THERMAL MANAGEMENT SYSTEM OF Li-ION BATTERIES USING INORGANIC PHASE-CHANGE MATERIALS

Svetlana Ushak[1,2], Yana Galazutdinova[1], Andrea Gutierrez[1], Luisa F. Cabeza[3], Mohammed M. Farid[4], and Mario Grágeda[1,2]

[1] Department of Chemical Engineering and Mineral Processing and Center for Advanced Study of Lithium and Industrial Minerals (CELiMIN), Universidad de Antofagasta, Campus Coloso, av. Universidad de Antofagasta, 02800 Antofagasta (Chile)

[2] Solar Energy Research Center (SERC-Chile), Av Tupper 2007, Piso 4, Santiago, Chile

[3] GREA Innovació Concurrent, Universitat de Lleida, edifici CREA, Pere de Cabrera s/n, 25001 Lleida (Spain)

[4] Department of Chemical and Materials Engineering, The University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

Abstract

Today the main problem of Li-ion batteries using is their high tendency to ignition. This paper proposes the utilization of hydrated inorganic salts as phase-change materials (PCMs) to maintain thermal balance within battery cells, inasmuch as these salts are not prone to combustion, unlike their organic analogs. Studies of three inorganic salts with addition of PEG 600 and various nucleating agents to improve their thermophysical properties were conducted. Results show that adding 20% PEG 600 gives a more cycling stable PCM without considerable effect on its melting temperature but with decreasing its heat of fusion. This research shows that mixing an inorganic PCM with an organic additive can be a good option to improve the thermal performance of the PCM.

Key-words: phase-change material (PCM), latent heat, Li-ion batteries, thermal management systems, thermophysical properties of inorganic salts.

1. Introduction

Li-ion batteries have revolutionized the portable electronics industry by offering significantly larger power density and specific energy value than previous technologies. On the other hand, using Li-ion battery packs have also some inconveniences, the main disadvantage is that during the operating cycles they generate large amounts of heat, which adversely affects the lifetime of the battery and becomes a problem for its safe use.

Temperature of the battery cell is defined by the heat balance between the amount of generated heat and the heat dissipated by the cell. According to Balakrishan et al. (2006) when the cell gets heated to a certain temperature, exothermic chemical reactions between the electrodes and electrolyte set in and a temperature rise occurs within the cell. In a case when the cell is able to dissipate the generated heat, temperature will not increase strongly. Otherwise exothermic processes will occur in adiabatic-like conditions and fast temperature rise takes place. This temperature rise will further accelerate undesirable chemical reactions, which causes more heat production. Ultimately, it will lead to thermal runaway, whose initial temperature determines the safety limit of the device. Thus, the vicious circle turns out: the reaction rate increases due to an increase in temperature causing a further increase in temperature and hence a further increase in the reaction rate. Moreover, it was shown that the pressure generated in this process may provoke mechanical damage in cells, causing short circuits and premature cell death. Numerous cases of electric motors fires, explosions of laptops due to cell ignition are known.

Working temperature is important not only because battery operation at high temperatures can lead to a fire

or explosion. Operating a battery at elevated temperatures significantly reduces its life. It has been proved by Waldmann et al. (2014) that high temperature accelerate reactions of degradation, namely degradation of the cathode, leading to capacity fade and internal resistance increase. Thus, the degradation rate of Li-ion batteries is very temperature-dependent; they degrade much faster if stored or used at higher temperatures. The carbon negative electrode of the cell also generates heat. High charge levels and elevated temperatures (whether from charging or ambient air) accelerate capacity loss. Loss rates vary by temperature: 6% capacity loss at 0 °C, 20% at 25°C, and 35% at 40°C. The optimal operating temperature range for Li-ion batteries is from −10°C to +50°C. At lower temperatures, the battery is not able to convert its chemical energy into electrical energy. At higher temperatures, safety devices called positive temperature coefficient (PTC) resistors inside the battery prevent it from being used until the temperature falls. However, in event of extreme temperatures or prolonged overheating, those mechanisms do not work and Li-ion batteries may suffer thermal runaway and cell rupture. In extreme cases this can lead to combustion. Batteries that are used in very cold or very hot conditions for extended periods of time can be permanently damaged.

Therefore, there is an ongoing search for the most advanced thermal management system, which would be able to ensure safe operation of Li-ion batteries, even under extreme conditions. The most promising today is thermal management system with PCM application.

