Technical University of Denmark

The Influence of CO2 Poisoning on Overvoltages and Discharge Capacity in Non-aqueous Li-Air Batteries

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

Publication date:
2013

Citation (APA):
Mekonnen, Y. S., Knudsen, K. B., Mýrdal, J. S. G., Younesi, R., Højberg, J., Hjelm, J., ... Vegge, T. (2013). The Influence of CO2 Poisoning on Overvoltages and Discharge Capacity in Non-aqueous Li-Air Batteries. Poster session presented at Nordisk Batterikonferens 2013 (NORDBATT), Uppsala, Sweden.

The Influence of CO_2 Poisoning on Overvoltages and Discharge Capacity in Non-aqueous Li-Air Batteries

Yedilfana S. Mekonnen[1,2], Kristian B. Knudsen[1], Jon S. G. Mýrdal[1,2], Reza Younesi[1], Jonathan Højberg[1], Johan Hjelm[1], Poul Norby[1], Tejs Vegge[1,2]

[1]Department of Energy Conversion , Technical University of Denmark, Frederiksborgvej 399 Building 238, DK-4000 Roskilde, Denmark.

[2]Center for Atomic-scale Materials Design and Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark.

Introduction

The Li-O_2 couple is particularly attractive due to its high specific energy , ~5-10 times greater than currently available Li-ion batteries and mainly intended for onboard storage in vehicles.[1] As first reported by Abraham et al. in 1996, the Li-O_2 cell with aprotic solvent is shown to be rechargeable, when Li_2O_2 is formed during discharge.[2] However, Li_2CO_3 is also formed from the parasitic reactions between the Li_2O_2 and aprotic electrolytes, air impurities (e.g. CO_2) and the graphite.[1] Both Li_2O_2 and Li_2CO_3 are insulating materials with wide band gap of 4.9 and 8.8 eV, respectively. Hence, these materials deposit (5-10 nm) limit the conductivity and lead to sudden death.[3]

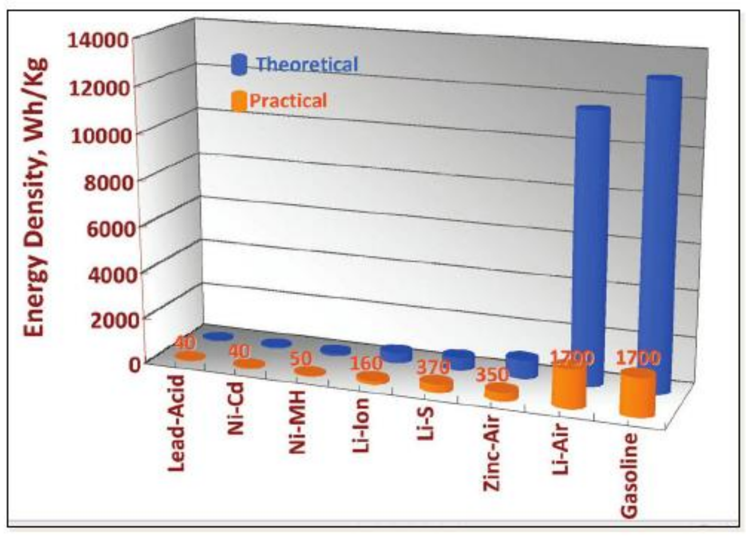

Fig1. Energy densities of M-air wrt Gasoline.

Methods

- ✓ Li-air cells were constructed using a Swagelok design. Each cell contained LiTFSI, DME and P50 cathodes. Experiments were performed using a galvanostat.
- ✓ DFT as implemented in GPAW code[4] via ASE. RPBE approximation is used. The stepped $(1\bar{1}00)$ Li_2O_2 surface with a super cell consisting of a 56-60 atoms slab with 18 Å vacuum layer and (4,4,1) kpoints are used.

Results

- ✓ CO_2 binds preferentially at step sites on the $(1\bar{1}00)$ Li_2O_2 surface and blocks the active nucleation sites.
- ✓ Both DFT and experimental results show that, CO_2 contamination strongly affects the recharging process.
- ✓ Higher overvoltages and large capacity losses are observed at 50 % CO_2.

