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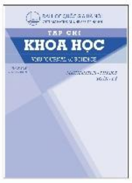

Original Article

Molecular Dynamics Simulation of Amorphous Vanadium Pentoxide

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Abstract: A molecular dynamics (MD) simulation has been carried out to explore the microstructure and diffusion pathway in amorphous vanadium pentoxide (V_2O_5) materials at room temperature and ambient pressure. We showed that the simulated model is a mix of basic units VO5 and VO6 connected to each other via 2 or 3 bridging oxygens. In the simulated model, there exist regions without atoms (cavity) in the form of clusters or channels. We found that 87% large pores, larger than or equal to oxygen atoms, overlap to form the largest tube.

Keywords: Vanadium pentoxide, amorphous, pore.

1. Introduction

For a long time, V_2O_5 materials have been manufactured and applied in science, technology and life. Many scientific publications [1-6] show that V_2O_5 materials exist in many different structures such as thin films, nanoparticles, nanorods, porous structure, and some polycrystalline. Because of these diverse structural morphologies, most studies focus on the characteristics and properties such as electronic, magnetic, electrical, electrochemical, optical, mechanical, and catalytic. Nanostructured V_2O_5 materials exhibit high energy density, high capacitance, good cyclic stability, and rapid electron transfer, so they can be used as supercapacitors and electrodes in batteries [2, 3, 6-9]. It is also used as gas sensing materials, biosensors, and electrochromic materials. The main change in the material properties of V_2O_5 is due to the change in band gap leading to the change in the conductivity.

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The V-O network is the most stable structure of the V_2O_5. Crystalline V_2O_5 materials have been studied and widely used in industry, especially in making electrodes in charge-carrying devices [10]. Recently, the amorphous V_2O_5 has attracted attention because its structural disorder has created natural conduction channels increasing the conductivity efficiency [8]. Since the 1980s, experimental scientists have studied the microstructure of V_2O_5 in both crystalline and amorphous states. The publications [10-13] have shown that the amorphous V_2O_5 is a structural network of structural units of VO4, VO5 and VO6. The number of VO4 structural units formed depends on the experimental conditions such as temperature, cooling rate or pressure. Structural units can be linked together by vertex- and edge- shared. The average V-O bond distance is 1.75 Å. The distance V-V between the vertex- or edge- share units is different, for example, in the edge- shared in VO5 bonds is 3.13 Å, in the vertex shared structural units it is 3.43 Å. Recent studies have shown that materials with disordered materials can form active diffusion pathways for ion diffusion [14-16]. Therefore, amorphous oxides are interesting in research because they have a high disorder degree. Research results on the $Li_2O.V_2O_5$, $Li_2O.SiO_2$ glass system show that the network structure of V_2O_5 and SiO_2 is relatively independent of the Li_2O concentration [17, 18]. In silicate systems such as $Na_2O.SiO_2$, $Li_2O.SiO_2$, the short ordered characteristics of the host atoms (Si, O) are almost unchanged compared to pure SiO_2. Li and Na atoms tend to be concentrated in clusters or channels and become very mobile. The chemical bonds of these mobile ions are very weak compared to the strong Si-O bonds. Their diffusion coefficients are ten times higher than those of Si and O. These atoms can move freely along natural diffusion pathways. For Li-ion battery application, the addition of lithium in V_2O_5 has been well documented and charge compensation occurs, however, studies regarding the use of amorphous vanadium oxide for storage energy is limited.

The free volume region in the amorphous V_2O_5 structure plays an important role in the diffusivity of cations that has not been studied commensurately with its importance in technology. For amorphous oxide materials such as SiO_2, Al_2O_3, the free volume region has been studied in detail and shown the porosity of the material [19-21]. The works also provide valuable information in fabrication of gas-sensitive materials. Currently, research on amorphous V_2O_5 materials in the field of battery manufacturing is attracting worldwide attention. So the study of this material in manufacturing electrical equipment is an objective requirement.

