Letter to the Editor

Comments on the structure of LiPON thin-film solid electrolytes

The development of novel solid-state electrolytes for application in lithium batteries has extended very rapidly in the last years through the materials science community. In particular, the advent of LiPON thin film electrolytes in the 90s at the Oak Ridge laboratories by Bates and coworkers [1,2] gave rise to a new field of research which has proven to be highly prolific. It has been clearly stated that nitrogen incorporation into the structure of the deposited film increases the electrical conductivity, apart from being electrochemically and mechanically stable, and that LiPON may also act as a barrier against dendrites growing from the Li anode [2]. Deposition of LiPON films from Li_3PO_4 targets under nitrogen atmosphere involves numerous factors which have to be controlled, e.g. time and temperature, N_2 pressure or radio-frequency power; however, no unique set of optimized parameters has been found that can best fulfill the requirements for the material performance. Furthermore, no concluding interpretation has been given to the effect of nitrogen on the electrical conductivity improvement through nitrogen incorporation.

The first explanation given for the increase in the electrical conductivity by nitrogen/oxygen substitution was based on the decreased electrostatic energy between LiPON and Li_3PO_4 reference material, as first proposed by Wang et al. when studying the electrical conductivity of lithium phosphate glasses [3]. Recently, some authors have suggested that it is rather the relative amount of tri-coordinated nitrogen species, N_t (–N<), which finally determine the capability of nitrogen to increase the electrical conductivity with respect to the oxide target [4–6]. Other authors, such as Fleutot et al. [7], however, provide an alternative explanation which is based on the variation of the different oxygen species found in the films by XPS, concluding that the decrease of the bridging oxygen/non-bridging oxygen ratio favors lithium ion mobility, and is at the origin of the conductivity improvement. It should be pointed out that this argument was previously proposed by Muñoz et al. [8] as the main reason for the improvement of electrical conductivity in bulk glasses of the system $Li_2O–P_2O_5$ due to nitridation, and that, even if this were valid for bulk glasses, it could not be of relevance for the LiPON deposited films obtained by Fleutot et al. [7].

In general, most authors have compared the atomic structure of the deposited LiPON films with that of the oxynitride bulk lithium phosphate glasses and its associated structural changes that occur through ammonolysis reaction of the phosphate melt. The purpose of the present letter is to bring to the attention of researchers the fact that the relationship between the atomic structure of LiPON electrolytes and the features attributed to oxynitride lithium phosphates as bulk glasses seems to have been misunderstood. Fig. 1 presents a diagram of the short-range structures in both a phosphate glass and an oxynitride glass.

For example, the model used by Hu et al. [4], and also by Jacke et al. [5], assumes that nitrided Li_3PO_4 can form a glass and that tri-coordinated and di-coordinated nitrogen atoms result from the reaction of adjacent phosphate chains with nitrogen. First, Li_3PO_4 will hardly form a glass and, furthermore, it is supposed that the targets the authors are using are made of crystalline Li_3PO_4. Second, in any case the structure of the Li_3PO_4 target cannot be based on phosphate chains, so that the mechanism of nitrogen incorporation into the LiPON structure should not be related in such a way to that occurring during thermal ammonolysis in a lithium phosphate melt [8]. In their work, Jacke et al. [5] stated that the relative amount of bridging oxygens (P–O–P) decreases with nitrogen in the films, as a consequence of the growth of triply coordinated nitrogen atoms, as also done by Fleutot et al. [7]. This observation refers also to the work of Wang et al. [3], in which the effect of nitrogen on the electrical conductivity of lithium phosphate glasses was studied. However, even though the bridging oxygen/non-bridging oxygen ratio decreases with nitrogen incorporation in phosphate glasses [9,10] this could not be so in the films. Indeed, bridging oxygens are half of the non-bridging ones per phosphorus atom in a lithium metaphosphate glass composition, which decreases with the increase of the Li_2O content in the $Li_2O–P_2O_5$ glass system. However, no bridging oxygens should be found in a Li_3PO_4 target. Both bridging and non-bridging oxygens would only be part of the resultant structure in LiPON film but not in the target.

