Enhanced Conductivity at the Interface of $Li_2O:B_2O_3$ Nanocomposites: Atomistic Models

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A theoretical investigation at density-functional level of Li ion conduction at the interfaces in $Li_2O:B_2O_3$ nanocomposites is presented. The structural disorder at the $Li_2O(111):B_2O_3(001)$ interface leads to reduced defect formation energies for Li vacancies and Frenkel defects compared to Li_2O surfaces. The average activation energy for Li^+ diffusion in the interface region is in the range of the values for Li_2O. It is therefore concluded that the enhanced Li conductivity of $Li_2O:B_2O_3$ nanocomposites is mainly due to the increased defect concentration.

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In the last decade, ion diffusion in nanocrystalline ceramics has received considerable interest. Conductivity in ceramic oxides has been observed in single-phase systems as well as in composites of different components [1–7]. Nanocomposite materials often show enhanced conductivity compared to the single-phase ceramic oxides which is attractive with respect to possible applications in battery systems, fuel cells or sensors. In recent experiments, it has been observed that the conductivity in $Li_2O:B_2O_3$ [1–3] and $Li_2O:Al_2O_3$ nanocomposites [6] is higher than in nanocrystalline Li_2O, although B_2O_3 and Al_2O_3 are insulators. This surprising effect was attributed to the increased fraction of structurally disordered interfacial regions and the enhanced surface area of the nanosize particles [3]. In nanocrystalline Li_2O, there are interfaces between similar crystallites, whereas, $Li_2O:B_2O_3$ nanocomposites contain three types of interfaces: between the ionic conductor grains, between the insulator grains and between the ionic conductor and the insulator grains.

Several classical models have been employed to describe the enhanced ionic conductivity in composite materials. The continuum percolation model was used to describe the dependence of the dc conductivity of $Li_2O:B_2O_3$ nanocrystalline composites on the insulator concentration [1]. A brick-layer type percolation model treating both the micro- and the nanocrystalline composites on the same footing [4] is also able to reproduce the experimental results for the conductivity as a function of composition. In a recent investigation [5], a more sophisticated Voronoi approach was used. All these stochastic models do not explicitly take into account the structure of the nanoparticles and of their surfaces. The aim of the present study was to investigate the effect of the atomic structure in the interface region on the ion mobility. We have developed atomistic models of the $Li_2O:B_2O_3$ nanocomposite based on periodic slabs. Investigations were performed to clarify whether the observed enhancement of Li conductivity in the $Li_2O:B_2O_3$ interface is due to a higher defect concentration (thermodynamically controlled) or to smaller activation barriers for local hopping processes (kinetically controlled). Models as proposed in the present study allow a direct simulation of the defect formation and mobility at atomic scale without any experimental input. They can give insight into the local bonding situation at the interface which is difficult to obtain from experiments.

We have modeled [8] the $Li_2O:B_2O_3$ nanocomposite interface as a combination of the energetically favorable $Li_2O(111)$ surface [14] and the most commensurate $B_2O_3(001)$ surface. A 4×4 supercell of the primitive $Li_2O(111)$ surface unit cell with surface lattice parameters $a = b = 12.9$ Å was used as model for the Li_2O surface [15]. The $B_2O_3(001)$ surface was modeled with a 3×3 supercell ($a = b = 13.1$ Å). Thus with the present combination of surface supercells, the lattice mismatch is only 1.3%. It is assumed that the nanoparticles can adjust their structure to minimize surface stress. Therefore the interlayer distance Z and the common surface lattice parameters $a = b$ were optimized [16]. Our model is infinite in two dimensions but nonperiodic in the direction of the surface normal. The atoms in the uppermost and lowest layers are exposed to vacuum. We therefore divided the atomic layers into an interface region and an outer region. The interface region containing 75 atoms is marked with a box in Fig. 1(a). It consists of two Li layers and one O layer of the Li_2O surface and one B layer and two O layers of the B_2O_3 surface. The Li layer close to the B_2O_3 surface is denoted as first layer, the other as second layer. All atoms in the interface region are fully relaxed. The remaining atoms in the outermost layers are kept fixed at bulklike positions in order to simulate the inner part of the nanoparticles. The final optimized structure is shown in Fig. 1(b). To our knowledge, this is the first atomistic model for the interface region between ionic conductor and insulator grains [19]. Metal-oxide interfaces and insulator-insulator oxide interfaces have been studied be-

