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Mn ion dissolution from MnS: a density functional theory study

The dissolution of MnS inclusions could induce pitting corrosion in stainless steels, but its dissolution mechanism is poorly understood at the atomic scale. With the help of *ab initio* molecular dynamics calculations, one inevitable step in the dissolution of MnS is studied by simulating the process of one

Mn ion leaving the surface. The reaction mechanism is determined to contain three steps with two large barriers and a small one, leading to two slow steps in the Mn ion dissolution. Comparing to the

Na ion dissolution from NaCl, the barriers of the Mn ion dissolution are much larger, which is a

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reflection of their different electronic structures.

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1. Introduction

The pitting corrosion of stainless steels causes huge losses in industrialized economies. The initiation of pitting corrosion starts from the dissolution of MnS inclusions in almost all cases.^{1–13} The dissolution of MnS inclusions may form crevices between MnS inclusions and the steel matrix and expose the fresh steel matrix to the corrosive environment, forming pits at these areas.¹⁴ The dissolution products of MnS inclusions may adsorb on the passive film nearby and thus destroy the passive film.^{15–17} Due to the dissolution of MnS inclusions, the areas near the inclusions become more sensitive to the pitting corrosion.^{4,7}

Because of its importance in the pitting corrosion of stainless steels, the mechanism of MnS dissolution has been studied extensively during the last several decades. Eklund carried out potentiostatic experiments and found that the dissolution products are sulfur and sulfate.³ The suggested reactions are presented as follows:

$$MnS \rightarrow Mn^{2+} + S + 2e^{-}$$
(1)

$$MnS + 4H_2O \rightarrow Mn^{2+} + SO_4^{2-} + 8H^+ + 8e^-$$
(2)

$$MnS + 2H^+ \rightarrow Mn^{2+} + H_2S.$$
(3)

Lott and Alkire anodically polarized 304 stainless steel and observed the electrochemical dissolution of MnS inclusions.¹⁴ Contrast to the results of Eklund, they found that the only dissolution product was thiosulfate. The related reactions are written as follows:

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$$2MnS + 3H_2O \rightarrow 2Mn^{2+} + S_2O_3^{2-} + 6H^+ + 8e^-$$
 (4)

$$MnS + 2H^+ \rightarrow Mn^{2+} + S + H_2.$$
(5)

As stated above, there are several proposed reaction mechanisms for the dissolution of MnS. A common point in all these mechanisms is that manganese appears as Mn^{2+} in the products. Thus, the dissolution of Mn ions is an inevitable step of the MnS dissolution. In this work, we studied the process of a Mn ion on the surface of the MnS crystal leaving its lattice site, entering the solution, and forming a hydrated Mn ion. This study could provide fundamental information about the dissolution of MnS.

The dissolution behaviors of different materials remain the objects of endless fascination by scientists in chemistry, geology, and pharmaceutics.¹⁸⁻²⁰ Many computational methods were developed to describe the dissolution processes,²¹⁻²⁹ but most of them are based on force fields. To describe the dissolution processes more accurately, density functional theory calculations are needed. Recently, Michaelides and co-workers studied the dissolution of NaCl in water by ab initio molecular dynamics (AIMD) and obtained a clear picture of the dissolution processes.³⁰⁻³² Thackeray and co-workers studied the dissolution of Li, Mn, and O ions from LiMnO4 by constrained density functional theory within the Blue Moon ensemble.33 The successes of these works demonstrate the feasibility of density functional theory calculations on the dissolution processes. In this paper, we use density functional theory calculations to study the dissolution process of Mn ions.

This paper is organized as follows: the second section describes the models and methods used in this paper; the third and forth parts present the results and discussion; and the last section summaries the main conclusions.

