

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

The Electrochemical Deposition Of Mercury On Glassy Carbon Electrodes

A thesis in partial fulfilment of the
requirements for the degree of
Masters of Science
in
Chemistry
At Massey University, Palmerston North
New Zealand

Giovanna Lucia Moretto
July 2000

ABSTRACT

The mechanism for the reduction of Hg^{2+} on glassy carbon in aqueous acetate and nitrate electrolyte was studied. This deposition process is of interest due to the wide electroanalytical applications of mercury thin film electrodes. It was found in the early stages of this work that even though the use of these electrodes is wide spread, there has been little investigation into how the deposition stage occurs.

The electrochemical techniques used were cyclic voltammetry and chronoamperometry. A range of experiments were undertaken including concentration dependence, rotation dependence, scan rate dependence, electrochemical-cleaning, and the dependence of the length of time left at open potential. The acetate experiments were carried out at a constant pH of 5.0 and all experiments were carried out at a constant temperature of 20°C.

Significant dependence was established in the cyclic voltammetry work for all the experimental conditions. In acetate electrolyte the development of peaks C1 and C2 were seen after cycling of the electrode without mechanical-cleaning. A shift in the reduction potential from a mechanically-cleaned electrode cycle to the next cycle without intervening cleaning was also observed. Two new anodic peaks, A2 and A3, were also seen in acetate electrolyte. At high concentrations cathodic current spikes were observed at the extreme cathodic limits of the voltammograms.

The response that was observed in nitrate electrolyte was dissimilar to that in acetate. The shift in reduction potential, current spikes, peaks C1, C2, A2, and A3, were never observed for the deposition of Hg^{2+} in nitrate electrolyte.

The chronoamperometry work on microelectrodes led to a number of new phenomena. Transients that were obtained from these experiments lead to the development of a quantitative nucleation and growth model for the growth of hemispherical mercury droplets. At the onset of reduction the transients follow a t^2 function which is in accordance with surface area dependence growth of the droplet. However, after a short length of time, the transients start to follow a function of $t^{1/2}$, which is suggestive of perimeter growth control. This is assumed to be due to the formation of a semi-passivating $\text{Hg}_2(\text{OAc})_2$ film over the mercury droplet where Hg_2^{2+} forms as a result of a disproportionation reaction.

A qualitative model was also developed to account for the observations of both the microelectrode results and most of the features seen in the cyclic voltammetry work.

ACKNOWLEDGEMENTS

First, I guess that I would like to thank my chief supervisor, Dr. Simon Hall, without whom I would have never have able to finish this thesis. Thank you Simon. For all your talks (of which a lot of the time you were saying the same thing over and over just in a different way, and I still didn't get it), your guidance and support, but most of all for just being you, it didn't matter when it was, you always found time to help.

Thanks must also go to my second supervisor, Dr. Simon Brown for his encouragement, guidance, and for always having time to see me.

I would like to thank the Massey University Research Projects and Funding Committee for the Stipend and consumables money provided throughout my MSc.

I would also like to thank the Institute of Fundamental Sciences Graduate Research Fund for the support they gave me to get to Australia to carry out some research and also to all the staff in IFS for the help each of them has given me over the years.

Thanks to all the 'kids' at Massey that have made the last few years great, Massey wasn't just a place to come and work, it was somewhere to see your friends to, and now it isn't going to be the same, I will miss you all. Special thanks must go to a few people though, Jo, Paul, Ant, Emad, Michael, Gav, and Steven.

To all my friends in Welly who have given me somewhere to run away to when Palmy got to much, but mostly Claire and Del.

To Adrian for being a good friend over the years and for making chemistry fun and exciting, without you there is a good chance that I would have a BCA and would be counting beans somewhere in an office.

The biggest thanks to my friends has to go to Justin. You the man! We have been through thick and thin together over the last few years, and you have made doing this thing at Massey great. It isn't going to be the same without you kid. I'm going to miss you beating me up every second day and just being there. What ever you end up doing you will do well, and wherever you go you better stay in touch.

