Unravelling the Catalytic Activity of MnO₂, TiO₂, and VO₂ (110) Surfaces by Oxygen Coadsorption on Sodium-Adsorbed MO₂ {M = Mn, Ti, V}

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ABSTRACT: Metal-air batteries have attracted extensive research interest owing to their high theoretical energy density. However, most of the previous studies have been limited by applying pure oxygen in the cathode, without taking into consideration the effect of the catalyst, which plays a significant role in the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Adsorption of oxygen on (110) Na-MO₂ is investigated, using density functional theory (DFT) calculations, which is important in the discharging and charging of Na-air batteries. Adsorption of oxygen on Na/MO₂ was investigated, and it was observed that the catalysts encourage the formation of the discharge product reported in the literature, i.e., NaO₂. The surface NaO₂ appears to have bond lengths comparable to those reported for monomer NaO₂.

1. INTRODUCTION

Metal-air batteries are ideal for applications where weight is a major consideration. Since oxygen is not stored in the battery, the cathode is much lighter compared to that of a lithium-ion battery. The metal-air battery has the potential of providing energy densities up to three times that of conventional lithium-ion batteries found in electronic devices, not to mention the incoming wave of electric vehicles. It is well-known that Na-air has a lower energy density compared to Li-air batteries; thus, we look at the effect of a catalyst in the formation of NaO₂. Lithium oxygen batteries have a theoretical gravimetric energy density of 3456 Wh kg⁻¹, assuming lithium peroxide (Li₂O₂) as the stable discharge product. The theoretical gravimetric energy density of sodium oxygen (NaO₂) batteries depends on the assumed discharge product and is 1605 Wh kg⁻¹ or 1105 Wh kg⁻¹ for sodium peroxide (Na₂O₂) or sodium superoxide (NaO₂), respectively. The attention given to sodium-air batteries is due to their high theoretical energy density but also because sodium is an abundant resource. The known discharge products in Na-air batteries are shown in the following equations:

Na + O₂ → NaO₂;  \( E^\circ = 2.27 \) V \hspace{1cm} (1)

Na + O₂ → Na₂O₂;  \( E^\circ = 2.33 \) V \hspace{1cm} (2)

Conversely, in a Na-air, the formation of the discharge products NaO₂ and Na₂O₂ competes due to the equilibrium potentials of 2.27 and 2.33 V, respectively shown in eqs 1 and 2. Importantly, Kang et al. concluded from computation that Na₂O₂ is more stable in the bulk phase, whereas NaO₂ is more stable at the nanoscale. Although both the peroxide and superoxide have been reported as the discharge products of a Na₂O₂ battery, which discharge product is favored is still not understood. The formation of NaO₂ may be kinetically preferred due to the requirement of only a one-electron transfer compared to two electrons for Na₂O₂.

In the absence of an oxygen evolution reaction catalyst, sodium-air batteries have a cycle life of 80 cycles; after an alloy catalyst was applied, the charge potential showed a decrease from over 4.0 V to below 2.7 V, resulting in an improved energy efficiency. The cells are cycled based on the reversible formation and decomposition of the discharge product, Na₂O₂·2H₂O. This is an improvement toward real applications in the field of energy storage of metal-air batteries. The oxygen crossover effect is largely suppressed by replacing the oxygen with air, whereas the dense solid electrolyte interphase formed on the sodium anode further prolongs the cycle life. The increased charge overpotential is likely due to the accumulation of side products on the air electrode to cover the active sites of the catalyst.

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Among transition metal oxides, manganese dioxide has been widely investigated as the catalyst in nonaqueous metal—oxygen batteries, mainly due to its environmental friendliness and easy preparation. A question has always been posed as to why MnO$_2$ is a preferred metal oxide (TiO$_2$ and VO$_2$) catalyst in metal-air batteries. To elucidate and gain a better comprehension of this observation, it is necessary to unravel how such a compound, together with other related metal oxides, plays a role in the promotion or inhibition of the growth of dominant discharge products Li$_2$O$_2$ or LiO$_2$ in Li-air batteries, or NaO$_2$ and Na$_2$O$_2$ in Na-air batteries, for example.