The principle of phase change material (PCM) is very simple: as the temperature of the medium increases, phase change occurs and the material passes from the solid state to liquid, absorbing heat and thus offsetting the rise in temperature. In the same way, when the temperature of the medium decreases, PCM passes from the liquid to the solid phase releasing heat to the medium and thus offsetting the decrease in temperature.

A material to be used as a phase change material should have high heat of fusion value and good thermal conductivity. Farid et al. (2004) indicated that for practical uses, the PCM should have a minimum subcooling, be chemically stable, non-toxic and non-corrosive. As well, they must have a low cost. Numerous publications in recent years have dealt with application of organic PCMs as a thermal management system in Li-ion batteries. Most organic PCMs are non-corrosive and chemically stable, they exhibit little or no subcooling, and have a high latent heat per unit weight. Their disadvantages are low thermal conductivity, high changes in volume on phase change and flammability. And since Li-ion batteries have the tendency to ignition, using of organic PCM seems to be very unsafe.

For that reason, if we consider the application of inorganic materials, among all the classes of inorganic compounds, hydrated salts are the best candidates to be used as PCMs. Hydrated salts have a high latent heat per unit volume, small volume changes on melting, high thermal conductivity, are non-flammable and low in cost in comparison to organic compounds. Inorganic PCMs having different melting points (7-120°C) are commercially available, thus it is possible to select suitable materials for specific heating and cooling applications; this why they are especially interesting and lend themselves to use in Li-ion batteries.

The main disadvantages that have been identified for this class of inorganic compounds are subcooling effects and phase instability (Loveday, 1988). The major drawbacks of hydrated salts are recrystallization and segregation of the salt during repeated cycles of charging and discharging (Rabin et al., 1995; Farid and Khalaf, 1994). Phase separation can cause a loss in enthalpy of solidification as reported by Cantor (1978). Several authors have conducted studies to reduce such phase segregation. It can be minimized by the addition of extra water, use of microcapsules, a rotary storage tank and thickening agents (Ryu et al, 1992). Another important problem common to salt hydrates is that of subcooling. At the fusion temperature, the rate of nucleation is generally very low. To achieve a reasonable rate of nucleation, the solution has to be subcooled and hence energy instead of being discharged at fusion temperature is discharged at much lower temperature. To prevent subcooling nucleating agents are used. The basic principle of their use is that the structure of nucleating agent has to be similar to salt hydrate structure.

Hence, the objective of this research is to explore the phase transitions of three hydrated inorganic salts using DSC method and thereafter, to use those inorganic salts as a thermal management system for Li-ion batteries. For that we study salts and saline mixtures for their application in Li-ion battery packs. To prevent phase segregation it is recommended to use gelling or thickening materials. Cabeza et al. (2005) pointed out that "gelling means adding a cross-linked material (e.g. polymer) to the salt to create a three dimensional network that holds the salt hydrate together. Thickening means the addition of a material to the hydrated salt that increases viscosity and thus holds the salt hydrate together". In our studies we used polyethylene glycol

(PEG), because we believe that this compound can cover both gelling and phase change material functions. Only a few authors have studied the application of PEG as an organic PCM (Ahmad et al., 2006; Feng et al., 2011). In addition, to settle the subcooling problem and to improve thermal performance of hydrated salts, we used different nucleating agents.

2. Materials and methods

2.1. Materials

For our measurements we used three certain inorganic salt hydrates widespread in the Northern Chile: $Na_2CO_3 \cdot 10H_2O$ (Merck), $Ca(NO_3)_2 \cdot 4H_2O$ (Merck), $Na_2SO_4 \cdot 10H_2O$ (Merck). Salts were selected according to their melting temperatures.

It has already been mentioned above that hydrated inorganic salts usually possess two serious shortcomings: subcooling and phase segregation during crystallization. Therefore, it was needed to select an optimal nucleating and thickening agent to solve both problems.

Polyethylene glycol from Merck (PEG 600) was used as a thickener additive to improve cycling stability. As nucleating agents we have also considered the regional minerals and by-products of non-metallic industry of Northern Chile: boric acid (Boric Acid 99.9% Granular), granulex (Granulex 10% Boron (Granulated Ulexite) $NaCaB_5O_9 \cdot 8H_2O$), quibor (Quibor 15% BORON (48% B_2O_3) $H_3BO_3 + Na_2B_{10}O_{16} \cdot 10H_2O$) and Ulexite (Powder Ulexite 9% BORON (Sodium Calcium Borate) $NaCaB_5O_9 \cdot 8H_2O$). All four reagents are from Quiborax.