Gino, thanks for always being there and being the best big brother someone would have.

Lastly, but by no means by least, I would like to thank my parents. Mum, Dad, thank you so much. Without you two I would never have been able to do everything that I have done

over the last 25 years. The both of you have always believed in me, even when I didn't, and have just always been there for me. No one could ask for two better parents than the ones that I have. I love you both.

TABLE OF CONTENTS

Abstract	i	
Acknowledgements	ii	
Table of Contents	v	
List of Figures	ix	
List of Tables	xiii	
List of Symbols	xiv	
List of Abbreviations	xvii	
CHAPTER 1	Introduction	1-13
1.1	Introduction	1
1.2	Overview of polarography	1
1.3	Stripping voltammetry	2
1.4	Mercury based electrodes	3
1.5	Glassy Carbon	5
1.6	Reasons for this work	7
1.7	Organization of this thesis	13
CHAPTER 2	Experimental Methods	14-26
2.1	Introduction	14
2.2	Instrumentation	14
	2.2.1 <i>Potentiostatic Equipment</i>	14
2.3	Electrode Systems	14
	2.3.1 <i>Working electrodes</i>	15
	2.3.1.1 Rotating Disc Electrode	15
	2.3.1.2 Microelectrodes	15
	2.3.2 <i>Counter electrode</i>	17
	2.3.3 <i>Reference electrode</i>	17
2.4	Working electrode pretreatment	17
	2.4.1 <i>Mechanical pretreatment</i>	17

2.4.2	<i>Electrochemical pretreatment</i>	17
2.5	Mass transport and the Levich Equation	17
2.5.1	<i>Turbulent and laminar flow</i>	20
2.5.2	<i>Calibration of Rotation Rate</i>	22
2.6	Reagents	23
2.6.1	<i>Mercuric Nitrate</i>	23
2.6.2	<i>Mercuric Acetate</i>	23
2.7	Determination of the pH of Mercuric Acetate solutions	23
2.8	Deoxygenation of electrolyte	26
CHAPTER 3		
Cyclic voltammetry studies		27-69
3.1	Introduction	27
3.2	Cyclic Voltammetry	27
3.3	Features of mercury deposition voltammograms in acetate media	28
3.3.1	<i>Peaks C1 and C2</i>	28
3.3.2	<i>Reduction overpotential</i>	28
3.3.3	<i>Peak A2</i>	29
3.3.4	<i>Current spikes</i>	29
3.4	Coulometry	29
3.5	Concentration Dependence	36
3.6	Scan Rate Dependence	37
3.7	Rotation Rate Dependence	50
3.8	Microelectrode studies	51
3.9	C1 and C2 after open circuit conditions	57
3.10	Cleaning potentials/ cleaning times	61
3.11	Electrochemical cleaning	63
3.12	Nitrate	63
CHAPTER 4		
Chronoamperometry Studies		70-93
4.1	Introduction	70
4.2	Chronoamperometry	70

4.3	RDE experimental observations	71
	4.3.1 <i>Concentration and potential dependence</i>	71
	4.3.2 <i>Rotation Dependence</i>	73
4.4	CA microelectrode work	74
	4.4.1 <i>Mechanically-cleaned MEs</i>	74
	4.4.2 <i>ME potential dependence</i>	81
	4.4.3 <i>Electrochemically-cleaned ME</i>	81
4.5	CA experiments in nitrate compared to those in acetate	88
CHAPTER 5 Discussion and Conclusions		94-137
5.1	Introduction	94
5.2	Observations from cyclic voltammetry and chronoamperometry	94
	5.2.1 <i>C1 and C2 peaks</i>	94
	5.2.2 <i>Current spikes</i>	95
	5.2.3 <i>Overpotential shift</i>	95
	5.2.4 <i>A1</i>	96
	5.2.5 <i>A2 and A3</i>	96
	5.2.6 <i>Steady state</i>	97
	5.2.7 <i>CA observations</i>	97
5.3	Scan rate	97
5.4	Levich Study	98
5.5	Koutecky-Levich Study	98
5.6	Koutecky-Levich study results	101
5.7	Levich Study	106
5.8	Coulometry	106
5.9	Mercury (I) formation	114
5.10	Microelectrodes	115
5.11	Electrochemical cleaning/ Overpotential shift	128
5.12	Mechanisms	129
	5.12.1 <i>Model I</i>	129
	5.12.1 <i>Model II</i>	129

