

# Molecular dynamics simulations of Li transport between cathode crystals

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## Abstract

The molecular dynamics (MD) computer simulation technique has been used to study the effect of an amorphous intergranular film (IGF) present in a polycrystalline cathode on Li transport. The solid electrolyte is a model lithium silicate glass while the cathode is a nanocrystalline vanadia with an amorphous  $V_2O_5$  IGF separating the crystals. Thin ( $\sim 1$  to a few nanometer thick) IGFs are known to be present in most polycrystalline oxide materials. However, the role of such a film on Li transport in oxide cathodes has not been addressed. Current scanning probe microscopy (SPM) studies have shown that the orientation of the layered nanocrystalline vanadia crystals near the cathode/solid electrolyte interface is not optimized for Li ion transport. While the precise structure of the material between the crystals has not been identified, initially it can be initially considered as likely to be a thin non-crystalline (amorphous) film. This is based on the ubiquitous presence of such a structure in other polycrystalline oxides. Also, and with more relevance to the materials used in thin film batteries, an amorphous film can be expected to form between nanocrystals that crystallized from an amorphous matrix, as would be the case in a deposited thin film cathode. Consistent with simulations of Li transport in amorphous vanadia, the current simulations show that Li ions diffuse more rapidly into the amorphous intergranular thin film than into the layered vanadia with the  $(0\ 0\ 1)$  planes parallel to the cathode/electrolyte interface.

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## 1. Introduction

Intergranular films (IGFs) are a ubiquitous component in most polycrystalline oxide materials. Often, they form because of the presence of minor (ppm level) contaminants in the starting materials. The contaminants segregate to the surface of the crystals during processing and create a very thin ( $\sim 1$  to a few nanometer thick) amorphous, or glassy, IGF that separates the crystals [1–4]. However, IGFs may also be present in pure materials that crystallize from a starting amorphous phase, as is the case of nanocrystal formation from a glassy matrix [5]. This latter aspect has specific relevance in the formation of a thin film polycrystalline cathode occurring during deposition and processing. (Here, the use of the phrase ‘thin film’ may become confusingly redundant, but ‘thick’ and ‘thin’ depend on perspective; thin film batteries are made of multi-micron thick layers of anode, electrolyte, and cathode; an IGF is a much thinner film of only a few nanometers separating crystals. Hence, a ‘thin film’ layer of cathode in a thin film battery is quite thick compared to the IGF). A deposited thin film cathode starts out amorphous, with possibly small ordered regions. Subsequent

heating enables crystallization to occur. The material between these crystals has not been studied, probably because of the very small volume percentage of the IGF. Nonetheless, the IGF is known to play an important role in the properties of ceramic materials. It may also play an important role in the transport properties in layered oxide cathodes.

Vanadia is a layered oxide that acts as a good model for understanding Li transport in layered oxides that have highly anisotropic behavior. Li ion transport in a layered oxide such as vanadia can be expected to be quite different across the crystalline layers ( $\langle 0\ 0\ 1 \rangle$  direction) than between them ( $\langle 0\ 1\ 0 \rangle$  or  $\langle 1\ 0\ 0 \rangle$  directions). In simulations of Li transport in vanadia, results showed that the activation energy for Li transport in the  $\langle 0\ 1\ 0 \rangle$  direction was  $\sim 0.8$  eV, while it was over twice as high across the layers in the  $\langle 0\ 0\ 1 \rangle$  direction [6]. The value 0.8 eV is similar to the value obtained in simulations of Li transport in silica glass. Experimentally,  $\sim 0.8$  eV is the activation energy found for Li transport in a variety of oxide glasses [7,8]. The implication is that the Li–O interactions, jump frequencies, and jump distances, which are all a part of the transition state theory of diffusion, are similar in these solid oxides. Previous simulations of Na diffusion in oxide glasses gave results consistent with experimental data [9]. The consistent trends of the alkali

