Examiner's Report on
a Poznan University of Technology Doctoral Dissertation

EXAMINER:	Professor Wataru Sugimoto Institute for Aqua Regeneration (ARG) Research Initiative for Supra-Materials (RISM) Shinshu University, Tokida 3-15-1 Ueda 386-8567 JAPAN
THESIS TITLE:	One-step assembly of metal-ion capacitors using redox-active electrolytes
SUBMITTED BY:	Adam Maćkowiak
FOR THE DEGREE OF:	Doctor of Philosophy
SCHOOL/FACULTY OF:	Faculty of Chemical Technology
FINAL REPORT SUBMITTED ON:	**10 December 2024**

Examiner's Recommendation Checklist

✓	The thesis meets the required standards in terms of the nature and quality of work undertaken, and the degree can be awarded without any further work by the candidate, other than the correction of a small number of typographical, or similar, minor errors in the final copy.
✓	**- The doctoral dissertation presents general theoretical knowledge of a person applying for a doctoral degree in a chemical sciences discipline**
✓	**- The doctoral dissertation indicates skills to conduct the scientific activity by the applicant applying for a doctoral degree;**
✓	**- The doctoral dissertation presents the original solution of a scientific problem and/or the original solution for the application of research results in the economic or social sphere.**
✓	**- The review is ended with a clearly expressed, unambiguous POSITIVE conclusion.**

10 December 2024

Wataru Sugimoto

Date **Examiner's Signature**

Detailed Examiner's report for the degree in Doctor of Philosophy

Candidate: Adam Maćkowiak

Title of Thesis: One-step assembly of metal-ion capacitors using redox-active electrolytes

Examiner: Wataru Sugimoto (Shinshu University, Japan)

General comments

The PhD thesis of Adam Maćkowiak concerns the development of a novel and innovative pre-lithiation method applicable, though not limited to, Lithium-ion Capacitors (LICs) and other Metal-ion Capacitors.

The thesis is a rich, well-documented and well-written monograph devoted to advancement in fast charging energy storage device application. Electrochemical capacitors are characterized by long cycle life coupled with a good balance between energy and power density, differentiating them from other energy storage systems such as Lithium-ion batteries. While the energy density is lower than LIBs, electrochemical capacitors have been implemented into various practical applications owing to its capability of storing/releasing energy in seconds. LICs are a type of hybrid electrochemical capacitor which combines double layer capacitor mechanism and a battery-type charge storage, leading to 10 times higher energy density than typical electrical double layer capacitors. One of the difficulties of LIC and other related hybrid capacitors is the pre-lithiation process. Commercial LICs use sacrificial lithium metal, which not only complicates the process, but poses safety issues, leading to high cost. Several new concepts of pre-lithiation have been proposed, but all use 'sacrificial' compounds leading to dynamic composition change in the positive electrode or electrolyte. The development of an efficient, inexpensive and safe pre-lithiation processes should provide users with a new option for fast energy storage systems, opening the doors to wide-spread usage in energy harvesting and load-leveling applications.

The doctoral dissertation is composed of a thematically related set of manuscripts published or is under review in highly reputed scientific journals and has 245 pages.

The dissertation consists of 3 published articles and 2 manuscripts that are under review. The applicant is one of the authors of 5 other published articles, but I have not included these in the Review as they have not been incorporated in the dissertation. The main research findings are grouped into 3 chapters (Chapter III, IV, and V) devoted to three main issues: Chapter III deals with the proof-of-concept

of the single-step pre-lithiation process using redox-active additive in the electrolyte, suitable for use in LIC processing and fabrication (A1 and M1). Chapter IV dives into the mechanistic understanding of the single-step pre-lithiation process using redox-active additive with SPECS analysis complemented by analysis with other techniques (A2 and M2). Chapter V expands the technique to other metal-ion capacitors, namely Na-ion Capacitors (A3).

Detailed specific comments

The introduction section (**Chapter I**), presents a general literature review of present energy storage systems with emphasis on the comparison of various charge storage mechanisms and materials, the deliverable energy and power performance, cyclability and advantages/disadvantages. In particular, electrochemical capacitors including hybrid capacitors (Li, Na, and K-ion capacitors) has been highlighted as they are the main topic in this dissertation. This chapter is well documented based on a comprehensive survey on background science and relevant literature to justify Adam Maćkowiak's objectives of this thesis, which are summarizes in **Chapter II**.

