Optimizing the Aqueous Processing of $Li_4Ti_5O_{12}$ Lithium-Ion Anodes

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Motivation and Aim

- Enable the aqueous processing of $Li_4Ti_5O_{12}$ (LTO) electrodes with sodium carboxymethyl cellulose (CMC) as binder
- Prevent Al current collector corrosion by optimizing the amount of phosphoric acid (PA) added to the slurry and the mixing parameters
- Development of an in-depth understanding of the impact of the slurry additive on the LTO active material
- Enhance the electrochemical performance of LTO lithium-ion anodes

Experiments

- Phosphoric acid (> 99%, Bernd Kraft; 33% in aqueous solution)
- Slurry mixing: ball milling at 1260 rpm, 1100 rpm, 1000 rpm, 900 rpm or 800 rpm for 2 h
- Electrolyte: LP30 (1M $LiPF_6$ in EC/DMC, 1:1 w/w)
- Galvanostatic cycling with cut-off voltages of 1.0 and 2.5 V at room temperature

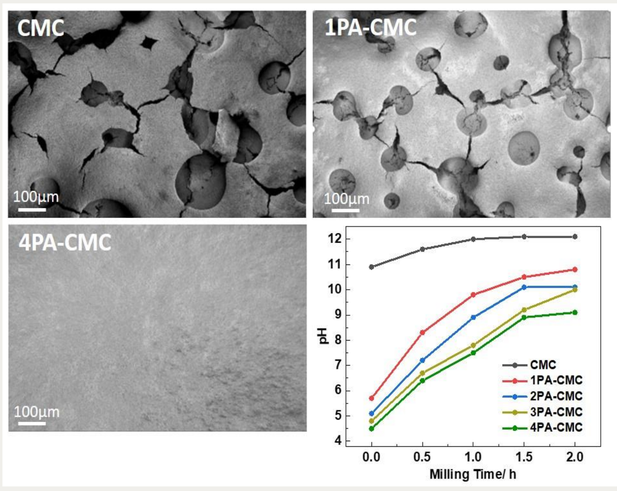
Impact of PA on the Electrode Morphology

Electrode formulation

88 wt% LTO, 5 wt% C45, 7 wt% CMC

- 1PA: 0.67 wt% of LTO
- 4PA: 2.68 wt% of LTO

At **1100 rpm**, 4PA is more efficient in eliminating Al corrosion than 1PA due to the lower pH value after ball milling for 2 h.

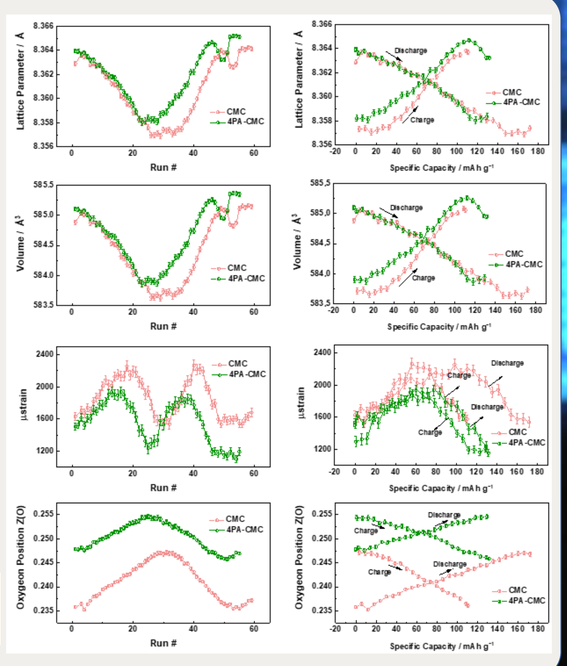


Effect of PA on the De-/Lithiation Mechanism

LTO electrodes containing 0PA and 4PA revel similar trends:

- Lattice parameter/unit cell volume reaches minimum at the end of discharge, whereas maximum oxygen position is observed.
- Maximum µstrain value appears for the medium state of charge or discharge.
- Variation of oxygen position is more obvious than that of lattice parameter or unit cell volume.