Three inorganic salts were analysed alone and in different combinations with PEG600 and four nucleating agents (Table 1).

Table 1. Samples composition of hydrated salts mixtures with PEG 600 and nucleating agents.

Sample	Composition (% w/w)
I	$Na_2SO_4 \cdot 10H_2O$
II	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (5%)
III	$Na_2SO_4 \cdot 10H_2O$ + Quibor (5%)
IV	$Na_2SO_4 \cdot 10H_2O$ + Granulex (4%)
V	$Na_2SO_4 \cdot 10H_2O$ + Boric acid (5%)
VI	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (5%) + Boric acid (5%)
VII	$Na_2SO_4 \cdot 10H_2O$ + Ulexite (4%)
VIII	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (20%) + Ulexite (1%)
IX	$Ca(NO_3)_2 \cdot 4H_2O$
X	$Na_2CO_3 \cdot 10H_2O$
XI	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (5%) + Boric acid (1%)
XII	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (5%) + Ulexite (1%)
XIII	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (5%) + Ulexite (5%)
XIV	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (20%) + Ulexite (5%)
XV	$Na_2SO_4 \cdot 10H_2O$ + PEG 600 (20%) + Ulexite (10%)

2.2 Methods

For the selected PCMs we have measured heat of fusion and fusion temperature. As well, stability of the PCMs has been analyzed, submitting them to cyclical variations of freezing-melting temperatures.

To determine the phase change temperatures and the latent heat of fusion a DSC 204 F1 *Phoenix* ® NETZSCH with N_2 atmosphere (volumetric flow 20 mL·min^{-1}) was used. Temperature and heat of fusion were measured in a range from 20°C to 70°C. Crucibles of aluminium with 25 μl volume capacity were used. Similarly, this DSC was used to cycle the samples between −15°C and 70°C to determine their cycling stability.

3. Results and discussions

3.1 Thermal properties

The results of the melting temperature are presented in Table 2. Table 2 also shows the results of heat of fusion for the samples, which are within the range from 81.86 J·g^{-1} to 262.5 J·g^{-1}.

Table 2. Temperature and heat of fusion of hydrated salts mixtures with PEG 600 and nucleating agents.

Sample	T_F [°C]	ΔH_F [J·g^{-1}]
Na$_2$CO$_3$·10H$_2$O	36.8	220.5
Ca(NO$_3$)$_2$·4H$_2$O	45.7	148.7
Na$_2$SO$_4$·10H$_2$O	37.4	262.5
Na$_2$SO$_4$·10H$_2$O + PEG 600 (5%)	37.7	181.6
Na$_2$SO$_4$·10H$_2$O + Quibor (5%)	33.1	184.7
Na$_2$SO$_4$·10H$_2$O + Granulex (4%)	37.5	221.9
Na$_2$SO$_4$·10H$_2$O + Boric acid (5%)	33.7	208.7
Na$_2$SO$_4$·10H$_2$O + PEG 600 (5%) + Boric acid (1%)	34.4	193.5
Na$_2$SO$_4$·10H$_2$O + PEG 600 (5%) + Boric acid (5%)	34.9	191.8
Na$_2$SO$_4$·10H$_2$O + Ulexite (4%)	36.6	208.2
Na$_2$SO$_4$·10H$_2$O + PEG 600 (5%) + Ulexite (1%)	35.8	135.1
Na$_2$SO$_4$·10H$_2$O + PEG 600 (20%) + Ulexite (1%)	35.9	137.7
Na$_2$SO$_4$·10H$_2$O + PEG 600 (5%) + Ulexite (5%)	35.0	133.5
Na$_2$SO$_4$·10H$_2$O + PEG 600 (20%) + Ulexite (5%)	35.4	103.8
Na$_2$SO$_4$·10H$_2$O + PEG 600 (20%) + Ulexite (10%)	30.8	81.86

3.2.Cycling stability

The cycling stability of samples was studied during six heating and cooling cycles. Ca(NO$_3$)$_2$·4H$_2$O (sample IX) and Na$_2$CO$_3$·10H$_2$O (sample X) have proven to be thermally unstable to the heating-cooling cycles, this why they were excluded from the further analysis; Na$_2$SO$_4$·10H$_2$O (Glauber's salt) has been chosen for our studies and we have focused on stabilizing its cycling properties.