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2. Computational details

All the calculations, including the AIMD, structure relaxation and transition state search, were performed using the VASP code.^{34,35} The Perdew–Burke–Ernzerhof (PBE)³⁶ exchange–correlation functional with gradient correction (GGA) was used with the projector-augmented wave (PAW) method.³⁷ The plane wave cutoff energy was 500 eV. Spin-polarized calculations of bulk MnS give the optimized lattice constant of 5.10 Å, an error of -2.3% from the experimental value. In AIMD calculations, the Nosé–Hoover chain thermostat was used with the temperature 360 K and the time step 0.5 fs. This elevated temperature was utilized to accelerate the motion of H₂O molecules so that the system could be equilibrated quickly. The TS of each elementary reaction was searched using the constrained minimization approach.^{38–40}

Considering that MnS and NaCl possess the same crystal structure, we constructed a defective MnS-H₂O interface model according to the defective NaCl-H₂O interface model used in the work of Michaelides and co-workers.³² Three atom layers (3×4 unit cell) and a defective layer of MnS (001) surface were cleaved to form the defective MnS-H₂O interface model with 46 H₂O molecules and a vacuum layer of 15 Å. The interface model is an orthogonal box which is shown in Fig. 1. The bottom layer of MnS was fixed in its optimized crystal lattice. The other Mn and S ions and all H₂O molecules were allowed to relax.

An AIMD calculation was carried out for this structure. After that, several geometries along the AIMD trajectory were selected to relax.



Fig. 1 The model of the defective $MnS-H_2O$ interface. The purple and yellow balls represent the Mn and S ions. Those in the defective layer are colored in blue (Mn) and green (S). Mn_c is shown as a bigger ball. It has three chemical bonds with its neighboring S ions, one normal bond (along the *z* axis) and two parallel bonds (in the *xy* plane). The H₂O molecules are shown in the stick style. This notation is used throughout the paper.

The one with the lowest total energy was adopted as the initial state (IS). The transition, intermediate and final states were determined in a two-step scheme. Firstly, several H2O molecules were placed at the periphery of the Mn ion at the corner site (Mn_c for short) and the reaction states in the dissolution process of Mnc were located. This step could be considered as the low-accuracy location of reaction states. Secondly, several dozens of H2O molecules were added into the supercells to let the total number of H₂O molecules in each supercell be 46. AIMD calculations were performed to equilibrate the H₂O molecules for each of the reaction states with the constraint that all Mn and S ions were fixed. Then, several geometries along the AIMD trajectories were chosen to do further relaxation or transition state search calculations to find the accurate reaction states. This step could be considered as the high-accuracy locations. For each structure, the AIMD time was 10 ps. For the initial state, a test run of 14 ps of AIMD was performed and the result was found to be the same as that of 10 ps. In our previous work, this approach was shown to be adequate, comparing to the free energy method.²⁹

3. Results

3.1 IS of the defective MnS-H₂O interface

Along the total 14 ps of the AIMD calculations, five geometries were chosen to relax in the last 10 ps and the one with the lowest total energy is shown in Fig. 2. As can be seen from the figure, the surface Mn ions tend to form hydrogen bonds with O atoms in H₂O molecules and the surface S ions tend to form hydrogen bonds with H atoms. The average height of S ions in the top layer is 0.37 Å higher than that of Mn ions. This difference can be understood from the fact that the number of S-H hydrogen bonds (the hydrogen bonds less than 3 Å are counted) is larger than that of Mn-O hydrogen bonds (9 vs. 4). The coordination number (CN) of Mn_c is two, *i.e.* there are two H₂O molecules which form hydrogen bonds with Mn_c. It is interesting to find that the two H₂O molecules are always around Mnc during the AIMD calculation and the distances between the Mnc and the two O atoms are in the range of 1.90-2.80 Å. This is the unique property of the IS. In other states, the Mn-O hydrogen bonds can be broken during the AIMD calculations.

