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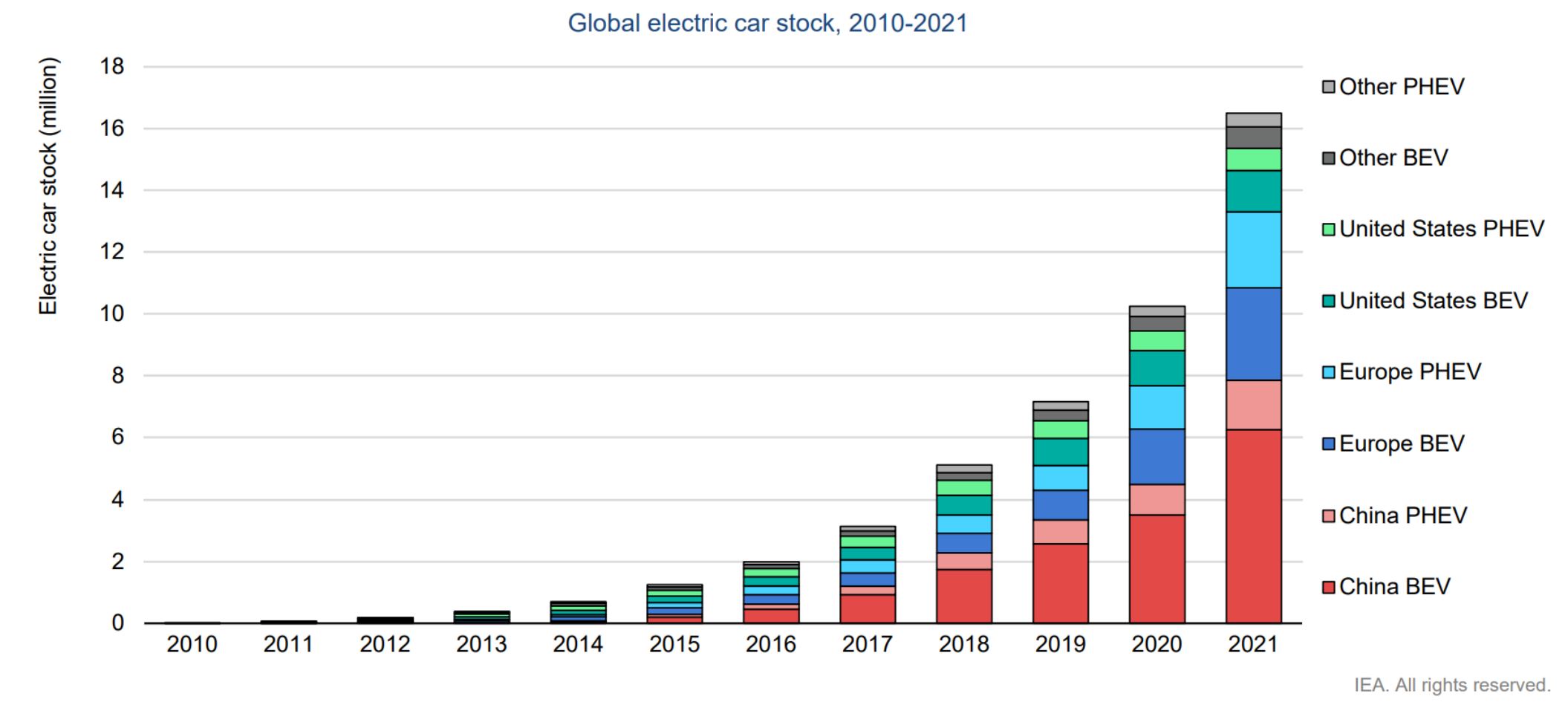
Analysis of Limiting Diffusion Processes within Li-ion Batteries

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Context & Objectives

To meet the ever-growing requirements of the transport sector, improvement of current Li-ion systems is needed in terms of energy density, safety, cycle life, and costs. Among the different strategies to increase battery autonomy, one focuses on electrode loading to increase the ratio of active materials to inactive components. However, by doing so, the output power density becomes strongly limited by the charge transport within the composite electrodes. (1)(2)

- Objectives**
- Study of battery power performance with respect to **electrode design (loading, porosity...)** as well as **temperature and ageing**
 - Determination of the **limiting current density (J_{lim})** and **effective limiting process** of power using an electrochemical approach
 - Optimization of the battery design to **maximize the energy/power**

Experimental

Electrode formulation

Active materials: **LFP & NMC-811**

| Electrode | Composition | Loading (mg.cm ⁻²) | Theoretical Capacity (mAh.cm ⁻²) | Porosity (%) | Temperature (°C) |
|------------------|----------------------------|--------------------------------|--|--------------|------------------|
| LFP / C65 / PVDF | 80/ 10/ 10 85/ 7,5/ 7,5 | 2-17 | 0,4-2,7 | 23-50 | 10°C-40°C |
| NMC / C65 / PVDF | 90/ 5 / 5 | 4-16 | 0,8-3,4 | 20-25 | 10°C-40°C |

