Łukasiewicz
Instytut Metali Nieżelaznych

Oddział w Poznaniu

Prof. dr hab. inż. Grzegorz Lota
Sieć Badawcza Łukasiewicz - Instytut Metali Nieżelaznych
Oddział w Poznaniu
ul. Forteczna 12, 61-362 Poznań
e-mail: grzegorz.lota@imn.lukasiewicz.gov.pl

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REVIEW OF THE DOCTORAL DISSERTATION OF CLAUDIA JANETH LIMACHI NINA

The doctoral dissertation prepared by Ms. Claudia Janeth Limachi Nina entitled "Sustainable and green batteries: fluorine-free lithium-ion cells" has been performed under supervision of Prof. Leszek Niedzicki and Prof. Michel Armand at Warsaw University of Technology, Faculty of Chemistry.

The Green Deal targets the European Union to be carbon neutral by 2050. Electrochemical power sources, which can safely provide clean energy, play an important role in achieving climate neutrality. Therefore, new electrochemical energy storage systems are constantly being researched and existing systems are being modified to be more environmentally friendly, but also to improve the operating parameters and the price of the end product. For more than 30 years, Li-ion batteries have been one of the most important electrochemical energy storage systems. Although there are now more of these systems in production than lead-acid batteries, the recycling of Li-ion batteries is still a problem. The thesis submitted for review is therefore important not only for improving the performance of Li-ion batteries, but also for protecting the environment.

The dissertation was submitted in the traditional form of a monograph and comprises 287 pages, 93 figures, 1 appendix figure, 58 tables, 5 appendix tables and 406 references. Ms. Limachi Nina's doctoral thesis consists of an abstract in Polish and English, a list of abbreviations, a table of contents, 14

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
61-362 Poznań, ul. Forteczna 12, Tel: +48 61 27 97 800
E-mail: claio@imn.lukasiewicz.gov.pl | NIP: 631 020 07 71, REGON: 000027542, BDO:000011457
Sąd Rejonowy w Gliwicach, X Wydział Gospodarczy | KRS: 0000853498
Bank SANTANDER nr konta: 73 1090 1346 0000 0000 3400 0300 PL
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chapters. Chapter 12 is a conclusion, chapter 13 is references and chapter 14 is appendices.

In the first chapter, the author presented the historical background of Li-ion batteries and the problems associated with the use of fluorine-based compounds in electrolytes and as binders for electrode materials. She presented the problems associated with the use of cobalt and nickel as cathode materials in Li-ion cells and the limitations associated with the use of graphite as an anode material. In the chapter, she presented the research objective, the research methodology related to the electrolyte and the electrode material used in the preparation of coin cells and pouch cells.

In the next 8 chapters of the theoretical part (chapters 2-9), the Ph.D. student described the processes related to energy storage in Li-ion systems in great detail, mainly using literature from the last 10 years. She went on to explain the principle of how a Li-ion battery works. She described in detail the salts, solvents and additives used to prepare the electrolytes used in Li-ion cells. She described cathode materials based on the nickel, manganese, cobalt system, but also LFP, LMFP, LMO and other types. She presented a broad characterisation of anode materials, from the use of graphite to the use of silicon, LTO and other systems. She described the binders used to make fluorine-based electrode materials (PVDF), but also those such as CMC and SBR that can be dissolved in water instead of toxic NMP. In the last two chapters of the theoretical part, the author focused on the degradation process in the Li-ion cell, the formation of the solid electrolyte interface (SEI) passive layer, and the determination of the mass ratio of positive to negative electrode material in a complete Li-ion cell to improve the cell's capacitive efficiency.

The experimental part of the thesis was presented by the Ph.D. student in two very extensive chapters (chapters 10 and 11). In chapter 10, the author described in detail the preparation of the fluorine-free salt LiPCP - lithium 1,1,2,3,3-pentacyanopropenide (based on the patent of Prof. Niedzicki), the electrolytes, cathode and anode materials used in the work, and the construction of coin cell and pouch cell test systems. It provided procedures for electrochemical and rheological testing, as well as electrode surface testing using a scanning electron microscope (SEM).

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In chapter 11, the Ph.D. student presented the results of her research. When investigating the conductivity of different solutions over a wide temperature range from 0°C to 50°C, she obtained the highest conductivity for the fluorine-free solution (0.8 mol kg^{-1} LiPCP in 3EC:7DMC) at a temperature of 20°C - 9.63 mS cm^{-1} (Table A.2). This electrolyte was selected for further research and was used to test cathode and anode materials and a fluorine-free Li-ion cells. As a result of the scaling, the Ph.D. student carried out tests from the Swagelok® system to coin cells to pouch cells. She demonstrated that fluorine-free systems can be scaled and that water-soluble systems can be used instead of binders such as PVDF. She modified the anode materials by using silicon oxide composite instead of graphite. Unfortunately, the use of silica composite did not improve the capacitive parameters of the cell during cyclability. The Ph.D. student used LFP as the cathode material, a material that does not contain critical elements such as cobalt and nickel. As part of her dissertation, the Ph.D. student demonstrated that it is possible to develop a more environmentally friendly Li-ion batteries without significantly affecting the cell's capacitive parameters.

Despite the very good assessment of the dissertation, I have a few questions that I hope the doctoral student will answer during the defence:

- Why did a Ph.D. student use the term molality (mol kg-1) instead of molarity (mol L-1) in her work?
  All the more so as the theoretical part refers to literature data using molarity (Tables 8-12).
- What was the reason for using different concentrations for the $LiPF_6$ (1 mol kg^{-1}) and LiPCP (0.8 mol kg^{-1}) solutions when comparing the conductivity test results?
- What causes the increase in anode potential during the first 20,000 seconds of charging (Figure 69)?
- Why is pitting corrosion visible on the aluminium current collector of the fluorine-free Li-ion battery (Figure 90a)?
- Did the Ph.D. student carry out corrosion research on a cathodic current collector?
- Does the Ph.D. student think that the fluorine-free Li-ion battery system presented has a chance of being commercialised?

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- Please present the candidate's academic achievements during the defence.

In summary, I think it is important to emphasise the practical importance of the results obtained. Taking into account the scientific value, I rate the dissertation high. Therefore, I am of the opinion that Ms. Claudia Janeth Limachi Nina is prepared for further scientific work and that the examined dissertation fully meets the statutory criteria and should be processed in further stages of the doctoral procedure (Ustawa z dnia 20 lipca 2018 r. - Prawo o szkolnictwie wyższym i nauce: Dz. U. z 2022 r. poz. 574 z późniejszymi zmianami).

Considering the importance of the research, the quality, high scientific value and potential application of the results obtained in the field of the development of electrochemical power sources, I recommend awarding the doctoral dissertation of Ms. Claudia Janeth Limachi Nina by the Council of the Chemistry Science Discipline of the Warsaw University of Technology.

Signed by / Podpisano przez:

Grzegorz Józef Lota

Date / Data: 2025-02-16 22:58

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
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