Electrochemistry of Conductive Polymers 46. Polymer Films as Overcharge Inhibitors for Lithium-Ion Rechargeable Batteries

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ABSTRACT :

Conducting polymer films grown from various aromatic compounds have been evaluated as overcharge protecting additives for lithium ion rechargeable batteries. The polymer films were grown electrochemically under the conditions similar to those encountered during the overcharging processes of lithium batteries and subsequently characterized by potentiodynamic, electrochemical quartz crystal microbalance, electrochemical impedance spectroscopic, and scanning electron microscopic experiments. Results indicate that bicyclic and polycyclic aromatic hydrocarbons would be poor candidates for inhibitors, while biphenyl, terphenyl, and benzene derivatives displayed excellent performances. Mixed polymer films grown from *o*-terphenyl and *p*-xylene show the best performance among the candidates.

Keywords : Overcharge inhibitor, Conducting polymers, Passivation, Lithium batteries.

Received August 5, 2010 : Accepted August 16, 2010

1. Introduction

Lithium-ion rechargeable batteries are widely used for cellular phones, personal computers, and other portable electronic devices. These batteries often encounter safety problems during a charging process. With two battery electrodes shorted or defective, charging currents may increase rapidly and the batteries become thermally unstable, which may sometimes lead to fires, explosions, and/or other mishaps. Thermal cut-off materials such as polyethylene-based separators, which melt down and plug up the ion transfer channels at high temperatures, and overcharge protection circuits are used in commercially available batteries to prevent high currents from flowing.¹⁾ However, the overcharge protection is not sufficient in many cases.

A number of fundamental studies have been undertaken

to protect the batteries from being overcharged, in which in-situ polymerization of a few aromatic compounds such as biphenyl (BP) and cyclohexylbenzene (CHB) is used to electrochemically grow insulating films at the cathode surface, passivating the battery cathodes and inhibiting high current flows.²⁻¹⁰⁾ In a previous report, we introduced an electrochemical impedance spectroscopic (EIS) measurement as a screening tool for the performance of additives before real abuse tests in lithium-ion cells. We had evaluated effects of varied compositions of BP and CHB by potentiodynamic, electrochemical quartz crystal microbalance (EQCM), spectroelectrochemical, and EIS measurements.⁸⁾ The results indicated that a mixed polymer film prepared from a solution containing BP and CHB was more effective than a polymer film grown from BP or CHB alone in that the mixed polymer film displayed favorable growth characteristics and higher electrical resistances. Surprisingly, these results are very consistent with real overcharge tests of lithium-ion cells.⁷⁾

In the present study, we extend our work by including

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some more aromatic compounds using the screening tool we have developed earlier. We then categorize the additives depending on their applicability to commercialized lithium ion batteries as an over-charge inhibitor and introduce the best combination among the candidates.

2. Experimental

BP (Aldrich), CHB (Aldrich), anthracene (Aldrich), naphthalene (Aldrich), fluorene (Aldrich), *o*-terphenyl (*o*-TP, Aldrich), *p*-terphenyl (*p*-TP, Aldrich), *p*-xylene (Aldrich), pyrrole (Aldrich), thiophene (Aldrich), propylene carbonate (PC, Aldrich), LiClO₄ (Aldrich), and H₂SO₄ (Aldrich) were used as received. A PC solution containing 1.0 M LiClO₄ was used as an electrolyte solution as it mimics those used in lithium batteries. Concentrations of additives were 0.10 M for all compounds with an exception of *p*-TP, for which a saturated concentration was used due to its low solubility in PC. The concentrations are significantly higher than those used in our earlier studies^{11,12)} in efforts to grow thick polymer films within a short period and yet to make them more easily passivated.

All electrolyte solutions were kept in a glove box, through which constantly regenerated dried argon was circulated to avoid or minimize contamination by water. All experiments were carried out in a glove box. We used a glassy carbon (0.030 cm²) electrode to examine the electrochemical behaviors of the additives because the electrodes made of LiMO_x (M = Co, Ni, Mn) type compounds, which are employed for cathodes in rechargeable batteries, have limited electrochemical windows due to their own electroactivity within the potential windows employed in this study. A Li wire and a Li foil were used as reference and counter electrodes, respectively. All potentials are referred to the Li reference electrode unless otherwise stated.