Cell Assembly

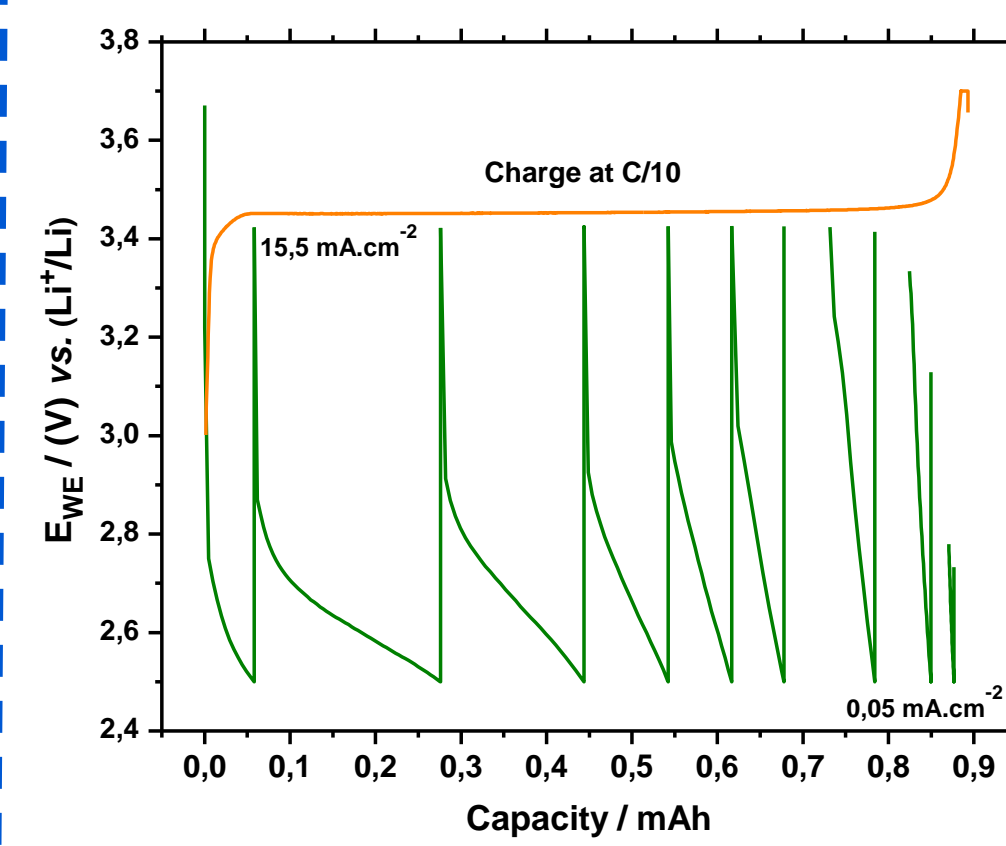
Coin cell CR2032

Electrode//LP30//Li

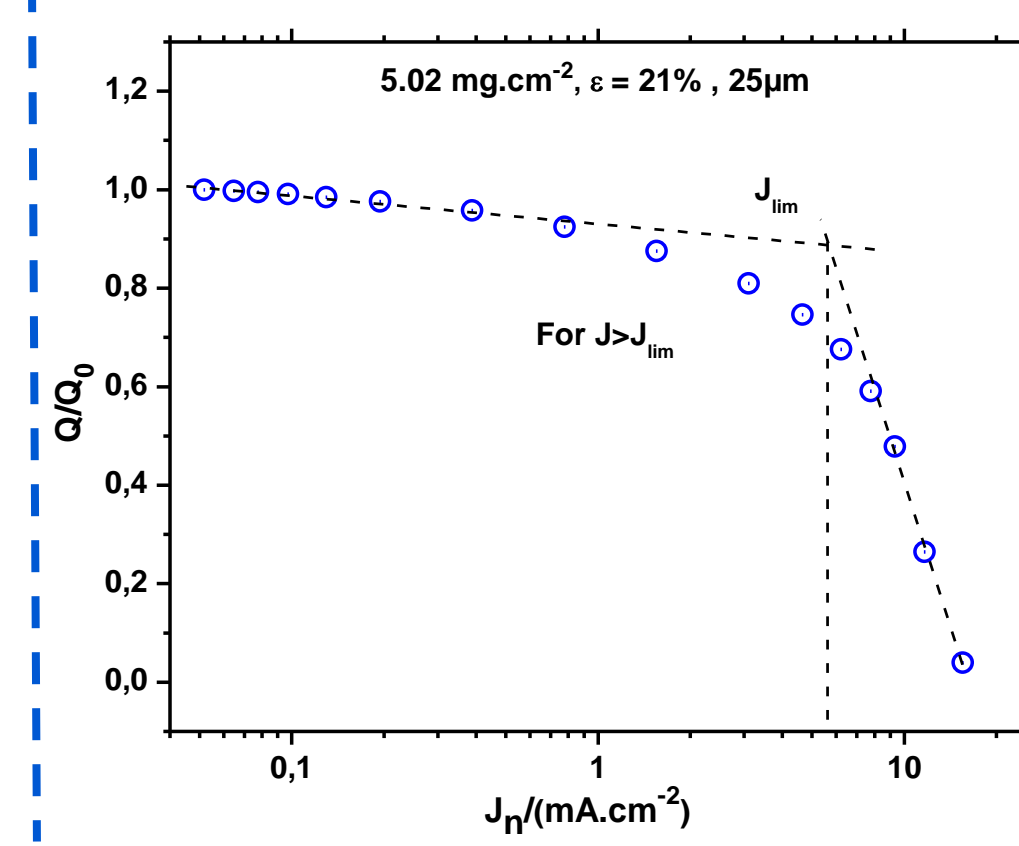


Methodology

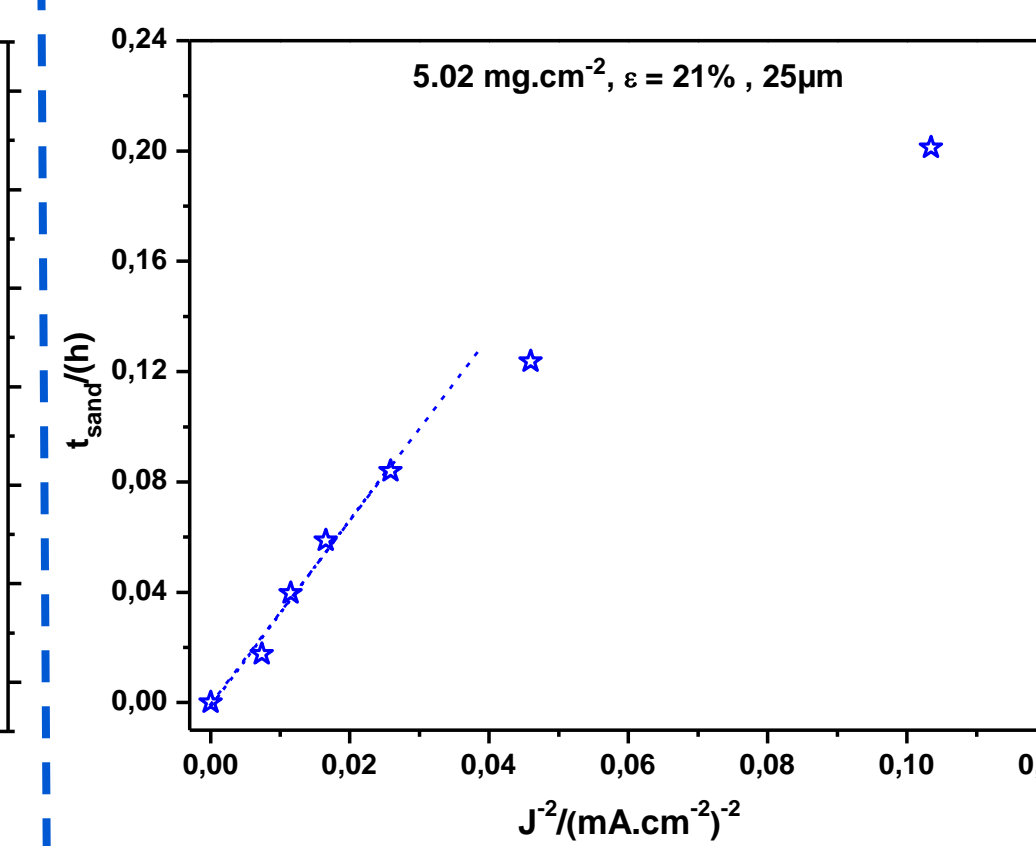
Cycling protocol (3)(4)



Power performance



Sand Plot



