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Polyaniline as a Functional Binder for $LiFePO_4$ Cathodes in Lithium Batteries

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Chemically synthesized polyaniline (PANI) can be used as a functional binder in the manufacture of the $LiFePO_4$ cathode of lithium batteries, and it provides $LiFePO_4$ particles with effective conduction paths, leading to a very low resistance electrode.

Conducting polymers have been broadly researched as electrode materials for electrochemical devices.[1,2] From among these, polyaniline (PANI), which has a highly stable oxidation state and good conductivity, has been studied as a polymeric cathode material for lithium batteries (LIBs).[3] However, the density of PANI is lower than that of transition-metal oxide cathode materials such as $LiCoO_2$. Therefore, the energy density of an LIB with a PANI cathode is smaller than that of present-day practical LIBs with transition-metal oxide cathodes. Kuwabata et al. reported that a composite electrode comprising PANI and V_2O_5 exhibits excellent charge and discharge performance. They used PANI as a double-functional material, namely, as a redox-active material and a binding material for the V_2O_5 particles. Apart from the pioneering work by Kuwabata et al.,[4] composite cathodes consisting of $LiFePO_4$ and conducting polymers including electropolymerized polypyrrole (PPy)[5a,5b] and chemically polymerized PANI[5c] were studied by several researchers. $LiFePO_4$ is a less expensive material than conventional $LiCoO_2$ cathodes, and extensive research[6] on this material is now being carried out to realize large-scale LIBs for electric vehicles. The redox of $LiFePO_4$ takes place at a potential of 3.5 V vs. Li/Li^+,[5] which is very close to the redox potentials of PANI and PPy. These conducting polymers also show good compatibility with the $LiFePO_4$ cathode for LIBs. However, the electropolymerization method[5a,5b] is not suitable for manufacturing composite $LiFePO_4$/conducting polymer cathodes using a practical production line in a battery factory. And compared with PPy, the capacity of PANI is usually high, which is strongly dependent on doping.[7] In conventional composite cathodes, binders, such as poly(vinylidene difluoride) (PVDF) and Teflon (PTFE), were used.[5] However, they were minimized for high energy density because of their low conductivity. In the present study, PANI was chemically synthesized and used as a binding material for the fabrication of a $LiFePO_4$ cathode for LIBs. For using PANI as the binder, improvements in the adhesion to the current collector foil and the capacity of the electrode were obtained.

PANI was prepared by the chemical oxidation of aniline, which is a convenient method for the synthesis of large quantities of PANI, as is described elsewhere.[4] Aniline (Wako Pure Chemical Industries, Ltd.) and ammonium persulfate (Wako Pure Chemical Industries, Ltd.) were reacted in a 2 mol dm^{-3} aqueous H_2SO_4 solution, forming PANI doped with SO_4^{2-}. This compound was reacted with hydrazine monohydrate/methanol (5/95, v/v) under a nitrogen atmosphere. Dedoped PANI was obtained as a gray powder. The $LiFePO_4$ composite cathode was prepared using PANI as the binding material (Figure 1). The composite cathode sheet was prepared as follows. A carbon-coated $LiFePO_4$ ($LiFePO_4$/C, carbon content: 1 wt %, SUMITOMO OSAKA CEMENT Co., Ltd.), acetylene black (AB, Denki Kagaku Kougyo), and PANI were mixed in the weight ratio shown in Table 1, and the mixture was thoroughly agitated in a solvent of *N*-methylpyrorridone (NMP) (Wako Pure Chemical Industries, Ltd.) using a mortar. The mixed paste was applied to an aluminium current collector using an automatic applicator. After drying the applied paste in vacuo at 100 °C for 24 h, the composite sheet was cut into a circular shape (14 mm diameter) and compressed using a uniaxial pressing machine at 100 kgf cm^{-2}. A composite cathode with a PVDF binder, which is generally used as the binding material in cathode electrodes, was also prepared to obtain reference data. The composite electrodes were stored in an argon-filled glove box to avoid the oxidation of PANI. The composite cathodes prepared using binders of PVDF and PANI are denoted as $LiFePO_4$–PVDF and $LiFePO_4$–PANI, respectively. To evaluate the charge–discharge performance of the composite cathodes, a hermetic cell was fabricated in an argon-filled glove box. Lithium metal foil (Honjo Metal Co., Ltd.) was used as the anode, and a porous polyolefin film (Celgard #2400) was used as the separator between the anode and the cathode. The electrolyte was 1 mol dm^{-3} $LiPF_6$ in a 1:1 solvent mixture of ethylene carbonate

