

# Mechanism of LTO Gassing and potential solutions

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# Overview

## Timeline

- Start: 10/01/2010
- End: 09/30/2014
- 15% completed

## Budget

- Total project funding FY 14
  - DOE - **\$1200K**
  - Contractor - \$ 0
- Funding received in FY10
  - **\$300K**
- Funding for FY10
  - DOE - **\$300K**

## Barriers

- Barriers addressed
  - Power fade of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  based lithium-ion chemistry
  - Gassing issues

## Partners

- EnerDel<sup>®</sup>
- University of Colorado



# Objectives of the work

- Identify gassing mechanism of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  based lithium-ion chemistries.
- Identify and develop advanced technologies to eliminate the gassing issue.
- Secure sufficient quantities of these advanced materials for further verification in big pouch cells (200 mAh) using either Argonne National Laboratory's new cell assembling line or with the help of an industrial partner.

# Approach

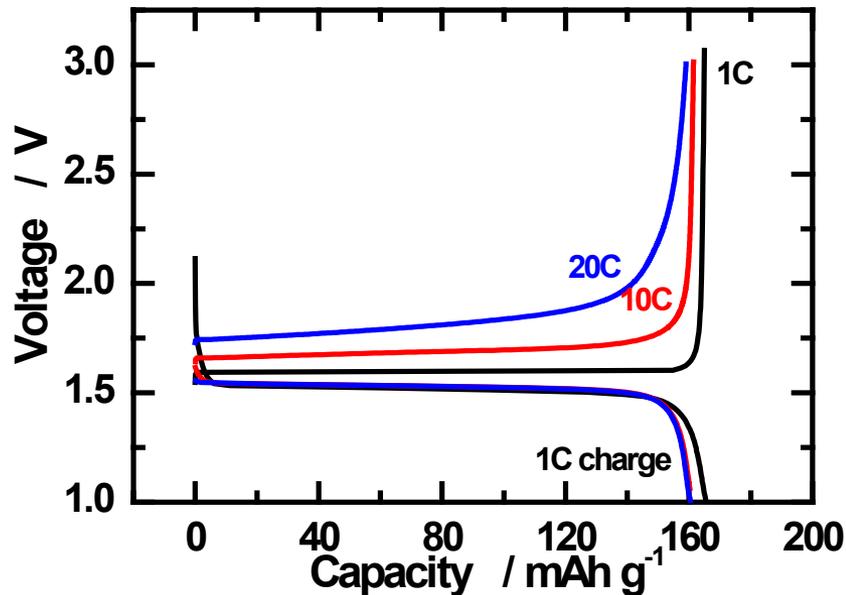
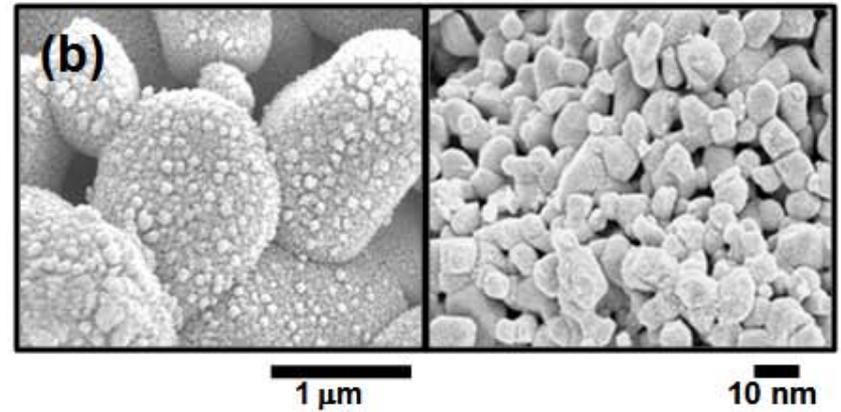
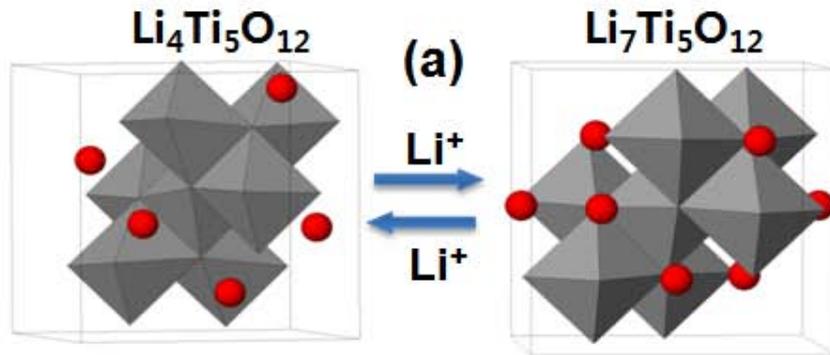
- Identify the conditions that lead to aggressive gassing of LTO.
- Characterize the gassing from LTO cells.
- Identify the real mechanism of gassing and provide possible solution to the LTO gassing

