Lithium/sulfur (Li/S) batteries have attracted substantial attention as a next-generation battery candidate because their theoretical energy density (~2500 Wh kg\(^{-1}\)) is much higher than the current C/LiCoO\(_2\) system (387 Wh kg\(^{-1}\)). In addition, sulfur exhibits several impressive characteristics, such as abundance in nature and low toxicity. However, Li/S batteries have several intrinsic problems that affect their practical application. Some of the issues associated with the sulfur cathodes include the low ionic and electronic conductivities of sulfur and Li-S, large volume expansion of sulfur upon lithiation (~80% expansion), and dissolution of intermediate products, namely lithium polysulfides (Li\(_x\)S\(_y\), where 4 ≤ x ≤ 8), into the electrolyte. This dissolution of polysulfide causes “redox shuttle phenomena,” which leads to overcharging (low coulombic efficiency) and rapid capacity fading.

Various strategies have been developed to solve these problems. Since Nazar’s group overcame the low conductivity problem of the sulfur cathode and achieved cycle stability by producing a sulfur–ordered mesoporous carbon (CMK-3) composite, various carbon materials have been studied as hosts for sulfur. In order to suppress polysulfide dissolution, anionic-liquid-based electrolytes have been investigated. Ionic-liquid-based electrolytes show excellent polysulfide dissolution inhibition, while batteries containing the ionic liquid-based electrolytes show relatively high resistances, owing to the high viscosities of these electrolytes. However, the high cost of ionic liquids hinders their practical application compared with commonly used organic electrolytes. There have been many reports on methods for suppressing dissolution of polysulfides by coating or modifying the surface of an active material with a polymer using chemical oxidative polymerization. Conductive polymers, such as poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS), polypyrrole, polythiophene, and polyaniline have also been used to coat sulfur. Many core-shell-structured sulfur composites have been reported. It is important to adjust the homogeneity of an electrode, and strict controls are needed to produce optimal nanostructures. Further improvements are needed to stop the dissolution of polysulfides completely to achieve better sulfur coatings.

Our team reported a novel sulfur-cathode structure consisting of a film formed on the sulfur-based electrode surface, wherein the film acted as a suppressor for polysulfide permeation to overcome the problem of polysulfide dissolution in the electrolyte. The polypyrrole (PPy) film was prepared via oxidative electropolymerization using a solution consisting of 1-methyl-1-butylpyrrolidinium bis(trifluoromethanesulfonfonyl)imide (BMP-TFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and pyrrole.

In this study, proper preparation conditions of the PPy film to prevent polysulfide dissolution and promote Li\(^+\) permeability were investigated by varying the PPy polymerization bath compositions and polymerization potential. In addition, a mechanism to prevent polysulfide dissolution and increase the Li\(^+\) transport number is discussed in this paper. We used a lithium-metal anode to evaluate the PPy-S/KB cathode performance.

**Experimental**

**Material synthesis.**—The S/KB composite was prepared via a previously described procedure. The PPy-S/KB cathode was prepared using oxidative electropolymerization in a three-electrode cell. An S/KB cathode, which was 10 mm × 10 mm in size was used. A platinum wire and lithium foil were used as the counter and the reference electrodes, respectively. Two types of polymerization baths, with and without a lithium salt, were prepared. The first type was composed of a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL), which is known to dissolve polysulfides easily. The above results suggest that the PPy film successfully inhibited polysulfide dissolution.