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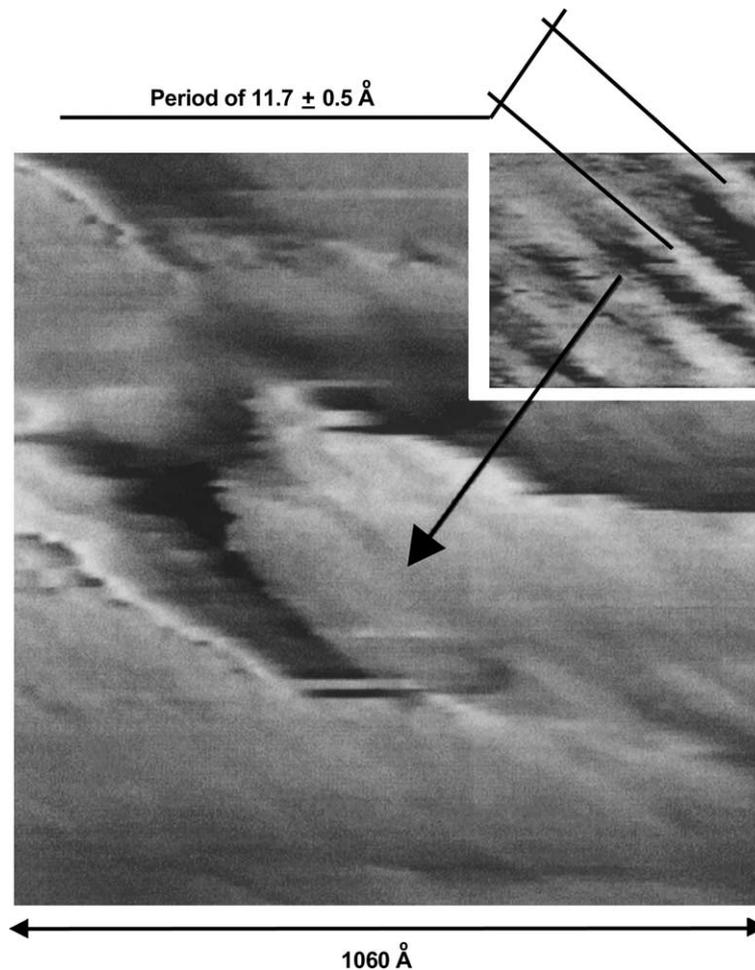


Fig. 1. SPM image of a plasma deposited thin film ( $\sim 30$  nm) of vanadia on a solid electrolyte glass [10]. Inset shows rows of vanadyls with the appropriate unit cell spacing in the  $\langle 1\ 0\ 0 \rangle$  direction, indicating the orientation of the vanadia layers near the interface.

metals in oxides and the similarity between experimental data and the simulations of Li as well as Na behavior in oxides offers confidence that the simulations provide a reasonable description of the anisotropy of Li transport in the layered vanadia crystals.

Recent scanning probe microscopy (SPM) studies of in-situ plasma deposited layers of vanadia cathode on a solid oxide electrolyte showed the orientation of the vanadia at the cathode/electrolyte interface [10]. The SPM studies clearly showed that a deposited film of vanadia orients such that the  $(0\ 0\ 1)$  planes are parallel to the crystal/electrolyte interface [10] (see Fig. 1). However, this is the slow transport direction based on the activation energies for Li transport. Nonetheless, Li transport in vanadia cathodes is reasonably good; that is, it is certainly not dominated by the very high activation barrier in the  $\langle 0\ 0\ 1 \rangle$  direction, even though, at the interface, this is the direction of Li transport into the cathode. Therefore, the role of the IGF on Li transport into oriented vanadia near the crystal/electrolyte interface was considered as a possible rapid transport path. Previous simulations [11] showed that the Li diffusion into amorphous vanadia is faster than in the crystal in the  $\langle 0\ 0\ 1 \rangle$  direction. Since the IGF

should behave somewhat like the amorphous phase previously studied, the role of the IGF on Li diffusion between vanadia crystals was initiated using molecular dynamics (MD) simulations. The role of an amorphous IGF between crystals in a cathode on Li ion transport has not been studied previously.