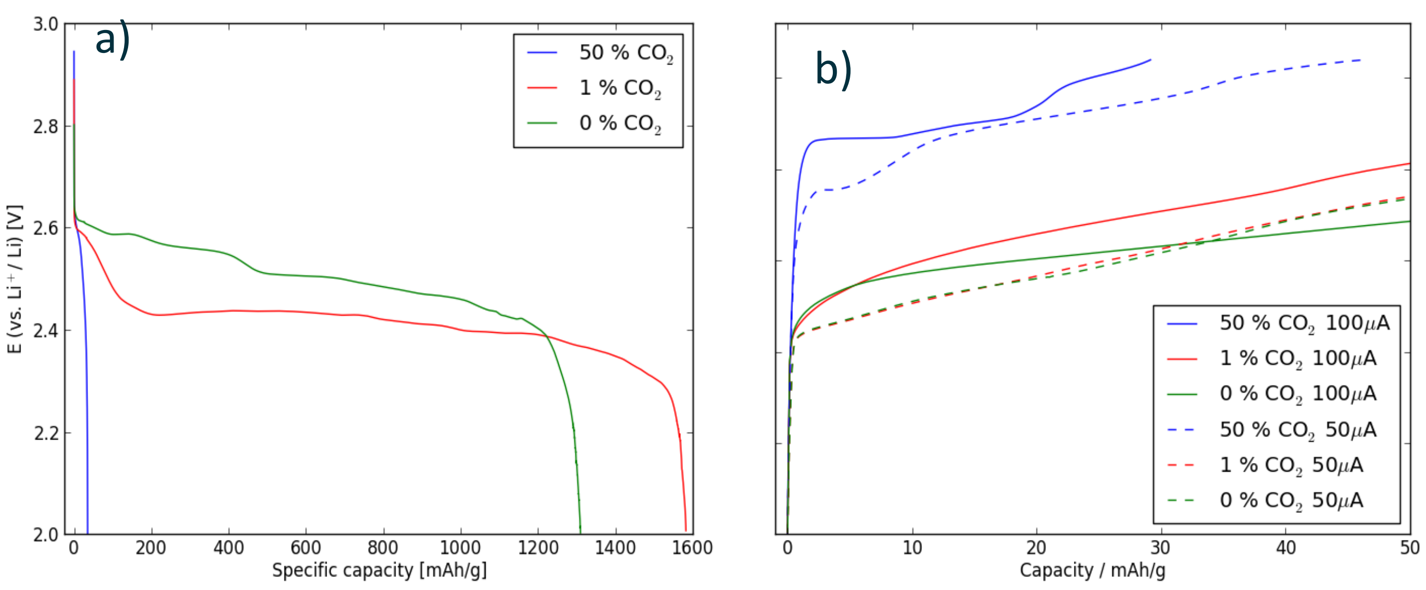

Fig2: a) Discharge, b) Charge curves for pure & CO_2 contaminated cells.

A four step, $2Li_2O_2$, growth mechanism on $(1\bar{1}00)$ Li_2O_2 surface[5] with CO_2

