Al-Microcapsules with a Self-Sacrificial Oxidation Method for High-Temperature Thermal Energy Storage

Sisi Tian, Yu Jiang, Yan Si, Bo Guan, Qian Wang,* and Tong Zhao

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ABSTRACT: Traditional high-temperature energy utilization systems employ conventional solid sensible heat storage (SHS) for energy storage. Latent heat storage (LHS) serves as a surrogate for energy storage as opposed to the SHS system due to the presence of phase-change materials (PCMs). In this paper, we report the production and characterization of Al microencapsulated PCM (MEPCM) through a simple one-step self-sacrificial oxidation fabrication process, where the core−shell type microencapsulated with Al microsphere (mean diameter 35 μm, melting temperature 669 °C) acted as the core (PCM) and Al_2O_3 as the shell. During the oxidation process, the surface layer of the Al microparticle was sacrificed to form a stable Al_2O_3 shell, which was only about 50 nm thick presented by means of a focused ion beam (FIB). In terms of the analyses of FIB and X-ray photoelectron spectroscopy (XPS), it is apparent that Al_2O_3 is successfully formed on the surface of Al microparticles, which can keep a stable solid shell structure during solid−liquid phase transitions. The latent heat of MEPCM was 310.4 kJ/kg, and the melting temperature was 668 °C. Thus, the one-step self-sacrificial heat-oxidation technique can lead to better commercialization and environmental friendliness of next-generation LHS-based high-temperature thermal energy storage materials.
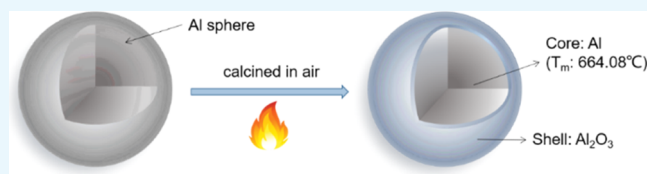
1. INTRODUCTION

In the field of renewable energy utilization, the development of integrated high-temperature thermal energy storage systems
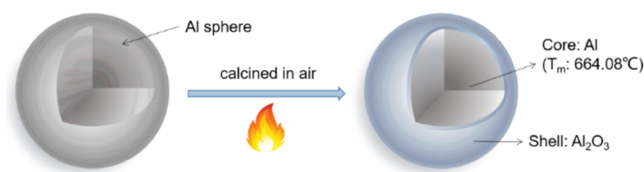

Figure 1. Illustration of Al MEPCM with the self-sacrificial oxidation method.

with high working temperatures has become a key requirement for the cost-effective generation of renewable energy utilization.[1] Thermal energy storage technology has attracted interest because it can provide a buffer against the temporal and spatial mismatches between the energy supply and demand processes. Sensible heat storage, latent heat storage, and chemical latent heat are the primary ways of thermal energy storage. Most basic heat utilization technologies for high temperature are only available in sensible heat storage (SHS), such as rocks, metal, concrete, and oxide ceramics.[2,3] However, the conventional solid SHS storage method has insufficient heat storage capacity and insufficient transfer and recycling of heat.[4−6]

Latent heat storage (LHS) has been considered an advantageous alternative to SHS as a thermal energy storage system. LHS is based on the storage or release of latent heat when a phase-change material (PCM) undergoes a phase transition, which provides 5−14 times more heat per unit compared to SHS. Additionally, LHS can be a constant heat source, and the reversible phase-change process makes PCM a reusable source.[7] Molten salts such as chloride,[8,9] sulfate,[10] fluoride,[11,12] and carbonate,[13] which have melting temperatures (T_m) over 500 °C, have been considered PCM candidates for high-temperature applications. Yet, poor thermal stability, high corrosion rate, and low thermal conductivity restrict functional applications of molten salt. Metals and alloys (i.e., aluminum (Al), copper (Cu)) have been explored as high-temperature PCMs due to the better stability and higher heat storage capacity.[7]

