A Rechargeable Battery Using Electrochemically-Doped Poly(3-vinylperylene) as an Electrode Material

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A rechargeable battery using electrochemically-doped poly(3-vinylperylene) as a cathode and lithium as an anode was fabricated, and its performance characteristics were examined. The battery exhibits a flat discharge cell voltage at current densities up to 0.8 mA cm^{-2} with high coulombic efficiency and good cyclability.

Electrically conducting polymers have recently attracted attention for their potential technological applications as well as academic interest. An interesting application of conducting polymers is as electrode materials for secondary batteries. The batteries using conducting polymers are expected to have higher energy and power densities than conventional ones using lead–acid or Ni–Cd owing to the light weight of organic polymers. Fabrication of secondary batteries using electrically conducting polymers and examination of their performance characteristics have been a subject of recent studies. Wholly π-conjugated linear polymers, such as polyacetylene,[1–4] poly(p-phenylene),[5,6] polythiophene,[7–9] polypyrrole,[10,11] and polyaniline,[12–14] have been studied for use as electrode materials.

For the purpose of developing a new class of electrically conducting polymers, we have been studying electrochemical doping of non-conjugated, vinyl-type polymers containing pendant π-electron systems,[15–21] and properties and functions of doped polymers.[22–26] Since the standard oxidation/reduction potentials of non-conjugated polymers containing pendant π-electron systems do not change with doping level, it is expected that secondary batteries using these polymers as electrode materials should maintain a flat cell voltage during the discharge process. Based on this idea,[22] we have been studying the performance characteristics of lithium secondary batteries using non-conjugated polymers containing pendant π-electron systems as the cathode material. We have shown that batteries using poly(N-vinylcarbazole) as an electrode material exhibit a flat cell voltage during the discharge process and have good cyclability with high coulombic efficiency.[22,25]

Recently, we have found that among vinyl-type conducting polymers, electrochemically-doped poly(3-vinylperylene) exhibits a relatively high room-temperature conductivity of the order of 1×10^{-5} S cm^{-1}.[20,26] In the present work, we have studied the application of poly(3-vinylperylene) (PVPe) as an electrode material for secondary batteries. We report here fabrication and performance characteristics of a lithium secondary battery using a mixture of PVPe and graphite as the cathode material.

Experimental

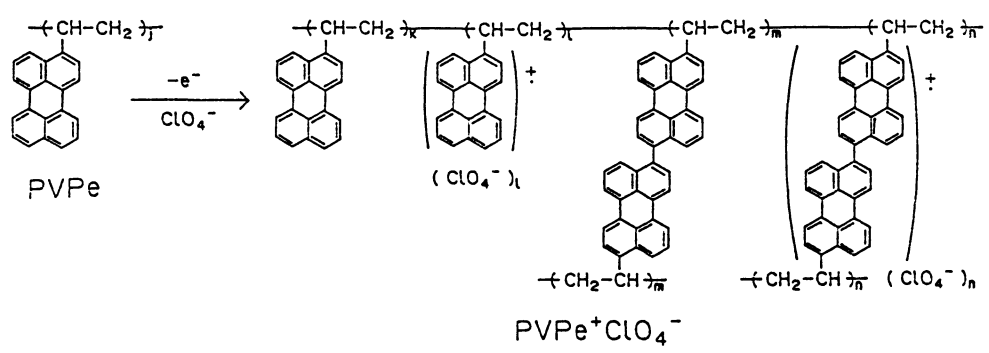
Materials. Poly(3-vinylperylene) (PVPe) was prepared by radical polymerization of 3-vinylperylene in benzene using 2,2′-azobisisobutyronitrile as an initiator, and purified by repeated reprecipitation from chloroform–methanol.[26] Propylene carbonate (PC) (Nacalai Tesque, extra pure reagent) was dried with molecular sieves (Wako Pure Chemical Industries, Ltd., 5A 1/16) for 4 d, and then distilled at 75 °C/1 mmHg (1 mmHg=133.322 Pa). Lithium perchlorate ($LiClO_4$) (Wako Pure Chemical Industries, Ltd., guaranteed reagent) was recrystallized three times from acetonitrile, and then dried at 160 °C under vacuum for one day prior to being dissolved in PC. Lithium metal foil (Furuuchi Chemical, Ltd.) and graphite powder (Wako Pure Chemical Industries, Ltd.) were used as received.

