2CO_3$  concentrations from 7.22 to 15.9%, for samples containing less water, the temperature dependency of conductivity follows the Vogel–Tamman–Fulcher (VTF)-type relation, that is

$$\sigma = \frac{A}{\sqrt{T}} \exp \left[ -\frac{B}{k_B(T - T_0)} \right]$$

where  $A$  is a preexponential factor,  $B$  is a pseudoactivation energy, and  $T_0$  is a thermodynamic glass-transition temperature that is usually lower than the glass-transition temperature  $T_g$  measured by DSC experiments. The results suggested that, for lower water content, ionic conductivity depends both on the polymer segmental motion and on interstitial water pathways present in the polymer matrix.

In excess of 15.9%  $K_2CO_3$ , the  $K_2CO_3$  crystal particles in gel begin to yield, the solid gel becomes soft, and the partial structure of polymer matrix can change. The above-mentioned results are verifiable by ESEM and FTIR analyses, and thus the measurement on the changes of conductivity of solid gel containing  $K_2CO_3$  over 15.9% versus reciprocal temperature was not carried out in this study.

### Microstructure of solid gel

In preparation of PAAM gel doped with  $K_2CO_3$ , it was found that solid-gel electrolytes became more opaque and softer with increasing  $K_2CO_3$  concentration. This is identified by the microstructure of solid hydrogels

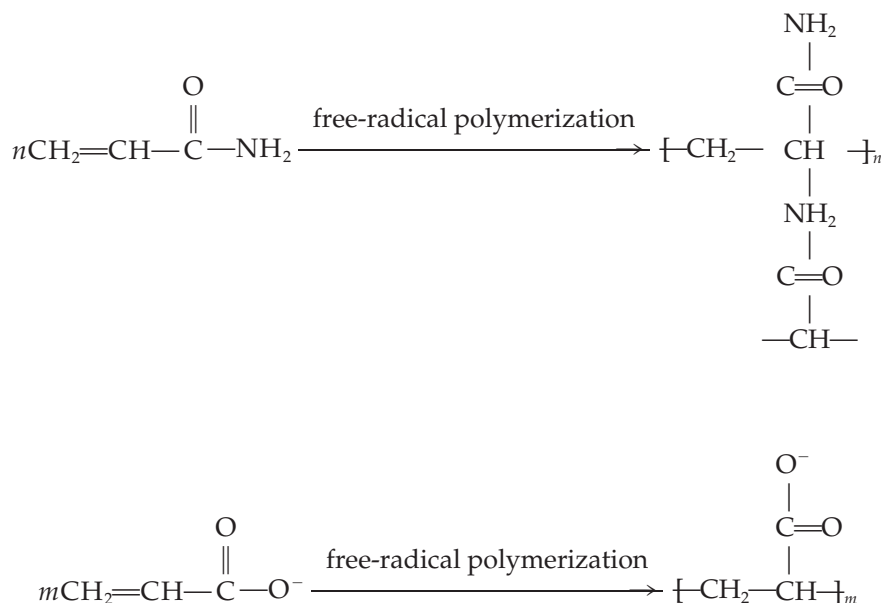
shown in Figure 4(a)–(c). Figure 4(a) shows that the sample is homogeneous without  $K_2CO_3$  addition. As shown in Figure 4(b), phase separation can be observed but no  $K_2CO_3$  crystal particle occurs. Figure 4(c) clearly exhibits the occurrence of crystal particles of  $K_2CO_3$ . The reason for these phenomena is not clear, although it is conjectured to be attributed to both the decrease of  $K_2CO_3$  solubility in the hydrogels and the accelerated flocculation of hydrogels with the increase of  $K_2CO_3$  concentration.

### FTIR studies of solid gel without any impurities

Figure 5 presents the IR spectra of the dried gels with and without addition of  $K_2CO_3$  in their preparation, from which little difference can be observed. The symmetric-stretch N—H vibration peaks at 3417 and 3208  $cm^{-1}$  in spectrum a and those at 3381 and 3221  $cm^{-1}$  in spectrum b show the existence of  $-NH_2$  in the two samples, respectively. However, the absorption of the peak at 3208  $cm^{-1}$  in spectrum a is stronger than that at 3221  $cm^{-1}$  in spectrum b, which indicates a higher fraction of  $-NH_2$  in sample a. In addition, the bending vibration peak of  $-NH_2$  at 1616  $cm^{-1}$  in spectrum a with a strong absorption, which is the characteristic of  $-CO-NH_2$ , can be observed, although only a weaker absorption peak occurs at the same position in spectrum b. The two peaks at 1564 and 1405  $cm^{-1}$  in spectrum b constitute the asymmetric-stretch  $-COO^-$  vibration peak and the symmetric-stretch  $-COO^-$  vibration peak, respectively. These phenomena show the coexistence of  $-CO-NH_2$  and  $-COO^-$  in sample

b. This may be attributed to the free-radical polymerization of AAM and MBAA accompanied by partial hydrolysis of their amide group to form carboxyl group at higher concentration of  $K_2CO_3$  (see reaction equations below). In addition, the partial hydrolysis of

MBAA results in the decrease of crosslinking degree in the solid-gel electrolyte. The above discussions can account for the solid-gel electrolytes becoming softer with the increase of  $K_2CO_3$  concentration in the preparation process of solid-gel electrolytes.



## CONCLUSIONS

It has been demonstrated that PAAM-based gels after being doped with  $K_2CO_3$  exhibit ambient temperature conductivities in the range  $10^{-2}$  to  $10^{-1}$  S/cm. The conductivity depends on the concentration of  $K_2CO_3$  in the PAAM hydrogels. With the increase of  $K_2CO_3$  concentration, the ionic conductivity rapidly increases initially, and then slowly increases and achieves the highest conductivity (0.118 S/cm) when  $K_2CO_3$  concentration is 15.9 mass %; the conductivity finally begins to decrease when  $K_2CO_3$  concentration exceeds 15.9 mass %. For  $K_2CO_3$  concentration below 7.22 mass %, the temperature dependency of conductivity is characteristically an Arrhenius type. For  $K_2CO_3$  concentration from 7.22 to 15.9 mass %, the temperature dependency of conductivity follows the VTF-type relation. When the  $K_2CO_3$  concentration exceeds 15.9

mass %, the  $K_2CO_3$  crystal particles exist in the solid-gel electrolytes (confirmed by ESEM) and there is a partial polyacrylate structure in the hydrogels.

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