5.13	Conclusions	133
5.14	Future work	136
REFERENCES		138-144

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1 Schematic structural model for GC.	8
2.1 The flow patterns created by a RDE.	19
3.1 A voltammogram displaying C1, C2, A1, and the steady state current. Direction of the forward and reverse sweeps also indicated.	30
3.2 Two voltammograms displaying E_{red} for a mechanically-cleaned and a cycled electrode.	31
3.3 A voltammogram displaying A2.	32
3.4 A voltammogram displaying cathodic current spikes.	33
3.5 A voltammogram where C1 and C2 have formed.	34
3.6 A coulometric plot of Figure 3.5.	35
3.7 Concentration dependence experiments with 2.0, 5.0, and 10.0 mM $[Hg^{2+}]$.	39
3.8 Concentration dependence experiments with 0.5, 1.0, and 2.0 mM $[Hg^{2+}]$.	40
3.9 Scan rate dependence experiments for $[Hg^{2+}] = 10.0$ mM.	43
3.10 Scan rate dependence experiments for $[Hg^{2+}] = 5.0$ mM.	44
3.11 Scan rate dependence experiments for $[Hg^{2+}] = 2.0$ mM.	45
3.12 Scan rate dependence experiments for $[Hg^{2+}] = 1.0$ mM.	46
3.13 An expanded view of the region where A2 is found in Figure 3.12.	47
3.14 Scan rate dependence experiments for $[Hg^{2+}] = 0.5$ mM.	48
3.15 An expanded view of the region where A2 is found in Figure 3.14.	49
3.16 Rotation dependence experiments for $[Hg^{2+}] = 10.0$ mM.	52
3.17 Rotation dependence experiments for $[Hg^{2+}] = 5.0$ mM.	53
3.18 Rotation dependence experiments for $[Hg^{2+}] = 2.0$ mM.	54

3.19	Rotation dependence experiments for $[\text{Hg}^{2+}] = 1.0 \text{ mM}$.	55
3.20	Rotation dependence experiments for $[\text{Hg}^{2+}] = 0.5 \text{ mM}$.	56
3.21	The difference between mechanically-cleaning, electrochemically-cleaning, and not cleaning, a ME.	58
3.22	Scan rate dependence experiments for $[\text{Hg}^{2+}] = 20.0 \text{ mM}$ using a ME.	59
3.23	Increasing time left at open potential experiment.	60
3.24	Electrochemical-cleaning experiment.	64
3.25	The first and second voltammograms recorded after mechanical-cleaning in nitrate electrolyte.	66
3.26	The first and second voltammograms recorded after mechanical-cleaning in a acetate electrolyte.	67
3.27	Scan rate dependence experiments in nitrate for $[\text{Hg}^{2+}] = 5.0 \text{ mM}$.	68
3.28	Rotation rate dependence experiments in nitrate for $[\text{Hg}^{2+}] = 5.0 \text{ mM}$.	69
4.1	A general CA transient displaying a steady state current, a falling transient, and a peak which develops.	72
4.2	A series of transients with decreasing E_2 potentials. $[\text{Hg}^{2+}] = 2.0 \text{ mM}$.	75
4.3	A series of 4 transients with decreasing E_2 potentials. $[\text{Hg}^{2+}] = 5.0 \text{ mM}$.	76
4.4	A series of transients of varying rotation rate. $[\text{Hg}^{2+}] = 10.0 \text{ mM}$, $E_2 = +200 \text{ mV}$.	77
4.5	A series of transients of varying rotation rate. $[\text{Hg}^{2+}] = 10.0 \text{ mM}$, $E_2 = -50 \text{ mV}$.	78
4.6	A series of transients of varying rotation rate. $[\text{Hg}^{2+}] = 5.0 \text{ mM}$, $E_2 = -250 \text{ mV}$.	79
4.7	A series of single smooth ME growth transients. $[\text{Hg}^{2+}] = 20.0 \text{ mM}$ $E_2 = +100 \text{ mV}$.	82

