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Shell-driven localized oxide nanoparticles determine thermal stability of micro-encapsulated phase change material

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ABSTRACT: Not all encapsulation techniques are universally apt for every type of phase change materials (PCM), highlighting the imperative for methodological precision. This study addresses the challenges of microencapsulated PCM (MEPCM) arising from the immiscible pairing of α -Al₂O₃ nanoparticles with Sn microparticles. The High-Speed Impact Blending

(HIB) dry synthesis technique is employed, facilitating large volume production of Sn@ α -Al₂O₃ MEPCMs. The resulting MEPCMs not only seamlessly endure 100 cycles of melting-solidification, but with the strategic incorporation of a glass frit, the MEPCMs composite also exhibits remarkable thermal durability, withstanding up to 1000 melting-solidification cycles. Even under ultra-fast thermal fluctuations, the α -Al₂O₃ shell remained resilient through 100 cycles. A marked reduction in supercooling is observed, attributed to the formation of SnO and SnO₂ nanoparticles within the α -Al₂O₃ crystal lattice. The atomically resolved interface dynamics between SnO₂ and α -Al₂O₃ play a pivotal role, lowering the energy barrier for Sn nuclei formation during solidification. This affects an accelerated Sn nucleation rate, effectively suppressing supercooling. Such insights offer a deeper understanding of the interplay between nanoscale crystal lattice imperfections and their implications for energy storage applications.

INTRODUCTION

The substituent of thermal energy storage: phase change materials (PCMs) are poised to amplify the efficacy of renewable energy utilization by enabling the innovative harnessing of exergy through the recuperation of industrial waste heat, bolstering the efficiency of solar thermal power generation, and providing foundational support to the emerging field of Carnot batteries.¹⁻⁵ In the case of inorganic PCM, its success has been associated to advancements in encapsulation techniques from the past two decades.⁶ Thereafter, not all encapsulation methods are universally suitable for every type of PCM. For example, while both the complex coacervation and spray-drying methods have been deemed appropriate for encapsulating PCMs for solar energy storage,⁷ they may not be ideal for PCMs with low melting points,⁸ sensitivity to viscosity, or a diverse particle size distribution.

Previous studies demonstrated the successful creation of micro-encapsulation PCMs (MEPCMs) with an α -Al₂O₃ shell making on metal/alloy PCM systems, achieved through a sequential process of chemical coating with an AlOOH layer followed by a heat-oxidation treatment in an O₂ atmosphere. The MEPCM technology has been excellent – selectable metals^{9, 10} or their alloys¹¹⁻¹³ for corrosion resistance PCMs, capable of storing $\sim 1 \text{ GJ} \cdot \text{m}^{-3}$ latent heat,¹⁴ exhibit compatibility with catalyst integration,¹⁵ versatility in composite molding,¹⁶⁻¹⁸ and a proven durability over thousand cycles of thermal stability tests.^{19, 20} Nevertheless, the practical extension of the current method remains an endeavor, with the persistent phenomenon of supercooling and its underlying mechanism yet to be comprehensively elucidated.

This work showcases the advancements in MEPCM technology, effectively addressing the encapsulation challenges inherent to the immiscible pairing of an α -Al₂O₃ shell with Sn microparticles (Sn@ α -Al₂O₃). This is achieved via a dry synthesis technique – High-Speed Impact Blending (HIB). This method, which epitomizes an environmentally friendly approach, not only facilitates the production of MEPCM with high yield and rigid shell structure but also ensures its durability in prolonged and rigorous thermal cyclic tests. The distinctive shell architecture, a byproduct of the encapsulation by α -Al₂O₃ nanoparticles, plays a pivotal role in supercooling suppression. This study provides valuable insights into surface dynamics and defect interactions, laying the foundation for refining the synthesis of the next generation of advanced energy storage materials.

RESULTS and DISCUSSION

Hybridization of Sn@ α -Al₂O₃ MEPCMs. Figure 1a displays the schematic of HIB experiment, in which pre-mixed Sn@ α -Al₂O₃ MEPCMs collide with each other (Figure 1b) under the influence of high-speed rotating blades (detailed experiments in Table S1, Supporting Information). The rapid rotation circulates the Sn@ α -Al₂O₃ MEPCMs through a looping tube

due to Ar gas pressure. This facilitates the adherence of α -Al₂O₃ nanoparticles to the Sn surface, resulting in the hybridization of Sn@ α -Al₂O₃ MEPCMs. To achieve uniform shelling, the rotor rotation speed, duration, and number of input batches were set to 80 m·s⁻¹, 3 min, and four, respectively. Each batch weighed 30 g, and the process can be repeated continuously to produce larger volumes. The hybridized Sn@ α -Al₂O₃ MEPCMs are then collected through a discharge valve. As shown in Figure 1c and Figure S1, the HIB process effectively creates distinct and uniform α -Al₂O₃ nanoparticles that form a shell-like structure on the Sn surface.

To examine the robust interfacial adhesion between the α -Al₂O₃ shell and Sn core, a cross-sectional focused ion-beam (FIB) lamellar cut was processed. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image reveals an uneven Sn surface at the Sn core/ α -Al₂O₃ interface (Figure 1d), a result of the collisions during HIB. In contrast, the α -Al₂O₃ nanoparticles appear densely packed with voids (Figure 1e). Near the Sn core/ α -Al₂O₃ interface, the voids size is ~50 nm, increasing to ~200 nm towards the outer shell. The shell's thickness measures ~2 μ m. Interestingly, localized Sn nanoparticles (~10 nm) are present on the α -Al₂O₃ surface and cross-section (Figure 1f–h, Figure S2b). Notwithstanding the immiscibility of Sn with α -Al₂O₃, this indicates nanosized Sn penetration into α -Al₂O₃ during HIB. A metastable Sn-Al-O surface (Figure 1i), which forms in a crystalline-amorphous state, may facilitate this Sn penetration. The Sn {101} and α -Al₂O₃ {024} TEM diffraction spots (Figure 1j) correspond to crystalline Sn/ α -Al₂O₃, while nanopores (Figure 1i and Figure S4b) indicate the amorphous nature of Sn-alumina. Given the thickness variation of 44–70 nm (Figure S2d–e), its nano-porosity increases towards the outer region, providing an active site for the formation of an oxide layer under thermal treatment. In the STEM-energy dispersive X-ray (EDX) map (Figure 1k), Sn is proportionally mixed with Al, while oxygen has a ratio four times that of Al.

The emergence of a metastable Sn-Al-O surface can be attributed to the incessant collisions between the MEPCMs during the HIB process. Notably, such an amorphous edge surface is absent in the pristine α -Al₂O₃ nanoparticles (Figure S5c). Moreover, during HIB, coolant water (~20 °C) was circulated around the central rotor region to mitigate excessive temperature escalation. Consequently, the collisions induced by HIB likely engendered a quasi “melted” Sn amalgamated proportionally with Al, thereby causing the formation of the metastable Sn-Al-O surface. Importantly, the EDX map of metastable surface (Figure 1k) exhibits 1–2 nm Sn deposits, which are likely the result of partial volatilization of Sn nanoparticles localized on the edge surface (Figure 1f) during HIB. This phenomenon contributes to variations in Sn nanoparticle size and distribution within the α -Al₂O₃ matrix, indicating a dynamic process during the HIB treatment. Given the presence of oxygen vacancies (V_O) in the inner regions of α -Al₂O₃ (P2 vs. P1 in Figure S2c), it is conceivable that HIB also introduced lattice defects within the α -Al₂O₃ nanoparticles, thereby paving the way for the genesis of localized Sn nanoparticles within the α -Al₂O₃ matrix. This pathway is discernable in the locally disrupted atomic configuration of the α -Al₂O₃ (104) lattice (Figure S4b-d) depicted in Figure 1h. Alongside V_O , this disrupted region also underscores a deficiency in Al atoms, facilitating Sn diffusion. Herein, Sn appears to permeate towards the inner α -Al₂O₃ lattice, as corroborated by the Sn EDX map spanning the inner α -Al₂O₃ (Figure S3c). Intriguingly, the diminishing thickness of the α -Al₂O₃ lattice (Position 6-9 in Figure S2e) in proximity to the Sn nanoparticle (Figure 1h) signifies a heightened concentration of V_O (Figure S2f), potentially accommodating Sn localization. This intricate nanoscale migration of Sn within the shell is instrumental in dictating the heat storage capacity and thermal durability of the Sn@ α -Al₂O₃ MEPCMs.

