PAUL SCHERRER INSTITUT

BATTERIES

ELECTROCHEMISTRY LABORATORY

Gas Evolution Reactions on Conductive Carbon Additives in Lithium-Ion Batteries

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Introduction & Purpose

❖ **Conductive carbon additive**

- **Main goal:** Increase the electronic conductivity (~ 10% weight ratio of electrodes)
- **Desirable:** Easily dispersed, highly conductive, light weight, chemically inert

❖ **Gas evolution reactions**

- **Safety:** Increase of internal cell pressure → Thermal runaway & cell leakage
- **Performance:** Irreversible capacity loss & increased impedance

❖ **Differential electrochemical mass spectrometry (DEMS)**

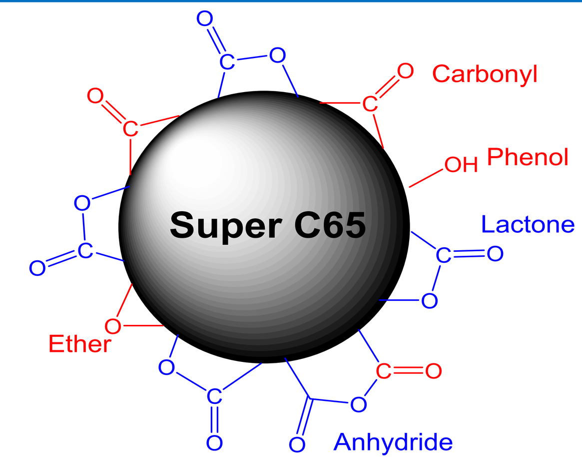
Investigate gas evolution *in situ*:

- **What:** Discriminate gases
- **How much:** Quantify the amount
- **When:** At what time/potential *(Differential)*

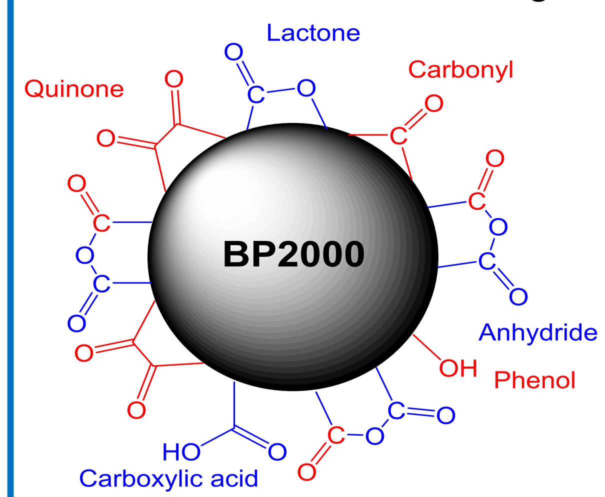
❖ **Aims**

- Determine the **type**, **extent** and **implication** of gas reactions on carbon additives in typical **LP30** carbonate electrolytes (LP30 = 1M $LiPF_6$ in 1:1 EC:DMC)
- Exploit **gas evolution** as **analytical probe** of carbon surface chemistry

