# TOWARDS THE USE OF SOLID OXIDE FUEL CELLS FOR THE CHEMICAL CONVERSION AND PRODUCTION OF ENERGY FROM BIODIESEL WASTE STREAMS

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF

PHILOSOPHY

MATTHEW JAMES DREWERY

B. ENG (NEWCASTLE), B. SCI (NEWCASTLE)



Department of Chemical Engineering

The University of Newcastle, Australia

March 2018

This research was supported by an Australian Government Research Training Program (RTP) Scholarship

## STATEMENT OF ORIGINALITY

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision.

The thesis contains published scholarly work of which I am a co-author. For such work a written statement, endorsed by the other authors, attesting to my contribution to the joint work has been included.

The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

26<sup>th</sup> March 2018

Matthew Drewery

## STATEMENT OF CONTRIBUTION OF OTHERS

I, the undersigned, hereby attest that Research Higher Degree candidate, Matthew James Drewery, has carried out the experiments, result analysis and writing in all papers included in this thesis.

26<sup>th</sup> March 2018

Prof. Michael Stockenhuber

#### ACKNOWLEDGEMENTS

I first would like to thank my supervisors, Professor Michael Stockenhuber, Professor Eric Kennedy and Professor Bogdan Dlugogorski for their support and advice throughout the course of my studies. I appreciate the insights and challenges they have presented me with. I am especially thankful to Professor Stockenhuber who offered this project and who's unwavering confidence in my abilities contributed significantly to the completion of this thesis.

I am indebted to the University of Newcastle for financial assistance through scholarships awarded and Bloomfield Collieries for assistance with establishing the project.

Thank you to the administrative and technical staff in the Faculty of Engineering at the University of Newcastle Jane Hamson, Matt Laver and Jane Power who provided guidance and advice. I would also like to highlight the significant help provided by Glenn Bryant, who helped with interpretation of results and operation of analytical equipment and Scott Molloy who provided significant assistance with the design, development and operation of electrical equipment. I appreciate my fellow researchers at the University of Newcastle and the contributions they have made to my studies. I extend sincerest thanks to Cameron Keast, Dr Gizelle Sanchez and Dr Jerry Li not only for their friendship and support, but also for extensive conversations, both research and non-research related, and their help in completing experiments, particularly Luke Harvey and Jarrod Friggieri who gave a significant amount of their own time in assisting with the completion of the final experiments for my thesis. I need to thank my family for their continued and unwavering support, my father, Robert, sister Michelle and brother Michael for their love and encouragement. My grandfather, Charlie, who unfortunately was unable to see the finished result but nevertheless encouraged me to pursue this postgraduate degree. While he was unable to impart information relating directly to the field under investigation, he was able to share a wealth of knowledge obtained throughout his life and provide an example as a person I aspire to be. To Christine, my mother, who always put everyone else's needs before her own, particularly mine, thank you for your encouragement and motivation, for pushing me and believing in my abilities.

Finally, my wife Sharni who came with me on this journey and shared the experience of the ups and downs of research. I would not have been able to complete my research without her endless patience and unwavering support. From early morning motivations, dinner deliveries during after-hour lab work and late-night discussions, I could not have gotten through without her.

#### ABSTRACT

Pressure to address the adverse environmental impact and issues of sustainability associated with the use of petroleum has resulted in the commercial development of biodiesel as a diesel replacement. The transesterification of fatty acids, which is used industrially in the production of biodiesel, also produces approximately 10 wt% glycerol as a major bi-product, rendering industrial synthesis of glycerol obsolete and causing its market value to drop significantly. The need to process the waste glycerol and value add to reduce the overall costs associated with biodiesel production has dramatically increased research into the use of glycerol as a platform chemical. There is also the opportunity to utilise solid oxide fuel cells to process this waste to produce energy through highly efficient electrochemical reactions.

This research examines the potential for using glycerol as a fuel, either through direct oxidation or pre-reforming, in a solid oxide fuel cell. In this instance, a cell consisting of a nickel-based anode, 150 µm scandia-doped zirconia electrolyte and LSM cathode sourced from Fuel Cell Materials was used to examine potential feed streams, with an indigenous dynamic load cell used to evaluate performance.

