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Characterization of highly conducting lithium salt doped polyaniline films prepared from polymer solution

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Abstract

We have developed a new method for preparing conducting polyaniline (Pani) films and investigated their chemical and physical properties by means of UV–Vis, FT-IR, EPR, XPS, and dc conductivity measurements. Conducting polyaniline films are prepared by casting from the solution of polyaniline with lithium salt. The free-standing films have relatively high dc conductivity without further treatment with HCl. The effects of lithium salts, such as $LiBF_4$, $LiPF_6$, and $LiClO_4$, and their concentrations on dc conductivity are studied. The dc conductivity of Pani–$LiBF_4$ film has been found to be better than those of Pani–$LiPF_6$ and Pani–$LiClO_4$ films. The dc conductivity of the systems increases with increasing lithium salt concentration in the range from 0.025 to 0.1 M, and exhibits a maximum value of $\sim 10^{-1}$ S/cm when 0.1 M $LiBF_4$ is doped. © 2001 Published by Elsevier Science Ltd.

Keywords: Solution processing; Infrared spectroscopy; UV–Vis absorption

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1. Introduction

A great deal of research on conducting polymers has been made because of their applications in electronics, optoelectronics and energy storage devices. Among the known conducting polymers, polyaniline has attracted much attention due to its ease of fabrication and stability in air [1,2]. Conducting Pani has been prepared by chemical treatment of Pani with protonic acid such as HCl. MacDiarmid et al. [3] have systematically investigated the change of electrical conductivity of Pani by protonic acid doping. They reported the variation of electrical conductivity as a function of pH (concentration of HCl solution) for emeraldine salt (ES) prepared by electrochemical and chemical treatments.

However, ES form of Pani doped with HCl is insoluble in organic solvents, which is restricted to a practical application. Recently, it has been found that conducting Pani films were cast from conducting solution of Pani with organic acid dopants and showed the conductivity of about 100–400 S/cm [4]. Those films, however, were very brittle and used toxic solvents. As a new class of dopants, lithium and zinc salts, such as $LiClO_4$, $LiBF_4$, $Zn(ClO_4)_2$, and LiCl, have been investigated. Chen and Lin [5] prepared the Pani doped with ionic salts such as $LiClO_4$, $LiBF_4$, and $Zn(ClO_4)_2$, and investigated the structure of those materials by using various spectroscopic techniques. Angelopoulos et al. [6] studied the morphology of Pani in the effect of LiCl on the properties of Pani base and the effect of LiCl on doped Pani. Giotto et al. [7] reported on the study of Pani, doped with $LiClO_4$ via pseudoprotonation, by NMR, morphology analysis, electrical conductivity, and thermal analysis. Recently, we reported the lithium salt-doped Pani samples prepared by the immersion of emeraldine base form of Pani film into the electrolyte solutions containing lithium salt [8]. The electrical conductivity, XPS, and EPR were investigated with respect to the doping level.

According to a conventional method to prepare conducting polymer, non-conducting powder or film form of polymers have been chemically treated in a certain manner to achieve the conducting state. In this paper, we report a new and simple method to synthesize a conducting polymer film cast from the conducting solution in which a dopant contains an organic solvent. We investigate the doping state in polymer solution and their physical properties by using FT-IR, EPR, XPS, and electrical conductivity experiments. In order to increase the conductivity, we perform the double doping with protonic acid on the polymer film.

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2. Experimental

Pani powders were synthesized from the oxidative polymerization of aniline using ammonium peroxydisulfate in aqueous acid solution (1 M HCl). This conventional synthesis yielded green polymer powders (ES) that were converted to insulating dark blue Pani powders (EB) by deprotonation with 0.1 M NH_4OH. This EB powder was used as a starting material for further synthesis of conducting Pani films.

