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Comparison of lithium//polyaniline secondary batteries with different dopants of HCl and lithium ionic salts

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Abstract

Polyanilines doped either with a protonic acid (HCl) or an electrolytic solution containing a lithium ionic salt ($LiPF_6$ or $LiBF_4$) are prepared and their electrochemical characteristics for use as polymer electrodes of lithium secondary batteries are investigated. An emeraldine base (EB) film doped with HCl has the highest d.c. conductivity ($\sim$ 10 S/cm). An EB-$LiPF_6$ film has higher conductivity ($\sim$ 0.52 S/cm) than an EB-LiBF4 ($\sim$ 0.082 S/cm) film. X-ray photoelectron spectroscopic analysis of the films shows that some of the quinoid rings in EB are transformed into benzeniod rings through a doping process to generate polarons. The charge–discharge characteristics of lithium secondary batteries using the polyaniline films as positive electrodes are determined. The cell using the EB-$LiPF_6$ film and an electrolytic solution containing $LiPF_6$ exhibits the highest specific discharge capacity ($\sim$ 50 mA h/g), whereas the cell using EB-HCl and $LiPF_6$ solution has superior performance in the rapid saturation of discharge capacity and in stability. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polyaniline; Lithium salt doping; Polymer electrode; Lithium secondary battery

1. Introduction

A conducting polymer has π-conjugated electrons spread along the polymer backbone and has a delocalized electron structure after doping. Polyaniline is one of the most stable and popular conducting polymers [1]. After Angelopoulos et al. [2] found that *N*-methyl-2-pyrrolidinone (NMP) is a good solvent for emeraldine base (EB), many researchers have attempted to verify the intrinsic property of polyaniline in processing technology. MacDiarmid et al. [3] systematically investigated the change of electric conductivity of polyaniline by protonic acid doping. They reported the variation of electrical conductivity as a function of pH (concentration of HCl solution) for emeraldine hydrochloride prepared by electrochemical and chemical methods.

Lithium secondary batteries are one of the most important applications of electrically conducting polymers. Various conducting polymers have been studied to examine their electrochemical properties. Some conducting polymers such as polyaniline, polypyrrole, and polythiophene are expected to be promising materials for the electrodes of secondary batteries because they are stable in air and have good electrochemical properties [4]. Since the specific capacity of a Li//conducting polymer secondary battery is very small, it is only used as the power sources for memory back-up and small electronic machines.

Many researchers have examined the use of polypyrrole as a positive electrode for lithium secondary batteries because it can be doped easily with cations and anions and is also stable in air. Conventionally, polyaniline is doped with protonic acid, and the resulting film has appropriate electrochemical properties for the positive electrode. However, the use of polyaniline in secondary batteries has been rarely studied because doping with ionic salt, and not protonic acid, is quite difficult.

Chen and Lin [5] investigated the properties of polyanilines doped with ionic salts such as $LiClO_4$, $LiBF_4$ and $Zn(ClO_4)_{24}$ by using various spectroscopic techniques. Doping was carried out by dissolving polyaniline, ionic salt, and NMP, and then casting the resulting solution into a film. By contrast, Yang et al. [6] investigated a

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Li//polyaniline cell in which the polyaniline was the emeraldine salt form doped with protonic acid.

Previously, we have reported [7] details of lithium salt-doped polyaniline samples prepared by the immersion of the EB form of polyaniline film in electrolyte solutions containing lithium salt. The doping level of the samples was investigated through measurements of electrical and magnetic parameters. The performance of a Li//polyaniline cell was also examined to the electrochemical reaction mechanism during the charge–discharge processes [8].

This study is concerned with the electrical properties and structural changes of polyaniline films prepared separately by doping with a protonic acid (1 M HCl) and a lithium salt solution ($LiBF_4$ or $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)). The electrode characteristics of Li//polyaniline cells which use the polyaniline films as positive electrodes, are also discussed.

