Titration Methods for the Determination of Hydroxides and Carbonates in Lithium Transition Metal Oxide Cathode Materials

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MOTIVATION

Contact with humidity of Li transition metal oxide cathode materials leads to…

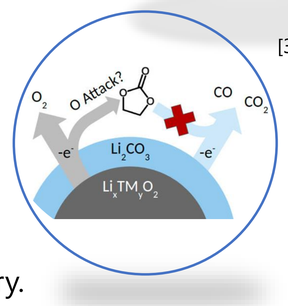
- Loss of Li^+ ions: [1,2]
  - Formation of LiOH.
  - Corrosion of the current collector.
- Formation of Li_2CO_3: [3]
  - Degradation of electrolyte and cathode material.
  - CO_2 outgassing while cycling.

[2]

Reaction mechanism:

$$Li^+ + H_2O \rightarrow H^+ + LiOH$$
$$LiOH + CO_2 \rightarrow LiHCO_3$$
$$LiOH + LiHCO_3 \rightarrow H_2O + Li_2CO_3$$

[3]

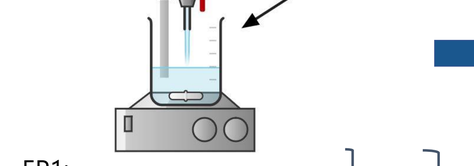


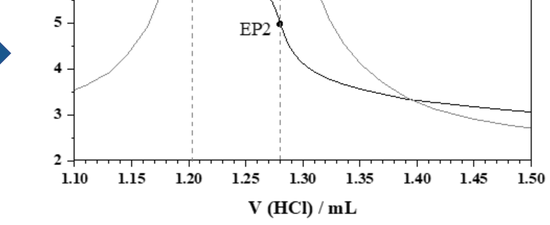
- Capacity loss & reduced cycle life of the battery.

AIM: Quantification of carbonate and hydroxide surface impurities on battery materials, with focus on minor quantities and using as little material as possible.

WARDER TITRATION

- First described by R.B. Warder back in 1881.[4]





EP1:

$$2OH^- + 2H^+ \rightarrow 2H_2O$$
$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

V_1

EP1 to EP2:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

V_2

Concentration LiOH

$$c(OH^-) = (2V_1 - V_2) * c(HCl) * \frac{1}{V_{sample}}$$

Concentration Li_2CO_3

$$c(CO_3^{2-}) = (V_2 - V_1) * c(HCl) * \frac{1}{V_{sample}}$$

LiOH in ppm

$$c(OH^-) * \frac{V_{H2O}}{m_{powder}} * M_{LiOH} * 1{,}000{,}000$$

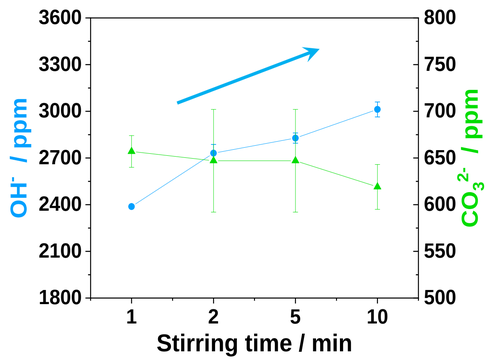
Li_2CO_3 in ppm

$$c(CO_3^{2-}) * \frac{V_{H2O}}{m_{powder}} * M_{Li_2CO_3} * 1{,}000{,}000$$

INFLUENCE OF STIRRING TIME

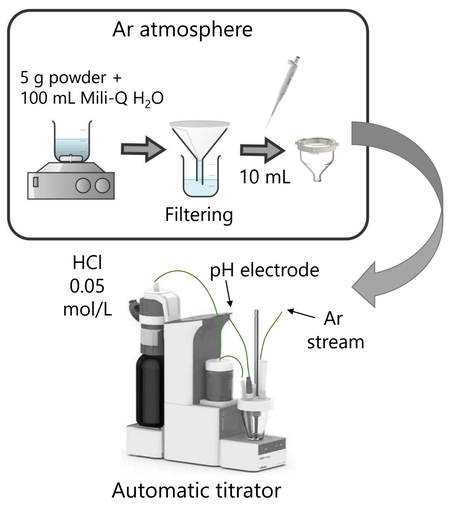
	OH^-	CO_3^{2-}
1 min	**2388 ± 10 ppm**	**657 ± 17 ppm**
2 min	2731 ± 56 ppm	647 ± 55 ppm
5 min	2828 ± 33 ppm	647 ± 45 ppm
10 min	3012 ± 48 ppm	619 ± 24 ppm

