CHEMICAL REACTIONS INVESTIGATION AT THE ELECTRODE / ELECTROLYTE INTERFACE THROUGH PHOTOEMISSION AND RELATED SURFACE TECHNIQUES

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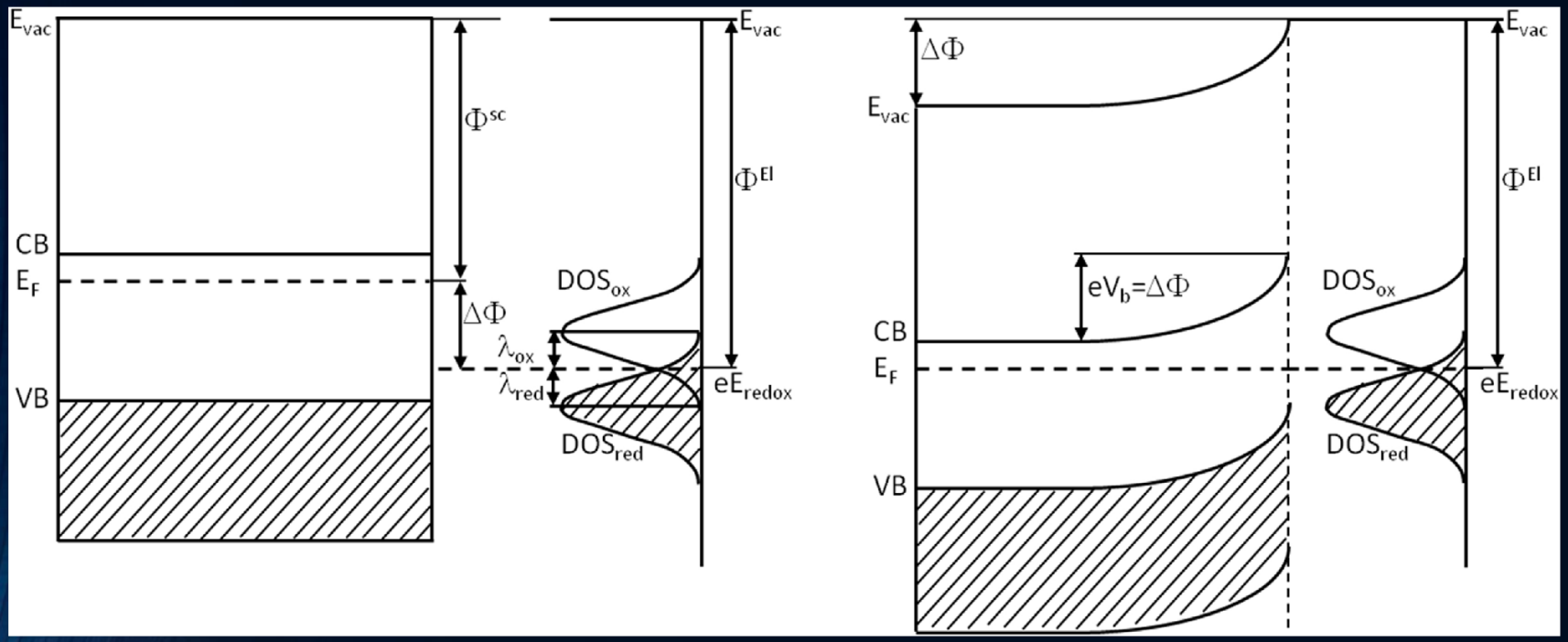
LAYOUT

- What's an *electrode/electrolyte interface*?
- Some examples…
- Why use photoelectron spectroscopy?
- Focus on materials for Li-oxygen cells

