

Simulations of lithium-air batteries

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Outline

- New challenges for battery research
- Lithium-ion batteries
- Lithium-air batteries
- Density functional simulations for research on lithium-air batteries

Introduction

- In the next future there will be an increased fraction of energy from renewable sources
- Most of renewable sources of energy are irregular:
Sun, wind, waves,...
- Energy is not harvested when it is available, not when it is needed
- Increased role of energy storage in the energy infrastructure

Energy storage

- Currently, possibilities to store large amounts of electricity are very limited: pumping up water in hydroelectric plants
- Main response today: to adapt production to instantaneous needs: few hours to run on and off a gas power plant
- With renewables, storage will gain importance

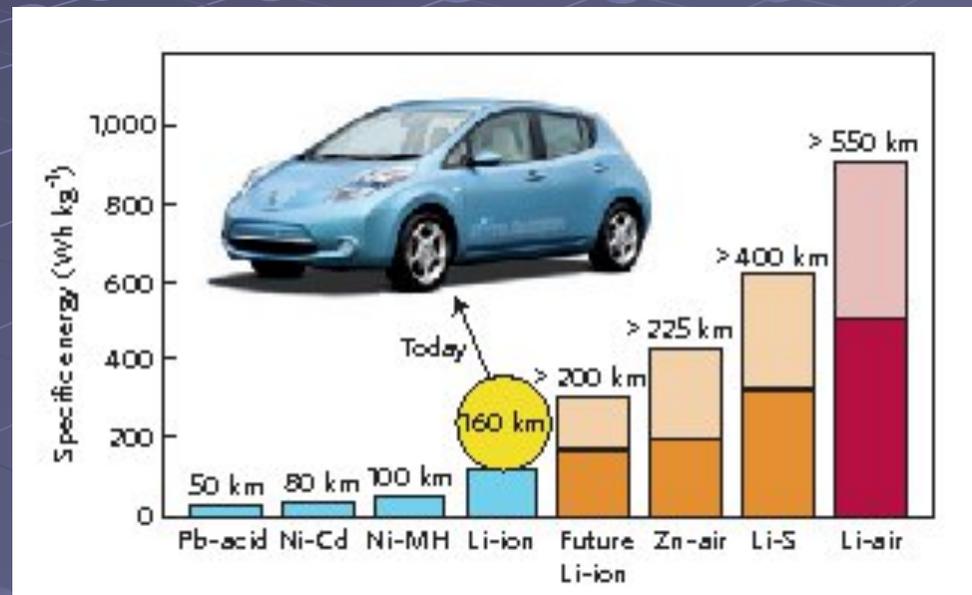
Electric mobility

- Moving away from fossil fuels means also developing electric cars
- Advantages on global scale (independence from limited resources) but also on local scale (less pollution in towns)
- Electric motors are very efficient, BUT the big problem is the battery

Batteries for the automotive sector: problems of existing batteries

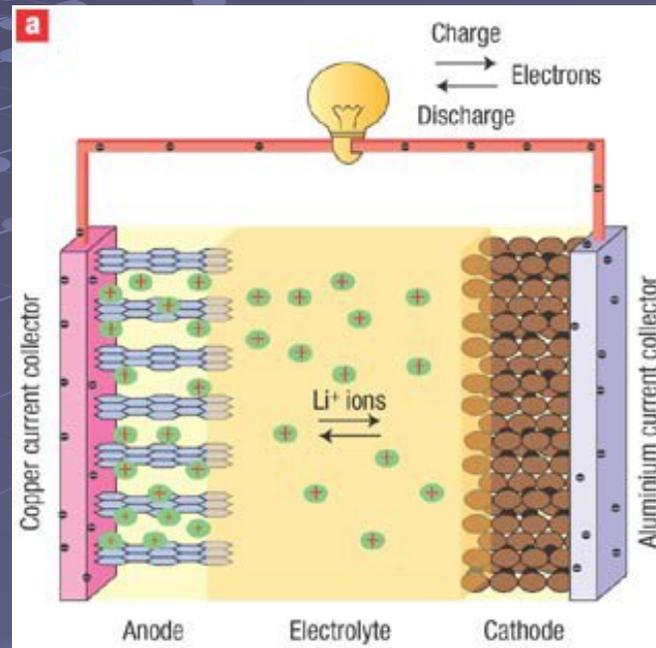
- Energy density: hundreds of Watt-hours/Kg (gasoline: thousands)
- Power density
- Durability

Batteries for the automotive sector: limited range



Bruce et al., Nat. Mater. 11, 19 (2012)

Lithium-ion batteries



B. Scrosati, Nature
Nanotechnology 2, 598
(2007)

During discharge, Li ions migrate from the anode to the cathode. Cathode is a transition metal oxide in conventional lithium-ion batteries, and contributes considerably to the total weight

