# 論文 / 著書情報
# Article / Book Information

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| 題目(和文) | |
| Title(English) | Elucidating the Influence of Carbonaceous Electrodes and Metal/Metal Oxide Promoters in Non-aqueous Li-O2 Batteries |
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| 出典(和文) | 学位:博士(工学),<br>学位授与機関:東京工業大学,<br>報告番号:甲第10525号,<br>授与年月日:2017年3月26日,<br>学位の種別:課程博士,<br>審査員:脇 慶子,金 有洙,肖 鋒,沖野 晃俊,平山 雅章,田巻 孝敬 |
| Citation(English) | Degree:Doctor (Engineering),<br>Conferring organization: Tokyo Institute of Technology,<br>Report number:甲第10525号,<br>Conferred date:2017/3/26,<br>Degree Type:Course doctor,<br>Examiner:,,,,, |
| 学位種別(和文) | 博士論文 |
| Category(English) | Doctoral Thesis |
| 種別(和文) | 論文要旨 |
| Type(English) | Summary |

（博士課程）
Doctoral Program

# 論 文 要 旨

THESIS SUMMARY

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| 専攻：<br>Department of | 創造エネルギー　専攻 | 申請学位（専攻分野）：<br>Academic Degree Requested | 博士<br>Doctor of　（　工学　） |
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）


The realization of electrochemical energy storage with ultra-high energy densities is one of the most pressing needs in the area of transportation and renewable energy. Amongst post Li-ion batteries, the non-aqueous lithium-oxygen ($Li-O_2$) battery is attractive as it processes the high theoretical specific energy (~3.5 kWh $kg^{-1}$), one of the highest of all battery chemistries. The ideal electrochemistry of gaseous oxygen and lithium ions in an aprotic electrolyte yields the reversible reaction, $2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$ ($E^o$ = 2.96 V vs $Li/Li^+$), with insoluble and insulating $Li_2O_2$ forming as the discharge product. The $Li-O_2$ is still much in its infancy with its many challenges and our approach is to investigate this potential next generation battery chemistry in the following ways:

In Chapter 1, the broader context of the present work relating to global warming and climate change acting as an impetus for the improvement in electrochemical energy storage is introduced. Additionally, related background on electrochemistry, redox reactions, and the dependence of energy density on battery chemistry is introduced. The central topic of the thesis relating to $Li-O_2$ batteries is discussed including the discharge and recharge electrochemistry, and the current shortcomings, challenges and which are hampering $Li-O_2$ battery development consisting of electrolyte and electrode instability, poor reversibility and cycleability, low rate capability and lower-than-theoretical capacity.

In Chapter 2, the experimental methods used throughout this thesis is elaborated upon, the electrochemical cells, testing conditions, and post-mortem analysis techniques. Our analyses can be separated into three categories, where we complement standard electrochemical testing with (1) morphological (2) chemical and (3) quantitative analysis. Our approach of correlating these three characterisation aspects allows for a much more complete picture of the processes occurring in our $Li-O_2$ cells. Of particular emphasis is quantitative *in situ* on-line electrochemical mass spectrometry (OEMS) to evaluate gas evolution and reversibility. We discuss the construction and utilization of OEMS including the operating principles and importance within the $Li-O_2$ battery field.

In Chapter 3, we highlight the importance of carbon surface chemistry towards the behavior of $Li-O_2$ cells by systematically investigating the role of surface properties by decoupling oxygen functional groups, defective edges, and graphitization in carbon nanotubes. Our findings show that discharge capacity is enhanced with the increasing degree of order and uniformity of the carbon surfaces causing an absence of nucleation sites and bias towards solvation-based nucleation and growth of $Li_2O_2$. The subsequent recharge potential is predominantly dependent on the $Li_2O_2$ structure formed from the preceding discharge, where the presence of oxygen-functional groups promotes the formation of amorphous $Li_2O_2$ which

can more facilely decompose in comparison to crystalline $Li_2O_2$. The highly active oxygen-functional groups and defective edges, however, inactivate during cycling, providing insights into future strategies regarding enhancement of chemical stability as electrode platform. Our study provides improved understanding of the general role of carbonaceous electrode surfaces towards discharge capacity, the notorious rise in recharge potential and stability.

In Chapter 4, we address the issue regarding the use of nanostructured metal and metal oxides towards mitigating the large polarization (>1 V) observed on recharge. The origin of the large recharge overpotential has been attributed to the sluggish kinetics of $Li_2O_2$ decomposition and to concurrent formation of side products arising from electrolyte and carbon electrode degradation which require high potential to decompose (> 4 V). We synthesized metal and metal-oxide nanoparticles (NPs) of Au, Pt, Pd, Ru and $Co_3O_4$ on carbon nanotubes to investigate their efficacy in reducing the recharge overpotential, the predominant cell processes and lastly, the probable reasons for the observed behavior. We identify that while the metal/metal oxide NPs (exception is Au) reduce the recharge overpotential with Ru exhibiting the lowest recharge potential. More importantly, we reveal that the reduced overpotential is not accompanied by an increase in reversibility (all exhibit ~60% $O_2$ reversibility). Our findings identify that that metal/metal oxide NPs (in particular Pt and Ru) have activity toward electrolyte oxidation. We extend this study to examine the effect of particle size, where we find that when the NP particle size is <10 nm, there is a weak correlation between recharge potential and NP size. Our findings indicate that metal and metal oxide NPs do not mitigate the underlying issue of reversibility, reaffirming the need to identify electrolyte and electrode materials that promote reversible Li-$O_2$ electrochemistry.

In Chapter 5, we conclude this thesis with a broader perspective of the lessons learned within the Li-$O_2$ battery field and potential directions for future work. Lessons learned is highlighted by the importance of a comprehensive array of characterization techniques with the emphasis on quantitative analysis which allows for a fuller picture of the process occurring in Li-$O_2$ cells. Recent developments occurring after the experimental work of this thesis was completed, is mentioned including the detection of singlet oxygen, and the potential promising development of molten nitrate electrolytes.



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