Fabrication of Battery. An anode was made by pressing lithium metal onto a nickel wire. A cathode, composed of a mixture of 40 mg PVPe and 20 mg graphite, was compressed to form a pellet of 1.3 cm in diameter. A platinum wire was used as a collector. A battery was constructed by sandwiching a glass filter paper(0.02 cm thick) as a separator between the PVPe–graphite cathode and the lithium anode. This assembly was carefully inserted into a glass vessel containing activated neutral alumina. The electrodes were covered by a 1.0 mol dm^{-3} $LiClO_4$/PC electrolyte solution, and the vessel sealed by an epoxy resin.

Measurement. Charge/discharge tests were carried out at constant current density ranging from 0.1 to 1.0 mA cm^{-2} using a charge/discharge unit (HJ-201B, Hokuto Denko, Ltd.). The discharge of the cell was terminated when the cell voltage dropped to 3.0 V. All experimental procedures were performed under dry argon.

Results and Discussion

Poly(3-vinylperylene) (PVPe) prepared by radical polymerization of 3-vinylperylene is an oligomer with molecular weights of M_n=1300 and M_w=1600, as determined by gel permeation chromatography with polystyrene as a standard.[26] Electrochemically-doped PVPe is a partially oxidized radical-cation salt of pendant perylene and biperylene moieties, the latter of which is formed by the coupling reaction of the perylene radical cation, as suggested from cyclic voltammetry of PVPe and insolubility of the dedoped polymer.[26]



Charge/discharge reactions of the rechargeable battery using PVPe as a cathode and lithium as an anode take place according to Eqs. 1 and 2. In the charge process, the PVPe is oxidized with concurrent incorporation of ClO_4^- from the supporting electrolyte dissolved in propylene carbonate (PC) as a counter ion for the positively charged polymer cations. At the same time, lithium cations of the supporting electrolyte are reduced at the lithium anode. During discharge, these ions diffuse back into the electrolyte. At the initial stage of charging of the Li/$LiClO_4$, PC/PVPe–graphite battery, cross-linking will take place as a result of the coupling reaction of the perylene radical cation.

$$\underset{\text{(cross-linked)}}{\text{PVPe}} + \text{ClO}_4^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} \text{PVPe}^{+}\text{ClO}_4^- + e^- \qquad (1)$$

$$\text{Li}^+ + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} \text{Li} \qquad (2)$$

Figure 1 shows charge/discharge curves of the Li/$LiClO_4$, PC/PVPe–graphite battery. The charge/discharge curve of the Li/$LiClO_4$, PC/graphite cell is also shown. The voltage of the cell using graphite only as a cathode increases and decreases monotonically during charge and discharge processes, and the cell acts like a capacitor. On the other hand, the Li/$LiClO_4$, PC/PVPe–graphite battery exhibits a flat cell voltage during discharge. The result indicates that the redox reaction of PVPe plays an important role in the cell reaction. The open-circuit voltage (V_{oc}) of the Li/$LiClO_4$, PC/PVPe–graphite battery was ca. 4.0—4.2 V depending on charge current densities. These values are approximately in accord with the value estimated from the standard oxidation/reduction potential of Li/Li^+ (E_0: −3.0 V vs. NHE) and that of PVPe/$PVPe^{+}$ (E_0: ca. 1.0 and 1.3 V vs. NHE for biperylene moiety and perylene moiety, respectively). The V_{oc} of the battery using PVPe–graphite as the cathode and lithium as the anode is higher than those of the corresponding batteries using wholly π-conjugated polymers such as polyacetylene (3.7 V),[3] polythiophene (3.8 V),[9] and polyaniline (3.6 V).[14] This is due to the higher standard oxidation/