Adsorption of oxygen on sodium-adsorbed surfaces was carried out where oxygen atoms were placed in a bulk-like composition, and oxygen molecules were placed in a peroxo form on Na-MO$_2$. Coadsorption of oxygen was performed in order to simulate the discharge cycle of the metal-air battery whereby oxygen molecules from the atmosphere combine with Na from the anode to form discharge products of Na-air batteries.

Comparison between the metal oxides was investigated in order to validate which of the metal oxides make a better catalyst based on the discharge products’ stability and formation, and whether the catalyst encourages formation of the products or not.

2. RESULTS

2.1. Oxygen Adsorption on MO$_2$ Surfaces. To discuss the redox properties of MO$_2$’s (110) surface, we calculated the adsorption energies of various stoichiometries. We only took into account variations in the oxygen content (the number of M atoms is fixed). If we stick to bulk-like oxygen positions, there are five possible values of $\Gamma$ (stoichiometric surface), $\Gamma = 1$ and 2. Total oxidation refers to the addition of a full layer of oxygen ions generating manganyl-like, titanyl, and vanadyl terminations on top of the previously unsaturated M sites. “Mono-peroxo” and “bridging-peroxo” modes of O$_2$ adsorption are shown in Figure 1.

The oxygen adsorption energies for MnO$_2$ have been discussed previously discussed in detail together with those on the VO$_2$ (110) surface. The adsorption energy of an oxygen atom on a five-fold coordinated Ti site (where $\Gamma = 1$) yielded 2.41 eV. When compared to other configurations, the configuration with $\Gamma = 2$ has more electron transfer from the titanium atom to the adatom.

The calculated adsorption energy obtained in this configuration is 0.69 eV and implies that oxidation of the surface has undergone an endothermic process; hence, it is thermodynamically unfavorable. We further adsorbed oxygen as bridging-peroxo unit (O$_2^{\Gamma=1}$), split between two Ti surface cations, which requires the least charge transfer per Ti cation of all oxidation possibilities. The mononuclear configuration gives the adsorption energy of 0.070 eV, and the bridging configuration gives 0.37 eV; these values show that the processes are endothermic, which implies a nonspontaneous process shown in Table 1. The mononuclear configuration is energetically most stable configurations where the oxygen molecule is adsorbed in different orientations. The adsorption energies shown in Table 1 reveal that VO$_2$ adsorbs oxygen strongly both in the form of an atom or molecule.

2.2. Adsorption of Oxygen on Na/MO$_2$ (110) Surface. We then interrogated the impact of MnO$_2$, TiO$_2$, and VO$_2$ catalysts on the formation of NaO$_2$ and Na$_2$O$_2$ during the cycling of Na-air batteries. Figure 2 shows structures of possible discharge products and their related O–O separations, i.e., bulk NaO$_2$ in pyrite (1.34 Å), marcasite (1.28 Å), Fm$ar{3}$m polymorphs, and the corresponding NaO$_2$ monomer (1.43 Å). Moreover, the bond lengths of O–O in the bulk (1.49 Å) and monomer (1.56 Å) Na$_2$O$_2$ are depicted. A variety of oxygen adsorption configurations have been investigated, with some assuming molecular bonding and others assuming dissociative adsorption. Figure 3 depicts four different stable configurations that have been discovered.

The first considered configuration is where one oxygen atom is directly located on top of each Na as a stationary point, which is in fact unstable, since this arrangement subsequently relaxes (if the symmetry of the initial configuration is broken) to a peroxo where two oxygen atoms are bonded to one Na atom, as shown in Figure 3(i). In the superoxide configuration, the oxygen adsorption energy is $-2.18$ eV/O$_2$, $-3.94$ eV/O$_2$, and $-5.33$ eV/O$_2$ for metal oxides surfaces shown in Figure 3. The resulting bond length of 1.29 Å for the O–O associated...
with the MnO₂ catalyst is consistent with those of the bulk marcasite phase of NaO₂. Furthermore, this configuration is the most stable for all MnO₂-based catalysts. For NaO₂, the bond length of 1.44 Å (O−O) induced by the TiO₂ catalyst is consistent with that of the NaO₂ (1.43 Å) monomer and is the second most stable configuration for TiO₂. However, the bond length of (O−O) in NaO₂ where VO₂ is the supporting catalyst compares well with the bond length (O−O) in the pyrite form of NaO₂, which is 1.34 Å, and it is the least stable configuration.