Chapter III is based on a published article (A1) and a submitted work under review (M1) and focuses on a novel and innovative solution to the problematic pre-lithiation process which is essential to the assembly of LICs. Commercial LICs are fabricated using Li metal in the cell and uses this as the lithium source to prepare Li pre-doped graphite Li_xC_6 (a graphite intercalation compound with Li^+ in the interlayer). While this is a practical solution to prepare Li_xC_6, the use of Li metal, complicated cell structure, need to precisely control the lithiation process leaves room for improvement. Several alternative methods have been reported in literature including the use of over-lithiated positive electrodes and high Li+ concentration electrolytes. These methods suffer from dead mass or change in conductivity of the electrolyte. As a new pre-lithiation process, the use of redox-active salt dissolved in the electrolyte has been developed. This new concept is based on a redox-active salt (LiSCN) which upon positive potential scan oxidizes SCN anion at the positive electrode and intercalates Li^+ at the negative graphite negative electrode. The process is a one-step one where there is no need to take apart and reassemble the cell and does not leave any dead space (voids) after the pre-lithiation procedure. The key to this new additive is to use an anion that will be oxidized below the potential of positive electrode degradation and the oxidized products will not be reduced back (irreversible reaction). The conclusion is derived from characterization of the negative electrode structure by various analytical methods including FT-IR, Raman spectroscopy, X-ray diffraction X-ray spectroscopy, GC-MS analysis of the decomposition

products It has been found that this simple one-step method results in 1.6 times increase in energy density and slightly higher power performance. The process is also applicable to Na-ion capacitors.

Chapter IV is based on a published article (A2) and a submitted work under review (M2) and is devoted to a deeper understanding of the electrochemical properties of the one-step lithiation of graphite with redox-active LiSCN added into the electrolyte via Step-Potential Electrochemical Spectroscopy (SPECS) supplemented with Galvanostatic Intermittent Titration Technique (GITT). Different concentrations of LiSCN were tested to identify the optimal condition for lithium intercalation/deintercalation into graphite. In this Chapter, first, the applicability of the SPECS technique to electrochemical reactions involving Li^+ intercalation is considered with a model Li/graphite cell (previous studies of SPECS have been conducted on capacitive or pseudo-capacitive processes, whereas lithiation of graphite is a Faradaic process). SPECS analysis was utilized to deconvolute the contribution from double-layer charging (non-Faradaic charge accumulation) and residual capacity (Faradaic intercalation process), obtain the diffusion coefficient at each reaction stage, and elucidate the optimal additive concentration. The results were compared to GITT analysis; not only was it confirmed that the SPECS data are consistent with GITT showing its applicability to battery reactions, but the moment of polarization change differed from the two techniques. While both analytical methods provide similar results, Maćkowiak concludes from the analysis that the use of both methods in combination is affords a more in-depth and comprehensive view of the reactions. After confirming the applicability of SPECS to Faradaic reactions with the simplified model cell, SPECS is then applied to the evaluation of physiochemical parameters for LICs using redox-active LiSCN in the electrolyte. The contribution from total capacity, double layer capacitance, diffusion-limited capacitance, and residual component were evaluated from half-cell testing with Li/activated carbon and graphite/Li cells as well as a full cell Li_xC_6/AC. It was shown that the use of redox active LiSCN facilitates better lithium intercalation and results in a lower resistance.

Chapter V is based on a published article (A3) and attempts to find an alternative compound to the redox-active salt LiSCN. Preliminary studies of various Li salts identified lithium acetate (LiOC) as a candidate, and the applicability of this salt was studied for Li- and Na-ion capacitors. The electrochemical behaviour was studied by galvanostatic charge-discharge using full cells with a reference electrode to evaluate the progress of the individual electrodes. LiOAc and NaOAc were effective for pre-lithiation of Li- and Na-ion capacitors, achieving 104 Wh/kg and 368 W/kg for LIC and 89 Wh/kg and 22 W/kg for Na-IC. Marginal degradation of the cell was observed, nonetheless, the initial energy and power densities were comparable or slightly improved compared to conventional metal-ion capacitors. The pre-metallization process was assessed by studying the oxidized products with GC-MS. In the case of LIC, it

was found that the initial oxidation product CO_2, but subsequently reduced to various organic compounds. On the other hand, for the Na-ion capacitor, significant CO2 emission was observed; the difference was suggested to occur from the difference in lithiation or sodiation behaviour into carbonaceous materials.

