Communication: The influence of CO2 poisoning on overvoltages and discharge capacity in non-aqueous Li-Air batteries

Mekonnen, Yedilfana Setarge; Knudsen, Kristian Bastholm; Mýrdal, Jón Steinár Garðarsson; Younesi, Reza; Højberg, Jonathan; Hjelm, Johan; Norby, Poul; Vegge, Tejs

Published in:
Journal of Chemical Physics

Link to article, DOI:
10.1063/1.4869212

Publication date:
2014

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

Link back to DTU Orbit

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Communication: The influence of CO2 poisoning on overvoltages and discharge capacity in non-aqueous Li-Air batteries

Yedifana S. Mekonnen, Kristian B. Knudsen, Jon S. G. Mýrdal, Reza Younesi, Jonathan Højberg, Johan Hjelm, Poul Norby, and Tejs Vegge

Citation: The Journal of Chemical Physics 140, 121101 (2014); doi: 10.1063/1.4869212
View online: http://dx.doi.org/10.1063/1.4869212
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/140/12?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Ideal design of textured LiCoO2 sintered electrode for Li-ion secondary battery
APL Mat. 1, 042110 (2013); 10.1063/1.4824042

Charging-induced defect formation in Li x CoO2 battery cathodes studied by positron annihilation spectroscopy
Appl. Phys. Lett. 102, 151901 (2013); 10.1063/1.4801998

First-principles study of the oxygen adsorption and dissociation on graphene and nitrogen doped graphene for Li-air batteries

Communications: Elementary oxygen electrode reactions in the aprotic Li-air battery

Improvement of discharge capacity of LiCoO 2 thin-film cathodes deposited in trench structure by liquid-delivery metalorganic chemical vapor deposition
Appl. Phys. Lett. 82, 3345 (2003); 10.1063/1.1571958
Communication: The influence of CO₂ poisoning on overvoltages and discharge capacity in non-aqueous Li-Air batteries

Yelidifana S. Mekonnen,1,2 Kristian B. Knudsen,1 Jon S. G. Mýrdal,1 Reza Younesi,1 Jonathan Højberg,1 Johan Hjelm,1 Poul Norby,1 and Tejs Vegge1, a)
1Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark
2Center for Atomic-scale Materials Design, Technical University of Denmark, DK-2800 Lyngby, Denmark
(Received 31 January 2014; accepted 11 March 2014; published online 24 March 2014)

The effects of Li₂CO₃ like species originating from reactions between CO₂ and Li₂O₂ at the cathode of non-aqueous Li-air batteries were studied by density functional theory (DFT) and galvanostatic charge-discharge measurements. Adsorption energies of CO₂ at various nucleation sites on a stepped (1100) Li₂O₂ surface were determined and even a low concentration of CO₂ effectively blocks the step nucleation site and alters the Li₂O₂ shape due to Li₂CO₃ formation. Nudged elastic band calculations show that once CO₂ is adsorbed on a step valley site, it is effectively unable to diffuse and impacts the Li₂O₂ growth mechanism, capacity, and overvoltages. The charging processes are strongly influenced by CO₂ contamination, and exhibit increased overvoltages and increased capacity, as a result of poisoning of nucleation sites: this effect is predicted from DFT calculations and observed experimentally already at 1% CO₂. Large capacity losses and overvoltages are seen at higher CO₂ concentrations. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4869212]

I. INTRODUCTION

As energy storage needs are growing rapidly, there is also an increase in research into high energy density materials for energy storage. Significant attention has been given to metal-air batteries, particularly Li-air batteries, as future environmentally friendly high energy density storage for vehicles, where the capacity offered by existing Li-ion technology is too low to solve the increasing demands on batteries.1 The Li₂O₂ couple is particularly attractive and could have ~5–10 times greater specific energies than currently available Li-ion batteries, though there are severe scientific and technical challenges that need to be addressed.2,3 Such as a clear understanding of the Li₂O₂ growth mechanisms, transport processes, interfacial phenomena, air impurities, and stability of the key components are vital parts of non-aqueous rechargeable Li-air cell research.4

