



Lithium-Air Batteries with split  
Oxygen Harvesting and Redox processes

**3rd "European Green Cars Initiative" Projects Clustering Event**

# LABOHR - Consortium



ALMA MATER STUDIORUM  
UNIVERSITÀ DI BOLOGNA



**Chemetall**



UNIVERSITY OF  
**Southampton**



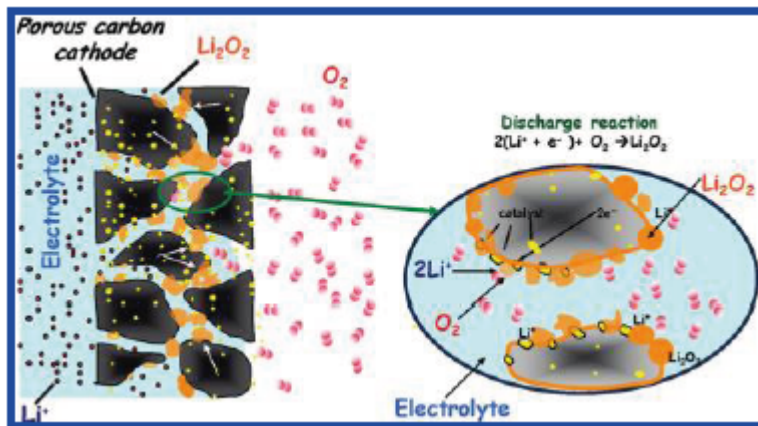
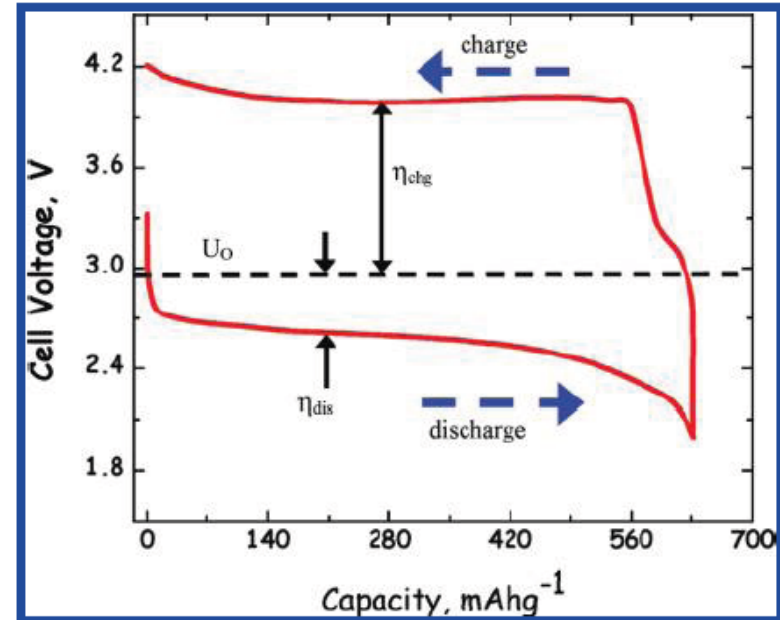
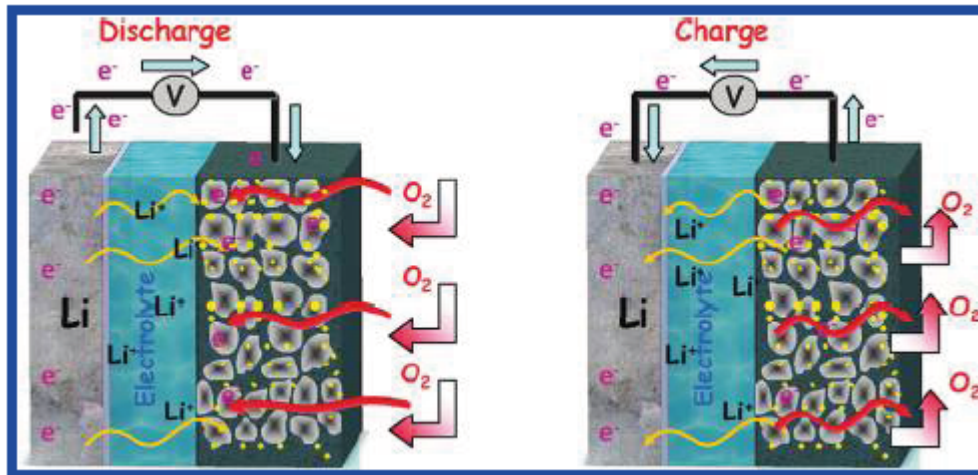
Oliver Panzer



Coordinator: Stefano Passerini, Münster



# Li-Air is a tough choice



anode, cathode, electrolyte, and packaging need to be improved

# Current Li-Ion technology

- ✓ Long cycle life
- ✓ Energy density high enough for electric commuting cars
- ✗ Safety issues: low flash point carbonates used in electrolyte, oxygen release from cathode materials

