

**REDOX MEDIATORS AND
ELECTROLYTES FOR
HIGH-PERFORMANCE
Li-O₂ BATTERIES**

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for the degree of

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Certificate of Original Authorship

I, Anastasiia Tkacheva, declare that this thesis is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences, Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Table of Contents

Certificate of Original Authorship	ii
Acknowledgements.....	iii
List of Figures	4
List of Tables	10
List of Schemes	11
List of Abbreviations	12
Publications Arising from This Work	17
Abstract.....	18
Overview	20
Chapter 1: Redox Mediators and Electrolytes in Li-O₂ Batteries.....	24
1.1. General Theoretical Considerations for Batteries	24
1.1.1. Voltaic Cells.....	24
1.1.2. Primary and Secondary Batteries	25
1.1.3. Theoretical Voltage, Capacity, and Energy	26
1.1.4. Discharge, Charge, Cycle Life, Coulombic Efficiency, State of Charge, Definitions Related to Voltage.....	28
1.2. Redox Mediators and Electrolytes in Aprotic Li-O ₂ Batteries.....	29
1.2.1. Operating Principles and Composition of Li-O ₂ Batteries.....	30
1.2.2. Shortcomings of Li-O ₂ Batteries.....	48
1.2.3. Redox Mediators	54
1.3. Conclusion	62
1.4. Research Approach and Methods.....	62
Chapter 2: Experimental Section	68
2.1. General	68
2.2. Synthesis of TEMPO-ionic Liquids (TEMPOImILs).....	69
2.3. Synthesis of Substituted 2-Phenyl-nitronyl Nitroxides (RPTIOs).....	80
2.4. Electrochemical Characterisation.....	82
2.4.1. General	82

2.4.2. Preparation of Carbon-Based Cathodes	84
2.5. Description and Justification of Characterisation Techniques	85
2.5.1. Thermal Analysis	85
2.5.2. Cyclic Voltammetry	86
2.5.3. Electrochemical Impedance Spectroscopy.....	88
2.5.4. UV-visible Spectroelectrochemistry	90
2.5.5. Galvanostatic Cycling	91
2.5.6. Scanning Electron Microscopy	93
2.5.7. X-ray Diffraction.....	94
Chapter 3: TEMPO-ionic Liquids as Redox Mediators and Solvents for Li-O₂ Batteries	96
3.1. Introduction	96
3.2. Synthesis of TEMPOImILs.....	99
3.3. General Characterisation of TEMPOImILs	100
3.4. Ionic Conductivity of TEMPOImILs	101
3.5. Cyclic Voltammetry of TEMPOImILs	103
3.5.1. The Effect of Ferrocene on TEMPOImILs	104
3.5.2. Cyclic Voltammetry Studies with LiTFSI	106
3.5.3. Cyclic Voltammetry Studies with TBATFSI.....	113
3.6. Galvanostatic Cycling of the Li-O ₂ Batteries with TEMPOImILs	114
3.7. Summary	119
Chapter 4: Nitronyl-nitroxide-based Redox Mediators for Li-O₂ Batteries	122
4.1. Introduction	122
4.2. Synthesis of RPTIOs	126
4.3. Cyclic Voltammetry Studies with LiTFSI	127
4.4. Cyclic Voltammetry Studies with TBATFSI.....	131
4.5. Spectroelectrochemistry of PTIO.....	132

4.6. Reactions in Li-O ₂ Batteries upon the Addition of the Redox Mediators	134
4.7. Performance of Li-O ₂ Batteries with RPTIOs	138
4.8. Summary	142
Chapter 5: Conclusions	144
Appendix	147
A.1. TGA and DSC Data for TEMPOImILs.....	147
A.2. An Investigation of Methylated Ferrocenes as RMs for Li-O ₂ Batteries.....	152
A.2.1. Introduction	152
A.2.2. Results and Discussion.....	152
A.2.3. Summary	154
References	156