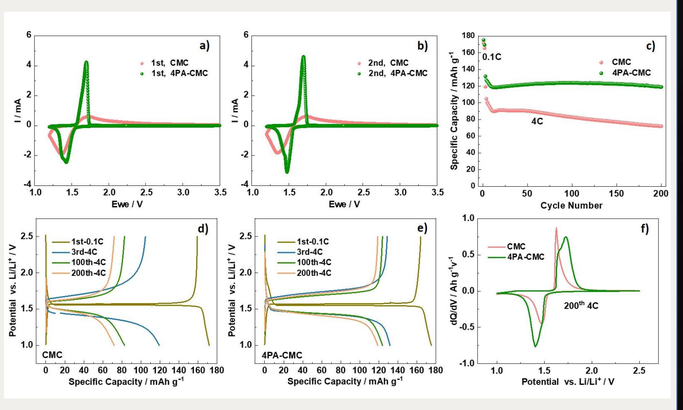
4PA electrode exhibits a **lower µstrain** than the **0PA electrode** during the first dis-/charge process.



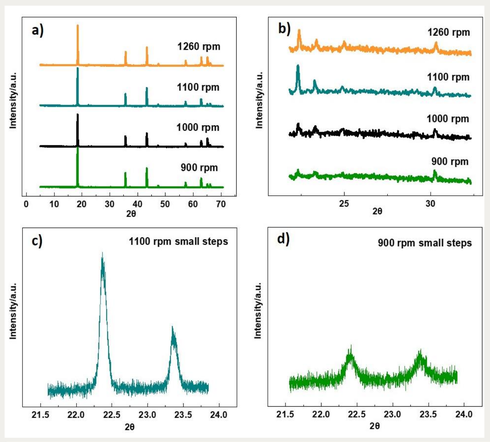
Electrochemical Characterization of 0PA and 4PA Electrodes (1100 rpm)

- **CV (a, b):** **4PA** electrode shows well-defined and intense redox peaks and small peak separation.
- **GC cycling at 4C (c, d, e):** after 200 cycles, the capacity of the **0PA** electrode is **72** mAh g^{-1} compared to **119** mAh g^{-1} for the **4PA** electrode.
- **dQ/dV (f):** The 4PA electrode exhibits broader peaks, but greater symmetry.

The addition of 4PA enhances the cycling performance of LTO electrodes.



Effect of the Ball-Milling Speed



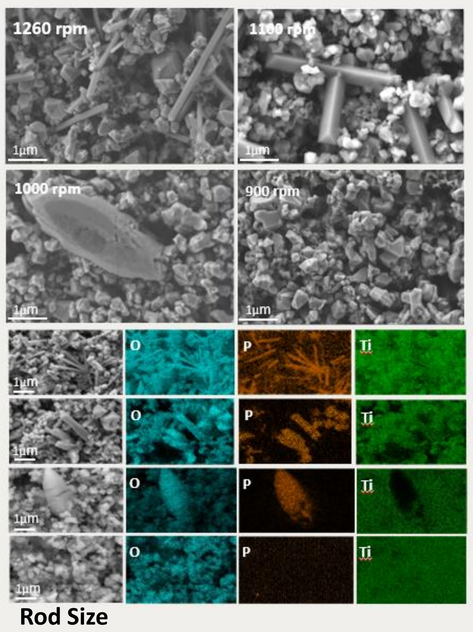
Do the rod-shaped particles contain Ti?

(from top to bottom)

- 1260 rpm: yes
- 1100 rpm: yes
- 1000 rpm: no
- 900 rpm: uniform

New phase with reflections at 2θ angles of **22.3°** and **23.3°**

- **1100 rpm** and **1260 rpm**: clearly visible additional reflections
- **1000 rpm** and **900 rpm**: less intense additional reflections



