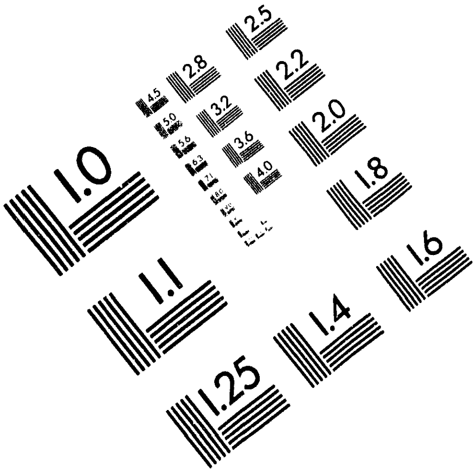

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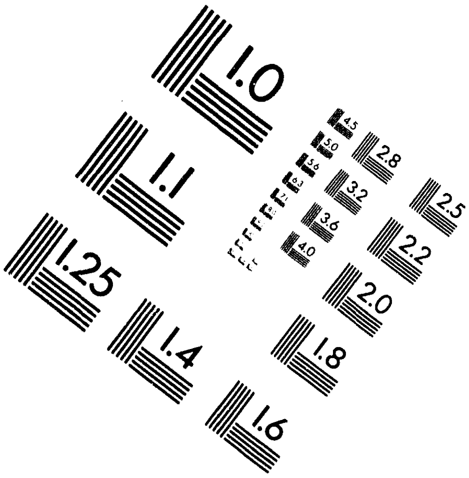

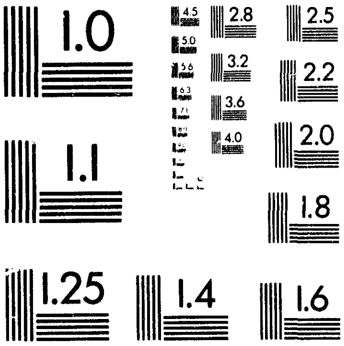

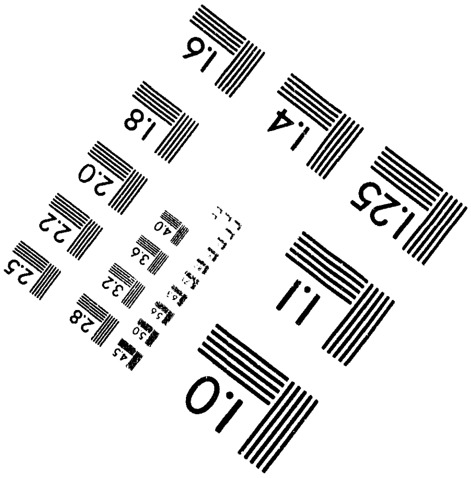

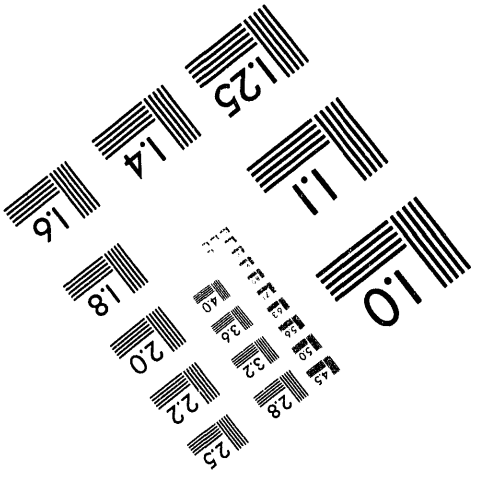

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BNL-60652

The Development of a New Plasticizer for Poly(ethylene oxide) Based Polymer Electrolyte and the Investigation of Their Ion-pair Dissociation Effect

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ABSTRACT

One approach to increasing the ionic conductivity of polymer electrolyte is to add plasticizers to the polymer-salt complexes[1]. Recently, we have synthesized a new plasticizer, modified carbonate (MC3), by attaching three ethylene oxide units to the 4-position of ethylene carbonate[2]. AC impedance studies[2] showed that an ionic conductivity of $5x10^{-5}$ S cm^{-1} could be achieved at room temperature, by adding 50 wt% of MC3 into PEO-$LiCF_3SO_3$ complex. This is two orders of magnitude higher than that found in PEO-$LiCF_3SO_3$ electrolyte without a plasticizer, and one order of magnitude higher than that found when using same amount of propylene carbonate (PC) as plasticizer. Temperature dependent conductivity measurement and thermal analysis show that this new plasticizer increased the ionic conductivity throughout the entire complex system, while the conventional plasticizers only create a high conductivity path way through the plasticizer itself. The samples are free standing films with good mechanical properties. When MC3 is used as a plasticizer, the ionic conductivity increase is much higher than using PC as a plasticizer at high

temperature (65 °C), implying an increase in the number of charge carriers. Therefore, we believe that MC3 has a stronger ion pair dissociation effect than PC, when used as a plasticizer. The ion pair dissociation effect was studied by Raman, FTIR, and near edge x-ray absorption fine structure (NEXAFS) spectroscopy.

INTRODUCTION

Polyethylene oxide (PEO)-salt systems are an important new class of electrolytes that are being considered for use in high specific energy rechargeable lithium batteries. However, their room temperature conductivity is low, typically 10^{-7} S/cm. Conventional poly(ethylene oxide) (PEO)-Li salt complexes reach conductivities of 10^{-4} S/cm at about 100 °C. Widespread application of these electrolytes require conductivities of $\sim 10^{-4}$ S/cm at ambient temperature. One approach to increasing the conductivity is to add plasticizers to the polymer-salt complexes[1]. Kelly *et al.*[3] have studied poly(ethylene glycol) (PEG) as a plasticizer for PEO-$LiCF_3SO_3$ complex. They reported a conductivity increase from $3x10^{-7}$ S/cm to 10^{-4} S/cm at 40 °C when 65 mol% PEG was added to a PEO-$LiCF_3SO_3$ complex. However, the hydroxyl end groups of PEG react with lithium metal so such a system would not be suitable for batteries. Another good candidate, propylene carbonate (PC), with a dielectric constant of 64.4, is widely used as a plasticizer. However, an ionic conductivity of 10^{-4} S/cm can not be reached at room temperature unless high concentrations of PC are used, which degrade the mechanical properties, and cause creep. We have synthesized a new plasticizer that combines the high dielectric constant of PC and the good compatibility of PEG with PEO. The plasticizer is a modified carbonate (MC3) made by replacing the CH_3 group at the 4-position on PC with three ethylene oxide (EO) units. AC impedance studies showed that an ionic conductivity of $5x10^{-5}$ S/cm can be achieved at 25 °C, by adding 50% of MC3 by weight of PEO to the PEO-$LiCF_3SO_3$ complex. Furthermore, the samples are free standing films with good mechanical properties.

Raman spectroscopy was used to study the ion pair dissociation effect by probing the stretching mode of free and paired (or aggregated) anion groups. Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, on the other hand, was used to probe the cation environment. FTIR spectroscopy was used to answer why MC3 has stronger ion pair dissociation effect.

EXPERIMENTAL

Materials: PEO with average molecular weight of 5,000,000, propylene carbonate (PC), $LiCF_3SO_3$, and KCF_3SO_3 salt were purchased from Aldrich, and used without further purification. The modified carbonate was synthesized in our laboratory. The details of the preparation procedure and characterization are reported separately[2]. The chemical structures of MC3 and PC are shown in Fig. 1.