It has been reported that the development of micro-encapsulated PCMs (MEPCMs) can retain both the mature technologies of SHS and the high thermal capacity of LHS. The shells of MEPCMs can prevent leakage of liquid PCM
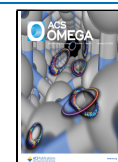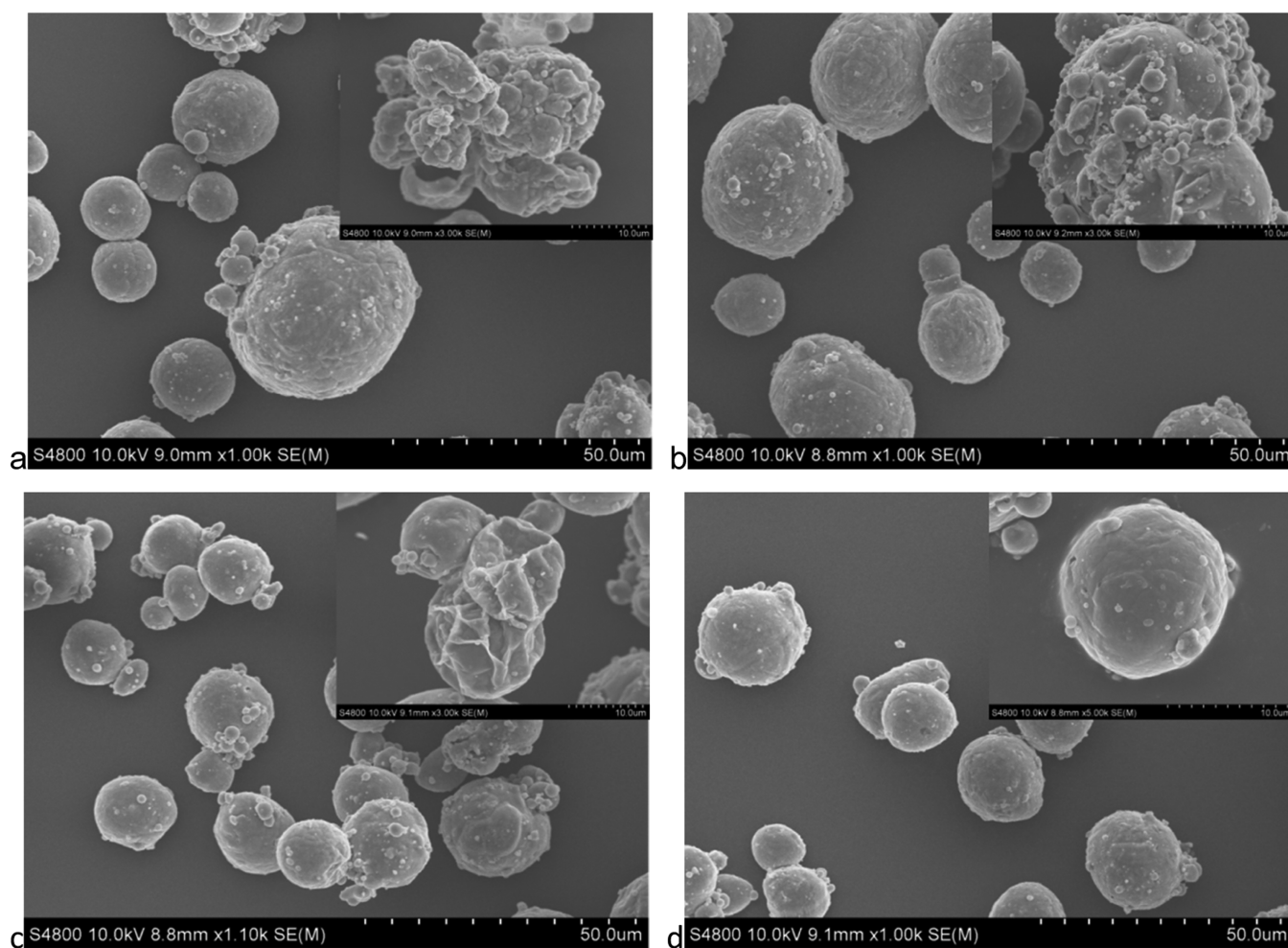
Figure 2. Scanning electron microscopy images of raw Al and MEPCM after heating at 700 °C in an argon atmosphere. (a) Raw aluminum powder and calcined at 700 °C (inset figure); (b) MEPCM prepared at 400 °C for 20 h and calcined at 700 °C (inset figure); (c) MEPCM prepared at 500 °C for 20 min and calcined at 700 °C (inset figure); and (d) MEPCM prepared at 500 °C for 30 min and calcined at 700 °C (inset figure).