The polymers were potentiodynamically grown at a scan rate of 50 mV/s. Cyclic voltammograms (CVs) were recorded using an EG&G Princeton Applied Research model 273A potentiostat, which was controlled by M270 electrochemistry software. Scanning electron microscopic (SEM) images of the polymer films were obtained using a Philips XL 30S FEG-SEM.

EIS measurements were made after steady-state CVs were obtained while the potential was cycled between 3.0 and 5.5 V. The impedance data were acquired in the presence of monomer molecules after the film was grown in order to mimic a real operating battery system, in which monomers should also be present. The EIS experiments

employed an EG&G model 273A potentiostat/galvanostat in conjunction with a Solartron SI 1255 HF frequency response analyzer, which was driven by EG&G M398 electrochemical impedance software. An ac wave of ± 5 mV (peak-to-peak) was overlaid on a DC bias potential at which the measurements were made. The measurements were made at a rate of 10 points per decade between 100 kHz and 1 Hz at the glassy carbon disk electrode. The EG&G ZSimpWin software program was used for analysis of the impedance data. The program simulated the measured impedance data to numerically fit a variety of electrical circuits. The program, combined with a general nonlinear least squares fit procedure, allowed an appropriate equivalent circuit to be constructed, whose simulated responses fit the measured data well.¹³⁻¹⁵⁾

Electrochemical quartz crystal microbalance (EQCM) measurements were carried out using a Biomechatron model 1000L EQCN quartz crystal analyzer (Jeonju, Korea). An AT-cut, 9 MHz gold-plated quartz crystal (0.20 cm²) was used as a resonator and an electrode.

In situ UV-visible absorption spectra were obtained concurrently, while a CV was recorded, with a 75 W xenon lamp and an Oriel InstaSpec[®] IV spectrometer having a charge-coupled device (CCD) array detector. The cell was configured in a near normal incidence reflectance mode using a bifurcated quartz optical fiber.¹⁶⁻¹⁸⁾ The white-light beam was brought onto the electrode surface via one branch of the bifurcated optical fiber from the light source such that the beam would be near normal to the surface. Reflected light from the electrode surface (area = 0.30 cm²) was then guided into a grating through another branch, which dispersed the white beam onto the CCD array detector. The wavelength of the spectrograph was calibrated using a small mercury lamp.

3. Results and Discussion

3.1. General Considerations: Requirements for Battery Overcharge Inhibitors

Our criteria for selecting an additive for an overcharge inhibitor are that it should: (1) not decrease the battery capacity significantly during normal charge-discharge cycles; (2) have a lower oxidation potential than those of the electrolyte and the solvent but a more anodic potential than that of cathode oxidation; and (3) form a uniform, stable, and highly resistive layer in a reasonably short period on the cathode surface during an overcharging process. Usually, a lithium-ion battery with a LiCoO₂ cathode is charged to a cell voltage of about 4.2 V, which

becomes $\text{Li}_{0.5}\text{CoO}_2$. The oxidation potential of the additives must be somewhere between the fully charged voltage (4.2 V vs. LiC_6 , 4.3 V vs. Li) and the anodic decomposition potential of the solvents (e.g., ~5 V vs. Li) for most lithium-ion batteries. This is because the additive must remain inert during the normal operation of lithium-ion batteries but become active before massive electrolyte decomposition occurs when they are overcharged. The third criteria for a film resistance can be evaluated by impedance measurements,⁸⁾ and we thus employed the EIS measurement as a screening tool for the performances of overcharge inhibitors.

Another important requirement for the additive is that the film must grow evenly to a certain extent and then become passivated before it gets too thick.⁸⁾ The film electrodeposited while the battery is overcharged must be conductive enough in its initial stage to grow fast enough to a desired thickness. When the thick polymer film is passivated, it reduces a possibility of a direct contact between the anode and the cathode of the cell at high temperature while the cell is being overcharged. The polymer film must thus become passivated before it gets too thick, preventing a large current from flowing. In our previous report, a thick polymer film was produced initially by oxidation of BP, which was then completely passivated by the formation of another highly resistive film generated upon oxidation of CHB. In other words, the polymer film grown in a mixed solution containing both BP and CHB provided a good performance by taking advantage of the fast film growth at the initial stage and then rapid passivation of the resulting film.⁸⁾

3.2. Surface Coverage: SEM study

Fig. 1(a) shows a SEM image for the poly(*p*-phenylene) (PPP) film deposited on the electrode surface by oxidation

of biphenyl. PPP is shown to grow as a flat polymer film and cover the entire electrode surface. A few cracks seen in this image must have resulted from washing and drying processes. In lithium-ion batteries, there would not be as many cracks as seen in this image when the polymer film is wet. SEM images of mixed polymer films prepared from solutions containing BP and CHB showed similar morphologies (not shown). As seen from this image, the polymer films produced by oxidation of aromatic compounds used in this study were shown to satisfactorily cover the entire electrode surface.

