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Article

Change phase materials: Wax Paraffin encapsulated in SiO_2 and SiO_2-Fe_3O_4

Materiales de cambio de fase: Parafina encapsulada en SiO_2 y SiO_2-Fe_3O_4

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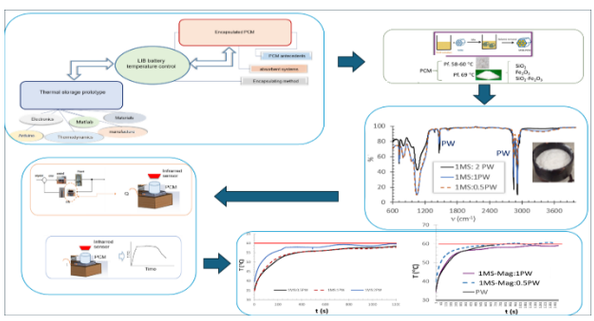
Abstract

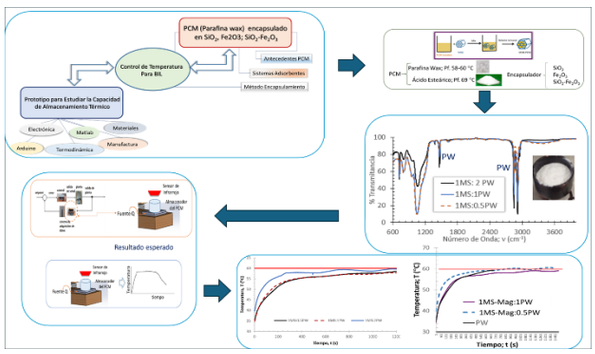
Energy storage has become an essential aspect of modern energy processes, with a particular focus on enhancing the performance of thermal devices such as lithium batteries, which are widely regarded as a key technology in the transition to electric vehicles. In instances where the placement of heat removal systems is necessary to prevent the device from heating up, this paper study the storage capacity of a bioorganic phase-change material (PCM) encapsulated in silica nanoparticles. This PCM is obtained from sodium silicate (MS) and its modification with magnetite (MS-Fe_3O_4). The PCM was integrated into the silica matrix through impregnation, and infrared spectroscopy demonstrated the presence of its primary functional groups. Furthermore, thermal characterization curves were obtained, indicating a significant impact on the temperature holding time when the PCM was absorbed into the silica matrix modified with magnetite.



PCM; SiO_2; SiO_2/Fe_3O_4; energy

Resumen

El almacenamiento de energía es vital para mejorar diferentes procesos energéticos entre los cuales se encuentran la mejora de dispositivos térmicos como son las pilas de litio empleadas en los autos eléctricos. Donde se requiere colocar sistemas removedores de calor para evitar el calentamiento del dispositivo, es por ello que en este proyecto se propone estudiar la capacidad de almacenamiento de un PCM bio-orgánico encapsulado en nanopartículas de sílice, obtenidas a partir de silicato de sodio (MS) y su modificación con magnetita (MS–Fe_3O_4). El PCM se integró a la sílice por impregnación y la espectroscopia de infrarrojo indicó la presencia de los principales grupos funcionales de éste; por otra parte, se obtuvieron las curvas de caracterización térmica observando un efecto en el tiempo de sostenimiento de temperatura cuando se absorbe el PCM en la sílice modificada con la magnetita.



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Introduction

Lithium batteries have transformed numerous industries, including consumer electronics and electric vehicles, due to their high energy density and rechargeability. However, they are subject to several challenges, with temperature rise being one of the most significant. When a lithium battery is overheated, it may experience several adverse effects that compromise its performance and safety. One of the most serious consequences is the accelerated deterioration of internal components, including electrolytes and electrodes. This can result in a reduction in storage capacity and an overall decrease in battery lifespan, Oró (2012), Villasmil (2019), Mohammadian (2017), Rao (2011), Jeon (2011).