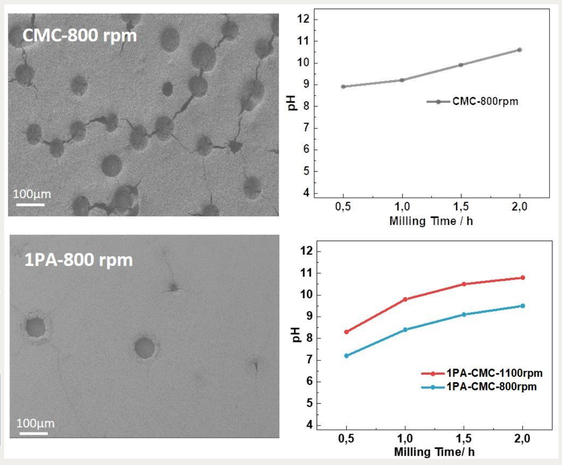
Rod Size

- 1260 rpm: the smallest
- 1100 rpm: a bit bigger
- 1000 rpm: larger (agglomerate)

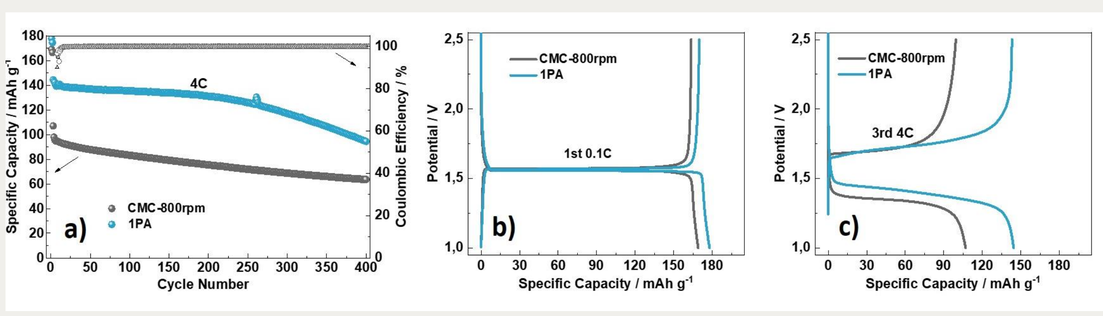
Effect of the Ball-Milling Speed on the pH Evolution and Electrode Morphology

- At 800 rpm, the 0PA electrode shows a reduced slurry pH and crack size.
- The same was observed for the 1PA electrode prepared at 800 rpm.

The **amount of PA** and the **ball-milling speed** are both affecting the **pH value** of the electrode slurry.



Electrochemical Characterization of 1PA Electrodes (800 rpm)

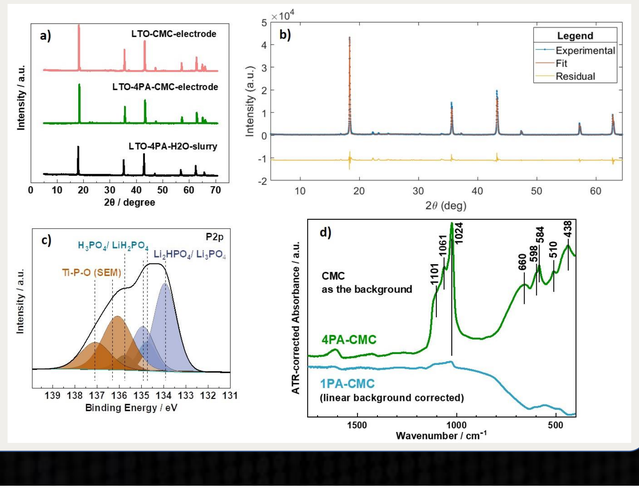


LTO electrodes with optimized electrode formulation and mixing parameters show superior capacity and lower polarization.

Chemistry of the Rod-shaped Particles

Pristine 4PA electrode (1100 rpm)

- **XRD (b):** LTO/Li_3PO_4 is around 9/1
- **XPS (c):** Ti-P-O; P $2p_{3/2}$: 136.1 eV
- **ATR-IR (d):** bands at 660, 598, 584, 510, 438 cm^{-1} related to the CMC binder and LTO, and additional bands at 1101, 1061, 1024 cm^{-1} for lithium titanium phosphate
- ICP-OES: more Li dissolved in water than Ti



Summary

- The addition of PA suppresses the Al corrosion, reduces the **µstrain** upon cycling, and enhances the electrochemical performance.
- The amount of PA added AND the mixing parameters (i.e. the ball-milling speed) affect the pH evolution and, thus, the electrode morphology.