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Senate
Warsaw University of Technology

Evaluation of the Doctoral Dissertation
titled

»Comparative analysis of synthesis routes and aluminum doping effects on NMC type cathode material«

Submitted by: **Yu-Sheng Chen**, M.Sc.

Program: Destiny – European Research Institute

Supervisors: Prof. Dr. Władysław Wieczorek and Prof. Dr. Robert Dominko

I was appointed as a reviewer of the dissertation of M.Sc. Yu Sheng-Chen on 18.02.2025. Based on the final version of the dissertation dated 20 February 2025, received by email, I hereby provide an independent evaluation.

ANALYSIS OF THE DISSERTATION AND ORIGINALITY OF THE SCIENTIFIC CONTRIBUTION

The dissertation presented by PhD candidate Yu-Sheng Chen deals in detail with lithium-ion batteries (LIBs), in particular with the nickel-containing cathode material - nickel- manganese-cobalt- oxide in an atomic ratio of 8:1:1 (NMC811), which is already available as a high-voltage cathode material in commercial vehicles, e.g. BMW iX3. However, there are still some challenges related to improving power density, shortening charging time and ensuring long-term cycle stability, which are crucial for further integration and scalability in the newer generation e-mobility sector. This is also reflected in the numerous research activities and publications of recent years.

In this context, Mr. Chen’s dissertation addresses a critical issue related to the chemical composition and improvement of NMC811 material. The development of NMC811 is of particular importance given the increasing demand for sustainable energy storage and the associated electromobility. A major strength of the work lies in its systematic approach to improving the performance of the cathode material, taking into account the cost and availability of the key raw material cobalt, which is both expensive and geopolitically critical. By investigating aluminum, an inexpensive and abundant element, as a dopant in the NMC structure, the candidate aimed to reduce the material cost and improve the structural and electrochemical stability. This makes the presented thesis attractive and scientifically relevant, yet original. The thesis not only addresses the synthesis routes and strategies for doping NMC

with aluminum, but also investigates how the incorporation of aluminum into the crystal structure affects the cycling behavior, structural integrity, and electrochemical performance of the material. The focus of the research is on the optimization of defined monocrystalline forms of NMC811 as well as polycrystalline counterparts. The scientific contribution of the dissertation is reflected in two peer-reviewed publications published in the Journal of Applied Physics A and Batteries.

ALIGNMENT WITH THE TOPIC PROPOSAL

Not applicable for the evaluated PhD thesis.

STRUCTURE OF THE DISSERTATION

The dissertation is well organized and includes a clear introduction, a detailed experimental section, comprehensive results and discussions, and a coherent summary. It meets all academic standards and requirements for the documentation of a doctoral thesis.

Introduction:

Introduction is divided into 11 sections. The chapter opens with an overview of lithium-ion batteries (Sections 1–3), followed by an examination of layered oxide cathodes in Section 4. Sections 5–10 discuss synthesis methods, material modification techniques such as doping and coating, and electrochemical characterization. Lastly, section 11 briefly outlines the experimental techniques used.

Experimental Part:

This chapter defines the research scope and objectives, with the author highlighting a central focus on stabilizing cathode interfaces and interphases, particularly in relation to the interaction between aluminum dopants and the NMC host structure. The study seeks to improve both structural integrity and electrochemical performance by optimizing synthesis routes for single-crystalline and polycrystalline materials. Two primary methods are employed: co-precipitation and molten salt calcination.

Results and Discussion:

Chapter Results and Discussion is divided into three sections. The first outlines experimental methods, including Rietveld-refined XRD, SEM-EDX, ICP-MS, HR-TEM, STEM-EELS and EC experiments. The second presents key findings on ten NMC811 cathodes. The section offers a detailed analysis of structure, morphology, and composition, while STEM-EELS data for four samples show that only the Ni signal in Al-doped polycrystalline material was notably affected. Electrochemical testing revealed no capacity gain for single-crystalline materials, while PC cathodes showed improved performance depending on the doping method. Co-precipitation was ineffective; post-calcination doping yielded better results. The last section summarizes everything and concludes.

Future Study:

The last chapter, Future Study, explores how electrolyte composition affects cathode stability.

Ten different electrode/electrolyte combinations were examined, with particular attention given to the specific additive. The chapter concludes with a focused and well-founded subsection on future directions and development, outlining potential research paths and highlighting unresolved questions for further investigation.

METHODS USED

The candidate employed a comprehensive range of characterization techniques to analyze the synthesized Al-doped NMC811, crucial for investigating its performance in lithium-ion batteries. These methods provide a full understanding of the structural, morphological, elemental, and electrochemical properties of the materials used in energy storage systems. The employed techniques include X-ray Diffraction (XRD) to study the crystallographic structure and phase composition, Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM-EDX) for analyzing surface morphology and elemental composition, and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for precise determination of elemental composition and trace elements. High-Resolution Transmission Electron Microscopy (HR-TEM) was used to explore fine structural features and nanomorphology, while Scanning Transmission Electron Microscopy with Electron Energy Loss Spectroscopy (STEM-EELS) provided detailed chemical analysis at the nanoscale, offering insights into elemental composition and bonding environments. Additionally, electrochemical tests were performed to evaluate the material's electrochemical performance and cycling stability in lithium-ion batteries. Together, these techniques offer a thorough investigation of the material's characteristics, supporting its potential for use of the synthesized materials.

HYPOTHESES VALIDATION

Not applicable for the evaluated PhD thesis.

ORIGINALITY AND VALUE

The dissertation contributes original and valuable knowledge to the field of lithium-ion battery research, particularly in optimizing cathode materials for improved performance and durability. Part of the findings have been partially published in two scientific articles, emphasizing their relevance and scientific merit:

- Chen, YS., Dominko, R., Marczewski, M. et al. Optimizing high-energy lithium-ion batteries: a review of single crystalline and polycrystalline nickel-rich layered cathode materials: performance, synthesis and modification. Appl. Phys. A 130, 740 (2024). https://doi.org/10.1007/s00339-024-07897-7
- Chen, Y.-S.; Tchernychova, E.; Hočevar, S.; Dominko, R.; Wieczorek, W. Comparative Analysis of Synthesis Routes and Aluminum Doping Effects on Nickel-Manganese-Cobalt Type Cathode Material. Batteries 2025, 11, 72. https://doi.org/10.3390/batteries11020072

STYLE AND LANGUAGE

The proposed work is written in a professionally correct manner. It uses established

terminology, symbols, and abbreviations, and the structure of the work is logical and flows smoothly.

CONCLUSION

The doctoral dissertation of **Yu-Sheng Chen** is an independent, significant, and original contribution to the field of Materials Science. All requirements for the title of Doctor of Science have been met. I recommend that the Senate of WUT accept this evaluation and allow the candidate to defend the dissertation.

Assoc. Prof. Dr. Boštjan Genorio

Boštjan Genorio

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