Glycerol has been identified as a potential solid oxide fuel cell feed owing to the presence of hydroxyl functional groups which are hypothesised to inhibit coke formation. Glycerol itself was shown to be a viable fuel feed for direct oxidation in solid oxide fuel cells, with reasonable power densities and minimal deactivation identified. Potential pre-reforming products were also examined as a feed,

V

including synthesis gas, acrolein and allyl alcohol, with the later species used in conjunction with a  $H_2O/D_2O$  isotope study and  $C_3$  mono-ol/diol study to investigate the interactions of OH species.

It was found that hydroxyl species play an important role in anode surface chemistry, facilitating a transfer reaction from the anode to electrolyte for electrochemical oxidation, which through the use of isotopes was highlighted as a potential rate limiting process. It was also shown that oxygenated hydrocarbons are less likely to deactivate the anode via coke formation, with increasing the number of hydroxyl inhibiting carbonisation. The importance of hydroxyl interactions was seen in comparisons to similar molecules acrolein and allyl alcohol, common derivatives of glycerol, where it was found the hydroxyl containing allyl alcohol was directly oxidised on the anode surface while the carbonyl of the acrolein resulted in rapid carbon formation and anode deactivation.

The highly oxygenated nature of glycerol also allows it to be utilised as a solid oxide fuel cell feed, where it was found that when fed into the anode chamber the fuel would oxidise (as opposed to internal reforming) without significant deactivation for over 90 hours operation. Industrial production of glycerol results in a number of potential impurities, in particular salts formed from the homogeneously catalysed transesterification reaction. It was identified that selection of these catalysts based on the salts produced (or modifications to heterogenous catalysis) needs to be considered, with the presence of sodium chloride resulting in the formation of nickel chloride on the anode surface causing anode deactivation.

VI

## LIST OF PUBLICATIONS

#### Peer Reviewed Journal Articles

DREWERY, M., KENNEDY, E., ALENAZEY, F., DLUGOGORSKI, B., STOCKENHUBER, M. (2015). "The effect of synthesis gas composition on the performance of Ni-based solid oxide fuel cells." <u>Chemical Engineering Research</u> and Design **101**: 22 – 26.

DREWERY, M., HARVEY, L., BRYANT, G., KENNEDY, E. M., STOCKENHUBER, M. "Utilization of glycerol and its derivatives in a nickel-based SOFC." <u>Energy and Technology</u>

#### **Conference Papers**

DREWERY, M., KENNEDY, E., ALENAZEY, F., DLUGOGORSKI, B., STOCKENHUBER, M. (2014). "The effect of syn gas composition on SOFC performance." *CHEMECA2014*, Perth, Australia.

DREWERY, M., MOLLOY, S., KENNEDY, E., DLUGOGORSKI, B., STOCKENHUBER, M. (2016). "Examining the role of water in performance of solid oxide fuel cells; an isotopic investigation." *9<sup>th</sup> International Conference on Environmental Catalysis*, Newcastle, Australia.

DREWERY, M., MOLLOY, S., KENNEDY, E., DLUGOGORSKI, B., STOCKENHUBER, M. (2017). "Conversion of glycerol on nickel-based solid oxide fuel cell anodes." 6<sup>th</sup> Sino-Australian Symposium on Advanced Biomass Utilisation Technologies, Perth, Australia.

DREWERY, M., MOLLOY, S., KENNEDY, E., DLUGOGORSKI, B., STOCKENHUBER, M. (2018). "Utilisation of solid oxide fuel cells for the conversion of glycerol derivatives." *4<sup>th</sup> International Symposium on Chemistry for Energy Conversion and Storage*, Berlin, Germany.

# TABLE OF CONTENTS

List	t of Fi	gures .		XIII	
List	t of Ta	ables		XXI	
1.	Intro	ductior	٦	1	
2.	Liter	erature Review6			
	2.1	The	motivation driving the development of alternative	energy	
		source	es	7	
	2.2	Fuel C	Cells	11	
		2.2.1	Polymer Electrolyte Membrane Fuel Cells	14	
		2.2.2	Solid Oxide Fuel Cells	15	
	2.3	Possil	ble Fuel Sources	19	
		2.3.1	Coal as a fuel supply	19	
		2.3.2	Biomass as a fuel supply	21	
		2.3.3	Hydrocarbons as a fuel supply	27	
	2.4	The ro	ole of water in solid oxide fuel cells	29	
	2.5	Gaps	in knowledge	36	
	2.6	Refer	ences	39	
3.	Experimental Procedure46				
	3.1	Mater	ials	47	
		3.1.1	Solid oxide fuel cell test fixture	47	
		3.1.2	Solid oxide fuel cell test fixture construction	48	
	3.2	Cell P	Preparation	50	
		3.2.1	Cell Reduction	50	
		3.2.2	Leak Checking	51	

