

In situ Gas Analysis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Based Electrodes at Elevated Temperatures

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Goal: Understand the severe gassing issue of LTO at elevated temperatures

Closed system – total pressure

Open system – partial pressure

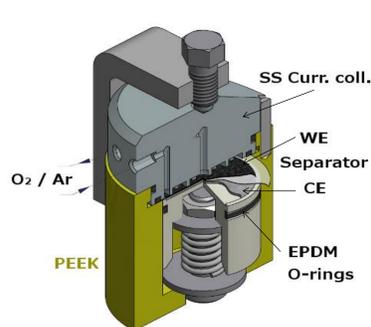
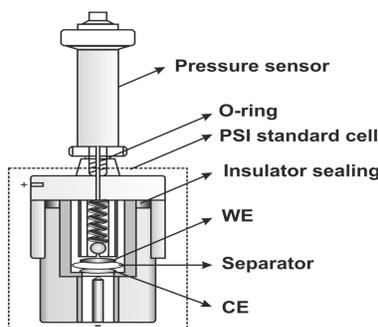
In situ pressure set-up

Pressure cell

OEMS cell

Online electrochemical mass spectrometry

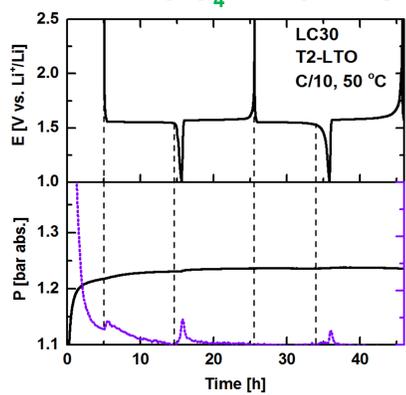
Methodology



Electrolyte



1 M LiClO_4 in EC:DMC

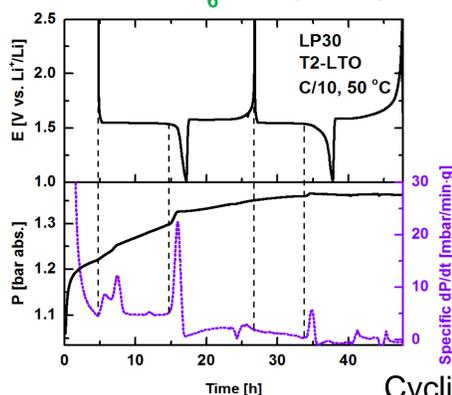


Lithium salts influence

LiClO_4 salt



1 M LiPF_6 in EC:DMC

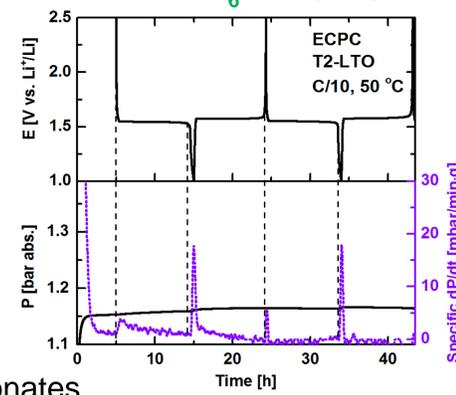


Solvents influence

Cyclic alkyl carbonates



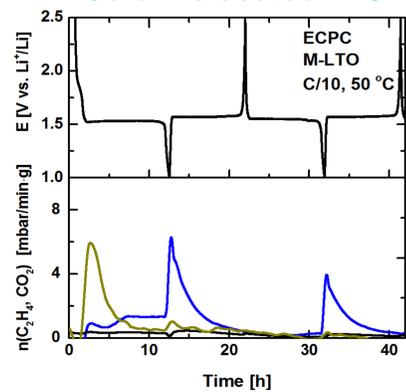
1 M LiPF_6 in EC:PC



Coating

LTO

Ceramic coated LTO

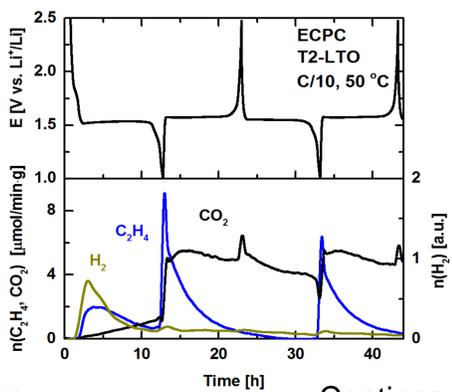


Coating influence

Ceramic coatings



Non-coated LTO

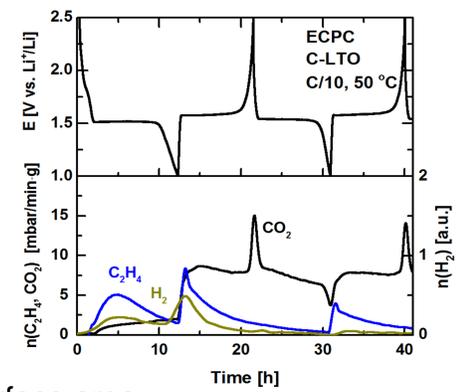


Coating influence

Coatings with high surface area



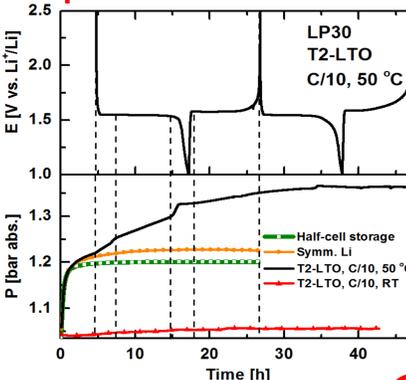
Carbon coated LTO



Temperature



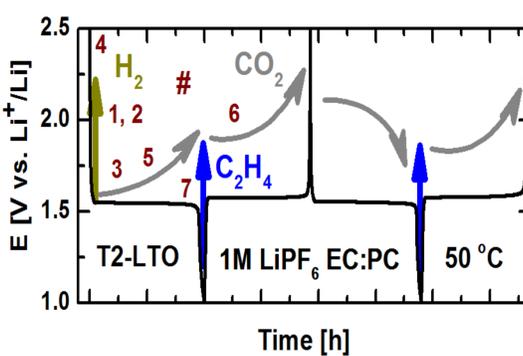
