

# Spectroscopic investigation of the gel polymer electrolytes based on methy methacrylate-styrene copolymers

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## Abstract

Gel polymer electrolytes composed of methyl methacrylate-styrene copolymers (PMS) and electrolyte solution (LiTFSI in EC/DMC) were prepared and characterized. Depending on the molar composition of the copolymer, these gel polymer electrolytes exhibited different electrochemical and mechanical properties. In order to investigate the physical interactions among organic solvents, polymer, and lithium ions occurred in the gel polymer electrolyte, Raman spectroscopy and solid state <sup>7</sup>Li NMR spin–spin relaxation measurements were performed. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Gel polymer electrolyte; Methyl methacrylate-styrene copolymer; Raman spectroscopy; Solid state <sup>7</sup>Li NMR; Spin–spin relaxation time

## 1. Introduction

In the past two decades, the progress of the portable consumer electronic devices has made it an urgent need to develop new batteries with a high energy density and design flexibility. Among them, lithium-ion polymer batteries are now being widely studied and developed, because they can be produced in a variety of forms, thus permitting portable batteries of the required shapes to be produced readily and enabling customization of portable power driven electronic equipment to be produced [1–3]. Gel polymer electrolytes (GPEs) exhibit high ionic conductivity at ambient temperature and, thus can be a good candidate for practical use.

In our previous studies [4,5], we synthesized methyl methacrylate(MMA)-styrene(ST) copolymer (hence, abbreviated as PMS) as a matrix polymer for preparing gel polymer electrolytes. In the copolymer, it is considered that the ST unit can improve the mechanical strength of gel polymer electrolyte due to a low affinity for electrolyte solution,

whereas MMA unit can achieve high ionic conductivity due to a good affinity for electrolyte solution. Content of MMA unit in the copolymer was proven to significantly affect the uptake of electrolyte solution and the degree of gelation. In this work, in order to investigate effect of MMA content on the specific interactions occurred in the gel polymer electrolytes, Raman and solid state <sup>7</sup>Li NMR spectroscopic measurements were performed.

## 2. Experimental

### 2.1. Preparation of gel polymer electrolytes

PMS was synthesized by emulsion polymerization, as previously reported [4]. PMS copolymers are designated PMS(*x*/*y*) for brevity, where *x* and *y* indicate the mol% of MMA and ST units in the copolymer, respectively. PMS was dissolved in an anhydrous tetrahydrofuran. After the polymer was completely dissolved, the solution was cast on a glass plate. It was then immersed in water bath to form the porous structure by phase inversion. After drying the porous membrane in a vacuum oven at 80 °C for 24 h, it was soaked

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in 1 M lithium trifluorosulfonyl imide (LiTFSI)-ethylene carbonate (EC)/dimethyl carbonate (DMC) solution (1:1 by volume) to make gel polymer electrolyte. GPE was cut into squares of  $4\text{ cm}^2$  and sandwiched between two stainless steel (SS) electrodes. AC impedance measurements were performed for conductivity measurement using Zahner Elektrik IM6 impedance analyzer over the frequency range of 100 Hz to 100 KHz.

## 2.2. Spectroscopic measurements

The Raman spectra were recorded with a Bruker RFS 100/S Fourier transform Raman spectrometer. The wavelength of the laser was 1064 nm Nd:YAG laser, and the power from the laser was 200 mW.  $^7\text{Li}$  NMR spectroscopy was measured at a frequency of 155.5 MHz (corresponding to a field of 9.4 T) with a Bruker DSX-400 MHz spectrometer. Spectra were obtained by a single pulse sequence at room temperature, spin-spin relaxation time ( $T_2$ ) was measured with  $\pi/2-\tau-\pi$  sequence pulse.

