Łukasiewicz
Instytut Metali Nieżelaznych

Oddział w Poznaniu

dr hab. inż. Mariusz Walkowiak

Sieć Badawcza Łukasiewicz
- Instytut Metali Nieżelaznych
ul. Forteczna 12
61-362 Poznań

Poznań, 01.09.2024

Review of PhD thesis submitted by Aginmariya Kottarathil, M.Sc., entitled „Highly Concentrated Electrolytes for Lithium-Sulfur Batteries"

Foreword

Devices for electrical energy storage that utilize electrochemical processes, primarily cells and batteries, have recently become an obvious and indispensable part of life. Among them, lithium-based technologies hold a special position. The Li-ion variant has undergone an unimaginable evolution, increasing its energy density nearly fourfold since its first commercialization by Sony in 1991, thereby enabling the unprecedented spread of mobile electrical devices, particularly consumer electronics and electric vehicles. Although Li-ion technologies in their various forms are currently the first choice for most applications requiring both high energy and power densities, some experts believe that "classic" Li-ion cells are reaching the limits of their development potential. Further progress is expected to be incremental, with major qualitative leaps anticipated from future solutions described as "post-Li-ion" and "post-Li," such as lithium-sulfur, sodium-ion, or magnesium-ion systems. This progress is possible thanks to intensive material research, primarily in the areas of anode, cathode, and electrolyte materials. The electrolyte, in particular, is often an underestimated component of the Li-ion cell. Indeed, it does not directly determine the cell's capacity, but it has an indirect influence and contributes to all critical operational parameters of the power source. Even when setting aside the vast research related to solid electrolytes, there is still a clear trend towards finding new, more optimal solutions in the area of solvents, salts, and functional additives within "traditional" liquid electrolytes. In Li-S cells,

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
61-362 Poznań, ul. Forteczna 12, Tel: +48 61 27 97 800
E-mail: claio@claio.poznan.pl | NIP: 631 020 07 71, REGON: 000027542, BDO:000011457
Sąd Rejonowy w Gliwicach, X Wydział Gospodarczy | KRS: 0000853498
Bank SANTANDER nr konta: 73 1090 1346 0000 0000 3400 0300 PL
Bank SANTANDER nr konta: 40 1090 1346 0000 0001 3343 4042 EUR | KOD SWIFT: WBKPPLPP

the role of the electrolyte is particularly critical, extending far beyond merely conducting ions, due to the completely different operating mechanisms of these cells. This necessitates intensive basic and applied research to understand the processes involved and to bring them closer to commercialization. From this perspective, Aginmariya Kottarathil's dissertation fits into an important stream of applied scientific research with a very high potential for industrial application.

Comments on the Concept, Formal Aspects, and Editorial Layer of the Dissertation

The dissertation submitted for review consists of 107 pages, including a total of 39 figures (6 of which are in the appendix) and 5 tables (2 of which are in the appendix). The dissertation is divided into three main parts: the theoretical introduction (14 pages), the experimental section along with computational techniques (15 pages), and the discussion of original research (Current work) (34 pages). In addition, the work includes acknowledgments, an abstract in two languages, a list of the candidate's publications, a list of abbreviations, a list of symbols, appendices, and a bibliography.

In the theoretical introduction, the candidate first briefly presents the broader context of her work in relation to current technological trends in battery technology, then focuses on lithium-sulfur batteries as the subject of her research. This section begins with a paragraph describing the history of batteries. Here is a minor critical remark: if the candidate decided to include such a subsection, it would be advisable to expand it further to cover the most important milestones in the history of battery development, between the earliest experiments of Volta and Galvani and modern times. The section of the introduction dedicated to lithium-sulfur cells is very concise but generally well-written from a substantive standpoint. It includes essential information about the history of this technology, the basic components of the cell, and the mechanisms of the processes occurring during cell operation, with particular attention to the issue of polysulfide solubility

