Financial support from BASF SE is gratefully acknowledged.

**CE**: Li metal.

**Li**

**Detection limit for Li oxide/carbonate products in discharged cathodes**

**Method**: limited to species

Conversion of Li oxide species to Li carbonate upon air exposure.

Changes at 2.0 V suggest depletion of solvated Li***.

**New Li compounds form at 2.0 V even under Ar. CO₂ formation starts already at 3.6 V on GC and 4.1 V on Au-GC.**

**Conclusions & Outlook**

**DRIFTS**:

- Li-O₂ cell: Li oxides form inside the cell and convert to Li₂CO₃ in minutes upon air exposure.
- Method: limited to species comprising ≥ 10 %wt of active material.

**SRIFTS**:

- Li-(Ar)O₂ 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 O₂.
- CO₂ formation: onset already at 3.6 V on GC and 4.1 V on Au-GC.
- Further oxidative decomposition reactions: formation of water/hydroxides, CO₂, carboxyls, carboxylates/carbonates with onset potentials ≥ 3.3 V.
- Solid decomposition products: formation by carbonyl polymerization?
- Li metal anode: non-innocent?

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**References**