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## Review of the doctoral dissertation by Ms. Abeer Sami Dheyab, M.Sc. entitled "Polymer Electrolytes Comprising Oligomeric Lithium Borate Salts and Poly(ethylene oxide)"

The doctoral dissertation of Ms. Abeer Sami Dheyab, M.Sc., submitted for review under the above title, was prepared at the Faculty of Physics, Warsaw University of Technology, under the supervision of Professor Michał Marzantowicz, Ph.D., D.Sc.

The reviewed dissertation focuses on research into new compositions of polymer electrolytes based on oligomeric lithium borate salts and poly(ethylene oxide) (PEO) for use in Li-ion cells. The subject matter is highly relevant and aligns well with global research and the ongoing technological race in the field trends of electrochemical energy storage. According to recent reports by (including Benchmark Mineral analytical agencies Intelligence, McKinsey, and Roland Berger), the energy storage market (encompassing Li-ion, Na-ion, and flow batteries) is expected to reach a demand of 4.7 TWh/year by 2030. As of the end of 2024, global production of Li-ion cells has already exceeded 1.5 TWh/year (a 30% increase compared to 2023), with China alone accounting for 1.2



TWh/year, underscoring its dominant position and the global dependency on its production capacity.

This rapid growth in the lithium-ion battery market is clearly tied to the widespread adoption of electric vehicles (EVs) and the ongoing, necessary global energy transition toward greater reliance on renewable energy sources. Energy storage systems based on Li-ion batteries and, in the near future, Na-ion systems—are poised to play a key role in stabilizing power grids that rely on intermittent renewable energy by providing energy buffering and power balancing.

Key functions of battery energy storage systems (BESS), such as operational safety and overall efficiency, depend heavily on the physicochemical properties of the active materials (electrodes) and electrolytes, as well as their interactions under operating conditions. While the energy and power output of a cell primarily depend on the properties of the electrode materials (cathode and anode), the service life, efficiency, and safety of a Li-ion cell are largely determined by the interactions between the electrolyte and the electrode materials, as well as by the behavior of the resulting reaction products.

In a full cell, the electrolyte serves as the medium for charge and mass transport. Its composition including solvents, conducting salts, and additives, plays a critical role in determining the efficiency of electrochemical processes and the reactivity toward electrode materials. The reaction mechanisms between the components (salts and solvents) of the liquid electrolyte and the active materials are complex and highly specific to the particular electrode/electrolyte system. Additionally, interactions with the products of the counter electrode reactions may also occur.

Replacing reactive and flammable liquid solvents with a polymer matrix (e.g., PEO) can significantly enhance the safety and durability of Li-ion cells. However, the use of a polymer electrolyte often results in reduced ionic conductivity. Therefore, developing new conducting salt systems compatible with the PEO polymer matrix, such as oligomeric Wydział Chemii



lithium borate salts, was essential. This goal lies at the heart of the dissertation under review and falls within the realm of both basic and applied research in the chemical and physical sciences.

The reviewed doctoral dissertation was written in English and published in the form of a typical WUT monograph, consisting of a total of 112 pages. The work comprises six main chapters, preceded by a summary, table of contents, a list of 48 figures, and a list of 12 tables.

In the first chapter ("Introduction"), the PhD student briefly outlines the purpose and context of the study. Chapter 2 ("Polymer Electrolytes – General Overview") serves as the theoretical background, spanning 23 pages and addressing key issues related to polymer electrolytes. However, this chapter also includes a brief popular science section on Li-ion cells (subchapter 2.1), which, although informative, is thematically broader than the main focus of the dissertation. Similarly, subchapter 2.2, which discusses types of electrolytes used in batteries, covers a broader scope. In my opinion, subchapters 2.1 and 2.2 should have been expanded and presented as a separate, introductory chapter preceding the discussion specifically focused on polymer electrolytes.

The remainder of Chapter 2 covers ionic conduction mechanisms in polymer electrolytes (2.3), types of polymer electrolytes and their components (2.4–2.7), and the basic physical properties of semicrystalline polymer electrolytes based on the PEO matrix (2.8–2.10). This section provides a solid foundation for the subsequent presentation and interpretation of results.

Chapter 3 is dedicated entirely to explaining the physical principles behind the research techniques used in the dissertation, namely differential scanning calorimetry (DSC) (3.1) and AC impedance spectroscopy (3.2), including interpretation methods relevant to ionic conductors. Subchapter 3.3 describes how transference numbers in electrolytes are determined, using the Bruce–Vincent and Watanabe methods. This chapter offers a well-structured

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and informative introduction to the methodological and experimental aspects of the research.

The experimental section of the dissertation spans 60 pages and begins with Chapter 4, which details the preparation of materials (salts and electrolytes) and the methodology used. The components of the electrolyte compositions and their sources (suppliers) are listed in a table. The primary components, oligomeric lithium trialkoxybutylborate salts, were synthesized at the Faculty of Chemistry, University of Warsaw, based on a process developed by Zygadło-Monikowska et al. at the Faculty of Chemistry, Warsaw University of Technology (group of Prof. Z. Floriańczyk) [J. Power Sources 195 (2010) 6055–6061].

This is a two-step process: (1) the formation of trialkoxyborates from  $B_2O_3$  and respective oxyethylene glycol monomethyl ethers (with EO units of 1, 2, 3, and 7.5), with water removed as a toluene azeotrope, and (2) the subsequent reaction of the trialkoxyborates with n-butyllithium. At this point, I must note an error on page 56: the stoichiometric coefficient "2" is missing from the products side of the first reaction.

