

DOCTORAL THESIS

Electrochemical pretreatment of carbon electrodes and the electroanalytical applications

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**Electrochemical Pretreatment of Carbon Electrodes
and the Electroanalytical Applications**

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A thesis submitted in partial fulfillment of the requirements

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Abstract

Electrochemical pretreatment of glassy carbon electrode is usually conducted by potentiostatic polarization at oxidizing potentials or by potential cycling in a wide potential range. Surface adsorption properties of glassy carbon can be improved by electrochemical pretreatment. Glassy carbon electrodes obtained by electrochemical pretreatment in acidic solution have found their applications in electroanalysis. We have reported in Chapter 2, possibly the first work on the electroanalytical applications of electrochemically activated glassy carbon electrodes. Chapter 2 and 3 illustrate respectively the preconcentration/electroanalysis of copper and lead species at the activated electrodes. The anodic peak current resulted from the adsorbed species usually gives linear responses to the cation concentration at micromolar level. High sensitivity and good linear correlation for the determination can be achieved. On the other hand, rapid preconcentration/determination of uric acid at activated glassy carbon is reported in Chapter 4. Uric acid can be analyzed with excellent sensitivity and selectivity. The uric acid in urine samples can be determined satisfactorily. Additionally, selective preconcentration/electroanalysis of vitamin B₂ in multi-vitamin tablets has been demonstrated in Chapter 5. The proposed method seems to offer a much better dynamic range for the determination of vitamin B₂ when compared with the AOAC standard method.

The surface structures of electrochemically activated glassy carbon have been examined by scanning tunneling microscopy in Chapter 6. Experimental results demonstrate that there are two different types of electrode surface sites, corresponding to the bundles and bundle edges of the fibrous microcrystallinities. Electrochemical activation also results in the formation of new void spaces of

different sizes. The void volume resulted from cyclic potential activation is usually smaller than that obtained by constant potential activation. The electrochemical behaviors of the activated electrode are related to both the new void structures and the size of the electroactive species employed.

In Chapter 7, the adsorption behaviors of metal cations and a number of quinone derivatives have been investigated in detail. Different adsorbents would preferentially adsorb to two different types of surface adsorption sites. The adsorption characteristics of these adsorption sites resemble those of the basal and edge planes of graphite electrodes. Adsorption behaviors show some dependence on the void structures. Inside the larger void space, the adsorption appears at the basal plane surfaces through hydrophobic interactions. Smaller voids and oxygen-containing surface functional groups show adsorption characteristics similar to the edge plane structures. Experimental results suggest that electrostatic interactions or hydrogen bonding are also involved, in addition to hydrophobic interactions. The adsorbents were located at different depth of the void spaces, dependent on their respective sizes.

Chapter 8 reports the kinetic studies on the electron transfer reaction occurring at the activated electrodes. Experimental results suggest that homogeneous electron transfer between the activated electrode and the adsorbents with higher hydrophobic characters proceeds at a faster rate. On the other hand, electrochemical activation usually results in improvements in the heterogeneous electron transfer. Hydrophobic electron transfer sites might be related to carbon moieties including microcrystalline defects and oxidized carbon moieties, while hydrophilic electron transfer sites should involve the oxygen-containing surface functionalities.

Table of Contents

Declaration	i
Abstract	ii
Acknowledgements	iv
Table of Contents	v
List of Tables	xi
List of Figures	xiii
List of Symbols and Abbreviations	xxiv

Part I Introduction**Chapter 1 Introduction**

1.1 The sp^2 -hybridized carbon	1
1.2 Glassy carbon	5
1.3 Electrochemically activated glassy carbon	7
1.3.1 Surface structures	7
1.3.2 Adsorption properties	8
1.3.3 Electron transfer kinetics	9
1.4 Objectives and experimental methods	10
1.5 References	13

***Part II Electroanalytical applications of electrochemically activated
glassy carbon electrodes*****Chapter 2 Determination of copper species at electrochemically activated glassy
carbon electrode**

2.1 Introduction	20
------------------	----

2.2 Experimental	22
2.3 Results and Discussion	23
2.3.1 Activation of glassy carbon surfaces	23
2.3.2 Preconcentration of copper species at activated glassy carbon electrodes	27
2.3.3 Mechanism of copper incorporation at PGCE	31
2.3.4 Effects of pH	33
2.3.5 Concentration dependence of electroanalytical response	38
2.3.6 Interference studies	42
2.4 Conclusions	43
2.6 References	44
Chapter 3 Determination of lead species at electrochemically activated glassy carbon electrode	
3.1 Introduction	46
3.2 Experimental	47
3.3 Results and discussion	49
3.3.1 Uptake of Pb^{2+} at electrochemically activated glassy carbon electrode	49
3.3.2 Effects of pH	51
3.3.3 Effects of preconcentration time	54
3.3.4 Reproducibility and Reusability	55
3.3.5 Calibration	58
3.3.6 Effects of other metal cations on desorption of lead species at PGCE	58
3.4 Conclusions	61
3.5 References	62
Chapter 4 Determination of uric acid at electrochemically activated glassy	