## 3. Results and discussion

Fig. 1 illustrates ionic conductivity and amount of the electrolyte solution absorbed by the porous membrane after soaking in the electrolyte solution, as a function of MMA content in the PMS copolymer. It can be seen that an increase of MMA content in the PMS copolymer enabled the porous membranes to absorb more electrolyte solution, which resulted in increase of ionic conductivity. This result is due to the fact that the MMA unit is more compatible with the carbonate-based liquid electrolyte as compared to the ST unit. However, higher uptake of electrolyte solution caused the reduction of mechanical strength of the gel polymer electrolyte, which is due to the gelation of PMS. This result suggests that gelation of PMS by electrolyte solution can be controlled by MMA content in the PMS polymer. In Fig. 1, an inflection

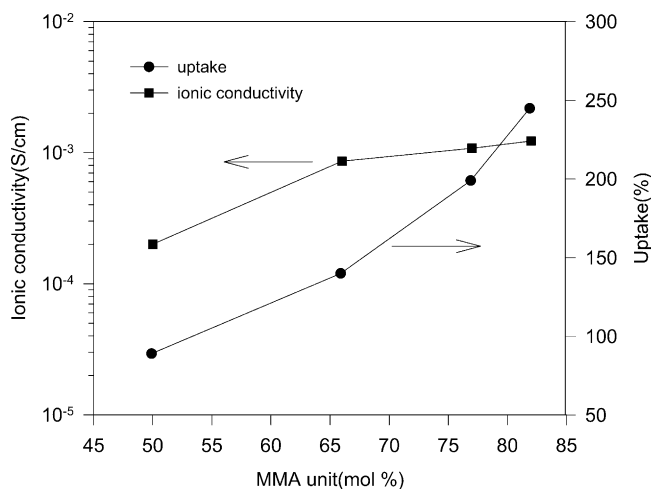


Fig. 1. Ionic conductivity and amount of the electrolyte solution absorbed by the PMS membrane as a function of the MMA content.

point for ionic conductivity can be observed at 66 mol% of MMA unit. This may be related to the change of conducting pathway in the gel polymer electrolyte. As the amount of electrolyte solution increases, it is possible to construct a local effective pathway in liquid phase. When MMA content exceeds about 66 mol%, the electrolyte solution absorbed by the porous membrane can form a local solvent channel for ionic conduction, which is major medium governing the ionic conductivity.

In order to investigate the specific interactions occurred in the electrolyte, Raman spectroscopy was measured. Fig. 2 shows the Raman spectra in the region of  $690\text{--}780\text{ cm}^{-1}$  (a) and  $860\text{--}940\text{ cm}^{-1}$  (b) as a function of salt concentration. As the salt concentration increases from 1 to 5 M, the Raman spectra shows obvious changes. As shown in Fig. 2(a), the peak appeared at the  $717\text{ cm}^{-1}$  for C=O bending of EC decreases, and the band observed at  $731\text{ cm}^{-1}$  for EC and  $\text{Li}^+$  ion interaction increases with salt concentration. The peak appeared at the  $894\text{ cm}^{-1}$  for C=O breathing of EC decreases, and the band of  $904\text{ cm}^{-1}$  for EC and  $\text{Li}^+$  ion