Curves of heating-cooling cycles for I-VIII samples from Table 2 are shown below (2nd, 4th and 6th cycles are shown). Curves are stable during cycles, with temperatures of fusion from 30.8°C to 45.7°C. The crystallization temperatures vary greatly, depending on nucleating agent or thickening agent (PEG 600) additive.
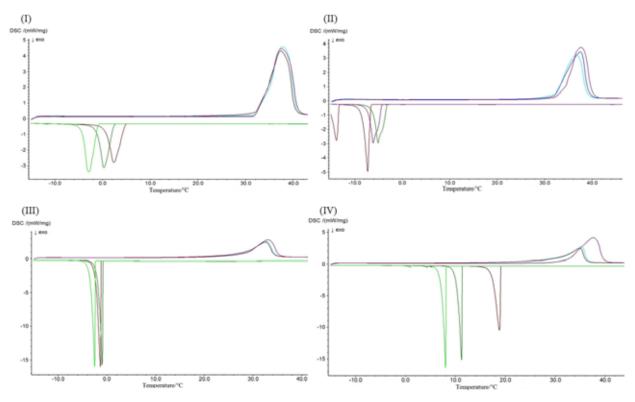
Figure 1. 2nd, 4th and 6th DSC curves of 6 heating-cooling cycles. (I) pure Na$_2$SO$_4$·10H$_2$O, (II) Na$_2$SO$_4$·10H$_2$O + PEG 600 (5%), (III) Na$_2$SO$_4$·10H$_2$O + Quibor (5%) and (IV) Na$_2$SO$_4$·10H$_2$O + Granulex (4%).

Figures disposed show the comparison of thermophysical properties between pure Glauber's salt and mix of Glauber's salt, nucleating agent and PEG600. Ulexite proved to be the most suitable nucleating agent for Na$_2$SO$_4$·10H$_2$O. As can be seen from Figure 2 (VII) the addition of Ulexite deals with the problem of incongruent melting and subcooling, however the crystallization temperature varies greatly. On the other hand, mixing of Glauber's salt with just PEG 600 neither shows a good result (Figure 1 (II)), giving both phase segregation and subcooling. Addiction of PEG 600 together with Ulexite is able to handle with these two problems.

Having analyzed DSC curves, it was concluded that sample VIII (Na$_2$SO$_4$·10H$_2$O + PEG 600 (20%) + Ulexite (1%)) revealed the best result. By the addition of PEG 600 it was managed to cope the phase segregation and the addition of Ulexite partially solved the subcooling problem. In all cases the addition of both PEG 600 and nucleating agent causes a significant reduction in the heat of fusion (for example, for the most stable sample XVIII from 262.5 J·g^{-1} to 137.7 J·g^{-1}). However that is justified, because completely suppresses phase segregation. Moreover, the value of heat of fusion remains more than 100 J·g^{-1}, which means that this material still can be used as a PCM.

The aim of further work is to search for such additives which wouldn't cause serious decrease in heat of fusion, but at the same time would cope with stabilization of phase segregation and improving nucleation properties of inorganic salt hydrates. Resultant mixtures will correspond to a hydrated salt plus nucleating agents and gelling or thickening materials, or the mixture of hydrated salts.
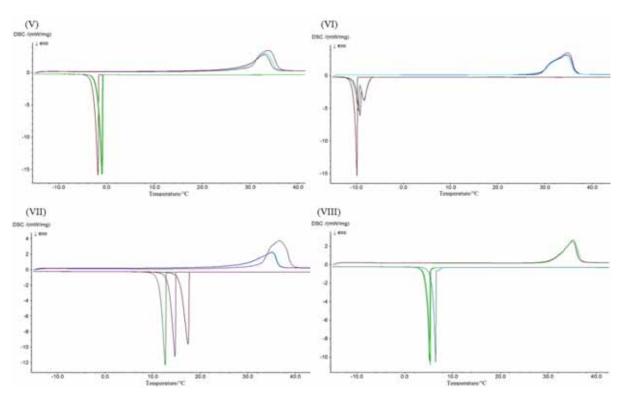
Figure 2. 2nd, 4th and 6th DSC curves of 6 heating-cooling cycles. (V) Na$_2$SO$_4$·10H$_2$O + Boric acid (5%), (VI) Na$_2$SO$_4$·10H$_2$O + PEG 600 (5%) + Boric acid (5%), (VII) Na$_2$SO$_4$·10H$_2$O + Ulexite (4%) and (VIII) Na$_2$SO$_4$·10H$_2$O + PEG 600 (20%) + Ulexite (1%).

