Supplementary Information

Impact of *in coin cell* atmosphere on lithium metal battery performance

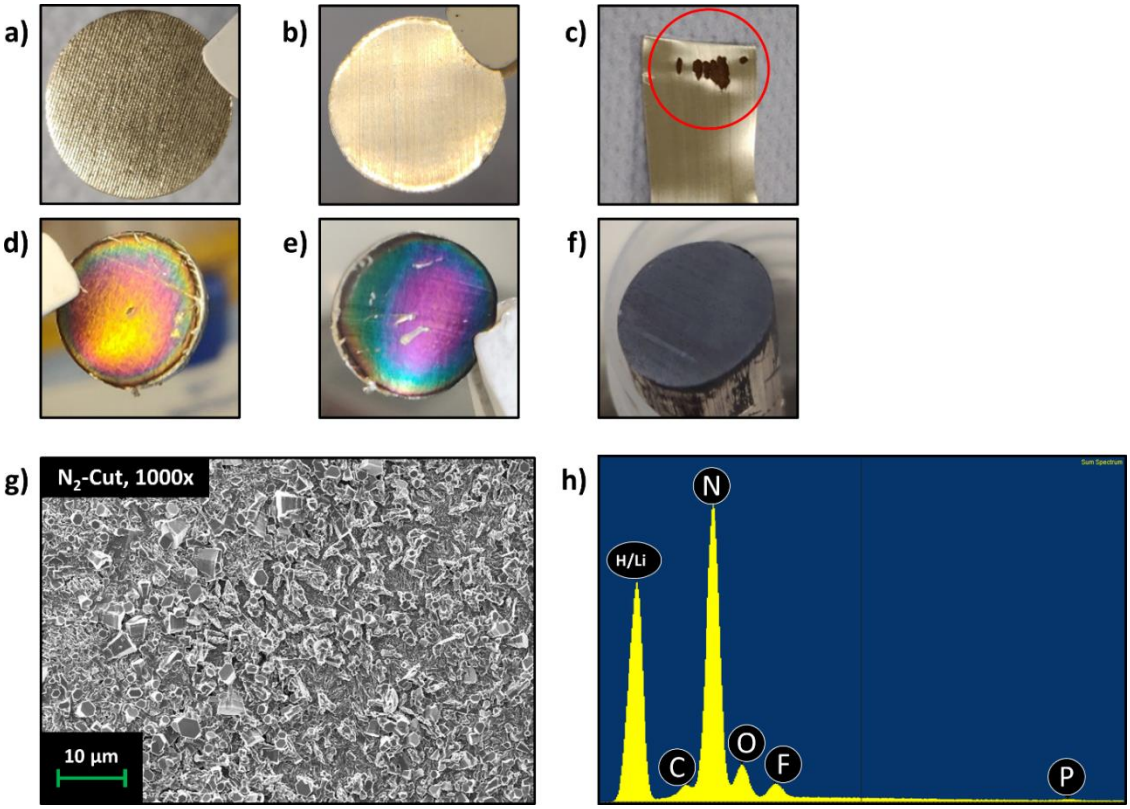
Sebastian P. Kühn[1], Matthias Weiling[1], Diddo Diddens[1], Masoud Baghernejad[1], Martin Winter[1,2], Isidora Cekic-Laskovic[1]

[1]Helmholtz-Institute Münster, Forschungszentrum Jülich GmbH, Münster 48149, Germany.
[2]MEET Battery Research Center, University of Münster, Münster 48149, Germany.

Correspondence to: Dr. Isidora Cekic-Laskovic, Ionics in Energy Storage (IEK-12), Helmholtz-Institute Münster, Forschungszentrum Jülich GmbH, Corrensstrasse 46, Münster 48149, Germany. E-mail: i.cekic-laskovic@fz-juelich.de

