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Quinone Diimine Part of Polyaniline Is Electrochemically Inactive in Nonaqueous Electrolytes

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ABSTRACT: An electrochemical and Raman spectroscopic study on polyaniline consisting of 1,4-iminophenylene (IP, $-NHC_6H_4-$) and nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene (NP, $-N{=}C_6H_4{=}NC_6H_4-$) units has proved that the NP part is electrochemically inactive in nonaqueous electrolytes in spite of its conjugated structure of single and double bonds. The IP part can be doped but the doped regions of polyaniline with more NP content are less uniform and have larger bond orders. Increase in the NP content decreases electrical conductivity and discharged capacity of polyaniline. Hence, polyaniline containing the NP structure is not suitable for the positive electrode material of a rechargeable lithium battery.

Introduction

Recently, polyaniline has attracted much attention because of its excellent electrical characteristics.[1-5] Elucidation of the relationships between its electrical properties and molecular structure is extremely important because it takes various forms with different physicochemical properties, depending critically on treatments after polymerization. Vibrational spectra of most of the forms of polyaniline have been studied extensively, and the relationships between the spectra and structure are established.[6,7] There are four possible unit structures in polyaniline, and the physicochemical properties depend on their composition: the four unit structures being imino-1,4-phenylene (abbreviated to IP), the cation of IP (IP^+), the radical cation of IP ($IP^{\bullet+}$), and nitrilo-2,5-cyclohexadiene-1,4-diylidenenitrilo-1,4-phenylene (NP).[7] XPS spectra have been consistently analyzed and turned out to be useful in estimation of the composition.[8] A comparison between the structure and electrical conductivity has revealed that $IP^{\bullet+}$ plays an important role in electrical conduction.[7,8] On the other hand, the role of the NP part in doped polyaniline has not been fully clarified yet. MacDiarmid et al. have pointed out the possibility that the NP structure has a degenerate ground state, like $(CH)_x$, and might exhibit defect states in the form of solitons.[9] Genies et al.[10] and Pistoia et al.[11] have proposed schemes that NP might be doped in nonaqueous electrolyte and would be converted to $NP^{\bullet+}$. Whether NP is active in nonaqueous solution or not is important, because some devices such as a polyaniline–lithium battery have been constructed on the basis that the NP part is not electrochemically active in nonaqueous solution. If it is active, polyaniline containing the NP part may be utilized for such devices. If it is not, however, the presence of NP would deteriorate the performance such as discharged capacity and internal resistance of the battery.

We studied Raman spectra, cyclic voltammograms, and electrical conductivities on several polyaniline samples of different NP contents and reference compounds of low molecular weights. It has turned out that the NP part is not doped in nonaqueous solution at standard conditions. The details are reported in this paper.

Experimental Section

The synthetic methods of polyaniline films are generally the same as those reported earlier[7,8] except for some details. A polyaniline film (as-prepared film, termed 2S[7,8]) was deposited by electrochemical oxidation of aniline in aqueous acid solution on a 2 cm × 2 cm platinum electrode under an electric current of 10 mA/cm^2, with a total electric charge of 16 C. The electrolyte solution contained 2 M hydrofluoroboric acid and 1 M aniline. During the electrochemical polymerization, the potential of the platinum electrode was in the range 950–1300 mV against a NaCl-saturated HS-305DS Ag/AgCl reference electrode (Toa Electronic Ltd.). The potential at the end of polymerization was +550 mV vs Ag/AgCl.

Polyaniline 1A. A 2S film was immersed in 1 M hydrazine hydrochloride for 24 h and then dipped in an aqueous solution containing 30 w/v % hydrazine for 48 h. The resulting film was washed with acetonitrile and dried under dynamic vacuum (1A). The presence of only IP units in this film was confirmed by the infrared spectrum.[7]

Polyaniline 2A. A 2S film was immersed in degassed sodium hydroxide for 72 h, followed by washing with distilled water and drying under dynamic vacuum (2A).[7]

Polyaniline 2A(x). 2S films were electrochemically reduced at 0, 250, and 500 mV vs Ag/AgCl in 1% hydrofluoroboric acid. These conditions correspond to −550, −300, and −50 mV from the resting potential of polymerization. The resulting films were immersed in degassed sodium hydroxide for 72 h, washed with degassed distilled water, and dried under dynamic vacuum. These films are named 2A(0), 2A(250), and 2A(500), respectively.

