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The Effect of CO₂ Contamination in Rechargeable Non–Aqueous Sodium–Air Batteries

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Abstract

Metal–air batteries have higher theoretical specific energies than existing rechargeable batteries including Li-ion batteries. Among metal-air batteries, the Na–O₂ battery has gained much attention due to its low discharge/charge overpotentials (~100 mV) at relatively high current densities (0.2 mA/cm²), high electrical energy efficiency (90%), high theoretical energy density, and low cost. However, there is no information reported regarding the effect of CO₂ contamination in non-aqueous Na–air batteries. Density functional theory (DFT) has here been applied to study the effect of low concentrations of CO₂ contamination on NaO₂ and Na₂O₂ growth/depletion reaction pathways and overpotentials. This was done on step surfaces of discharge products in non-aqueous Na–air batteries. Adsorption energies of CO₂ at various nucleation sites for both step surfaces were determined and results revealed that CO₂ preferentially binds at the step valley sites of (001) NaO₂ and (1¯100) Na₂O₂ surfaces with binding energies of ~0.65 eV and ~2.67 eV, respectively. CO₂ blocks the step nucleation site and influences the reaction pathways and overpotentials due to carbonate formation. The discharge electrochemical overpotential increases remarkably from 0.14 V to 0.30 V and 0.69 V to 1.26 V for NaO₂ and Na₂O₂ surfaces, respectively. CO₂ contamination is thus drastically impeding the growth/depletion mechanism pathways, and increases the overpotentials of the surface reaction mechanism hampering the performance of the battery. Avoiding CO₂
contamination from intake of gas and electrolyte decomposition is thus critical in development of Na–air batteries.

I. Introduction

The demand for high energy density, affordable and long–lasting energy storage materials is growing rapidly. Batteries are useful for renewable energy systems as stationary energy storage units and play a vital role in today’s and future automobile industry.\textsuperscript{1–3} However, the capacity offered by the current state-of-the-art Li-ion technology is too low to solve the increasing demands.\textsuperscript{4} Therefore, to meet the increasing demand for energy storage technologies, significant attention is given to research and development of metal-air batteries (Li–, Na– and Zn–O\textsubscript{2}/air batteries).\textsuperscript{4–7} Metal–air batteries have higher theoretical specific energies than existing rechargeable batteries including Li-ion batteries. Though metal–air batteries certainly show promise, there are several scientific and technical challenges which must be addressed before commercialization. These include low accessible capacity\textsuperscript{8}, poor conductivity and rechargeability\textsuperscript{7,9–13}, instability of electrodes\textsuperscript{14–17}, electrolytes\textsuperscript{18} and salts\textsuperscript{19,20} and high sensitivity to trace gases.\textsuperscript{21–26}

Despite its lower capacity and potential than the Li–O\textsubscript{2} battery, the Na–O\textsubscript{2} battery has gained much attention due to its low discharge/charge overpotentials (\textasciitilde 100 mV) at relatively high current densities (0.2 mA/cm\textsuperscript{2}) and high electrical energy efficiency (90\%). Na–O\textsubscript{2} batteries can be operated over multiple cycles with chemical reversibility.\textsuperscript{27–31} Additionally, sodium is more abundant and cheaper than lithium.\textsuperscript{8,27–31}

In Na-O\textsubscript{2} batteries, depending on the electrolyte used and other experimental conditions different discharge products have been reported such as sodium superoxide (NaO\textsubscript{2})\textsuperscript{6,9,27,29,32,33}, sodium peroxide (Na\textsubscript{2}O\textsubscript{2})\textsuperscript{34,35}, sodium carbonate (Na\textsubscript{2}CO\textsubscript{3})\textsuperscript{28}, hydrated sodium peroxide (Na\textsubscript{2}O\textsubscript{2}\cdot2H\textsubscript{2}O)\textsuperscript{36,37} and sodium hydroxide (NaOH)\textsuperscript{34}. However, sodium peroxide (Na\textsubscript{2}O\textsubscript{2})\textsuperscript{34,35} and sodium superoxide (NaO\textsubscript{2})\textsuperscript{6,9,27,29,32,33} are the two dominant discharge products in non-aqueous sodium–air batteries. Charging overpotentials have been found to depend greatly on the discharge product, as NaO\textsubscript{2} can be decomposed
with low charging overpotentials (∼100 mV),\textsuperscript{9,27,29} while decomposition of Na\textsubscript{2}O\textsubscript{2} exhibit large overpotentials (> 1.3 V).\textsuperscript{34} In addition to the high overpotential, poor rechargeability (< 10 cycles) has been observed for battery cells in which Na\textsubscript{2}O\textsubscript{2} is formed. Many of the drawbacks are similar to those observed in the Li–O\textsubscript{2} system.\textsuperscript{29}