**Electrochemical measurements.**—A potential range and a scan rate of a linear sweep voltammogram (LSV) were open-circuit potential. A novel polypyrrole (PPy) film was investigated to determine the optimal conditions for operation in a Li/S battery. The PPy film was prepared by oxidative electropolymerization to improve the Li/S battery performance, as reported in our previous paper. In such a system, the PPy film was coated directly on the S/Ketjenblack cathode to solve the problem of polysulfide dissolution. The optimum PPy film preparation conditions to prevent polysulfide dissolution and to promote Li\(^+\) permeability were determined by varying the PPy polymerization bath composition and polymerization potential. As a result, the inclusion of 1.0 M lithium bis(trifluoromethanesulfonfonyl)imide (LiTFSI) in the polymerization bath (0.1 M pyrrole in 1-methyl-1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide) was found to be the most important factor for producing a PPy film with a high Li\(^+\) transport number (t\(_{\text{Li}^+}\) ≈ 1). A polymerization potential of 4.5 V versus Li/Li\(^+\) was shown to be optimum for the promotion of Li\(^+\) permeability. The mechanism by which the PPy film prevents polysulfide dissolution and increases Li\(^+\) permeability is discussed by analyzing the SEM, CV, XPS, and \(^{13}\)C solid-state NMR data.
Material characterization.—The microstructure of the PPy film formed directly on the Ni substrate was observed using a field-emission scanning electron microscope (FE-SEM, S4500S, Hitachi High-Technologies). The Li\(^{+}\) transport number for the PPy film was determined at 80°C through the method used by Bakker et al.\(^{23}\) The measurement method was the same as previously reported.\(^{22}\) For X-ray photoelectron spectroscopy (XPS) measurements, the PPy films, after polymerization, were rinsed thoroughly with ethanol and dried overnight under vacuum. The XPS measurements were carried out using a VersaProbe2 surface analysis instrument (ULVAC-PHI). All XPS spectra were referenced to the C 1s neutral carbon peak at 284.8 eV to compensate for surface-charging effects. The intensities of the XPS spectral peaks were normalized to compare peak positions. Surface elemental stoichiometry was obtained from peak area ratios corrected with the appropriate instrument sensitivity factors. This system had a maximum error of ±10%. Prior to \(^{13}\)C solid-state nuclear magnetic resonance (NMR) analysis, the films were peeled from the Ni substrates, washed thoroughly with ethanol, and dried overnight under vacuum. The films were then crushed and ground with NaCl to avoid arcing in a magnetic field. Magic angle spinning (MAS) was used with a spinning speed between 5 and 8 kHz. The analysis was performed using a JNM-ECA400 (JEOL) instrument, equipped with a solid-state probe operating at 100.53 MHz. Cross-polarization (CP) from \(^1\)H was used to enhance the \(^{13}\)C signal. The number of scans required to attain an adequate signal-to-noise ratio was 20,000.

Results and Discussion

The polymerization solvent and polymerization potential affected the formation and electrochemical properties of the PPy film. The PPy-S/KB cathodes were prepared using ionic liquid polymerization baths with and without Li\(^{+}\) to investigate the effects of the presence of Li\(^{+}\) in the polymerization bath. Figures 1a and 1b show the linear sweep voltammetry (LSV) results for (a) 1.0 M LiTFSI BMP-TFSI and (b) BMP-TFSI with and without 0.1 M pyrrole. In the polymerization bath with Li\(^{+}\), the polymerization current of pyrrole was less than half that of the bath without Li\(^{+}\). This lower current resulted from the high viscosity caused by Li\(^{+}\) moving with the anions in the ionic liquid. Hence, the polymerization current of pyrrole in the polymerization bath with Li\(^{+}\) was limited by Li\(^{+}\) ion diffusion. From these LSV results, three polymerization potentials of 4.0, 4.5, and 5.0 V versus Li/Li\(^{+}\) were selected. At 4.0 V, which is close to the onset potential of pyrrole polymerization, the polymerization current of pyrrole was dominant. At 4.5 V, which is greater than the onset potential of pyrrole polymerization and less than the onset potential of the polymerization bath decomposition, a greater PPy polymerization current flowed than at 4.0 V. At 5.0 V, the polymerization bath decomposition affected the current.