Lithium-air batteries

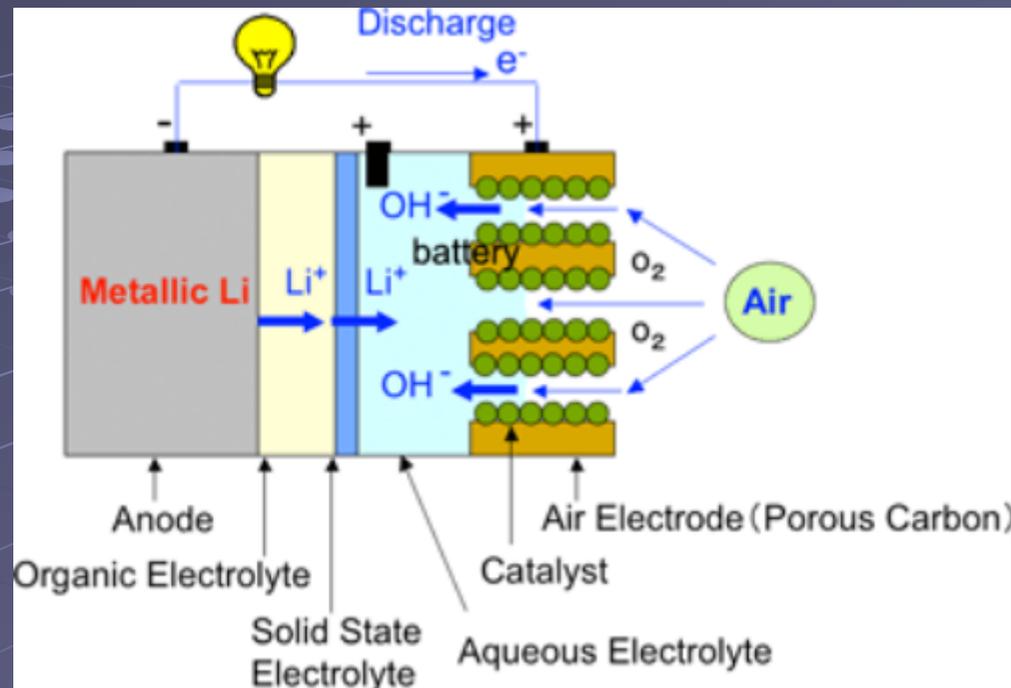
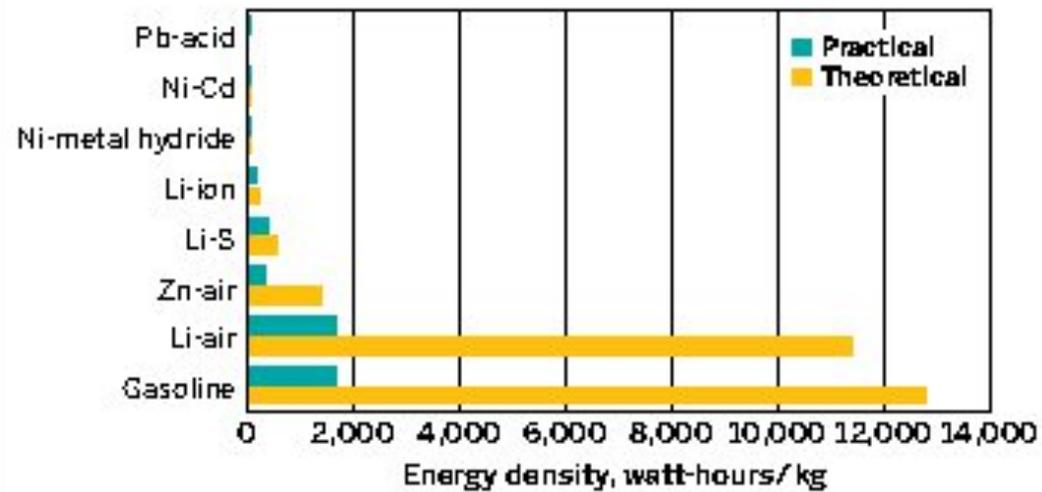


Image: AIST

- During discharge, Li ions migrate to the cathode and in contact with air they form Li_2O_2 nanoparticles
- Demonstrated re-chargeability in 2006 (Ogasawara et al., J. Am. Chem. Soc. 128, 1390 (2006))

The potential of lithium-air batteries

ENERGY-PACKED On a per-weight basis, lithium-air batteries' energy density soars over that of other battery types and even rivals that of gasoline.



SOURCE: *Journal of Physical Chemistry Letters*

Chemical & Engineering News, 11/2010

Lithium-air batteries: open problems

- Slow kinetics (low power density)
- High overpotentials for re-charging
- Bad cyclability

More later...

Lithium-air batteries: open problems

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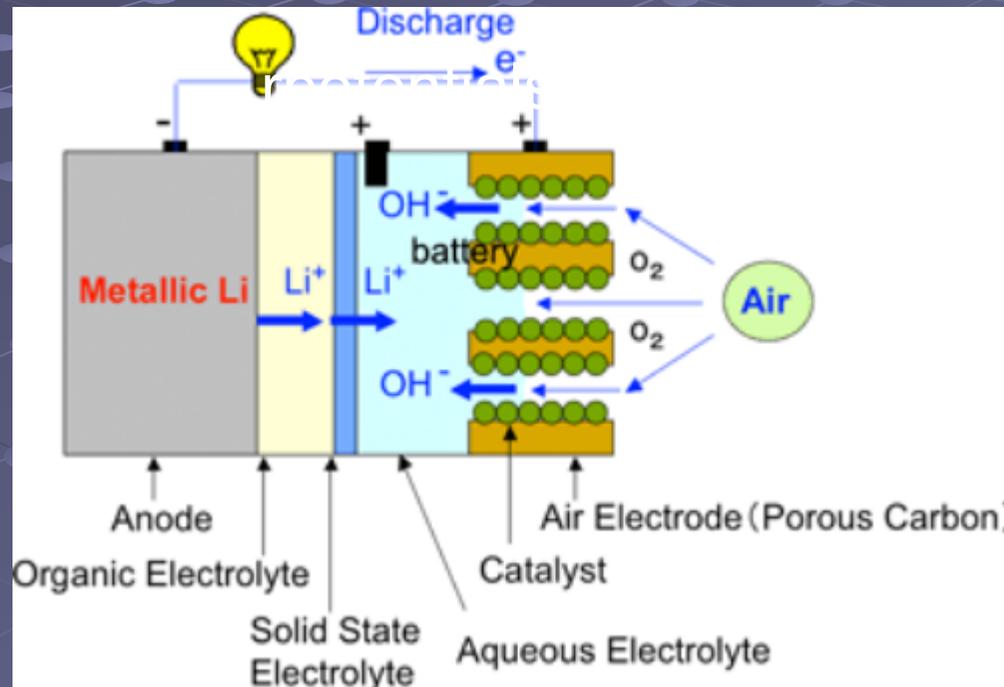


