Preparation of Polymer-Modified Electrodes: A Literature and Experimental Study

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Preparation of Polymer Modified Electrodes
Literature and Experimental Study

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At Stony Brook
The Graduate School

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ABSTRACT

A literature review is presented on the field of polymer modified electrodes which can be electrochemically generated. It is suggested that a possible application of these polymer modified electrodes is as a regeneratable catalysis packing material for use in counter-current exchange columns. Secondly, there is a presentation of experimental results dealing with possible electrode modification using difluoro- and dimethyl- phenols and fluorinated derivatives of styrene, benzoquinone and hydroquinone. It appears that dimethylphenol shows the most potential of the monomers experimentally tested in providing a stable polymer modified electrode surface.

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LIST OF ABBREVIATIONS

A	(a) electrode area; (b) ampere
Å	angstrom
Ag/Ag ⁺	silver/silver ion electrode (AgNO ₃ in Acetonitrile solution)
Ag/AgCl	standard silver/silver chloride electrode
C	degree celcius
CH ₃ CN	Acetonitrile
CME	chemically modified electrodes
CV	cyclic voltammetry, cyclic voltammogram
DFP	2,6-Difluorophenol
DMP	2,6-Dimethylphenol
DRA	Diffused Reflectance Accessory
E _{ad}	peak potential where adsorption occurred
E _{diff}	peak potential due to diffusion process
E _p	peak potential
ΔE _p	E _{p_a} - E _{p_c} in CV
E _{p_a}	anodic peak potential
E _{p_c}	cathodic peak potential
F	the Faraday
i	current
i _{ad}	peak current due to adsorption process
i _{diff}	peak current due to diffusion process

M	molarity
n	electrons per mole of species oxidized or reduced
PFS	2,3,4,5,6-Pentafluorostyrene
PG	pyrolytic graphite
PPO	polyphenylene oxide
Pt	platinum
Q	(a) charge; (b) quinone
Q/H ₂ Q	quinone/hydroquinone
RHE	real hydrogen electrode
SCE	standard KCl-saturated calomel electrode
SCE/MeOH	calomel electrode with KCl saturated Methanol
t	time
TEATFB	tetraethylammonium tetrafluoroborate
TFHQ	tetrafluorohydroquinone
TFQ	tetrafluoro-1,4-benzoquinone
V	volt
∇	potential sweep rate

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CHAPTER 1. LITERATURE SURVEY

The subject of this report is that of chemically modified electrodes from the viewpoint of possible preparation of a new type of electrically conductive column-packing for a two-phase countercurrent contact column. A packing whose surfaces are chemically modified may provide chemical environments which are variable through in-situ control of the electrochemical potential of the packing. In addition, the packing may act as a support for catalysts whose selectivity and specificity may also be adjusted as in-situ variables.

Chemically modified electrodes (CME) are electrodes whose surface characteristics have been deliberately modified by immobilizing a chemical species on the surface so that the electrode would then display the chemical, electrochemical, optical and other properties related to the immobilized molecules. The CMEs have also been called "derivatized", "functionalized", "electrostatically trapped", and "polymer-coated". The consequences of unintentional adsorption of ions and molecules on electrode surfaces are not usually included in discussions of CMEs [1-7].

(1) Methods of Surface Modification

The electrode modifier can be electrochemically reactive or non-reactive. The active modifiers are those which can exchange electrons with the substrate electrode surface. They are more interesting than the electrochemically inactive modifiers, because the redox states of the active modifiers are controlled by varying the electrode potential. Thus, they may be useful as electron

transfer agents, selective electron transfer mediator-catalysts, and photosensitizers for semiconductor electrodes.

The first deliberate chemical modification of an electrode is credited to R. W. Murray's group in the mid-1970s [1]. Since then, studies of the CME have proliferated [2-9]. Surfaces of metals, metal oxides, semiconductors and carbonaceous materials have been chemically modified through coverage by monomers [1, 10-35], polymers with anchor molecules [36-38], and polymers without anchors [39-48]. The anchors link the modifier molecules to the substrate surfaces by chemical, mostly covalent, bonds using oxygen-functional groups on the substrate. The surface derivatization without anchors has been accomplished by electrochemical [49-75], thermal [76, 77], and plasma [37, 78-80] polymerizations of monomers directly on the substrates.

(2) Past applications and the New Application as Column Packing

There have been more interesting developments of CMEs as column packing and catalyst carrier for a counter-current contact column. The wettability of electroactive modifiers appears to be adjustable through electrochemical control of the average redox state of the modifier molecules [81, 82]. Therefore, an in-situ control of hydrophobicity and other properties, such as selectivity in catalysis, may be possible. The counterions of polymer-modified electrodes can be ion-exchanged with other anions using electrolyte solutions containing the new anions [23, 59, 82-85]. Thus, the counterions from the polymerization media can be replaced with ions more suitable for specific applications of the modified electrode. As an ion-gate [86-88], a film of poly(pyrrole), PP, in its reduced state is impermeable to chloride ions, but the anion permeability

of PP in its cationic form is a thousand times higher. Thus, the ionic environment of CME can be controlled in-situ. Fine aggregates of metals can be electrochemically imbedded in a polymer film formed on a substrate electrode [23, 76, 77, 90]. The metal could be a catalyst metal. The technique may be useful to enhance the electric conductivity of the polymer film. The CME column packing may be fabricated in the form of a flow-through electrode, FTE, [91]. In addition to application to electroanalytical chemistry [92-96], the FTE has been a subject of active investigation in its relation with photoelectrolysis of water [97] and fuel cells [98-101].

It is conceivable that a column packing made of a chemically modified electrode, also acting as a catalyst support, may be useful for (a) controlling the packing efficiency, (b) increasing the catalyst activity and/or catalyst selectivity, and (c) changing the chemical reaction pathway in various other ways. This may be accomplished by simply changing the electrochemical potential of such a CME. This concept is different from conventional electrocatalysis in that the latter requires expenditure of electric power as energy input to drive the catalyzed reaction, while the present concept only needs the current to change the redox state of the surface modifier.

(3) Feasibility of In-Situ Regeneration of Catalyst Activity

One of the primary problems associated with the use of a heterogeneous catalyst is its chemical poisoning and crystallographic surface deterioration. However, it is well known that catalytic activities of platinized platinum in laboratory-scale electrochemistry can be restored by repeated cycling of its

potential between cathodic and anodic voltages [102-104]. This is at least partially due to regeneration of the active sites during the potential cycling [103-109]. In addition, some groups claim that the restoration of the catalytic activity is also due to elimination of chemical poisons from the surfaces. [103, 104, 110, 111].

Common chemical poisons of platinum are nucleophiles: (a) inorganic and organic compounds of Group Va and Group VIa elements, which include water and hydroxyl compounds, ammonia, pyridine, sulfides and thiophene, (b) complex ions of transition metals with their outermost d-shells more than half filled, and (c) unsaturated compounds [112, 132-137]. It is well known that the oxygen functionalities on platinum surfaces can be removed by the cathodic-anodic excursions of potential [113-115]. Studies of underpotential deposition and stripping voltammetry on platinum surfaces have indicated that the deposition of the transition metal is in general reversible with a few exceptions, e.g., mercury and lead [116-120].

Our research group [121] has demonstrated that, in the fluid-dynamic conditions simulating that of packed columns, two to three cycles of a triangular potential wave completely restores the clean polycrystalline platinum surfaces which have been deliberately poisoned by sulfite or transition metals, including lead. The transition metals tested were the common constituents of stainless steel of various types and other chemically stable metallic structural materials of industrial plants. A reproducibly clean platinum surface was obtained by an electrochemical procedure [121] using an ultrapure sulfuric acid solution made from the acid supplied by Johnson Matthey and ultrapure water prepared in our laboratory. Our ultrapure water has been demonstrated [121] to be of higher purity than Conway's pyrocatalytically distilled water [122].

(4) Polymer-Modified Electrodes

Table I lists representative polymers that have been used for chemical modification of electrodes. The requirements that must be satisfied by a successful modifier-polymer for the purpose of the CME-packing-carrier application are discussed below.

(a) Electrochemical polymerization. Table I is a compilation of π -conjugated polymers generated by anodic polymerization directly on an electrode surface. The necessary conditions for a successful anodic polymerization, other than the high electrical conductivity (σ) of the polymer's oxidized state, have been discussed by Diaz [123]. Electropolymerization has been done in many ways such as by potentiostating at an anodic potential e.g. polyphenylene (152, 153, 155, 156, 158), polyquinone (73), polyphenol (140), polynapthol (143), and poly(methylsalicylate) (144) or by linear anodic potential sweep e.g. polypyrrole (66, 68, 74, 138), polyfluorene (65, 67, 70), polythiophene (69), polyazulene (72), polynapthoquinone (141, 142), polyphenylene (149, 150, 151, 155, 157), polyphenylene oxide (145-148), polyphenol (140), polynapthol (143), and polynapthoquinone (141, 142) or by linear sweep in the cathodic direction e.g. polypyrrole (75) and polyperfluorocyclopentene (71) or by polymerization at constant current e.g. polypyrrole (139) and polyphenylene (139). Most of the electropolymerizations were done at anodic potentials where the deposition of impurity cations at the anode can be eliminated. The radical cations of these π -conjugated compounds are usually more stable with respect to decomposition and side reactions.