Fig. 1(b) displays an image for a typical conducting polymer, polythiophene, which were grown under the same experimental conditions. As can be seen from the image, the morphology is completely different from that of PPP shown in Fig. 1(a). The polythiophene film shows many protruded growth sites, providing inhomogeneous thicknesses and porous structures. This is because the protruded part has higher conductivity than other areas; the polymer growth takes place preferentially at these sites.¹⁹⁾ The sharp polymer structures can provide charge collecting points, which could be dangerous in electrochemical power storage devices. We also tried to make other well known conducting polymer films in PC, and they all showed three dimensional structures although their shapes may be different from that shown in Fig. 1(b). Thus, conducting polymers of high electrical conductivity, such as polypyrrole, polythiophene, and polyaniline, are not suitable for use as protective films during the uncontrollable overcharging process due to their uneven film formation even though they can be successfully passivated and become very resistive.^{9,10)}

3.3. Bicyclic and Polycyclic Aromatic Hydrocarbons

Fig. 2(a) shows CVs of naphthalene oxidation during

Fig. 1. SEM images for (a) PPP and (b) polythiophene, which have been electropolymerized from 0.10 M monomer and 1 M LiClO_4 in PC by potentiodynamically cycling at 50 mV/s.

Fig. 2. A series of CVs recorded during potential cycles in PC solutions containing (a) 0.10 M naphthalene and (b) 0.10 M *o*-TP as well as 1 M LiClO₄ between 3.0 and 4.7 V at a glassy carbon electrode at 50 mV/s.

the potential cycling between 3.0 and 4.6 V. Naphthalene has been shown to be polymerized at its onset oxidation potential of about 4.35 V,²⁰⁾ and the slow polymer film growth is shown as displayed by slow increase in currents for polymer oxidation and reduction between 3.6 and 3.9 V. During the successive potential cycling, the reduction current at ~4.2 V, which is attributed to reduction of electro-generated radical cations, also increases during the potential reversal, indicating that its radical cations are relatively stable. However, the onset oxidation potential of naphthalene is not positive enough, which may lead to a decrease in the battery capacity during normal charge-discharge cycles.

Anthracene oxidation shows similar characteristics to those of naphthalene except that its onset potential is less positive at about 4.0 V due to more extensive conjugation. During the voltage sweeps, oxidation and reduction peaks at 3.9 and 3.8 V, which are assigned to redox reactions of its dimers, tetramers, and/or anthraquinone,²¹⁾ grow continuously. A critical drawback for anthracene is that its oxidation potential is too low to be used for a 4 V class lithium-ion battery. Other polycyclic hydrocarbons such as tetracene and rubrene have limited solubility; their oxidation potentials are even more negative and the radical cations are very stable.²²⁾ Thus, polycyclic hydrocarbons are not suitable candidates for overcharge inhibition.

3.4. Biphenyl and Terphenyl Derivatives

Fig. 2(b) show a series of CVs of *o*-TP recorded in the potential range of 3.0–4.7 V. As *o*-TP is the same as BP with one phenyl group substituted at its *o*-position, its electrochemical characteristics are similar to those of BP except that its polymerization is more effective, and thus the oxidation and reduction current peaks observed for its

polymer at about 4.1 and 3.7 V, respectively, are significantly smaller. As the potential cycling was continued, the polymer redox currents increase for the first 10 cycles but the polymer was seen to be passivated beyond the 10th cycle as evidenced by the decrease in the currents.