Sample preparation for ionic conductivity: PEO with molecular weight of 5,000,000 was dissolved in acetonitrile to make a 2 wt.% solution. Various amounts of $LiCF_3SO_3$ were added to the solution to make PEO-$LiCF_3SO_3$ complexes with different Li/O mole ratios (1/8, 1/16, 1/24, 1/32 etc.). Additions of 20 %, 50 %, or 100 % of MC3 by weight of PEO were added to the solutions to form the hybrid systems. All percentages for the plasticizers, quoted in this paper, are normalized with respect to the weight of PEO. PEO-$LiCF_3SO_3$ complex solutions with additions of 50 % of PC were also prepared for conductivity studies. The hybrid and complex films were cast on a 0.95 cm^2 nickel foil disk. The cast films were kept under vacuum (0.5 torr) for 24 hours at 50

° C before the impedance measurements in order to evaporate the solvent. The hybrid samples were free standing films with good mechanical strength. IR spectra were taken for the casting solution and cast film after drying process. By comparing the intensity ratio of absorption peaks at 1800 cm^{-1} (carbonyl stretching mode for MC3 or PC) and 2900 cm^{-1} (CH_2 stretching mode for PEO and MC3) for the liquid and dried film samples, it was assured that the MC to PEO ratio did not change significantly during the drying process. PEO-$LiCF_3SO_3$ complex solutions with additions of 50 % and 100 % PC by weight of PEO were also prepared for comparative studies. Due to the lower boiling temperature, the evaporation of PC during the film drying process can not be ignored. Therefore, the cast films initially containing 100 % PC by weight of PEO were dried under vacuum at room temperature and tested for PC concentration by IR spectroscopy for every 30 minutes until a 50 % weight ratio was reached. The residue of acetonitrile was negligible judged by the IR spectra. The sample with 50 % PC weight ratio was then mounted into cell for AC impedance measurements right away.

<u>Sample preparation for NEXAFS studies</u>: A new potassium salt, di-potassium N,N'-Jeffamine dipropanesulfonate (JDPS) was also synthesized in our laboratory. The starting material, with the commercial name Jeffamine was supplied by Texaco Chemical Company. The chemical structure of di-potassium JDPS is shown in Fig. 1. These type of salts were initially synthesized for use in the single ion conductivity studies. For our x-ray absorption study, this salt offers two outstanding properties: First, it has a clear white line splitting as a signature of K^+-SO_3^- pairing. Secondly, the K^+ ions in this JDPS salt are wrapped by the Jeffamine chains, make it difficult to dissociate them from SO_3^- anions by PEO or other solvents. This provided us a system which facilitated the investigation of ion pair dissociation effects by PEO, PC, and MC3 in a controlled manner. Five

systems were studied: (1) a di-potassium JDPS - PEO complex; (2) di-potassium JDPS in a PC solution; (3) di-potassium JDPS in a MC3 solution; (4) a di-potassium JDPS - PEO complex with various amounts of PC; and (5) a di-potassium JDPS - PEO complex with various amount of MC3. The results of system (2) and system (3) will be discussed in this paper, the rest of them will be reported separately[4]. In the PC-di-potassium JDPS and the MC3-di-potassium JDPS system, 100/40, 100/100, and 100/200 of salt/PC(or MC3) solutions were obtained by adding PC or MC3 to the salt solution in acetonitrile. The solutions were added dropwise on Kapton tape and the acetonitrile was evaporated under vacuum at room temperature.

Conductivity Measurements: Conductivity measurements were carried out using a Hewlett-Packard 4129A Impedance Analyzer in the frequency range from 5 Hz to 10 MHz. Temperature control was achieved by a Du Pont Instruments Column Compartment. The hybrid and complex films were sandwiched between two nickel foil ion-blocking electrodes (0.95 cm^2 cross section) in a sealed glass cell. The samples were kept under a dry atmosphere except a brief exposure to air when mounting the samples in the cell. Conductivity measurements were made in the temperature range of 25 °C to 65 °C on hybrid films of the PEO-$LiCF_3SO_3$ complex that had MC3 as a plasticizer. A large variety of compositions was studied. For comparison, measurements were also performed on films without a plasticizer and on films using PC as a plasticizer.

NEXAFS measurements: NEXAFS measurements were made at Beam Line X19A of the National Synchrotron Light Source. The data were collected as fluorescence excitation spectra using a large solid angle ionization chamber as the fluorescence detector. As the incident x-ray energy was scanned through the potassium *K*-edge, the ejected photoelectrons sequentially probe empty electronic levels of the sample being studied, resulting in fine structure in the near edge absorption spectrum. The relaxations of these excited states take place by either the emission of Auger electrons or fluorescence photons. The spectrum depends on bonding, valence, and coordination symmetry of the potassium atoms in the sample. However, unlike the NEXAFS spectra for low Z atoms such as carbon and oxygen, where the individual spectral features can be assigned to particular transitions, the interpretation of NEXAFS spectra for potassium is more complicated. Reference systems are, therefore, required for spectral interpretation.

RESULTS AND DISCUSSION

Conductivity: The temperature dependence of the conductivities (second heating cycle, ie. after being heated to 65 °C, then cooled to 25 °C) for PEO-MC3-$LiCF_3SO_3$ (50 wt.% MC3), PEO-PC-$LiCF_3SO_3$ (50 wt.% PC), and PEO-$LiCF_3SO_3$, with Li/O ratio of 1/24 are plotted in Figure 2. The room temperature conductivity of PEO-MC3-$LiCF_3SO_3$ is two orders of magnitude higher than that found for a PEO-$LiCF_3SO_3$ electrolyte without plasticizer, and one order of magnitude higher than that found when using propylene carbonate (PC) as a plasticizer. Cameron et al[5]. could only explain the improvement of conductivity on the addition of PC, and the dependence of the conductivity on the PC and salt concentrations, by postulating the existence of separate ionic pathways through the plasticizer. They proposed that these conducting pathways exist in the PEO matrix, and that the ionic motion is decoupled from that of the polymeric solvent. The result is a decrease the activation energy for ion movement which reduces the gradient of the Arrhenius curve. So the conductivity increase at low temperature is much more significant than that at high temperature. In addition to a reduction in the slope of the Arrhenius curve, the PEO-MC3-$LiCF_3SO_3$ film had a much higher conductivity at high temperature (65 °C). This indicates an increased number of charge carriers in the polymer electrolyte, due to the strong ion-pair dissociation effect of MC3. The Arrhenius curve of PEO-PC-$LiCF_3SO_3$ system shows similar effects but with a much smaller increase in conductivity at higher temperatures. In the case of the PEO-MC3-$LiCF_3SO_3$ film the Arrhenius curve had a discontinuity point accompanied with a slope change at 45 °C, whereas the curves for PEO-$LiCF_3SO_3$ and PEO-PC-$LiCF_3SO_3$ films were smooth up to 65 °C. The temperature dependent conductivities for the PEO-MC3-$LiCF_3SO_3$ system (50 wt.% MC3) with Li/O ratios of 1/16, 1/24, and 1/32 are plotted in Figure 3 as curve (a), (b), and (c). All three curves have a discontinuity point between 45 °C and 55 °C. This type of discontinuity has been reported by Armand[6] for PEO-$LiCF_3SO_3$ complexes at 68 °C, which is the melting temperature of pure PEO in crystalline state. The discontinuity observed in PEO-MC3-$LiCF_3SO_3$ system is an indication of the existence of a low melting point (below 65 °C) phase in this system. By comparison, the temperature dependent conductivity curves of PEO-PC-$LiCF_3SO_3$ films, did not show any discontinuity below 65 °C. As the discontinuity point moved to a lower temperature, (curve (a) and (b), as compared to curve (c)), the overall conductivity increased to a higher value.

