

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

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

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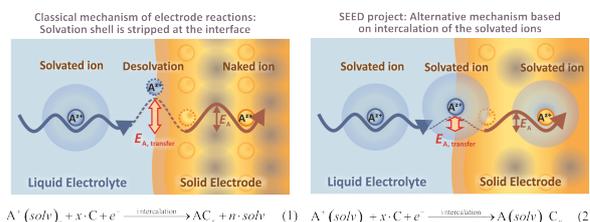
### In Short

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

Lithium-ion batteries (LIBs) has become the go-to energy storage device in portable electronics and in electrical vehicles - which are expected to become more and more common. Moreover, with the ongoing transition to transient renewable energy sources the use of stationary storage is projected to grow exponentially [1]. To meet future demands for energy storage, several next generation batteries are being investigated. One such next generation battery technology is the sodium-ion battery (SIB) which performs similarly to LIBs, but have several advantages in terms of safety and raw materials [2].

A key difference between sodium and lithium cations is how they interact with graphite - the anode of choice for LIBs. Lithium cations are intercalated between the graphene sheets at a low potential vs. lithium metal, yielding a high specific capacity. This, however, does not occur in the case of sodium, due to unfavourable interactions between the sodium cations and graphite host structure [3,4], hence hard carbon has been the main negative electrode employed in SIBs [5]. It was recently discovered, however, that sodium can form a ternary graphite intercalation compound (t-GIC), whereby the cation is intercalated along with its solvation sheath, Figure 1, when glyme based electrolytes are used [6]. What enables this process is currently unknown, but the structure and stability of the solvation shells around the cations are thought to be of great importance.

The first funding round focused on these solvation shell in these glyme based electrolytes. Glymes have a very flexible structure, with several stable conformations. We first investigated whether the population of the different conformations changes upon the addition of a salt - Preliminary analysis saw no such changes. Previous DFT studies has

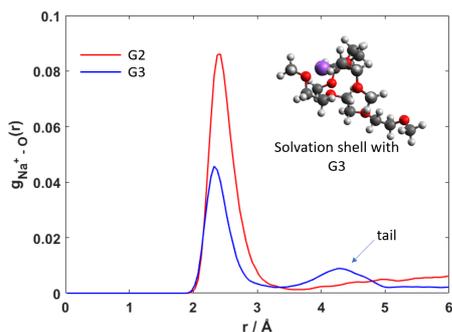


**Figure 1:** In the classical electrode reactions the solvation shell is stripped during charge transfer from the electrolyte to the solid electrode in a desolvation process (left), while the SEED project (right) studies a phenomenon where the solvents of the solvation shell are partially, or fully, 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

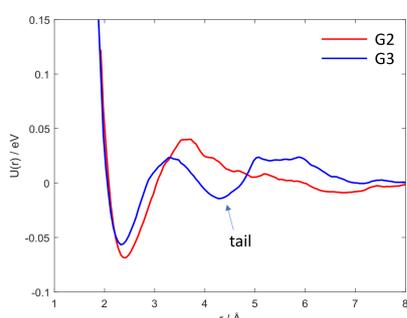
identified the maximally elongated all trans conformation as one of the more stable ones, and even if our initial geometries contained several glymes in this conformation they quickly evolved to other conformations and none were present at the end of the production run, indicating that previous DFT studies on glyme conformations fail to accurately describe the population of different conformations. This is possibly due to the DFT simulations often being of a single molecules in vacuum, or with an implicit solvent, and thus do not account for the dynamic environment around the molecules, which are more accurately represented in molecular dynamics. The CPMD trajectories shows that  $Na^+$  has a coordination number of 6 in these electrolytes, consistent with other typical battery electrolytes [7]. Preliminary analysis also shows that triglyme (G3) cannot wrap around  $Na^+$  the same way diglyme (G2) can. The solvation shells are therefore substantially larger when using G3, where a tail like feature sticks out of the solvation shell, as can be detected as an additional bump in the radial distribution function (RDF) of the system (Figure 2).

The potential of mean force  $U(r) = -k_B T \ln g(r)$ , Figure 3, shows that G3 binds more weakly to  $Na^+$  than G2, and that the tail of the solvation shell in the G3 electrolyte is loosely bound, indicating that it, along with the rest of the G3 molecule, more easily detaches. This, along with the larger size of the G3 molecule, is thought to be the root cause of the lower capacity seen when using G3 compared with G2.

Recently we have uncovered a set of novel electrolytes where we use a mixture of G2 and another solvent that previously was not known to co-



**Figure 2:** RDF of G2 (red) and G3 (blue) based electrolyte, along with a solvation shell with G3 - showing how the molecules are too large to completely wrap around the cation, instead creating a tail on the solvation shell.



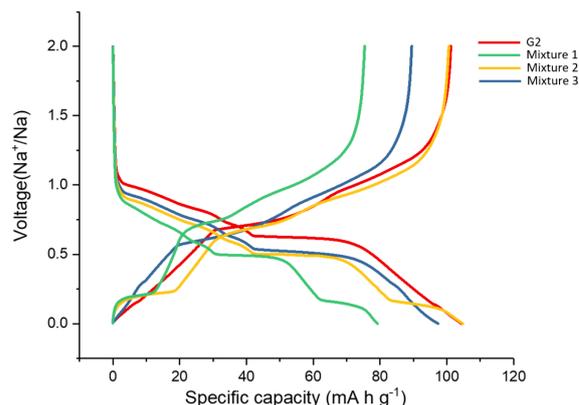
**Figure 3:** Potential of mean force for G2 (red) and G3 (blue), showing that G3 binds more weakly to  $\text{Na}^+$  than G2.

intercalate. Preliminary results (Figure 4) indicate that this electrolyte enables higher energy densities as the capacity can be kept constant, compared with a pure G2 based electrolyte, while the voltage is lowered. Moreover, these electrolytes can operate with a much lower salt concentration, reducing the cost of the electrolyte by almost a magnitude. Finally, using these new electrolytes a low voltage plateau emerges indicating a change in the electrochemical process occurs in these batteries.

The goal of this continuation is to study the structure and stability of the solvation shell in these new electrolytes as a function of the ratio between glymes and salt, and glymes and the new solvent, using Car-Parrinello molecular dynamics (CPMD). In particular, we want to investigate if the contribution of glymes in the solvation shell is reduced, along with the volume of the solvation shell, compared with the electrolytes already simulated in the first funding round of this project. Moreover, special emphasis will be put on computing the energy required to remove a glyme molecule from the solvation shell in these new electrolytes.

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Voltage profiles – second cycle

**Figure 4:** The new electrolytes (green, orange and blue) show clear differences in their voltage profile compared to when a pure G2 based electrolyte (red) is used. The overall voltage is lowered - leading to higher energy density - and a new plateau emerges at low voltages, indicating that another electrochemical process occurs at low voltages when using these new electrolytes.

### More Information

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