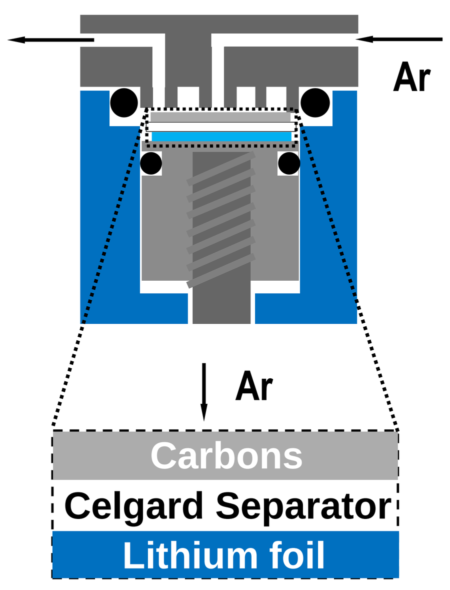
Carbons / Cell / DEMS



BET surface area: 62 m^2/g

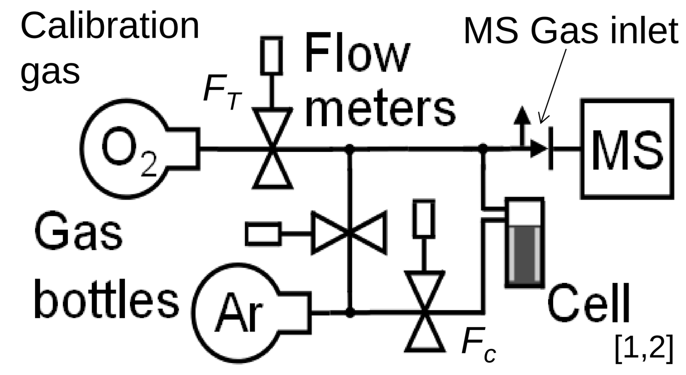


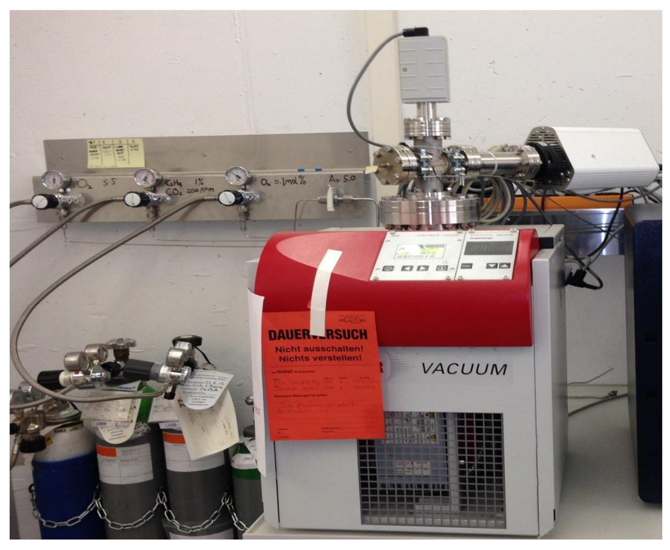
BET surface area: 1244 m^2/g



LP30 electrolyte

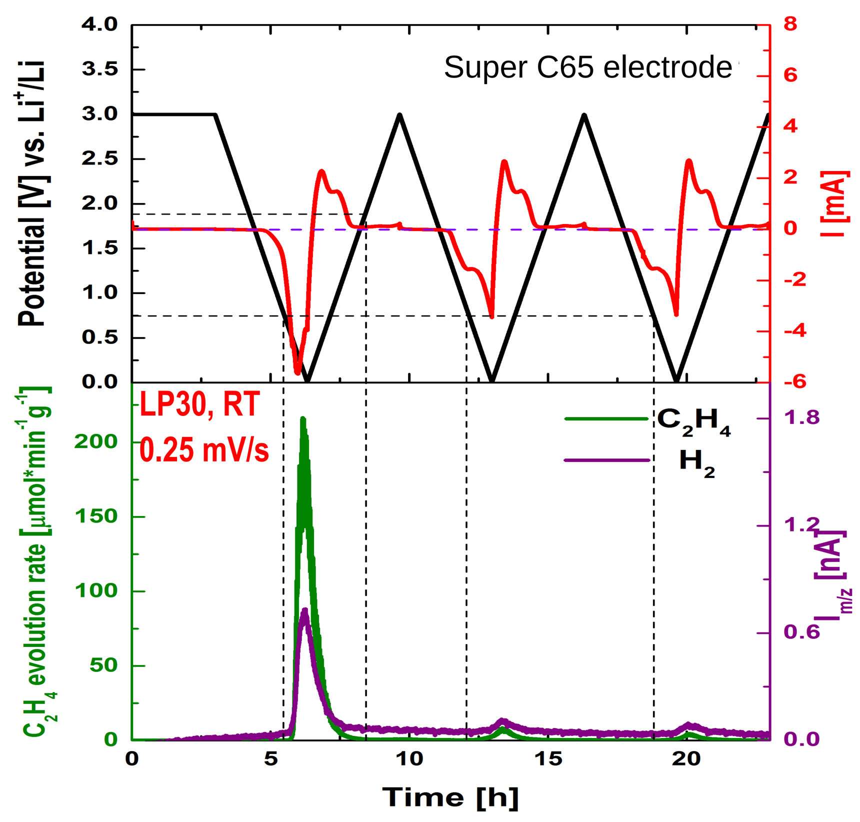
Electrochemical cell

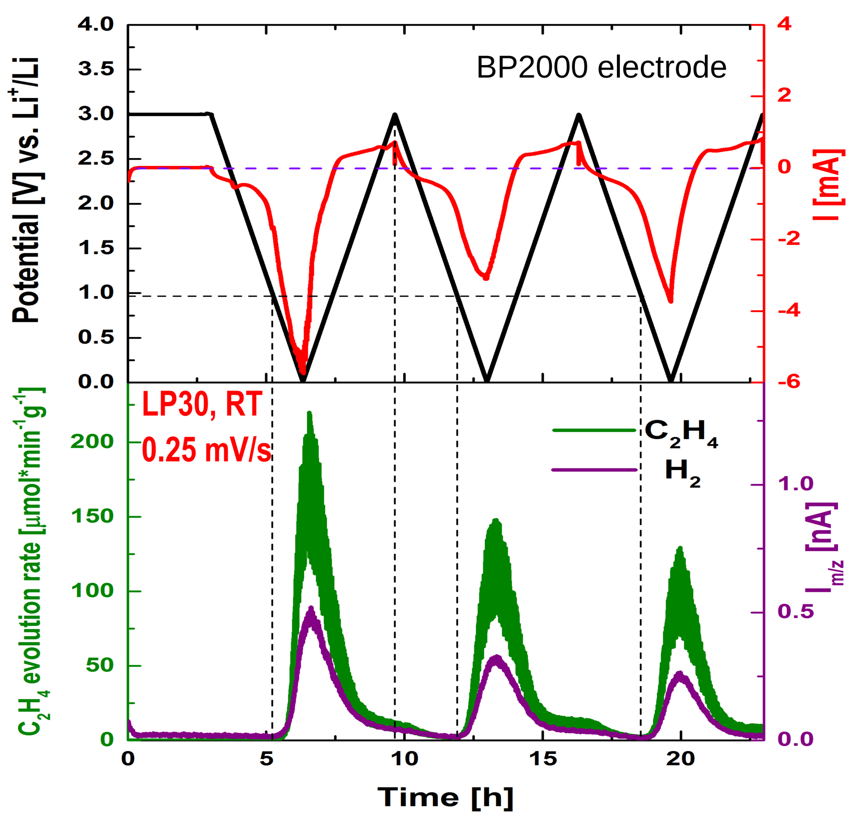




Differential electrochemical mass spectrometry (DEMS)

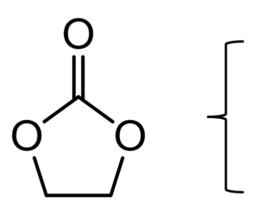
Reduction reactions (5 mV-1.5 V vs. Li^+/Li)





C_2H_4 quantity ← correlated → pore size distribution			
Carbon type	1st CV cycle	2nd cycle	3rd CV cycle
Super C65	7.7 mmol/g	0.4 mmol/g	0.3 mmol/g
BP2000	15.7 mmol/g	12.3 mmol/g	9.3 mmol/g

C_2H_4&H_2 evolution (0.8 V–5 mV)

