A Rechargeable Battery using Electrochemically Doped Poly(*N*-vinylcarbazole)

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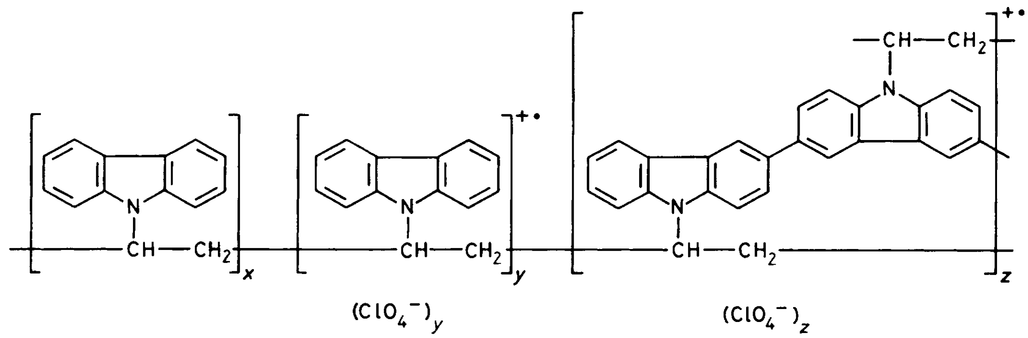
Electrochemically doped poly(*N*-vinylcarbazole) functions as a positive electrode material for a secondary lithium battery.

Recently there has been growing interest in the fabrication of devices using organic electrical conductors. Rechargeable batteries using polyacetylene as electrode materials have attracted attention,[1—3] and the assembly of secondary batteries using other all-π-conjugated polymers, *e.g.*, poly(*p*-phenylene),[4] activated carbon fibre,[5] polyaniline,[6] *etc.*, have also been reported. The cell performance is based on reversible electrochemical doping and undoping.

We have reported the transformation of insulating, non-conjugated pendant polymers, *e.g.*, poly(*N*-vinylcarbazole) (PVCz), into electrically conducting polymers by electrochemical doping.[7,8] We report here the application of the electrochemically doped PVCz as a positive electrode material for a secondary lithium battery. In the case of non-conjugated pendant polymers, it is expected that the standard oxidation–reduction potential will not change with the doping level, and hence a flat voltage is maintained during the discharge process.

Electrochemically doped PVCz with ClO_4^- as a dopant was prepared according to the method described previously:[7,8] it was deposited on a platinum plate (3.0×1.5 cm^2) by controlled potential electrolysis of PVCz (Luvican M170) dissolved in CH_2Cl_2 (5.0×10^{-3} M) containing $Bu^n_4NClO_4$ (0.1 M) at a potential of 1.0 V (*vs.* Ag/Ag$^+$, 0.01 M, reference electrode) for 60 min. A battery was constructed under an argon atmosphere by immersing the electrochemically doped PVCz deposited on the platinum electrode and a lithium plate (2.0×3.5 cm^2) in a purified, dry propylene carbonate solution



Electrochemically doped PVCz (PVCz$^{+\bullet}$).

containing $LiClO_4$ (1.0 M) as an electrolyte in a glass vessel. The separation of the two electrodes was 1 cm, a glass filter paper being inserted between them to avoid the contact of the electrodes. Activated neutral alumina was placed at the bottom of the vessel in order to keep the solution dry. Charge and discharge of the battery were carried out at constant current densities.

The electrochemically doped, greenish PVCz is a partially oxidized cation radical salt with ClO_4^- as a counter anion. Its structure contains the dicarbazolyl moiety owing to the intermolecular (and intramolecular) coupling reaction of the carbazole cation radical at the 3- and/or 6-position of the carbazole ring, as evidenced from the i.r. spectrum and the cyclic voltammogram.[7,9,10] The oxidation process of PVCz is irreversible in the initial stage; however, it becomes reversible when the coupling reaction occurs to a certain extent as seen in the cyclic voltammograms, which exhibit two anodic and corresponding cathodic waves, the first and the second anodic waves (*ca.* 0.6 and *ca.* 0.8 V *vs.* Ag/Ag^+, 0.01 M) being ascribed to the oxidation of the conjugated dicarbazolyl moiety and the isolated carbazole ring, respectively.

Charge and discharge reactions of the cell consisting of the electrochemically doped PVCz as the positive electrode and lithium as the negative electrode take place as shown in equations (1) and (2).

$$\mathrm{PVCz} + \mathrm{ClO_4^-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} \mathrm{PVCz^{+\bullet}ClO_4^-} + e^- \tag{1}$$

$$\mathrm{Li^+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} \mathrm{Li} \tag{2}$$

The open circuit voltage of the cell initially made was 3.86 V, going up to 4.15 V after a cycle of discharge and charge at a current density of 11.1 $\mu A\ cm^{-2}$. This value is approximately in accord with the value estimated from the oxidation–reduction potentials of Li/Li^+ (E° −3.02 V *vs.* normal hydrogen electrode, NHE) and $PVCz/PVCz^{+\bullet}$ (E° *ca.* 1.10; 1.30 V *vs.* NHE). The cell exhibited short-circuit currents of 2.2 and 6.0 $mA\ cm^{-2}$ when charged at 2.2 and 11.1 $\mu A\ cm^{-2}$, respectively. Figure 1 shows charge and discharge characteristics of the cell at three constant current densities. The coulombic efficiency was 90% at a current density of 4.4 $\mu A\ cm^{-2}$ and 86% at a current density of 11.1 $\mu A\ cm^{-2}$. The cell exhibited a fairly good flat voltage during discharge, and when 1 h charge and discharge processes were cycled 100 times, no appreciable change in the characteristics was observed. These results indicate that the electrochemically doped PVCz, a non-conjugated pendant polymer, functions as a positive electrode material for a rechargeable battery.

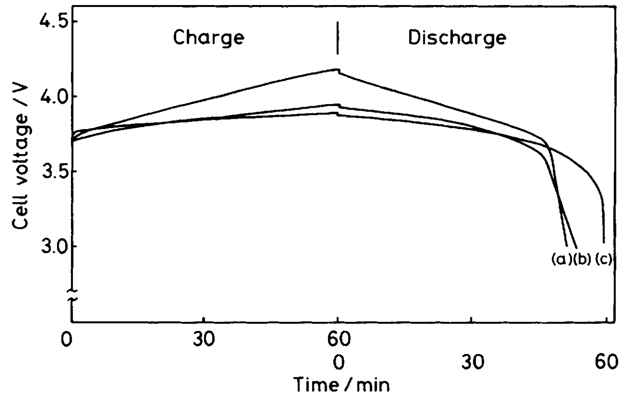


Figure 1. Charge–discharge characteristics of the cell, $Li/LiClO_4$ in propylene carbonate/electrochemically doped PVCz. Current density ($\mu A\ cm^{-2}$): (a) 11.1, (b) 4.4, (c) 2.2.

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