As illustrated in Figure 1, the lithium-ion battery (LIB) is constructed according to the configuration of an electrochemical cell, comprising a cathode and anode separated to prevent a short circuit. The cathode (positive charge) is composed of lithium oxide (Li_2O) and varying quantities of transition metals (specifically, nickel, Ni; magnesium, Mg; and cobalt, Co). In contrast, the anode (negative charge) is formed of graphite. The transfer of electrons occurs from the anode to the cathode.

The anode is connected to the cathode via an electrolyte medium, which facilitates the transfer of charge carriers, namely Li^+ ions, dissolved in an aprotic medium, such as diethyl carbonate or conductive polymers, including polyvinylidene fluoride (PVDF) and polyvinyl fluoride (PVP).

Box 1

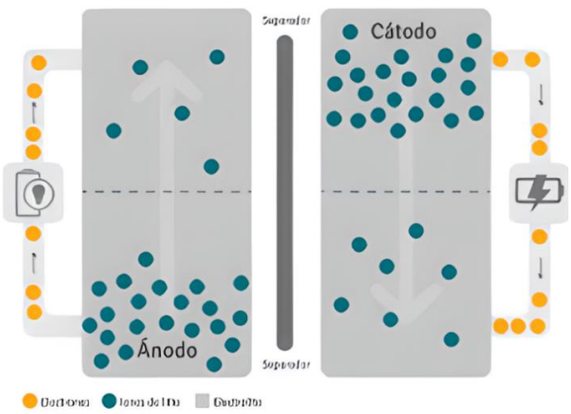

Figure 1
Operation of a lithium-ion battery (LIB)

The flow of electrons from the anode to the cathode is responsible for producing the battery voltage. The movement of Li^+ ions through the electrodes maintains equilibrium between the external current and the system, ensuring that the positive charge of the Li^+ ions does not neutralize the external charge (Mohammadian 2017).

One of the limitations of this energy storage system is the generation of heat during the charging and discharging cycle of the LIB, which, if not adequately managed, can cause damage to some components within a relatively short time frame. Furthermore, if the temperature rises to the point of melting the lithium (180°C), the metal will be subject to an exothermic reaction and will explode. Such temperatures can be reached in high-voltage storage systems. This requires the implementation of temperature regulation systems (60-85°C) (Rao 2011), such as phase change materials (PCM), which possess a high latent heat (melting or boiling) or sensible heat and are used as thermal energy storage (Jeon 2011).

Therefore, these materials have been using as prospective new energy storage systems, specifically in the context of thermal energy storage (TES). Figure 2 shows the storage principle, which involves the absorption of energy by the material, followed by its release upon a change in temperature.

This release may occur as latent or sensible heat. The storage of energy using sensible heat ($Q=Cp\Delta T$) requires that the material possess a high Cp value. The quantity of energy that can be stored is dependent upon the temperature differential (ΔT) to which the PCM is subjected.

Therefore, the temperature of both the storage and the energy release are not constant. However, storage through latent heat (phase change) occurs at the temperature at which the phase change of matter (solid-liquid; solid-gas; liquid-gas; liquid-gas) is generated, which occurs at a constant temperature or in a very limited temperature range for all materials (Jeon 2011, Hussain 2016).

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Box 2

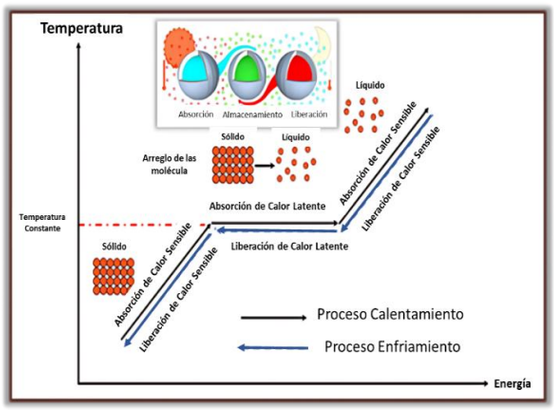

Figure 2

Operation of PCM as an energy storage device [5,6]

Consequently, the aim of this project is to investigate the potential of kerosene wax as a temperature controller for a LIB (Figure 3). The aim is to determine the ability to control the temperature of the system at 60°C. To improve the stability of the PCM, it is encapsulated in three different systems. The materials under consideration are magnetite (a thermal conductor), mesoporous silica (a thermal insulator), and silica modified with magnetite (a hybrid material).

