# **Characteristics of Aqueous Polycarbazole Batteries**

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**ABSTRACT:** The characteristics of electrochemically prepared polycarbazole (PCARB) as the cathode active material for secondary batteries are studied in aqueous electrolytes. The cell of the type  $\text{Zn/Zn}(\text{CIO}_4)_2/\text{PCARB}$  has a specific capacity of 30 Ah/kg and an energy density of 46 Wh/kg. The coulombic efficiency is about 80–90% and is dependent on the thickness of PCARB films. Cole-Cole plots for PCARB electrodes by impedance measurements have been obtained at different oxidation potentials as a function of doping. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 145–150, 1999

Key words: polycarbazole; batteries

## INTRODUCTION

Polymer batteries offer the advantages of high energy density, high output voltage, design flexibility and longer electrode life due to the absence of mechanical changes in electrode dimensions. But the major problems in their commercialization arise due to the lack of charge retention, processability, environmental stability, and inefficient current collection at the polymer-substrate interface.<sup>1-2</sup> Copolymerization, incorporation of electroactive anions as fixed charge compensators, use of polymer composites with inorganic oxide materials and molten salt electrolytes with aluminium as counter electrode are some of the recent strategies applied to improve the performance of polymer batteries.<sup>3–8</sup> Another significant development is the recent work involving the use of solid polymer electrolytes such as polyethylene oxide and polyacrylonitrile as battery electrolytes.<sup>9–11</sup> Their light weight and flexibility will enable the realization of ultrathin batteries with

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very high energy densities. The low shelf life and poor charge retention of these polymer batteries has prevented their commercialization.

It is significant to note that of the number of conducting polymers reported so far, polyacetylene, poly(p-phenylene), polyazulene, polypyrrole, polythiophene, poly(3-methylthiophene), polyaniline, poly(2-methylaniline) and poly(N-vinylcarbazole) have been investigated for battery applications. Of these polypyrrole and polyaniline have been recently commercialized by BASF (Germany) and Bridgestone Corporation (Japan), respectively. In view of the newness of the field and the potentially large number of synthesizable conducting polymers, further research has become necessary to identify suitable polymers for charge storage applications.

Carbazole having a structure of pyrrole ring with two fused benzene rings beside it, has been reported to form a conducting polymer with conductivity of 0.1–1 Scm<sup>-1</sup>. The linkage of monomers occurs via 3,6 positions.<sup>12</sup> The attraction of polycarbazole (PCARB) lies in its stability in air. Carbazole can be viewed either as a derivative of pyrrole or as that of aniline. Our studies on the electroactivity and proton doping of PCARB<sup>13</sup> and

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Figure 1 Schematic of the  $Zn/Zn(ClO_4)_2/PCARB$  battery.

also earlier studies by other authors<sup>14–16</sup> have shown that PCARB resembles more of polyaniline than it does polypyrrole. Polypyrrole and polyaniline are known to possess good stability and their battery performance in aqueous electrolytes have been reported.<sup>7,17–18</sup>

We report here the charge-discharge characteristics of PCARB/Zn( $ClO_4$ )<sub>2</sub>/Zn cell to examine the possibility of useage of PCARB film in aqueous rechargeable battery.

## **EXPERIMENTAL**

Carbazole (Merck) was recrystallized from methanol. Perchloric acid, methanol and other chemicals were of reagent grade and were used as supplied. Thick green PCARB films were deposited on a platinum plate  $(1 \text{ cm}^2)$  by potentiostatic oxidation of carbazole at 0.7 V versus Ag/AgCl reference in a medium containing 75% of methanol and 25% of 5 M HClO<sub>4</sub>. Film thickness was controlled by monitoring the charges passed during polymerization. Charging-discharging tests were performed in aqueous zinc perchlorate at pH 1.3, which was prepared by dissolving 1 g of zinc in 3 ml of perchloric acid (70%) and diluting it to 20 ml with distilled water. A slightly amalgamated zinc foil served as the anode. No gas evolution was observed at the zinc anode and it could be repeatedly used for several cycles. The weight of the polymer was 2.3 mg/cm<sup>2</sup> at 2.5 C/cm<sup>2</sup>. Schematic of a batterey with PCARB film as cathode and Zn as anode is shown in Figure 1.