2. Experimental

EB powder was dissolved in NMP solvent to yield 3 wt.% EB solution. The solution was poured on a slide glass and dried at 80°C in a convection oven to prepare a free-standing film. For protonic acid doping, the film was immersed in a 1 M HCl solution for 15 h and dried in a vacuum oven for 15 h. For ionic salt doping, an equivolume mixture of EC (Mitsubishi Chemical) and DMC (Mitsubishi Chemical) with 1 M $LiPF_6$ or 1 M $LiBF_4$ was used. The EB film was immersed in the lithium salt solution for 72 h in a dry box. The doped film was then washed with ethyl ether and dried in vacuum oven for 15 h. The conductance of doping solutions was measured to determine the dissociation factor of lithium salt in the solution. For the quantity of H^+ ion in the doping solution, a pH paper which was already dried in a vacuum oven for 24 h was used.

A four-probe method and a cryogenics closed cycle refrigerator system (CCS-100) were employed to measure d.c. conductivity ($\sigma_{\text{d.c.}}$). Four thin gold wires (0.1 mm thick and 99.95% pure) were attached in parallel on the sample surface by graphite glue (Acheson Electrodag 502) to eliminate constant resistance. X-ray photoelectron spectroscopy (XPS) was performed for the films by means of a VG ESCALAB Mkll spectrometer (Al Kα 1486.6 eV photons). The neutral peak of carbon 1*s* (C1*s*) at 284.6 eV was used as a reference to correct the shift by surface-charging effects.

The electrochemical cell consisted of the polyanilne film doped with HCl or lithium salt, lithium metal as the anode, glass filter as the separator, and EC:DMC:$LiPF_6$ or $LiBF_4$ (1:1:1 M) as the electrolyte solution. The lithium, separator, electrolyte solution, and doped polyaniline film were assembled in sequence as a sandwich in a test cell holder in a dry box. The cell was tested with a galvanostatic charge–discharge cycler in the voltage range from 2.0 to 3.9 V with a constant current density of 0.05 mA/cm^2.

3. Results and discussion

In order to identify indirectly the degree of dissociation of lithium salt, the conductance of doping solutions, was determined. The conductance is approximately proportional to the amount of ionic salt dissociated. The conductance of EC:DMC:$LiPF_6$ or $LiBF_4$ solution is 10.44 or 5.14 mS/cm, respectively. The quantity of H^+ ion in the doping solution is reflected as pH = 2.8–3.0 or –4, respectively. Thus, it may be said that the quantity of H^+ ion in the solution does not affect the conductivity of the polyaniline film because if pH of the doped polyanilne with protonic acid is 3–4, the conductivity should be about 10^{-5}–10^{-10} S/cm [2]. Nonetheless, it is considered that a small quantity of H^+ ions still exist as an impurity in this solution.

The temperature dependence of the d.c. conductivity, $\sigma_{\text{d.c.}}$, for the doped polyaniline films is given in Fig.1. The $\sigma_{\text{d.c.}}$ of polyaniline samples varies with the dopant used. EB-HCl film has the highest conductivity ($\sim$ 10 S/cm), and $\sigma_{\text{d.c.}}$ for the EB-$LiPF_6$ film is higher ($\sim$ 0.52 S/cm) than that of the EB-$LiBF_4$ film ($\sim$ 0.082 S/cm) at room temperature. To define the conduction mechanism, the temperature dependence of the d.c. conductivity was determined for the samples. A quasi one-dimensional (1D) variable range hopping (VRH) model provides the best fitting for $\sigma_{\text{d.c.}}(T)$ of polyaniline doped with lithium salts, i.e.:

$$\sigma_{\text{d.c.}}(T) = \sigma_0 \exp\left[-(T_0/T)^{1/2}\right], \tag{1}$$

where: T_0 is the temperature corresponding to $16/[k_B D(E_F) L_{\parallel} L_{\perp}^2]$; σ_0 is the $\sigma_{\text{d.c.}}$ at T_0; $D(E_F)$ is the density of states at the Fermi level E_F; k_B is the Boltzmann constant; $L_{\parallel}$ and $L_{\perp}$ are the localization lengths in

