

Solvation shell structure and dynamics of glyme based electrolytes for sodium-ion batteries

Ab initio molecular dynamics study of glyme based electrolytes used in co-intercalation sodium-ion batteries

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In Short

- The structure and dynamics of solvation shells of common electrolytes showing co-intercalation behaviour
- Car-Parrinello molecular dynamics of glyme based electrolytes
- Size, and content of solvation shell
- Stability of solvation shell

Rechargeable batteries in the form of the lithium-ion battery (LIB) has become ubiquitous in modern day society. From its entry unto the market in 1991 LIBs has enabled wide spread usage of portable electronics, most noticeably in the form of laptops and smartphones, and has become the prime energy storage unit in electrical vehicles. Moreover, the usage of rechargeable batteries is projected to increase by two to three orders of magnitude. But, it is not only in the electromobility sector where the usage of batteries will increase. With the current transition to a society powered by renewable energy sources, such as solar and wind, there is a growing need for practical and efficient energy storage due to the transient nature of these energy sources, and the use of stationary storage is thus projected to grow exponentially [1].

LIBs rely on the availability of lithium and natural graphite, and to a certain extent on cobalt, concentrated in third world countries and conflict zones, whose long term supply for the growing energy storage demands is insufficient [2]. Besides the issues of the sustainability of the raw material needed to produce LIBs, several improvements to the current battery technology is sought after, including greater energy and power densities, improved safety aspects and cycle life, recyclable, reduction in cost, fast charging capabilities. Therefore, several possible next generation battery technologies are being investigated, with the aim of replacing the LIB in several key applications. One such next generation battery technology is the sodium-ion battery (SIB). These batteries show similar performance levels to LIBs, but are safer and can be constructed from abundant and sustainable natural resources [2–5]

One of the main differences between SIBs and LIBs is the negative electrode. In LIBs graphite is used as a negative electrode, where lithium cations are intercalated between the graphene sheets, yielding a high specific capacity, and occurs at a low potential vs. lithium metal, setting the stage for a high energy density system. Such high capacity systems can not form with sodium cations, due to an unfavourable interaction between the sodium cations and graphite [7–10], and instead hard carbon has been the main negative electrode employed in SIBs [11]. Recently, it was discovered that graphite can be used in conjunction with sodium using diglyme (G2) based electrolytes, through the formation of ternary graphite intercalation compounds (t-GICs), $[\text{Na}(\text{G}2)_x]^{+} + e^{-} + \text{C}_y \rightarrow [\text{Na}(\text{G}2)_{x'}] \text{C}_y + \text{G}2_z$, $x = x' + z$, where the solvated cation is intercalated, along with solvent molecules, into graphite [12]. These systems show a remarkable cycle life, being able to charge/discharge several thousands of times without losing a significant portion of its capacity, and show excellent power performance due to the possible lack of a desolvation step in the intercalation process, Figure 1. But, these systems lack, at the moment, the necessary specific capacity for commercial applications, and suffers from large volume expansion. The discovery sparked an interest in t-GICs for SIBs and several other electrolytes displaying this mechanism was soon found, although the electrochemical performance of the systems differs greatly [13 ??], showing that this phenomenon might open up a rich new avenue of chemistries utilizing graphite in SIBs.

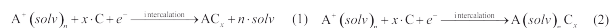
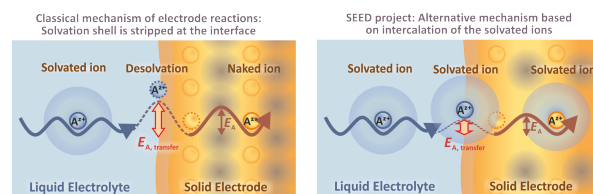


Figure 1: In the classical electrode reactions the solvation shell is stripped during charge transfer from the electrolyte to the solid electrode in a desolvation process (left), while the SEED project (right) studies a phenomenon where the solvents of the solvation shell are partially, or fully, co-intercalated with the working cation. This has a large impact on the redox reaction, as well as the kinetics of the reaction, along with the change in the structure of the electrode upon accepting a solvation shell. Courtesy Adelhelm / ERC Consolidator Grant SEED

Several key characteristics of the systems forming ternary intercalation compounds through redox reactions are still open for debate, including the above stoichiometry of the reversible co-intercalation process, were the number of co-intercalated G2 are thought to be either 1 or 2, ratio of carbon atoms to solvated complex is between 16-22 and it is unknown if any desolvation process occur, and if they do occur, if they take place inside or outside of the graphite host [13]. Thus, the theoretical capacity is currently unknown. Moreover, the voltages that these reaction take place at is dependent on the solvent and the structure and dynamics of the solvation shell they form around the cation - traditionally in LIBs and SIBs the redox reaction is independent of the solvent - and hence the possible energy densities of these systems are unknown.

The goal of this study is to in detail characterize the structure and dynamics of the solvation shell, along with investigating the electrochemical stability for several electrolytes of interest for the co-intercalation phenomenon in SIBs using Car-Parrinello molecular dynamics (CPMD). In particular, we aim at uncovering the value of the number of solvents, and the stability of the solvation shell prior to co-intercalation occurs and compared with standard LIB and SIB electrolytes, in order to identify properties which are of importance for the co-intercalation phenomenon.

WWW

<https://www.chemie.hu-berlin.de/en/forschung-en/electrochemistry/>

More Information

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Funding

ERC Consolidatory Grant number 864698, Solvated Ions in Solid Electrodes: Alternative routes towards rechargeable batteries based on abundant elements (SEED).