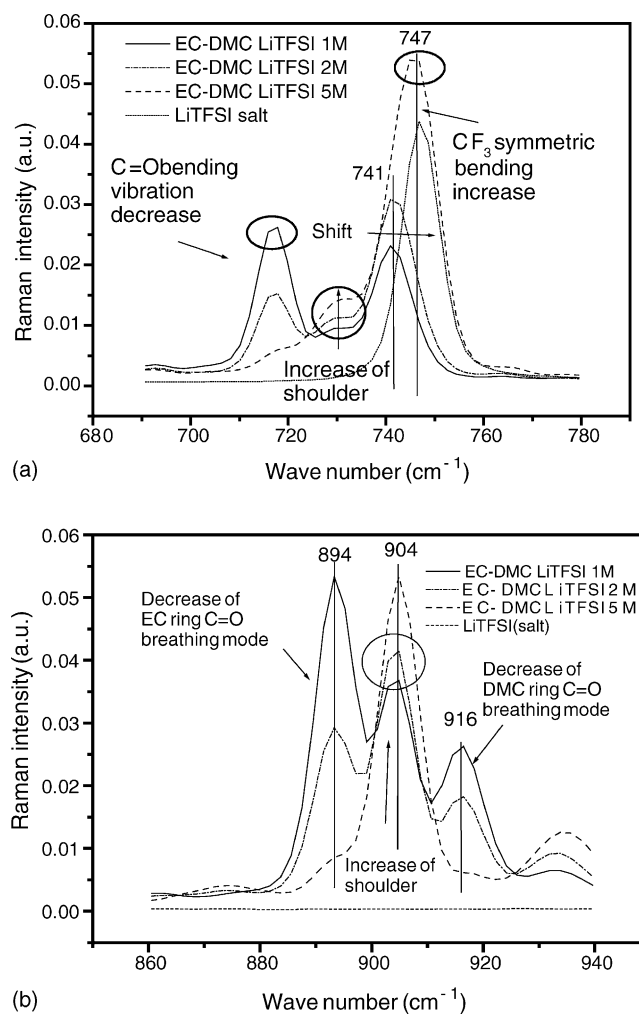


Fig. 2. Change of Raman spectra in the region of  $690\text{--}780\text{ cm}^{-1}$  (a) and  $860\text{--}940\text{ cm}^{-1}$  (b) with salt concentration.

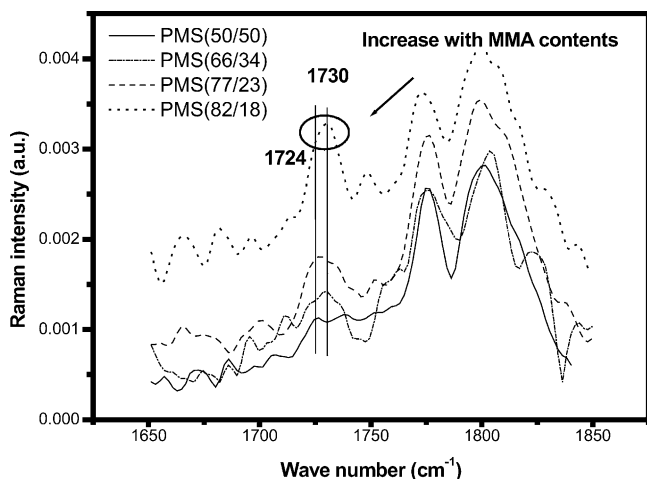


Fig. 3. Raman spectra for carbonyl band in MMA unit as a function of MMA content in the PMS-based gel polymer electrolyte.

increases with increasing salt concentration, as can be seen Fig. 2(b). These results suggest that the concentration of free  $\text{Li}^+$  ions decreases with increasing salt concentration, which is an evidence of formation of solvent-shared ion pairs and agglomerates. These phenomena are consistent with the previous works, which has been studied in the polymer electrolyte prepared with poly(ethylene oxide) [6] or poly(acrylonitrile) (PAN) [7]. Fig. 3 represents the change of carbonyl band in PMMA, as a function of MMA content. It can be clearly seen that the peak appeared at  $1730\text{ cm}^{-1}$  for MMA and  $\text{Li}^+$  ion interaction increases with MMA content, which means that the specific interaction between  $\text{Li}^+$  ion and carbonyl of MMA unit increases. This result suggests that the polar functional group of MMA unit in the PMS copolymer also can contribute the solvation of the lithium salt.

To study the effect of MMA content on interaction between EC and LiTFSI, the peaks observed at  $700\text{--}800\text{ cm}^{-1}$  were resolved into three peaks with fitting program, the results are shown in Fig. 4. In this figure, each peak can be assigned as follows:  $717\text{ cm}^{-1}$  (C=O bending vibration mode of EC),  $730\text{ cm}^{-1}$  (interaction between EC and LiTFSI) and  $743\text{ cm}^{-1}$  (symmetric bending of  $\text{CF}_3$ ). The peak corresponding to the interaction between EC and LiTFSI is shown to increase with MMA content, while other peaks observed at  $717$  and  $743\text{ cm}^{-1}$  are little changed with MMA content. This result suggests that interaction between EC and Li salt can be also affected by the MMA unit in the PMS copolymer.