Thermal stability over 100 cycles. Figure 2a illustrates the latent heat storage functionality of the MEPCMs, characterized by a cyclical progression of endothermic and exothermic reactions.

A testament to the efficacy of this application is the conspicuous absence of Sn leakage, even after prolonged melting-solidification cycles. Initially, a series of 100 cycles were carried out in an air atmosphere to assess the MEPCMs post-HIB. Owing to the α -Al₂O₃ encapsulation, the Sn core registered a latent heat capacity of approximately 50 J·g⁻¹ during both melting and solidification phases (Figure 2b), which is marginally lower than the 56 J·g⁻¹ observed for pure Sn (Figure S6). In its pure condition, the phase transitions of Sn manifested a supercooling of 23 °C, based on the melting temperature (T_m) and solidification temperature (T_s) onset difference (Table S2). Subsequently, the degree of supercooling escalated to 72 °C for the Sn@ α -Al₂O₃ MEPCMs. Evidently, these attributes are a direct consequence of the α -Al₂O₃ encapsulation. Similar behavior was observed by Sheng *et al.* concerning the irregular particle morphology of Sn@SnO₂ MEPCMs, where an approximate supercooling of 89 °C was noted under SnO₂ encapsulation, in contrast to the 87 °C observed in their pure Sn.²¹ The markedly reduced supercooling observed in the present study can be ascribed to the enhanced sphericity of Sn. Notably, the non-uniform nature of the Sn microparticles in the study by Sheng *et al.*, with their potentially larger surface area and unknown purity, could have introduced variations in the interfacial energy, influencing nucleation behavior and thus supercooling. As elucidated in subsequent sections, the delay in crystal nucleation during the melting phase is intrinsically linked to the supercooling event.²² Post completion of 100 melting-solidification cycles, the MEPCMs displayed intact integrity, devoid of any leakage or α -Al₂O₃ shell fractures (as corroborated by the scanning electron microscopy (SEM) images shown in Figure 2b and Figure S7), emphasizing their robustness throughout the cyclic test. Concurrently, the recurrent supercooling was suppressed over the 100 cycles, resulting in a decline of approximately 16% in both the solidification latent heat (ΔH_s) and melting latent heat (ΔH_m) of the MEPCMs (Figure 2b,c).

The differential scanning calorimetry (DSC) curves history over 100 cycles is plotted in Figure 2d to monitor the progression of the supercooling suppression. When subjected to a heating/cooling rate of $50\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, the T_m peak remains at $247.2\text{ }^{\circ}\text{C}$. In contrast, the T_s peak exhibits a gradual shift, transitioning from 130.3 to 137.7 to $141.7\text{ }^{\circ}\text{C}$ (Figure 2c). The initial shift in the T_s peak becomes discernable by the 10th cycle, with a subsequent $\sim 4\text{ }^{\circ}\text{C}$ shift observed by the 25th cycle, stabilizing thereafter up to the 100th cycle. This stabilization in T_s post the 25th cycle is clearly observed in Figure 2d. Additionally, the latent heat variations during the melting and solidification phases show a decline up to the 60th cycle, reaching a plateau that persists through the 100th cycle. Post-oxidation treatments conducted in an air atmosphere (Figure S8) indicate that $500\text{ }^{\circ}\text{C}$ represents the maximal utilization temperature for prolonged heat storage and release using the MEPCMs.

Thermal stability under 1000 cycles. The practical application of the MEPCMs can be compromised due to potential oxidation of the Sn core. However, leveraging their distinct microparticle morphology, it is feasible to create a composite pellet of the MEPCMs by incorporating a glass frit. This approach not only caters to the pellet form but also allows for modifications into various shapes such as honeycombs and balls. Utilizing this glass frit, composites of MEPCMs have previously been demonstrated fit for high-temperature applications ($555\text{--}575\text{ }^{\circ}\text{C}$) using Al-Si alloy-based MEPCMs.^{16, 23} For Sn, a specific glass-frit (ASF-1100, AGC Electronics Co., Ltd) designed for relatively low firing conditions ($460\text{ }^{\circ}\text{C}$, 30 min) was chosen. This frit, comprising Bi_2O_3 and B_2O_3 , served as an effective binder for the MEPCMs (inset Figure 2e) (detailed methodology for $\text{Sn}@ \alpha\text{-Al}_2\text{O}_3$ MEPCMs composite making in Supporting Information). In addition, the incorporation of active metals into MEPCMs, enhancing their catalytic properties, has been previously demonstrated.¹⁵ Owing to the facile dry synthesis approach outlined in this study, the multifunctional properties of MEPCMs can be feasibly achieved. For the $\text{Sn}@ \alpha\text{-Al}_2\text{O}_3$ MEPCMs, the binding process was

executed without compromising the structural integrity of the MEPCMs, as exhibited in Figure S10a. Post-sintering, the pellet demonstrated latent heat values of $\Delta H_m = 30 \text{ J}\cdot\text{g}^{-1}$ and $\Delta H_s = 25 \text{ J}\cdot\text{g}^{-1}$ (Figure 2e). However, considering the intact nature of the $\text{Sn}@ \alpha\text{-Al}_2\text{O}_3$ MEPCM and the diluting effect of the glass frit, the pellet accounts for 60% of the MEPCMs' sensible heat capacity.

This assertion was further validated after subjecting the composite to 1000 melting-solidification cycles under conditions analogous to its powdered form, where heating/cooling was conducted at $400 \text{ }^\circ\text{C}/40 \text{ }^\circ\text{C}$ in an air atmosphere. The extended cyclic test was carried out in a custom-built quartz furnace. Cross-sectional observations (Figure S10b) revealed that the MEPCMs maintained their morphology post the 1000 cycles, albeit with a slight reduction in ΔH_m and ΔH_s values to 25 and $24 \text{ J}\cdot\text{g}^{-1}$, respectively. In comparison, previous research on the $\text{Al-25wt.\%Si}@ \alpha\text{-Al}_2\text{O}_3$ MEPCM composite established a benchmark for thermal durability over 300 cycles^{16, 18, 23} – a threshold that this study surpassed. Notably, in composite form, $\text{Al-25wt.\%Si}$ exhibits a considerably higher latent heat energy than Sn, registering at $120\text{--}160 \text{ J}\cdot\text{g}^{-1}$. Despite this, the enhanced durability of the MEPCMs in pellet form substantiates their practical significance. Given the retained structural integrity, the latent heat decrease is both logical and acceptable for such extended thermal cyclic durability. Furthermore, akin to the results post 100 cycles, the results post 1000 cycles revealed a suppression in supercooling (T_s : from 134.8 to $146.4 \text{ }^\circ\text{C}$), highlighting the role of the robust $\alpha\text{-Al}_2\text{O}_3$ shell structure in fortifying the thermal stability of the MEPCMs.

Ultra-fast thermal cycling. Drawn from the findings of the extended 1000 cyclic test of the composite, further investigations delved into the resilience of the $\text{Sn}@ \alpha\text{-Al}_2\text{O}_3$ MEPCM under more rigorous conditions, specifically assessing the performance of the MEPCM under ultra-fast heating/cooling rates using an advanced Flash-DSC 2+ (Mettler Toledo) machine. A single

Sn@ α -Al₂O₃ MEPCM ($\phi \approx 20 \mu\text{m}$) was placed on a Flash-DSC chip sensor using silicon oil to ensure sustained particle-sensor contact during the rapid thermal transitions. Preliminary heating to 400 °C for 1s was employed to eliminate any residual Si oil. The experiment encompassed heating/cooling rates of 1000, 5000, and 8000 °C·min⁻¹ for a total of 100 cycles in an air environment, with the temperature varying between 400 and 40 °C.