NEXAFS Spectra: Figure 4 shows x-ray absorption curves, at the potassium *K* edge, for (a) the di-potassium JDPS) salt (b) a di-potassium JDPS salt solution in MC3 with a salt/MC3 weight ratio 100/80 and (c) with a ratio of 100/100. The large "white line" peak above the edge is due to dipole-allowed transitions to final states of *p* symmetry[7,8]. In curve (a), the white line is split into two peaks, labeled A and B. This splitting is the result of the removal of degeneracy of the final *p* states due to the electric field surrounding the K^+ ions caused by the paired SO_3^- ions. This type of white line splitting has been observed in other potassium salts such as KI and $K(CH_3)_3CO$ crystal[9]. Although the details of the splitting vary from salt to salt, the splitting is a clear signature of ion-pairing. In curve (c), with salt/MC3 weight ratio of 100/100, the white line splitting was smeared into a single broad peak with a shoulder A. This is a typical spectrum of unpaired potassium ions coordinated with oxygen atoms. Similar spectra have been reported for KI-18-crown-6 complex[9] and a dilute KI-PEO complex[9] (K/O ratio < 1/20). Therefore, curve (c) was used as a reference for dissociated ion pairs. In curve (b), at higher salt concentration (a salt/MC3 weight ratio 100/80), an increase in the white line splitting was observed through the increase in intensity of peak A but the effect is not as strong as in curve (a). This spectrum is representative of moderate ion-pairing. These three curves were used as references for the qualitative study of ion pair dissociation. Figure 5 shows the NEXAFS spectra of two di-potassium JDPS salt solutions in PC with weight ratios of (a) 100/100 and (b) 100/200. Feature B was significantly broadened in curve (a) indicating a strong ion pair dissociation effect caused by PC. The spectrum, curve (b), for the more dilute solution with a salt/PC weight ratio of 100/200, is almost the same as curve (c) in Fig. 4, indicating a high degree of ion pair dissociation. In comparing Fig. 5 to Fig. 4, we found that the level of ion pair dissociation in the di-potassium JDPS salt/MC3 solution with a salt/MC3 weight ratio of 100/100 was higher than that found for a salt/PC solution with salt/PC ratio of 100/100. Actually the data indicated that degree of dissociation was comparable to that found for a salt/PC ratio of 100/200. Therefore, we concluded that the MC3 solvent has a stronger ion pair dissociation effect for the salt. This enhancement must accrue from the ethylene oxide (EO) groups in MC3 which may complex with K^+ ions and prevent them from pairing with the SO_3^-. This will be further discussed in the FTIR studies. Since both PC and MC3 were used as plasticizers, we further studied the three component systems of di-potassium JDPS salt/PEO/MC3 and di-potassium JDPS salt/PEO/PC. The results reported in reference 4 show that when MC3 was used as plasticizer, it also has stronger ion pair dissociation effects on potassium salt than PC.

Raman spectra: The symmetric stretching mode of the SO_3 group of the CF_3SO_3 anion for $LiCF_3SO_3$ in organic solution has been used as a sensitive probe of the ion pairing and aggregation state of $CF_3SO_3^-$ anions[10,11]. The spectra of 1M and 1.5M $LiCF_3SO_3$ dissolved in CH_3CN are shown in figure 6. Three peaks are apparent in the band profile. They represent free $CF_3SO_3^-$ anions at 1033 cm^{-1}, Li^+-$CF_3SO_3^-$ ion pairs at 1042 cm^{-1}, and larger, less-well-specified aggregates at 1050 cm^{-1}. The concentration dependence of these three peaks is consistent with their assignments. Figure 7 shows Raman spectra of the SO_3 symmetric stretching mode for $LiCF_3SO_3$ in PC at Li:PC mole ratios of (a) 1:3 and (b) 1:6. In the spectrum of less concentrated sample with Li:PC molar ratio of 1:6, a weak peak centered at 1033 cm^{-1} representing free $CF_3SO_3^-$ ions was detectable. The spectrum is dominated by a peak located at 1042 cm^{-1} representing ion-pairing. Features representing larger aggregates at Raman shift greater than 1055 cm^{-1} are almost as strong as the ion-pairing peak. When the salt concentration was increased to a molar ratio of 1:3, the free ion peak essentially disappeared, the intensity of ion-pair peak was reduced, and the larger cation-anion aggregate peaks became the dominating ones. Figure 8 shows Raman spectra of the SO_3 symmetric stretching mode for $LiCF_3SO_3$ in MC3 at Li:MC3 mole ratios of (a) 1:3 and (b) 1:6. In contrast to the $LiCF_3SO_3$/PC solutions in Fig. 7, the Raman spectra of $LiCF_3SO_3$ dissolves in the modified carbonates (MC3) indicate that these systems contain substantial amounts of free ions. In the spectrum of less concentrated 1:6 molar ratio solution, the free ion peak dominates the much weaker ion-pair peak. For the more concentrated 1:3 molar ratio solution, the intensity of ion-pair peak increased to the same strength as the free ion peak. The features representing larger aggregates are not detectable in both MC3 solutions. Therefore, we conclude that when MC was used as a solvent, it has much stronger ion-pair dissociation effect on $LiCF_3SO_3$ salt than using PC as a solvent.

FTIR spectra: The interaction between the lithium ion and the carbonyl oxygen with and without polyether side-chain was studied by FTIR spectroscopy. The carbonyl stretching band at 1800 cm^{-1}

is sensitive to the complexation of Li^+ cations to the carbonyl oxygen and was used to probe this complexation. Figure 9 shows the FTIR spectra of the carbonyl stretching region for PC (top), $LiCF_3SO_3$ in PC at Li:PC molar ratios of 1:6 (middle) and 1:3 (bottom curve). As increasing amounts of $LiCF_3SO_3$ are added to PC, its carbonyl band broadens and shifts to lower frequencies in a manner consistent with previously reported FTIR spectra on $LiClO_4$ dissolved in PC[12]. Figure 10 shows the FTIR spectra of the carbonyl stretching region for MC-3 (top), and $LiCF_3SO_3$ in MC-3 at Li:MC-3 molar ratios of 1:6 (middle) and 1:3 (bottom curve). When the same molar amounts of $LiCF_3SO_3$ are added to MC-3, the Li^+ induced broadening and shifting of the carbonyl band are significantly smaller. The perturbation to the carbonyl band in the presence of Li salts arises from complexation of Li^+ cation to the carbonyl oxygens, the more extensive the complexation, the larger the spectral perturbation. Thus our FTIR results clearly demonstrate that Li^+ cations are associated less tightly with the carbonyl of MC3 than with the carbonyl of the PC. This is indirect evidence that the Li^+ is somehow complexed to the polyether side-chain of MC3.

CONCLUSION

A new type of plasticizer, 2-keto-4-(2,5,8,11-tetraoxadodecyl)-1,3-dioxolane, which in this paper is called modified carbonate (MC3), has been synthesized. By adding 50 wt% of MC3 in PEO-$LiCF_3SO_3$ complex, the room temperature ionic conductivity could be increased by two orders of magnitude while still maintaining good mechanical properties. NEXAFS studies at the potassium *K*-edge of di-potassium JDPS salt in PC or MC3 solutions show that MC3 has much stronger ion pair dissociation effect than PC. The ion pair dissociation effect was also studied by Raman and FTIR spectroscopy. The attached EO groups on the MC3 complex potassium cations dissociated by the carbonate group and prevent them from forming ion pairs with SO_3^- anions.

ACKNOWLEDGEMENT

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Figure 1. Chemical structure of propylene carbonate (PC), modified carbonate (MC3), Jeffamine ED-900, and di-potassium N,N'-Jeffamine dipropanesulfonate (JDPS)

Figure 2. Arrhenius plots for conductivity in PEO-MC-$LiCF_3SO_3$ (50 wt.% MC of PEO) (a), PEO-PC-$LiCF_3SO_3$ (50 wt.% PC of PEO) (b), and PEO-$LiCF_3SO_3$ (c) systems, with Li/O ratio of 1/24.

Figure 3. Arrhenius plots for conductivity in PEO-MC-$LiCF_3SO_3$ system (50 wt.% MC of PEO) with Li/O ratio of 1/16 (a), 1/24 (b), and 1/32 (c).

