

REVIEW

*on the PhD thesis for awarding the educational and scientific degree “Doctor”
in professional field 4.2. Chemical sciences, PhD program Theoretical chemistry
(Computational chemistry)*

PhD candidate: Hristo Georgiev Rasheev, full-time student, Faculty of Chemistry and Pharmacy, Sofia University “St. Kliment Ohridski”

Dissertation title: “**Molecular modelling of components for post-lithium-ion batteries**”

Supervisors: Prof. Dr. Alia Tadjer and Prof. Dr. Radostina Stoyanova

by Assoc. Prof. Dr. Silvia Emilova Angelova,
Institute of Optical Materials and Technologies “Acad. J. Malinowski”- BAS,
member of the scientific jury, appointed by order № RD-38-86/07.02.2022,
of the Rector of Sofia University “St. Kliment Ohridski”

I. Biographical information

Hristo Georgiev Rasheev graduated in 2012 from National Gymnasium of Natural Sciences and Mathematics “Acad. Lyubomir Chakalov” (Chemistry) in Sofia. As a student he participated in many national and international competitions in chemistry and won numerous awards. In the period 2012-2018 he was a student at Sofia University “St. Kliment Ohridski” and acquired a Bachelor's degree in Chemistry and a Master's degree in Computational chemistry in 2016 and 2018, respectively. In 2019 he was enrolled as a full-time doctoral student at the Laboratory of Quantum and Computational Chemistry, Department of Physical Chemistry, FCP-SU. Hristo Rasheev joined this group in 2014 and gained solid theoretical knowledge and research experience, which he expanded through short-term internships/trainings abroad (UK and Sweden). As a student he actively participates in governing bodies in FCP-SU - he is a member of the Faculty Council, the Faculty Student Council, a commission for a competition for young scientists and postdoctoral students at FCP-SU. His teaching experience is impressive - a teacher at NGNSM “Acad. L. Chakalov” (“Structure of matter”), teacher of chemistry in English at Darbi College, leads exercises and seminars for students of various specialties in FCP, consultant on 2 theses (BSc and MSc). His excellent performance as a student and PhD student is highly appreciated - he received an Olympic scholarship from the American Foundation for Bulgaria and a scholarship from the Evrika Foundation - Talents program, finalist in the PhD scholarship competition of the Karoll Knowledge Foundation.

II. General description of the dissertation

The submitted for review dissertation on “Molecular modeling of components for post-lithium ion batteries” has a total volume of 140 pages (of which 11 pages of references and 3

pages of application) and is structured traditionally - consists of introduction, objectives and tasks, literature review, theoretical methods, results and discussion, conclusions, contributions, bibliography and application. The bibliography includes 188 literature sources. The cited literature is focused on the researched scientific problem. The exposition in the dissertation is accurate, precise, supported by high-quality illustrative material and tables. The dissertation is accompanied by an abstract of 39 pages, which is designed according to the requirements, contains all sections of the dissertation (excluding the literature review) and adequately presents the dissertation content in a concise form.

The research in the dissertation is focused on the so-called “post-lithium” batteries, i.e. batteries that surpass the popular lithium-ion batteries (LIBs), currently the most promising and fast-growing technology for the production of rechargeable batteries. Lithium-ion batteries power almost everything around us - from smartphones and laptops to electric vehicles. They have a unique ability to store and produce energy, they are compact, which makes them an indispensable part of modern mobile devices. Expectations for the next generation of batteries are even higher. One such new generation of batteries could be that of hybrid batteries, i.e. metal-ion batteries with mixed charge carriers.

The objective of the dissertation is modeling of solvation and desolvation in electrolytes containing two kinds of cations with account of the environment’s effect in order to establish whether the cations compete or cooperate. According to the author, there is little experimental data on the processes of solvation/desolvation of ions in the electrolyte and especially in the vicinity and in contact with the electrode surface, which are subject to speculative interpretation. The methods of modern theoretical chemistry are suitable for explaining processes or phenomena by modeling and studying model systems in order to obtain information that cannot be obtained from the experiment. To achieve research objective, the following tasks are set:

- Development of an appropriate computational protocol for geometry optimization of finite and infinite systems comprising neutral and charged particles;
- Selection of a reliable scheme for assessment of the thermodynamic parameters characterizing the electrochemical behavior of the targets of study;
- Choice of combinations of cations, anions, solvent and electrode surface, closest to the available technological production schemes.

