

## Review

on a thesis entitled: "*Molecular modeling of components for post-lithium-ion batteries*", submitted by **Hristo Georgiev Rasheev** for awarding the educational and scientific degree "**Doctor**" in Professional field 4.2. „Chemical Sciences“ (Theoretical Chemistry - Computational Chemistry)

Hristo Rasheev graduated from the Faculty of Chemistry and Pharmacy at Sofia University "St. Kl. Ohridski" in 2018 with a master's degree in Computational Chemistry. Right after the graduation, in the period 2019-2022, he was a full-time PhD student (program Theoretical Chemistry) in Laboratory of Quantum and Computational Chemistry, Department of Physical Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, under the supervision of Prof. Dr. Alia Tadjer (Faculty of Chemistry and Pharmacy at Sofia University) and Prof. Dr. Radostina Stoyanova (Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences). The approbation of the PhD thesis took place on January 28, 2022 by the complemented with external experts Council of the Department of Physical Chemistry at the Faculty of Chemistry and Pharmacy, Sofia University.

The topic of Hristo Rasheev's PhD thesis is motivated by the idea of increasing the efficiency of metal-ion batteries by using mixed charge carriers. The development of such batteries is at an early stage and their improvement is a big challenge due to the complex interactions between the components in the electrolyte and at the electrode/electrolyte interface. The theoretical study of these complex interactions with an emphasis on the solvation/desolvation processes in electrolytes containing a combination of two types of cations, is the main goal of this thesis. By means of quantum-chemical calculations, carried out exhaustively within the Density Functional Theory, close-to-the-known combinations of cations, anions, solvents and electrode surface have been modeled. Original computational schemes are proposed for optimization of objects of finite and infinite size, neutral and charged particles, taking into account the influence of the environment. The research topic is innovative and relevant, and the results obtained are an indisputable contribution and progress in the field, as they can be used to improve existing and model future components for post-lithium-ion batteries.

The dissertation is written on 137 pages and includes 41 tables and 55 figures, which give a clear representation of the structural models and correlations studied and testify to the volume and depth of the performed calculations. The Synopsis correctly presents the content of the thesis, which is structured in three standard sections: *Literature overview*, *Computational methods*, *Results and discussion*, preceded by *Introduction*, *Purpose and Tasks*, and ends with *Conclusions*, *Contributions*, *Bibliography and Appendix*. The main goal of the research and the accompanying tasks are clearly and concretely defined. The *Literature overview* of the existing research on molecular modeling of the components of metal-ion batteries is analytical and comprehensive and describes the need of theoretical studies. 183 literature sources and 5 websites were cited proving the good knowledge of Hristo Rasheev on modeling of components for post-lithium-ion batteries, which allows him to critically evaluate literature data and propose new constructive solutions. The *Computational methods* are presented concisely and competently, and their specific application is

argued in the various stages of the study. The *Results and Discussion* section chronologically presents the results of the research in three parts.

In the first part, "*Theoretical assessment of the electrochemical stability of electrolyte solvents for rechargeable batteries*", an in-depth analysis of the possible conformations and electrochemical stability of different solvents in electrolytes for rechargeable batteries is made. By estimation of the absolute electrochemical potential of oxidation and reduction, Hristo Rashev proposed an improved scheme for determining the electrochemical stability window of solvents for non-aqueous electrolytes, as well as an original strategy for its expansion by adding "sacrificial molecules".

The research in the second part, "*Modeling of solvation and desolvation processes in mono- and dual-cation electrolytes*", is essential to achieve the main goal of the dissertation. It is important to note that for the first time are reported results from simulations of electrolytes with mixed ions. Hristo Rashev successfully has developed a computational approach based on molecular models simulating binuclear cationic complexes of homonuclear cation pairs ( $\text{Li}^+/\text{Li}^+$ ,  $\text{Na}^+/\text{Na}^+$  and  $\text{Mg}^{2+}/\text{Mg}^{2+}$ ) as well as heteronuclear cation pairs: a) with the same charges but different ionic radii ( $\text{Li}^+$  and  $\text{Na}^+$ ), b) with different charges but commensurate ionic radii ( $\text{Li}^+$  and  $\text{Mg}^{2+}$ ) and c) with different charges and different ionic radii ( $\text{Na}^+$  and  $\text{Mg}^{2+}$ ). The modeling was performed correctly, taking into account the influence of the environment, with a suitable for this type of complexes method, B3LYP/6-31G (d,p), providing reliable results in a reasonable computational time. SMD solvent model was used, specially parametrized to reproduce free energy values. The performed model calculations are important for the research on the topic, as they help to assess important structural and energetic characteristics of the complexes that are difficult or inaccessible for experimental determination (stability, solvation energy and desolvation energy). Some of the established dependencies are particularly valuable as they explain experimental facts, for which there is no reasonable interpretation up to the moment. On the other hand, they can be useful in the selection of a mixed electrolyte composition for the construction of new hybrid metal-ion batteries. The original contributions of Hristo Rashev to the research are the proposed models and computational schemes for quantitative assessment of the propensity of binuclear complex formation, by analyzing structural characteristics of ion-solvent clusters and the polarizing effect of cations and by estimating the energetics of the ion-solvent interactions. Some important new results and correlations from the research in this part of the thesis are given briefly below.