In this work, we build an amorphous V_2O_5 model at room temperature and investigate microstructural features such as pair bond distance, bond angle distribution and coordinate distribution. The free volume region is surveyed through the pore distribution, thereby showing the degree of diffusion of charge carriers (such as Li^+, Zn^+) in the structural network. The diffusion pathway was also shown by the structural visualization method.

2. Calculation Method

The model V_2O_5 consisting of 3000 atoms is built by molecular dynamics (MD) at 300 K and 0 GPa pressure, under periodic boundary conditions. The Born-Meyer interaction potential used in model building has the form:

$$U_{ij}(r) = q_i q_j \frac{e^2}{r_{\text{ij}}} + B_{ij}\, exp(-\frac{r_{\text{ij}}}{R_{ij}}) - \frac{C_{\text{ij}}}{r_{\text{ij}}^6} - \frac{D_{\text{ij}}}{r_{\text{ij}}^8}$$

where the ionic charges of V and O are: q_V=5, q_O=-2, respectively. The pair interaction coefficients B_{V-V}=0, B_{V-O}=2970, B_{O-O}=1500 eV and R_{ij}=29 pm. The dipole-dipole and dipole-quadrupole interaction coefficients C_{ij} and D_{ij} are ignored. We use these interaction potentials because they allow reconstruction of the amorphous V_2O_5 structure giving results that are in good agreement with the experimental data.

Coulomb interactions at long distances were calculated using the Ewald-Hansen technique. The model density was taken from the experiment and received a value of 3.35 g/cm^3. Verlet algorithm is used with an MD time step of 0.4 fs. The initial configuration was built at 3,000 K and at 0 GPa pressure to achieve equilibrium and no disturbances. This liquid model was then rapidly cooled down to a temperature of 300 K and a pressure of 0 GPa after about 10^5 MD steps. The system is then continued to run until a stable equilibrium is reached. To investigate the microstructural features, the radial distribution function was averaged over 1,000 configurations. The distribution of coordination numbers is determined through the first minimum of the radial distribution function. The characteristics of near-distance, mid-range, and angle distribution are also determined.

To provide information about the possibility of inserting impurity atoms into the structural network, we also survey the distribution of pores in the model. The V and O atoms have radii of 1.22 Å and 0.73 Å, respectively. A pore is defined as a sphere that is in contact with four neighboring atoms and contains no atoms inside. To calculate pore, we take 4 neighboring atoms with the condition that any 2 atoms in them have a distance of 10.5 Å. The pore is then inserted inside and in contact with these 4 atoms. If any pore is overlapped with a V or O atom, it will be removed. The pores can stand alone or overlap together to form clusters or tubes. If the two overlap pores that large pore occupies 2/3 of the volume of the small pore, the small pore will be removed. A large pore stands in the center and there are small pores located around it, it will form a pore cluster. And every two interserve pores with their cross-sectional area greater than or equal to the oxygen atom, forming a pore tube. A pore tube is made up of 2 or more pores. These clusters and tubes are natural pathways for O atoms to diffuse easily within it. From these analyzes we show large pores play a role as vacancies and clusters and tubes also are natural diffusion pathways in the network, thereby evaluating the diffusion possibility of mobile ions (Li$^+$, Zn^{2+}, etc.) inside it.

3. Results and Discussion

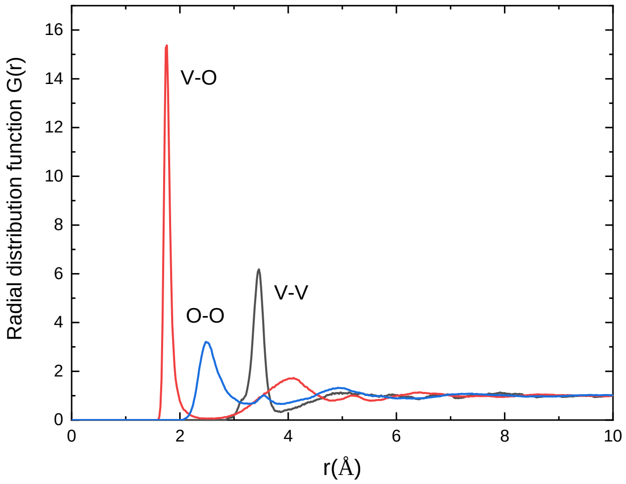

Figure 1. The radial function distribution of V_2O_5 at 300K, 0 GPa.