A similar result was observed for the electrochemical polymerization of *p*-TP (data not shown). Fluorene, which has the same chemical structure as biphenyl with two phenyl groups are linked by a methylene carbon at their *o*-positions, shows the best defined electrochemistry for its oxidation. This is because two phenyl rings are much more extensively conjugated and yet cannot rotate around the single bond linking two phenyl rings upon electrochemical oxidation or photochemical excitation. As a result, it has the lowest

Table 1. Oxidation potentials of additives

Additives	E _{ox} (V) vs. Li	References
Anthracene	4.00	*
Naphthalene	4.35	*
Fluorene	4.35	*
1,2,4,5-Tetramethylbenzene	4.40	5
Tetrahydronaphthalene	4.45	4
<i>p</i> -Terphenyl	4.45	*
Hydrogenated terphenyl	4.45	4
Diphenylether	4.50	6
Diphenyleneoxide		4
<i>o</i> -Terphenyl	4.50	*
Biphenyl	4.55	*
1,2,4-Trimethylbenzene	4.60	5
<i>p</i> -Xylene	4.70	*
Cyclohexylbenzene	4.75	*
Toluene	4.75	5
Benzene	4.95	5

* This work.

oxidation potential of bi- and ter-phenyl derivatives (Table 1) and the highest polymerization efficiency. The redox currents for electrochemically produced polymers from this class of hydrocarbons are in the order of fluorene > *o*-TP > *p*-TP $\approx$ BP. The polymers undergo reversible redox chemistry indicating that their passivation is not effective enough to be used as overcharge inhibitors.

3.5. Benzene Derivatives

Fig. 3 shows a series of CVs recorded for 0.1 M *p*-xylene (a) and CHB (b). Electrochemical oxidation of *p*-xylene displays similar characteristics to those shown by CHB (Fig. 3(b)), toluene, and benzene with the oxidation potential of benzene most positive of all. The decrease in monomer oxidation currents of benzene derivatives as the cycle number increases was more dramatic than that of biphenyl derivatives, indicating that the film was more rapidly and severely passivated. Their onset oxidation potentials depend on the position and the number of substituted methyl groups at the benzene ring (Table 1). With the number of methyl groups increasing, the onset oxidation potential of the benzene derivatives shifts distinctly to a less positive potential due to the electron donating property of the methyl group.⁵⁾

Fig. 4(a) compares linear sweep voltammograms for a few aromatic compounds: (i) fluorene, (ii) *o*-TP, and (iii) CHB. Oxidation of fluorene shows the highest peak current, and the oxidation peak current of *o*-TP is about twice of that of CHB. This indicates that the electron transfer is more efficient for the fluorene molecule, which is more conjugated than the two other molecules due to its planar geometry, leading to more efficient polymerization. Thus, the thicknesses of electrodeposited polymers are expected to be in an order of polyfluorene >

Fig. 4. (a) Linear sweep voltammograms for 0.10 M: (i) fluorene, (ii) *o*-TP, and (iii) CHB; (b) EQCM results for 0.10 M: (1) naphthalene, (2) fluorene, (3) BP, (4) *o*-TP, (5) saturated *p*-TP, (6) CHB, and (7) *p*-xylene for 10 potential cycles. During the EQCM measurements, the potential ranges were from 3.0 V to monomer oxidation onset potential (E_{onset}) + 0.25 V. The other experimental conditions were the same as those used for Fig. 2.

Fig. 3. A series of CVs for: (a) 0.10 M *p*-xylene and (b) 0.10 M CHB between 3.0 and 4.85 V under the same experimental conditions as those used for Fig. 2.

poly(*o*-TP) > polyCHB from the peak potentials, which was shown to be the case from EQCM results in Fig. 4(b). During the EQCM measurements, the potential ranges were adjusted with regard to each monomer oxidation onset potential (E_{onset}). Thus, the potential cycling range was from 3.0 V to $E_{\text{onset}} + 0.25$ V. Results indicate that the amounts of the polymer accumulated during oxidation of naphthalene and fluorene are larger than for other compounds. Although CHB and *p*-xylene were oxidized at potentials close to ~ 5.0 V, the amounts of the polymer accumulated on the electrode surface are significantly smaller in comparison to those for biphenyl and terphenyl derivatives. However the thin polymer films displayed higher resistances as will be shown by impedance experiments (*vide infra*).