# Recent Accomplishments and Progress

- **Identified conditions that lead to aggressive gassing issue**
  - The gassing issue was only limited to chemistries using  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode.
  - No gassing was observed at fully discharged state.
  - Gassing was barely observed at room temperature ( $25^\circ\text{C}$ ).
  - Severe gassing was observed at fully charged state and at elevated temperatures ( $\geq 55^\circ\text{C}$ ).
  - Similar phenomena was not observed for cells using carbon anodes.
- **Proposed preliminary hypothesis on gassing mechanism**
  - Gassing is believed to be generated from the chemical reduction of solvent (carbonates) on surface of  $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ .
  - The high catalytic activity of titanium oxides might be a promoter to the chemical reduction reaction.
  - Surface modification was proposed to change the catalytic activity of  $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ .



# Why $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ?



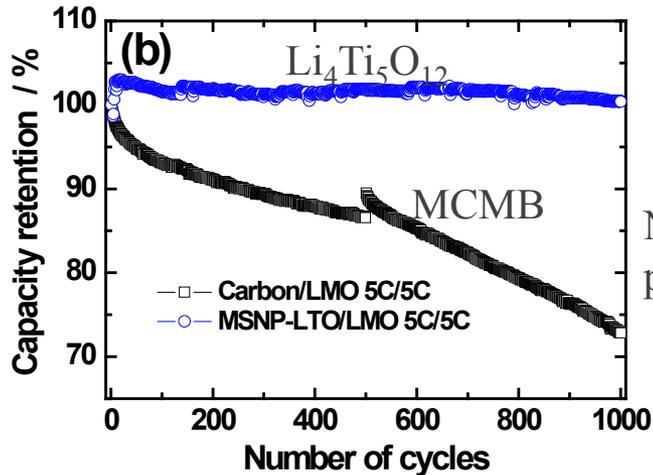
- No volumetric change after lithium insertion. – Zero strain for extreme long term stability.
- Specially designed nano-structured material for higher packing density and extremely high rate capability (> 20C).



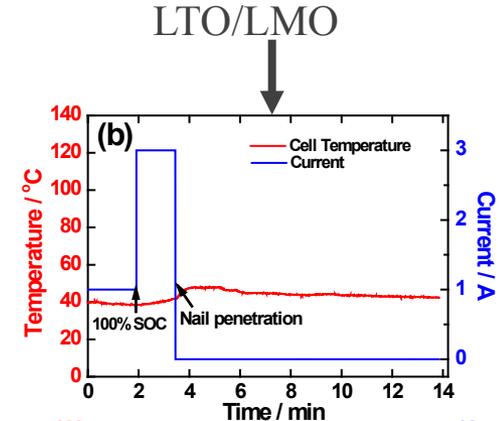
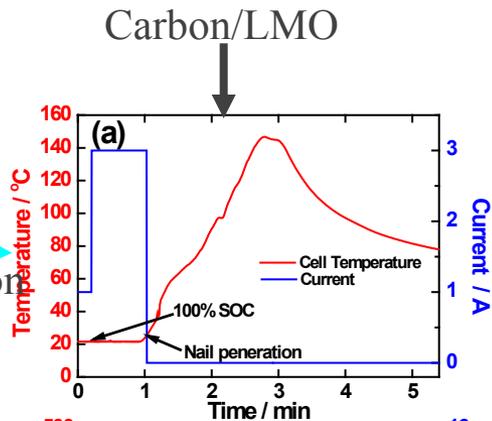
# Outstanding electrochemical and safety performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ cells

