



Short communication

Redox active poly(*N*-vinylcarbazole) for use in rechargeable lithium batteries

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ABSTRACT

The performance of poly(*N*-vinylcarbazole) (PVK) for use in rechargeable lithium batteries was investigated. The positive-electrode (cathode) using PVK as an active material exhibited a discharge capacity of more than 120 mAh g⁻¹ (PVK) with a mean potential of 3.7 V vs. Li⁺/Li. The PVK-electrode showed a stable cycle-life performance. In addition, the application of this polymer as a redox active binder material was also examined using a composite electrode with lithium iron phosphate (LiFePO₄). The LiFePO₄-PVK composite electrode showed a higher total discharge capacity than the conventional LiFePO₄-PVDF electrode.

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1. Introduction

Lithium-based batteries have recently become one of the major power sources for day-to-day portable devices. Various materials have been proposed to significantly increase their energy densities. In addition, another demand has recently been increasing due to concerns about the resource scarcity and environmental issues; namely, rare metal-free and low-polluting safe materials are desirable especially for the positive-electrode materials, and organic materials that do not include any heavy metals have recently been attracting attention as alternative active materials [1–11].

Several types of organic positive-electrode materials have already been proposed. Among them, classical conductive polymers, represented by polyaniline and polythiophene, which have π -conjugated chain structures that form electron pathways, have been studied because of their potentially high energy densities [3]. However, their capacities observed in experiments are much lower than the expected theoretical values due to the relatively low upper limit of their doping level.

Another group of organic positive-electrode polymers is a series of pendant-type polymers, which are characterized by nonconjugated backbones and redox centers localized in pendant groups, such as tetramethylpiperidine-*N*-oxyl (TEMPO) [4] and ferrocene [5]. These polymers tend to exhibit moderate discharge capacities which are close to their theoretical capacities, although their electronic conductivities are generally low. Among the pendant-type polymers, poly(*N*-vinylcarbazole) (PVK or PVCz) (Fig. 1) is known

as a photoconductive polymer and has been studied as a functional material for use in electroluminescence and photovoltaic devices [12]. The conduction mechanism of PVK is different from other conventional conductive polymers carrying π -conjugated chain structures; its electronic pathway is formed by the π -stacked structure of the carbazole moiety in the polymer [13]. In addition, the carbazole moiety is known to undergo a redox reaction above 1 V vs. NHE [14–17], which implies the possibility of a polymer having this moiety as a positive electrode material.

From the viewpoints of such an electrochemical property and unique structure of PVK, we focused our attention on this polymer as a positive-electrode active material for use in rechargeable lithium batteries. The preliminary battery performance of PVK was first reported a few decades ago [18] followed by a few papers [19,20]. However, these reports only described some partial charge/discharge curves, and the utilization ratio limit of this polymer as a battery material was unknown [18–20]. In this study, we re-evaluated the battery performance of PVK as an active material, and found that this polymer shows a high doping level during the charge/discharge process and a stable cycling stability. In addition, we found that PVK can be used as a binder material which replaces the electrochemically inactive binder and augments the total capacity of the conventional inorganic electrode.

2. Experimental

2.1. Materials

Poly(*N*-vinylcarbazole) (PVK) (average molecular weight: 1.1×10^6 g mol⁻¹, density: 1.2 g cm⁻³) was purchased from the Sigma-Aldrich Corp. and used without further purification.

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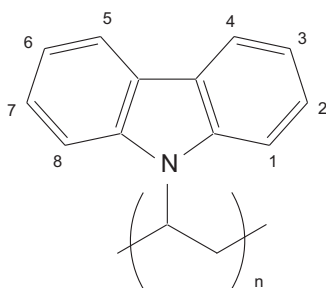


Fig. 1. Chemical structure of PVK.

Polyvinylidene fluoride (PVDF) powder and its solution in *N*-methyl-2-pyrrolidone (NMP) (KF Polymer L#1120) were purchased from the Sigma–Aldrich Corp. and the Kureha Corp., respectively. The carbon layer deposited lithium iron phosphate (LiFePO_4) (primary particle diameter: 70–100 nm), which was used in the preparation of the composite electrodes, was provided by Mitsui Engineering & Shipbuilding Co., Ltd. [21–23].

