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# Atomistic simulation of the surface structure of electrolytic manganese dioxide

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ABSTRACT

Atomistic simulation methods were used to investigate the surface structures and stability of pyrolusite and ramsdellite polymorphs of electrolytic manganese dioxide (EMD). The interactions between the atoms were described using the Born model of Solids. This model was used to calculate the structures and energies of the low index surfaces {0 0 1}, {0 1 0}, {0 1 1}, {1 0 0}, {1 0 1} and {1 1 0} for both pyrolusite and ramsdellite. Pyrolusite is isostructural with rutile and similar to rutile the {1 1 0} surface is found to be the most stable with the relaxed surface energy 2.07 J $m^{-2}$. In contrast, for ramsdellite the {1 0 1} surface is the most stable with a surface energy of 1.52 J $m^{-2}$. Pyrolusite {1 0 0} and ramsdellite $\{1\ 0\ 0\}_b$ surfaces have equivalent energies of 2.43 J $m^{-2}$ and 2.45 J $m^{-2}$, respectively and similar surface areas and hence are the likely source for the intergrowths. Finally, comparison of the energies of reduction suggests that the more stable surfaces of pyrolusite are more easily reduced.



## 1. Introduction

Manganese dioxide is used as an electrode in dry cells of the Leclanché type. One of the recent improvements to these dry cells has been the substitution of naturally occurring manganese dioxide by a synthetic variety, in particular electrolytic manganese dioxide (EMD) [1]. EMD is not expensive and has the ability to maintain high discharge rates, a good performance over a wide temperature range and a long storage life. Consequently, EMD is the most widely used cathode material for alkaline batteries and has also found application in rechargeable batteries [2–4].

The structural and electrochemical properties of manganese dioxide have been reported widely for several years [5,6]. XRD patterns were used to give a comprehensive description of the structure of EMD in terms of an intergrowth of pyrolusite and ramsdellite domains and microtwinning [7–10]. The pyrolusite crystal structure is isostructural with rutile-$TiO_2$ and is similar to ramsdellite. The main difference between the polymorphs is the way in which the manganese atoms are arranged on their hexagonal layers [11]. Structural changes upon proton intercalation and heat treatment were studied using in situ neutron powder diffraction [12]. However, an extensive review by Chabre and Pannetier [6] has pointed out a need for alternate methods to check and complement diffraction techniques.

Simulation techniques have been used successfully to study a wide variety of oxide structures, including $MnO_2$ [13]. In particular, different defect models of EMD were generated and relaxed using classical lattice energy minimisation, and those that re-produced experimental X-ray diffractions patterns were identified [14]. First principles calculations were carried out on proton intercalation in the pyrolusite and ramsdellite polymorphs of $MnO_2$ [15], and to understand the effect of other point defects on the structural stability [16]. Recently, simulated amorphisation and recrystallisation studies of nano [17] and bulk [18] $MnO_2$ have produced defect rich microstructures whose structural properties compare reasonably with experimental results. The formation of extended defects, such as intergrowths in EMD, together with the prediction and control of crystal growth can be better understood if surface properties, are known. However, owing to the complexity of the material experimental investigations of the surfaces are difficult and to date have not been reported. One approach that could provide reliable models of the surfaces is atomistic simulation techniques.

In this work atomistic simulation methods are used to predict the surface structures, stabilities and morphologies of pyrolusite and ramsdellite. Crystal surfaces observed in nature also contain structural defects, such as point defects, dislocations or steps; hence defects on surfaces will be investigated for both systems.

## 2. Methodology

The surface energies and structures of pyrolusite and ramsdellite were calculated using the computer code METADISE (*Minimum Energy Technique Applied to Dislocations, Interfaces and Surface Ener-*

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*gies*) [19]. The code is designed for modelling dislocations, interfaces and surface energies. The crystal is divided into two blocks (block II and I) each consisting of two regions; region I and region II. Region I contains ions close to the interface and are allowed to relaxed whereas region II contains ions further away from the surface and are held fixed. During the minimisation process, the ions in region I are allowed to relax relative to region II. Region I and II need to be sufficiently large for the energy to converge. The energies of the block are the sum of the energies of the interaction between the ions. The surface energy, $\gamma_i$, of a particular Miller index plane is given by

$$\gamma_i = \left[\frac{(U_{\text{surf}} - U_{\text{bulk}})}{A}\right] \quad (1)$$

where $U_{\text{surf}}$ is the energy of the surface block of the crystal, $U_{\text{bulk}}$ is the energy of the same number of bulk ions and $A$ is the surface area. It is necessary to ensure that a sufficient number of layers are modelled so that the energy of the block has converged. In the calculation of a particular Miller index there may be multiple unique repeat units. The surfaces are classified according to the scheme identified by Tasker [20], i.e. Type I where the surface unit cell is comprised of planes containing cations and anions in stoichiometric ratio, Type II is comprised of a stack of charged planes where the repeat unit has no dipole moment perpendicular to the surface, Type III has a stack of charged planes where the repeat unit has a dipole moment perpendicular the surface. However, the Coulombic sum for such a surface cannot be evaluated, as it is divergent [21], and if such surfaces are to be studied then the surface must be reconstructed such that the dipole is cancelled [22]. Thus for each surface the different terminations are identified and if a Type III surface is further reconstructed to remove the dipole perpendicular to the surface. If there are multiple unique repeats units, then the lowest energy cut should be most representative of the experimental surface structure. This is further complicated by the presence of asymmetric cuts. Symmetric repeat unit $(hkl)_{\text{sym}}$ has the same surface at the top and at the bottom whereas asymmetric repeat unit $(hkl)_{\text{asym}}$ has different surfaces at the top and bottom. If the crystal space group has a centre of inversion then each asymmetric surface will have its own inverse $(hkl)_{\text{iasym}}$ and the asymmetric cut is treated independently.