The semiconductor/electrolyte interface

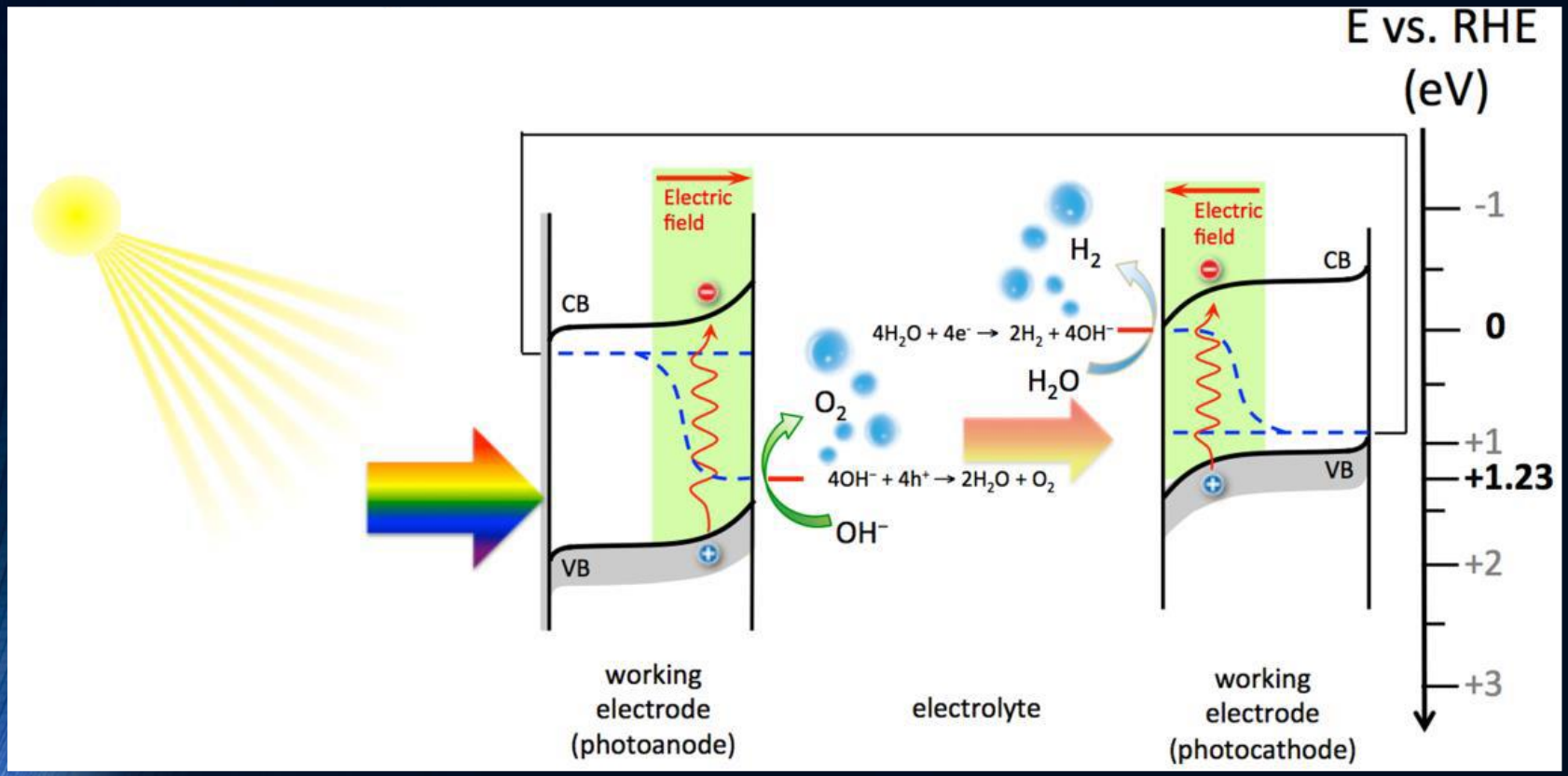


Before contact

After contact

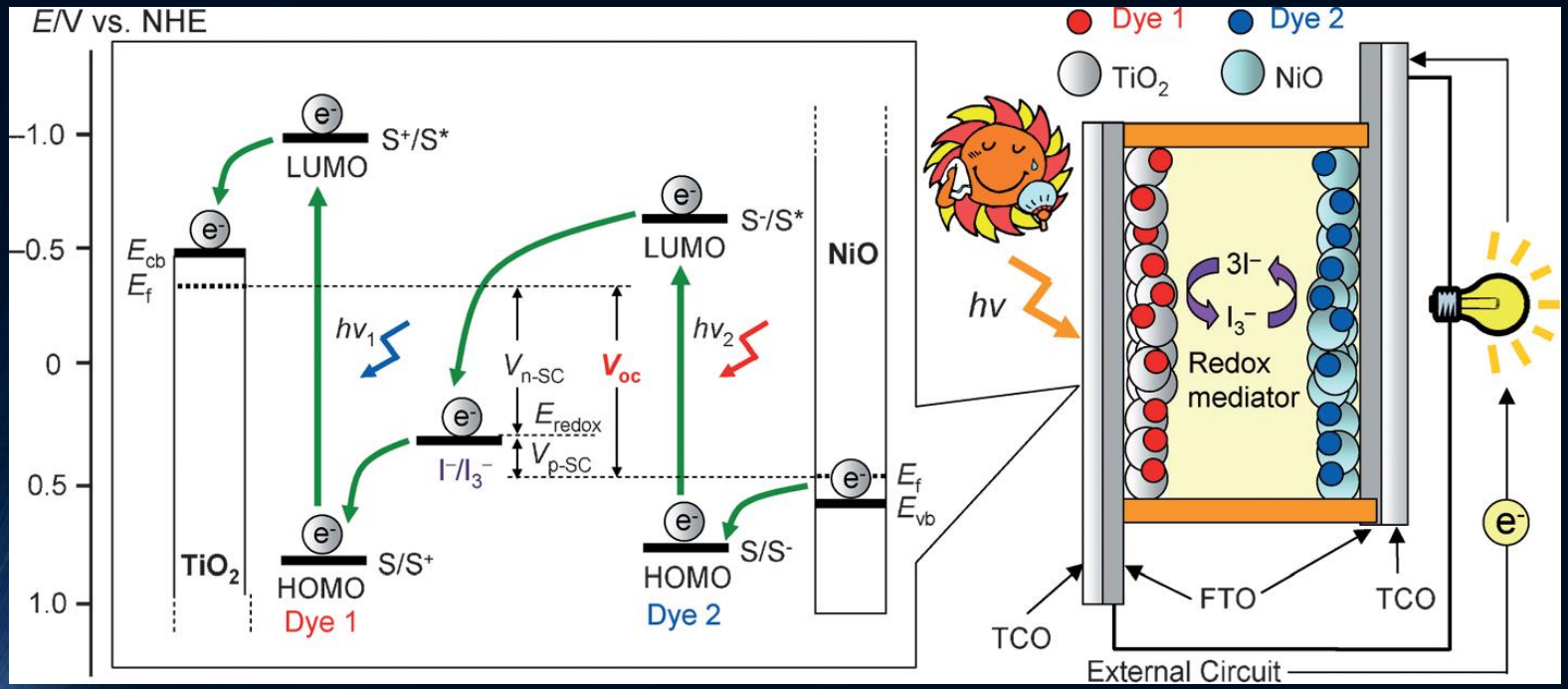
Schottky limit approximation: $eV_b = \Delta\Phi$

The semiconductor/electrolyte interface…*illuminated*!



