

Short communication

Electrochemical activity of polypyridine in aqueous acidic media

Takakazu Yamamoto ^{a,*}, Toshihiko Nishiyama, Gaku Harada ^b, Masataka Takeuchi ^c

^a Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^b Energy Devices Division, Engineering Department, NEC, 1120 Shimokuzawa, Sagamihara, Kanagawa 229-1198, Japan

^c Central Research Laboratory, Showa Denko, 1-1-1 Oonodai, Chiba, Midori-ku, 267-0056, Japan

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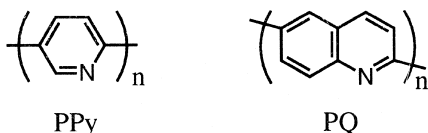
Abstract

Polypyridine (PPy) cast on carbon fibre is reduced at about -0.20 V vs. Ag/AgCl in an aqueous solution of poly(vinyl sulfonic acid), PVSA. The cyclic voltammetric trace is stable for over a thousand scans and gives a discharge capacity of 117 C per gram of polypyridine. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Polypyridine; Cyclic voltammogram; Negative electrode active material

1. Introduction

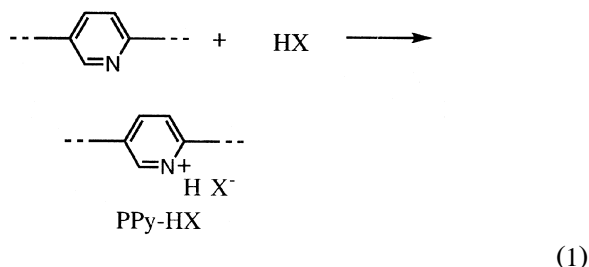
π -Conjugated aromatic polymers containing imine nitrogen are the subject of recent interest [1–4]. The following polypyridine, PPy, and polyquinoline, PQ, are typical polymers of this kind.



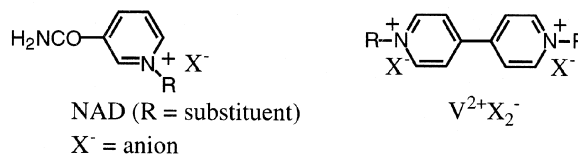
These polymers are susceptible to reduction because they contain electron-withdrawing imine nitrogen, and electrochemical reduction (or n-doping) of these polymers in

non-aqueous solutions has been reported [5]. The electrochemical response of these polymers and their derivatives in acidic media has, however, received much less attention [6].

The polymer will be protonated in acidic media, and the protonated structure resembles those of NAD and viologene dyes ($V^{2+}X_2^-$) which are electrochemically redox active, e.g.,

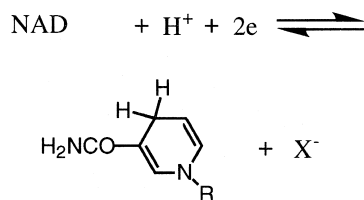
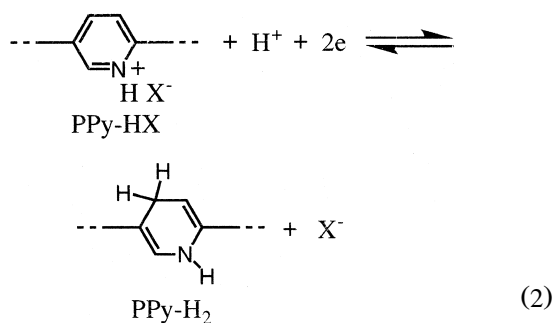


Analogous compounds:

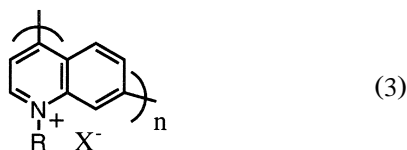


* Corresponding author. Tel.: +81-45-924-5220; Fax: +81-45-924-5276; E-mail: tyamamot@res.titech.ac.jp

la7If PPy–HX accepts electrochemical redox reactions similar to those of NAD and $V^{2+}X_2^-$, i.e.,



then it can serve as a negative electrode active material in battery. Based on these considerations, we have studied the electrochemical response of PPy in an acidic medium. Electrochemical responses of the following polyquinolines quaternized with RX in aqueous media have been reported [6].



2. Experimental

Polypyridine, PPy [4], and polyaniline [7] were prepared according to the methods reported in the literature. A carbon fibre (Showa Denko crystalline VGCF) sheet (electrical conductivity = 60 S cm^{-1} ; packing density = 0.054 g cm^{-3}) was impregnated with a formic acid solution of PPy and dried under vacuum. The carbon fibre sheet was then dipped in an aqueous dispersion of Nafion, dried, and used for the electrode. A commercially available aqueous solution of poly(vinyl sulfonic acid), PVSA, (6 M of the monomer unit) was used as the acidic aqueous solution for the electrochemical study.

3. Results and discussion

A cyclic voltammogram (CV) for PPy laid on the carbon electrode in an acidic aqueous solution of PVSA is shown in Fig. 1. The voltammogram shows that PPy undergoes electrochemical reduction in a range of about -0.1 to $-0.3 \text{ V vs. Ag/AgCl}$. Reverse scanning gives a discharging anodic current with a peak at $-0.11 \text{ V vs. Ag/AgCl}$. The CV data depicted in Fig. 1 correspond to a discharge capacity of $117 \text{ C per gram of PPy}$. Without PPy, the carbon electrode does not give such an electrochemical redox cycle and, consequently, the redox reaction is due to PPy. Since electrochemical reduction of $V^{2+}X_2^-$ [8] and quarternized polyquinoline [6] takes place at an analogous potential (about $-0.5 \text{ V vs. Ag/AgCl}$), the electrochemical reactions expressed by Eq. (2) are possible. Attachment of the electron-withdrawing [4] PPy backbone at the pyridine ring in Eq. (2) appears to facilitate the reduction of the protonated pyridine ring.