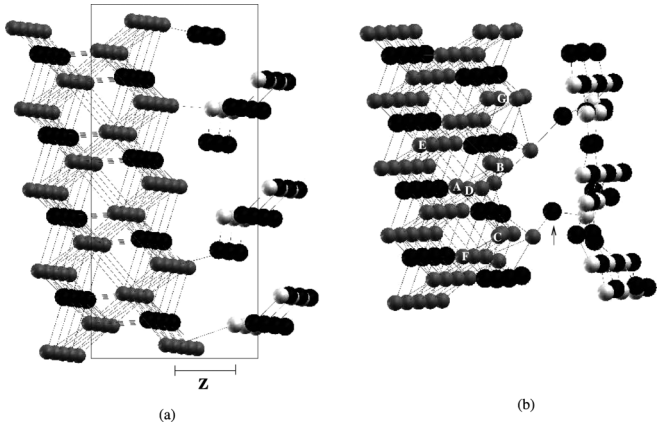

FIG. 1. The interface of Li_2O:B_2O_3 nanocomposite; (a) after the optimization of Z and a and (b) after optimization of the interface region taking the optimized Z and a. Dark gray, black, and light gray spheres represent Li, O, and B, respectively.

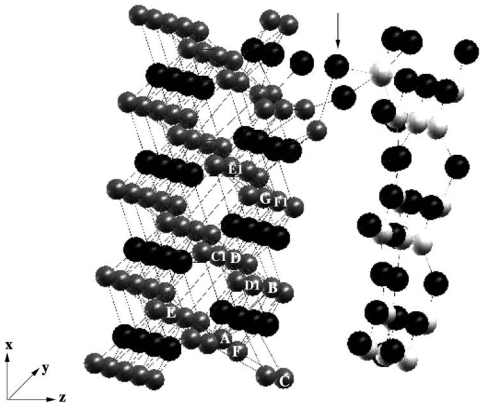

FIG. 2. Possible pathways for Li^+ migration in the Li_2O:B_2O_3 interface.

fore with slab models at density-functional theory level and with classical force-fields [21,22].

As a main result of the optimization, we observe the formation of a new boron-oxygen bond in the interface region. One of the oxygen atoms of the Li_2O surface [marked by an arrow in Fig. 1(b)] is pulled out of the surface layer towards a neighboring boron atom of the B_2O_3 surface. As consequence of this dislocation, the coordination of a Li atom in the second layer is reduced from four to three [Li (A) in Fig. 1(b)]. The remaining fourfold coordinated Li atoms in the second layer are denoted as type D, E, and F. The threefold-coordinated lithium atoms of the first layer [B, C, and G in Fig. 1(b)] do not change their coordination. It is assumed that reduced Li coordination and geometrical distortion due to the movement of the oxygen atom affect the energetics of defect formation in the interface region. This was investigated by calculating the lithium vacancy defect formation energy E_V [23] for types A–G, and the Frenkel formation energy E_F [24] for representative Li atoms (types A and B) in the interface region. In Table I, the calculated values of E_V and E_F of the Li_2O:B_2O_3 nanocomposite are compared with theoretical values of bulk Li_2O [12,17] and the $Li_2O(111)$ surface and also with available experimental data [18]. E_V varies from 5.04 to 5.91 eV for the considered lithium types of the interface model. As expected, the defect formation energy for Li(A) with reduced coordination is the smallest (5.04 eV). Also, the other threefold-coordinated lithium atoms B, C, and G in the top layer have smaller defect formation energies (5.08, 5.16, and 5.50 eV, respectively) than the fourfold coordinated lithium atoms D, E, and F in the second layer (5.70, 5.63, and 5.91 eV, respectively). Li(B) and Li(C) are closer to the dislocated oxygen than Li(G) and, correspondingly, their bond strength is smaller.

For all considered sites E_V is smaller in the Li_2O:B_2O_3 interface than in the Li_2O bulk (6.0 eV, Table I), and of the corresponding lithium atoms (A1 and G1) in the $Li_2O(111)$ surface (5.63 and 5.16 eV, respectively). A similar effect was observed for the Frenkel defect formation (Table I). E_F is much smaller in the Li_2O:B_2O_3 nanocomposite (1.17 eV) than in bulk Li_2O (2.24 eV). Our calculated bulk value is in agreement with experiment (2.53 eV) [18], and a previous DFT-LDA study (2.20 eV) [17]. As found for the vacancy formation, E_F in Li_2O:B_2O_3 nanocomposite is smaller than in the $Li_2O(111)$ surface (1.60 eV).

