SYNTHESES AND ELECTROCHEMICAL PERFORMANCE OF COMPOSITE AND CORE-SHELL LITHIUM-RICH OXIDES CATHODE FOR LITHIUM-ION BATTERY

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JANUARY, 2022

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY (Ph.D) IN INDUSTRIAL CHEMISTRY IN THE DEPARTMENT OF CHEMISTRY, COLLEGE OF SCIENCES AND TECHNOLOGY, COVENANT UNIVERSITY, OTA, OGUN STATE, NIGERIA.

JANUARY, 2022

ACCEPTANCE

This is to attest that this thesis is accepted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Industrial Chemistry in the Department of Chemistry, College of Science and Technology, Covenant University, Ota, Nigeria.

Mr. John A. Philip **……………………………………**
(Secretary, School of Postgraduate Studies) **Signature and Date**

Prof. Akan B. Williams **………………………………….**
(Dean, School of Postgraduate Studies) **Signature and Date**

DECLARATION

I, AJAYI, SAMUEL OLUWAKAYODE (18PCC01865) declare that this research was carried out by me under the supervision of Prof. Kolawole O. Ajanaku and Dr. Cyril O. Ehi-Eromosele of the Department of Chemistry, College of Sciences, Covenant University, Ota, Nigeria. I attest that the thesis has not been presented either wholly or partially for the award of any degree elsewhere. All sources of data and scholarly information used in this thesis are duly acknowledged.

AJAYI, SAMUEL OLUWAKAYODE ……………………………

Signature and Date

CERTIFICATION

We certify that this thesis titled **"SYNTHESES AND ELECTROCHEMICAL PERFORMANCE OF COMPOSITE AND CORE-SHELL LITHIUM-RICH OXIDES CATHODE FOR LITHIUM-ION BATTERY"** is the original research work carried out by **AJAYI, SAMUEL OLUWAKAYODE (18PCC01865)** in the Department of Chemistry, Covenant University, Ota, Ogun State, Nigeria under the supervision of Prof. Kolawole O. Ajanaku and Dr. Cyril O. Ehi-Eromosele. We have examined and found this work acceptable as part of the requirements for the award of Doctor of Philosophy (Ph.D) degree in Industrial Chemistry.

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DEDICATION

This thesis is dedicated to God Almighty who alone is worthy of all my praise and adoration and whom I recognize as my divine source, from whom I tapped all the wisdom and favour for the completion of this work.

ACKNOWLEDGEMENTS

My utmost appreciation goes to God, the source of divine wisdom, knowledge, and understanding for the privilege and grace bestowed on me to complete the Ph.D programme. I am highly indebted to the Chancellor and Chairman of the Board of Regents, Covenant University, Dr. David O. Oyedepo, for providing a platform that has given me the opportunity not only to pursue my academic career but also to be a part of the glorious vision that Covenant University is driving. I must sincerely thank the Vice-Chancellor of Covenant University, Prof. Abiodun H. Adebayo, the Registrar, Dr. Oluwasegun P. Omidiora, and the entire management team for their leadership role towards the success of this programme. I appreciate the Dean, School of Postgraduate Studies (SPS), Prof. Akan B. Williams, and the Sub-Dean, SPS, Dr. Emmanuel A. Amoo. The Dean, College of Science and Technology (CST), Prof. Victor T. Omotosho, is also appreciated.

My immense gratitude goes to my supervisor, Prof. Kolawole O. Ajanaku, and co-supervisor, Dr. Cyril O. Ehi-Eromosele for their patience, love, supports, untiring commitments, enthusiastic guidance, meticulousness, constructive criticisms, thoughtful comments, and contributions towards the successful completion of this programme. You are great mentors that are willing to sacrifice all for my success and see the best in me. I must not fail to mention the role you both played in sourcing for the AvH fellowship that funded this project and the help you rendered during my research work. Indeed, my path crossing your paths is a divine favour from God that I will never take for granted; I am highly indebted to you both, sirs.

My sincere appreciation goes to the Head of Department, Prof. Joseph A. O. Olugbuyiro for his positive influence, assistance in the processing of my PG forms, and motivation throughout the Ph.D programme. I must not fail to appreciate Dr. Joseph A. Adekoya, the departmental PG coordinator for his support and love during this programme. I deeply appreciate the Faculty and Staff of the Department of Chemistry for their contributions, inputs, and constructive criticisms at all the stages of this work.

This study was carried out at Covenant University, Ota, and at the Institute of Applied Materials-Energy Storage Systems (IAM-ESS), Karlsruhe Institute of Technology. I sincerely acknowledge the funding of this project and financial support by the Alexander von Humboldt (AvH) Foundation that enabled me to finish up this programme. I am grateful to my host, Prof. Dr. Helmut Ehrenberg, who gave me the opportunity to work in the IAM-ESS. I deeply appreciate Dr. Sylvio Indris, my group leader, and the assistance of the IAM-ESS technical staff during the research work. I also appreciate Mrs. Asmau Gebi and other doctoral students in the IAM-ESS for their useful discussions and contributions during my research work.

My profound gratitude also goes to the immediate past Vice-Chancellor, Dean, CST and Head of Department (HOD) of Chemistry Covenant University, Prof. Aaron A.A Atayero, Prof. Kolawole O. Ajanaku, and Prof. Olayinka O. Ajani, respectively for approving my study leave to Germany. I am highly indebted to Prof. Matthew O. Olabemiwo and Prof. Mary A. Oladipo for their kind support and encouragement in the course of the programme. I deeply appreciate my parents; Mr. and Mrs. Simeon Ajayi for their love, spiritual investment, and moral support during the course of the programme, Thank you so much for everything, you shall live long in sound health to eat the fruit of your labour. I deeply appreciate my siblings; Ajayi Julius Oluwafunminiyi and Ajayi Juliana Oluwafunmilayo for their love and unwavering support during my Ph.D study.