List of Figures

Figure 1. Schematic diagram of aprotic Li-O ₂ battery. ⁹	30
Figure 2. Discharge/charge profiles of Li-O ₂ batteries with IL/DMSO electrolyte at a capacity of 1000 mAh g ⁻¹ (left) and 500 mAh g ⁻¹ (right). ⁵⁸	36
Figure 3. Schematic diagram of a hybrid Li-O ₂ battery with a protected anode. ⁴⁹	37
Figure 4. Charge-discharge curves of Li-O ₂ batteries based on (a) P(VdF–HFP)/TEGDME GPE (b) liquid TEGDME electrolyte obtained at a fixed capacity of 500 mAh g ⁻¹ . ⁹² ..	42
Figure 5. Cycle life of Li-O ₂ batteries with PMMA based GPE. ⁸⁶	43
Figure 6. Electrochemical performance of Li-O ₂ battery with PAN-based GPE and LiNO ₃ at a fixed capacity of 400 mAh g ⁻¹ (a) charge-discharge profiles; (b) cycling stability. ⁸⁹	44
Figure 7. Preparation and appearance of ETPTA-based GPE with and without 1% w/w of glass microfillers. ⁹⁸	45
Figure 8. Electrochemical performance of Li-O ₂ battery with LAGP-PMS hybrid electrolyte at 50 °C at a fixed capacity of 1000 mAh g ⁻¹ (a) power output capability at different current densities (b), (c) charge-discharge curves and cyclability at a current density of 200 mAh g ⁻¹ . ⁸⁷	46
Figure 9. Gravimetric specific energies of various rechargeable batteries with gasoline. ²⁷	49
Figure 10. Scanning electron microscope image showing dendrites in a Li secondary battery. ¹⁰⁶	50
Figure 11. (a) The mechanism of OER with RM; (b) Charge-discharge profiles of Li-O ₂ battery with or without RM. ¹⁰	55

Figure 12. The mechanism of DBBQ facilitating ORR. ¹³⁵	57
Figure 13. Structure of TEMPOImILs.	64
Figure 14. Structure of RPTIOs.	65
Figure 15. Potential sweep in cyclic voltammetry.	86
Figure 16. A typical cyclic voltammogram.....	87
Figure 17. Example of a Nyquist plot.	89
Figure 18. a) Full discharge curves; ¹⁵⁶ b) discharge/charge curves with a capacity restricted to 1000 mAh g ⁻¹ . ⁸⁸	92
Figure 19. Cycling profile of a battery. ¹⁵⁸	93
Figure 20. Structure of TEMPOImILs studied in this work.	98
Figure 21. TGA curves of TEMPOImILs in N ₂ atmosphere.	100
Figure 22. TGA and DSC data for TEMPOImIL 5e	101
Figure 23. Temperature vs. ionic conductivity plots for pure TEMPOImILs 5a–e	102
Figure 24. Temperature vs. ionic conductivity plots for pure TEMPOImILs 6a–e	103
Figure 25. Temperature vs. ionic conductivity plots for pure TEMPOImILs 5a, c tested up to 80 °C.	103
Figure 26. Cyclic voltammetry plots for 10 mmol TEMPOImILs 5a, b, e in 0.1 M LiTFSI/DMA with and without added ferrocene.....	105
Figure 27. Cyclic voltammograms of TEMPOImILs 5a, e, 6a, e (10mM) in LiTFSI/TEGDME under an oxygen atmosphere, 1 st cycle.....	107
Figure 28. Cyclic voltammogram of TEMPOImIL 5a demonstrating the effect on the OER, 10 cycles.....	108

Figure 29. Cyclic voltammograms demonstrating the effect on the OER of TEMPOImILs 6a (a), 5e (b), 6e (c), 10 cycles.....	109
Figure 30. Cyclic voltammogram of TEMPOImIL 5b (10mM) in LiTFSI/MeCN under an argon atmosphere.	112
Figure 31. Cyclic voltammograms of TEMPOImILs 5a , e , 6a , e (10mM) in TBATFSI/TEGDME, 20 cycles.....	113
Figure 32. Cyclic voltammogram of TEMPOImIL 5a (10mM) in TBATFSI/TEGDME, 100 cycles.....	114
Figure 33. Cycle life of Li-O ₂ batteries with TEMPOImILs/LiTFSI and TEGDME/LiTFSI operated at a fixed capacity of 0.13 mAh cm ⁻² in the voltage range of 2.0–4.2 V at 73 °C.	115
Figure 34. Galvanostatic discharge/charge profiles of Li-O ₂ batteries with TEGDME/LiTFSI and TEMPOImIL 5b /LiTFSI at 73 °C.	117
Figure 35. Full charge and discharge profiles of Li-O ₂ batteries with TEGDME/LiTFSI and TEMPOImIL 5d /LiTFSI at 73 °C.....	118
Figure 36. The structure of PTIO.....	123
Figure 37. Photographs of the crushed crystals of RPTIO compounds: (a) NMe ₂ PTIO, (b) MeOPTIO, (c) PTIO, (d) NO ₂ PTIO.	127
Figure 38. Cyclic voltammograms of RPTIOs (10 mM), LiTFSI (0.1 M) in TEGDME under an argon atmosphere.	128
Figure 39. Cyclic voltammograms of RPTIOs (10 mM) in LiTFSI/TEGDME under an argon atmosphere in different potential ranges.....	130

