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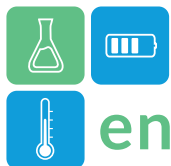
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Solid-Solid Phase Change Materials for the Thermal Management of Li-Ion Batteries

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Abstract

With the escalating demand for high-performance lithium-ion (Li-ion) batteries across diverse applications, ensuring effective thermal management is imperative for safety, longevity, and optimal functionality. Current literature limitations underscore the crucial necessity for innovative solutions, leading to the exploration of solid-solid phase change materials (SS-PCMs). This study focuses on the potential of hybrid organic-inorganic layered perovskites, a unique class of SS-PCMs, for thermal management in Li-ion batteries. These materials boast higher thermal stability, minimizing the risk of leakage and enhancing overall safety. Moreover, they offer improved energy density, extended cycle life, and efficient heat absorption/release. This research delves into the synthesis, characterization, and future perspectives of integrating these materials into various battery components for optimized thermal control and enhanced overall performance.

Keywords: Li-ion batteries, thermal management, SS-PCMs, hybrid layered perovskites.

Introduction

Thermal energy storage is a critical concern, especially given the prevalence of heat-intensive processes in final energy applications. Latent heat storage, characterized by a high enthalpy of phase change, presents distinct advantages over sensitive storage methods, offering energy densities three to five times higher. The isothermal nature of latent heat storage, coupled with the ability to adjust temperatures through material design, renders it suitable for applications like thermal management in Li-ion batteries. The demand for high-performance Li-ion batteries has seen a significant rise across diverse applications, underscoring the critical need for efficient thermal management. This is essential not only for ensuring safety but also for enhancing the longevity and optimal functionality of these batteries. In this context, phase change materials (PCMs), particularly hybrid solid-solid PCMs (SS-PCMs) like 2D perovskites, have emerged as promising candidates for thermal energy storage (Wankhede et al., 2022). These materials exhibit reversible transitions between crystalline and semi-crystalline or amorphous states, displaying minimal volume variation and the absence of a liquid phase related leakages. Notably, they offer enhanced energy density, extended cycle life, and efficient heat absorption and release, making them valuable for advanced thermal energy storage applications (Fallahi et al., 2017).

Despite being identified as promising materials for thermal management in the 1980s (Busico et al., 1980),

employing 2D perovskites as hybrid SS-PCMs have received little attention until now (Seo et al., 2022). In fact, hybrid SS-PCMs with a generic chemical formula $(C_nH_{2n+1}NH_3)_2M^II X_4$ (M = divalent metal; X = halogen) have demonstrated potential for heat transfer with controllable phase change temperatures (Landi and Vacatello, 1975). This paper discusses the synthesis, characterization, and potential of copper and zinc-based solid-solid phase change materials for thermal management in today's applications.

Methodology

Hybrid SS-PCMs $(C_nH_{2n+1}NH_3)_2M^II X_4$, where M =Cu, Zn; X =Cl; n =12, 16 were synthesized via solution chemistry. The synthesis involved the mixing of inorganic salts (zinc chloride, copper chloride - SigmaAldrich) and alkyl amines (dodecylamine, hexadecylamine - SigmaAldrich) in ethanol under reflux conditions at elevated temperatures (70-82°C), with the addition of slight quantities of HCl (37%). Notably, the synthesis protocol was implemented at different scales, ranging from 50 mL to 600 mL, ensuring scalability and reproducibility. Four hybrid SS-PCMs were synthesized:

- Bis(n-dodecylammonium)Tetrachlorocuprate $(C_{12}H_{28}N)_2CuCl_4$ (denoted as CuC12)
- Bis(n-dodecylammonium)Tetrachlorozincate $(C_{12}H_{28}N)_2ZnCl_4$ (denoted as ZnC12)
- Bis(n-hexadecylammonium)Tetrachlorocuprate $(C_{16}H_{34}N)_2CuCl_4$ (denoted as CuC16)
- Bis(n-hexadecylammonium)Tetrachlorozincate $(C_{16}H_{34}N)_2ZnCl_4$ (denoted as ZnC16)

The obtained SS-PCMs underwent a comprehensive characterization using a multi-technique approach. Thermal performance was assessed using micro-differential scanning calorimetry (DSC, Setaram, Calvet 3D) and simultaneous thermal analysis (STA coupling TGA and DSC, Jupiter F3-Netzsch). The structural features were investigated using X-ray diffraction (XRD, Bruker D8 Advance), attenuated total reflection (ATR, Bruker Invenio), small-angle X-ray scattering (SAXS, Xenocs), and synchrotron techniques. Scanning electron microscopy (SEM, Zeiss LEO 1530) was used for microscopic analyses.