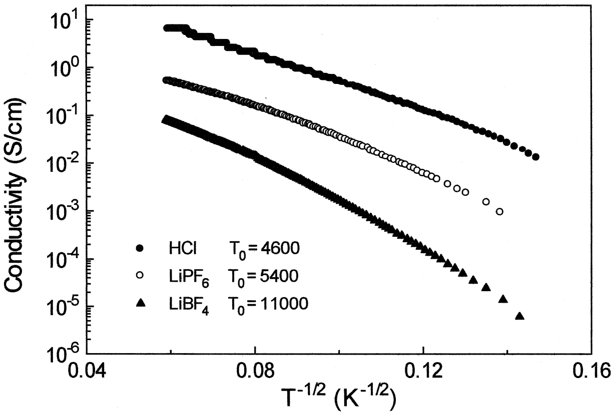

Fig. 1. Temperature dependence of d.c. conductivity of polyaniline doped with HCI and lithium salts.

a direction parallel and perpendicular to the polymer chain, respectively [9,10]. Based on the $\sigma_{\text{d.c.}}(T)$ results, a quasi-1D charge transport mechanism is deduced for these polyaniline systems. The slope of T_0 implies an effective energy separation between localized states. The system becomes a more highly conducting state as the value of T_0 decreases. The T_0 of the EB-HCI film is ~4600 K and that of EB-LiPF$_6$ or LiBF$_4$ films is ~5400 or ~11,000 K, respectively. EB-HCI and EB-LiPF$_6$ films are in a more highly conducting state than the EB-LiBF$_4$ film.

Information about various intrinsic redox states and the doping level of conducting polymers can be obtained from XPS experiments [11,12]. The nitrogen 1*s* (N1*s*) XPS core level spectra of the EB, EB-HCI, EB-LiPF$_6$, and EB-LiBF$_4$ films at room temperature are presented in Fig. 2. The major peak line may be separated into three peak lines. The lines corresponding to nitrogens in imine and amine units are centred at 398.1 and 399.3 eV, respectively, while the line of positive nitrogen is centred at 401.0 eV.

The oxidation states of polyaniline are very important because they determine the physical and chemical properties [3,13]. From the XPS results for the EB sample, as shown in Fig. 2(a), the oxidation state of the EB form with the area ratio of amine to imine peaks can be calculated. When EB is in the perfectly intermediate state ($1-y=0.5$), the area ratio must be 1.0. When this area ratio is larger than 1.0, EB is in a slightly reduced state, and when the ratio is less than 1.0, EB is in a slightly oxidized state. The present sample of EB is in a slightly reduced state because the value of $1-y$ is 0.435. The peak of positive nitrogen in the EB sample is detected as in Fig. 2a. This originates from the residual doped state in the preparation step of EB. That is, the polyaniline was synthesized as the emeraldine salt state doped with HCI, and treated with NaOH as a de-doping agent to make the EB state. If the emeraldine salt is not fully de-doped in this process, the EB as final product is in the partially doped state with HCI.

After doping with HCI and lithium salt, the imine peak area becomes smaller than that of the EB sample. The peak area ratio due to the positive nitrogen is ~28%, ~31%, and ~18%, which implies the generation of charged nitrogen sites when doping. This result agrees with the conductivity trend of the EB-LiPF$_6$ and EB-LiBF$_4$ films. The EB-HCI film, however, has higher conductivity than the EB-LiPF$_6$ film although its area of positive nitrogen peak is smaller.

The XPS results imply that some quinoid rings in the EB form of polyaniline are transformed into benzenoid rings through the HCI, LiPF$_6$, and LiBF$_4$ doping process to form polarons. It is not clear in lithium salt doping process, however, that the polarons can be separated like the doping process with HCI. XPS analysis (and also Fig. 2) shows that some portions of the quinoid rings exist after doping because the lithium ion is a heavy and inhomogeneous atom.