Figure 4. Near-edge x-ray absorption spectra for the *K* edge of potassium for di-potassium JDPS salt in MC3 solution with salt/MC3 weight ratios of (a) 100/0, (b) 100/80, and (c) 100/100.

Figure 5. Near-edge x-ray absorption spectrum for the *K*-edge of potassium for the di-potassium JDPS salt in a PC solution with salt/PC weight ratios of (a) 100/100 and (b) 100/200.

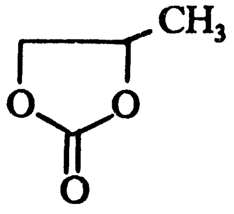
Figure 6. Raman spectra of the SO_3 symmetric stretching mode for $LiCF_3SO_3$ in CH_3CN solution: (a) 1M; (b) 1.5M

Figure 7. Raman spectra of the SO_3 symmetric stretching mode for $LiCF_3SO_3$ in PC at Li:PC mole ratios of (a) 1:3 and (b) 1:6.

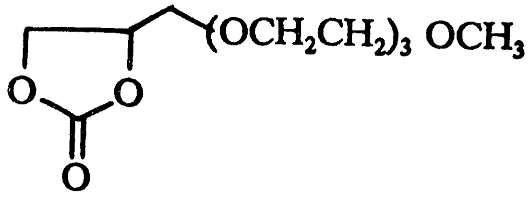
Figure 8. Raman spectra of the SO_3 symmetric stretching mode for $LiCF_3SO_3$ in MC3 at Li:MC3 mole ratios of (a) 1:3 and (b) 1:6.

Figure 9. FTIR spectra of the carbonyl stretching region for PC (top), and $LiCF_3SO_3$ in PC at Li:PC molar ratios of 1:6 (middle) and 1:3 (bottom curve).

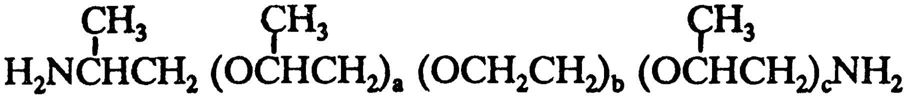
Figure 10. FTIR spectra of the carbonyl stretching region for MC-3 (top), and $LiCF_3SO_3$ in MC-3 at Li:MC-3 molar ratios of 1:6 (middle) and 1:3 (bottom curve).



propylene carbonate (PC)

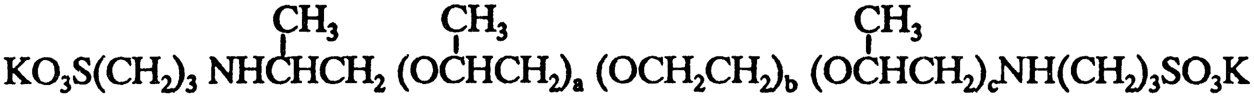


modified carbonate (MC3)



$$\mathrm{H_2N\overset{CH_3}{C}HCH_2\,(O\overset{CH_3}{C}HCH_2)_a\,(OCH_2CH_2)_b\,(O\overset{CH_3}{C}HCH_2)_cNH_2}$$

Jeffamine 900: $a+c=2.5$ $b=15.5$



$$\mathrm{KO_3S(CH_2)_3\,NH\overset{CH_3}{C}HCH_2\,(O\overset{CH_3}{C}HCH_2)_a\,(OCH_2CH_2)_b\,(O\overset{CH_3}{C}HCH_2)_cNH(CH_2)_3SO_3K}$$

Dipotassium Jeffamine-N,N'-dipropanesulfonate

Fig. 1. X.Q. Yang et al

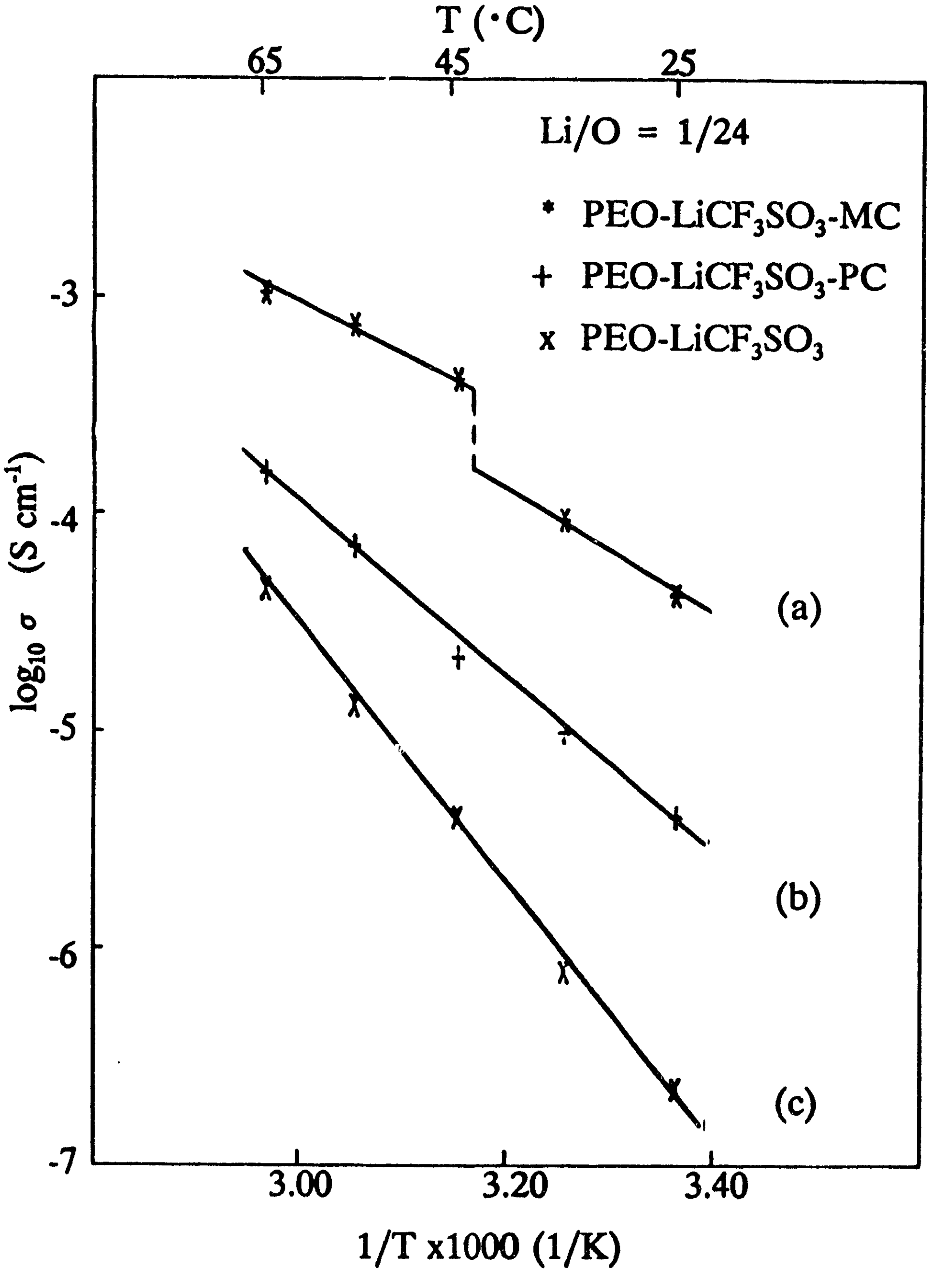


Fig. 2 X.Q. Yang et al.

