Energetic basis of catalytic activity of layered nanophase calcium manganese oxides for water oxidation

Nancy Birkner, Sara Nayeri, Babak Pashaei, Mohammad Mahdi Najafpour, William H. Casey, and Alexandra Navrotsky

Previous measurements show that calcium manganese oxide nanoparticles are better water oxidation catalysts than binary manganese oxides ($\text{Mn}_n\text{O}_m$, $\text{Mn}_3\text{O}_4$, and $\text{MnO}_2$). The probable reasons for such enhancement involve a combination of factors: The calcium manganese oxide materials have a layered structure with considerable thermodynamic stability and a high surface area, their low manganese oxide materials have a layered structure with considerable thermodynamic stability and a high surface area, their low manganese oxide materials have a layered structure with considerable thermodynamic stability and a high surface area.

Calcium manganese oxide nano-particulate of $\text{CaMnO}$ phases, measures their surface energies, and provides insight into their redox reactions and catalytic function.

Two suites of CaMnO samples with varying surface areas and $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratios were synthesized by slight modifications of established methods (10) from similar starting solutions with different Ca and Mn concentrations. The surface enthalpies and heats of formation were determined by calorimetry. The methodology involves high-temperature oxide-melt solution calorimetry (21–28) using a molten oxide solvent, $3\text{Na}_2\text{O}-4\text{MnO}_3$, at 700 °C on a suite of nanoparticle samples having different surface areas determined by nitrogen adsorption measurements (29) and water contents measured by thermal analysis. Chemical analysis determined the manganese and calcium content. Thermogravimetry provided total weight loss due to oxygen and water evolution, and iodometric titration determined the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio (Methods and SI Text).

Table 1 presents the composition (normalized to 1 mol of manganese) of both suites of CaMnO samples, along with their Brunauer–Emmett–Teller (BET) surface area. Their X-ray diffraction (XRD) patterns (Fig. S1) are consistent with layered structures showing a lack of long-range order between the layers. Sintering of the samples resulted in the same XRD pattern (Fig. S2) for all. Layered morphology was verified using transmission electron microscopy (TEM) (Fig. S3). SEM (Fig. S4) shows that the CaMnO samples consist of aggregates of nanoparticle particles below 100 nm in size. Thermogravimetric (TG) differential scanning calorimetry (DSC) (Fig. S5) shows an endotherm for water loss at 142 °C and two additional endotherms at 745 °C and 887 °C, which may represent both water and oxygen loss, as well as an exothermic peak at 650 °C possibly caused by sample coarsening. Consistent with previously reported lamellar structures for other Mn-oxide materials (15–20), similar structures for these CaMnO materials are suggested by XRD (Fig. S2) and confirmed by low-resolution TEM (Fig. S5).

The broad diffraction peaks and pattern of intensities suggest highly disordered materials with little long-range coherence among layers; however, because crystallography was not the focus of the present work, a detailed diffraction study was not pursued.

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The authors declare no conflict of interest.

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Table 1. Sample composition, average manganese oxidation state, and surface area

<table>
<thead>
<tr>
<th>Composition</th>
<th>Measured $\Delta H_{\text{ox}}$, kJ/mol</th>
<th>$\Delta H_{\text{ds,ox}}$ of the oxide, kJ/mol$^a$</th>
<th>$\Delta H_{\text{ds,ox}}$, kJ/mol</th>
<th>BET surface area, m$^2$/g and molar surface area, m$^2$/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.29}$·0.01H$_2$O</td>
<td>174.05 ± 1.46 (12)</td>
<td>132.49 ± 1.46</td>
<td>−52.29 ± 3.02</td>
<td>924.56 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.33}$·0.48H$_2$O</td>
<td>168.20 ± 1.45 (12)</td>
<td>135.05 ± 1.45</td>
<td>−52.29 ± 3.02</td>
<td>902.95 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.35}$·0.43H$_2$O</td>
<td>165.65 ± 1.67 (10)</td>
<td>135.82 ± 1.67</td>
<td>−50.89 ± 3.24</td>
<td>891.05 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.37}$·0.30H$_2$O</td>
<td>158.00 ± 1.26 (10)</td>
<td>137.28 ± 1.27</td>
<td>−50.99 ± 2.85</td>
<td>854.52 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.37}$·0.28H$_2$O</td>
<td>158.25 ± 1.20 (8)</td>
<td>138.62 ± 1.20</td>
<td>−52.33 ± 2.79</td>
<td>850.18 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.37}$·0.28H$_2$O</td>
<td>154.12 ± 2.03 (8)</td>
<td>124.42 ± 2.03</td>
<td>−55.89 ± 3.62</td>
<td>889.49 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.37}$</td>
<td>154.87 ± 1.42 (10)</td>
<td>125.61 ± 1.42</td>
<td>−58.18 ± 2.99</td>
<td>896.70 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.37}$</td>
<td>150.69 ± 1.41 (8)</td>
<td>126.48 ± 1.41</td>
<td>−53.60 ± 2.98</td>
<td>880.44 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.37}$</td>
<td>142.12 ± 0.94 (8)</td>
<td>126.77 ± 0.95</td>
<td>−54.41 ± 2.59</td>
<td>843.34 ± 2.22</td>
</tr>
<tr>
<td>Ca$<em>{0.39}$Mn$</em>{(3^{0.01})}$O$_{2.37}$</td>
<td>137.99 ± 1.73 (8)</td>
<td>127.67 ± 1.73</td>
<td>−54.63 ± 3.30</td>
<td>823.06 ± 2.22</td>
</tr>
</tbody>
</table>