Remarkably, even under these aggressive thermal rates, the encapsulation exhibited commendable robustness, particularly at 1000 and 5000 °C·min⁻¹ (Figure S11b,c). However, the 8000 °C·min⁻¹ rate unveiled the encapsulation threshold, evidenced by discernable cracking (Figure S11d). The Flash-DSC curves (Figure 2f) revealed several observations: a shift in both T_m and T_s towards elevated temperatures with increasing rates, and a noticeable expansion in the area under the melting/solidification curves. While certain inconsistencies were noted for the T_m peaks, these could be attributed to factors such as limitations of the Si oil and variations in the thickness of the α -Al₂O₃ shell. The sensitivity of the Flash-DSC nanocalorimetry to specimen thickness further corroborates this observation.²⁴ Nonetheless, the consistent upward shift in T_s peaks affirms the ability of the MEPCM to suppress supercooling even under extreme thermal conditions.

Oxides formation in the Sn@ α -Al₂O₃ MEPCMs. X-ray diffraction patterns (XRD) reveal that the Sn @ α -Al₂O₃ MEPCMs, post-HIB, retained their crystalline integrity (Figure 3a). The initial shift in the solidification peak during the 10th cycle suggests the formation of SnO, which, by the completion of 100 cycles, progressively transitions to SnO₂. The presence of SnO and SnO₂ was further validated by X-ray photoelectron spectroscopy spectra. A distinct 0.07–0.08 eV difference in the peak assignment of Sn 3d for SnO and SnO₂ was observed (Figure S22a), consistent with previously reported values.²⁵ Moreover, the O 1s spectra of the samples showed peaks at 531.32 eV (10 cycles) and 531.12 eV (100 cycles), corroborating the

presence of V_O (Figure S22b). To elucidate these oxide formations, HAADF-STEM analysis was performed on cross-sectional MEPCM samples from both the 10th and 100th cycles. The 10th cycle MEPCM's core/shell interface mirrors the HIB sample (Figure 1d, Figure S16), with the luminous contrast nanoparticles on the cross-sectional $\alpha\text{-Al}_2\text{O}_3$ particle being identified as SnO crystals (Figure 3b). Given the congruence in nanoparticle distribution with the HIB shell (Figure 1f), it is inferred that the Sn nanoparticles (Figure 1h) acted as nucleation sites for SnO genesis. Subsequent cyclic tests led to the oxidation-driven densification of these nanoparticles, forming a 10–20 nm SnO_2 layer on the $\alpha\text{-Al}_2\text{O}_3$ particle surface (Figure 3c), while SnO_2 nanoparticles persisted within the inner $\alpha\text{-Al}_2\text{O}_3$ lattice (Figure 3d).

The HAADF image shown in Figure 3d reveals a diminished Al-O column intensity at the SnO_2 (101) lattice and $\alpha\text{-Al}_2\text{O}_3$ interface, accentuating the significance of lattice defects in relation to the earlier HIB-induced Sn localization. Figures 3e,f substantiate this phenomenon, with the variation in Al-O intensity being evident on the $\alpha\text{-Al}_2\text{O}_3$ (104) lattice. Notably, the darker contrast in the initial 3 nm area of Figure 3e(A) exhibits a diminished Al-O intensity relative to that in Figure 3e(B). Concurrently, the $\alpha\text{-Al}_2\text{O}_3$ surface layer comprises SnO_2 nanoparticles (Figure S17a,b), and even with fewer surface nanoparticles, the internal SnO_2 nanoparticles remain localized (Figure S17c). Density functional theory (DFT) results discussed later will shed light on the electronic states accompanying the formation of SnO_2 on the $\alpha\text{-Al}_2\text{O}_3$ lattice. This is not merely restricted to the SnO_2 nanoparticle observed in Figure 3d; SnO_2 nanoparticles pervade the entirety of the $\alpha\text{-Al}_2\text{O}_3$ lattice (Figure S17a). Figure 3e and its EDX mapping (Figure S17b) bolster the hypothesis that despite the absence of visible SnO_2 nanoparticles, the $\alpha\text{-Al}_2\text{O}_3$ crystal is replete with defects, facilitating the continuous penetration and oxidation of Sn within the $\alpha\text{-Al}_2\text{O}_3$ lattice during the 40–400 °C cyclic test. This penetration is particularly facilitated by $\alpha\text{-Al}_2\text{O}_3$ voids (Figure 1e) during Sn volatilization, aided by the Sn seeds (Figure 1h) and Sn-Al-O metastable surface (Figure 1i).

Figure 3g presents a HAADF-resolved atomic configuration of the SnO₂ (110)/ α -Al₂O₃ ($\bar{1}02$) interface, obtained to further investigate the potential interface effects on supercooling suppression. Notably, lattice strains are distinctly confirmed on α -Al₂O₃. In the delocalized region (orange-pink lines region), sequences of Al atom columns exhibit both stretching (B-C) and compression (A-B), with distances of 3.0 and 1.4 Å, respectively (Figure 3h). Despite the absence of discernable strains on Sn atoms, local delocalization is plausible, given the V_O detected by STEM-EDX in this interface region. The evolution of SnO₂ formation and its impact on supercooling suppression under standard DSC is depicted in Figure 3i. During HIB, Sn nanoparticles (Figure 3i-1) found localization within the α -Al₂O₃ matrix, attributed to the quasi “melted” state of Sn coupled with lattice defects in α -Al₂O₃. This facilitated the permeation of Sn into the void interspersed between the α -Al₂O₃ during the melting phase, with these voids retaining Sn upon solidification. Subsequently, influenced by the localized Sn seeds (Figure 1g), SnO and SnO₂ nanoparticles progressively built-up over the span of 10 to 100 cycles (Figure 3i-2,3). The Sn nuclei formation accelerates with stronger morphology of SnO and SnO₂ crystals, resulting in suppression of supercooling. The Flash-DSC experiment corroborated the DSC findings, indicating that SnO₂ nanoparticles can be densely populate beneath the α -Al₂O₃ (Figure 3i-4, Figure S12) at the Sn/ α -Al₂O₃ interface, thereby reinforcing the shell structure and stabilizing the latent heat (60th cycle onwards in Figure 2d). Furthermore, due to their abundant localization in the shell region, SnO₂ nanoparticles exhibit an affinity for lattice energies, resulting in their spontaneous enrichment at the α -Al₂O₃ shell.

The Sn core/ α -Al₂O₃ shell interface after 100 cycles was also examined, in scenarios where the SnO₂ layer asserted dominance. However, contrary to expectation, a discernable Sn/ α -Al₂O₃ shell interface structure emerged (Figure 4a); instead of layer formation, SnO₂ nanoparticles are localized within the α -Al₂O₃ crystal. The HAADF image of the Sn [101] projection axis (Figure 4b) unequivocally suggests that the Sn crystal exhibits a propensity to

extend toward the α -Al₂O₃ particle shell. The SnO₂ formed at the 2 μ m agglomerated α -Al₂O₃ particles (Figure 1e) acted as a binder—extending the rigidity of the α -Al₂O₃ shell. It is imperative to note that a substantial amount of SnO₂ nanoparticles is likely to be present at the interface beyond 100 cycles. Conversely, an interfacial SnO₂ layer can be formed in the HIB samples through heat treatment in an O₂ flow prior the cyclic test. This scenario can then be synergistically integrated with composite fabrication, aiming to surpass the benchmark of 1000 cyclic tests while simultaneously enhancing the heat storage capacity. This discussion will be reported in the near future. Presently, this report focuses on the fundamentals and mechanistic aspects of the HIB-fabricated Sn@ α -Al₂O₃ MEPCM, building towards those improvements, particularly with regards to the suppressed supercooling.

Supercooling suppression in the Sn@ α -Al₂O₃ MEPCMs. The supercooling degree decreased from 72 to 61 °C after 100 cycles, i.e., the crystallization rate during liquid-solid Sn phases became faster. This has already begun in the 25th cycle, whereafter the T_s peak (141.7 °C) stabilized toward 100 cycles (Figure 2c). As discussed above, only SnO₂ concentration buildup occurred over these cycles, resulting in the latent heat decrement until the 60th cycle (Figure 2d). During solidification, the built SnO₂ nanoparticles (Figure 3c and Figure 4a) play an instrumental role in promoting faster Sn nuclei formation. These nuclei, discernible within the fissured regions of the Sn core (Figure 4c), evolved as a consequence of the attenuated Sn density post the cyclic test. They are indeed spherical in shape ($\phi \approx 30$ nm) and densely populated on the Sn core, as indicated by the yellow markers. Moreover, the nuclei are single crystal in nature, as indicated by the clear Sn (220) lattice (Figure 4d, Figure S18). It is formed through lattice reorganization, emanating from the proximal granular seeds (Figure 4d), a process enhanced by the SnO₂ nanoparticles.