ICCA = *in Coin Cell* Atmosphere; DR = Dry room; GB = Glovebox

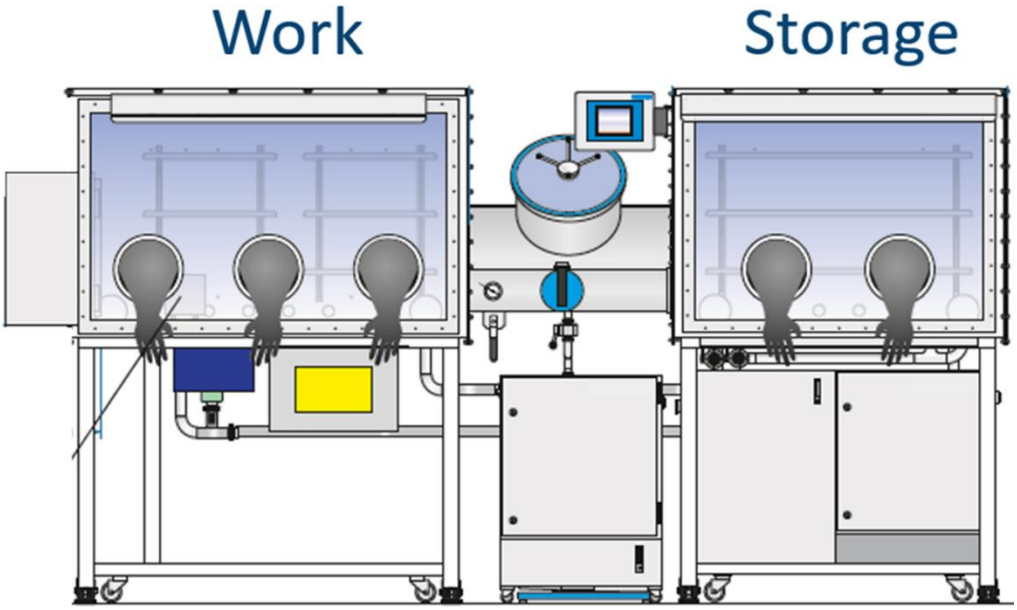
1 Gas reaction of lithium metal



Supplementary Figure 1. Optical analysis of different types of lithium. Commercially available lithium chips (a) and cut outs of battery grade lithium foil (b). Decomposition of battery grade lithium (c) in contaminated storage conditions upon a scratched off native passivation layer. Surface reaction of freshly cut lithium slices in contaminated Ar-filled glovebox (d, e) ultimately resulting in a black surface, equal to the one formed upon the generation of a fresh lithium surface in an N_2- filled glovebox (f). SEM (g) and EDX analysis (h) of the black surface formed on a fresh Li slice in an N_2-filled glovebox.

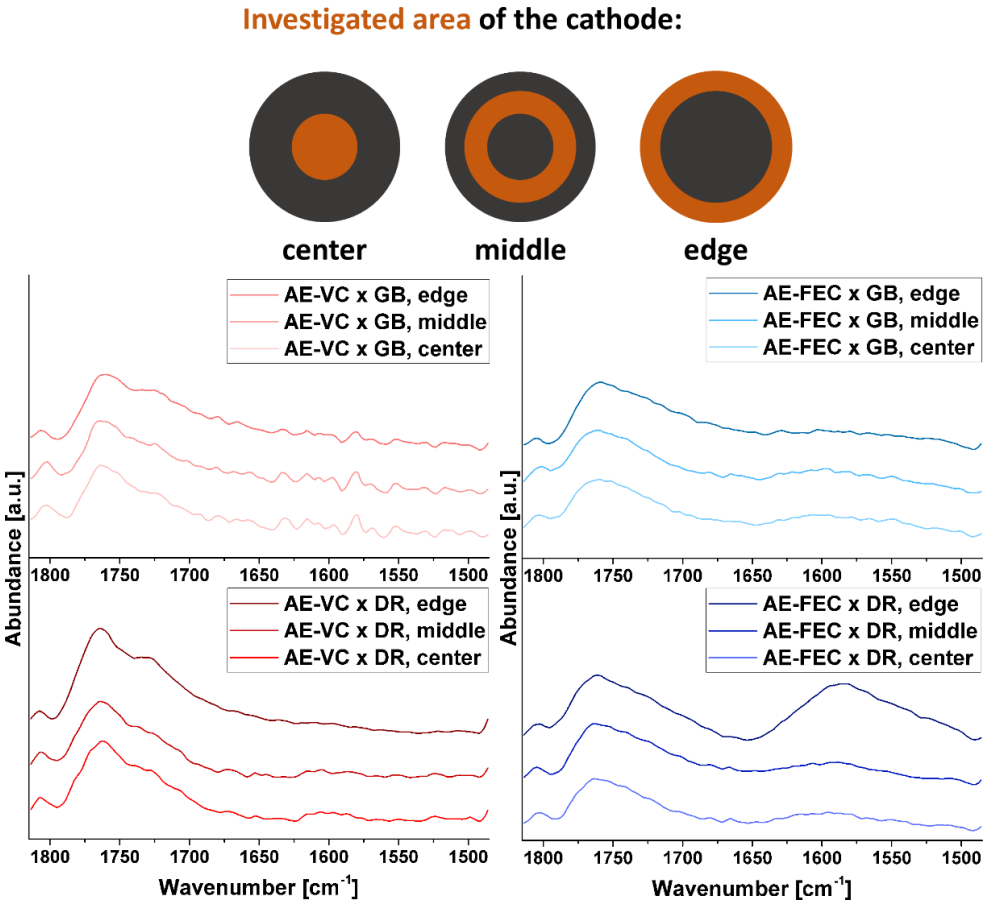
ICCA = *in Coin Cell* Atmosphere; DR = Dry room; GB = Glovebox

