

Advanced investigation of oxygen release during cycling of HE-NCM

Elias Castel, Erik J. Berg, Patrick Lanz, Claire Villeveille, and Petr Novák

Paul Scherrer Institut, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland
petr.novak@psi.ch

Lithium-ion batteries

$\text{Li}_2\text{MnO}_3\cdot\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ (HE-NCM) → Promising material to replace LiCoO_2 .
→ Cycling to 5V vs. Li^+/Li .

Surface reactions & interfaces → Side-reactions at interfaces → Detrimental to LiB long-term performance.

Electrolyte unstable → Study of gas evolution by Differential Electrochemical Mass Spectrometry (DEMS).

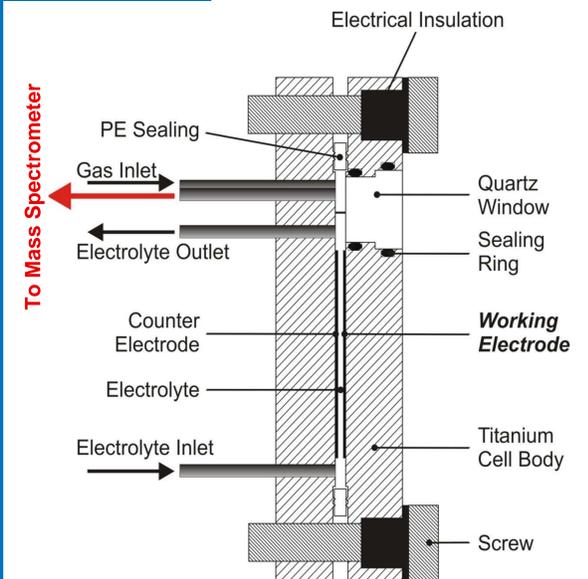
Experiments

DEMS setup: Electrochemical cell purged during cycling to bring any electrochemically developed volatile products to quadrupole MS for analysis.

HE-NCM electrodes cycled at C/10 between 2 to 5 V vs. Li^+/Li in:

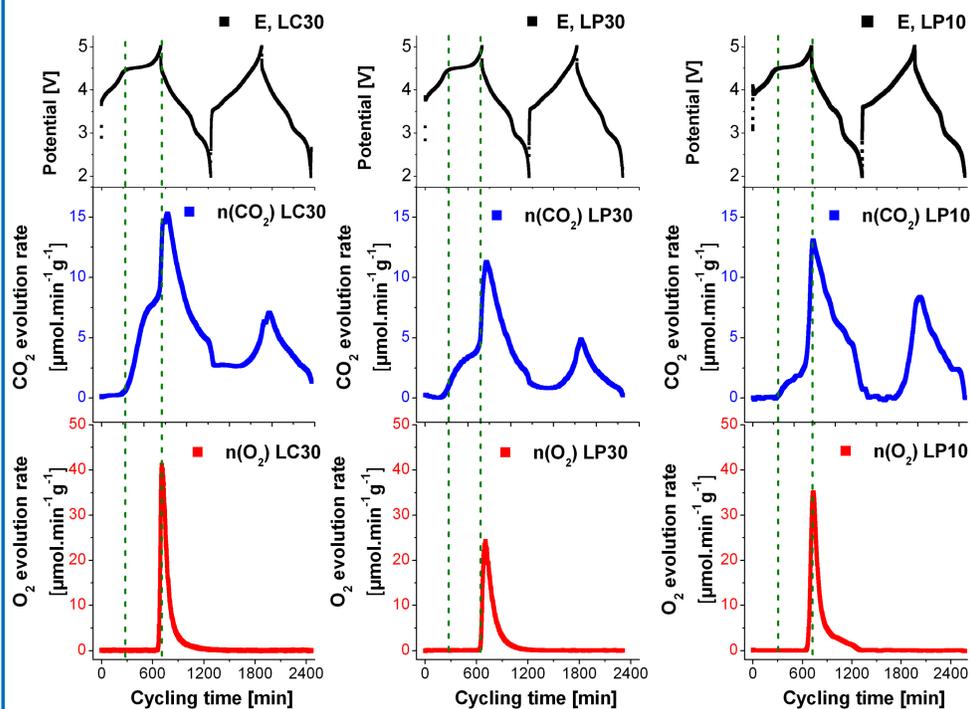
- LP30 1M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC), 1:1
- LP10 1M LiPF_6 in EC/DMC/diethyl carbonate (DEC), 3:3:4
- LC30 1M LiClO_4 in EC/DMC, 1:1