Box 3

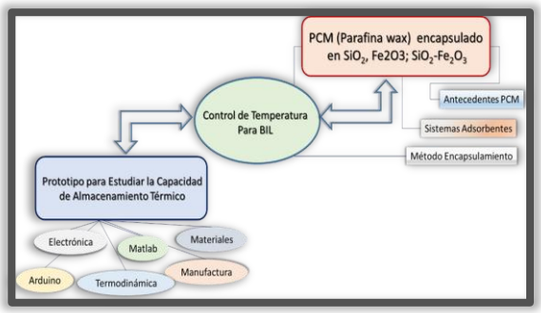

Figure 3

Plan for obtaining a temperature controller for lithium-ion batteries (LIB)

Experiments

To implement the analysis, a series of steps were undertaken to identify an appropriate material for the temperature controller function. Figure 4 shows the general methodology developed for this project. Stage 1 involved encapsulating the PCM in SiO_2, Fe_3O_4, and SiO_2/Fe_3O_4 systems. Stage 2 required adapting the equipment to obtain data. Stage 3 focused on thermal characterization of the materials, with results presented in graphical form for comparison.

Box 4

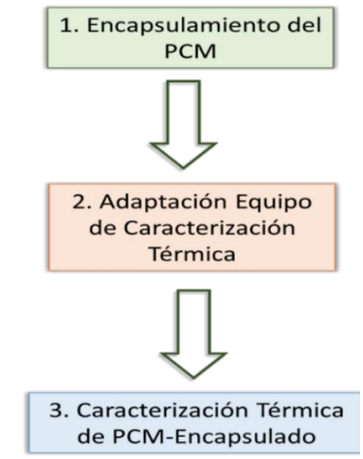

Figure 4

General project methodology

Magnetite synthesis and characterization

The synthesis of magnetite was conducted via precipitation techniques, in accordance with the conditions set forth in Equation 1, with a $2Fe^{3+}$:Fe^{2+} ratio. In a 250-ml flask, 5.27 g of $FeSO_4$ and 2.7 g of $FeCl_3$ were dissolved in 200 ml of water under constant stirring. The pH was then adjusted to 10–11 with NH_4OH, and the system was placed at reflux for 24 hours. At the conclusion of the specified period, the magnetite was retrieved through filtration and subjected to a 12-h drying process at 75°C. The magnetite was subjected to powder XRD analysis, which was conducted on a Rigaku Ultima IV X-ray diffractometer.

$$2FeCl_3 + FeSO_4 + 8NH_4OH \rightarrow Fe_3O_4 + (NH_4)2SO_4 + 6NH_4Cl + 4\,H_2O \quad (1)$$

Magnetite MS synthesis and modification

The synthesis of mesoporous silica materials was conducted using sodium silicate and P–123 as a molecular sieve, according to the methodology proposed by Salazar et al. (Salazar-Hernández 2020). Silicic acid is obtained and aged for 24 h, then used as a precursor in the formation of the inorganic network. The magnetite is anchored in the silica by modifying it with amino groups. Finally, 0.167 moles of the mesoporous silica are suspended in 100 mL of ethanol. A solution of 0.0416 moles of the modifying agent 3–aminopropyltrimethoxysilane (90%, Aldrich) was prepared, and 1 mL of NH_4OH was added.

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The system was then subjected to reflux for 24 h. At the conclusion of this period, the solid was recovered and washed with two portions of 10 mL of ethanol and 10 mL of acetone. It is then subjected to a 12 h drying process at 75°C in an oven. The anchoring of the magnetite in the modified silicas was conducted by placing 1 g of the synthesized Fe_3O_4 under reflux with 10 g of MS-NH_2 for 12 h. Then, the material was recovered by filtration and dried at 70°C for 12 h.

Wax paraffin encapsulation

The PCM used was wax paraffin (99%; Aldrich) with a melting point between 58 and 60 °C. The encapsulation process was conducted via impregnation (Figure 5), employing the quantities specified in Table 1. The PW was placed in a boiling flask and heated until complete melting occurred. Then, the encapsulant was added and mixed homogeneously, and the mixture was allowed to cool to room temperature.

