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Electrocrystallization of Quinhydrone[1]

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Synopsis. Quinhydrone crystals were deposited at 2.0 V vs. Ag onto SnO_2-coated glass substrates from aqueous solutions of hydroquinone in the presence of NaCl, HCl, or NaOH. The crystals were observed with backscattered image SEM, and characterized with X-ray diffraction and IR spectroscopy. In situ visible absorption spectra were measured and a mechanism of deposition is discussed.

Quinhydrone is a representative charge-transfer (CT) complex between hydroquinone (HQ) as a donor and *p*-benzoquinone (BQ) as an acceptor. It is not only a conventional CT complex which has been studied for many years,[2] but also a novel type of molecular compound whose properties, such as a phase transition associated with the proton transfer,[3] have drawn attention. Quinhydrone is usually prepared by mixing HQ and BQ, or by chemical oxidation of HQ with iron(III) ammonium sulfate.[4]

Electrodeposition, in general, is a method with the following advantages: (1) The reaction is highly controllable by means of exterior physical conditions such as potentials, currents, charges, and so on. (2) Chemically active species, such as oxidizing reagents, are not necessary, i.e. the system is clean.[5] (3) Crystals of high quality can be easily obtained, particularly in the cases of CT complexes and ion radical salts, which are not soluble in most solvents.[6] However, there have been very few attempts to synthesize quinhydrone by electrocrystallization.

The objective of this work was to prepare quinhydrone crystals of high quality by electrodeposition. The conversion of HQ to quinhydrone involves electron transfer coupled with proton transfer.[7] Thus proton acceptors are needed for the conversion. Therefore, the electrochemical oxidation of HQ was carried out in aqueous solutions. The obtained crystals were characterized by some standard techniques. In addition, in situ visible absorption spectra were measured in order to clarify the mechanism of quinhydrone generation.

Experimental

Chemicals. HQ (purchased from Kanto Chemicals) was recrystallized from hot water. Hydrochloric acid, sodium chloride, and sodium hydroxide were used without further purification. Deionized water was used for the preparation of the solutions.

Electrocrystallization. An electrolytic glass cell equipped with a Ag counter electrode was used. A piece of SnO_2-coated glass (supplied from Showa Denko) served as the working electrode. HQ (0.4 $\mathrm{mol\,dm^{-3}}$) in the aqueous solution was oxidized in the presence of NaCl, HCl (both 0.2 $\mathrm{mol\,dm^{-3}}$), or NaOH (0.1 $\mathrm{mol\,dm^{-3}}$) by applying a potential of 2.0 V vs. Ag.

Measurements. Backscattered image scanning electron microscopy was performed with a JOEL JSM-5300 scanning electron microscope. The reason why backscattered image SEM was used is that Au thin films could not be evaporated onto the quinhydrone crystals, which sublimed easily. X-Ray diffraction of the powder was measured with a Riguku RU-3 diffractometer. IR spectra were measured with a Hitachi 215 IR spectrometer by a KBr method. In addition, in situ visible absorption spectra were measured with a Shimadzu MPS-2000 spectrophotometer, using a quartz cell equipped with SnO_2-coated glass and Ag electrodes.

Results and Discussion

Characterization of the Crystals. When a potential of 2.0 V vs. Ag was applied in the aqueous solutions of HQ in the presence of NaCl, HCl, or NaOH for two hours, dark brown crystals were deposited on the electrode. According to the elemental analyses results, the observed contents of C and H were in good agreement with the calculated values. Both the Na and Cl contents were within acceptable error (less than 0.3 and 0.9 wt% for Na and Cl, respectively).

Figure 1 shows an SEM image of a crystal produced from NaCl solution. Because quinhydrone sublimes easily, the specimen could not be coated with Au for ordinary SEM observation. The backscattered image SEM method was applied without a conductive coating. The photograph shows hexangular prisms with a length of hundreds of micrometers, which are characteristic of quinhydrone single crystals.[8] The diffraction patterns were in agreement with those predicted from monoclinic simple lattice.[8] We cannot see typical hexangular prisms in the SEM images for the specimens produced from HCl and NaOH solutions. However, the X-ray diffraction data support that these specimens consist of monoclinic quinhydrone.

