Review Report of Doctoral Dissertation

Title: Structural Characterization of Materials for Energy Applications Using NMR Spectroscopy

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Brief Summary of the Thesis and Its Results

The dissertation focuses on the structural characterization of materials for energy applications, specifically polymer electrolytes, conductive polymers, and inorganic semiconductors of the perovskite type. The primary techniques employed are both liquid and solid-state NMR spectroscopy. While standard NMR techniques form the basis of the study, the research also incorporates advanced methodologies such as T1 and T2 relaxation time measurements, pulse-field gradient NMR for ion diffusion studies, exchange spectroscopy (EXSY) for investigating Li-ion exchange, and ultra-wideband WURST-QCPMG experiments for semiconductor structure analysis.

In addition to these established methods, the thesis introduces novel approaches such as the calculation of Li+ cation self-diffusion rates using T1 and T2 relaxation data, particularly useful for cases of low ion mobility where standard pulse-field gradient methods are ineffective. The development of software for processing spikelet ultra-wide NMR spectra represents another innovative contribution. The results of this research have been disseminated through six peer-reviewed journal articles, with a seventh under review.

Commentary on Individual Aspects of the Thesis

1. Introduction and Theoretical Background:

The introduction provides a solid theoretical background on the NMR experiments utilized in the study. It effectively sets the stage for the subsequent chapters by explaining the fundamental principles of NMR spectroscopy and detailing the specific techniques employed. The second part of the introduction offers a comprehensive literature review and explanation of the specific types of energy materials studied. This section effectively contextualizes the research within the broader field of energy materials science, highlighting the relevance and importance of the work.

2. Results and Discussion:

The summary of the results section describes six independent investigations of various properties of different materials, unified by the application of NMR spectroscopy to elucidate the relationship between the structure of the materials and their properties. The results presented in the thesis are robust and well-supported by experimental data. The discussion provides a thorough interpretation of the findings, linking them to the broader context of materials science and energy applications. The explanation of the novel methodologies and their impact on the field is particularly clear and convincing.

3. Research Significance and Innovation:

The dissertation successfully demonstrates the application of both standard and already established advanced NMR techniques to the study of materials relevant to energy applications. The inclusion of novel methodologies, such as the Li+ self-diffusion rate calculation and the development of specialized software, showcases the author's innovative contributions to the field.

4. Methodological Rigor:

The author exhibits a strong command of NMR spectroscopy, employing a diverse array of techniques to obtain comprehensive structural insights. The use of T1 and T2 relaxation time measurements, pulse-field gradient NMR, EXSY NMR, and WURST-QCPMG experiments is well-justified and effectively applied. The interdisciplinary nature of the work, bridging chemistry and physics, is particularly noteworthy.

Specific Comments on Professional, Linguistic, and Formal Aspects

Professional Aspects:

The thesis demonstrates a high level of professionalism in its experimental design, data analysis, and presentation of results. The interdisciplinary approach enriches the research, reflecting a deep understanding of both chemistry and physics.

Linguistic Aspects:

The dissertation is written in clear, comprehensible English, with only a small number of typographical errors found. The language is precise and appropriate for the scientific content, making the complex subject matter accessible to a broader audience.

Formal Aspects:

The structure of the thesis is logical and well-organized. Figures, tables, and references are used effectively to support the text.

Final Evaluation and Recommendation

The dissertation presents a considerable contribution to the field of materials science, specifically in the application of NMR spectroscopy to energy-related materials. The combination of standard and advanced NMR techniques, along with the introduction of novel methodologies, underscores the research's innovative nature.

Apart from correcting the minor mistakes and typographical errors listed in the appendix, I recommend the author to make the USS software open source. Adding an open-source license and publishing the source code on GitHub would improve its visibility and sustainability.

Given the thoroughness of the experimental work, the clarity of the writing, and the relevance of the findings, I highly recommend this thesis for defence.

Reviewer:

Dr Tomas Lebl
Senior Scientific Officer
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24 May 2024

Appendix 1 - Questions:

1. The sentence on the page 26 "The cross-peaks may have the same or opposite phase with respect to diagonal peaks depending on the size of investigated moieties." is not entirely true because the size of moiety is only one of the factors that determines whether NOE effect, and consequently phase of cross-peak in NOESY spectrum, is positive or negative. Could you elaborate on the fundamentals of NOE effect origin and explain why NOE effect can be positive or negative?

2. On the page 63, it is mentioned that water molecules are immobilized due to their coordination to the perchlorate anion. Can you explain in more detail the bonding mechanism between water and perchlorate anion and can you rationalise why coordination of water molecules to Al^{3+} or Cl^{-} ions is weaker than to the perchlorate anion?

Appendix 2 – List of corrections

1. The equation 1.1 does not seem to be right. Both spin quantum number *I* and gyromagnetic ratio γ are scalars. A product of two scalars yields a scalar but nuclear magnetic moment is a vector. Gyromagnetic ratio γ is proportionality factor between two vectors nuclear magnetic moment and spin angular momentum. Some amendments in preceding paragraph are also needed to make this part right.
2. Page 8, Paragraph - Chemical shielding interaction, line 1: "eternal" should be "external".
3. Page 38, line 16: "stability of the electrolyte stability" delete the second "stability" word
4. Page 58, Figure 4.13. caption for part (b) is missing, caption line 3: "trnsdport" should be "transport",
5. Page 62, line 17: "with" should be "which".
6. Page 79, Figure 4. 27. caption mentions labels (a, d and c) but the labels are missing in the image.