In the introduction to the literature review the author very logically and in accessible language acquaints the reader with LIBs, their structure and mode of operation, their advantages and disadvantages, the need to improve existing technologies and materials. It is stated that an alternative approach to achieve higher efficiency of metal ion batteries is the replacement of LIB with hybrid ones, i.e. metal-ion batteries with mixed type current carriers. The three main parts of the literature review are devoted to electrolytes for metal-ion batteries, the electrode/electrolyte interface and the electrode materials, respectively.

In the section on electrolytes, it is clarified that “electrolyte” in the scientific and technical literature means a mixture of dissolved salt and solvent, as salt contains a metal ion, which acts as a carrier of electric charge between the electrodes during battery operation. Then suitable salts (with maximum bulk counterion and low charge) and different classes of non-aqueous/organic solvents are considered - cyclic ethylene carbonate (EC), propylene carbonate (PC) and acyclic dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylmethyl

carbonate (EMC). The possibility of using solid-state electrolytes and ionic liquids as an alternative to liquid ones is mentioned. It has been explained that the electrochemical stability of the electrolyte depends mainly on the redox properties of the solvents, as the dissolved salt is more resistant to electrochemical oxidation and reduction. The available literature data on quantum chemical and/or molecular dynamic treatment of the metal ion-solvent system are described in detail, while the available data on the interactions and diffusion of electrolyte ions are scarce.

The electrode/electrolyte interface section of the literature review compactly and concisely describes the complex processes that take place at the anode-electrolyte and cathode-electrolyte interface, as well as the nature and function of the anode decomposition products layers (Solid Electrolyte Interface, SEI) and of the cathode (Cathode Electrolyte Interface, CEI). The methods of computational chemistry have been used to study the probable mechanisms by which the SEI layer is formed and to model the adsorption of solvent molecules on the electrode. The electrode materials are also examined in detail, tracing the evolution of anode and cathode materials and outlining the prospects of promising candidates.

The clearly structured and informative literature review is proof that the PhD candidate is well aware of the state of the problem. This allowed the specific definition of the tasks and the choice of methods for their implementation. The basics of the theoretical methods used to conduct the research in the dissertation are presented compactly and concisely. The way they are presented shows that the PhD candidate has mastered the tools of theoretical chemistry and handles them easily.

III. Main scientific results

Results and discussion consists of three chapters – A, B and C, focused on three different aspects of the study. For each of the three sections a different methodology/computational protocol is used, argued and described in detail.

A. *“Theoretical assessment of the electrochemical stability of electrolytes solvents for rechargeable batteries”*

In this section, the oxidative and reductive stability of four solvents used in rechargeable batteries was assessed: ethylene carbonate (EC) and dimethyl carbonate (DMC) for LIBs; propylene carbonate (PC) for LIBs and sodium-ion batteries, and diglyme (G2) for sodium- and magnesium-ion ones. The theoretical calculation of the electrochemical potential is based on assessment of the free energy of the processes of electron(s) acceptance or abstraction followed by evaluation of the respective electrode potential of reduction or oxidation. An important factor influencing the energy of the process is the presence of a dielectric medium, so all optimizations are performed in an implicit solvent medium with the corresponding dielectric constant of each solvent, testing two models - PCM and SMD. As an estimate for the performance of different methods (MP2 + 9 DFT functionals, different basis sets = 16 methods in total) compared to experimental results, the ionization energy of a Li atom in the gas phase is calculated and the absolute potential of Li^+/Li^0 couple in water is evaluated using tabular data for ΔG of metal lithium atomization. The closest to the experimental values of ionization energy are the values obtained at theoretical levels MP2 (full)/6-31+G(d,p) and $\omega\text{B97XD}/6-311+G(d,p)$. The conformers of dimethyl carbonate and diglyme are also studied with a wide range of methods. For the other two solvents (ethylene carbonate and propylene

carbonate) no conformational isomers are reported due to the presence of a cycle and the absence of a mobile side chain. The oxidation and reduction potentials of the solvents are calculated and the results obtained are critically discussed.

The contribution of the studies described in this chapter is to refine a computational protocol for determining the window of electrochemical stability of solvents for non-aqueous electrolytes. The proposed scheme for the assessment of Electrochemical Stability Window (ESW) differs from the classical one. It is shown that theoretical results are improved by using a sufficiently large basis set (at least triple- ζ) and an implicit model for accounting for the environment. A strategy is proposed to expand the ESW by adding “sacrificial additives”.

B. “Modelling of solvation and desolvation in dual-cation electrolytes”

This chapter presents the results of modeling of mixed Li/Na, Li/Mg and Na/Mg ionic electrolytes. In order to determine whether two metal ions compete in solvation in solution and what the specific characteristics of this competition are, models containing two identical or two different metal ions and an increasing number of solvent molecules is built. To establish a correlation between structural and energy characteristics and charge density, the model binuclear complexes are composed of homo- and heteronuclear pairs of cations, the latter having:

- same charges but different ionic radii (Li^+ and Na^+);
- different charges, but commensurate ionic radii (Li^+ and Mg^{2+});
- different both charges and ionic radii (Na^+ and Mg^{2+}).