- The coordination numbers of the ions, the spatial organization and the stability of the possible mono- and binuclear complexes, their structural and energetic characteristics have been established. The charge transfer has been analyzed. Correct structural models are proposed.
- A new important for the practice relationship between the solvation energy of the charge carriers ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ) and their transport properties in the electrolyte has been proven. The addition of  $\text{Na}^+$  to  $\text{Li}^+$  and  $\text{Mg}^{2+}$ -electrolytes has been found to improve the ionic mobility, altering the solvation pattern by forming heteronuclear  $\text{Na}^+/\text{Li}^+$  and  $\text{Na}^+/\text{Mg}^{2+}$  pairs.
- From the profiles of the free desolvation energy in gas phase and in implicit solvent it was found that it increases with decreasing the solvent molecules, which correlates well with the aspiration

of the ions to solvation and compensation of their charge (especially for  $\text{Mg}^{2+}$ - $\text{Mg}^{2+}$  complexes). It has been proven that the desolvation process becomes energetically favorable when the number of the solvent molecules is higher than the optimal coordination numbers of  $\text{Li}^+$  and  $\text{Mg}^{2+}$ . In line with available experimental data, the monovalent homo- and heteronuclear complexes of  $\text{Na}^+$  (in gas phase and in implicit solvent) showed the easiest desolvation.

- The finding that the binding of  $\text{Li}^+$  or  $\text{Na}^+$  to  $\text{Mg}^{2+}$  in binuclear complexes leads to easier desolvation of the ions compared to mononuclear ones, is very important as it may explain the experimentally established fact that double salt electrolytes containing both  $\text{Li}^+$  (or  $\text{Na}^+$ ) and  $\text{Mg}^{2+}$  are superior to single cation electrolytes.
- It has been proven that the  $\text{PF}_6^-$  counter-ion has a negligible effect on the geometry of the complexes, has minor participation in the redistribution of electron density with the solvent and thus does not play a significant role in the solvation and desolvation of the cations in both mono- and binuclear configurations.

The third part, „*Modelling of interactions at the electrode/electrolyte interface*”, describes calculations with two types of atomistic electrode models: a  $\text{TiO}_2$  molecule (minimalistic model) and spinel-type electrode surface of lithium titanate,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (realistic model). Physically correct periodic models have been constructed with the proven preferred topology of cation-EC- $\text{TiO}_2$  clusters. The most preferred adsorption positions on the surface for  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  have been determined. More important results and dependencies of the research in this part are as follows.

- In accordance with experimental data, the geometric optimization of the adsorbed EC molecule predicted a dehydrogenation reaction. The calculated free energies have shown that the interaction with the model electrode facilitates the desolvation of the cations.
- The adsorption and desolvation of mononuclear complexes of general formula  $(\text{M}_n^+(\text{EC})_{1-3})$  is simulated and studied by molecular models of single cations with 1 to 3 EC molecules adsorbed on the fixed surface of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  at two different sites for each cation. The calculated desolvation energy values of the three ions are the highest in vacuum, followed by those on the surface and the lowest ones are in implicit solvent. Weak dependence of the results on the layer thickness was found. Reliable for analysis geometric, energetic and charge characteristics of the structures are obtained, from which useful for the practice correlations are derived.
- The desolvation of binuclear complexes of the type  $\text{M}_1^{n+}\text{M}_2^{m+}(\text{EC})_{0-3}$  (for the heteronuclear combinations of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ ) is clarified by means of detailed modeling of complexes on the surface. Valuable information has been obtained about the interactions and the competition between the cations. It has been found that in mixed electrolytes the binuclear complexes desolvate at the electrode/electrolyte interface more easily than the mononuclear ones.

The dissertation is characterized by good scientific style and correct terminology. The text of the dissertation convinces me of Hristo Rashev's in-depth knowledge of the topic, his excellent theoretical training and capacity for independent scientific research. The results obtained are discussed in depth and critically and there is no doubt that they are the personal work of Hristo

Rashev. The dissertation is based on two scientific articles in high-ranking journals: ChemPhysChem (Q1, IF, 3.102) and ACS Omega (Q1, IF, 3.512). In both articles, Hristo Rashev is the first author and co-author only with his supervisors, which once again confirms his high personal contribution. Hristo Rashev has participated in other three publications related to the topic of the thesis. He reported results on the topic at nine scientific forums in the country and abroad. Hristo Rashev participated very successfully in three completed doctoral projects at Scientific Research Fund of Sofia University, in 2 national research projects and in 2 national projects with European co-financing. He has participated many times in national and international Olympiads and competitions, received a number of scholarships and awards and has teaching experience in exercises and seminars. He was a member of the Faculty Council of Faculty of Chemistry and Pharmacy, a member of the Faculty Student Council of Faculty of Chemistry and Pharmacy and a member of the commission for the competition for young scientists and postdoctoral students at Faculty of Chemistry and Pharmacy at Sofia University. All these scientometric and biographical data are an excellent certificate for Mr. Rashev and present him as a successful and promising researcher.

**Conclusion.** The theoretical research described in the thesis was performed at a high scientific level, competently and comprehensively. The results obtained are an indisputable contribution to the development of electrolytes for post-lithium-ion batteries. The conclusions from the research have not only theoretical significance but also practical usefulness for the field and can be used as a good basis for future experimental research of these and similar systems. Based on the above, I believe that the proposed thesis fully satisfies all the requirements of the Law for development of the academic staff in Republic of Bulgaria and the Recommended Criteria for obtaining scientific degrees and holding academic positions at Sofia University for the Professional field "Chemical Sciences". Taking into account the level and the volume of research done, the quality of the thesis and the contributions of Hristo Rashev in it, I find it reasonable to give my positive assessment and propose to the esteemed Scientific Jury to award the educational and scientific degree "Doctor" to Hristo Georgiev Rashev in Professional Field 4.2 "Chemical Sciences" (Theoretical chemistry - Computational Chemistry)

Reviewer:

March 29, 2022, Sofia

(Natasha Trendafilova, Prof. Dr.)