3.6. Screening Overcharge Inhibitors

Table 1 summarizes oxidation potentials of the candidates for inhibitors. The compounds of low oxidation potentials (< 4.4 V) cannot be used for an overcharge inhibitor as they would interfere with the battery charging process and significantly decrease their capacities due to their participation in redox reactions during charge-discharge cycles. The compounds whose oxidation potentials are in the range of 4.4–4.6 V may serve as candidates for overcharge inhibitors when they form thick polymer films, which reduce a possibility of a direct contact between the anode and cathode while the cell is overcharged. The compounds of high oxidation potentials of 4.6–4.8 V can be candidates for a resistive polymer group due to their capability of complete passivation upon formation of the polymer layer. Finally, compounds showing too high oxidation potential of more positive than 4.8 V may not be suitable due to the slow response during the overcharging process because their oxidation reactions overlap with those of solvent decomposition.

Resistances of the polymer films were evaluated by impedance measurements. The films were prepared by 10 potential cycles between 3.0 V and 5.5 V in a solution containing 0.10 M monomers. Fig. 5(a) shows Nyquist plots obtained at 5.0 V for the polymer films in the same solutions as ones in which the films were prepared, and Figs. 5(b) and c show equivalent circuits used for impedance data analysis. In the equivalent circuits, a constant phase element, Q , was used instead of a capacitor, C . Deviations from ideal capacitive behaviors led to the use of Q due to highly porous polymer structures. All the data shown in Fig. 5(a) were satisfactorily described by the circuit shown in Fig. 5(b) or 5(c) depending on the potential region.

Fig. 5. (a) Impedance data and their simulated lines (—) for the polymer films at 5.0 V in 1 M LiClO₄ PC in solutions containing the same concentration of each monomer as that from which the polymer films were prepared. The films were prepared by 10 potentiodynamic cyclings between 3.0 V and 5.5 V from solution containing 0.10 M: (1) naphthalene, (2) fluorene, (3) BP, (4) *o*-TP, (5) saturated *p*-TP, (6) CHB, and (7) *p*-xylene; (b) and (c) equivalent circuits used for fitting the impedance data. Here R_s is the solution resistance; R_1 and R_2 are the polarization resistances; Q_1 and Q_2 are constant phase elements.

The resistances of the polymer films are in the order of polyxylene > poly(*p*-TP) > poly(*o*-TP) > polyCHB > polyBP > polyfluorene > polynaphthalene. When the resistances were normalized with the film thickness, the same order was maintained with even more differences in their values. This is because the more resistive films have smaller thicknesses and their normalized resistances became even greater.

We used a notation, total resistance (R_{tot}), which is $R_s + R_1$ for the circuit with a single semicircle shown in Fig. 5(b), while it is $R_s + R_1 + R_2$ for the circuit with two semicircles displayed in Fig. 5(c). Fig. 6 shows the changes in R_{tot} values for seven different polymer films when the potential was varied. The resistances hit their minimum values at 4.6 V or 5.0 V and increase back

Fig. 6. Total resistances, R_{tot} , plotted as a function of potential for the polymer films grown in 1 M LiClO₄ PC solutions containing each monomer: (a) naphthalene, (b) fluorene, (c) BP, (d) *o*-TP, (e) *p*-TP, (f) CHB, and (g) *p*-xylene.

to larger values at 5.3 V. This is because the films become most conductive at 4.5–5.0 V due to maximum rates of electron transfer for doping the polymer films. However, they become passivated upon further oxidation at higher potentials. Single component polynaphthalene (a) and polyfluorene (b) films showed highly conductive properties throughout the wide range of potential, although they were thicker than the others as was judged from the CV peak currents of the polymer films and EQCM results. Films grown from BP (c), *o*-TP (d) and *p*-TP (e) showed intermediate resistivity while that prepared from *p*-xylene (g) showed the highest resistance values throughout the entire overpotential region. The poly(*p*-xylene) film turned out to be more resistive than that grown from CHB (f). The results indicate that bicyclic and polycyclic aromatic hydrocarbons are poor candidates with too high conductivity, biphenyl and terphenyl derivatives can be good candidates as a thick polymer layer, and benzene derivatives can be excellent candidates thanks to a highly insulating layer of the cathode surface during the overcharge process.