The fabrication process of Pani films doped with various Li salts is shown in Fig. 1. Conducting polymer such as Pani was dissolved little by little in *N*-methyl-2-pyrrolidinone (NMP) solvent that can solve both the lithium salt and polymer and had a polarity. A deep blue colored solution was obtained. The lithium salt such as $LiPF_6$, $LiBF_4$, and $LiClO_4$ with various concentrations 0.1 ~ 0.025 moles was completely dissolved in the polymer solution by stirring it with a magnetic stirrer in a dry box for about 1 h. Since the concentration of the lithium salt influences significantly the electrical conductivity of the polymer film, it is needed to control carefully the concentration of the lithium salt, preferably in the range from 0.1 to 0.025 moles. However, when the concentration was over 0.15 mole, polymer films were difficult to be cast as free-standing film. And when the concentration was below 0.02 mole, the doping was not effective and their conductivity was very low. The solution obtained through the above processes was filtered and residual polymer particles were removed. This solution was poured onto a glass or a substrate to cast film and dried at ~80°C for 15 h.

If the polymer film produced through the above process was demanded to be a higher conducting state, it is possible to perform 'the double doping' with protonic acid on this polymer film. We doped with various concentrations of HCl on the Pani–Li salt films with dipping method.

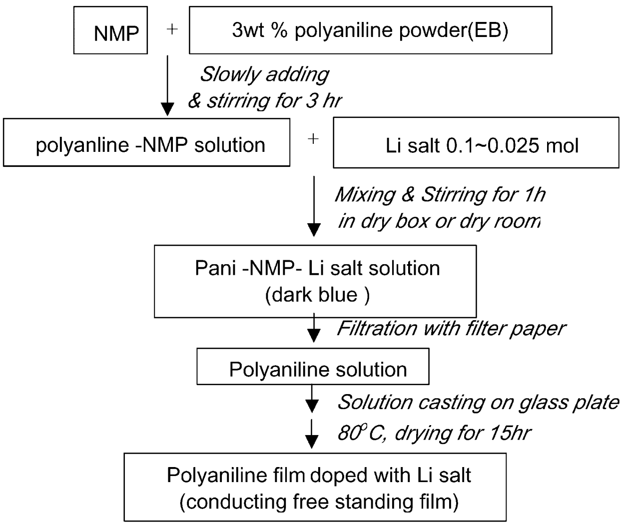

Fig. 1. The process for fabrication of the Pani films doped with various Li salts.

The UV–Vis spectroscopic data were collected by using Shimadzu Model UV-3100 (1000–300 nm). FT-IR spectra were obtained by using Perkin Elmer System 2000 FT-IR in the range from 4000 to 500 cm^{-1}. The FT-IR data were collected from the samples coated on quartz substrates. Brucker ESP300 spectrometer (X-band) was used to obtain the EPR spectra. Samples were put in EPR tube (Wilmad 707), and pumped with a diffusion vacuum pump ($\leq 10^{-5}$ Torr). In order to XPS sputtering experiments, the XPS data were measured by using VG ESCALAB MkII spectrometer (AlK_α 1486.6 eV photons). Neutral peak of carbon 1s (C1s) at 284.6 eV was used as a reference to correct the shift by surface charging effects of XPS experimental. The surface of the samples was etched by the sputtering of Ar ion beam with the energy of 3 keV for 10 min. The dc conductivity was measured using a four-probe method.

3. Results and discussion

Fig. 2 compares UV–Vis spectra for the EB and Pani–Li salt solution using NMP. The absorption bands at ~327 and 638 nm for the EB solution are not shifted by the doping of lithium salt. This indicates that the doping does not occur on polymer chains in the solution state. When Pani is solved in NMP solvent, the color of the solution becomes blue. If this polymer solution is chemically treated (e.g. with a protonic acid such as HCl), a large percent of the Pani solved in the solution is separated as a precipitate (deep green). The precipitate is commonly insoluble in any organic solvents. We can observe that the color of the doped polymer changes with an acid treatment in the solution. This change in color is due to the variation of a band gap between LUMO and HOMO of π-orbital molecules.