2 Dual-Box



Supplementary Figure 2. A special dual-glovebox, equipped with H_2O, O_2, N_2 and solvent purifier as well as temperature control (set to 25 °C) and CO_2 sensor. The right chamber of the Dual-Box has been used to store battery components and prevent any degradation of material (anodes, cathodes, electrolytes) to ensure equal starting conditions for all experiments. The left chamber has been used for battery assembly and is the origin of the GB ICCA referenced in the main text.

3 ATR-FTIR Analysis



Supplementary Figure 3. Additional ATR-FTIR spectra measured on different parts of the electrode (highlighted in orange).

ICCA = *in Coin Cell* Atmosphere; DR = Dry room; GB = Glovebox

4 Electrolyte formulations

Electrolytes used in this study have been designed based in an equal molar approach to enhance and ensure comparability between the utilized additive containing electrolytes AE-VC and AE-FEC.

Supplementary Table 1. Baseline electrolyte (BE)

Compound	**wt%**	**m [g] for 1000g**	**n [mol]**	**mol%**
$LiPF_6$	15.10	151.00	0.99	10.36
EC	25.50	255.00	2.90	30.18
EMC	59.40	594.00	5.71	59.46

Supplementary Table 2. Electrolyte, containing vinylene carbonate as electrolyte additive (AE-VC)

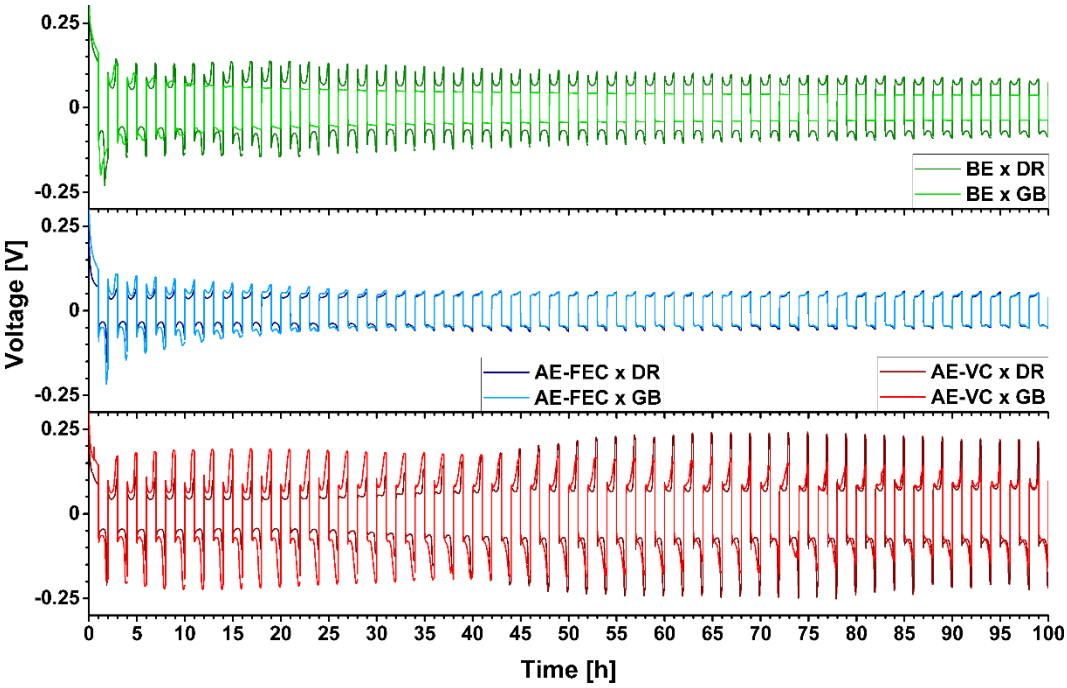
Compound	**wt%**	**m [g] for 1000g**	**n [mol]**	**mol%**
$LiPF_6$	14.40	144.00	0.95	9.78
EC	24.10	241.00	2.74	28.23
EMC	56.50	565.00	5.43	55.99
VC	5.00	50.00	0.58	5.99