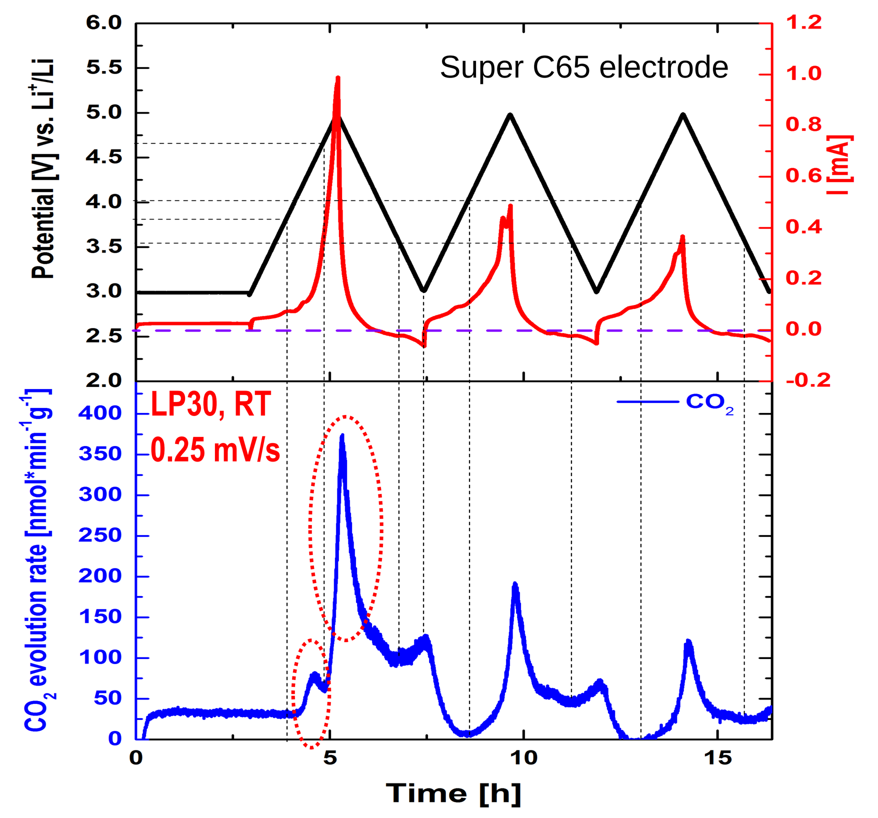


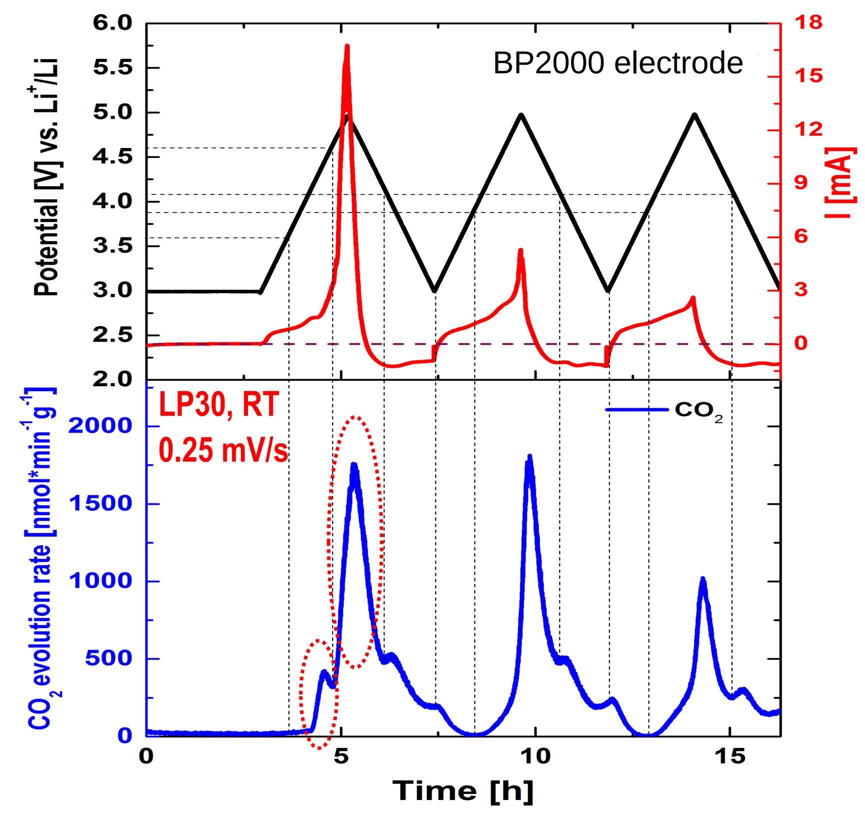
$Li_2CO_3 + C_2H_4\uparrow$

$(CH_2OCO_2Li)_2 + C_2H_4\uparrow$

$H\cdot + H\cdot \rightarrow H_2\uparrow$

Oxidation reactions (3.8 V-5 V vs. Li^+/Li)

