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VACUUM DECOMPOSITION THERMODYNAMICS AND EXPERIMENTS OF RECYCLED LEAD CARBONATE FROM WASTE LEAD ACID BATTERY

by

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Lead acid batteries have been widely used in different fields, so abundant waste lead acid battery was generated. Waste lead acid battery is regarded as a toxic material due to the metallic lead and the lead paste compounds. Once lead and its compounds enter the human body and the environment, which will cause serious threats. At present, the waste lead acid batteries are mainly recovered in the form of metal lead, which has many problems. Thus, this paper put forward a novel technology to recycle waste lead acid battery. Vacuum thermal decomposition was employed to treat recycled lead carbonate from waste lead acid battery. Thermodynamics analysis and experiments were finished from the reaction free energy of lead carbonate decomposition and vacuum furnace. The results showed that the recycled lead carbonate began to be decomposed when the temperature reached 250 °C. Above 340 °C, most of intermediate $PbCO_3 \cdot 2PbO$ were converted to red α-PbO and then transformed to yellow β-PbO when the temperature was raised further to 460 °C. Furthermore, the study provided the fundamental data for the preparation of α-PbO and β-PbO in vacuum, which also demonstrated a new way for the reuse of spent lead acid battery resource and an outlook of sustainable production.

Key words: *waste lead acid battery, thermodynamics, recycled lead carbonate, vacuum decomposition*

Introduction

Lead acid battery is the most important energy storage device to supply power in fields of transportation, communication, medical treatment and other aspects due to its excellent characters of stable and reliable performance, low production cost, resource recycling and big capacity [1-3]. Undoubtedly, the wide use of lead acid battery can cause a large amount of waste lead acid batteries. Thus, the recovery of waste lead acid batteries containing toxic lead compounds such as $PbSO_4$ was regarded as the requirement from the perspective of both economic and ecological [4, 5]. Commercially, pyrometallurgy and hydrometallurgy, this two traditional

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technologies methods are considered to be the most frequently-used process transforming waste lead acid battery into metallic lead [6].

The pyrometallurgical method helps waste lead acid battery, obtain metallic lead across the oxidization and reduction processes, which exists high energy consumption and generates SO_2 gas and lead dust pollution [7]. Thus hydrometallurgical technology was put forward that effectively solves the previous problems [8, 9]. Generally, the metallic lead obtained from waste lead acid battery needs to be reoxidized into lead oxide by the ball-mill and the Barton-pot methods for making renew lead acid battery as the negative and positive electrode plate, the lead oxidizing process requires exhausting more energy and tends to producing secondary lead dust pollution [10, 11]. Therefore, in order to better deal with the environments and energy consumption problems, the study for synthesizing PbO instead of metallic lead from the waste lead acid battery is necessary [3].

Sonmez *et al.* [12,13] obtained the intermediate $Pb(C_6H_6O_7)H_2O$ through citric acid treatment lead acid battery, then the intermediate $Pb(C_6H_6O_7)H_2O$ was roasted can make lead oxide. Pan *et al.*[14] in China adopted the method *lead paste catalytic conversion-desulfurization and recrystallization* to convert the lead paste into $PbSO_4$, and then desulfurization and recrystallization with NaOH solution were used to obtain lead oxide with a purity of more than 99.99%. Gao *et al.* [15] obtained lead oxide by desulfurizing the lead paste with $(NH_4)_2CO_3$ and sodium carbonate.

However, the utilization of those technologies for making PbO from waste lead acid battery still exist some problems such as reagent volatile, high energy consumption, and lead dust pollution so on. Consequently, more attention was paid to the exploration of new techniques for making PbO from waste lead acid battery. Vacuum decomposition technology avoided the distractions of gas molecules, the reaction rate could be accelerated, and reaction temperature can be lowered, compared with the traditional thermal decomposition technology at the same time, and the vacuum decomposition technology is energy saving [16, 17].