Experiments were performed on an Electrochemical Interface (SI 1286, Schlumberger Instruments Ltd.) and data were recorded on a Hewlett Packard ColorPro plotter. Impedence measurements were made by using an impedance analyzer (Model HP 4192A). The film morphology was examined by using a scanning electron microscope (Hitachi model 450).

# **RESULTS AND DISCUSSION**

Figure 2(a) shows cyclic voltammograms of polycarbazole obtained at different scan rates in 5 M perchloric acid. The anodic and cathodic peak potentials obtained at a sweep rate of 10 mVs<sup>-1</sup> are 0.33 V and 0.12 V versus Ag/AgCl, respectively. The peak currents scale linearly with the sweep rate (inset Fig. 2). The anodic and cathodic peaks correspond to the doping and undoping of perchlorate ions, respectively. The anodic peaks become sharper with increasing sweep rates and several linear regions are involved at the highest sweep rate of 100 mVs<sup>-1</sup> (Fig. 2), whereas the cathodic peak is virtually unaltered. This may perhaps be attributed to a change in film resistivity that is coupled with electrochemical switching.<sup>19</sup>

Figure 3(a,b) shows the cyclic voltammograms at higher anodic limits. When a virgin film is swept in the potential range -0.2 to 0.7 V, a second anodic spike can be observed in the first scan only. However, on the anodic limit being extended to 1.25 V, a third irreversible anodic peak is also observed. During the first scan the second anodic spike is present, but from the second scan onwards only the first and third peaks are observed. Successive scans in this potential range led to the redox characteristics of the first couple. These observations are similar to those



**Figure 2** (a) Cyclic voltammogram (CV) of polycarbazole at different scan rates in 5 M HClO<sub>4</sub>. (b) Plot of the peak current  $(I_P)$  versus the scan rate (v).



**Figure 3** CV (20 mVs<sup>-1</sup>) of carbazole modified electrodes in 5 M HClO<sub>4</sub> for varying potential ranges. (a) -0.2 to 0.7 V: (1) first scan, (2) second scan. (b) -0.2 to 1.2 V: (1) first scan, (2) second scan.

made by Mengoli et al.<sup>14–15</sup> who speculated the second and third peaks to be due to the formation of some oligomers and degradation products. However, as long as the anodic potential limit does not exceed 0.45 V, the first redox process remains fairly stable for more than 100 scans, and it represents the stable form of PCARB associated with electrochromism.

Figure 4(a) shows the cyclic voltammograms of PCARB in zinc perchlorate solution, with zinc as the anode. The anodic peak attains the shape after a few "activating" scans (2 to 5 scans) and the peak currents tend to increase to 10-15% during the subsequent scans. After about 80 scans, the peak current decrease with the oxidation peak becoming less intense and the reduction peak, broader [Fig. 4(b)].

The results of elemental analysis correspond to the empirical formula  $C_{12}H_{13}N(ClO_4)_{0.45}$ . The oxidized film contains one perchlorate ion for every two carbazole rings. This is in accordance with the literature reports.<sup>12,14</sup>

The scanning electron micrograph (Fig. 5) shows a partially crystalline and rough morphol-



**Figure 4** (a) CV of polycarbazole in  $Zn(ClO_4)_2$ . Scan rate = 20 mVs<sup>-1</sup>, film formation charge = 150 mC. Current gradually increased with potential cycling and reached a steady voltammogram. (b) Continuous CV of polycarbazole obtained in  $Zn(ClO_4)_2$  electrolyte solution. Cycle numbers are shown in figure.

ogy, which may facilitate the doping and undoping processes in PCARB electrodes.<sup>20</sup> Results of preliminary X-ray diffraction studies indicate the



**Figure 5** SEM of polycarbazole on Pt surface prepared at 5 M  $HClO_4$  at magnification of 600 Hz.



**Figure 6** Self discharge characteristics of Zn/Zn-(ClO<sub>4</sub>)<sub>2</sub>/PCARB battery.

semi crystalline nature of the electrochemically prepared PCARB film.

Figure 6 shows the variation of open-circuitvoltage with time. It can be seen that initially the cell voltage is 1.67 V which decreases fast. The observed fast rate of self-discharge initially may be attributed to some redox reactions in the electrolytic medium. It is significant to note that the cell voltage reaches an equilibrium value of 1.47 V in about 5 h and remains constant thereafter. This indicates that the PCARB is quite stable in the aqueous solution.