Supplementary Table 3. Electrolyte, containing fluoroethylene carbonate as electrolyte additive (AE-FEC)

Compound	**wt%**	**m [g] for 1000g**	**n [mol]**	**mol%**
$LiPF_6$	14.23	144.00	0.95	9.78
EC	23.82	241.00	2.74	28.23
EMC	55.85	565.00	5.43	55.99
FEC	6.09	61.62	0.58	5.99

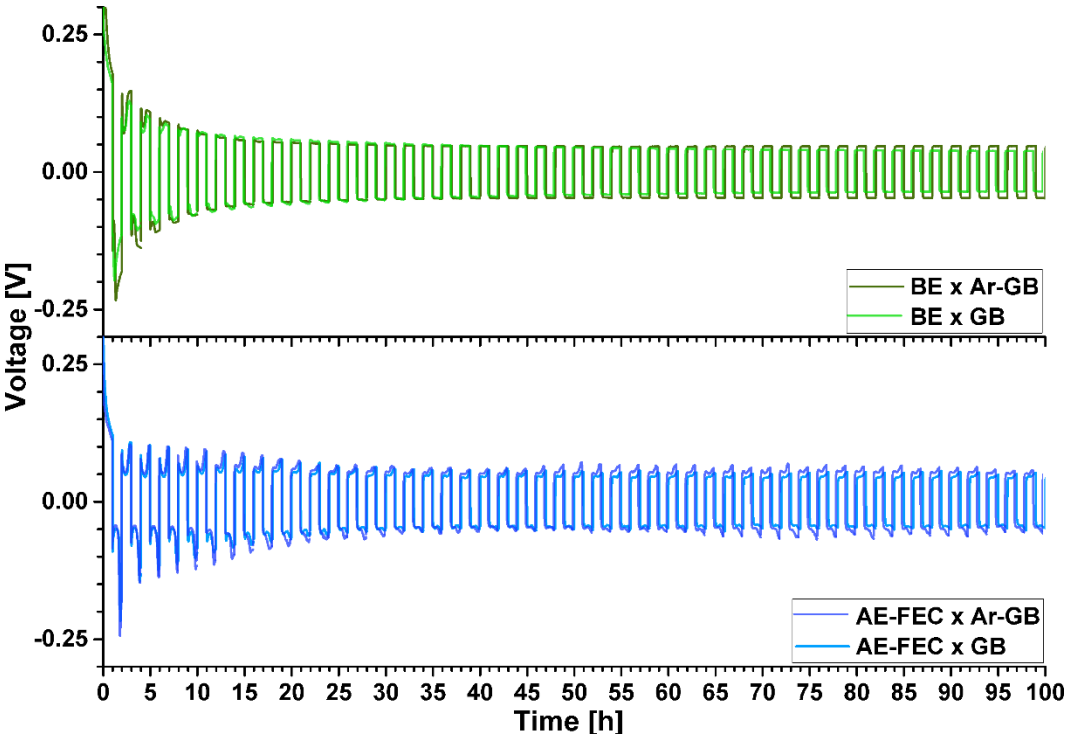
5 Stripping/plating data of Li||Li symmetric cells

