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Senate
Warsaw University of Technology

Evaluation of the Doctoral Dissertation
titled

»Design and Characterization of $CsPbCl_3$ Perovskite-Based Anodes and Artificial SEI in Lithium Batteries«

Submitted by: **Juhi**, M.Sc.

Program: Destiny – European Research Institute

Supervisors: Prof. Dr. Władysław Wieczorek and Prof. Dr. Robert Dominko

I was appointed as a reviewer of the dissertation of Juhi M.Sc. on 21.10.2025. Based on the final version of the dissertation dated 17^{th} of November 2025, received by mail, I hereby provide an independent evaluation.

ANALYSIS OF THE DISSERTATION AND ORIGINALITY OF THE SCIENTIFIC CONTRIBUTION

This thesis addresses one of the most critical challenges in state-of-the-art lithium-ion battery (LIB) research i.e. the development of advanced anode materials and interfacial engineering strategies to meet the growing demand for higher energy density, improved safety, and long-term cycling stability. By investigating cesium lead chloride ($CsPbCl_3$) both as an active anode material and as an artificial solid electrolyte interphase (ASEI) coating, the work presents a comprehensive and original approach that bridges materials chemistry, electrochemistry, and interfacial science.

The thesis is well motivated, clearly positioning its research objectives within the limitations of state-of-the-art anodes. While graphite remains the commercial benchmark, its limited theoretical capacity and unstable SEI formation restrict further performance gains. Lithium metal, despite its ultrahigh capacity, suffers from severe dendritic growth and interfacial instability. The candidate convincingly argues that halide perovskites such as $CsPbCl_3$ offer a unique opportunity to address these issues due to their mixed ionic–electronic properties and chemical reactivity with lithium.

The thesis makes a substantial and original contribution to the field of lithium-based energy storage. Its key strengths lie in the systematic investigation of $CsPbCl_3$ across multiple roles, the strong mechanistic understanding supported by complementary characterization techniques, and the clear relevance to practical battery configurations. The work is generally well structured, scientifically rigorous, and clearly presented. Nevertheless, the thesis also identifies important avenues for future research. Further optimization through nanostructuring, carbon-based compositing, and binder engineering could mitigate volume changes and improve conductivity when $CsPbCl_3$ is used as an active material. Electrolyte engineering and deeper investigation of electrolyte–perovskite interactions are necessary to better control SEI growth. Moreover, advanced operando techniques such as operando XRD and XPS would be valuable for elucidating lithium transport mechanisms within the ASEI. Validation of $CsPbCl_3$-coated graphite and silicon anodes in full-cell configurations with commercial cathodes would further strengthen the practical relevance of the findings.

ALIGNMENT WITH THE TOPIC PROPOSAL

Not applicable for the evaluated PhD thesis.

STRUCTURE OF THE DISSERTATION

The dissertation is clearly and logically structured, featuring a well-defined introduction that outlines the research objectives, a thorough and transparent experimental section, comprehensive presentation and discussion of the results, and a coherent concluding summary. The quality of the writing and organization meets the academic standards and formal requirements expected of a doctoral thesis.

Introduction:

Introduction is divided into 6 sections and it outlines the role of lithium-based batteries in enabling the energy transition, describing the basic operation of lithium-ion batteries and the limitations of current anode materials. It highlights lithium-metal batteries as next-generation systems with higher energy density but significant stability challenges. The focus then shifts to metal halide perovskites (MHPs), emphasizing their tunable composition, phase behavior, and fundamental properties that govern their interaction with lithium. The potential of MHPs as advanced anode materials and ASEI layers is discussed, leading to the thesis objective of exploring MHP-based strategies to improve the performance and stability of lithium-based energy storage systems. The chapter finishes with thesis aim and objectives.

Experimental Part:

This chapter describes the materials and experimental methods used in this work, beginning with the list of chemicals and the synthesis of $CsPbCl_3$-based materials using both mechanochemical and solution-based approaches. The fabrication of battery components, including $CsPbCl_3$ anodes, $LiFePO_4$ cathodes, and $CsPbCl_3$-protected electrodes, is detailed along with coin and pouch cell assembly procedures. Structural characterization techniques such as SEM, XRD, and XPS are employed to analyze morphology, crystallinity, and surface chemistry. Finally, electrochemical performance is evaluated through galvanostatic cycling, cyclic voltammetry, and electrochemical impedance spectroscopy to assess the charge storage behavior, kinetics, and interfacial properties of the assembled cells.

Results and Discussion:

This chapter presents a systematic investigation of $CsPbCl_3$ in lithium-based battery systems, exploring its dual functionality as a conversion–alloying anode material and, more importantly, as an effective interfacial coating that stabilizes lithium metal and conventional anodes through the formation of a robust artificial solid electrolyte interphase.

In the first part of the work, $CsPbCl_3$ is explored as a conversion–alloying anode material in half-cell configurations with liquid electrolytes. The material delivers a high initial discharge capacity of approximately 600 mAh g^{-1}, significantly exceeding that of graphite. Through a combination of electrochemical testing, XRD, and XPS analyses, the candidate provides a detailed mechanistic understanding of the Li-storage process. The results demonstrate that $CsPbCl_3$ undergoes an irreversible conversion reaction during the first discharge, forming metallic Pb, Li–Pb alloys, and Cs/Cl-containing salts. Subsequent cycling is dominated by reversible Pb alloying/dealloying, while inactive salt phases and continuous SEI growth contribute to capacity fading. This mechanistic insight represents a valuable contribution to the limited literature on halide perovskites as battery anodes. At the same time, the thesis critically acknowledges the intrinsic limitations of $CsPbCl_3$ in its bulk form, particularly the pronounced irreversible capacity loss and long-term instability.