A computational study by Kang \textit{et al.}\textsuperscript{38} shows that NaO\textsubscript{2} is more stable than Na\textsubscript{2}O\textsubscript{2} at the nanoscale level (up to 5 nm), whereas bulk Na\textsubscript{2}O\textsubscript{2} is thermodynamically stable at standard conditions (in agreement with experimental observations). Moreover, a combined experimental and computational study revealed that bulk NaO\textsubscript{2} is thermodynamically stable up to a temperature of 120 K, while bulk Na\textsubscript{2}O\textsubscript{2} is thermodynamically stable above 120 K.\textsuperscript{6} Kinetic studies showed that the overpotentials for growth/depletion of Na\textsubscript{2}O\textsubscript{2} were significantly larger than those for NaO\textsubscript{2}.

Additional insight into the growth/depletion mechanisms of discharge products is desired in the development. The previous computational work by Mekonnen \textit{et al.}\textsuperscript{6} showed that steps on reconstructed (001) NaO\textsubscript{2} and (1\textoverline{1}00) Na\textsubscript{2}O\textsubscript{2} surfaces act as nucleation sites to achieve the lowest discharge overpotentials. Adsorbed species at surfaces can potentially block these nucleation sites, and therefore, alter the growth directions, overpotentials, and discharge capacities. For instance, carbonate species were formed in Li–air batteries by parasitic side reactions between the discharge products/intermediates (Li\textsubscript{2}O\textsubscript{2}/LiO\textsubscript{2}) and carbon containing species in the cell. The main sources of carbon in metal-air batteries are trace gases such as CO and CO\textsubscript{2}\textsuperscript{39}, graphite\textsuperscript{15} and decomposition of aprotic electrolytes.\textsuperscript{18} The parasitic reactions lead to carbonate accumulation at the C–Li\textsubscript{2}O\textsubscript{2} and Li\textsubscript{2}O\textsubscript{2}–electrolyte interfaces.\textsuperscript{15,40} These carbonate species are responsible for a large potential increase during recharge and a vast decrease in exchange current density. Adsorption of CO\textsubscript{2} and sulfur containing compounds on oxide surfaces of Li–O\textsubscript{2} battery could very well dictate the electrochemical growth mechanism.\textsuperscript{23,41} The formation of Na\textsubscript{2}O\textsubscript{2} in the solution-based mechanism is found to be suppressed in high DN-electrolytes like DME and DMSO. However, studying the effect of electrolytes by explicitly adding electrolyte in the cell is beyond the scope of this work, which is focused on the surface-based mechanism.
To our knowledge, only few studies have reported information regarding the effect of CO$_2$ contamination in Na–air batteries. Among air contaminants, CO$_2$ is the most critical due to its high solubility in aprotic electrolytes and high reactivity with NaO$_2$ and Na$_2$O$_2$ to form an insulating material containing carbonate species, which requires high overpotentials to decompose.

Herein, we investigate the effect of CO$_2$ contamination on growth mechanisms on stepped (001) NaO$_2$ and (1100) Na$_2$O$_2$ surfaces using density functional theory (DFT). This allows us to obtain the theoretical minimum discharge and charge overpotentials for surface growth/depletion in non–aqueous CO$_2$ contaminated Na–air batteries.