2.2. Preparation of electrodes and cells

The electrodes and coin-type sealed cells for the battery tests were prepared as follows. A slurry for the positive electrode was first prepared by mixing PVK, ketchen black (KB), and vapor-grown carbon fiber (VGCF) as the conductive additives, and PVDF as the binder in a weight ratio of 5:2:2:1 with NMP. The prepared slurry was laid on an aluminum-sheet current collector, and the resultant electrode was dried, and then roll-pressed. To evaluate the binder property of PVK, a composite electrode was prepared and compared with a conventional one using PVDF as the binder. In this case, the carbon layer deposited LiFePO_4 was used as a main positive-electrode active material. For these composite electrodes, slurries made of the LiFePO_4 powder, PVK or PVDF, and KB in the weight ratio of 16:3:1 with NMP were used. The prepared positive-electrode and lithium metal sheet as a negative-electrode were placed into an IEC R2032 coin type cell case with a glass filter as the separator. After an electrolyte of the mixed solvent of ethylene carbonate and diethyl carbonate (1:1) containing 1.0 mol L^{-1} lithium hexafluorophosphate was added, the cell case was sealed.

2.3. Measurements

For the charge/discharge cycle-life test of the cell using the PVK electrode, the prepared coin-type cell was galvanostatically charged at a current density of $20 \text{ mA g}^{-1} (\text{PVK})$ with a cutoff potential of 4.7 V vs. Li^+/Li , and galvanostatically discharged at the same current density to a cutoff potential of 2.0 V vs. Li^+/Li . The high-rate capability of the electrode was examined by discharging at various current densities after several cycles. In this paper, the obtained capacities are expressed in terms of per mass of the active materials. For the LiFePO_4 -based composite electrodes, the prepared coin-type cells were charged and discharged at a current density of $30 \text{ mA g}^{-1} (\text{LiFePO}_4)$ in the same potential range. The charge/discharge tests were performed using a computer-controlled system (BLS series, Keisokuki Center Co., Ltd.) equipped with a thermostatic chamber at 30°C .

Differential scanning calorimetry (DSC) tested the PVK powder to clarify the thermal stability using a thermoanalytical apparatus (DSC8230HP, Rigaku Corp.) at the heating rate of $10^\circ\text{C min}^{-1}$ under a hydrogen atmosphere.

In order to assess the mechanical strength of PVK as a binder, we carried out the tensile strength test against shear stress on PVK

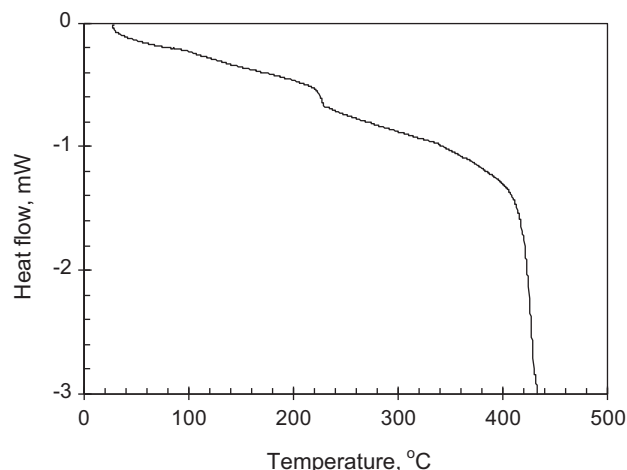


Fig. 2. DSC thermogram of PVK powder.

and PVDF. Two sheets of polypropylene were stuck each other with $10 \mu\text{L}$ of the polymer solutions (25 g L^{-1} , PVDF or PVK in NMP) in such a way that the bonding area be 1 cm^2 . The force needed to shear apart the polypropylene sheets were measured using a digital force gauge (ad-4932a-50N, A&D). The results were expressed as the average of six runs \pm the standard deviation.

The morphology of the prepared electrode was examined using a scanning electron microscope (SEM) (JSM-6390, JEOL, Ltd.).