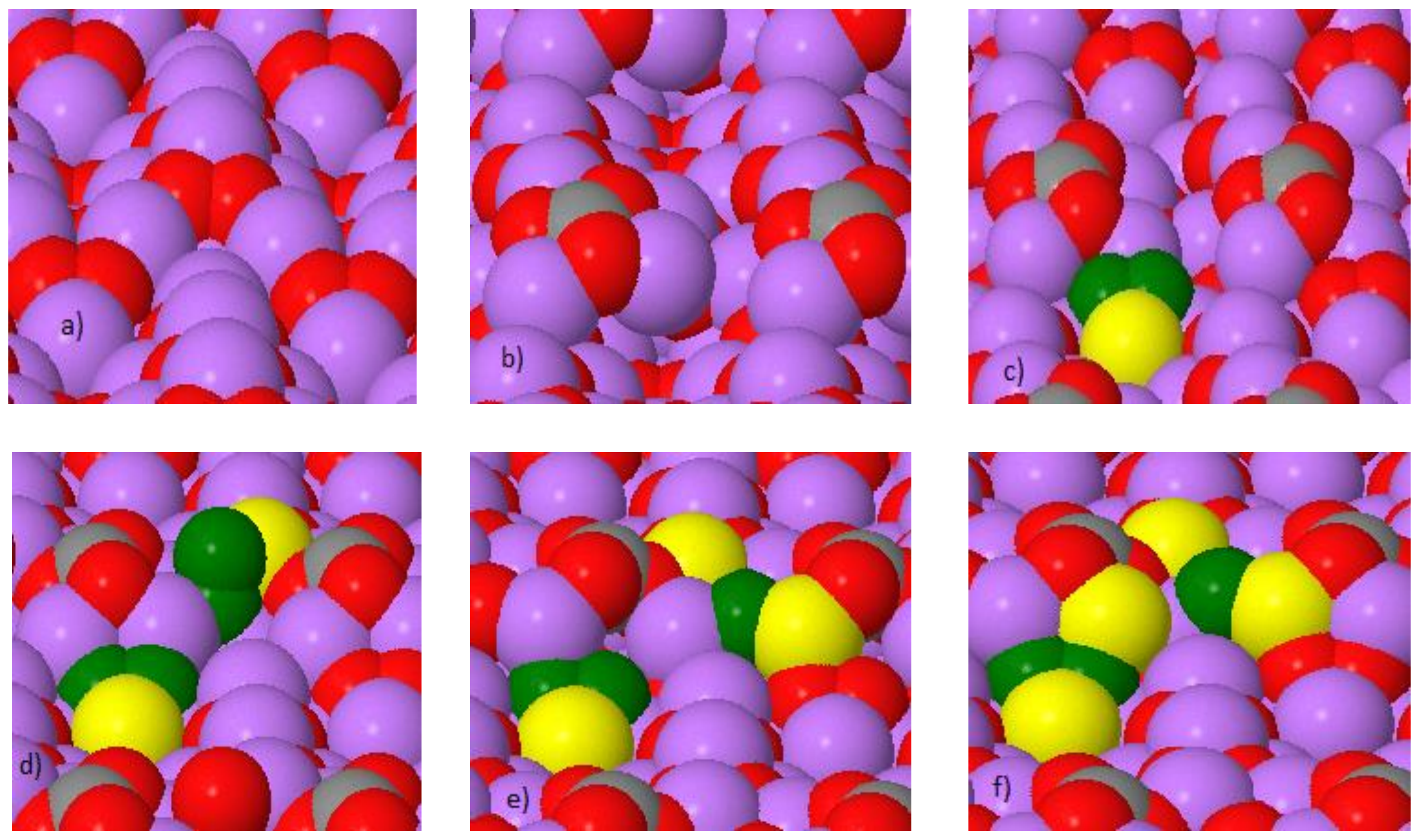

Fig3: a) Stepped Li_2O_2 surface. b) CO_2 adsorbs at step. c) 1st LiO_2 binds. d) 2nd LiO_2 binds. e) 1st Li binds. f) 2nd Li binds to the surface; end up with 2 Li_2O_2 growth.

