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REVIEW OF THE DOCTORAL DISSERTATION
OF YU-SHENG CHEN

The doctoral dissertation prepared by Yu-Sheng Chen entitled „*Comparative analysis of synthesis routes and aluminum doping effects on NMC type cathode material*" has been performed under supervisions of Prof. Wladyslaw Wieczorek (Warsaw University of Technology) and Prof. Dr. Robert Dominko (Slovenian National Institute of Chemistry). The doctoral thesis has been carried out in a collaboration between Warsaw University of Technology and Slovenian National Institute of Chemistry within *Destiny – Marie Curie European Doctoral Program*.

This dissertation focuses on important aspects of the battery material research, in particularly, with respect to the high energy density requirement. Because of the reasonably high energy and power densities and the moderately low cost of lithium-ion batteries, they are the key energy-storage technology to meet the needs of next-generation electric vehicles. Special attention has been paid to studies of the nickel-rich layered (NCM) cathodes, such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811), for the reasons that they are promising candidates, offering broad range of advantages due to their high specific capacities. The Author describes synthetic methods and studies effects of aluminum doping on nickel-manganese-cobalt (NMC) 811 cathode materials, with a focus on improving their structural and electrochemical stability. Yu-Sheng Chen concentrates on comparison of two synthesis techniques: the hydroxide co-precipitation followed by solid-state calcination for creating polycrystalline (PC) cathodes, as well as the molten salt calcination for single-crystalline (SC) cathodes. The Author focuses on the introduction of aluminum dopants at various stages of these processes to understand how they affect the structural, morphological, and electrochemical characteristics of NMC cathodes. The results, which have been described and discussed in the dissertation, are certainly of importance to the development of high-energy lithium-ion batteries. The obtained results are also of significance from the view-point of the development of materials chemistry and engineering.

The doctoral dissertation of Yu-Sheng Chen is organized in a way that it consists of four chapters. The chapters are preceded by Acknowledgements, Abstract of the thesis in English and in Polish, List of publications, Table of contents, and List of abbreviations. The first part is *Introduction* (Chapter I), in which crucial items of information concerning batteries, cathodes for electric vehicles (EVs) and overview of Ni-rich cathodes are provided. The Author's attention is focused on comparison single crystalline (SC) with polycrystalline (PC) cathodes, mainly with respect to the degradation mechanisms, synthesis and modification of SC and PC Ni-rich cathodes. Single-crystal and polycrystalline Ni-rich cathodes exhibit distinct electrochemical properties, thus making them promising candidates for high-energy lithium-ion batteries. In the reviewer's opinion, the literature part of the work addresses the most important achievements in the above-mentioned fields. At the end of Chapter I, the Author describes techniques, methods, and procedures used to evaluate properties of Nickel-Manganese-Cobalt (NMC) cathode materials, such as X-ray diffraction (XRD), Inductively Coupled Plasma (ICP), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Electron Energy Loss Spectroscopy (EELS), and galvanostatic cycling as a fundamental electrochemical technique used to evaluate the performance of battery electrodes. In Chapter II, the Author concentrates on synthesis and preparation of NMC811 cathodes. The Author discusses the initial experimental setup for precursor synthesis and synthesis parameter optimization. At the end this Chapter, the Author describes and compares two synthetic techniques: hydroxide co-precipitation followed by solid-state calcination for creating polycrystalline (PC) cathodes, and molten salt calcination for single-crystalline (SC) cathodes. It is noteworthy that the Author has systematically incorporated aluminum dopants into these materials by integrating aluminum sulfate ($Al_2(SO_4)_3$) in stoichiometric proportions of 1–2 mol% with other transition metal salts. In Chapter III, Yu-Sheng Chen shows results and discusses properties of selected samples of NMC811. Fifteen samples have been subjected to analysis to estimate how various doping levels and the synthesis methods influence their performance. The Author describes analytical techniques employed to evaluate the structural, chemical, and electrochemical properties of the synthesized cathode materials. The contents of Chapter IV refer to future studies. Yu-Sheng Chen concentrates on investigating the impact of various electrolyte additives. The Author has studied the effect of different concentrations (1%, 2%, and 5%) of DTDPh (1,3,2-benzodioxathiole 2,2-dioxide) added to the commonly used LP40 (1M $LiPF_6$ in EC/DEC 1:1 wt) electrolyte. The sample with 2% DTDPH demonstrated enhanced cycling stability, with a slower decline in capacity, when compared to the baseline of the NMC811 sample without additives. According to the Chen’s opinion, the future directions for improving NMC-based cathodes involve not only optimizing electrolyte additives but also advancing the solid-state battery technology by increasing the nickel content, while maintaining stability, as well as exploration of new dopants and coatings. The Author states that these research efforts aim at pushing the boundaries of energy density, cycle life, and safety, ultimately supporting the development of more powerful and reliable lithium-ion batteries. At the end of the doctoral dissertation, Yu-Sheng Chen places references in a form of the list of 132 publications.

Going to the substantive evaluation of the dissertation, I would like to mention the important observations and achievements described therein. Yu-Sheng Chen examined different approaches to synthesizing NMC811 cathode materials in two forms: polycrystalline and single-crystal structures. The Author specifically analyzed how aluminum could be introduced as a doping element, utilizing both co-precipitation techniques and high-temperature solid-state reaction processes. The important observations are as follows. The samples, which were crystallized in the R-3m space group, showed sharp peaks indicative of high crystallinity (based on X-ray powder diffraction). Furthermore, doping using solid-state methods led to sharper peaks, possibly due to the introduction of small amounts of aluminum compounds. Based on Scanning Electron Microscopy images, it was postulated that, regardless of the synthesis method, the particles formed irregular agglomerations; and the chemical composition analysis (by inductively coupled plasma) confirmed that the elemental ratios of nickel, cobalt, and manganese matched in all samples theoretical stoichiometric values, though the aluminum doping during co-precipitation caused slight deviations. The galvanostatic cycling experiments demonstrated that the aluminum doping influenced positively the capacity and rate performance of the polycrystalline NMC cathode, particularly at a doping level of 2% mol.

I am convinced that the work has been prepared correctly, and I have no doubt that the measurements have been carried out carefully. Furthermore, the results obtained are convincing. A similar statement applies to conclusions.

I have got a few questions or comments that could be easily answered or explained during the doctoral defense.

(1) What was the accuracy of the elemental analysis measurements? Are the proposed stoichiometries reliable?

(2) More information how the degradation mechanism of samples changes depending on stoichiometry and doping would be helpful.

(3) Novel aspects of synthetic procedures, relative to the existing literature, should be more strongly emphasized.

In conclusion, I would like to express my appreciation to the efforts of the Author, emphasize high scientific value of the obtained results and evaluate very positively the doctoral dissertation. Furthermore, I would like to state that the dissertation meets the formal and customary criteria and expectations for doctoral works in the area of exact and natural sciences and chemistry discipline. Thus I am convinced that Yu-Sheng Chen should be admitted readily to the public doctoral defense at Warsaw University of Technology.

Iwona Rutkowska