The polymer electrolytes were prepared in a dry glovebox via a casting method using anhydrous acetonitrile solutions containing PEO and lithium borate salts of various oligomeric lengths (different numbers of EO units). This stage of laboratory work, involving the preparation of polymer electrolytes with varied compositions, is particularly important for interpreting the experimental results. Here, I would like to request a comment on the precision of the component weightings and the resulting error in the reported "intrinsic" EO:Li ratio. Additionally, what was the repeatability of the polymer membrane casting process? Were multiple membranes tested for each electrolyte composition?

The polymer electrolytes were then subjected to electrochemical characterization using a gas-tight sample holder (electrochemical cell) with a controlled spring load and sample thickness measurement.

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Impedance spectroscopy measurements were performed using an Alpha-N frequency response analyzer (Novocontrol), and temperaturedependent measurements were conducted using a Peltier-based thermostat. DSC measurements were carried out using a TA Q2000 heat-flux calorimeter with an autosampler, and hermetically sealed employed. aluminum pans were The complementary lithium transference number measurements presented in the dissertation are based on the work of Karol Pożyczka, which was part of his PhD thesis, and these results contribute to a deeper understanding of the studied electrolyte systems.

Chapter 5, titled *"Results and Discussion,"* presents the experimental results obtained for the pure oligomeric lithium borates and the polymeric conducting membranes derived from them and PEO, covering various thermal and transport properties. The chapter also includes a discussion of lithium transference numbers determined using the symmetric polarization method.

Regarding the scientific value of this section, I would like to emphasize the extensive amount of valuable experimental data presented. The analysis of DSC thermal properties of the pure salts reveals an interesting discontinuity in behavior as a function of oligomer chain length. Specifically, both short (n=1) and long (n=7.5) oligomeric chains exhibit a semicrystalline state, whereas the intermediate-length systems (n=2 and 3) are fully amorphous. These amorphous systems also display the greatest reduction in glass transition temperature (T<sub>g</sub>). This prompts the question: what is the nature of this ordering and crystallization behavior?

DSC thermograms of the PEO/lithium borate salt polymer electrolytes with oligomeric chain lengths of n=1, 2, and 3 show a similar thermal profile. A relatively intense endothermic effect is observed, attributed to melting in the range of  $T_m = 59-76$  °C, along with a glass transition in the range of  $T_g = -80$  to -43 °C. The melting peak can be attributed to the semicrystalline PEO polymer matrix, and no significant influence of

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salt content on the degree of crystallinity was observed. However, a clear influence of oligomer chain length on the decrease in  $T_g$  was found; for the n=2, 3, and 7.5 systems,  $T_g$  dropped below that of pure PEO ( $T_g = -54$  °C), with the lowest value (Tg = -80 °C) recorded for n=3.

Given the casting and drying method used to form the electrolyte membranes, it must be considered that the drying dynamics could influence the ordering and interaction between PEO macromolecules and the oligomeric salts. Were different drying conditions (e.g., temperature, time) tested? And again, I raise the question: what was the repeatability of the membrane casting process? In summary, the results of the DSC calorimetric studies show that incorporating an optimized amount of oligomeric lithium borate salt into the PEO matrix results in a synergistic effect that improves the thermal properties of the polymer electrolyte. This is, in my opinion, a significant achievement.

Electrical properties measurements of the oligomeric borate salts demonstrate increased ionic conductivity with increasing oligomer chain length. These results are consistent with the DSC findings. However, the study of electrical conductivity in the polymer membranes (PEO/oligomeric lithium borate salts) indicates a more complex mechanism involving interactions affected by measurement conditions. It was noted that conductivity values varied across subsequent heating and cooling cycles, which may be due to membrane relaxation or improved contact conditions. Still, the possibility that these variations were influenced by pressure from the sample holder spring cannot be excluded. This variability posed a challenge for evaluating the results, which makes the findings all the more valuable. It was observed that for amorphous polymer electrolytes at 70 °C, ionic conductivity was higher than in the pure salts. At room temperature, the relationship was more complex, likely due to the semicrystalline nature of the polymer, resulting in values comparable to or lower than those of the pure salts.

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The results presented in this chapter are broad in scope, covering many variables. As such, they serve as a solid basis for future optimization studies on this system. Importantly, the results suggest that it is possible to obtain a conductive polymer membrane based on the PEO/oligomeric lithium borate system with ionic conductivity comparable to that of the pure salts. Moreover, the physical properties of these membranes allow them to function simultaneously as a separator in a battery cell, eliminating the need for liquid and flammable solvents in the electrolyte.

As noted in the dissertation, there is a synergistic interaction between the PEO macromolecules and the branched salt anions that affects ion mobility and, consequently, lithium transference numbers. This is a particularly interesting phenomenon, which deserves further study and optimization, especially in the context of applications involving lithium metal anodes, for example, in All-Solid-State Batteries (ASSBs).

The final conclusions in the thesis summarize the most important findings and key observations made by the PhD student regarding the systems based on the PEO polymer matrix and oligomeric lithium borate salts. From an editorial standpoint, it must be emphasized that the dissertation is carefully and clearly written. My earlier critical remarks are intended solely as constructive feedback and do not in any way diminish the scientific merit of the work.

According to the Scopus database, the PhD student is a coauthor of one publication, published in the reputable journal *Electrochimica Acta*, which includes results presented in the dissertation.

In summary, I conclude that the doctoral dissertation submitted by Ms. Abeer Sami Dheyab, M.Sc., constitutes an original scientific achievement of high substantive quality. The work introduces significant elements of scientific novelty and clearly fulfills the conditions and requirements for doctoral dissertations, as outlined in



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Article 187 of the Act of July 20, 2018 – Law on Higher Education and Science (Dz.U. 2023 poz. 742). On this basis, I hereby recommend to the Scientific Council of the Discipline of Physical Sciences at the Warsaw University of Technology that the doctoral candidate be admitted to the subsequent stages of the doctoral procedure.

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