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RESEARCH UNIVERSITY

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Review of the doctoral dissertation by Abeer Sami, M.Sc.
entitled: „Polymer electrolytes comprising oligomeric lithium borate salts and poly(ethylene oxide)"

legal basis: Formal letter No. RPW/47747/2024 N dated 25th October 2024 received from prof. dr hab. inż. Tomasz Woliński, chairman of the Scientific Council Discipline of Physical Sciences of the Warsaw University of Technology.

1. General information

The doctoral dissertation of Ms. Abeer Sami entitled "Polymer electrolytes comprising oligomeric lithium borate salts and poly(ethylene oxide)", supervised by prof. Michał Marzantowicz, Ph.D., D.Sc. was developed at the Warsaw University of Technology in the discipline of Physical Sciences and the field of Natural Sciences. The work is experimental, and the submitted dissertation takes the form of a monograph summarizing materials conducting lithium ions. The main object of study is the correlation between electrolyte composition and ionic conductivity, as well as its dielectric and thermal properties. The main goal is to achieve high ionic conductivity in a polymeric system and, at the same time, limit anion mobility. I consider the undertaken scientific goal of this dissertation as important and current, because materials of this type are used, among others, in lithium-ion batteries. It constitutes a significant contribution to the existing state of knowledge in the discipline of Physical Sciences.

2. Work structure

The doctoral dissertation was written in English in the form of a scientific monograph. It has 112 pages and consists of 6 main chapters. The work contains 12 tables, 48 figures, 18 of which are in the introductory part, and 92 literature references. The layout of the dissertation is typical. First chapter is entitled "Introduction" and presents the motivation for undertaking the research problem and formulates the objectives of the doctoral thesis. The second chapter gives a general review of polymer electrolytes, divided into subchapters devoted to different electrolyte materials in lithium-ion batteries and physicochemical parameters characterising these compounds. Next, the experimental techniques are characterized and the details of synthesis procedure as well as measurement procedure are given. In the 5th chapter the obtained results are presented and discussed. Final conclusions are summarized in the 6th chapter. The division of the dissertation into individual parts well reflects the content, systematically introducing subsequent issues discussed in the work. However, a valuable addition would be to include a list of abbreviations and symbols in the work, which would make it easier to read, especially for people who are not specialists in the subject matter covered by the dissertation.

The work is written in correct, understandable language, although the author did not avoid minor editorial errors, such as the last sentence in the Polish Abstract ("Streszczenie") of the work. However, this does not detract from the overall positive reception of the work.

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3. Substantive assessment of the dissertation

3.1 Evaluation of the references

The cited 92 references contain not only articles and scientific books from the last 15 years, but also older papers from the end of 20th century. Older references are usually the so-called fundamental works, on the basis of which the existing state of knowledge was developed. However, what leaves me unsatisfied is the fact that when discussing the current state of knowledge, the author did not refer to at least several articles published after 2020. In the context of the content, the literature has been selected properly and demonstrates the author's good knowledge in the topic undertaken.

3.2 Scientific goals

The author is interested in oligomeric salts with a developed anion structure in order to limit charge transport through anions and increase the conductivity of lithium ions. Thus, these materials could be interesting candidates for electrolytes in lithium-ion batteries.

The first goal of this study was to achieve high ionic conductivity in a polymeric system by developing new lithium salts aimed at delocalization of anion charge, which lowers the melting temperature of the salt and promotes dissociation. The second goal, at the same time, was to limit anion mobility by development of salts with large, oligomeric anions, which are expected to have low mobility and thus increase lithium transference number.

The goals formulated in this way determined the subsequent stages of the research work, starting from the synthesis of new electrolytes obtained by mixing oligomeric borate salts with long molecular weight poly(ethylene oxide), through the characterization of their electrical and thermal properties.

In the work, a logical chain of reasoning is noticeable, resulting in a good selection of subsequent stages of the experiment and consistently aiming to obtain answers to the questions posed. In view of the above, the goals of the work should be considered as successfully achieved, and the obtained research results can be further used and developed.

3.3 Experimental methods

The lithium borate salts were prepared by a two-step synthesis process, containing fabrication of trialkoxyborates from B_2O_3 and respective oxyethylene glycol monomethyl ethers with the removal of the produced water in the form of an azeotrope with toluene and the conversion into the form of lithium salts in the reaction with n-butyllithium. The obtained branched structure of borate salts included three oligomeric oxyethylene segments of various length *n* and a butyl group. Four different lengths of oligomeric arms were studied (n=1;2;3 and 7.5).

The electrolytes were obtained by solvent-casting method, using acetonitrile as the solvent. The weight proportions of polymer and oligomeric salts were chosen so that they represent certain molar proportions of ethylene oxide units to lithium: 50:1, 32:1, 16:1, and 10:1.

The investigated systems were analysed by the Differential Scanning Calorimetry (DSC) to determine their thermal properties, particularly the T_g and the melting point, as well as by the Electrochemical Impedance Spectroscopy (EIS) to measure their ionic conductivity, dielectric properties and to estimate the transference number.

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I hereby state that the research plan, the applied characterization techniques and the method of analyzing the results and assessing the uncertainty of measurements are correct from the point of view of achieving the objectives of the doctoral thesis of Ms. Abeer Sami.

3.4 Discussion and evaluation of research results

The reviewed doctoral dissertation contains interesting results that were achieved as a result of research conducted by Ms. Abeer Sami. I consider the most important results described in this dissertation to be:

1. Electrolytes obtained by addition of high molecular weight poly(ethylene oxide) to oligomeric borate lithium salts present ionic conductivity comparable to that of the pure borate salts.

