

MOLECULAR DYNAMICS SIMULATIONS OF RAPID TRANSPORT PATHS FOR Li DIFFUSION IN NANOSTRUCTURED LAYERED CATHODES

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Molecular dynamics (MD) computer simulations have been used to study Li migration from the solid electrolyte glass into a nanocrystalline vanadia cathode in a solid state oxide thin film battery. Previous simulations have shown that Li transport into the cathode crystal is effected by the orientation of this layered crystal at the interface, with the largest activation barriers to diffusion in the $\langle 001 \rangle$ direction and the lowest barrier in the $\langle 010 \rangle$ direction¹.

However, scanning probe microscopy (SPM) studies of an in-situ deposited thin film oxide glass electrolyte and layered vanadia cathode (on a Li source) showed that the (001) planes are parallel to the electrolyte/cathode interface, providing the slow $\langle 001 \rangle$ direction for Li transport into the cathode².

Previous MD simulations have also shown that Li transport in amorphous vanadia is nearly as rapid as that in the fast $\langle 010 \rangle$ direction of the layered crystal¹. Thin (~1-5 nm thick) amorphous intergranular films are known to be present in many polycrystalline oxide materials³ and also believed to be present between nanocrystals crystallized within an amorphous matrix⁴, but their role in the polycrystalline cathodes of battery and EC devices has not been well studied.

We have used MD computer simulations using a multibody potential and variable charge on the vanadium ions as a function of Li intercalation to evaluate transport of Li ions in a model system containing a Li-conducting solid glassy electrolyte and a nanocrystalline layered vanadia cathode. The vanadia was studied with amorphous V_2O_5 intergranular films of different thicknesses separating the nanocrystals.

Transport behavior of Li ions in the solid state device will be discussed, with emphasis on the effect of an amorphous intergranular film in the nanocrystalline cathode on Li transport. Additional discussion will include diffusion within the glassy electrolyte, diffusion within the layered cathode as a function of direction, and diffusion across the glassy electrolyte/cathode interface.

While the experiments show that the slowest diffusion direction is perpendicular to the interface, thus inhibiting diffusion, our MD simulations show possible rapid diffusion paths in nanocrystalline vanadia that would offset the natural orientation of these crystals at the cathode/electrolyte interface (see figure 1). Our

results also show the diffusion of Li into the crystals via the amorphous vanadia phase, indicating the rapid transport mechanism. However, our results also show that, because of edge effects between the amorphous vanadia and the crystalline vanadia, the width of these diffusion paths affect Li diffusion and an optimum width will be discussed.

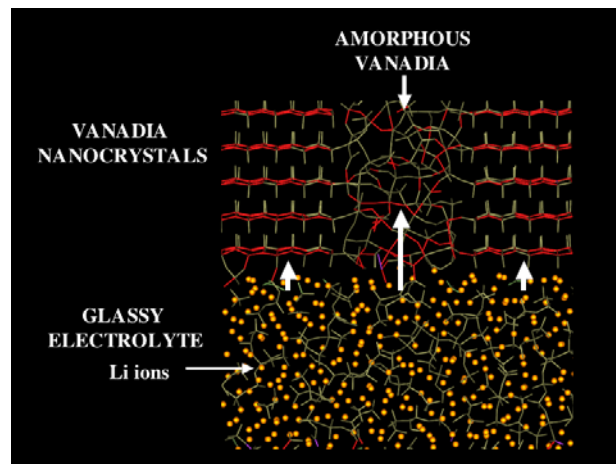


FIGURE 1. Side view of the simulated cathode (on top) and electrolyte glass (on bottom), showing V-O and Si-O bonds, as well as spheres indicating Li ions at the start of the simulation of Li diffusion near 1.5nm amorphous vanadia intergranular film between nanocrystals of vanadia. Based on previous simulations of Li ion transport in amorphous vanadia, more rapid transport of Li ions is expected in the amorphous vanadia than across the (001) planes of the crystal, in the $\langle 001 \rangle$ direction, as implied by length of up arrows. In addition, diffusion of Li from the amorphous vanadia into the crystals will depend on the orientation of the crystals with the amorphous vanadia.

References

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