Figure 40. Cyclic voltammograms with and without RPTIOs (10 mM) in LiTFSI/TEGDME under an O ₂ and Ar atmosphere. “No RM” refers to 0.1 M LiTFSI in TEGDME.....	131
Figure 41. Cyclic voltammograms of PTIO (10 mM) in TBATFSI/TEGDME under an oxygen atmosphere: (a) full scan range, (b) enlarged region at higher positive potentials.....	132
Figure 42. UV-Visible spectral changes during stepwise electrochemical oxidation of PTIO solution in TBAPF ₆ /MeCN. The potential was recorded vs. Ag/Ag ⁺ reference electrode.....	133
Figure 43. UV-Visible spectral changes during stepwise electrochemical reduction of PTIO solution in TBAPF ₆ /MeCN. The potential was recorded vs. Ag/Ag ⁺ reference electrode.....	134
Figure 44. Full discharge curves of the batteries with RPTIOs (10 mM) in LiTFSI/DEGDME and pure LiTFSI/DEGDME electrolyte in argon (a) and oxygen (b).	135
Figure 45. SEM images of CB cathodes: (a) pristine, (b) discharged containing PTIO, (c) discharged without PTIO, (d) charged containing PTIO, (e) charged without PTIO..	136
Figure 46. SEM images of discharged (top) and charged (bottom) CB cathodes with RPTIOs: a), d) MeOPTIO; b), e) NMe ₂ PTIO; c), f) NO ₂ PTIO.....	136
Figure 47. XRD patterns of pristine, discharged and charged CB cathodes with and without PTIO. Note: discharged cathodes remained attached to the stainless steel current collectors, peaks assigned to stainless steel are indicated in the diffraction patterns by **.....	137

Figure 48. XRD patterns of pristine, discharged and charged CB cathodes with and without RPTIOs.	138
Figure 49. Galvanostatic discharge/charge curves of RPTIOs (10 mM) in LiTFSI/DEGDME (1 st cycle).....	139
Figure 50. Galvanostatic cycling profiles of batteries (RPTIO (10 mM) in LiTFSI/DEGDME): (a) NMe ₂ PTIO, (b) MeOPTIO, (c) PTIO, (d) NO ₂ PTIO, and (e) pure LiTFSI/DEGDME electrolyte.....	140
Figure 51. Galvanostatic cycling profiles of the batteries with 10 mM MeOPTIO in LiTFSI/DEGDME and pure LiTFSI/DEGDME electrolyte at fixed capacities of 0.25 mAh cm ⁻² (a) and 0.5 mAh cm ⁻² (b).....	141
Figure A1. TGA and DSC data for TEMPOImIL with n = 4, R = H.	147
Figure A2. TGA and DSC data for TEMPOImIL with n = 4, R = Me.	148
Figure A3. TGA and DSC data for TEMPOImIL with n = 5, R = H.	148
Figure A4. TGA and DSC data for TEMPOImIL with n = 5, R = Me.	149
Figure A5. TGA and DSC data for TEMPOImIL with n = 6, R = H.	149
Figure A6. TGA and DSC data for TEMPOImIL with n = 6, R = Me.	150
Figure A7. TGA and DSC data for TEMPOImIL with n = 7, R = H.	150
Figure A8. TGA and DSC data for TEMPOImIL with n = 7, R = Me.	151
Figure A9. TGA and DSC data for TEMPOImIL with n = 8, R = Me.	151
Figure A10. Full discharge/charge curves of the Li-O ₂ batteries with pure LiTFSI/DEGDME electrolyte (“no OMeFc”) and 0.01 M OMeFc in LiTFSI/DEGDME electrolyte.....	153