$^a$Sample compositions are normalized to 1 mol of manganese.
$^b$Quality control was run between different samples of CaMnO using a reference standard of manganese dioxide (Sigma–Aldrich) for the Murray titration method for manganese AOS and speciation.
$^c$Error is 2 SDs of the mean. Value in parentheses is number of experiments performed. Uncertainties are propagated in subsequent calculations.
$^d$Heats of formation of $\Delta H_{\text{ds,ox}}$ were computed using standard thermochromical cycles that included the use of measured drop solution enthalpies ($\Delta H_{\text{ds}}$) of the CaMnO samples and of $\Delta H_{\text{ds}}$, CaO = (−90.70 ± 1.69) kJ/mol (30), $\Delta H_{\text{ds}}$, Mn$_2$O$_3$ = 154.87 ± 1.00 kJ/mol (30). Heats of formation of $\Delta H_{\text{ox}}$ were computed using standard formation enthalpies (33) of binary oxides from the elements and heat content (33) of O$_2$. CaMnO sample contains 43.06 ± 0.01 wt% manganese (0.78a mol) and 12.40 ± 0.01 wt% calcium (0.30a mol).
CaMnO sample contains 49.00 ± 0.01 wt% manganese (0.89a mol) and 15.28 ± 0.01 wt% calcium (0.38a mol).
relating the corrected $\Delta H_{fs}$ (Table 2) and molar surface area (Table 1) yields the surface enthalpy (SE; essentially equivalent to surface energy) for the hydrous surfaces (Fig. 1). The thermochemical cycle used to compute the SE is provided in SI Text. The SE for the hydrous surfaces of the samples of suite “a” with a manganese average oxidation state (AOS) of 3.89 (Table 1) is $0.75 \pm 0.11$ J/m$^2$. The SE for the samples of suite “b” with a manganese AOS of 3.68 (Table 1) is $0.57 \pm 0.12$ J/m$^2$. These values overlap within the experimental uncertainty, especially when one propagates the error arising from scatter in the calorimetric measurements and from uncertainty in the measured water content. One must also bear in mind that such nanophase samples may not be totally homogeneous in Ca/Mn ratio, Mn oxidation state, and water content, and that all these sources of error may combine to form a nonrandom distribution of uncertainties. Thus, we conclude that the measured surface energies of the two suites of samples are best considered as being the same within experimental error. The layered structure CaMnO samples have substantially lower SE values than those previously reported (30) for Mn$_3$O$_4$ (SE = $0.96 \pm 0.08$ J/m$^2$), Mn$_2$O$_3$ (SE = $1.29 \pm 0.10$ J/m$^2$), and MnO$_2$ (SE = $1.64 \pm 0.10$ J/m$^2$).

Formation enthalpies (Table 2) for the CaMnO samples were computed using thermochemical cycles (SI Text). The enthalpies of formation from the binary oxides (thermochemical cycles are discussed in SI Text) are calculated directly from differences in the appropriate $\Delta H_{fs}$ of reactants and products; those from the elements added the stoichiometrically weighted enthalpies of formation of the binary oxides from the elements (Table S1) as given in standard tabulations. The enthalpies of formation from the binary oxides for layered structure CaMnO samples are exothermic, which indicates the strongly basic nature of the CaO that combines with the relatively acidic Mn-oxides. Enthalpy of formation from CaO, Mn$_2$O$_3$, and O$_2$ ($\Delta H_{fs}$*) is more exothermic than that from CaO, Mn$_3$O$_4$, and MnO$_2$ ($\Delta H_{fs}$ na), which reflects the exothermic oxidation of trivalent to tetravalent manganese. Likewise, the standard formation enthalpies from the elements, $\Delta H_f^0$, of the CaMnO samples (Table 2) are strongly exothermic. The formation enthalpies (Table 2) include the effects of calcium incorporation and structural change, as well as the variable manganese oxidation state, in the suite of samples. To focus on the energetic effect of the manganese oxidation state within the layered structure, Fig. 2 shows the enthalpy of formation from CaO, Mn$_2$O$_3$, O$_2$, and H$_2$O for the reaction:

$$m\text{CaO} + 0.5\text{Mn}_2\text{O}_3 + 0.25\text{O}_2 + n\text{H}_2\text{O} = \text{Ca}_n\text{Mn}_m\text{O}_{(1.5n+0.5m)} + n\text{H}_2\text{O},$$

plotted vs. the number of moles of oxygen (0.25y) in the reaction. The enthalpy of formation becomes more exothermic linearly with the number of moles of O$_2$ used, independent of the Ca/Mn ratio (different in the two suites) or the average oxidation state. The slope then gives the change in enthalpy of formation per mole of O$_2$ added, which represents the enthalpy of internal oxidation (internal in the sense of being within the layered structure with no phase change) and yields a value of $-100.0 \pm 8.4$ kJ per mole of O$_2$. This enthalpy is exothermic but significantly less so than the enthalpy of oxidation of Mn$_2$O$_3$ to MnO$_2$ ($-168.1$ kJ per mole of O$_2$) (30). The intercept at zero excess oxygen ($-67.0 \pm 1.7$ kJ/mol) is the enthalpy of formation of the hypothetical layered CaMnO phase containing only trivalent manganese and is a measure of the stabilizing interaction of CaO, Mn$_2$O$_3$, and H$_2$O to form the layered structure. For a hypothetical CaMnO with only Mn$^{IV}$, the corresponding enthalpy of formation would be $-92.0 \pm 8.6$ kJ/mol from CaO, Mn$_2$O$_3$, O$_2$, and H$_2$O or $-28.3 \pm 8.9$ kJ/mol from CaO, MnO$_2$, and H$_2$O. This suggests that a fully oxidized layered material would be stable relative to CaO, MnO$_2$, and H$_2$O. However, we did not try to extend the range of manganese oxidation states in these materials to lower or higher values than those achieved in the indicated syntheses.

