A Drastic Influence of Point Defects on Phase Stability in MnO2

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ABSTRACT

Despite its importance as a cathode material in primary alkaline batteries, the structure of γ-MnO2 is still not well determined. Different authors have suggested that a number of different polymorphs, as well as highly disordered phases, may be present in γ-MnO2. The origin of this structural complexity remains largely unexplained. In this paper we use first principles methods to explore the energetics of the MnO2 system. We find a number of low-energy polymorphs with similar energies, suggesting that relatively small changes in the energetics might influence the stable phases. Using nonzero-temperature models we demonstrate that thermal disorder is not the cause of structural disorder in these materials. However, we then show that point (Ruetschi) defects, even in surprisingly low concentrations, have a dramatic effect on the phase stability. We propose that Ruetschi defects may be the key to some of the structural complexity in γ-MnO2, and that any realistic structural study must take them into account.

INTRODUCTION

The alkaline Zn/MnO2 system is the dominant chemistry used for primary batteries. The electrochemically active form of MnO2 presently used in alkaline batteries is commonly referred to as γ-MnO2. [1] It is often produced by electrolytic methods, in which case it is referred to as Electrolytic Manganese Dioxide (EMD). The γ-MnO2 polymorph does not denote a unique structure but has been suggested to be either a single phase with considerable disorder [1,2], or a multi-phase assembly, with some of the phases possibly being disordered [3,4]. However, all of the relevant phases of MnO2 that have been proposed consist of a (possibly distorted) hexagonal close packed lattice of oxygen ions with Mn cations occupying half the octahedral sites. Specific common Mn polymorphs have been given standard names: pyrolusite (β-MnO2, believed to be the most stable structure), ramsdellite (R-MnO2, often, in a defected form, believed to be the dominant component of γ-MnO2), and ε-MnO2 (generally described as a stochastic distribution of Mn on the octahedral sites of the oxygen framework) [5]. All polymorphs seen in nature (except perhaps ε-MnO2) have perfect Mn-Vacancy-Mn-Vacancy ordering along the c-axis of the hcp oxygen lattice.

METHODOLOGY

The energies of all configurations in this work are computed in the Generalized Gradient Approximation (GGA) to spin-polarized Density Functional Theory using ultra-
soft pseudopotentials, as implemented in the Vienna Ab Initio Simulation Package (VASP). [6] Paramagnetic energies were calculated from a Heisenberg model fit to a number of collinear spin configurations. [7]

The order-disorder temperature is obtained by mapping the first-principles energies onto a simplified and easily calculated cluster expansion Hamiltonian, [8] whose order-disorder properties can be studied using Monte Carlo methods. Further details of this methodology are given in. [9]

PURE MnO\textsubscript{2} ENERGETICS

We calculated energies of 38 different Mn-Vacancy configurations and the results for a number of structures that have been previously identified in the literature are given in Table 1. For most polymorphs only the ferromagnetic energies were calculated. However, it is clear from the energy values that the ferromagnetic energies do not predict the correct pyrolusite groundstate. Since these systems are expected to be paramagnetic at room temperature, the paramagnetic energies were obtained by fitting a Heisenberg model to the energy of a large number of magnetic configurations for several Mn-Vacancy orderings. The correct pyrolusite groundstate is predicted from the paramagnetic energies.

There are a number of polymorphs with energies fairly close to pyrolusite. These structures all have perfect c-axis order, as is generally the case for structures found experimentally, and among them are many of the commonly seen MnO\textsubscript{2} polymorphs. This suggests that the common polymorphs are frequent, at least in part, because they are not too unstable compared to pyrolusite. However, even though there are many structures close in energy to pyrolusite, it is still unclear what might stabilize them. Two possible factors we explore below are thermal effects and point defects.

Table 1: Energies for some structures which have been previously identified in the literature. The second and third columns list the energy obtained for ferromagnetic and paramagnetic Mn spin arrangements, respectively. All energies are relative to the energy of paramagnetic pyrolusite. Energies are ordered by paramagnetic energy when available, otherwise by ferromagnetic energy. References are provided for further information on the structures.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ferro Energy (meV/FU)</th>
<th>Para Energy (meV/FU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pyrolusite[1]</td>
<td>67</td>
<td>0</td>
</tr>
<tr>
<td>2 (ε') [4]</td>
<td>58</td>
<td>16</td>
</tr>
<tr>
<td>3 (Ramsdellite) [1]</td>
<td>64</td>
<td>22</td>
</tr>
<tr>
<td>4 (α-PbO\textsubscript{2}\textsuperscript{+}) [1]</td>
<td>80</td>
<td>37</td>
</tr>
<tr>
<td>5 (D33) [10]</td>
<td>85</td>
<td>40</td>
</tr>
<tr>
<td>6 (Twinned-Ramsdellite) [1]</td>
<td>114</td>
<td>--</td>
</tr>
<tr>
<td>7 (Birnessite) [1]</td>
<td>163</td>
<td>162</td>
</tr>
</tbody>
</table>
PURE MnO$_2$ THERMODYNAMICS