- Time-saving methodology
- One charge, followed by successive discharges at ever-decreasing C-rates

Sand Equation (4)(5)

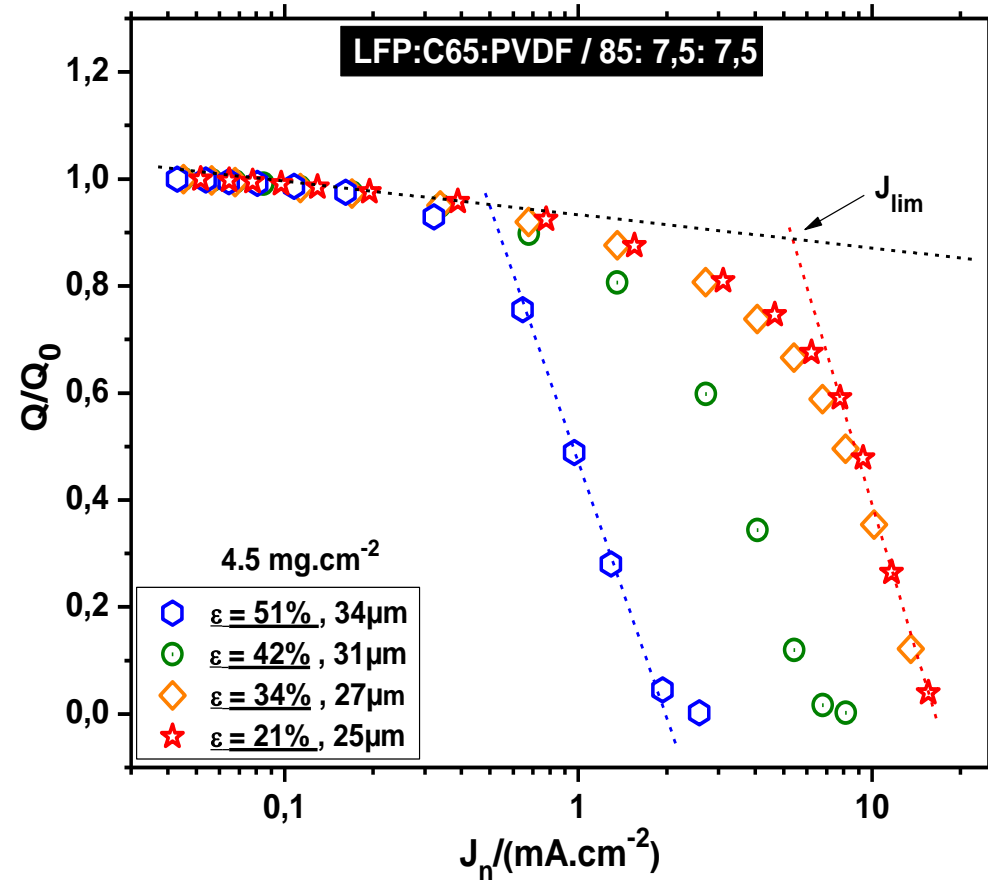
$$t_{sand} = \pi \cdot D_{eff} \left(\frac{n \cdot S \cdot F \cdot C_{max}}{2 \cdot J} \right)^2$$