The consistently apparent SnO₂ (101) lattice (Figure 3d and Figure 4a) has an orientation dependency on the α -Al₂O₃ (104) lattice, suggesting a promotion of faster Sn nuclei formation due to specific SnO₂ lattice surface energy. This is in conjunction with a study by Martin *et al.*, wherein the nucleation dynamics are postulated to be intertwined with the surface plane normal to the solidifying liquid.²⁶ However, a lattice mismatch between a unit cell parameter is not deemed to be the key determining factor. The SnO₂ (101)/ α -Al₂O₃ (104) interface has a lattice mismatch of 7.2%. Subsequent insight gleaned from DFT analyses shows that the SnO₂ (110) lattice suffice a smaller 5.5% lattice mismatch with the α -Al₂O₃ ($\bar{1}02$) surface. DFT studies on SnO₂ (110) are popular owing to its low surface energy.^{27, 28} However, it is necessary to acknowledge that the coexistence of both SnO₂ (101) and SnO₂ (110) lattices within the α -Al₂O₃ shell promote Sn nuclei formation. These nanoparticles, characterized by their specific SnO₂ lattice structures, spontaneously agglomerate into 30 nm Sn nuclei to form the Sn core.

A higher density of SnO₂ nanoparticles at the Sn/ α -Al₂O₃ interface is preferable to accommodate the kinetics of Sn nucleation (Figure 3i-4). However, there are fewer nanoparticles at this interface compared with the SnO₂ density observed in Figure 3c. This disparity can potentially be attributed to the 50 °C·min⁻¹ heating/cooling rate implemented by the combined thermogravimetry (TG)-DSC analyzer, which enabled the SnO₂ nanoparticles that spontaneously formed during solidification to slowly diffuse into the α -Al₂O₃ shell. This observation aligns with the outcomes of the Flash-DSC experiments. The Flash-DSC scan results (Figure 2f) resembles a suppressed supercooling behavior, as in Figure 2b. Crucially, the predominance of SnO₂ (101) nanoparticles at the Sn/ α -Al₂O₃ interface (Figure S12) predicates that the Sn nucleation rates are bound to the density of the SnO₂ nanoparticles. This also infers that a nanoscale solidification phase in an encapsulated PCM transpires under conditions of rapid temperature decrease rate.

Electronic states in the $\text{SnO}_2/\alpha\text{-Al}_2\text{O}_3$ interface. Valence electron energy-loss spectroscopy (VEELS) in STEM (STEM-VEELS) measurements and DFT calculations were carried out centered on the SnO_2 (110)/ $\alpha\text{-Al}_2\text{O}_3$ ($\bar{1}02$) interface (Figure 3g). An interface incorporating SnO_2 (101)/ $\alpha\text{-Al}_2\text{O}_3$ (104) (Figure 3d) is desirable, which however is not perpendicular to electron probe suitable for independent EEL collection from each SnO_2 region, the interface, and $\alpha\text{-Al}_2\text{O}_3$, as shown in Figure 5a. To verify the effects of V_O within the interface, a single oxygen atom was removed from both the SnO_2 and $\alpha\text{-Al}_2\text{O}_3$ structures comprising the SnO_2 (110)/ $\alpha\text{-Al}_2\text{O}_3$ ($\bar{1}02$) interface model (Figure 5b). Indeed, similar strains of $\alpha\text{-Al}_2\text{O}_3$ observed in the $[\bar{1}00]$ viewed model, where the first Al atoms column in contact with SnO_2 had compressive strain. There was no indication of oxygen shuffling during model relaxation, where stretching of both Al and O is more pronounced at the vicinity of V_O point. Within the SnO_2 domain, a distinct delocalization of Sn atoms near to the V_O point was observed, which explains the shape irregularities in the HAADF image of the Sn atoms shown in Figure 3g. A comparable interfacial behavior is inherent to the SnO_2 (101)/ $\alpha\text{-Al}_2\text{O}_3$ (104) interface, given that the $[0\bar{1}0]$ view of the interface model (Figure 5b) has an equivalent $\alpha\text{-Al}_2\text{O}_3$ (104) lattice arrangement.

Hereinafter, the STEM-VEELS map result shows single scattering distribution (SSD) obtained from each designated region: SnO_2 (Figure 5c), the interface (Figure 5d), and $\alpha\text{-Al}_2\text{O}_3$ (Figure 5e). The VEEL spectrum imaging (SI) data were collected in 2D array mode, employing a window size of 135×60 , centered on the targeted interface. The probe dwell time was 15 ms. The SSD spectra are taken from the averaged area of each SnO_2 , interface, and $\alpha\text{-Al}_2\text{O}_3$ region (Figure 5a). Then, the energy-loss function (ELF) calculation results obtained from the V_O -incorporated SnO_2 , interface, and V_O incorporated $\alpha\text{-Al}_2\text{O}_3$ models were compared. The SSD spectra represent the complex permittivity ϵ of each region, but without

energy dependencies requisite to give the real and imaginary parts (ϵ_1 and ϵ_2) of the permittivity.²⁹ Therefore, Kramers–Kronig analysis (KKA)²⁹ of the SSD is necessary for direct comparison with the computed ELF. However, there is a caveat for the KKA given by the probability of underlying α -Al₂O₃ under SnO₂ and vice versa, even though the measured interface thickness is 45 nm (via the absolute Log-ratio method). The 45 nm thickness lends credence to a negligible plural-scattering,³⁰ thereby increasing the reliability of the collected VEEL spectra. Thereafter, the ELF from each region is plotted against the SSD. In the SnO₂ region (Figure 5c), a harmonious alignment of two peaks is discerned between the SSD and calculated ELF at 2.0 and 14.0 eV. As shown by the partial density of states (PDOS), these peaks are linked to V_O in SnO₂ and the Sn-*p* orbital (Figure 5f). The calculated interface ELF resonated profoundly with the experiment (Figure 5d), especially with scattering intensities exceeding 6.0 eV. Moreover, a nuanced shoulder peak at 1.2 eV (inset of Figure 5d) unravels the presence of a specific low-energy electronic state within the SnO₂/ α -Al₂O₃ interface.

The caveat in KKA is recognized here from the consistent 1.2, 2.0, and 4.0 eV peaks across all regions. The 4.0 eV peak belongs to V_O in α -Al₂O₃ (Figure 5e,h). Note that a mere 1.4% of V_O is effective in the calculated $2 \times 2 \times 1$ α -Al₂O₃ supercell (Table S7). The actual V_O concentration can be higher, considering charge compensation mechanisms necessitated by the spanning SnO₂ localization within the α -Al₂O₃. The broad 2.5–6 eV SSD peak indicates the presence of multiple, distinct V_O peaks originating from the α -Al₂O₃, which seem to overlap and scatter within this energy spectrum while maintaining the α -Al₂O₃ bandgap ($E_g = 8.8$ eV). This hypothesis can be substantiated by exploring variations in supercell dimensions, the spatial positioning, and the concentration of V_O within the α -Al₂O₃ matrix. As an alternative approach, computational analyses involving Sn-doping, Al vacancies, and a combination of V_O can provide further insights. In contrast, the 2.0 eV peak is consistent in all regions, which implies an approximate 2.1% V_O in the SnO₂. Beyond 6.0 eV, the plots for SnO₂ and α -Al₂O₃

diverge. This suggests the simultaneous capture of two distinct inelastic scattering events within each region: (i) the layered interaction of SnO_2 and $\alpha\text{-Al}_2\text{O}_3$ atoms and (ii) the interfacial dynamics of $\text{SnO}_2/\alpha\text{-Al}_2\text{O}_3$. This is inevitable given the primordial metastable Sn-Al-O surface and the inherent lattice defects within the $\alpha\text{-Al}_2\text{O}_3$ lattice. Furthermore, the SSD profile from the interface mirrors that of the $\alpha\text{-Al}_2\text{O}_3$ region, highlighting the diffusion dynamics of SnO_2 within the $\alpha\text{-Al}_2\text{O}_3$ lattice, in addition to the localized presence of SnO_2 nanoparticles.