(b) Stability over a large potential range. Sufficiently wide potential range for the reversible electrochemical redox reaction is necessary to accom-

moderate various potential excursions (see below).

(c) Sufficiently high hydrophobicity is needed, if a hydrophobic catalyst is being formulated. The contact angles between water (or dilute aqueous solutions) and non-cationic form of polymer of more than 90° are preferred. In addition, a strong dependence of the hydrophobicity on the electrode potential will make its usage more flexible. The hydrophobicity of organic substances are more or less predictable on the basis of Zisman's work [128-131]. The potential-dependence of the hydrophobicity of electroactive polymers has been studied by Willman and Murray [81] and Diaz [82].

(d) Reasonably high electrical conductivity in its reduced form. Under ideal conditions a high conductivity will not be required for steady state operation of the gas-liquid contact columns. However, a high conductivity is desirable for in-situ catalyst regeneration while the columns are in operation. Studies by Murray's group show that, after a PP film potential is stepped down to a very cathodic level (e.g., -0.9V vs. SCE), it takes a few tens of minutes for the film to be reduced to a limiting state [88-90]. On the other hand, studies by Street [124, 125] indicate that partially oxidized PP films are significantly conductive. In the potential range well above the hydrogen evolution potential in aqueous solutions, the conductivity of PP is several orders of magnitude higher than that of the completely reduced PP [89]. In general, the oxidized form of polymers have very high conductivities compared to the reduced form, and the conductivity is strongly dependent on the identity of the counter-ion. The conductivity can be enhanced by doping the polymers with metal or carbon particles via various electrodeposition techniques [90, 126].

(e) Long-term chemical, electrochemical and mechanical stability of the

film in various aqueous solutions, in air, and with respect to repeated potential cycling is necessary for industrial applications. The mechanical stability includes strong adherence of the polymer to the substrate electrode.

Our research group has investigated the electropolymerization of various monomers in order to find a modifying polymer which satisfies these requirements. To date, the most promising one is poly(terphenyl), found by Leonard Krebs [138]. The poly(terphenyl) films are formed by anodic electropolymerization of p-terphenyl in anhydrous acetonitrile and using various supporting electrolytes. The film preparation is reproducible and stable in aqueous solutions between the hydrogen evolution potential and almost 1.5V (vs. RHE).

Table I. Survey of Electrochemically Prepared Polymer Films

Polymer	Counter Ions	E_{Pa} (V) ^(a)	Conductivity (S cm ⁻¹) ^(h)	References
Poly(pyrrole) [PP]	CH ₃ SO ₃ ⁻	-	50	123
	BF ₄ ⁻	-0.10	100	127, 57
	BF ₄ ⁻	1.50	-	66
	BF ₄ ⁻	1.19 ^(b)	-	68
	ClO ₄ ⁻	-0.09	200	127, 123
	ClO ₄ ⁻	1.85 ^(d)	-	138
	ROSO ₃ ⁻	-	60-110	139
	PF ₆ ⁻	0.6	-	74
Poly(N-methylpyrrole)	BF ₄ ⁻	0.52	1x10 ⁻³	127, 57
	BF ₄ ⁻	1.36	-	66
Poly(3-methylpyrrole) [PMP]	BF ₄ ⁻	0.50	4	57
Poly(N-phenylpyrrole)	BF ₄ ⁻	0.70	1x10 ⁻³	127, 123
	BF ₄ ⁻	1.64	-	66
Poly(N-(p-hydroxy)ethylpyrrole)	BF ₄ ⁻	1.40	-	66
Poly(3-carboethoxy,4-methyl-pyrrole)	BF ₄ ⁻	1.43	-	66
Poly(2-carboxy,3-carboethoxy,4-methylpyrrole)	BF ₄ ⁻	1.98	-	66
Poly(2,5-dimethylpyrrole)	BF ₄ ⁻	0.90	-	66

(Continued)

(Table I ; continued)

Polymer	Counter ions	E_{P_a} (V) ^(a)	Conductivity (S cm ⁻¹) ^(h)	References
Poly(pyrrole-2-carboxylic acid)	BF ₄ ⁻	1.71	-	66
Poly(pyrrole-2-aldehyde)	BF ₄ ⁻	1.88	-	66
Poly(2-(β -hydroxy)ethylpyrrole)	BF ₄ ⁻	1.13	-	66
Poly(2-carboethyloxypyrrole)	BF ₄ ⁻	1.30	-	66
Poly(3,4-dichloropyrrole)	ClO ₄ ⁻	0.97 ^(b)	2x10 ⁻⁴	62
Poly(3,4-dibromopyrrole)	ClO ₄ ⁻	0.70 ^(b)	8x10 ⁻³	62
Poly(3,4-diiodopyrrole)	ClO ₄ ⁻	0.60 ^(b)	9x10 ⁻⁴	62
Poly(3-bromopyrrole)	ClO ₄ ⁻	0.3 ^(b)	0.03	62
Poly(thiophene) [PT]	BF ₄ ⁻	0.96	0.02	57
		1.44 ^(e)	-	69
	PF ₆ ⁻	-	0.02	56
Poly(3-methylthiophene) [PMT]	BF ₄ ⁻	0.72	-	57
	PF ₆ ⁻	-	1	57
Poly(3-bromothiophene)	BF ₄ ⁻	1.06	-	57
Poly(3,4-dibromothiophene)	BF ₄ ⁻	1.33	-	57
Poly(azulene)	BF ₄ ⁻	0.7	0.02 - 1	56
	ClO ₄ ⁻	0.7	0.01 - 1	56
	ClO ₄ ⁻	0.88	-	72

(Continued)

(Table I ; continued)

Polymer	Counter ions	E_{p_a} (V) ^(a)	Conductivity (S cm ⁻¹) ^(h)	References
Poly(furan) [PF]	BF ₄ ⁻	1.85 ^(c)	10-80 ⁽ⁱ⁾	55
Poly(aniline)	BF ₄ ⁻	0.08	0.01	51, 123
Poly(pyrene)	ClO ₄ ⁻	1.1	0.1 - 1	56
Poly(carbazole)	ClO ₄ ⁻	0.95	1x10 ⁻³	56
Poly(indole)	ClO ₄ ⁻	1.26	0.020	58
Poly(5-carboxylic acid indole)	ClO ₄ ⁻	1.40	0.024	58
Poly(5-cyanoindole)	ClO ₄ ⁻	1.70	0.014	58
Poly(fluorene)	BF ₄ ⁻	1.82	1x10 ⁻⁴	64
	BF ₄ ⁻	1.80	1x10 ⁻¹ -1	67
	BF ₄ ⁻	1.75 ^(e)	1x10 ⁻³	70
	ClO ₄ ⁻	1.49 ^(e)	1x10 ⁻³	70
	PF ₆ ⁻	1.69 ^(e)	1x10 ⁻³	70
Poly(1-methoxyfluorene)	BF ₄ ⁻	1.66	1x10 ⁻¹ -1	67
Poly(1-methylfluorene)	BF ₄ ⁻	1.78	1x10 ⁻¹ -1	67
Poly(2-chlorofluorene)	BF ₄ ⁻	1.76	1x10 ⁻¹ -1	67
Poly(2-bromofluorene)	BF ₄ ⁻	1.78	1x10 ⁻¹ -1	67
Poly(9-hydroxyfluorene)	BF ₄ ⁻	1.80	1x10 ⁻¹ -1	67
Poly(9-chlorofluorene)	BF ₄ ⁻	2.18	1x10 ⁻¹ -1	67
Poly(9-phenylfluorene)	ClO ₄ ⁻	1.50 ^(e)	1x10 ⁻³	70

(Continued)

(Table I ; continued)

Polymer	Counter ions	E_{p_a} (V) ^(a)	Conductivity (S cm ⁻¹) ^(h)	References
Poly(vinyl diquat)	ClO ₄ ⁻	0.90	-	53
Poly(perfluorocyclopentene)	ClO ₄ ⁻	-1.26	-	71
Poly(p,p'-biphenol)	ClO ₄ ⁻	1.20	-	140
Poly(5-aminonap ⁺ hoquinone)	ClO ₄ ⁻	-.83, -1.36	-	73
Poly(1,5-diaminoanthraquinone)	ClO ₄ ⁻	-1.1, -1.56	-	73
Poly(1-aminoanthraquinone)	ClO ₄ ⁻	-1.03, -1.55	-	73
Poly(2-aminoanthraquinone)	ClO ₄ ⁻	-.99, -1.62	-	73
Poly(5-hydroxy-1,4-naptho- quinone)	OH ⁻	0.70 ^(c)	-	141, 142
Poly(5-hydroxy-2-methyl-1,4- napthoquinone)	OH ⁻	-	-	141
Poly(1-naphthol)	ClO ₄ ⁻ , BF ₄ ⁻	-	1x10 ⁻²	143
Poly(methyl salicylate)	OH ⁻	2.2 ^(b)	-	144
Poly(phenyl salicylate)	OH ⁻	1.2 ^(b)	-	144
Polyphenyleneoxide films by:				
2,6-xylenol	OH ⁻	0.8 ^(c)	-	145
	ClO ₄ ⁻	1.1, 1.5 ^(e)	1.5x10 ⁻⁴	147
hydroxybenzyl alcohol	OH ⁻	0.35 ^(c)	-	146
hydroxybenzaldehyde	OH ⁻	0.35 ^(c)	-	148