• Excellent capacity retention at 55°C

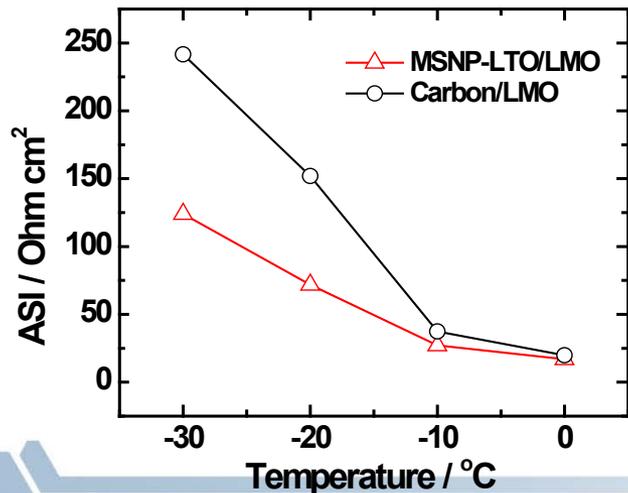
• Unmatched abuse tolerance



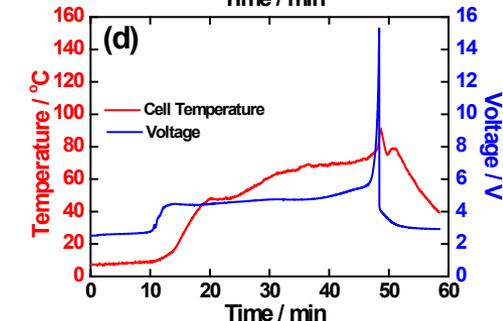
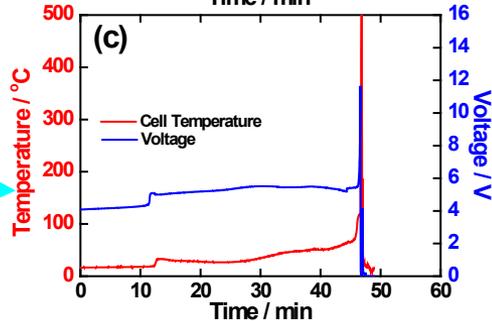
Nail penetration



• Better low temperature performance



Over-charge



Higher energy density can be achieved by coupling LTO with high voltage cathodes like  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ .



# Key issue that hinders the deployment of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ based chemistry

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  (200 mAh cell)