The low-energy states identified in the calculations above suggest that there may be low-energy excitations in this system, leading to significant thermal disorder, even at low temperatures. We therefore study the state of order as a function of temperature. Unfortunately, first-principles approaches generally give energies only for zero temperature. Nonzero-temperature calculations require thermal averages over many such energies, and direct first-principles calculation is prohibitively time consuming. Therefore, to investigate the thermodynamics of the MnO$_2$ system we map the energies of different Mn-Vacancy arrangements onto a simplified Hamiltonian by the cluster expansion method. [8] This simplified Hamiltonian can then be used in Monte Carlo simulations to study configurational disorder as a function of increasing temperature. The cluster expansion is fit to paramagnetic energies. However, since only a limited number of these were calculated, a hybrid scheme which also makes use of the ferromagnetic values was used (see Ref. [9] for details). Monte Carlo methods were used to calculate the energy as a function of increasing temperature, and the results are shown in Figure 1. The simulation starts in the pyrolusite groundstate, and there are essentially no thermal excitations until the Mn-Vacancy arrangement disorders at $\sim$3900 K. The real material would decompose at much lower temperatures, but our constrained model allows us to simulate how the configurational disorder evolves without other transformations that would normally be associated with heating.

The near total absence of thermal excitations for any practical temperatures demonstrates that equilibrium thermal disorder plays no significant role in this material. This appears somewhat paradoxical in light of the low-energy structures observed above, which one might expect to appear as excitations on a much lower temperature scale. However, the paradox is resolved by realizing the nature of excitations in this system.

**Figure 1**: Monte Carlo Energy as a function of temperature for MnO$_2$. 

![Energy vs Temperature Plot](image-url)
Because essentially all low-energy arrangements involve c-axis ordering, an excitation requires moving a whole column of atoms, rather than just a single one. Thus the thermal energy required scales with the correlation length along the c-axis. The energies given in Table 1 are in this sense misleading, since they are given per a formula unit. To transform between structures, columns of formula units along the c-axis must be moved, and the energy required is actually quite large. Since the c-axis correlation is the essential feature constraining disorder, we expect the order-disorder temperature to be determined primarily by the interactions along the c-axis. From our cluster expansion it is clear that these interactions are quite strong, e.g., the first nearest neighbor coupling, directly along the c-axis, is 439 meV. It is the strong c-axis interactions which set the very high order-disorder temperature in this material.

**POINT DEFECTED MnO$_2$ ENERGETICS**

Point defects in MnO$_2$ are generally believed to come in the form of Ruetschi defects, a missing Mn ion compensated by four hydrogen atoms. \[11\] We have calculated the energy of Ruetschi defects in a number of different Mn-Vacancy arrangements. The relative energies, given per a Ruetschi defect, are show in Figure 2.

**Figure 2:** Effect of Ruetschi defects on the structural energy for a number of different polymorphs and defect concentrations. "Rams" refers to ramsdellite and "Tw_Rams" refers to fully twinned ramsdellite. Mn1 and Mn3 refer to two distinct sites in the twinned ramsdellite, with 3 and 5 nearest-neighbor Mn, respectively.
Surprisingly, the defects show a wide range of stability, spreading over nearly 0.9 eV in just the few cases we have considered. This shows that the Mn arrangement will affect where Ruetschi defects are stable, and reciprocally, the presence of Ruetschi defects will affect which Mn arrangements are most stable.

The origin of this powerful coupling between Mn order and Ruetschi defect stability is easy to understand when the Ruetschi defects are considered in more detail. Although Ruetschi defects are a point defect, in that they are associated with a single missing atom, they are a conglomerate of four hydrogen atoms, which makes them both large and flexible. The hydrogen atom arrangement is quite variable, since it must attempt to satisfy a number of constraints: the hydrogen must try to stay near the defect to keep local charge neutrality, also make covalent and hydrogen bonds to the oxygen, and simultaneously avoid Mn and H to minimize the electrostatic energy. How well all these constraints can be met depends on the Mn arrangement, which gives rise to the strong coupling between Ruetschi defect stability and Mn ordering. The least stable defect among those we calculated is in Birnessite. Birnessite consists of layers of Mn and Vacancies. The unscreened oxygen repel each other, making it impossible for hydrogen to find stable covalent and hydrogen bonds in those layers. This forces all the hydrogen to reside in the Mn filled layers, placing hydrogen close to the Mn and other hydrogen, and creating a less stable defect. By contract, the ramsdellite structure has large 2x1 tunnels well suited to hydrogen stability. By making use of these tunnels the Ruetschi defect can form a very stable configuration.

As a concrete example of the potential importance of Ruetschi defects, consider the relative stability of pyrolusite and ramsdellite. Our paramagnetic calculations show that, in the pure material, pyrolusite is more stable by about 22 meV per Mn. However, each Ruetschi defect stabilizes ramsdellite over pyrolusite by about 600 meV. Therefore, at a Ruetschi defect concentration of approximately 4%, the relative stability of the two phases will switch, and ramsdellite will become more stable.

CONCLUSIONS

We have used first-principles calculations to demonstrate that there are a number of MnO₂ polymorphs close in energy to the stable pyrolusite phase. We show that despite these structures having comparable energies, there is no thermal disorder at practical temperatures, and the pyrolusite Mn arrangement does not disorder until about 3900 K. Strong c-axis ordering causes the thermal excitations to be very high in energy. We demonstrate that the extended flexible structure of Ruetschi defects creates a strong coupling between defects and Mn order. This combination of the small energy differences between many MnO₂ polymorphs and the strong coupling of Ruetschi defects to Mn order implies that even at low concentrations the Ruetschi defects will have a dramatic impact on MnO₂ structure. These results demonstrate that any analysis of MnO₂ structure must take Ruetschi defects into account.

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REFERENCES