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Review of the Doctoral Dissertation by M.Sc. Eng. Claudia Janeth Limachi Nina, entitled "Sustainable and Green Batteries: Fluorine-Free Lithium-Ion Cells"

This review was prepared based on the letter dated November 20, 2025, addressed by the Chairman of the Scientific Discipline Council of Chemical Sciences, Prof. dr hab. inż. Wojciech Wróblewski of the Warsaw University of Technology. The thesis was prepared under the guidance of two supervisors: Dr hab. inż. Leszek Niedzicki, prof. PW, and Prof. Dr. Michel Armand. It was structured in a standard book-like format.

The main focus of the thesis centers on the development of fluorine-free lithium-ion (Li-ion) cells, representing a possible, significant step toward the production of sustainable and environmentally friendly batteries. Li-ion technology plays a pivotal role in the ongoing energy transition. These cells not only power smartphones and laptops but have also become indispensable for electric vehicles and, in recent years, a critical component of emerging electrochemical energy storage systems. These systems are essential for integrating intermittent renewable energy sources, such as solar and wind, into reliable power grids. Undoubtedly, the high energy density, lightweight design, and long cycle life of Li-ion batteries have revolutionized how people store and utilize energy. Global production of Li-ion cells, encompassing various chemistries, sizes, and shapes, has shown exponential growth, with billions of units already manufactured. However, the widespread adoption of Li-ion technology comes with numerous challenges, particularly concerning the use of environmentally harmful and hazardous chemicals in the commercialized designs. Recycling these cells has become a crucial issue, as improper handling could undermine the environmental benefits of this technology. It is known that among the most problematic substances are fluorinated compounds, such as lithium hexafluorophosphate ($LiPF_6$), a widely used electrolyte salt, and polyvinylidene difluoride (PVDF), a common binder. As rightly identified by the Author, eliminating fluorine from Li-ion batteries is critical, not only to address environmental concerns, but also to enable more effective recycling and enhance the overall sustainability of the technology. This task, however, is highly challenging. Fluorinated compounds play a vital role in ensuring the performance and stability of Li-ion cells, and finding alternatives with suitable physicochemical properties has proven very difficult. **From this perspective, the issue undertaken by M.Sc. Claudia Janeth Limachi Nina is highly relevant, scientifically compelling, and technologically significant. The challenge is undoubtedly demanding and, by its very nature, complex.**

The thesis was written in English, following a standard structure that includes an abstract (also provided in Polish), nine chapters dedicated to the literature review, one chapter focused on the methodology and description of the experiments (divided into sections A, B, and C with corresponding sub-chapters), and an extensive main chapter presenting the Author's original results, also divided into sections A, B, and C (and numerous sub-chapters). This is further supplemented by a conclusions chapter, an extensive list of references (over 400), appendices, and lists of figures, tables, and abbreviations, along with acknowledgments. The entire document spans over 280 pages, with chapters 1-9 covering pages 19 to 117.

After a brief introduction to the topic, the Author clearly outlined the main problem and research objectives in the initial chapter, titled "Importance and Objectives of Developing Green and More Sustainable Lithium-Ion Cells". It is immediately evident to the reader that, while the core focus lies in the development and investigation of a novel fluorine-free lithium salt (intended for electrolyte preparation), both electrodes, made from selected active materials, must also be processed in an aqueous environment using alternative binders. Simultaneously, a more practical goal is to demonstrate the feasibility of the design through the assembly and testing of coin and pouch cells. For the experiments, the Author selected olivine-type phosphate cathode materials, as well as synthetic graphite and silicon oxide/carbon composite (SOX) anode materials. In addition to defining the aims, M.Sc. Claudia Janeth Limachi Nina also provided key details about the tasks involved and an overview of the general methodology in this chapter.

The subsequent chapters provide an overview of selected topics related to energy storage, lithium-ion batteries, nonaqueous electrolytes, cathode and anode materials, as well as binders and solvents used in electrode preparation. The literature review is further enriched with a discussion on degradation mechanisms in Li-ion batteries and the fundamental technological aspects. Overall, the logical arrangement of the chapters and their respective subchapters is well-structured, and their content aligns with the topics addressed in the dissertation. The scientific depth and quality of the language used in the discussion are satisfactory and do not raise any significant concerns. The Author has selected timely and relevant issues, presenting them in a clear and concise manner. However, given the large number of subsections, each addressing different groups of materials, it is understandably challenging to provide an in-depth and comprehensive discussion of all the compounds and issues covered. At this point, the reviewer feels compelled to note that devoting a similar level of attention to numerous groups of candidate compounds and materials may not be the optimal approach for the literature review section of a doctoral dissertation. This strategy makes it difficult to provide a deep and thorough discussion of each topic without exceeding a reasonable page count for the thesis. This approach is likely also the reason for the relatively limited number of figures (graphs, schematics, etc.) cited from the literature, which makes the whole section less engaging for the reader, who is often compelled to consult the numerous referenced sources for additional clarity or information.