5.1 Close up of first 100 h



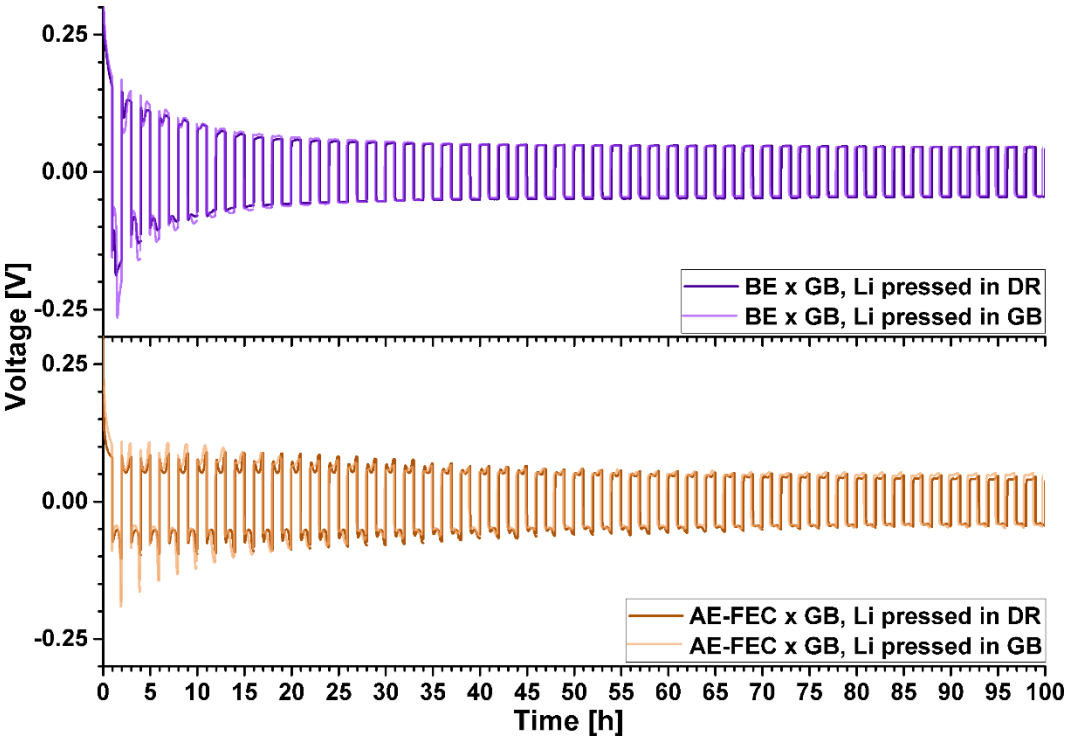
Supplementary Figure 4. Close up (100 h/ 50 cycles) of voltage profiles (0.5 mA cm^{-2}, 1 h charge and discharge) of six different Li||Li cell setups. Top: BE×DR – dark green, BE×GB – light green; Middle: AE-FEC×DR – dark blue; AE-FEC×GB – light blue; Bottom: AE-VC×DR – dark red; AE-VC×GB – light red.

5.2 N_2-free vs. standard Ar-GB: striping/plating performance comparison



Supplementary Figure 5. Close up (100 h/ 50 cycles) of voltage profiles (0.5 mA cm^{-2}, 1 h charge and discharge) of four different Li||Li cell setups comparing ultra-pure N_2 free and "standard" argon glovebox atmosphere (Ar-GB). Top: BE×Ar-GB – dark green, BE×GB – light green; Bottom: AE-FEC×Ar-GB – blue; AE-FEC×GB – light blue.