Photoelectrochemical devices for the production of «solar» fuels

The semiconductor/molecule/electrolyte interface…*illuminated*!



Photoelectrochemical devices for the conversion of solar energy

The electrode/molecule/gas/electrolyte interface

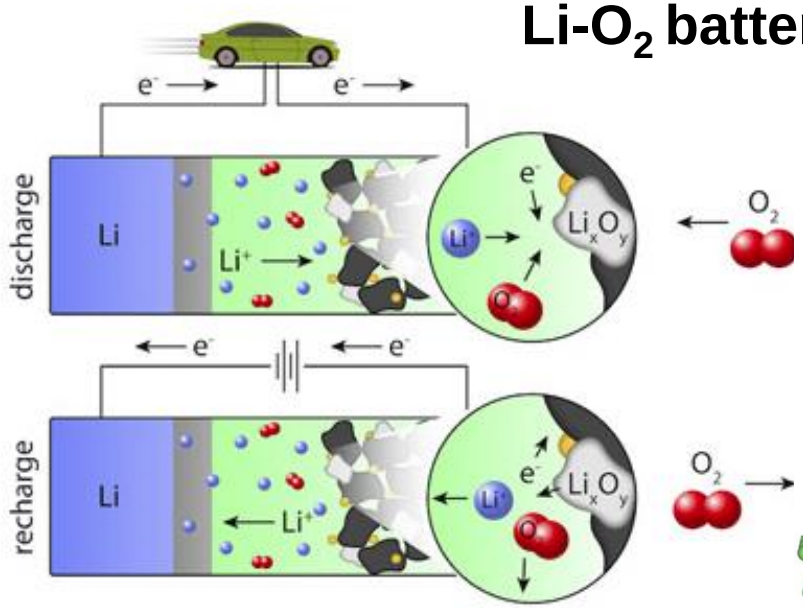
Reactions on discharge:

$Li^+ + O_2 + e^- \rightarrow LiO_2$ 1^ monoelectronic reduction

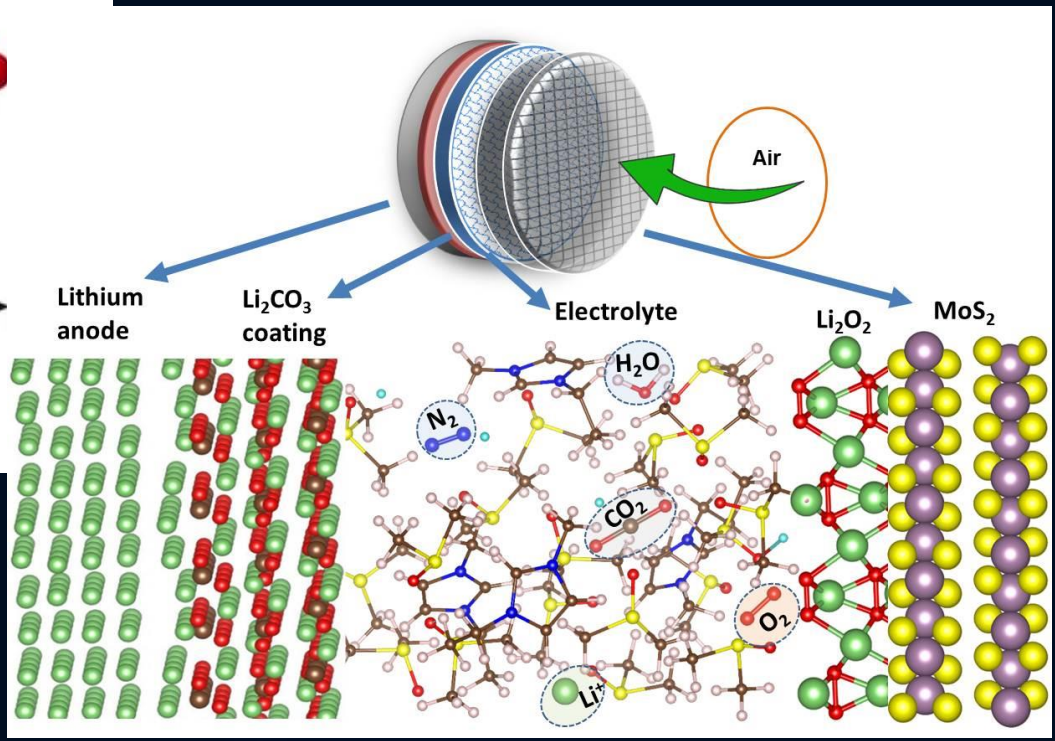
$LiO_2 + Li^+ + O_2 + e^- \rightarrow Li_2O_2$ 2^ monoelectronic reduction