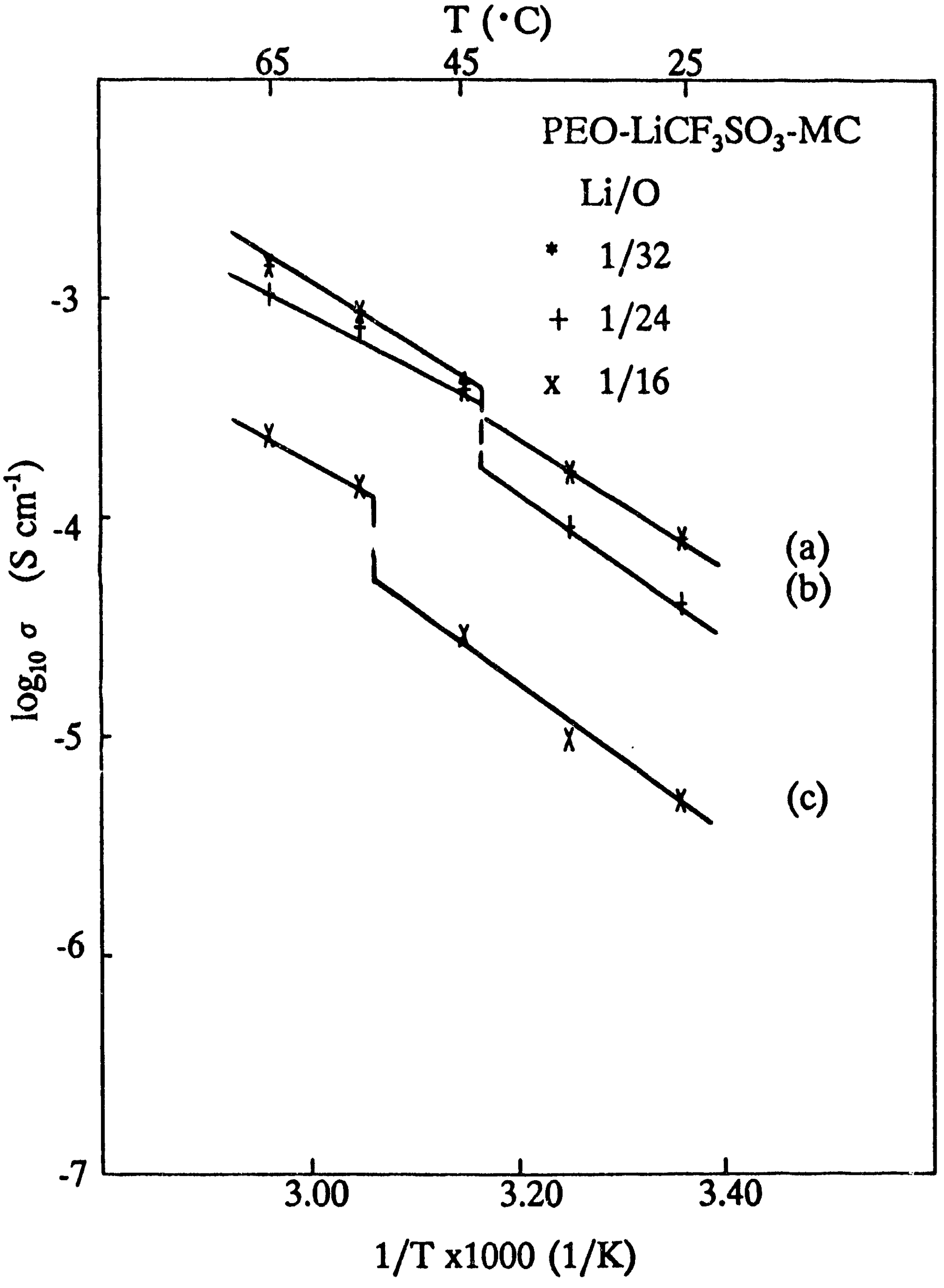


Fig. 3. X. Q. Yang et al.

