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Published in:
Journal of Chemical Physics

Link to article, DOI:
[10.1063/1.5141931](https://doi.org/10.1063/1.5141931)

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Benti, N. E., Mekonnen, Y. S., Christensen, R., Tiruye, G. A., García Lastra, J. M., & Vegge, T. (2020). The effect of CO₂ contamination in rechargeable non-aqueous sodium–air batteries. *Journal of Chemical Physics*, 152(7), [074711]. <https://doi.org/10.1063/1.5141931>

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Cite as: J. Chem. Phys. **152**, 074711 (2020); <https://doi.org/10.1063/1.5141931>

Submitted: 09 December 2019 . Accepted: 04 February 2020 . Published Online: 19 February 2020

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Submitted: 9 December 2019 • Accepted: 4 February 2020 •

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Note: This paper is part of the JCP Special Topic on Interfacial Structure and Dynamics for Electrochemical Energy Storage.

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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 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 (1100) 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 from 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.

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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.¹⁻³ However, the capacity offered by the current state-of-the-art Li-ion technology is too low to solve the increasing demands.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-O₂/air batteries).⁴⁻⁷

Metal-air batteries have higher theoretical specific energies than existing rechargeable batteries including Li-ion batteries. Although metal-air batteries are promising, there are several scientific and technical challenges that must be addressed before commercialization. These include low accessible capacity,⁸ poor conductivity and rechargeability,^{7,9-13} instability of electrodes,¹⁴⁻¹⁷ electrolytes,¹⁸ and salts,^{19,20} and high sensitivity to trace gases.²¹⁻²⁶

Despite its lower capacity and potential than the Li-O₂ battery, 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) and high electrical energy efficiency

(90%). Na–O₂ batteries can be operated over multiple cycles with chemical reversibility.^{27–31} Additionally, sodium is more abundant and cheaper than lithium.^{8,27–31}

In Na–O₂ batteries, depending on the electrolyte used and other experimental conditions, different discharge products have been reported such as sodium superoxide (NaO₂),^{6,9,27,29,32,33} sodium peroxide (Na₂O₂),^{34,35} sodium carbonate (Na₂CO₃),²⁸ hydrated sodium peroxide (Na₂O₂•2H₂O),^{36,37} and sodium hydroxide (NaOH).³⁴ However, sodium peroxide (Na₂O₂)^{34,35} and sodium superoxide (NaO₂)^{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 NaO₂ can be decomposed with low charging overpotentials (~100 mV),^{9,27,29} while decomposition of Na₂O₂ exhibits large overpotentials (>1.3 V).³⁴ In addition to the high overpotential, poor rechargeability (<10 cycles) has been observed for battery cells in which Na₂O₂ is formed. Many of the drawbacks are similar to those observed in the Li–O₂ system.²⁹

A computational study by Kang *et al.*³⁸ shows that NaO₂ is more stable than Na₂O₂ at the nanoscale level (up to 5 nm), whereas bulk Na₂O₂ is thermodynamically stable under standard conditions (in agreement with experimental observations). Moreover, a combined experimental and computational study revealed that bulk NaO₂ is thermodynamically stable up to a temperature of 120 K, while bulk Na₂O₂ is thermodynamically stable above 120 K.⁶ Kinetic studies showed that the overpotentials for growth/depletion of Na₂O₂ were significantly larger than those for NaO₂.

Additional insight into the growth/depletion mechanisms of discharge products is desired in the development. The previous computational work by Mekonnen *et al.*⁶ showed that steps on reconstructed (001) NaO₂ and (1100) Na₂O₂ 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 (Li₂O₂/LiO₂) and carbon containing species in the cell. The main sources of carbon in metal–air batteries are trace gases such as CO and CO₂,³⁹ graphite,¹⁵ and decomposition of aprotic electrolytes.¹⁸ The parasitic reactions lead to carbonate accumulation at the C–Li₂O₂ and Li₂O₂–electrolyte interfaces.^{15,40} These carbonate species are responsible for a large potential increase during recharge and a vast decrease in exchange current density. Adsorption of CO₂ and sulfur containing compounds on oxide surfaces of the Li–O₂ battery could very well dictate the electrochemical growth mechanism.^{23,41} The formation of Na₂O₂ in the solution-based mechanism is found to be suppressed in high DN-electrolytes such as dimethoxyethane (DME) and dimethyl sulfoxide (DMSO). However, studying the effect of electrolytes by explicitly adding electrolytes into 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 CO₂ contamination in Na–air batteries. Among air contaminants, CO₂ is the most critical due to its high solubility in aprotic electrolytes and high reactivity with NaO₂ and Na₂O₂ to form an insulating material containing carbonate species, which requires high overpotentials to decompose.

