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Review of the doctoral dissertation of M. Sc. Eva del Campo Ortiz entitled *Operando Raman Microscopy Studies on Next Generation Positive Electrode and Electrolyte Materials*

The doctoral thesis was carried out under the supervision of Prof. Marek Marcinek from the Faculty of Chemistry of Warsaw University of Technology and Prof. Laurence Hardwick from the Department of Chemistry of the University of Liverpool. The research was supported by the DESTINY Doctorate Programme, founded by the European Commission through the Horizon 2020 Marie Sklodowska-Curie COFUND PhD Programme.

Novel efficient lithium–ion batteries receive broad attention due to the increasing demand for energy storage devices. The Raman operando studies are a prerequisite for understanding the working and possible mechanisms of degradation of electrode materials. The dissertation fits into this research trend. The thesis has been written in English in the form of a concise monograph. It begins with the general introduction to lithium-ion batteries' functionality and working principles (LIB), including the historical background of the current LIB research. Mrs. del Campo Ortiz focuses further on $LiNiO_2$ cathode materials, which are the main object of her studies. The structure and physicochemical properties of $LiNiO_2$ are described comprehensively, giving a good overview of the potential issues limiting the practical applications of such electrodes. Though, some minor inaccuracies could be found, like on page 13: The symbol "R-3m" means the trigonal space group with a threefold symmetry axis and symmetry plane, so the term "hexagonal R-3m" sounds confusing.

The next chapter describes the basics of Raman spectroscopy to emphasise the choice of this experimental technique for studying the electrode properties. The description of Raman basics is rather extensive. All basic features are well explained, though the division into the classic approach (chapter 3.1) and the quantum mechanics approach (chapter 3.2) is rather unnecessary, because these approaches overlap, and the Author herself puts the Schrödinger equation into the classic approach and the Placzek polarisation theory into the quantum part. It would be much easier for the reader if these two chapters were one. Despite this remark, the description of the Raman effect is clearly written in general and emphasises issues used in the experimental part of the thesis. The possible problems using Raman spectroscopy are very well described in Chapter 3.6. including the possible interferences on Raman signals and the in situ operando Raman spectroscopy principles. Chapter 3.7 focuses on the description of Raman operando studies and formulates the goal of the PhD project, which is the study of electrode properties in real time during the cycling process in order to understand the mechanisms that affect the battery longevity deeply.

Chapter 4 describes details of the Raman setup, such as the spatial resolution of the measurements. The most essential details are collected in the very clear Table. The Author thoroughly describes the experimental details of the spectroelectrochemical cell, methodically considering all issues important for the cell performance and the Raman experiment. The studied cathode materials were prepared at the Warsaw University of Technology and the University of Liverpool. The differences between the studied materials are collected in Table 4, where the cathodes studied in the operando experiments are marked in bold letters. Such a comparison facilitates the understanding of the experiment design. The data handling methods used in the PRISMA program are also thoroughly described.

The results and discussion of results begin with Chapter 5. A few of the studied materials are characterised by SEM to show the homogeneity and the influence of the calcination temperature on the morphology. Further most materials are tested for the long term stability and compared with the commercial $LiNO_2$ from BASF. Comparing Figure 19 and Table 4 explains the choice of materials studied further by Raman operando. The materials with the highest capacity, smaller capacity but good long-term stability and the one with lower capacity (LiNi)2_B1) were further studied. The choice is excellent as the reader can see, though the Author could describe it straightforwardly in the text. The following subchapters discuss the electrochemical properties, particularly the potential profiles in the spectroelectrochemical and coin cell configurations. It becomes evident that the free-standing electrodes are not suited for further studies and that the casting strip electrodes behave similarly to the coin cells. The galvanostatic and the differential plots are analysed. The effect of doping on the phase transition is clearly shown. Further, the effect of additives on the electrolyte is studied and described well.

