UNIVERSITI TEKNOLOGI MARA

SYNTHESIS OF DOPED $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC 111) USING COMBUSTION METHOD AND THEIR ELECTROCHEMICAL PERFORMANCE AS CATHODE MATERIALS FOR Li-ION BATTERIES APPLICATION

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ABSTRACT

The NMC 111 cathode materials possess compelling characteristics in terms of high energy density and low cost, making them highly promising for the next generation of high-energy lithium-ion batteries. However, they still encounter challenges, particularly rapid capacity degradation, especially under high C rates. In this study, we employed the combustion method to synthesize the NMC 111 cathode materials. The work was divided into three parts: (i) synthesis of the NMC 111 materials using three different fuels to investigate their phase, structure, morphology, and battery performance, (ii) synthesis of doped NMC 111 materials with two dopants (Titanium and Aluminium) to examine their impact on the structural, morphological, and battery performance, and (iii) optimization of the synthesis process to identify the best materials, NMCT, and evaluate their effects on the structure, morphology, and battery performance. In the first part, pristine NMC 111 materials synthesized using citric acid (NMC_C) as a fuel demonstrated the most favorable performance, exhibiting the highest initial discharge capacity of 130.80 $mAhg^{-1}$ and an efficiency of 89.84% after 30 cycles. Several factors contributed to this performance, including the highest enthalpy of combustion ($\Delta cH°$ solid), which influenced the crystal growth and ordered structure of the material, as well as a stable structure with reduced cation mixing and uniform distribution of particle size, resulting in a larger surface area that facilitated the movement of Li ions during the charge-discharge process. In the second part, NMCT, which is NMC 111 doped with Titanium, exhibited superior performance compared to the Al-doped and pristine samples, delivering a higher initial discharge capacity of 142.51 $mAhg^{-1}$ and an efficiency of 82.63% after 30 cycles. This enhanced performance can be attributed to factors such as increased crystallinity, a well-defined layered structure, improved cation ordering, and a smaller crystallite size. In the third part, the NMCT materials underwent annealing at various temperatures and durations. The NMCT annealed at 800 ˚C for 72 hours demonstrated excellent cycling stability, showcasing a higher initial discharge capacity of 148.6 $mAhg^{-1}$ and capacity retention of 96.8% after 30 cycles. The exceptional performance of this material can be attributed to its superior structural integrity, characterized by larger parameters of the c-axis, minimal cation mixing, larger Li-O atomic distance, and a smaller potential difference (ΔE). In conclusion, the NMCT annealed at 800 ˚C for 72 hours emerged as the most favorable cathode material, exhibiting great potential for application in lithium-ion batteries.

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CHAPTER 1
INTRODUCTION

1.1 Background of the Study

A battery, comprised of one or multiple electrochemical cells, serves as a significant source of electrical power. By receiving an electrical charge, the battery can generate a stable potential for power supply. The battery performs two essential functions: providing sustained power output over a specific duration and storing electrical energy. Batteries are classified into two categories: primary (non-rechargeable) and secondary (rechargeable). Non-rechargeable batteries are characterized by irreversible electrochemical reactions, immediately producing current upon assembly [1]. These batteries offer several advantages, including ease of use, low initial cost, versatility for various consumer applications, extended shelf life, and high energy density. On the other hand, rechargeable batteries are composed of one or more electrochemical cells with electrically reversible reactions. Despite having a higher upfront cost, rechargeable batteries prove more economical in the long run as they can be recharged multiple times [2].

A rechargeable battery technology with promising potential is the lithium-ion battery (LIB), widely utilized in advanced battery systems. At the core of its electrochemical composition are lithium ions, which migrate from the negative electrode to the positive electrode during discharge, and vice versa during charging. Different variations of lithium-ion batteries employ diverse chemistries, resulting in variations in performance, cost, and safety characteristics [3]. LIBs find applications in numerous products such as handheld power tools, electronic devices, toys, small and large appliances, electric vehicles (EVs), hybrid electric vehicles (HEVs), and electrical energy storage systems [4]. The utilization of lithium-ion batteries offers several advantages, including cost-effectiveness, ease of maintenance, high power density, significant specific capacities, excellent stability, high open circuit voltage, absence of memory effect, and a