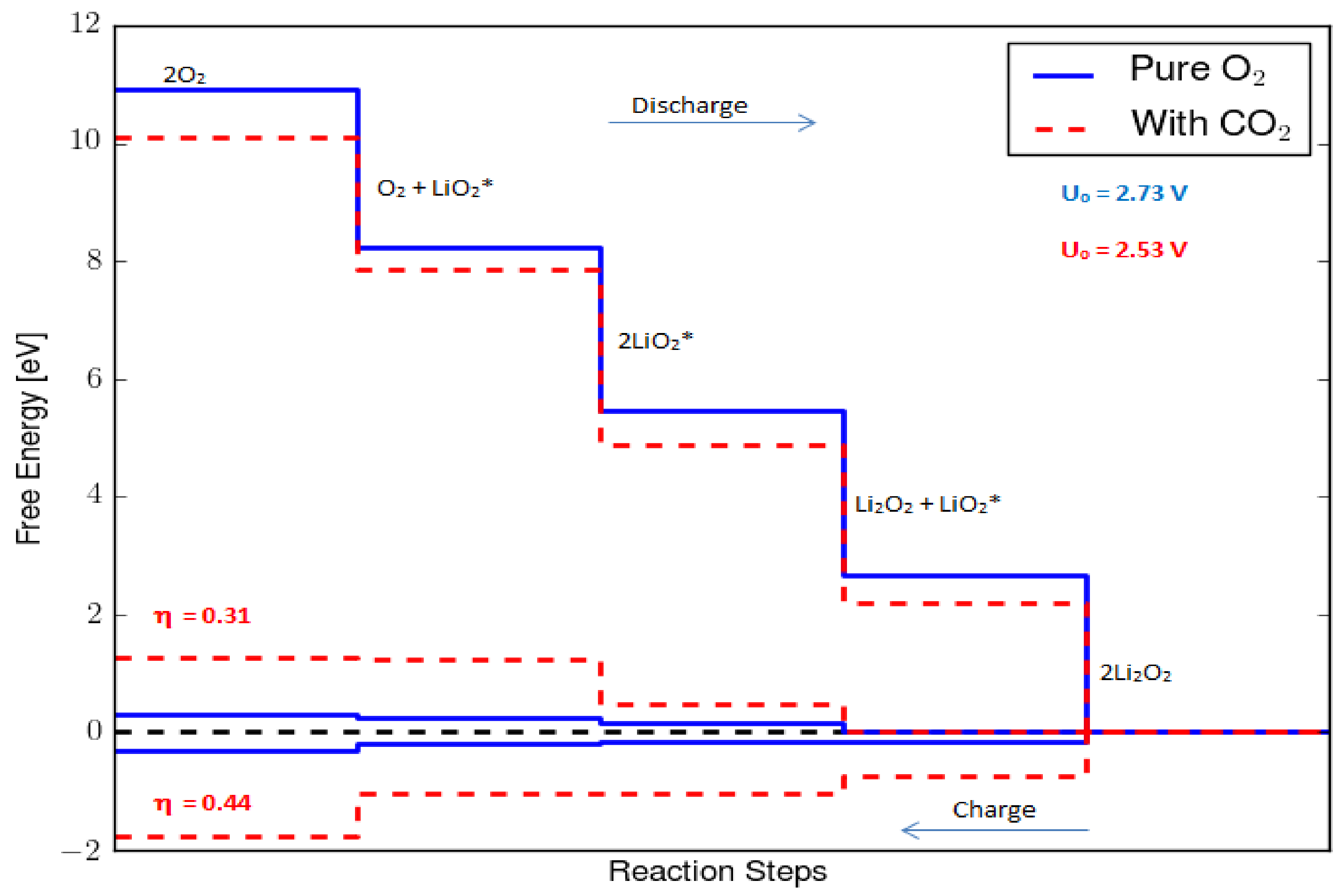

Fig4: Free energy diagrams for discharge mechanism of Li_2O_2 on Cathode surface with and without CO_2.

Conclusions

- ✓ CO_2 is the most critical due to its high solubility in aprotic electrolytes & high reactivity with Li_2O_2 to form Li_2CO_3.
- ✓ CO_2 binds favorably at steps sites on Li_2O_2 surface and once it is adsorbed at the step site, it is unlikely to diffuse elsewhere.
- ✓ The recharging process is strongly influenced by CO_2, and exhibits higher charging overvoltage, which is observed already at 1 % CO_2 while at 50 % CO_2 a large capacity loss is seen.

References

1. McCloskey et al (2012). J. Phys. Chem. Lett., 3, 997−1001.
2. Abraham, K. M.; Jiang, Z., J. Electrochem. Soc. **1996**, 143, 1-5.
3. Gowda et al (2013). Phys. Chem. Lett., 4, 276−279.
4. Enkovaara et al (2010). J. Phys. Condens. Matter, 253202, 253202
5. Hummelshøj et al (2010). J. of Chem. Phys., 132, 071101.

Funded by ReLiable Project

DTU Energy Conversion
Department of Energy Conversion and Storage