The CV cycle is stable and essentially the same CV trace is obtained even at the 1000th cycle. Without the Nafion layer (see Section 2), which coats the PPy layer, the CV trace is unstable, and about half the discharge capacity is obtained after the 100th cycle. This is presumably due to partial dissolution of PPy into the acidic medium.

Because of the excellent cyclability of the electrochemical redox reaction of PPy, the following secondary cell has been constructed by using PPy laid on the carbon electrode, PVSA, and polyaniline (PAn) laid on the carbon electrode, i.e., C/PPy/PVSA(aq)/PAn/C. A discharge curve for the cell with an excess amount of PAn is shown in Fig. 2. The electromotive force of the cell agrees with the redox potentials of PPy (about $-0.1 \text{ V vs. Ag/AgCl}$,

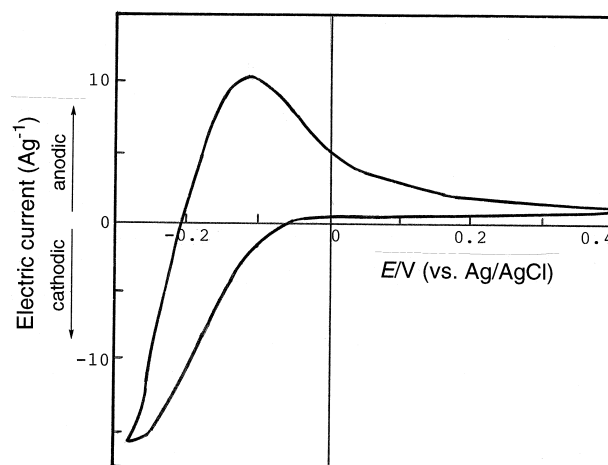


Fig. 1. Cyclic voltammogram for polypyridine laid on carbon fibre electrode in acidic aqueous solution of poly(vinyl sulfonic acid). Scanning rate = 20 mV s^{-1} .

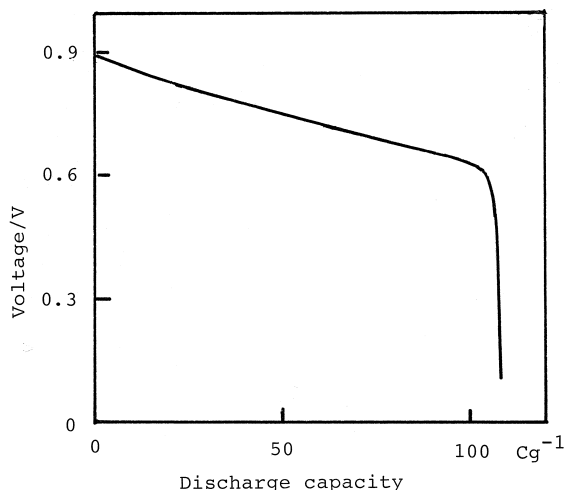
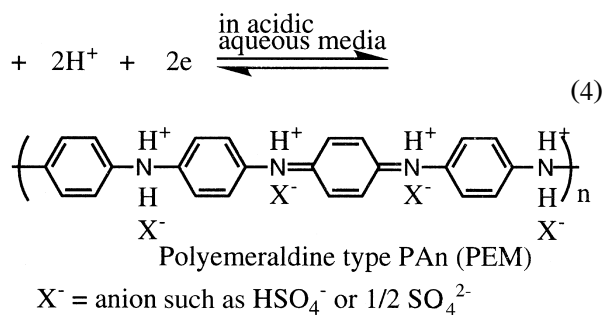
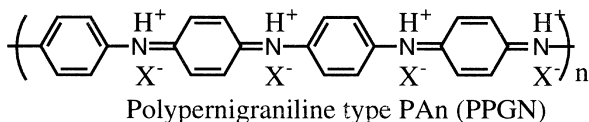


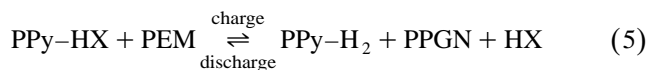
Fig. 2. Discharge curve for C/PPy/PVSA(aq)/PAn/C cell at a 0.1 C discharge rate. After charging for 300 s at 0.9 V. At 7th discharge. The discharge capacity is given in coulomb per gram of PPy.

see, Fig. 1) and oxidized PAn (polypernigraniline, about 0.8 V vs. Ag/AgCl [9,10]).



Such electrochemical reactions of PAn have been studied extensively, and the assumption of the electrochemical

reaction expressed by Eq. (2) gives the following total cell reaction (Eq. (2) + Eq. (4)):



The discharge capacity estimated for discharge voltage range of 0.9 to 0.63 (Fig. 2) is 98 C per gram of PPy and corresponds well to the discharge capacity evaluated from the CV trace.

As described above, PPy can serve as a new type of negative electrode active material in acidic aqueous media, although its discharge capacity is not large. The reduction of the pyridine ring (Eq. (2)) appears to be facilitated by the electron-withdrawing PPy chain (*vide ante*), but such a facilitation effect may be weakened by partial conversion of the pyridine ring of PPy into the reduced pyridine $-\text{H}_2$ ring. This will render reduction of the remainder of pyridine ring difficult and will, therefore, yield a relatively small discharge capacity. This problem may, however, be overcome by the introduction of an electron-withdrawing substituent (e.g., the $\text{NH}_2\text{CO}-$ group in NAD, *vide ante*) to the pyridine ring of PPy. Studies along these lines are now in progress.

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