On the other hand, the dried Pani–Li salt films show different IR vibration characteristics from the undoped Pani film as shown in Fig. 3 and Table 1. Most vibration frequencies (e.g. a mode of QNH^+B) of Pani–Li salt films

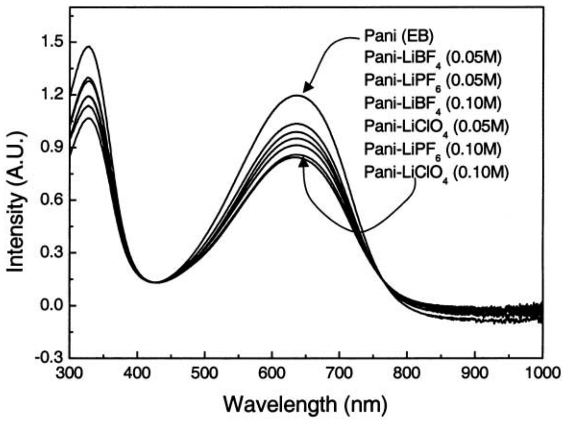

Fig. 2. UV–Vis spectra for the EB and the Pani–Li salt solution using NMP.

Table 1
The positions of vibration of FT-IR for Pani–Li films

	Stretching of NQN (cm^{-1})	Stretching of NBN (cm^{-1})	C–N str. in QBQ (cm^{-1})	C–N str. in QBQ, QBB, BBQ (cm^{-1})	C–N str. in BBB (cm^{-1})	A mode of QNH^+ B (cm^{-1})	C–H out of plane bending (cm^{-1})	Aromatic ring deformation (cm^{-1})
Pani (EB)	1593	1503	1379	1306	1238	1166	833	X
Pani–$LiPF_6$	1580	1499	1373	1302	1247	1141	836	561
Pani–$LiBF_4$	1579	1498	1375	1301	1247	1140	827	X
Pani–$LiClO_4$	1588	1501	1376	1305	1244	1144	832	625

are shifted to lower wavenumbers (e.g. ~ 1443 cm^{-1}) compared to those of the undoped Pani film (e.g. 1466 cm^{-1}). When the wavenumber shifts to higher, it means that the electron density increases on the ring. From the results, the resonance stabilization due to the presence of the counter anion by doping process of the nitrogen groups increases and the peaks are shifted to lower wavenumbers [9]. Therefore, we know that the doping does not occur in Pani–Li solution. However, when the solvent is evaporated, the doping occurs in drying state just like in the film.

The intensity of the EPR signal, which is due to unpaired electrons, for Pani–$LiBF_4$ samples increases with increasing concentration of Li salt, as shown in Fig. 4. The results suggest that the Pani film doped with high concentration Li salt makes more unpaired electrons (polaron) than that doped with low concentration Li salt. Therefore, the former Pani film with high concentration Li salt has high a doping state resulting in high conductivity.

Fig. 5 compares room temperature dc conductivity ($\sigma_{R.T.}$) of Pani–Li films cast from a solution as a function of Li salt concentration. The $\sigma_{R.T.}$ increases with increasing concentration of lithium salt. The Pani–$LiBF_4$ films have higher conductivity than Pani–$LiPF_6$ and Pani–$LiClO_4$ films. The highest conductivity of the systems is 0.16 S/cm for Pani–$LiBF_4$ (0.1 M). The variation in conductivity with different lithium salts originates the differences in solubility product (K_{sp}) and/or the degree of solvation.

Fig. 6 shows the XPS peaks of the counter ions (F1s) of Pani–$LiPF_6$ (0.1 M) and Pani–$LiBF_4$ (0.1 M) samples as a function of sputtering time. The normalized area of F1s XPS core level spectra of the Pani–$LiPF_6$ and Pani–$LiBF_4$ samples continuously decreased as the sputtering time increased. This is explained by the solvation effect. The NMP solvent is evaporated from surface. However, since the dried films may have a small quantity of solvent inside, the relatively large amount of Li^+ and counter ions effectively doped on surface. Therefore, a relatively large amount of dopants or counter ions exists on the surface in films, and the distribution of Li^+ and counter ions is a gradient through the films. Nevertheless, this distribution of Li^+ and counter ions is more uniform than that of films doped with dipping method. Therefore, the Li^+ and counter ions are deeply placed inside the Pani–$LiPF_6$ and Pani–$LiBF_4$ samples. The films fabricated from polymer solution are more effectively doped than that of films doped with dipping method.