(Continued)

(Table I ; continued)

Polymer	Counter ions	E_{P_a} (V) ^(a)	Conductivity (S cm ⁻¹) ^(h)	References
hydroxyacetophenone	OH ⁻	0.35 ^(c)	-	148
hydroxypropiophenone	OH ⁻	0.54 ^(c)	-	148
hydroxybenzophenone	OH ⁻	0.39 ^(c)	-	148
4-(p-hydroxyphenyl)- 2-butanone	OH ⁻	0.18 ^(c)	-	148
Polyphenylene films by:				
Benzene	CLO ₄ ⁻	1.7 ^(e)	1x10 ⁻³	149
	BF ₄ ⁻	1.85 ^(e)	1x10 ⁻³	149
	F ⁻	0.55 ^(f)	-	150
	F ⁻	-	1x10 ⁻³	151
	Cl ⁻	-	2.4x10 ⁻⁴	152
	BF ₄ ⁻ , AsF ₆ ⁻	-	2x10 ⁻¹	153
	AsF ₆ ⁻	-	100	156
Biphenyl	CLO ₄ ⁻	1.2, 1.4 ^(e)	1x10 ⁻³	149
	CLO ₄ ⁻	1.50	-	154
	BF ₄ ⁻	1.2, 1.8 ^(e)	1x10 ⁻³	149
	BF ₄ ⁻	1.7 ^(e)	-	155
	BF ₄ ⁻	1.5 ^(b)	-	157
	CLO ₄ ⁻	2.0 ^(b)	-	157

(Continued)

(Table I ; continued)

Polymer	Counter ions	E_{p_a} (V) ^(a)	Conductivity (S cm ⁻¹) ^(h)	References
Biphenyl	BF ₄ ⁻	-	-	158
o-Terphenyl	CLO ₄ ⁻	1.47 ^(g)	-	154
m-Terphenyl	CLO ₄ ⁻	1.48 ^(g)	-	154
p-Terphenyl	CLO ₄ ⁻	1.32 ^(g)	-	154
Triphenylene	CLO ₄ ⁻	1.40 ^(g)	-	154

- (a) E_{p_a} is the peak potential in the anodic scan, expressed in volts with respect to the saturated sodium calomel electrode (SSCE).
- (b) E_{p_a} values are with respect to the Ag/AgCl reference electrode.
- (c) E_{p_a} value is for the peak (oxidation) potential of the monomer with respect to the saturated calomel electrode (SCE).
- (d) E_{p_a} value is with respect to polished silver wire quasi reference electrode (QRE).
- (e) E_{p_a} value is with respect to Ag/AgNO₃(0.1M in CH₃CN) reference electrode.
- (f) E_{p_a} value is with respect to Pd/H₂ reference electrode.

- (g) E_{p_a} value is with respect to Ag/AgClO_4 (0.1M in CH_3CN) reference electrode.
- (h) Polymers are in their cationic states.
- (i) This value for the conductivity seems excessively high. We note that these authors also reported conductivities of poly(thiophene) which are equally high, in contrast to the reports by other authors.

CHAPTER 2. EXPERIMENTAL

The purpose of this chapter is to present the description of all equipment, chemicals, experimental techniques and instrumentation used in this research. A detailed description of all procedures is also presented.

(1) Electrochemistry

(1.1) Instrumentation. Electrochemical experiments were performed using EG&G/PAR model 362 Scanning Potentiostat. The voltammograms, cyclic voltammograms and chronoamperograms were recorded by an IBM PC/AT computer equipped with ASYSTANT+ data acquisition software or by a Houston Instrument Model 200 XY Recorder. Triangular waveforms and half triangular waveforms for cyclic voltammograms and voltammograms respectively were generated directly by the potentiostat. The squarewave waveforms for chronoamperometry were generated and controlled by the function generator in ASYSTANT+. The potentials were recorded against either a standard KCl-saturated calomel electrode (SCE), a calomel electrode with KCl saturated methanol (SCE/MeOH), a standard silver/silver chloride electrode, or a silver/silver ion electrode (Ag/Ag^+ 0.1M AgNO_3 in CH_3CN) depending on the solvent used.

(1.2) Electrochemical cells. All electrochemical experiments were done using two configurations of electrochemical cell.

(1.2.1) Electrochemical cell 1 [EC1]

EC1 is a one compartment electrochemical cell as shown in figure1.

FIGURE 1. ELECTROCHEMICAL CELL [EC1]

- A: 9 mm I.D. port with threaded O.D., made from a sample vial with a flat teflon washer.
- B: 1/4" I.D. port, made from a #7 ACE fitting with a teflon adapter.
- C: Cell body, made from a 50 X 60 mm weighting bottle.

It has five ports on the lid of the cell which are for the working electrode, the reference electrode, the counter electrode, and the nitrogen inlet port. There is a nitrogen outlet port connecting to the cell body. The purpose of this arrangement is to eliminate any gas generated at the counter electrode during electrochemical processes such as oxygen in aqueous solution.

(1.2.2) Electrochemical cell 2 [EC2]

EC2 is a one compartment electrochemical cell as shown in figure 2. The cell body and all ports except the nitrogen outlet port were made out of Ace Glass joints. The working electrode port was at the bottom of the cell where a working electrode is mounted up side down to prevent trapped gas on its surface. This configuration provided a much better environmental control than EC1 because gasses from outside cannot enter the electrochemical cell.

(1.3) Electrodes.

(1.3.1) Platinum electrode

A Platinum slug (99.99+%, AESAR) tightly fit in a cylindrical teflon holder was used as a working electrode (Figure 3). The Pt/stainless steel piece is screwed to the stainless steel rod thus it can be removed for cleaning, polishing and surface characterization purposes. The exposed surface of the Pt acts as the substrate on which we can immobilize any chemical modifier of our choice. Prior to every electrochemical modification process, the Pt was polished to a mirror like finish with LECO GP20 Grinder/Polisher and solutions of diamond powder (1/2-1 μ and 1/4-1/2 μ). It was then sonicated in many portions of distilled water for 10-15 minutes to remove diamond particles and then dipped in hot chromic acid solution for 5 minutes to remove any organic matter from the surface. It was then rinsed and sonicated with several

FIGURE 2. ELECTROCHEMICAL CELL [EC2]

- A: 7 mm I.D. port, made from #7 ACE fitting with a teflon adaptor.
- B: Glass ball gas outlet.
- C: Cell body, made from 50 mm I.D. #7646 ACE glass joint clamped together with teflon o-ring seal in between.

FIGURE 3. PLATINUM SLUG ELECTRODE

- A: 1/8" O.D. stainless steel extension rod.
- B: 1/4" O.D. stainless steel rod, screwed onto A and silver soldered to C.
- C: Platinum slug (6.35 mm O.D. X 12.7 mm)
- D: Cylindrical teflon covering piece.
- E: Cylindrical teflon sleeve tight fit to B and C.

portions of distilled water. Right before use, it was rinsed with acidic permanganate distilled water and used immediately in aqueous solution or partially dried and rinsed with distilled organic solvents of choice.

(1.3.2.) Pyrolytic graphite electrodes [92, 159, 160]

Graphite is a form of carbon whose atoms are arranged as giant sheets of fused aromatic molecules stack coplanarly. Pyrolytic graphite (PG) is a type of graphite with an orderly arrangement of individual planes. Thus it is anisotropic and its user must be careful to properly align PG in the desired orientation (Figure 4).

Plane *ab* which parallels to the graphite layers is called the basal plane. It is non-ionic, has low polarity, hydrophobic and rich in π electron density. The population of chemical functionalities is low and only found along surface imperfections. Without alteration, the basal plane is unreactive to synthetic coupling reactions. But because of its high π electron density, it is conducive to strong chemisorptive interaction, especially with unsaturated and aromatic compounds. We can use this adsorptive property of the basal plane for chemisorptive electrode modification.

Plane *ab* and *bc* which are perpendicular to the graphite layers are called edge planes. The edge planes are thought to contain oxygenic functional groups such as phenolic, quinone, carboxyl, lactone and other ketonic functionalities. Edge planes are polar, hydrophilic and contain ionic sites which cause double layer capacitance of the edge plane to be higher than that of the basal plane. Therefore edge planes are attractive for chemical coupling and modification procedures. One must keep in mind that the characteristics of the portion of the edge and basal plane exposed on a surface depends on surface pretreatment.

FIGURE 4. SCHEMATIC REPRESENTATION OF THE LAYERED STRUCTURE OF PYROLYTIC GRAPHITE.