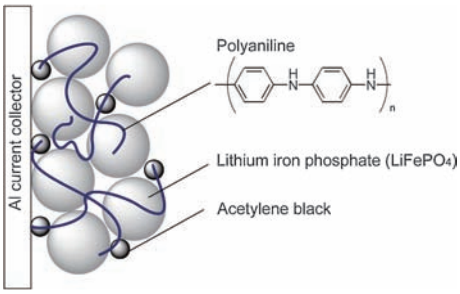

Figure 1. Schematic illustration of the composite polyaniline/$LiFePO_4$ cathode.

Table 1. Compositions of the composite cathodes

Sample name	$LiFePO_4$/C /wt %	AB /wt %	PANI /wt %	PVDF /wt %
PANI	—	—	100	—
$LiFePO_4$–PVDF	85	9	—	6
$LiFePO_4$–PANI	85	9	6	—

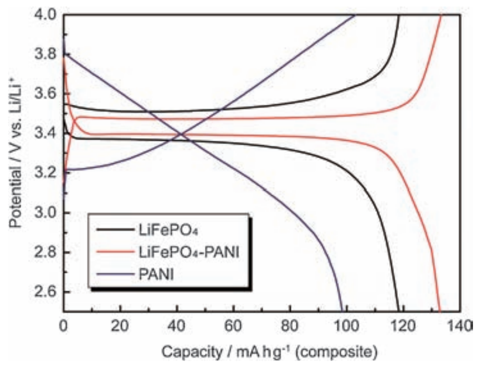

Figure 2. Fifth charge–discharge curves for the [Li metal|1 M $LiPF_6$/EC–DEC|PANI, $LiFePO_4$–PVDF, or $LiFePO_4$–PANI] cells measured at 1 C rate.

and diethyl carbonate (EC–DEC) purchased from Kishida Chemical Co., Ltd. In this paper, the charge and discharge capacities of the cathode were calculated based on the total mass of the composite ($LiFePO_4$/C + AB + binder).

Bending tests were carried out to evaluate the adherence of the composite film to Al. The composite film fabricated on Al foil was bent to 90°, three times. The $LiFePO_4$–PANI composite film showed good adhesion to the Al current collector, while the $LiFePO_4$–PVDF composite film partially peeled off (Supporting Information; SI, Figure S1).[10] Therefore, it is evident that PANI has an improved adhesive ability compared to the PVDF binder.

To check the electrochemical behavior of the chemically synthesized PANI, a PANI film without AB and $LiFePO_4$/C was prepared by casting the PANI/NMP solution on an Al foil. After drying the PANI film, galvanostatic charge and discharge measurements were performed using a [PANI film on Al foil|1 M $LiPF_6$/EC–DEC|Li metal] cell (SI, Figure S2).[10] The PANI film electrode showed redox behavior in the voltage range of 3.2–4.0 V. During the charge, the oxidation of PANI took place and the counter anion, PF_6^-, was inserted into the film. Anion dedoping occurred during the course of discharge. The charge and discharge capacity of pure PANI in this voltage range was ca. 100 mA h g^{-1}, which is in good agreement with previous reports.[4]