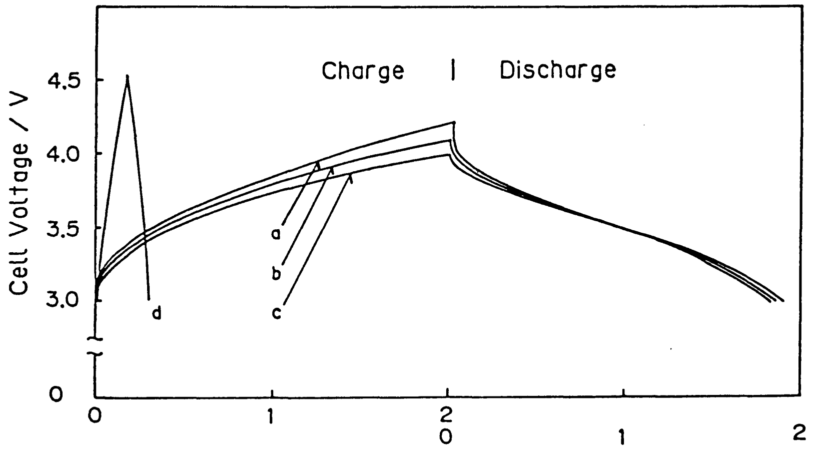


Fig. 1. Charge/discharge curves of Li/$LiClO_4$, PC/PVPe–graphite battery at constant current densities of (a) 0.8, (b) 0.6, and (c) 0.4 mA cm^{-2}, together with that of (d) Li/$LiClO_4$, PC/graphite cell at 0.1 mA cm^{-2}. The curves (a), (b), and (c) were obtained for a sample which had been subjected to 50 cycles of 1 h charge/discharge at a current density of 0.1 mA cm^{-2}. Each curve was obtained after 10 cycles at the given current density.

reduction potential of PVPe than those of the wholly π-conjugated linear polymers.

The PVPe batteries show coulombic efficiencies higher than 90 % at charge/discharge current densities up to 0.8 mA cm^{-2}. No degradation of these characteristics was observed after 100 cycles of the charge/discharge process. Figure 2 shows how the coulombic efficiency of the Li/LiClO$_4$, PC/PVPe-graphite battery varies depending on charge/discharge cycles at a current density of 0.1 mA cm^{-2}. In the first cycle, the coulombic efficiency was 43%. When the charge/discharge cycle was repeated ca. 30 times, the coulombic efficiency increased to 92 %, and then became constant. The lower coulombic efficiency at the initial 30 cycles of charge/discharge is considered to be partly due to incomplete dedoping and partly due to the formation of the biperylene moiety as a result of the coupling reaction of the pendant perylene radical cation.

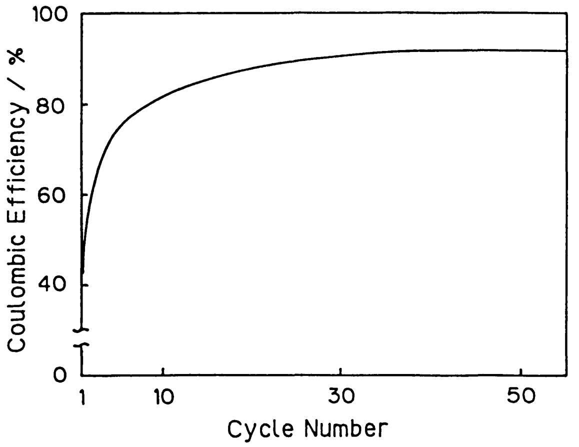


Fig. 2. Dependence of coulombic efficiency of Li/LiClO$_4$,PC/PVPe-graphite battery on the cycle number of charge/discharge.