Image: AIST

Complicated system, complicated processes

Lithium-air batteries: DFT simulations

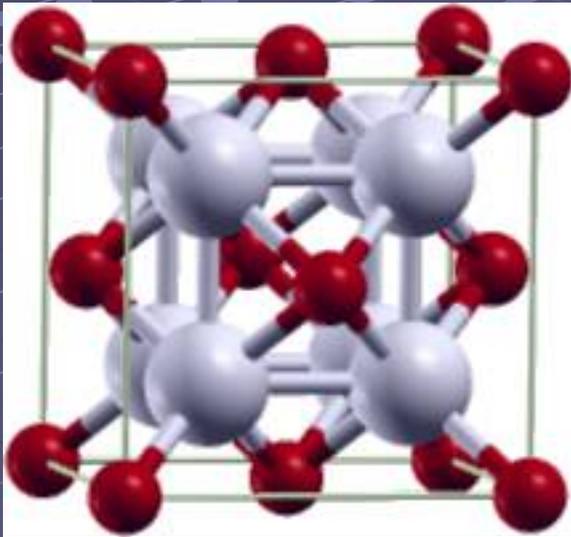
- Pinpoint essential features
- Divide and conquer strategy
- Investigate single components and simple processes with DFT

First step: lithium oxidation

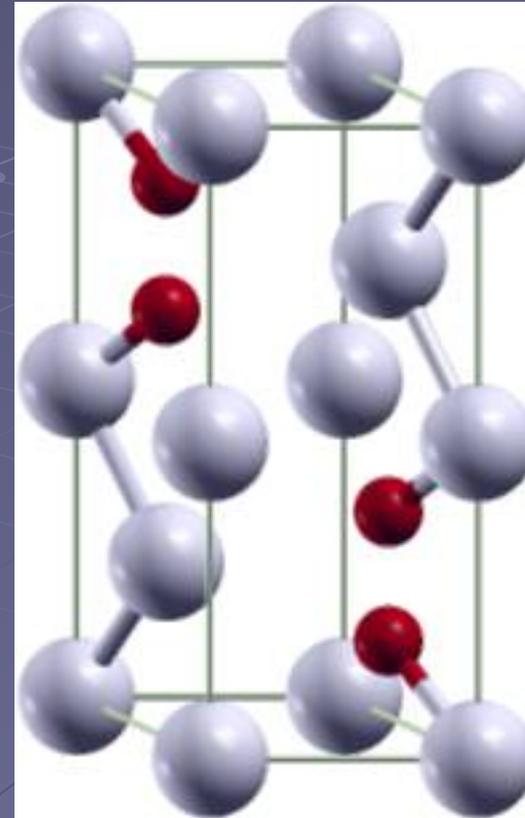
DFT simulations of lithium oxidation

- First step: to study lithium oxidation
- For now, we get rid of the battery and we are left only with lithium and oxygen
- Investigate thermodynamics of the oxidation process

Lithium oxides



Cubic Li₂O



Hexagonal Li₂O₂

Lithium peroxide: possible structures

Two proposals to explain XRD:
Feher et al. (1953) and Föppl (1957)

Only recently settled:

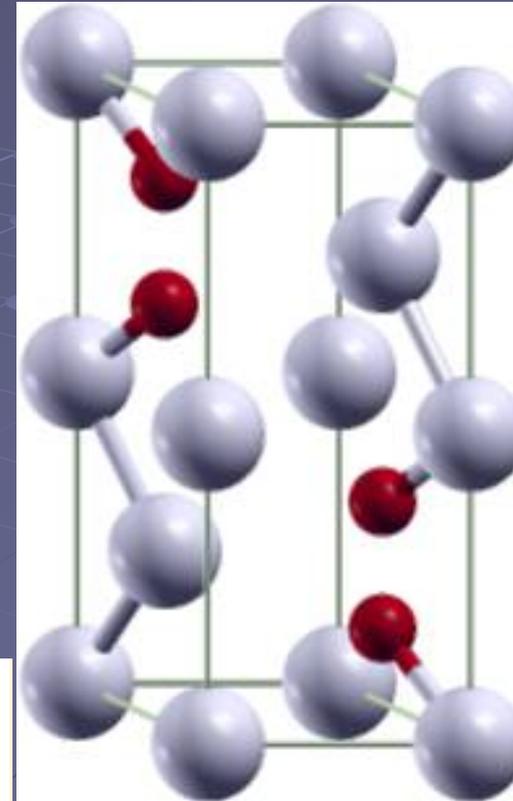
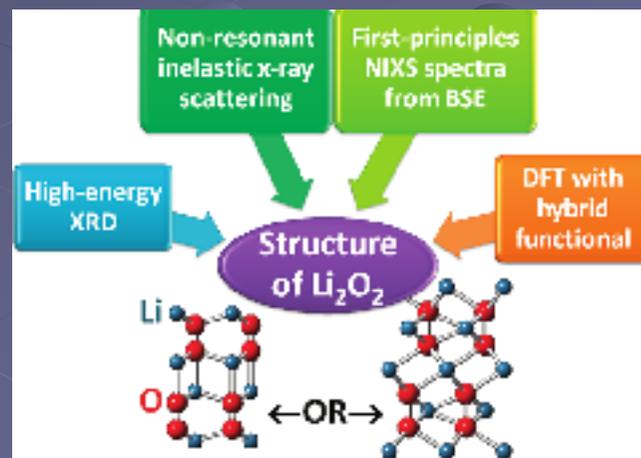
DFT structural relaxation and
energies:

Cota and De La Mora, Acta Crystallogr. B 61,
133 (2005)

Seriani, Nanotechnology 20, 445703 (2009)

Experiment
and DFT:

Chan et al.,
J. Phys. Chem.
Lett. 2, 2483 (2011)



Hexagonal Li_2O_2

Ab-initio thermodynamics

- Density functional theory gives the ground-state energy of a system
- We are interested in the oxidation of a metal in contact with gas at (T,p)
- Ab-initio thermodynamics is a method to calculate free energies from DFT total energies taking into account the chemical potential, e.g. of the oxygen gas.

- $$\Delta G_{\text{LiO}_x} = G_{\text{LiO}_x} - G_{\text{Li}} - x * G_{\text{O}}$$

Ab-initio thermodynamics

- $G_{\text{bulk}} = E_{\text{tot}}(\text{DFT}) + F_{\text{vib}}(\text{DFT})$
- $G_{\text{O}} = \frac{1}{2} E_{\text{tot}}(\text{DFT}) + \Delta\mu_{\text{O}}(T,p)$
- E_{tot} and F_{vib} can be calculated by DFT, the free energy of the oxygen can gas is taken from thermodynamic tables (see e.g. Reuter et al., PRB 65, 035406 (2002))

Lithium-air batteries

Ab-initio thermodynamics calculations of free energy of formation reproduce experimental voltage

$$\Delta g_{\text{LiOx}}^f = g_{\text{LiOx}}^{\text{bulk}} - g_{\text{Li}}^{\text{bulk}} - x/2 g^{\text{gas}}(\text{O}_2)$$

DFT voltage: 2.49 V

Exp. voltage^{**}: 2.5-2.7 V

^{**}Ogasawara et al., JACS 128, 1390 (2006)

N. Seriani, Nanotechnology 20, 445703 (2009)

Lithium-air batteries: open problems

- Slow kinetics (low power density)
- High overpotentials for re-charging
- Bad cyclability

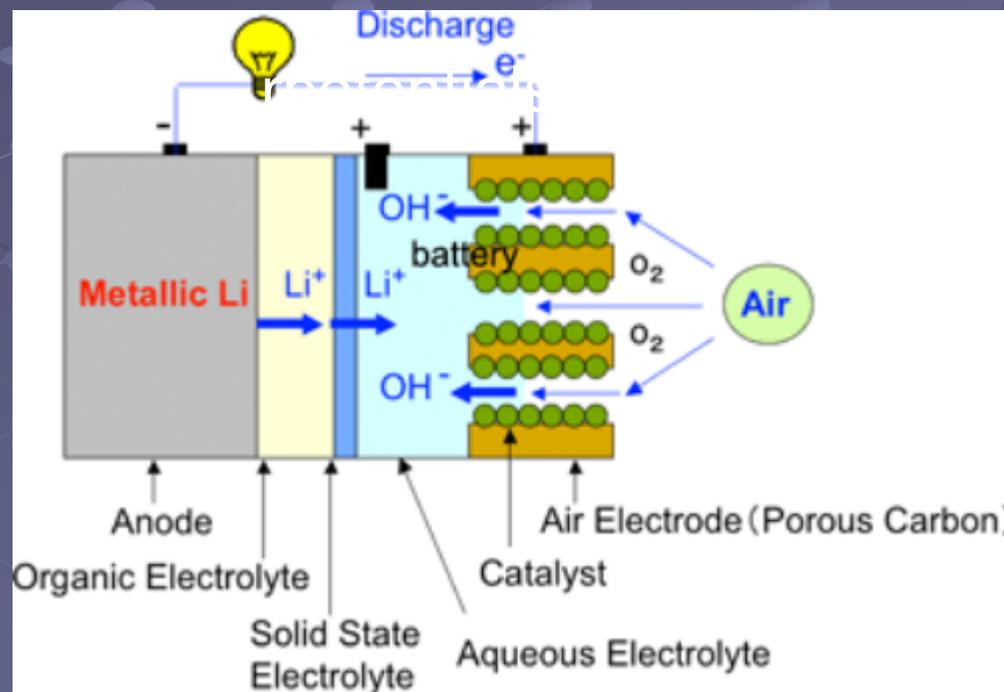


Image: AIST

Lithium-air batteries: open problems

System level

- Slow kinetics (low power density)
- High overpotentials for re-charging
- Bad cyclability