NMC811, in H_2O



→ **LiOH** is **continuously increasing** during stirring in water while Li_2CO_3 stays nearly constant. [5]

ADAPTING THE TITRATION SET-UP TO LAB SCALE



	OH^-	CO_3^{2-}
5g/100mL	2374 ± 182 ppm	602 ± 59 ppm
2.5g/100mL	**2338 ± 150 ppm**	**646 ± 54 ppm**
1g/100mL	1034 ± 28 ppm	519 ± 72 ppm

NMC811, in H_2O, 1 min stirring

- **Ar atmosphere** prevents additional CO_2 uptake from the air.
- Only **10 mL** of filtered solution necessary for titration.
- Automatic titrator: small **dosing steps of 0.1 µL** possible.

→ Material input can be reduced by 50% to 2.5g/100mL to obtain the same results.

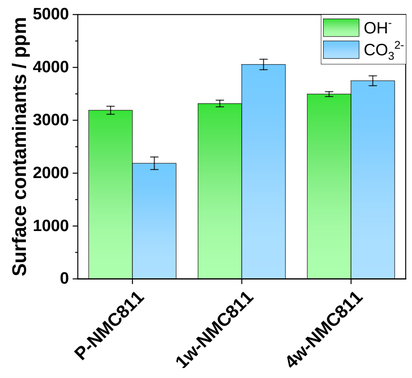
IMPACT OF HUMID STORAGE ON CAM

- NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$) was exposed to 75% relative humidity for 1 week and 4 weeks.

	OH^-	CO_3^{2-}
P-NMC811	3189 ± 132 ppm	2186 ± 206 ppm
1w-NMC811	3316 ± 109 ppm	4055 ± 172 ppm
4w-NMC811	3495 ± 80 ppm	3747 ± 162 ppm

In H_2O, 1 min stirring, 2.5g/100mL

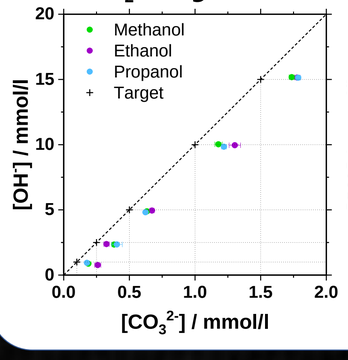
- Increase of carbonate species with prolonged storage.



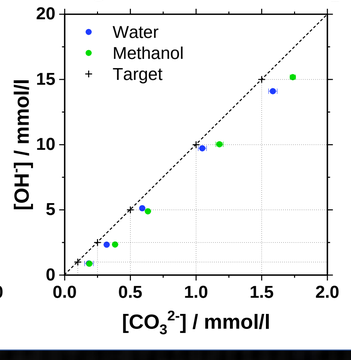
RECOVERY RATE IN VARIOUS TITRATION MEDIA

- Preparation of **test solutions** with **defined concentrations** of hydroxide and carbonate.
- Low concentrations were chosen to reflect the small concentrations found on cathode active materials.
- Each value was determined **with repeat measurements**.

70:30 H_2O:Organic solvent



Organic solvents vs. H_2O



- Organic solvents: supposed to **enhance EP** in titration curve.
- Greater **deviation** from target for **org. solvents**, especially for very **low concentrations** (target: lab-scale quantities!).

→ **H_2O** was chosen for further titration experiments.

SUMMARY

- **Warder titration** was examined as a measure to determine carbonate and hydroxide contents in Li ion battery CAM.
- The titration procedure was adjusted to the lab scale.
- Different **solvents** were investigated of which H_2O was selected for further work.
- Titration was used to confirm the **increase of carbonate species** on NMC811 after storage in humid environments.

REFERENCES

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