After stored at  
63°C & 100%  
SOC for 1 year

Before

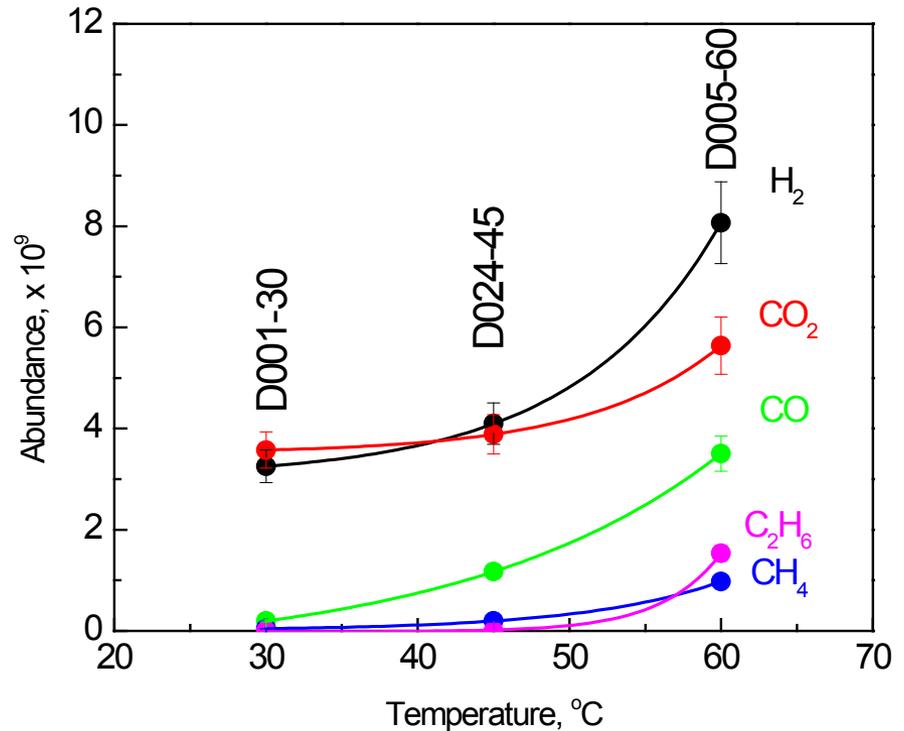
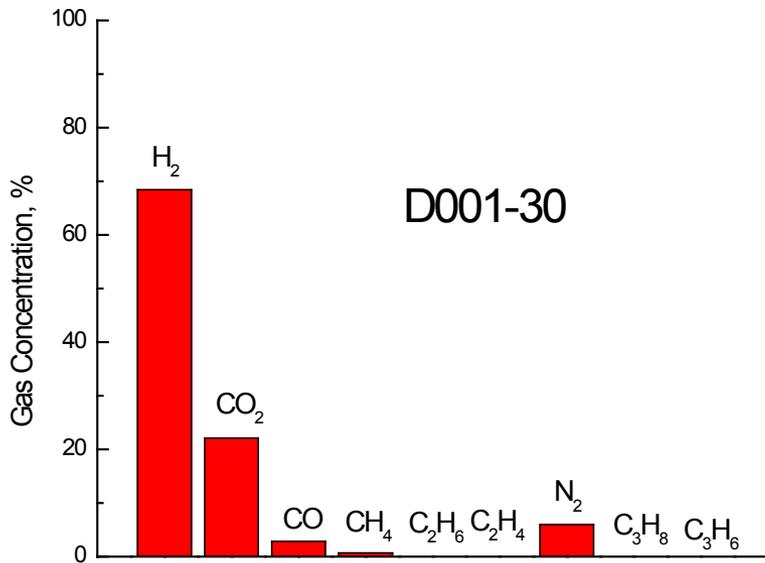
After stored at  
63°C & 100%  
SOC for 1 year

Before

- Release large amount of gas after high temperature storage.