II. Computational Methodology

DFT$^{42,43}$ calculations were performed with the grid–based projector–augmented wave method (GPAW) code$^{44,45}$ through the atomic simulation environment (ASE).$^{46}$ A real space grid basis set$^{47,48}$ was used with 0.18 Å grid point spacing. To approximate the electron exchange and correlation, the PBE functional$^{49}$ was used as it, albeit inability to properly capture some features of Na$_x$O$_2$ species such as electronic conduction, is expected to present the best compromise of reliable free energy calculations and computational cost $^{50–53}$. Previous DFT calculations found that reconstructed stepped (001)NaO$_2$ and (1100) Na$_2$O$_2$ surfaces are stable and have favorable nucleation sites for low overpotential growth/depletion pathways.$^6$ They are thus also used as model surfaces in this study.

The applied approach is based on analysis of the free energy of the reaction intermediates without explicitly identifying and quantifying possible kinetic barriers for the redox reactions. The reported values should therefore be viewed as theoretical minimum values for the overpotentials. For the (001) NaO$_2$ stepped surface (with $P\alpha\bar{3}$ space group), we used a super cell consisting of a 60–72 atoms slab The super cell was sampled with $2 \times 4 \times 1$ k–points in a Monkhorst–Pack mesh and all the calculations were spin–polarized (ferromagnetic phase) with an initial magnetic moment value of 0.5 assigned to each O atom in NaO$_2$. A previous theoretical study reported the ferromagnetic phase to
be more stable than the antiferromagnetic phase by 15 meV per formula unit.\textsuperscript{54} The Na\textsubscript{2}O\textsubscript{2} growth/depletion mechanism with and without CO\textsubscript{2} was studied on the stepped (1\,\overline{1}00) surface of Na\textsubscript{2}O\textsubscript{2} in the \textit{P}\overline{6}2\textit{m} space group. The super cell consisted of a 88–96 atoms slab. \textit{k}–points were sampled with a $2 \times 2 \times 1$ Monkhorst–Pack mesh. For both surfaces, approximately 20 Å spacing were added between repetitions of the slab caused by the periodic boundary conditions in the direction perpendicular to the surface. Dipole corrections were also applied in this direction. The positions of the atoms in the bottom layers of the slabs were fixed with lattice constants as in bulk to emulate a large bulk rather than a thin sheet. For structure optimization, all the calculations were continued until all forces are less than 0.03 eV/Å. Four formula units of NaO\textsubscript{2} and two formula units of Na\textsubscript{2}O\textsubscript{2} were added to the slab systems to examine the growth mechanisms. These additions would in absence of CO\textsubscript{2} correspond to a reforming of the initial surface termination.

Similar to the lithium electrode approach used for Li–air batteries\textsuperscript{55,56}, the computational sodium electrode approach was used for the free energy calculations in this work. At zero applied potential ($U = 0$), the bulk Na anode and Na ions in electrolyte solution were assumed to be in equilibrium ($\text{Na} \leftrightarrow \text{Na}^{+} + \text{e}^{-}$). The free energy change of the reaction is shifted by $-n\text{e}U$ at an applied bias $U$, where \textit{n} is the number of electrons transferred. At a given applied potential, the change in free energy ($\Delta G$) between two consecutive intermediates/steps can be calculated as,

$$\Delta G_{i,U} = \Delta G_{i} - \text{e}U$$ \hspace{1cm} (1)

At neutral bias all reaction steps are downhill. The limiting discharge potential ($U_{\text{discharge}}$) is determined by the smallest free energy step, $\Delta G_{i,\text{min}}$, along the reaction path at $U=0$, as this is the first to become uphill at an applied potential. The value of $U$ at which this occurs is a theoretical maximum for the discharge potential. Likewise, the largest free energy step, $\Delta G_{i,\text{max}}$, is last to become downhill for the charging reaction, and thus determines the limiting charge potential ($U_{\text{charge}}$) during the charging reaction. It is, likewise, a theoretical minimum for the charging potential, which could be larger in actual operation.
The calculated effective equilibrium potential can be obtained from the free energy of the full reaction as \( U_o = \Delta G / n_e \). Large systematic errors in the description of superoxides, peroxides and monoxides have previously been documented by various groups and accounted for in various ways.\(^{38,57,58}\) Here, we adopted the approach of Christensen \textit{et al.}\(^{58}\) using NaCl as an indirect reference for sodium in order to better account for the oxidation state of Na in the Na–O\(_2\) system. The approach is chosen as it reduces the systematic errors significantly, while allowing consistent calculation of surfaces with oxide species in different oxidation states. The energy of Na with the NaCl reference, \( E^{\text{NaCl ref}}(\text{Na}) \) is given by: \(^{58}\)

