

First Electrochemical Intercalation of Lithium into Fullerenated Poly(*N*-vinylcarbazole)

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SYNOPSIS

Lithium batteries are attractive for energy storage because of their high theoretical energy densities. A mechanism of an electrochemical intercalation reaction is suggested for the discharge of the first Li-fullerenated poly(*N*-vinylcarbazole) battery on the basis of experimental data obtained from cyclic voltammetry, FTIR, XRD, and ESR. The above battery has a higher open-circuit voltage (ca. 3.2 V), and its discharge may be ascribed to the electrochemical intercalation process of lithium in fullerenated poly(*N*-vinylcarbazole) for positive electrode materials. The effect of the discharge of the electric cell on the structure and paramagnetic property of fullerenated poly(*N*-vinylcarbazole) is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The electrochemical behaviors of fullerenes, particularly C_{60} and its derivatives, have been investigated extensively in recent years¹⁻⁶ due to their unusual structure and a high electron affinity ($E_A = 2.6-2.8$ eV).⁷ Electrochemical methods have demonstrated that C_{60} readily accepts electrons to form fulleride anions and its degenerate LUMO can accept up to six electrons.⁶ However, limited attention^{4,8} has been given to the electrochemical intercalation of alkali metal into fullerene C_{60} and its derivatives. A potential advantage of the application of electrochemical intercalation is that it may provide another synthetic route⁸ to alkali-metal-intercalated fullerenes M_xC_{60} ($M = K, Na, Rb, Cs$) in addition to previously described chemical methods,^{9,10} in particular, for the superconducting compounds with $x = 3$,¹¹ and may offer an appropriate approach to develop novel and efficient lithium intercalated batteries¹²⁻¹⁴ modified by fullerenes. At present, alkali-metal intercalation compounds of C_{60} have attracted a great deal of interest¹⁵ due primarily to the existence of superconductivity in some members of the family but also to the richness of the binary phase equilibria

vs. metal concentration x , temperature T , and hydrostatic pressure P . A generic feature of all intercalation compounds is the variety of equilibrium guest-host superlattice structures which result from minimizing free energies $F(x, T, P)$ by tradeoffs among attractive and repulsive interactions, free volume, and entropy, all of which are concentration-dependent.^{16,17} Experimental results^{4,8} show that small cations (Li^+, Na^+, K^+, Cs^+) should be intercalated more easily into the spaces of the lattice formed by the C_{60} molecules. Here, we report the first electrochemical intercalation of lithium into photoconductive¹⁸⁻²⁰ fullerenated poly(*N*-vinylcarbazole).

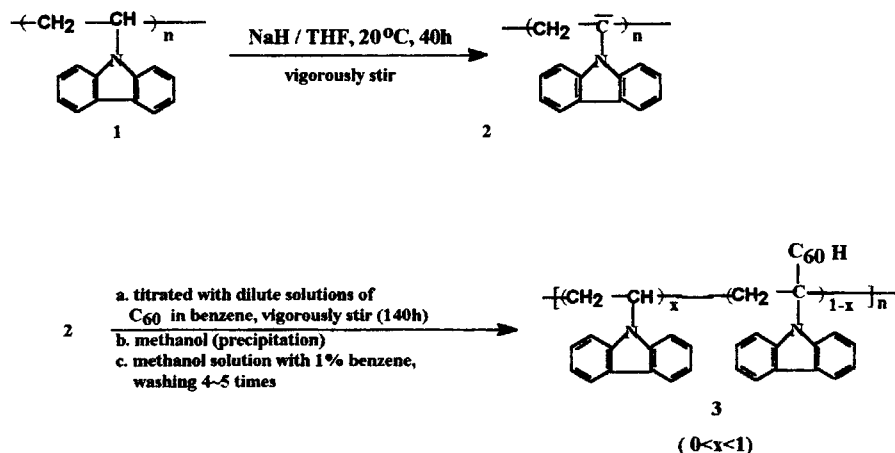
EXPERIMENTAL

A pure C_{60} sample was synthesized and purified according to the literature²¹; solvent residues were removed by vacuum-drying at 200°C for several hours. HPLC analysis shows C_{60} in a purity of 99.5%. The soluble fullerenated poly(*N*-vinylcarbazole) containing 3.85% of C_{60} was prepared by the following method under a purified nitrogen atmosphere (shown in Scheme I). The confirmation of the structure²² and photoconductivity of fullerenated poly(*N*-vinylcarbazole), which has a visibly earthy yellow cast when com-