Because the structural nature of PG having two different types of surfaces separately, it is convenient to perform an experiment where the type of exposed surface can be controlled. This is the reason why we chose to have our preliminary work done on PG instead of normal graphite or glassy carbon where both planes are intertwined and a controlled experiment is impossible to conduct.

We designed two PG electrodes with the same style, but different in dimension (Figure 5). Each will expose either the basal or the edge surface to the environment only. The opening of the holders were designed to be as wide as possible and with a minimal depth to eliminate diffusional problems and trapped gasses. We have found the tapered design of the opening was satisfactory.

Due to its fragile property, a piece of PG (Union Carbide) was cut with a Low Speed Diamond Wheel Saw (South Bay Technology) or drilled into a rod shape using a Diamond Core Drill (Lapcraft).

PG pieces were cleaned by Soxhlet extraction in hexane for 20 hours to remove any contamination from machining and handling. They were baked at 140°C for 12 hrs to remove hexane. Then the extraction process was repeated in methanol for 24 hours to remove any polar contaminant that may have remained after hexane extraction. After that they were dried in an oven at 140°C for 12 hrs.

We followed the polishing procedure that Hu, Karweik and Kuwana [161] used for their glassy carbon except that we found diamond powder (Kay Industrial Diamond Corp.) a more suitable polishing medium than alumina powder because alumina particles tends to accumulate between PG layers and are very difficult to remove. Because our PG pieces were very small and we wanted to

FIGURE 5. PYROLYTIC GRAPHITE ELECTRODE

- A: Cylindrical electrode extension, made of Kel-F.
- B: Cylindrical electrode hood, made of Kel-F and has tapered opening to eliminate diffusion obstacles.
- C: 1/4" O.D. stainless steel with contacting disk.
- D: Pyrolytic graphite rod.

prevent any contamination from handling during polishing and the cleaning processes, latex finger cots were worn. We also designed a polishing fixture (Figure 6) to hold the small PG pieces so that only the desired surface was exposed and that the surface would be polished true and prevent the unintentional generation of dual surfaces during polishing.

(2) Supporting Electrolytes and solvents. Tetraethylammonium tetrafluoroborate 98%, TEATFB, was purchased from Johnson Matthey. Sodium hydroxide 99.99% semiconductor grade, NaOH, was purchased from Aldrich. Potassium chloride ACS grade, KCl, was purchased from Fischer. All three electrolytes were used as received without further purification.

Acetonitrile (Fisher, HPLC grade) was refluxed with calcium hydride (to remove water) under a nitrogen atmosphere (Figure 7). The lower boiling point fractions were discarded and the solvent was distilled as needed. We have found this purification process produces dry and pure acetonitrile that results in clean cyclic voltammograms.

Water was obtained by distilling distilled water from acidic permanganate solution after letting the solution sit for at least two days before the distillation (Figure 8). This water was free from any organic contaminant.

Methanol (Fischer, HPLC grade) was doubly distilled before used. Hexane (Fischer, HPLC grade) was used as received.

(3) Additional Instrumentation

(3.1) Fourier-Transform infrared spectrometer (FTIR) A Nicolet Model 5PC FTIR equipped with a Diffused Reflectance Accessory (Harrick Scientific) was used to characterize the modified surfaces. The samples were put in the DRA

FIGURE 6. POLISHING FIXTUE

- A: 2.75" O.D. optical pyrex glass disk, attached to B by stainless steel screw.
- B: 1.375" O.D. stainless steel (shaded area).
- C: 0.75" O.D. cylindrical teflon piece, tight fit to B.
- D: Micrometer, press fit to B.

FIGURE 7. ACETONITRILE DISTILLATION APPARATUS

Distillation was conducted under nitrogen atmosphere.
All pyrex and teflon.

FIGURE 8. WATER PURIFICATION APPARATUS BY DISTILLATION
FROM ACIDIC PERMANGANATE SOLUTION.

Distillation was conducted under nitrogen atmosphere.

and the spectra were generally obtained by 200 scans at 2 cm^{-1} resolution. All spectra were taken under nitrogen atmosphere. Clean, polished platinum surface was used as background.

(3.2) Goniometer A NRL Goniometer Model 100-00 (Ramé-Hart) was used to measure contact angles of clean and modified surfaces. We used the sessile drop method (Appendix 2) to measure an angle between the interface of a 2 μL drop of acidic permanganate distilled water and the solid surface of interest. All measurements were done in an enclosed environmental chamber (Ramé-Hart Model 100-07) under an acidic permanganate distilled water saturated nitrogen atmosphere.

(4) Experimental Procedures

(4.1) Cyclic voltammetry of platinum in sulfuric acid solution The procedure described here had been used in our lab to establish a clean platinum surface and calculate its real electrochemical area. This procedure was adapted from the work of Conway et al [122]. The Pt surface was polished to mirror smooth as described previously. The Pt electrode was then placed in a fresh portion of 0.05 M H_2SO_4 and potential cycled at 500 mV/s between -0.225 to +1.250 V_{SCE} for 15 min while bubbling N_2 through the solution. The solution was then replaced with a new portion and potential cycling processes were repeated until a clean Pt CV was obtained. This CV will be used to calculate Pt electrochemical area by assuming $210\text{ }\mu\text{C}/\text{cm}^2$.

(4.2) Cyclic voltammetry of Pt in basic solutions A Pt disk was used in

the following solutions: 0.2 M NaOH (aq), 0.2 M NaOH/0.1 M MeOH (aq) and 0.2 M NaOH/MeOH. The Pt was polished and cleaned before it was potential cycled at a scanrate of 500 mV/s in the above solutions between -0.95 to 0.7 V_{SCE}. The solution was then discarded and was replaced with a fresh portion. The potential cycle was continued until a well defined CV was obtained. All experiments were done under N₂ atmosphere.

(4.3) Electropolymerization of 2,6-Dimethylphenol [DMP] A solution of DMP was prepared with 0.2 M NaOH in MeOH. All polymerizations were done on a clean Pt disk electrode by the potential scanning technique under nitrogen atmosphere. All potential were recorded against SCE/MeOH reference electrode. The polymer modified electrode was characterized by FTIR, contact angle and the stability of the polymer film was also tested in 0.05 M H₂SO₄.

(4.4) Electropolymerization of 2,3,4,5,6-Pentafluorostyrene [PFS] PFS (98%, Aldrich) is a clear liquid with a unique faint odor and was used as received. A clean Pt surface was prepared in electrochemical cell EC1 before it was transfer into an electrochemical cell EC2 for the polymerization. The working solution was 5 mM PFS in 0.2 M TEATFB in CH₃CN. All polymerization potential were measured against an Ag/Ag⁺ reference electrode. All experiments were conducted under nitrogen atmosphere.

(4.5) Electropolymerization of Tetrafluoro-1,4-benzoquinone [TFQ] and Tetrafluorohydroquinone [TFHQ] TFQ (97%) and TFHQ (98%) were purchased from Aldrich and used as received. The working electrode was a Pt disk which was

polished and cleaned before each use. The polymerization solutions were 0.1 M TFQ or 0.1 M TFHQ in 0.1 M TEATFB/ CH_3CN . The CV of each compound was obtained. The potential were recorded against Ag/Ag^+ reference electrode. The modified Pt surface was compared to a clean Pt by CVs in 0.05 M H_2SO_4 . All experiments were done under N_2 atmosphere.

CHAPTER 3. PREPARATION OF CMES BY ELECTROPOLYMERIZATION OF 2,6-DMP

We are looking for suitable chemical modifiers for pyrolytic graphite electrodes which must satisfy the requirements mentioned previously under the heading "Polymer-Modified Electrodes". Many compounds were chosen as potential candidates, all of them contain aromatic rings which may result in π -conjugated polymers after anodic polymerization. This structure is a primary requirement for sufficient conductivity of the polymers. At this initial stage, most studies were done on 2,6-dimethylphenol which is known to form polyphenylene oxide polymer under anodic polymerization (141, 142, 145, 146, 148). We are in the process of establishing a suitable electropolymerization method as well as explaining the polymerization mechanism which will be used as a basis for us to move on to the fluorinated members.

(1) Polyphenylene oxide modified electrodes Dubois et. al. [141, 142, 145, 146, 148] demonstrated that electrochemical methods can be used to generate polyphenylene oxide [PPO] films on metal electrode surfaces by selectively oxidizing the hydroxyl group of phenol derivatives in basic alcohol medium. They reported that the PPO films passivate the metal surface. The films are both adhesive and hydrophobic and are suitable for forming a protective coating on metallic surfaces.

The ability to generate these hydrophobic films electrochemically interested us a great deal. We chose to work on the simple phenol derivative 2,6-Dimethyl phenol [DMP] before moving on to the fluorinated derivatives.

(2)   Preliminary study   Electropolymerization of DMP was done on a Pt disk electrode in a solution of 0.1 M DMP in 0.2 M NaOH/MeOH. The polymerization potential for DMP was obtained using linear sweep voltammetry. The potential was scanned from -0.5 to 1.0 V _{SCE/MeOH}. During the scan, an intense yellow color was observed near the working electrode. This yellow persists in the solution if the applied potential is terminated and/or if the electrode is removed from the electrochemical cell. The color intensity diminished as the potential increases past the peak maximum. The color observed could be an intermediate species formed as a result of the oxidation of DMP. As the potential increases, the electrode reaction occurs at a faster pace such that all of the intermediate is converted immediately into product resulting in the diminished intensity of the yellow color. Afterward, a thin uniform blue film is observed on the Pt surface. This result agrees well with Dubois et. al. [145]. Dubois used gas chromatography to identify this yellow product as dimethylbenzoquinone.