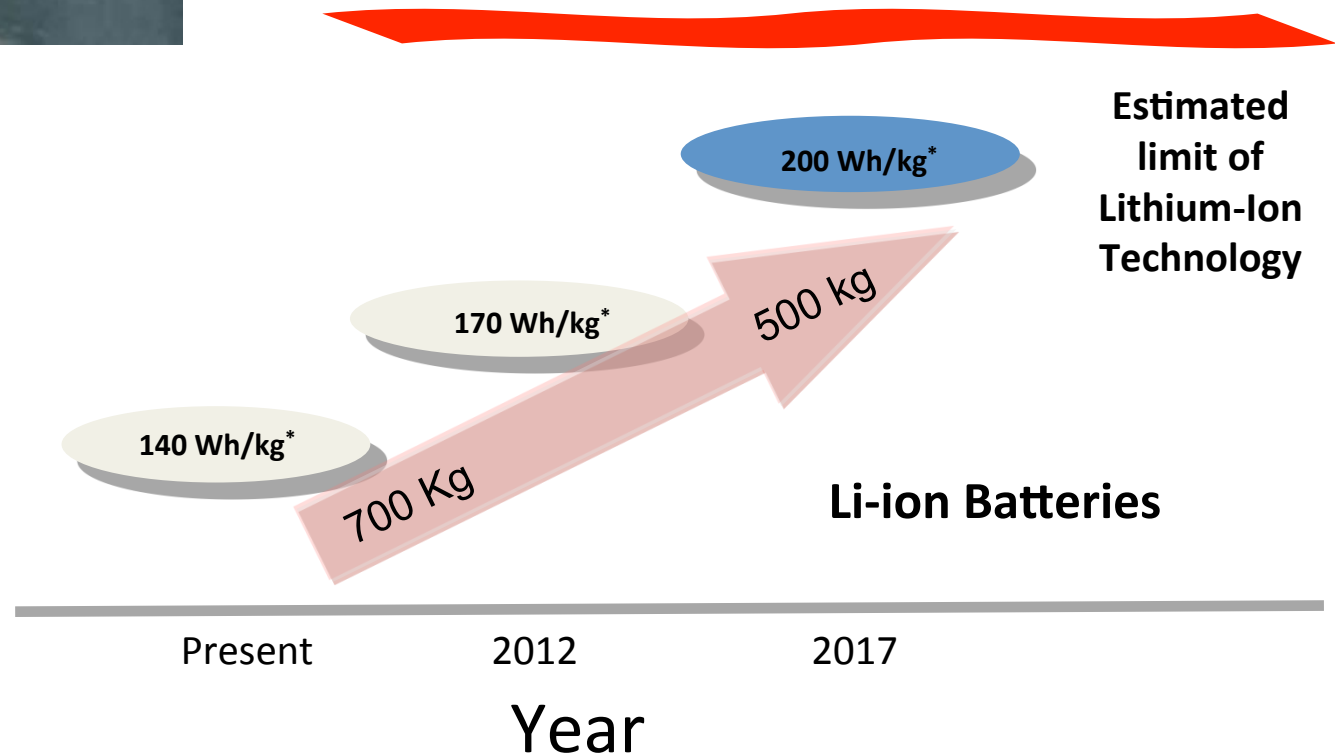




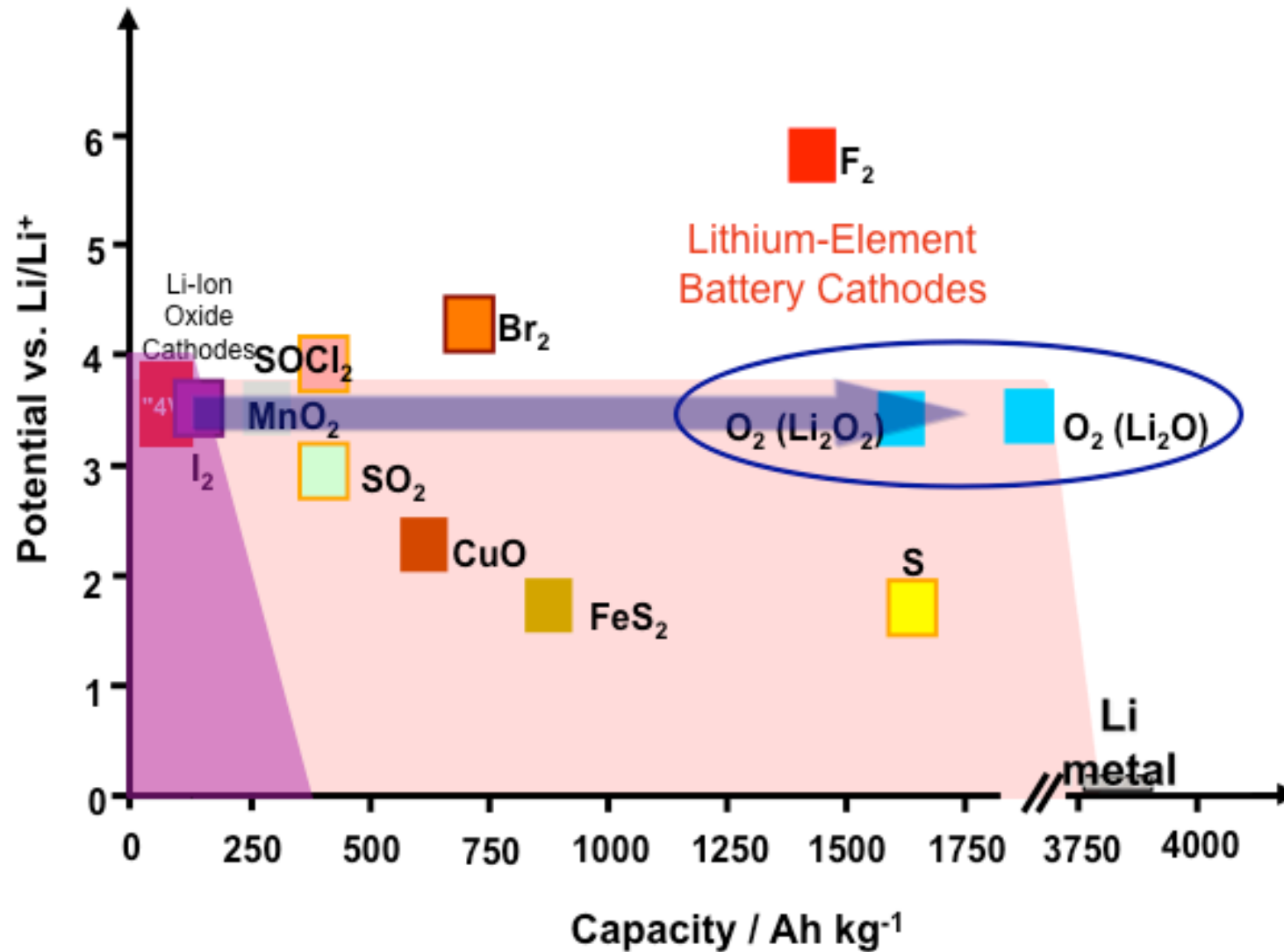


**Pb-acid** 3000 kg  
**Ni-MH** 1200 kg

✗ Practical energy density limit can't be pushed much further: Theoretical thermodynamic limit



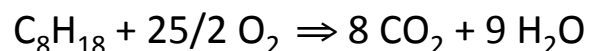
# Lithium-Air Battery: energy perspectives



# Lithium-Air Battery: energy perspectives

Combustion Energy of Gasoline

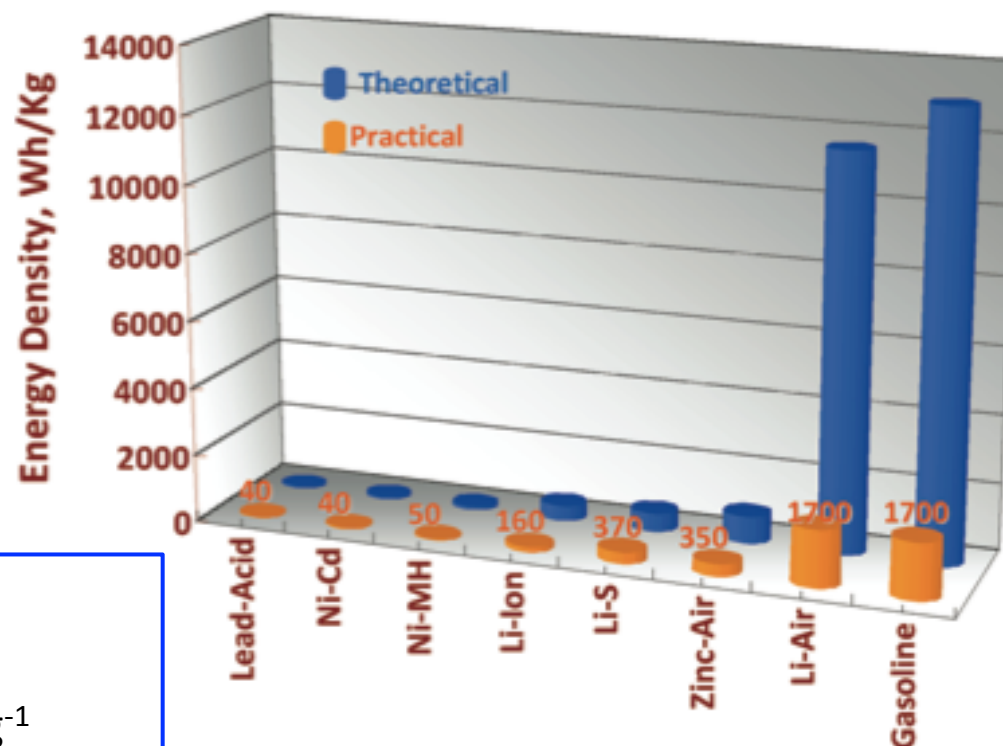
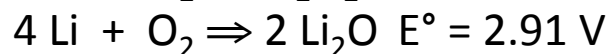
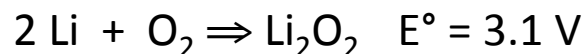
Theor. Energy: **13500 Wh/kg**



**Tank to Wheel** (EU) efficiency 20%  
corresponding to only **2700 Wh/kg**

Theor. Energy ( $\text{O}_2$  not included)