$2LiO_2 \rightarrow Li_2O_2 + O_2$ disproportion

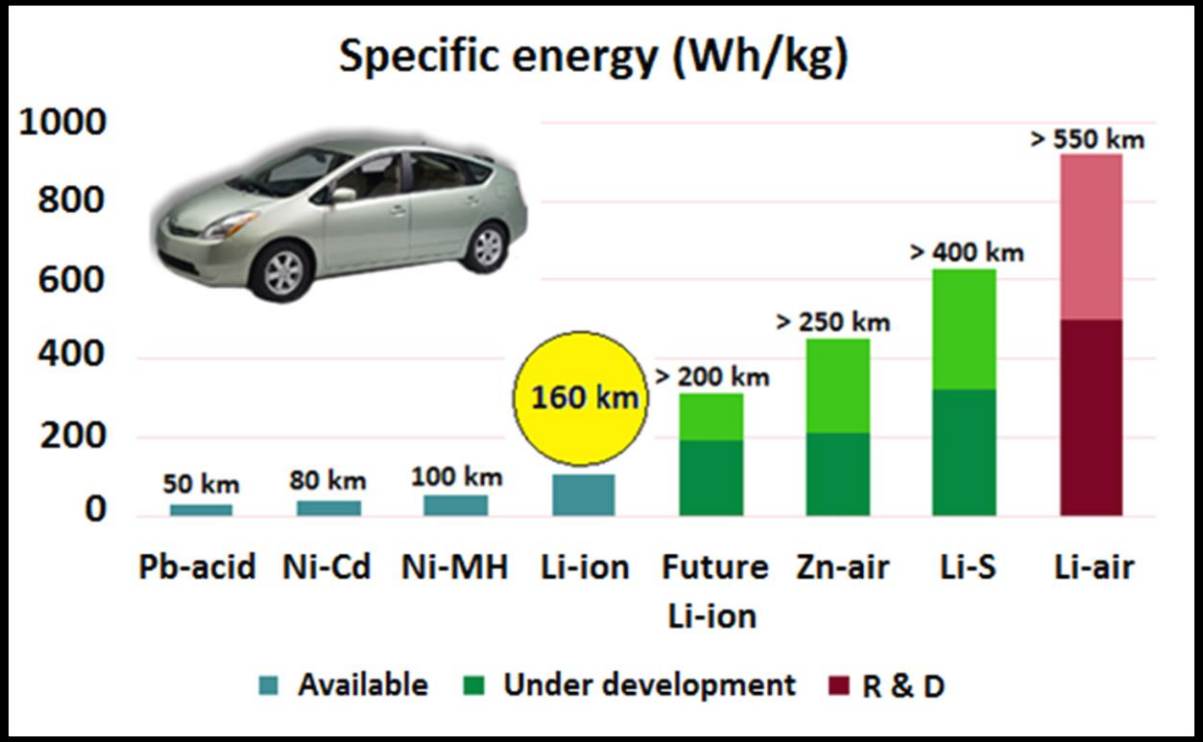
$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$ two-electrons reduction



Li-air battery!