Chapter 4, titled "Nonaqueous Electrolytes for Lithium-Ion Batteries," provides valuable insights into the critical properties of lithium salts from the perspective of nonaqueous liquid electrolyte formulation. It includes a detailed description of the most commonly used and studied lithium salts, including fluorine-free alternatives, and is supplemented with tabulated data on conductivity and aluminum passivation potential (measured at near room temperature with typical solvents). The chapter also lists the advantages and drawbacks of specific salts, describes common solvents, and discusses various electrolyte additives. In the reviewer's opinion, however, the most interesting and scientifically significant part of Chapter 4 is the section dedicated to the criteria essential for designing new lithium salts for liquid electrolytes, with composition and design principles gathered in Figure 4. Addressing the outlined challenges, such as simplified synthesis, reduced hazards, hydrolysis resistance, thermal stability, solvent compatibility, low-temperature performance, and solid electrolyte interphase (SEI) formation, would undoubtedly enable the successful development of a novel and effective lithium salt.

Chapter 5 presents an overview of positive electrode materials, divided into sub-chapters focusing on layered (NMC-type) oxides, polyanion olivine-type materials, and spinels. The Author correctly identifies the key challenges associated with each group of candidate electrode materials, providing valuable, though somewhat brief, descriptions of potential strategies to address these issues. For instance, in the case of $LiFePO_4$ olivine, methods for improving electronic conductivity, lithium-ion diffusion, tap density, and low-temperature performance are discussed. However, the sub-chapters remain relatively concise and lack graphs or figures, which would have been helpful in enhancing the reader's understanding of the fundamental issues. A similar approach is evident in Chapter 6, which discusses a wide range of negative electrode materials. While the descriptions are informative, the lack of visual aids similarly impacts comprehension. The final sub-chapters in both sections, which explore the sustainability perspectives of cathode and anode materials, are particularly engaging and provide a more interesting context within the scope of the thesis. The functions and types of binders are discussed in Chapter 7, which includes also a comparison between conventional and aqueous binders, as well as insights into future perspectives for potential improvements and modifications.

Chapter 8 provides valuable information on various known degradation mechanisms that lead to capacity fade in cells during cycling. The systematic approach used to present this data is particularly noteworthy and enhances the clarity of the discussion. The final in this section Chapter 9 offers only a brief overview of selected technological issues related to the manufacturing of electrode layers and cells.

A review of the discussed part of the dissertation indicates that M.Sc. Claudia Janeth Limachi Nina possesses a general and up-to-date theoretical knowledge required for a candidate applying for the doctoral degree in the discipline of Chemical Sciences. However, it is the role of the reviewer to point out any questions or weaker aspects of the description, which are outlined below in the form of a list of detailed comments regarding the theoretical section of the dissertation.

1. The list of abbreviations is helpful, however, the absence of a corresponding list of symbols leaves the reader without proper explanations in some instances. For example, the equations in Table 1 are not clarified, even though standard symbols were used in their formulation.
2. The Author states on page 26 that "(...) the voltage of lithium batteries is significantly higher than that of Pb-acid and Ni-metal hydride, due to lithium being the most electropositive element (...)". This statement is questionable, as the cell voltage depends on both electrodes. A more in-depth explanation is needed to adequately justify this claim.
3. The Author has largely omitted the critical aspect of the transference numbers of anions and cations in liquid electrolytes. This omission is surprising and negatively impacts the overall discussion on the properties of various salts and electrolytes.
4. What is the meaning of the conductivity data for a TMO content of 100 vol%, as presented in Table 7?
5. It is unclear (page 55, Table 14) under what conditions the reported specific capacity was measured. Additionally, the claim that the average potential is almost independent of the chemical composition of NMC is questionable and requires further clarification.
6. In the reviewer's opinion, the thesis would benefit from a more in-depth discussion of the relationship between the intrinsic physicochemical characteristics of the materials selected for the experiments and their functional properties. This applies not only to the lithium 1,1,2,3,3-pentacyanopropenide (LiPCP) salt but also to the selected materials such as $LiFePO_4$, $LiMn_{0.6}Fe_{0.4}PO_4$, synthetic graphite, silicon oxide composites, and binders. While the initial Chapters 1-9 are generally informative, a more explicit correlation between the intrinsic properties of these materials and their observed performance would enhance the discussion. In other words, although the thesis provides substantial information on "how it is," it sometimes lacks sufficient insight into "why it is that way."