**11680 Wh.kg<sup>-1</sup>** → **3000-5000 Wh.kg<sup>-1</sup>**





# What makes a good battery

Cyclability-lifetime

Recyclability-toxicity

Energy efficiency = faradaic efficiency + voltage difference between charge and discharge

$$\text{Specific energy} = \text{Specific capacity} * \text{Voltage}$$

Li<sup>+</sup> based battery:

- Number of Li<sup>+</sup> transferred from one electrode to another  
= e<sup>-</sup> circulating in the external circuit

- Total weight/volume of the battery

Reactions at each electrode  
(insertion, intercalation,  
conversion, Li plating):

Thermodynamic + overvoltages

# Problems to solve

Realize a Li-air battery, not a Li-O<sub>2</sub> battery

Prevent the electrolyte to evaporate

Prevent O<sub>2</sub> from migrating or reacting at the negative (Li) electrode

Find the best conditions for the reaction  $2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2$  to be reversible and take into account the necessary changes in the electrolyte chemistry at the negative electrode:



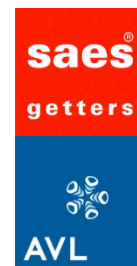
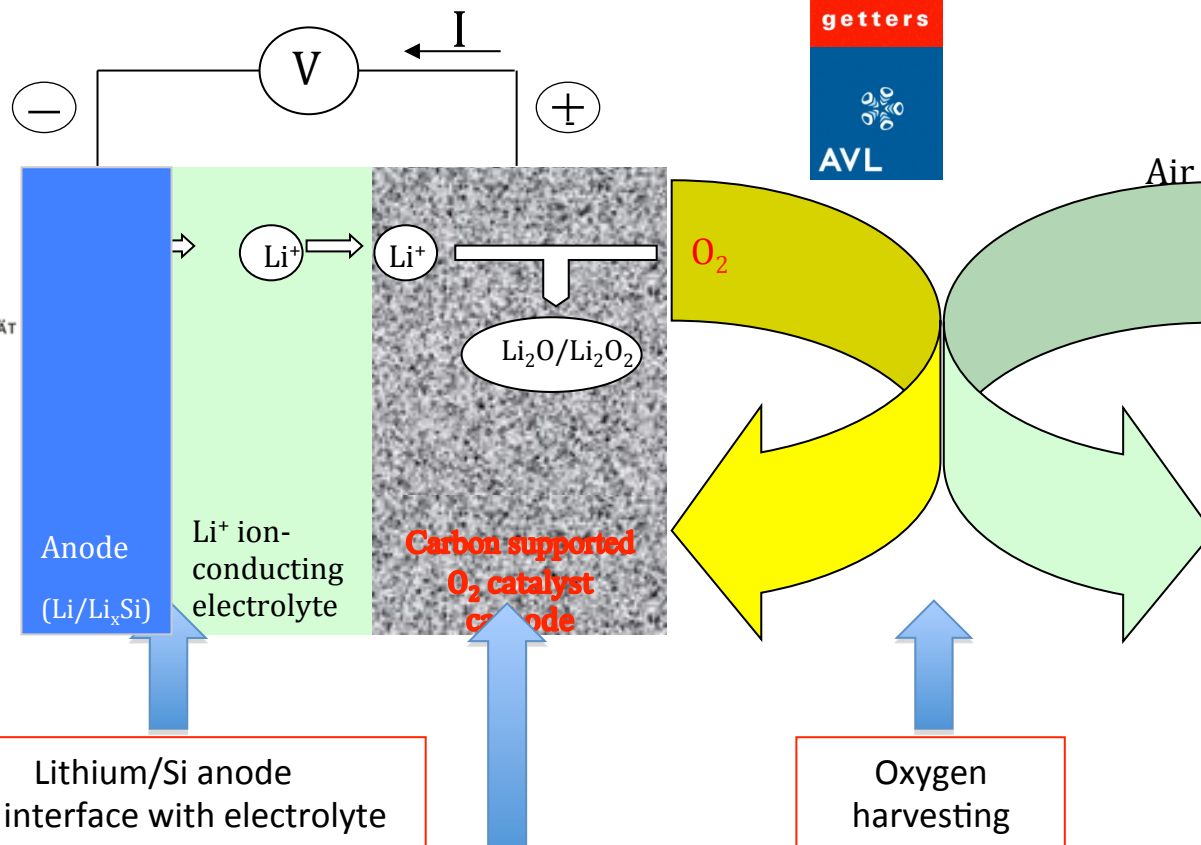
- Traditional carbonate-based electrolytes, are involved (degraded/ consumed) in the electrochemical reactions<sup>1</sup>.
- Evaporation, same risks as in a Li-ion battery.

