PAUL SCHERRER INSTITUT

ELECTROCHEMISTRY LABORATORY

BATTERIES

FTIR SPECTROSCOPY TOOLS FOR THE CHARACTERIZATION OF ELECTRODE / ELECTROLYTE INTERFACES IN BATTERIES

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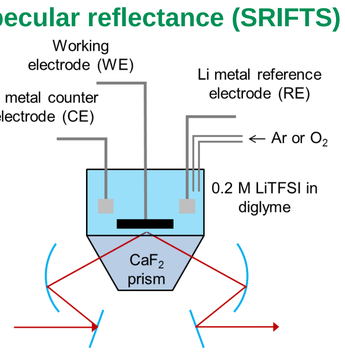
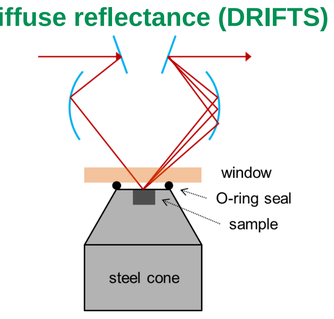
Cells / Approach / Aim

Specular reflectance (SRIFTS)



Diffuse reflectance (DRIFTS)



Approach

- **IR:** Facile analysis of solid, liquid and gaseous samples; particularly sensitive to CO, CO_2, carbonyl, carboxyl, carbonate and hydroxide species.
- ***Ex situ* DRIFTS:** Allows for analysis of real (amorphous) working electrodes.
- ***In situ* SRIFTS:** Avoids relaxation & determines the exact potential of electrochemical processes.

Aim

- Improve lifetime and cyclability by understanding interface reactions and their dependence on the gaseous, liquid and solid components present AND forming inside **Li-O_2** and **Li-Ion** batteries.[1]

Conclusions & Outlook

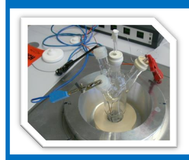
DRIFTS:

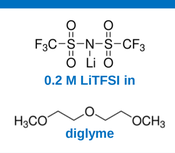
- Li-O_2 cell: Li oxides form inside the cell and convert to Li_2CO_3 in minutes upon air exposure.
- Method: limited to species comprising ≥ 10 %wt of active material.

SRIFTS:

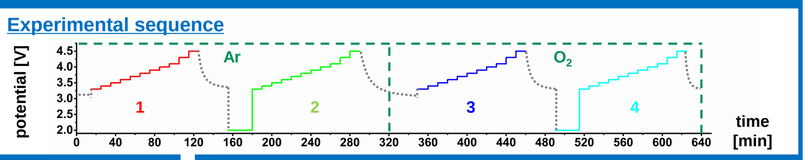
- Li-(Ar)O_2 cell: Li^+ incorporated into new Li compounds at 2.0 V. even in Ar.
- Carboxylate salt/carbonate formation at 2.0 V: stronger in Ar than in O_2.
- CO_2 formation: onset already at 3.6 V on GC and 4.1 V on Au-GC.
- Further oxidative decomposition reactions: formation of water/hydroxides, CO_2, carbonyls, carboxylates/carbonates with onset potentials ≥ 3.3 V.
- Solid decomposition products: formation by carbonyl polymerization?
- Li metal anode: non-innocent?

In situ SRIFTS





Experimental sequence



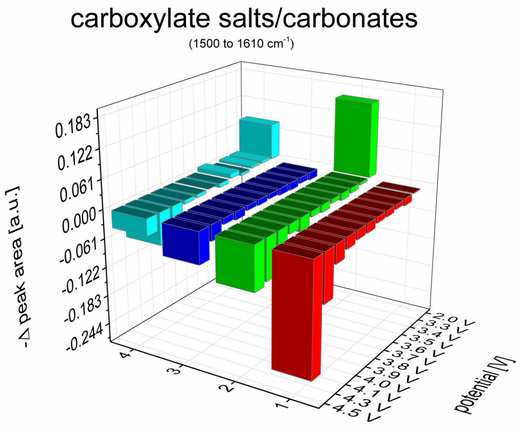
Ex situ DRIFTS

Experimental conditions

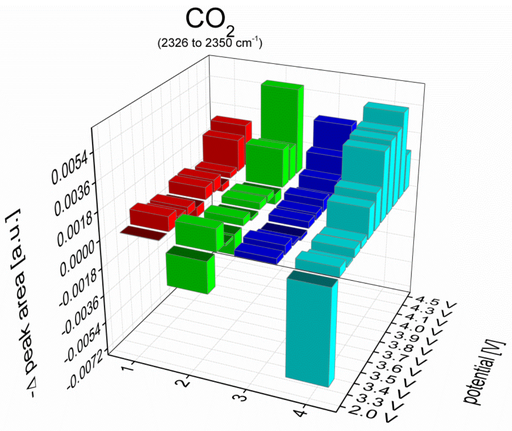
- WE: 80 %wt carbon, 20 %wt Nafion, 200 µm on glass fibre separator.
- CE: Li metal.
- Electrolyte: 0.2 M LiTFSI in diglyme.
- Galvanostatic cycling at ± 0.3 mA.