DEMS cell



1/ Gas evolution rate

- Similar evolution rate whatever the electrolyte
- O_2 and CO_2 only evolved. O_2 appeared only during the 1st charge
- On the plateau (4.5V vs. Li^+/Li) only CO_2 detected
- >4.7V vs. Li^+/Li O_2 detected followed by a strong CO_2 signal

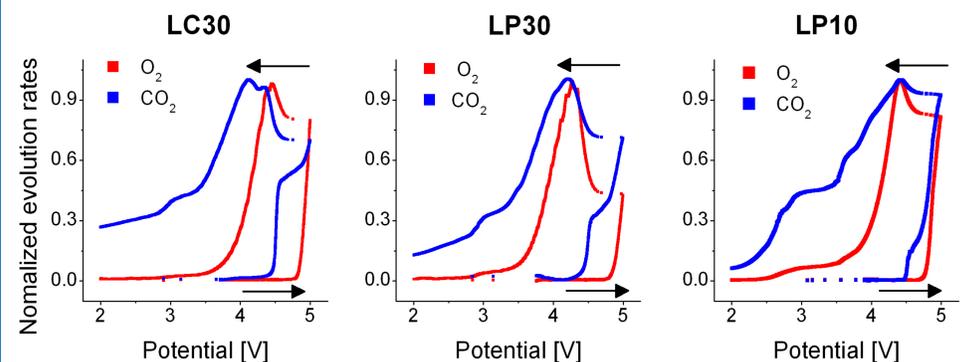


- 1st discharge: O_2 and CO_2 peaks are maximal. O_2 evolution rate decreases faster than CO_2
- 2nd cycle less CO_2 gas

2/ Gas detection onset

1st charge process:

- CO_2 detected at ca. 4.25V vs. Li^+/Li for LC30 and LC30 and 4.5V for LP10
- Between 4.5V and 4.7V vs. Li^+/Li , CO_2 evolution decelerated
- O_2 is detected at 4.7V vs. Li^+/Li , CO_2 evolution accelerated
- Formation of O_2 and CO_2 are correlated



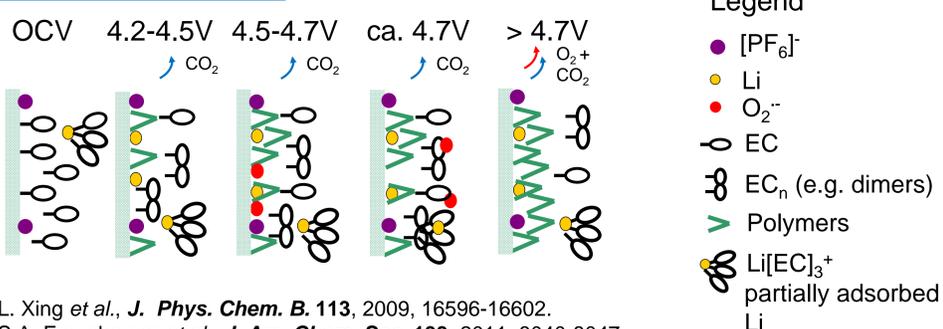
1st discharge process:

- Correlation of O_2 and CO_2 peaks
- Evolution of O_2 decreased faster than CO_2
- Additional CO_2 peaks observed between 2.8 to 3.5V vs. Li^+/Li

Further observations:

Less CO_2 evolution observed for LP10 electrolyte compared to LC30 and LP30 during the initial charging step.

3/ Interpretation



Conclusion

- Electro-oxidation of carbonates at high potentials. No clear difference between the used electrolytes
- More CO_2 detected during the 1st cycle when O_2 is released by the active material

Acknowledgments

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