during the solid−liquid phase transformation, which means that all of the basic SHS technologies with various structures can be retained in the new LHS system by substituting the SHS material with the MEPCMs.[7,14] Many high-temperature MEPCMs have been synthesized. The Al−Si alloy MEPCM was prepared in two steps consisting of boehmite coating and heat-oxidation treatment at 105 °C overnight.[15] The Al−Si alloy MEPCM was also synthesized by the sol−gel process with the help of a silane coupling agent followed by treatment at 120 °C for 24 hours.[16] NaNO$_3$ MEPCMs were obtained by coating the NaNO$_3$ particles with perhydropolysiazane (PHPS) and then heated in a muffle furnace at 350 °C for 1 h in an air atmosphere.[17] Previous research reported an Al MEPCM prepared by a three-step process: removing surface-dense Al$_2$O$_3$, modifying with Ni, and calcining at 400−800 °C after being dried at 110 °C for 24 h.[18] Also, an Al/Al$_2$O$_3$ MEPCM prepared by the three-step boehmite-precipitation treatment process with Al(OH)$_3$ was reported.[19] Yet, these processes showed limitations such as a lower heat capacity and a complicated manufacturing process. All of the above MEPCMs were synthesized with two or more steps involving the solvent process and heat treatment.

In this study, we propose a one-step self-sacrificial heat-oxidation technique to form a core−shell type Al MEPCM, in which no chemical solvent is involved and no chemical waste is formed. The facile one-step microencapsulation method is used via a simple heat-oxidation treatment of the PCM in an air atmosphere to oxidize out-layer Al to a stable Al$_2$O$_3$ outer shell (Figure 1). Once a dense Al$_2$O$_3$ shell coating forms on the surface of the Al microsphere, the inner Al will be isolated from air and will not be oxidized. The stable shell can prevent the leakage of the Al MEPCM when the inner Al core melts. The morphology of the MEPCM and the thickness of the shell along with the stability of the Al$_2$O$_3$ shell outside the Al particles were discerned. The Al$_2$O$_3$ shell was only about 50 nm, which is quite thinner than the reported MEPCMs', such as the 3−5 μm shell of Al-Si/Al$_2$O$_3$[16] and the 6−8 μm shell of Al/Al$_2$O$_3$.[18] In addition, the one-step heat-oxidation method is an advantageous process due to its lower cost, environmentally friendly nature, and facile construction for large-scale industrial production.

2. MATERIAL AND METHODS

2.1. Material. Microsphere particles of Al with a mean diameter of 35 μm (purity: 99.0%, Hikari Material Industry Co., Ltd.) were used as raw materials and PCMs.

2.2. Methods. MEPCM was prepared using a simple one-step heat-oxidation treatment. Briefly, the dried Al microspheres were directly subjected to heat-oxidation treatment in a tube furnace. The samples were heated from room

temperature to 300, 400, and 500 °C at the rate of 5 °C/min in an air atmosphere and kept for a period of time. Afterward, the MEPCMs were cooled down to room temperature.

2.3. Characterization of MEPCM. To verify the chemical structure and study the composition of the prepared MEPCM, the following techniques and methods were used. The surface morphology of the MEPCM was observed after coating with gold with the help of scanning electron microscopy (S-4800, Hitachi, Japan) at an accelerated voltage of 20 kV. The sample was subjected to a micron lamellar specimen using a focused ion beam (FIB) (Helios Nanolab G3 CX, FEI), and the element mapping was analyzed by an energy-dispersive spectrometer (EDS). The composition of the MEPCM was analyzed by Fourier transform infrared (FT-IR) spectra. In a typical procedure, samples were mixed with KBr to make pellets. FT-IR spectra in the absorbance mode were recorded using an FT-IR spectrometer (TENSOR 27, Bruch GmbH, Germany). The thermal stability of the MEPCM was studied using a thermal gravimetric analyzer (STA 409 PC, NETZSCH Group, Germany) in the temperature range from 20 to 800 °C under air at a flow rate of 20 mL/min and at a heating rate of 10 °C/min. The thermodynamic properties (phase-change and heat storage capacity) of MEPCM were investigated by the differential scanning calorimeter instrument (DSC, Mettler-Toledo, TGA/DSC 1) at a heating or cooling rate of 10 °C/min in a flow of argon. X-ray photoelectron spectroscopy (XPS, ESCALAB250XI, Thermo Fisher Scientific) was used to measure the binding energy of the Al and O atoms.

