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Lithium and copper transport properties in phosphate glasses: A Molecular Dynamics study

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ABSTRACT

Recently glasses have been considered as potential candidates for solid-state batteries applications due to the peculiar properties that they show if compared to crystalline ones. In this work, the dynamic properties of copper (Cu^{1+}) and lithium (Li^{1+}) ions in phosphate glasses, in which Cu_2O was progressively substituted to Li_2O, were investigated and correlated with the glass structure analysis by using Molecular Dynamic (MD) simulations.

The diffusion of Li^+ ions and how it is influenced by Cu^{2+} and Cu^{1+} ions were highlighted. In this vitreous system, the Cu^{1+} ions diffuse interacting with the lithium diffusion.

This results in the general increase of the activation energy of Li^{1+} as a function of the Cu_2O content in these glasses. At the same time the substitution of Li_2O by Cu_2O leads to the decrease of the Ea of the Cu^{1+}, mainly due to structural changes that promote the disruption of the Li^{1+} pathway and the creation of more stable Cu^{1+} sites. This explains the increased migration of this ion in higher copper content system.

1. Introduction

In last decades, the fast evolution and growth of the consumer electronics market (laptops, mobile phones, smartphones, etc.) have entailed a strong development of the materials constituting these devices. Today, Lithium ion batteries are widely used in portable electronic devices such as mobile phones and laptop computers, but in recent years they attracted considerable attention for their application in plug in electric vehicles (PHEV) and full electric vehicles (EV), with the challenge to progressively overcome the limits of these systems mainly related to safety and reliability issues as well as to energy density ones [1–3].

Among the materials investigated for lithium batteries, glasses have been recently considered as potential candidates for the next generation of lithium ion batteries [4–6]. The interest in glass-based materials is due to the advantages that they show in term of compositions, isotropic properties, absence of grain boundaries and easy film formation [7–10]. Furthermore, the disordered structure takes several advantages in the manufacturing process: amorphous structures allow easier coupling between the various components of the Solid State Batteries (SSBs), avoiding the mismatches that occur between crystal lattices.

Glasses behave as super-ionic, mixed ionic-electronic, or simply electronic conductors, depending by the composition and the concentration of different modifiers in the glass matrix [11–13] For instance, the presence of cations in multiple oxidation states promotes the small polaron hopping phenomena empathizing the electronic contribution to conductivity [14–18], while the presence in the matrix of ions with smaller ionic ratio leads to increased ionic conductivity [19]. Thus, based on the dominant conductive behaviour, glasses can be proposed as electrolytes (ionic conductors) or cathodes (mixed ionic-electronic conductivity).

Glasses for SSB have been widely studied because of their liquid like structure [2], their disorder glass structure is characterized by an "open" structure, which promotes the diffusion of small ions, i.e. lithium, inside the matrix and induce a good ionic conductivity [20]. Several methods have been proposed to further boost the ions transport. The most diffuse method is to obtain the so called "mixed mobile ion effects" or "mixed former effect", mixing two different anions species [2,21,22].

In lithium containing glasses, an increase of the conductivity with Li^{1+} concentration have been demonstrated however, the introduction of other ions species can strong influence the behaviour of the diffusion. This effect is mainly due to changes in the structure or the concurrent movement of ions of different nature, which can improve or inhibit the diffusion [21,22].

Previous experimental works performed on lithium meta-phosphate glasses ($50\text{-}xLi_2O\text{-}xCu_2O\text{-}50P_2O_5$, x = 0, 5, 10, 15 and 20 mol%) showed that the conductivity has a predominant ionic conductivity

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behaviour in this system, mainly due to Li^{1+} diffusion. Moreover, the conductivity value decreases by two to three orders of magnitude when lithium oxide is replaced by copper oxide and the activation energy tends to increase, suggesting that copper ions probably contribute to the conduction mechanism [23].

This strong change in conductivity might be caused by mixed mobile ions effect (MMIE), arising from the presence of two different mobile ions Li^+ and Cu^+ [23]. Two main effects have been considered to explain the observed conductivity results [24]: firstly, the mobility of the Cu^+ ions are much lower in the network structure that is optimized for smaller Li^+ ions. On the other hand, the presence of relatively immobile Cu^{2+} in the glass matrix, promotes a short-intermediate range structure, produced by the substitution of P—O—Li bonds by relatively covalent P—O—Cu^{2+} bonds, leading to a more cross-linked structure and a progressive reduction of the optimum sites for the jumping of both Li^+ and Cu^+, in agreement with the increase of the energy barrier for ion transport [24].

In this work, Molecular Dynamics (MD) simulations were performed to further detail the observed experimental conductivity in this glass system, stressing on the diffusion transport properties (mean square displacement, velocity auto-correlation function, Van Hove correlation function, etc.) of Cu^{1+} and Li^{1+} ions.

2. Simulation details

Five compositions were simulated to evaluate the influences of different ions contents on the transport properties. In particular, as benchmark composition was chosen the lithium meta-phosphate glass system, in which Li_2O was gradually substituted by Cu_2O until 20 mol %, which represents the today experimental limit to obtain a vitreous material [23,24].