3. Results and Discussion

3.1. Thermal behavior of PVK and morphology of the prepared electrode

To evaluate the thermal behavior of the PVK, a DSC measurement was first carried out. Fig. 2 shows the DSC thermogram. A slight endothermic effect at around 200°C corresponds to the glass transition point of PVK, and the following intense endothermic reaction at around 400°C corresponds to its decomposition. Throughout the tested temperature range, PVK showed an endothermic behavior. In contrast, the conventional positive-electrode material of lithium cobalt oxide (LiCoO_2) shows an exothermic reaction at the decomposition temperature accompanied by oxygen evolution [24], which accelerates the thermal runaway phenomenon of batteries. The observed endothermic behavior of PVK over a wide range of temperatures is considered to be an important feature for the safety of rechargeable lithium batteries.

Fig. 3 shows an SEM image of a positive-electrode using PVK as the active material (before the press process). In the figure, needle-like fibers represent the shape of the conductive carbon fiber (VGCF) additive. A wide field observation indicated that the electrode materials, such as PVK, VGCF, and KB, are well dispersed in the electrode. PVK is soluble in the solvent/suspending agent (NMP) used for the electrode-preparation process, which is considered to contribute to the good dispersibility of the electrode materials.

3.2. Battery performance of the PVK electrode

Fig. 4 shows the first several charge/discharge curves of an electrode prepared using PVK. The electrode exhibits smooth discharge curves with a mean potential of 3.7 V vs. Li^+/Li . There have been some studies on the redox potentials of carbazole derivatives and the reported potentials correspond to about 4 V vs. Li^+/Li under the present conditions [14–19]. This estimated potential approximately agrees with the observed charge and discharge potentials

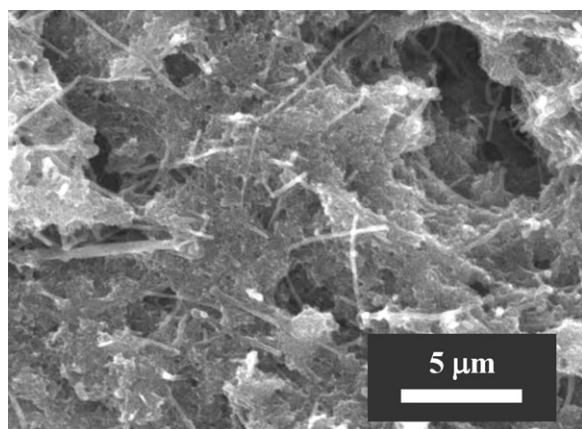


Fig. 3. SEM image of the PVK-based electrode.

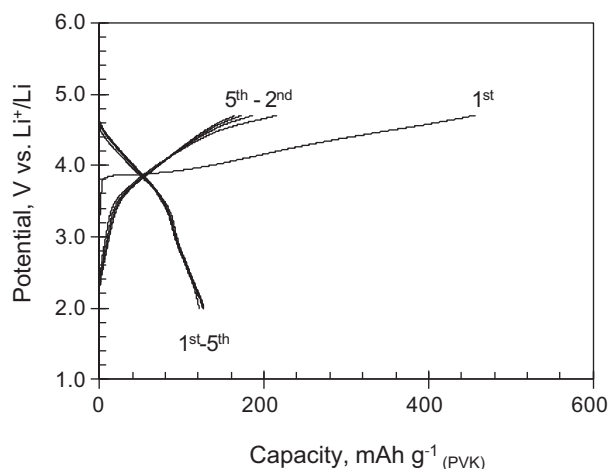


Fig. 4. Charge/discharge curves of the electrode using PVK during early cycling (current density: $20 \text{ mA g}^{-1}(\text{PVK})$, potential range: 2.0–4.7 V vs. Li^+/Li).

of our measurements. The coulomb efficiency (discharge capacity/charge capacity) in the first cycle is poor; however, it gradually became better upon cycling (details are given below). The obtained discharge capacity of about $125 \text{ mAh g}^{-1}(\text{PVK})$ is close to the theoretical value of $139 \text{ mAh g}^{-1}(\text{PVK})$ based on the assumption of a