Herein, we investigate the effect of CO₂ contamination on growth mechanisms on stepped (001) NaO₂ and (1100) Na₂O₂ 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 CO₂ 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} using 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 functional⁴⁹ was used as it, albeit its inability to properly capture some features of Na_xO₂ 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)NaO₂ and (1100) Na₂O₂ 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 the 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) NaO₂ stepped surface (with *Pa*3 space group), we used a supercell consisting of a 60–72 atoms slab. The supercell was sampled with 2 × 4 × 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 NaO₂. A previous theoretical study reported the ferromagnetic phase to be more stable than the antiferromagnetic phase by 15 meV per formula unit.⁵⁴ The Na₂O₂ growth/depletion mechanism with and without CO₂ was studied on the stepped (1100) surface of Na₂O₂ in the *P62m* space group. The supercell consisted of a 88–96 atoms slab. k-points were sampled with a 2 × 2 × 1 Monkhorst–Pack mesh. For both surfaces, approximately 20 Å spacing was 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 structural optimization, all the calculations were continued until all forces are less than 0.03 eV/Å. Four formula units of NaO₂ and two formula units of Na₂O₂ were added to the slab systems to examine the growth mechanisms. These additions would, in absence of CO₂, correspond to a reforming of the initial surface termination.

Similar to the lithium electrode approach used for Li–air batteries,^{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 (Na ↔ Na⁺ + e[−]). The free energy change of the reaction is shifted by −*neU* at an applied bias *U*, where *n* is the number of electrons transferred. At a given applied potential, the change in free energy (Δ*G*) between two consecutive intermediates/steps can be calculated as

$$\Delta G_{i,U} = \Delta G_i - eU. \quad (1)$$

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 the last to become downhill for the charging reaction and thus determines the limiting charge potential (U_{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 $U_o = \Delta G/ne$. 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 *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–O₂ 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 by⁵⁸

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

where $E(\text{NaCl})$ and $E(\text{Cl}_2)$ are the calculated energies per formula unit of NaCl and Cl₂, 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:

$$E(X) = E_X^{\text{DFT}} + \text{ZPE}(X) + \int_0^T C_p dT(X), \quad (3)$$

where E_X^{DFT} 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 the work of Christensen *et al.*,⁵⁸ an energy correction was applied to O₂ (g), which, otherwise, is very difficult to correctly describe within DFT. In the computational approach used here, the optimal energy correction of O₂ is -0.33 eV. Hence, a corrected energy per formula unit of O₂ was calculated according to the following equation:

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

The enthalpies of formation of NaO₂ and Na₂O₂ using the energy corrected O₂ and sodium chloride (NaCl) references are thus given as ($x = 1$ for NaO₂ and $x = 2$ for Na₂O₂)

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

or

$$\Delta H'^{\text{NaCl}}(\text{Na}_x\text{O}_2) = E(\text{Na}_x\text{O}_2) - x * \left[E(\text{NaCl}) - \frac{1}{2}E(\text{Cl}_2) - \Delta H_{\text{NaCl, exp}} \right] - E^{\text{Corr}}(\text{O}_2). \quad (5)$$

The free energies of NaO₂ and Na₂O₂ are calculated as

$$\Delta G^{\text{NaCl}}(\text{Na}_x\text{O}_2) = \Delta H'^{\text{NaCl}}(\text{Na}_x\text{O}_2) - \{T\Delta S(\text{Na}_x\text{O}_2) - T\Delta S(\text{O}_2) - x * T\Delta S(\text{Na})\}, \quad (6)$$

where $T\Delta S$ is the entropy at standard temperature and pressure (STP). The entropy for solid phases, i.e., Na metal, NaO₂, and Na₂O₂, were, for simplicity, assumed to be identical to the entropy in bulk crystals. The entropy for O₂ in the gas phase [$T\Delta S(\text{O}_2)$] is 0.63 eV.