Figures 2a–2f show the charge–discharge voltage profiles of the PPy-S/KB cathode polymerized, 2(a)–2(c), with Li\(^{+}\), and 2(d)–2(f), without Li\(^{+}\), at 4.0, 4.5, and 5.0 V, respectively. The inserted plots in Figs. 2a–2e show discharge capacity and coulombic efficiency versus cycle number. The PPy-S/KB cathode polymerized with Li\(^{+}\) did not show any overcharge caused by polysulfide dissolution. However, a significant overcharge was observed in the initial cycles, and rapid capacity degradation occurred on the PPy-S/KB cathode polymerized without Li\(^{+}\). In the case of the PPy-S/KB cathode polymerized without Li\(^{+}\), the PPy-S/KB cathode polymerized without Li\(^{+}\) at 5.0 V, the charge current continued to flow even after the capacity reached the theoretical value during the 1st cycle, and additional cycles could not be completed, as shown in Fig. 2f. The PPy-S/KB cathode polymerized with Li\(^{+}\) did not show any overcharge caused by polysulfide dissolution. However, a significant overcharge was observed in the initial cycles, and rapid capacity degradation occurred on the PPy-S/KB cathode polymerized without Li\(^{+}\). In the case of the PPy-S/KB cathode polymerized without Li\(^{+}\), the PPy-S/KB cathode polymerized without Li\(^{+}\) at 5.0 V, the charge current continued to flow even after the capacity reached the theoretical value during the 1st cycle, and additional cycles could not be completed, as shown in Fig. 2f. The PPy-S/KB cathode polymerized with Li\(^{+}\) showed 939 and 570 mA h g\(^{-1}\) at the 1st and 50th cycle, respectively, with over 97% coulombic efficiency, as shown in Fig. 2a. In addition, a slight shoulder at ~2.8 V was noticeable in the discharge curves. This shoulder resulted from the redox reaction of PPy, and it will be discussed in detail below with the presentation of Fig. 5. The PPy-S/KB cathode polymerized with Li\(^{+}\) at 4.5 V demonstrated a high capacity of 1037 mA h g\(^{-1}\) at the 1st cycle and good capacity retention of 691 mA h g\(^{-1}\) after the 50th cycle (with over 99% coulombic efficiency), as shown in Fig. 2b. The PPy-S/KB cathode polymerized at 5.0 V exhibited capacities of 491 and 193 mA h g\(^{-1}\) at the 1st and 50th cycles, respectively, as shown in Fig. 2c. The PPy-S/KB cathode polymerized without Li\(^{+}\) at 4.0 V exhibited 1020 and 472 mA h g\(^{-1}\) at the 1st and 50th cycles, respectively, with a low coulombic efficiency of 82% during the initial cycles, as shown in Fig. 2d. As we saw in the charge-discharge profiles with Li\(^{+}\), a slight shoulder at ~2.8 V was seen in the discharge curves without Li\(^{+}\). For the PPy-S/KB cathode polymerized without Li\(^{+}\) at 4.5 V, the 1st discharge capacity was 1047 mA h g\(^{-1}\) with significant overcharge, and the 50th was 509 mA h g\(^{-1}\). Hence, it is evident that the PPy film polymerized without Li\(^{+}\) has a low Li\(^{+}\) transport number. In addition, if the PPy film was polymerized with Li\(^{+}\), the Li\(^{+}\) permeability of the PPy film is likely to differ by the polymerization potential. The Li\(^{+}\) transport number was determined for the PPy films polymerized at 4.0 and 4.5 V with and without Li\(^{+}\) using the technique previously reported.\(^{22}\) The PPy films polymerized with and without...
Li⁺ at 5.0 V could not be evaluated because they were difficult to prepare as self-supporting films, as described later in Fig. 4f. The lithium-titanium oxide (LTO) electrode separated by the PPy film was immersed in a sample solution with a LTO reference electrode and analyzed by measuring the potential shift between the electrodes. Figure 3 shows the potential shift of the PPy film versus the Li⁺ concentration of the sample solution. The reference for the potential shift was the potential of a 1.0 M LiTFSI solution. The theoretical slope calculated using the Nernst equation and Nernst constant at 80 °C and 70 mV is plotted in the figure. The potential shift of the PPy film polymerized without Li⁺ at 4.0 and 4.5 V did not drop below 30 and 6 mV, respectively, even though the Li⁺ concentration of the sample solution was changed from 10⁻¹ to 10⁻³ M. We confirmed that the PPy film polymerized without Li⁺ has a low Li⁺ transport number. Thus, the PPy film polymerized without Li⁺ allowed passage of Li⁺ and TFSI⁻. Presumably, the polysulfide passed through the PPy film because the sizes of TFSI⁻ and S₄⁻, which is a major polysulfide anion, are almost same. Therefore, both overcharging and rapid capacity degradation, caused by polysulfide dissolution, occurred when the PPy-S/KB cathode was polymerized without Li⁺, as shown in Figs. 2d–2f. In contrast, for the PPy film polymerized with Li⁺, the magnitude of the potential shift decreased as the Li⁺ concentration in the solution decreased. We have already reported that the Li⁺ transport number through the PPy film polymerized with Li⁺ at 4.5 V was close to unity, which is also shown in Fig. 3 for the reference. Since the slope of the measured plots for the PPy film polymerized with Li⁺ at 4.0 V was similar to the theoretical slope, we concluded that this PPy film also has a high Li⁺ transport number. It is presumed that the PPy film polymerized in the bath including Li⁺, Li⁺ is incorporated into the film along with the TFSI⁻ as shown in the following data in Fig. 6. Therefore, a Li⁺ conducting path can be formed to retain a high Li⁺ transport number.