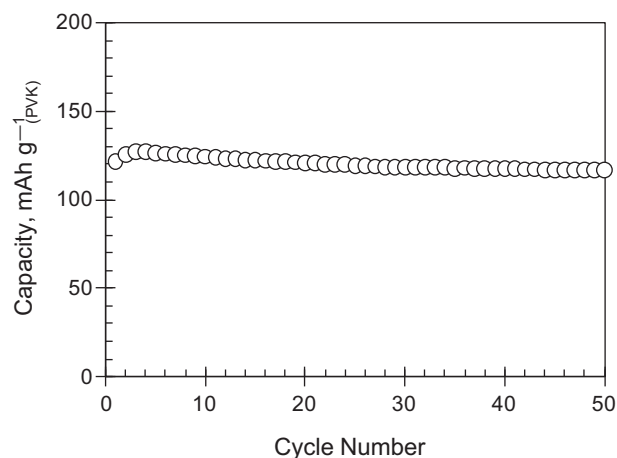


Fig. 6. Cycle-life performance of the electrode using PVK (current density: $20 \text{ mA g}^{-1}(\text{PVK})$, potential range: 2.0–4.7 V vs. Li^+/Li).

one-electron transfer redox reaction between the neutral state and cation radical state of the carbazole moiety as shown in the reaction equation in Fig. 5a. This capacity also implies that a high doping level is possible for PVK during the charge/discharge process. The obtained discharge capacity and the potential of PVK are comparable to those of the conventional positive-electrode materials such as LiCoO_2 (140 mAh g^{-1} , 3.8 V vs. Li^+/Li) or LiFePO_4 ($140\text{--}160 \text{ mAh g}^{-1}$, 3.4 V vs. Li^+/Li).

The capacity retention is shown in Fig. 6. The electrode using PVK shows no appreciable decay in capacity upon cycling and maintains $117 \text{ mAh g}^{-1}(\text{PVK})$ even after 50 cycles. Among the reported organic active materials [4–11], the cycle-life performance of PVK is relatively good. In general, the dissolution of the redox active site into the electrolyte solution causes the capacity decay upon cycling; however, the observed good cycle stability indicates that the dissolution of PVK into the electrolyte solution is negligible.

As already mentioned, the coulomb efficiency for the first cycle is poor (ca. 30%). This behavior should reflect the coupling reaction between the adjacent carbazole moieties. According to some reports [14–16], the 3- and 6-positions of the cation radical state of the carbazole are reactive, and these positions cause the coupling reaction. Our quantum calculations based on the density functional theory also implied the high spin densities at these positions. Therefore, the redox reaction of the resulting cross-coupled

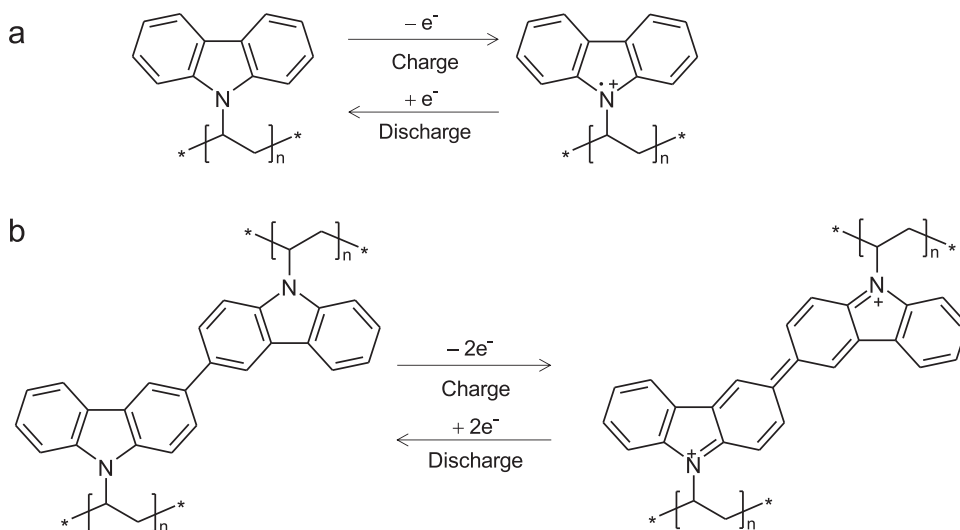


Fig. 5. Conceivable drawings of the redox reactions of (a) PVK and (b) cross-linked PVK.