The weights of the films (1A, 2A, and 2A(x)) were in the range 5.6–5.8 mg.

Doped 1A, Doped 2A, and Doped 2A(x). Nonaqueous electrochemical cells were constructed in a drybox (Mecaplex Ltd.) filled with ultrahigh-quality argon (Toyo Sanso Co., Ltd.). Electrochemical solvent was 1 M lithium tetrafluoroborate/propylene carbonate (electrolyte for a lithium battery, Mitsubishi Petrochemical Co., Ltd.). Lithium–aluminum alloy (Li 80 wt %) and lithium metal (Foote Mineral Co.) were used as the counter and reference electrodes, respectively. Each of 1A, 2A, 2A(0), 2A(250), and 2A(500) was oxidized in the electrochemical cell at +3.6 V vs the reference electrode: the oxidized films are termed doped 1A, doped 2A, doped 2A(0), doped 2A(250), and doped 2A(500), respectively.

Electrodes Made of Low Molecular Weight Reference Compounds. *N,N′*-Diphenyl-*p*-phenylenediamine (BBB, $C_6H_5NHC_6H_4NHC_6H_5$) (Wako Pure Chemical) was purified by sublimation and recrystallization from ethanol solution several

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Table I
Discharged Capacities and Electrical Conductivities in Various Doped Forms of Polyaniline

forms	discharged capacity, mA·h/g	electrical conductivity, S/cm
doped 1A	110	6–25
doped 2A(0)	105	0.7–3
doped 2A(250)	90	0.1–0.5
doped 2A(500)	84	2×10^{-2}–0.1
doped 2A	80	3×10^{-3}–1×10^{-2}

times until the crystals became colorless. *N,N'*-2,5-Cyclohexadiene-1,4-diylidenebis(benzamine) (BQB, $C_6H_5N{=}C_6H_4{=}NC_6H_5$) was prepared by oxidation of BBB.[12] Each compound was mixed with Teflon paste (polyflon D-1, Daikin Industries, Ltd.) and adhered on a platinum collecting electrode (BBB-electrode or BQB-electrode).

Electrochemical Measurements. The doped polyaniline samples were discharged at +2.0 V vs the reference for 168 h using the nonaqueous electrochemical cell described above. Electrical discharged capacity was monitored on a HF-201 coulomb/ampere-hour meter (Hokuto Denko Ltd.). Discharged capacity for each sample is listed in Table I. Cyclic voltammograms were recorded at 3 mV/s between 2.0 and 4.3 V vs the reference on a HECS 318 high-sensitivity potentiostat and a HECS 321B potential sweep unit (Huso Electrochemical System) with a Graphtec WX2400 X-Y recorder. Performances of polyaniline and BBB- and BQB-electrodes were examined with the electrochemical cell.

Electrical conductivity was measured for the doped polyaniline samples at room temperature by the four-probe method,[8] and the values are listed in Table I.

Raman spectra of polyaniline films at liquid-nitrogen temperature were obtained on a JEOL JRS-400D double monochromator or a Jasco CT-80D polychromator equipped with a multichannel detector.[7]

Results

Electrochemistry. A BBB-electrode was successfully oxidized in the electrochemical cell by applying +3.8 V vs the reference electrode. During this procedure, the colorless BBB-electrode turned blue and formation of a radical cation $BBB^{\bullet+}$ was ascertained by visible absorption and Raman spectroscopy.[7] A BQB-electrode, on the other hand, could not be oxidized with an electric potential up to +4.2 V vs the reference. This electrode could not be doped with cation (Li^+) by applying a negative potential (−0.5 V vs the reference electrode), although the supporting platinum plate was alloyed with lithium. Consistently, the Raman spectra of the BQB-electrode remained unchanged after such treatments.