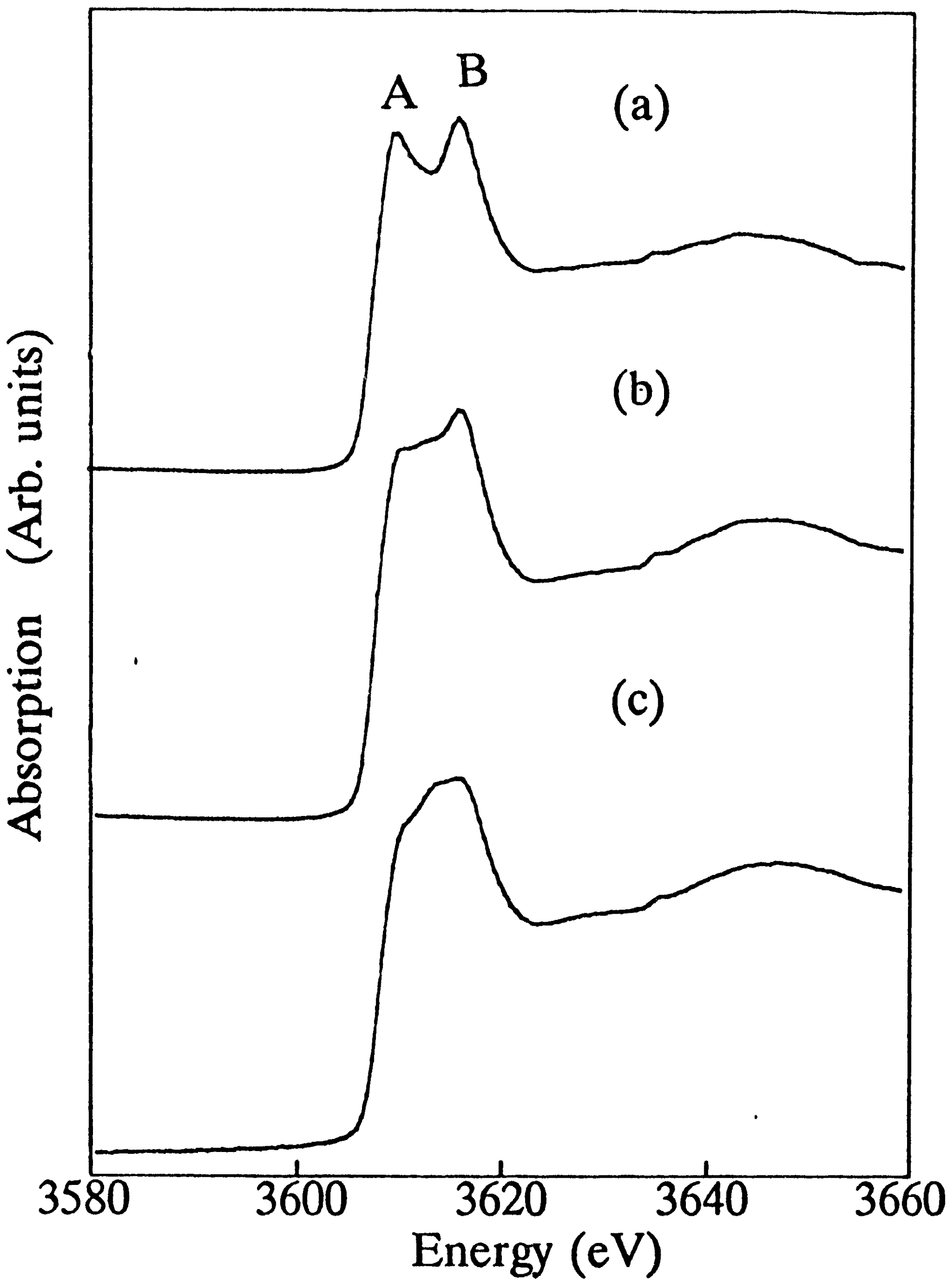


Fig. 4. X-a. Yang et al

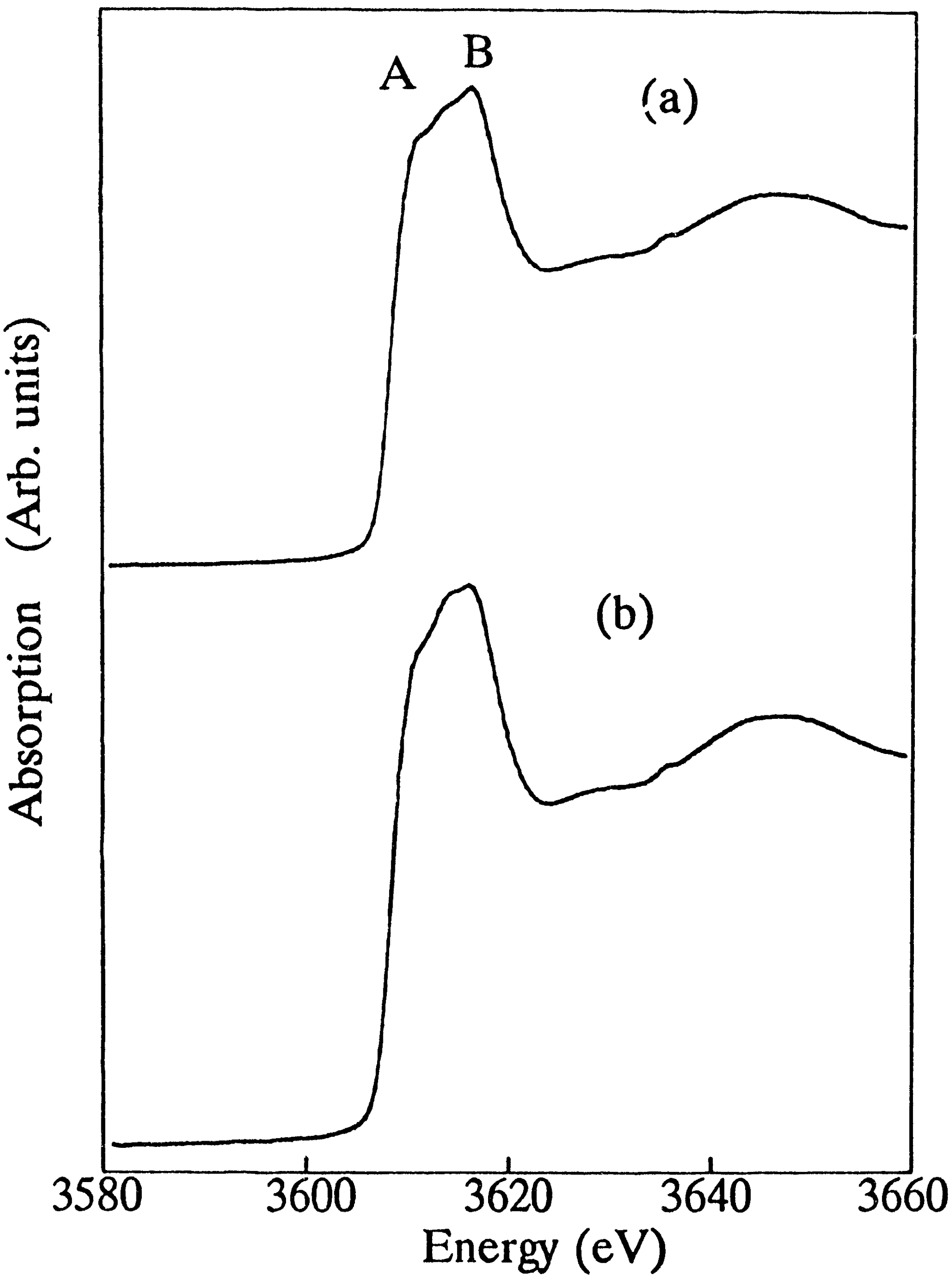


Fig. 5. X.Q. Yang et al

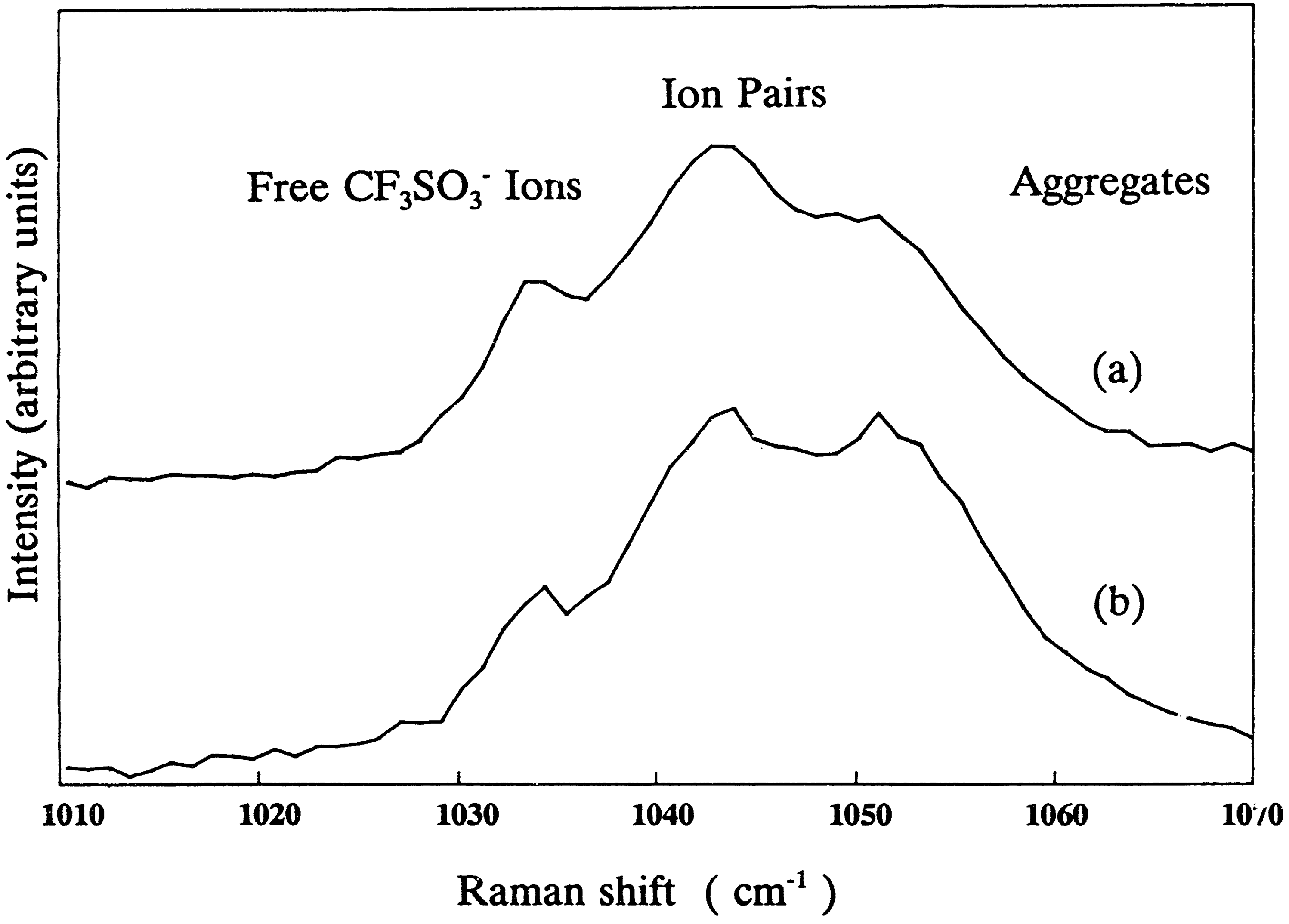


Fig. 6. X. Q. Yang et al.