Meanwhile, as for vacuum thermal decomposition technology has achieved good applications and obtained expectant results. Zhou *et al.* [18] proved that the vacuum thermal decomposition of molybdenite concentrate was feasible to produce crude molybdenum and sulfur. Gron *et al.* [19] applied that the vacuum thermal decomposition technology on GaN obtaining the Ga element. Yong *et al.* [20] confirmed that AlN chlorination route can extract aluminum from aluminum nitride under vacuum. The use of vacuum heat treatment can obviously decreased the reaction temperature comparing the temperatures of nitrogen, and air atmospheres [21]. The $CdCO_3$ had a higher decomposition rate and a lower decomposition temperature in vacuum than those in air [22]. Decomposition of solid alumina in the presence of carbon in vacuum make the decomposition of solid Al_2O_3 possible [23]. The decomposition technology in vacuum has a good performance and application.

In this paper, vacuum decomposition thermodynamics and experiments of recycled lead carbonate from waste lead acid battery was finished. Various methods have been developed to recycle lead carbonate from the waste lead acid battery and those technologies are extremely mature so that almost nobody still focused on the research of recovering lead carbonate from waste lead acid battery, so the investigation started with lead carbonate as the raw material. Thermodynamics for assessing the likelihood of a reaction of decomposition process was vital. The thermodynamics were certified by vacuum decomposition process of recycled lead carbonate from waste lead acid battery. The thermodynamics also give the reaction the onset temperatures. Another important part of vacuum decomposition is worthy to be paid closed attention to experiments. For knowing the experiments process in vacuum decomposition is very vital to analyzing

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the decomposition products. It is important to understand that the vacuum decomposition process of the recycled lead carbonate from waste lead acid battery. The research in this paper is to obtain the basic data of the thermal decomposition method of waste lead-acid batteries under vacuum, and provides a new research idea for the secondary resource recovery of these batteries.

Methodology

The employed lead carbonate for decomposition

The lead carbonate employed was obtained from waste lead acid battery in a china factory. Generally, waste lead acid battery were preferentially split to collect the lead paste in industry. Then, the lead paste of waste lead acid battery were treated by the steps: desulfurization, leaching, and carbonation. According to the above mentioned treatments, the lead paste of waste lead acid battery would entirely be converted to lead carbonate with the purity more than 99.9% [7]. The process for obtaining lead carbonate from waste lead acid battery would not be elaborated deeply. On the contrary, starting from the decomposition of lead carbonate is of great research value because it can greatly reduce cost, save energy and eliminate environmental effect for the preparation of lead oxide. To identify the phase composition, the XRD pattern of the raw material was presented in fig. 1, which clearly confirmed that lead carbonate was the major phase without the others occurring.
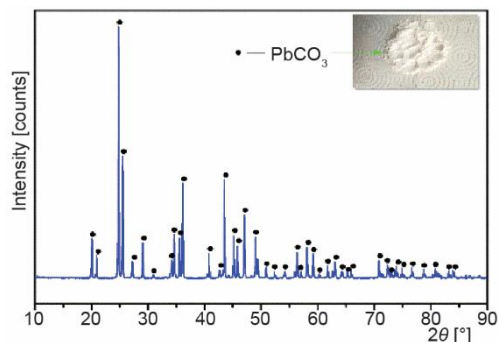

Figure 1. The XRD pattern of the raw material

Vacuum decomposition set-up

The schematic diagram of vacuum decomposition furnace was shown in fig. 2. There were mainly several sections (a main heater, insulated, crucible, macintosh vacuum gauge, and vacuum pump systems) composed for controlling experimental conditions in vacuum furnace. Specially, the crucible was used to place the recycled lead carbonate and decompose it. Main heater and insulated were employed to control temperature. Mechanical pump and diffusion pump ensured vacuum condition by moving the decomposition gases from vacuum system to the air. Also, this vacuum furnace can be set to 15-step decomposing procedure. Each heating section can adjust different heating rate and holding time. Also, the heater power was switched off after the end of heating period, but vacuum pump must continuously run until the temperature in the furnace is below 25 °C. Finally, the decomposed product was taken out for analysis.
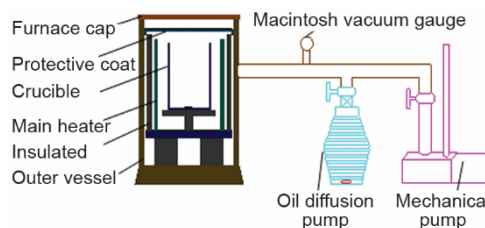