## 2. Computational procedure

The details of the computational procedure have been previously presented [6,11,12]. A multi-body potential with both two-body and three-body terms is used to describe all interatomic interactions. A change in the charge on the V ions due to the presence of nearby Li ions is incorporated in the algorithm [11].

A fifth-order Nordsieck–Gear predictor–corrector algorithm was used to solve Newton’s equation of motion. Both NVE (microcanonical ensemble) and NpT (canonical) simulations were performed. NpT simulations were run using a modified Berendsen [13] algorithm to take into account non-isotropic conditions [14]. Surfaces and interfaces were formed in the manner previously presented [12].

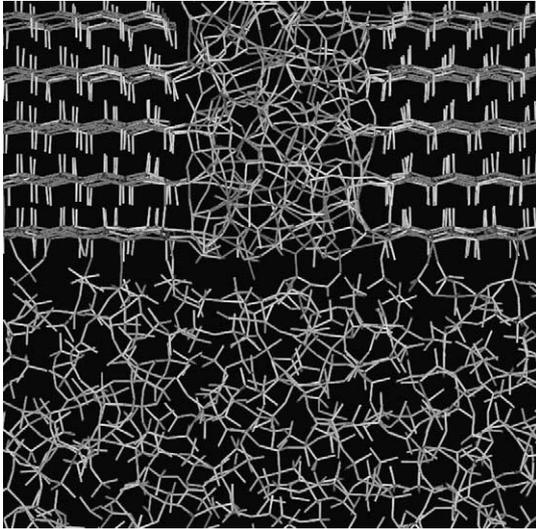


Fig. 2. Side view of the simulated cathode (on top) and electrolyte glass (on bottom). Only V–O and Si–O bonds are shown in the cathode and electrolyte, respectively. The 1.5 nm vanadia IGF is shown separating the vanadia crystals.

The IGF was made by creating a bulk (three-dimensional periodic boundary conditions, PBC) vanadia crystal and freezing the lowest two-third of the atoms in the  $\langle 010 \rangle$  direction. The crystal was heated and the remaining atoms allowed to melt. A subsequent quenching procedure through intermediate temperatures formed the glassy IGF. At lower temperatures, all atoms in the crystal/IGF were allowed to move under a constant pressure simulation. The resultant crystal/IGF is seen in Fig. 2 (where the crystal/IGF was shifted in the  $\langle 010 \rangle$  direction to center the IGF in the image). The crystal/IGF was then interfaced with the lithium silicate solid electrolyte glass, creating the system shown in Fig. 2. Fig. 2 shows a side view of the crystal/electrolyte glass interface. Separating the ordered crystals is an  $\sim 1.5$  nm amorphous

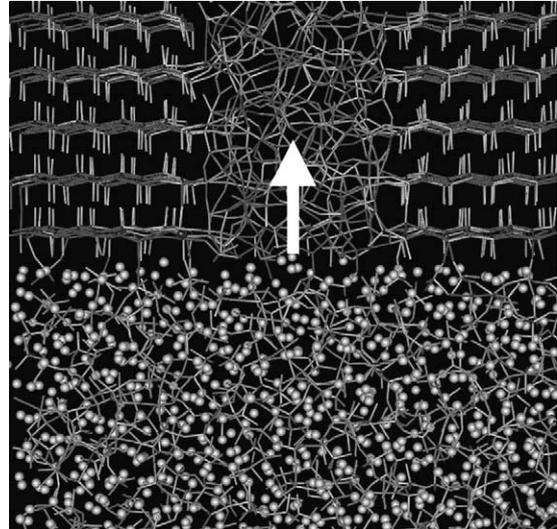


Fig. 3. Side view of the simulated cathode (on top) and electrolyte glass (on bottom), similar to Fig. 2, but with Li ions included. Based on previous simulations of Li ion transport in amorphous vanadia, rapid transport is expected along direction of the arrow, in the IGF.

vanadia IGF. Only the Si–O bonds in the electrolyte and V–O bonds in the cathode (crystal and IGF) are drawn. All atoms in the system were allowed to relax in the subsequent simulations except for those in the glassy electrolyte farthest from the crystal/electrolyte interface, similar to previous work [12].