Chapter 10 of the thesis (pages 119-130), titled "Experimental Section, Materials and Methods," provides detailed information on the preparation and investigation of selected fluorine-free electrolytes, the fabrication of electrode layers and cells, and the surface characterization of optimized electrodes. Sections A, B, and C are further divided into sub-chapters where the Author outlines the preparation and measurement procedures, as well as the experimental conditions. Overall, the chosen methods are highly relevant to the scope of the thesis and reflect current experimental approaches for evaluating the ionic conductivity of liquid electrolytes, passivation phenomena, the electrochemical stability window, and the morphological characteristics of electrode layers. The methodology employed for processing electrode layers and studying their electrochemical properties, such as reversible capacity and rate capability, is appropriate and consistent with the objectives of the dissertation. The construction and testing of coin and pouch cells were also carried out effectively. Given that the active materials used for preparing electrode layers were commercially sourced, it is understandable that techniques typically used for structural and surface characterization of solids were practically not applied. It is worth noting that a significant portion of the methodology involves technical and engineering-oriented procedures and tests, which, while not purely scientific, are nonetheless highly relevant to the dissertation's objectives. Although it is not explicitly stated, it can reasonably be assumed that M.Sc. Eng. Claudia Janeth Limachi Nina designed and conducted most of the experiments herself, which further underscores her hands-on involvement in the research.

In summary of this part of the review, the reviewer would like to highlight the appropriateness of the selected measurement techniques, the logical organization of the research tasks, as well as the proper planning and execution of the experiments. Taken as a whole, this indicates that M.Sc. Eng. Claudia Janeth Limachi Nina has demonstrated the required ability to conduct independent scientific research. Naturally, some questions arise in this context as well, which are presented below in the accompanying list.

1. Why were no methods employed to characterize the formation of the SEI when using novel LiPCP-based electrolytes? Is this already well-established knowledge concerning the anode materials used? A similar question can be raised regarding the formation of the CEI.
2. What was the purity of the synthesized LiPCP? Is this salt stable during prolonged storage?
3. For the electrode layers used in the pouch cells, how uniform were the thickness and the local mass loading of the anodes and cathodes?
4. The methodology description has a shortcoming in that it often lacks detailed information regarding the potential occurrence of measurement errors and their estimated magnitude.

It should be emphasized, however, that the above remarks are largely of a technical nature and stem more from the reviewer's curiosity. Considering the type of samples and the objectives of the research, it should once again be highlighted that the selection of methods and their scope of application are appropriate, and the execution of the experiments is proper.

The next chapter of the doctoral dissertation (Chapter 11, pages 133-249), which presents the Author's original research results, constitutes its main part. As previously mentioned, it is logically divided into three sections and numerous subsections.

Initially, M.Sc. Eng. Claudia Janeth Limachi Nina conducted research to develop a novel LiPCP-based electrolyte, exploring different salt concentrations (0.1-1.2 mol kg^{-1}) and various solvents, commonly abbreviated as EC, DMC, DEC, and EMC. The ionic conductivity studies, performed over a temperature range of 0-50 °C and including reference data for $LiPF_6$-based electrolytes, allowed for the determination of total conductivities. However, as previously noted, no transference number data were reported. Linear sweep voltammetry demonstrated that additives such as vinylene carbonate (VC) and acetonitrile (AN) are beneficial for extending the high-voltage stability window of the electrolyte. Also, data obtained from impedance spectroscopy were used to analyze variations in the resistance of the passivation layer on lithium electrodes with the selected electrolytes. These results revealed differing behaviors between LiPCP- and $LiPF_6$-based electrolytes, which were noted and commented upon, though not explored in detail.

The subsequent parts of Section A present results on the fabrication of various cathodes ($LiFePO_4$ and $LiMn_{0.6}Fe_{0.4}PO_4$) and anodes (synthetic graphite and silicon oxide-based) in Swagelok cells, along with the corresponding cyclic voltammetry and other electrochemical tests. The selected electrolyte consisted of 0.8 mol kg^{-1} LiPCP in a solvent mixture of EC:DMC (30:70 wt%) with 1 or 5 wt% VC additive. Through the optimization of electrode constituents and their ratios, optimal designs were identified. Notably, when compared to the standard $LiPF_6$-based electrolyte, the data for cells utilizing the new electrolyte are quite promising. However, the results also revealed that $LiMn_{0.6}Fe_{0.4}PO_4$ poses significant challenges, likely requiring entirely new electrolyte compositions to mitigate the observed high polarization. It should also be emphasized that the studies conducted on cells with a reference lithium metal electrode are crucial for further research and the optimization of so-called full cells.

