A Novel Approach to Lithium-ion Battery Thermal Management: Poly(vinylidene fluoride-co-hexafluoropropylene) Composite Separators with Phase Change Materials

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Introduction

Separator membranes play an essential role in determining lithium-ion battery overall performance [1]. Some of the main detrimental issues of current lithium-ion battery systems are the ones related to battery safety and, in particular, with their thermal regulation [2].

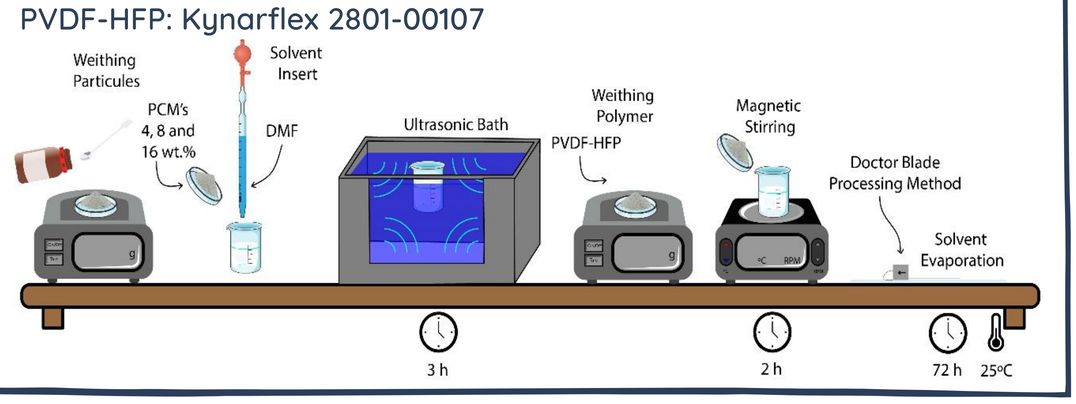
This manuscript offers a suitable solution by developing separator membranes with thermal regulation through the inclusion of phase change materials (PCM) microspheres [3].

Methodology

- Composite membranes of PVDF-HFP were fabricated using **varying amounts** of **phase change materials (PCM) microspheres** (0, 4, 8 and 16 wt.%).

PCMs: acrylic core–shell particles, CrodaTherm ME 29P) with a melting temperature at 29 °C

PVDF-HFP: Kynarflex 2801-00107



Results

- **SEM** images show that the membranes have a **porous microstructure** with **different pores sizes.** It is also observed that the inclusion of microencapsulated PCM affects the morphology of the membrane (Figure 1b-d), i.e., the size of the pores and their distribution, both along the cross section and the surface of the samples.

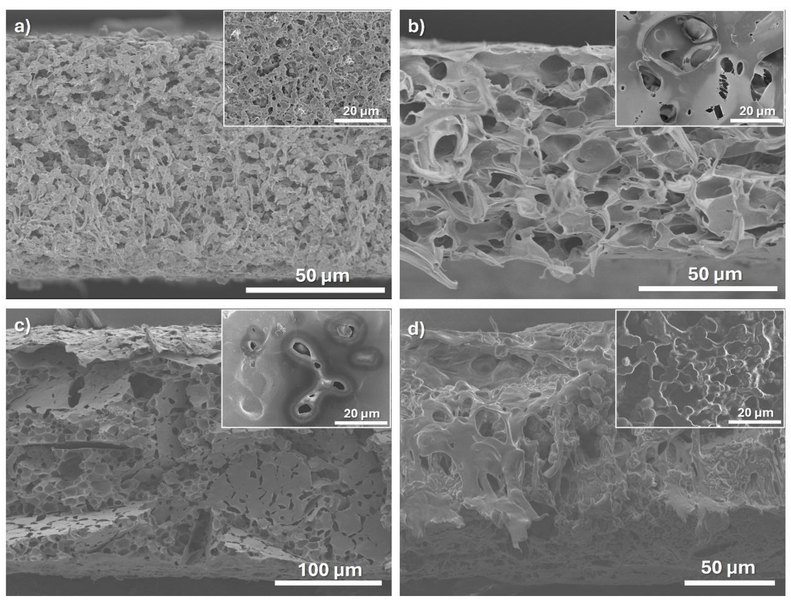


Figure 1: SEM images of the cross-section and surface (inset) of the different PVDF-HFP composite membranes with a) 0, b) 4, c) 8 and d) 16 wt.% microencapsulated PCM content. .

- Composite membranes with PCM (Figure 2b and c) present uniform thermal distribution at different temperatures compared to neat PVDF-HFP (Figure 2a).

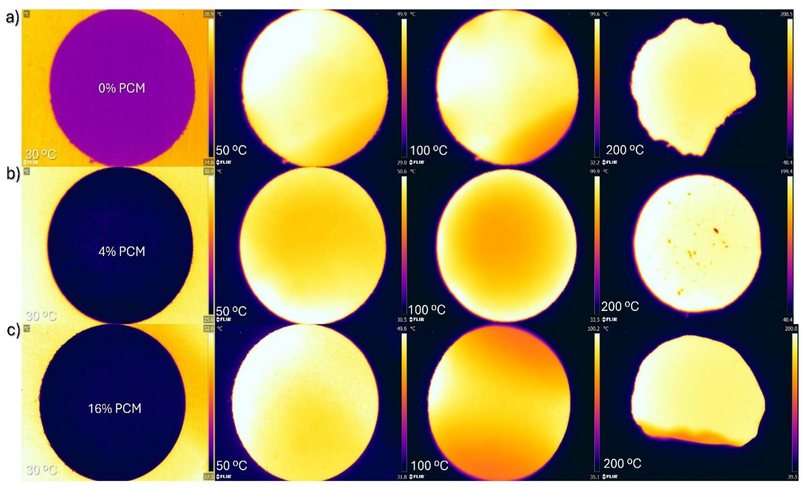


Figure 2: Optical images at different thermal temperatures, 30, 50, 100 and 200 °C, for composite separator membranes with a) 0, b) 4, and c) 16 wt.% microencapsulated PCM content, respectively. The diameter of the separators is 19 mm..