<sup>1</sup>S. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák, P. G. Bruce, *JACS* **133** (2011) 8040

# LABOHR approach: splitting



Chemetall



Lithium/Si anode and interface with electrolyte

Oxygen Redox reaction

Oxygen harvesting

Target:  
500Wh/Kg & 200W/kg  
at the battery pack level



Coordinator  
Involved in all aspects of  
the project (provides IL-  
based electrolytes)



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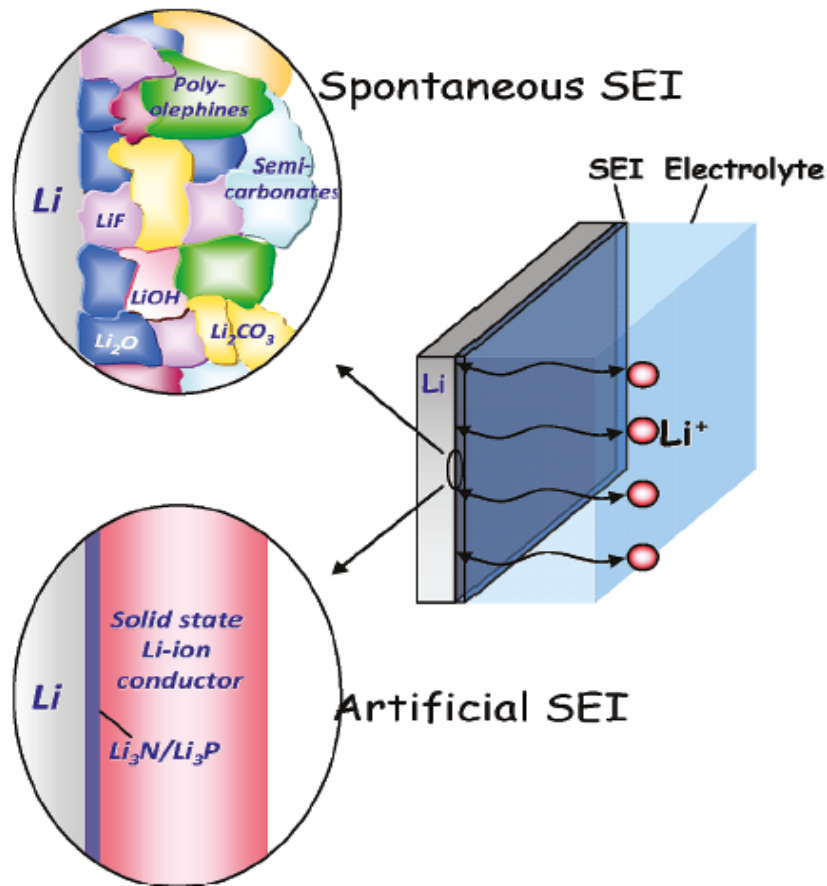


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# Li (or Si) /electrolyte interface

The stability of the electrolyte toward Li (or for Li-ion battery versus lithiated graphite) is linked to the presence of a SEI (Solid Electrolyte Interphase)<sup>1</sup>



Emanuel Peled from Tel Aviv University (TAU) invented the term and concept in 1979. TAU is now working on artificial SEI and Si negatives

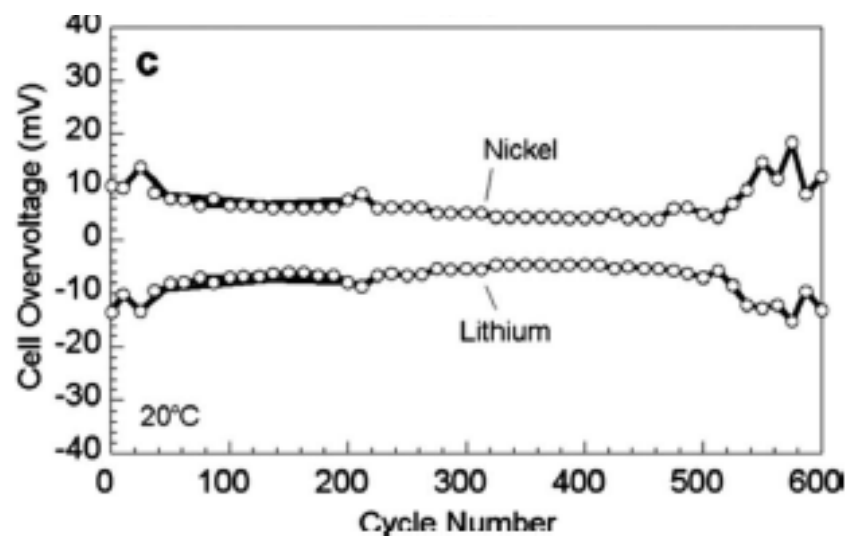
KNUTD is also working on Si based negatives

Münster will investigate the Lithium/ electrolyte interface using ILs-based electrolytes, liquid or solid (including polymer)

<sup>1</sup>E. Peled, *J. Electrochem. Soc.* **126** (1979) 2047

# Li cycling in ILs based electrolytes

State of the art lithium metal battery using ILs<sup>1</sup> or polymer/ILs based electrolytes<sup>2</sup> by Münster



0.26 mA.cm<sup>-2</sup> at 20°C in  
0.9 PYR<sub>14</sub>FSI - 0.1 LiFSI  
99.1% efficiency per cycle