The structural features of the model are shown in Figure 1. The first position of the pair radial distribution function shows the average pair bond distances of V-V, V-O and O-O are 3.46, 1.76, and 2.52 Å, respectively. These pair bond distances obtained from experiments are of 3.45, 1.75 and 2.70 Å [2,3]. The simulation results are in good agreement with the experimental data. The average bonding distance O-O differs from the experimental one by about 7% due to the high degree of structural disorder of the constructed model by numerical method. Experimental studies in [6] also show that the structural order and properties of V_2O_5 is affected by the fabrication conditions and methods.

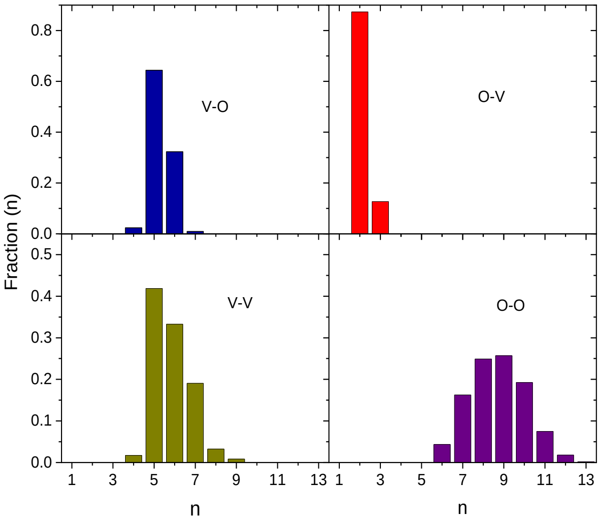

Figure 2. The coordination number distribution of V_2O_5 at 300K, 0 GPa.

The local ordering environment around each type of atom is determined by the coordination number distribution. To calculate the distribution of coordination numbers, we use the cut-off distance as the minimum position of the pair radial distribution function. Information about the distribution of coordination numbers is plotted in Figure 2.

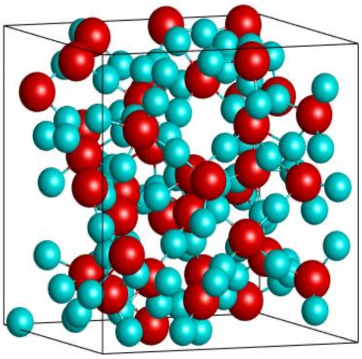

Figure 3. The structural network of model V_2O_5 at 300K, 0GPa, V (red color) and O (blue color).

The Figure 2 shows that V atoms are coordinated 5 and 6 by O atoms in which 5 coordination is the highest percentage (75.2%), number of coordinates 6 accounts for 19.2%. The coordination number of 4 and 7 is only about 6%. Thus, the structure network of V_2O_5 consists of the basic structural units VO5 and VO6 connected via shared O atoms and agree with experiment data in [2, 3, 13]. The coordination number of O atoms is 2 and 3, in which the fraction of OV2 and OV3 are 94% and 6%, respectively. This shows that the basic structural units VO5 are mainly connected together by bridging O atoms (BO). At the average distance of 3.46 Å the V atoms are also coordinated 5 and 6 by atoms of the same type. The coordination number distribution O-O is more widespread and is mainly in the range 7-10. Compared with the porous amorphous SiO_2 (99% Si with coordinate 4 and 87% O with coordinate 2) [12], the V_2O_5 structure is higher disordered. The coordination number distribution of V and O atoms at 300K, pressure 0 GPa is visualized in Figure 3.