glassy carbon (GC)

carboxylate salts/carbonates (1500 to 1610 cm^{-1})

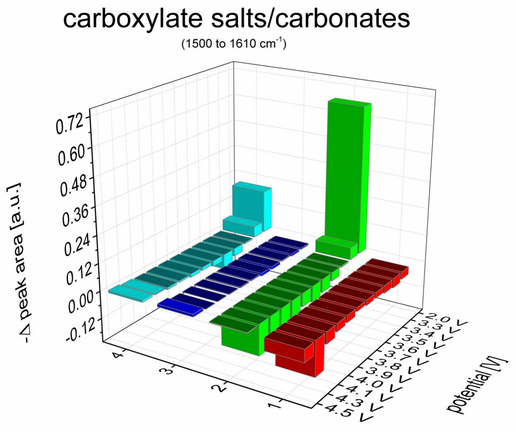


CO_2 (2326 to 2350 cm^{-1})

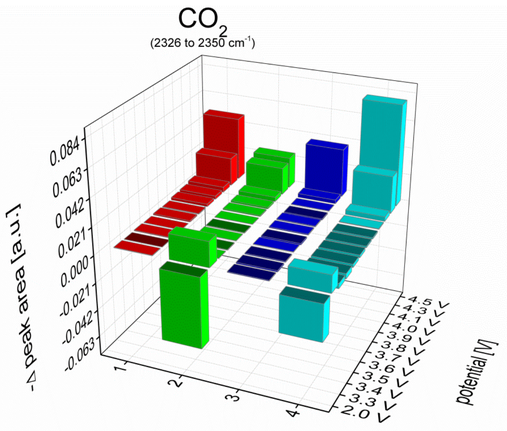


Au on glassy carbon (Au-GC)

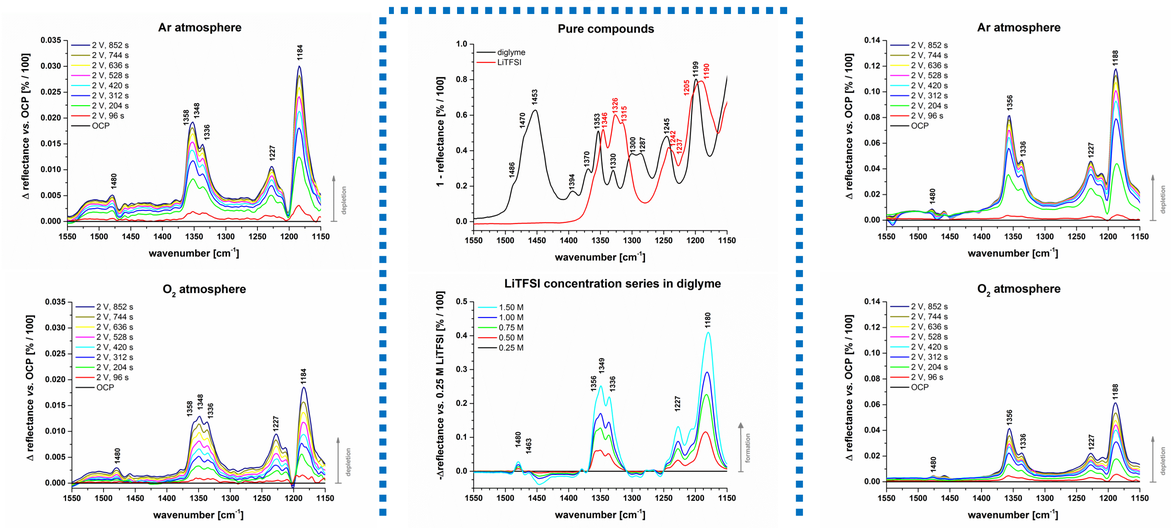
carboxylate salts/carbonates (1500 to 1610 cm^{-1})



CO_2 (2326 to 2350 cm^{-1})



- More carboxylate salts/carbonates[2] during reduction (2.0 V) in Ar.
- CO_2 formation facilitated on GC in O_2 (GC: ≥ 3.6 V, Au-GC: ≥ 4.1 V).