3.2 The process of the Mn ion entering the solution

As shown in Fig. 1, Mn_c has three chemical bonds with its neighboring S ions. It should be interesting to know which one will break preferentially. To this end, two series of calculations were performed on the surface model without any H₂O molecules. The surface model was fully relaxed except the ions in the bottom layer and the energies of the surface model is set to be zero (the reference state). Then, the *y* coordinate (see Fig. 1) of Mn_c was gradually changed to produce a series of structures. Each structure was relaxed with the constraint that the *y* coordinate of Mn_c was fixed. This series of calculations was used to simulate the breaking of one of the parallel bonds. Another series of calculations was used to simulate the breaking of the normal bond. In these calculations, the *z* coordinate



Fig. 2 Side (a) and top (b) views of the structure of the initial state. The two molecules forming hydrogen bonds with Mn_c are shown in the ball style. The black lines in (b) show the lattice of the supercell.



Fig. 3 The energy changes when dragging ${\rm Mn}_{\rm c}$ in the normal and parallel directions from the MnS surface without water.

of Mn_c was gradually changed to produce a series of structures and each structure was relaxed with the constraint that the *z* coordinate of Mn_c was fixed. The two energy curves are shown in Fig. 3. From this figure, we can see that to break one parallel bond, Mn_c has to overcome a higher energy barrier. Namely, the normal bond may break preferentially.

Having obtained the results without H_2O molecules, TS searches were carried out in the presence of H_2O molecules. The first TS (TS1) is reached when the normal bond is 3.17 Å (0.73 Å longer than that in the IS, Fig. 4a), which is 0.80 eV higher than the IS. The bond lengths of the two parallel bonds are 2.40 and 2.73 Å, respectively, a little longer than those in the IS. After overcoming the TS1, an intermediate state (IM1) was found, where Mn_c is on the bridge site of the two S ions. The bond length of the normal bond is 4.35 Å (about 2 Å longer than that in the IS). The two parallel bonds are 2.50 Å and 2.66 Å, respectively, and they are now tilted, as can be seen in Fig. 4b. The total energy of the IM1 is 0.49 eV lower than that of the TS1.

Then the second TS (TS2) was searched. It was found that the process of Mn_c overcoming the TS2 is the stretching of the longer one of the two tilted bonds. In the TS2, this Mn–S bond is 3.22 Å, 0.56 Å longer than that in the IM1. This state is only 0.02 eV higher than the IM1. After overcoming this small barrier, Mn_c would reach the IM2 where Mn_c is on the top site of one S ion. The IM2 is more stable than the IM1 by an energy difference of 0.13 eV. In the TS3 and the FS, the bond lengths of



Fig. 4 The states during the Mn_c dissolution process. (a–f) are the structures of different states as labeled.

 $\ensuremath{\text{Table 1}}$ The energy barriers and the stretchings of the specific Mn–S bonds of the three TSs

	$E_{\rm a}/{ m eV}$	$D_{ m str}/{ m \AA}$
TS1	0.80	0.73
TS2	0.02	0.56
TS3	0.89	1.05

the Mn–S bond are 3.39 Å and 5.00 Å, respectively. The barrier from the IM2 to the TS3 is 0.89 eV and the reverse reaction barrier from the FS to the TS3 is 0.66 eV. All the states of the Mn ion dissolution process are shown in Fig. 4. The energy barriers (E_a) and the stretchings (D_{str}) of the specific Mn–S bonds of the three TSs are given in Table 1. It can be seen that the barrier of the TS3 is the largest and that of the TS2 is very small, which will be analysed in the next section. The trend of the energy barriers is qualitatively consistent with that of the stretchings. For each TS, the stretching is the difference of the specific Mn–S bond in the TS and the previous state.

4. Discussion

4.1 The energy profile of the Mn ion dissolution

Fig. 5 shows the energy profile of the whole dissolution process. It can be seen that the TS1 and the TS3 are the two peaks and their shapes are similar to each other. The barriers of the two TSs are also similar (see Table 1), which indicates that there are two important steps in the Mn ion dissolution. The effective barrier of the Mn ion dissolution is 1.07 eV. It means that the dissolution of MnS in water is difficult, which coincides with the fact that MnS is an insoluble material in water.