\[
E^{\text{NaCl ref}}(\text{Na}) = E(\text{NaCl}) - \frac{1}{2} E(\text{Cl}_2) - \Delta H_{\text{NaCl,exp}} \quad (2)
\]

Where, \( E(\text{NaCl}) \) and \( E(\text{Cl}_2) \) are the calculated energy per formula unit of NaCl and Cl\(_2\), respectively, and \( \Delta H_{\text{NaCl,exp}} \) is the experimental enthalpy of formation of NaCl. The calculated energy per formula unit of X was obtained using the following expressions:

\[
E(X) = E^{\text{DFT}}_X + ZPE(X) + \int_0^T C_p dT(X) \quad (3)
\]

Where, \( E^{\text{DFT}}_X \) is the ground–state DFT energy, ZPE is the zero–point vibrational energy and the integral is over the constant-pressure heat capacity. In line with Christensen \textit{et al.}\(^{58}\), an energy correction was applied to O\(_2\) (g), which otherwise is very difficult to describe correctly within DFT. In the computational approach used here, the optimal energy correction of O\(_2\) is \(-0.33\) eV. Hence, a corrected energy per formula unit of O\(_2\) was calculated according to equation 4.

\[
E^{\text{Corr}}(\text{O}_2) = E^{\text{DFT}}_{\text{O}_2} + ZPE(\text{O}_2) + \int_0^T C_p dT(\text{O}_2) - 0.33\text{eV} \quad (4)
\]

The enthalpies of formation of NaO\(_2\) and Na\(_2\)O\(_2\) using the energy corrected O\(_2\) and sodium chloride (NaCl) references are thus given as (\( x = 1 \) for NaO\(_2\) and \( x = 2 \) for Na\(_2\)O\(_2\))

\[
\Delta H'^{\text{NaCl}}(\text{Na}_x\text{O}_2) = E(\text{Na}_x\text{O}_2) - x \cdot \left[ E^{\text{NaCl ref}}(\text{Na}) - E^{\text{Corr}}(\text{O}_2) \right]
\]

Or

\[
\Delta H'^{\text{NaCl}}(\text{Na}_x\text{O}_2) = E(\text{Na}_x\text{O}_2) - x \cdot \left[ E(\text{NaCl}) - \frac{1}{2} E(\text{Cl}_2) - \Delta H_{\text{NaCl,exp}} \right] - E^{\text{Corr}}(\text{O}_2) \quad (5)
\]
The free energies of NaO$_2$ and Na$_2$O$_2$ are calculated as:

$$\Delta G^{NaCl}(Na_xO_2) = \Delta H^{NaCl}(Na_xO_2) - \{T\Delta S(Na_xO_2) - T\Delta S(O_2) - x \ast T\Delta S(Na)\}$$ (6)

where, $T\Delta S$ is the entropy at standard temperature and pressure (STP). The entropy for solid phases, i.e., Na metal, NaO$_2$ and Na$_2$O$_2$, were for simplicity assumed to be identical to the entropy in bulk crystals. The entropy for O$_2$ in the gas phase ($T\Delta S(O_2)$) is 0.63 eV.