coefficient

Quick access to the effective diffusion

Results & discussions

LFP based electrode : 1) Porosity effect

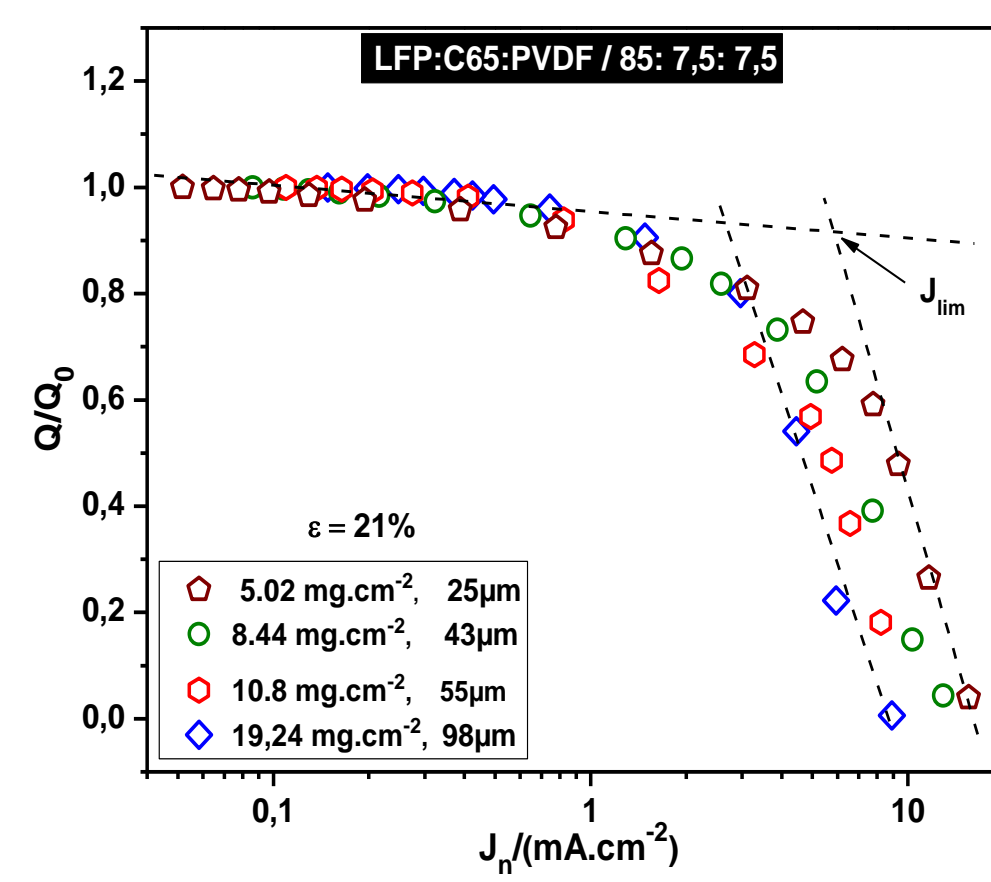


- Lower porosity results in higher J_{lim} , and higher operating C-rates

→ Calendering enhances contact particle-particle and particle-current collector

| Porosity (%) | 53 | 22 |
|---|-----------------------|-----------------------|
| J_{lim} (mA.cm ⁻²) | 0,7 | 5 |
| D_{eff} (cm ² .s ⁻¹) | 2,2.10 ⁻¹⁵ | 1,7.10 ⁻¹⁴ |