carbon electrode	
4.1 Introduction	64
4.2 Experimental	65
4.2.1 Reagents	65
4.2.2 Apparatus	65
4.2.3 Procedures	66
4.3 Results and Discussion	66
4.3.1 Uptake of uric acid at activation of glassy carbon electrode	66
4.3.2 Effects of pH on the uptake of uric acid	69
4.3.3 Determination of uric acid by square-wave voltammetry	71
4.3.4 Preconcentration	71
4.3.5 Regeneration of activated electrode and reproducibility	75
4.3.6 Calibration	77
4.3.7 Interference studies	77
4.3.8 Determination of uric acid in real sample	80
4.4 Conclusions	81
4.5 References	82
 Chapter 5 Selective determination of vitamin B₂ in multivitamin tablets at electrochemical activation glassy carbon electrode	
5.1 Introduction	84
5.2 Experimental	86
5.3 Results and Discussion	88
5.3.1 Adsorption of vitamin B ₂ on activated glassy carbon electrode	88
5.3.2 Effects of activation methods	92

5.3.3 Effects of preconcentration time	95
5.3.4 Effect of pH	97
5.3.5 Calibration curve	99
5.3.6 Interferences	101
5.3.7 Determination of Vitamin B ₂ in Multivitamin Tablets	103
5.4 Conclusions	104
5.5 References	105
 <i>Part III Structures and properties of electrochemically activated glassy carbon electrodes</i>	
 Chapter 6 Structural studies on electrochemically activated glassy carbon electrode	
6.1 Introduction	107
6.2 Experimental	111
6.3 Results and Discussion	112
6.3.1 Scanning tunneling microscopic (STM) studies	112
6.3.2 Voltammetric response of activated glassy carbon obtained by different activation methods	121
6.3.2.1 Redox reaction of copper species	121
6.3.2.2 Effects of chloride anions on the redox reactions of copper species	123
6.3.2.3 Catalytic oxidization of NADH at 3,4-DHB incorporated-PGCE	128
6.4. Conclusions	133
6.5 References	135
 Chapter 7 Study on the adsorption mechanism at electrochemically activated	

glassy carbon electrode	
7.1 Introduction	139
7.2 Experimental	142
7.2.1 Reagents and Apparatus	142
7.2.2 Procedures	142
7.2.2.1 Electrode pretreatment	142
7.2.2.2 Adsorption process	143
7.2.2.3 Desorption process	143
7.2.2.4 X-ray photoelectron spectroscopy (XPS)	144
7.3 Results and Discussion	144
7.3.1 Adsorption behaviors	144
7.3.2 XPS studies	147
7.3.2.1 Organic adsorbents	147
7.3.2.2 Inorganic metal cations	149
7.3.3 Adsorption of organic adsorbents	154
7.3.4 The desorption process in different solvents	161
7.3.5 Effects of surface active species on the adsorption/desorption process	165
7.3.5.1 Effects of surface active species on the desorption	165
7.3.5.2 Interference of surface active species on the uptake	167
7.3.6 Adsorption of metal cations at the activated electrode	172
7.3.6.1 Effects of adsorbed quinone species	172
7.3.6.2 Effects of surfactants	176
7.3.7 Effects of void space	181
7.3.8 Other factors	185

7.3.8.1 Effects of pH on adsorption	185
7.3.8.2 Effects of controlled potential on adsorption	190
7.4 Conclusions	195
7.5 References	197
Chapter 8 Electron transfer kinetics at electrochemically activated glassy carbon electrode	
8.1 Introduction	201
8.2 Experimental	204
8.3 Results and discussion	205
8.3.1 Homogeneous electron transfer at the activated electrode	205
8.3.1.1 Electrochemical behaviors of adsorbed quinone derivatives	205
8.3.1.2 Effects of scan rate on the redox process of the adsorbents	211
8.3.1.3 Effects of adsorbent coverage on the homogeneous electron transfer rate	215
8.3.2 Heterogeneous electron transfer at the activated electrode	220
8.4 Conclusions	235
8.5 References	236
<i>Part IV Overall conclusions and future work</i>	
Chapter 9 Overall conclusions and future work	
9.1 Overall conclusions	240
9.2 Future work	241
9.3 References	243
List of Publications	244
Curriculum Vitae	245
