



[54] TWO-TERMINAL VOLTAMMETRIC MICROSENSORS

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[56] References Cited

U.S. PATENT DOCUMENTS

4,545,382	10/1985	Higgins et al.	204/415
4,717,673	1/1988	Wrighton et al.	436/68
4,895,705	1/1990	Wrighton et al.	422/68
4,929,313	5/1990	Wrighton	204/433
4,936,956	6/1990	Wrighton et al.	204/153.21

OTHER PUBLICATIONS

Hammond, et al. "Synthesis, N.m.r. Spectra, and Structure of Macrocyclic Compounds Containing the Ferrocene Unit" *J. Chem. Soc. Perkins Trans. I* 707-715 (1983).

Medina, et al. "Ferrocenyldimethyl-[2.2]-cryptand: Solid State Structure of the External Hydrate and Alkali and Alkaline-earth-dependent Electrochemical Behaviour" *J. Chem. Soc. Chem. Commun.* 290-292 (1991).

Shu, et al. "Synthesis and Charge-Transport Properties of Polymers Derived from the Oxidation of 1-Hydro-1'-(6-(pyrrol-1-yl)hexyl)-4,4'-bipyridinium Bis(hexafluorophosphate) and Demonstration of a pH-Sensitive Microelectrochemical Transistor Derived from the

Redox Properties of a Conventional Redox Center" *J. Phys. Chem.* 92:5221-5229 (1988).

Nuzzo, et al. "Adsorption of Bifunctional Organic Disulfides on Gold Surfaces" *J. Am. Chem. Soc.* 105:4481-4483 (1983).

Brown, et al. "Illustrative Electrochemical Behavior of Reactants Irreversibly Adsorbed on Graphite Electrode Surfaces" *J. Electroanal. Chem.* 72:379-387 (1976).

Bain, et al. "Depth Sensitivity of Wetting: Monolayers of ω -Mercapto Ethers on Gold" *J. Am. Chem. Soc.* 110:5897-5898 (1988).

Fackler and Porter "Gold Rings That Do Not Glisten. The Crystal and Molecular Structures of Two Novel Gold (II) Compounds Containing 12- and 13-Atom Gold-Sulfur Rings, $[\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{S}_8$ and $[\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{S}_9$ " *J. Am. Chem. Soc.* 108:2750-2751 (1986).

(List continued on next page.)

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[57]

ABSTRACT

Self-assembly of a chemically insensitive redox material, such as ferrocenyl thiol, and a chemically sensitive redox material, such as a quinone thiol, onto microelectrodes forms the basis for a two-terminal, voltammetric microsensor having reference and sensor functions on the same electrode. Detection is based on measuring the potential difference of current peaks for oxidation and reduction of the reference (ferrocene) and indicator (quinone) in aqueous electrolyte in a two-terminal, linear sweep voltammogram using a counterelectrode of relatively large surface area. Use of microelectrodes modified with monolayer coverages of reference and indicator molecules minimizes the size of the counterelectrode and the perturbation of the solution interrogated. Key advantages are that the sensor requires no separate reference electrode and the sensor functions as long as current peaks can be located for reference and indicator molecules.

14 Claims, 6 Drawing Sheets

