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Development of a New Cathode for Aqueous Rechargeable Batteries

A thesis presented in partial fulfilment of the
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Abstract

The demand for low-cost energy storage is a current issue. Existing batteries are unable to meet this constraint due to the high raw material prices, in particular the metal content. The risk of fluctuating metal prices and future availability will not meet the market demand and therefore alternative materials need to be considered.

The focus of this project was to develop a non-metal based battery electrode specifically for stationary battery systems. This study presents fundamental concepts required to form a rechargeable electrochemical storage device utilising hydrogen peroxide as the electroactive species. This involved two key aspects: immobilisation of hydrogen peroxide in order to prevent self-discharge and catalytic regeneration of hydrogen peroxide from hydroxide ions. Although the construction of the device was not within the scope of this project, the chemical and electrochemical analysis of potential compounds were evaluated at a molecular level. In particular, the synthesis and molecular behaviour of a urea-based 'binder' that will immobilise hydrogen peroxide, and an oxoammonium 'catalyst' to reform hydrogen peroxide during recharge of the battery. Additionally, the attachment of these compounds to a surface was also evaluated.

Analysis of the interactions between substituted ureas ('binder') and hydrogen peroxide proved challenging. Although these findings suggest that adduct formation is occurring, the methods undertaken were not able to determine the equilibrium constant or strength of binding. They did however give an indication of the quantity of hydrogen peroxide in the synthesised adducts and this methodology can be applied to the range of hydrogen peroxide adducts. Additionally, functionalisation of surfaces with a diazonium-containing substituted urea was achieved and is a viable method for attaching the 'binder' to the electrode substrate material.

The second key step is to incorporate a rechargeable aspect to the battery system. An oxoammonium cation was proposed to act as a 'catalyst' to replenish H_2O_2 during charging. Details regarding the synthetic methodology for synthesis of nitroxide-containing compounds, incorporating diazonium functionalities for attachment to a surface, were obtained. Of particular interest was the amido-TEMPO structure that was electrochemically attached to a carbon surface electrode. Evaluation of its ability to form H_2O_2 was achieved using a bi-potentiostat where a current density of 0.21 A m^{-2} was observed. This novel idea shows promise and demonstrates the ability for the catalyst to replenish H_2O_2 in an aqueous battery system.

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Abbreviations and Symbols

δ	chemical shift
AAS	atomic absorption spectroscopy
AcOH	acetic acid
Ah	ampere hours
aq	aqueous
Ar	aromatic
ATR	attenuated total reflectance
ax	axial
BDMS	bromodimethylsulfonium bromide
BET	Brunauer-Emmett-Theory
Boc	<i>tert</i> -butoxycarbonyl
CA	chronoamperometry
CDCl ₃	deuterated chloroform
CDI	<i>N,N'</i> -carbonyldiimidazole
CE	counter electrode
CEP	concerted electron transfer process
conc.	concentrated
COSY	correlation spectroscopy
CV	cyclic voltammetry
DCC	<i>N,N'</i> -dicyclohexylcarbodiimide
DCE	dichloroethane
dba	dibenzylideneacetone
DFT	density functional theory
DMDQ	2,5-dimethoxy-1,4-benzoquinone
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethyl sulfoxide
DPU	diphenylurea
eq.	equivalent
Eq.	equatorial
ESI	electrospray ionisation
EtOAc	ethyl acetate

EtOH	ethanol
EDG	electron donating group
EDTA	ethylenediaminetetraacetic acid
EPR	electron paramagnetic resonance
eV	electron volts
EWG	electron withdrawing group
Fc	Ferrocene
Fc ⁺	Ferrocenium
Fmoc	fluorenylmethyloxycarbonate
FT	fourier transform
GC	glassy carbon
HOBT	hydroxybenzotriazole
HOMO	highest occupied molecular orbital
HR-MS	high resolution mass spectrometry
IR	infra-red spectroscopy
ITC	isothermal titration calorimetry
kJ	kilojoules
kW	kilowatts
kWh	kilowatt hour
LUMO	lowest unoccupied molecular orbital
(m)	medium
mAh/g	milliampere hours per gram
<i>m</i> CPBA	<i>meta</i> -chloroperoxybenzoic acid
MAS	magic angle spin
ME	microelectrode
MeCN	acetonitrile
MeOH	methanol
mV/s	millivolts per second
MW	megawatts
MS	mass spectrometry
mp	melting point
MP2	Møller-Plesset
<i>m/z</i>	mass/charge

NEt ₃	triethylamine
NMM	N-methylmorpholine
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
PAN	polyacrylonitrile
Ph	phenyl
PG	protecting group
ppm	parts per million
PTC	phase transfer catalyst
RE	reference electrode
RDE	rotating disk electrode
RF	radio frequency
RRDE	rotating ring disk electrode
RT/rt	room temperature
s	solid
(s)	strong
sec	seconds
ss	solid-state
SEM	scanning electron microscope
TBAH	tetrabutylammonium hydroxide
TEMPO	2,2,6,6-tetramethylpiperidin-1-yloxy
TFA	trifluoroacetic acid
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMIO	1,1,3,3-tetramethyl-2,3-dihydroisoindol-2-yloxy
TMS	trimethylsilylacetylene
TLC	thin layer chromatography
UHP	urea hydrogen peroxide
UV-Vis	ultraviolet-visible spectroscopy
US	United States
V	volts
(w)	weak

WE	working electrode
Wh/kg	watt hours per kilogram
Wh/L	watt hours per litre
W/kg	watts per kilogram
W/L	watts per litre

