

Theoretical and Computational Investigation of Electrolytes for Sodium-ion Batteries: What We Have Learned So Far

¹Tuanan C. Lourenço (PQ), ¹Luis G. Dias (PQ), ²Juarez L. F. Da Silva (PQ).^{1*}

lourenco.tuanan@gmail.com

¹São Carlos Institute of Chemistry, University of São Paulo, Av. Trabalhador São-carlense, 400, Parque Arnold Schimidt, 13560-970, São Carlos, SP, Brazil; ²Chemistry Department, FFCLRP, University of São Paulo, 14040-901, Ribeirão Preto, SP, Brazil

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Highlights

Classical molecular dynamics (MD) simulations are a powerful approach in the investigation of electrolytes, which can provide insightful information about the dependence of the electrolyte composition and performance at the atomistic level.

Abstract

Sodium-ion batteries (SIBs) are one of the most promising energy storage technologies among the post-lithium batteries, which is mainly due to the SIBs low production cost due to the large abundance of sodium in the planet, combined with the possibility of using low-cost metals in the battery device and the possibility of using the lithium-ion production facilities. However, the performance of SIBs is still lower than that of the actual lithium-ion batteries (LIBs) available in the market, which is mainly due to the physicochemical limitations of the materials. Then, one of the main steps in the improvement of SIB performance rely on the development of new materials. In this context, we have used classical molecular dynamics simulations to evaluate the relationship between the electrolyte composition and performance for ionic liquids (ILs) and deep eutectic solvents (DES) based electrolytes. In this context, we observed a clear dependence between sodium salt concentration and electrolyte transport properties, where large salt concentrations lead to a reduction in the chemical species mobility resulting from the increase in viscosity and the strong Na⁺-anion interactions implemented in the systems. Moreover, on the basis of small structural changes in electrolyte chemical species, it is possible to tune the transport properties to control the impact of the sodium salt in the electrolyte properties or to improve the mobility of the chemical species. In this context, we highlight the use of asymmetrical anions, which lead to the formation of heterogeneous solvation shells around the Na⁺ ion, the use of weakly coordinate anions to weaken the Na⁺-anion interactions, or the use of protic ILs, which in general have viscosities lower than those of aprotic ILs, which is mainly attributed to the h-bonds formed between the ions. Although MD simulations are widely applied to electrolyte studies, we have also focused on the evaluation/development of different workflows and routes to ensure the reliability of the MD data and also to investigate in deeper details atomistic properties such as the sodium-ion diffusion mechanism. From that we observed that the use of scaled charges are mandatory to ensure a better correlation between the experimental and simulated data. The use of periodic density functional theory (DFT) calculations to obtain the bulk phase charge for the electrolyte species has also been shown to be a promissory route to improve not only the description of the transport properties, but also the structural reorganization of the electrolyte due to the indirect description of the impact of charge transferring and polarizabilities in the chemical species. Therefore, it is clear that with the appropriate methodology, classical MD simulations can provide a clear path to the development of new and improved electrolytes for sodium-ion batteries.

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