The second and most impactful part of the thesis focuses on the use of $CsPbCl_3$ as a protective interfacial coating for lithium metal anodes. A simple and scalable drop-casting method is employed, enhancing the practical relevance of the work. Electrochemical evaluations in symmetric (Li|Li), asymmetric (Li|Cu), and full-cell (Li|LFP) configurations clearly demonstrate the effectiveness of the coating. The $CsPbCl_3$-coated lithium anodes exhibit suppressed dendrite formation, reduced overpotential growth, and improved Coulombic efficiency. Notably, the candidate reveals an enhanced CE of 98% for coated Li|Cu cells compared to 96.1% for bare lithium. Operando electrochemical impedance spectroscopy and post-mortem XPS analyses provide strong evidence that the $CsPbCl_3$ coating reacts with lithium to form a hybrid SEI composed of Pb, Li–Pb alloys, LiCl, and modified organic/inorganic species. This hybrid SEI effectively suppresses the formation of high-surface-area lithium (HSAL), reduces interfacial resistance, and stabilizes lithium plating/stripping. The successful demonstration of improved long-term performance in Li|LFP full cells—achieving nearly 99.5% capacity retention after 250 cycles—strongly supports the practical significance of this interfacial strategy.

In the final part of the thesis, the versatility of the $CsPbCl_3$ coating is further demonstrated through its application to graphite and silicon anodes. In both systems, the coated electrodes show enhanced reversible capacity, improved capacity retention, and better interfacial stability compared to uncoated counterparts. SEM analysis confirms that the coating maintains structural integrity during repeated cycling. These results indicate that $CsPbCl_3$ functions effectively as an ASEI layer by regulating SEI formation and protecting the electrode surface, thereby extending its applicability beyond lithium metal systems.

METHODS USED

The thesis employs a combination of materials synthesis, electrode fabrication, and advanced characterization techniques to investigate the role of $CsPbCl_3$ in lithium-based battery systems. $CsPbCl_3$ is synthesized using both mechanochemical and solution-based approaches, followed by the fabrication of anodes, cathodes, and $CsPbCl_3$-coated electrodes. Electrochemical performance is evaluated in half-cell, symmetric, asymmetric, and full-cell configurations using galvanostatic cycling, cyclic voltammetry, Coulombic efficiency measurements, and electrochemical impedance spectroscopy, including operando EIS. Structural and interfacial properties are analyzed using scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy, complemented by post-mortem analysis to elucidate lithium-storage mechanisms and SEI/ASEI formation. Together, these methods provide a comprehensive assessment of both bulk electrochemical behavior and interfacial stability.

HYPOTHESES VALIDATION

Not applicable for the evaluated PhD thesis.

ORIGINALITY AND VALUE

The dissertation contributes original and valuable knowledge to the field of lithium-ion battery research, particularly in optimizing anode materials for improved performance and durability. Part of the findings have been partially published in two scientific articles, emphasizing their relevance and scientific merit:

- JUHI, Juhi, VARGAS ORDAZ, Mariana, DRVARIČ TALIAN, Sara, TCHERNYCHOVA, Elena, WIECZOREK, Władysław, LEWIŃSKI, Janusz, DOMINKO, Robert. Cesium lead chloride as an artificial solid electrolyte interphase for enhanced anode protection in lithium metal batteries. Chemistry of materials. 2025, vol. 37, iss. 21, str. 8745–8754, ilustr. ISSN 1520-5002. https://pubs.acs.org/doi/full/10.1021/acs.chemmater.5c01666
- JUHI, Juhi, SASKI, Marcin, KOCHANIEC, Maria K., WIECZOREK, Władysław, DOMINKO, Robert, LEWIŃSKI, Janusz. Exploring metal halide perovskites as active architectures in energy storage systems. Journal of materials chemistry. A, Materials for energy and sustainability. [Online ed.]. 2025, vol. 13, iss. 45, str. 38753-38789, ilustr. ISSN 2050-7496. https://pubs.rsc.org/en/content/articlelanding/2025/ta/d5ta04267d

STYLE AND LANGUAGE

The proposed work is written in a professionally correct manner. It uses established terminology, symbols, and abbreviations, and the structure of the work is logical and flows smoothly.

CONCLUSION

The doctoral dissertation of **Juhi** is an independent, significant, and original contribution to the field of Materials Science. This thesis successfully demonstrates the potential of $CsPbCl_3$-based perovskites as both conversion–alloying anode materials and multifunctional interfacial coatings. Despite certain limitations, the work provides important mechanistic insights and establishes a solid foundation for future development of halide-perovskite-based strategies in high-performance lithium-ion and lithium-metal batteries.

All requirements for the title of Doctor of Science have been met. I recommend that the Senate of WUT accept this evaluation and allow the candidate to defend the dissertation.

Assoc. Prof. Dr. Boštjan Genorio

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