Box 5

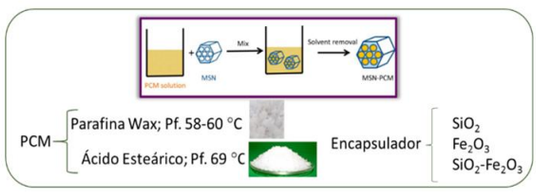

Figure 5

Impregnation method of PCM in encapsulation systems

Box 6

Table 1

Aggregate of PCM added to each encapsulator

PCM (g)	0.05	0.1	0.2
% weight	10	20	40

Thermal characterization

To obtain the data from the various samples, an experimental setup will be designed in accordance with the specifications depicted in Figure 6. This setup is intended to facilitate temperature measurements, which will be conducted on the different PCM encapsulations.

The measurements will be conducted with the use of a PID thermometer. To ensure accurate temperature control, a REX-100 thermostat will be employed as the heat source.

The thermostat will enable the regulation of the temperature supplied via a resistor connected to the thermometer. This experimental approach will provide the controlled conditions necessary for the accurate and systematic measurement of the thermal behavior of the encapsulated PCMs.

Box 7

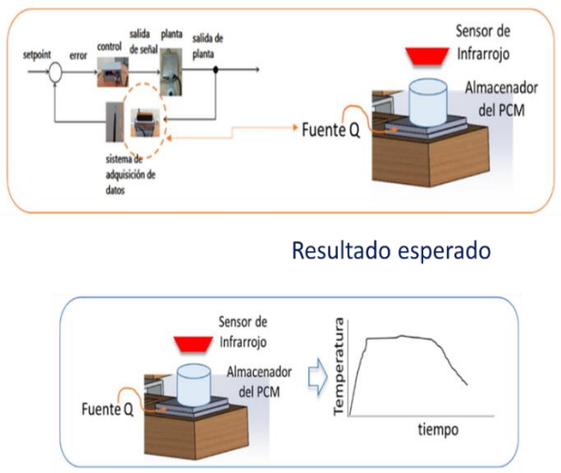

Figure 6

Apparatus for thermal characterization.

Results

PCM impregnation in encapsulators

The encapsulation method used was simple impregnation. Figure 7a shows the infrared spectra for the wax paraffin, which presents signals corresponding to a C–H hydrocarbon at 2900 cm^{-1}, ν and 1400 cm^{-1}, δ. Additionally, the spectra identify a C=C at 680 cm^{-1}. While the MS shown signals corresponding to the inorganic network, specifically Si–O–Si at 1100 and 780 cm^{-1}, as well as a shoulder at 980 cm^{-1}, which is associated with Si–OH. Magnetite is not active in the infrared, therefore, in the MS modification with magnetite, only a broadening of the Si–O–Si band (1100 cm^{-1}) is observed. Figure 7b shows the diffractogram for magnetite, in which the characteristic planes were identified. These are 2θ at 30.1, 35.4, 43.1, 54.5, 57.6, and 62°, which correspond to magnetite according to Mohammadi et al. (Mohammadi [2021]).

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Box 8

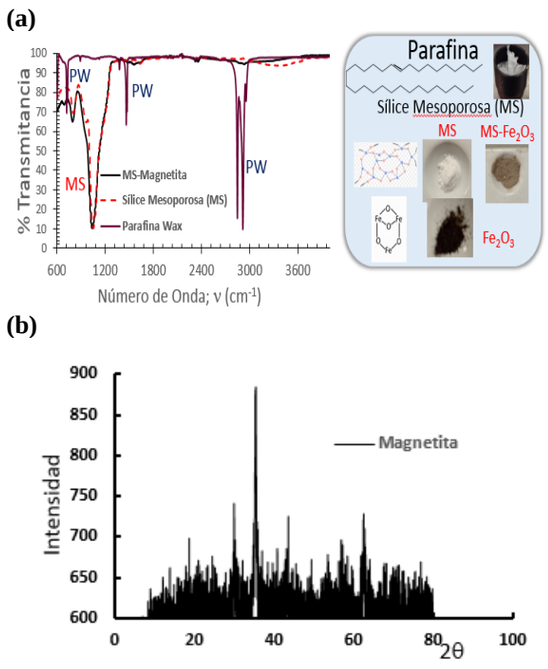

Figure 7

Base materials (a) Infrared spectra for encapsulators and PCM (b) XRD for magnetite