An interesting feature of this energy profile is that the energy barrier of TS2 is very small compared with those of TS1 and TS3. The reason for this very small energy barrier may be due to the existence of a repulsive Mn–Mn interaction. Fig. 6 illustrates the local bonding around Mn_c in the IM1 and the TS2, which shows the Mn–Mn distance being only 3.43 Å, shorter than the nearest equilibrium distance (3.61 Å) between Mn ions in bulk MnS. This repulsive interaction is reduced (3.43 Å in the IM1, 3.63 Å in the TS2) when Mn_c reaches the TS2. The reduction of the repulsive interaction will lower the energy of the TS2, resulting in the very small energy barrier of the TS2.

Because of the small energy barrier of the TS2 and the fact that the energy of the IM1 is higher than that of the IM2, the IM1 can be considered an unstable state. To further confirm this suggestion, an AIMD calculation was performed for the optimized structure of the IM1 with fixing the bottom layer only. The IM1 is transformed into the IM2 only after 3 ps: Fig. 7 shows the length changes of the two Mn–S bonds in the IM1 along the AIMD trajectory; one Mn–S bond breaks after about 3 ps.

4.2 The comparison between MnS and NaCl dissolution

Our results appear to be reasonable: in the IS, Mn_c bonds with three S atoms and there are three bonds to be broken during



Fig. 5 The energy profile of Mn ion dissolution. The three inserts shows the local structures of the three TSs. The Mn–S bonds to be broken are shown as dashed lines.



Fig. 6 The local bonding of Mn_c in the IM1 (a) and the TS2 (b). To show the local bonding more clearly, only the top two layers of MnS and the H₂O molecules forming hydrogen bonds with Mn_c are displayed. The arrows indicate the Mn–Mn distances.



Fig. 7 The bond lengths of the two Mn–S bonds of Mn_c in IM1 as a function of the AIMD simulation time, averaged in 0.5 ps. One Mn–S bond breaks after about 3 ps.

the dissolution process. Therefore, three TSs located in our work, corresponding to the breaking of three S- Mn_c bonds, make chemical sense. However, comparing our work with that of Michaelides and co-workers,³² a major difference can be found: in the process of NaCl dissolution, Michaelides and co-workers reported only two TSs during the dissolution process of the Na ion. This may seem to be odd because the two materials possess the same crystal structure and the atomic model used in this work is almost the same as that about NaCl dissolution, although the methods used in these two works are different (total energy calculations in MnS ν s. free energy calculations in NaCl).

Comparing the atomic structures of these states in the Mn ion dissolution to those of the Na ion carefully, it is found that the two TSs in the Na ion dissolution are almost the same as the TS1 and the TS3 in the Mn ion dissolution and the IM in the Na ion dissolution is similar to the IM2 in the Mn ion dissolution. As already shown in Section 4.1, the IM1 in the Mn ion dissolution is kinetically very unstable, which may not exist in the free energy landscape. Hence, the calculation results of the two systems are in fact in accordance with each other. The similarity of the calculation results of the two systems shows the effectiveness of our calculation method.

Table 2 The z coordinates of ions in the corner sites for NaCl and MnS in the models with and without H_2O molecules and their differences. The unit is Å

	Na	Cl	Mn	S
w/o H ₂ O	2.50^{a}	2.80^{a}	7.76	8.13
w/ H ₂ Õ	2.90^{a}	3.30^{a}	7.93	8.22
Difference	0.40	0.50	0.17	0.09
^{<i>a</i>} These numbe	rs are estimated	l from Fig. 3 of	ref. 32.	