The Na-peroxo adsorption configuration is not the only stable peroxo adsorption configuration: a peroxo group perpendicular to the surface and binding to Na on one end and to M on the other end, as in Figure 3(ii) (E_{ads} = −1.55 eV/O₂, −3.40 eV/O₂, −3.91 eV/O₂ for the metal oxides as they are shown in Figure 3), are stable. In the case of MnO₂ and TiO₂ catalysts such configuration is least stable, whereas for VO₂ it is the most stable arrangement. The molecular form of oxygen is maintained with a bond length ranging from 1.40 to 1.44 Å, which is comparable to the O−O bond length of 1.43 Å in the NaO₂ monomer. The length of such a bond is likewise closer to that of the bulk NaO₂, namely, 1.49 Å.

Another configuration occurs when locating oxygens above two previously unsaturated M cations, as in Figure 3(iii). Upon relaxation, the oxygens remain separated with bond lengths ranging from 2.55 to 3.07 Å, mainly suggesting a dissociated configuration, which is, however, stable as shown by the adsorption energies (E_{ads} = −1.91 eV/O₂, −4.98 eV/O₂, −5.68 eV/O₂ for MnO₂, TiO₂, and VO₂ respectively). The configurations in Figure 3(iii) are the second most stable for MnO₂ and VO₂, but for TiO₂, it is the most stable. Figure 3(iv) shows an additional stable dissociative configuration with an oxygen atom on the “bulk-like” positions on top of each of the M cations but with additional bonds formed with the Na adatoms, as in Figure 3(iv) (E_{ads} = −1.73 eV/O₂, −3.62 eV/O₂ and −5.96 eV/O₂). In general, it is the second least stable configuration in Figure 3. Large O−O separations ranging from 2.93 to 3.09 across all metal oxides further confirm the dissociation.

There is no trend in terms of the most stable surface; for MnO₂, the most stable configuration is the peroxo group on sodium, which clearly shows or encourages the formation of NaO₂. The most stable configuration for the adsorption of oxygen on the Na-TiO₂ is the configuration with the peroxo on

Figure 2. Structures of NaO₂ (a–d) pyrite, marcasite, Fm̅3m, and a monomer, respectively, and structures of Na₂O₃ (e, f) P̅6m and its monomer respectively showing the relaxed O−O distances.¹

Figure 3. (i–iv) Various configurations that can be adopted by Na−O₂ peroxos when oxygen is adsorbed on different sodiated metal oxide surfaces.
Ti, while the most stable configuration for the adsorption of oxygen on Na-VO$_2$ is the configuration with peroxo on the surface V and adsorbed Na. The adsorption energy for oxygen adsorption on Na-MO$_2$ is negative, indicating an exothermic reaction that does not require energy to occur and is therefore spontaneous.

The dissociated and peroxo on Ti/Na are the least stable configurations relative to other configurations but still stable compared to pure TiO$_2$ surface which depicts similar tendencies as MnO$_2$.

Oxidation on Na/VO$_2$ is also stable relative to the Na free surface that is shown in Figure 5, which extends to $-1$ eV and which is 0.9 eV below the threshold of the Na free surfaces. According to the order of the plots, it is observed that the most stable configuration is the peroxo on V/Na followed by the dissociated, whereas the superoxide and the dissociated are the least stable configurations.

All plots for different compositions (Figures 4, 5, and 6) appear to be most stable in all three metal oxides because the relative surface free energies are negative with a very slight increase in the oxygen chemical potential. The order of stability on the plots is in agreement with the calculated adsorption energies of the oxygen adsorption on Na-MO$_2$.