The discharge curves and specific discharge capacity for 30 cycles for the Li//EB-HCI cell using a EC:DMC:1

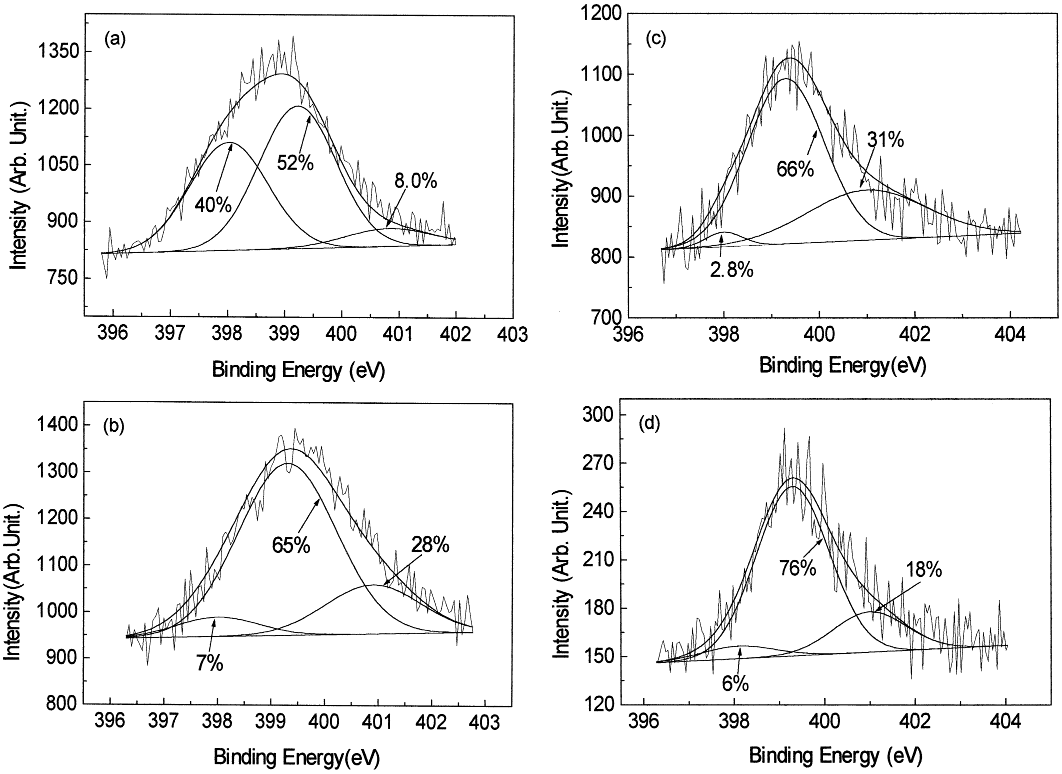

Fig. 2. N1*s* XPS core spectra of (a) EB, (b) EB-HCI, (c) EB-LiPF$_6$, and (c) EB-LiBF$_4$ films at room temperature.

M $LiPF_6$ or 1 M $LiBF_4$ electrolytic solution are given in Fig. 3. For EC:DMC:1 M $LiPF_6$ solution, the discharge capacity continuously increases with cycling. The saturated capacity cannot be obtained due to the continual increase over the 30 cycles. The specific discharge capacity at the 30th cycle is ~ 10 mA h/g and the coulombic efficiency is ~ 95%. For EC:DMC:1 M $LiBF_4$ solution, however, the discharge capacity becomes saturated at an early stage of cycling (~ 3rd cycle). This capacity is ~ 21 mA h/g, which is only about 17% of the theoretical capacity (142.6 mA h/g for a polyaniline unit doped by lithium salt). The corresponding coulombic efficiency is ~ 94%.

