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Synthesis of Conducting Thin Films by Electro-oxidative Polymerization of Phenol

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Electro-oxidative polymerization of phenol leads to conducting, thin polymer films with electrical conductivities of *ca.* 10^{-8} to 10^{-1} S cm^{-1}, depending on the nature of the supporting electrolytic solution.

A number of aromatic compounds have been employed recently to produce new conducting, semiconducting, or non-conducting polymer films by electropolymerization. However, only a few OH-containing aromatic compounds (*e.g.* phenol and 2,6-dimethylphenol) have been used.[1—9] It has been reported that the electropolymerization of phenols leads to electroinactive polymeric films and in some cases electroactive dimeric compounds, depending on the electrolysis conditions.[1—8]

We have found that the electro-oxidative polymerization of phenol in acetonitrile solutions with basal-plane pyrolytic graphite (BPG) electrodes gives electroactive, conducting polymer films with electrical conductivities of *ca.* 10^{-8} to 10^{-1} S cm^{-1}, depending on the nature of the supporting electrolyte, and now describe the preliminary characterization and some properties of the polyphenol films prepared.

The electro-oxidative polymerization was carried out in a nitrogen atmosphere under potentiostatic conditions at room temperature, using a three-electrode, two-compartment cell.[4,5] Phenol was dissolved (50 mM) in acetonitrile together with supporting electrolyte (0.2 M; $NaClO_4$, Bu_4NClO_4, Bu_4NBF_4, or Bu_4NPF_6). Typically, film formation was achieved on BPG electrodes by constant-potential electrolysis at 1.7 V *vs.* a sodium chloride saturated calomel electrode (NaCl s.c.e.) or by potential-sweep electrolysis between 0 and 1.6 V at 50 mV s^{-1} [Figure 1(a)]. A homogeneous, black, thin polyphenol film was formed on the BPG anode. The thicknesses (ϕ) of the polyphenol films prepared by changing the amount (q) of charge passed during electropolymerization were measured by use of a surface texture measurement instrument as described previously.[10] The thickness ϕ was linearly related to q, with q in the range 0.2 to *ca.* 4 C cm^{-2}, and the slope of the ϕ *vs.* q plot was 1.5 μm C^{-1} cm^2.

The i.r. spectrum of the film [ν (C=C)1608 and 1500, ν(C=O) 1690 and 1655, ν(C–O)1370 and 1220, ν(C–O–C) 1265, ν(O–H) 3230, γ(C–H)850 and 755, and $\nu(ClO_4^-)$1100 and 630 cm^{-1}]† indicated that the polyphenol contains quinone moieties, ether bonds, hydroxy groups, and electrolyte anions (ClO_4^-) as dopant and that it possesses 1,2-, 1, 4-, 1, 2, 4-, and/or 1, 2, 3, 5-substituted benzene fragments as unit structures,[11,12] linked *via* C–C and/or C–O–C bonds. Elemental analysis indicated an average doping level of one ClO_4^- ion for every six monomer units. The polyphenol film was insoluble in the commonly used organic solvents and acids.

All the polyphenol films prepared in various supporting electrolytes were electroactive in aqueous solution [Figure 1(b)], but not in acetonitrile solution. The apparent molar coverage of electroactive sites, estimated by cyclic voltam-

