

Temperature Dependence of Ion Diffusion in Chromium Oxide Cr_2O_3

Penghui Cao,¹ Daniel Wells,² and Michael Short^{*1}

¹*Department of Nuclear Science and Engineering, Massachusetts Institute of Technology*

²*Electric Power Research Institute (EPRI), Charlotte, NC 28262*

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We apply molecular dynamics simulation to probe ion diffusion in chromium oxide Cr_2O_3 . Point defects such as vacancy and interstitial assisted diffusion mechanism is investigated, and their corresponding temperature dependent diffusion coefficients are also computed. Temperature-dependent diffusion anisotropy is observed in our simulation. At low temperature, ion diffusion is found to be strong anisotropic, which disappeared above 1800K. Migration energy barriers of point defects show the origin of this anisotropic diffusion and explain why it disappears at higher temperature.

PACS numbers:

I. INTRODUCTION/BACKGROUND

- Cr_2O_3 Oxides formed on steam generator alloy, ion diffusion is related to oxide growth and metal ion release.
- experimental studies
 1. Sabioni et al. studied the role of oxygen and chromium ion diffusion on oxidation process and found chromium diffusivity is lower than the corresponding oxygen diffusivity.¹
 2. Lobnig et al. studied the diffusion coefficients of Cr, Ni and Fe in Cr_2O_3 Oxides.²
 3. Tsai³ probe growth mechanism of Cr_2O_3 Oxides by measuring oxygen and chromium diffusion.
 4. Hoshino et al. measured Cr diffusion in plane and out of plane in single crystal of Cr_2O_3 and found diffusion along c axis is higher.⁴
- MD studies
 1. Ion diffusion⁵ and surface properties⁶ have been studied by Vaari, Sun et al in chromium oxide by using MD.
 2. Ion diffusion by atomistic simulation.⁷

Cr_2O_3 oxide scales are usually formed on the surface of high chromium-bearing alloys and this chromium oxide layer plays an important role in protecting metallic alloys against corrosion. *Need to add something in LWRs, relate it to CRUD formation*. To understand oxidation and metal ion release processes, studying ions diffusion mechanism is desirable.

The diffusion of chromium and oxygen ions in Cr_2O_3 has been investigated experimentally¹⁻⁴ and computationally^{5,7}. In Hoshino's experiment, self-diffusion of chromium ion has been found highly depends

on diffusion direction. We found that ion diffusion in Cr_2O_3 has been little studied by using atomistic simulation. Just recently molecular dynamics simulation was applied to compute ion diffusivity due to Schottky type point defects. However, the directional anisotropic diffusion in Cr_2O_3 is still need to be uncovered.

The aim of this study is to understand point defects assisted diffusion mechanism in Cr_2O_3 . We studied vacancy and interstitial diffusion of ion for a range of temperatures by means of MD simulation and found that temperature can affect diffusion anisotropy. The ion diffusion is found to be strong anisotropic at low temperature and the anisotropy disappears when temperature becomes higher. We then compute the activation energy barrier of ion migration by using Nudged Elastic Band (NEB) to interpret the origin of anisotropic diffusion.

II. COMPUTATIONAL METHODS

In our present work, we modeled the interaction between ions by the combination of short range Buckingham potential and long range Coulombic potential. The potential for the interaction between ions i and j at a distance r is defined as

$$U_{ij}(r) = A_{ij}e^{-r/\rho_{ij}} - \frac{C_{ij}}{r_{ij}} + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where the parameters A , ρ and C can be found in previous study⁷.

Like $\alpha - \text{Al}_2\text{O}_3$ and Fe_2O_3 , Cr_2O_3 has the corundum structure. **Add unit cell description and figure** Our simulations were carried out using a $18 \times 18 \times 18$ hexagonal super cell system that contains 58320 atoms. We use periodic boundary conditions in all three directions. To study vacancy and interstitial assisted ion diffusion, we randomly delete or insert ionic atoms in the system. In our simulation model, vacancy or interstitial has defects concentration of 0.0008. Before the diffusion coefficient calculation, the system is relaxed at zero pressure for 100 ps in the NPT (constant number of atoms, pressure and temperature) and another 100 ps run is performed in the NVT ensemble (constant number of atoms, volume

*Corresponding author: hereiam@mit.edu

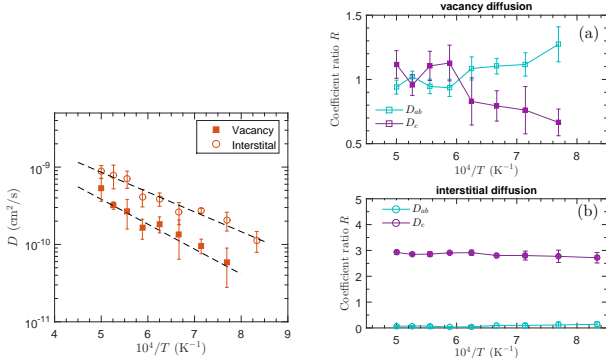


FIG. 1: Chromium ion diffusivities in 3 dimensions, along c axis and in ab plane. (left) Oxygen vacancy and interstitial diffusion coefficients as function of temperature, (right) (a) normalized chromium vacancy diffusivities D_{ab} and D_c in ab plan and along c axis, (b) normalized chromium interstitial diffusivities in ab plan and along c axis

and temperature). The Nose-Hoover thermostat is used in time intergration and the time step is set to be 1 fs.