Fig. 7 shows the schematic structure of non-doping state in solution and doping state in the form of film. When lithium salts are solved, the ions are dissociated in NMP that has a weak polarity ($P^1 = 6.7$) [10]. When lithium salts are solved and positive and negative ions are dissociated in the solvent, the ions are surrounded with NMP molecules (solvation). Then, doping does not occur and the color does not change like the results of Fig. 2. However, when the solution is poured onto a glass plate and heated, NMP is evaporated. The number of positive and negative ions surrounded by NMP molecules will be relatively

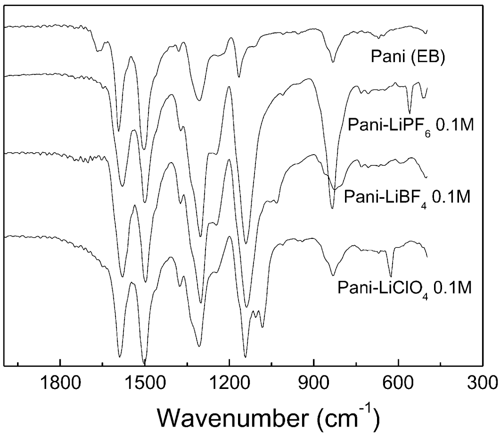

Fig. 3. IR spectra for EB, Pani–Li salt samples.

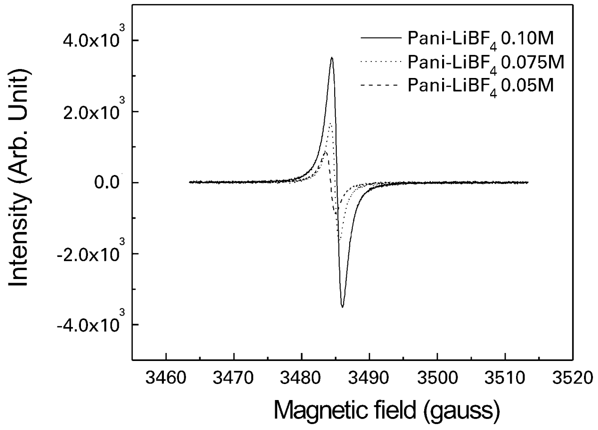

Fig. 4. The intensity of the EPR signal for Pani–$LiBF_4$ samples.

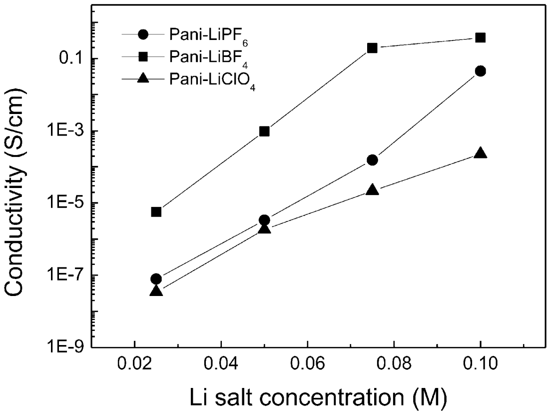

Fig. 5. The conductivity ($\sigma_{R.T.}$) of Pani–Li films cast from a solution as a function of Li salt concentration.

decreased so that ions of ionic salt are not surrounded by NMP. The positive ions (Li^+) easily migrate toward doping site on polymer chain and cause doping by nucleophilic reaction.

In order to increase conductivity of Pani–Li salt samples, we doped with HCl on the systems. Fig. 8 shows $\sigma_{R.T.}$ of Pani–Li salt doped with various concentrations of HCl. When the concentration of a lithium salt is 0.1 M, the conductivity of Pani–Li salt films doped with 0.05, 0.1, and 1 M HCl is increased and, however, the conductivity of Pani–Li salt films doped with 0.001, 0.005, and 0.01 M HCl is decreased as shown in Fig. 8(a). When the concentration of a lithium salt is 0.075 M, the conductivity of Pani–Li salt films doped with all concentrations of HCl except 0.001 M is increased as shown in Fig. 8(b). When the concentration of a lithium salt is 0.05 and 0.025 M, all the conductivity of Pani–Li salt films is increased except that of Pani–LiPF$_6$ (0.05, 0.025 M) and Pani–LiClO$_4$ (0.025 M) as shown in Fig. 8(c) and (d). For the Pani–Li salt samples with various concentrations, the additional doping of HCl induces the variation of $\sigma_{R.T.}$ as the doping level of HCl increases from 10^{-3} to 10^{-1} mole. Above 0.1 mole, the $\sigma_{R.T.}$ of the systems is saturated at ~10 S/cm, which is the same value of fully doped Pani–HCl. We observe the increase of $\sigma_{R.T.}$ for Pani–Li salt samples with low concentrations such as 0.05 and 0.025 M. The results show that the additional doping with protonic acid on the