The PDOS plots explain the formation of interface SSD (Figure 5g). The PDOS is taken from five atomic columns (region marked in blue in Figure 5b) equivalent to the averaged SSD area of the interface (Figure 5a). As a result, coupling takes place between the Sn-*p* (green line) and Al-*p* (maroon line) orbitals, where both states originally resided in the 14 eV regions in SnO_2 w/ V_O and $\alpha\text{-Al}_2\text{O}_3$ w/ V_O . However, due to band bending, the established interface precipitated an energy descent, initiating from 4.0 eV and peaking in the vicinity of 8–9 eV, subsequently becoming predominantly governed by the Al-*p* orbital at elevated energies. The spectral broadening commencing from 4.0 eV appears to be predominantly influenced by the V_O effect emanating from the $\alpha\text{-Al}_2\text{O}_3$ lattice, hinting at a V_O concentration ranging between 1.0–1.4% within the interface. The 1.0% value is extrapolated from the V_O present in the Al₆₄O₉₅ compositional model of the interface. Consequently, the V_O distribution within the interface model predominantly functions as point defects, shedding light on the phenomenon of electron delocalization during the interfacing process. Notably, the 1.0 eV ELF peak is discernible even in the optimized interface model devoid of V_O . In conjunction with the synergistic interplay of Sn-*p* and Al-*p* orbitals, it becomes apparent that the $\text{SnO}_2/\alpha\text{-Al}_2\text{O}_3$ interface plays a pivotal role in attenuating potential energy during the Sn nucleation phase of solidification. This, in turn, accelerates the nucleation rate, culminating in the suppression of supercooling.

Such submicron functional nanoparticles in α -Al₂O₃ crystals are profoundly fascinating, especially since electrons and holes transport in α -Al₂O₃ have been widely studied for applications in silicon devices. Within the purview of this research, the HIB methodology attests the multifaceted applicability of MEPCM, transcending its conventional role in energy storage materials to encompass dynamic nanoscale crystallographic alterations.

CONCLUSION

In summary, the HIB methodology is a streamlined approach to fabricate Sn@ α -Al₂O₃ MEPCM. Given its inherent dry synthesis characteristic, it paves the way for scalable production, aligning with industrial requisites. The MEPCMs registered a 50 J·g⁻¹ latent heat capacity and seamlessly endured 100 melting-solidification cycles. Through the incorporation of a glass frit, the MEPCMs composite was successfully obtained, ensuring thermal durability over 1000 cycles. The α -Al₂O₃ shell, characterized by its structural rigidity, withstood 100 cycles even under the rigors of ultra-fast thermal fluctuations. A notable attenuation in supercooling was discerned throughout the cyclic tests, attributable to the genesis of SnO and SnO₂ nanoparticles within the α -Al₂O₃ crystal. Conventionally, the supercooling dynamics are influenced by the emergence of SnO or SnO₂ crystals as oxide layers. However, the HIB-induced metastable Al-Sn-O surface coupled with lattice anomalies in α -Al₂O₃ facilitated the strategic positioning of Sn seeds within the α -Al₂O₃ matrix, thereby catalyzing the genesis of SnO and SnO₂ nanoparticles. DFT analyses indicate that the formation of the SnO₂/ α -Al₂O₃ interface culminates in a reduced energy threshold, instigating the formation of Sn nuclei during the solidification phase. Consequently, there is an uptick in the Sn nucleation velocity, suppressing supercooling. This investigation illuminates the intricate interplay of nanoscale

crystal lattice imperfections in energy storage materials and paves the way for synthesizing multi-functional energy storage materials with improved properties.

EXPERIMENTAL SECTION

HIB experiment. Microspherical Sn particles ($\phi \approx 38 \mu\text{m}$, 99.95%, Hikari Material Industry Co., Ltd., Japan) obtained from the spinning disk atomization method were used as the PCM. For shelling, Sn and $\alpha\text{-Al}_2\text{O}_3$ particles (99.99%, Kojundo Chemical Lab. Co., Ltd., Japan) were initially pre-mixed in a volume ratio of 8:2. Subsequently, HIB was conducted using a hybridization system (NHS-0, Nara Machinery Co., Ltd., Japan) in an Ar atmosphere. Table S1 provides a detailed summary of the HIB experiment.

Surface observations and chemical analyses. The surface morphology and EDX analyses of the $\text{Sn}@ \alpha\text{-Al}_2\text{O}_3$ MECPM were conducted using field-emission type scanning electron microscopy (FE-SEM, JEOL, JSM-7001FA). Cross-sections of the surface were obtained using a cross-section polisher (JEOL, IB-09010CP). Phase compositions were characterized by powder XRD using a 1D silicon strip detector (Rigaku Miniflex600, D/tex Ultra2) with Cu-K α radiation ($\lambda = 1.5045 \text{ \AA}$). Peak fitting was performed with reference to JCPDS cards 4-0673, 78-3877, 72-1012, and 88-0287 for Sn, $\alpha\text{-Al}_2\text{O}_3$, SnO, and SnO₂, respectively.

Thermal stability test. Latent heat (ΔH) measurements and cyclic stability tests were conducted using a combined TG-DSC analyzer (Mettler Toledo, TGA-DSC-3). Both analyses were performed under an air flow at a rate of $100 \text{ mL} \cdot \text{min}^{-1}$. For the latent heat measurement, 30 mg samples were placed in an Al_2O_3 crucible and subjected to a heating/cooling rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The temperature range was set from 40 to 400 $^\circ\text{C}$. The 100 cycles test was conducted at the same temperature range and a heating/cooling rate of $50 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

Nanostructure characterizations. For STEM imaging, a cross-sectional TEM sample was prepared using 30 kV Ga ions in a FIB milling system (JEOL, JEM-9320FIB). HAADF-STEM imaging, VEELS, and EDX were conducted using a JEM-ARM200F (JEOL) instrument. Both HAADF and EDX analyses were performed at 200 keV. VEEL spectra were acquired at 80 keV in dual-eels mode with a convergence angle of 24.71 mrad and a collection angle of 41.75 mrad. With an energy dispersion of 0.01 eV/channel, the FWHM of the zero-loss peak (ZLP) was 0.45 eV. The SI data were calibrated using the ZLP, and denoising was applied through principal component analyses (HREM Research Inc.). The fitted logarithm tail method was employed for ZLP removal. Subsequently, to obtain the single scattering distribution (SSD), plural-scattering removal was applied using the Fourier-Log function.

First-principles calculations. First-principles calculations were performed based on the density functional theory (DFT) using CASTEP codes³¹ (Academic release, *ver.* 21.11) and employing on-the-fly generated norm-conserving pseudopotentials. The exchange-correlation functional at the generalized gradient approximation (GGA) was described using the Perdew–Burke–Ernzerhof (PBE) functional. The GGA + U method was implemented for bulk SnO, SnO₂, and α -Al₂O₃ calculations, with the parameters summarized in Table S7. The resultant bandgaps for SnO, SnO₂, and α -Al₂O₃ are 0.705, 3.628, and 8.806 eV, respectively (Figure S21), which is consistent with reported bandgaps of these systems.³²⁻³⁴ The calculation of the SnO₂ (110)/ α -Al₂O₃ ($\bar{1}02$) interface was performed on the basis of the HAADF-STEM image (Figure 3g). $2 \times 2 \times 4$ SnO₂ (110) and $1 \times 3 \times 4$ α -Al₂O₃ ($\bar{1}02$) surfaces were cleaved to ensure an iso-stoichiometric SnO₂/ α -Al₂O₃ interface comprising 96 atoms from SnO₂ and 160 atoms from α -Al₂O₃. Both surfaces were aligned with a 15 Å vacuum slab on both ends, yielding an $a = 6.635$ Å, $b = 13.3266$ Å, $c = 56.4809$ Å interface structure. The lattice mismatch was as follows: $\Delta u = 9.82\%$, $\Delta v = 6.83\%$. Following convergence criteria for supercell shown in Table S7, the ionic positions were optimized with a Monkhorst–Pack k-point grid of $4 \times 2 \times 1$. The

density of states and energy-loss function were calculated using a k-point grid of $6 \times 3 \times 1$. The same convergence criteria and k-point grid were applied for calculation of the $\text{SnO}_2/\alpha\text{-Al}_2\text{O}_3$ interface with V_O .