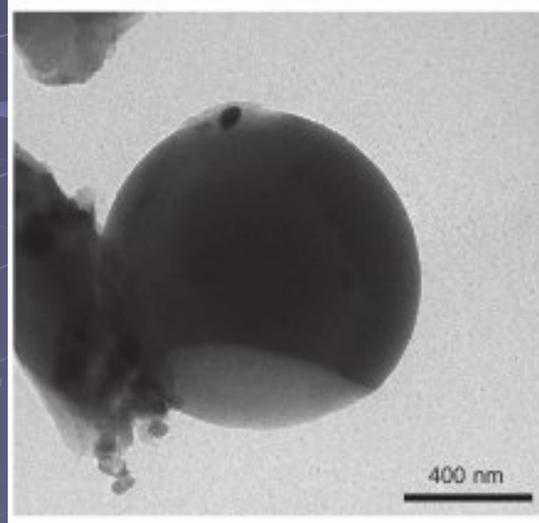
Component level

- Mechanisms of formation of lithium peroxide
- Role of the catalyst
- Mechanisms of electronic conductivity in lithium peroxide
- Mechanisms of dissolution of lithium peroxide
- Mechanisms of capacity loss: parasitic reactions

Lithium-air batteries: issues

- Mechanisms of formation of lithium peroxide at the cathode
- Role of the catalyst
- Mechanisms of electronic conductivity in lithium peroxide
- Mechanisms of capacity loss: parasitic reactions

Mechanisms of electronic conductivity in lithium peroxide



Jung et al., Nature Chemistry 4, 579 (2012)

Mechanisms of electronic conductivity in lithium peroxide

Band gap of perfect Li_2O_2 :

Method	Band gap (eV)
PBE	1.88 ¹
HSE	4.50 ²
G_0W_0	4.91 ¹

¹ Hummelshøj et al., J. Chem. Phys. 132, 071101 (2010)

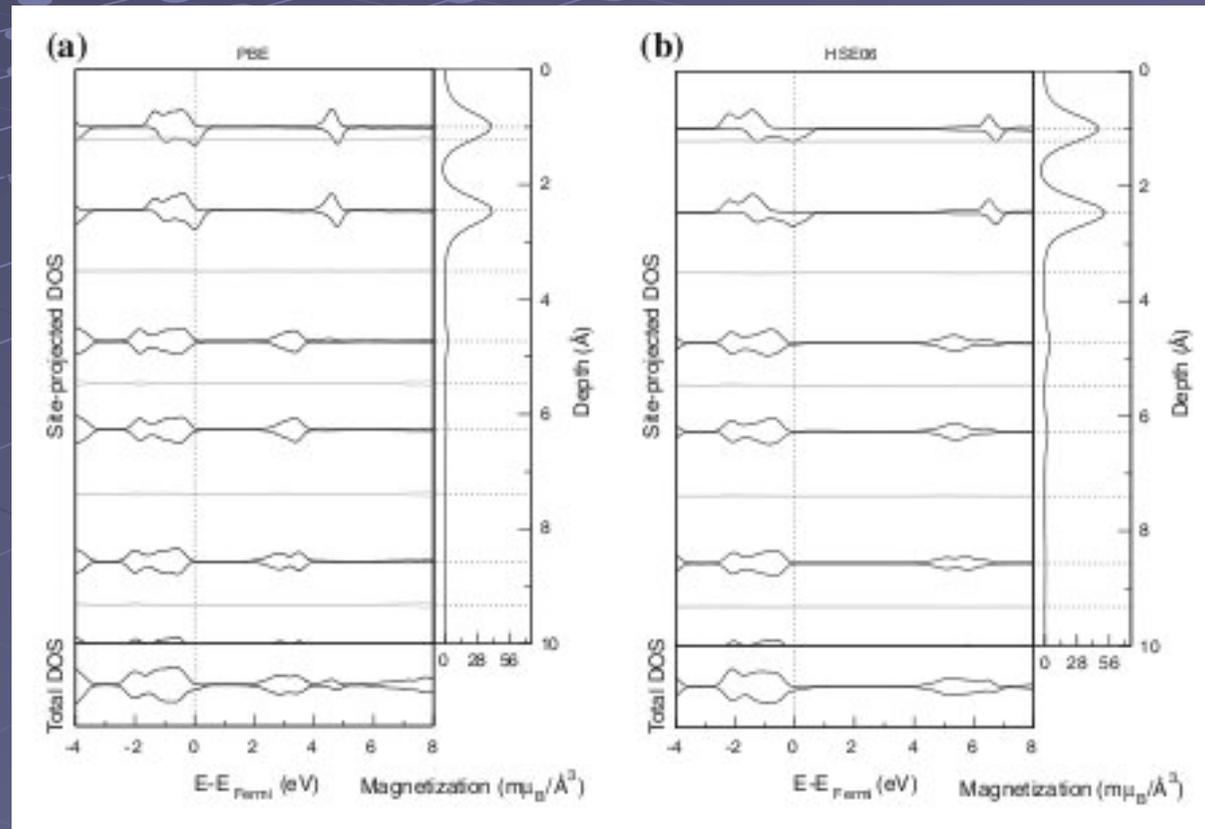
² Kang et al., Phys. Rev. B 85, 035210 (2012)

Still, 100 nm thick films have been observed in cathode before re-charging

Mechanisms proposed: Surface conduction
Polaron hopping
Vacancy-related conduction