2) Loading effect

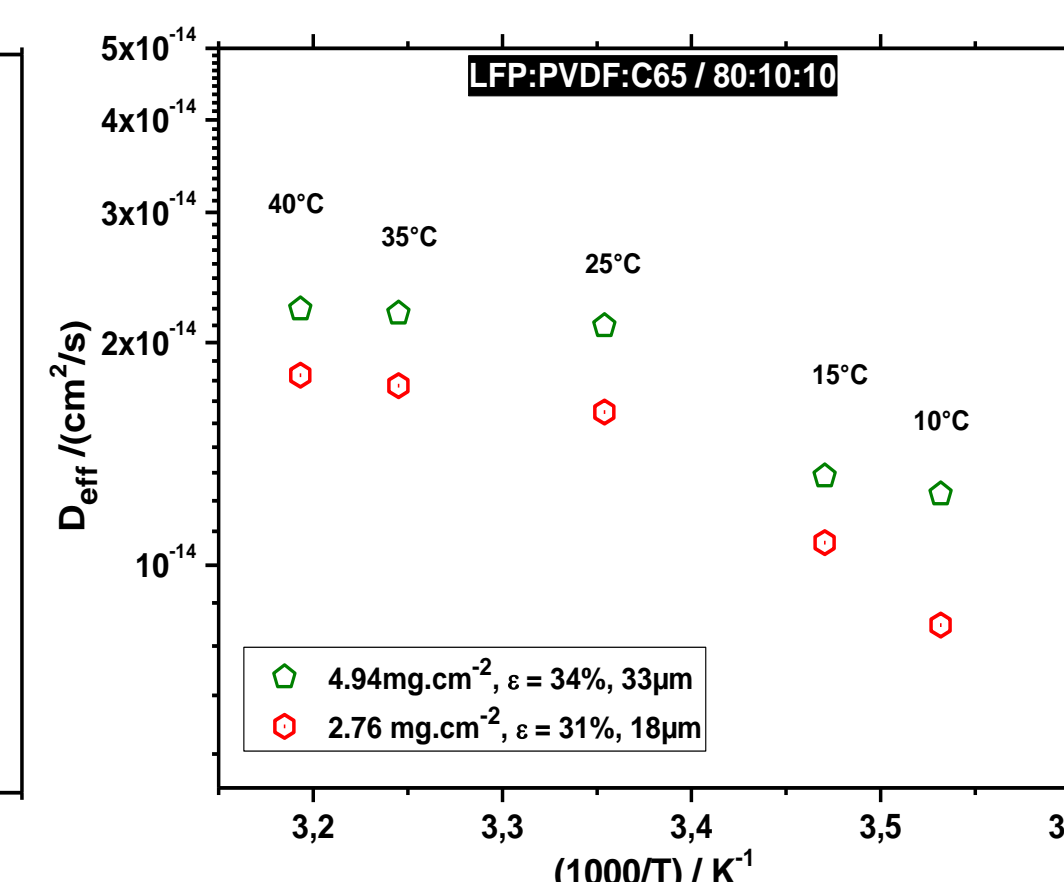
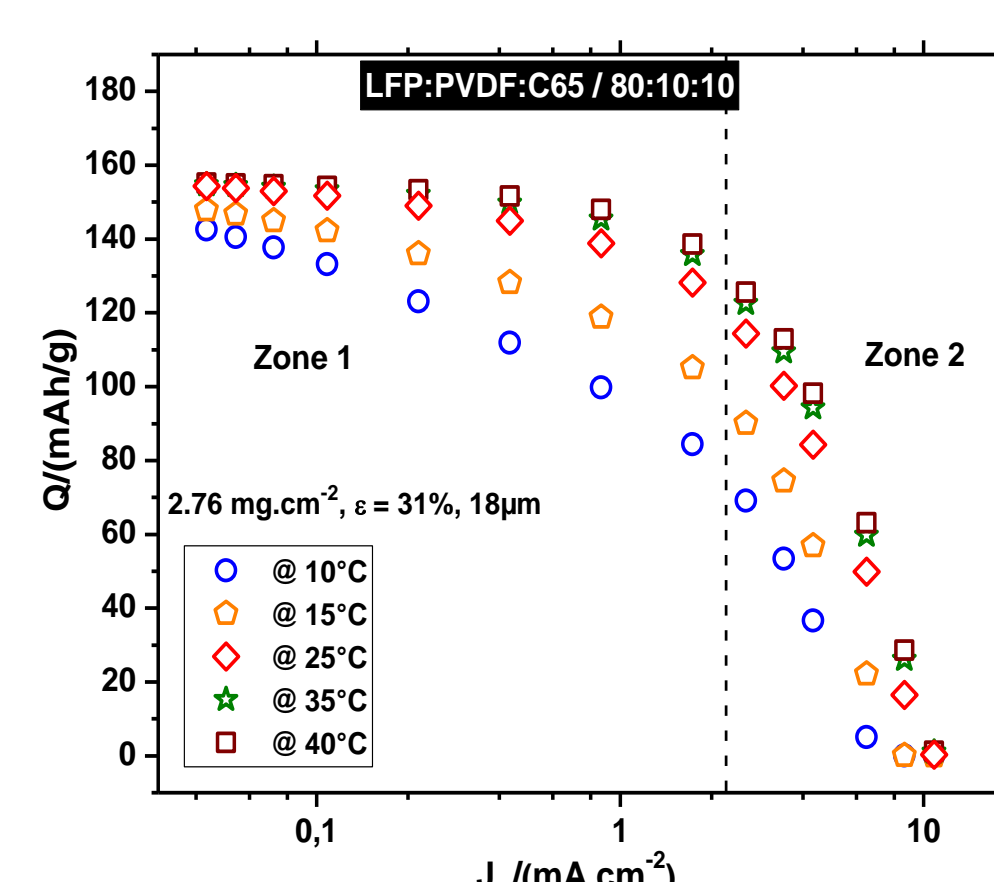


