

# Revisiting Grignard Reagent Based Electrolytes in Magnesium-Ion Battery : A First-Principles Study

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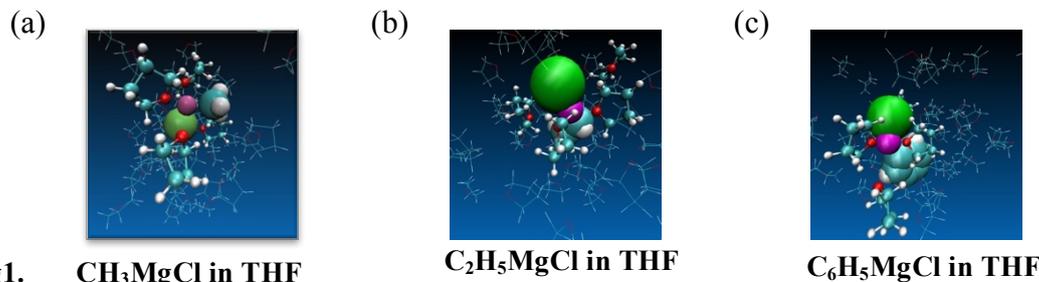
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Magnesium-ion batteries (MIBs) have gained considerable attention as an alternative energy storage to Li-ion batteries in the past few decades [1]. Grignard reagent (R-Mg-X: X=halogen) with ether has been one of the most studied and efficient solutions for MIB. However, the microscopic behaviors in the electrolyte solution are still under debate. To gain insight of the solvation and dissolution/deposition on the atomic scale, we performed the first-principle molecular dynamics samplings of such MIB electrolytes using the CPMD code. The study was also motivated for understanding the fundamental mechanisms of electrolytes for 2+ cation and the underlying differences instead of 1+ cation.

We carried CPMD simulations of a single R-Mg-X (where R=Methyl, Ethyl and Phenyl) in different cubic boxes with 44 tetrahydrofuran(THF) molecules, the edge length of each simulation box is 18.23 Å. We employed the dispersion corrected PBE-D2 functional. After the equilibration, statistical averages were computed from trajectories of 50 ps.

The compatibility of electrolyte for reversible dissolution/deposition of Mg<sup>2+</sup> is a most important factor to determine Coulombic efficiency of the battery. Therefore, the solvation structure of R-Mg-X in THF is studied through radial distribution functions (RDFs) and vibrational shift in power spectra. The strong solvation of Mg<sup>2+</sup> with THF is revealed through the RDFs well-structured peaks. The RDFs differences for different R groups in R-Mg-X (R=Methyl, Ethyl and Phenyl) shows that R=Phenyl, has most closely packed solvation shell and the order of such packing is Ph>Me>Et. However, the coordination number of THF's in RMgX solvation shell follow the order Ph<Et≈Me. Power spectra of THF in the solvation shell of Mg<sup>2+</sup> ion for the RMgX shows red shift for the -C-O- frequencies, compared to bulk THF, which also support the strong solvation of Mg<sup>2+</sup> ion with THFs. Such spectral findings are also verified through experiments. These calculation results will provide useful insight of solvation and dissolution/deposition process in MIBs.



## References:

[1] D.Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich and E. Levi, Nature 407, 724 (2000).