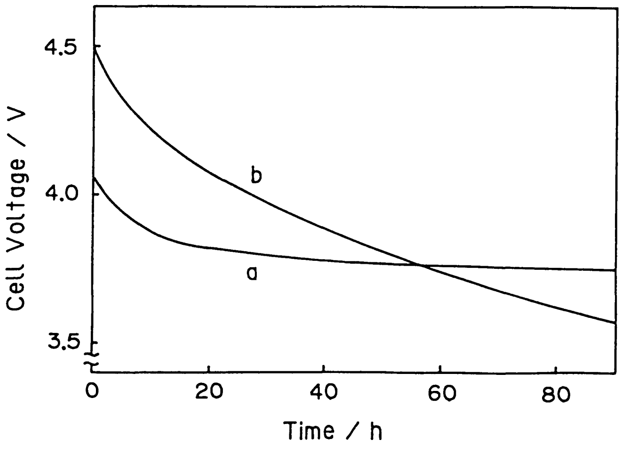


Fig. 3. Storage-time dependence of the open-circuit voltage of (a) Li/LiClO$_4$, PC/PVPe-graphite battery and (b) Li/LiClO$_4$, PC/graphite cell. The PVPe-graphite battery was charged for 3 h at a current density of 0.5 mA cm^{-2} after 10 cycles of 3 h charge/discharge at 0.5 mA cm^{-2}. The graphite cell was charged for 10 min at a current density of 0.1 mA cm^{-2}.

Figure 3 shows the time dependence of the open-circuit voltage (V_{oc}) of the Li/LiClO$_4$, PC/PVPe-graphite battery together with that of the Li/LiClO$_4$, PC/graphite cell. Whereas the V_{oc} of the cell using graphite only as the electrode material rapidly decreased (Fig. 3b), that of the PVPe-graphite battery decreased slightly from 4.05 to 3.75 V at the initial stage, but then no further significant decrease was observed (Fig. 3a).

The self-discharge test was carried out for the Li/LiClO$_4$, PC/PVPe-graphite battery. Figure 4 shows how the coulombic efficiency varies with the period of time for which the charged battery is left to stand at room temperature. The result shows that the coulombic efficiency decreases from the initial value of ca. 92 to ca. 70% in 12 h, but thereafter the coulombic efficiency does not significantly decrease, gradually dropping to ca. 62% after one week.

Performance characteristics of the Li/LiClO$_4$, PC/PVPe-graphite secondary battery are listed in Table 1. When the period of time for charge/discharge increased from 1 h to 2 and 3 h at the same current density (0.4 or 0.6 mA cm^{-2}), the energy density of the battery increased twice and three times, respectively. No appreciable difference was observed in the coulombic efficiency when the battery was charged for 1 h or 2 h; however, when charged for 3 h under the same total charge capacity condition (40 A h kg^{-1}), the coulombic efficiency was found to decrease slightly from 93 to 86 %. It is suggested that when the battery is charged at a lower current density under the condition of the same total charge capacity, undesirable side reactions such as electrolytic decompositions of the electrolyte solution can be prevented, but the self-discharge of the battery

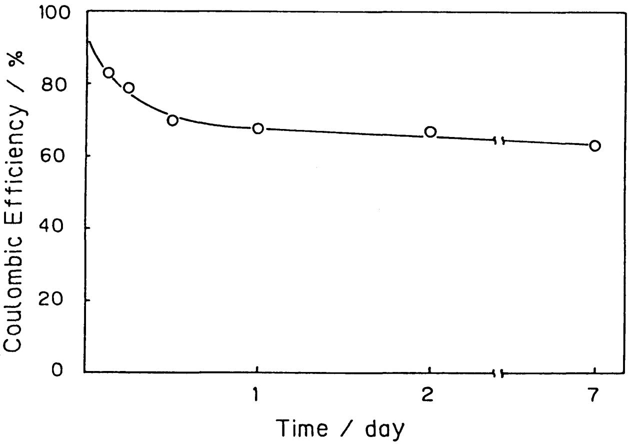


Fig. 4. Self-discharge of Li/LiClO$_4$, PC/PVPe-graphite battery. After 50 cycles of 1 h charge/discharge at 0.1 mA cm^{-2} were carried out, the battery was charged for 2 h at a current density of 0.1 mA cm^{-2} and then left to stand at room temperature in argon atmosphere.

