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Kraków, January 6th, 2025

Review of Ph.D. thesis by Abeer Sami, M. Sc. „Polymer Electrolytes Comprising Oligimeric Lithium Borate Salts and Poly(ethylene oxide)"

1) Legal basis

This review report has been prepared at the request of the Scientific Council of the Discipline of Physical Sciences at Warsaw University of Technology, in accordance with Article 187 of the Act of July 20th, 2018, Law on Higher Education and Science.

2) Topic of the thesis

The present doctoral dissertation was conducted at the Faculty of Physics, Warsaw University of Technology, under the supervision of Dr. hab. inż. Michał Marzantowicz, Professor at WUT. The focus of the dissertation is on ionically conductive polymers composed of lithium oligomeric borate salts embedded in poly(ethylene oxide) matrix, investigated with a goal to maximise their ionic conductivity and achieve high lithium transference number and serve as Li^+-conducting solid electrolyte membrane. The studied compounds do not contain rare elements and utilise a facile synthesis procedure, so if successfully fabricated, such materials would be of great importance for applications in electrochemical cells such as Li-ion batteries, electrochromic devices, sensors, etc. therefore I found the topic of this thesis relevantly selected and timely.

3) Description of the thesis

The Ph.D. thesis of Abeer Sami, M.Sc., spans 112 pages and is organized into six chapters, an abstract in English and Polish, a table of contents, a list of figures, a list of tables, and references. The dissertation incorporates 48 figures, 12 tables, and 92 references to scientific articles and books.

Chapter 1, entitled "Introduction", provides a concise overview of the motivations underlying this research, which are focused on the development of novel types of solid electrolytes for rechargeable lithium batteries. It also enumerates the essential properties of candidate materials for this application. The Author sets out the objective of the research as the achievement of high ionic conductivity of the polymer electrolyte, coupled with low anion mobility. This objective is pursued by incorporating a lithium salt comprising an oligomeric borate anion, which was predicted to exhibit low mobility. The research scope encompasses the comparison of the thermal and electrical properties of four distinct oligomeric anions at varying concentrations, with the aim of identifying the most suitable candidate solid electrolyte.

In Chapter 2, the Author provides a review of polymer electrolytes, comparing them with other groups of electrolytes with regard to their advantages and disadvantages for application in lithium-ion batteries. The chapter then goes on to describe solid polymer electrolytes, with a particular focus on those based on poly(ethylene oxide) and various lithium salts, particularly lithium oligomeric borate. Basic rules behind the mechanism of ion conduction are discussed, as are the effects of crystallinity and other factors affecting ionic conductivity. The final subchapter provides a brief overview of dielectric relaxation phenomena in polymer electrolytes as a function of frequency and temperature, based on the Debye model.

The third and fourth chapters of this thesis provide a background of the experimental techniques employed in this study. These include differential scanning calorimetry, AC impedance spectroscopy and transference number measurements. The chapters also offer detailed insights into the experimental setup and the materials used in the study.

Chapter 5 presents and discusses the obtained results and is divided into three sections: (i) thermal properties of the studied system, (ii) electrical properties of the studied system and (iii) transference numbers. These results have been published by M. Marzantowicz, A. Sami, Karol Pożyczka, A. Chodara, D. Gładka, E. Zygadło-Monikowska, and F. Krok under the title "Polymer electrolytes comprising oligomeric lithium borate salts and poly(ethylene oxide)" in Electrochimica Acta 469 (2023) 143203.

Firstly, the melting point, glass transition temperature, and heat of fusion for pure oligomeric borate salts were evaluated using the DSC technique. Subsequently, the same values were determined for the PEO-salt system for several different concentrations of the salt, starting from pure PEO up to a PEO/salt weight ratio of 0.08 (see Table 4.2). It was observed that both salt concentration and length of the oligomeric groups affected the transition temperatures and heat of fusion. While no obvious trend could be determined, some of the investigated compositions revealed lower glass transition temperature, lower melting point and lower heat of fusion than pure PEO, suggesting that the dissolved salt created a significant amount of disorder in the polymer structure, which is a promising indication for its potential application as a solid electrolyte. It is noteworthy that compositions with n = 3 and 7.5 exhibited particularly low glass transition temperatures, low melting points, and low heat of fusion values.

Secondly, the electrical conductivity of the samples of the same compositions was measured using AC impedance spectroscopy within the temperature range of -50°C to +90°C. The highest observed conductance was $2.3\cdot10^{-5}$ S cm^{-1} for n=2 and EO:Li = 50:1 at 70°C, while at 25°C the highest conductance of $4.5\cdot10^{-7}$ S cm^{-1} was achieved for n=3 and EO:Li=10:1. In addition to the ionic conductivity values themselves, other relevant parameters were calculated on the basis of these experiments. These included the ideal glass transition temperature, T_0, a parameter from the Vogel-Tammann-Fulcher equation describing the temperature at which polymer chain motion is activated, and the decoupling index, R_τ, describing the relation between the motion of ions and polymer chains. The observed evolution of measured values was then linked to the values of glass transition temperature, melting point and heat of fusion. The effect of heating and cooling cycles was measured and is briefly described, however without detailed information on cooling and heating procedures nor numerical values for ionic conductivity.

Thirdly, an analysis of the dielectric properties was conducted on the basis of AC impedance measurements. The real and imaginary parts of the dielectric function and the conductivity dispersion were modelled and discussed. The shift of the characteristic relaxation frequencies towards higher values for the polymer electrolyte indicated faster motion of the polymer chains in comparison with the pure PEO polymer. The dispersion of conductivity revealed two characteristic regions: long-range DC conductivity and short-range, high-frequency. This enabled a deeper insight to be gained into the ionic transport mechanism.