A series of potential scan polymerizations of DMP was conducted using various scanrates (Figure 9). All voltammograms show large peaks with preceding shoulders. All except the scan at 5 mV/s show shoulders following the main peak. The existence of these shoulders needs to be explained as well as the anodic shift of the main peak as the scanrate increase. Another interesting feature of these voltammograms are the changes in peak shape as the scanrate changes.

Another series of potential scan polymerizations of DMP was done. This time the Pt was potential cycled once in blank solution before starting the polymerization process (Figure 10). These voltammograms have a different shape than the first set (Figure 9). All of them show more intense preceding shoul-

FIGURE 9. VOLTAMMOGRAMS OF DMP AT DIFFERENT SCANRATE

solution is 0.1 M DMP/0.2 M NaOH/MeOH
 working electrode is Pt disk (6.35 mm.O.D.)
 potential range -0.5 to 1.0 $V_{SCE/MeOH}$

FIGURE 10. VOLTAMMOGRAMS OF DMP AT DIFFERENT SCANRATES

solution is 0.1 M DMP/0.2 M NaOH/MeOH
 working electrode is Pt disk (6.35 mm.O.D.)
 potential range -0.5 to 1.0 $V_{SCE}/MeOH$

The Pt electrodes were scanned in 0.2 M NaOH/MeOH
 before being transferred to this solution.

ders. The changes in the peak shape and the shift in the main peak potential as the scanrate varied are similar to the first set.

These features of the voltammograms and their variations present clues to the mechanism of the polymerization process. In the following sections I will develop a qualitative description of this mechanism.

(3) Cyclic voltammetry of Pt in NaOH (aq) In attempting to answer the questions encountered during my preliminary study, I decided to first establish a procedure for obtaining a clean Pt CV in aqueous sodium hydroxide solution. The best results obtained after several attempts and changes are presented in figure 11. The shape of these CVs is very similar to that obtained in sulfuric acid solution. There are 3 hydrogen desorption peaks at -0.88 , -0.64 and -0.54 V_{SCE} respectively. The hydrogen adsorption peak is found at -0.66 V_{SCE} and the increasing of the cathodic current around -0.90 V_{SCE} is the beginning of hydrogen gas evolution. The oxygen adsorption peaks are found in the region of -0.20 to 0.7 V_{SCE} and the oxygen desorption peak located at -0.34 V_{SCE} . These CVs have the combined features of the Pt single crystal low index planes (100, 110, 111) in 0.1 M NaOH [163]. Since our Pt electrode is polycrystalline Pt which is theoretically composed of 10% Pt(100), 66% Pt(110) and 24% Pt(111) [164], it is not surprising that we observe the combination of these features in our CVs. The data is very reproducible and we will use these CVs as a basis for Pt in alkaline medium.

(4) Cyclic voltammetry of Pt in aqueous MeOH/NaOH The electrocatalytic oxidation of methanol on a Pt electrode has been extensively studied [165 and ref. therein]. Most of these studies were done in acidic media. Mechanistic

FIGURE 11. CYCLIC VOLTAMMOGRAM OF Pt IN 0.1 M NaOH

potential range -0.95 to 0.7 V_{SCE}
scanrate 500 mV/s

and adsorbed intermediates such as CO_{ad} , HCHO_{ad} were postulated. Since I will be using MeOH as a solvent, it is necessary to know if these adsorbed molecules will block Pt sites and inhibit polymerization. These experiments were done using a Pt electrode in 0.1 M NaOH/0.1 M MeOH (aq) solution. The cyclic voltammograms were recorded for a series of scans (figure 12). I will now compare these CVs to the CV of Pt in NaOH (aq) (Figure 11) which was recorded over the same potential range. On the anodic sweep, there is a peak located at $-0.160 \text{ V}_{\text{SCE}}$. The current dropped after the peak maximum was reached and there was no increase in current until the very end of the anodic sweep, which is the same as the oxygen region of Pt in aqueous NaOH. When comparing these CVs to a Pt CV in aqueous NaOH (figure 11), it is obvious that the peak at $-0.16 \text{ V}_{\text{SCE}}$ is new and must belong to methanol. The species causing this peak appears to have suppressed the fine details in the hydrogen region. This indicates the existence of a surface bound intermediate which blocks the hydrogen binding sites. The reduction peak around $-0.2 \text{ V}_{\text{SCE}}$ has a much lower current. Based on a theory developed by Wopchall and Shain [167], these features fit a case where the reactant is weakly adsorbed on the electrode surface. The adsorption of the methanol on the surface reduces the amount of material diffusing away from the electrode during the reverse scan, which gives rise to a decrease in cathodic peak current. The increase in anodic peak current after subsequent scans is a result of adsorbed methanol. These species after being reduced by the reverse scan do not diffuse far from the electrode vicinity. Especially, when the scan rate is high (the experiment was done at 500 mV/s), very little of the material has time to diffuse away before the potential switches direction. This results in the increase of the anodic peak current due to the accumulation of methanol and its oxidation product(s) in the vicinity of the electrode.

FIGURE 12. CYCLIC VOLTAMMOGRAMS OF Pt IN 0.1 M NaOH/0.1 M MeOH (aq)

Pt disk electrode (6.35 mm.O.D.), scanrate 500 mV/s
 potential range -0.95 to 0.70 V_{SCE}

— first scan

- - - fifth scan

..... after continuous scan for 30 minutes

Beden et. al. [166] reported that when the concentration of MeOH is low (less than 10^{-2} M), the cathodic peak is superimposed on the MeOH oxidation peak with almost equal magnitude of the peak current. This is possible only if there is no strongly bound intermediate which would irreversibly block the electrode active sites. The shape of the CV becomes stable after continuous cycling for 20 minutes. After which, the concentration of the adsorbed species has reached a maximum and no change is observed.

(5) Cyclic voltammetry of Pt in 0.2 M NaOH/MeOH From the study of MeOH electro-oxidation in aqueous NaOH solution, the adsorbed intermediate was determined. Since I will be working with MeOH as a solvent, the coverage of the Pt surface with methanolic residues will be important. To determine the extent to which they will affect my results, a series of Pt CVs in 0.2 M NaOH/MeOH were recorded (Figure 13). During the first scan, the CV appears similar in shape to the CV of methanol electro-oxidation on Pt in aqueous media (Figure 12) except that anodic peak is shifted to a much higher potential. This anodic shift suggests that methanol oxidation becomes more difficult in nonaqueous solutions. The free energy of adsorption of methanol on platinum in the absence of water increases, thus the oxidation peak shifts to a higher potential. The peak current increased until it reached a limiting value after 15 minutes of continuous cycling. After 15 minutes, the shape of the CV was stabilized and no change was observed for periods of up to 30 minutes. The initial increase in the peak current is a result of the accumulation of an adsorbed methanol and methanol oxidation intermediate as mentioned before. The current reached a stable value when all Pt sites were occupied. It should be noted that the voltammetric curves of both the positive and negative sweeps,

FIGURE 13. CYCLIC VOLTAMMOGRAMS OF Pt IN 0.2 M NaOH/MeOH

Pt disk electrode (6.35 mm.O.D.), scanrate 500 mV/s
potential range -0.95 to 0.70 V_{SCE}

— first scan

- - - fifth scan

- · - · - after continuous scan for 15 minutes

once stabilized, are almost superimposable. This indicates the absence of a strongly bound intermediate. Dubois [168] concluded from a MIRFTIRS study of MeOH oxidation on Pt in alkaline medium that the electro-oxidation of MeOH on Pt is retarded by an intermediate methanolic residue which blocks the electro-active sites. This residue could be CO_{ad} which undergoes further electro-oxidation at the electrode surface when the potential is sufficiently positive, about $+0.40 \text{ V}_{\text{SCE}}$. They proposed CO_2 as the main product which agrees well with my experiments. Gas bubbles were observed on the Pt surface when the anodic limit was increased to higher values. The results of this study indicates that the Pt surface was covered by MeOH electro-oxidation intermediates. These species are weakly bound and may not obstruct the polymerization process via competitive adsorption with the monomer. In all cases a polymer film was observed served on the Pt surfaces.

(6) Electropolymerization of 2,6-Dimethylphenol Polymerization of DMP was done by the potential scanning technique. The working potential range was chosen to be from -0.5 to $1.0 \text{ V}_{\text{SCE/MeOH}}$. A typical voltammogram of DMP in 0.2 M NaOH/MeOH is presented in figure 14. The experiments were done under the same conditions with scanrate as the variable. As the potential increases during a sweep, DMP in solution moves toward the working electrode where it will be oxidized. Some of the DMP was oxidized to form an adsorbed product on the surface whereas some was oxidized and remained in solution. The free energy of adsorption facilitates the oxidation of DMP into adsorbed products thus its peak precedes the oxidation peak of DMP as dissolved product. Since the pre-wave is a result of adsorption it will be called the adsorption peak and its peak potential and peak current will be referred as E_{ad} and i_{ad} , respectively.