3. RESULTS AND DISCUSSION

Aluminum, the most abundant metal element in the earth's crust with a melting temperature of 660 °C, is an ideal PCM
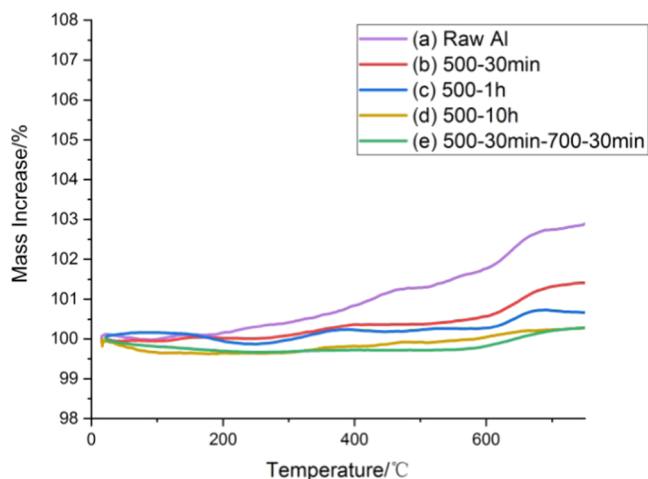

Figure 3. Thermogravimetric analysis. Al raw material (a) and the samples obtained by calcining it at 500 °C for 30 min (b), 1 h (c), and 10 h (d) in an air atmosphere. Sample obtained by calcining it at 500 °C for 30 min with further calcination at 700 °C for 30 min in an air atmosphere (e).

candidate material, but it has not been widely used due to its flammable property and difficulty in capsulation. In this work, Al MEPCM was prepared by oxidation of the raw Al particles under an air atmosphere. During the oxidation process, the surface layer of the Al microparticle was sacrificed to form a stable Al_2O_3 shell. In the experiment, raw aluminum particles with a mean diameter of 35 μm (Figure 2a) were oxidized in
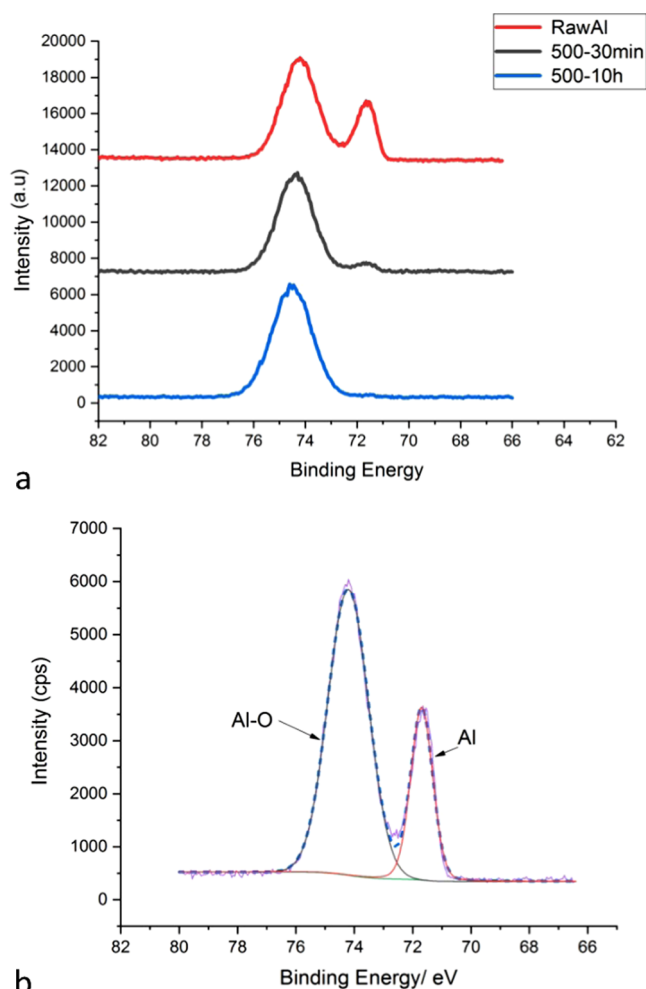

Figure 4. (a) XPS spectra in the Al 2p region for the Al raw material and calcining at 500 °C for 30 min. (b) Deconvoluted Al 2p spectra of raw Al obtained showing the XPS data.