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pared with the unreacted polymer and is soluble in some organic solvents, DMF, CS₂, CHCl₃, THF, and so on, is by a variety of techniques such

as UV-vis, FTIR, ESR, XRD, ¹³C-NMR, and SEM and the transient photocurrent measuring technique:



Scheme I

Electrochemical experiments were performed using a JH2C potentiostat and XFD-8 super-low-frequency signal generator with associated ancillary equipment. Data were collected using a conventional LZ3-200 function recorder. Experiments were performed in cells of conventional design. Two fresh lithium foils were used as a reference electrode and a negative electrode, respectively. The positive electrode area of the electrochemical cell, in which fullereneated poly(*N*-vinylcarbazole) was employed as positive composite electrode materials, was 0.58 cm². The electrolyte was 1M LiClO₄/propylene carbonate (PC). Experimental solutions were routinely degassed with argon and all measurements were carried out in a dry box under a positive argon pressure.

FTIR spectra were recorded on the Nicolet-FTIR-5DX spectrometer, ESR spectra were recorded on Bruker ER200D-SRC spectrometer, and *g*-values were determined by calibration to DPPH. XRD spectra were measured on a Science D/Max-Rb diffractometer (CuK α radiation $\lambda = 1.54050 \text{ \AA}$).

RESULTS AND DISCUSSION

The cyclic voltammograms on the positive electrode of electric cell (a) [fullereneated poly(*N*-vinylcarbazole) (50 mg)|Li (LiClO₄ + PC)] at a different potential scan rate are shown in Figure 1. Chabre et al.⁸ reported that three well-defined reduction peaks of the first redox cycle for pure C₆₀ are apparent at 2.3, 1.9, and 1.5 V, respectively, vs. Li, and the absence of trailing current after the above three

peaks proves that all the available sites were occupied in the C₆₀ solid at each of these reduction steps. The only reduction peak of voltammograms of cell (a) appears at near 2.3 V vs. Li, corresponding approximately to lithium intercalation into fullereneated poly(*N*-vinylcarbazole), particularly C₆₀ attached to the polymer backbone. Furthermore, the dramatic separation (roughly 1.6 V) between the oxidation peak and the reduction peak may relate to the magnitudes of thermodynamic equilibrium "b" for the intercalation reaction and resistance of the electrode and electrolyte solution.²³ Figure 2 shows the dependence of the anodic peak current *I*_{pa} on the second root of the scan rate $V^{1/2}$; it is

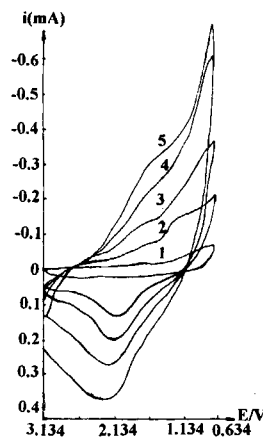


Figure 1 The cyclic voltammograms on the positive electrode of electric cell (a): fullereneated poly(*N*-vinylcarbazole) (50 mg)|Li (LiClO₄ + PC) at different potential scan rates. Scan rate: v_1 1.37 mV s⁻¹; v_2 10 mV s⁻¹; v_3 20 mV s⁻¹; v_4 40 mV s⁻¹; v_5 80 mV s⁻¹.

