UNIVERSITI TEKNOLOGI MARA

SYNTHESIS AND OPTIMIZATION OF NITROGEN-DOPED ACTIVATED CARBON ELECTRODE FOR ENHANCED LITHIUM POLYSULFIDE ADSORPTION IN LITHIUM-SULFUR BATTERIES

MOHD SAUFI BIN MD ZAINI

Thesis submitted in fulfilment
of the requirements for the degree of
Doctor of Philosophy
(Chemical Engineering)

College of Engineering

May 2025

ABSTRACT

The polysulfide shuttle effect significantly impedes the commercial viability of lithium-sulfur (Li-S) batteries by causing rapid capacity fading and low coulombic efficiency. Incorporating porous carbon materials as the cathode host is a promising approach to address this issue. Biomass-derived carbon materials offer substantial advantages due to their abundance, renewability, and cost-effectiveness. Palm kernel shell biomass (PKS), generated in vast amounts in Malaysia, holds exceptional promise for conversion into composite electrodes with sulfur for Li-S batteries. This approach not only enhances resource efficiency but also contributes to the circular economy. Enhancing the lithium polysulfide (LiP) adsorption capacity of carbon materials requires modifying surface functionalities and pore properties. Factors such as impregnation ratio, activation temperature, and activation time are critical and require systematic optimization. This study aims to synthesize activated carbon (AC) from PKS with chemical modifications to enhance polysulfide adsorption capacity for improved Li-S battery performance. Potassium hydroxide (KOH) was used as the activation agent, while urea was utilized for nitrogen doping. Response surface methodology (RSM) and artificial neural networks (ANN) were employed to optimize and predict LiP adsorption on the nitrogen-doped activated carbon (NDAC). Although recent studies have focused on using AC cathodes for their strong affinity to lithium polysulfide, there has been limited investigation into the quantitative adsorption of lithium polysulfide with varying ratios of urea doping in AC. Thus, this study aimed to quantitatively assess the polysulfide adsorption capacity uptake for high performance of AC-cathode in lithium sulfur batteries. The results of this study indicate that increasing the urea ratio improves the AC's porosity and enhances LiP adsorption. The NDAC with the biomass-to-urea ratio of 1:3 exhibited the most remarkable adsorption uptake capacity of 12.94 mmol/g, attributed to the well-developed porosity (BET surface area of 1902.99 cm^2/g and a pore volume of 0.92 cm^3/g) and high nitrogen functionalization on the carbon surface, which contributes to the formation of physical and chemical bonds between polarized lithium polysulfide and the carbon matrix. RSM analysis indicated that the impregnation ratio was the most significant factor affecting LiP adsorption, with optimal NDAC achieved at an activation temperature of 880°C, an impregnation ratio of 2.0, and an activation time of 80 minutes. The experimental results from RSM were used to train the predictive capabilities of the ANN for LiP adsorption. A comparison between ANN and RSM revealed that both methods provided high-quality predictions, with R^2 values of 0.9901 and 0.9756, respectively. However, ANN exhibited superior prediction accuracy with a lower Mean Squared Error (MSE) of 0.003 compared to RSM's 0.007. The NDAC synthesized under optimal conditions exhibited a large specific surface area of 2303.28 m^2/g and a pore volume of 1.27 cm^3/g, featuring a variety of pore sizes in the micro and meso ranges. The sulfur composite cathode (NDAC/S) demonstrated excellent electrochemical performance, with an initial discharge capacity of 1043.35 mAh/g at 0.1C and retaining a capacity of 686.52 mAh/g after 100 cycles. This capacity is five time higher than commercial lithium-ion batteries of 278 mAh/g. This outstanding electrochemical performance is due to the synergistic effect of the hierarchical pore structure, large surface area, substantial pore volume, and the presence of doped nitrogen, which provides strong chemical bonding with LiP. Overall, this study provides valuable insights into the utilization of PKS-derived NDAC as a promising host matrix for future Li-S batteries, potentially advancing their commercial viability.