The CO₂ adsorption free energies (G_{ads}) on surfaces of NaO₂ and Na₂O₂ were calculated using the following equation:

$$G_{\text{ads}} = E_{\text{ads}} + \text{ZPE} - TS. \quad (7)$$

The CO₂ adsorption energies (E_{ads}) were calculated by subtracting the DFT energies of the reactants from the energy of the product using the following equation:

$$E_{\text{ads}} = E(\text{CO}_2 @ \text{Na}_x\text{O}_2) - [E(\text{Na}_x\text{O}_2) + E(\text{CO}_2)]. \quad (8)$$

The change in entropic energy of CO₂ is approximated by the entropy of the gaseous CO₂ used as reference [$TS(\text{CO}_{2(g)}) = 0.64$ 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 CO₂, which is expectedly small. ZPE is calculated for the adsorption sites by comparing the zero point vibrational energy of gaseous CO₂ and an O₂ dimer on the surface with the carbonate species formed during adsorption. These will, to a large extent, offset each other such that the largest (absolute) value observed for ΔZPE 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 DMSO⁶⁰ to assess the solvation effect on gaseous species and select adsorption geometries. Solvation was found to destabilize CO₂ adsorption by less than 0.15 eV with 0.09 eV of the destabilization originating from the stabilization of the CO₂ reference state.

Identification of a solution based reaction mechanism as an alternative to the here examined growth reaction also requires consideration of the electrolyte. The reaction free energies of superoxide ions with Li⁺, Na⁺, and CO₂ 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 to be significantly more prone to react with alkali ions than CO₂, which itself is more stabilized by adsorption than reaction with superoxide. Thus, we do not expect that systematic inclusion of the 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 CO₂ molecules at different sites were calculated to identify the preferred site for CO₂ adsorption. The sites with strong adsorption energies were identified on both NaO₂ and Na₂O₂ stepped surfaces. Second, the growth/depletion pathways of NaO₂ and Na₂O₂ were investigated. It should be remarked that we only consider the adsorption of a single CO₂ molecule in the model system, i.e., possible interaction between close range CO₂ adsorbents is not considered. We are thus restricted from examining the effect of high CO₂ concentrations. With the used model structures and computational unit cells, we are also unable to determine the effect of very small CO₂ concentrations.

A. CO₂ adsorption energies on the surfaces of NaO₂ and Na₂O₂

The binding energies of a single CO₂ molecule at various nucleation sites (see Fig. 1) on NaO₂ and Na₂O₂ surfaces were investigated, and the corresponding adsorption energies are presented in Table I. It shows that CO₂ preferentially binds at the left step valley site of the (001) NaO₂ surface with a binding energy of -0.65 eV [see Figs. 1(a) and 1(b)] forming Na_{*n*}CO₃-like species. Similarly, for the stepped (1100) Na₂O₂ surface, CO₂ is favorably adsorbed

at both the front (B') and back (E') step valley sites with binding energies of -2.67 eV and -2.57 eV, respectively. Moreover, CO₂ is weakly adsorbed at the terrace sites of both surfaces compared to the binding energies of front and back step valley sites of Na₂O₂ (see Table I). Comparatively, the adsorption energy of a CO₂ molecule is 3–4 times stronger on the stepped valley on Na₂O₂ surfaces than on stepped NaO₂ and Li₂O₂²³ surfaces.

B. Effect of CO₂ contamination on NaO₂ growth/depletion mechanisms

In the following, the effect of CO₂ poisoning on the NaO₂ growth/depletion mechanisms by adsorbing CO₂ at the step valley site is analyzed [Fig. 2(b)]. 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 NaO₂[•] species) and chemical (involving O₂ species) reaction steps were taken into account. The thermodynamically favorable path (i.e., the lowest overpotential path) was determined after CO₂ adsorption. The first intermediate step in the growth mechanism was found to be the addition of a NaO₂ species at the

FIG. 1. (a) CO₂ adsorption at various sites of the stepped (001) NaO₂ surface. A—step ridge, B—left step valley, C—right step valley, D—step kink, and E—step terrace. (b) CO₂ adsorption at various sites of the stepped (1100) Na₂O₂ surface. A'—front terrace, B'—front step valley, C'—top front terrace, D'—top back terrace, and E'—back step valley. Na, O, and C atoms are shown in purple, red, and yellow, respectively. CO₂ adsorption on both surfaces form Na_{*n*}CO₃-like species, and in the formation of CO₃²⁻, the sources of oxygen atoms are from CO₂ (green) and surfaces (blue).