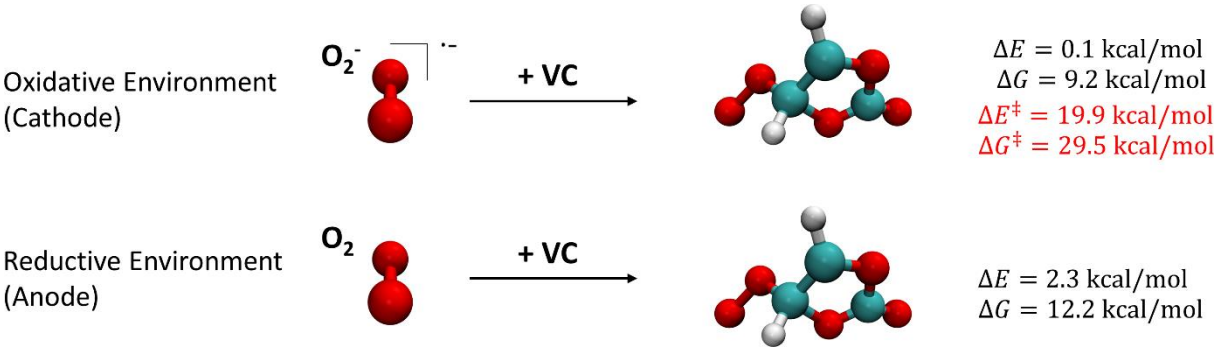
5.3 DR- vs. GB-Atmosphere lithium surface modification: stripping/plating performance comparison



Supplementary Figure 6. Close up (100 h/ 50 cycles) voltage profiles (0.5 mA cm^{-2}, 1 h charge and discharge) of four different Li||Li cell setups assembled using either lithium electrodes prepared in a GB or DR atmosphere.[7,39] Top: BE×GB, Li pressed in DR – dark purple, BE×GB, Li pressed in GB – light purple; Bottom: AE-FEC×GB, Li pressed in DR – dark brown; AE-FEC×GB – light brown.

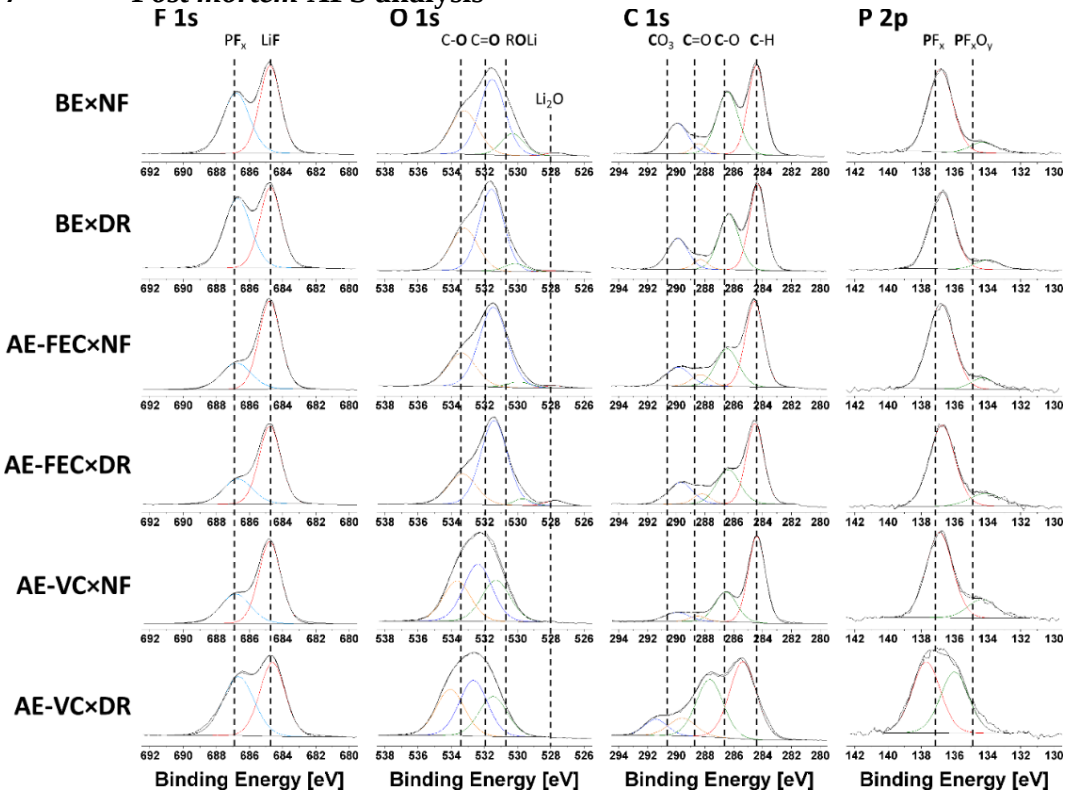
ICCA = *in Coin Cell* Atmosphere; DR = Dry room; GB = Glovebox

