Crystal-isotropicity dependence of ionic conductivity enhancement at strained interfaces

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A B S T R A C T

In the solid state ionic field, lattice strain is ubiquitous at heterostructural crystal interfaces and can lead to enormous variation in the transport efficiency of ions along the as-formed strained interfaces. In particular, substantial experimental work has been focused on Y-doped ZrO_2 (YSZ), the O^{2-} ionic conductivity of which can be enhanced ~10^4 times under a 4% lattice strain. Despite the consistence that theoretical modeling and computing finds with such an experimental enhancement, a fundamental investigation into the isotropicity dependence of ionic conduction in strained crystal interfaces is still lacking. In this report, we investigate the isotropicity dependence of ionic conduction in arbitrary orthorhombic crystals and reveal the intrinsic conduction enhancement upon applying strain at any designated crystal orientation. Our work provides fundamental basis for rational strain engineering of a crystal in general, the ionic conduction of which is subject to enhancement for energy applications.

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1. Introduction

The transport efficiency of ionic species in solid-state materials is of pivotal importance for a number of applications. In particular, ensuring efficient electrical conduction of ions in solid crystals is the prerequisite to achieve fuel cell and battery systems with high energy density and fast charge/discharge [1,2]. In the field of solid oxide fuel cells (SOFCs), the advantage of high chemical–electrical conversion efficiency is compromised largely by the high operation temperatures, typically well above 500 °C [3–7]. Such an operation temperature is necessary to maintain an applicable ionic conductivity in the ion-conducting electrolytes including Y-doped ZrO_2 (YSZ), CeO_2, etc. To mitigate this devastating drawback, a number of methods have been developed to improve the ionic conductivity of the aforementioned electrolyte crystals, including doping various elements in existing crystals and preparing multi-element nanocomposites [8–11]. Strain engineering, which is ubiquitous and known to lessen the energy barrier of ionic transport within a crystal, has exhibited unprecedented capability of enhancing the ionic conduction within an ion-conducting solid crystal [12–15]. For instance, by introducing 3%–5% lattice strain to YSZ, the ionic conductivity of the material is enhanced by nearly four orders of magnitude [16–21]; the ionic conductivity of Gd doped CeO_2 (GDC), Sm doped CeO_2 (SDC), Er doped Bi_2O_3 (ESB), are all efficiently enhanced by a few magnitudes by introducing certain extents of lattice strain [22–23]. As two materials with lattice mismatch are deposited to form nanostructures, the interface/bulk atom ratio increases significantly and the ionic conduction enhanced by the interface strain can be more dominant compared with the bulk ionic conduction [24,25]. Although substantial conductivity enhancement has been achieved frequently through strain engineering, few analytical models have been developed to investigate the isotropicity-dependence of such conductivity enhancement. In particular, the authors derived an analytical model to evaluate the conductivity enhancement versus strain correlation recently, but the model is based on pure isotropic crystals [26]. Indeed, understanding well the selectivity of lattice orientation is one of the keys to realizing high-performance heterostructural crystals. In this report, we employ a volume expansion-versus-conductivity enhancement model to investigate insightfully the isotropicity-dependence of ionic conductivity enhancement for a general ionic-conducting crystal. Our study provides an efficient fundamental basis for rational strain engineering towards improved applicability of electrolyte and electrode crystals in the areas of fuel cells and ion-based batteries.

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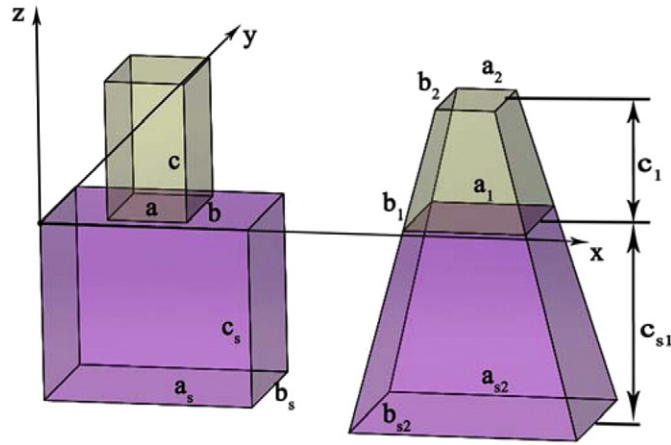[1] These authors contributed equally to this work.