For doped polyanilines, the discharged capacity was highest in doped 1A and decreased in doped 2A(0), doped 2A(250), doped 2A(500), and doped 2A, in that order (Table I). Electrical conductivity as well, was highest in doped 1A and decreased in the same order (Table I). It was lower than 10^{-5} S/cm for 1A, 2A, and 2A(*x*).

The general features in cyclic voltammograms of 1A, 2A(0), 2A(250), and 2A(500) (Figure 1) are similar to each other, although the first peak around 3.1 V corresponding to the formation of doped polyaniline becomes lower in that order, paralleling the trends in conductivity and discharged capacity.

Raman Spectra. Raman spectra of 2A, 2A(500), 2A(250), and 2A(0) with 514.5-nm excitation are shown in Figure 2. The spectral patterns of the latter three (Figure 2b–d) generally resemble that of 2A, which has been confirmed to consist of IP and NP.[6,7] However, the intensities at 1474 and 1220 cm^{-1} arising from ν_Q (a mixed mode of the C=N stretch and the C=C stretch) and the C–N stretch of the NP part,[6,7] relative to that at 1614 cm^{-1} assigned to a ring stretch mode of the IP part,[6,7] are largest in 2A [e.g., area 9.33 (peak 3.40) for ν_Q] and decrease in 2A(500), 2A(250), and 2A(0) in that order [8.89 (3.24), 6.28 (2.30), and 5.88 (1.98), respectively], indicating decrease in the NP content in the same order.

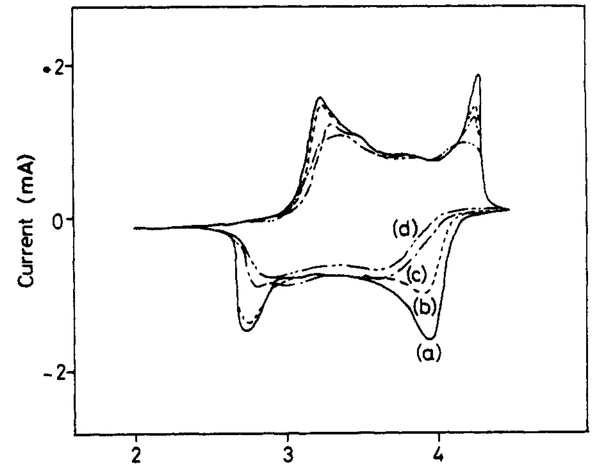

Figure 1. Cyclic voltammograms of (a) polyaniline 1A, (b) 2A(0), (c) 2A(250), and (d) 2A(500). As to the notations, see text.

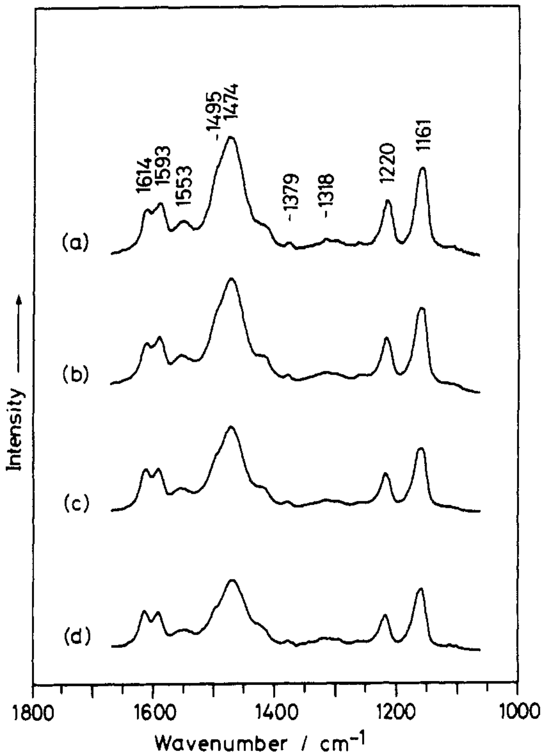

Figure 2. Raman spectra of (a) polyaniline 2A, (b) 2A(500), (c) 2A(250), and (d) 2A(0) with 514.5-nm excitation.