Figure 2 shows the IR spectra of the electrocrystallized products. We can see absorption bands which are characteristic of quinhydrone for each kind of specimen: 3240 $\mathrm{cm^{-1}}$ (OH stretching), 1634 $\mathrm{cm^{-1}}$ (C=O stretching), 1592 $\mathrm{cm^{-1}}$, 1310 $\mathrm{cm^{-1}}$ (C=C stretching), 1085 $\mathrm{cm^{-1}}$ (CH in-plane deformation), and 898 $\mathrm{cm^{-1}}$ (CH out-of-plane deformation).[9] The spectra for the products obtained from the three kinds of solution were similar to each other, except for some fine structures. For example, the absorption peaks at 1094 and 1085 $\mathrm{cm^{-1}}$ appeared in all the products, whereas the absorption peak at 1090 $\mathrm{cm^{-1}}$ appeared only in the product obtained from HCl solution. The difference may be based

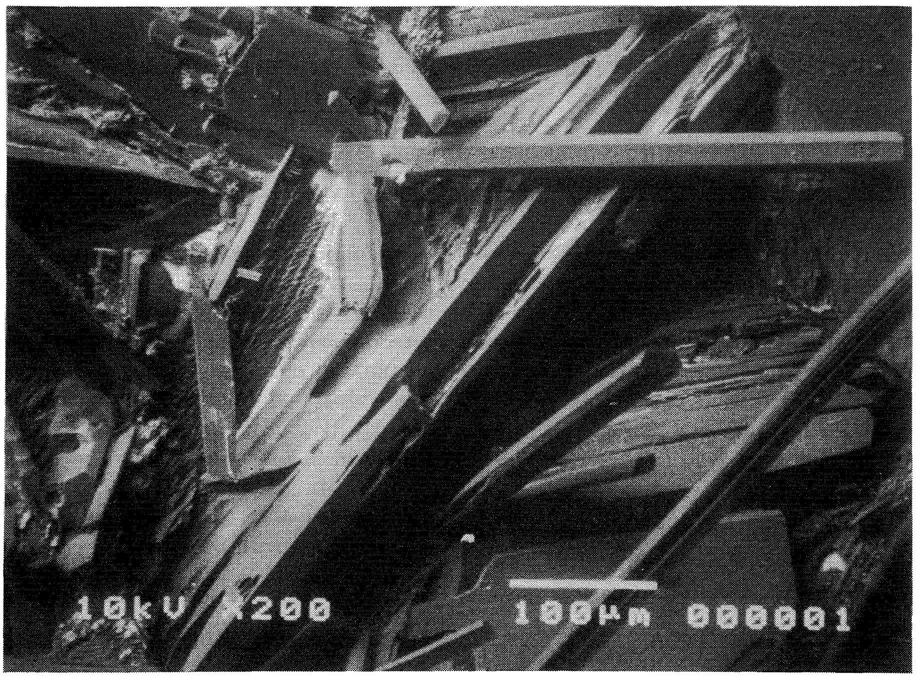


Fig. 1. SEM image of crystals of quinhydrone. Specimen produced from NaCl solution.

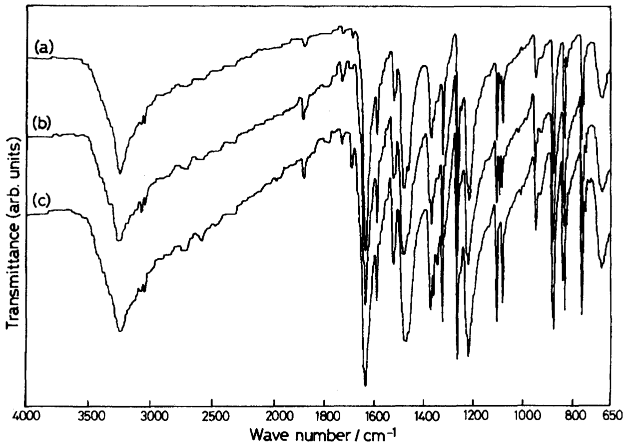


Fig. 2. IR spectra of the electrocrystallized quinhydrone. Specimens produced (a) from NaCl, (b) from HCl, and (c) from NaOH solutions.

on protonation on the surface of the crystal.

The specimen was diamagnetic as shown by the ESR results. Such a result suggests that the degree of charge transfer is about zero in the ground state.

Mechanism for Electrodeposition. Figure 3 shows the in situ visible absorption spectra, each of which was measured every 10 min. In addition to the spectra observed on application of a potential of 2.0 V vs. Ag, Fig. 3 also shows the spectra after the removal of the potential (broken lines).