Chapter VI briefly summarizes the key findings reported in this dissertation followed by a list of articles not included in this dissertation, scientific accomplishments, copyrights, and co-authorship statements. It is worth noting that Adam Maćkowiak is the first author of all five manuscripts included in this dissertation, showing that the individual is a scientifically established and mature young scientist with the ability to conduct research at a very high standard. Adam Maćkowiak is also first author of one paper and co-author of 4 other papers not included in the dissertation in well reputed peer-reviewed journals.

Overall conclusion

Overall, the thesis submitted by Adam Maćkowiak is very novel and comprehensive and provides a substantial contribution to advancement in metal-ion capacitor science and technology. It has been carefully written with negligible errors, the experiments have been carried out carefully, and the discussion based on the results are convincing. Finally, I would like to state that the dissertation meets the formal and customary requirements and expectations for a doctoral work in this discipline. Thus, I am in strong favour of Adam Maćkowiak proceeding to the public doctoral defence stage.

Minor suggestions

I have a few questions or comments that could be easily answered or explained during the doctoral defence and minor grammatical suggestion that may be modified after the defence.

1. Page 18: Present fuel cells do not use platinum black, but carbon supported platinum or platinum alloys. Suggest re-phrasing.
2. Page 18: What criteria did the author consider for the choice of references for this section? In general, when citing references for a general statement, I would choose a representative review paper from well-established reputed research groups.
3. Page 18, last sentence: Suggest to removing “such as the mentioned hydrogen-powered buses)”, as this has not been mentioned previously.

4. Page 21: Suggest to spell-out KERS (although it is listed in the abbreviations section).

5. Page 24: Consider re-phrasing “1999 Conway defined a term “supercapacitor”. “Supercapacitor” was trademarked by NEC 1978, now transferred to TOKIN.

6. Page 27: The statement “smaller pores, the greater capacitance” is miss-leading. It would be better to define the pore-size (below or above 1 nm) and if it is areal, gravimetric, or volumetric capacitance.

7. Page 41: I would choose Mi-MH instead of Ni-Cd here. Ni-Cd is used for very specific applications and availability is not common compared to Ni-MH.

8. Page 43 and 45: Change ‘anode electrode’ to ‘anode’ or ‘negative electrode’

9. Page 45: Change ‘polyacenic semiconductive’ to ‘polyacenic semiconductor’. The reference here maybe a mistake. I believe the correct paper is https://doi.org/10.1016/S0379-6779(97)81181-2.

10. Page 56: Please re-check the cited reference for Figure 16. I could not find this figure in this paper.

11. Page 57: The abbreviation ‘GCPL’ is not commonly used. Electrochemistry textbooks term this method as chronopotentiometry or constant current potentiometry (CP). This is also not a technique, but a method (also applicable to CV). The same for ‘PEIS’, simply ‘EIS’ is more commonly used.

12. Page 58: Define I_R before equation 3.

13. Page 59: A brief comparison of pros/cons of SPECS vs GITT as a table would help readers to understand the advantages of SPECS.

14. Page 64 line 12: Consider rephrasing ‘operation of electrical double-layer capacitors’ to ‘mechanism of capacitive and pseudo-capacitive systems’. An electrical double-layer capacitor is a full cell system. SPECS has been applied to MnO2 and RuO2 which are not classified as materials for electrical double-layer capacitors.

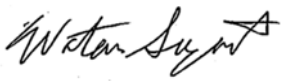
15. Page 105 line 4 from bottom: It would be nice to comment here on the total charge necessary to fully react (consume) SCN and compare this value to the amount of LiSCN actually added in the electrolyte.

16. Page 107: Suggest reporting XRD data of the lithiation process as supporting information, or mention that this has been studied in another part of this dissertation.

17. Page 107-108: Figure 3 and 4a seems be a reproduction from A1. Suggest to state so in the caption.

18. Page 150: It is mentioned that EDLCs have a long lifespan of 1 million cycles, and then 100,000 cycles later on. Fix inconsistency.

19. Page 173 lines 4 and 8: Change ‘won’t’ to ‘will not’.



Wataru Sugimoto

10 December 2024