# Major gas in the LTO cell is hydrogen



**Amount of H<sub>2</sub> in the cell increase with temperature**

# Locating the reaction mechanism

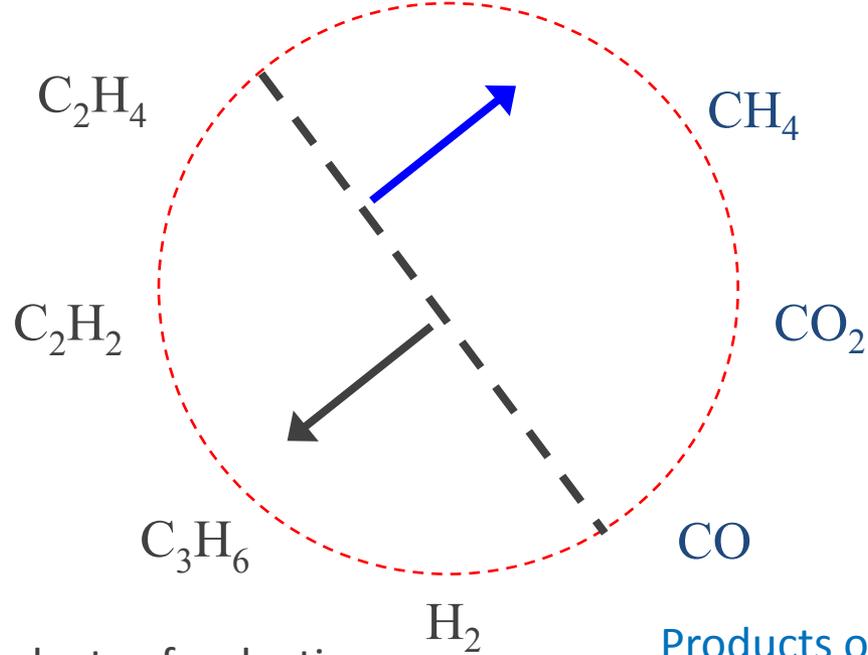
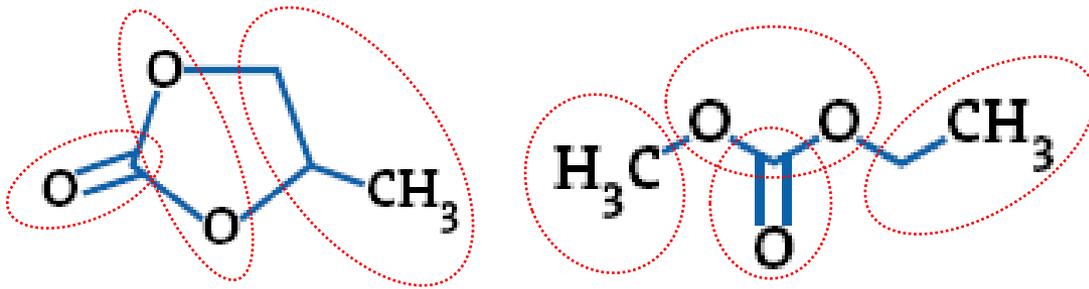
## (Where does the gas come from in the LTO based Cell?)

- $H_2$  is a key component of the gas. Blocking the reaction pathway for  $H_2$  might be a solution for the gas issue.
- $Li_4Ti_5O_{12}$  and  $Li_{1+x}Mn_{2-x}O_4$  have no source of H element, they will not generate  $H_2$  by themselves.
- Trace amount of moisture in the electrolyte and electrode has no way to explain the huge amount of gas generated, and that no gas was observed for carbon-based cells.
- Electrolyte has H source (carbonates) but is stable at ambient temperature.
- The possible mechanism is,

Chemical or electrochemical decomposition of the H source (electrolyte) on the electrode surface (metal oxides), serving as the catalysis.