an air atmosphere at 300, 400, and 500 °C for different times. Then, the as-prepared MEPCM and raw aluminum particles were calcinated at 700 °C in a tube furnace under an argon atmosphere separately. The raw aluminum particles were melted after being heated at 700 °C, which was higher than the fusion point of 660 °C. The raw aluminum particles agglomerated into a cube after being cooled down to room temperature. The phase-change materials that leak from the microcapsules can stick the MEPCM together; thus, whether the MEPCM can bear the heat treatment over its fusion point can be used to testify the stability of the MEPCM's core–shell structure. The samples oxidized at 300 and 400 °C for 1–20 h were all agglomerated after being calcinated at 700 °C under an argon atmosphere. The MEPCM samples oxidized at 500 °C for 10 and 20 min were agglomerated slightly. On the contrary, the MEPCM samples oxidized at 500 °C for 30 min to 20 h were still in a powder form after being calcinated at 700 °C under an argon atmosphere. The result shows that the MEPCM samples oxidized at 500 °C for longer than 30 min can bear the calcination at 700 °C. Thus, the shortest oxidation time for 500 °C was confirmed to be 30 min.

The microstructure of the MEPCM was investigated. The surface morphology and the size of the particles were the same as before (Figure 2a) and after being oxidized (Figure 2b–d). However, after being calcinated at 700 °C in an argon
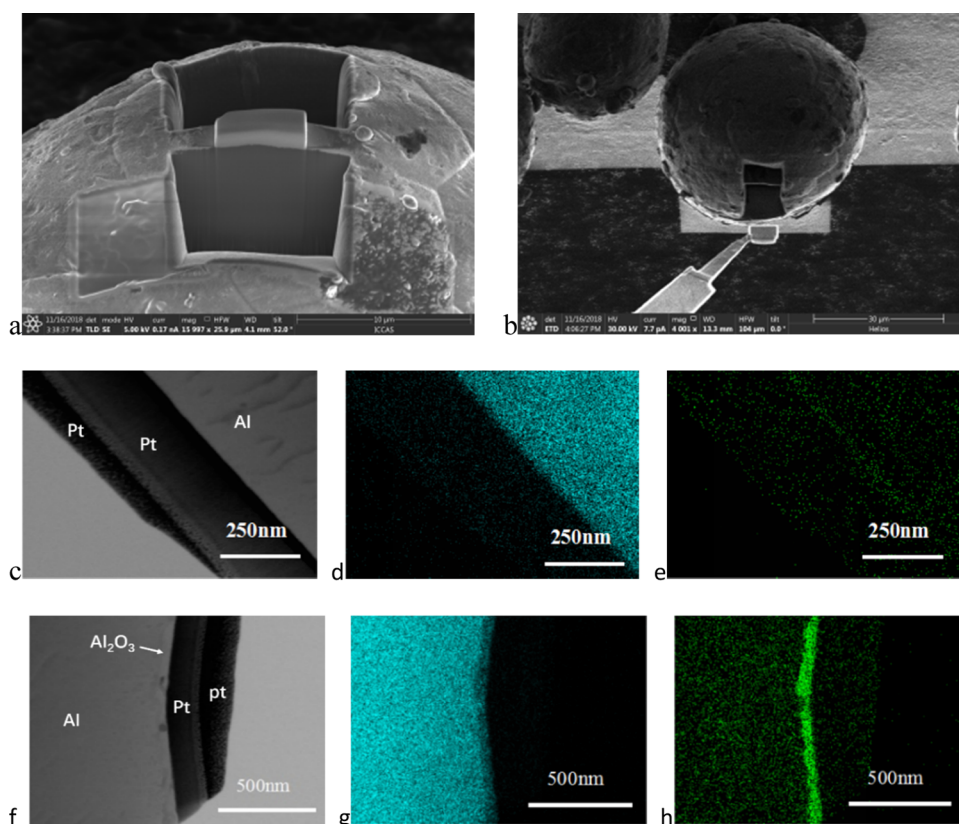
Figure 5. SEM images of steps in the process of FIB extracting and transferring a lamella from the particles to a Cu TEM grid (a, b). EDS analysis of the slice of raw aluminum powder (c) scanning area; (d) Al mapping; (e) O mapping. EDS analysis of sections of a 500 °C calcined 10 h sample (f) scanning area; (g) Al mapping; (h) O mapping.

atmosphere, the samples oxidized at 300 and 400 °C could not keep the sphere figure. Some particles were destroyed, and most particles were stuck together (Figure 2a−c). Compared with the MEPCM samples oxidized at 400 °C for 20 h (Figure 2b) and at 500 °C for 20 min (Figure 2c), the samples treated over 30 min can keep the spherical shape after being calcined at 700 °C (Figure 2d). Rough and lumpy surfaces of MEPCM remain consistent with raw particles, and no liquid PCM leakage was observed. All of the microstructures were consistent with the macroscopic phenomenon, which implied the successful formation of encapsulated PCM with a dense and stable shell.