2. Presence of crystalline phase in mixed PEO-borate systems leads to a decreased conductivity caused by crystallization, but it can be partially compensated by their low glass transition temperature T_g.

3. Some of the investigated systems, for example, electrolytes composed of borate salt with average length n=7.5 and molar ratio EO:Li of 32:1 and 50:1 exhibit values of the glass transition temperature lower than the values obtained for pure PEO and pure borate salt, which is also reflected in characteristic frequency of the dielectric relaxations related to segmental chain motion (the frequencies of segmental relaxation which promotes ion transport were shifted to higher frequencies in respect to the parent compounds).

4. The semicrystalline character of the investigated mixed borate salt-linear PEO systems is reflected by the dispersion of conductivity and the presence of high and low frequency plateaus in impedance spectral plots of conductivity. It is suggested that the low frequency plateau depends rather on sample crystallinity, while the high frequency plateau reflects the conductivity of amorphous domains, and may be interpreted as a limit of conductivity possible to achieve if crystallization could be suppressed.

5. The addition of poly(ethylene oxide) to oligomeric borate lithium salts increases the apparent lithium transference numbers (t^+) in comparison to the neat salt. Author suggests that it may be due to promoting salt dissociation by the presence of PEO chains and subsequent transport of lithium cations across the electrolyte, as well as by the improved selectivity of the electrolyte by obstructing the movement of branched anions.

I state that the reviewed doctoral dissertation is an original, valuable solution to the undertaken scientific problem. The topic, which is the search for new materials for electrolytes for lithium-ion batteries, has a significant application character. Creating and investigating materials based on poly(ethylene oxide) - oligomeric borate lithium salt system makes an important contribution to the existing state of knowledge about materials from the group of oligomeric salts with a developed anion structure.

The reviewer's interest in the topic and the discovery of a few inconsistencies in the dissertation led to several questions/comments of a polemical nature, which I would like to ask for clarification during the public defense of the doctoral dissertation.

3.5 Comments and questions

1) It has been found that most of the results presented in this dissertation, as well as some big parts of the text, were previously published in the paper by Michał Marzantowicz, **Abeer Sami**, Karol

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Pozyczka, Agnieszka Chodara, Dorota Gładka, Ewa Zygadło-Monikowska and Franciszek Krok of the same title as the revised dissertation: "Polymer electrolytes comprising oligomeric lithium borate salts and poly(ethylene oxide)" (Electrochimica Acta 469 (2023) 143203). It is surprising that the PhD student does not refer to this scientific paper anywhere, even though the publication in the journal Electrochimica Acta, which is highly respected in the field of solid state ionics, is undoubtedly a great achievement. Please, comment on that.

2) The author investigated different lengths of oligomeric segments and different EO:Li proportions. The thermal analysis indicates a different nature of these materials, therefore the comparison between them is difficult to be performed. The conclusions should be rather taken separately on each system. Please, consider if it was possible to make this work more systematic. If yes, how it can be done?

3) In the discussion of Fig.5.6 the Author comments on an unexpected behaviour of the investigated system. It is written that: 'studied system can be regarded rather as a mixture of domains of borate salt and domains of pure PEO, rather than a typical polymer-salt complex.' Are there any experimental methods to verify this hypothesis?

4) The Author found that 'two salts may exhibit problems with stability when subjected to prolonged heating and cooling treatment'. What about the long-term stability at room temperature? Was it investigated? How long the samples remained unchanged?

5) Fig. 5.9 appears in the dissertation without any comment. Please, describe and justify the use of that particular equivalent circuit for fitting of impedance spectra. The physical nature of each element should be explained.

6) In the discussion of conductivity measurements the Author explains some differences in the obtained results by the microstructure of surface foils which were in contact with the electrodes. I wonder if this is a hypothesis or was there any visual inspection to prove this explanation? Are there any images to confirm these differences in the microstructure?

7) In the 'Dielectric properties' section the Author claims: 'not all of these phenomena can be undoubtedly deconvoluted from an impedance spectrum measured at a single temperature. Therefore, a more accurate and reliable result can only be obtained by analyzing measurements made over a wide temperature range.' Can the Author suggest any other method of impedance spectra analysis that may give a deeper insight view into the nature of such electrolyte materials for lithium-ion batteries?

8) It is written that the section 5.3 'Transference numbers' presents results measured during doctoral studies of Karol Pożyczka. What was Ms. Abeer Sami's input on these measurements? It's not clear for the reviewer.

4. Final conclusions

I state that the scientific issue addressed in the reviewed dissertation is important and current. The work is written in a correct, accessible language, and the inaccuracies found are of lesser importance. The topic taken up is very complex, and many questions still remain unresolved and leave a certain dissatisfaction. Despite this, it should be stated that the applied research methods and the presented analysis of the results are sufficient for a doctoral dissertation in the discipline of experimental physics.

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I hereby declare that the doctoral dissertation submitted to me for evaluation by Ms. Abeer Sami, MSc titled: "Polymer electrolytes comprising oligomeric lithium borate salts and poly(ethylene oxide)" - prepared under the supervision of prof. Michał Marzantowicz, Ph.D., D.Sc., meets the customary and statutory requirements for doctoral dissertations. In connection with the above, I recommend to the Discipline Council of Physical Sciences of the Warsaw University of Technology that the candidate is admitted to the next stages of the PhD procedure.

Beata Bochentyn

dr hab. inż. Beata Bochentyn, prof. PG

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