4.8	A selection of ME growth transients exhibiting more than one single smooth growth transient. $[\text{Hg}^{2+}] = 20.0 \text{ mM}$, $E_2 = +100 \text{ mV}$.	83
4.9	Current decreases for ME growth transients. $[\text{Hg}^{2+}] = 20.0 \text{ mM}$, $E_2 = +100 \text{ mV}$.	84
4.10	4.10 Current decreases for ME growth transients. $[\text{Hg}^{2+}] = 20.0 \text{ mM}$, $E_2 = +100 \text{ mV}$.	85
4.11	A selection of ME growth transients with E_2 potentials more cathodic than 0 mV. $[\text{Hg}^{2+}] = 20.0 \text{ mM}$.	86
4.12	A selection of ME growth transients which have undergone electrochemical-cleaning. $[\text{Hg}^{2+}] = 20.0 \text{ mM}$, $E_2 = +100 \text{ mV}$.	87
4.13	A series of transients in nitrate electrolyte with varying E_2 potentials. $[\text{Hg}^{2+}] = 2.0 \text{ mM}$.	90
4.14	A series of 4 transients at fixed concentration comparing the response obtained in acetate and nitrate over 5000 msec.	91
4.15	A comparison between acetate and nitrate transients. $[\text{Hg}^{2+}] = 5.0 \text{ mM}$, $E_2 = +300 \text{ mV}$.	92
4.16	A comparison between acetate and nitrate transients. $[\text{Hg}^{2+}] = 5.0 \text{ mM}$, $E_2 = +100 \text{ mV}$.	93
5.1	A plot of A1 peak height as a function of square root of the scan rate.	99
5.2	Diffusion coefficients for Hg^{2+} as a function of $[\text{Hg}^{2+}]_{\text{bulk}}$.	104
5.3	Koutecky-Levich plots for a range of $[\text{Hg}^{2+}]_{\text{bulk}}$ in acetate.	107
5.4	Koutecky-Levich plots for a range of $[\text{Hg}^{2+}]_{\text{bulk}}$ in nitrate.	108
5.5	Levich plots for a range of $[\text{Hg}^{2+}]_{\text{bulk}}$ in acetate.	109
5.6	Calculated ME growth transients.	120
5.7	ME current as a function of hemispherical radius.	121

5.8	Schematic diagram of three growth possibilities on MEs.	123
5.9	ME current as a function of time.	124
5.10	Early stages of the ME current as a function of radius.	125
5.11	Schematic diagram of a second nucleus joining a larger nucleus.	127
5.12	Schematic diagram of Model I.	130
5.13	Schematic diagram of Model II.	134
5.14	Schematic voltammogram with features of Model II.	135