FIGURE 14. VOLTAMMOGRAMS OF 0.1 M DMP/0.2 M NaOH/MeOH

Pt disk electrode (6.35 mm.O.D.)
 potential range -0.95 to 0.70 V_{SCE}
 — 20 mV/s
 ..... 50 mV/s
 ----- 100 mV/s

In a similar manner, the peak potential and peak current of the soluble DMP species will be referred as E_{diff} and i_{diff} because they are the result of a diffusion control process.

The plot of i_{diff} verses square root of the scanrate (Figure 15) proves that this peak is a result of a diffusion controlled electron transfer process [162]. For an adsorption process, i_{ad} varies with scanrate. But from figure 14, i_{ad} increases as the scanrate increases but reaches a limit. The ratio of i_{ad} to i_{diff} should increase with the square root of the scanrate when the product is strongly adsorbed on the surface [167]. This plot, using data from figure 14, is shown in figure 16, the result of which is the opposite from that derived from theoretical analysis.

Figure 17 shows a series of voltammograms under the effect of DMP concentration. As the bulk concentration increases, the surface coverage increases and there become fewer available sites for DMP to be oxidized and remains as adsorbed product on the surface. This results in a decrease in i_{ad} which is as expected in figure 17. On the other hand, the occupied sites has almost no effect on the oxidation of DMP forming a soluble product, thus i_{diff} remains reasonably constant over the range [167].

(7) Physical characterization of polyphenylene oxide film After the electropolymerization of DMP, the Pt surface was covered with a thin blue film. The film would uniformly and completely cover the Pt surface only when extreme care was used during the cleaning, polishing and handling of the electrode. A small amount of contamination is sufficient to inhibit the polymerization process. This may be due to the blocking the approach of the DMP molecules to the Pt surface. Only the uniform blue films, determined by observa-

FIGURE 15. A PLOT OF THE DIFFUSION CURRENT AND $\nu^{1/2}$
from the data of figure 14

FIGURE 16. A PLOT OF THE RATIO OF i_{ad}/i_{diff} AND $\sqrt{\text{scanrate}}$
from the data of figure 14

FIGURE 17. VOLTAMMOGRAMS OF DMP/0.2 M NaOH/MeOH

Pt disk electrode (6.35 mm.O.D.), scanrate 50 mV/s
potential range -0.95 to $0.70 V_{SCE}$

—— 0.07 M DMP
..... 0.1 M DMP
----- 0.2 M DMP

tion using a X125 microscope, were characterized.

a. Contact angle The contact angles of the films were measured by the sessile drop method using a 2 μ L drop of acid permanganate distilled water. The contact angle values varied from 101° to 104° which indicate that the PPO film of DMP is hydrophobic.

b. FTIR The IR spectra of a PPO film of DMP and the standard spectra are shown in figure 18. Both spectra match peak for peak. The analysis of spectra B is as follows:

wavenumber (cm^{-1})	mode	functional group
2917	C-H stretching	methyl
1607, 1479	C=C bending	aromatic
1385	C-H bending	methyl
1306, 1203, 1023	C-O stretching	ether
961, 818	C-H oop bending	aromatic

c. Film stability in sulfuric acid solution The stability of the PPO film in sulfuric acid solution was examined by cyclic voltammetry in 0.05 M H_2SO_4 (Figure 19). The shape of the CVs were similar to a Pt CV in sulfuric acid. The film was tested by potential cycling between -0.225 to 1.250 V_{SCE} for 12 minutes. The film was stable throughout the continuous scanning and the physical appearance of the film through a X125 microscope was the same. The stability of the film was also confirmed by FTIR after this continuous scanning. These results were satisfying.

FIGURE 18. IR SPECTRA OF POLYPHENYLENE OXIDE OF 2,6-DIMETHYLPHENOL

- A: standard spectrum of PPO
- B: our PPO film from electropolymerization of DMP on Pt
by potential scanning in 0.1 M DMP/0.1 M NaOH/MeOH

FIGURE 19. CYCLIC VOLTAMMOGRAMS OF PPO FILM OF DMP IN 0.05 M H_2SO_4

(8) Polymerization mechanism of 2,6-Dimethylphenol From the data presented in the previous sections, a general mechanism of the polymerization process can be deduced. Methanol which is used as the solvent throughout the study is oxidized within the polymerization potential range, but its oxidation product does not retard the polymerization of DMP. The thin blue film of PPO is always obtained as a product. The yellow color observed during the polymerization suggests the existence of reaction intermediate. This intermediate must be available at all time during the polymerization. The shape of the voltammogram which consists of an adsorption prepeak and a diffusion peak that there are two pathways that DMP can follow during the polymerization.

Equation (2) is required for the initial step of attaching the polymer to the surface. Equation (1) is necessary for polymer chain propagation.

Dubois et. al. [145] in their work on polyphenylene oxide films suggested that the initial step is the oxidation of a phenolate ion to a radical species. This radical has large spin density at its ortho and para positions. Other radicals will attached at these positions and the polymer film will be obtained. A parallel mechanism is presented in figure 20. All DMP molecules are assumed to be present in the form of phenolate ions due to the high pH of the working solution (0.2 M NaOH/MeOH). During the chain propagation steps, DMP radical is constantly generated in the vicinity of the electrode surface. They can be further oxidized to dimethylbenzoquinone (the yellow color [145]) or other products. This radical has high electron density at ortho and para posi-

tions, but because both ortho positions are occupied by the methyl groups, the polymer chain can only grow via the para position and a straight chain polymer results. This fact is confirmed by IR spectra which does not show an OH peak. If the polymer chain is branched, there should be more than one OH group per branched chain. The intensity of this peak would be greater and could be used to estimate the degree of branching. This feature is not observed at all.

Initiation:

Propagation:

Overall reaction:

FIGURE 20. ELECTROPOLYMERIZATION MECHANISM OF 2,6-DMP

CHAPTER 4. PREPARATION OF OTHER CHEMICALLY MODIFIED ELECTRODES

(1) Electropolymerization of 2,3,4,5,6-Pentafluorostyrene

My first attempt in electrode modification was done with 2,3,4,5,6-Pentafluorostyrene [PFS]. I chose this compound because of the similarity in its structure to styrene, the monomer of polystyrene (an addition polymer). During an addition polymerization, a double bond is spent in the process of adding another monomer unit on. We can predict that the resultant polymer is nonconducting due to the lack of a conjugated system (Figure 21).

On the other hand, in the process of anodic polymerization, a cationic radical is generated. This radical activates a chain polymerization and it is possible that the polymer product may contain conjugated double bonds in its backbone and thus be conducting (figure 22). The possibility of this result was very exciting, so I started my investigation with the anticipation of developing a pyrolytic graphite/PFS modified electrode.

(1.1) Results and Discussion

The electrochemistry of PFS was determined in a system of 5 mM PFS/0.2 M TEATFB/CH₃CN using a Pt electrode. I found that its oxidation peak begins at 1.8 V_{Ag/Ag+} and reaches a peak current maximum at 2.36 V_{Ag/Ag+}. No reduction peak was observed down to -1.0 V_{Ag/Ag+}. The highest usable anodic potential for pyrolytic graphite in this system is 1.6 V_{Ag/Ag+}. But since the polymerization potential of PFS must be higher than 1.8 V_{Ag/Ag+}, I could not continue

FIGURE 21. STRUCTURE OF STYRENE ADDITION POLYMERS

A: styrene and polystyrene

B: 2,3,4,5,6-pentafluorostyrene and polyfluorostyrene

FIGURE 22. ANODIC POLYMERIZATION MECHANISM OF PFS

this phase of my research using pyrolytic graphite, instead I continued my study using Pt.

Polymerization of PFS was done by the potentiostating technique. In this technique, a polymerization potential is selected (preferably at a potential where monomer oxidation commences) and a squarewave waveform is applied. The applied waveform starts at an initial potential where no polymerization occurs then rises to the polymerization potential and is kept there for a specific period of time after which the potential is returned to its initial value. A current-time curve is recorded simultaneously. Integration of this curve gives the amount of electrical charge that was used during the polymerization process. This value was corrected by subtracting the charge produced during a blank run. (Appendix 1)

The total charge spent during the potentiostating of a monomer solution was 10 times higher than the total charge spent for a blank solution under the same conditions. This indicated the occurrence of some electrode reactions. Since the system of TEATFB/ CH_3CN is stable within the range of +2.97 to -2.47 $V_{\text{Ag}/\text{Ag}^+}$, I am certain that the polymerization must have occurred at the electrode surface. Based on the mechanism shown in figure 22, I assumed the consumption of one electron per monomer unit. The calculation shown in Appendix 1 indicates that a uniform coverage of the Pt surface would contain approximately 6×10^{13} polymer sites with roughly 1550 monomer units per chain. This gives a film thickness of approximately 280 Å.