Figure 8a shows the magnetite modified with PCM, wherein all the corresponding signals for the hydrocarbon (PW) and a broad band of 700–1100 cm^{-1}, indicative of the interaction of Fe_3O_4 with paraffin, are observed. Furthermore, the solid formed with low (1:0.2) and high (1:2) concentrations of PCM solid pastes were obtained. In contrast, mesoporous silica (Figure 8b) forms powder-type solids at low PCM concentrations (1:0.5), granulated solids at 1:1 concentration, and pastes at 1:2 concentrations.

The intensity of the PW signals increases with increasing PW content in the material, reaching a maximum at the 1:2 concentration (Figure 8c). For MS-magnetite, the PW forms a granular solid at a concentration of 1:0.5, while a paste was observed at the other two concentrations, 1:1 and 1:2, respectively. In the spectra for the 1:0.5 concentration, the intensity of the silica and PW signals is relatively similar.

However, at a concentration of 1:1, the PW signals show a clear predominance in intensity.

Box 9

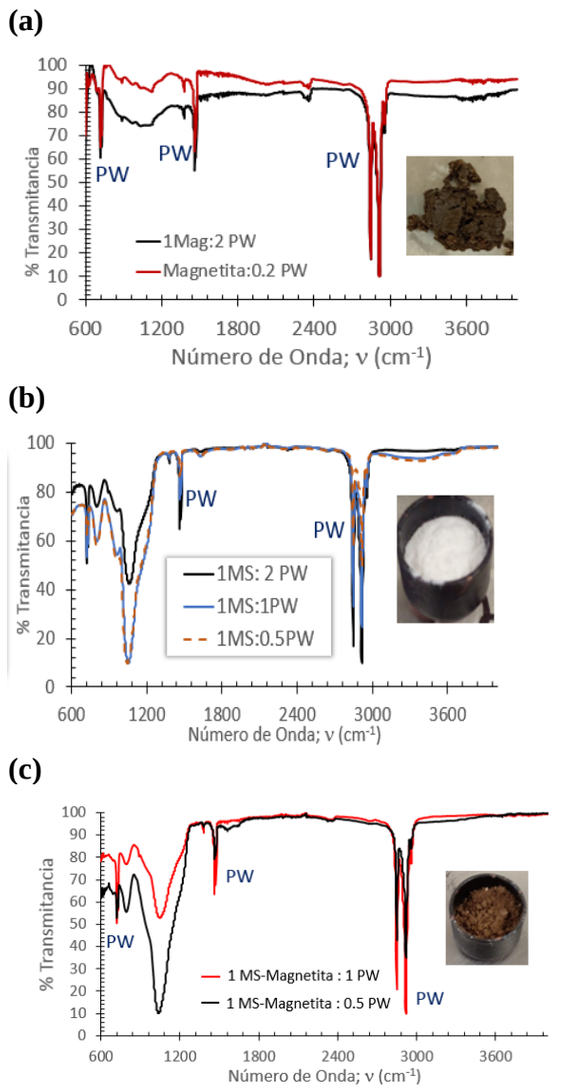

Figure 8

Encapsulation of PCM. (a) Paraffin Wax (b) Magnetite (c) Mesoporous Silica (MS)

Thermal characterization

Once the PW has been successfully melted, it forms a cover on the vessel and is unable to recover its initial volume (Figure 9a). This behavior has also been observed with magnetite as an encapsulator. However, in the case of MS and MS-magnetite, the volumes remain constant.