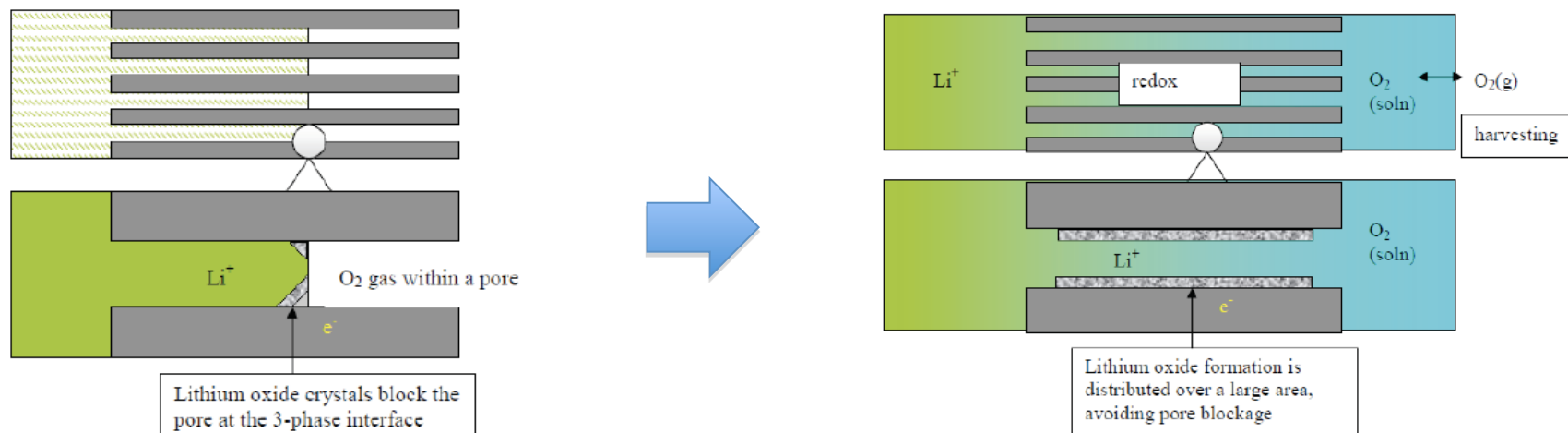


The rate should be improved, and O<sub>2</sub> prevented to react

<sup>1</sup>E. Paillard, Q. Zhou, W. A. Henderson, G. B. Appetecchi, M. Montanino, and S. Passerini *J. Electrochem. Soc.* **156**, A891 (2009)

<sup>2</sup>G. T. Kim, G. B. Appetecchi, M. Carewska, M. Joost, A. Balducci, M. Winter, S. Passerini, *J. Power Sources* **195** (2010) 6130

# Oxygen Redox Reaction



Southampton University (John Owen) and Bologna University (Marina Mastragostino) are in charge (with Münster) of the fundamental studies (O<sub>2</sub> electrochemistry in ILs/Li salts electrolytes, O<sub>2</sub> diffusion in the positive electrode pores)

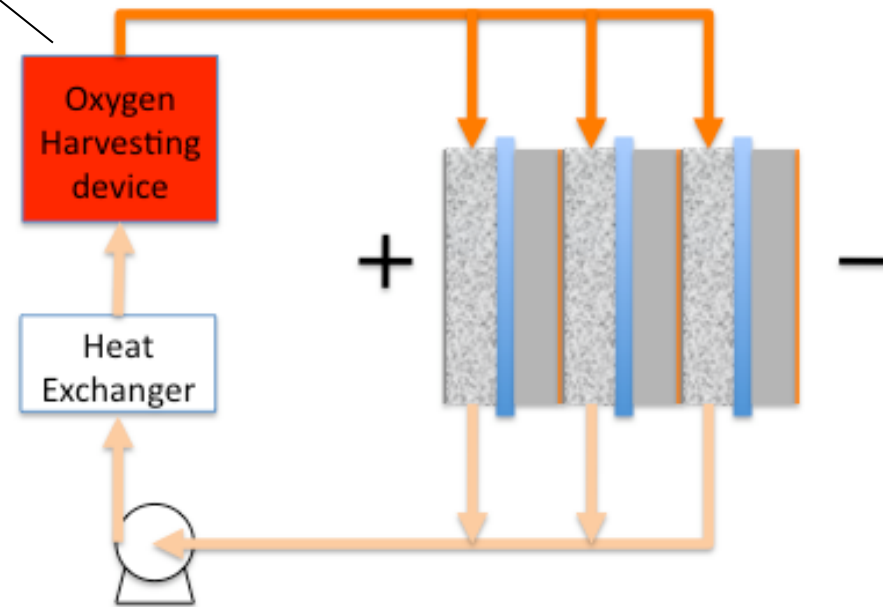
as well as of the development of composite positives with KNUTD (Kiev) and CSIC (Spain). The task requires:

- 1 - The choice of the right catalyst: influence on the voltage, but also on the achievable capacity
- 2 - The right morphology/porosity of carbon (template synthesis): O<sub>2</sub> diffusion, storage of Li<sub>2</sub>O<sub>2</sub>/Li<sub>2</sub>O



