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The Electrochemical Deposition Of Mercury On Glassy Carbon Electrodes

A thesis in partial fulfilment of the
requirements for the degree of
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in
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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 $Hg_2(OAc)_2$ 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.

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LIST OF SYMBOLS

Symbol		Unit
A	area	cm^2
A_s	area of a sphere	cm^2
A_h	area of a hemisphere	cm^2
A1	first anodic peak	
A2	second anodic peak	
A3	third anodic peak	
c_b	bulk concentration	mM
c_s	surface concentration	mM
C1	first cathodic peak	
C2	second cathodic peak	
D	diffusion coefficient	$\mathrm{m}^2\mathrm{s}^{-1}$
E	potential	mV
E_{red}	reduction potential	mV
E_{ox}	oxidation potential	mV
E_1	initial potential	mV
E_2	finial potential	mV
f	rotation rate	rps
F	Faraday constant	$\mathrm{C\ mol}^{-1}$
h	height	cm
$[\mathrm{Hg}^{2+}]_{\mathrm{bulk}}$	bulk mercury concentration	mM
$[\mathrm{Hg}^{2+}]$	surface mercury concentration	mM
i	current density	$\mathrm{mA\ cm}^{-2}$

i_{Al}	Al 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	$\mathrm{m}^{-2}\mathrm{s}^{-1}$
k	rate constant	m s^{-1}
k_{f}	heterogeneous electron transfer rate constant	m s^{-1}
$k_{\mathrm{red,nuc}}$	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	
v	kinematic viscosity	$m^2\ s^{-1}$
v	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
$Hg_2(OAc)_2$	mercurous acetate
ME	microelectrode
RDE	rotating disc electrode
RE	reference electrode
rpm	revolutions per minute
SHE	standard hydrogen electrode
WE	working electrode