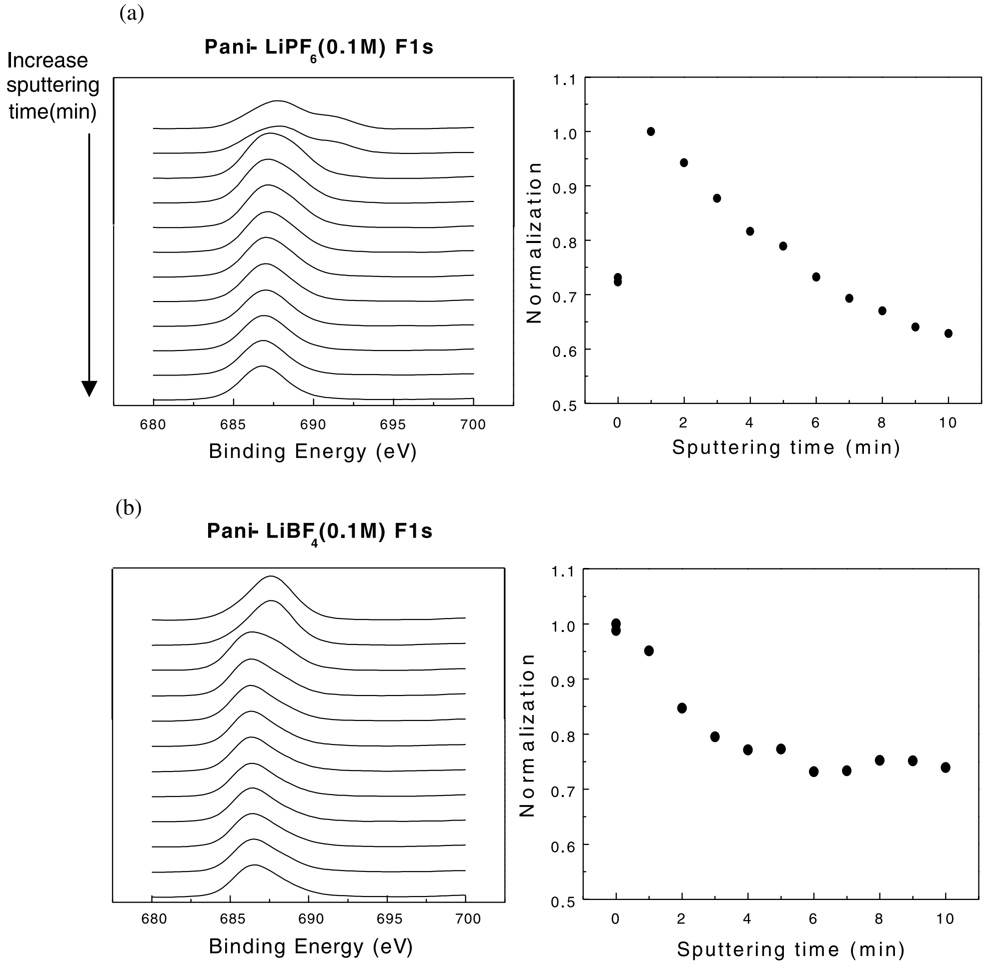

Fig. 6. The variation of XPS peaks of the counter ions (F1s) of (a) Pani–LiPF$_6$ (0.1 M) and (b) Pani–LiBF$_4$ (0.1 M) samples as a function of sputtering time.