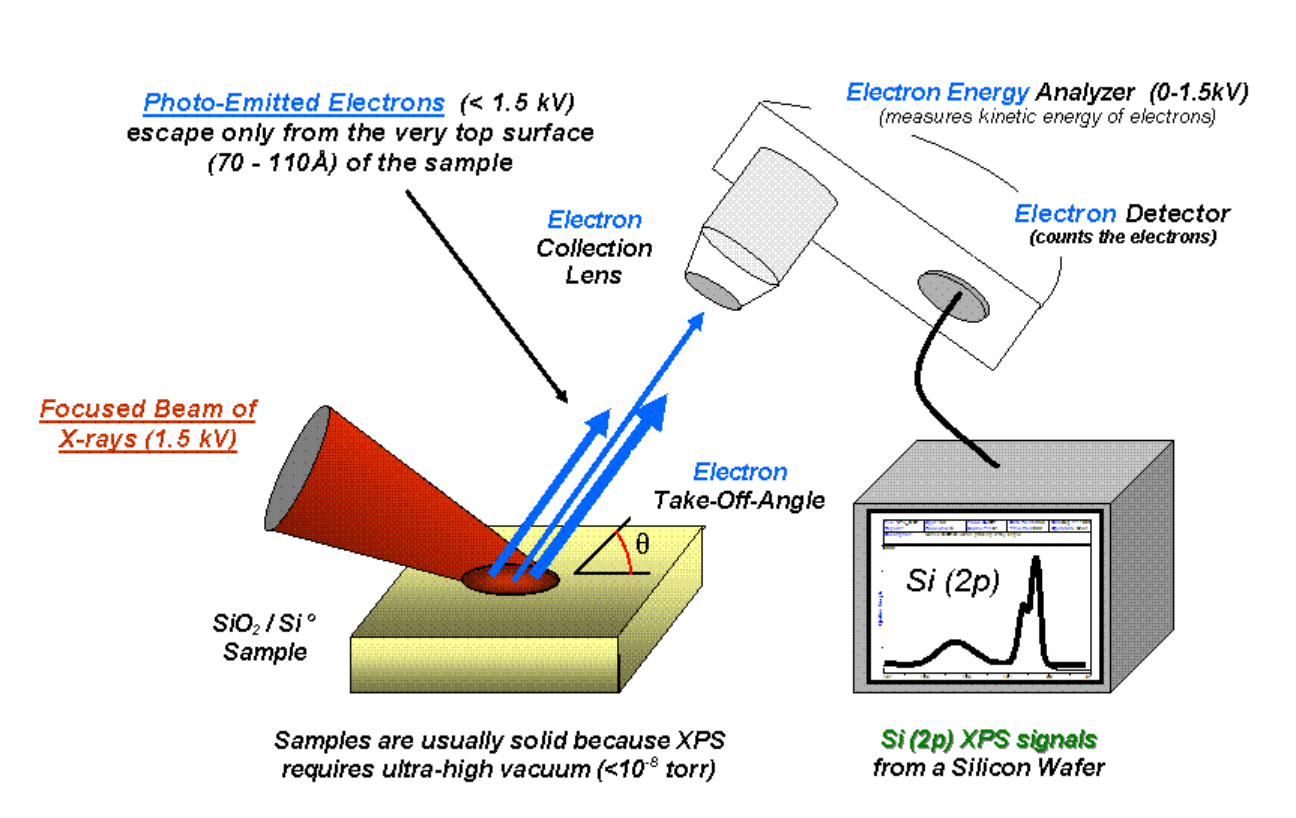
INTRODUCING Li-O_2 BATTERIES



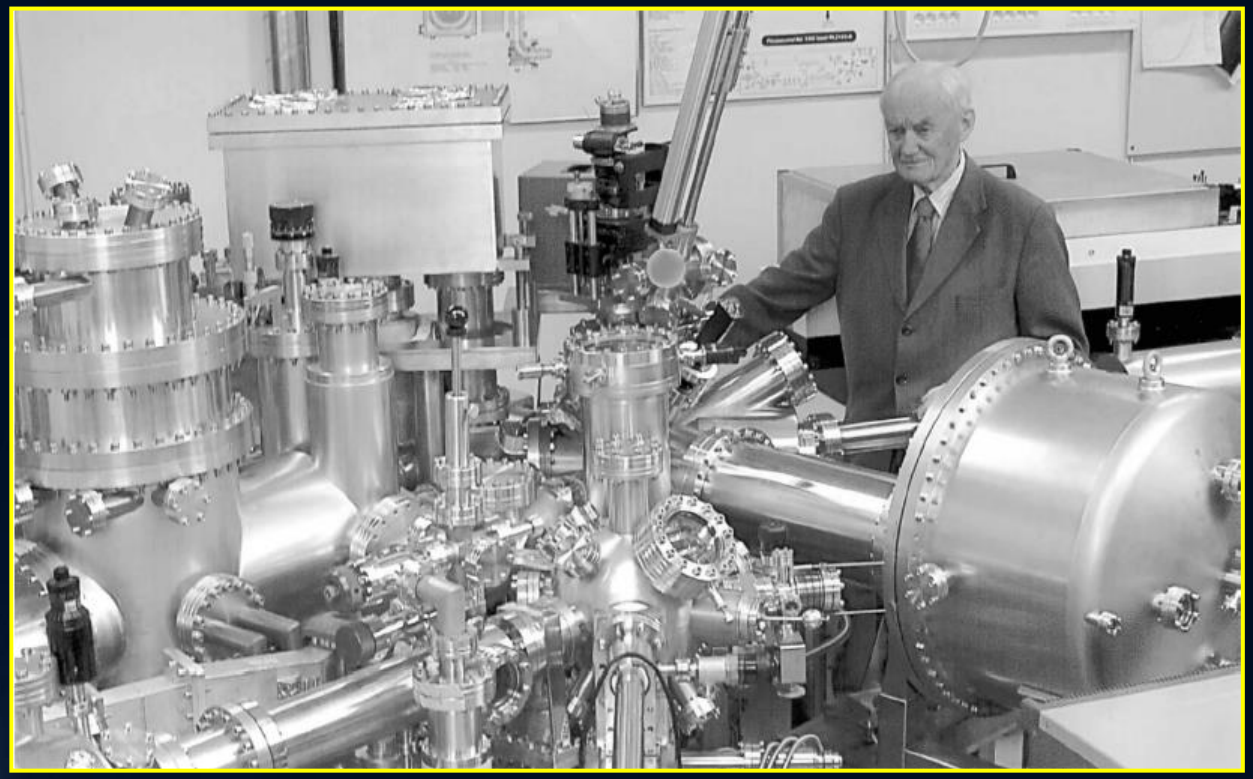
- ✓ High specific energy
- ✓ Low-cost
- ✓ High reversibility
- ✓ Zero emission
- ✓ High efficiency
- ✓ High thermal stability
- ✓ Long life
- ✓ Environment friendly

Photoemission spectroscopy

…that is photoelectric effect!



- Hertz 1887
- Einstein 1905 (Nobel 1921)

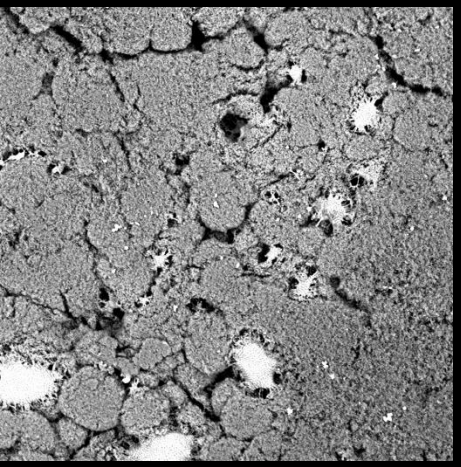


professor Kai Siegbahn Nobel Prize in Physics 1981

“…for his contribution to the development of high-resolution electron spectroscopy."