Figure 2 shows the charge–discharge curves of the fifth cycle of [Li metal|1 M $LiPF_6$/EC–DEC|PANI, $LiFePO_4$–PVDF, or $LiFePO_4$–PANI] cells measured at 303 K. The charge–discharge measurements for the PANI, $LiFePO_4$–PVDF, and $LiFePO_4$–PANI composite electrodes were performed at current densities of 33, 230, and 190 μA cm^{-2}, respectively (approximately 1 C rate). As expected, the $LiFePO_4$–PVDF electrode showed plateaus at 3.5 and 3.4 V during the charge and discharge, respectively, due to the redox of $Fe^{2+/3+}$ in the olivine framework structure. The discharge capacity of the $LiFePO_4$–PVDF electrode was 119 mA h g^{-1} based on the total mass of the composite, which corresponds to 81% utilization of the active material ($LiFePO_4$). The $LiFePO_4$–PANI composite electrode showed a discharge capacity of 132 mA h g^{-1}, which is larger than that of $LiFePO_4$–PVDF electrode. The capacity due to the redox of PANI also contributed to the capacity. However, since the PANI content is only 6 wt % in the $LiFePO_4$–PANI composite, the capacity added due to the redox of PANI should be 6 mA h g^{-1} composite, assuming that the specific capacity in this voltage range is 100 mA h g^{-1} PANI. Therefore, it is presumed that the utilization of the active material ($LiFePO_4$) was increased by using PANI as a binder. Furthermore, the polarization during the galvanostatic charge and discharge of $LiFePO_4$–PANI is clearly smaller than that of $LiFePO_4$–PVDF. The $LiFePO_4$ itself has very low electric conductivity; therefore, the $LiFePO_4$ particles are generally carbon coated to achieve effective current collection from the particles in the cathode.[8] In addition to carbon coating, conductive agents such as AB are mixed into the cathode to reduce the electrical resistance of the cathode. However, the unstable contact between the $LiFePO_4$/C particles and the AB particles may cause high resistance, leading to significant polarization during charge and discharge. It seems that the good conductivity of PANI in the $LiFePO_4$–PANI composite cathode reduces the electronic resistance between the $LiFePO_4$/C and AB particles. It is well known that anion-doped PANI has a high electrical conductivity.[9] The intimate contact between the $LiFePO_4$/C particles and PANI, which are formed during cathode fabrication, is effective in diminishing the resistance of the composite cathode.

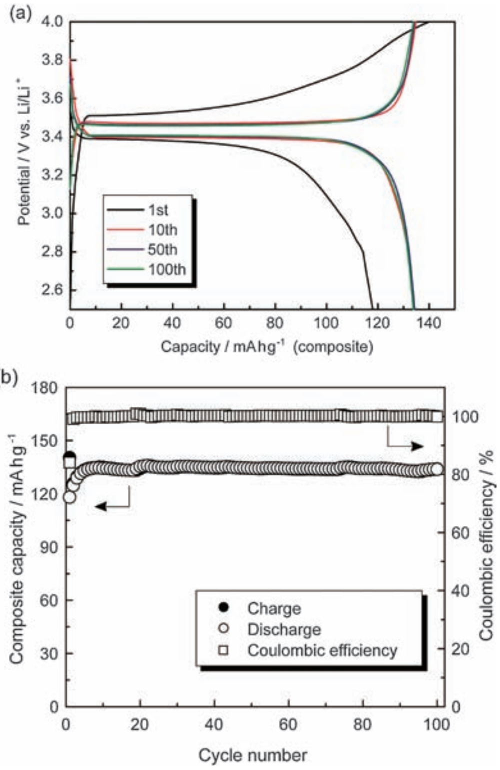

Figure 3. (a) First, 10th, 50th, and 100th charge–discharge curves and (b) cycling properties during 100 cycles for the [Li metal|1 M $LiPF_6$/EC–DEC|$LiFePO_4$–PANI composite electrode] cell measured at 1 C rate.

