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Microporous Aluminum Oxide Films at Electrodes

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Physical properties and structure of electrode polymeric films, which have been most frequently used as a means of reagent immobilization,[1] play an important role in determining the kinetics of electron transport within such films.[2] In electrocatalytic applications of modified electrodes, transport of solution substrate into an electrode film also depends strongly on its structure.[2c,3] We report here the development of rigid, nonpolymeric electrode films consisting of porous aluminum oxide films of well-characterized and controllable microstructure. We give an experimental assessment of the film porosity and describe its properties as a matrix for immobilization of electroactive reagents. Electrode modification with layers of rigid inorganic materials such as clays and zeolites has recently been reported.[4] In those instances, however, the microporosity of the inorganic matrices was of molecular dimensions and exhibited, as a result, electron-transport rates comparable to poorly swelled polymeric electrode films.[1]

The porosity of the aluminum oxide films consists of an array of parallel, cylindrical pores, perpendicular to the film surface. The structure of an aluminum oxide film can be best judged by transmission electron microscopy (see Figure 1). The diameter of an individual pore can be varied in the range of approximately 200–1500 Å.

These types of aluminum oxide films are prepared by electrooxidation of aluminum substrates in acidic media, typically in sulfuric, phosphoric, or oxalic acids.[5] The pore diameter of the film is determined, to a good approximation, by the formation voltage alone; film thickness is proportional to the time of electrooxidation.[5] Our estimate for the pore diameter, based on the transmission electron microscopy data for the oxides formed in 4% phosphoric acid, at voltages between 25 and 100 V, is 14 ± 1.4 Å/V and agrees well with commonly quoted values.[5]

Following the electrochemical formation, a porous film is separated from the aluminum substrate by amalgamation. Since the impervious barrier layer (a few hundred angstroms in thickness) constitutes one side of the oxide film, the untreated oxide film deposited at a platinum electrode forms a passivating layer.[6] Removal of the barrier layer (often referred to as a thinning process) is accomplished by a dropwise chemical dissolution with 1 M NaOH during which only the barrier layer side of the oxide film is exposed to the sodium hydroxide solution in order to prevent simultaneous dissolution of the entire oxide structure.

The progress of the thinning process can be monitored by the rotating disc electrode method with the standard Koutecky–Levich

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(2) See, for example: (a) Majda, M.; Faulkner, L. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *169*, 77–95. (b) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685–689. (c) Anson, F. C.; Sevēant, J. M.; Shigehara, K. *J. Am. Chem. Soc.* **1983**, *105*, 1096–1106. (d) Nakahama, S.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *158*, 303–322.

(3) (a) Albery, W. J.; Hillman, A. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *170*, 27–49. (b) Anson, F. C.; Savēant, J. M.; Shigehara, K. *J. Phys. Chem.* **1983**, *87*, 214–219. (c) Anson, F. C.; Savēant, J. M.; Shigehara, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *145*, 423–430. (d) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savēant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *131*, 1–35. (e) Rocklin, R. D.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 2104–2112.

(4) (a) Ghosh, P. K.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 5691–5693. (b) Ghosh, P. K.; Man, A. W. H.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *169*, 315–317. (c) Kamat, P. V. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *163*, 389–394. (d) Murray, C. G.; Nowak, R. J.; Rolison, D. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *164*, 205–210.

(5) For a review, see: Wood, G. C. In "Oxides and Oxide Films"; Diggle, J. W., Ed.; Marcel Dekker: New York, 1973; Vol. 2, pp 167–279.