Figure 2. Schematic diagram of vacuum decomposition furnace

The TG/DSC analysis of recycled lead carbonate from waste lead acid battery and XRD characterization of after decomposition of recycled lead carbonate

The 10 mg raw material, recycled lead carbonate was heated from 25 °C to 610 °C using the TG/DSC analyzer (NETZSCH STA 449F3 STA 449F3A-0046-M) with the different

heating rate of 1 K per minute, 5 K per minute, and 10 K per minute in a vacuum system pressure of 0.2 atmosphere, respectively. Thermal decomposition of lead carbonate will give valuable information of its behavior in a chemical process. This evaluation may be carried out by using HSC Chemistry® 6.0 software with the HSC Equilibrium module for studying the effects of different variables on the chemical system at equilibrium. The characterization of decomposed products was detected by the XRD instrument Rigaku (Japan) D/max-3B, radiation in the range from 10° to 90° (2-θ°) with a scanning rate 2° per minute, and using copper target as α-ray radiation.

Results and discussion

Thermodynamics analysis in vacuum decomposition process of lead carbonate

The CO_2 gas will be released in the process of thermal decomposition of lead carbonate, the reactions existed are complex and diverse with $PbCO_3 \cdot PbO$, $PbCO_3 \cdot 2PbO$, α-PbO, and β-PbO several intermediate compounds based on the results of literature study, and the partial pressure of CO_2 will seriously affect the results of decomposition products [24, 25]. Therefore, the control on the partial pressure of CO_2 is pretty important because the CO_2 gas released disturbed the heat transfer in the form of a gas film by wrapping unreacted particles [24].

As mentioned in section Introduction, with the assistance of vacuum atmosphere will be better to complete the decomposition of lead carbonate in certain degree. That's to say that the CO_2 gas released will be quickly pumped out by the vacuum pump to eliminate the CO_2 gas side effects. As far as at present there is no relevant analysis available on the thermodynamic calculation for the possible intermediates of the thermal decomposition of lead carbonate under vacuum atmosphere, it has not been completed in a proper way, the following thermodynamic analysis of lead carbonate and its intermediates fully discussing the possibility and degree of the reactions. The possible decomposition reactions of lead carbonate in vacuum was listed in tab. 1.

Table 1. Possible reactions of vacuum decomposition of lead carbonate

Reaction process	Number	Reaction
PbCO$_3$ thermal Decomposition (25-400 °C)	R1	$PbCO_3 = 1/2(PbCO_3 \cdot PbO) + 1/2(CO_2)$
	R2	$PbCO_3 = 1/3(PbCO_3 \cdot 2PbO) + 2/3(CO_2)$
	R3	$PbCO_3 = \alpha\text{-}PbO + CO_2$
	R4	$PbCO_3 = \beta\text{-}PbO + CO_2$
PbCO$_3$·PbO thermal decomposition (25-400 °C)	R5	$(PbCO_3 \cdot PbO) = 2/3(PbCO_3 \cdot 2PbO) + 1/3(CO_2)$
	R6	$PbCO_3 \cdot PbO = \alpha\text{-}PbO + CO_2$
	R7	$PbCO_3 \cdot PbO = \beta\text{-}PbO + CO_2$
PbCO$_3$·2PbO thermal decomposition (25-400 °C)	R8	$PbCO_3 \cdot 2PbO = 3(\alpha\text{-}PbO) + CO_2$
	R9	$PbCO_3 \cdot 2PbO = 3(\beta\text{-}PbO) + CO_2$
Phase transition process (25-700 °C)	R10	$\alpha\text{-}PbO = \beta\text{-}PbO$
	R11	$\beta\text{-}PbO = \alpha\text{-}PbO$

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As shown in tab. 1, *reaction free energy function method* is applied to estimate the response under the condition of different pressure of reaction free energy $\Delta_r G_m$ and temperature t [°C]. In general, the relationship between $\Delta_r G_m$ and t can be computed as:

$$\Delta_r G_m = \Delta_r G_m^\theta + R(t + 273) \ln \left(\frac{P}{P^\theta} \right)^n \tag{1}$$

where $\Delta_r G_m$ [kJ] is the reaction free energy, $\Delta_r G_m^\theta$ [kJ] – the standard free energy, P [Pa] – the partial pressure of CO_2 gas approximately equal to the systematic pressure because the pump is running continuously, P^θ – the standard atmosphere pressure 101325 Pa, t [°C] – the reaction temperature, R – the gas constant 8.314 J/molK, and n – the reactive coefficient of carbon dioxide).