3. DISCUSSION

3.1. Effect of Metal Oxide Catalysts in the Cathode Reaction in a Na-Air Battery. Na-air batteries have emerged parallel to the study of Li-air batteries as an alternative, based on the substitution of lithium by sodium, in spite of their lower theoretical energy density, which can exhibit better reversibility and much lower overpotentials compared to lithium-based cells.\textsuperscript{19,20} During the battery discharge process, molecular oxygen is reduced in the cathode, in the presence of Na cations and electrons, forming sodium superoxide (NaO$_2^-$):

$$\text{O}_2 + \text{Na}^+ + e^- \rightarrow \text{NaO}_2^-$$

This is subsequently decomposed upon charging in the reverse reaction (Na$^+$ + O$_2^-$ + e$^-$ $\leftrightarrow$ NaO$_2$). Other less prevalent discharge products such as sodium peroxy (Na$_2$O$_2^-$) and peroxy dehydrate (Na$_2$O$_2$·2H$_2$O) have been reported.\textsuperscript{21–23} This is in contrast to nonaqueous Li-air batteries, where Li$_2$O$_2$ was unequivocally identified as the final discharge.

The effects concerned with the MnO$_2$ (110) surface as a catalyst are summarized in Figure 7. First, three bulk polymorphs, $Fm\overline{3}m$, marcasite, and pyrite, of the Na-O$_2$ battery superoxide discharge product, NaO$_2$, are shown in Figure 2, and their respective formation energies are $-2.14$, $-2.69$, and $-2.74$ eV,\textsuperscript{18,24} with corresponding O-O bond lengths of 3.80, 1.28, and 1.34 Å. A competing discharge product is the peroxo Na$_2$O$_2^-$ (symmetry $P6\bar{2}m$) with a formation energy of $-2.63$ eV and related O-O bond length of 1.49 Å. Furthermore, it is apparent that energies of formation of bulk marcasite ($-2.74$ eV) and pyrite ($-2.69$ eV) NaO$_2$ are lower than adsorption energies of sodium oxides at the MnO$_2$ (110) surface for all configurations, i.e., from the least stable ($-1.55$ eV) to the most stable ($-2.18$ eV) arrangements. In addition, the energy of the bulk $P6\bar{2}m$ peroxo Na$_2$O$_2$ is also lower than those of all MnO$_2$ surface-catalyzed products, which implies that surface MnO$_2$ promotes nucleation and formation of the discharge products.

This is consistent with the experimental observation that NaO$_2$ is the main product of the cathode reaction in Na-air batteries, with some Na$_2$O$_2$ as a byproduct (both in the
presence and in the absence of MnO

Indeed, the O−O bond length of the most stable surface configuration (1.29 Å) is nearly equivalent to that of the marcasite (1.28 Å) and not adversely far from one of the pyrite (1.34 Å) phases. On the other hand, the length of the O−O bond of the least stable configuration (1.40 Å) is 6% smaller than that of the bulk phase of the peroxo NaO2. Formation of the dissociated configurations, corresponding to large O−O separations, is also enhanced by the MnO2 catalyst. All such evidence suggests the MnO2 catalyst for promoting nucleation and growth of NaO2 and Na2O2 discharge products.

We now consider the TiO2 (110) surface as a viable catalyst for the formation of NaO2 products during discharge. A closer look at the energies of formation of bulk NaO2 polymorphs Na2O2 is shown in Figure 8; the energy of formation of the surface sodium oxide at configuration (peroxo on Ti/Na, dissociated, dissociated’, and superoxide) indicates that the former (bulk) is higher by 0.93 eV/Na, 2.29 eV/Na, 1.25 eV/Na, and 0.71 eV/Na respectively in all stable configurations for oxygen adsorption on Na-TiO2 surfaces. This means that the formation of Na2O2 and Na2O2 will be discouraged in such configurations because the clusters are too stable and will stick to the surface. In all configurations, the initial reduction of oxygen in the cathode occurs less favorably, i.e., peroxo on Ti/Na, dissociated, and superoxide. Although the energetics do not show the benefit of the TiO2 (110) surface as a catalyst in the formation of expected discharge products, their associated O−O bond lengths are closer to those of Na2O2 bulk and dissociated configurations.