Tests on cathode materials for aprotic Li-O_2 cells

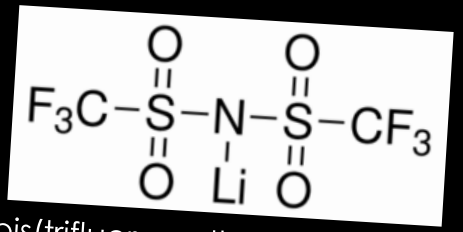
Cathode materials



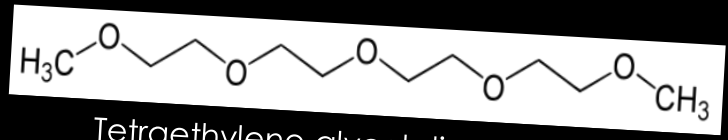
Super P carbon cloth + fluorinated polymeric binder

- Unexpensive and largely available
- Porous
- Catalyst for discharge reactions
- Subject to oxidative chemical attacks

Electrolyte

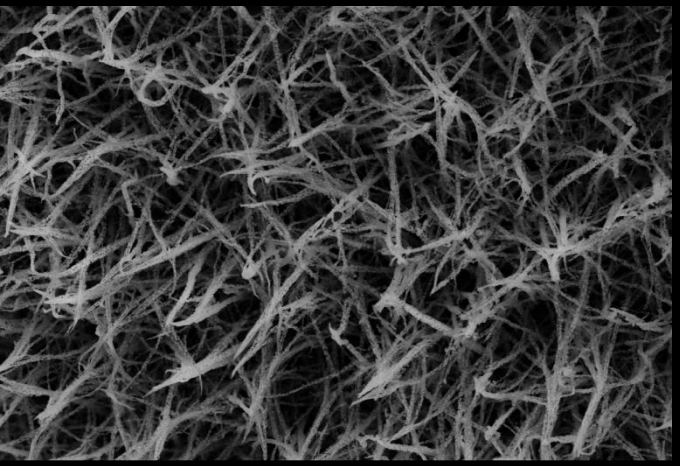


Lithium bis(trifluoromethane sulfonyl) imide (**LiTFSI**)



Tetraethylene glycol dimethyl ether (**TEGDME**)

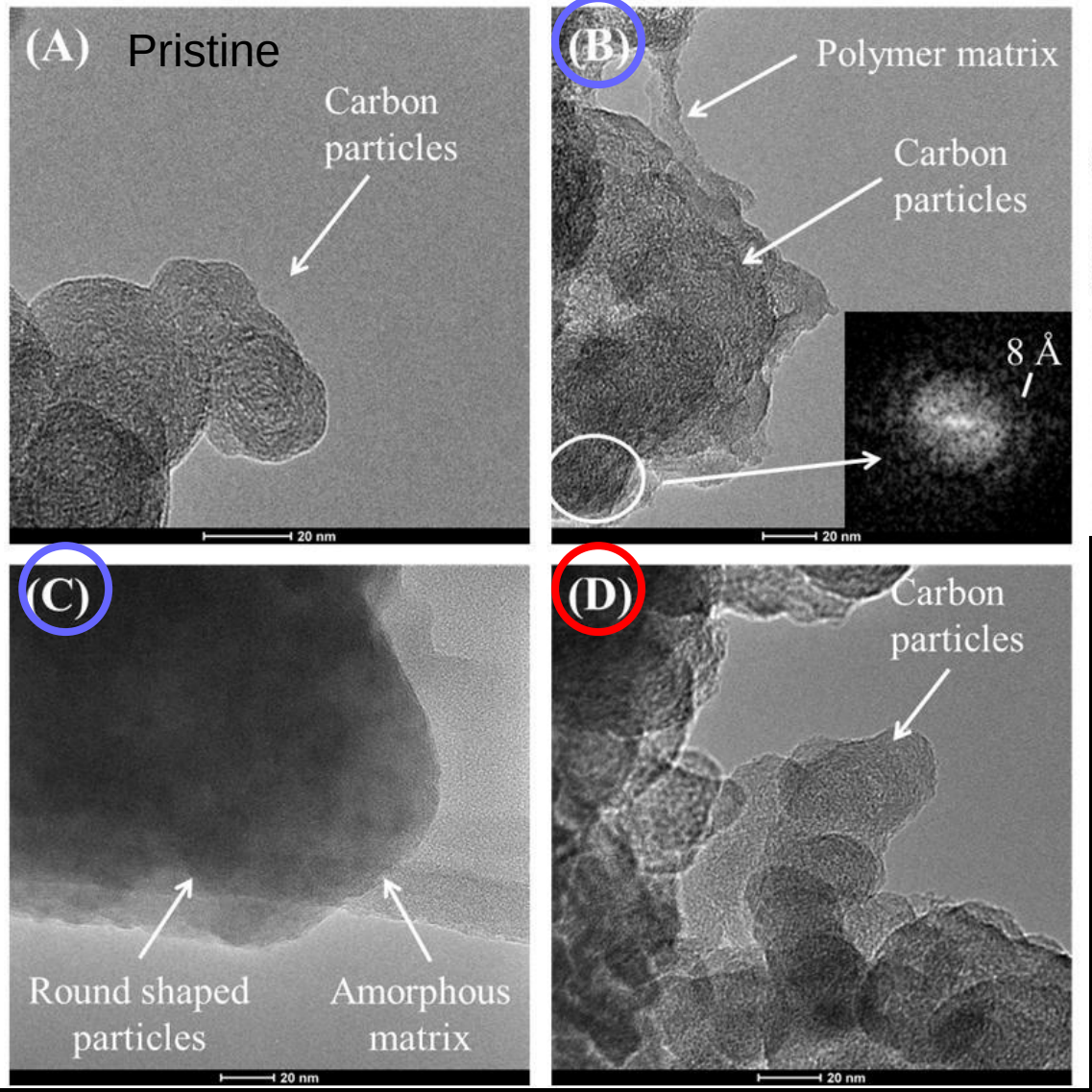
A novel cathode material for Li-O_2 cells