Figures

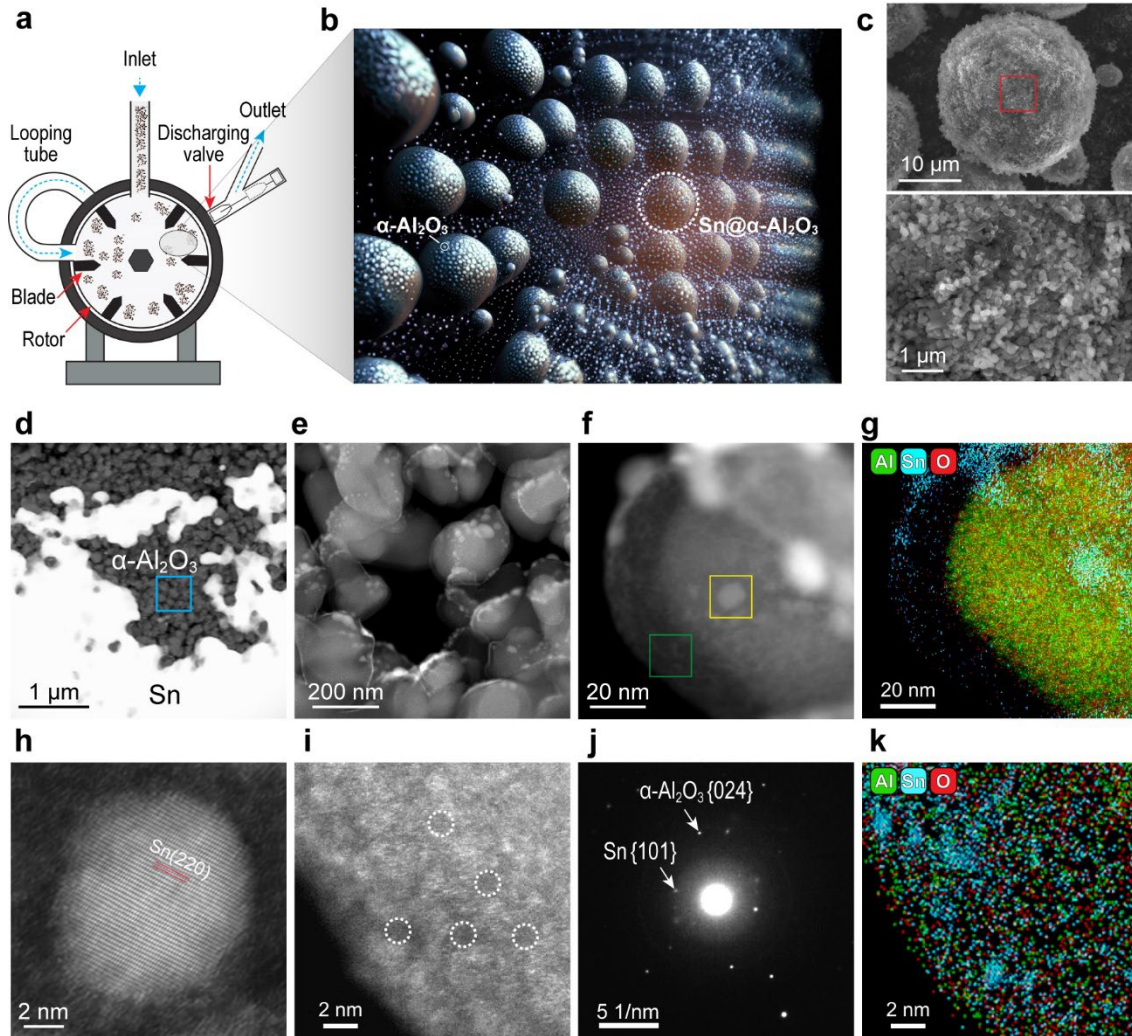


Figure 1. (a) Schematic of the HIB experiment for $\text{Sn}@\alpha\text{-Al}_2\text{O}_3$ MEPCM synthesis. (b) Depiction of MEPCM collision dynamics during HIB. (c) SEM image of a single $\text{Sn}@\alpha\text{-Al}_2\text{O}_3$ MEPCM; the red marker indicates the $\alpha\text{-Al}_2\text{O}_3$ nanoparticles shell (bottom image). (d) HAADF-STEM image of the FIB lamellar section, showing the Sn core and the $\alpha\text{-Al}_2\text{O}_3$ interface. (e) Close-up view of $\alpha\text{-Al}_2\text{O}_3$ nanoparticles from the blue marked region in (d). (f–g) Single $\alpha\text{-Al}_2\text{O}_3$ nanoparticle and its corresponding overlay STEM-EDX (Al K α , Sn L α , O K α) map. (h) Atomic resolution HAADF image of a localized Sn ($d_{220} = 2.07$ Å) nanoparticle,

taken from the yellow marked area. (i) HAADF image of metastable Sn-Al-O surface, taken from green marked region; white circles denote nanopores. (j) TEM SAED pattern of the metastable Sn-Al-O surface. (k) Overlay STEM-EDX (Al $K\alpha$, Sn $L\alpha$, O $K\alpha$) map of (i).

