

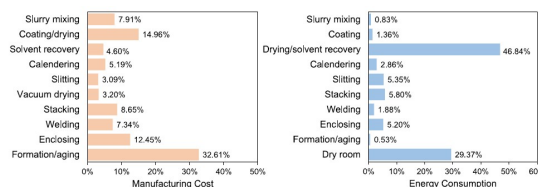
# Evaluation of processing strategies for the manufacturing of Li-ion battery positive electrodes using non-solvent extrusion process

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## > Context & Objectives

- Positive electrode manufacturing needs the use of **toxic N-methyl-2-pyrrolidone (NMP) solvent** → critical step: high energy consumption for drying stage, need for safety protocols, solvent recovery and recycling facilities [1]
- Alternatives towards **dry process manufacturing** are considered to reduce cost and energy consumption [2,3]
- Advantages of **twin-screw extrusion** for producing electrode mixtures: continuous process combining both mixing and layer forming steps, limited use of solvent (or even eliminated), small footprint, easy scale-up
- Main issues for Li-ion (Gen3) electrode manufacturing: solvent-free extrusion is **challenging to obtain highly-filled electrodes** and usually leads to **very dense electrodes** → not enough porosity to allow liquid electrolyte to wet the electrodes
- Objective:** develop specific extrusion-based processes with no need for organic solvent and low temperature treatment



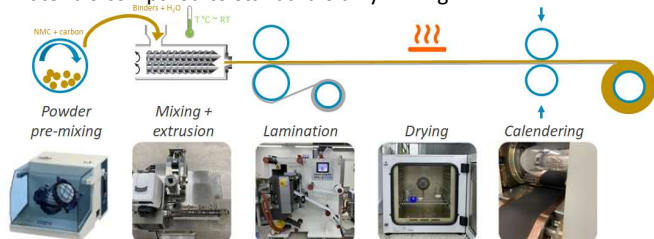
Example of cost and energy breakdown for a cell manufacturing facility [1]

[1] Liu, Y. et al., *iScience* 24, 102332 (2021)  
[2] Verdier, N. et al., *Polymers* 13 (3), 323 (2021)  
[3] Li, Y. et al., *Materials Today* 55, 92–109 (2022)

## > Materials & Methods

### Water-assisted extrusion

- Moving from NMP- to **water-based continuous cathode mixing** [4,5]
- Cathode formulation: **NMC 622 + carbon black + CMC + latex**; similar materials compared to standard slurry mixing



[4] Seeba, J. et al., *Chemical Engineering Journal*, 402, 125551 (2020)  
[5] Haarmann, M., Griebel, D., Kwade, A., *Energy Technology*, 9 (10), 2100250 (2021)

### Melt extrusion with CBA additive

- Inspired strategy from plasturgy → **chemical blowing agent CBA** [6]
- Cathode formulation: **NMC 532 + carbon black + binder + CBA**
- Selection of **HNBR** as polymer binder for melt processing

TGA	CBA additive	T <sub>dec</sub> decomp. (°C)	Residual (%)
	Azodicarbonamide (AZO)	200	0 ✓
	Ammonium oxalate (AOX)	220	0 ✓
	Polypropylene carbonate (PPC) [7,8]	180	0 ✓
	Sodium bicarbonate	120	62 ✗

[6] Coste, G., Negrelli, C., & Caillol, S., *European Polymer Journal* 140, 110029 (2020)

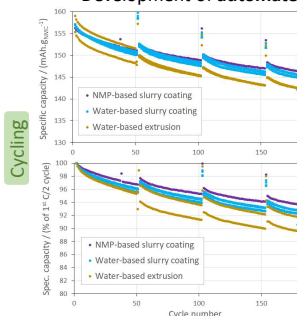
[7] Astafyeva, K. et al., *Batteries & Supercaps* 3 (4), 341–343 (2020)  
[8] El Khakani, S. et al., *Journal of Power Sources* 454, 227884 (2020)

- Optimization to obtain **cohesive electrodes masses**: binder fraction, material premixing, shear rate...
- Characterization of **porosity microstructure** after thermal treatment



## > Results

- Process and formulation optimization:
  - Increase of **solid content** from 70 % (slurry) to **90 % with extrusion**
  - Optimization of **screw profile** to allow proper introduction of liquid components (CMC, latex), decrease of CMC content to help polymer solubilization
  - Development of **automated lamination equipment** towards R2R process

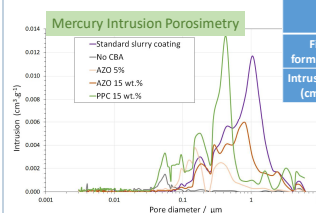


- Cycling tests:
  - Slightly lower performances with water-based coated electrode compared to NMP-based one → **sensitivity of NMC 622 in contact with water**
  - Decrease of capacity of extruded electrodes compared to coated ones, lower reproducibility → **non optimized electrode morphology**

NMC vs. Graphite (slurry-based) single layer pouch cells  
C/3 CCCV (4.2V) charge - C/2 discharge - 23 °C  
Electrolyte 1M LiPF<sub>6</sub> in EC:PC:DMC (1:1:3) + 2 % VC

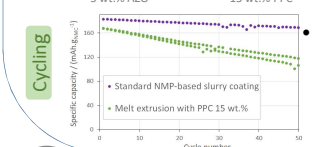
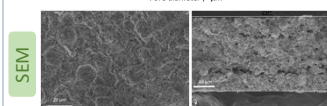
- Morphology after calendering:
  - Better homogeneity and binder distribution** for coated electrode
  - Binder agglomerates** at the surface after extrusion step, revealed by lamination/calendering
  - Further process improvement should improve electrode morphology

Water-based slurry coating : a) x 1000, b) x 10 000  
Water-based extrusion : c) x 1000, d) x 10 000



	Std slurry coating (NMP)	Extrusion - No CBA	Extrusion - AZO 15 wt. %	Extrusion - AOX 15 wt. %	Extrusion - PPC 15 wt. %
Final formulation	95/5/5	95/5/5	88.2/5.9/5.9	88.2/5.9/5.9	88.2/7.7/4.1
Intrusion vol. (cm³.g⁻¹)	0.083	0.018	0.055	0.065	0.119

- Only slurry coated electrode with major pore fraction ~ **1 μm diameter** (target for electrochemical application)
- Lower pore size distribution** for all CBA
- From 5 to 15 wt.% CBA: increase of the intruded volume
- Higher intruded volume** with PPC polymer compared to powder AZO and AOX
- Very dense composites**, some visible cavities for PPC-based electrode



- Cycling tests:
  - Cycling is possible with PPC-based electrode, but no response for both AZO and AOX electrodes

NMC vs. Li metal (coin cells)  
C/10 CCCV (4.3 V) charge - C/10 discharge - 45 °C  
Electrolyte 1M LiPF<sub>6</sub> in EC:DMC:EMC (1:1:1)

## > Conclusion & Perspectives

- Promising results for water-based extrusion process, optimization towards roll-to-roll process should enable to compete with standard slurry coating.
- High impact of CBA on porosity microstructure, to be optimized with polymers; electrochemical performances still need to be demonstrated.