	3.3	React	or Characterisation	53
		3.3.1	Reactor Function	53
		3.3.2	Characterisation of Cell Power	54
		3.3.3	Calculation of Cell Efficiency	54
	3.4	Initial	Fuel Cell Experiments - Characterisation of fuels by cell p	ower
		and m	nass balance	55
	3.5	Analy	tical Techniques	57
		3.5.1	Gas Chromatography	58
		3.5.2	Mass Spectrometry	63
		3.5.3	X-Ray Photoelectron Spectroscopy	66
		3.5.4	Fourier Transform Infra-Red Spectroscopy	69
		3.5.5	Galvanostat	73
		3.5.6	Impedance Spectroscopy	74
	3.6	Refer	ences	79
4.	Exar	mining	the role of water on the performance of solid oxide fuel cell	s; an
isotopic study			81	
			luction	82
			85	
		4.2.1	Fuel Cell Preparation	85
		4.2.2	Analysis	86
		4.2.3	Solid Oxide Fuel Cell Operation	86
4.3 Results and discussion			ts and discussion	87
	4.4	Concl	usion	98
	4.5	Refer	ences	100

5. The effect of synthesis gas composition on the performance of nickel			
	l oxide fuel cells103		
	5.1	Introduction104	
	5.2	Experimental109	
		5.2.1 Fuel Cell Preparation	
		5.2.2 Analysis	
		5.2.3 Operation of Solid Oxide Fuel Cell110	
	5.3	Results and discussion111	
	5.4	Conclusion125	
	5.5	References126	
6.	Ope	ration of solid oxide fuel cells on short chain alcohols; investigation of fuel	
	feed oxygen content130		
	6.1	Introduction131	
	6.2	Experimental133	
		6.2.1 Fuel Cell Preparation	
		6.2.2 Analysis	
		6.2.3 Solid Oxide Fuel Cell Operation134	
	6.3	Results and discussion135	
	6.4	Conclusion143	
	6.5	References145	
7.	Utilis	sation of glycerol derivatives in solid oxide fuel cells	
	7.1	Introduction149	
	7.2	Experimental154	
		7.2.1 Fuel Cell Preparation154	
		7.2.2 Analysis	

		7.2.3 Solid Oxide Fuel Cell Operation155	
	7.3	Results and discussion156	
	7.4	Conclusion	
	7.5	References167	
8.	Ope	ration of solid oxide fuel cell on neat and contaminated glycerol;	
	opp	ortunities for waste hydrocarbon utilisation173	
	8.1	Introduction174	
	8.2	2 Experimental17	
		8.2.1 Fuel Cell Preparation	
		8.2.2 Analysis	
		8.2.3 Solid Oxide Fuel Cell Operation	
	8.3	Results and discussion179	
	8.4	Conclusion	
	8.5	References188	
9.	Con	clusion and recommendations195	
Ap	pendi	x A: Solid oxide fuel cell construction201	
Ap	pendi	x B: Indigenous dynamic load cell schematics	
	B.1	Galvanostat204	
	B.2	Electrical Impedance Spectrometer211	
Ар	pendi	x C: In situ FTIR sample holder assembly216	

# LIST OF FIGURES

Figure 2.1:	Typical composition of coal fired power station flue gas8
Figure 2.2:	Flow diagram of external fuel processing required for a proton
	exchange membrane fuel cell15
Figure 2.3:	Schematic of a solid oxide fuel cell
Figure 2.4:	Potential fuels for use with solid oxide fuel cells
Figure 2.5:	Voltage at constant current of solid oxide fuel cell anode during
	redox cycling
Figure 2.6:	Hydrogen adsorption on zirconia surface and subsequent water
	desorption32
Figure 3.1:	Exploded view of solid oxide fuel cell assembly48
Figure 3.2:	Temperature program for heating solid oxide fuel cell50
Figure 3.3:	Schematic indicating gas losses for solid oxide fuel cell
Figure 3.4:	Reactor function measured using helium53
Figure 3.5:	Schematic of solid oxide fuel cell test system57
Figure 3.6:	User interface of micro-GC58
Figure 3.7:	Schematic of typical gas chromatogram setup59
Figure 3.8:	Schematic of basic thermal conductivity detector61
Figure 3.9:	Typical chromatograms produced with (a) Molsieve 5Å and (b)
	PoraPLOT Q columns equipped with TCD62
Figure 3.10:	Schematic of mass spectrometry63
Figure 3.11:	Schematic of principle of quadrupole mass spectrometer65
Figure 3.12:	Ejection of photoelectron from core levels in XPS analysis66
Figure 3.13:	Schematic of X-ray Photoelectron Spectrometer67
Figure 3.14:	Sample output from XPS68