Then, the as-prepared MEPCM particles were further analyzed by thermogravimetry under an air atmosphere by heating from room temperature to 750 °C at a heating rate of 10 °C/min (Figure 3). Figure 3a shows the rapidly increased mass gain of the raw material (Al microsphere) around 600 °C. Compared to the raw material, the MEPCM prepared at 500 °C for longer than 30 min presented a better thermal stability (Figure 3b−d). The MEPCM prepared at 500 °C for 10 h showed nearly no weight gain (Figure 3d). The slight mass gain of the MEPCM prepared at 500 °C for 30 min (Figure 3b) could be explained by the lower density of the Al_2O_3 shell compared to the MEPCM prepared at 500 °C for 10 h. However, the shell was dense enough to bear the phase change of Al (Figure 2d). Furthermore, the sample obtained by calcining at 500 °C for 30 min was then calcined at 700 °C for another 30 min in air (Figure 3e). Neither leakage nor weight gain was observed in the sample, which indicated that the Al

inner core of the MEPCM was protected by a compact alumina shell.

Surface chemical characterization was performed by XPS. Figure 4 shows the Al 2p XPS spectra of the raw Al microsphere and the MEPCMs prepared at 500 °C for 30 min. The Al 2p band of the raw Al microsphere showed a peak located at 74.20 eV and a peak located at 71.69 eV, which corresponds to the Al−O form and the Al metal form, respectively.[20,21] This result illustrated that the surface of the raw Al particle can be slightly oxidized in an ambient temperature. However, the raw Al particle can be melted when heated to 700 °C. A slight Al metal form peak intensity was detected in the MEPCM prepared at 500 °C for 30 min, which indicated that the Al_2O_3 on the MEPCM surface was not dense enough. Consistent with the thermogravimetric analysis (Figure 3b), the MEPCM prepared at 500 °C for 30 min had a visible weight gain as the temperature increased. As shown in Figure 4, the Al 2p band of the MEPCM prepared at 500 °C for 10 h showed higher intensity peaks of the Al−O form than raw aluminum powder, and no Al was detected, hence indicating that the compact Al_2O_3 shell was formed, which was consistent with the TGA curve (Figure 3d).

To express the thickness of the A_2O_3 shell, FIB was used to extract a lamellar specimen from the MEPCM particle prepared at 500 °C for 30 min and a raw aluminum particle separately. The elemental mapping of Al and O (oxygen) of the specimen was analyzed by EDS equipped on the transmission electron microscope (Figure 5). The Al element uniformly distributed in the raw aluminum specimen (Figure 5d). Some oxygen was detected on the surface of the particle
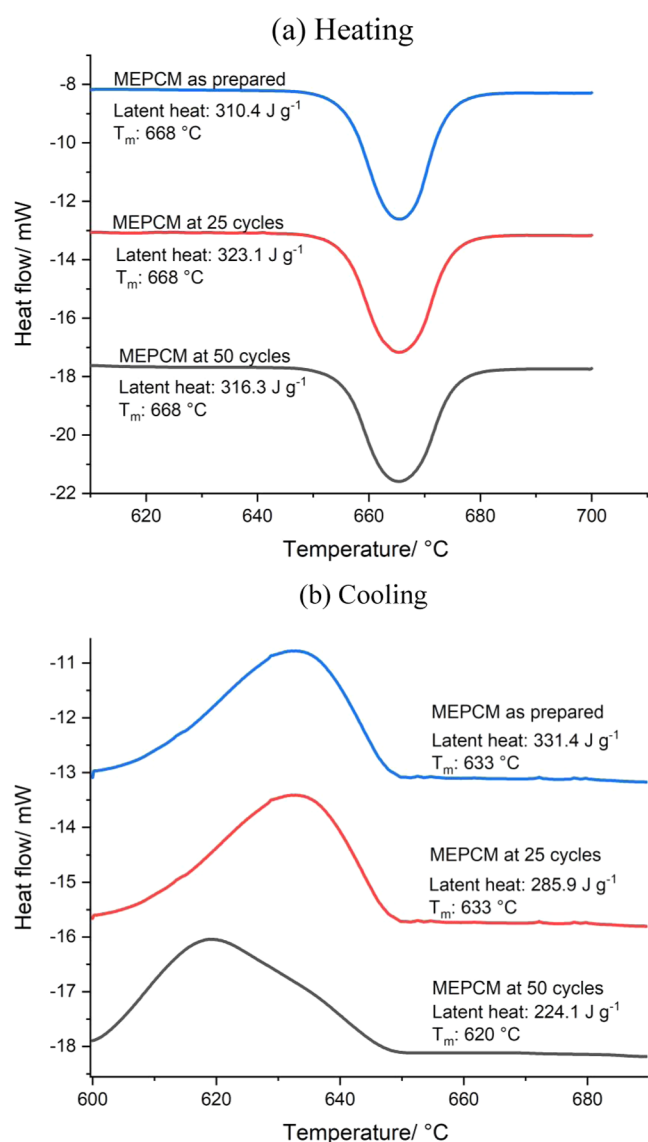
Figure 6. (a) Heating and (b) cooling DSC result of the Al MEPCM as prepared and obtained at 25 and 50 cycles of repeated melting and freezing (argon atmosphere, 10 °C/min).