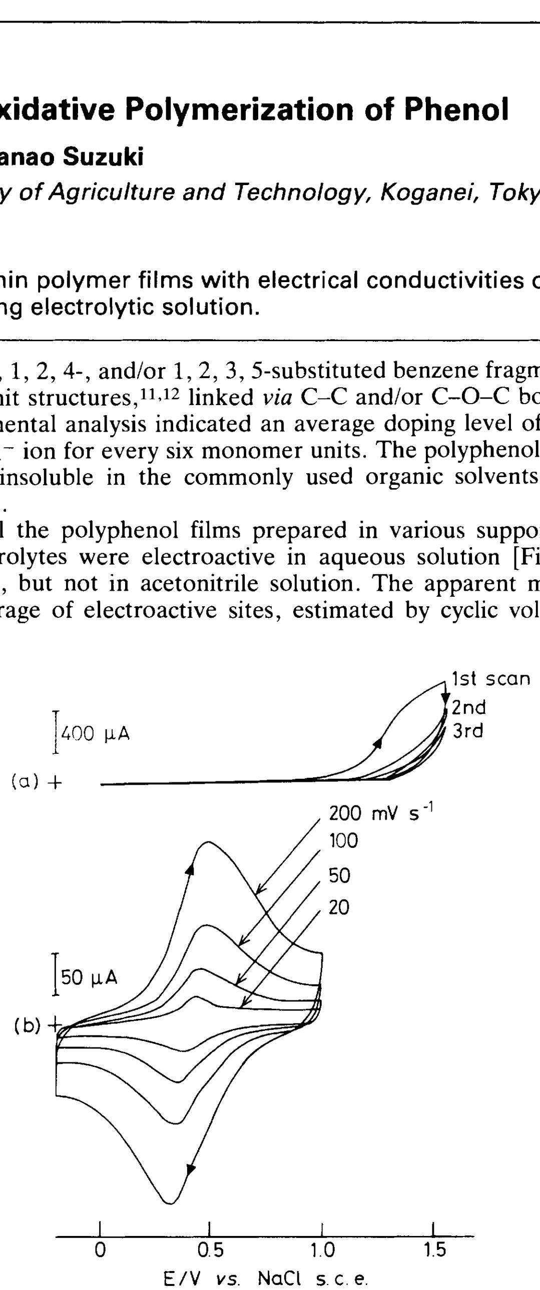

Figure 1. (a) Cyclic voltammograms recorded during the electrochemical oxidation of phenol on BPG electrode (area 0.2 cm^2) in acetonitrile solution containing 0.2 M $NaClO_4$ and 50 mM phenol. Potential scan rate 50 mV s^{-1}. (b) Cyclic voltammogram representing the electroactivity of the polyphenol film in an aqueous solution containing 0.2 M $NaClO_4$ + $HClO_4$ (pH 1.0) at various potential scan rates.

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† ν: Stretching vibration: γ: out-of-plane bending vibration.

metry, was 1.6×10^{-8} mol cm^{-2} for the film with ϕ 0.075 μm, corresponding to *ca.* 160 monolayers based on a monolayer coverage of *ca.* 10^{-10} mol cm^{-2}. At a given pH, the formal redox potential ($E^{\circ\prime}$), estimated as the average of the anodic and cathodic peak potentials ($E_p{}^a$ and $E_p{}^c$), was almost the same as that (*e.g.* 0.0 V *vs.* NaCl s.c.e. at pH 7.0) for a monomeric quinone/hydroquinone (Q/H_2Q) redox couple,[13] and a linear $E^{\circ\prime}$ *vs.* pH plot with slope *ca.* −60 mV per pH unit was obtained, indicating that protons and electrons take part in the electrode reaction in 1:1 ratio as expected for the Q/H_2Q couple. The films could be cycled repeatedly without any significant decay between 0 and 0.7 V in aqueous solution.

The electrical conductivities (σ) of the polyphenol films, measured by a d.c. four-probe technique at 25 ± 1 °C, were found to depend on the supporting electrolytes used. The σ values were 1.4×10^{-8}, 3.0×10^{-8}, 1.2×10^{-4}, and 5.0×10^{-1} S cm^{-1} for films prepared in $NaClO_4$, Bu_4NClO_4, Bu_4NBF_4, and Bu_4NPF_6 solutions in acetonitrile, respectively. A similar large variation in σ with supporting electrolyte anion has previously been reported for polypyrrole,[14,15] polythiophene,[15—17] and poly(3-methylthiophene)[17] films. The conductivities remained substantially unchanged even after 1 year in contact with air, suggesting possible applications. A detailed discussion of the properties will be given elsewhere.

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