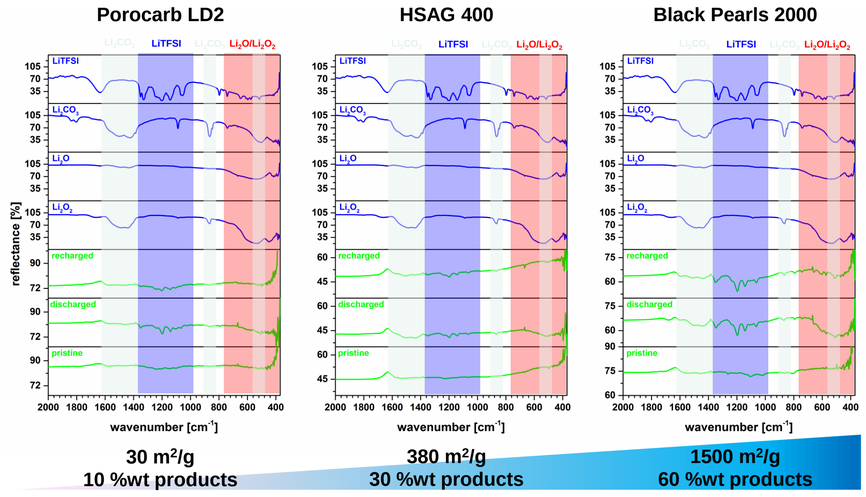
- Changes at 2.0 V suggest depletion of solvated Li^+.

☞ **New Li compounds form at 2.0 V even under Ar.**

☞ **CO_2 formation starts already at 3.6 V on GC and 4.1 V on Au-GC.**

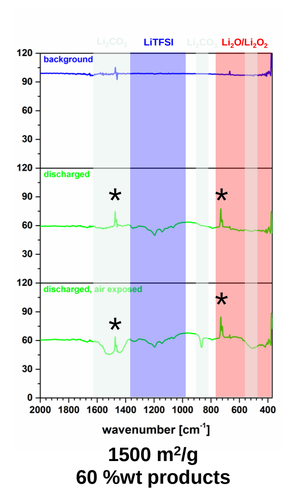
Li-O_2 cathodes

Cathodes with different specific surface areas, air exposed samples



30 m^2/g 10 %wt products — **380 m^2/g 30 %wt products** — **1500 m^2/g 60 %wt products**

Controlled air exposure



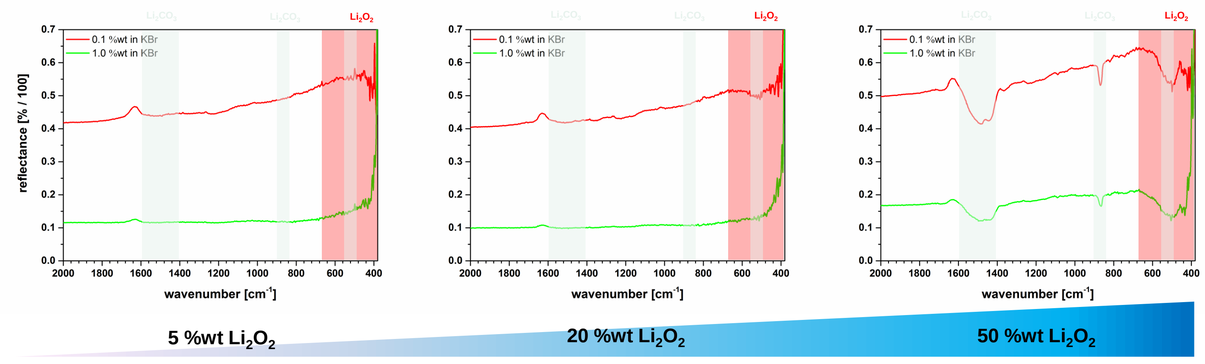
1500 m^2/g 60 %wt products

- Detection limit for Li oxide/carbonate products in discharged cathodes approximately 10 %wt.
- Conversion of Li oxide species to Li carbonate upon air exposure.

*** HDPE foil artifacts**

Carbon – Li_2O_2 blends

Blend composition: x %wt Li_2O_2, 100-x %wt (85 %wt Black Pearls 2000, 15 %wt PTFE)



5 %wt Li_2O_2 — **20 %wt Li_2O_2** — **50 %wt Li_2O_2**

- Detection limit for Li peroxide/carbonate in blends: 5 to 20 %wt.

Acknowledgements

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References

[1] Cairns et al., *Annu. Rev. Chem. Biomol. Eng.*, **2010**, 1, 299-320.
[2] Wijnja et al., *Spectrochim. Act. Part A*, **1999**, 55, 861-872.

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