The CO$_2$ adsorption free energies ($G_{ads}$) on surfaces of NaO$_2$ and Na$_2$O$_2$ were calculated using equation 7.

$$G_{ads} = E_{ads} + ZPE - TS$$ (7)

The CO$_2$ adsorption energies ($E_{ads}$) were calculated by subtracting the DFT energies of the reactants from the energy of the product using equation 8.

$$E_{ads} = E(CO_2@Na_xO_2) - [E(Na_xO_2) + E(CO_2)]$$ (8)

The change in entropic energy of CO$_2$ is approximated by the entropy of the gaseous CO$_2$ used as reference ($T\Delta S(CO_2_{(g)}) = 0.64$ eV). The majority of this entropic energy is due to translation and rotational degrees of freedom, which are largely lost upon adsorption. By simply using 0.64 eV as the change in entropic energy we neglect the vibrational energy contribution of the adsorbed CO$_2$, which is expectedly small. $\Delta ZPE$ is calculated for the adsorption sites by comparing the zero point vibrational energy of gaseous CO$_2$ and an O$_2$ dimer on the surface with the carbonate specie formed during adsorption. These will to large extend offset each other such that the largest (absolute) value observed for $\Delta ZPE$ is smaller than 0.08 eV.

The effect of the electrolyte has not been included in this study. It should be remarked that electrolytes can have a very significant effect on the growth/depletion mechanisms. 59 Proper systematic inclusion of electrolyte effects does, however, fall outside the scope of this study as it will be very computational resource demanding. An implicit electrolyte model has been applied to simulate DMSO 60 to assess the solvation effect on gaseous species and select adsorption geometries. Solvation was found to destabilize CO$_2$
adsorption by less than 0.15 eV with 0.09 eV of the destabilization originating from stabilization of the CO$_2$ reference state.

Identification of a solution based reaction mechanism as alternative to the here examined growth reaction also requires consideration of the electrolyte. The reaction free energies of superoxide ions with Li$^+$, Na$^+$, and CO$_2$ in DMSO were calculated using both the GPAW code$^{44,45,60}$ and the molecular ADF code with an implicit solvation model.$^{61,62}$ Within these method limitations, superoxide ions are found significantly more prone to react with alkali ions than CO$_2$, which itself is stabilized more by adsorption than reaction with superoxide. We do thus not expect that systematic inclusion of DMSO electrolyte with the implicit solvation model will significantly change the presented findings but should stress that simulation with different electrolyte models and/or electrolytes might.

III. Results and Discussion

The binding energies of CO$_2$ molecules at different sites were calculated to identify the preferred site for CO$_2$ adsorption. The sites with strong adsorption energies were identified on both NaO$_2$ and Na$_2$O$_2$ stepped surfaces. Secondly, the growth/depletion pathways of NaO$_2$ and Na$_2$O$_2$ were investigated. It should be remarked that we only consider the adsorption of a single CO$_2$ molecule in the model system, i.e. possible interaction between close range CO$_2$ adsorbents is not considered. We are thus restricted from examining the effect of high CO$_2$ concentrations. With the used model structures and computational unit cells we are also unable to determine the effect of very small CO$_2$ concentrations.

3.1. CO$_2$ adsorption energies on the surfaces of NaO$_2$ and Na$_2$O$_2$

The binding energies of a single CO$_2$ molecule at various nucleation sites (see Figure 1) on NaO$_2$ and Na$_2$O$_2$ surfaces were investigated and the corresponding adsorption energies are presented in Table 1. It shows that CO$_2$ preferentially binds at the left step valley site of the (001) NaO$_2$ surface with a binding energy of $-0.65$ eV (see Figure 1a b) forming Na$_{n-1}$CO$_3$ like species. Similarly, for the stepped (1100) Na$_2$O$_2$ surface, CO$_2$ is
favorably adsorbed both at the front (B’) and back (E’) step valley sites with binding energies of -2.67 eV and -2.57 eV, respectively. Moreover, CO\textsubscript{2} is weakly adsorbed at the terrace sites of both surfaces compared to the binding energies of front and back step valley sites of Na\textsubscript{2}O\textsubscript{2} (see Table 1). Comparatively, the adsorption energy of a CO\textsubscript{2} molecule is 3–4 times stronger on the stepped valley on Na\textsubscript{2}O\textsubscript{2} surfaces than on stepped NaO\textsubscript{2} and Li\textsubscript{2}O\textsubscript{2} surfaces.