According to the defect formation energies, the interface region of Li_2O:B_2O_3 nanocomposites contains higher concentrations of both defect types than bulk Li_2O and the $Li_2O(111)$ surface. The similarity of the trends obtained for E_V and E_F is not surprising since both defects involve the formation of an empty Li lattice site [25]. In previous theoretical work [17] it has been shown that the migration barrier of the Li interstitial mechanism is higher than that of the vacancy mechanism. This is supported by more recent experimental investigations on the Li^+ migration in Li_2O [3], Li_2O:B_2O_3 [1,2] and Li_2O:Al_2O_3 nanocomposites [6] where a vacancy mechanism was proposed. Therefore we concentrated on the vacancy mechanism in our model calculations. As first step, a single neutral Li atom was removed from the Li_2O:B_2O_3 slab. This is a

TABLE I. Calculated formation energies of a Li vacancy, E_V (eV) and a Frenkel defect, E_F (eV)

	Li_2O:B_2O_3[a]							Li_2O		$Li_2O(111)$[a]	
Li	A	B	C	D	E	F	G	Calc.	exp.	$A1$	$G1$
E_V	5.04	5.08	5.16	5.70	5.63	5.91	5.50	6.0 [12]		5.15	5.63
E_F	1.17							2.20 [17], 2.24[a]	2.53 [18]	1.60	

[a]This work.

TABLE II. Comparison of measured and calculated activation energies ΔE (eV) for Li hopping

	$Li_2O:B_2O_3$												Li_2O		$Li_2O:Al_2O_3$
	Calc.										Exp. [2]	Calc.		Exp. [3]	Exp. [6]
a	A (second layer close to O4)					G (first layer far from O4)									
b	B	C	D	E	F	B	$C1$	$D1$	$E1$	$F1$					
ΔE_{ab}	0.10	1.08	2.04	0.56	2.72	1.18	0.22	2.00	0.39	1.88	0.34 ± 0.04	0.33 [12] (0.34 [17])		0.31	0.30 ± 0.02
ΔE_{ba}	0.09	0.68	1.37	0.29	1.68	1.06	0.05	1.97	0.18	1.80					

simplification of the real situation where Li remains in the lattice and may affect the movement of other Li atoms. But in the present investigation, we are only interested in the activation barriers for hopping processes between regular lattice sites. Li migration may then occur from a tetrahedral site to a cation vacancy in the interface which is threefold-coordinated to oxygen atoms, or vice versa. Another possibility is a hopping process between an occupied and an unoccupied threefold-coordinated site of the first layer. In both cases, one or two oxygen atoms are shared by the migrating Li^+ and the cation vacancy [26].

In Fig. 2, selected lithium atoms are labeled to represent possible migration pathways for the Li^+ movement in the interface of $Li_2O:B_2O_3$ nanocomposite. As possible starting points, we selected two representative Li atoms, the second layer Li(A) which becomes threefold-coordinated due to the dislocation of one oxygen (O4), and the first-layer Li(G) which has a large distance (6.45 Å) from the dislocated oxygen. Migration of Li^+ can occur in a zigzag pathway, via hopping from site $A \leftrightarrow B$, $A \leftrightarrow C$, $A \leftrightarrow E$, $G \leftrightarrow B$, $G \leftrightarrow C1$, or $G \leftrightarrow E1$. Alternatively, migration can occur straight along the x direction ($A \leftrightarrow D$ or $G \leftrightarrow D1$), or along the y direction ($A \leftrightarrow F$ or $G \leftrightarrow F1$). The calculated values for the activation energy, ΔE, for all these possible migration pathways are presented in Table II. Since the hopping processes can occur in both directions and the two Li sites are not equivalent in the $Li_2O:B_2O_3$ interface, we distinguished ΔE_{ab} for the process ($a \rightarrow b$) and ΔE_{ba} for the migration in opposite direction [27]. Their smaller activation energies (0.1–1.2 eV) indicate that the zigzag pathways are more accessible than the migrations along the straight lines, either along the x direction ($\Delta E = 1.4$–2.0 eV) or the y direction ($\Delta E = 1.7$–2.7 eV). Several calculated ΔE, e.g., for the processes $B \rightarrow A$ (0.10 eV) and $C1 \rightarrow G$ (0.22 eV), are much smaller than the experimental ΔE of nanocrystalline Li_2O, 0.31 eV [3]. They are also smaller than the measured activation enthalpies in $Li_2O:B_2O_3$ nanocomposites (0.34 ± 0.04 eV [2]) and in $Li_2O:Al_2O_3$ nanocomposites (0.30 ± 0.02 eV [6]). However, it has to be taken into account that in these experiments an average over the manifold of local hopping processes is obtained. Since the measurements have been performed at 300–500 K, it can be assumed that activation energies larger than 1 eV cannot be overcome in the time scale of NMR experiments. This excludes all straight pathways and also some of the zigzag pathways. The average of the remaining nine calculated activation energies is 0.28 eV, in close agreement to the reported experimental values.