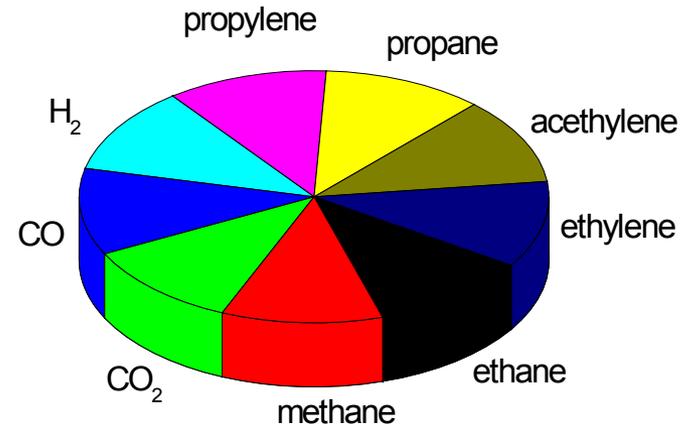


# Where the gases come from?



Products of reduction

Products of decomposition



# Detailed observations on gassing issue

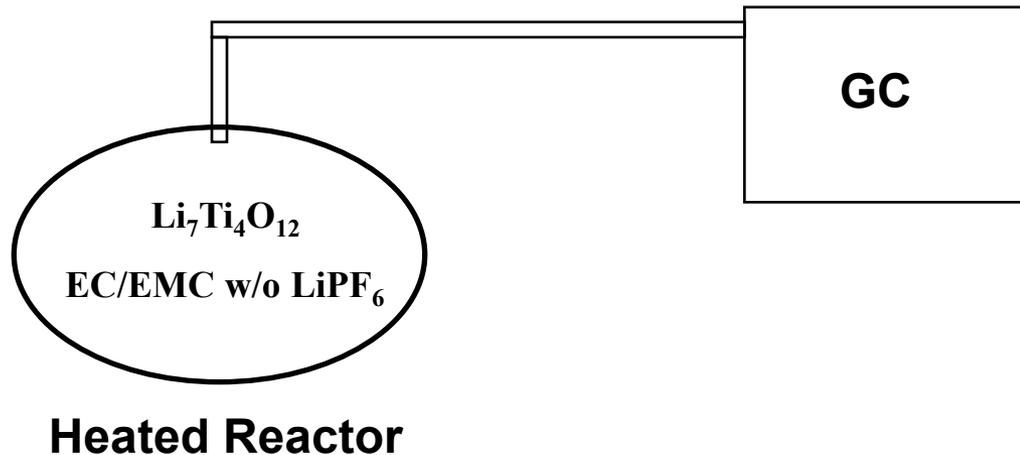
Observation for  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO)/ $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  (LMO) cells:

- Baking  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  → less gas
- At completely discharged state (55°C) → no gas
- At charged state (55°C) → severe gas
- At discharge state (55°C) → no gas
- Replacing LMO with NCA or NCM → severe gas at charged state and 55°C
- Replacing LTO with carbon anodes → no gas
  
- GC-MS data shows that the gas include  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$ .  $\text{H}_2$  is the dominated component.
- SEM, XRD and electrochemical test of aged electrodes shows no damage to the electrode materials (both LTO and LMO).



# Quantification of H<sub>2</sub> generation using GC-MS

- (1) A 200 mAh pouch cell using LTO/LMO was charged to 2.8V (fully charged).
- (2) The pouch cell was then opened and the negative electrode was harvested from the cell.
- (3) Lithiated LTO recovered from the negative electrode was then mixed with solvent or electrolyte and sealed in a heated reactor.
- (4) A online gas chromatography (GC) was deployed to detect the evolution of H<sub>2</sub> from the mixture.



# GC results of reaction between $\text{Li}_7\text{Ti}_5\text{O}_{12}$ and solvents w/o $\text{LiPF}_6$

- **Reaction between  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  and electrolyte (1.2M  $\text{LiPF}_6$  in EC/EMC=3/7)**

At 80°C,  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  : 0.402g =  $8.37 \times 10^{-4}$  mol;    **Electrolyte:** 25ml

$\text{H}_2$  produced: ~ **30mL**

Assume the following reaction:  $\text{Ti}^{3+} + \text{H}^+ \rightarrow \text{Ti}^{4+} + \frac{1}{2} \text{H}_2$

In theory, 0.402g  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  will produce about **28 mL**  $\text{H}_2$  based on above reaction, agreeing quite well with the experimental data.