Finally, a comparison of the energy of formation of bulk Na2O2 and Na2O2 shown in Figure 9, and the energy of formation of the sodium oxides on the VO2(110) surface (dissociated, dissociated’, superoxide, and peroxo on V/Na) is informative.

It indicates that the energy of formation for the bulk is higher compared to those of all stable sodium oxide configurations induced by the VO2 (110) surfaces. This suggests that formation of Na2O2 and Na2O2 will not be enhanced by the VO2 (110) surface catalyst since the clusters are too stable and would stick to the surface.

Consequently, nucleation and growth of discharge products will not be enhanced by such metal oxides. However, the O−O bond lengths of generated sodium oxides, which are mediated by the catalysts, though not energetically feasible, are closer to those of NaO2 pyrite (1.36 Å), Na2O2 (1.44 Å), and dissociated configurations (3.07 Å).

Similar to rechargeable Li−O2 batteries, recent studies have alluded to the importance of catalysts in enhancing the performance of Na−O2 batteries. Carbonaceous materials have been used to accelerate the sluggish behavior of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics in rechargeable Na−O2.22,23,24,26 Although transition metal oxides catalysts have been employed extensively in Li-O2 batteries,27−33 owing to the advantages of low cost, high abundance, being environmentally benign, and having considerable catalytic activity in both aqueous and aprotic electrolytes, their use in Na−O2 batteries is limited.
It has, however, been clearly shown that the porous micro-nanostructured CaMnO₃ electrode is an efficient electro-catalyst in Na-air batteries and delivers a high rate capacity and enhanced cyclability. In addition, a composite of NiCo₂O₄ nanosheets/Ni foam, as a carbon-free and binder-free electrode for Na-air, has been identified as a highly efficient electrode for nonaqueous Na-air cells. The nanosheets of the discharge products, composed of Na₂O and Na₂CO₃ were observed after discharging in sodium-air batteries. Similarly, our current study has demonstrated that MnO₂, as a catalyst, promotes nucleation and growth of both Na₂O and Na₂O₂. On the contrary, other metal oxides such as TiO₂ and VO₂ do not depict this catalytic effect toward the formation of discharge products in Na-O₂ batteries.

It is further interesting to discuss the current results in light of computations reported by Ceder et al. (2014), which were carried out in the absence of catalysts. They showed that while sodium peroxide (Na₂O₂) is the stable bulk phase of Na in an oxygen environment at standard conditions, sodium superoxide (NaO₂) is considerably more stable at the nanoscale regime. Hence, the superoxide requires much lower nucleation energy than the peroxide, which explains why NaO₂ is reported as the discharge product in some Na-O₂ batteries. Our study proposes that the presence of catalysts, such as the MnO₂ (110) surface, would further lower the nucleation energy for the superoxides and peroxides, and enhance their growth, whereas the TiO₂ and VO₂ would not be effective.

Figure 10 summarizes the surface adsorption and coadsorption of Li and oxygen atoms in comparison to the formation energies of different bulks of NaO₂, as illustrated in Figures 4–6. This clearly shows the stability of the adsorbed surfaces and the formation energies of the bulk for the metal oxides. The more stable the adsorption energy of the catalyzed systems (compared to the formation energy of the bulk NaO₂), the more unfavorable the configuration, which implies that NaO₂ will stick to the surface, and thus the catalytic property of the metal oxide is not recommended.