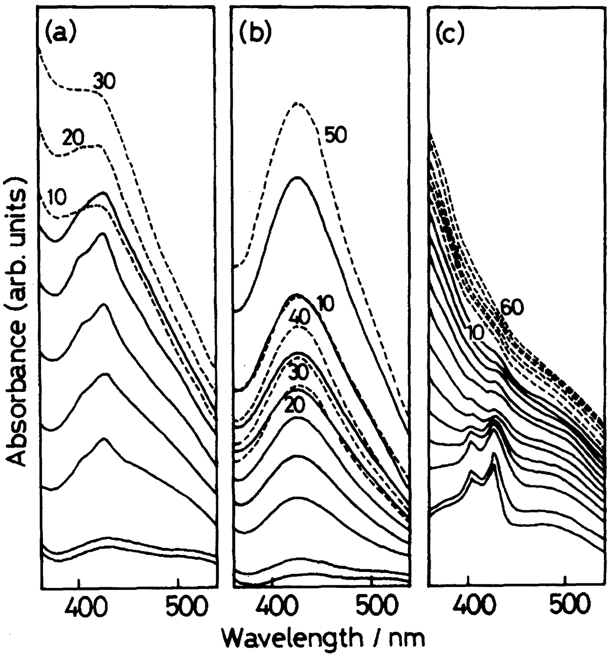
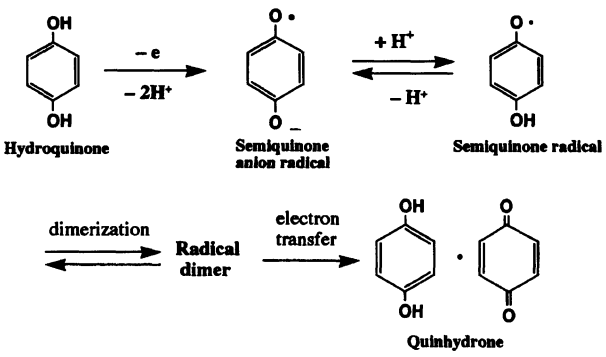


Fig. 3. In situ visible absorption spectra, measured in (a) NaCl, (b) HCl, and (c) NaOH solutions. Solid lines, observed on application of the potential; broken lines, observed after the removal of the potential every 10 min. Numerals beside the broken lines mean the time passed (in min).

The in situ spectra strongly depended on the electrolytic solutions: (a) NaCl, (b) HCl, and (c) NaOH. In the cases of (a) and (c), sharp absorption peaks appeared at 402 and 428 nm and grew gradually on application of the potential. Such twin peaks can be assigned to the semiquinone anion radical; Kimura et al.[10,11] have determined the wavelengths of the absorption bands for the semiquinone anion radical, formed



Scheme 1.

by irradiation of UV light in ethanol solution at 77 K, as 407 and 432 nm. Fukuzumi et al.[12] have determined these values, for the radical formed by chemical oxidation with MnO_2, to be 404 and 430 nm.

On the contrary, in the case of (b), i.e., at low pH, a broad band appeared around 430 nm and grew on application of the potential. In this case, perhaps a protonated species, neutral semiquinone radical, is predominant. According to Kimura et al.,[10] semiquinone radical shows four peaks at 391, 399, 406, and 415 nm. The broad band around 430 nm suggests the coexistence of neutral semiquinone radicals and semiquinone anion radicals.

Even at higher pH, after the potential was removed, the absorption band also became broader. This can be ascribed to protonation of the semiquinone anion radicals, followed by dimerization of the neutral semiquinone radicals. Kimura et al.[11] have reported that the semiquinone anion radicals dimer shows an absorption band at 585 nm. In addition, semiquinone radicals can perhaps make a dimer with an absorption band around such a long wavelength. However, no absorption bands were observed in this region. This can be explained in terms of a short life of this dimer; the dimer could suffer rapid electron transfer from one radical to the other and deposition onto the electrode.

The suggested mechanism of quinhydrone generation is as the scheme shows (Scheme 1).

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References

1) Partially presented at the Tohoku District Meeting of the United Societies of Chemistry, Kôriyama, October 1992.

2) "Beilsteins Handbuch der Organischen Chemie," 4th ed, Verlag von Julius Springer, Berlin (1925), Band VII, p. 617.

3) T. Mitani, G. Saito, and H. Urayama, *Phys. Rev. Lett.*, **60**, 2299 (1988).

4) "The Merck Index," 11th ed, Merck, Rahway (1989), p. 1282.

5) A. Fujishima, M. Aizawa, and T. Inoue, "Denki-Kagaku Sokutei-hô," Gihôdô Shuppan, Tokyo (1984), Chap. 18.

6) J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz, and M. -H. Whangbo, "Progress in Inorganic Chemistry," ed by S. J. Lippard, John Wiley & Sons, New York (1987), Vol. 35, p. 79.

7) V. D. Parker, *Electrochim. Acta*, **18**, 519 (1973).

8) H. Matsuda, K. Osaki, and I. Nitta, *Bull. Chem. Soc. Jpn.*, **31**, 611 (1958).

9) M. A. Slifkin and R. H. Walmsley, *Spectrochim. Acta, Part A*, **26A**, 1237 (1970).

10) K. Kimura, K. Yoshinaga, and H. Tsubomura, *J. Phys. Chem.*, **71**, 4485 (1967).

11) K. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).

12) S. Fukuzumi, Y. Ono, and T. Keii, *Bull. Chem. Soc. Jpn.*, **46**, 3353 (1973).