Raman spectra of doped 2A with 457.9-, 488.0-, 514.5-, and 632.8-nm excitation are shown in Figure 3. The spectra excited at shorter wavelengths (Figure 3a,b) are similar to those of doped 1A, which have been assigned to the IP part remaining undoped in doped 1A.[7] With 514.5-nm (or 632.8-nm) excitation, additional bands at 1597 (1591), 1498 (1500), 1324 (1372–1318), and 1249 (1262) cm^{-1} are reasonably assigned to the $IP^{\bullet+}$ part: the 1324-cm^{-1} band (the C–N stretch characteristic of radical cation $IP^{\bullet+}$)[7] exhibiting the largest downshift of −7 cm^{-1} on ^{15}N substitution (Figure 3e) as expected.[6,7] Two other bands at 1478 (1467) and 1220 (1223) cm^{-1} are definitely assigned to ν_Q[6,7] and ν_{CN}[7] of the NP unit, because their ^{15}N shifts of −13 and −5 cm^{-1} (Figure 3), respectively, resemble those

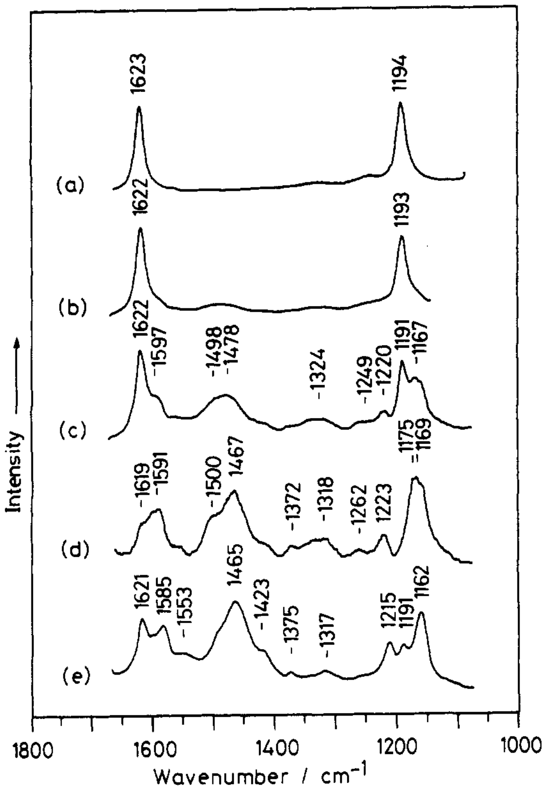

Figure 3. Raman spectra of polyaniline doped 2A excited at (a) 457.9, (b) 488.0, (c) 514.5, and (d) 632.8 nm and a Raman spectrum of ^{15}N-substituted polyaniline doped 2A (e) excited at 514.5 nm. Intensity patterns in (c) and (e) are different because the ^{15}N sample was prepared in small scale and the compositions of the unit structures resulted different from those of the ordinary doped 2A sample.

of the corresponding bands in 2A (−13 and −3 cm^{-1}).[6] The band around 1167 (1175–1169) cm^{-1} arises from an overlap of the CH bending vibrational bands of IP$^{•+}$ and NP.[6,7] Both the 1318- and 1372-cm^{-1} peaks in the 632.8-nm spectrum are assigned to the C–N stretch in the IP$^{•+}$ part. The wavenumber of this mode is sensitive to electron delocalization around the CNC part; i.e., it is lower for a more delocalized IP$^{•+}$ structure and converges to ca. 1310 cm^{-1}.[7] For short oligomers where the electron delocalization is limited, it is 1401–1383 cm^{-1} in BBB$^{•+}$[7] and 1386 cm^{-1} in B4$^{•+}$.[13] The broad band (with peaks at 1372 and 1318 cm^{-1}) indicates that the structure of the IP$^{•+}$ parts in the sample is not uniform but various parts of differently electron-delocalized structures are present. In fact, the spectral pattern around 1420–1310 cm^{-1} can be different for every doped sample, reflecting sensitively the distribution of the CNC structures. Hence, all the bands of doped 2A can be assigned to one of IP, IP$^{•+}$, and NP units, and no new bands assignable to NP$^{•+}$ were observed, which evidences that the NP part is not electrochemically oxidized in nonaqueous solution at standard conditions. Incidentally, NP does not seem either to be reduced electrochemically (at −0.5 V vs the reference), because the Raman spectrum of a 2A sample treated in that way was practically the same as that of untreated 2A.