Table 1. Performance Characteristics of Li/LiClO$_4$, PC/PVPe–Graphite Battery[a]

Charge/discharge current density	Charge capacity	Degree of doping	Coulombic efficiency	Open-circuit voltage V_{oc}/V	Short-circuit current I_{sc}/mA	Maximum power density[e]	Energy density[f]
mA cm^{-2}	Ah kg^{-1}	%	%			kW kg^{-1}	W h kg^{-1}
0.4	13	14[b]	90	4.0[b]	95	2.3	42
0.6	20	21[b]	93	4.0[b]	110	2.5	63
0.4	27	28[c]	95	4.0[c]	130	2.9	79
0.6	40	41[c]	93	4.1[c]	140	3.1	115
0.8	53	55[c]	92	4.2[c]	140	3.0	134
0.3	30	31[d]	89	4.0[d]	135	3.0	85
0.4	40	41[d]	86	4.1[d]	135	3.0	104

a) Performance characteristics were evaluated for a sample which had been subjected to 50 cycles of 1 h charge/discharge at a current density of 0.1 mA cm^{-2}. The data were obtained after 10 cycles at the given current density. b) Values for 1 h charge. c) Values for 2 h charge. d) Values for 3 h charge. e) $V_{\mathrm{oc}} I_{\mathrm{sc}}/4W$, where W is the sum of the mass of the doped polymer and the mass of lithium consumed in the discharge reaction. f) Calculated from the equation $V{\cdot}I{\cdot}t/W$, where V represents discharge voltage, I discharge current, t discharge period of time, and W the sum of the mass of the doped polymer and the mass of lithium consumed in the discharge reaction.

becomes appreciable. The use of graphite in combination with PVPe as the cathodic material permits much higher charge/discharge current densities, because its contact with PVPe prevents the formation of an insulating layer during discharge as appears to be the case for the electrode using the polymer alone.

Performance characteristics of the Li/LiClO$_4$, PC/PVPe–graphite battery are similar to those of the corresponding battery using poly (*N*-vinylcarbazole), but the battery using PVPe exhibits improved performance over the poly(*N*-vinylcarbazole) battery; namely, higher short-circuit current and hence higher maximum power density, and higher coulombic efficiency at higher charge capacity. Whereas the coulombic efficiency for the poly(*N*-vinylcarbazole) battery decreases to less than 90% when the charge capacity increases to 40 A h kg^{-1}, the battery using PVPe exhibits a coulombic efficiency of more than 90% at a charge capacity of 53 A h kg^{-1}. The self-discharge behavior of the battery using PVPe is similar to that of the battery using poly(*N*-vinylcarbazole).

Higher doping level can be achieved for the battery using PVPe as the electrode material (55% as described in Table 1) than for the batteries using polyacetylene (7%),[3] polythiophene (24%),[9] and polypyrrole (24%).[10] It is expected that the higher doping level generally leads to a higher energy density of the battery. When the Li/LiClO$_4$, PC/PVPe-graphite battery was charged at a current density of 0.8 mA cm^{-2} for 2 h, the energy density was 134 W h kg^{-1} on the basis of the weight of the electrode-active material. This value of energy density for the Li/LiClO$_4$, PC/PVPe–graphite battery is comparable to or higher than those reported for the corresponding polythiophene (140 W h kg^{-1})[9] and polypyrrole (86 W h kg^{-1})[10] batteries, but lower than those for polyacetylene (255 W h kg^{-1})[3] and polyaniline (400 W h kg^{-1})[14] batteries. The lower energy density of the PVPe battery relative to polyacetylene and polyaniline batteries is partly due to the higher molecular weight of the vinylperylene unit (M_{w}= 278) than the acetylene (M_{w}=13) or aniline (M_{w}=92) unit.

Secondary batteries using non-conjugated polymers containing pendant π-electron systems have the following advantages over the corresponding batteries using wholly π-conjugated linear polymers. a) Flat cell voltage is achieved owing to the invariance of the standard oxidation/reduction potential of the pendant polymers irrespective of the doping degree. b) Higher energy density is expected to be achieved due to higher doping level. c) Higher V_{oc} is expected by the choice of pendant chromophores with relatively high oxidation potential. The disadvantages of these batteries are relatively low conductivities of the doped polymers and relatively high molecular weight of the monomer units.

The present study has demonstrated that electrochemically-doped poly(3-vinylperylene) functions as a new type of cathode-active material for a lithium rechargeable battery. The battery exhibits high coulombic efficiency and flat cell voltage in the discharge process at current densities up to 0.8 mA cm^{-2}.

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