### 5. COMPUTATIONAL METHODS

Periodic density functional theory (DFT) computations were carried out using the Vienna Ab initio Simulation Package (VASP) code in the form of the Perdew, Burke, and Ernzerhof (PBE) exchange correlation functional in the generalized gradient approximation (GGA). A cutoff kinetic energy of 600 eV was utilized to determine the number of planewaves, and the Monkhorst–Pack Brillouin zone sampling approach with 6 × 6 × 9 and 6 × 6 × 1 k-points mesh for the bulk and surface structures, respectively, was used. We adopted Liechtenstein’s nonsimplified rotationally invariant Hubbard correction with the effective Coulomb parameter set U = 2.8 eV and exchange parameter J = 1.2 eV and U = 4.6 eV and exchange parameter J = 0.0 eV. The VO₂ calculations were done without the Hubbard correction and were not spin calculations. We first considered the stability of the (110) surface by performing periodic calculations in a slab with stoichiometric composition, thicknesses 14 Å (depending on the oxidation state), and vacuum gaps of ~14 Å (Figure 1). The two surfaces of each slab are symmetrically equivalent, and this equivalence was kept during all of the calculations, preventing the formation of the electric dipole moments that can be associated with asymmetric slabs.

With variances of roughly +0.8% and −3.1% for a and c, respectively, and 1.6% in the cell volume for the MO₂ indicated in Table 2, the lattice parameters were in good agreement with the experimental results. When the bulk structure was allowed to relax fully and cleaved a (110) surface which was allowed to

### Table 2. MnO₂, TiO₂, and VO₂ Bulk Lattice Parameters

| structure  | a (Å)  | c (Å)  | V (Å³) |
|------------|--------|--------|--------|
| β-MnO₂     | 4.366  | 4.410  | 2.961  |
| β-TiO₂     | 4.627  | 4.954  | 3.008  |
| β-VO₂      | 4.617  | 4.554  | 2.774  |

The formation of surface sodium oxide (NaO₂) is more energetically favorable than the formation of gas-phase sodium superoxide (NaO₂) monomers but is less favorable than the formation of NaO₃ bulk, implying that the presence of β-MnO₂ in the cathode of a Na-air battery lowers the energy for the initial reduction of oxygen. In the presence of TiO₂ and VO₂, the formation of the surface NaO₂ is more favorable than the monomer and NaO₂ bulk, which implies that the discharge products will stick to the surface.

For the most stable configurations in the most favored or preferred catalyst, which is MnO₂ in the case for Li-MO₂ and Na-MO₂, it is observed that the stable products predicted are indeed Li₂O and Na₂O₂, which are observed in the dissociated composition for the Li-MnO₂ surface, while it is the most stable configuration in the Na-MnO₂ surface, which encourages the formation of NaO₂. The discharge products formed in Li-air batteries supported by the metal oxide surface catalyst (MnO₂, TiO₂, and VO₂) have the same bond lengths with their bulk and monomer structures. In summary, in Li-air batteries, that Li₂O is not the only product formed; there is a trace of LiO₂, which is confirmed by the bond length similar to that of the calculated LiO₂ monomer.

The metal oxide catalyst employed in this study (MnO₂, TiO₂, and VO₂) supports the formation of NaO₂ in Na-air batteries, which is the most stable discharge product, and this was supported by the bond length comparison of the clusters (NaO₂) formed with the bulk Na₂O and NaO₂ monomer calculations.

Figure 10. MO₂ surface (110) adsorption and sodium oxide bulk energetics.
converge as well, and the surface energy was obtained using the expression

\[ \gamma = \frac{E_{\text{slab}} - E_{\text{bulk}}}{2A} \]  

(4)

where \( E_{\text{slab}} \) denotes the energy per slab unit cell, \( E_{\text{bulk}} \) denotes the energy of an equivalent amount of bulk solid, and \( A \) is the surface area. The adsorption and coadsorption of sodium and oxygen on clean (110) surfaces are carried out in such a way that stoichiometry and symmetry are maintained throughout the calculations. More information on the methodology can be found elsewhere.\(^{6,44,45}\)

\[ E_{\text{ads}} = E_{\text{system}} - (E_{\text{slab}} + E_{\text{adsorbate}}) \]  

(5)

Equation 5 is used to calculate the adsorption energy where \( E_{\text{ads}} \) is the adsorption energy, \( E_{\text{system}} \) is the energy of the slab together with its adsorbate, and \( E_{\text{adsorbate}} \) is the energy of the adsorbate.

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Notes

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