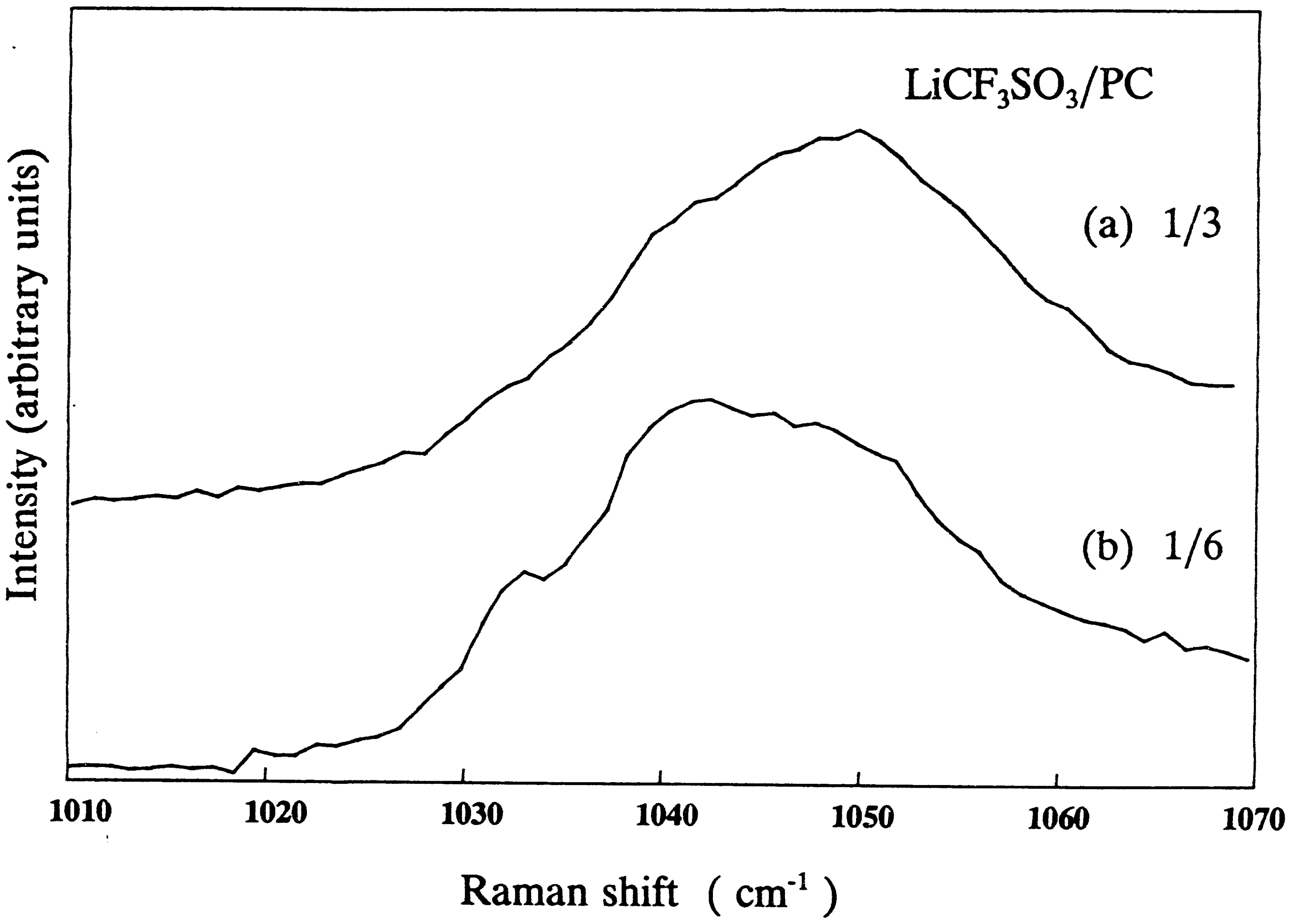
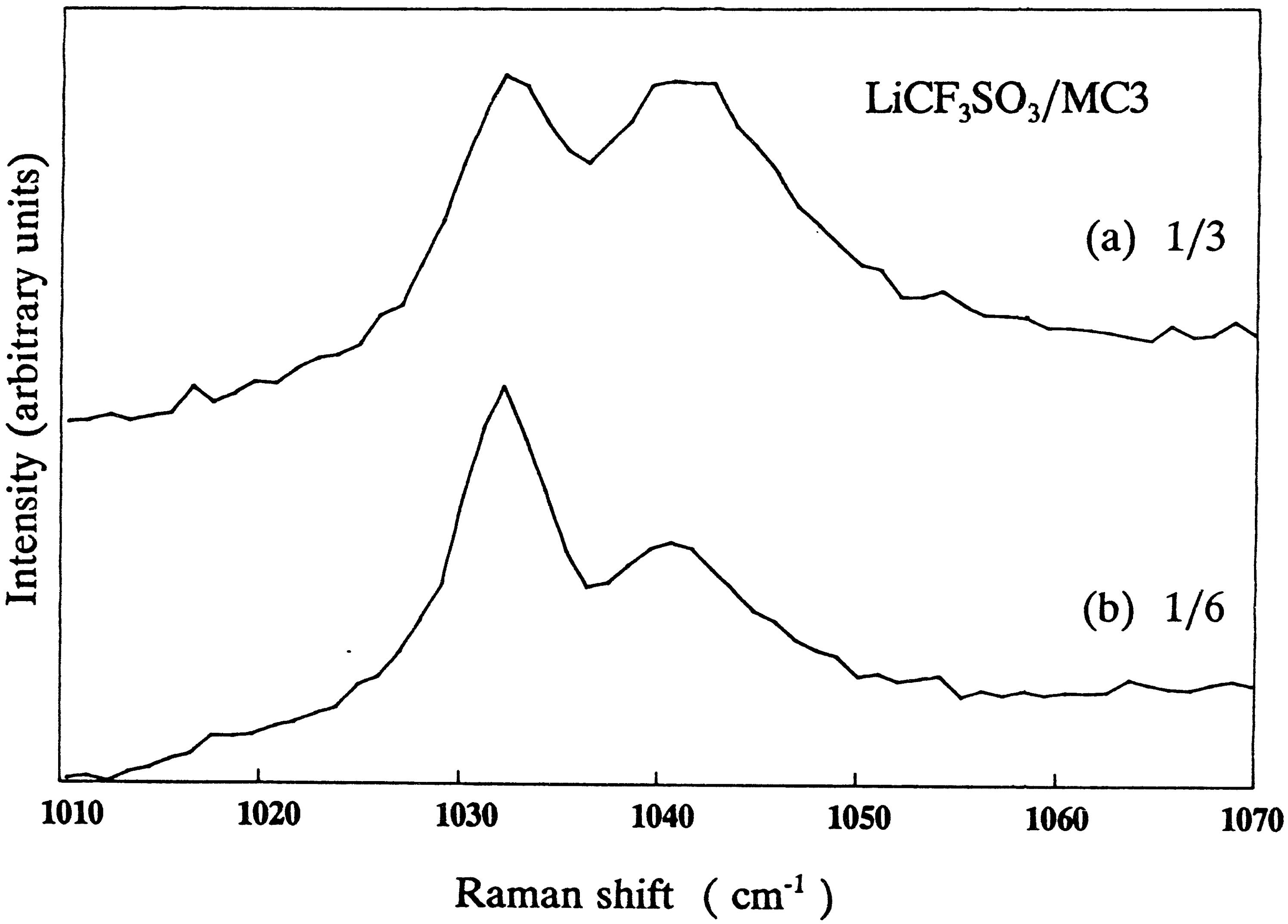


Fig 7 X Q Yang et al



LiCF$_3$SO$_3$/MC3
(a) 1/3
(b) 1/6
Intensity (arbitrary units)
1010
1020
1030
1040
1050
1060
1070
Raman shift (cm^{-1})