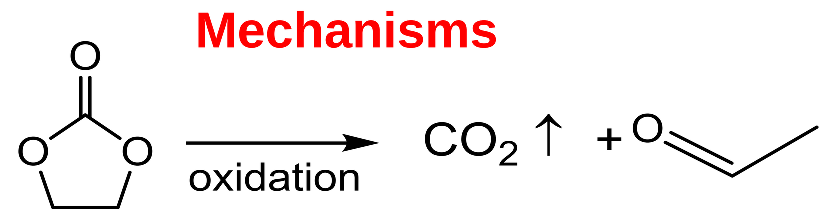




CO_2 evolution onsets

- 3.8 V–4.6 V: Surface groups oxidation
- 4.6 V–5.0 V: EC & DMC oxidation

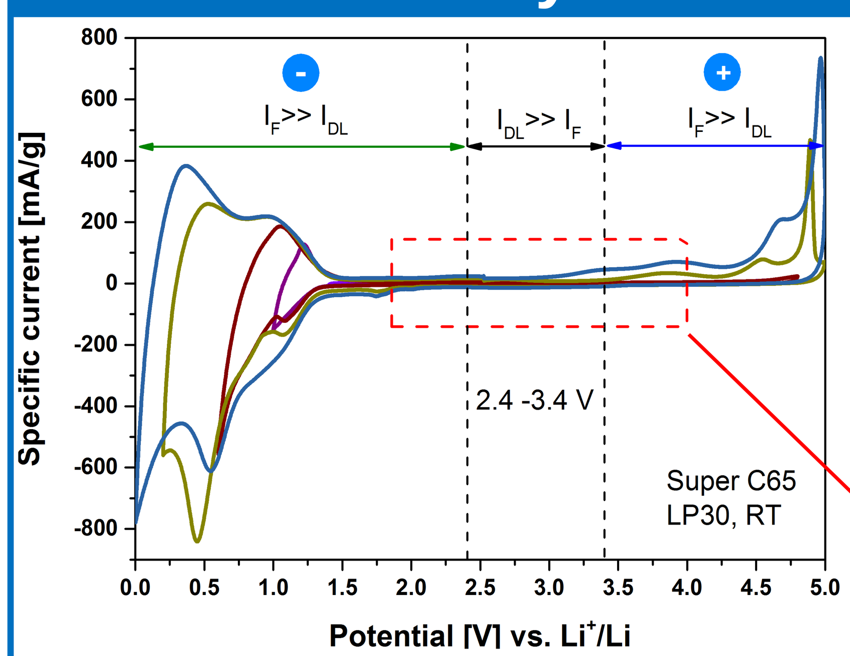
Mechanisms

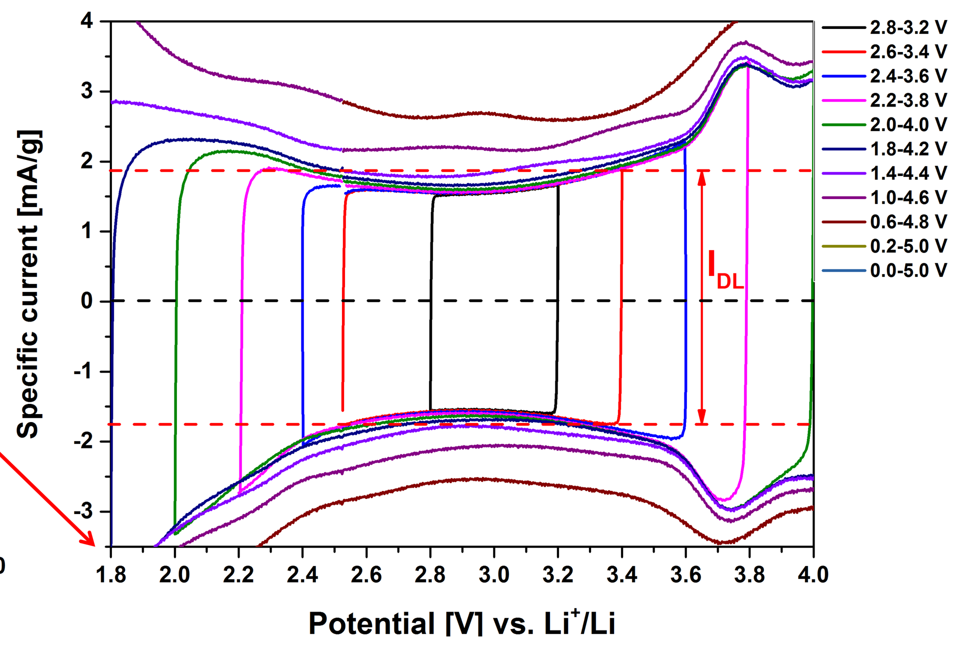


$CO_2\uparrow + $

CO_2 quantity ← proportional active surface area		
Carbon type	1st oxidation	2nd oxidation
Super C65	1.2 μmol/g	15.0 μmol/g
BP2000	9.0 μmol/g	104.9 μmol/g