As the ionic conductivity is determined by the product of the number of carrier ions and their mobility, it is important that the contribution to ionic conductivity is resolved into these two factors. According to previous works [8–10], the spin–spin relaxation time ( $T_2$ ) and the fraction of mobile lithium ions can be estimated from  $^7\text{Li}$  NMR spin–spin relaxation experiments. Echo traces obtained by spin-echo technique in the gel polymer electrolytes could be resolved into two components. One had a longer  $T_2$  and the other had a shorter  $T_2$ , and it was found that the sum of the two com-

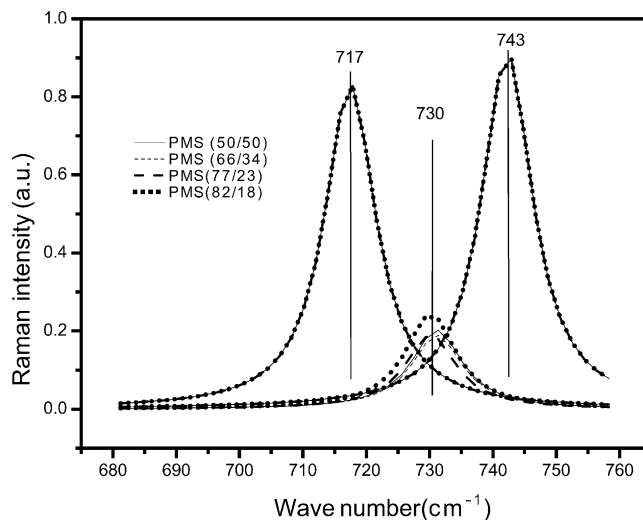


Fig. 4. Peak resolution of Raman band observed in the region of  $700\text{--}800\text{ cm}^{-1}$  for gel polymer electrolyte prepared with PMS and LiTFSI-EC/DMC.

Table 1

The relative fraction of free lithium ion ( $X_F$ ) and its spin–spin relaxation time ( $T_2$ ) in the gel polymer electrolytes containing 1.0 M LiTFSI-EC/DMC

Polymer	$T_2$ (s)	$X_F$
PMS(50/50)	2.3	0.70
PMS(66/34)	3.7	0.89
PMS(77/23)	29.6	0.98

ponents,  $M(t) = M_1(t) + M_2(t)$ , where  $M_1(t)$  and  $M_2(t)$  stand for the nuclear magnetization of the mobile lithium nuclei and the tightly bound lithium nuclei, respectively, could be fitted to the traces. The atom portions of Li belonging to mobile lithium ions were calculated, using the equation of  $X_F = M_1(0)/[M_1(0) + M_2(0)]$ . The  $T_2$  values and relative intensities ( $X_F$ ) of mobile lithium are summarized in Table 1. It is apparent that  $X_F$  increases with MMA content, which indicates that MMA unit in the PMS copolymer also plays a role in solvating the lithium salt. This is consistent with the Raman spectroscopic results, as discussed above. The  $T_2$  value, proportional to the mobility of mobile lithium ion, is also found to be increased with MMA content. As MMA content increases, electrolyte uptake increases, which results in plasticizing the polymer matrix, so the mobility of the free lithium ions is enhanced. When comparing the values of  $T_2$  and  $X_F$  with MMA content, it is found that an increase of  $T_2$  is more significant than that of  $X_F$ . From these results, it is concluded that an increase of ionic conductivity with MMA content in the PMS-based gel polymer electrolytes mainly originates in the increase of the ionic mobility rather than that of the number of the free ions.

#### 4. Conclusions

Specific interactions among Li ions, solvents, and polymer occurred in the PMS-based gel polymer electrolytes

were investigated by Raman spectroscopy. Formation of ion pairs and ion agglomerates with salt concentration were confirmed, and the polar functional group of MMA unit in the PMS copolymer was proven to contribute the solvation of the lithium salt. With solid state  $^7\text{Li}$  NMR relaxation, the increase of ionic conductivity with MMA content in the PMS-based gel polymer electrolytes is proven to be related to the ionic migration process rather than the generation process of the free ions.

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