5. Conclusions

Thermophysical properties for three different inorganic salts of Northern Chile, Na$_2$CO$_3$·10H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O, and Na$_2$SO$_4$·10H$_2$O, were considered. The results of preliminary measurements reveal that only sodium sulfate decahydrate (Glauber's salt) possesses decomposition stability within heating-cooling cycles. Mixtures of Glauber's salt with four different nucleating agents (Boric acid, Granulex, Quibor, and Ulexite) and PEG 600 as a thickener agent were determined to stabilize the thermal properties during cycles of heating and cooling.

Ulexite proved to be the most suitable nucleating agent for Glauber's salt, which deals with the problem of incongruent melting and subcooling, however the crystallization temperature varies greatly. On the other hand, mixing of Glauber's salt with just PEG 600 neither shows a good result. Addiction of PEG 600 together with Ulexite is able to handle incongruent melting as well as subcooling.

For the new mixtures the temperature and heat of fusion were in the temperature range from 20°C to 70°C. The results obtained for the most stable sample VIII (Na$_2$SO$_4$·10H$_2$O + PEG 600 (20%) + Ulexite (1%)) were: T$_F$ 35.9ºC and ΔH$_F$ 137.7 J·g^{-1}. The heating and cooling cycling were measured in the temperature range from −15°C to 70°C. The most stable sample turned out to be Na$_2$SO$_4$·10H$_2$O + PEG 600 (20%) + Ulexite (1%) with a constant subcooling of about 28ºC.

As expected, the addition of PEG 600 and nucleating agent to Glauber's salt did not change the melting temperature of Na$_2$SO$_4$·10H$_2$O considerably, but did decrease its heat of fusion, which became 137.7 J·g^{-1} instead of 262.5 J·g^{-1}. As this value remains higher than 100 J·g^{-1}, this material can be used as PCM yet. In our case this addition is justified since it deals with a problem of incongruent melting and weak nucleation properties, still our challenge remains to search for thickening and nucleating agents which do not produce such drawbacks.

This research has shown that PEG is a good additive to improve cycling stability of PCM, furthermore, Ulexite reveals to be a proper addition to settle the subcooling problem. Also, it was ascertained that mixing an inorganic PCM with an organic additive can be a good option to improve the thermal performance of the PCM. We have demonstrated that Glauber's salt in combination with Ulexite and PEG600 may serve as a phase-change material and could be potential used as a thermal management system for Li-ion battery packs.

Acknowledgements

References

Ahmad, M., Bontemps, A., Salle, H., Quenard, D. Experimental invstigation and computer simulation of thermal behaviour of wallboards containing a phase change material, 2006. Energy and Building, 38, 357-366.

Balakrishnan, P.G., Ramesh, R., Prem Kumar, T. Safety mechanisms in lithium-ion batteries, 2006. Journal of Power Sources 155, 401–414.

Cabeza, L., Heinz, A., Streicher, W. Report C2 of Subtask C, Inventory of Phase Change Materials (PCM), 2005. University of Lleida, Spain-Graz University of Technology Austria.

Cantor, S. DSC study of melting and solidification of salt hydrates, 1978. Thermochimica Acta, Vol. 26, 39-47.

Farid, M.M, Khudhair, A.M., Razack, S.A.K.., Al-Hallaj, S. A review on phase change energy storage: materials and applications, 2004. Energy Conversion and Management, 45, 1597–1615.

Farid, M.M, Khalaf, A.N. Performance of a direct contact latent heat storage unit with two hydrated salts, 1994. Solar Energy, 52, 179–89.

Feng, L., Zheng, J., Yang, H., Guo, Y., Li, W., Li, X. Preparation and characterization of polyethyleneglycol/active carbon composites as shape-stabilized phase change materials, 2011. Sol. Energy Mat. and Solar Cells, 95, 644–650.

Loveday, D.L. Thermal performance of air-heating solar collectors with thick, poorly conducting absorber plates, 1988. Solar Energy, 41, 6, 593–602.

Rabin, Y., Bar-Niv, I., Korin, E., Mikic, B. Integrated solar collector storage system based on a salthydrate phase change material, 1995. Solar Energy, 55, 6, 435–444.

Ryu, H. W., Woo, S. W., Shin, B. C., Kim, S. D. Prevention of supercooling and stabilization of inorganic salt hydrates as latent heat storage materials, 1992. Sol. Energy Mater. and Sol. Cells, Vol. 27, 161-172.

Waldmann, T., Wilka, M., Kasper, M., Fleischhammer, M., Wohlfahrt-Mehrens, M. Temperature dependent ageing mechanisms in Lithium-ion batteries e A Post-Mortem study, 2014. Journal of Power Sources 262, 129–135.