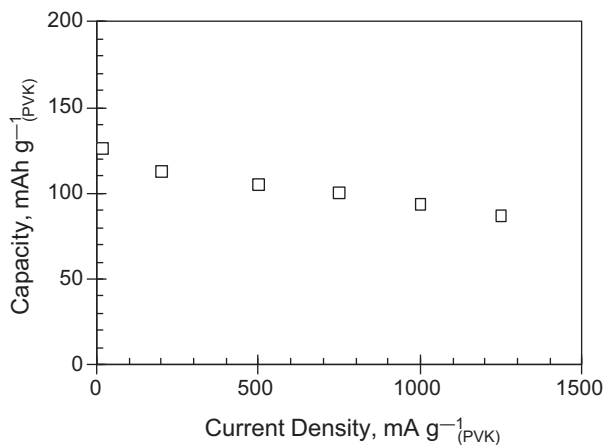


Fig. 7. Rate capability of the electrode using PVK (potential range: 2.0–4.7 V vs. Li^+/Li).

PVK schematically shown in Fig. 5b is also considered to contribute to the charge/discharge process of the PVK electrode [15,16,18,19]. Additional chemical modifications of the reactive positions by some protecting groups will stabilize the cation radical state of the carbazole moiety [14], which may improve the coulomb efficiency during the charge/discharge process.

The high-rate capability of the electrode using PVK was also examined by discharging at various current densities after several cycles. Fig. 7 shows the relationship between the discharge capacity and the applied current density. The discharge capacity decreases as the current density increases, as is generally seen for conventional electrodes. However, even at $1250 \text{ mA g}^{-1}(\text{PVK})$, which corresponds to a rate of about 10-C, the electrode still showed $87 \text{ mAh g}^{-1}(\text{PVK})$, which correspond to 69% of the capacity observed at the low current density of $20 \text{ mA g}^{-1}(\text{PVK})$. The obtained high-rate performance of PVK is good, and application for high-power use can be expected.

3.3. Battery performance of the LiFePO_4 -PVK composite electrode

During the normal preparation process of conventional electrodes, some polymeric compounds, such as PTFE and PVDF, are used in the electrode as binder materials. These polymers are necessary to immobilize the active material powder, although these electrochemically inactive binders sacrifice the total gravimetric

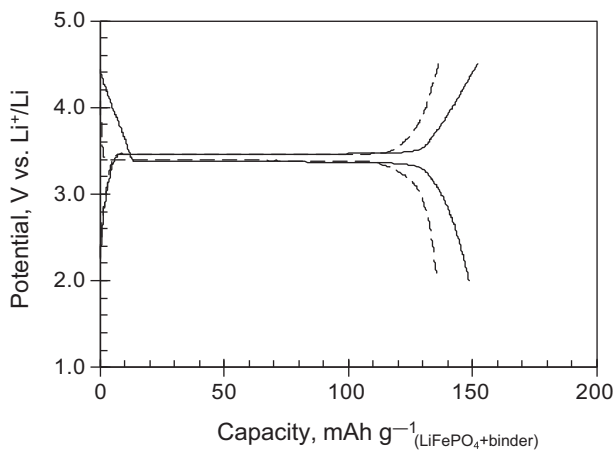


Fig. 8. Charge/discharge curves of the composite electrodes. (solid line: LiFePO_4 -PVK; broken line: LiFePO_4 -PVDF). (current density: $30 \text{ mA g}^{-1}(\text{LiFePO}_4)$, potential range: 2.0–4.7 V vs. Li^+/Li).