Figure A11. Full discharge/charge curves of the Li-O₂ batteries with pure LiTFSI/DEGDME electrolyte (“no DMeFc”), 0.01 M DMeFc in LiTFSI/DEGDME electrolyte, and a mixture of both. 154

List of Tables

Table 1. Chemical structures and redox potentials of the redox mediators tested in Li-O ₂ batteries.	58
Table 2. Abbreviations and description of the structures of RPTIOs	65
Table 3. Potentials of TEMPOImILs with and without added ferrocene.....	106
Table 4. Shifts in cathodic peak potentials (E_{pc}) of TEMPOImILs after the 1 st cycle.....	110
Table 5. Redox potentials for the oxidation of RPTIOs.....	128

List of Schemes

Scheme 1. Synthesis of TEMPOImILs.....	99
Scheme 2. Redox processes in nitroxide radicals.....	106
Scheme 3. Protonation of hydroxylamine anion.	110
Scheme 4. Redox processes in nitronyl nitroxide radicals.	123
Scheme 5. Resonance structures in nitronyl nitroxide radicals.....	124
Scheme 6. Synthesis of RPTIO compounds.....	126

List of Abbreviations

<i>Abbreviation</i>	Explanation
% w/w	percentage by mass
$^1\text{O}_2$	singlet oxygen
<i>AC</i>	alternating current
<i>Ah</i>	ampere-hour
<i>CB</i>	carbon black
<i>CNT</i>	carbon nanotubes (cathode material)
<i>CP</i>	carbon paper
<i>CV</i>	cyclic voltammetry
<i>DBBQ</i>	2,5-di- <i>tert</i> -butyl-1,4-benzoquinone
<i>DEGDME</i>	diethylene glycol dimethyl ether, diglyme
<i>DFT</i>	density functional theory
<i>DMA</i>	<i>N,N</i> -dimethylacetamide
<i>DME</i>	ethylene glycol dimethyl ether, glyme, dimethoxyethane
<i>DMeFc</i>	decamethylferrocene
<i>DMF</i>	dimethylformamide
<i>DMTFA</i>	<i>N,N</i> -dimethyltrifluoroacetamide
<i>DMSO</i>	dimethyl sulfoxide
<i>DOL</i>	1,3-dioxolane

<i>DSC</i>	differential scanning calorimetry
<i>E</i>	discharge voltage
$E^0_{(cell)}$	standard cell potential
<i>EIS</i>	electrochemical impedance spectroscopy
<i>EMS</i>	ethylmethanesulfonate
$E^{\circ'}$	formal redox potential
E_{pa}	anodic peak potential
E_{pc}	cathodic peak potential
<i>ETPTA</i>	ethoxylated trimethylolpropane triacrylate
<i>Fc</i>	ferrocene
<i>GPE</i>	gel polymer electrolyte
<i>HMD</i>	2,2,4,4,5,5-hexamethyl-1,3-dioxolane
<i>I</i>	current
<i>IL</i>	ionic liquid
<i>i-PrOH</i>	isopropyl alcohol
<i>IR</i>	infrared
<i>LiRCO₂</i>	lithium alkyl carbonates (R = alkyl)
<i>LiTFSI</i>	lithium bis(trifluoromethanesulfonyl)imide
<i>MeCN</i>	acetonitrile
<i>MeO</i>	methoxy

<i>Nafion</i>	a sulfonated tetrafluoroethylene based fluoropolymer-copolymer
<i>NMe₂</i>	dimethylamino
<i>NMR</i>	nuclear magnetic resonance
<i>NN</i>	nitronyl nitroxide
<i>O₂⁻, O₂^{•-}</i>	superoxide anion, superoxide anion radical
<i>OCV (E_{OC})</i>	open-circuit voltage
<i>OER</i>	oxygen evolution reaction
<i>OMeFc</i>	octamethylferrocene
<i>ORR</i>	oxygen reduction reaction
<i>P(VdF-HFP)</i>	poly(vinylidene fluoride-co-hexafluoropropylene)
<i>PAN</i>	polyacrylonitrile
<i>Pc</i>	phthalocyanine
<i>PEO</i>	poly(ethylene oxide)
<i>PTIO</i>	2-phenyl-4,4,5,5,-tetramethylimidazoline-1-oxyl 3-oxide
<i>PMMA</i>	poly(methyl methacrylate)
<i>PMS</i>	poly(methyl methacrylate-styrene)
<i>PTFE</i>	poly(tetrafluoroethylene)
<i>PVA</i>	poly(vinylalcohol)
<i>Q_{nom}</i>	nominal capacity