To provide more detailed information about the short- and mid-order, the bond distance and bond angular distributions between neighboring atoms are also investigated and shown in Figures 4 and 5.

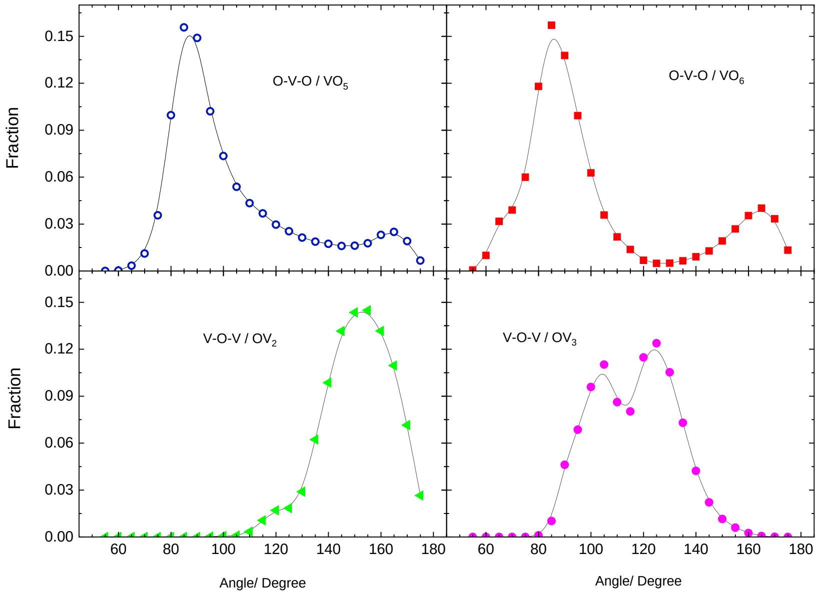

Figure 4. The bond angle distribution of V_2O_5 at 300K, 0 GPa.

It can be seen that the O-V-O bond-angle distribution in both VO5 and VO6 has a main peak at 85 ± 3^0 and a shoulder at 165 ± 3^0. The average V-O bond distance in VO5 is 1.74 Å and in the range from 1.62–1.98 Å. This result is consistent with the experiment [2] that the V-O distance is from 1.53–1.97Å and the mean value is 1.75 Å. The average distance V-O in VO6 is 1.78 Å. The mid-range order was investigated through the V-O-V angle distribution and the connection distance between two basic structural units adjacent to the O-V. Each base structure unit VOx (x=5, 6) is vertex or edge bonded to 2 or 3 nearest structural units by a shared O atom. The mean V-O-V angle distribution between two neighboring VOxs obtains a main peak at 155 ± 3^0 and distributes in the range from 135–170^0. The mean O-V distance in OV2 is 1.78 Å, equal to the mean V-O distance in VO6 units. Average V-O-V angle distribution in units OV3 has 2 main peaks at 105 ± 3^0 and 125 ± 3^0. The average O-V distance is 1.88 Å and the width of the peak shows that this distribution is more disordered. Thus, the lattice structure of amorphous V_2O_5 consists of the basic structural units VO5 and VO6 linked together by 2 or 3 O atoms.

Each O atom is bonded to 2 or 3 V atoms to form a highly disordered mixed V-O network. The bond distances in a structural unit VO5 and VO6 are the same, but the O bond distances with 2 or 3 V atoms are different, indicating that the VOx structural units are randomly localized to form a mixed network.