# Prototyping and stack modeling

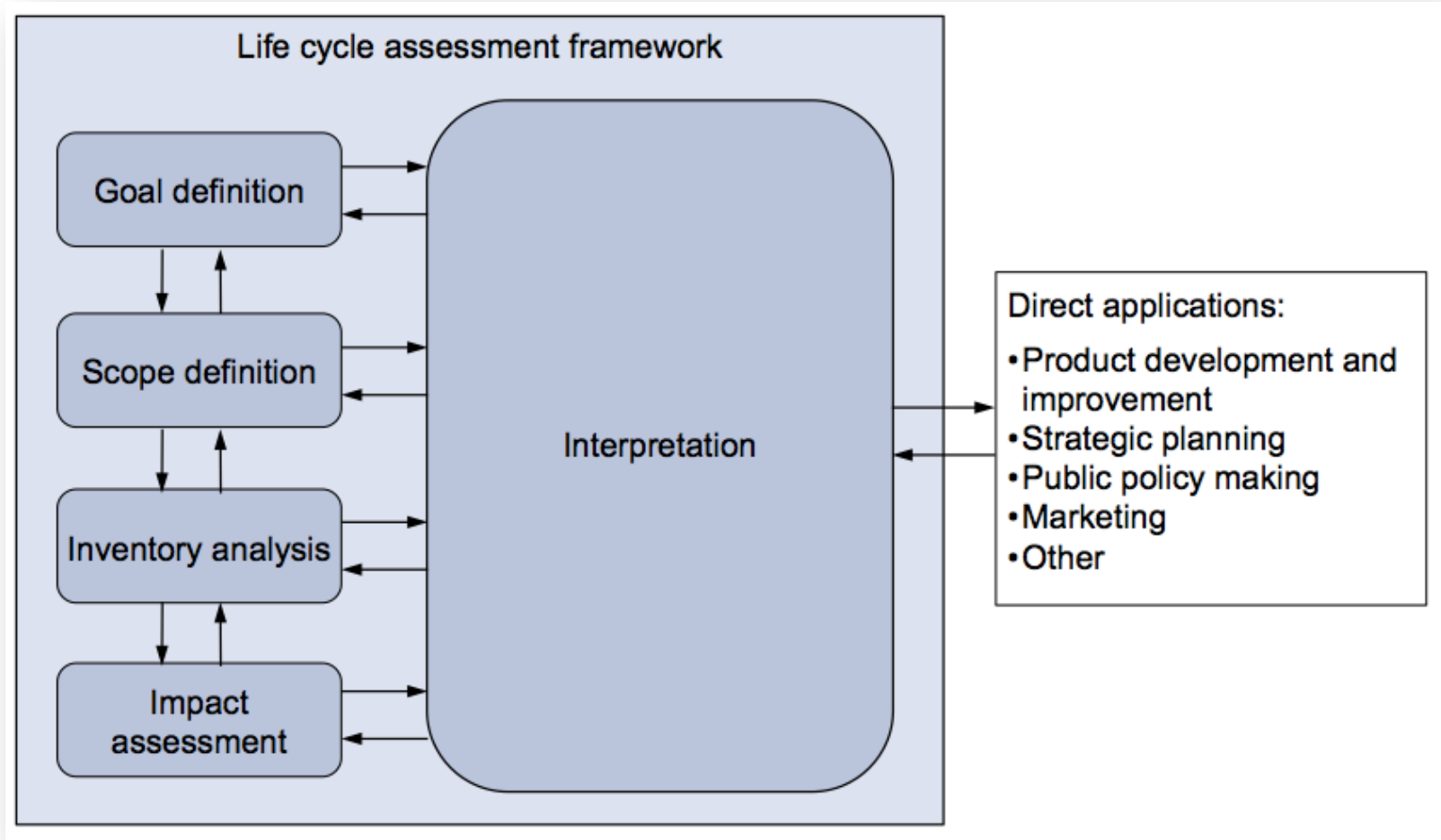
SAES getters (Italy) / AVL (Austria)



AVL (Graz, Austria) is in charge of the cell design, and of providing the hardware and ancillary systems. The full stack for car powering will be modeled