Q_{theor}	theoretical capacity
$RPTIOs$	substituted 2-phenyl-4,4,5,5,-tetramethylimidazoline-1-oxyl 3-oxides
rGO	reduced graphene oxide (cathode material)
RH	relative humidity
RM	redox mediator
$S\ cm^{-1}$	siemens per centimeter
SEI	solid electrolyte interface
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SPE	solid polymer electrolyte
$TBAPF_6$	tetrabutylammonium hexafluorophosphate
$TBATFSI$	tetrabutylammonium bis(trifluoromethanesulfonyl)imide
t_D	discharge time
$TEGDME$	tetraethylene glycol dimethyl ether, tetraglyme
$TEMPO$	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
$TEMPOImILs$	TEMPO-substituted ionic liquids
$TEMPO-OH$	4-hydroxy-TEMPO
$TFSI$	bis(trifluoromethanesulfonyl)imide
TGA	thermogravimetric analysis

U	actual specific energy
U_{theor}	theoretical energy
$UV-visible$	ultraviolet-visible
V	volt
Wh	watt-hour
XRD	X-ray diffraction

Publications Arising from This Work

1. J. Zhang, B. Sun, Y. Zhao, A. Tkacheva, Z. Liu, K. Yan, X. Guo, A. M. McDonagh, D. Shanmukaraj, C. Wang, T. Rojo, M. Armand, Z. Peng, G. Wang, A versatile functionalised ionic liquid to boost the solution-mediated performances of lithium-oxygen batteries. *Nature Communications* **2019**, *10*, 602.
2. D. Zhou, A. Tkacheva, X. Tang, B. Sun, D. Shanmukaraj, P. Li, F. Zhang, M. Armand, G. Wang, Stable Conversion Chemistry-Based Lithium Metal Batteries Enabled by Hierarchical Multifunctional Polymer Electrolytes with Near-Single Ion Conduction. *Angewandte Chemie International Edition* **2019**, *58* (18), 6001-6006.
3. Zhou, D.; Shanmukaraj, D.; Tkacheva, A.; Armand, M.; Wang, G., Polymer Electrolytes for Lithium-Based Batteries: Advances and Prospects. *Chem* **2019**, *5*, 1-27.
4. Tkacheva, A.; Zhang, J.; Sun, B.; Zhou, D.; Wang, G.; McDonagh, A. M., TEMPO-Ionic Liquids as Redox Mediators and Solvents for Li-O₂ Batteries. *The Journal of Physical Chemistry C* **2020**, *124* (9), 5087-5092.
5. A. Tkacheva, B. Sun, J. Zhang, G. Wang, A. M. McDonagh, Nitronyl-nitroxide-based redox mediators for Li-O₂ batteries, *The Journal of Physical Chemistry C* **2021**, <https://doi.org/10.1021/acs.jpcc.0c08466>.

Abstract

The predicted theoretical energy density of a Li-O₂ battery is close to that of gasoline, which makes it one of the most promising forms of energy storage. To allow Li-O₂ batteries to achieve their full potential, multiple issues need to be overcome. One issue is the large charge and discharge overpotentials caused by sluggish kinetics of the reactions within the battery and the solid, insulating nature of the discharge product Li₂O₂. Applying soluble electrocatalysts (redox mediators or RMs) that aid the formation and decomposition of the Li₂O₂ can help to reduce the overpotentials. Other challenges associated with the Li-O₂ battery include instability, leakages, flammability and volatility of commonly used aprotic electrolytes. In this thesis, two series of compounds are investigated as solutions to these issues: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) substituted imidazolium ionic liquids (TEMPOImILs) with different lengths of alkyl linkage between the TEMPO and imidazole moieties and with either H or CH₃ on the 2-position of the imidazole ring, and phenyl nitronyl nitroxides (RPTIOs) with varied substituents on the benzene ring. The compounds were characterized using NMR and FTIR together with elemental analysis, TGA, DSC and EIS for TEMPOImILs. Redox processes were studied using cyclic voltammetry and, for RPTIOs, UV-visible spectroelectrochemistry. The effect of the RMs on the battery performance was tested by assembling and cycling Li-O₂ batteries. For RPTIOs, cathodes were analysed after cycling of the batteries using SEM and XRD, and battery tests in argon were conducted to determine if there was a contribution to the capacity from redox shuttling of the RM. It was found that TEMPOImILs can serve both as charging RMs and safer electrolyte solvents for Li-O₂ batteries, while RPTIOs not only catalyse the charge process but also provide some improvement of the discharge performance. The length of alkyl chain in TEMPOImILs did not have any noticeable effect on the battery performance, whereas TEMPOImILs with 1-methylimidazolium cations provided substantially longer cycle life than those with 1,2-dimethylimidazolium cations. The charge potentials of the batteries with RPTIOs with the electron-donating groups were the lowest, showing that altering the structures of nitronyl-nitroxide-based RMs can