As first reported by Abraham and Jiang in 1996, the Li-O₂ battery with aprotic solvent is shown to be rechargeable, when Li₂O₂ is formed during discharge at the cathode.5 Detailed understanding of the Li₂O₂ growth mechanism is important to solve the problem associated with the practical limitations of the battery. Previous theoretical works by Hummelshøj et al.6 and Radin et al.7,8 showed that steps on a reconstructed (1100)surface could act as nucleation sites for low discharge overvoltage and facets such as (0001), (1100), and (1120) have similar surface energies. Hummelshøj et al.9 have also shown that surfaces are potential dependent and vary during discharge and charge. According to GαW0 calculations, both Li₂O₂ and Li₂CO₃ are insulating materials with wide band gap of 4.9 and 8.8 eV, respectively.10–12 Therefore, as these materials deposit at the cathode surface during discharge they will limit the electronic conduction and lead to sudden death during discharge within 5–10 nm thick Li₂O₂ deposits.13,14 However, recent DFT calculations found that hole and electron polaronic transports at the surface and in bulk Li₂O₂ and Li₂CO₃ can take place. Using a PBE+U (Hubbard-corrected Perdew–Burke–Ernzerhof) exchange correlation functional, Garcia-Lastra et al.11 revealed that the hole polarons have higher mobility than electron polarons and Li₂CO₃ exhibits lower conduction than Li₂O₂. Recent works by Luntz et al. have shown that hole tunneling should dominate and polaronic transport is only expected to be significant in Li₂O₂ at elevated temperatures and low current densities.15,16

Li₂CO₃ like crystalline species are formed by parasitic side reactions between the Li₂O₂ or LiO₂ and carbon sources from air impurities such as CO and CO₂ gases,17 the graphite itself, or the decomposition of aprotic electrolytes. Younesi et al.18,34 reported the degradation of various electrolytes by Li₂O₂ and documented Li₂CO₃ as a decomposition product from aprotic electrolytes. Likewise, McCloskey et al.3 have shown that carbonates accumulate at the C-Li₂O₂ and Li₂O₂-electrolyte interfaces and are responsible for a large potential increase during recharge and a huge decrease in exchange current density. This makes growth of Li₂O₂ on Li₂CO₃ an equally important process to investigate, but this is beyond the scope of this communication. As reported by Siegfried et al.19 and Myrdal and Vegge20 adsorption of sulfur containing compounds on oxide surfaces could also control the electrochemical growth mechanism. Adsorbed species at surfaces can potentially block the nucleation sites, and therefore, alter the growth directions, overvoltages, and capacities.

In this communication, we address the influence of CO₂ contamination on the Li₂O₂ growth mechanism, discharge/charge overvoltages, and capacity in non-aqueous
Li-air batteries using density functional theory (DFT) and galvanostatic measurements. Among other air contaminants, CO$_2$ is the most critical subject due to its high solubility in aprotic electrolytes and high reactivity with Li$_2$O$_2$ to form an insulating material Li$_2$CO$_3$.

II. COMPUTATIONAL RESULTS AND ANALYSIS

DFT$^{21–23}$ as implemented in the GPAW (grid-based projector-augmented wave method) code$^{24}$ is used to perform the presented calculations through the atomic simulation environment (ASE). GPAW is built on real space grids and non-valence electrons are described by PAW (projector augmented-wave method). Electron exchange and correlation is approximated by the revised Perdew–Burke–Ernzerhof (RPBE) functional. The stepped (1 ¯100) Li$_2$O$_2$ surface with a super cell consisting of a 56–64 atoms slab with a 18 Å vacuum layer between periodic images along the z-axis, see Fig. S1 in the supplementary material. Since the oxygen rich (0001) facet will also be exposed, in particular under charging conditions, and subsequent investigations should be performed to analyze the detailed mechanisms of CO$_2$ bonding to this facet. Recent computational DFT results for SO$_2$ adsorption on stepped (0001) and (1100) surfaces do, however, show preferential bonding to the (1100) facets, which is investigated here. The k-points are sampled with a (4,4,1) Monkhorst-Pack mesh and 0.15 grid points is used. Atomic energy optimization calculations are performed until all forces are less than 0.01 eV/Å. Energy barriers are calculated by the climbing image nudged elastic band (CINEB) method.$^{29–31}$