Spectroelectrochemical experiments were performed to observe the polymer oxidation states and to obtain UV-visible spectra supporting EIS results. Fig. 7 shows the results obtained at 5.0 V during potential sweep for a few aromatic hydrocarbons. Fig. 7a shows the spectrum for the polyfluorene film during its growth. The 430 nm peak is assigned to the band gap transition of the undoped neutral polymer while bands at longer wavelengths are due to the quinoid structure (500 nm) and free carriers (800 nm), indicating that the polyfluorene is highly conductive. Fig. 7(b) shows a spectrum for poly(*p*-TP)

Fig. 7. Spectra recorded at 5.0 V during potential sweep in a 1.0 M LiClO₄ solution containing (a) fluorene, (b) *p*-TP, (c) CHB. The potential sweep rate was 50 mV/s.

film, in which the free carrier band at about 700 nm is significantly low. Here, absorption peaks or shoulders were observed at 375 nm, 480 nm and 700 nm upon oxidation of *p*-TP. Thus, the poly(*p*-TP) film would be significantly more resistive than polyfluorene. The spectral patterns of PPP and poly(*o*-TP) were very similar to that of poly(*p*-TP) (not shown). Fig. 7c shows a UV-visible spectrum for a film grown from CHB. Again, the free carrier band is almost nonexistent. This explains why the poly-CHB was not as conductive as polyTPs and the polymer growth was so much slower.

Fig. 8. First and fifth CVs recorded during 10 potential cycles between 3.0 and 5.5 V for mixed monomer solutions: (a) 25 mM *o*-TP and 75 mM CHB, (b) 25 mM *o*-TP and 75 mM *p*-xylene; (c) and (d) impedance data obtained at 5.0 V for the polymer films prepared from potential cyclings as shown in (a) and (b). The experimental conditions were the same as those used for Fig. 2, and the solutions used for EIS measurements are the same as those in which the polymer films have been grown.

Fig. 8 shows CVs recorded for the first and 5th cycles during the polymer growth from solutions containing a mixture of: (a) *o*-TP and CHB and (b) *o*-TP and *p*-xylene with their respective concentrations of 25 and 75 mM to make up a total concentration of 0.10 M each. When the two monomers were mixed, two clearly resolved peaks were observed in their CVs during the first cycle. This is because the degree of passivation is not too severe when the *o*-TP concentration is low and, thus, both peaks corresponding to oxidation of CHB and *p*-xylene are observed. From the second cycle on, however, the oxidation peaks of CHB and *p*-xylene were completely blocked due to the highly passivated surface. In CVs of the fifth potential cycle, current scales were extremely low, because the polymer films were effectively passivated due to potential cycling between 3.0 V and a high over-voltage of 5.5 V.

Resistances of the polymer films thus obtained were also evaluated by the impedance measurements. Figs. 8(c) and (d) show EIS results acquired at 5.0 V for the polymer films

prepared from the potential cyclings. The polymer films prepared from the solutions containing mixed monomers show significantly higher resistances in comparison to those of single component polymer films, although the mixed polymer films are thinner than the poly(*o*-TP) film as judged from the CVs shown in Figs. 4 and 8. The mixed polymer films show much better performances as an over-charge inhibitor than their single component counterparts.

4. Conclusion

The effects of many aromatic additives of different chemical structures on the safety of lithium ion batteries during charge-discharge cycles have been systematically evaluated for the first time. Current scales of CVs and impedance data of the films electrodeposited in solution containing various aromatic compounds clearly demonstrate which would serve as an appropriate overcharge inhibitor. Our results indicate that biphenyl and terphenyl

derivatives are good candidates for the preparation of thick polymer films, while benzene derivatives are good candidates for making thin resistive layers. When the candidates from each group are used together in a mixed solution, the mixed polymer film grown thereof gives a better performance than those obtained from solutions containing a single component in that reasonably thick films grow and have higher resistances. This is because polymer films grow quickly from the biphenyl and terphenyl derivatives during initial stages of overcharging processes, which are then subsequently passivated by the polymerization of benzene derivatives.

The polymer film prepared from the solution containing BP and CHB showed a high resistance of 600 k Ω .⁸⁾ However, the resistances of the mixed polymer films grown from the mixed *o*-TP and *p*-xylene solution are much higher than 600 k Ω . Therefore the mixed polymer film grown from *o*-terphenyl and *p*-xylene should be a better choice than the film grown from BP and CHB.

Acknowledgments

This work was supported by the WCU Program (R31-2008-000-20012-0) granted to UNIST.

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