Subchapter 5.6 shows basic features of Raman spectra of powdered cathode materials and discusses the choice of laser wavelength for further operando studies. The Author convinces that the 633nm laser causes less heating, less fluorescence background, and penetrates deeper into the sample. These are good arguments for choosing this wavelength. Though, the remark that "compared to 532 nm, 633 nm laser line offers a better signal-to-noise ratio" is surprising, because Figure 29 shows the opposite. Further, the details and challenges of the Raman data interpretation are described, showing how much work has been put into this work.

Chapter 6 presents general remarks about the interpretation of Raman data from the operando experiments. Finally, Chapter 7 describes operando Raman studies of the selected $LiNiO_2$ materials. Generally, the reversible changes were observed for the $LiNiO_2$_5 cathode except the band position of the Eg mode, which showed a 5 cm^{-1} shift after the whole cycle in comparison to its initial value, which was interpreted as the effect of vacancies formed upon the delithiation. The Author lists other reasons for the band shift, such as cation mixing. Such an interpretation agrees with observations of similar materials in the literature. The interpretation of Raman intensities relating them to phase transitions and the Jahn-Teller effect is very interesting. It is very well discussed and compared with the literature. The results for the doped materials (Figures 39 and 40) are clearly different from those for undoped LiNiO, which the authors correlate with differences in phase transitions, which is an elegant explanation of these changes. Other studied cathodes show less reversible characteristics.

The minor critical remark concerns the citation Quentin et al. (https://doi.org/10.1002/aenm.202401413). Quentin is the first name. This person's family name is Jacquet, and the family name is usually used in the citation.

Figures 35 and 42 present results for the materials prepared at identical synthesis conditions. The differences in analysis by PRISMA are surprisingly different, which the Author attributes to poor focus. If one compares Figures 33 and 44, it is visible that in 44, the intensities of the electrolyte bands are much higher. Can this influence the results from PRISMA?

Chapter 7.9 presents a novel approach to analysing the Raman operando data. The multivariate analysis is applied to find components in the data set for $LiNiO_2$_A. The three identified components correspond to the lithiated and delithiated $LiNiO_2$, and the remaining part is attributed to the electrolyte changes. A plot of the component contents versus the capacity (Figure 55) reproduces changes expected upon cycling. Such data presentation is an original idea and facilitates the interpretation of data.

In the Conclusions Chapter, Mrs. del Campo Ortiz emphasises that materials showing low variation in positions and intensity of Raman peaks are characterised by high performance. She also notices that the reversibility of Raman changes does not always correspond to the highest electrochemical performance. She proposed further research to confirm her findings. There are several important conclusions about the method of preparation of materials based on the combination of electrochemical and spectroscopic experiments.

I would like to emphasise that the thesis presents valuable data. Collecting such data sets required several tedious and time-consuming experiments. Handling such big data sets is not simple. The Author of the thesis showed several ideas on how to do that, starting from the individual fitting of Raman bands, using the PRISMA package and finally employing the multivariate analysis to illustrate the structural changes of the cathode during cycling. The work contains essential research novelty. It is also important for practical applications. Mrs. Del Campo Ortiz has co-authored one scientific publication before the thesis was completed. The following publications are probably prepared.

There are two points, which I hope I will have the opportunity to discuss during the defense of the thesis. These are:

1. Can you correlate the changes in the Raman intensities of the Eg and A1g modes with the long-term stability of the cathode in general?
2. Why could the Raman experiments, which went out of focus, not be repeated?

Considering the very good scientific level of the work and important elements of scientific novelty, I conclude that the reviewed dissertation meets the requirements for doctoral theses specified in Art. 187 of the Act of July 20, 2018 Law on Higher Education and Science (Dz. U. z 2024 r., poz. 1571 with later changes). Therefore, I am recommending Mrs. Eva del Campo Ortiz's admission to the next stages of the doctoral process.

Sincerely,

Podpisany elektronicznie przez
Barbara Jadwiga Pałys
16.09.2025
9:30:25 +02'00'