Adsortion energies of CO$_2$ at various nucleation sites on a stepped (1100) Li$_2$O$_2$ surface were determined, see Table I. CO$_2$ binds preferentially at the step valley site and weakly binds at the step ridge site. NEB calculations show that once CO$_2$ is adsorbed at step valley site, it is bound by barriers upwards of 3 eV, see Fig. S2 in the supplementary material. Since the CO$_2$ molecule is required to desorb from the surface prior to re-adsorbing at the step site. The detailed nature of a conversion of adsorbed CO$_2$ to Li$_2$CO$_3$ warrants further investigations, but we find that the adsorption of a single CO$_2$ molecule forms a Li$_3$CO$_3$-type complex (Fig. 1(b)), which could act as a nucleation site for further growth of Li$_2$CO$_3$.

The computational lithium electrode approach is used in the free energy calculations.$^{6,32}$ Defined as, $U = 0$, when bulk Li anode and Li ions in solution (Li$^+$ + e$^-$) are at equilibrium. The free energy change of the reaction is shifted by $-neU$ at an applied bias, where $n$ is the number of transferred electrons; other assumptions are listed in the supplementary material.$^{35}$ As reported by Hummels$øj$ et al., kinks and steps sites of the stepped (1100) Li$_2$O$_2$ surface are favorable nucleation sites for a low overvoltage Li$_2$O$_2$ growth mechanism. The influence of CO$_2$ poisoning on the Li$_2$O$_2$ growth mechanism is studied while CO$_2$ is already adsorbed at step valley site (Fig. 1(b)).

The free energy diagram in Fig. 2 shows a four steps, two formula units Li$_2$O$_2$ growth mechanism on the stepped (1100) Li$_2$O$_2$ surface with and without CO$_2$. The first step in the presence of CO$_2$ is adsorption of LiO$_2$ species (Fig. 1(e)), and which reduces the binding energy by 0.44 V compared to the pure discharge. The next step is the addition of a second LiO$_2$ species (Fig. 1(d)), which is the potential limiting charge step that raises the binding energy by 0.20 V compared to pure Li$_2$O$_2$. This is followed by subsequent additions of two Li (Figs. 1(e) and 1(f)) with relatively small binding energies with respect to a pure discharge. In the pure O$_2$ discharge mechanism, unlike in the presence of CO$_2$, addition of the first Li is the limiting charge potential step. The 2Li$_2$O$_2$ growth at the step surface effectively displaces CO$_2$ from the step to the less stable terrace site.

Hummels$øj$ et al. have reported that the pure Li$_2$O$_2$ growth mechanism follows a 4 steps reaction mechanism, where all reaction steps are electrochemical, similar to what is seen in the presence of CO$_2$. The equilibrium potential can be obtained as $U_0 = -\Delta G/2e$. The effective equilibrium potential on a pure surface becomes 2.73 V (experimental value, $U_{\text{Discharge}} = 2.85$ V), while in the presence of CO$_2$, this is effectively reduced to 2.53 V for the first cycle due to the shift in binding energy of CO$_2$ from a step valley to terrace site. As a result, discharge at other facets may become activate.$^9$ At neutral bias all reaction steps are downhill, but at an applied potential, the free energy difference changes for each step calculated as

$$\Delta G_{i,U} = \Delta G_i - eU.$$  

(1)

The lowest free energy step, $\Delta G_{\text{min}}$, along the reaction path becomes uphill first at an applied potential called limited discharge potential, $U_{\text{Discharge}}$, while the largest free energy step, $\Delta G_{\text{max}}$, that is last to become downhill for the reversed reaction at an applied potential called limited charge potential, $U_{\text{Charge}}$, obtained as

$$U_{\text{Discharge}} = \min \left[ -\Delta G_i/e \right] \text{ and } U_{\text{Charge}} = \max \left[ -\Delta G_i/e \right].$$  

(2)