Raman spectra of doped 2A(500), doped 2A(250), and doped 2A(0) with 632.8-nm excitation are similar to that of doped 2A (Figure 4), and each of them can be explained as an overlap of those of IP$^{•+}$, NP, and IP at a certain composition. (The presence of IP is better identified with 457.9-nm excitation.) It is easy to analyze the spectra if we compare the band shapes in the 1550–1450-cm^{-1} region, because the peaks around 1500 and 1470 cm^{-1} are characteristic of IP$^{•+}$ and NP, respectively. Apparently, the composition of NP is largest in doped 2A(500) and decreases in the order of doped 2A(250) and doped 2A(0), while the order in composition of IP$^{•+}$ reverses. The low-frequency peak of the C–N stretch band around 1380–1310 cm^{-1} due to IP$^{•+}$ is strongest in doped 2A(0) and becomes weaker in doped 2A(250) and doped 2A(500), which reflects the compositions of highly electron-delocalized CNC parts in the samples. Other spectral features are consistent with this interpretation. It is noticed that the spectrum of doped 2A(500) resembles very much that of doped 2A, indicating similar compositions of IP$^{•+}$ and NP in the two samples.

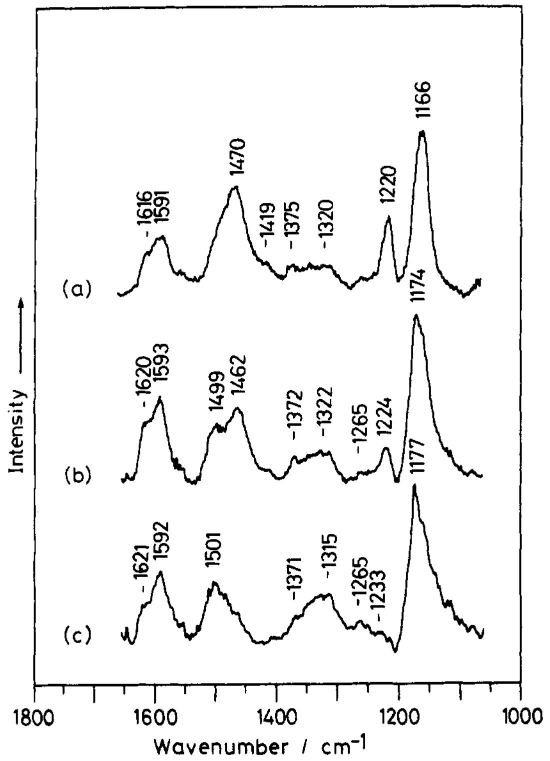

Figure 4. Raman spectra of (a) polyaniline doped 2A(500), (b) doped 2A(250), and (c) doped 2A(0) excited at 632.8 nm.

A difference spectrum between those of doped 2A and 2A excited at 514.5 nm is compared with the spectrum of doped 1A in Figure 5. Apart from the band intensities, which are differently scaled for a and b, the spectral patterns are mostly the same for the two. This observation signifies that the NP part in 2A is certainly not doped and the proportion of IP and IP$^{•+}$ is similar for doped 1A and doped 2A at the doping levels of the samples. However, comparison of the spectral pattern around 1380–1310 cm^{-1} clearly indicates that the structures of the CNC linkage in the IP$^{•+}$ part are more homogeneous and the electrons more delocalized in doped 1A than in doped 2A. The band around 1257 cm^{-1} in b is assigned to a benzene ring mode in the IP$^{•+}$ part, on the basis of a downshift (−27 cm^{-1}) on deuterium substitution at the benzene ring.[14] The frequency of this band seems to be affected by the electron delocalization, because this region also is much different between a and b.