Figure 7(a,b) shows the charging-discharging curves of the zinc/PCARB battery at constant current densities. The PCARB electrode is doped electrochemically with perchlorate ion when charging reactions 1 and 2 occur at the polymer and zinc electrodes, respectively. When discharging, the reverse reactions occur.

$$(P)_{n} + 0.45nClO_{4}^{-} \rightarrow (P^{0.45}(ClO_{4}^{-})0.45)_{n} + 0.45ne^{-}$$
(1)

$$0.225nZn^{2+} + 0.45ne^{-} \rightarrow 0.225nZn$$
 (2)

The coulombic efficiency shows a slight decrease with increase in the film formation charge. The coulombic efficiency is about 91% for the thin film (0.5 Ccm<sup>-2</sup>) and 81% for the thicker film (2.5 Ccm<sup>-2</sup>). The voltage drop observed at the point of polarity change becomes more pronounced by increasing the current density for the thicker films. This indicates that the reversibility of doping-undoping process at thicker film becomes lower than that of thin PCARB film prepared at 0.5 Ccm<sup>-2</sup> charge. The average discharge voltage is

about 1.55 V and the short-circuit current is 13 mA when charged at 100  $\mu$ A cm<sup>-2</sup>. The cell has a maximum capacity of 30 Ahkg<sup>-1</sup> and an energy density of about 46 Whkg<sup>-1</sup>. It may be of interest to note that PCARB and poly(N-vinylcarbazole)-lithium batteries in propylene carbonate/LiClO<sub>4</sub> electrolyte show open-circuit voltages of 3.95 and 4.15 V and coulombic efficiencies of 80.7% (1 mAcm<sup>-2</sup>) and 86% (11.1  $\mu$ Acm<sup>2</sup>), respectively.<sup>2,21</sup> The PCARB/Zn battery has a specific capacity of 51.2 Ahkg<sup>-1</sup> and an energy density of about 140 Whkg<sup>-1</sup> with a self-discharge of 7.7% and can withstand about 14 cycles. Performance characteristics of some conducting polymer batteries are shown in Table I.

Figure 8 shows typical Cole–Cole plots for the PCARB film at different anode potentials of the cyclic voltammogram. From Figure 9 it is ob-



**Figure 7** (a) Charge and discharge of the cell containing  $0.4 \text{ mg/cm}^2$  of polycarbazole at different current densities. (b) Charge and discharge of the cell containing  $2.3 \text{ mg/cm}^2$  of polycarbazole at different current densities.

Cell config. –/Elec/+	0.c.v. (V)	Energy Density Wh/kg	Coulumbic Efficiency (%)	R
C/PANI/ZnCl <sub>2</sub> —NH <sub>4</sub> Cl/Zn	1.0	50-100	70–100	18
Zn/1MZnSO <sub>4</sub> /PANI		111	100	17
Zn/ZnCl <sub>2</sub> /PMA-Pt	1.3	110.3	100	22
Li/LiClO <sub>4</sub> —PC/PANI	3.1	382	100	23
Li/LiClO <sub>4</sub> —PC/PVCz	3.86	_	90	21
Zn/Zn(ClO <sub>4</sub> ) <sub>2</sub> /PCARB	1.47	46	80–90	Present work

Table I Performance Characteristics of Conducting Polymer Batteries

served that the reduced film has a very low capacitance. As soon as the oxidation of the film begins, the capacitance rises to reach a maximum at about 1.6 V, whereafter it decreases. This is in agreement with the cyclic voltammogram data (Fig. 4) where the oxidation peak is at 1.6 V. Thus, the capacitance is directly proportional to the amount of oxidized polymer but is independent of the electrode potential once the polymer film is converted into its oxidized form.<sup>24</sup> The impedance data show that the behaviour of PCARB is typical of a thin redox and electronically conductive polymer film. The semicircle in the high frequency part of the figure indicates charge transfer domination and is characteristic



**Figure 8** The Cole–Cole plots for impedance of polycarbazole at different potentials during doping at different oxidation potentials: ( $\triangle$ ) 1.0 V; ( $\bigcirc$ ) 1.2 V; ( $\times$ ) 1.4 V; ( $\bullet$ ) 1.6 V; ( $\blacktriangle$ ) 1.8 V. The film formation charge = 2 Ccm<sup>-2</sup>. The numbers labelling points on the curves are frequencies (Hz).