- **Reaction between  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  and solvents (EC/EMC=3/7) plus some residue  $\text{LiPF}_6$**

At 80°C,  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  : 0.402g =  $8.37 \times 10^{-4}$  mol;    **Solvent:** 25ml

$\text{H}_2$  produced: ~ **5mL**

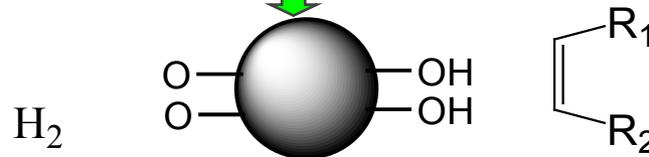
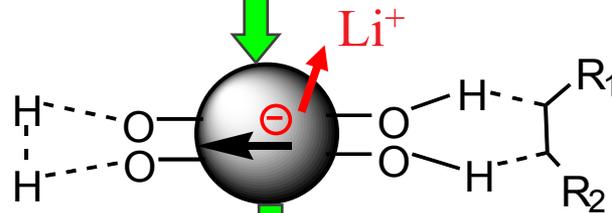
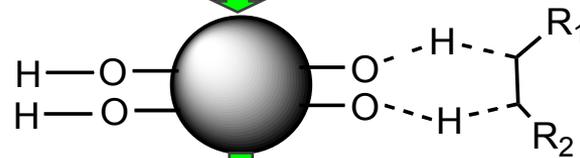
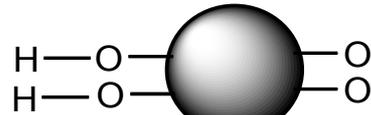
Might have  $\text{LiPF}_6$  residue on  $\text{Li}_7\text{Ti}_5\text{O}_{12}$ , resulting in low  $\text{LiPF}_6$  concentration; not purely solvent.

**Gas comes from the chemical reduction reaction of solvent by  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  with the help of  $\text{LiPF}_6$ .**



# Assembling of reaction model to explain experimental observations

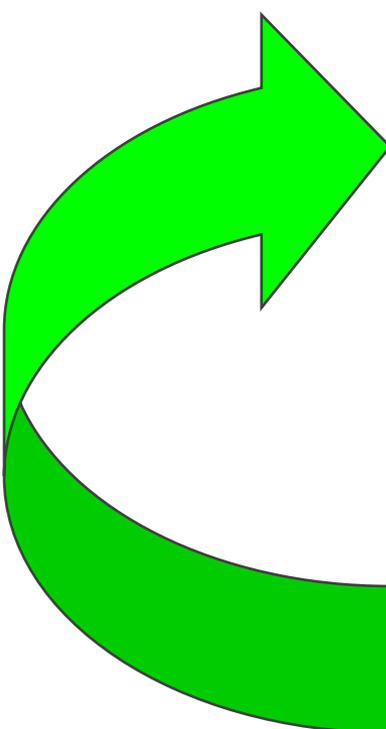
Metal oxide ( $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ )



Absorption of solvent on LTO surface.

Reduction of hydroxyl group and release  $\text{H}_2$ .

Chemical decomposition of solvent.



# Future work

- Understanding the true mechanism is the key to resolve the problem. Following items are key components for the future work.
  - (a) Investigate the reaction kinetics using in situ XANES (X-ray Absorption Near-Edge Structure).
  - (b) Using the kinetics data obtained from XANES to quantify the effectiveness of surface modification agents.
  - (c) Explore additives and “poisoning” agents to suppress the catalytic activity of LTO.
  - (d) Explore coating LTO to eliminate the catalytic reactivity at the surface of LTO.



# Summary

- Nano-structured  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is a promising anode materials for high power lithium-ion batteries with extremely long life and unmatched tolerance to overcharge and thermal abuses.
- Gassing of  $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$  at elevated temperature is the remaining issue that hinders the deployment of this chemistry.
- A hypothesis on the gassing reaction was proposed.
- More fundamental research is needed to reveal the true mechanism and to completely resolve the problem.



# Collaborations

- EnerDel

- Fabrication of 200 mAh LTO/LMO lithium-ion cells to verify the effectiveness of surface modification.

- Colorado University

- Surface Modification using ALD process