Double layer domain (2.4 V-3.4 V vs. Li^+/Li)





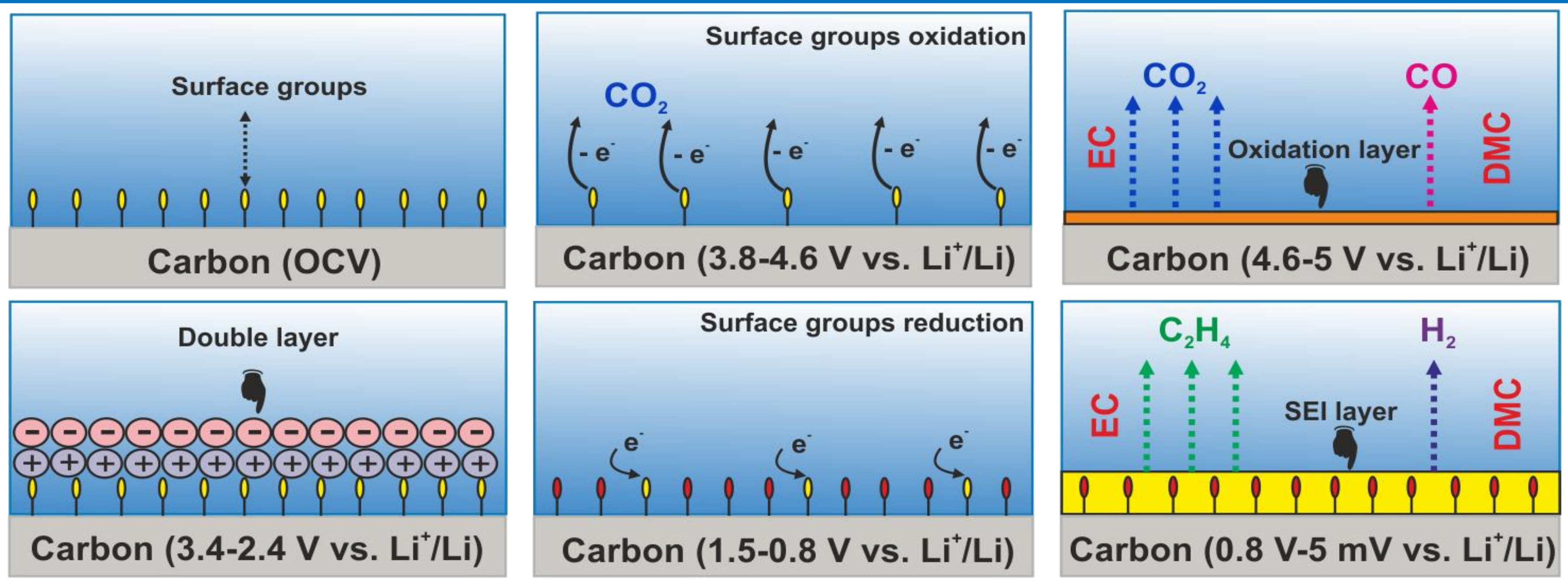
$$I_{Total} = I_{DL} + I_F$$ → Double layer current + Faradic current

Li-ion batteries active material operating potential ranges:

- (−) Negative: 5 mV < U < 2.4 V vs. Li^+/Li
- (+) Positive: 3.4 V < U < 5 V vs. Li^+/Li

Significant faradic currents from surface reactions in both ranges!

Summary & Conclusions



1. Onsets and types of side reactions on carbon additives are determined by DEMS.

❖ 5 mV-0.8 V vs. Li^+/Li: C_2H_4 and H_2 are detected as a result of the electrolyte reduction.

❖ 2.4-3.4 V vs. Li^+/Li: The double layer behavior dominates.

❖ 3.8-5 V vs. Li^+/Li: Carbon surface groups and electrolytes are oxidized to evolve CO_2.

2. Gas quantities are correlated to carbon surface areas & pore size distributions.

3. Gas evolution from carbon additives is often disregarded, but is considerable.

References

[1] P. Novák et al., *J. Pow. Sources.* **2005**, *146*, 15-20.

[2] R. Imhof, P. Novák, *J. Electrochem. Soc.* **1999**, *146*, 1702-1706.

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