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

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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 Li2O2 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 Hummelsøj 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. Hummelsøj et al.9 have also shown that surfaces are potential dependent and vary during discharge and charge. According to G0W0 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, García-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 Li2O 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.10 and Myrdal and Vegge19 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, CO₂ is the most critical subject due to its high solubility in aprotic electrolytes and high reactivity with Li₂O₂ to form an insulating material Li₂CO₃.

II. COMPUTATIONAL RESULTS AND ANALYSIS

DFT²¹–²³ as implemented in the GPAW (grid-based projector-augmented wave method) code²⁴ is used to perform the presented calculations through the atomic simulation environment (ASE).²⁵ GPAW is built on real space grids and non-valence electrons are described by PAW (projector augmented-wave method).²⁶,²⁷ Electron exchange and correlation is approximated by the revised Perdew–Burke–Ernzerhof (RPBE) functional.²⁸ The stepped (1100) Li₂O₂ 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.³⁵ Since the oxygen rich (0001) facet will also be exposed, in particular under charging conditions,²⁹ and subsequent investigations should be performed to analyze the detailed mechanisms of CO₂ bonding to this facet. Recent computational DFT results for SO₂ adsorption on stepped (0001) and (1100) surfaces do, however, show preferential bonding to the (1100) facets,³⁰ 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

Adsorption energies of CO₂ at various nucleation sites on a stepped (1100) Li₂O₂ surface were determined, see Table I. CO₂ binds preferentially at the step valley site, 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

<table>
<thead>
<tr>
<th>Species</th>
<th>Sites</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</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>

The lowest free energy step, ΔGₘᵟᵡ, along the reaction path becomes uphill first at an applied potential called limited discharge potential, Uₐₖₜ, while the largest free energy step, ΔGₘᵢₓ, that is last to become downhill for the reversed reaction at an applied potential called limited charge potential, U_chₜ, obtained as

\[ U_{\text{discharge}} = \min \left[ -\frac{\Delta G_i}{e} \right] \text{ and } U_{\text{charge}} = \max \left[ -\frac{\Delta G_i}{e} \right]. \]

In the presence (absence) of a single CO₂ molecule, this discharge occurs as described in Fig. 1, resulting in \( U_{\text{discharge}} = 2.21 \) V (2.66 V), and \( U_{\text{charge}} = 2.97 \) V (2.81 V) and the discharge and charge overvoltages in the presence (absence) of CO₂ are \( \eta_{\text{discharge}} = 0.31 \) V (0.07 V), and \( \eta_{\text{charge}} = 0.44 \) V (0.08 V). The calculated 0.44 V overvoltage for charge corresponds to low CO₂ concentrations, where only a single CO₂ molecule is adsorbed on the Li₂O₂ step forming a Li₃CO₃ 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 LiO₂ species: in total desorbing 2 Li₂O₂ units from the surface and returning to the configuration in Fig. 1(b).
FIG. 1. Stepped Li2O2 (110) surface before and after adsorption of CO2 and 4 steps Li2O2 growth pathways during discharge. (a) Pure stepped Li2O2 surface. (b) CO2 adsorbs to step valley site forming a Li∼3CO3 type complex. (c) 1st LiO2 adsorbs. (d) 2nd LiO2 adsorbs. (e) 1st Li. (f) 2nd Li adsorbs to the surface completing growth of 2 Li2O2 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 CO2 (e.g., 1%). For higher CO2 concentrations, the formation of crystalline Li2CO3 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 O2 and H2O). Each battery contained a 200 μl 1 M LiTFSI (99.95%, Sigma-Aldrich) and 1,2-dimethoxymethane, DME, (H2O < 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 Bio-Logic VMP3 Multichannel galvanostat (Bio-Logic, Claix, France). Batteries were operated in two galvanostatic modes: First, at 100 μA (127.3 μA/cm2) where cells were discharged to 2 V and charged to 4.6 V vs. Li+/Li. Second, at 50 μA (63.6 μA/cm2) using the same potential limits.

To investigate the effect of gaseous CO2, the assembled cells were purged with three different atmospheres: 0/100 CO2/O2, 1/99 CO2/O2, and 50/50 CO2/O2. 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% CO2 cells and is likely caused by the high concentration of electrochemically inactive CO2. A similar effect was observed, by Gowda et al.17 for a pure CO2 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% CO2 with respect to pure O2 cells. Interestingly, a higher discharge capacity was observed for the 1% CO2 cells in respect to the pure O2 cells as shown in Fig. 3 (inset). A possible explanation is the dissolution of Li2CO3 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 O2 cells as suggested by Myrdal and Vegge.20 Such morphological changes could increase the total electrodeposited layer and lead to higher capacities.

All CO2 cells have higher discharge overvoltages compared to cells with pure O2 at a discharge rate of 127.3 μA/cm2, which may be caused by the blocking of the
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35. See supplementary material at http://dx.doi.org/10.1063/1.4869212 for Figs. S1–S5.