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1.1 Properties of glassy carbon.	6
1.2 Summary of mercury deposition conditions using non-modified GC electrodes.	10
1.3 Summary of mercury deposition conditions using modified GC electrodes	12
2.1 Rotation rate calibration for the RDE.	24
2.2 The composition of standard buffer solutions over the pH range of 4.0 to 6.0.	25
3.1 E_{red} as a function of $[\text{Hg}^{2+}]$.	38
3.2 Total cleaning times as a function of cleaning potentials.	62
3.3 Total times for electrochemical-cleaning at +1300 mV, as a function of $[\text{Hg}^{2+}]$.	62
5.1 Analysis of the acetate Koutecky-Levich plot listing the slope and the error in the slope, plus the intercept and the error in the intercept, as a function of $[\text{Hg}^{2+}]$.	102
5.2 Calculated D_{Hg} plus the positive and negative errors as a function of $[\text{Hg}^{2+}]$.	103
5.3 Analysis of the nitrate Koutecky-Levich plot listing the slope and error in the slope, together with the calculated D_{Hg} plus the positive and negative errors, as a function of $[\text{Hg}^{2+}]$.	105
5.4 Q_A/Q_C values for varying $[\text{Hg}^{2+}]$ as a function of rotation rate.	111
5.5 Q_A/Q_C values for varying $[\text{Hg}^{2+}]$ as a function of scan rate.	112
5.6 A comparison between nitrate and acetate for Q_A/Q_C , as a function of rotation rate.	113
5.7 Listings of the x and $E_{\text{red,nuc}}$ value for a series of ME growth transients.	119

LIST OF SYMBOLS

<u>Symbol</u>		<u>Unit</u>
A	area	cm^2
A_s	area of a sphere	cm^2
A_h	area of a hemisphere	cm^2
A_1	first anodic peak	
A_2	second anodic peak	
A_3	third anodic peak	
c_b	bulk concentration	mM
c_s	surface concentration	mM
C_1	first cathodic peak	
C_2	second cathodic peak	
D	diffusion coefficient	m^2s^{-1}
E	potential	mV
E_{red}	reduction potential	mV
E_{ox}	oxidation potential	mV
E_1	initial potential	mV
E_2	final potential	mV
f	rotation rate	rps
F	Faraday constant	C mol^{-1}
h	height	cm
$[\text{Hg}^{2+}]_{\text{bulk}}$	bulk mercury concentration	mM
$[\text{Hg}^{2+}]$	surface mercury concentration	mM
i	current density	mA cm^{-2}

i_{A1}	A1 peak current	mA cm^{-2}
i_d	diffusion current	mA cm^{-2}
i_L	limiting current	mA cm^{-2}
i_k	kinetic current	mA cm^{-2}
i_{ss}	steady state current	mA cm^{-2}
I	current	mA
j	flux	$\text{m}^{-2}\text{s}^{-1}$
k	rate constant	m s^{-1}
k_f	heterogeneous electron transfer rate constant	m s^{-1}
$k_{\text{red,nuc}}$	rate constant for nucleus growth	m s^{-1}
l	length of electrode	cm
M	concentration	mol L^{-1}
M	molecular weight	g mol^{-1}
n	number of electrons	
n_{Hg}	moles of mercury	mol
Q	charge	
Q_A	total anodic charge	
Q_{ra}	accumulated non-faradic charge	
Q_{oc}	charge where oxidation occurs	
r	radius of electrode	cm
r_s	radius of a sphere	cm
r_h	radius of a hemisphere	cm
Re	Reynolds number	
t	time	sec

t_0	time nucleus first forms	sec
x	distance	cm
x	power function	
ν	kinematic viscosity	$\text{m}^2 \text{s}^{-1}$
ν	scan rate	mV s^{-1}
ν	velocity of the electrode	
V	volume	cm^3
ω	angular velocity	rad s^{-1}
δ	Nernst diffusion layer thickness	cm
ρ	density	g cm^{-3}

LIST OF ABBREVIATIONS

BAS	Bioanalytical Systems Inc.
CA	chronoamperometry
CE	counter electrode
CV	cyclic voltammetry
Hg^0	mercury metal
Hg^{2+}	aqueous mercury
Hg_2^{2+}	mercurous dimer
$\text{Hg}_2(\text{OAc})_2$	mercurous acetate
ME	microelectrode
RDE	rotating disc electrode
RE	reference electrode
rpm	revolutions per minute
SHE	standard hydrogen electrode
WE	working electrode