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ACCEPTED MANUSCRIPT

On the determination of ion transport numbers in molten salts using molecular dynamics

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Individual transport numbers provide a measure of the charge ratio which is carried by each ionic species of an electrolyte. However, unlike the electrical conductivity or diffusion coefficients, this quantity lacks a clear definition from the statistical mechanics point of view. In practice, it is measured via complex experimental setups, and most of the interpretation of the available data is made by using the Nernst–Einstein approximation. Here we show that this approach is not suitable in molten salts due to the large contributions of the cross-terms due to the ionic interactions in the total ionic conductivity. We propose a partition scheme that allows to attribute these cross-terms to the various ions, allowing for an estimate of the transport numbers in a series of molten salt formed by mixing NaF and AlF_3 at various compositions. The results are interpreted using the speciation of the melt, which is characterized by the formation of various AlF_x clusters. At large AlF_3, the Na^+ ions are shown to contribute almost totally to the ionic conductivity.

I. INTRODUCTION

The total ionic conductivity describes the ability of the electrolytes to transport the charge. It contains contributions from all the species without distinction, so that transport numbers (or transference numbers) are often introduced in order to estimate all the individual contributions. These quantities, which are well defined when the ions are infinitely diluted in a solvent, are however much more ambiguous in concentrated electrolytes. Indeed, from experiments, the various methods that were introduced to determine transport numbers either employ setups in which the system is open from the thermodynamic point of view or their interpretation involves strong approximations [1]. In simulation studies, there is also no definition that would allow to determine transport numbers, unlike the ionic conductivity. These difficulties are due to the large cross-terms that arise due to the strong cation-anion interactions [2].

The resulting lack of data on partial charge transport properties is limiting, for instance, the design and the optimization of energy efficiency of many industrial processes. The aim of this work is to fill this gap by proposing a partitioning scheme allowing to measure a set of transport numbers of every ionic species in a molten salt. As a case study, we have considered the NaF-AlF_3 melts, for which we have calculated the partial charge transport properties at 1293 K for $X_{AlF_3} \leq 0.5$. This system is interesting from both a practical and theoretical point of view. Indeed, in the aluminium production industry (Hall-Héroult cells), the electrolyte used to dissolve the alumina is mainly constituted of 3·NaF-AlF_3. Optimizing the electrical properties of the electrolyte requires an accurate knowledge of the partial charge transport properties, and could improve the electrical efficiency of the electrolysis cells. This has a potential to impact positively the aluminum production industry from both an economical and environmental point of view. From a theoretical perspective, the NaF-AlF_3 system is interesting for studying the different aspects of the chemical effects upon the charge transport properties. NaF-AlF_3 is also non-ideal since it displays a rather large heat of mixing (∼-37 kJ/mol)[3]. In terms of chemical interactions and structure, the system is non symmetric, the maximum short range ordering is observed at around $X_{NaF} = 0.68$ [3] (X represent the mole fraction). In addition, several coordination complexes coexist around this composition. Therefore, depending on the composition, the NaF-AlF_3 system gives us a chance to study several aspects, with different degrees of complexity, of the link between chemistry and charge transport within ionic mixtures.

To simulate the molten salts of interest, we employ equilibrium molecular dynamics (EMD) simulations. In this method, the trajectories are calculated by solving the classical equations of motion (Newton's second law). The interactions are calculated using the polarizable ion model, which was developed by Madden and co-workers [4, 5]. It was shown to predict with good accuracy a large set of thermodynamic, structural, dynamic and physical properties of different types of molten salts mixtures, with different degrees of complexity in the chemical interactions [6–13]. In short, the interactions between ions are parameterized from Density Functional Theory (DFT) calculations, using a generalized force-fitting strategy. In the case of NaF-AlF_3, we have recently shown that the simulations were yielding ionic conductivities and self-diffusion coefficients in a very good agreement with experiments [14]. In combination with further DFT calculations, the trajectories were further used to interpret the NMR spectra of the melts. In this

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