The general pictures of the dissolution processes of the Na ion and the Mn ion can be considered almost the same, but there are also some differences in the detail. The two barriers of the Na ion dissolution are 0.30 eV and 0.22 eV,³² respectively, and the corresponding barriers of the Mn ion dissolution are 0.80 eV and 0.89 eV, respectively. The difference in dissolution barriers can be understood from their different electronic structures. Fig. 8 shows the electronic charge density difference diagrams of the two materials. From these two diagrams, we can see that the bonds between Na and Cl ions are almost ionic while the bonds between Mn and S ions are partially ionic and partially covalent. There exists charge accumulation between Mn and S ions. A Bader analysis⁴¹ shows that the effective charges of Mn and S in bulk MnS are +1.1 e and -1.1 e, differing considerably from their formal charges, while the calculated effective charges of Na and Cl in bulk NaCl are +1 eand -1 e, respectively. This means that the Mn–S bonds are more difficult to break by H2O molecules than the Na-Cl bonds. It explains the higher barriers of the Mn ion dissolution.

Another difference in the detail is the structures of the two ISs. Table 2 shows the *z* coordinates of the ions in the corner sites of the two ISs. It can be seen that the *z* coordinates of both Na and Cl ions are heightened in the presence of H₂O molecules compared to those without H₂O molecules while the changes in MnS are much smaller (Na: 0.40 Å, Cl: 0.50 Å, Mn: 0.17 Å, S: 0.09 Å), illustrating that the solvation effect of H₂O molecules on the *z* coordinates of ions in the corner site is more obvious for NaCl than MnS.

5. Conclusions

This work combines *ab initio* molecular dynamics, structure relaxation and the transition state search to study the dissolution process of the Mn ion at the corner site on the (001) surface of MnS. The total energy profile and an understanding about



Fig. 8 The charge density difference diagrams of MnS (a) and NaCl (b). The unit is e Å⁻³ and the slices are obtained by cutting the (001) planes.

this process is obtained. The main conclusions are summarized as follows:

(1) For the dissolution of the Mn ion at the corner site on the (001) surface of MnS, there are three transition states and two intermediate states between the initial and final states. The three barriers are 0.80, 0.02, and 0.89 eV, respectively. It indicates that there are two slow steps in the Mn ion dissolution. The effective barrier of the whole process is 1.07 eV.

(2) In the two IMs, the IM1 is kinetically unstable. One S-Mn_c bond in the IM1 can easily break, leading to the transformation from the IM1 to the IM2.

(3) The general pictures of the dissolution processes of the Na ion and the Mn ion are very similar, which originates from the same crystal structure of MnS and NaCl.

(4) The barriers of the Mn ion dissolution are much larger than those of Na, which is due to the difference in the bonding nature of NaCl and MnS. The former is a pure ionic crystal and the later is partially ionic and partially covalent.

References

- 1 G. Wranglen, Corros. Sci., 1969, 9, 585-602.
- 2 G. Wranglen, Corros. Sci., 1974, 14, 331-349.
- 3 G. S. Eklund, J. Electrochem. Soc., 1974, 121, 467-473.
- 4 R. Ke and R. Alkire, J. Electrochem. Soc., 1992, 139, 1573–1580.
- 5 M. A. Baker and J. E. Castle, *Corros. Sci.*, 1993, 34, 667–682.
- 6 H. Bohni, T. Suter and A. Schreyer, *Electrochim. Acta*, 1995, 40, 1361–1368.
- 7 M. P. Ryan, D. E. Williams, R. J. Chater, B. M. Hutton and D. S. McPhail, *Nature*, 2002, **415**, 770–774.
- 8 H. Krawiec, V. Vignal, O. Heintz, R. Oltra and E. Chauveau, *Metall. Mater. Trans. A*, 2006, **37A**, 1541–1549.
- 9 I. Muto, Y. Izumiyama and N. Hara, J. Electrochem. Soc., 2007, 154, C439–C444.
- 10 I. Muto, D. Ito and N. Hara, *J. Electrochem. Soc.*, 2009, **156**, C55–C61.
- 11 S. J. Zheng, Y. J. Wang, B. Zhang, Y. L. Zhu, C. Liu, P. Hu and X. L. Ma, *Acta Mater.*, 2010, 58, 5070–5085.
- 12 D. E. Williams, M. R. Kilburn, J. Cliff and G. I. N. Waterhouse, *Corros. Sci.*, 2010, **52**, 3702–3716.
- 13 Y. J. Wang, P. Hu and X. L. Ma, *J. Phys. Chem. C*, 2011, **115**, 4127–4133.
- 14 S. E. Lott and R. C. Alkire, J. Electrochem. Soc., 1989, 136, 973-979.
- 15 P. Marcus, A. Teissier and J. Oudar, *Corros. Sci.*, 1984, 24, 259–268.
- 16 V. Vignal, H. Krawiec, O. Heintz and R. Oltra, *Electrochim. Acta*, 2007, **52**, 4994–5001.