Similarly, Fleutot et al. [7] have studied the variation of the different oxygen species through XPS, distinguishing three types of oxygen atoms in the films: P=O (non-bridging), P–O⁻ (non-bridging) and P–O–P (bridging), as identified through direct relationship with the structure of a phosphate glass. They showed that P–O–P decreases with nitrogen content, although its amount is much lower than the sum of P=O and P–O⁻ contents for all N/P ratios [7]. However, this attribution of the oxygen types is, again, based on a model describing the structure of an alkali metaphosphate glass, which, again, introduces a new source of confusion because the target sample from which the LiPON film is formed is not a metaphosphate glass. The authors go on to propose a mechanism by which bridging oxygens are substituted first, forming mainly tri-coordinated nitrogen. Additionally, a serious problem arises from the fact that no XPS data are provided between the non-nitrided film and up to N/P = 0.4, so there is no distinction made between N_t and N_d and their correlation with the type of oxygens. Finally, P–O–P could not be substituted to form N_t because no P–O–P exists in the crystalline Li_3PO_4 target, and also P=O and
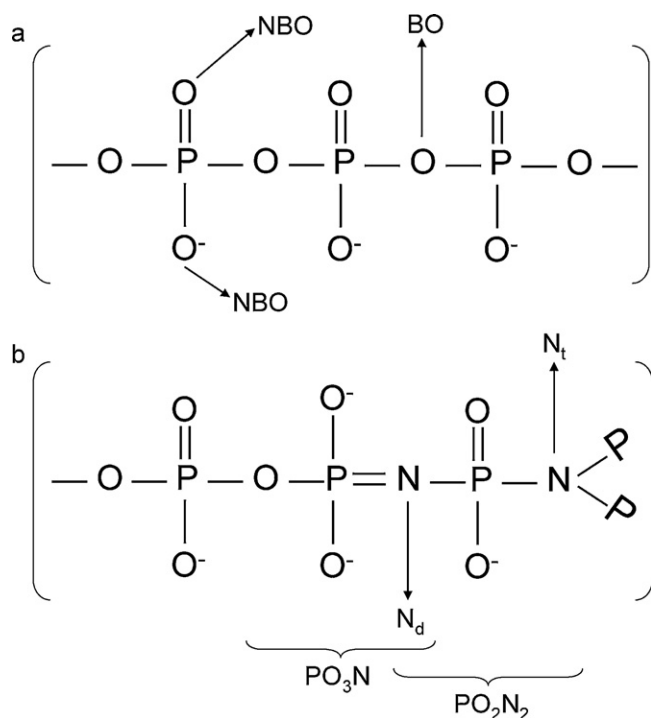
Fig. 1. Schematic representation of the structural features found in a phosphate glass (a), and an oxynitride phosphate glass (b). For a metaphosphate glass composition, the structure is built up of PO_4 tetrahedra with 2 non-bridging oxygens (NBO) per group and 1 bridging oxygen (BO). Each BO is shared by two adjacent phosphate groups. In an oxynitride glass structure, either di-coordinated nitrogen atoms (N_d), or tri-coordinated ones (N_t), substitute for oxygens in PO_4 groups, giving rise to a glass formed by two additional building units, PO_3N and PO_2N_2 tetrahedra.

$P–O^-$ would not be distinguishable, according to the structures of Li_3PO_4 polymorphs [11].

It should thus be clearly stated that whether bridging oxygens are formed or not in the LiPON films will not depend on the structure of the crystalline Li_3PO_4 target material, because no such structural feature is present in it. Alternative interpretations should, therefore, be provided without directly referring to the atomic structure of an alkali phosphate glass. The nitridation mechanism has been well studied in phosphate glasses and it is of course relevant for the interpretation of the electrical conductivity improvement that arises with the incorporation of nitrogen in thin film LiPON electrolytes. However, the starting materials and, more importantly, the processing route by which oxynitride lithium phosphates and bulk oxynitride glasses are obtained are quite different. Any comparison, therefore, must be made with care to prevent misleading interpretations in current research work before finding the suitable relationships between both types of materials.

References

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