Because the oxidation state in these CaMnO materials can be varied over a significant range at constant calcium content, charge balance in the structure must involve species in addition to calcium. Indeed, the Ca/Mn(III) stoichiometry exceeds 1:1. Given that calcium is divalent, this seems to imply that it cannot only be stabilizing excess charge due to Mn(III). The other well-known cause for excess structural charge is the presence of Mn(IV) vacancies (31–33). Thus, these highly disordered materials may contain both Mn(III) “defects” and Mn(IV) vacancies. More detailed crystallographic and spectroscopic studies, outside the scope of the present study, are needed to investigate these structural features.
The important thermodynamic observation is that because the enthalpies of the two suites of samples fall on the same line in Fig. 2, the formation and redox energetics in the layered structure are not sensitive to the Ca/Mn ratio (or to the water content) and are independent of the Mn\(^{3+}\)/Mn\(^{4+}\) ratio. This result indicates that all the layered CaMnO samples provide a similar energetic environment for manganese redox reactions.

**Discussion**

Previous experiments (2, 4) have shown that the efficiency of CaMnO water oxidation catalysis decreases in the following order: CaMnO >> Mn\(_2\)O\(_3\) > MnO\(_2\), Mn\(_3\)O\(_4\). The existence of mixed valence (Mn\(^{3+}\) and Mn\(^{4+}\)) is probably critical to catalysis and efficient electron transfer in solution and at the solid-solution interface. This point has been made before (8), but several unique observations in the present study give further insight into these processes. In contrast to the two-phase Mn\(_2\)O\(_3\)/MnO\(_2\) assemblage with limited redox capability within each phase, the CaMnO materials allow a much wider range of Mn\(^{3+}\)/Mn\(^{4+}\) ratios within a single structure. The less exothermic oxidation enthalpy for the layered structure CaMnO phases than in the binary oxides (the Mn\(_2\)O\(_3\)/MnO\(_2\) couple) means that the equilibrium between Mn\(^{3+}\) and Mn\(^{4+}\) is more closely balanced and oxidation or reduction does not require a profound structural change. This can occur, with energetics independent of the Mn\(^{3+}\)/Mn\(^{4+}\) ratio, within this constant layered environment. Furthermore, the thermodynamic stability of the Ca-containing layered structure phases permits these redox reactions to proceed without phase change or decomposition.

The low SE of the layered structure CaMnO materials (significantly smaller than for Mn\(_2\)O\(_3\), Mn\(_3\)O\(_4\), or MnO\(_2\)) suggests that water is not strongly bound to the surface sites, because, for many oxides, the enthalpy of H\(_2\)O chemisorption becomes more exothermic with increasing SE (28, 34). In comparing TiO\(_2\) and SnO\(_2\) (rutile structure), Ma et al. (35) have argued that the better gas-sensing ability of the latter stems from a lower surface energy, lower water coverage on the surface, and weaker binding of surface water, enabling energetically easier access of other gas molecules to the SnO\(_2\) surface. Indeed, Castro and Quach (36) proposed recently that measurement of water adsorption enthalpy can be used as a proxy to estimate surface energy. Loosely bound water on CaMnOs may be readily displaced, making sites on the catalyst surface more accessible to other species. Such accessibility also connects the solution chemistry to the catalyst performance. During the water-splitting reaction, reactive intermediates are presumed to form and bind to the surface of the catalytic oxide, with the strength of binding depending on the nature of the transition metal and the structure of the oxide (37). A low binding energy and high mobility for water and counterions may make surface sites near the transition metal more accessible and favor the binding of these activated oxygen species. A simplistic and strictly local view of the O\(_2\)-generation reaction would have two nearby terminal oxo groups link as bonded atoms are oxidized to form peroxide or O\(_2\). However, the layered structure suggests a more nuanced view that emphasizes interlayer chemistry and delocalized charges on the layers, which are only a few nanometers in dimension. Increases in layer charge that accompany O\(_2\) generation require proton transfer and charge adjustment. These are best accomplished via reactions involving solutes in the interlayer region, including Brønsted acids/bases that allow rapid proton transfers. Thus, we speculate that the catalytic performance of the Mn-oxides will be favored in the layered structure phylلومanganates, such as birnessites, which facilitates reversibility and transport by allowing rapid charge compensation. It also has a point-of-zero charge near the pH conditions, where sacrificial oxidants like cerium ammonium nitrate are used (pH 1).

Additionally, the nanoparticle size and disorder of the layered structure CaMnO materials increase the ability of the solid structure to support Mn(III) defects and to have a large number of nonbridging oxygen sites for ligand exchange and catalysis. The major role of calcium in the CaMnO materials may be to stabilize the layered structure rather than to take part in the catalytic reactions, although one can imagine incorporation of acids/bases that facilitate proton transfer in the interlayer. At highly acidic pH, such as near the pH at which sacrificial oxidants like cerium ammonium nitrate are used (pH 1), much of the Ca\(^{2+}\) in the structure may be progressively replaced by H\(^+\), with calcium released to aqueous solution. However, although the Ca\(^{2+}\) is slowly leached out of the material in acid (8), manganese is conserved by repeated reductive dissolution, followed by reoxidation at the solid surface. Takashima et al. (38, 39) argue that the strong pH dependence of catalytic activity can be explained by the effect of pH on the disproportionation of Mn\(^{3+}\) to Mn\(^{2+}\) and Mn\(^{4+}\), with the divalent manganese dissolving in the aqueous solution. For such equilibrium to be maintained during catalysis, adsorption of manganese species on the surface and their transport into, or out of, the structure must be rapid and reversible, as is likely to be the case here.