From this estimation, the polymer film was thick enough for surface characterization by FTIR and contact angle analysis. If the film has color, I would be able to visually see the altering of the platinum surface. But the FTIR data did not show any existence of the functional groups of the polymer (Figure 23).

FIGURE 23. INFRARED SPECTROGRAMS OF PFS

- A: standard IR spectrogram of PFS
- B: FTIR spectrum of a Pt surface after potentiostating at 2.2 V_{Ag/Ag⁺} for 90 sec. in a solution of 5 mM PFS in 0.2 M TEATFB/CH₃CN. The spectrum shows peaks of water and carbon-dioxide only.

The contact angle values were less than 90° but were 10° higher than the value for a clean Pt surface. This does not agree well with a prediction that PFS should polymerize into a highly hydrophobic polymer (contact angle greater than 90°). The small change in the value of the contact angle only indicates an altering of the Pt surface during the electrochemical process, but together with the FTIR results, shows no surface modification due to formation of PFS polymer on the surface.

The PFS polymerization was attempted with oxidized and reduced Pt surfaces under the same conditions as was done with the Pt neutral surface. Results indicate that the reduced Pt surface facilitated the polymerization process since the total charge consumed during a polymerization was twice as much as when it was performed on an oxidized surface. Based on the mechanism shown in figure 22, it can be understood that a cationic radical generated in the vicinity of the working electrode would have a higher affinity for the reduced Pt surface due to electronic attraction of opposite charges and thus more units of them can move close to the electrode. Despite all the possibilities, there was not a trace of any polymer on any Pt surface.

(1.2) Conclusion

It is conclusive enough to say that PFS polymerized but its polymer did not stay on a Pt surface (grey particles were observed at the bottom of the electrochemical cell). PFS contains a bulky aromatic moiety which probably obstructs itself from attaching to the surface. Another possibility is that it underwent an addition polymerization as shown in figure 21 and generated a nonconducting polymer. It is impossible to generate a long chain of a noncon-

ducting polymer electrochemically. A short chain must peel off from the surface in order to keep the polymerization process going.

Because of its high oxidation potential (exceeds the oxidation potential limit for pyrolytic graphite) and inability to undergo a surface attached electropolymerization, PFS is not a suitable modifier for our purposes.

(2) Quinone/hydroquinone modified electrodes

The redox reaction of quinone/hydroquinone $[Q/H_2Q]$ was discovered in 1904 by Haber and Russ. But it was not until 1921 when scientists realized the potential of this discovery and a new kind of electrode called the Quinhydrone electrode had been invented. This new kind of reference electrode has a potential that responds to pH and is reproducible to within a few millivolts. The reversibility and sensitivity to pH made the quinhydrone electrode very useful for coulometric titrations prior to the invention of the glass electrode. The Q/H_2Q couple could be an exceptional electrode modifier because the redox reaction is straight forward. The reaction involves multiple electrons in non-aqueous solutions whereas it involves multiple protons in aqueous solutions. These natures are useful for the study of coupled ions and electrons transfer [5,169, 170].

Q/H_2Q has been used to modify electrodes for example, Anson et. al. [12-14] modified glassy carbon and pyrolytic graphite with compounds containing reactive Q/H_2Q functional groups. The modification was done by simply dipcoating the carbon electrodes in suitable solutions of Q/H_2Q . The adsorptions were irreversible and the modified electrodes were as reactive as the unbound modifiers. Kuwana [20] covalently attached Q/H_2Q compounds with a terminal amino

group to carboxylic acid functionalities on a carbon surface. Miller et. al. [40-44] coated carbon electrodes with synthetic polymer films containing Q/H₂Q moiety, however, many of these polymers exhibited poor stability or incomplete electroactivity in aqueous solutions. From the literature, we see that it is possible to use Q/H₂Q compounds as an electrode modifier. Our main question now is if it is possible to electropolymerize Q/H₂Q and obtain a polymer that is hydrophobic and that still retains the reactivity of Q/H₂Q. To answer this question, I chose to work on two compounds, tetrafluorohydroquinone [TFHQ] and tetrafluoroquinone [TFQ], which if polymerized will be highly hydrophobic.

(2.1) Results and discussion

(2.1.1) Tetrafluoro-1,4-benzoquinone The oxidation and reduction potentials of TFQ was determined using a Pt electrode. I have found that TFQ can undergo two redox reactions, one located at -0.110 and -0.260 V_{Ag/Ag+}, and the second at -0.920 and -1.240 V_{Ag/Ag+} (Figure 24). This behavior indicates that the electrochemical reduction of TFQ occurs in two steps corresponding to the formation of the anion-radical and then the dianion respectively. The first redox reaction has a peak separation of 150 mV, which is larger than a value of 58 mV given for the theoretical equivalence of a one electron transfer reversible process. The shape of the CVs did not become distorted during a series of potential cycles which indicates that the reaction is reversible. Peak separation exceeding 58 mV can be accounted for by an uncompensated ohmic drop due to the solvent, since it is known that CH₃CN is a high resistance solvent. The second redox reaction peaks were often deformed. An explanation for this could be that the dianion after formation can react with quinone and

FIGURE 24. CYCLIC VOLTAMMOGRAM OF TETRAFLUORO-1,4-BENZOQUINONE

Pt disk (6.35 mm.O.D.) in 0.1 M TFQ/0.1 M TEATFB/CH₃CN
 potential range 0.4 to -1.5 V_{Ag/Ag⁺}, scanrate 500 mV/s

generate two anion-radicals, thus the peak current for the dianion oxidation would be small. From figure 25, the peak current depended on the scanrate and the plot of peak current versus the scanrate is linear which indicates that the redox reaction is of surface bound species. No surface film was observed on this modified Pt surface via a X125 microscope. When checking the stability of the modified surface in 0.05 M H_2SO_4 , the CV was found to be distorted from that of a clean Pt CV in 0.05 M H_2SO_4 (Figure 26). There is a peak with shoulder starting at 0.10 V_{SCE} to 0.38 V_{SCE} and reaching maximum at 0.20 V_{SCE} . The hydrogen peaks were diminished but the oxygen adsorption peak increased. Potential cycling the electrode in 0.05 M H_2SO_4 did not give a CV indicative of clean Pt which indicates a permanent poisoning of the Pt surface. Molecules of TFQ on the Pt surface occupy some of the dihydrogen adsorption region, this explains why both hydrogen regions were diminished. The quinone functionality of TFQ also undergoes an electron transfer reaction at the electrode, this explains why there was an increase in the oxygen adsorption region.

(2.1.2) Tetrafluorohydroquinone The oxidation-reduction peaks of TFHQ were recorded using a Pt disk electrode (figure 27). The first pair was at -1.225 and -0.675 $\text{V}_{\text{Ag}/\text{Ag}^+}$ and the second pair at -0.100 and +0.050 $\text{V}_{\text{Ag}/\text{Ag}^+}$. The second pair had a peak separation of 50 mV which indicates a reversible one electron transfer while the first pair had a peak separation that was very large. The increase in current at the oxidation end may be due to the irreversible oxidation or decomposition of TFHQ because during the process of potential cycling the solution which was a pale clear beige color at the start turned darker. No film was observed on the Pt surface when observed by a X125 microscope. The modified surface was rinsed with CH_3CN followed by distilled

FIGURE 25. CYCLIC VOLTAMMOGRAMS AT DIFFERENT SCANRATE OF TFQ

Pt disk (1 mm.O.D.) in 5 mM TFQ/0.1M TEATFB/ CH_3CN
 potential range 0.4 to -1.5 $\text{V}_{\text{Ag}/\text{Ag}^+}$

scanrate were 10, 20, 50, 100, and 200 mV/s

FIGURE 26. CYCLIC VOLTAMMOGRAM OF Pt AND TFQ MODIFIED Pt

Pt (6.35 mm.O.D.) in 0.05 M H_2SO_4 , scanrate 500 mV/s

potential range -0.225 to 1.250 V_{SCE}

A:---- clean Pt, contact angle = 60.5°

B:— modified Pt surface, the CV was stable through
30 minutes continuous potential cycling.

FIGURE 27. CYCLIC VOLTAMMOGRAM OF Pt IN TETRAFLUOROHYDROQUINONE

Pt disk (6.35 mm.O.D.) in 0.1 M TFHQ/0.1 M TEATFB/ CH_3CN
 potential range -1.50 to 1.7 $\text{V}_{\text{Ag}/\text{Ag}^+}$, scanrate 500 mV/s.

water before placing it in a solution of 0.05 M H_2SO_4 (Figure 28). The modified surface gave a CV in which the hydrogen and oxygen regions were smaller. There was a small peak centered @ 0.200 V_{SCE} on the anodic scan, this peak had a matching reduction peak at a slightly lower potential. This indicates that a film of TFHQ is absorbed onto the surface of the Pt (blockage of hydrogen and oxygen sites) and that the film is electrically conducting (redox reaction of the absorbed molecules centered @ 0.200 V_{SCE}).