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
61-362 Poznań, ul. Forteczna 12, Tel: +48 61 27 97 800
E-mail: claio@claio.poznan.pl | NIP: 631 020 07 71, REGON: 000027542, BDO:000011457
Sąd Rejonowy w Gliwicach, X Wydział Gospodarczy | KRS: 0000853498
Bank SANTANDER nr konta: 73 1090 1346 0000 0000 3400 0300 PL
Bank SANTANDER nr konta: 40 1090 1346 0000 0001 3343 4042 EUR | KOD SWIFT: WBKPPLPP

and the so-called redox shuttle effect. Next, the candidate explores the topic of electrolytes in greater detail, with particular attention to the issue of highly concentrated electrolytes, which forms the core of her research work. In the chapter titled *Scope of the Thesis*, the candidate clearly and transparently presents the objectives of her doctoral work and its substantive scope. Figure 1.5, which graphically depicts this scope, is particularly helpful. The literature review is generally well-written, although it is rather concise and does not provide an in-depth analysis of the topic. However, the most important information relevant to the subsequent discussion of the results is provided, and it manages to avoid any glaring errors. The selection of cited literature is appropriate. In Chapter II, the candidate presents and discusses the experimental techniques used in her doctoral research. This chapter is thoroughly written, and in some cases, it briefly includes the theoretical foundations of the techniques employed. In Chapter III, the results of the candidate's own research are presented along with their discussion. The core of this research is comprised of two sections (III.3 and III.4) dedicated to the study of electrolytes. Additionally, the candidate has included sections on machine learning (Chapter III.5) and operando studies using Raman spectroscopy. The scientific results achieved will be discussed in further detail later in this review. From a formal perspective, a small portion of the results has been included as an appendix. The rationale behind this approach is somewhat debatable given the aforementioned limited overall volume of the research material. Nevertheless, the reviewer does not intend to critically challenge the candidate's choice. The bibliography is relatively extensive for the relatively small volume of the entire dissertation, containing 137 references, including some very recent ones, which is an asset and indicates doctoral candidate's good familiarity with the subject literature.

The overall structure of the dissertation is clear, it is carefully prepared in terms of editing, and it is free from glaring formal errors. The English language used in the dissertation is correct.

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
61-362 Poznań, ul. Forteczna 12, Tel: +48 61 27 97 800
E-mail: claio@claio.poznan.pl | NIP: 631 020 07 71, REGON: 000027542, BDO:000011457
Sąd Rejonowy w Gliwicach, X Wydział Gospodarczy | KRS: 0000853498
Bank SANTANDER nr konta: 73 1090 1346 0000 0000 3400 0300 PL
Bank SANTANDER nr konta: 40 1090 1346 0000 0001 3343 4042 EUR | KOD SWIFT: WBKPPLPP

Detailed Substantive Comments on the Research Results.

The doctoral candidate in her research on concentrated electrolytes for lithium-sulfur batteries studied a total of five lithium salts: LiTFSI, LiTf, LiTDI, LiPDI, and LiHDI. In the first part of the research, she focused on "classic" salts (LiTFSI, LiTf) and included LiTDI, a Hückel salt, for comparison. In the second part, she concentrated solely on Hückel salts (LiTDI, LiPDI, and LiHDI) at a selected concentration. The main idea of the first part was to investigate the influence of salt concentration on the physicochemical properties of electrolytes and the electrochemical characteristics of cells. For the study of local structure and speciation, the doctoral candidate prepared solutions with a fairly wide range of concentrations, reaching 7m, 5m, or 2m concentration depending on the salt. Using Raman spectroscopy, she was able to determine the percentage contribution of various fractions (free ions, ion pairs, aggregates) and correlate this data with ionic conductivity and viscosity, which is a valuable scientific outcome. In her study of ion transport processes, the doctoral candidate identified and explained the unexpected lack of a straightforward correlation between specific conductivity and the viscosity of electrolytes. The discussion of this phenomenon reflects the candidate's relatively good understanding of the literature in the field. In the section dedicated to the electrochemical studies in cells, the candidate generally obtained accurate charge/discharge characteristics for her samples. She was able to demonstrate an increase in cell capacity with rising salt concentration. However, in the case of LiTFSI salt, the candidate decided to exclude the highest concentrations (4m and 7m) from her experiments, citing the existence of similar studies in the literature. This decision leaves a slight sense of incompleteness, as it would have been interesting to see this data analyzed by the candidate for a more comprehensive picture. The surprisingly low capacity of the cells at low concentrations of LiTf is also noteworthy. The explanation that assumes high

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
61-362 Poznań, ul. Forteczna 12, Tel: +48 61 27 97 800
E-mail: claio@claio.poznan.pl | NIP: 631 020 07 71, REGON: 000027542, BDO:000011457
Sąd Rejonowy w Gliwicach, X Wydział Gospodarczy | KRS: 0000853498
Bank SANTANDER nr konta: 73 1090 1346 0000 0000 3400 0300 PL
Bank SANTANDER nr konta: 40 1090 1346 0000 0001 3343 4042 EUR | KOD SWIFT: WBKPPLPP

polysulfide solubility seems to be an oversimplification based on a preconceived notion, as at concentrations around 1m, the capacities should be higher.

