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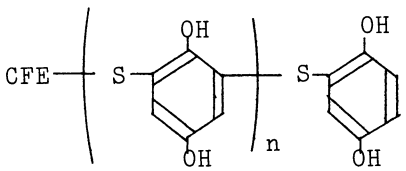
PREPARATION OF CARBON ELECTRODES MODIFIED WITH POLY(MERCAPTOHYDROQUINONE)S AND THEIR FUNCTIONS AS pH SENSOR

Gorou ARAI,* Takashi KOIKE, and Iwao YASUMORI
Department of Applied Chemistry, Faculty fo Engineering,
Kanagawa University, Kanagawa-ku, Yokohama 221

Carbon fiber electrodes (CFE) were modified with either a poly(mercaptohydroquinone) film or a poly(methylmercaptohydroquinone) film by means of electrochemical oxidation. The modified CFE thus prepared showed an excellent Nernstian response to H^+ ion over the pH range from 2 to 9.

There have been a great deal of interests in the chemical modification of electrodes for electrocatalytic,[1] analytical,[2] or selective synthetic properties.[3] Especially the modification method by electrochemical polymerization can give easy preparation of polymers with a regular structure.[4] In a previous paper[5] we have described the preparation of heavy metal ion sensors using the quinonoid polymer electrode modified with mercaptides. Here we wish to report the preparation of carbon electrodes modified with poly(mercaptohydroquinone) (1) and poly(methylmercaptohydroquinone) (2) films and their functions as pH sensors. These electrodes were prepared as follows : Mercaptohydroquinone(4×10^{-1} mM, 1 M = 1 mol dm^{-3}) or methylmercaptohydroquinone(4×10^{-1} mM) was oxidized in a Britton-Robinson buffer (pH 5.0, 20 vol% EtOH) at +0.5 V vs. SCE for 30 min using a carbon fiber electrode (CFE) with 7 μm in diameter and ca. 1 mm in effective length.[6] Before the electrochemical oxidation, the CFE was rinsed with acetone and was then electropolished at -1.5 V vs. SCE for 30 min in the Britton-Robinson buffer (pH 5.0) for the purpose of cleaning the CFE surface. The CFE's modified with the two types of quinonoid polymer films thus prepared were throughly rinsed with pure water and then reduced at -0.5 V vs. SCE for 30 min in the Britton-Robinson buffer (pH 5.0) to give the CFE's modified with 1 and 2.



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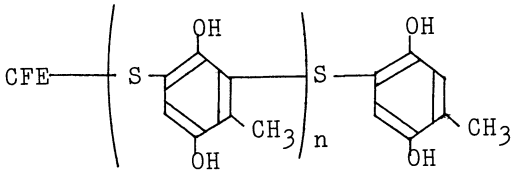

2

The CFE modified with 1 or 2 was attached with Ag paste to an end of Cu wire which was coaxial as shown in Fig. 1. Potentials of the modified CFE were measured as described previously.[5] The Britton-Robinson ($2 < pH < 11$) and a Clark-Lubs buffer ($pH < 2$) solutions were used as standard pH solutions.

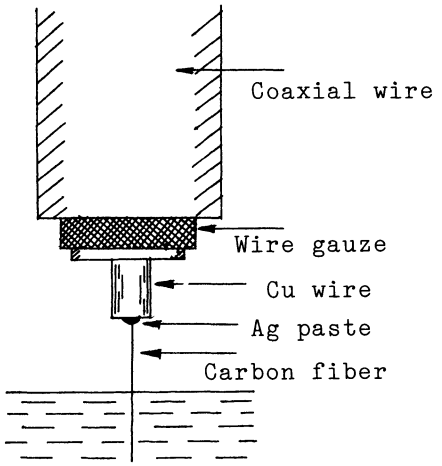

Fig. 1. The CFE modified with poly(mercaptohydroquinone)s-film.

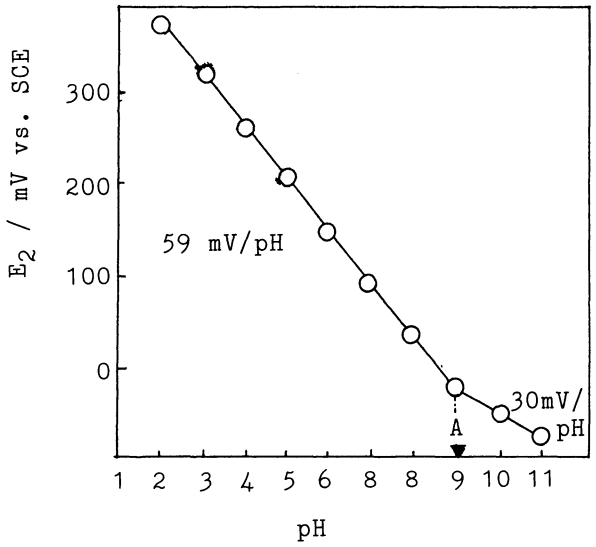

Fig. 2. Relationship between E_2 and pH.

As shown in Fig. 2, the potentials of the CFE modified with 2 (E_2) showed an excellent Nernstian response to pH over the pH range from 2 to 9. A point A shown in Fig. 2 approximates to the negative logarithm of the first dissociation constant (pK_1) of methylhydroquinone moiety in 2. It is therefore assumed that the pH response mechanism of these CFE's modified with 1 and 2 correlates with dissociation equilibrium of two hydroxyl groups on the hydroquinones in 1 and 2. The CFE modified with 1 and 2 reached steady-state potentials within 2 s in solutions having pH larger than 3, but required more response time below pH 3 and could not work well below pH 1.5. The CFE modified with 1 and 2 showed reproducible Nernstian response curves for at least 20 d when stored in a weak acidic Britton-Robinson buffer. Furthermore, the Nernstian response measured with these modified CFE's was found to be unaffected by the presence of reducing agents 0.1 M Na_2SO_3 and 0.1 M $Na_2S_2O_3$ which seriously influence potentials of a quinhydrone electrode.[7] These results show that the CFE modified with 1 or 2 possesses some excellent functions as a pH microsensor.

References

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6) The effective length means the length of CFE dipped in the buffer solutions.
7) E. Biilmann, Bull. Soc. Chim., 41, 213 (1927).

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