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The Electrochemical Oxidation Of Hydrogen Peroxide On Platinum Electrodes At Phosphate Buffer Solutions

A thesis presented in partial fulfilment of the
requirements for the degree of
Doctor of Philosophy
in
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ABSTRACT

The kinetics and mechanism for the electrochemical oxidation of H_2O_2 on platinum electrodes in phosphate buffers were studied.

A mechanistic model for this reaction was developed that involves binding sites, on the surface of the electrode, that are thought to be based on some form of hydrous platinum oxide, initially identified as $Pt(OH)_2$. Hydrogen peroxide adsorbs onto the binding sites to form the complex $Pt(OH)_2{\cdot}H_2O_2$. The complex then undergoes internal electron transfer to form a reduced platinum site, Pt, with the release of the products water and oxygen. The binding sites regenerate electrochemically to give rise to an amperometric signal together with the release of protons.

Two side reactions were proposed, the first involved a competitive inhibition of the binding sites by oxygen to form the species $Pt(OH)_2{\cdot}O_2$. The second involved a non-competitive inhibition of the complex $Pt(OH)_2{\cdot}H_2O_2$ by protons.

A rate equation was derived to account for all electrode sites involved in the proposed mechanism, with kinetic parameters for electrode reactions, and was validated over a range of bulk $[H_2O_2]$, rotation rates, potentials, temperatures, buffer concentrations and pH.

The kinetic and equilibrium constants for the model were optimised using a SIMPLEX procedure. The equilibrium constants were found to be potential- and temperature-invariant ($K_1 = 6.38 \times 10^{-3}$ m^3 mol^{-1}, $K_4 = 0.128$ m^3 mol^{-1} and $K_5 = 0.053$ m^3 mol^{-1}). The diffusion coefficient for H_2O_2 was found to be in the range $0.55 - 0.66 \times 10^{-9}$ m^2 s^{-1}. These values were lower than those reported in the literature. The rate constants, k_2N and k_3N, were found to vary with potential and temperature, and pseudo-activation energies for k_2 were found to range from 70 – 40 kJ mol^{-1} (dependent on the potential).

The model was further developed to account for the formation of the platinum binding sites (labelled as Pt_{BS}) from precursor sites, Pt_{PS}. A series of experiments employing phosphate buffers with a range of concentration and pH were performed. It was found that steady-state responses for the oxidation of H_2O_2 increased with increasing phosphate concentration. In the absence of phosphate, an alternative binding mechanism was evident.

A maximum response was found at pH 6.8 and decreased markedly at more basic or acidic conditions. This pH-dependence suggested that $H_2PO_4^-$ was the species involved in the formation of the binding sites. The decrease in response at pH > 6.8 being caused by the decrease in $[H_2PO_4^-]$, whilst an inhibition of the precursor site by protons was proposed to account for the depression in electrode response at pH < 6.8.

The influence of chloride upon the kinetics of H_2O_2 oxidation was examined and described qualitatively in terms of the new model. It was found that the rate of oxidation was decreased markedly in the presence of chloride. Two possible inhibition modes for chloride were identified and it was established that a non-competitive inhibition of the precursor sites was likely to be the dominant cause for the chloride inhibition.

The work described in this thesis has not only identified a new and comprehensive mechanism for the oxidation of H_2O_2 at platinum electrodes, but also provides information that may prove useful when designing sensors that rely upon this reaction. In particular the important role of hydrodynamic conditions, buffer composition and concentration are clearly identified.

Publications arising from this work

i) Electrochemical oxidation of hydrogen peroxide at platinum electrodes. An adsorption-controlled mechanism. S. B. Hall, E. A. Khudaish and A. L. Hart, *Electrochim. Acta*, 1998 (43) 579.

ii) Electrochemical oxidation of hydrogen peroxide at platinum electrodes. Effect of potential. S. B. Hall, E. A. Khudaish and A. L. Hart, *Electrochim. Acta*, 1998 (43) 2015.

iii) Electrochemical oxidation of hydrogen peroxide at platinum electrodes. Effect of temperature. S. B. Hall, E. A. Khudaish and A. L. Hart, *Electrochim. Acta*, 1999 (44) 2455.

iv) Electrochemical oxidation of hydrogen peroxide at platinum electrodes. Phosphate buffer dependence. S. B. Hall, E. A. Khudaish and A. L. Hart, *Electrochim. Acta*, 1999 (44) 4573.

v) Electrochemical oxidation of hydrogen peroxide at platinum electrodes. Inhibitory effect by chloride ions. S. B. Hall, E. A. Khudaish and A. L. Hart, *Electrochim. Acta*, submitted for publication.

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LIST OF SYMBOLS

Symbol	Description	Unit
A	electrode geometric area	cm^2
A_o	true surface area of electrode	cm^2
$[A]$	concentration of species A at electrode surface	$mol\ m^{-3}$
$[A]_{bulk}$	concentration of species A in the bulk	$mol\ m^{-3}$
C_{dl}	double-layer capacitance	$\mu F\ cm^{-2}$
c	Concentration	$mol\ L^{-1}$
D	diffusion coefficient	$m^2\ s^{-1}$
E	potential	mV
E°	standard potential	mV
F	Faraday constant	$C\ mol^{-1}$
f	electrode rotation rate	rpm or rps
f	fraction of free surface sites	
ΔH	enthalpy change	$kJ\ mol^{-1}$
i	current density	$mA\ cm^{-2}$
i_L	limiting current	$mA\ cm^{-2}$
i_d	diffusion current	$mA\ cm^{-2}$
i_k	kinetic current	$mA\ cm^{-2}$
I	current	mA
I_{dl}	double-layer charging current	mA
I_f	faradaic resistance current	mA
j	heterogeneous rate	$mol\ m^{-2}\ s^{-1}$
j_{max}	maximum heterogeneous rate	$mol\ m^{-2}\ s^{-1}$
k_2	heterogeneous rate constant	$m\ s^{-1}$
k_3	heterogeneous rate constant	$m\ s^{-1}$
K_1	equilibrium constant	$m^3\ mol^{-1}$
K_4	equilibrium constant	$m^3\ mol^{-1}$
K_5	equilibrium constant	$m^3\ mol^{-1}$

K_M	Michaelis constant	mol m^{-3}
m	molality	mol kg^{-1}
$\overline{m}$	average mass	g
n	number of electrons	
R_f	faradaic resistance	ohm
δ	thickness of diffusion layer	cm
η	absolute viscosity	kg m^{-1} s^{-1}
θ	fructional surface coverage	
ρ	density	kg m^{-3}
τ	efflux time	s
ν	kinematic viscosity	m^2 s^{-1}
ω	angular velocity	rad s^{-1}

LIST OF ABBREVIATIONS

A/D	analog/digital
CA	chronoamperometry
CE	counter electrode
CPE	carbon paste electrode
CV	cyclic voltammetry
FIA	flow-injection analysis
GOD	glucose oxidase
H_2O_2	hydrogen peroxide
ME	microelectrode
$Pt(OH)_2$	hydrous platinum oxide
RDE	rotating disc electrode
RE	reference electrode
rpm	revolutions per minute
SCE	saturated calomel electrode
SCP	staircase potentiometry
SHE	standard hydrogen electrode
WE	working electrode