6 Quantum chemical calculations



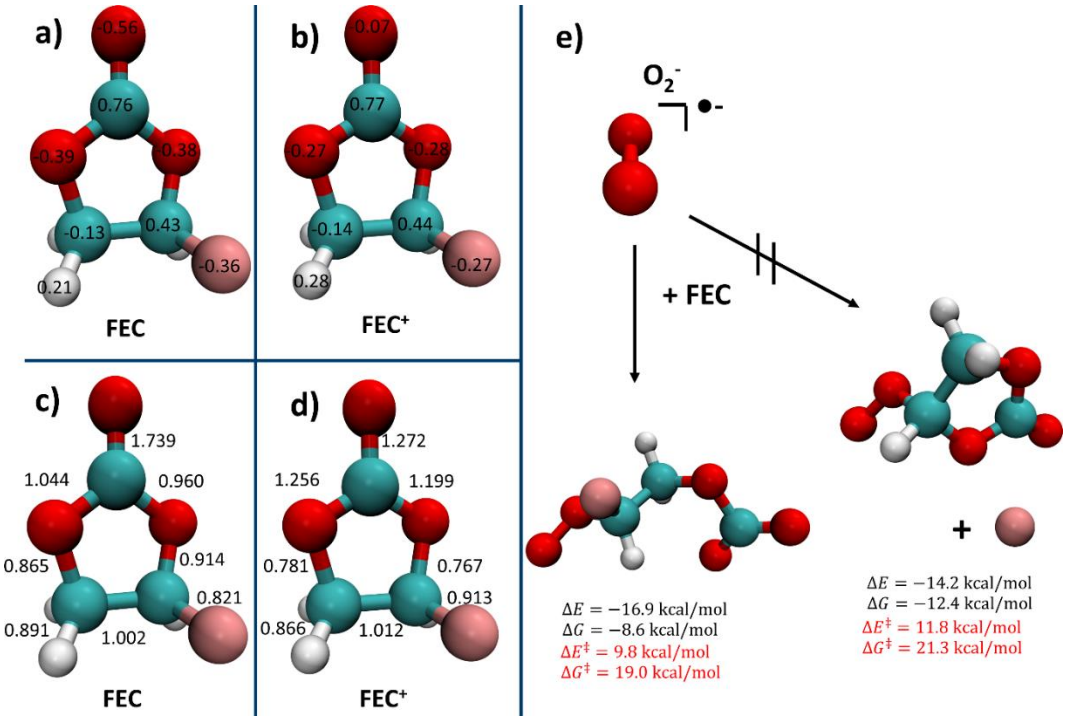
Supplementary Figure 7. Quantum chemical calculations of the possible reactions of VC with oxygen in an oxidative or reductive environment.

7 *Post mortem* XPS analysis



Supplementary Figure 8. Individual chemical resonance of the *post mortem* XPS analysis of Li electrodes harvested from Li||Li symmetric cells after 100 h of stripping/plating experiment (0.5 mA cm^{-2}, 0.5 mAh cm^{-2}).

ICCA = *in Coin Cell* Atmosphere; DR = Dry room; GB = Glovebox



Supplementary Figure 9. Quantum chemical calculations as basis for the FEC decomposition mechanism on NMC811 in the presence of oxygen. Mulliken charges (a,b) and bond orders (c,d) of FEC (a, c) and FEC^+ (b, d, representing coordinated an FEC-Li^+ system). E) Free energy (black) and energy barrier (red) values for the nucleophilic attack of the superoxide radical on FEC, supporting a ring opening mechanism over a fluorine cleavage.

ICCA = *in Coin Cell* Atmosphere; DR = Dry room; GB = Glovebox