- 17 H. Krawiec, V. Vignal and J. Banas, *Electrochim. Acta*, 2009, 54, 6070–6074.
- 18 B. Miller-Chou, Prog. Polym. Sci., 2003, 28, 1223-1270.
- 19 A. Dokoumetzidis and P. Macheras, *Int. J. Pharm.*, 2006, 321, 1–11.
- 20 C. A. Ohlin, E. M. Villa, J. R. Rustad and W. H. Casey, *Nat. Mater.*, 2010, 9, 11–19.
- 21 Y. Xiao and A. C. Lasaga, *Geochim. Cosmochim. Acta*, 1994, 58, 5379–5400.
- 22 Y. Yang, S. Meng, L. Xu, E. Wang and S. Gao, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, 72, 012602.
- 23 J. M. Park, A. Laio, M. Iannuzzi and M. Parrinello, J. Am. Chem. Soc., 2006, 128, 11318–11319.
- 24 Y. Yang, S. Meng and E. G. Wang, J. Phys.: Condens. Matter, 2006, 18, 10165–10177.
- 25 S. Nangia and B. J. Garrison, J. Phys. Chem. A, 2008, 112, 2027–2033.
- 26 Y. Yang and E. G. Wang, J. Comput. Theor. Nanosci., 2008, 5, 247–268.
- 27 S. Nangia and B. J. Garrison, *J. Am. Chem. Soc.*, 2009, 131, 9538–9546.
- 28 A. V. Marenich, C. J. Cramer and D. G. Truhlar, J. Phys. Chem. B, 2009, 113, 6378–6396.
- 29 T. Song and P. Hu, J. Chem. Phys., 2006, 125, 091101.
- 30 L. Liu, M. Krack and A. Michaelides, J. Am. Chem. Soc., 2008, 130, 8572–8573.
- 31 L.-M. Liu, M. Krack and A. Michaelides, J. Chem. Phys., 2009, 130, 234702.
- 32 L.-M. Liu, A. Laio and A. Michaelides, *Phys. Chem. Chem. Phys.*, 2011, **13**, 13162–13166.
- 33 R. Benedek, M. M. Thackeray, J. Low and T. Bučko, J. Phys. Chem. C, 2012, 116, 4050–4059.
- 34 J. Hafner, J. Comput. Chem., 2008, 29, 2044-2078.
- 35 G. Kresse and J. Furthmuller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, 54, 11169–11186.
- 36 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- 37 P. E. Blochl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, 50, 17953–17979.
- 38 A. Alavi, P. Hu, T. Deutsch, P. L. Silvestrelli and J. Hutter, *Phys. Rev. Lett.*, 1998, **80**, 3650–3653.
- 39 Z.-P. Liu and P. Hu, J. Am. Chem. Soc., 2003, 125, 1958–1967.
- 40 A. Michaelides and P. Hu, J. Am. Chem. Soc., 2000, 122, 9866–9867.
- 41 G. Henkelman, A. Arnaldsson and H. Jonsson, *Comput. Mater. Sci.*, 2006, **36**, 354–360.