Results and Discussion

Batches of CuC12, CuC16, ZnC12, and ZnC16 synthesized at different scales between 50 and 600 mL were characterized by ATR and XRD. The obtained XRD patterns exhibited characteristic peaks corresponding to the parent materials despite the increase in synthesis scale (Figure 1), signifying the reproducibility and scalability of the followed synthesis protocol for each of the four-studied SS-PCMs. Similarly, no changes in the recorded ATR profiles were observed, indicating the preserved structure and coordination after the scale up.

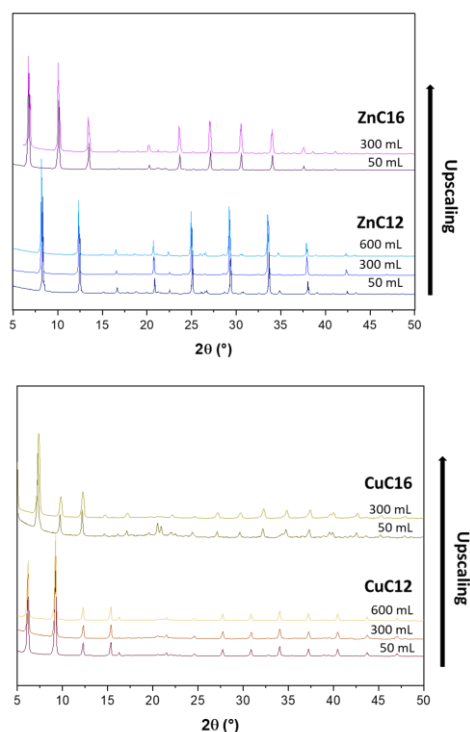


Figure 1: PXRD results showing the reproducibility of synthesis protocol at different synthesis scales.

Moreover, the thermal performance of the different materials was studied by STA and DSC. The obtained results revealed an increase in the transition temperature with the increase in the alkyl chain length

for both Cu and Zn based materials. The effect of the cation on the configuration was also observed. Copper-based samples presented transition temperatures lower than those of zinc based ones (Figure 2).

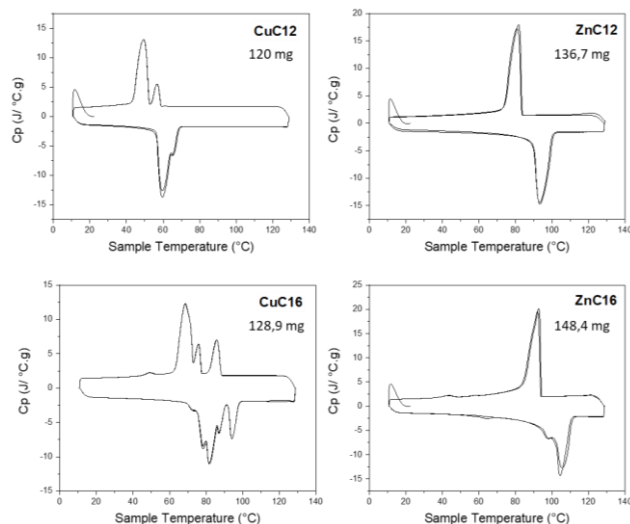


Figure 2: DSC profiles recorded after two consecutive cycles between 10-130°C at a rate of 1 Kmin⁻¹. Measurements were performed under air in closed crucibles.

Correspondingly, STA measurements have shown that the synthesized samples presented a high thermal stability up to 3 times the transition temperature in case of copper, and 2 in case of zinc (Figure 3).