of a parallel net work formed by a resistor and capacitor.  $^{25-27}$ 

### CONCLUSIONS

PCARB/Zn(ClO<sub>4</sub>)<sub>2</sub>/Zn cell has a specific capacity of 30 Ah/kg and an energy density of 46 Wh/kg. Depending upon the thickness of PCARB films the coloumbic efficiency has been experimentally determined as about 80–90%. These results indicate that the electrochemically doped PCARB, can be used as a cathode active material in aqueous rechargeable battery. Although, presently the energy density and specific capacity of this PCARB battery is low; however, attempts are being made to improve its performance.

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**Figure 9** Capacitance versus oxidation potential for polycarbazole-coated electrodes.

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# REFERENCES

- Yoneyama, H.; Li, Y.; Kuwabata, S. J Electrochem Soc 1992, 139, 28.
- Morishita, Masao; Abe, Sueki. Elect Eng Japan 1987, 107, 1.
- Naoi, K.; Ueyama, K.; Osaka, T.; Smyryl, W. H. J Electrochem Soc 1989, 136, 1385.
- 4. Osaka, T.; Naoi, A. J Electrochem Soc 1989, 136, 13.
- Santhanam, K. S. V.; Gupta, Neeraj. Trends Poly Sci 1993, 1, 284.
- Kuwabata, S.; Kishimoto, A.; Tanaka, T.; Yoneyama, H. J Electrochem Soc 1994, 141, 10.
- Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. J Electrochem Soc Chem Commun 1987, 327.
- Koura, N.; Ejiri, H.; Takeishi, K. J Electrochem Soc 1993, 140, 602.
- Momma, T.; Kakuda, S.; Yarimizu, H.; Osaka, T. J Electrochem Soc 1995, 142, 1766.
- Osaka, T.; Momma, T.; Nishimura, K.; Kakuda, S.; Ishii, T. J Electrochem Soc 1994, 141.
- Kakuda, S.; Momma, T.; Osaka, T.; Battista Appetecchi, G.; Scrosati, B. J Electrochem Soc 1995, 142, L1.

- Waltman, R. J.; Bargon, J. Can J Chem 1986, 64, 76.
- Verghese, M. M.; Sundaresan, N. S.; Basu, T.; Malhotra, B. D. J Mat Sci Lett 1995, 14, 401.
- Mengoli, G.; Musiani, M. M.; Schreck, B.; Zecchin, S. J Electroanal Chem 1988, 246, 73.
- Cattarin, S.; Mengoli, G.; Musiani, M. M.; Scherck, B. J Electroanal Chem 1988, 246, 87.
- Hino, S.; Iwasaki, K.; Matsumoto, K. Synth Met 1994, 64, 259.
- Kitani, A.; Kaya, M.; Sasaki, K. J Electrochem Soc 1986, 133, 1069.
- Trinidad, F.; Montemayor, M. C.; Fatas, E. J Electrochem Soc 1991, 138, 3186.
- Gottesfeld, S.; Redondo, A.; Rubinstein, I.; Feldberg, S. W. J Electroanal Chem 1989, 265, 15.
- Osaka, T.; Naoi, K.; Ogano, S.; Nakamura, S. J Electrochem Soc 1987, 134, 2096.
- 21. Kakuta, T.; Shirota, Y.; Mikawa, H. J Chem Soc Chem Commun 1985, 553.
- Popkirov, G. S.; Barsoukov, E. J Electroanal Chem 1995, 383, 155.
- 23. Shaolin, Mu; Bidong, Q. Synth Metals 1989, 32, 129.
- Osaka, T.; Nakajimo, T.; Naoi, K.; Owens, B. B. J Electrochem Soc 1990, 137, 2139.
- Hunter, T. B.; Tyler, P. S.; Smyrl, W. H.; White, H. S. J Electrochem Soc 1987, 134, 2198.
- Jow, T. R.; Shacklette, L. W. J Electrochem Soc 1988, 135, 541.
- Naoi, K.; Ueyama, K.; Osaka, I.; Smyrl, W. H. J Electrochem Soc 1990, 137, 494.