- Thicker is the electrode; lower is J_{lim}

→ At high loading, the limiting process is probably the diffusion within the porous electrode

| Loading (mg.cm ²) | 5 | 19 |
|--|-----------------------|-----------------------|
| J_{lim} (mA.cm ⁻²) | 5 | 2,5 |
| D_{eff} AM limitation (cm ² .s ⁻¹) | 1,7.10 ⁻¹⁴ | 2,5.10 ⁻¹⁵ |
| D_{eff} electrolyte limitation (cm ² .s ⁻¹) | 5,2.10 ⁻⁷ | 1,1.10 ⁻⁶ |

3) Temperature effect



- For $J > J_{lim}$ (zone1), the slope Q vs J increases when T decreases

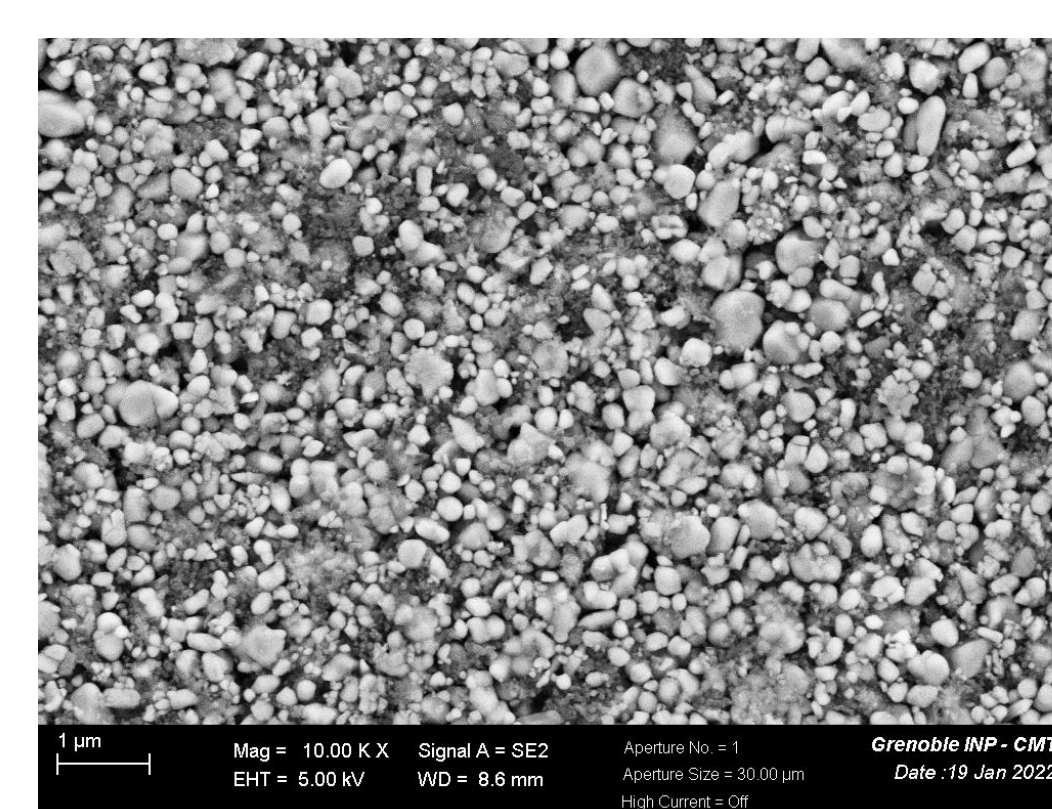
- The variation of D_{eff} with $1/T$ shows two linear portions