The discharge curves and specific discharge capacity for a Li//EB-lithium salt cell is presented in Fig. 4. When using $LiPF_6$ as both the doping agent and the electrolytic salt, the discharge capacity slowly increased with cycling and saturates at ~ 15th cycle. The saturated specific discharge capacity is ~ 50 mA h/g, which is about 35% of the theoretical capacity. For $LiBF_4$, the discharge capacity rapidly increases with cycling and saturates at > 15th cycle. The saturated specific discharge capacity is ~ 45 mA h/g, which is about 28% of the theoretical capacity. These phenomena may be explained as follows. Since the EB-$LiPF_6$ sample has more active sites or reaction paths induced from electrochemical reaction by $LiPF_6$ doping,

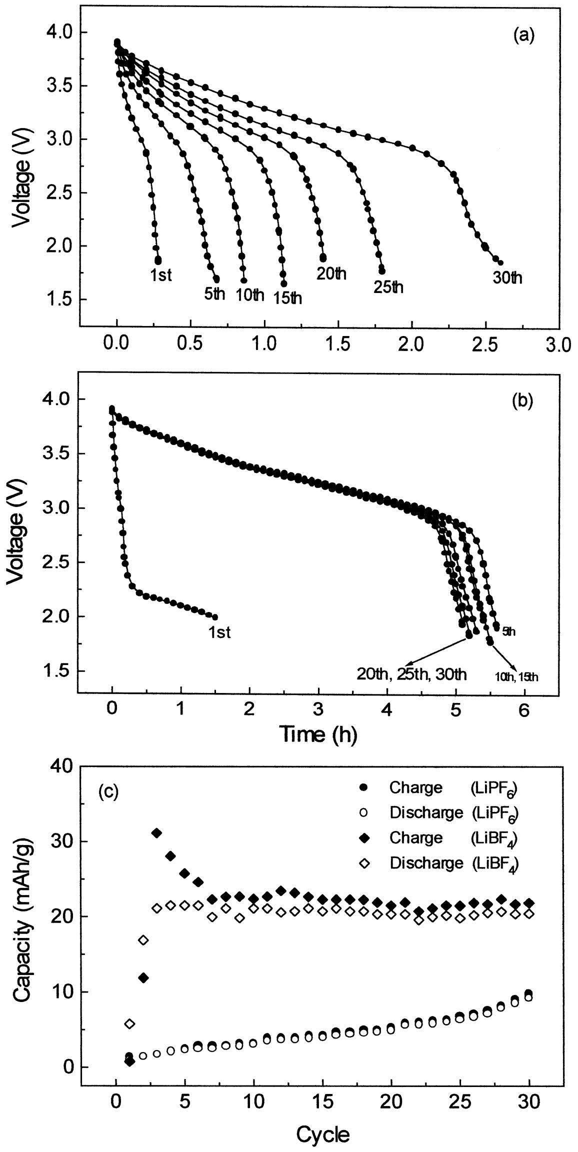

Fig. 3. Discharge curves of Li//EB-HCI cells when electrolytic solutions of (a) EC:DMC:1 M $LiPF_6$ and (b) EC:DMC:1 M $LiBF_4$ are used. (c) Specific charge–discharge capacities for 1–30 cycles.