TABLE I. Adsorption energies (G_{ads}) of a CO₂ molecule on some selected sites of stepped (001) NaO₂ and (1100) Na₂O₂ surfaces (sites are shown in Fig. 1). Boldface indicates the preferential binding energy.

(001) NaO ₂			(1100) Na ₂ O ₂	
Species	Site	G_{ads} (eV)	Site	G_{ads} (eV)
CO ₂	Step ridge (A)	-0.12	Front bottom terrace (A')	-0.95
	Left step valley (B)	-0.65	Front step valley (B')	-2.67
	Right step valley (C)	-0.60	Top front terrace (C')	-2.08
	Step kink (D)	-0.05	Top back terrace (D')	-0.54
	Step terrace (E)	-0.61	Back step valley (E')	-2.57

FIG. 2. Stepped NaO_2 (001) surface before and after adsorption of a CO_2 molecule and the four steps of NaO_2 growth during discharge. (a) Pure stepped NaO_2 surface. (b) CO_2 adsorbs to the step valley site. (c) 1st NaO_2 , (d) 2nd NaO_2 , (e) 3rd NaO_2 and (f) 4th NaO_2 adsorb to the surface completing the growth of four NaO_2 formula units. Na and O atoms are shown in purple and red, respectively. Deposited atoms C, Na, and O are shown in yellow, blue, and green.

site illustrated in Fig. 2(c) (bottom left site). The second intermediate step was again the adsorption of a NaO_2 species [Fig. 2(d)]. It is identified as the potential limiting step for charging. The third and fourth intermediate steps, Figs. 2(e) and 2(f), were the adsorption of two NaO_2 species across the two NaO_2 species previously adsorbed, respectively. The fourth step yields the lowest potential of the reaction pathway in the presence of CO_2 .

As it can be seen in Fig. 3, the reaction pathways and the potentials were altered by the presence of CO_2 gas in the system. In the absence of CO_2 , the first and fourth steps were identified as the steps limiting the discharge and charge potentials, respectively.⁶ The carbonate species get embedded within the NaO_2 structure.

The effective equilibrium potential on a pristine stepped NaO_2 surface has previously been calculated to be 2.34 V (experimental

value, $U_{0,\text{Exp}} = 2.27 \text{ V}$),⁶³ which is reduced to 2.28 V in the presence of CO_2 . In the presence of CO_2 , overpotentials increase from 0.14 V to 0.30 V during discharging and from 0.19 V to 0.31 V during charging. Although increased, the overpotentials in the presence of CO_2 on NaO_2 are still less than the overpotentials previously calculated for pristine Na_2O_2 .⁶ As shown in Fig. 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).

It is plausible that at higher CO_2 concentrations, the effect on overpotentials and capacity will be larger as it is the case for Li-air batteries.^{15,23}

C. Effect of CO_2 contamination on Na_2O_2 growth/depletion mechanisms

The effect of CO_2 contamination on the Na_2O_2 growth/depletion mechanisms was studied with CO_2 adsorbed at the front step valley site [Fig. 4(b)] of the initial surface structure. The reaction mechanism yielding the lowest theoretical overpotential has been determined. As illustrated in Fig. 4 and the free energy diagram in Fig. 5, the mechanisms are four-step reaction mechanisms. On the stepped (1100) Na_2O_2 surface, all reaction steps are electrochemical and involve either Na^* or NaO_2^* added to/removed from the step surface successively to grow/deplete two formula units of Na_2O_2 .

In the presence of CO_2 , the addition of NaO_2 species at the site illustrated in Fig. 4(c) is found to be the preferred initial intermediate step for the growth reaction mechanism. The reaction is followed by the addition of another NaO_2 species at the top right site [Fig. 4(d)] 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_2O_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

FIG. 3. Calculated free energy diagram for a four step growth/depletion mechanism for a stepped (001) NaO_2 surface with and without adsorbed CO_2 .