Figure 1: (a) CO\textsubscript{2} adsorption at various sites of stepped (001) NaO\textsubscript{2} surface. A) Step ridge, B) Left step valley, C) Right step valley D) Step kink and E) Step terrace. b) CO\textsubscript{2} adsorption at various sites of stepped (1\overline{1}00) Na\textsubscript{2}O\textsubscript{2} surface. A’) Front terrace, B’) Front step valley, C’) Top front terrace, D’) Top back terrace and E’) Back step valley. Atoms are labeled as: Na (Purple), O (red) and C (yellow). CO\textsubscript{2} adsorption on both surfaces form Na\textsubscript{~n}CO\textsubscript{3} like species, in the formation of CO\textsubscript{3}\textsuperscript{2−} the source of oxygen atoms are from CO\textsubscript{2} (green) and surfaces (blue).
Table 1: Adsorption energies of a CO$_2$ molecule on some selected sites of stepped (001) NaO$_2$ and (1\overline{1}00) Na$_2$O$_2$ surfaces, sites are shown in Figure 1.

<table>
<thead>
<tr>
<th>Species</th>
<th>Site</th>
<th>$\Delta G_{\text{ads}}$ (eV)</th>
<th>Site</th>
<th>$\Delta G_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>Step ridge (A)</td>
<td>-0.12</td>
<td>Front bottom terrace (A')</td>
<td>-0.95</td>
</tr>
<tr>
<td></td>
<td>Left Step valley (B)</td>
<td><strong>-0.65</strong></td>
<td>Front step valley (B')</td>
<td><strong>-2.67</strong></td>
</tr>
<tr>
<td></td>
<td>Right Step valley (C)</td>
<td>-0.60</td>
<td>Top front terrace (C')</td>
<td>-2.08</td>
</tr>
<tr>
<td></td>
<td>Step kink (D)</td>
<td>-0.05</td>
<td>Top back terrace (D')</td>
<td>-0.54</td>
</tr>
<tr>
<td></td>
<td>Step terrace (E)</td>
<td>-0.61</td>
<td>Back step valley (E')</td>
<td><strong>-2.57</strong></td>
</tr>
</tbody>
</table>

3.2. Effect of CO$_2$ contamination on NaO$_2$ growth/depletion mechanisms

In the following, the effect of CO$_2$ poisoning on the NaO$_2$ growth/depletion mechanisms by adsorbing CO$_2$ at step valley site is analyzed (Figure 2b). The lowest theoretical overpotential pathways were identified by comparing the free energies of (electro) chemical reaction steps.

In order to generate entire reaction pathways to determine the minimum theoretical overpotential both electrochemical (involving either Na$^+$ or NaO$_2$ species) and chemical (involving O$_2$ species) reaction steps were taken into account. The thermodynamically favorable path (i.e. the lowest overpotential path) was determined after CO$_2$ adsorption. The first intermediate step in the growth mechanism was found to be addition of a NaO$_2$ specie at the site illustrated in Figure 2c (bottom left site). The second intermediate step was again adsorption of a NaO$_2$ specie (Figure 2d). It is identified as the potential limiting step for charge. The third and fourth intermediate steps, Figure 2e and 2f, respectively, were adsorption of two NaO$_2$ species across the two NaO$_2$ species previously adsorbed. The fourth step yields the lowest potential of the reaction pathway in presence of CO$_2$.

As it can be seen in Figure 3, the reaction pathways and the potentials were altered by the presence of CO$_2$ gas in the system. In absence of CO$_2$, the first and fourth steps were
identified as the steps limiting discharge and charge potentials, respectively.\textsuperscript{6} The carbonate species get embedded within the NaO\textsubscript{2} structure.

![Figure 2: Stepped NaO\textsubscript{2} (001) surface before and after adsorption of a CO\textsubscript{2} molecule and the four steps of NaO\textsubscript{2} growth during discharge. (a) Pure stepped NaO\textsubscript{2} surface. (b) CO\textsubscript{2} adsorbs to step valley site. (c) 1\textsuperscript{st} NaO\textsubscript{2}, (d) 2\textsuperscript{nd} NaO\textsubscript{2}, (e) 3\textsuperscript{rd} NaO\textsubscript{2} and (f) 4\textsuperscript{th} NaO\textsubscript{2} adsorbs to the surface completing growth of four NaO\textsubscript{2} formula units. Atoms labeled as: Na (purple) and O (red). Deposited atoms labeled as: C (yellow), Na (blue) and O (green).]