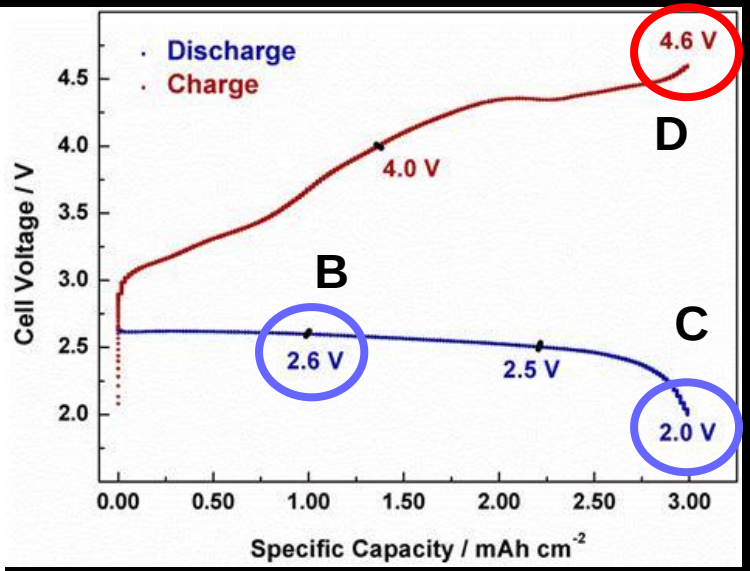


Cr^{3+}- doped $NiCo_2O_4$@Ni foam synthesized by means of an hydrothermal method

- Porous
- More active catalyst for discharge and charge reactions
- Inert to oxidative chemical attacks

Carbon cathodes: TEM images





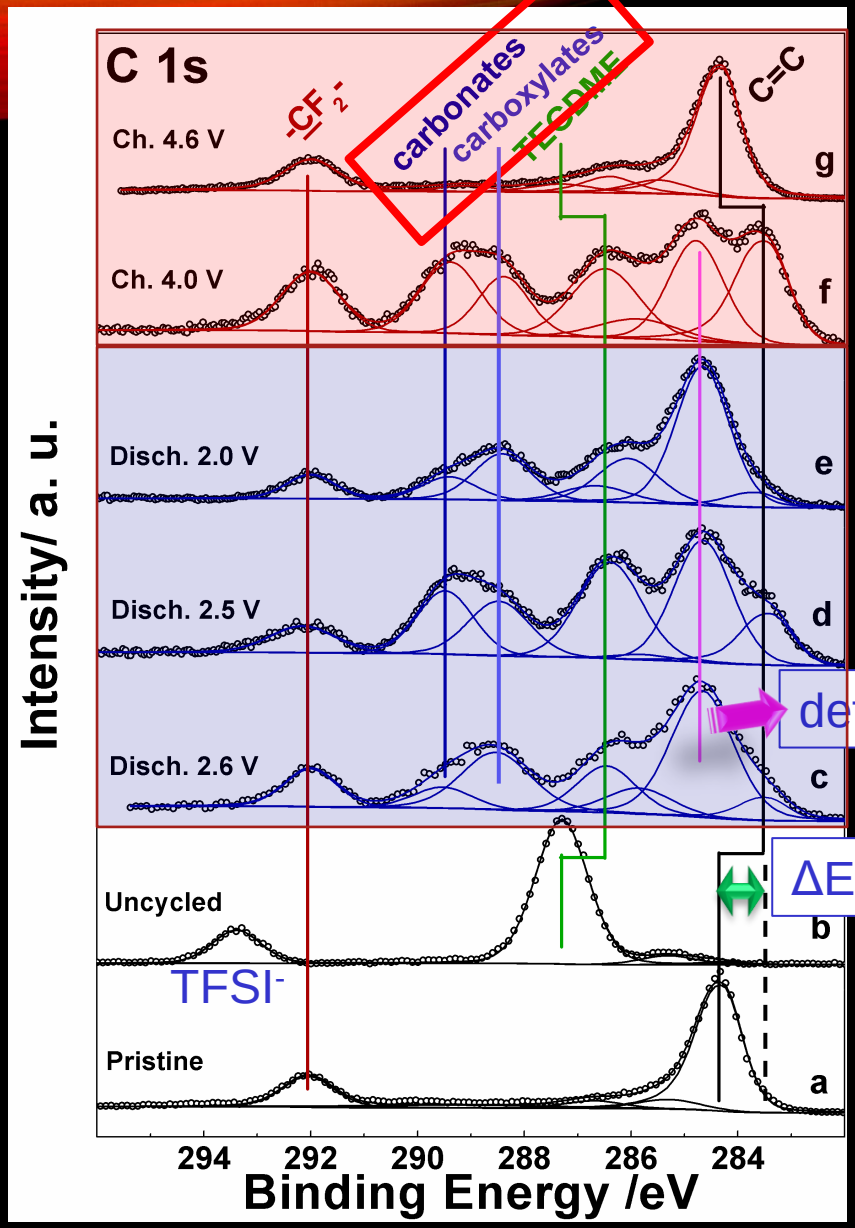
Discharge at 2.6 V: degradation products and nanoparticles, possibly constituted by Li_2O_2 .

Discharge at 2.0 V: amorphous matrix and shadows of pristine round shaped carbon particles.

Charge at 4.6 V: partial recovery of the original morphology.