Fig. 8 X. Q Yang

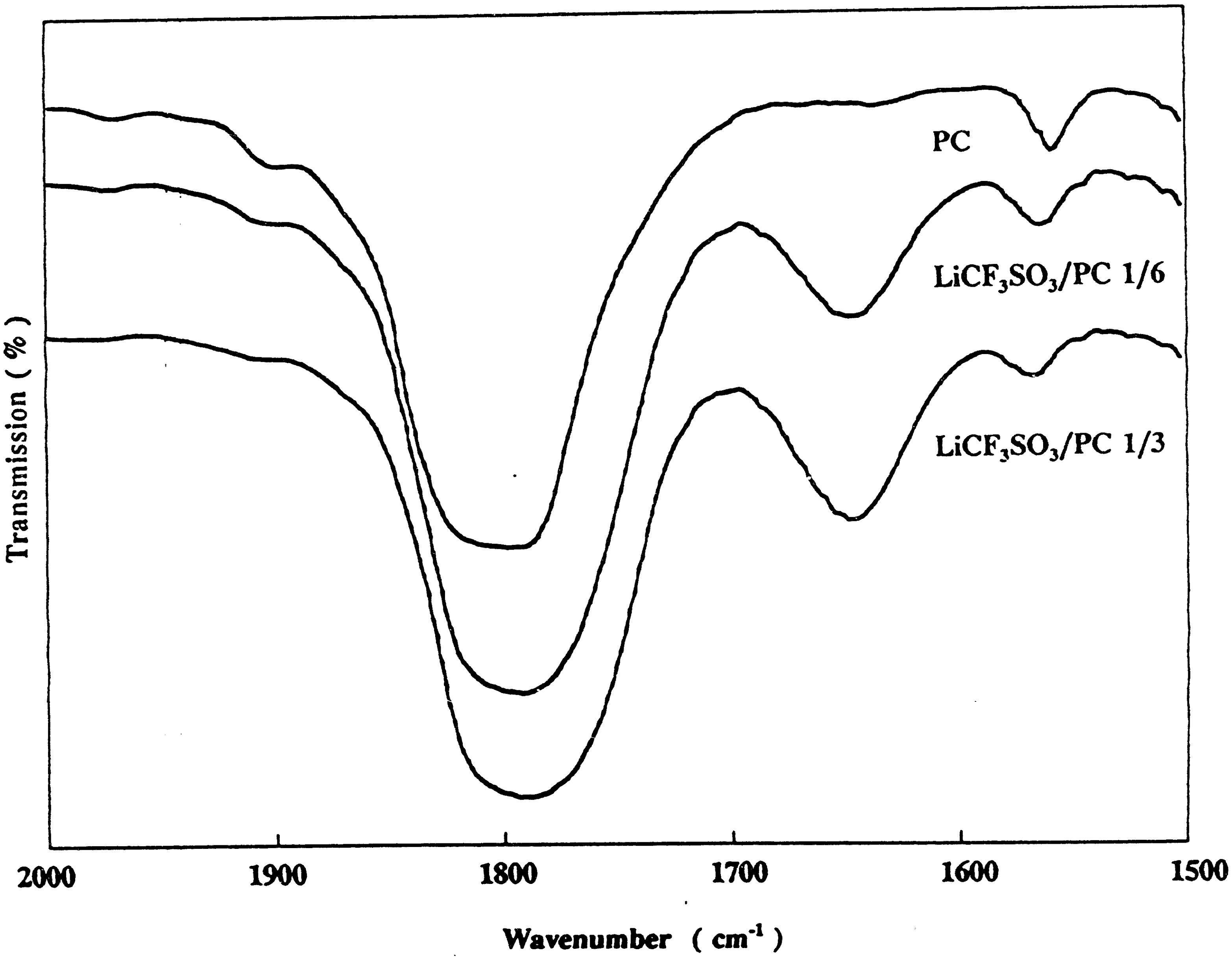

PC
LiCF3SO3/PC 1/6
LiCF3SO3/PC 1/3
Transmission (%)
2000
1900
1800
1700
1600
1500
Wavenumber (cm-1)

Fig. 9 Xu et al.

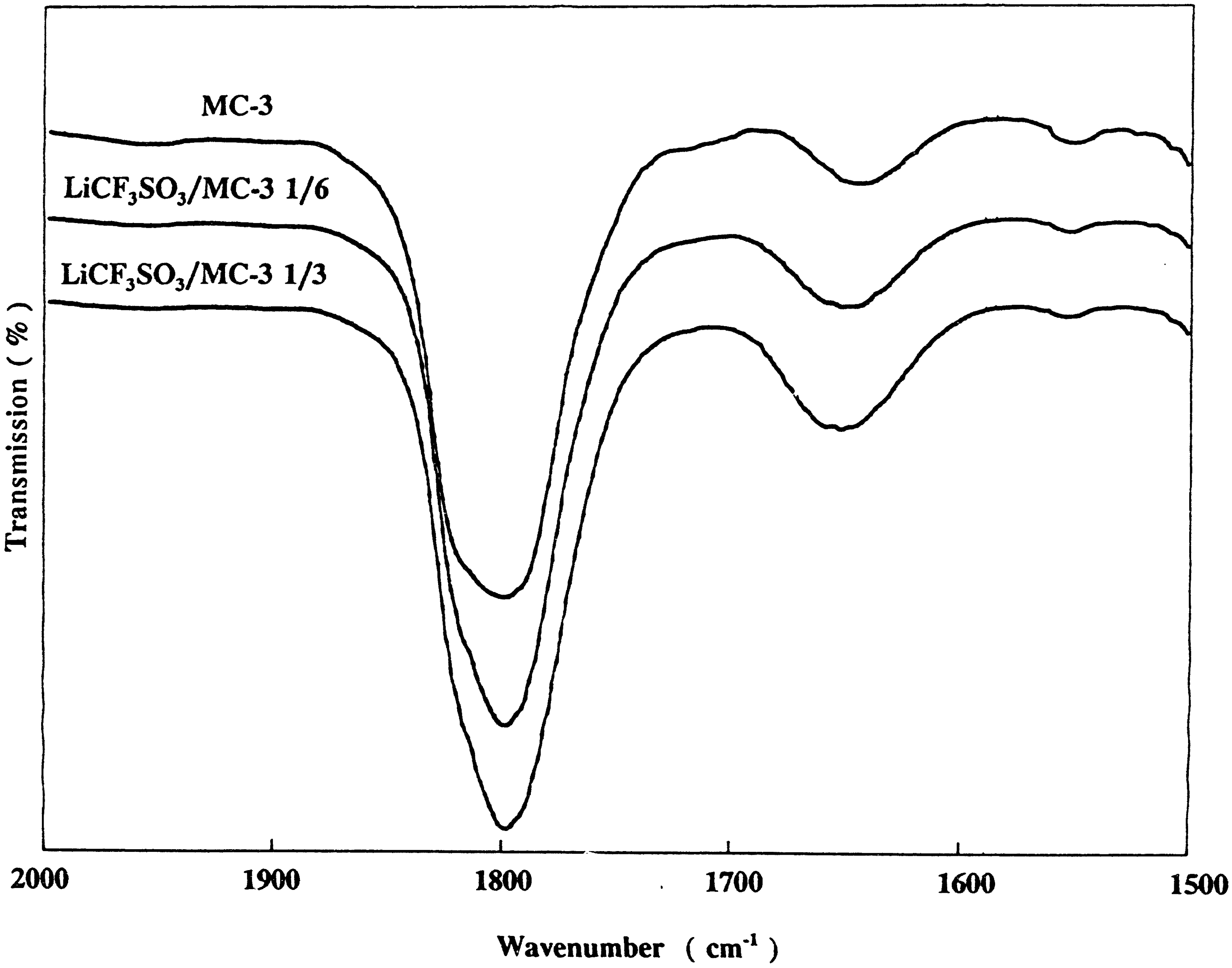


Fig 10 X. H etal.

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