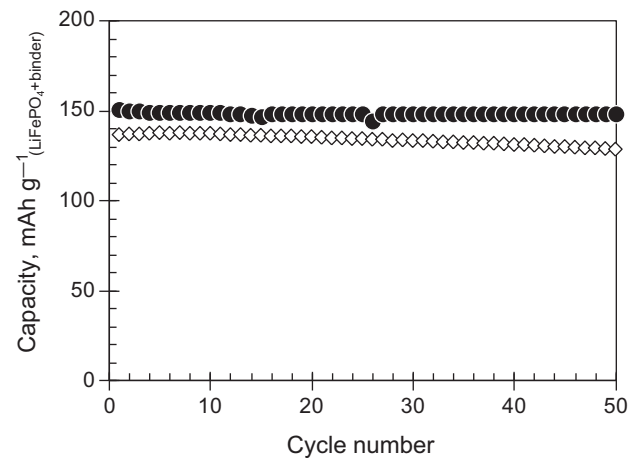


Fig. 9. Cycle-life performance of the composite electrodes (●: LiFePO_4 -PVK; ◇: LiFePO_4 -PVDF). (current density: $30 \text{ mA g}^{-1}(\text{LiFePO}_4)$, potential range: 2.0–4.7 V vs. Li^+/Li).

discharge capacity of each electrode. Application of a redox active polymer as the binder instead of the redox inactive conventional ones can overcome this problem. In this section, the property of PVK, of which the good cycling stability was proved, as a redox active binder was examined using lithium iron phosphate (LiFePO_4) as the main active material.

As a preliminary test to evaluate the binder property of PVK, a tensile strength was measured and the result was compared with that of PVDF. In this measurement, 24 ± 6 and $10 \pm 3 \text{ N cm}^{-2}$ of force were required for PVK and PVDF, respectively, to shear away the two bonded polypropylene sheets, implying that PVK matches or exceeds PVDF in the mechanical strength.

Fig. 8 shows a comparison of the typical charge/discharge curves of the normal LiFePO_4 -PVDF-type electrode and the LiFePO_4 -PVK-type composite electrode. As shown, the normal LiFePO_4 -PVDF electrode has a discharge capacity of $136 \text{ mAh g}^{-1}(\text{LiFePO}_4+\text{PVDF})$. The observed value can be converted to 161 mAh g^{-1} for the mass fraction of LiFePO_4 , which is close to its theoretical value of 170 mAh g^{-1} . On the other hand, the LiFePO_4 -PVK composite electrode, in which PVK was used instead of PVDF, has the higher capacity of $149 \text{ mAh g}^{-1}(\text{LiFePO}_4+\text{PVK})$ due to the additional capacity of PVK. (In this case, a 10% increase was observed.) Assuming the capacity that originated from LiFePO_4 was 160 mAh g^{-1} , the contributed capacity from PVK as a redox active binder was calculated to be 90 mAh g^{-1} . The methodology of using a redox active polymer as a binder is proved to increase the total energy density of batteries.

Fig. 9 shows a comparison of cycle-life performance of these electrodes. The cycle-life performance of the composite electrode using PVK is comparable to that of the PVDF-based electrode, i.e., the composite electrode using PVK showed almost no decay during 50 cycles with a higher capacity. This result indicates the usefulness of PVK as a binder material. Furthermore, the use of a redox active binder material was revealed to be an effective way to increase the total discharge capacity of the electrodes.

4. Conclusions

The performance of poly(*N*-vinylcarbazole) (PVK) was investigated as a positive electrode active material for use in rechargeable lithium batteries. This polymer showed about $125 \text{ mAh g}^{-1}(\text{PVK})$ with a mean potential of 3.7 V vs. Li^+/Li at the current density of $20 \text{ mA g}^{-1}(\text{PVK})$. The obtained capacity and the potential are comparable to those of conventional positive electrode materials, such as LiCoO_2 .

Furthermore, the application of this polymer as an electrochemically active binder material was also examined. A composite electrode of LiFePO₄ using PVK as a binder showed a good cycle-life performance by maintaining its capacity supplemented by the redox of PVK binder. This methodology of using a redox active polymer as a binder will increase the total energy density of batteries.

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