ENERGY STORAGE AND DISTRIBUTED RESOURCES DIVISION

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REVIEW OF THE PH.D. THESIS
"Operando Raman Microscopy Studies on Next Generation Positive Electrode and Electrolyte Materials"
by Eva del Campo Ortiz, M. Sc.

The Thesis is is written in correct scientific English and the Thesis composition, presentation and conclusions are concise, accurate and sufficiently documented to constitute a consistent and valid piece of graduate work. The Thesis is well-structured, and the author demonstrates a thorough understanding of the research topic. The initial sections provide proper acknowledgements, abstracts (in English and Polish) and a list of publications that resulted from the research carried out during the Ph.D. study. Two publications are listed, of which one somewhat relevant to the subject of the Thesis includes candidate's contribution and has been already accepted by a journal (no specific information provided), whereas the second report, which is still in the manuscript preparation phase, refers to the original research in this study with the Ph.D. candidate listed as the first author.

The dissertation begins by introducing the significance of Li-ion batteries in modern energy storage and the need for developing sustainable and high-performance electrode materials. The technical focus of this Ph.D. Thesis refers to the current S&T challenges related to Li-ion battery technology. $LiNiO_2$ is a popular cathode material for lithium-ion batteries due to its high theoretical capacity, relatively low cost, and environmental friendliness. The primary motivation of this study is well positioned regarding material performance limitations, which prevent its widespread adoption. Those important impediments are carefully addressed and discussed in Section 2 namely – (i) thermal stability and safety, (ii) cycle life and capacity fade, (iii) voltage fluctuations and phase transitions, (iv) nickel dissolution, (v) moisture sensitivity, (vi) cation mixing, (vii) oxygen loss, (viii) difficulty in synthesis, and (ix) high cutoff voltage.

To overcome these challenges, the Ph.D. the author has summarized various technical strategies such as - (i) doping with other elements (e.g., cobalt, manganese, or aluminum), (ii) surface modification and coating, (iii) developing new synthesis methods, and (iv) optimizing cell design and operating conditions. These challenges and potential solutions associated with $LiNiO_2$ cathodes in Li-ion cells provide a solid foundation for the proposed research plan and technical approach.

In operando Raman spectroscopy and confocal microscopy were chosen as primary tools in this work to study the structure, composition, and properties of composite $LiNiO_2$ cathodes in model Li-ion cells. In fact, Raman spectroscopy can provide information on the molecular structure and composition of materials. In the context of Li-ion battery cathodes, Raman spectroscopy is often used to **i**dentify phase composition in the cathode material, analyze lattice vibrations to understand its structural properties, such as crystallinity and disorder, and detect surface species, which can form during the synthesis or cycling of the cathode material.

The Thesis provides an extensive description of the basic Raman excitation principles and confocal optical setup. By combining Raman spectroscopy and confocal microscopy, the author could gain a more comprehensive understanding of the structure, composition, and properties of Li-ion battery cathodes. This reviewer just wishes that this section was put more in the context of vibrational behavior of Li-ion cathode materials, including $LiNiO_2$ to introduce the reader into unique intricacies of the analytical approach and relevant experimental approach specific for the chem-phys. properties of this class of materials. A more profound discussion of the shortcoming and advantages of the used experimental tools vs. other diagnostic methods would also be commendable.

Otherwise, the author clearly outlines the research objectives, which focus on employing operando Raman microscopy to study the structural and chemical changes occurring in next-generation positive electrode and electrolyte materials during electrochemical cycling. The undertaken experimental approach is a fine junction of expertise of the two academic centers: Warsaw University of Technology and University of Liverpool, which renowned for their work in the area of Li-ion batteries electrode materials, electrolytes and advanced characterization.

The author has employed a well-established technique (Raman spectroscopy) to investigate a relevant research topic (Li-ion battery materials). However, the study also presents some novel aspects, such as the application of operando Raman microscopy to next-generation cathode materials. The results presented in the dissertation are thorough and well-documented. The author provides a detailed analysis of the Raman spectroscopic data, which reveals valuable insights into the electrochemical behavior of the investigated materials. The discussion of the results is clear, and the author effectively relates her findings to the broader context of Li-ion battery research.

The $LiNiO_2$ material synthesis methods, *in situ* Raman spectroscopy cell configurations, overall experimental approach and advanced data processing machine learning algorithm (PRISMA) for the high-throughput analysis of Raman spectra have been reproduced from the prior work published in the open literature. The SEM images of the composite electrodes show a fairly uniform mixture of the $LiNiO_2$ composite electrode constituents. However, the images of the electrode cross section raise some concerns about the electronic and mechanical contact between the composite and Al current collector.

This raises concerns about the quality of the composite electrode manufacturing and its effect on the electrochemical performance in different test cell configurations, unrelated to the $LiNiO_2$ material intrinsic properties, not to mention the effect of Ti or Cu doping. Also, the resultant local electronic resistance barriers in the composite electrode percolation network could affect the uniformity of the electrode active material electrochemical response and its local spectral signature. These uncertainties together with the. corresponding data error analysis would substantiate the observed results trends and conclusions.

I would also argue that some conclusions may appear to be made based on limited data. This is especially concerning in study cases where the entire analysis is based on data obtained from just one characterization technique. This work would greatly benefit from some additional experimental evaluation using structure sensitive instrumental techniques such as common XRD, TEM etc.

In summary, the work reported by Eva del Campo Ortiz, M. Sc. is a solid example of fundamental study of the basic of properties of the $LiNiO_2$ cathode material, which reveals some new important information on the mechanism of its function and operation in Li-ion cells. The research has been performed well according to the widely accepted standards of the relevant scientific fields (electrochemistry, materials science, advanced characterization), and that originality and the significance of the outcomes with regard to the current state of the art meets the core academic standards. The dissertation demonstrates a sufficient level of scientific quality and originality.

I strongly suggest that this work and its key findings are organized in a series of manuscripts and submitted to peer-reviewed journals for further evaluation and discussion by the scientific community.

The dissertation presents two primary findings and conclusions:

1. **New insights into cathode material degradation:** The author provides evidence of structural and chemical changes occurring in doped and undoped $LiNiO_2$ materials, and their differences during electrochemical cycling, which contributes to the understanding of operation and degradation mechanisms, especially upon charging to high potentials.

2. **Operando Raman microscopy as a powerful tool:** The study demonstrates the potential of operando Raman microscopy as a powerful tool for investigating the electrochemical behavior of Li-ion battery materials in real-time.

Overall, the author has demonstrated a good level of scientific knowledge, and the study has the potential to contribute to the advancement of Li-ion battery research. The study provides valuable insights into the electrochemical behavior of next-generation positive electrode and electrolyte materials, and the author demonstrates a good understanding of the research topic.

Following a thorough evaluation, I confirm that the doctoral dissertation submitted by Ms. Eva del Campo Ortiz fulfills the requirements outlined in Article 187 of the Act on Higher Education and Science of 20 July 2018. I therefore recommend that it be approved for defense.

With my best regards,

Robert Kostecki