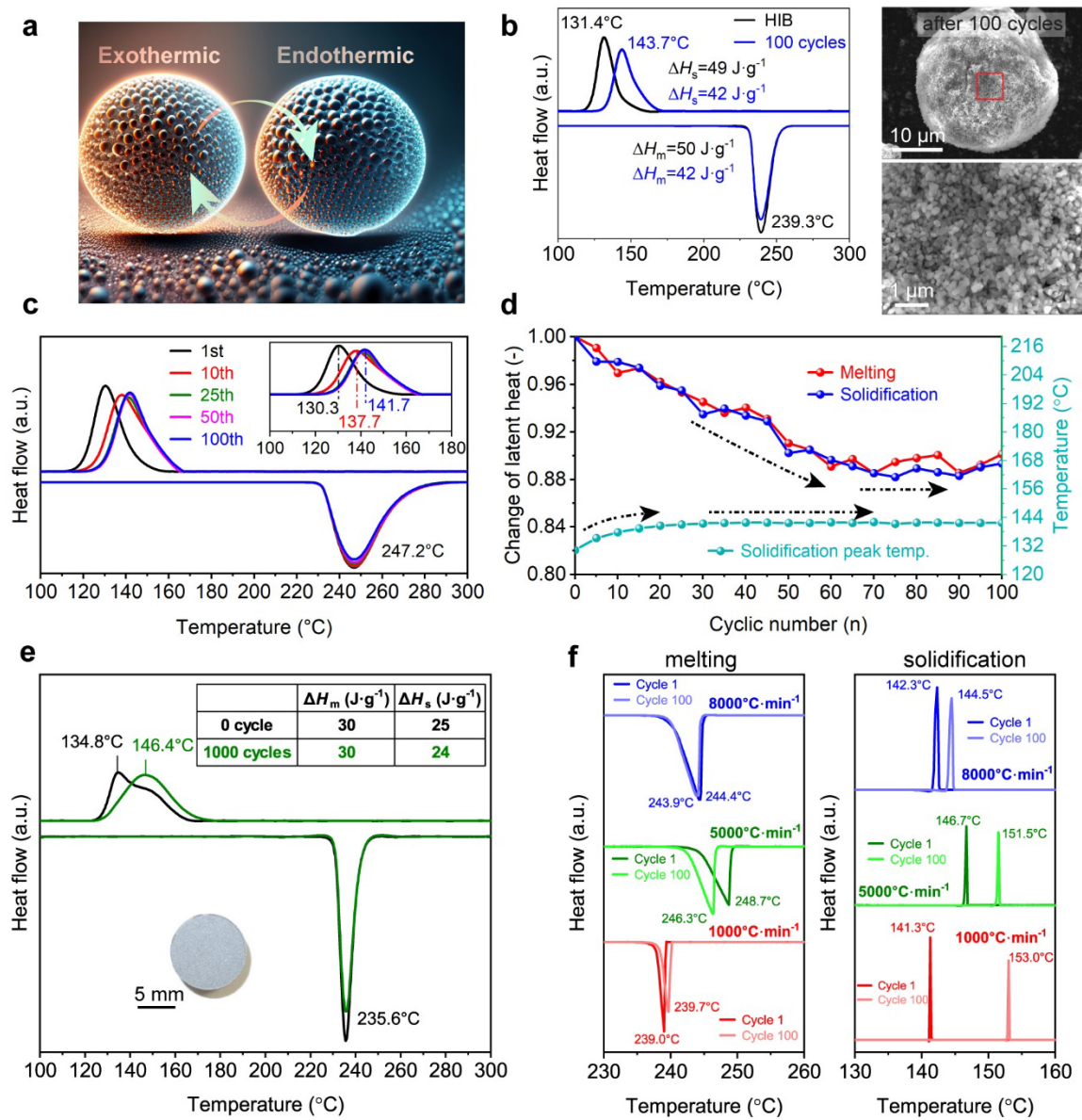


Figure 2. (a) Illustration of the thermal cycle of the MEPCM through endothermic and exothermic phases. (b) DSC curves of the Sn@ α -Al₂O₃ MEPCMs post-HIB and after 100 cycles in an air atmosphere. (ΔH_m : melting latent heat; ΔH_s : solidification latent heat). (c) DSC history over 100 cycles; the inset highlights solidification peak shifts. (d) Latent heat changes for melting and solidification every 5 cycles and the solidification peak temperature. (e) DSC curves of the Sn@ α -Al₂O₃ MEPCMs composite before and after 1000 cycles in air; the inset

shows the composite sintered with an ASF-1100 glass frit. (f) DSC curves of a single Sn@ α - Al_2O_3 MEPCM before and after the 100 cycles test under ultra-fast heating/cooling rates of 1000, 5000, and 8000 $^\circ\text{C}\cdot\text{min}^{-1}$ in air.

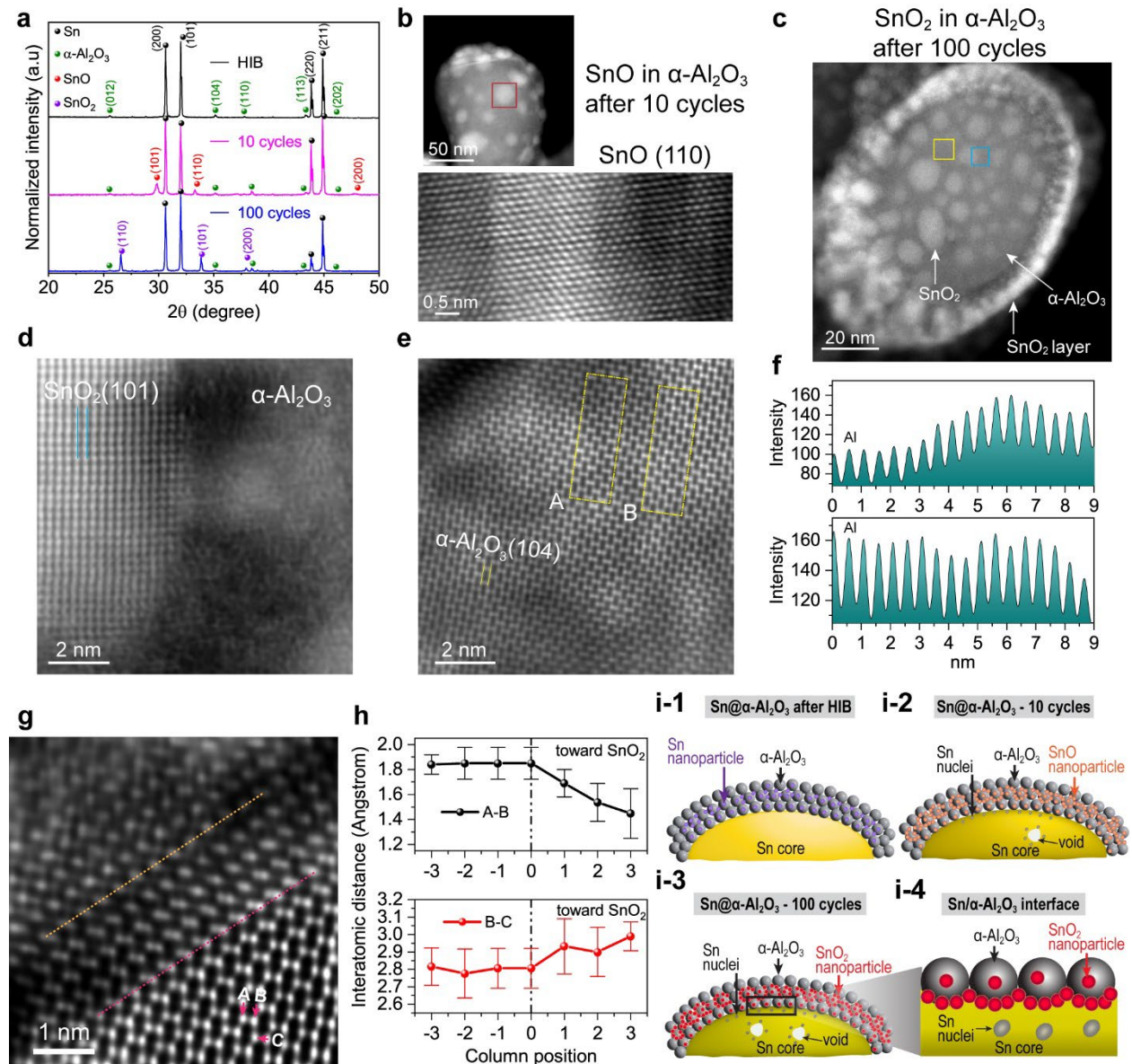


Figure 3. (a) XRD patterns of MEPCMs post-HIB after 10 and 100 cycles. (b–c) Cross-sectional HAADF-STEM images of α - Al_2O_3 after 10 and 100 cycles, respectively. The bottom of (b) is the SnO (110) ($d_{110} = 2.93$ Å) lattice from the red marked area. (d) SnO₂ (101) ($d_{101} = 2.74$ Å) lattice on α - Al_2O_3 from the blue marked area in (c). (e) α - Al_2O_3 (104) ($d_{104} = 2.55$ Å) lattice from the yellow marked area in (c). (f) Al-O intensity profiles from A and B areas in (e); peaks and troughs correspond to Al and O atoms, respectively. (g) HAADF-STEM of SnO₂

(110, $d = 3.51 \text{ \AA}$)/ $\alpha\text{-Al}_2\text{O}_3$ ($\bar{1}02$, $d = 3.71 \text{ \AA}$) interface at the $\alpha\text{-Al}_2\text{O}_3$ surface. The pink dotted line denotes the boundary between non-delocalized and delocalized $\alpha\text{-Al}_2\text{O}_3$; the orange line marks the SnO_2 interfacing region. The A-B notion indicates Al atoms belonging to the (104) plane, while B-C is the Al atoms sequence in the ($\bar{1}02$) plane. (h) A-B and B-C interatomic distances in each three columns before and after the pink boundary line, respectively. Error bars correspond to the standard deviation. (i) Schematics of (i-1) localized Sn nanoparticles in $\alpha\text{-Al}_2\text{O}_3$ post-HIB, (i-2) SnO formation during 10th cycle's solidification, (i-3) SnO_2 formation during solidification from the 10th to 100th cycle, and (i-4) final SnO_2 population at the Sn/ $\alpha\text{-Al}_2\text{O}_3$ interface.