As experimentally known, cuprous ions tend to oxide during the melt-quenching procedure and part of Cu^{1+} ions convert into Cu^{2+} ions. To obtain an accurate simulation of glass structures, the ratio of Cu^{1+}/Cu^{2+} ions was included into the modelling approach by considering both valence states, whose percentage derived by experimental XPS analysis [24] performed by Mugoni et al. on the same compositions and reported in Table 1.

The initial configuration was obtained by randomly placing around 10,000 atoms in a cubic box, where the size length depends on the experimental density [23]. Based on the compositions in mol% of oxides (Table 1), for each species, a specific number of atoms was settled to respect the correct ratios among the species. Subsequently, part of Cu^{1+} ions was changed in Cu^{2+} ions in accordance with the Cu^{2+}/Cu_{tot} ratio, as listed in Table 1, and the number of oxygen ions was corrected in order to achieve the overall charge neutrality of the entire system [25].

The system was described by Pedone potential [26], which defines the interactions between the various ions in terms of Morse and Coulombic contributions. However, the original force field lacked the parameters that describe the Cu^{2+}–O interactions, which were further implemented by Ori et al. [27]. Moreover, to improve the description of coulombic interactions, a partial charge model was used to consider the effects of covalence. The parameters used in the simulations are listed in Table 2.

Table 1
Label of the studied glass compositions, compositions, Cu^{2+}/Cu_{tot} ratio determined from XSP analysis, density and atoms number as a function of glass composition.

Sample ID	P_2O_5 (mol%)	Li_2O (mol%)	Cu_2O (mol%)	Cu^{2+}/Cu_{tot}	Density (g/cm^3)	Atoms number
CG0	50	50	0	/	2.40 ± 0.01	10,000
CG5	50	45	5	0.74 ± 0.05	2.49 ± 0.01	10,070
CG10	50	40	10	0.84 ± 0.05	2.51 ± 0.01	10,160
CG15	50	35	15	0.80 ± 0.05	2.69 ± 0.01	10,240
CG20	50	30	20	0.82 ± 0.05	2.88 ± 0.01	10,320

Table 2
Potential parameters.

Pair	Dij (eV)	Aij (Å^{-2})	r0 (Å)	Cij (eV Å)
$P^{+3.0}$-$O^{-1.2}$	0.831326	2.585833	1.800780	1.0
$Cu^{+0.6}$-$O^{-1.2}$	0.090720	3.802168	2.055405	1.0
$Cu^{+1.2}$-$O^{-1.2}$	0.011856	1.643080	3.065264	3.0
$Li^{+0.6}$-$O^{-1.2}$	0.001114	3.429506	2.681360	1.0
$O^{-1.2}$-$O^{-1.2}$	0.042395	1.37930	3.61870	22.0

The amorphous structures were obtained by simulating a conventional melt-quenching procedure, using DL-POLY code version 2.19 [25,28]. Each system was heated at 4000 K and equilibrated for 40 ps. Afterwards, the system was cooled down from 4000 K to 300 K in 740 ps with a nominal cooling rate of 5 K/ps and then equilibrated for 40 ps. Berendsen thermostat with time constant parameter for the frictional coefficient set to 0.4 ps was used to control the temperature during the whole simulation [29]. Integration of the equations of motion was performed using the Verlet Leapfrog algorithm with a time step of 1 fs. Coulombic interactions were calculated by the Ewald summation method with a cutoff of 11 Å and an accuracy of 10^{-6}, while for the short range interactions a cutoff of 8 Å was used.

As previously reported, the focus of this work is to analyse the transport properties of the mobile ions (Li^+ and Cu^+) in glass matrices. Simulations at constant temperature were performed to obtain trajectories that accurately describe the ions movements. The systems were systematically studied in the range between 300 and 3000 K and for each temperature; they were firstly equilibrated in NVT while the production was performed in NVE ensemble, for a total of 1,000,000 timesteps (1 ns). Trajectories were collected every 20 steps (20 fs), during the NVE runs and totally 9000 final configurations were obtained. From the trajectories collected during the NVE simulations, the transport properties were analysed using mean square displacement (MSD), velocity auto-correlation function (VACF) and Van Hove correlation function ($G_s(r, t)$) [30–35].

Nosè-Hoover thermostat [36,37] was used to control the temperature with a frictional coefficient of 0.5 and a timestep of 1 fs was chosen during the simulations.

3. Results

The MD analysis, reported in this paper, aims to further investigate the experimental trends observed for these glasses, structural and conductivity results, obtained by MD, were widely investigated to increase the knowledge about the transport properties of Li^{1+} and Cu^{1+} ions that are supposed to be the diffusing species in the glass network. The glass structure resulting by MD were validated in terms of short range order and medium environment by comparing the pair distribution function (PDF) and Qn species distribution respectively. The data resulting from the MD (Table 3) show a good agreement with the experimental ones observed lithium and copper phosphate glasses allow to validate the computational procedure used [38,39].

The temperature range from 300 to 3000 K was investigated to evaluate the stability of the systems at the considered temperatures, utilised to calculate the transport properties. The energy and the pressure plots in function of the temperature provide information on the stability of the system: the presence of anomalies in the plot could denote that the system exceeds the transition temperature (Tg) which would involve the vibration and movement of all the species in the matrix, comprised the network former [35].

Fig. 1-**A** and 1-B shows the averaged energy and the pressure values in function of the temperature: the plots do not show any sort of discontinuity (e.g. rapid change of slope) and the systems can be