The findings above provide insight into why the poorly ordered crystalline-layered structure CaMnO materials are better catalysts than well-ordered crystalline binary Mn-oxide minerals (Mn\(_2\)O\(_3\), Mn\(_3\)O\(_4\), and MnO\(_2\)). However, it is possible that the well-ordered materials may evolve under repeated electrochemical cycling to resemble birnessites more closely (with charge balance coming from various cations, including H\(^+\)) (40). One must also ask whether calcium is unique or whether birnessites with other strong electrolyte cations, particularly Na\(^+\) and K\(^+\), behave analogously. Further study of the effect of different exchangeable interlayer cations on thermodynamics and catalytic activity is in progress.

**Conclusion**

The present study suggests that the high surface area, thermodynamic stability, constant and closely balanced redox energetics over a large variation in the Mn\(^{3+}\)/Mn\(^{4+}\) ratio, low surface energy, and weakly bound surface water act together to provide a highly favorable environment for water oxidation catalysis in layered CaMnOs and possibly other birnessite-related structures. The findings in this work can be generalized to guide the search for new and better oxides for water oxidation catalysis. One should look for materials providing easy accessibility and a low binding energy for water (often associated with a low surface energy) in which the redox-active cations can exist, with modest and constant energy difference, over a wide range of Mn\(^{3+}\)/Mn\(^{4+}\) ratios without disrupting the structure.

**Methods**

The CaMnOs had been synthesized previously using a minor modification of published methods (10). Overall, the synthesis involved reaction of potassium permanganate, Mn(II) acetate, and calcium chloride in the presence of potassium hydroxide, and calcium chloride in the presence of potassium hydroxide. The first change was in the use of a very highly concentrated solution of potassium hydroxide, and the second was the discontinuation of the hydrothermal conditions. It is believed that this assisted the formation of small particles because it promoted rapid precipitation. Conversely, hydrothermal treatment, which promotes crystal growth, was removed from the procedure to maintain nanoparticles. The two suites of CaMnO samples are similar but vary in their calcium, manganese, oxygen, and water content; average particle size; and surface area. The syntheses are detailed in SI Text.

All phases were confirmed by powder XRD using a Bruker D8 Advance X-ray diffractometer (Cu K\(_\alpha\) radiation) operated at 45 kV and 40 mA. The XRD patterns were collected with a 0.02° two-θ step size and 10-s dwell time, and they were analyzed by Jade software (version 6.11, 2002, Materials Data, Inc.) to evaluate the phase(s) present and to estimate the average nanoparticle size. All samples displayed XRD patterns appropriate to a layered structure phase, with significant peak broadening particularly evident in the low-angle range (Fig. S1). The samples were measured as received as well as after heating to 1,000 °C during TG analysis. Heated samples
crystallized to an ∼50-50 mixture of CaMnO4 (marokite) and MnO2 ( hausmannite) as shown in Fig. 52.

Samples were heated to 1,000 °C at a rate of 10 K/min under a flow of argon (75 mL/min) in platinum crucibles using the Setaram Labys Evo instrument and associated Calisto software. The TG data were corrected for buoyancy by running an empty crucible. H2O content was determined from the weight difference (obtained on a microbalance for highest accuracy) before and after annealing the samples overnight at 1,000 °C. Samples heated at 1,000 °C lost all their water and crystalized to a mixture of CaMnO4 (marokite) and MnO2. Part of the measured total weight loss was due to loss of oxygen, because Mn3+ in the original sample was reduced on heating, and part was due to dehydration. The former was calculated from the difference in manganese oxidation state between the pristine sample and annealed sample measured by Murray (41) titration. This was subtracted from the total weight loss to give the weight loss due to water. Other than serving as reference material for determining the oxygen and water content of the initial samples, these sintered samples were not considered further because they no longer possessed the layered structures characteristic of the CaMnO4 catalysts.

Surface area was measured by N2 adsorption at −196 °C using a five-point BET (29) technique on a Micromeritics ASAP 2020 in the P/P0 (relative pressure) range of 0.05–0.3. Before analysis, the samples were degassed under nitrogen gas at 200 °C for 12 h. XRD patterns for each phase after similar heating process were collected by a Scintag XDS diffractometer. The diffraction patterns were analyzed using PowderCell software to assess the crystallinity of the samples. XRD patterns for each phase after similar heating process were collected by a Scintag XDS diffractometer. The diffraction patterns were analyzed using PowderCell software to assess the crystallinity of the samples.

Details of methodology; thermochemical cycles; figures for XRD, TEM, SEM, and TG-DSC; and calculation details of the manganese average oxidation state, manganese speciation, water-corrected ΔHΔ, and formation enthalpies are provided in SI Text. Details of the method and calculations are provided in SI Text.

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Synthesis
The two suites of samples were produced by the laboratory of one of the authors (M.M.N.) using similar starting solutions with different Ca and Mn concentrations. For both suites of samples, the first sample was made at 0 °C and each subsequent sample was produced at a temperature ~20 °C higher (IR temperature probe) than the temperature of the previous sample. Additionally, each subsequent sample synthesis involved an increase in the amount of potassium hydroxide (KOH) by 10 g, starting with 10 g of KOH for the first sample reaction in ~400 mL of 18-MΩ water. For both sample suites, a starting concentration of calcium to manganese in the reaction reagents reflected that of the final sample composition (Table 1). The resulting products were extremely fine particulates. The reaction was complete within about 2 h, but the products were allowed to wet-age for an additional 6 h. The particulates were recovered from the aqueous reaction matrix using centrifugation (660 × g for 12 min) and subsequently washed by means of the addition of 18-MΩ water until the rinses were no more than 0.14 mS (conductivity meter), which indicated all extraneous ions were washed away from the product. The samples were dried in a vacuum drier at room temperature to complete dryness (~18 h for 500-mg amount of sample). Chemical analysis by actively coupled plasma (ICP) optical emission spectrometry (OES) indicated no presence of potassium in any of the samples. The samples were not specially treated intentionally to modify the average oxidation state (AOS) of manganese; that was all Mother Nature’s doing.