Figure 3a shows the first, 10th, 50th, and 100th charge–discharge curves of the [Li metal|1 M $LiPF_6$/EC-DEC|$LiFePO_4$–PANI composite electrode] cell. Small, irreversible capacity was observed in the first cycle. However, the Coulombic efficiency after the second cycle was greater than 99%. The irreversible capacity was probably due to the partially irreversible anion doping of PANI; indeed, similar irreversible behavior was observed for the PANI film electrode (SI, Figure S2).[10] In the

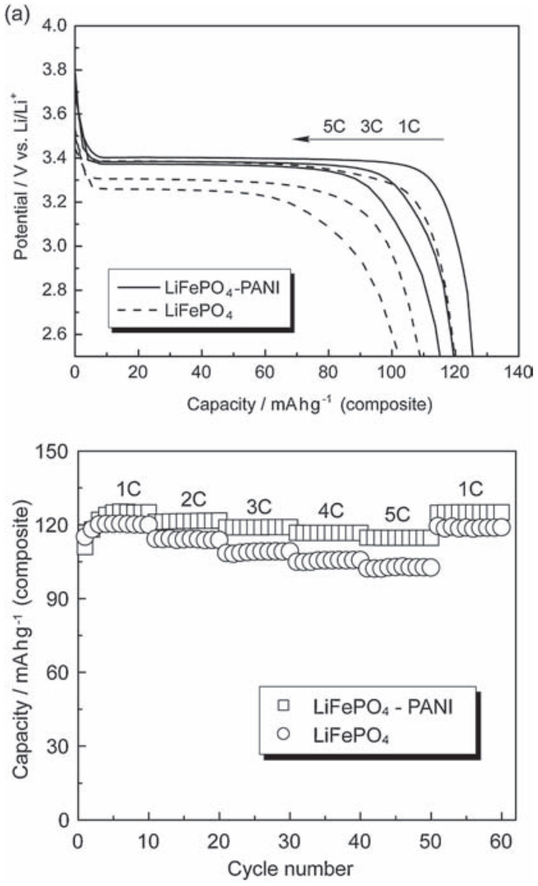

Figure 4. (a) Discharge curves and (b) discharge capacities of [Li metal|1 M $LiPF_6$ EC–DEC|$LiFePO_4$–PVDF or $LiFePO_4$–PANI composite electrode] cells measured at various C-rates.

first cycle, the polarization of charge and discharge was relatively high compared to those of subsequent cycles. The mass-transfer resistance of the electrolyte in the pristine $LiFePO_4$–PANI composite was probably high because the PANI was not swollen with electrolyte. The swelling of PANI might occur due to the absorption of solvents and anion doping during the first charge process, resulting in a decrease in the mass-transfer resistance in the subsequent cycles. After the second cycle, the $LiFePO_4$–PANI cathode exhibited a high capacity of 134 mA h g^{-1} and a good Coulombic efficiency of 99%, as shown in Figure 3b.

Figure 4 shows the rate capability of the [Li metal|1 M $LiPF_6$/EC–DEC|$LiFePO_4$–PVDF or $LiFePO_4$–PANI composite electrode] cells measured at 303 K. All charging processes were performed at 1 C, and discharge was performed at 1, 2, 3, 4, and 5 C, and then 1 C again for 10 cycles. The discharge voltage plateau and discharge capacity of the $LiFePO_4$–PVDF composite cathode decreased with an increase in the current density. The voltage decrease suggests that the iR drop increased with increasing current density. On the other hand, a remarkable increase in polarization was not observed for the $LiFePO_4$–PANI composite electrode even at a 5 C rate. Furthermore, the discharge capacity of the $LiFePO_4$–PANI composite at the 5 C rate was as high as 116 mA h g^{-1}. Clearly, the rate of $LiFePO_4$–PANI is better than that of $LiFePO_4$–PVDF. It seems that the intimate contacts between the $LiFePO_4$/C particles and PANI improves the electronic conductivity between the $LiFePO_4$/C and AB particles, resulting in the good rate of the composite cathode.

In summary, we prepared a composite cathode composed of $LiFePO_4$/C and PANI for LIBs. PANI showed a nice binding ability to form a composite electrode on an Al foil substrate. In addition, PANI contributes to the charge and discharge capacities of the composite cathode through anion doping and dedoping. The high electrical conductivity of the anion-doped PANI decreased the resistance of the cathode, leading to a high rate of the $LiFePO_4$–PANI composite electrode. In conclusion, this study demonstrates that the chemically synthesized PANI can be used as a functional binder for the $LiFePO_4$ cathodes of LIBs.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.