(2.2) Conclusion

TFQ and TFHQ do not polymerize but instead they are adsorbed on a Pt surface. The adsorption is an irreversible process and the clean Pt surface can not regenerate from potential cycling method. Even though the adsorbed layer block the hydrogen and oxygen binding sites on Pt surface, it is electrically conductive. TFQ and TFHQ or other compounds with reactive Q/H₂Q functional group might be useful to us in our future work by adding them to the polymer chain to increase conductivity.

(3) Electropolymerization of 2,6-Difluorophenol A study of the electropolymerization of 2,6-Difluorophenol [DFP] is in progress. From the preliminary results, DFP polymerized on Pt electrode under similar conditions as DMP except that the polymerization occurred at higher anodic potential (figure 29) A rainbow colored polymer film was observed on the Pt surface. The film is stable after 12 minutes potential scanning in 0.05 M sulfuric acid (Figure 30). The IR spectrum of the film is shown in figure 30, the analysis of the

spectra is summarized in the table below:

wavenumber (cm^{-1})	mode	functional group
2950, 2835	C-H stretching	methyl
2363, 2345	C-O stretching	carbon dioxide
1620, 1490	C=C bending	aromatic
1380	C-H bending	methyl
1300, 1093	C-O stretching	ether
1250, 1027	C-F stretching	aryl fluoride
838, 785	C-H oop bending	aromatic

FIGURE 28. CYCLIC VOLTAMMOGRAMS OF Pt AND TFHQ MODIFIED Pt

Pt disk (6.35 mm. O.D.) in 0.05 M H_2SO_4 , scanrate 500 mV/s
potential range -0.225 to $1.250 V_{SCE}$

A:----- clean Pt, contact angle = 60°

B:—— TFHQ modified Pt, the CV was stable through 30
minutes continuous potential cycling.

FIGURE 29. VOLTAMMOGRAM OF 2,6-DIFLUOROPHENOL

solution is 0.1 M DFP/0.2 M NaOH/MeOH
 working electrode is Pt disk (6.35 mm. O.D.)
 potential range -0.2 to 1.6 V_{SCE/MeOH}

FIGURE 30. CYCLIC VOLTAMMOGRAMS OF PPO OF DFP IN 0.05 M H_2SO_4

FIGURE 31. IR SPECTRA OF 2,6-DIFLUOROPHENOL.

PPO film from electropolymerization of DFP on Pt
by potential scanning in 0.1 M DFP/0.2 M NaOH/MeOH

CHAPTER 5. FINAL CONCLUSION

The initial goal of this research was to find an electropolymerization method to generate a hydrophobic (and conducting) polymer on pyrolytic graphite. The polymer must be stable in aqueous solutions such as 0.05 M sulfuric acid. Fluorinated compounds were selected due to their greater hydrophobic nature. The following compounds with high probability for polymerization were selected: 2,3,4,5,6-pentafluorostyrene [PFS], tetrafluoro-1,4-benzoquinone [TFQ], tetrafluorohydroquinone [TFHQ], and 2,6-difluorophenol [DFP]. I have found that the oxidation potential of these compounds are high due to the fluorine moiety. Some of these compounds oxidize beyond the workable potential for pyrolytic graphite. As a result most of this work was done using Pt as the substrate. PFS polymerized but the polymer did not remain attached to the surface. Even though TFQ and TFHQ did not polymerize, but were adsorbed onto the surface, these adsorbed molecules did exhibit reversible surface electron transfer which may be useful for future research. Perhaps they may be immobilized within the polymer film and used to generate or increase the polymer redox character. Most of my work was done on 2,6-Dimethylphenol [DMP] and the results are satisfying. In the study with DMP I was able to generate a polymer film electrochemically. The resultant polymer is hydrophobic and stable in 0.05 M sulfuric acid solution. The IR data is positive and agrees well when compared to the standard spectrum. It is also possible to electropolymerize DFP.

Most of the problems encountered in the course of this research were due to the high oxidation potentials of fluorinated compounds which lies beyond

workable potential of pyrolytic graphite. The high electronegativity of fluorine is the cause of this problem. I was able to obtain a hydrophobic polymer from DMP which does not contain any fluorine moiety. This suggests that a new line of research on compounds containing hydrophobic groups with low electronegativity should be considered.

The best electropolymerization method and conditions are still to be established. A detailed study of the polymer properties such as film thickness, conductivity and its stability in sulfuric acid solutions needs to be fulfilled. The polymerization model and mechanism need to be established. The work will not be complete until a polymerization is performed on pyrolytic graphite.

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APPENDIX 1

Calculation of polymer film thickness

From a chronoamperogram (i-t curve), the total charge can be calculated from an integration of area under the curve.

$$Q_{\text{total}} = \int_0^t i dt \quad (1)$$

From the Nernst Equation

$$i = \frac{nFdN}{dt} \quad (2)$$

$$\int i dt = \frac{\int dN}{nF} \quad (3)$$

$$\frac{Q_{\text{total}}}{nF} = N_{\text{total}} \quad (4)$$

where Q_{total} = integration area of the i-t curve, (C)
 n = number of electrons per redox reaction
 F = Faraday
 N_{total} = number of moles of monomer

The following calculation refers to the chromatogram shows at the end of this Appendix and the mechanism presents in figure 22.

Charge (Q) = (integration area) x (time scale) x (current scale)
 let Q_m = charge used by monomer
 Q_b = charge used by blank solution

$$\begin{aligned} Q_m &= 252.24 \text{ cm}^2 \times 2.5 \text{ s/cm}^2 \times 25 \text{ mAs/cm}^2 \\ &= 1.58 \times 10^2 \text{ C} \end{aligned}$$

$$\begin{aligned} Q_b &= 59.05 \text{ cm}^2 \times 2.5 \text{ s/cm}^2 \times 10 \text{ mAs/cm}^2 \\ &= 1.43 \times 10^3 \text{ C} \end{aligned}$$

$$\begin{aligned} Q_{\text{total}} &= Q_m - Q_b \\ &= 1.58 \times 10^2 - 1.48 \times 10^3 \\ &= 1.43 \times 10^2 \text{ C} \end{aligned}$$

The number of monomer molecules can be calculated from equation (4)

$$\begin{aligned} \# \text{ of molecules} &= \frac{1.43 \times 10^2 \text{ C}}{96500 \text{ C/mol}} \\ &= 1.48 \times 10^7 \text{ mole} \times 6.02 \times 10^{23} \text{ molecules/mole} \\ &= 8.93 \times 10^{16} \text{ molecules} \end{aligned}$$

Top view

Side view

$$r = r_{\text{C}} \approx 1.4 \text{ \AA}$$

$$\begin{aligned} \text{Area of platinum surface} &= \pi r^2 \\ &= \pi (0.3175 \text{ cm})^2 \\ &= 0.32 \text{ cm}^2 \times (10^8 \text{ \AA/cm})^2 \\ &= 3.2 \times 10^{15} \text{ \AA}^2 \end{aligned}$$

$$\begin{aligned} \text{cross section of a polymer bundle} &= \pi r^2 \\ &= \pi (3 \times 1.4 \text{ \AA})^2 \\ &= 55.4 \text{ \AA}^2 \end{aligned}$$

$$\begin{aligned} \# \text{ of occupied sites} &= \frac{3.2 \times 10^{15} \text{ \AA}^2}{55.4 \text{ \AA}^2} \\ &= 5.78 \times 10^{13} \text{ sites} \end{aligned}$$

$$\begin{aligned} \# \text{ of monomer per chain} &= \frac{2.93 \times 10^{16} \text{ molecules}}{5.78 \times 10^{13} \text{ sites}} \\ &\approx 1550 \text{ monomer/chain} \end{aligned}$$

If there were 8 polymer chains per bundle, there will be approximately 200 molecules of monomer per chain. If the polymer has the structure as assumed for this calculation, the chain length is about 280 Å. Or the polymer film has a thickness of 280 Å when assumed complete surface coverage.

Appendix 2

Wetting and Contact Angle

A drop of liquid on a clean solid surface may spread out into a thin film or may form a drop of various shapes. Film forming liquids have a high affinity for the solid and the solid-liquid contact is maximized by the spreading of the film while liquids with weaker affinity will only collect themselves into beads. This affinity is referred to as wettability.

If the drop is small enough so that the influence of gravity can be neglected, the balance of forces can be derived at each interface.

There are three interfaces among the solid, liquid and gas phases. Three interfacial tensions: γ_1 , γ_2 , γ_3 as shown in the above figure are interfacial tensions between solid-gas, liquid-gas, and liquid-solid respectively. θ is called the contact angle.

The interfacial tensions can be taken as forces between the solid-liquid interfaces. The force balance at point O along the horizontal contact line is

$$\gamma_1 = \gamma_{12} + \gamma_2 \cos \theta \quad (1)$$

$$\text{or} \quad \gamma_1 - \gamma_{12} = \gamma_2 \cos \theta \quad (2)$$

equation (2) is known as Young's equation. This equation is valid only when adsorption does not exist at the interface.

Contact Angle (θ) (degree)	$\cos(\theta)$	Physical description
0	1	completely wetting
$0 < \theta < 90$	$0 < \cos\theta < 1$	
90	0	
$90 < \theta < 180$	$0 > \cos\theta > -1$	
180	-1	completely nonwetting

END

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