Characterization
High-Temperature Oxide-Melt Solution Calorimetry. Solution calorimetric studies of nanoparticles of varying size provide a direct measurement of the variation of enthalpy with surface area; a linear relation implies a constant surface enthalpy (SE; surface energy) (1–5). Because oxides are generally poorly soluble in aqueous solvent, the well-established technique of high-temperature oxide-melt solution calorimetry, in which small pellets of sample are dropped from room temperature into a molten oxide solvent held in the calorimeter at high temperature, was used to dissolve the oxides and to control the final oxidation state (6, 7). The measured enthalpy, called the heat of drop solution, ∆Hdrop, contains several contributions: the heat content of the sample, its enthalpy of dissolution at calorimetric temperature, and any enthalpy of oxidation-reduction or gas evolution associated with the process. To interpret the data properly, both the initial state (chemical composition, structural state, and surface area of the solid sample) and the final state (complete dissolution, changes in oxidation state, and evolution of gases) must be characterized. Additionally, surface water contributes to the total heat effect and must be accounted for, as previously described (8). Contribution of bulk H2O was subtracted from the experimental enthalpy using the appropriate thermochemical cycle as discussed below. The scope of the line relating the water-corrected heat of solution to surface area provided the SE. When the enthalpy associated with the H2O is taken as that of bulk water for the process H2O (liquid, 25 °C) → H2O (gas, 700 °C), the calculated SE represents the enthalpy of the hydrated surface (1, 9). We note that the SE is essentially the same as the surface energy and is a good representation of the surface free energy because both the volume change and entropy change on forming nanoparticles from bulk material are small (10, 11).

Manganese AOS and Manganese Speciation. Titration of Mn(III) and Mn(IV) oxidation states used a modified Murray method (12). We describe here the methods of standardization and titration in addition to detailing calculations for both manganese AOS and manganese speciation. As far as we know, this information is not detailed elsewhere in the literature and is not taught as a standard analytical chemistry procedure. We provide the details so that a potential user does not have to do an extensive literature survey.

The method involves iodometry, which has become widely used after its development from the Winkler method (13) for dissolved oxygen measurement in aqueous media. Iodometric titrations for manganese AOS determination were first presented by Murray (12); hence, we refer to the method of manganese oxidation state titration as Murray titration. The procedure involves the reaction of dissolved manganese ions with a large excess of iodide (I−) in an acidic medium to produce triiodide (I3−), which is then titrated with a standardized solution of S2O32−. This method was used successfully to measure manganese AOS in natural manganese oxides (Mn-oxides) and ferromanganese oxides of medium-range order mineral structure phases (12), as well as in bacterio-anoxic layered Mn-oxides (14); thus, the method should translate well to synthetic layered structure Mn-oxides.

The method titrates the iodine produced by reaction of iodide with manganese ions directly and can be performed at room temperature. The titrant solution is highly concentrated in I−; I3− is formed according to the equilibrium I2 + I− → I3−, where I2 is molecular iodine. Because I2 is volatile, an excess of iodide (as sodium iodide) must be present in the acidified aqueous matrix containing the manganese ions from the sample to maintain the iodine as a water-stable I3− complex. After the redox reaction is complete between the Mn ions with an excess of I− to produce I3−, the resulting iodine is titrated with a volume of standardized thiosulfate solution. The number of moles of thiosulfate that react with the I3− provides the number of moles of manganese that are reduced during the process of iodide oxidation by manganese species having a greater than +2 oxidation state (aqueous manganese cannot be further reduced than to divalent).

It is important to note that the use of nitrogen gas-sparged 18-MΩ/cm water drives off dissolved gases from the aqueous matrix that may oxidize some portion of the excess iodide. Another potential source of error for the titration is the volatility of iodine, which can effectively be prevented by adding excess iodide and by keeping all solutions at a temperature not exceeding 25 °C. Nitrite and copper ions, in addition to UV light, will catalyze conversion of iodide to iodine; thus, exposure to these must be minimized. For protracted titrations, some analytical chemists suggest addition of dry ice to the titration mixture to displace air from the Erlenmeyer flask to prevent air oxidation of iodide to iodine. Calculations of manganese AOS and manganese speciation in the calcium manganese oxide (CaMnO) samples require that the total composition of manganese, as well as calcium, be known for each sample. Total Mn and total Ca can be measured using different analytical methods (ICP-MS, ICP-OES, or microprobe).

Two chemical equilibrium equations are involved in the standardization process:

\[
\text{IO}_3^- + 8\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2^- + 3\text{H}_2\text{O.} [S1]
\]

\[
\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}. [S2]
\]

Iodate (IO3−) is the primary standard used to standardize a sodium thiosulfate secondary standard solution. An I3− ion is obtained from the primary standard [potassium iodate (KIO3)], and 3 mol of I3− is obtained in solution for each IO3− ion (3:1...
ratio). However, the iodine species that is reactive in an aqueous matrix exists not as iodate IO$_3^-$ ion, molecular iodine I$_2$, or iodide I$^-$; instead, it exists as I$_3^-$, which is what reacts with the thiosulfate [S$_2$O$_3^{2-}$]. Thus, 2 mol of S$_2$O$_3^{2-}$ is required to neutralize each mole of I$_3^-$. Further details of the titration procedure are given below.