FE-SEM images of PPy films polymerized at 4.0, 4.5, and 5.0 V in a bath with Li⁺ were prepared to investigate the effects of the

Figure 2. Charge–discharge voltage profiles of coin cells consisting of [PPy-S/KB // LiTFSI DME/DOL (1:1 vol%) // Li] cycled at 0.03 C (25 μA). The PPy-S/KB cathode polymerized with Li⁺ at (a) 4.0, (b) 4.5, and (c) 5.0 V versus Li/Li⁺, and polymerized without Li⁺ at (d) 4.0, (e) 4.5, and (f) 5.0 V versus Li/Li⁺. The dashed lines represent the first cycle, and the solid lines represent subsequent cycles. The inserted plots in (a)–(e) show discharge capacity and coulombic efficiency versus cycle number.
polymerization potential on morphology. Figures 4a–4c show the top-surface views (× 6.0 k) and Figs. 4d–4f show the cross-sectional views (× 10.0 k) of the PPy films polymerized at 4.0, 4.5, and 5.0 V, respectively. Fig. 4a showed a smooth and uniform surface. In contrast, rough surfaces with a PPy aggregation size varying from less than 1 micron to several microns were observed in Figs. 4b and 4c. The thickness of the PPy film decreased as the polymerization potential increased (5.2 μm at 4.0 V, 3.6 μm at 4.5 V, and 3.0 μm at 5.0 V), even though the amount of charge passed was fixed at 1.0 C cm$^{-2}$. This result may have been caused by the difference in conductivity of the PPy films. The cross-sectional form of the PPy films polymerized at 4.0 and 4.5 V have a constant cross-sectional shape. On the other hand, the PPy film polymerized at 5.0 V has a non-uniform cross-sectional shape with some visible voids. The surface roughness of PPy depends upon the formation potential. When PPy was polymerized at 4.0 V, the polymerization process proceeded rather slowly. The slow polymerization process smoothed the surface. In contrast, an increase in the growth rate of the films due to the higher applied potential of 5.0 V resulted in a rougher film. The morphology of the PPy film polymerized at 4.5 V has characteristics between the other two films.