Mechanisms of electronic conductivity in lithium peroxide: 1. Surface conduction

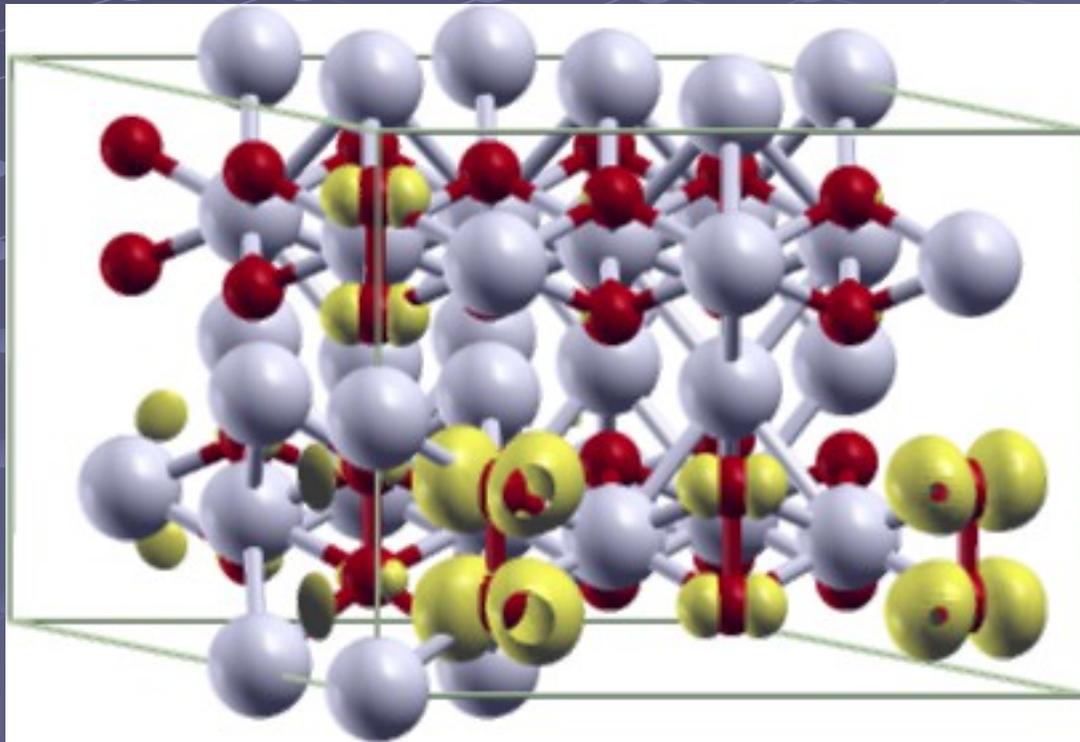
$\text{Li}_2\text{O}_2(0001)$ is semimetallic:



Radin, Tian, Siegel, J. Mater. Sci. 47, 7564 (2012)

Mechanisms of electronic conductivity in lithium peroxide: 2. hole polaron

In presence of a hole, Li_2O_2 gains 0.25 eV by distorting the crystal and localizing the hole:

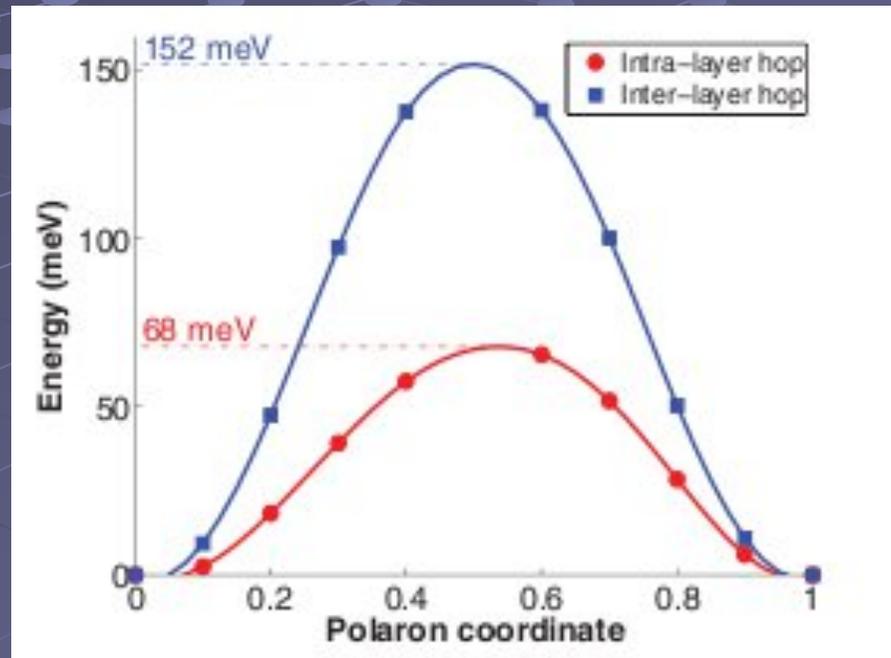


Hole associated with local distortion of the lattice:

$$d_{\text{hole}}(\text{O-O}) = 1.35 \text{ \AA} \text{ vs. } d_{\text{perfect}}(\text{O-O}) = 1.55 \text{ \AA}$$

Mechanisms of electronic conductivity in lithium peroxide: 2. hole polarons

Extremely low barrier for hole polaron diffusion:



A barrier of 68 meV along the easy direction
If binding to Li^+ vacancies considered, barrier of 360 meV

Ong, Mo, Ceder, PRB 85, 081105(R) (2012)

Mechanisms of electronic conductivity in lithium peroxide: summary

Low barriers for hole polaron diffusion

Half metallic surface $\text{Li}_2\text{O}_2(0001)$

Improved understanding of (some) elementary processes, overall picture still rather confuse