In summary, we have developed an atomistic model of nanocrystalline $Li_2O:B_2O_3$ composites. With this model, a quantum-chemical investigation of the defect properties and ionic conductivity in the interface region was performed. It was found that Li-O bonds are weakened and simultaneously B-O bonds are formed at the boundary between the two surfaces. This preference of oxygen bonding with B (or Al in $Li_2O:Al_2O_3$) plays a key role in generating low-coordinated Li [28]. The removal of surface oxygen from Li_2O is responsible for the increased vacancy defect concentration in $Li_2O:B_2O_3$ (or $Li_2O:Al_2O_3$) nanocomposite materials. We propose that nanocomposites of ionic compounds (containing weakly bound and therefore mobile cations) with highly covalent compounds (with strong metal- or nonmetal-oxygen bonds) are in general promising candidates for high ionic conductivity. Our model calculations show that the most likely mechanism for Li^+ migration is in a zigzag pathway rather than in a straight line along a direction parallel to the interface plane. The averaged calculated activation energy for Li^+ migration in the $Li_2O:B_2O_3$ interface is similar to the experimental values of bulk Li_2O, $Li_2O:B_2O_3$ and $Li_2O:Al_2O_3$ nanocomposites. We therefore conclude that the experimentally observed enhanced Li mobility in the $Li_2O:B_2O_3$ interface region is thermodynamically and not kinetically controlled.

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[16] The optimized values of Z and $a = b$ are 5.0 and 12.4 Å corresponding to a substantial lateral contraction of 3%–4%. For comparison we calculated the defect formation energy of Li A (Table I) with lattice constant $a = 13.0$ Å. Although the total energies of the defected and the stoichiometric reference model changed substantially, the calculated defect formation energy only slightly increased from 5.04 to 5.07 eV.

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[23] The defect formation energy E_V is calculated with the following equation,

$$E_V = E(\text{Li}_{2-x}\text{O:B}_2\text{O}_3) + E(\text{Li}, g) - E(\text{Li}_2\text{O:B}_2\text{O}_3),$$

where $E(\text{Li}_{2-x}\text{O:B}_2\text{O}_3)$ and $E(\text{Li}_2\text{O:B}_2\text{O}_3)$ denote the total energy of the $Li_2O:B_2O_3$ nanocomposite with and without vacancy, respectively, and $E(\text{Li}, g)$ is the energy of the free Li atom.

[24] The Frenkel formation energy E_F is the energy needed to move a Li^+ ion from its regular lattice site to an interstitial site. The lowest converged value was obtained for a distance of 3.15 Å (Li A) and 4.77 Å (Li B) between the interstitial and the regular sites.

[25] Because of the different references, the absolute values of E_F are much smaller than those of E_V. The two defect types can be regarded as extreme cases of real lattice defects, where the dislocated Li is close to the vacancy (Frenkel defect) or at infinite distance (hole vacancy).

[26] Spin polarization plays an important role for the Li^+ migration. It was observed that the unpaired electron, created due to the cation vacancy, is localized on the $2p$ orbital of one of the surrounding oxygen atoms. The same situation was observed for the Li^+ diffusion in crystalline Li_2O [12] and $Li_2B_4O_7$ [13].

[27] For each process the activation energies ΔE_{ab}, ΔE_{ba} were approximated as energy difference of a transition structure where Li is halfway between the two sites, and the initial situation where Li is on site a and site b is empty, or vice versa. Effects from the zero point energy were neglected.

[28] The effect can be predicted from the average Li-O and B-O (or Al-O) bond strengths of the bulk materials. Taking into account the atomic coordination numbers, 4 (Li) and 8 (O) in Li_2O, and 3 (B) and 2 (O) in B_2O_3-I, and the enthalpies of atomization, 1154 kJ/mol [29] and 3127 kJ/mol [30], formal bond energies of 144 kJ/mol (Li-O) and 521 kJ/mol (B-O) are obtained for Li_2O and B_2O_3, respectively. At this point it is important to note that theoretically obtained binding energies are accurate enough to be used for such an analysis if experimental data are unavailable. This has been repeatedly demonstrated, e.g., in our own studies of Li_2O and B_2O_3 bulk properties [11,12].

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