FIG. 4. Stepped (1100) Na_2O_2 surface before and after adsorption of CO_2 and Na_2O_2 growth during discharge. (a) Pure stepped Na_2O_2 surface. (b) CO_2 adsorbs to the step valley site forming a $\text{Na}\dots\text{nCO}_3$ type complex. [(c) and (d)] NaO_2 species consecutively adsorbed followed by the addition of Na species at (e) and (f) to the surface completing growth of two Na_2O_2 formula units. Na and O atoms are shown in purple and red. C, Na, and O atoms (deposited) are shown in yellow, blue, and green.

the discharge potential, which is smaller than that of the pure system [see Figs. 4(e), 4(f), and 5]. The full growth mechanism is completed with the formation of two formula units of Na_2O_2 at the front of the stepped surface.

Unlike NaO_2 , the presence of CO_2 on a Na_2O_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, $U_{0,\text{Exp}} = 2.33 \text{ V}$ ⁶³). In both cases, an O_2 ion (peroxide in Na_2O_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_2O_2 . In NaO_2 , CO_3^{2-} will occupy

an O_2^{2-} site with a moderate distortion to the local structure. In Na_2O_2 , it will occupy a Na site with a severely undercoordinated Na adsorbed near to it. Thus, an explanation for the larger change in equilibrium potential caused by CO_2 for Na_2O_2 than for NaO_2 could be that the density of NaO_2 is lower than that of Na_2O_2 . Carbonate can thus fit into the NaO_2 crystal structure, while it cannot in Na_2O_2 .

In the presence of CO_2 , 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 Fig. 4 and from right to left in Fig. 5]. In the presence of CO_2 , the growth/depletion pathways, as well as the limiting discharge and charge potentials, have changed compared with the pristine Na– O_2 system.⁶

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_2O_2 . According to GW calculations, NaO_2 and Na_2O_2 are insulating materials with bandgaps of 5.30 eV and 6.65 eV, respectively.⁵⁴ Therefore, the cathode surface is passivated when NaO_2 and Na_2O_2 are deposited during the discharging process and electrons cannot reach the surface, leading to the so-called “sudden death” of the battery. Similar to earlier studies on Li_2O_2 ,^{64,65} Yang and Siegel⁵⁴ identified hole polarons (localized on O_2 dimers) and negative sodium vacancies as the main charge carriers in Na_2O_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_2O_2 .⁵⁴ The smaller conductivity in Na_2O_2 relative to that of NaO_2 would increase the difference in overpotentials under operando conditions even further than the difference caused by CO_2 .

FIG. 5. Calculated free energy diagram for the four step discharge/charge mechanism on a stepped (1100) Na_2O_2 surface with and without adsorbed CO_2 .

IV. CONCLUSION

The effect of CO₂ contamination on growth/depletion pathways and overpotentials on stepped surfaces of NaO₂ and Na₂O₂ discharge products in sodium–air batteries is investigated using density functional theory. Adsorption energies of CO₂ at various nucleation sites of stepped (001) NaO₂ and (1100) Na₂O₂ 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 NaO₂ ions. Results show that CO₂ molecules preferentially bind at the step valley sites of NaO₂ and Na₂O₂ stepped surfaces, with binding energies of −0.65 eV and −2.67 eV, respectively. Moreover, CO₂ increases the overpotentials for NaO₂, particularly the discharge potential, which increases from 0.14 V to 0.30 V with small reduction in equilibrium potential with the presence of CO₂. Similarly, the discharge (charge) overpotentials for the reaction mechanisms of Na₂O₂ in the presence of CO₂ increased from 0.69 V (0.68 V) to 1.26 V (0.92 V). The presence of CO₂ further resulted in a decrease in equilibrium potential from 2.37 V to 2.20 V. In general, the DFT calculations show that in both cases, with and without CO₂, the cells that discharge with NaO₂ exhibit relatively low overpotentials compared to those of Na₂O₂. The present study finds that small amount of CO₂ 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.

ACKNOWLEDGMENTS

The authors acknowledge support from the thematic research project (Project Nos. TR/012/2016 and VPRIT/PY-026/2018/10) funded by Addis Ababa University. N. E. Benti would like to acknowledge Jigjiga University for sponsorship.

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