The ion diffusion was determinated measuring mean square displacement (MSD) of ions as a function of time at a range of temperatures. The MSD of ion is described by

$$\langle \Delta r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N [\mathbf{r}_i(t+t_0) - \mathbf{r}_i(t_0)]^2 \quad (2)$$

where N is total number of the ion in the system, $\mathbf{r}(t_0)$ is initial reference position at time t_0 and $\mathbf{r}(t)$ is position at time $t+t_0$. The diffusivity that relates MSD to the observe time t is defined as

$$D = \frac{\langle \Delta r^2(t) \rangle}{2d \times t} \quad (3)$$

where d is dimensionality of the system. Then diffusivity of ion along c axis, in ab plane and in three dimensions can be calculated by $D_c = \langle \Delta r_c^2(t) \rangle / 2t$, $D_{ab} = \langle \Delta r_{ab}^2(t) \rangle / 4t$, $D_3 = \langle \Delta r_{abc}^2(t) \rangle / 6t$. The diffusion coefficient D is calculated by fitting the MSD as a function of time. All diffusion simulations are performed in NVT emsamble by extensive simulation time of 1 ns to ensure adequate statistical sampling.

III. RESULTSS

A. Temperature-dependent ion diffusivities

Our simulation are performed at temperature ranging from 1200 K to 2000 K ad the diffusion coefficients determined at vacancy defect interstitial defect are shown in Fig. 1 and 2.

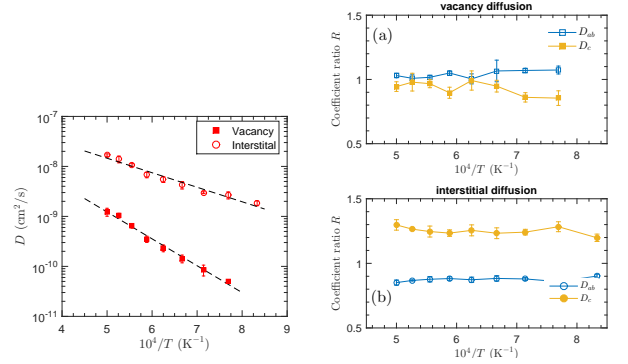


FIG. 2: Oxygen ion diffusivities in 3 dimensions, along c axis and in ab plane. (left) oxygen vacancy and interstitial diffusion coefficients as function of temperature, (right) (a) normalized oxygen vacancy diffusivities D_{ab} and D_c in ab plan and along c axis, (b) normalized oxygen interstitial diffusivities in ab plan and along c axis

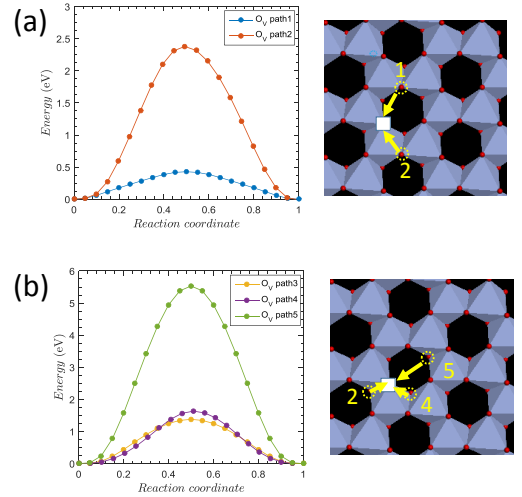


FIG. 3: Oxygen vacancy migration pathways. (a) paths in ab plane, (b) out of plane paths

B. Point defects migration pathways

- Oxygen vacancy migration pathways, Fig. 3
- Chromium vacancy migration pathways, Fig. 4
- Chromium interstitial migration pathway, Fig. 5

IV. DISCUSSION

Our diffusivity results are obtained at a defects concentration of 0.0008. However, we note that the diffusion coefficients of ion depends both on the concentration of defects and the mobility, as shown by

$$D(T) = \alpha a^2 C \omega = \alpha a^2 C f e^{-E_m/k_B T} \quad (4)$$

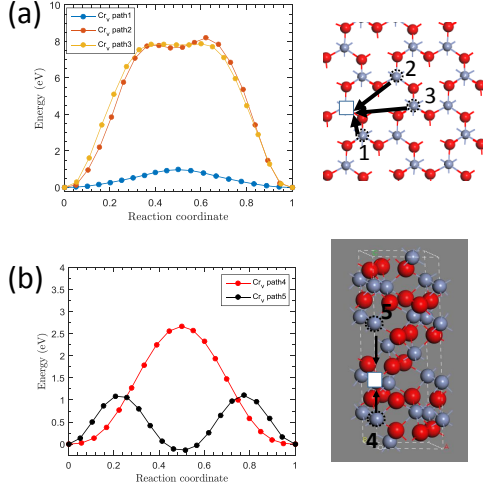


FIG. 4: Chromium vacancy migration pathways. (a) paths in ab plane, (b) out of plane paths

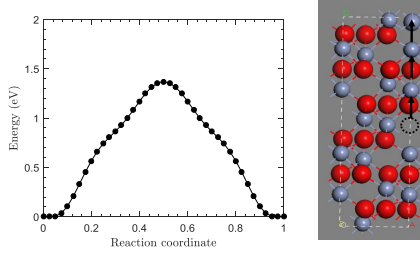


FIG. 5: Chromium interstitial migration pathway

where ω is successful jump frequency, f_{Debye} is trial frequency, E_m is defect migration energy, k_B is the Boltzmann constant, T is system temperature, α is constant, a is jump distance and C_{defect} is concentration of defect. We also note that concentration C can be defined as

$$C = e^{-E_f/k_B T} \quad (5)$$

where E_f is defect formation energy. The above diffusivity equation can be written as

$$D(T) = \alpha a^2 f e^{-E_f/k_B T} e^{-E_m/k_B T} \quad (6)$$

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