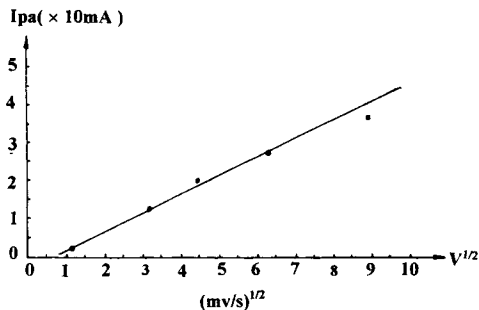


Figure 2 Dependence of anodic peak current I_{pa} on second root of scan rate $v^{1/2}$.

clear that I_{pa} has better linear relations with $V^{1/2}$, indicating a kinetic control mechanism for the electrode reaction that occurred at the positive electrode that is ascribed to the diffusion control of lithium in fullerenated poly(*N*-vinylcarbazole).

The infrared spectra shown in Figure 3 from fullerenated poly(*N*-vinylcarbazole) which underwent discharge treatment at a current density of $30 \mu\text{A cm}^{-2}$ for 26 h and the parent fullerenated poly(*N*-vinylcarbazole) were basically similar; they differed apparently in the presence of new peaks at 503.12 (vs), 1025.0 (vs), 1212.5 (vs), 536.0 (w), 556 (w), 637 (w), 625 (w), and 1803 (vw) cm^{-1} and the dramatic increase of the peak intensities at 1125.0 and 1156.2 cm^{-1} . Meanwhile, after the discharge of cell (a), the peaks at 471.87 (vw), 615.0 (vw), 575.0 (vw), and 528.12 (w) cm^{-1} disappeared completely; the latter peaks at 575.0 and 528.12 cm^{-1} were ascribed to the two characteristic vibration peaks of pure C_{60} [see Fig. 3(a)]. A possible reason for the above feedings is that in the discharging process the lithium atom lost an electron to participate in the big π -electron orbital motions of the carbazyl of the polymer and fullerene C_{60} attached to the polymer backbone, whereas the Li^+ ion might enter into the framework structure of C_{60} and carbazyl rings of the polymer to form an intercalation compound.^{8,24} However, specific locations of Li^+ in fullerenated poly(*N*-vinylcarbazole) and assignments of all the above new peaks require further research.

The X-ray diffraction scan for the fullerenated poly(*N*-vinylcarbazole) which underwent the discharge treatment is shown compared with that from the parent fullerenated poly(*N*-vinylcarbazole) in Figure 4. It is obvious that after the discharge of cell (a) the intensities of two main diffraction peaks centered at $2\theta = 20.36^\circ$ (4.358 Å) and 7.82° (11.296 Å) [see Fig. 4(a); the magnitude in the parentheses represents the corresponding d -value for the 2θ peak], in which the former is an amorphous halo

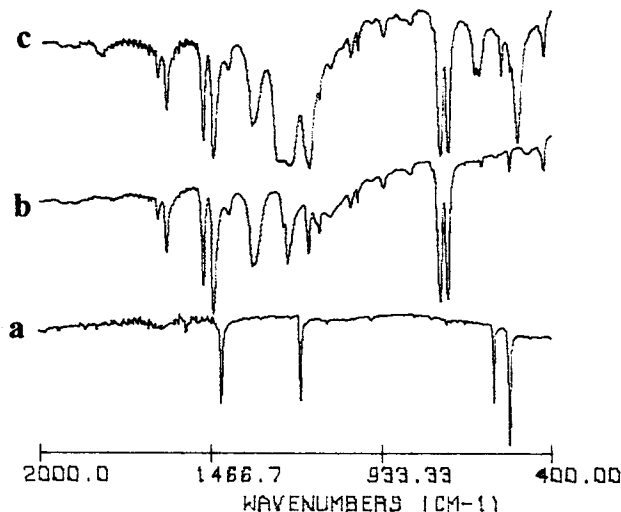


Figure 3 FTIR spectra of the samples: (a) C_{60} ; (b) fullerenated poly(*N*-vinylcarbazole) containing 3.85% C_{60} ; (c) fullerenated poly(*N*-vinylcarbazole) which underwent the discharge treatment at a current density of $30 \mu\text{A cm}^{-2}$ for 26 h.