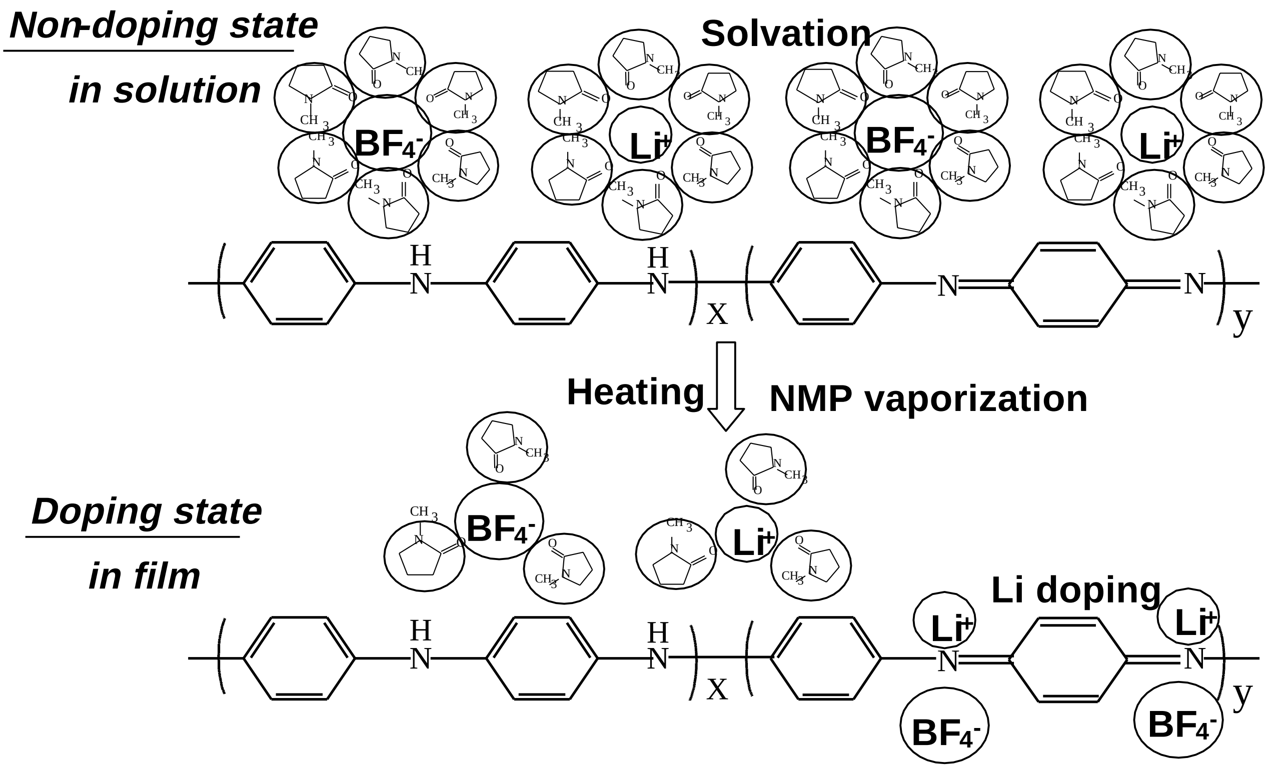

Fig. 7. The schematic structure for non-doping state in solution and doping state in film.