In the presence (absence) of a single CO$_2$ molecule, this discharge occurs as described in Fig. 1, resulting in $U_{\text{Discharge}} = 2.21 \text{ V (2.66 V)}$, and $U_{\text{Charge}} = 2.97 \text{ V (2.81 V)}$ and the discharge and charge overvoltages in the presence (absence) of CO$_2$ are $\eta_{\text{Discharge}} = 0.31 \text{ V (0.07 V)}$, and $\eta_{\text{Charge}} = 0.44 \text{ V (0.08 V)}$. The calculated 0.44 V overvoltage for charge corresponds to low CO$_2$ concentrations, where only a single CO$_2$ molecule is adsorbed on the Li$_2$O$_2$ step forming a Li$_3$CO$_3$ type complex (see Fig. 1). Here, the charging process follows the same reaction steps as the discharge, but in reverse (from right to left in Fig. 2), i.e., the first two steps are desorption of two Li and followed by desorption of 2 LiO$_2$ species: in total desorbing 2 Li$_2$O$_2$ units from the surface and returning to the configuration in Fig. 1(b). Quantitative agreement with

---

**Table I.** Adsorption energies of CO$_2$ in the gas phase at (1100) Li$_2$O$_2$ surface.

<table>
<thead>
<tr>
<th>Species</th>
<th>Sites</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>Step valley</td>
<td>-0.73</td>
</tr>
<tr>
<td></td>
<td>Terrace valley</td>
<td>-0.21</td>
</tr>
<tr>
<td></td>
<td>Step ridge</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 192.38.67.112 On: Fri, 04 Apr 2014 08:55:28
FIG. 1. Stepped Li$_2$O$_2$ (1100) surface before and after adsorption of CO$_2$ and 4 steps Li$_2$O$_2$ growth pathways during discharge. (a) Pure stepped Li$_2$O$_2$ surface. (b) CO$_2$ adsorbs to step valley site forming a Li$_3$CO$_3$ type complex. (c) 1$^{st}$ LiO$_2$ adsorbs. (d) 2$^{nd}$ LiO$_2$ adsorbs. (e) 1$^{st}$ Li. (f) 2$^{nd}$ Li adsorbs to the surface completing growth of 2 Li$_2$O$_2$ formula units. Atoms labeled as: C (gray), Li (purple), and O (red). Deposited atoms shown as: Li (yellow) and O (green).

experimental overvoltages can therefore only be expected for low concentrations of CO$_2$ (e.g., 1%). For higher CO$_2$ concentrations, the formation of crystalline Li$_2$CO$_3$ would be expected, resulting in significantly larger overvoltages.3

III. EXPERIMENTAL RESULTS AND ANALYSIS

Li-air batteries were constructed using a Swagelok design and assembled inside an Ar-filled glovebox (≤3 ppm O$_2$ and H$_2$O). Each battery contained a 200 μl 1 M LiTFSI (99.95%, Sigma-Aldrich) and 1,2-dimethoxymethane, DME, (H$_2$O < 20 ppm, BASF) electrolyte. Cathodes consisted of P50 AvCarb carbon paper (Fuel cell store), which were sonicated using 2-propanol (99.5%, Sigma-Aldrich) and acetone (≥99.8%, Sigma-Aldrich), introduced into a glovebox where they were rinsed with DME before drying in vacuum at 80°C for 12 h. Cathodes were supported by a 316 steel mesh. A 10 mm diameter lithium foil (99.9%, Sigma-Aldrich) was used as anode. Two Celgard separators 2500 (Celgard) were placed in between the two electrodes. The separators were sonicated in EtOH (99.9%, Sigma-Aldrich), transferred to a glovebox, and rinsed with DME before drying in vacuum at 80°C for 12 h. Experiments were performed using a BioLogic VMP3 Multichannel galvanostat (Bio-Logic, Claux, France). Batteries were operated in two galvanostatic modes: First, at 100 μA (127.3 μA/cm$^2$) where cells were discharged to 2 V and charged to 4.6 V vs. Li$^+/$/Li. Second, at 50 μA (63.6 μA/cm$^2$) using the same potential limits.

To investigate the effect of gaseous CO$_2$, the assembled cells were purged with three different atmospheres: 0/100 CO$_2$/O$_2$, 1/99 CO$_2$/O$_2$, and 50/50 CO$_2$/O$_2$. Three individual batteries were assembled and investigated for each atmosphere and each curve presented in Figs. 3 and 4 is therefore an average of three cells with the equal atmosphere as shown in Fig. S3 in the supplementary material.35 The lowest discharge capacity was observed for the 50% CO$_2$ cells and is likely caused by the high concentration of electrochemically inactive CO$_2$. A similar effect was observed, by Gowda et al.17 for a pure CO$_2$ cell, where the cell potential immediately dropped. It should however be noted that Takechi et al.33 observed, quite to the contrary of our observations, higher discharge capacities up to 70% CO$_2$ with respect to pure O$_2$ cells. Interestingly, a higher discharge capacity was observed for the 1% CO$_2$ cells in respect to the pure O$_2$ cells as shown in Fig. 3 (inset). A possible explanation is the dissolution of Li$_2$CO$_3$ species in DME and/or, as also suggested by Gowda et al., or a change in deposition morphology compared to that deposited in the pure O$_2$ cells as suggested by Myrdal and Vegge.20 Such morphological changes could increase the total electrodeposited layer and lead to higher capacities.