Capacity loss

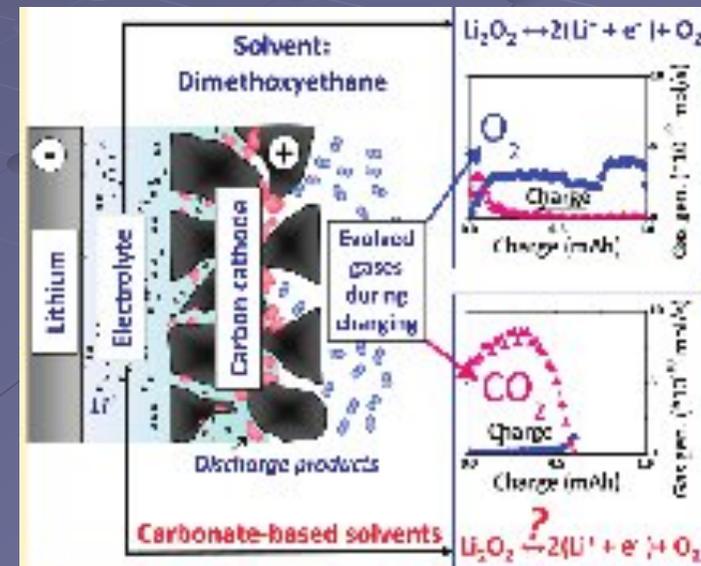
First batteries would have a high loss of capacity upon cycling (discharging – recharging)

Initially difficult to pinpoint one effect

It has been recently shown at IBM that carbonate based solvents decompose during operations

(McCloskey et al., J. Pys. Chem. Lett. 2, 1161 (2011), J. Am. Chem. Soc. 133, 18038 (2011), Laino and Curioni, Chemistry-A European Journal 18, 3510 (2012))

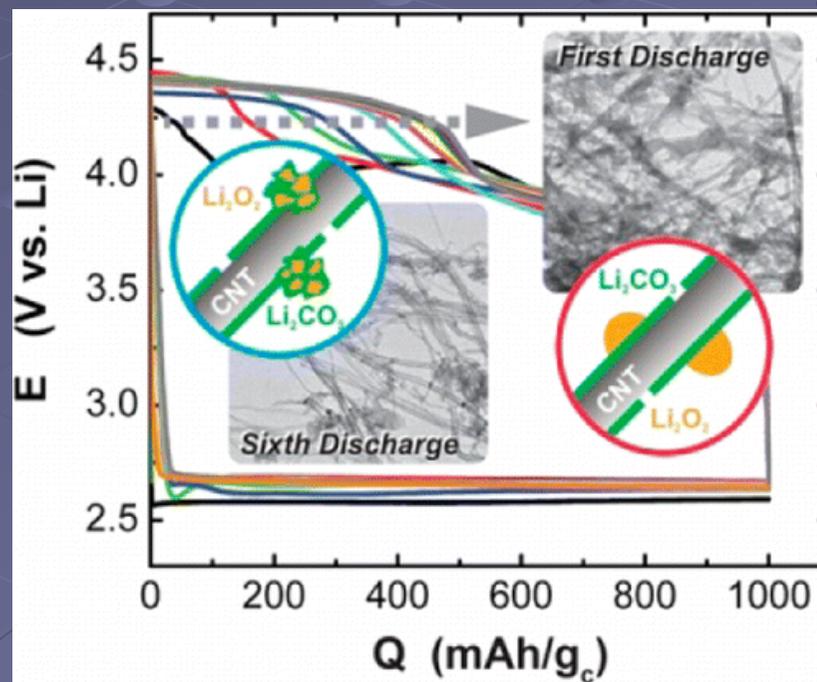
This could be the end of the story...



Capacity loss

In fact, it seems that also the carbon cathode partially decomposes

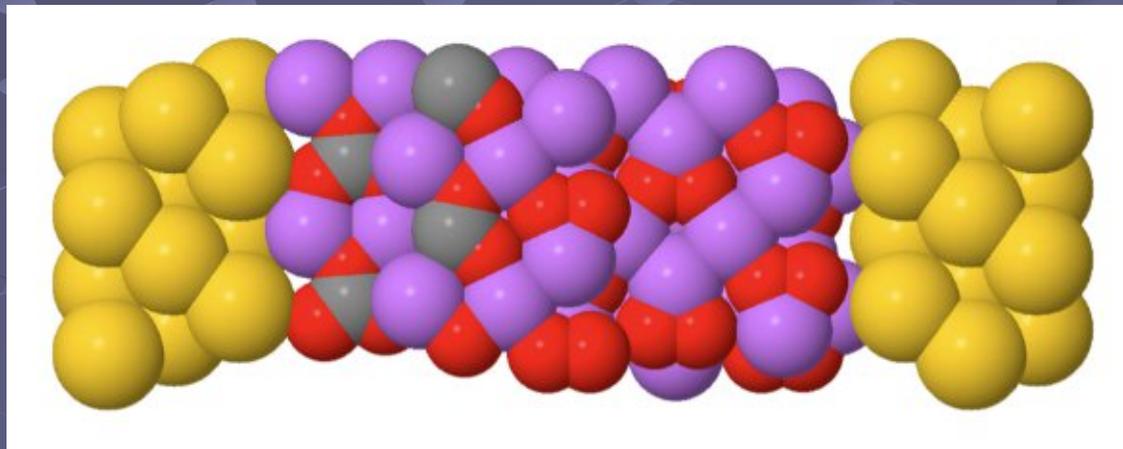
Small layer of carbonate between Li_2O_2 and carbon cathode seen in XANES, selected-area electron diffraction (SAED)