The final section of Chapter 5 summarizes the findings from Karol Pożyczka's earlier doctoral thesis, which was conducted within the same research group. In his thesis, Dr. Pożyczka measured Li^+ transference numbers for the specific oligomeric group length (n = 7.5) and various salt concentrations in PEO. The conclusion drawn from this work was that the Li^+ transference number is below 0.4 at 80°C and is independent of the salt concentration above a certain threshold concentration, while neat salt was characterised by a much lower transference number of approximately 0.05. It is important to note that this section does not introduce new findings beyond those presented in K. Pożyczka's thesis. As such, it should be regarded as an appendix, rather than a regular chapter of the thesis. The value of this section would be greatly enhanced if the results for polymer electrolytes with other oligomeric chain lengths and different temperatures were also discussed.

The thesis text is generally written in good scientific English, and the presentation of plots and tables is accurate and adheres to standard scientific conventions.

4) Content assessment

The most significant result presented in Abeer Sami's doctoral thesis is the systematic investigation and coupling between the thermal properties and electrical conductivity of solid electrolytes based on polyethylene oxide and borate oligomeric salts for various oligomeric chain lengths. I believe that this study provides a deeper understanding of polymer-based solid electrolytes and has the potential to contribute to the development of new polymer electrolytes in the future.

Following a thorough examination of the doctoral dissertation, it is concluded that the solution proposed is an original contribution to the scientific community. Furthermore, the dissertation confirms the PhD candidate's comprehensive theoretical foundation and demonstrates their capacity for autonomous scientific research.

5) Comments and questions

Following a thorough examination of the thesis I found several open topics or doubts, which I would like to be addressed during the doctoral defence.

1. What was the purity of the borate salt and poly(ethylene oxide) samples that were investigated, and how could potential impurities affected the conductivity and stability of the electrolytes that were obtained? The conductivity reported of pure PEO electrolyte seems to be rather high: approximately 10^{-6} S cm^{-1} at 70°C. Could this be due to impurities?

2. What effect does the loading force from the spring have on the properties of the polymer electrolyte? Is it possible to utilise this factor in the practical construction of devices incorporating such an electrolyte?
3. For some of the samples Author suggested (pp. 72-73) that borate salts with n=2 and n=3 might exhibit a multiphase inhomogeneous nature. Could this affect the ionic conductivity? Was this hypothesis pursued in more details?
4. How the relationship between the ionic conductivity and T_m, T_g and T_0 established in this work compares to other Li^+-conducting polymer electrolytes, for example the $LiPF_6$:PEO system?
5. What effect did the heating/cooling rate have on the crystallinity and ionic conductivity of the studied electrolytes? Was the ionic conductivity in the heating cycle the same as during cooling, and was the cooling/heating rate the same in the DSC and impedance spectroscopy experiments? If not, how could this affect the results? The Author stated (p. 81) that some electrolytes improved in subsequent heating/cooling cycles and interpreted this effect as related to improved contact with the electrode. Can this be alternatively explained as related to changes of the crystallinity?
6. The Author suggested (pp. 75, 77) that borate salts with n=2 and n=3 lack stability during investigation. Have further studies been conducted on this effect? Could the stability be increased by narrowing the applied temperature range?
7. In the discussion, the Author employed the term 'stiffening' (pp. 77, 79) to denote the alterations in the properties of the polymer electrolyte. Could you please define this term? How does it differ from the concepts of glass transition or crystallization?
8. In order to calculate the decoupling index, ionic conductivity values were extrapolated down to the glass transition temperature, which was more than 30°C lower than the lowest experimental temperature, as illustrated in Figure 5.18. Could the Author please estimate the uncertainty of this procedure?
9. The values obtained for the Li^+ transference number in the oligomeric borate salt are similar to those observed for the classic $LiPF_6$:PEO system. Does the Author have a hypothesis why more bulky oligomeric anions did not allow an increase in the cation transference number?

As previously stated, the aforementioned questions do not in any way detract from the results or value of this dissertation. Rather, they serve to initiate a more profound scientific discourse. In addition to the aforementioned remarks, the thesis contains some unclear statements, inaccuracies, including typographical errors and inconsistencies. These are listed below:

- Table 5.1. Table caption does not match the table's content, values of T_0 are not given in the table.
- Table 5.2. Melting point values for n=7.5 given in the table differ from those in Fig. 5.5.
- Pp. 77-78, Fig. 5.10: description given in the paragraph do not match the data presented in the figure. E.g. the text says that pure borate salt with n=2 has the lowest conductivity, while in the fig. it is among the highest, as least in the low temperature range.
- P. 78. The temperature values at the upper x-axis are incorrect.
- P. 85. The discussion of the results seem to be unclear: is it dissolution or dissociation of the salt, which is affecting the ionic conductivity for borate salts with short oligomeric chains?
- Table 5.4. Table presents Log(σ) instead of σ, as suggested by the table cation.

6) Final conclusion

Based on the above, I can state that the doctoral dissertation of Abeer Sami, M.Sc. submitted for review meets the requirements set out in the Law on Higher Education and Science of 20th July 2018. The dissertation presents the general theoretical knowledge of the Author, demonstrates the ability to independently conduct scientific work and is an original solution to a scientific problem in the field polymer solid electrolytes. Taking all this into account, I apply to the Scientific Council of the Discipline of Physical Sciences of the Warsaw University of Technology to admit the work to further stages of the procedure for awarding the degree of doctor in the discipline of physical sciences.

Signature

Władysław Wieczorek ....