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Report: Operando Raman microscopy studies on next generation positive electrode and electrolyte materials
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The PhD thesis titled "Operando Raman Microscopy Studies on Next-Generation Positive Electrode and Electrolyte Materials" explores the synthesis of $LiNiO_2$ using four different methods. Each sample was compared with a commercial material from BASF. Scanning Electron Microscopy (SEM) was used to analyse particle size distribution and morphology, linking these characteristics to electrochemical performance. Among the synthesised materials, LiNO2_B (Liverpool University) showed higher specific capacity, while LiNO2_C demonstrated superior long-term cycling performance, comparable to the BASF sample. The study also investigated doping $LiNiO_2$ with titanium (UoL) and copper (WUT), and found that adding 2% LiTDI to the electrolyte improved long-term cycling stability.

From the literature the structural phase transitions associated with the lithium extraction and insertion processes during electrochemical cycling. It has been reported that the hexagonal structure (H1) present during OCP transforms into monoclinic (M) structure followed by two further phase transitions into (H2) and finally the (H3) structures. The aim of the thesis is to use Operando Raman spectroscopy to characterise the different samples during galvanostatic cycling to identify the various phase transitions to improve the electrochemical performance of the material and to research how the synthesise and doping modify the structural properties of $LiNiO_2$.

The thesis begins with a brief introduction, providing justification for the choice of material and outlining the theory behind lithium-ion batteries. However, it lacks a clear statement of the thesis aims, which would have enhanced the understanding of the work. This is followed by a detailed section on "Ni-rich layered oxides and their properties". The structure of this chapter is clear and well written. It describes limitations identified with $LiNiO_2$ and the benefits with doping the material. Chapter 3 introduces the theories behind Raman spectroscopy and data analysis. This chapter is clearly written and easy to apprehend. It also includes a short discussion on the limitations with Raman spectroscopy. However, a more in-depth discussion around limitations regarding the operando Raman measurements is missing. Chapter 4 describes the different synthesis methods applied in the thesis, which is based on traditional solid-state synthesis techniques. One of the novelties with this thesis is the application of the PRISM app, which allow close to "on-the-fly" measurements by removing the manual step previously needed to analyse the peaks in the Raman spectra. The thesis also use "Multivariant curve resolution" to perform "automated" deconvolution of the peaks to follow how the different components of a peak develop as a function of electrochemical cycling.

The result section is divided into three chapters. Starting with chapter 5 that discuss the characterisation of the as-synthesised materials comparing how $LiNiO_2$ perform electrochemically. It also presents the Raman characterisation of $LiNiO_2$ as pristine material and with electrolyte in the operando EL-Cell together with a justification of the use of the PRISM app in further data analysis. This chapter is clearly written but it lacks a discussion on the chemical purity of the material. This is particularly true when introducing the doped materials. It is acceptable that the thesis is not covering techniques, such as X-ray diffraction (XRD) or X-ray Absorption spectroscopy (XAS), however, a more in-depth discussion how impurities would be detected using Raman spectroscopy is missing. The spectrum for the pristine material presented only includes the A_{1g} and E_g peaks associated with $LiNiO_2$, which is an indication of phase purity, but this is not discussed in this chapter. Chapters 6 is short introducing the interpretation of the operando Raman spectra for $LiNiO_2$, followed by Chapter 7, which discuss in detail the performance of the different material and how the doping and additive changes the Raman spectra during electrochemical cycling, linking to the structural properties of the material. Both Chapters 6 and 7 are clearly written and figures are easy to read and discussed in detail in the text. The interpretation of the data is sound and contributes to the understanding of these materials, while introducing new solutions to how to improve the properties of $LiNiO_2$ and pushing the research field forward. This is high quality results and of interest to both industry and academia.

The final chapter, “Conclusion and Outlook,” give a good summary of the work presented in the thesis but it is too brief. It lacks a thorough summary of the work and a critical analysis of the results. The chapter should also outline future research directions and explain how the findings could be applied in industry. While the use of additives showed promising benefits, the thesis notes that BASF commercial powders did not improve cycling performance with these additives. It would be valuable to explore other additives and discuss how the research could be expanded and made relevant to industrial applications.

Overall, this thesis is well-presented and contains novel results that contribute meaningfully to the development of Ni-rich layered oxides. The use of Operando Raman spectroscopy to characterise the materials is particularly innovative, as it is not a standard technique widely available to research groups. Designing the cells and conducting the measurements is challenging, and interpreting the data adds further complexity. The candidate has produced high-quality work, and the results are impressive. The thesis is well-written and professionally presented. It is on the borderline of distinction; with a more comprehensive conclusion-including a deeper discussion of future research directions—and clearer articulation of the aims in the Introduction, it would merit a distinction.

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