All CO$_2$ cells have higher discharge overvoltages compared to cells with pure O$_2$ at a discharge rate of 127.3 μA/cm$^2$, which may be caused by the blocking of the
absolute nucleation sites by solubilized CO₂, forcing the reactions to follow pathways with higher overvoltages. This effect can even be seen at 1% CO₂, as illustrated in Fig. 3 above. The charge capacity, as seen in Fig. 4 and Fig. S4 in the supplementary material, is very dependent on the CO₂ concentration, with high concentrations limiting charge capacity and thereby the cell reversibly. The 50% CO₂ cells reach the lower potential limit (2.0 V) early, at approximately 35 mAh/g, while 1% CO₂ cells and pure O₂ cells continued until capacities in the range 1150–1600 mAh/g were reached depending on current density. The low charge capacity at high CO₂ contaminations should be attributed to the poor Li-CO₂ electrochemistry, also reported by Gowda et al. The charging overvoltages are a function of both current density and the level of CO₂ contamination. While there is no significant difference in overvoltages between cells charge at 127.3 and 63.6 µA/cm² for 50% CO₂ cells, which again can be attributed to the poor Li-CO₂ electrochemistry. At 127.3 µA/cm², there is an increase in overvoltage of about 0.4 and 0.3 V for 1% CO₂ cells and 0% CO₂ cells, respectively. The general increase in overvoltages with increasing current density can be explained by the Butler-Volmer model, while the larger overvoltage for the 1% CO₂ cells than 0% CO₂ cells is expectedly caused by the formation and oxidation of the carbonate like species (Fig. 1(b)). A second charge at 63.6 µA/cm² shows identical results for 1% and 0% CO₂. This can be ascribed to the evolution of CO₂ observed during the initial charge cycle, where CO₂ is released at 4.5 V, as shown in Fig. S5 in the supplementary material, resulting in residual CO₂ in the electrolyte causing blocking of the step sites in subsequent charging experiments.

IV. CONCLUSIONS

Influences of CO₂ poisoning at a stepped (1100) Li₂O₂ surface in non-aqueous Li-air battery were studied using DFT calculations and cells were characterized by electrochemical charge-discharge measurements. CO₂ preferentially binds at step valley site at the Li₂O₂ surface and the Li₂O₂ growth mechanism consists of four electrochemical steps, following the same sequence for both pure and contaminated systems. Accordingly, the first step of the growth mechanism is the adsorption of two LiO₂ species and followed by addition of two Li to form 2 Li₂O₂ at the cathode surface. For charge in the low CO₂ limit, a similar reaction will occur, but in reverse order.

Low concentrations of CO₂ (1%) effectively block the surface-active nucleation sites and alter the shape and growth directions of Li₂O₂ on the surface; resulting in an increased capacity of the battery at the expense of an increase in the overvoltage in the presence of CO₂. A similar behavior is seen in pure oxygen following charging to 4.5 V, resulting from decomposition reactions. The effective discharge potential is reduced by 0.20 V on a stepped (1100) Li₂O₂ surface, shifting the reaction to alternate nucleation sites. In general, the DFT calculations and experimental results show that the recharging process is strongly influenced by CO₂ contamination, and exhibits significantly increased charging overvoltage, which is observed already with 1% CO₂ contamination, while at 50% CO₂ a large capacity loss is also seen.

ACKNOWLEDGMENTS

The authors acknowledge support of this work from the ReLiable project (Project No. 11-116792) funded by the Danish Council for Strategic Research Programme Commission on Sustainable Energy and Environment.

35 See supplementary material at http://dx.doi.org/10.1063/1.4869212 for Figs. S1–S5.