Step 1 is to prepare unstandardized sodium thiosulfate solution (also known as a secondary standard). For a 0.05- to 0.06-M solution of sodium thiosulfate, dissolve ~12 g of Na$_2$S$_2$O$_3$ * 5H$_2$O (158.11 g/mol) in 1 L of freshly nitrogen gas-sparged 18-MΩ water. Sparing the 18-MΩ water with nitrogen gas drives off other dissolved gas species, which may be redox-active or may alter the pH. If the thiosulfate solution is too concentrated to obtain at least a 20-mL end-point titration volume for the analysis, one must do a simple dilution and then double-check the standardization against a reference material (MnO$_2$ of 99.99% purity from Sigma–Aldrich). The thiosulfate stock solution must be refrigerated to maintain freshness for up to a few weeks.

Step 2 is to prepare the treated iodate primary standard solution:

a) The primary standard KIO$_3$, available as a standard solution (Sigma–Aldrich), is chemically treated to obtain the stabilized I$_3^-$ species in water. A slight excess of I$^-$/I$_3^-$ is supplied by dissolving solid potassium iodide (KI). The H$^+$ can be supplied by adding a nonreactive acid, such as H$_2$SO$_4$. Starch indicator solution is prepared by dissolving 2 g of laboratory-grade soluble starch in 100 mL of hot distilled water, which is then stored in a medicine dropper bottle and kept under refrigeration.

b) Twenty-five milliliters of 0.1-N (0.01 M) KIO$_3$ (M$_r$ = 214) Primary Standard solution (Sigma–Aldrich) is pipetted into a 250-mL Erlenmeyer flask.

c) Two grams of KI (M$_r$ = 166) is added and stirred well using a magnetic stir bar to dissolve all solids.

d) Approximately 5 mL of 2 M H$_2$SO$_4$ is added to the solution, which is now ready to standardize the thiosulfate solution.

Step 3 is standardization of sodium thiosulfate secondary standard solution. The standardization of Na$_2$S$_2$O$_3$ occurs according to Eq. S2. The unstandardized thiosulfate solution is placed into a prepared 50.00-mL buret. Starch indicator is used to accentuate the end point and is added near the end of the titration, when the titrated solution is pale yellow (often referred to as straw-colored). Addition of the starch indicator, which complexes with solution iodine, produces black-blue solution coloration. When the end point is reached, in which all iodine has been reduced, the solution turns clear. Use the titrated volume to compute the actual molarity of the thiosulfate solution, and it is now standardized.

The steps of the Murray titration are described below for measuring the Mn-oxide samples.

To a 100-mL Erlenmeyer flask add:

i) Fifty milliliters of degassed, chilled 18-MΩ/cm water

ii) A weighed sample of ~50 mg of the Mn-oxide sample

\[ \alpha = 2 - \frac{\text{[(Volume of Na}_2\text{S}_2\text{O}_3 \times \text{Concentration of Na}_2\text{S}_2\text{O}_3 \times \text{Molar mass of Mn-oxide sample}]/\text{(mass of Mn-oxide sample)}}. \]

iii) Ten milliliters of sodium iodide (NaI) (or KI) excess reagent solution (70 g of NaI in 100 mL of degassed 18-MΩ/cm water)

iv) Five milliliters of 2 M H$_2$SO$_4$

The Mn-oxide sample dissolves in about 15 min (stirring will aid this process). Note that the standard reference MnO$_2$ requires more time to dissolve due to coarseness. The resulting solution is titrated with a triply standardized Na$_2$S$_2$O$_3$ solution.

For computing errors in manganese AOS, we report two SEs of measurement for each sample based on triplicate experiments. Although these errors are in the range of ±0.001 to ±0.005, we report the error as ±0.01 due to the limitations in measurement imposed by likely uncertainties in the volumetric glassware.

**Calculations to Obtain Manganese AOS.** Total oxidized equivalents, [OX], of manganese may be expressed as the manganese AOS obtained from the Murray titration:

\[ [\text{OX}] = 2 \times [\text{Mn(IV)}] + [\text{Mn(III)}]. \]

Subsequently, the O/Mn ratio, as in MnO$_x$, is calculated as:

\[ x = 1 + 1/2 \times \left( \frac{\text{Total oxidized equivalents}}{\text{Total moles of Mn}} \right), \]

where “total moles of Mn” is obtained from ICP-MS and “Total oxidized equivalents” is obtained from the Murray titration. In terms of x, 2 SDs of the mean can be very low (less than 0.002) with strict adherence to proper analytical methodology. Although a buret may only be read to an accuracy of 0.01 mL, the reproducibility of the method is outstanding.

In summary, this method determines the total oxidized equivalents from the moles of thiosulfate standard that went into the reaction. One then uses this value to compute both the O/Mn ratio and the manganese oxidation state speciation. In the present context then, the use of Eqs. S1 and S2 may be modified slightly to reflect the Mn-oxide as the oxidizing agent, and the resulting iodine species is titrated with thiosulfate to determine the moles of equivalent electrons that were involved in this process:

\[ \text{Mn-oxide} + \text{oxidized equivalents} \rightarrow \text{Mn}^{2+} + \text{thiosulfate}, \]

\[ \text{I}_3^- + 2\text{SO}_3^{2-} \rightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{3-}. \]

The Mn-oxide reacts with the iodide to produce iodine. This liberated iodine then gets titrated with a standardized sodium thiosulfate (Na$_2$S$_2$O$_3$) solution to a colorimetric end point (in this case, until complete disappearance of color). From the volume and concentration of titrated thiosulfate, the sample mass, and sample formula weight, we obtain the value for total oxidized equivalents.