As shown in Figure 9b, the wax paraffin is heated to reach 60°C. This temperature was reached in 761 seconds (12.68 minutes) in the PW and in 792 seconds (13.2 minutes) in the magnetite with 20% PW (1:0.2). After this point, the temperature begins to increase, rising by 1°C. This is due to the conductive capacity of magnetite (Fe_3O_4). The 1:2 mixture exhibited a higher heat adsorption rate, reaching 60°C at 418 seconds (6.97 minutes).

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Following this, the temperature was maintained at a range of 1–2°C above 60°C, with minor fluctuations.

Box 10

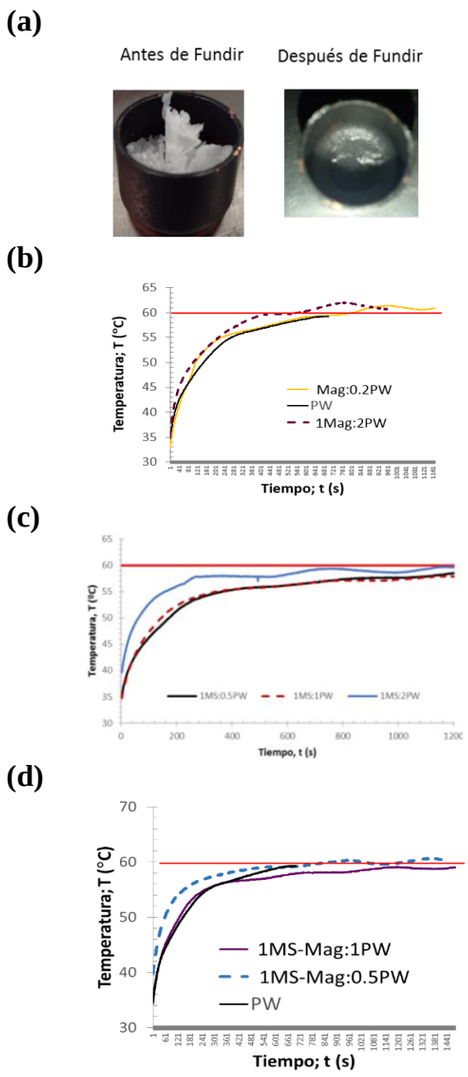

Figure 9

Thermal behavior (a) PCM volume change by the heating-cooling cycle (b) Thermal load curve of PCM encapsulated in Fe_3O_4 (c) Thermal load curve of PCM encapsulated in MS (d) Thermal load curve of PCM encapsulated in MS-Fe_3O_4.

Mesoporous silica behaves as a thermal insulator (characterized by low thermal conductivity), preventing the temperature from reaching 60°C. Consequently, at a ratio of 1:0.5 (Figure 9c), the temperature difference was observed to be 1.39–5 °C. At a ratio of 1:1, the temperature difference was 2–5°C, while at a ratio of 1:2, the temperature difference was 1–2 °C. The behavior of silica encapsulated with magnetite exhibited a hybrid character between that of a conductor and a thermal insulator, with a ΔT of less than ±0.5°C (Figure 9d).

Conclusions

The results of the infrared spectroscopy characterization indicate that the modification of silica with magnetite enhances the adsorption of PCM on the solid surface, as evidenced by the observed hybrid behavior between the insulator (SiO_2) and conductor properties of the magnetite.

Declarations

Conflict of interest

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

Author contribution

Salazar-Hernández, Carmen: Conception and design, data collection, analysis and interpretation of the data, critical revision of the manuscript.

Salazar-Hernández, Mercedes: Conception and design, data collection, analysis and interpretation of the data, critical revision of the manuscript.

Villegas-Alcaraz, José Francisco: Data collection, analysis and interpretation of the data, critical revision of the manuscript.

Mendoza-Miranda, Juan Manuel: Conception and design, data collection, analysis and interpretation of the data, critical revision of the manuscript.

Availability of data and materials

Data will be made available on request.

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Abbreviations

LIB	Lithium-Ion Battery
MS	Mesoporous Silica
PCM	Phase Change Material
PID	Proportional, Integral and Derivative controller
PVDF	Polyvinylidene fluoride
PVP	Polyviniyl fluoride
PW	Wax paraffin
XRD	X-ray Diffraction Analysis

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