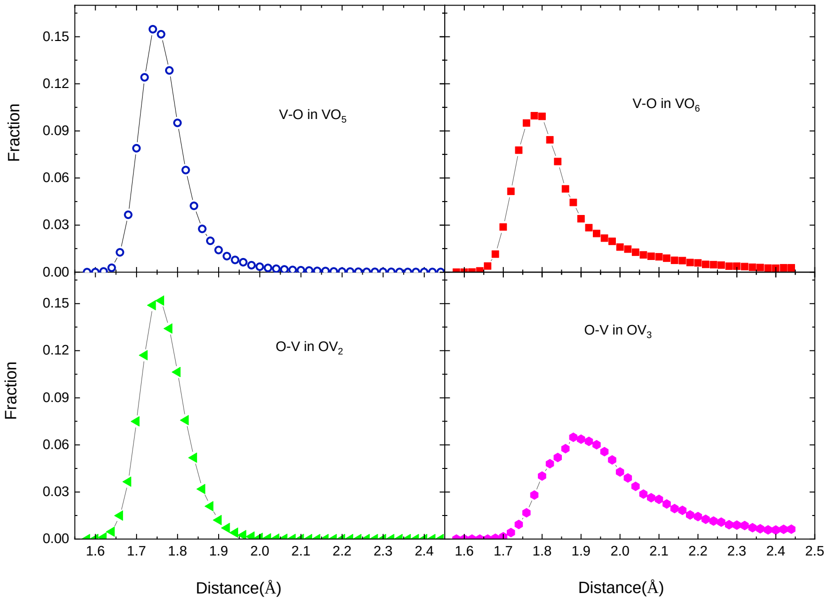

Figure 5. The bond distance distribution of V_2O_5 at 300K, 0 GPa.

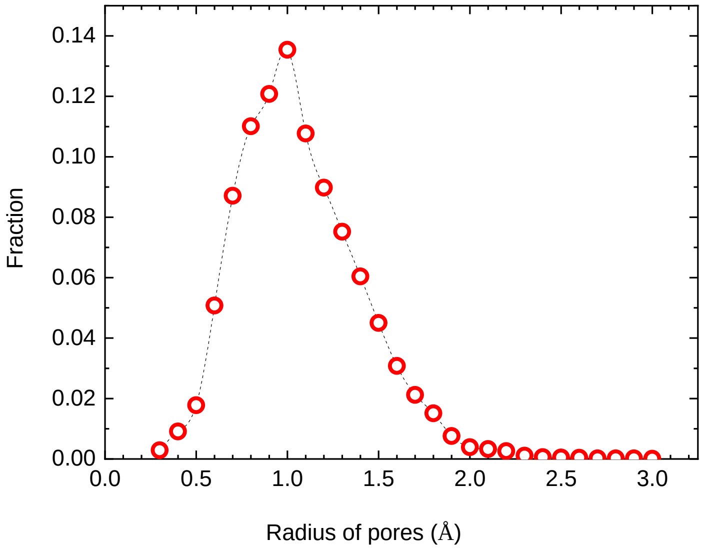

Figure 6. The radius distribution of pores in model V_2O_5 at 300K, 0 GPa.

It does not form clusters of the same structure units as in pure SiO_2 network [19]. Because of this mixing V^+ ions in the structural network have different valences, leading to chemical reactions with doping atoms to form a good charge carrier material.

To further elucidate the local disorder, we survey the distribution of pore spheres inside the structural lattice. The radius distribution of pores is shown in Figure 6. It can be seen that the average pore radius is 1.0 Å. The distribution spreads from 0.3–3.0 Å. Small pores with a radius smaller than the O atomic radius are called cavities. The survey results show that the number of pores with radius larger than the O atom accounting for 83% and the number of pores with radius larger than the V atom accounting for 27% of the total number of pores, which proves that the V_2O_5 network structure is porous. The number of pores that can contain Li atoms in the model is 13% of the total number of pores.

Table 1. The cluster distribution of pores in model V_2O_5 at 300 K, 0 GPa.