Fig. 1. 3D schematic of coherent solid ionic electrolyte interfaces with lattice mismatch, where Phase 1 has a lattice constant of a, b and c, and Phases 2 has a lattice constant of a_s. b_s and c_s. Among the parameters, $c < c_s$, $a < a_s$ and $b < b_s$. Interfacial tensile strain for Phase 1 is induced due to the lattice mismatch.

2. Models and calculation methods

Fig. 1 shows the 3D schematic of coherent solid ionic electrolyte interfaces between Phase 1 and Phase 2 with lattice mismatch. Phase 1 and Phase 2 are cubic, tetragonal or orthorhombic crystallographic ionic conductors. Phase 1 has lattice constants of a, b and c, and Phases 2 has lattice constants of a_s, b_s and c_s. If $a < a_s$ and $b < b_s$, tensile strain for Phase 1 is induced as the two phases form a coherent interface along xy plane. As a result, the unit cell parameters a and b expand to a_1 and b_1, respectively at the first atomic layer parallel to the interface, and to a_2 and b_2, respectively at the second atomic layer. According to the definition of lattice strain, we get Eqs. (1) and (2),

$$a_1 = a(\varepsilon_1 + 1), b_1 = b(\varepsilon_1 + 1) \tag{1}$$

$$a_2 = a(\varepsilon_2 + 1), b_2 = b(\varepsilon_2 + 1) \tag{2}$$

where ε_1 and ε_2 are the lattice strain of the first atomic layer and the second atomic layer, respectively. ε_1 and ε_2 can be calculated by Eq. (3) [27–29],

$$\varepsilon(x) = \varepsilon_1 \exp[-\alpha x] \tag{3}$$

where $\varepsilon(x)$ is the lattice strain at the x position from the interface to the investigated lattice position, and α is a constant, which is equal to 4–5 nm^{-1} for YSZ and CeO$_2$ [30]. The distance between the two atomic layers, c, changes to c_1, which is resulted from ab plane stretching, and the correlation between c and c_1 is expressed in Eq. (4) [31],

$$c_1 = c\left(1 - \frac{2v\varepsilon_1}{1-v}\right) \tag{4}$$

where v is the Poisson ratio of Phase 1.

According to our previous work, the correlation between lattice cell volume expansion and the tensile strain can be expressed as Eq. (5) [26],

$$\Delta V = \frac{1}{3}abc\left(1 - \frac{2v\varepsilon_1}{1-v}\right)\left((\varepsilon_1 + 1)^2 + \left(1 + \varepsilon_1 \exp\left[-\alpha c\left(1 - \frac{2v\varepsilon_1}{1-v}\right)\right]\right)^2 + (\varepsilon_1 + 1)\left(1 + \varepsilon_1 \exp\left[-\alpha c\left(1 - \frac{2v\varepsilon_1}{1-v}\right)\right]\right)\right) - abc. \tag{5}$$

The activation energy of ion transport derived from the interface strain, ΔG, can be calculated based on the Zener and Keyes strain-energy model [32,33],

$$\Delta G = \frac{-\Delta V E(2 + 2v)}{7 - 10v - 8v^2} \tag{6}$$

where E is Young's modulus. The correlation between ionic conductivity and tensile strain is expressed in Eqs. (7)–(8) [26],

$$\ln\left(\frac{\sigma_t}{\sigma_0}\right) = -\frac{\Delta G}{k_B T} \tag{7}$$

$$\ln\left(\frac{\sigma_t}{\sigma_0}\right) = \frac{\frac{1}{3}abc\left(1 - \frac{2v\varepsilon_1}{1-v}\right)\left((\varepsilon_1 + 1)^2 + \left(1 + \varepsilon_1 \exp\left[-\alpha c\left(1 - \frac{2v\varepsilon_1}{1-v}\right)\right]\right)^2 + (\varepsilon_1 + 1)\left(1 + \varepsilon_1 \exp\left[-\alpha c\left(1 - \frac{2v\varepsilon_1}{1-v}\right)\right]\right)\right) - abc}{k_B T (7 - 10v - 8v^2)/(2E_1(1 + v))} \tag{8}$$