D. Giacco, M. Carboni, S. Brutti, A. G. Marrani, *ACS Appl. Mater. Interfaces* **2017** 10.1021/acsami.7b05153

Carbon cathodes: XPS hv = Al Ka 1486.7 eV



Discharge

- Enhancement of carbon defects
- Deposition of carboxylates/carbonates
- Build-up of an electric potential gradient due to degradation by-products

Reactivity of solvent and cathode material with freshly generated oxygen radicals

Charge

- Electrochemical oxidation of COO^- /carbonates to CO_2
- Partial oxidation of C texture (epoxy)
- Recovery of carbon defectivity
- Recovery of electric potential gradient

D. Giacco, M. Carboni, S. Brutti, A. G. Marrani, *ACS Appl. Mater. Interfaces* **2017** 10.1021/acsami.7b05153

Let's try a new carbon-free cathode material!

Why Cr^{3+}-doped $NiCo_2O_4$@Ni foam?

Ni foam

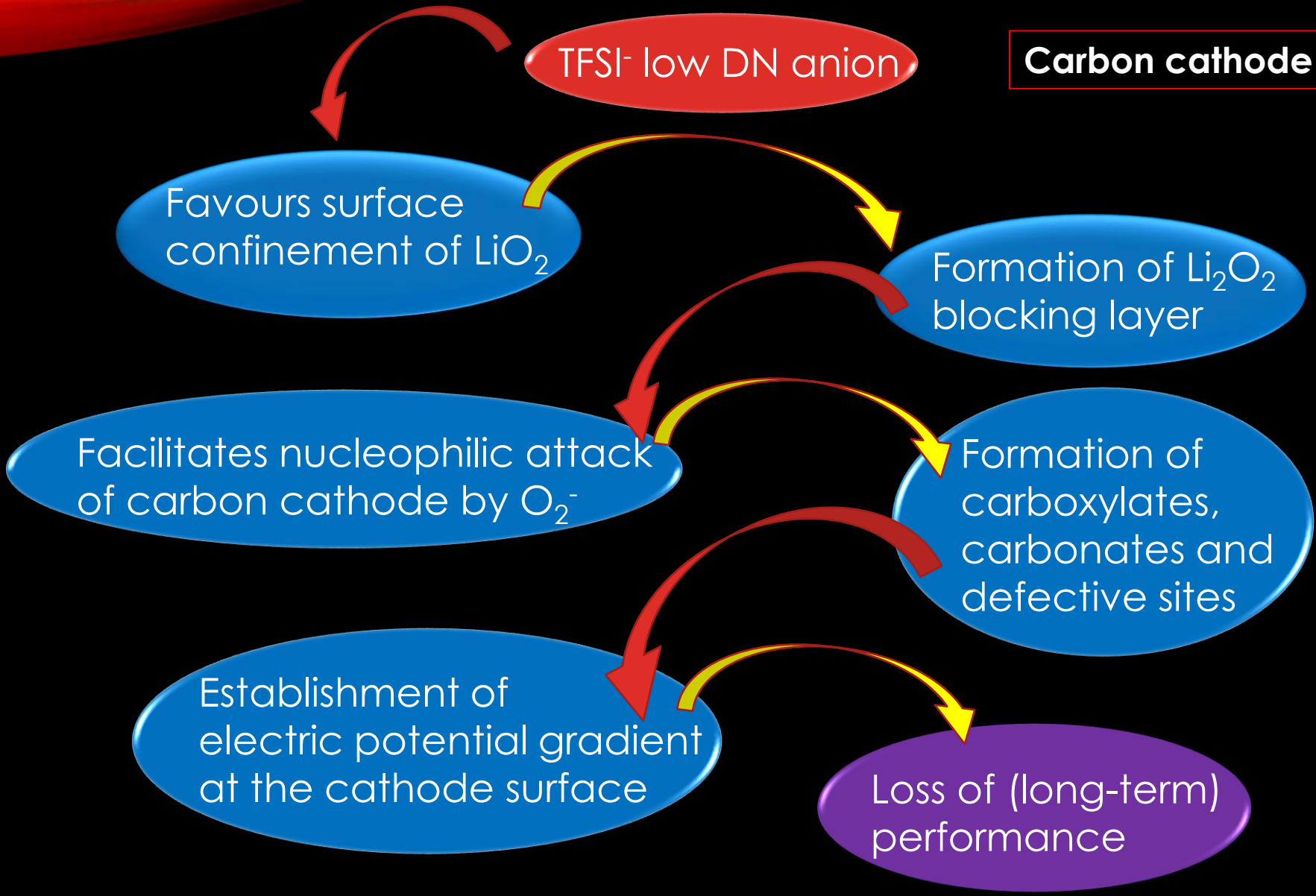
- Porous current collector
- Low overvoltages

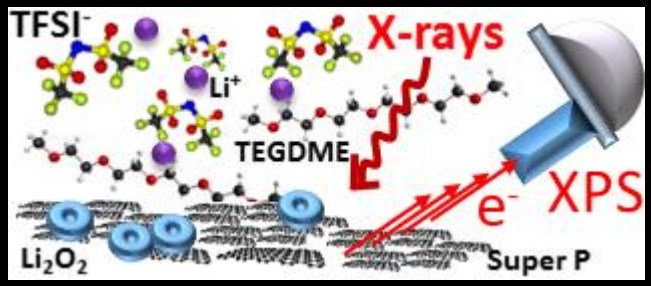
$NiCo_2O_4$

- Carbon-free
- High porosity
- Catalyst for ORR and OER
- Good electrochemical performance with the electrolyte LiTFSI/TEGDME

M^{n+}-doping of $NiCo_2O_4$ (M^{n+} = transition metal cations)
Possible increment of the catalytic activity →
Higher discharge capacity and reversibility, lower overvoltages.

Summary: XPS helped understand…





Thanks for your kind attention

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