Number of pore in a cluster	1	2	3	4	5	6	7	23
Number of clusters	1727	483	256	161	85	44	15	1

The pore cluster distribution is listed in Table 1. It shows that in the structural network, separate standing pores are predominant. Specifically, there are 1,727 pores standing alone, accounting for 62% of the total number of pores. The number of clusters decreases with the increasing number of pores in a cluster. We also found the largest cluster containing 23 pores. Figure 7a is a visualization of the clusters obtained in the V_2O_5 model.

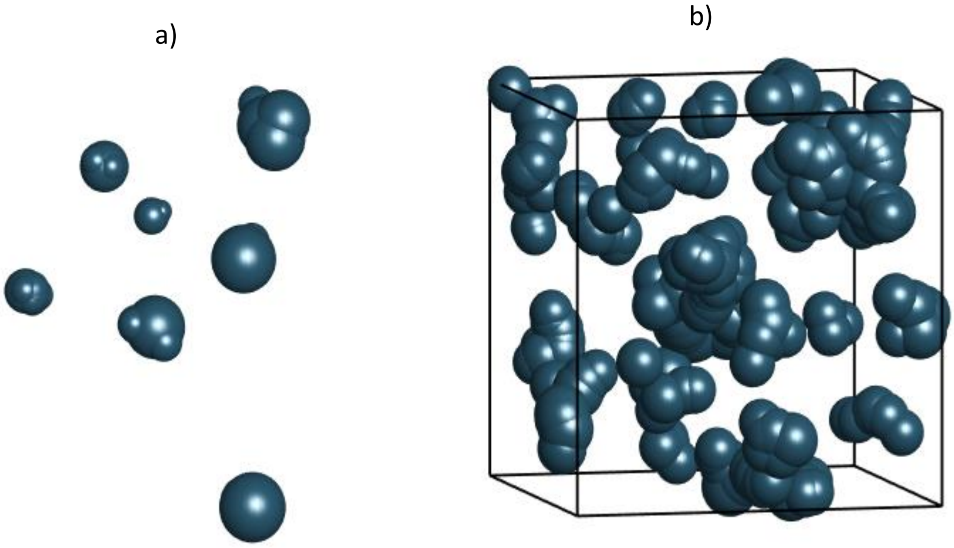

Figure 7. The distribution of clusters (a) and tubes (b) in size 10×10×10 (Å). In the model, some tubes are overlapped to form the largest tube that percolates over whole system.

The tube contains two or more pores with a radius greater than the radius of the oxygen atom, and each pore in a tube must overlap at least one pore adjacent by a shared circle. The pore tube distribution was also investigated and showed that 265 pore tubes are made up of 11,853 pores. The largest tube is made up of 11,468 overlapping pores. Figure 7b is a snapshot of the pore tubes and parts of the largest tube located in the 10×10×10Å space of the system. Note that this snapshot does not show the full length and shape of the largest tube.

Cluster and tube distribution show a picture of the natural path for doping atoms to diffuse in the structural network. With a range of pore radii from 0.73–3.04 Å, we provide information for finding suitable ions dissolved in the V_2O_5 network. This is the basis for applying the material in making electrodes that carry mobile ions moving inside it as well as making gas-sensitive devices.

4. Conclusion

Using method of molecular dynamics simulation, we have successfully built an amorphous V_2O_5 model that is in a good agreement with experimental data. The structural features analyzed in detail indicate that the amorphous V_2O_5 structure is a mix network of basic structural units VO5 and VO6. The V atom has 5 or 6 neighboring O atoms and each O atom has coordinate numbers 2 and 3 by V atoms. The structural units VOx are distributed randomly to form a disordered V-O network. The free volume region, where atoms do not occupy up to 63% of the model volume, appears as clusters or tubes, which are the ideal natural environment for the diffusion of impurity atoms in the V-O network.

In summary, the analysis of amorphous V_2O_5 microstructure has shown a high disorder of the structural network V-O. First, the random arrangement of the structural units VOx leads to a chemical disorder of the V atoms. The disorder is also present in the free volume region with different sizes percolating over the whole system. This is the ideal diffusion pathway to promote ion diffusion.

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