It was anticipated that preferential Li diffusion might occur along the IGF, as indicated by the arrow in Fig. 3.

### 3. Results and discussion

The result of initial simulations at 300 K, which allow for sufficiently fast Li migration without affecting the structure of the glassy or crystalline phases, is shown in Fig. 4. Fig. 4a

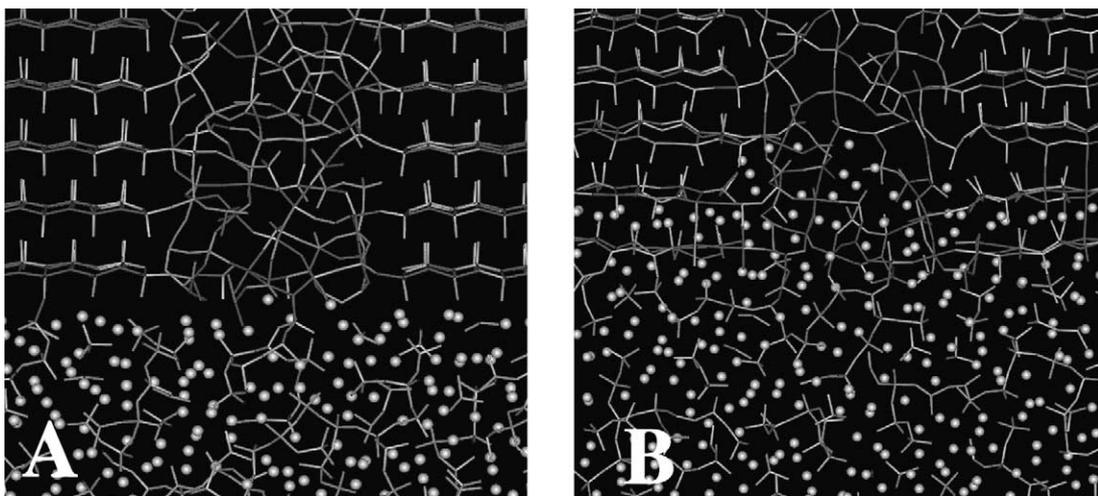


Fig. 4. (A) Side view of a thin section (into the page) of cathode/electrolyte interface at the start of the simulation: Si–O and V–O bonds drawn. Filled circles are Li ions. (B) Side view of a thin section (into the page) of cathode/electrolyte interface at the end of 150,000 moves: Li ions diffuse more rapidly into the IGF part of the cathode than the crystalline part.

shows the starting view of a thin section in the third dimension for clarity. Li ions are shown as filled circles. Fig. 4b shows the results after 150,000 moves at temperature (the scale of the figures is slightly different). Li ions rapidly move into the cathode/electrolyte interface and into the first crystalline layer. However, diffusion of Li is more rapid in the IGF than in the crystalline part of the cathode. This is consistent with the more rapid transport of Li in the simulated amorphous vanadia in comparison to crystalline vanadia with the (0 0 1) planes parallel to the cathode/electrolyte interface [6,11]. Further studies are being performed to obtain a more detailed analysis of this behavior.

The current simulations clearly indicate a possible rapid path for Li migration at the cathode/electrolyte interface when the layered crystal is oriented with the slow transport direction in the crystal being perpendicular to the interface.

#### 4. Conclusions

The application of the MD computer simulation technique to studies of thin film lithium ion batteries has shown potentially important results regarding the role of an amorphous IGF between cathode crystals on Li ion transport. The simulations show that a rapid transport path exists in the IGF that could offset the deleterious orientation of the layered vanadia crystal at the cathode/electrolyte interface. Vanadia is used in these simulations as a model of layered oxide cathodes, where anisotropic diffusion is expected.

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