(6) Floating techniques were used to deposit sections of the oxide film (with surface area of 0.3–1.0 cm²) onto solid electrodes covering their entire surface. Subsequent drying with a heat gun makes the adhesion complete and permanent, particularly when the oxide thickness does not exceed ∼5000 Å.
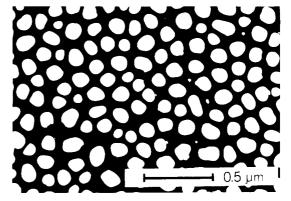

Figure 1. Structure of a porous aluminum oxide layer; transmission electron micrograph of 5000-Å-thick oxide film prepared by electrooxidation of Al substrate at 75 V in 4% H_3PO_4 at room temperature, average pore diameter, 1000 Å.

data analysis. We have used Gough's model[7] for membrane-covered electrodes to determine the porosity, ρ, of our aluminum oxide films as a function of the extent of thinning. The porosity increased in a representative series of experiments for the first 20 drops of barrier layer dissolution from 4% to 43% and remained at a constant level of 45–50% for the subsequent 5–10 drops. This porosity value agrees well with the ratio of the pores cross section to the oxide layer surface area assessed from the transmission electron micrographs and thus indicates the completeness of the barrier layer dissolution.

Aluminum oxide films were impregnated with poly(4-vinylpyridine) (PVP) in order to immobilize ferrocyanide ions.[8] In this procedure previously thinned aluminum oxide films, 1.5 μm in thickness (pore diameter of 800 Å), were exposed to a 0.5% PVP solution in methanol, blotted, and dried. One side of the PVP-impregnated oxide films was then vapor coated with gold in vacuum to assure the most intimate contact of the film with the gold.[9] Individual PVP-impregnated, gold-coated aluminum oxide films were then used to produce electrodes.

Unlike electrodes coated directly with PVP, a polymer that forms a passivating film in neutral solution, our Au/Al_2O_3–PVP electrode remains completely permeable to ferrocyanide ions in neutral solutions (Figure 2A). Apparently, the impregnating layer of PVP is only coating the inside walls of the oxide film pores, leaving the centers of the pores open. The presence of PVP within the oxide structure can be seen when the Au/Al_2O_3–PVP electrode is immersed in a 1 mM, pH 3.0 solution of $K_4Fe(CN)_6$ and then transferred to a supporting electrolyte solution of the same pH.[10] A stable voltammogram shown in Figure 2B demonstrates that the oxide structure is indeed impregnated with PVP and that the electrostatically bound ferri-/ferrocyanide ions remain electroactive. The quantity of incorporated ferrocyanide depends on the concentration of the PVP solution used to impregnate the porous Al_2O_3 films and ranges from 1.2×10^{-9} to 1.0×10^{-8} mol/cm² (for 1-μm-thick oxide films). Preliminary measurements of the effective diffusion coefficient, D_{eff}, by chronoamperometry yield values in the order of 10^{-8} cm²/s, somewhat higher than those reported for PVP film electrodes.[11] Interestingly, we have observed a linear increase of D_{eff} values with the increasing concentration of $K_4Fe(CN)_6$ in solution. The D_{eff}'s of 0.57×10^{-8}, 0.96×10^{-8}, 1.5×10^{-8}, and 1.9×10^{-8} cm²/s were obtained, for example, in 10, 30, 70, and 100 μM $K_4Fe(CN)_6$ solutions, respectively. This effect is likely due to the mediation of the bound

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(9) During the vapor-deposition process, the aluminum oxide substrates were positioned at approximately 45° above the gold source to avoid the possibility of gold penetration into the pores of the oxide film.

(10) The solution contained $Fe(CN)_6^{4-}$ ions at 30 μM level to prevent leaching of the PVP-bound hexacyanoferrate centers.

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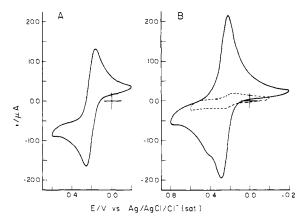
Figure 2. Steady-state cyclic voltammograms of $Fe(CN)_6^{3-/4-}$ at a gold electrode modified with 1.5-μm-thick porous Al_2O_3 film impregnated with PVP by contact with 0.5% (w/v) PVP solution in CH_3OH; (A) 1.0 mM $K_4Fe(CN)_6$, 0.1 M CF_3COONa, pH 8.0, v = 50 mV/s; identical voltammograms are produced in this solution at a bare gold electrode of the same geometric surface area. (B) Medium transfer experiment: the electrode from (A) was first exposed to a 1mM $K_4Fe(CN)_6$, pH 3.0 solution and then transferred to a 0.1 M CF_3COOH/CF_3COONa, pH 2.8 solution (continuous line);[10] dashed line, blank voltammogram, 30 μM $K_4Fe(CN)_6$, pH 8.0.[10]