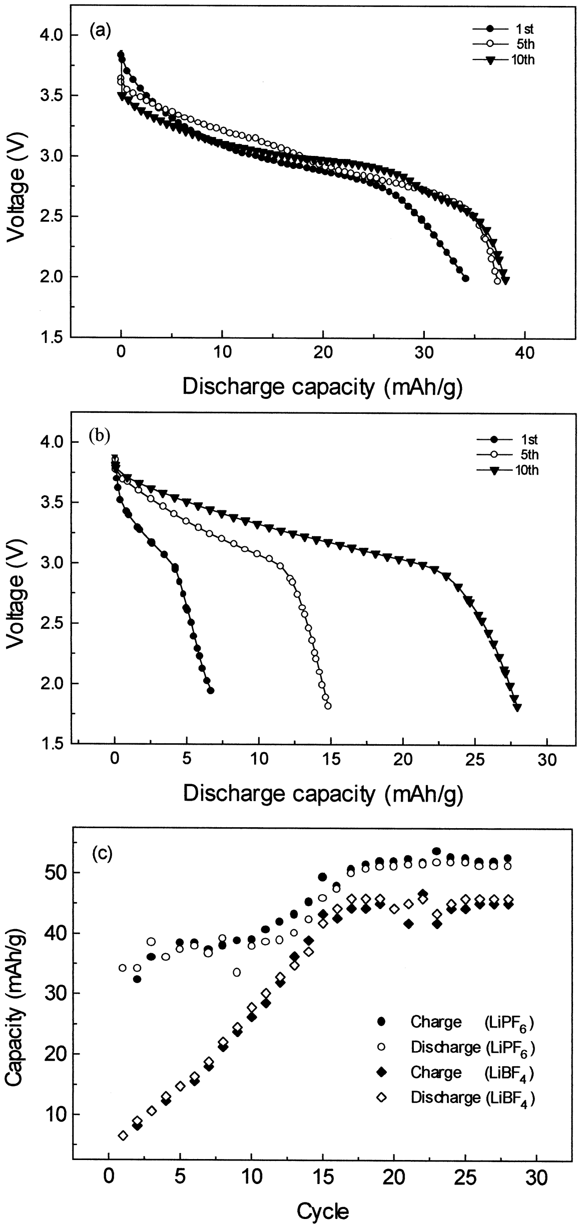

Fig. 4. Discharge curves of Li//EB-$LiPF_6$ or $LiBF_4$; discharge curves of 1st, 5th, and 10th cycles for (a) Li//EB-$LiPF_6$ cell and (b) Li//EB-$LiBF_4$ cell. (c) Specific charge–discharge capacities.

the capacity slowly increases from the first cycle. By contrast, the capacity of the Li//EB-$LiBF_4$ cell is considerably lower during the initial several cycles and rapidly increases during the next repeated cycles. This may be because the EB-$LiBF_4$ film has poor conductivity in the initial state and then generates continually the active sites and reaction paths during the repeated charge–discharge process. In addition, EB-HCl and EC:DMC:1 M $LiPF_6$ may belong to the above case.

From these results, it is seen that the cell using a EB-$LiPF_6$ electrode film and an EC:DMC:1 M $LiPF_6$ electrolytic solution has the highest specific discharge capacity. The cell with an EB-HCl film and an EC:DMC:1 M $LiBF_4$ electrolyte solution has the best performance in terms of rapid saturation of capacity and stability. Nonetheless, the measured electrical capacity and initial charge–discharge reversibility are too low for practical purposes. The use of a composite polyaniline electrode which is combined with other materials such as polymer, metal oxide, carbon, etc., to increase the conducting path or to support the structural reversibility is required.

References

[1] T.A. Skotheim, Handbook of Conducting Polymers, Marcel Dekker, New York, 1986.

[2] M. Angelopoulos, G.E. Asturias, S.P. Ermer, A. Ray, E.M. Scherr, A.G. MacDiarmid, Mol. Cryst. Liq. Cryst. 160 (1988) 151.

[3] A.G. MacDiarmid, J.C. Chiang, A.F. Richter, A.J. Epstein, Synth. Met. 17 (1987) 285.

[4] J.C. Chiang, A.G. MacDiarmid, Synth. Met. 13 (1986) 193.

[5] S.A. Chen, L.C. Lin, Macromolecules 28 (1995) 1239.

[6] L. Yang, W. Qui, Q. Liu, Solid State Ionics 86–88 (1996) 819.

[7] J. Joo, H.G. Song, C.K. Jeong, J.S. Baeck, J.K. Lee, K.S. Ryu, Synth. Met. 98 (1999) 212.

[8] K.S. Ryu, K.M. Kim, S.G. Kang, G.J. Lee, S.H. Chang, Solid State Ionics, submitted for publication.

[9] Z.H. Wang, C. Li, E.M. Scherr, A.G. MacDiarmid, A.J. Epstein, Phys. Rev. Lett. 66 (1991) 1745.

[10] N.F. Mott, E. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, 1979.

[11] M. Aldissi, S.P. Armes, Macromolecules 25 (1992) 2963.

[12] K.L. Tan, B.T.G. Tan, E.T. Kang, K.G. Neoh, Phys. Rev. B 39 (1989) 8070.

[13] A.G. MacDiarmid, A.J. Epstein, Faraday Discuss. Chem. Soc. 83 (1989) 317.