Gallant et al., J. Phys. Chem. C
116, 20800 (2012)

Capacity loss: ab-initio simulations

Conductivity calculations show that a small insulating (mono-)layer is enough to cause large increase in overall resistivity



McCloskey et al., J. Phys. Chem. Lett. 3, 997 (2012)

Capacity loss: ab-initio simulations

Conductivity calculations show that a small insulating (mono-)layer is enough to cause large increase in overall resistivity

Initial stages of Li_2O_2 formation and its interaction with the carbon cathode should be further investigated

DFT can give insight into elementary reactions

Role of the catalyst in lithium peroxide formation and dissolution

Presence of a catalyst in the cathode seems to improve kinetics

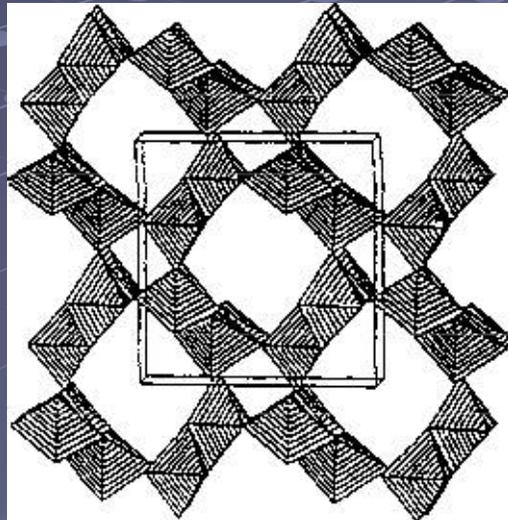
Still, some battery configurations work also without

Formation of solid phase of lithium peroxide of several hundreds of nanometers

Do relevant processes really take place on or near the catalyst?

α -MnO₂

Understanding the properties of the catalyst present at the cathode: α -MnO₂



Thackeray, Prog. Solid St. Chem.
25, 1 (1997)

Crystal structure formed by MnO₆ octahedra

Channels often with impurities

Complex magnetic behaviour

α -MnO₂

In some classes of transition metal oxides, the activity for oxygen evolution reaction seems to be correlated with the occupancy ~ 1 of a certain orbital (e_g) of the metal ions at the surface (Suntivich et al., Science 334, 1383 (2011))

Pure α -MnO₂ has indeed an occupancy of 0.9-1.0 (PBE...HSE)

Is this enough to conclude that important reactions take place at the catalyst?

Can this be changed by doping elements in channels?

Work in progress (with Yanier Crespo)

Summary

- Challenges for the understanding of processes taking place in lithium-air batteries can be overcome also with the help of ab-initio simulations
- To be able to apply DFT to battery research, it is necessary to individuate and isolate single processes and/or single materials
- Divide and conquer strategy

Summary: ab-initio simulations

- Bulk Li_2O_2 : thermodynamics
- Mechanisms of conductivity in lithium peroxide
- Parasitic reactions, effects of Li_2CO_3
- Properties and role of the $\alpha\text{-MnO}_2$ catalyst

Acknowledgements

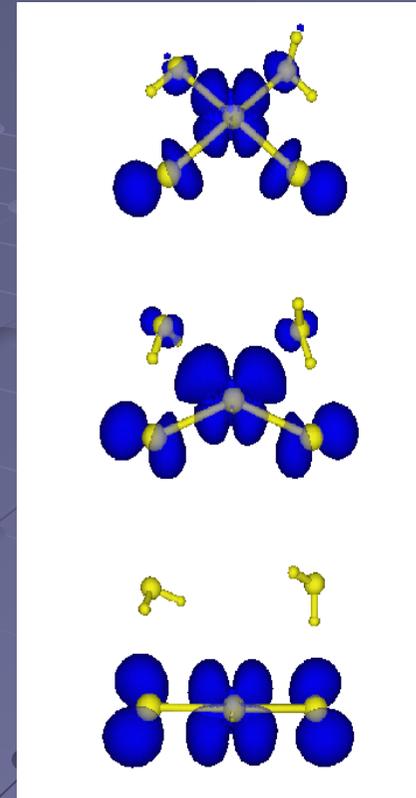
- Y. Crespo, A. Andreanov (ICTP)
- L. Colombi Ciacchi (Uni Bremen)
- A. Curioni (IBM)

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Computational resources: ICTP and CINECA

Ab-initio molecular dynamics

- *Model consists of atomic nuclei and electrons*
- *Atomic nuclei follow classical mechanics*
- *Electrons are quantum particles*
- *Adiabatic approximation → during motion, electrons are always in the instantaneous ground state*



Density functional theory

- Method to reduce the many-electron Schrödinger equation to equations for one-electron wavefunctions (Kohn-Sham equations)

Schrödinger equation

$$\left[-\sum_i^N \frac{\hbar^2}{2m} \nabla_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i, \vec{r}_j) \right] \Psi(\vec{r}_1, \dots, \vec{r}_N) = E \Psi(\vec{r}_1, \dots, \vec{r}_N)$$



$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(\vec{r}_i) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V_{xc}[n(\vec{r})] \right] \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$$

Kohn-Sham equation

Local density approximation and generalized-gradient approximation for V_{xc}