Finally, I would like to appreciate my friends Adejumo Temiloluwa, Osinowo Damilola, Nwogu Blessing, Makanjuola Toluwalope and Abiola Babawale for their moral support in the course of my Ph.D study.

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LIST OF ACRONYMS AND ABBREVIATION

XRD:	X-ray diffraction
SEM:	Scanning electron microscopy
TEM:	Transmission electron microscopy
SEM:	Scanning electron microscopy
LLO:	Layered lithium oxide
LIBs:	Lithium-ion batteries
ICP-OES:	Inductively coupled plasma optical emission spectroscopy
PVdF:	Polyvinylidene fluoride
TG:	Thermogravimetric
DSC:	Differential scanning calorimetry
ΔG^{O}:	Standard gibbs free energy
n:	Number of electrons transferred in an electrode reaction
F:	Faraday constant
SEI:	Solid electrolyte interface
EDS:	Energy dispersive X-ray analysis
EIS:	Electrochemical impedance spectroscopy
C-rate:	Rate of charge or discharge
E:	Cell voltage under non-standard conditions
E^{O}:	Standard battery potential
R:	Universal gas constant
T:	Temperature
NMP:	N-methyl-2-pyrrolidone
Mw:	Molecular mass of the electrode material
V_{OC}:	Open-circuit voltage
CE:	Coulombic efficiency
SOC:	State of charge

ABSTRACT

The layered lithium-rich oxide (LLO) cathode delivers higher capacity and excellent thermal stability compared to the conventional cathode materials but they demonstrate several performance limitations that affect their practical applications. The aim of this research work is to optimise the electrochemical performance of LLOs using different synthetic routes, LLO architecture (composite/core-shell), and stoichiometries. The effects of the nature of fuel [citric acid (CA) and ammonium acetate (AA)] in different proportions and annealing temperature on the structural properties and electrochemical performance of $Li_{1.2}Mn_{0.52}Ni_{0.2}Co_{0.08}O_2$ composite material synthesised by the solution combustion synthesis (SCS) were determined. The samples were analysed with TG-DSC, ICP-OES, powder XRD, Raman Spectrometer, and SEM/EDX. The 75%CA:25%AA fuel mixture samples had the largest particle size compared with 50%CA:50%AA and 100%CA samples. The electrochemical result revealed that 50%CA:50%AA samples gave the highest initial discharge capacities of 196 mAh/g and 215 mAh/g and a capacity retention of 99.9% and 86.7% after 30 cycles, for the sample annealed at 1000^{o}C/10 hr (5050-T1) and 900^{o}C/3 hr (5050-T2), respectively. The 75%CA:25%AA fuel mixture sample pre-annealed at 500^{o}C/3 hr and further annealed at 1000^{o}C/3 hr (7525-T3) gave the highest capacity retention of 121.4% after 30 cycles. A core-shell (CS) structure can be used to improve the electrochemical performance of LLO materials. Therefore, CS $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ ($Li_{1.2}Mn_{0.52}Ni_{0.2}Co_{0.08}O_2$) were synthesised through different synthetic routes (sol-gel and wet chemical synthesis). The sol gel synthesised sample gave an overall better electrochemical performance compared to the wet chemical synthesised sample. The effects of coating solvent and annealing temperature on the sol-gel synthesised CS sample were further examined. The initial discharge capacity and coulombic efficiency of the CS sample coated in distilled water and annealed at 1000^{o}C (CS-SG-W-1000) were 240 mAh/g and 76%, respectively while the same sample coated in aqueous ethanol (CS-SG-A-1000) gave 175 mAh/g and 28.2%, respectively. After 30 cycles, the discharge capacity and capacity retention of CS-SG-W-1000 sample was 215 mAh/g and 89.4%, while that of CS-SG-A-1000 was 138 mAh/g and 79.0%, respectively. The better overall electrochemical performance observed for CS-SG-W-1000 compared to CS-SG-A-1000 was attributed to the better dispersion in the water and the presence of better-layered and crystalline structure obtained at the highest annealing temperature. Finally, different LLO stoichiometric quantities of $xLi_{1.2}Mn_{0.6}Ni_{0.2}O_2$(LMO)·(1-x)$LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$(NCM) (x = 0.7, 0.5, 0.3) composite cathode materials were synthesised using solution combustion-mechanochemical synthesis. The initial discharge capacity and coulombic efficiency of the 0.7LMO-0.3NCM sample was 239 mAh/g and 67.9%, 0.5LMO-0.5NCM sample was 171.5 mAh/g and 63.2%, while the 0.3LMO-0.7NCM sample gave 213.1 mAh/g and 74.2%, respectively. After 30 cycles, the discharge capacity and capacity retention of 0.7LMO-0.3NCM were 209 mAh/g and 87.2%, 0.5LMO-0.5NCM sample were 155 mAh/g and 91.0%, while 0.3LMO-0.7NCM were 149.1 mAh/g and 70.0%, respectively. This study shows that the composite powders synthesised with only citric acid fuel gave the best electrochemical performance compared with those produced using the fuel mixtures. Also, the core-shell architecture improved the first coulombic efficiency of LLO material compared with the composite architecture.

Keywords: $Li_{1.2}Mn_{0.52}Ni_{0.2}Co_{0.08}O_2$, Composite, Core-shell, Coulombic efficiency, Electrochemical performance, Solution combustion synthesis