which is broad and diffuse, and the latter, a function of chain parallelism,²⁵ decreased dramatically and their peak positions (2θ angle) only varied slightly from 2θ 7.82° (11.296 Å), 20.36° (4.358 Å) to 7.90° (11.182 Å), 20.84° (4.259 Å), respectively, indicating that Li^+ ions intercalated into the crystal grating of the polymer. Furthermore, after electric cell (a) discharged, the three small sharp peaks centered at 14.62° (6.054 Å), 28.58° (3.121 Å), and 29.80° (2.988 Å) shown in Figure 4(a), which have been interpreted as being associated with the covalent attachment of C_{60} to the poly(*N*-vinylcarbazole) backbone,²⁶ disappeared and a very strong new peak

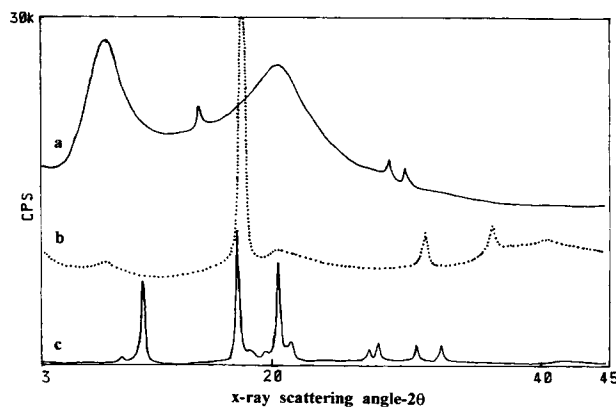


Figure 4 X-ray diffraction diagrams from (a) fullerenated poly(*N*-vinylcarbazole); (b) fullerenated poly(*N*-vinylcarbazole) which underwent the discharge treatment at a current density of $30 \mu\text{A cm}^{-2}$ for 26 h; (c) C_{60} .

at 17.92° (4.946 Å) and two weak new peaks centered at 2θ 31.40° (2.846 Å) and 36.42° (2.465 Å) were observed [Fig. 4(b)]. Meanwhile, the presence of possible new crystal gratings of Li_2O , Li_2O_2 , NiO , and LiClO_4 in the material for a positive electrode due to the discharge of cell (a) was not detected. Chabre et al.⁸ reported the electrochemical intercalation of lithium into solid C_{60} and found that preliminary X-ray studies on positive composite electrode materials reduced at 2.2 and 1.3 V (i.e., $x = 0.5$ and $x = 3$, respectively) give new diffraction patterns which do not correspond to those of the K and Rb compound structures.¹⁰ To further identify the assignments of the above three new peaks, the scattering for pure C_{60} shown in Figure 4(c) is also characterized by 11 peaks centered at 2θ 9.02° (9.796 Å), 10.60° (8.338 Å), 17.54° (5.052 Å), 18.52° (4.787 Å), 19.74° (4.494 Å), 20.58° (4.312 Å), 21.56° (4.118 Å), 27.30° (3.264 Å), 27.98° (3.186 Å), 30.74° (2.906 Å), and 32.66° (2.740 Å). Among these peaks, the peaks at 2θ 17.54° , 10.60° , and 20.58° are relatively strong diffraction peaks. The results show that the above three new peaks might result from electrochemical intercalation of lithium into fullerene C_{60} attached to the polymer backbone.