- At 2C-rate the obtained discharge capacities are 87 mAh.g^{-1}, 36 mAh.g^{-1}, 19 mAh.g^{-1} and 0 mAh.g^{-1} for the membranes with 16 wt.%, 8 wt.%, 4 wt.% and neat polymer membrane, respectively (Figure 3a). Excellent coulombic efficiency (~95%) is also observed with a good discharge capacity value at the C/10 rate after 200 cycles (Figure 3b).

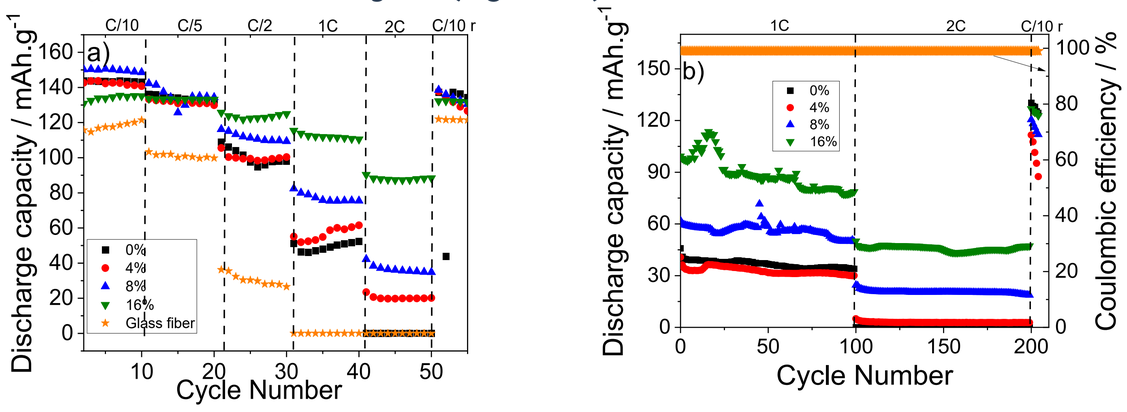


Figure 3: a) Rate performance and **b)** Cycle life behavior for all membranes and commercial glass fiber separator .

- This composite membrane can act as a security and active battery component once the observed pore size reduction can decrease the lithium-ion percolation acting as a thermal-shutdown (Figure 4).

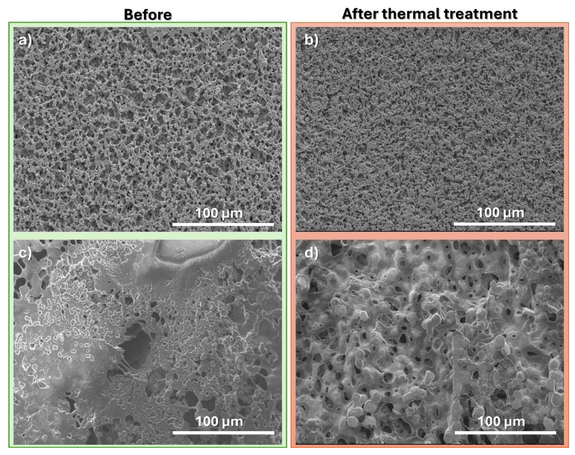


Figure 4: **a)** SEM surface images of a)-b) neat membrane and c-d) membrane with 16 wt.% PCM content, before and after thermal treatment at 80 °C..

Conclusion

- The **membranes** showed a **porous structure** with varying porosity and pore size.
- The PCM content improves the thermal distribution of the membrane and consequently guarantees its integrity.
- The membrane with 16wt.% of PCM microspheres of 87 mAh.g-1 after 200 cycles .
- The PCM microspheres improves the thermal regulation of the separator in which presents low thermal shrinkage and, therefore, improved mechanical stability upon heating.
- These separators are suitable for lithium-ion batteries with thermal regulation properties, allowing to prevent thermal runaway and, consequently, improve their safety.

References

[1] C. M. Costa, S. Lanceros-Mendez, Recent advances on battery separators based on poly(vinylidene fluoride) and its copolymers for lithium-ion battery applications, Current Opinion in Electrochemistry, 29 (2021), 100752

[2] X. Feng, D. Ren, X. He, M. Ouyang, Mitigating Thermal Runaway of Lithium-Ion Batteries, Joule. 4 (2020)743-770.

[3] J. P. Serra, at all, Improving Thermal Regulation of Lithium-Ion Batteries by Poly(vinylidene fluoride-co-hexafluoropropylene) Composite Separator Membranes with Phase Change Materials, ACS Appl. Energy Mater. 2025, 8, 3, 1847–1856

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