directly affect battery performance. Overall, the use of the RMs in combination with other measures discussed in the thesis can lead to high-performance Li-O₂ batteries.

Overview

There is currently an active search for alternatives to non-renewable energy resources. Alternative energy sources include sunlight, nuclear reactions, wind, and tide power. In some cases, the energy generated by these types of plants must be stored. Batteries are a common and important form of energy storage. Energy storage devices are also used in transportable electronics for civilian and military purposes, uninterrupted power supplies, battery storage power stations, power tools, and electric vehicles.¹⁻² The latter are particularly interesting as an alternative to conventional vehicles.³

Most of the existing electric vehicles utilise lithium-ion (Li-ion) or nickel-metal hydride battery packs with the former prevailing during the last few years due to a higher specific energy.⁴⁻⁵ However, the theoretical specific energy for Li-ion batteries does not exceed 600 Wh·kg⁻¹, which makes it difficult to compete with the internal combustion engine.⁶⁻⁷

Lithium-oxygen (Li-O₂) secondary batteries have attracted considerable attention because their theoretical specific energy is the highest of all known cathode and anode materials and is close to that of gasoline.^{6,8} In practice, there are many issues affecting the performance of Li-O₂ batteries. An important problem is the accumulation of the discharge product, Li₂O₂, that blocks the cathode surface leading to a high charge overpotential and poor cycle life.⁹⁻¹¹ To address this issue, soluble electrocatalysts (redox mediators) have been proposed that have a better contact area than traditionally used heterogeneous catalysts.⁹⁻¹⁰

Other drawbacks include the formation of Li metal dendrites, flammability, volatility and instability of all known liquid electrolytes in the presence of reactive oxygen species.^{9,12-13} New electrolytes targeting these issues need to be considered.

It was hypothesised here that new redox mediators that reduce the charge overpotential and improve the cyclability of Li-O₂ batteries could be synthesised. In addition, electrolytes could be chosen such that they suppress the dendritic Li growth and provide safer batteries. Overall, the project aimed to develop high-performance Li-O₂ batteries. Thus, the specific project aims are:

- To synthesise compounds with properties suitable for the use as redox mediators and/or electrolytes in Li-O₂ batteries.
- To fabricate and characterise Li-O₂ batteries that integrate the proposed redox mediators and/or electrolytes.
- To analyse the effect of implementing the new redox mediators and/or electrolytes on the charge and discharge overpotentials, charge and discharge capacity and cycle life of Li-O₂ batteries.

To satisfy these aims, two series of compounds have been proposed: (i) TEMPO-functionalised imidazolium ionic liquids and (ii) substituted phenyl nitronyl nitroxides. While the latter were used solely as redox mediators, the former compounds combined the properties of redox mediators and electrolyte solvents.

The thesis is organised as follows: Chapter 1 provides a brief overview of theory of batteries with some important definitions and analyses the information available in the literature about Li-O₂ batteries, *i.e.*, operating principles, drawbacks emphasising the need for new redox mediators and electrolytes, redox mediators and electrolytes applied to date. Chapter 2 contains a detailed explanation of the research approach and methods used in this

project, including synthetic methods and characterisation techniques, and presents experimental data. Chapter 3 focuses on the synthesis and general characterisation of TEMPO-functionalised imidazolium ionic liquids, followed by the analysis of electrochemical results. Chapter 4 presents and discusses the results obtained for experiments using substituted phenyl nitronyl nitroxides as RMs. Chapter 5 summarises the essential findings and suggests directions for future research. Appendices include figures containing TGA and DSC data for TEMPOImILs and a study investigating the potential of octa- and deca-methylferrocenes to be used as RMs for Li-O₂ batteries.