Figure 3.15:	Schematic of FTIR interferometer70
Figure 3.16:	Experimental schematic of <i>in situ</i> FTIR71
Figure 3.17:	Background spectra obtained via in situ FTIR72
Figure 3.18:	Custom sample holder for in situ FTIR analysis73
Figure 3.19:	Sinusoidal response in a linear system with V (excitation) and I
	(current response) represented by solid and dashed lines
	respectively showing response phase shift ( $\phi$ )75
Figure 3.20:	Impedance spectra for used alkaline cell77
Figure 4.1:	Current as a function of $H_2O$ concentration where $H_2$ concentrations
	are approximately 40% ( $\blacksquare$ ) and 70% ( $\blacktriangle$ ) in N <sub>2</sub> 88
Figure 4.2:	Measured OCV as a function of $H_2O$ concentration where $H_2$
	concentrations are approximately 40% ( $\square$ ) and 70% ( $\blacktriangle$ ) in N <sub>2</sub> with
	total anode flow rate of 300 cm <sup>3</sup> .min <sup>-1</sup> 89
Figure 4.3:	Measured $O_2$ consumption in cathode as a function of $H_2O$
	concentration where $H_2$ concentrations are approximately 40% ( $\square$ ),
	50% (●) and 70% (▲) in N₂90
Figure 4.4:	OCV measured as a function of SOFC temperature where $H_2$
	concentrations are approximately 40% ( $\blacksquare$ ), 50% ( $●$ ) and 70% ( $▲$ )
	in N <sub>2</sub> , with H <sub>2</sub> O and D <sub>2</sub> O humidification represented by filled and

- hollow markers respectively......92

- Figure 4.8: Electric impedance spectrometry plots of 70% H<sub>2</sub> in N<sub>2</sub> with total flow rate of 300 cm<sup>3</sup>.min<sup>-1</sup> humidified with H<sub>2</sub>O ( $\bullet$ ) and D<sub>2</sub>O ( $\Delta$ ) from 20 Hz to 2 KHz at (a) 700°C and (b) 800°C......97

- Figure 6.5: Cell performance comparison between isomers diluted to 30% in N₂ with anode flow rate of 300 cm<sup>3</sup>.min<sup>-1</sup> at 850°C. (a) Compares 1-propanol (▲) to 2-propanol (●) while (b) compares 1,2-propanediol (\*) to 1,3-propanediol (–). Voltage and power densities represented by shaded and hollow markers respectively .......140
- Figure 7.1: Overall reaction for production of biodiesel......149
- Figure 7.3: Possible reaction routes for glycerol dehydration ......152

- Figure 7.9: Difference FTIR spectra of acrolein in contact with SOFC cell at 300°C. Spectrum of unused SOFC has been subtracted .......164

Figure B.1:	Galvanostat system context and interconnections	.206
Figure B.2:	Galvanostat architecture	.206
Figure B.3:	Precision reference voltage	.207
Figure B.4:	Power transistor array schematic	.209
Figure B.5:	Load current amplifier schematic	.210
Figure B.6:	Electrical impedance spectrometer schematic	215
Figure C.1:	Exploded schematic of in situ FTIR sample unit	217

### LIST OF TABLES

1:	3
	1

- Table 2.2:
   Summary of fossil fuel reserves in Australia
   19
- Table 5.1:Maximum cell power measurements operating with 50% syngasdiluted in N2 with an anode flow rate of 300 cm $^3$ .min $^{-1}$ ......117
- Table 5.2:Maximum cell power measurements operating with 35% syngasdiluted in N2 with an anode flow rate of 300 cm $^3$ .min $^{-1}$ ......119

- Table 8.1:
   Synthesis gas ratios produced by glycerol pyrolysis and by reaction

   over Ni-YSZ
   176