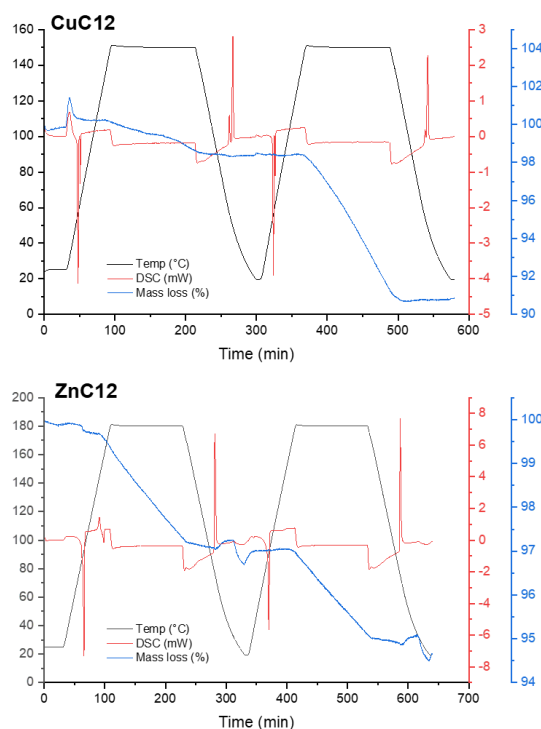


Figure 3: STA measurements recorded on CuC12 (26.3 mg) and ZnC12 (27.5 mg) after 2 cycles under air between 25-130°C at a rate of 2 Kmin⁻¹.

Table 1: Summary of results obtained by DSC and STA.

	CuC12	CuC16	ZnC12	ZnC16
ΔH (J/g)	72	72/103	85	80/100
T_{melting} ($^{\circ}\text{C}$)	54-56	69-71	80-83	92-95
Thermal Stability	150 $^{\circ}\text{C}$	150 $^{\circ}\text{C}$	180 $^{\circ}\text{C}$	180 $^{\circ}\text{C}$

Based on the obtained results, CuC12 can be nominated as an ideal material for thermal management of Li-ion batteries. CuC12 presents a phase transition temperature around 55 $^{\circ}\text{C}$ and a thermal stability at a temperature up to three times higher than its transition temperature with no degradation or liquidification. Further efforts are being put on the mechanical characterization of these materials, and a preliminary prototype is being under studies (Figure 4).

Conclusions

This study presents hybrid materials with high latent heat storage efficiency and thermal stability, even at temperatures double their transition temperature. Their unique thermal properties allow versatile shaping for optimized thermal exchanges, especially in Li-ion batteries. The employed advanced characterization techniques provided detailed insights into the materials' structure and behavior; the energy and transition temperature depend on both the length of the aliphatic chain and the nature of the cation. The possible successful design of the first thermally stable Li-ion battery employing SS-PCMs accentuates the innovative potential of these materials. Our work sets the stage for further exploration and optimization, emphasizing their transformative impact on energy storage technologies in terms of efficiency and

scalability. Future research may focus on refining synthesis methods, exploring additional applications, and advancing integration into diverse energy storage systems. Finally, it is worth mentioning that a pioneering commercial-scale synthesis protocol using 20L reactors is under investigation.

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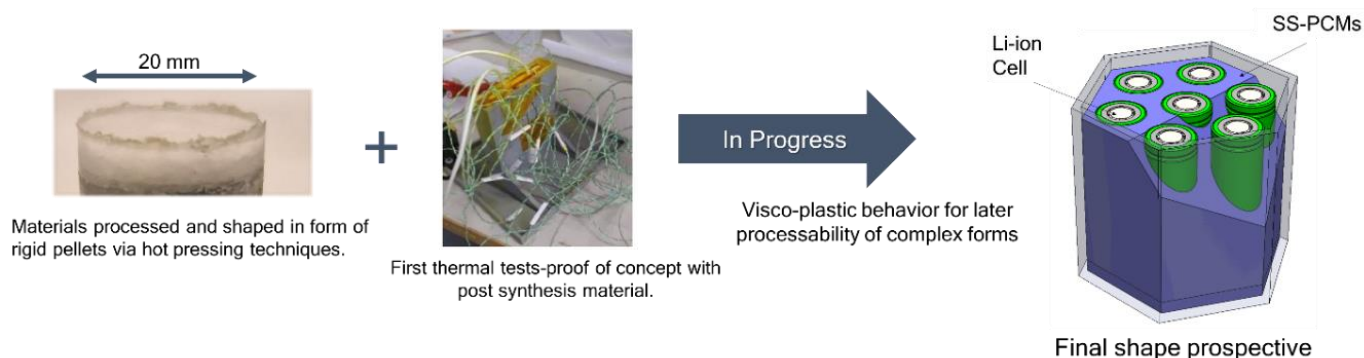


Figure 4: Work in progress covering the testing and shaping of materials for applying in a Li-ion battery system.