**Calculations for Manganese Speciation.** For manganese speciation (the number of manganese atoms in each oxidation state in the sample or analyte solution), we need to compute fractions of each Mn oxidation state relative to the total manganese content. This speciation is directly related to the total number of moles of electrons transferred during iodometric titration. We call the mole fraction of Mn$^{3+} \alpha$ and that of Mn$^{4+} \beta$, where $\beta = (1 - \alpha)$. From the Murray titration,

\[ \text{Then,} \]

\[ [\text{Manganese AOS}] = 2 \times [\text{Mn(IV)}] + [\text{Mn(III)}] = 2 \times (4 \beta) + (3 \alpha). \]

The ratio of oxygen to manganese remains O/Mn = 1/2 (Mn AOS). Furthermore, Ca is always in the +2 oxidation state,
which contributes one oxygen per calcium to the chemical formula. The chemical formula of the compound, normalized to 1 mol of Mn, neglecting water, is given by:

\[ m\text{Ca} \cdot \alpha\text{Mn(III)} \cdot \beta\text{Mn(IV)} \cdot O \ast \left[(2 \ast m\text{Ca}) + 3 \ast \alpha + 4 \ast \beta\right]/2, \]

where \( m = \) [total wt% Ca in sample/Ca atomic mass]/(total wt% Mn in sample/Mn atomic mass)].

\[ \text{Ca}_{1-m}\text{MnO}_{1.5 + m} \cdot \text{H}_{2} \text{O}_{(s, \text{nano}, 25 \degree C)} \rightarrow \text{Ca}_{1-m}\text{MnO}_{1.5 + m} \cdot \text{H}_{2} \text{O}_{(s, \text{dn}, 700 \degree C)} + n\text{H}_{2} \text{O}_{(g, 700 \degree C)} = \Delta H_{1} = \Delta H_{dh} \]

\[ n\text{H}_{2} \text{O}_{(g, 25 \degree C)} \rightarrow n\text{H}_{2} \text{O}_{(g, 700 \degree C)} = \Delta H_{2} = n(25.0 \pm 0.1 \text{ kJ/mol})^{(15)} \]

\[ n\text{H}_{2} \text{O}_{(lq, 25 \degree C)} \rightarrow n\text{H}_{2} \text{O}_{(g, 700 \degree C)} = \Delta H_{3} = n(44.0 \pm 0.1 \text{ kJ/mol})^{(15)} \]

\[ \{\text{Ca}_{1-m}\text{MnO}_{1.5 + m} \cdot \text{H}_{2} \text{O}_{(s, \text{nano}, 25 \degree C)} \rightarrow \{\text{Ca}_{1-m}\text{MnO}_{1.5 + m} \cdot \text{H}_{2} \text{O}_{(s, \text{dn}, 700 \degree C)} + n\text{H}_{2} \text{O}_{(g, 700 \degree C)} = \Delta H_{4} = \Delta H_{1} - \Delta H_{2} - \Delta H_{3}. \]

Here, sln means dissolved in 3NaO-4MoO3 at 700 °C, \( \Delta H_{1} = \Delta H_{dh} \) denotes values obtained using high temperature oxide melt solution calorimetry. \( \Delta H_{2} \) is the heat content of water as it is changing temperature over the range 25 °C to 700 °C (15). \( \Delta H_{3} \)

is the enthalpy of condensation (15). This water-corrected enthalpy of drop solution (\( \Delta H_{4} \)) is plotted against molar surface area, and the slope of the line gives the SE of the hydrated surface.

**Thermochemical Cycles and Calculations. Surface enthalpy.** First, we give the thermochemical cycle for bulk water correction for the CaMnO phases: \( \text{Ca}_{1-m}\text{MnO}_{1.5 + m} \cdot 0.5y\text{H}_{2} \text{O} \). Here, Mn(IV) is represented by “y” and Mn(III) is represented by (1 – y) because all calculations refer to 1 mol of manganese. The coefficients “m” and “n” account for moles of calcium and moles of water contained in the samples, respectively:

\[ m\text{CaO}_{(s, 25 \degree C)} \rightarrow m\text{CaO}_{(s, \text{dn}, 700 \degree C)} = \Delta H_{1} = m \ast (-90.7 \pm 1.69 \text{ kJ/mol})^{(16)} \]

\[ 1/2 (1 - y)\text{Mn}_{2} \text{O}_{3} \rightarrow 1/2 (1 - y)\text{Mn}_{2} \text{O}_{3 \text{dn}, 700 \degree C} = 1/2 (1 - y) \ast \Delta H_{2} = 1/2 (1 - y) \ast (154.87 \pm 1.00 \text{ kJ/mol})^{(17)} \]

\[ y\text{MnO}_{2} \rightarrow y\text{MnO}_{2 \text{dn}, 700 \degree C} = y \ast \Delta H_{3} = y \ast (124.92 \pm 1.03 \text{ kJ/mol})^{(17)} \]

\[ n\text{H}_{2} \text{O} \rightarrow n\text{H}_{2} \text{O}_{(g, 700 \degree C)} = n \ast \Delta H_{4} = n \ast (69.0 \pm 0.1 \text{ kJ/mol})^{(15)} \]

\[ m\text{CaO} - 1/2 (1 - y)\text{Mn}_{2} \text{O}_{3} \cdot y\text{MnO}_{2} \cdot n\text{H}_{2} \text{O} (s, 25 \degree C) \rightarrow \left[ m\text{CaO} + 1/2 (1 - y)\text{Mn}_{2} \text{O}_{3} + y\text{MnO}_{2} \right]_{(s, \text{dn}, 700 \degree C)} + n\text{H}_{2} \text{O}_{(g, 700 \degree C)} = \Delta H_{5} = \Delta H_{dh} \text{ sample kJ/mol.} \]

\[ \Delta H_{f - ox} = \text{kJ/mol} \]