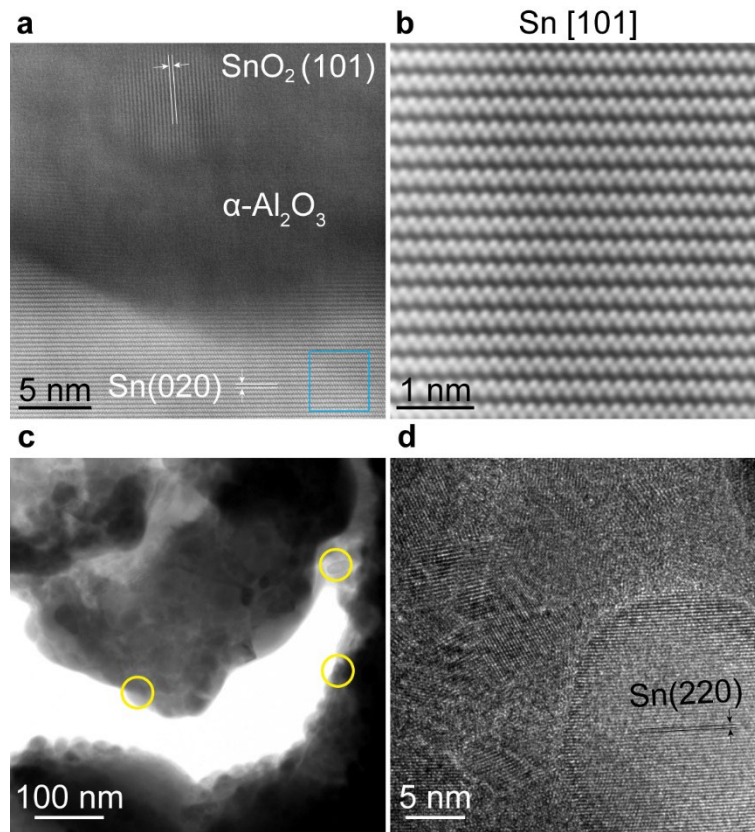


Figure 4. (a) HAADF-STEM image of the Sn core/ $\alpha\text{-Al}_2\text{O}_3$ interface, showing the SnO_2 (101) ($d_{101} = 2.67 \text{ \AA}$) lattice on $\alpha\text{-Al}_2\text{O}_3$. (b) Sn (020) ($d_{020} = 3.02 \text{ \AA}$) HAADF-STEM from blue-marked area in (a) along the Sn [101] direction. (c) TEM image of voids in the Sn core after 100 cycles. (d) HRTEM image of Sn(220) lattice.

100 cycles. Yellow markers indicate the Sn nuclei. (d) HR-TEM image of the Sn nuclei, displaying the Sn (220) ($d_{220} = 2.09 \text{ \AA}$) lattice.

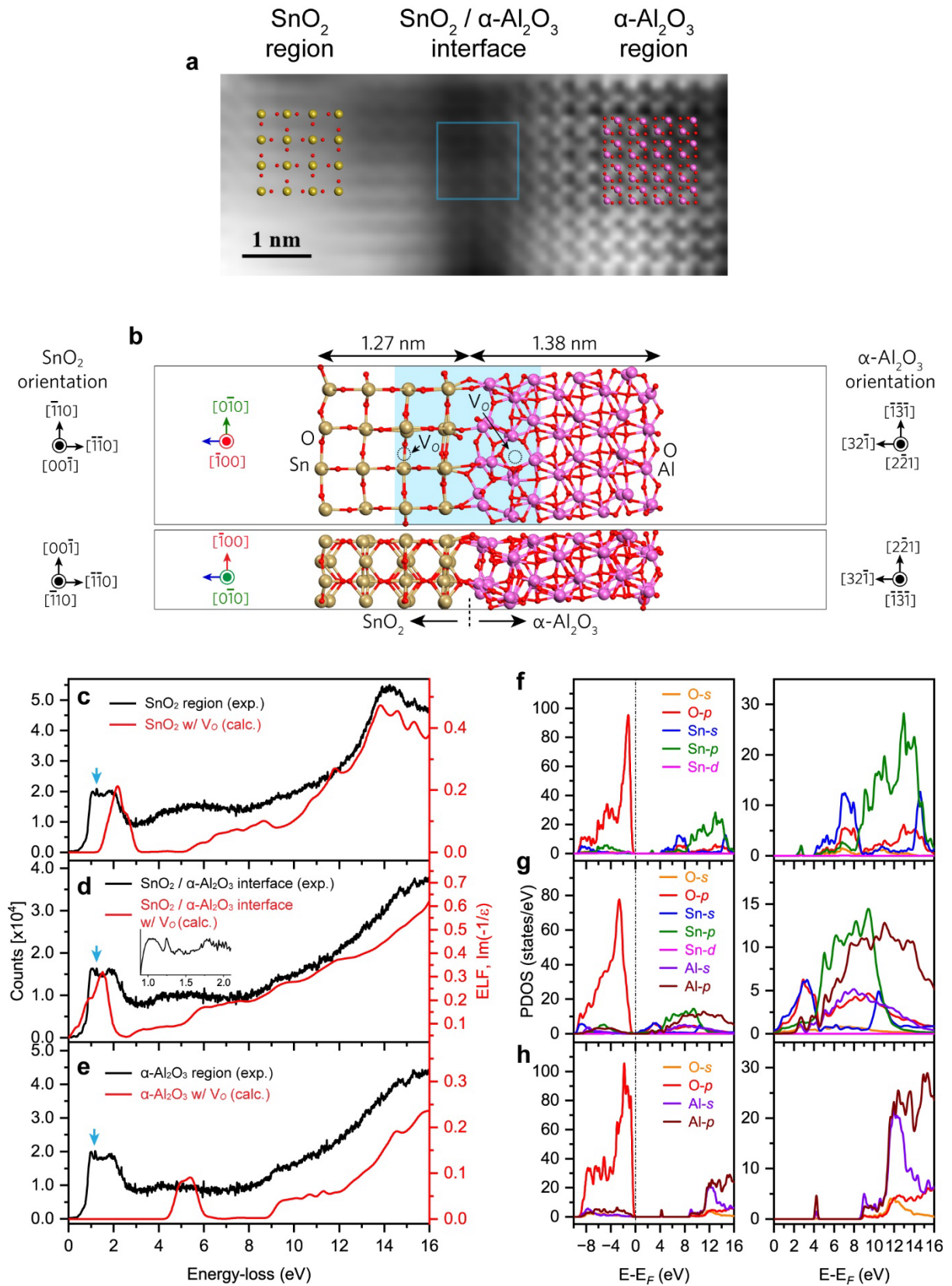


Figure 5. (a) ADF from STEM-VEELS map of the interface with VEEL spectra averaged over the SnO₂, interface, and α -Al₂O₃ regions, indicated by overlaid markers. (b) Optimized SnO₂ (110)/ α -Al₂O₃ ($\bar{1}02$) w/ V_O interface structure; top and bottom panels show the interface's $[\bar{1}00]$ and $[0\bar{1}0]$ view, respectively. Blue marked region is the targeted atoms for the PDOS plot. (c–e) STEM-VEELS experimental results vs. calculated (010) polarized ELF and PDOS for the SnO₂ region, SnO₂/ α -Al₂O₃ interface, and α -Al₂O₃ region, respectively. Left: SSD of the EEL spectra vs. calculated ELF with blue arrow pointing to the interfacing peak (magnified in the inset). (f–h) Calculated PDOS for SnO₂ w/ V_O, SnO₂/ α -Al₂O₃ interface w/ V_O, and α -Al₂O₃ w/ V_O. Right panels: Enlarged views of the PDOS plots.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/#####>

Additional summary of HIB experiment; Overview and cross-sectional SEM, S/TEM, EDX mapping analyses of the MEPCMs; STEM-EELS data on the cross-sectional α -Al₂O₃ nanoparticles; DSC curve of the pure Sn before HIB; DSC and TG profiles following heat oxidation treatment; Details of MEPCMs composite making; Additional Flash-DSC experimental results; HRTEM image of the Sn nuclei particle; Details of DFT calculations; Summary of Rietveld analyses; GGA + *U* calculated band structure (PDF)

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Notes

The authors declare no conflict of interest.

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