ferrocyanide oxidation along the oxide pores by the solution ferricyanide ions inside the pores.

Concluding, the open and well-characterized microstructure of these rigid aluminum oxide films is the most attractive and advantageous feature of this material as an electrode matrix. We have shown an example of reagent immobilization along the oxide pores by impregnation of the oxide structure with a polymer. Electron transport in these types of systems consists of a lateral electron or charge propagation along the pores and constitutes for us a separate problem of considerable interest.

Hydride Sponge: 1,8-Naphthalenediylbis(dimethylborane)

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The complexation of cations with rigid polydentate ligands has been studied in numerous research groups during the past 2 decades.[1] It is only very recently, however, that the converse problem of anion complexation by electron-deficient compounds has received widespread attention. Lehn et al.[2] and Schmidtchen[3] have elegantly determined the complexing abilities of rigid polyaza cations with their counterions. The work of Shriver and Biallas[4] on 1,2-diborylethanes and also that of Kuivila et al.[5] on distannylmethanes has demonstrated chelate effects in nonrigid bidentate Lewis acids interacting with Lewis bases. Shore et al.[6]

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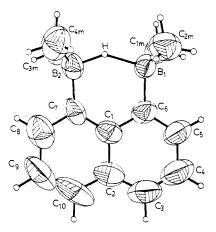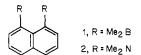

Figure 1. Perspective ORTEP drawing of $1\cdot H^-$ in crystalline $1\cdot KH\cdot$(dioxane)$_3$.

have prepared bridged hydrides from flexible 1,4-diborylbutanes. However, the synthesis and complexing properties of multidentate Lewis acids that are both rigid and uncharged have not been previously reported.

Conformationally defined oligoboranes are promising candidates for electron-deficient hosts that could engage in multidentate complexation with guest anions. As a prototypical example, we report the synthesis and hydride-abstracting ability of 1,8-naphthalenediylbis(dimethylborane) (1). This novel bis(borane) may be viewed as the electron-deficient counterpart of 1,8-bis-(dimethylamino)naphthalene (2), "proton sponge".[7] Just as 2

1, R = Me$_2$B
2, R = Me$_2$N

possesses a surprisingly high proton affinity due to the enforced interaction of its lone pairs, compound **1** might be expected to complex strongly with small anions by virtue of its convergent vacant p orbitals on the boranyl groups, which are forced substantially out of conjugation with the naphthalene ring by steric repulsion of the methyls on boron. The only previous mention[8] of an unbridged 1,8-diborylnaphthalene was an account of an unsuccessful attempt to prepare the bis(diiodoboryl) derivative.

A solution of 1,8-dilithionaphthalene[9] was prepared[10] by treating 3.43 g (9.0 mmol) of 1,8-diiodonaphthalene[11] dissolved in 100 mL of Et_2O with 7.1 mL (20 mmol) of 2.8 M n-BuLi at 0 °C for 10 min under Ar. The resulting dilithiate solution was cooled to –70 °C and transferred by cannula into a solution of Me_2BOEt^{12} (2.5 g, 29 mmol) in 20 mL of Et_2O, which also was held at –70 °C. The combined solution was stirred and allowed to warm to +10 °C, then recooled to –70 °C. Boron trifluoride etherate (2.46 mL, 2.84 g, 20 mmol) was added,[13] the solution was again allowed to warm to +10 °C, and then the volatile components were removed in vacuo. The residue was extracted at ambient temper-

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