Comparison at 25 °C and 50 °C



Elevated temperatures



Gas evolution onsets



Major gases: $\text{H}_2 + \text{CO}_2 + \text{C}_2\text{H}_4$

Mechanisms of gas evolution reactions

- | | |
|---|----------|
| $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2\uparrow$ | 1 |
| $2\text{H}\cdot \rightarrow \text{H}_2\uparrow$ | 2 |
| $\text{OH}^- + \text{EC} \rightarrow \text{radicals} + \text{CO}_2\uparrow$ | 3 |
| $\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + 2\text{HF} + \text{POF}_3\uparrow$ | 4 |
| $\text{POF}_3 + \text{EC/PC/DMC} \rightarrow \text{compounds} + \text{CO}_2\uparrow$ | 5 |
| $\text{Ti}^{4+} + \text{EC/PC/DMC} \rightarrow \text{Ti}^{3+} + \text{radicals} + \text{CO}_2\uparrow$ | 6 |
| $2\text{Li}^+ + \text{EC} \rightarrow \text{Li}_2\text{CO}_3\downarrow / (\text{CH}_2\text{CH}_2\text{OLi})_2\downarrow + \text{C}_2\text{H}_4\uparrow$ | 7 |

Conclusions

- Elevated temperatures significantly increase the kinetics of electrolyte degradation.
- H_2 , C_2H_4 , and CO_2 are the dominantly evolving gases for ethylene carbonate based electrolytes.
- Passivating the LTO surface by a proper coating, and/or exchanging the LiPF_6 salt, may effectively reduce gas evolution.