The energy of the crystal is described via interatomic potentials. The potential is comprised of parameterised analytical expressions describing the interactions between the atoms. We considered a number of potential models, but the most reliable was a partially charged model where the rigid ion potentials were obtained by modifying the parameters for the cation developed by Matsui [23] for isostructural $TiO_2$, using GULP (General Utility Lattice Programme) [24], so that they gave good agreement with the crystal structure of pyrolusite as shown in Table 2. Matsui has successfully applied this potential to study the stability of $TiO_2$ polymorphs as a function of temperature and pressure; and gave a good account of the bulk properties of rutile-$TiO_2$. Later surface studies by Purton [25] used the Matsui potential to model the ideal and defective surfaces of rutile-$TiO_2$. The potential model produced accurate surface relaxations for both the ideal and the defective (containing oxygen vacancies) surfaces. In addition, the potential model has been used to study surface structure properties of rutile and anatase-$TiO_2$ polymorphs [26]. The surface energies were calculated and the relaxed crystal morphologies agreed closely with experimentally observed crystals. The analytical expression for the interaction between a pair of atoms including electrostatic terms with short-range Buckingham potentials is depicted in Eq. (2)

$$U_{r_{ij}} = \left[\frac{q_i q_j}{r_{ij}} + A_{ij} e^{\left(\frac{-r_{ij}}{\rho_{ij}}\right)} - \frac{C_{ij}}{r_{ij}^6}\right] \quad (2)$$

where the parameters for ions $i$ and $j$, separated by a distance $r_{ij}$, are $q_i$ and $q_j$, and $A_{ij}$, $\rho_{ij}$ and $C_{ij}$ are variable parameters, $q_i$ and $q_j$ represent the charges. The second term represents the short-range repulsive interaction between the ions and the third term the attractive van der Waals forces.

In order to understand the surface reactivity of $MnO_2$, atomistic simulation technique was used to model defects in the surfaces. For the study of $Mn^{3+}$ defects, the interactions were modelled using the Buckingham potential for which the parameters are listed in Table 1.

**Table 1**
Interatomic potentials for pyrolusite and ramsdellite for the rigid ion model. The potential parameters describe the short-range potential terms between the component ions species of $MnO_2$ and $Mn_2O_3$. The cut-off of 10.0 Å was used.

| | $A$ (eV) | $\rho$ (Å) | $C$ ($e^6$Å) | Species | $q$ (e) |
|---|---|---|---|---|---|
| *Short-range interactions* | | | | | |
| $Mn^{2.2+}$…$O^{1.1-}$ | 15538.20 | 0.195 | 22.00 | $Mn^{2.2+}$ | 2.20 |
| $Mn^{2.2+}$…$Mn^{2.2+}$ | 23530.50 | 0.156 | 16.00 | | |
| $O^{1.1-}$……$O^{1.1-}$ | 11782.76 | 0.234 | 30.22 | $O^{1.1-}$ | −1.10 |
| $Mn^{1.65+}$…$O^{1.1-}$ | 18645.84 | 0.195 | 22.00 | | |
| $Mn^{2.2+}$…$Mn^{1.65+}$ | 28707.21 | 0.156 | 16.00 | $Mn^{1.65+}$ | 1.65 |
| $Mn^{1.65+}$…$Mn^{1.65+}$ | 33883.92 | 0.156 | 16.00 | | |

## 3. Structures of pyrolusite and ramsdellite

Pyrolusite and ramsdellite are two known crystalline polymorphs of manganese dioxide [27], and they have related structures due to the similarity of their oxygen frameworks. The pyrolusite structure may be described as infinite single chains of edge sharing octahedra, which are connected by corners to the other single chains, while the ramsdellite structure has double chains [28]. Pyrolusite is tetragonal with space group $P4_2/mnm$ [29] and ramsdellite is orthorhombic and has the space group $Pbnm$ [30]. In both cases each $Mn^{4+}$ atom is surrounded by six $O^{2-}$ atoms. In pyrolusite the oxygen atoms have primitive tetragonal packing [31] whereas ramsdellite oxygen atoms are based on a combination of body centred tetragonal packing [32] and hexagonal close packing [28]. The pyrolusite structural parameters and the corresponding structural results are given in Table 2. Since the crystal structures were used in the derivation of the parameters, it is not surprising that the agreement with experimental results is good. However, we also note, as with $TiO_2$ the c/a ratio is reproduced reasonably well using the partially ionic, rigid ion

**Table 2**
Calculated and experimental* [29] lattice and structural parameters of pyrolusite.

| | Calculated | Experimental* |
|---|---|---|
| *Lattice parameter* | | |
| $a$ (Å) | 4.401 | 4.414 |
| $c$ (Å) | 2.925 | 2.860 |
| $\alpha, \beta, \gamma$ (°) | 90.00 | 90.00 |
| *Fractional coordinates* | | |
| Mn core | 0.000 0.000 0.000 | 0.000 0.000 0.000 |
| O core | 0.302 0.302 0.000 | 0.306 0.306 0.000 |
| *Elastic constants (GPa)* | | |
| $C_{11}$ | 376.8 | |
| $C_{12}$ | 258.7 | |
| $C_{13}$ | 167.6 | |
| $C_{14}$ | 0.000 | |
| $C_{33}$ | 500.4 | |
| $C_{44}$ | 145.7 | |
| *Dielectric constants* | | |
| $\varepsilon_{11}$ | 3.13 | |
| $\varepsilon_{33}$ | 2.50 | |