Activation Energy

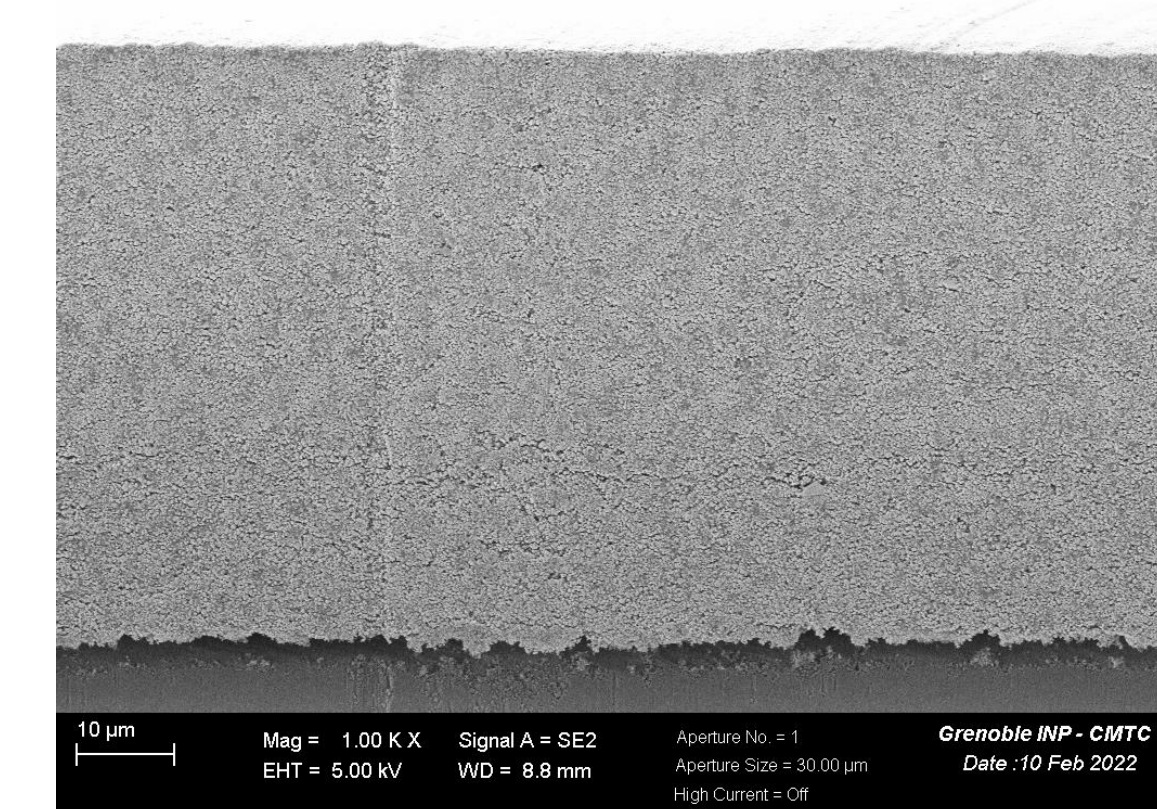
Ea (10-25°) 0,32 eV

Ea (25-40°) 0,06 eV

4) SEM images

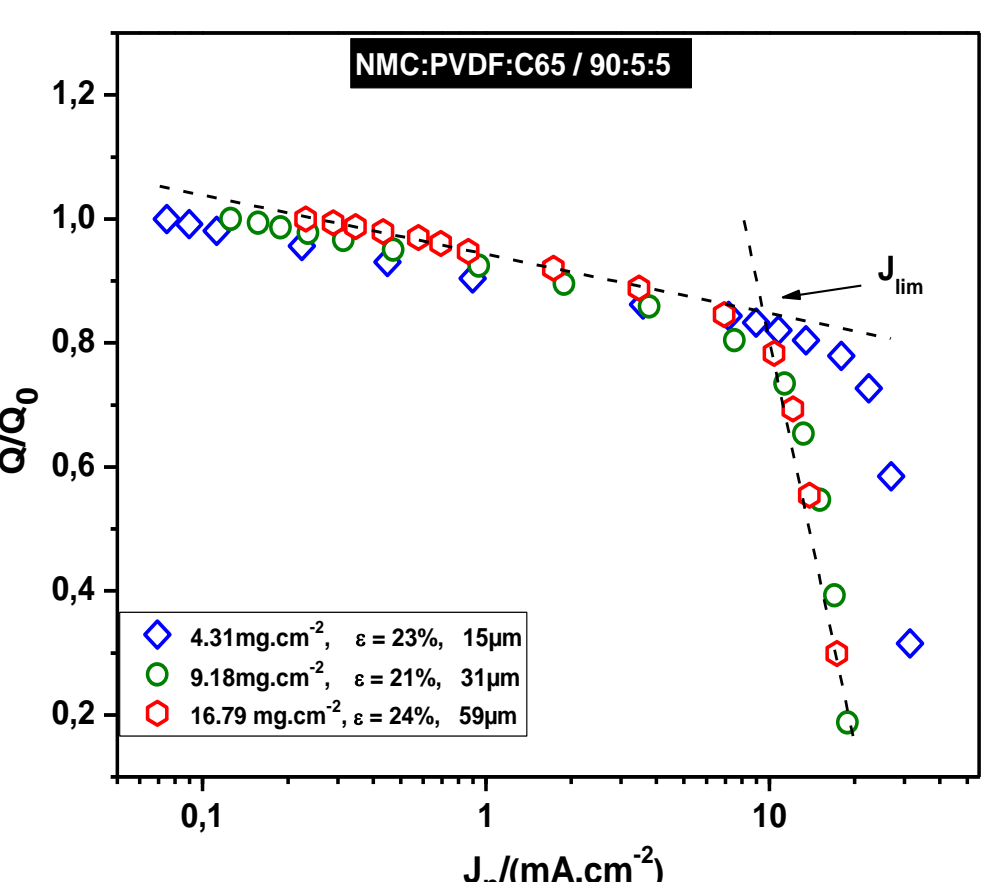


Cross-section



LFP electrode at 20% porosity

NMC based electrode : 1) Loading effect

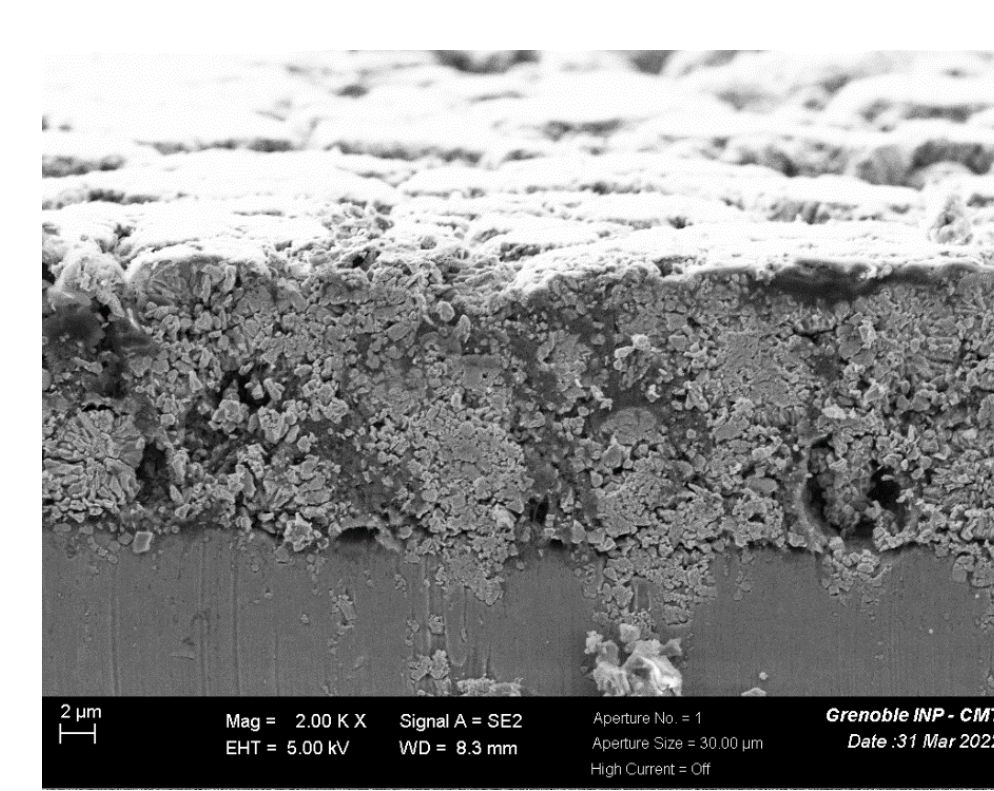
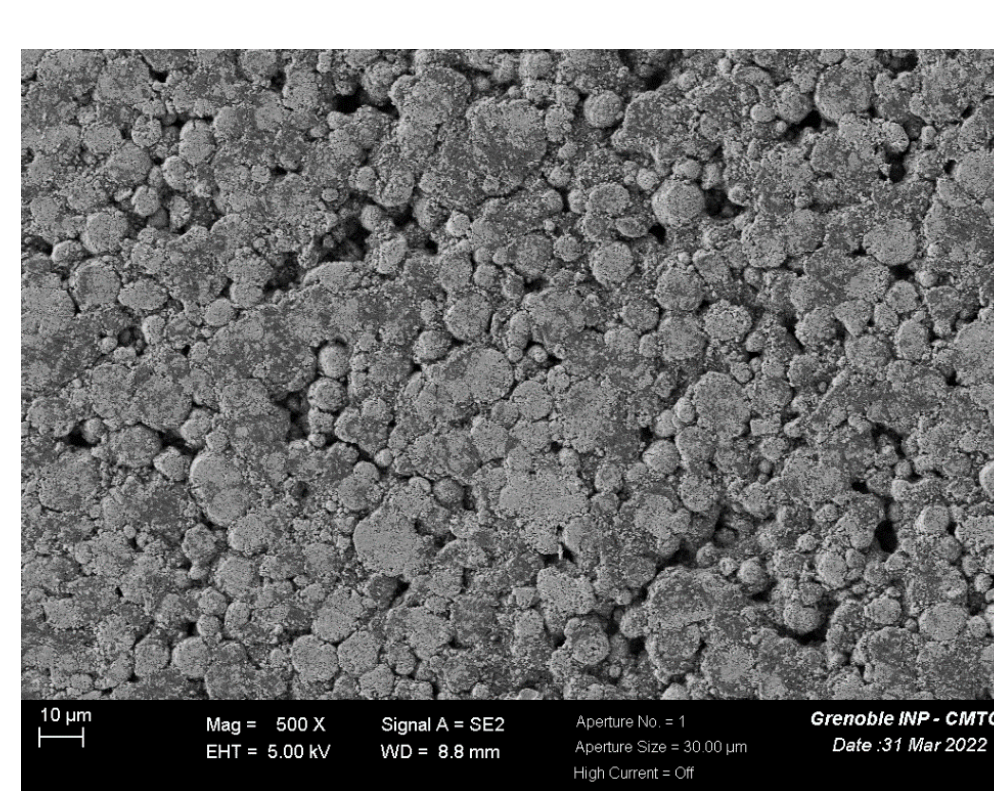


- NMC-based electrode shows higher J_{lim} , compared to LFP one.

| Loading (mg.cm ²) | 4 | 17 |
|--|-----------------------|-----------------------|
| J_{lim} (mA.cm ⁻²) | 15 | 10 |
| D_{eff} AM limitation (cm ² .s ⁻¹) | 3,6.10 ⁻¹² | 5,3.10 ⁻¹³ |
| D_{eff} electrolyte limitation (cm ² .s ⁻¹) | 1,9.10 ⁻⁶ | 4,4.10 ⁻⁶ |

- Same effect of loading on J_{lim} and power performance

2) SEM images



NMC electrode at 20% porosity

Conclusion

- Quick determination of limiting current density as well as limiting process of power.

- Electrode design (Porosity, loading, microstructure) has a substantial impact on the power performance of the battery.

In progress: Find a theoretical correlations

References

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