Table 1. Latent Heat and Melting Point of the Al MEPCM and Raw Al in the 50 Cycles

		cycle 1	cycle 10	cycle 25	cycle 40	cycle 50
Al MEPCM	latent heat (J/g)	310.4	316.4	323.1	322.9	316.3
	melting point (°C)	668	668	668	668	668
	freezing point (°C)	633	633	633	623	620
raw Al	latent heat (J/g)	317.1	327.2	324.4	325.8	320.3
	melting point (°C)	669	669	669	669	669
	freezing point (°C)	645	646	646	646	646
latent heat retention rate		97.9	96.7	99.6	99.1	98.8

(Figure 5e) because the surface layer of the raw aluminum can be slightly oxidized in an ambient environment. The MEPCM specimen (Figure 5h) clearly showed an O element layer of

about 50 nm in thickness, and the Al element in this 50 nm thick layer was darker than the inner part (Figure 5g). Thus, the outer surface layer of the MEPCM can be recognized as alumina. For a particle with a 10 μm diameter, the outer layer of 50 nm thickness accounts for only 1.49% of the volume. Thus, the thin layer of the alumina shell can retain a very high latent heat of the MEPCM.

The latent heat storage capacities of the MEPCM and raw Al were evaluated by means of DSC (Figure 6, Table 1). The melting points of Al and Al MEPCM were 669 and 668 °C, respectively (Table 1). The freezing points of Al and Al MEPCM were 645 and 633 °C, respectively (Table 1). The alumina shell with good conductivity can transfer heat from the external of the MEPCM to the internal Al core quickly. The latent heat values of Al and Al MEPCM were 317.1 and 310.4 J/g, respectively (Table 1). This latent heat retention rate was 97.9%, which was much higher than the previously reported Al−Si alloy and Al MEPCM results. This was due to the thin shell of the produced Al MEPCM, and no byproduct was generated during the process. The latent heat and latent heat retention rate of the MEPCM were consistently stable in the 50 heating cycles (Figure 6, Table 1) although the freezing point decreased slightly in the 50 cooling cycles.

4. CONCLUSIONS

In summary, this paper proposed a facile method to synthesize Al MEPCM with a higher melting temperature and a latent heat retention rate. The MEPCM consisted of an Al core (PCM) and an alumina shell gained by a one-step heat-oxidation method. The alumina shell was synthesized by sacrificing the outer layer of the raw Al particle into a thin alumina layer. The alumina was in situ formed without any additive solvent, and this 50 nm thick layer was robust enough to bear the leakage of the melted Al. This thin layer retained a very high latent heat retention rate, which was higher than 95%. The one-step self-sacrificial heat-oxidation technique can lead to better commercialization and environmental friend-liness of next-generation high-temperature thermal energy storage materials.

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Notes
The authors declare no competing financial interest.

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