**Enthalpy of formation from oxides CaO, Mn2O3, MnO2, and H2O.**

\[ m\text{CaO}_{(s, 25 \degree C)} \rightarrow m\text{CaO}_{(s, \text{dn}, 700 \degree C)} = m \ast \Delta H_{1} = m \ast (-90.7 \pm 1.69 \text{ kJ/mol})^{(16)} \]

\[ 1/2 \text{Mn}_{2} \text{O}_{3} \rightarrow 1/2 \text{Mn}_{2} \text{O}_{3 \text{dn}, 700 \degree C} = 1/2 \ast \Delta H_{2} = 1/2 \ast (154.87 \pm 1.00 \text{ kJ/mol})^{(17)} \]

\[ 1/4 \text{O}_{2} \rightarrow 1/4 \text{O}_{2 \text{dn}, 700 \degree C} = 1/4 \ast \Delta H_{3} = 1/4 \ast (21.84 \text{ kJ/mol})^{(18)} \]

\[ n\text{H}_{2} \text{O} (s, 25 \degree C) \rightarrow n\text{H}_{2} \text{O}_{(g, 700 \degree C)} = n \ast \Delta H_{4} = n \ast (69.0 \pm 0.1 \text{ kJ/mol})^{(15)} \]

\[ m\text{CaO} - 1/2 \text{Mn}_{2} \text{O}_{3} \cdot 1/4 \text{O}_{2} \cdot n\text{H}_{2} \text{O} (s, 25 \degree C) \rightarrow \left[ m\text{CaO} + 1/2 \text{Mn}_{2} \text{O}_{3} \right]_{(s, \text{dn}, 700 \degree C)} + \left[ n\text{H}_{2} \text{O} + 1/4 \text{O}_{2} \right]_{(g, 700 \degree C)} = \Delta H_{5} = \Delta H_{dh} \text{ sample kJ/mol.} \]

\[ \Delta H_{f - ox} = \text{kJ/mol} \]

**Enthalpy of formation from oxides CaO, Mn2O3, H2O, and O2.**
**Enthalpy of formation from the elements.** Enthalpy of formation from the elements, \( \Delta H^\circ_f \), of the CaMnO layer structure phases from the elements was calculated by adding the appropriate enthalpies of formation of the binary oxides from the elements, multiplied by the stoichiometric coefficients in the formation reactions. The values for binary oxides are listed below (Table S1).


![Fig. S1.](image-url) Typical X-ray diffraction (XRD) pattern of a layered structure CaMnO material before heating to 1,000 °C. The two broad peaks are consistent with a layered structure. The small sharp peak is a silicon diffraction peak coming from a scratch in the zero-background sample holder.
Fig. S2. Typical XRD pattern of CaMnO after heating to 1,000 °C. The scan line in the middle of the figure is the actual measured pattern and the overlay is the calculated pattern, as measured with whole-pattern profile fitting performed using Jade software (version 6.1, 2002). Additionally, as calculated with the Jade software package, the scan line in the upper part of the figure is the computed difference pattern and represents the difference between observed and theoretical intensities, whereas the lines in the lower part of the figure correspond to reference peak positions for marokite (with *) and hausmannite (without *). The compositions of the two mineral oxide phases, reported at the top of the figure as wt%, are 48.2% hausmannite and 51.8% marokite. syn, synthetic.

Fig. S3. Transmission electron microscopy (TEM) image of CaMnO shows layered structure morphology.
**Fig. S4.** SEM image shows that the CaMnO samples consist of aggregates of fundamental nanoscale particles (Pa) from 20 to 60 nm (or below 100 nm) in size. EHT, electron high tension; QBSD, quadrant back scattering detector; WD, working distance.

**Fig. S5.** Thermogravimetric (TG) differential scanning calorimetry (DSC) representative of the CaMnO samples. Analysis of the TG-DSC shows an endotherm for water loss at 142 °C (peak 1) and two additional endotherms at 745 °C (peak 3) and 887 °C (peak 4), which may represent both water and oxygen loss, as well as an exothermic peak at 650 °C (peak 2) possibly caused by sample coarsening. Exo, exothermic (exothermic peak direction in this context); green line, mass loss; blue line, heat flow; brown line, part of calculation for integration of the curve to determine total mass loss for the thermogravimetric analysis; diamonds, initial and final temperature used in the baseline; dotted lines, extrapolation of the baseline, which in the present case is linear due to the background subtraction; "x" marks the selection of the peak (indicated by the circle) and the analysis is used here to identify the temperature of the reported processes in the figure.

**Table S1. Summary of standard formation enthalpies of binary oxides ($\Delta H^\circ_f$)***

<table>
<thead>
<tr>
<th>Oxide</th>
<th>$\Delta H$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn}_2\text{O}_3$ (bixbyite)</td>
<td>$-959.0 \pm 1.0$</td>
</tr>
<tr>
<td>$\text{MnO}_2$ (pyrolusite)</td>
<td>$-520.0 \pm 0.7$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$ (liquid)</td>
<td>$-285.8 \pm 0.1$</td>
</tr>
<tr>
<td>CaO (lime)</td>
<td>$-635.1 \pm 0.9$</td>
</tr>
</tbody>
</table>

*Standard formation enthalpies are from a study by Robie and Hemingway (18).*