The effective equilibrium potential on a pristine stepped NaO\textsubscript{2} surface has previously been calculated to 2.34 V (experimental value, \(U_{0,\text{Exp}} = 2.27\) V)\textsuperscript{63}, which is reduced to 2.28 V in the presence of CO\textsubscript{2}. In the presence of CO\textsubscript{2}, overpotentials increase from 0.14 V to 0.30 V during discharging and from 0.19 V to 0.31 V during charge. Although increased, the overpotentials in the presence of CO\textsubscript{2} on NaO\textsubscript{2} is still less than the overpotentials previously calculated for pristine Na\textsubscript{2}O\textsubscript{2}.\textsuperscript{6} As shown in Figure 3, the depletion or charging process follows the same reaction steps as the growth or discharge process, but in reverse order (from right to left).
Figure 3: Calculated free energy diagram for a four steps growth/depletion mechanism for a stepped (001) NaO₂ surface with and without adsorbed CO₂.

It is plausible that at higher CO₂ concentrations the effect on overpotentials and capacity will be larger as it is the case for Li-air batteries.¹⁵,²³

3.3. Effect of CO₂ contamination on Na₂O₂ growth/depletion mechanisms

The effect of CO₂ contamination on the Na₂O₂ growth/depletion mechanisms were studied with CO₂ adsorbed at the front step valley site (Figure 4(b)) of the initial surface structure. The reaction mechanism yielding the lowest theoretical overpotential has been determined. As illustrated in Figure 4 and the free energy diagram in Figure 5, the mechanisms are four-step reaction mechanisms. On the stepped (11̅00) Na₂O₂ surface, all reaction steps are electrochemical and involve either Na⁺ or NaO₂⁺ added to/removed from the step surface successively to grow/deplete two formula units of Na₂O₂.
In the presence of CO$_2$, the addition of NaO$_2$ species at the site illustrated in Figure 4c is found to be the preferred initial intermediate step for the growth reaction mechanism. The reaction is followed by another NaO$_2$ species added at the top right site (Figure 4d) with a binding energy of $-3.12$ eV. This is the potential limiting step for the charge process. The binding energy is increased by $0.14$ eV compared to pure Na$_2$O$_2$. The last two steps are additions of two Na$^+$ species at the bottom left and bottom right sites with binding energies of $-1.97$ eV and $-0.94$ eV, respectively. The last step limits the discharge potential, which is smaller than that of the pure system; see Figure 4 (e and f) and Figure 5. The full growth mechanism is completed with the formation of two formula units of Na$_2$O$_2$ at the front of the stepped surface.

Unlike NaO$_2$, the presence of CO$_2$ on a Na$_2$O$_2$ surface significantly alters the equilibrium potential. The equilibrium potential is reduced from 2.37 V in pristine to 2.20 V in the presence of CO$_2$ (experimental value, $U_{\text{O, Exp}} = 2.33$ V$^{63}$). In both cases an O$_2$ ion (peroxide in Na$_2$O$_2$, superoxide in NaO$_2$) is broken spontaneously to form a carbonate ion on the surface and an O$^{2-}$ ion in the subsurface. As the structure grows, the carbonate will become enclosed in the structure of both NaO$_2$ and Na$_2$O$_2$. In NaO$_2$, CO$_3^{2-}$ will occupy an O$^{2-}$ site with a moderate distortion to the local structure. In Na$_2$O$_2$ it will occupy a Na site with a severely under coordinated Na adsorbing near to it. Thus, an explanation for the larger change in equilibrium potential caused by CO$_2$ for Na$_2$O$_2$ than for NaO$_2$ could be that the density of NaO$_2$ is lower than that of Na$_2$O$_2$. Carbonate can thus fit into the NaO$_2$ crystal structure while it cannot in Na$_2$O$_2$. 