Chapter 4 focuses on Huckel salts at relatively low concentrations, not exceeding 2m. The analysis of local structure and speciation is further enriched with FTIR spectroscopy, which is commendable. However, some inconsistency can be observed in the selection of concentrations. For the ion transport studies, only 1m and 2m concentrations were chosen, while for the electrochemical studies, only 2m was selected. Although the candidate justifies this by the high solubility of polysulfides at low salt concentrations, it would still have been valuable to include these in the research. Aside from that, the comparison of the three Huckel salts in the context of lithium-sulfur batteries is a rather interesting contribution to the research. In Figure 4.7, there is no data visible for LiHDI with the addition of LiNO3, which is mentioned in the discussion of the results and in the figure caption. It would be advisable to clarify whether this is an editorial error.

The solubility of lithium polysulfides in the electrolyte solution is a crucial phenomenon for the functioning of a lithium-sulfur cell, particularly in achieving favorable operational parameters. A solid understanding of the mechanisms by which sulfur transforms into polysulfides is therefore a challenging but essential task in the research of new electrolyte compositions. The candidate is aware of this, and the topic is consistently addressed throughout the dissertation in both experimental and theoretical contexts, which reflects well on the candidate's understanding of the issues she has undertaken to investigate. She dedicated Chapter 5 to attempts to predict the solubility of polysulfides using machine learning. The result is an interesting comparison between experimental and theoretically calculated solubility parameters of PS, showing a relatively high degree of correlation. In Chapter 6, she further delved into the mechanisms of PS dissolution and diffusion using the advanced technique of operando Raman spectroscopy. An interesting conclusion from the rather thorough analysis of Raman spectra, performed on cells both at open-circuit voltage and during cycling,

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
61-362 Poznań, ul. Forteczna 12, Tel: +48 61 27 97 800
E-mail: claio@claio.poznan.pl | NIP: 631 020 07 71, REGON: 000027542, BDO:000011457
Sąd Rejonowy w Gliwicach, X Wydział Gospodarczy | KRS: 0000853498
Bank SANTANDER nr konta: 73 1090 1346 0000 0000 3400 0300 PL
Bank SANTANDER nr konta: 40 1090 1346 0000 0001 3343 4042 EUR | KOD SWIFT: WBKPPLPP

is the lower concentration of lithium polysulfides near the lithium anode in more concentrated electrolytes. This was correctly interpreted as a decrease in polysulfide solubility or a reduction in their migration rate. This phenomenon undoubtedly warrants more in-depth investigation.

Summary and Conclusion

The doctoral dissertation submitted for review was carried out as part of the DESTINY PhD Programme and through scientific collaboration between the Warsaw University of Technology and Chalmers University of Technology. This is a valuable initiative that offers young scientists the opportunity for comprehensive development under the guidance of outstanding mentors, an opportunity that Ms. Kottarathil has undoubtedly benefited from. In her doctoral work, the candidate has achieved several interesting research results that expand our knowledge of electrolytes for lithium-sulfur batteries and logically continue the accomplishments of the Warsaw University of Technology team. She has demonstrated a good understanding of the relevant literature as well as the experimental and computational techniques used in battery component research. Thus, despite its relatively modest scope and length, as well as despite from some disputable choices that the candidate made, the work overall constitutes a significant contribution to the existing body of knowledge. Consequently, I believe that the dissertation meets the requirements set forth in the Law on Academic Degrees and Titles, and I recommend that M.Sc. Aginmariya Kottarathil be admitted to the subsequent stages of the doctoral proceedings.

Poznań 1.09.2024

Sieć Badawcza Łukasiewicz – Instytut Metali Nieżelaznych Oddział w Poznaniu
61-362 Poznań, ul. Forteczna 12, Tel: +48 61 27 97 800
E-mail: claio@claio.poznan.pl | NIP: 631 020 07 71, REGON: 000027542, BDO:000011457
Sąd Rejonowy w Gliwicach, X Wydział Gospodarczy | KRS: 0000853498
Bank SANTANDER nr konta: 73 1090 1346 0000 0000 3400 0300 PL
Bank SANTANDER nr konta: 40 1090 1346 0000 0001 3343 4042 EUR | KOD SWIFT: WBKPPLPP