The processes of solvation/desolvation at the molecular level in electrolytes with mixed cations are clarified by quantifying the tendency to form binuclear complexes, analyzing the structural characteristics of the ion-solvent clusters and the polarizing effect of cations and estimating the energy of the interactions ion-solvent. For comparison, solvation/desolvation data on mononuclear complexes of Li^+ , Na^+ and Mg^{2+} in the same solvent (ethylene carbonate) are used. The effects of the polarity of the medium and the presence of a counterion are also discussed.

Each element of the study is described in detail - the spatial organization of the complexes, the preferred coordination numbers, electron density distribution, solvent effect (implicit model, optimization) - solvation/desolvation, counterion effect (PF_6^-), including the so-called “assisted desolvation” - the participation of fluoride ions (by-product) in the interaction with cations that facilitates the desolvation of the metal cation.

Interesting dependences are found for dication non-aqueous electrolytes - in mixed Li-Na electrolytes binuclear complexes are preferred only in the area of depleted solvent, while in mixed Li-Mg and Na-Mg electrolytes binuclear complexes dominate over mononuclear ones even at higher solvation levels. The PF_6^- counterion has no significant effect on desolvation, but its degradation products such as F^- facilitate the complete desolvation of binuclear complexes.

C. “Modelling of interactions at the electrode/electrolyte interface”

A particularly interesting part of the study is the modeling of the electrode/electrolyte interface interactions with the inclusion of periodic calculations for non-minimalistic (realistic) models of the electrode surface. The minimalistic models of metal cation-EC- TiO_2 clusters

(B3LYP/6-31G**/SMD calculations with G09) are used as a guide for building periodic models.

To build the adsorption models, a layer (~ LTO) of 168 atoms is used - 32 lithium, 40 titanium and 96 oxygen atoms, as the positions of the atoms on the surface are fixed. The adsorption sites on the surface, the adsorption and desolvation of mononuclear metal cation-EC complexes, the influence of layer thickness, the desolvation of binuclear complexes, the influence of the counterion on the adsorption and desolvation of mono- and binuclear complexes are described consistently and logically. The PhD candidate critically notes the dependence of the results on the complexity/realism of the used model and the limitations arising from this in terms of the reliability of the predicted picture of the process. The model for simulating the electrode-electrolyte interface allows to explain some side effects of decomposition of the electrolyte components as a result of their interaction with the electrode surface.

IV. Contributions and significance of research

The dissertation contains scientific results that represent an original contribution to science. The results and theoretical considerations in the dissertation are presented in an excellently organized and extremely clear way. There is no doubt that the scientific contributions are personal work of the PhD candidate. The main contributions formulated by him (four in number) are excellently defined and accurately reflect the scientific results.

The contributions of the dissertation are in the field of fundamental research of processes occurring in metal-ion (lithium-ion and hybrid) batteries. Detailed knowledge (even only at theoretical level) of the interactions in the electrolyte and at the electrode interface supports the development of new, more efficient electrolytes and new electrode materials. This makes the research relevant, promising and significant.

V. Dissemination of results

The research on the topic of the dissertation was published in 2021 in two publications in reputable scientific journals - ChemPhysChem (IF=3.102, Q1) and ACS Omega (IF=3.512, Q1). The materials on the dissertation are presented at 9 national and international scientific events, at 4 of them the PhD candidate gave oral presentations.

VI. Critical remarks and recommendations

I have no critical remarks and recommendations on the dissertation. The presentation is excellent, illustrated with aesthetically pleasing and informative figures and tables. All this contributes to the overall excellent impression of the author's qualities and his ability to analyze, present and summarize the data obtained from theoretical modeling.

VII. Conclusion

The materials presented under the current procedure for awarding the educational and scientific degree "Doctor" meet the requirements of Development of Academic Staff in the Republic of Bulgaria Act (DASRBA), the Rules on the conditions and procedure for acquiring science degrees and holding academic positions in Sofia University "St. Kliment Ohridski" and the minimum national requirements in the professional field. The PhD candidate, despite his

short research experience, has significant scientific achievements and great potential for future development. I give a positive assessment of the dissertation and support the awarding of the educational and scientific degree “Doctor” to Hristo Georgiev Rashev in professional field “4.2. Chemical sciences”.

Sofia

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/Assoc. Prof. Dr. Silvia Angelova /