Figure 4: Stepped (1̅100) Na₂O₂ surface before and after adsorption of CO₂ and Na₂O₂ growth during discharge. (a) Pure stepped Na₂O₂ surface. (b) CO₂ adsorbs to step valley site forming a Na₃nCO₃ type complex. (c) and (d) NaO₂ species consecutively adsorbed followed by Na species added at (e) and (f) to the surface completing growth of two Na₂O₂ formula units. Colors: Na (purple), and O (red). Deposited atoms colors: C (yellow), Na (blue) and O (green).

In the presence of CO₂, the discharge and charge overpotentials increase significantly, from 0.69 V to 1.26 V and from 0.68 V to 0.92 V, respectively. A change of the potential limiting steps also occurs. Again, the charging process follows the same reaction steps as the discharge process but in reverse order (from f to b in Figure 4 and right to left in Figure 5). In the presence of CO₂, the growth/depletion pathways, as well as the limiting discharge and charge potentials, have changed compared with the pristine Na–O₂ system.⁶
Figure 5: Calculated free energy diagram for the four steps discharge/charge mechanism on a stepped (1\,\bar{1}00) Na$_2$O$_2$ surface with and without adsorbed CO$_2$.

In addition to the presence of CO$_2$ and other impurities, another important source of overpotentials in Na–air batteries is the low electronic conductivity of both NaO$_2$ and Na$_2$O$_2$. According to GW calculations, NaO$_2$ and Na$_2$O$_2$ are insulating materials with bandgaps of 5.30 and 6.65 eV, respectively.\textsuperscript{54} Therefore, the cathode surface is passivated when NaO$_2$ and Na$_2$O$_2$ are deposited during discharging process and electrons cannot reach the surface, leading to the so-called “sudden death” of the battery. Similar to earlier studies on Li$_2$O$_2$,\textsuperscript{64,65} Yang and Siegel\textsuperscript{54} identified hole polarons (localized on O$_2$ dimers) and negative sodium vacancies as the main charge carriers in Na$_2$O$_2$. Electron and hole polarons contribute equally to the intrinsic conductivity of NaO$_2$. NaO$_2$ exhibits higher electronic and ionic conductivity (~10 orders of magnitude) than Na$_2$O$_2$.\textsuperscript{54} The smaller conductivity in Na$_2$O$_2$ relative to that of NaO$_2$ would increase the
difference in overpotentials in operando conditions even further than the difference caused by CO$_2$.

IV. Conclusion

The effect of CO$_2$ contamination on growth/depletion pathways and overpotentials on stepped surfaces of NaO$_2$ and Na$_2$O$_2$ discharge products in sodium-air batteries is investigated using density functional theory. Adsorption energies of CO$_2$ at various nucleation sites of stepped (001) NaO$_2$ and (1100) Na$_2$O$_2$ surfaces were determined. Four–step growth/depletion mechanism pathways were considered in this study. All intermediate steps were found to be electrochemical involving either Na or NaO$_2$ ions. Results show that CO$_2$ molecules preferentially bind at the step valley sites of NaO$_2$ and Na$_2$O$_2$ stepped surfaces, with binding energies of $-0.65$ eV and $-2.67$ eV, respectively. Moreover, CO$_2$ increases the overpotentials for NaO$_2$, particularly the discharge potential, which increases from 0.14 V to 0.30 V with small reduction in equilibrium potential with the presence of CO$_2$. Similarly, the discharge (charge) overpotentials for the reaction mechanisms of Na$_2$O$_2$ in the presence of CO$_2$ increased from 0.69 V (0.68 V) to 1.26 V (0.92 V). The presence of CO$_2$ further resulted in a decrease in equilibrium potential from 2.37 to 2.20 V. In general, the DFT calculations show that in both cases, with and without CO$_2$, the cells that discharge with NaO$_2$ exhibits relatively low overpotentials compared to those of Na$_2$O$_2$. The present study finds that small amount of CO$_2$ contamination has the potential to dramatically alter the growth/depletion mechanism pathways, increase the overpotentials and consequently affect the performance of the Na-air battery.

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