Discussion

Raman spectral analyses clearly indicate that 2A and 2A(*x*)'s consist commonly of IP and NP units and the composition of NP is largest in 2A and 2A(500) and decreases in 2A(250) and 2A(0) in that order. 1A consists solely of IP.[7] When these samples are oxidized electrochemically in nonaqeous electrolyte, the IP domains are partly doped to give rise to IP$^{•+}$ units, whose content is

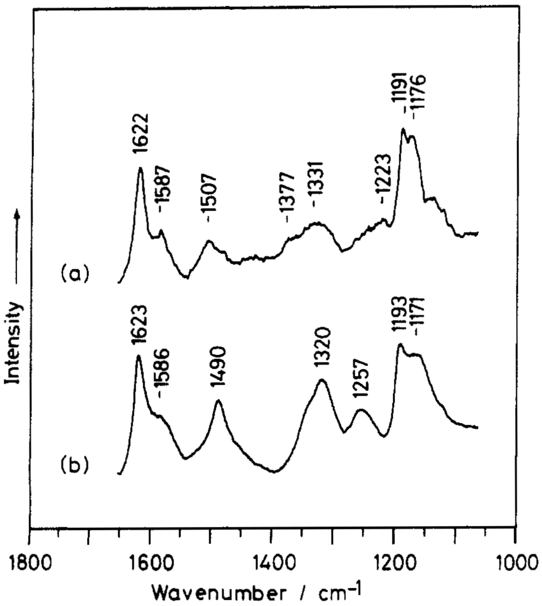

Figure 5. (a) Difference Raman spectrum (doped 2A–2A) and (b) Raman spectrum of doped 1A with 514.5-nm excitation.

largest in doped 1A and decreases in the following order: doped 1A > doped 2A(0) > doped 2A(250) > doped 2A (500) ≃ doped 2A. The NP part, on the other hand, is not oxidized (nor reduced), and hence the NP compositions in the undoped samples are retained in the doped samples. This was clearly exemplified by the similarity between the difference spectrum (doped 2A–2A) and the spetrum of doped 1A, which signifies that the electrochemical oxidation up to 3.1 V is simply a partial IP → IP$^{•+}$ process and does not involve the oxidation of the NP unit. The results on BBB- and BQB-electrodes that the former was electrochemically oxidized but the latter was not oxidized nor reduced are consistent with the Raman observations on polyaniline.

The cyclic voltammograms of 1a and 2A(x)'s were simple and similar to one another although the first-peak currents were different and the peak was steepest in 1A and broadened in 2A(0), 2A(250), and 2A(500) in that order. The differences can be explained in the light of the Raman observation that the NP unit is electrochemically inactive: the peak current decreases and the peak shape broadens in proportion to the composition of NP. The trend in discharged capacity in Table I is also explained by the same reason.

Apparently, the electrochemically inert NP part does not contribute to the electrical conductivity either. The conductivity is very low in 2A and 2A(x)'s, and the values of conductivity in the doped samples parallel the compositions of IP$^{•+}$. Conversely speaking, the more the content of NP in a doped sample, the lower is the conductivity. Hence, it is evident that only the radical cation IP$^{•+}$ is important in electrical conduction of polyaniline and intervening NP parts do not contribute to but hinder the electrical conduction.

When polyaniline is applied to the material for the positive electrode of a rechargeable lithium battery, which works in nonaqueous electrolyte, the NP-rich samples should be excluded because the NP parts decrease the discharged capacity and electrical conductivity and increase the internal resistance of the battery.

It may be stressed here, however, that the NP part is undesirable for limited practical devices, such as the polyaniline–lithium battery. When used in acid media, the quinone diimine part of the NP unit can be protonated to become conductive IP$^{•+}$.[7,15] Furthermore, photoinduced localized charged excitation[16] and a large photocurrent[17] in NP-containing polyaniline have been reported. A pH-sensitive transducer[18] and a photoelectric device[19] utilizing such properties of the NP part have been proposed.

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