The effect of the discharge of electric cell (a) on the paramagnetic electronic structure of fullerenedated poly(*N*-vinylcarbazole) was investigated by the ESR technique (Fig. 5). As shown in Figure 5(a), the ESR signal of pure poly(*N*-vinylcarbazole) was not detected. The ESR spectrum of fullerenedated poly(*N*-vinylcarbazole) before the discharge of electric cell (a) [Fig. 5(b), gain factor: 8×10^4] shows two peaks: a narrow peak I ($g = 2.0028$, $\Delta H_{pp} = 2.2\text{G}$) with respect to the interaction between the pendant C_{60} molecule and corresponding near-neighboring carbazole groups in the polymer, and a shoulder broad peak II ($\Delta H_{pp} = 11.2\text{G}$) assigned to the interaction between positively charged carbazyl and the adjacent rich-charged carbazyl.²⁷ It is obvious that two kinds of paramagnetic species in fullerenedated poly(*N*-vinylcarbazole) is in existence. After electric cell (a) discharged, the ESR spectrum from the fullerenedated poly(*N*-vinylcarbazole) for the positive electrode [Fig. 5(c), gain factor: 5×10^5] shows two new complicated signals, III' and IV', besides signal I' ($g = 2.0025$, $\Delta H_{pp} = 2.2\text{G}$) and signal II'. It is well known that relative ESR signal intensity is directly proportional to $Y'_m(\Delta H_{pp})^2$, where Y'_m is the amplitude of the peak and ΔH_{pp} is the peak-to-peak width. As ΔH_{pp} remains constant, the signal intensity is directly proportional to peak height. The ratio of peak height of signal I' and signal I was calculated as 0.3157 using the gain factor of 5×10^5 as the

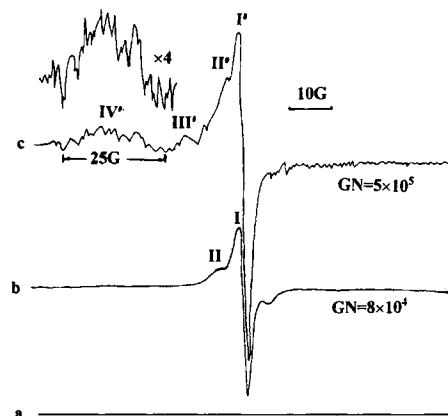


Figure 5 ESR spectra of (a) pure poly(*N*-vinylcarbazole); (b) fullerenedated poly(*N*-vinylcarbazole); (c) fullerenedated poly(*N*-vinylcarbazole) which underwent the discharge treatment at a current density of $30 \mu\text{A cm}^{-2}$ for 26 h.

calculated reference standard under the same experiment condition; i.e., the intensity of signal I shown in Figure 5(b) decreased 68.43% after the discharge of electric cell (a), implying that the interaction between the pendant C_{60} molecules and corresponding near-neighboring carbazole groups in the polymer weakened due to lithium intercalation into fullerenedated poly(*N*-vinylcarbazole). The above results demonstrated that the electrochemical intercalation of lithium into fullerenedated poly(*N*-vinylcarbazole) has an important effect on unpaired electron spinning concentration and the paramagnetic electric structure of the above material; this conclusion is in correspondence with that reported by Li.²³

CONCLUSION

We have demonstrated the synthesis of soluble fullerenedated poly(*N*-vinylcarbazole) through the reaction of carbanion intermediates with fullerene. A mechanism of an electrochemical intercalation reaction is suggested for the discharge of the first Li-fullerenedated poly(*N*-vinylcarbazole) battery on the basis of experimental data obtained from cyclic voltammetry, FTIR, XRD, and ESR. The above battery has a higher open-circuit voltage (ca. 3.2 V), and its discharge may be ascribed to the electrochemical intercalation process of lithium into fullerenedated poly(*N*-vinylcarbazole). Further characterization and study of the electrochemical properties of the positive composite electrode materials, as well as the physical and chemical behaviors of lithium ions

in fullerenated poly(*N*-vinylcarbazole), are currently being investigated.

We thank professor Zhi-Yu Jiang for helpful discussions. This work was supported by the National Natural Science Foundation of China and Science Foundation of Shanghai Committee of Science and Technology.

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Received July 10, 1995

Accepted November 9, 1995