Section B is extensive and focuses on the more technology-oriented aspects of fabricating electrodes for larger pouch cells. Scaling up any new technology is inherently challenging and demands an interdisciplinary approach, often requiring numerous additional experiments. This complexity is well-reflected in the structure of this section, which includes multiple sub-chapters addressing key aspects, such as the relationship between the formulation of anode and cathode slurries and their rheological properties and pH, thickness and area loading measurements, the role of calendaring, surface characterization using scanning electron microscopy, electrode sheet resistance evaluation, galvanostatic performance testing, and more. While these studies are somewhat less compelling from a purely scientific standpoint, they are essential for achieving the main goal of the thesis. This is highlighted in sub-chapter 11.11, which presents the electrochemical characterization of the proposed and developed fluorine-free pouch-type Li-ion cells, tying together the practical advancements made in this section. In this section, the Author presented data on the role of the critical parameter known as the N/P ratio, and elaborated on the charge/discharge curves of the constructed fluorine-free pouch cells. Notably, three-electrode configuration cells were also tested, allowing for independent monitoring of the voltages of both working electrodes. This approach provides valuable insights into the ongoing electrochemical processes. For instance, it enables the detection of potential negative voltage on the anode, which is often associated with the detrimental lithium plating effect. The Author also included significant data regarding reactions occurring at low potentials, highlighting irreversible processes and capacities exceeding theoretical limits. These effects were attributed to unstable SEI formation, electrolyte reduction, irreversible lithium consumption, and possibly, assembly inaccuracies. The final Section C provides comprehensive results on the surface properties of pouch cell electrodes before and after cycling, primarily obtained through scanning electron microscopy coupled with elemental analysis. These findings are valuable, offering insights such as the detection of sodium originating from the aqueous binder.

The review of Chapter 11 allows for the following observations. Overall, the structure is logical, and the included figures and tables are clear and effectively illustrate the discussed results. The language used in the description is precise and scientifically rigorous. The number of minor errors and typos is relatively small. Any questions or concerns related to this part of the dissertation are listed below.

1. Was the temperature of the cells monitored throughout all electrochemical tests?
2. While the SEM results for the electrodes before and after testing are quite comprehensive, it remains unclear whether there is a correlation between the morphological features and their distance from the current collector.
3. Could the Author comment on the repeatability of the calendaring process and the morphological properties of the electrodes used in the construction of pouch cells?
4. A similar question arises regarding the evaluation of electrode conductivity.
5. Could the Author discuss the potential influence of the surface characteristics of the metallic support on the preparation of the electrode layers?
6. For the SEM studies, how was it ensured that the samples were not affected by potential contact with the atmosphere, particularly after electrochemical tests?

The conclusions, briefly summarized in Chapter 12, effectively highlight the key findings of the research. It is reasonable to agree with the Author's assertion that the studies successfully demonstrated the viability and scalability of the developed fluorine-free cells. A novel fluorine-free electrolyte was developed, consisting of 0.8 mol kg^{-1} LiPCP in the EC:DMC mixture (30:70 wt%), which exhibits high conductivity and good stability at high voltages. Cathode and anode layers were fabricated using novel binders in aqueous conditions, thereby eliminating the need for fluorine-containing chemicals. The functional properties of these layers were optimized through extensive investigations and additional processing steps. Optimized electrode formulations were proposed and tested: a $LiFePO_4$-based cathode (LFP:KB:CMC:SBR = 93.5:5:0.75:0.75, following the standard literature notation), a synthetic graphite anode (SG:C-45:CMC:SBR = 95:2:1:2), and a silicon oxide-based anode (SiOx/C:C-45:CMC:SBR = 92:6:1:1). Relatively good (at this stage of the research) electrochemical properties were achieved in the pouch cells, particularly for the LFP/SG configuration. The role of the N/P ratio in the studied full cells was established, providing valuable insights. Additionally, studies using a three-electrode configuration revealed significant irreversible effects occurring at lower voltages, offering important insights into the ongoing electrochemical processes.

Based on the information presented above, it can be concluded that the subject of the reviewed doctoral dissertation constitutes an original solution to a scientific problem and that the stated objectives of the research have been successfully achieved. The topic undertaken by the Author is engaging, and the properties of the studied electrolytes, electrode layers, and constructed cells are often challenging to interpret. M.Sc. Eng. Claudia Janeth Limachi Nina has successfully addressed these challenges by providing her own interpretation of the measurement results. The comments and questions raised are largely of a polemical nature and do not significantly impact the reviewer's positive evaluation of the dissertation. The results obtained by the Author, along with the interpretations, represent a significant contribution to the discipline of Chemical Sciences. Furthermore, the research outcomes may have practical implications for the development of sustainable, fluorine-free lithium-ion cells.

In conclusion, I affirm that the doctoral dissertation meets all the requirements specified in Article 187 of the Act of July 20, 2018, on Higher Education and Science (Journal of Laws 2020, item 85, as amended). I recommend that the Scientific Discipline Council of Chemical Sciences at the Warsaw University of Technology admit M.Sc. Eng. Claudia Janeth Limachi Nina to the subsequent stages of the doctoral process.

prof. dr hab. inż. Konrad Świerczek

Kraków, January 17th 2025

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