Cyclic voltammograms of each PPy film were obtained to investigate the electrochemical properties of each PPy film polymerized directly on a Ni substrate with Li$^+$ at 4.0, 4.5, and 5.0 V. Figure 5 shows the 2nd cycle of the cyclic voltammogram for each PPy film. A PPy redox peak was observed at ∼3.0 and ∼3.3 V on the PPy film polymerized at 4.0 and 4.5 V, respectively. The PPy film polymerized at 5.0 V showed only an anodic peak at ∼3.5 V and almost no cathodic peak. We also confirmed a similar tendency for the PPy film polymerized without Li$^+$. Generally, a redox reaction of PPy proceeds via the doping–undoping reaction of the anion (TFSI$^-$, in this case). If an anion redox reaction occurs, polysulfide might pass through the film. This might occur because the sizes of TFSI$^-$ and S$_4^{2-}$ are approximately the same. However, it is known that when a large polyanion is doped in a PPy film, some cation exchange characteristics manifest themselves. On the other hand, when Li$^+$ with a large diffusion coefficient is present in the film, even with low-molecular-weight dopant anions (e.g., ClO$_4^-$, TOS$^-$, and TFSI$^-$), cation exchange characteristics also appear. Thus, we see that some redox peaks, corresponding to Li$^+$ expulsion/incorporation, are observed for
Figure 6. Core-level photoelectron peaks of F 1s, O 1s, N 1s, C 1s, S 2p, and Li 1s for PPy films polymerized with Li+ at 4.0, 4.5, and 5.0 V versus Li/Li+. The film properties of doped ions are discussed in the following paragraphs by the analysis of XPS and 13C solid-state NMR spectra. Figure 6 shows the F 1s, O 1s, N 1s, C 1s, S 2p, and Li 1s XPS core-level spectra of the PPy films polymerized at 4.0, 4.5, and 5.0 V. Typical peaks derived from PPy and the dopant anion (TFSI−) were observed in every spectrum. The main C 1s peak (284.8 eV) demonstrated the major contribution of the C=\(\text{C}\) bonds in PPy20 and the shoulder on the high energy side originated from the C–N bonds in PPy20 and the C–S bonds in TFSI−.30 The N 1s spectra showed two characteristic peaks of the neutral pyrrolylium nitrogen (N0) at a binding energy of 399 eV, and the positively charged nitrogen (N+) at 402 eV.29 The main F 1s peak (688.6 eV) and the peak at the highest binding energy (292.5 eV) on the C 1s spectra could be assigned to –CF3 in LiTFSI.30 The presence of –SO2 in LiTFSI was supported by the O 1s peak (532.5 eV) and the S 2p peak (168.5 eV).31 Some differences in the polymerization potentials were observed in the spectra of N 1s and C 1s. Comparing the ratios of N+ and N0 for each polymerization potential on the N 1s spectrum, the PPy film polymerized at 4.5 V demonstrated the greatest N+ ratio of 43%. On the C 1s spectrum, only the PPy film polymerized at 5.0 V showed a peak due to Li2CO3 at 289 eV.31 These results were consistent with the LSV results, which showed the decomposition reaction of the polymerization solvent occurring at ∼4.8 V (Fig. 1a). The molar ratios of TFSI−, N, and C, which were estimated from the atomic percentages of the main components in the film, are listed in Table I. The ratio of TFSI− was calculated using the atomic ratios of F 1s and S 2p. The ratios of N and C were obtained by subtracting the components contained in TFSI−. The amount of TFSI− in the PPy films was the greatest in the film polymerized at 4.5 V. Focusing on the ratio of N:C bonds in PPy20 and the C–S bonds in TFSI−,30 the PPy films polymerized at 4.0 and 4.5 V work well as Li+ permselective films, which result in good battery performance, as shown in Figs. 2a and 2b. On the other hand, the PPy film polymerized at 5.0 V did not show such a redox reaction due to extensive polymer decomposition. It was confirmed that the electrochemical activity of PPy decreased as the polymerization potential increased. PPy is a conductive polymer consisting of a π-conjugated system. However, when the polymerization potential is high enough, PPy gradually oxidizes, resulting in a shift of the redox peak to higher potentials. At 5.0 V, cleavage of the pyrrole ring and cross-linking occurs, breaking the π-conjugated system. Thus, the PPy film polymerized at 5.0 V without redox is no longer a conductive film.

| atm.% | F 1s | O 1s | N 1s | C 1s | S 2p | Li 1s | molar ratio TFSI− : N : C |
|-------|------|------|------|------|------|------|--------------------------|
| 4.0 V | 18.7 | 21.0 | 10.0 | 37.6 | 4.7  | 8.0  | 2.4 : 7.6 : 33.0          |
| 4.5 V | 25.2 | 15.6 | 7.8  | 38.2 | 7.5  | 5.6  | 3.8 : 4.0 : 30.7          |
| 5.0 V | 9.5  | 18.6 | 4.7  | 61.8 | 3.4  | 2.1  | 1.7 : 3.0 : 58.4          |
Figure 7. 13C solid-state NMR spectra of PPy films polymerized with Li+ at 4.0, 4.5, and 5.0 V versus Li/Li+. (•) Spinning sideband.

in order to estimate the composition of the PPy film polymerized at 4.0 V, the ratio was ∼1:4; for that at 4.5 V, it was ∼1:7; and for that at 5.0 V, it was ∼1:20. The N:C atomic ratio for the film polymerized at 4.0 V agreed reasonably well with the ideal PPy stoichiometry of 1:4. These results indicate an undamaged polymer structure at a low polymerization potential. At 4.5 V, the ratio of N was greater than that of the ideal PPy. On the other hand, a serious decomposition of the polymer and the solvent occurred at 5.0 V. Considering the previously described high proportion of oxidation state nitrogen in the PPy film polymerized at 4.5 V, BMP2+, which is a cationic component of the film liquid serving as the polymerization solvent, might have been incorporated in the PPy film. Some N+ species from oxidized pyrrole and the cations of the ionic liquid were detected via XPS when the films were grown in a quaternary ammonium ionic liquid. Further investigation of PPy films were conducted using 13C solid-state NMR.