ACKNOWLEDGEMENT

In the Name of Allah, the Most Beneficent and Merciful

With utmost gratitude, I express my thanks to Almighty Allah for His benevolence, mercy, and divine guidance. I have achieved a significant level of education and knowledge through His grace.

I extend my heartfelt appreciation and gratitude to my academic supervisors, Professor Ir. Dr. Syed Shatir Asghrar Syed Hassan and Associate Professor Ir. Dr. Syed Mutallib Al-Junid, for their continuous support, guidance, and advice throughout this project. I also sincerely apologize for any mistakes made during the experiments and thank them for their patience. Their best advice, "always put a sense of belonging into research," will always remain with me.

My profound gratitude goes to my friends, research team, and assistant engineers, particularly Mr. Mustafa Mokhtar, Pn. Siti Zaharah Roslan, Pn. Nur Faradilla Anuar, and Mr. Mohd Syazwan Mohd Ghazali, for their technical support and advice throughout this research.

I am also grateful to Professor Dr. Oskar Hasdinor Hassan and Professor Dr. Ab Malik Marwan Ali from the Ionic Materials and Devices (iMADE) Research Laboratory, Institute of Science, for their valuable support in enabling the manufacturing of batteries and their expert guidance on electrochemical performance.

My deepest gratitude to the Ministry of Education Malaysia and Universiti Teknologi MARA for providing financial assistance under the "Skim Latihan Akademik Bumiputra" scholarship. I am greatly indebted to them, as their support made it possible for me to pursue my studies.

Finally, I would like to express my gratitude and recognition to my wife, Latifah Musa; my children, Muhammad Sufyan As-Sauri, Iffah Aqilah, Iffatul Aufa, and Iffah Aliah; my late father, Md Zaini Zainal; and my beloved mother, , along with my other relatives, for their unwavering support, encouragement, and selfless contributions towards the successful completion of this project.

To them, I dedicate this thesis. Alhamdulillah.

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CHAPTER 1
INTRODUCTION

1.1 Research Background

The rapid technological progress of our society has led to a growing need for advanced energy storage technologies, particularly due to the increased demand for portable electronic devices (PEDs). These devices are crucial for modern lifestyles but face constraints due to limited energy supply, posing a critical challenge in designing high-performance, long-lasting rechargeable batteries. Currently, Li-ion batteries, such as nickel manganese cobalt oxide (NMC), are the most prevalent type of battery for PEDs, yet their theoretical gravimetric capacity of 278 mAh/g is insufficient for sustaining extended runtimes [1].

An alternative electrochemical energy storage device to address these challenges is the lithium-sulfur (Li-S) battery. The Li-S battery offers a significantly higher theoretical energy density of 1675 mAh/g, six times that of NMC batteries. In addition, sulfur is inexpensive and abundantly available, making it an attractive component for cost-effective systems. Due to their potential for higher energy density compared to conventional lithium-ion batteries, rechargeable Li-S batteries hold significant promises for powering PEDs in the future.

Li-S batteries operate on conversion chemistry rather than intercalation chemistry, where sulfur undergoes conversion to lithium sulfide at the cathode, while lithium is stripped and plated at the anode, as represented by the following equations:

$$\text{Lithium Anode} : 16Li \rightarrow 16Li^{+} + 16e^{-} \quad (1.1)$$

$$\text{Sulfur cathode} : S_8 + 16Li^{+} + 16e^{-} \rightarrow 8Li_2S \quad (1.2)$$

$$\text{Overall reaction} : S_8 + 16Li \rightarrow 8Li_2S \quad (1.3)$$

However, during the charge and discharge processes, the shuttle effect occurs, caused by polysulfide dissolution and migration between the anode and cathode, resulting in poor cycling stability, low conductivity, and shortened battery life. This challenge has hindered the commercialization and widespread use of Li-S batteries.