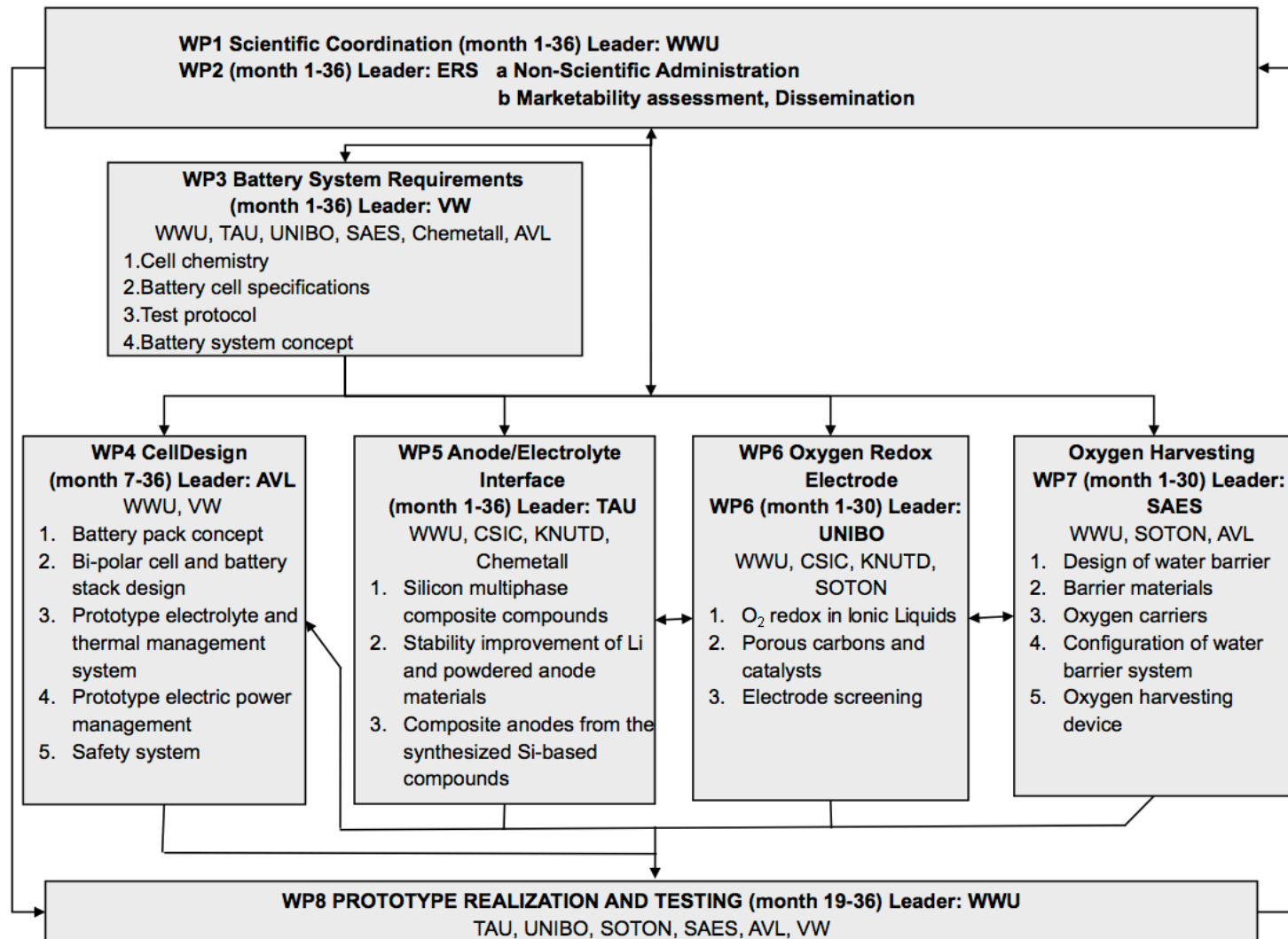
Münster is in charge of realizing the prototype (100 cm<sup>2</sup>, including an external O<sub>2</sub> harvesting device)

# LCA



*adapted from ISO 14044 by EU*

# LABOHR organisation





**Pb-acid** 3000 kg  
**Ni-MH** 1200 kg

**"Super- Battery" < 200kg**

>500 Wh/kg

Estimated  
 limit of  
 Lithium-Ion  
 Technology

200 Wh/kg\*

170 Wh/kg\*

500 kg

140 Wh/kg\*

700 Kg

**Li-ion Batteries**


Present

2012

2017

**Year**

# Please contact us via the website: labohr.eu




Lithium-Air Batteries with split  
Oxygen Harvesting and Redox processes

Events & ResultsThe ProjectThe TeamInternal

- › **2012 MRS (Material Research Society) Fall Meeting**  
November 25 - 30, 2012  
Hynes Convention Center - Boston, Massachusetts
- › **PRIME 2012**  
Honolulu, Hawaii | October 7-12, 2012  
Hawaii Convention Center and the Hilton Hawaiian Village
- › **5th International Conference on Advanced Lithium Batteries for Automobile Applications**  
September 17-20, 2012  
Istanbul, Turkey
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## The Team

**Prof. Dr. Stefano Passerini (WWU)**



Professor Stefano Passerini, Chemist, has been working since 1986 on basic and applied research devoted to study and characterize materials and systems for electrochemical energy storage. Since 2010 he holds a Chair in 'New Electrochemical Energy Devices', main topics are: Polymer electrolytes; inorganic sol-gel materials and ionic liquids; and lithium batteries. He is author/co-author of over 160 publications in 'peer reviewed' international scientific journals, 4 book chapters and about 10 international patents.

**Prof. Marina Mastragostino (UNIBO)**



Marina Mastragostino is Full Professor of Chemistry at Bologna University. Her research activity is mainly focused on basic and applied studies on inorganic, carbonaceous and polymeric nanostructured electrode materials for lithium-ion batteries, supercapacitors and fuel cells for transportation and stationary and portable applications. Electrochemical studies for enzymatic biofuel cells are also performed in her research group. Her experience in the field of the materials electrochemistry is proven by 180 papers published on international journals and books, by several invited presentations in International Meetings and by the participation as Scientific Responsible in several national and European projects for the development of advanced electrochemical systems, also with industrial partners.