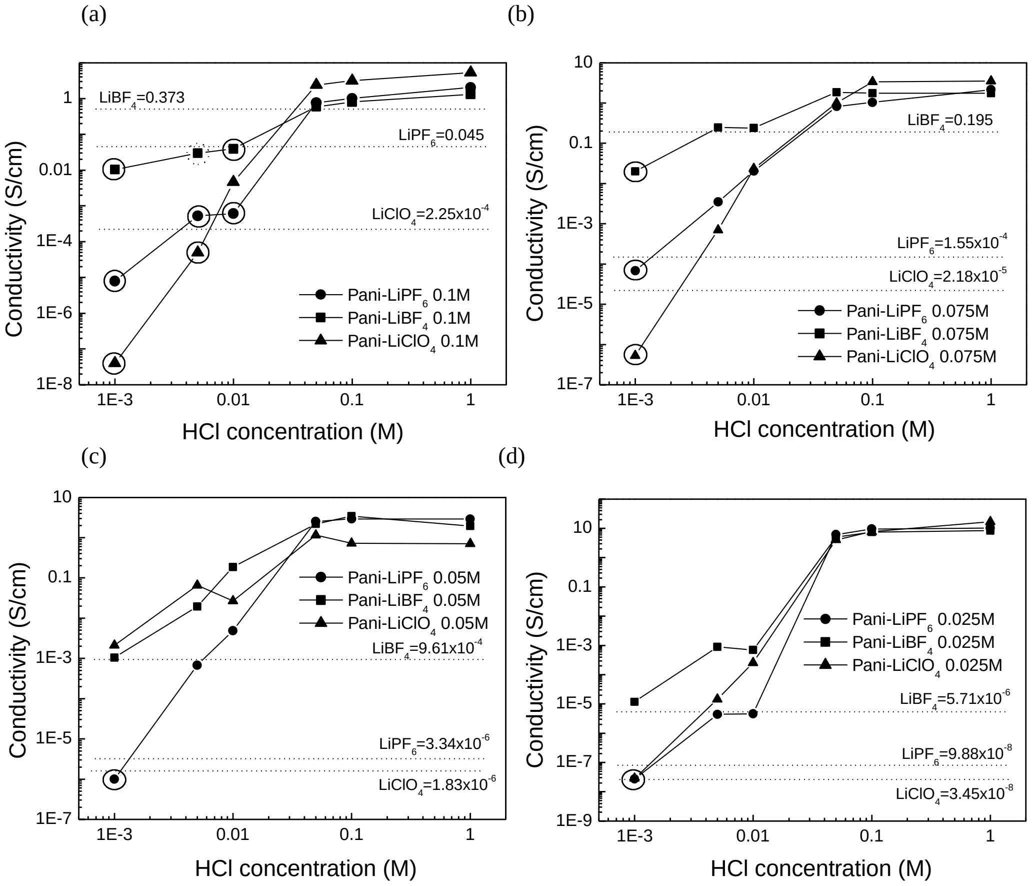

Fig. 8. The electrical conductivities of Pani–Li salt cast from polymer solution with the additional HCl doping.

Pani–Li salt samples is more effective at low concentration of doping agents.

4. Conclusion

We have synthesized highly conducting Li salt doped Pani films from the solution containing Pani and lithium salt. The doping does not occur on polymer chains in the solution state. However, doping occurs at the film state and this is confirmed from FT-IR data. The Pani film doped with high concentration Li salt makes more unpaired electrons (polaron) than the Pani film doped with low concentration Li salt. The electrical conductivity increases with increasing concentration of lithium salt. Pani–$LiBF_4$ films have higher conductivity than Pani–$LiPF_6$ and Pani–$LiClO_4$ films. The change in conductivity with different lithium salts might be associated with differences in solubility product (K_{sp}) and/or the degree of solvation. The non-doping state in solution and doping state in film state are explained with solvation effect. The Li^+ and counter ions deeply exist inside the Pani–$LiPF_6$ and Pani–$LiBF_4$ samples fabricated from polymer solution compared to the dipping samples. Therefore, the films directly fabricated from polymer solution are more effectively doped than the sample prepared by chemical treatment with protonic acid dopants. We observed the variation of the conductivity of Pani–Li salt samples with various concentrations through the additional doping of HCl.

References

[1] Nalwa HS. Handbook of organic conductive molecules and polymers, vol. 2. New York: Wiley, 1997 p. 595–619.
[2] Angelopoulos M, Asturias GE, Ermer SP, Ray A, Scherr EM, MacDiarmid AG. Mol Cryst Liq Cryst 1988;160:151–6.
[3] MacDiarmid AG, Chiang JC, Richter AF, Epstein AJ. Synth Met 1987:285–90.
[4] MacDiarmid AG, Epstein AJ. Synth Met 1994:103–16.
[5] Chen SA, Lin LC. Macromolecules 1995;28:1239–45.
[6] Angelopoulos M, Liao YH, Furman B, Graham T. Macromolecules 1996;29:3046–9.
[7] Giotto MV, Bonagamba TJ, Panepucci H, Valenciano GR, Mattoso LHC. Synth Met 1999;101:756–7.
[8] Jeong CK, Jung JH, Kim BH, Lee SY, Lee DE, Chang SH, Ryu KS, Joo J. Synth Met 2001;117:99–103.
[9] Hatchett DW, Josowiez M, Janata J. J Phys Chem 1999;B103:10992–8.
[10] Snyder LR. J Chromatogr 1974;92:223.