Figure 7 shows the 13C solid-state NMR spectra of the PPy films polymerized at 4.0, 4.5, and 5.0 V. The 13C NMR spectra of the PPy films show broad resonances centered around 120 ppm. It has been reported that PPy consists of essentially α-type linkages with the main carbon resonance at ∼120 ppm. The position of the high-frequency resonance at 143 ppm is consistent with the presence of the quinoid carbons of PPy, since these carbons were less shielded than their aromatic counterparts. Focusing on the signal-to-noise ratio, the film polymerized at 4.5 V had the sharpest signal derived from PPy, whereas the signal was broad in the film polymerized at 4.0 V, and could be barely seen in the film polymerized at 5.0 V. These PPy resonances can be reproduced by fitting three Gaussian peaks with chemical shifts at 120, 143, and 170 ppm with an accuracy of ±1 ppm. Comparing the 4.0 V with the 4.5 V spectra by the half width at half maximum (HWHM) of the peaks at 120 ppm, the 4.0 V signal was slightly narrower than the 4.5 V signal. For slowly tumbling molecules such as polymers, the T1 relaxation times can be quite long. The T1 relaxation time of the PPy film polymerized at 4.5 V was considered to have a broad signal due to its high PPy density.33

Combining the 13C NMR data with the XPS results suggests that, at 4.0 V, the film has become relatively dense having PPy and TFSI− as the main components. Hence, it is considered a low Li+ permeable film. On the other hand, a sharp signal was observed for the PPy film polymerized at 4.5 V, so it is considered a low-density PPy. In the spectrum of the PPy film polymerized at 4.5 V, the peak around 70 ppm was observed, which we interpreted as a spinning sideband (SSB). This SSB was observed because the intensity of the signal around 120 ppm was prominent. There was also significant signal intensity between 10 and 30 ppm, which corresponded to the alkyl chains of BMP2+ within the film.34 The PPy film polymerized at 4.5 V is supposed to contain TFSI−, Li+, and BMP2+ components of the ionic liquid. We confirmed that the percentages of TFSI−, BMP2+, and Li+ within the PPy film differed due to the polymerization potential. For the film polymerized at 5.0 V, the resonance of the PPy around 120 ppm was barely detectable. Therefore, the PPy backbone seems to have decomposed due to the high polymerization potential of 5.0 V. In electropolymerization, the stability of the intermediate radical cations of pyrrole can be determined mainly by the polymerization potential, solvent, and nucleophile anions. It has been reported that the distributions of α-ε, α-ɛ, and β-β type linkages within PPy change in ionic liquids. Therefore, the stability of pyrrole radical cations improved more in ionic liquids than in molecular solvents.35 In a typical organic solvent, in which the polymerization potential was much greater than the on set potential of PPy, the reactivity of the radicals was too high to react with substances around the radicals. However, such impaired reactions did not occur in ionic liquids, even at high polymerization potentials. The only change in the ionic liquid was the features and the materials incorporated into it. The addition of dopant anions and cationic components from the ionic liquid incorporated into the film was expected to have a significant effect on the Li+ permeability of the PPy film. Briefly, the PPy film had good enough Li+ permeability for a sulfur-cathode coating when polymerized at a relatively high potential of 4.5 V, in which TFSI− is incorporated abundantly in the film, as shown in Table I.

Conclusions

The optimal electropolymerization conditions for a Li+ permeable PPy film to prevent polysulfide dissolution on an S/KB cathode were investigated. Important factors for PPy preparation on an S/KB cathode were the presence of Li+ in the polymerization bath (0.1 M pyrrole and 1.0 M LiTFSI in BMP-TFSI) and a relatively high polymerization potential of 4.5 V versus Li/Li+. Adding LiTFSI to the polymerization bath had a major effect on the Li+ transport number for the PPy film. The polymerization potential affected the Li+ permeability of the PPy film because more TFSI− and BMP2+ are incorporated in the film at the higher polymerization potential of 4.5 V. Finally, the importance of optimizing the polymerization conditions of PPy on the S/KB cathode was demonstrated by considering a mechanism to improve the Li+ transport number of the PPy film.

Acknowledgments

This work was partly supported by the “Advanced Low Carbon Technology Research and Development Program, Specially Promoted Research for Innovative Next Generation Batteries (ALCA Spring)” from the Japan Science and Technology Agency (JST), Japan.

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