Then the determination of $\Delta_r G_m^\theta$ is crucial, which can be derived from eqs. (2)-(9).

$$\Delta_r G_m^\theta = \Delta_r H_m^\theta - T\Delta_r S_m^\theta \tag{2}$$

where $\Delta_r H_m^\theta$ and $\Delta_r S_m^\theta$ is a function of temperature, which can be obtained from eqs. (3) and (4).

$$\Delta_r H_m^\theta = \Delta_r H_m^\theta(298 \text{ K}) + \int_{298}^{T} \Delta C_{P,m} dt \tag{3}$$

$$\Delta_r S_m^\theta = \Delta_r S_m^\theta(298 \text{ K}) + \int_{298}^{T} \frac{\Delta C_{P,m}}{T} dt \tag{4}$$

The solution formula of standard free energy change is (5):

$$\Delta_r G_m^\theta = \Delta_r H_m^\theta(298 \text{ K}) + \int_{298}^{T} \Delta C_{P,m} dt - T\Delta_r S_m^\theta(298 \text{ K}) - T \int_{298}^{T} \frac{\Delta C_{P,m}}{T} dt \tag{5}$$

where $\Delta_r H_m^\theta(298 \text{ K})$, $\Delta_r S_m^\theta(298 \text{ K})$, and $C_{P,m}$ can be derived from eqs. (6)-(9). According to the parameters of the thermodynamic data for various carbonated and lead oxides from the HSC chemistry®6;

$$\Delta_f H_{m(\text{product})}^\theta(298 \text{ K}), \quad \Delta_f H_{m(\text{reactant})}^\theta(298 \text{ K}),$$

$$\Delta_f S_{m(\text{product})}^\theta(298 \text{ K}), \quad \Delta_f S_{m(\text{reactant})}^\theta(298 \text{ K}), \text{ and } C_{P,m}$$

can be easily obtained from HSC chemistry®6.

$$\Delta_r H_m^\theta(298 \text{ K}) = \sum v_i \Delta_f H_{m(\text{product})}^\theta(298 \text{ K}) - \sum v_j \Delta_f H_{m(\text{reactant})}^\theta(298 \text{ K}) \tag{6}$$

$$\Delta_r S_m^\theta(298 \text{ K}) = \sum v_i \Delta_f S_{m(\text{product})}^\theta(298 \text{ K}) - \sum v_j \Delta_f S_{m(\text{reactant})}^\theta(298 \text{ K}) \tag{7}$$

$$C_{P,m} = A + 10^{-3} BT + 10^5 CT^{-2} + 10^{-6} DT^2 \tag{8}$$

$$\Delta C_{P,m} = \sum [v_i C_{P,m}(\text{product})] - \sum [v_j C_{P,m}(\text{reactant})] \tag{9}$$

where the coefficients *A, B, C,* and *D* are given for the heat capacity functions using by HSC chemistry®6, v_i – the product coefficient of the reaction, and v_j – the reactant coefficient of the reaction.

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The computations were performed using the module of reaction equations with the assistance of HSC chemistry®6, which input the corresponding equation R1-R11(As shown in tab.1) and calculated the relevant standard free energy $\Delta_r G_m^\theta$, then enabled to get the calculation values of reaction free energy $\Delta_r G_m^\theta$ based on eq. (1) under different pressure conditions. The temperature was varied in the range from 25 °C to 400 °C (the melting point of lead carbonate, $t = 400$ °C) and from 25 °C to 800 °C (the highest measurement temperature of the thermocouple used, $t = 800$ °C), and all calculation of R1 to R11, the pressure was set to $P = 30$ Pa (based on the experimental vacuum pump system), 100 Pa, 1000 Pa, and 101325 Pa, respectively.

Combined the reaction R1 to R11 and eqs. (1)-(9) under different pressures, we can obtain the following calculation results of the relationship between $\Delta_r G_m$"and t [°C], respectively.

Thermodynamic analysis of thermal decomposition of PbCO₃

The thermodynamics calculation results of thermal decomposition of PbCO₃ are shown in fig. 3.
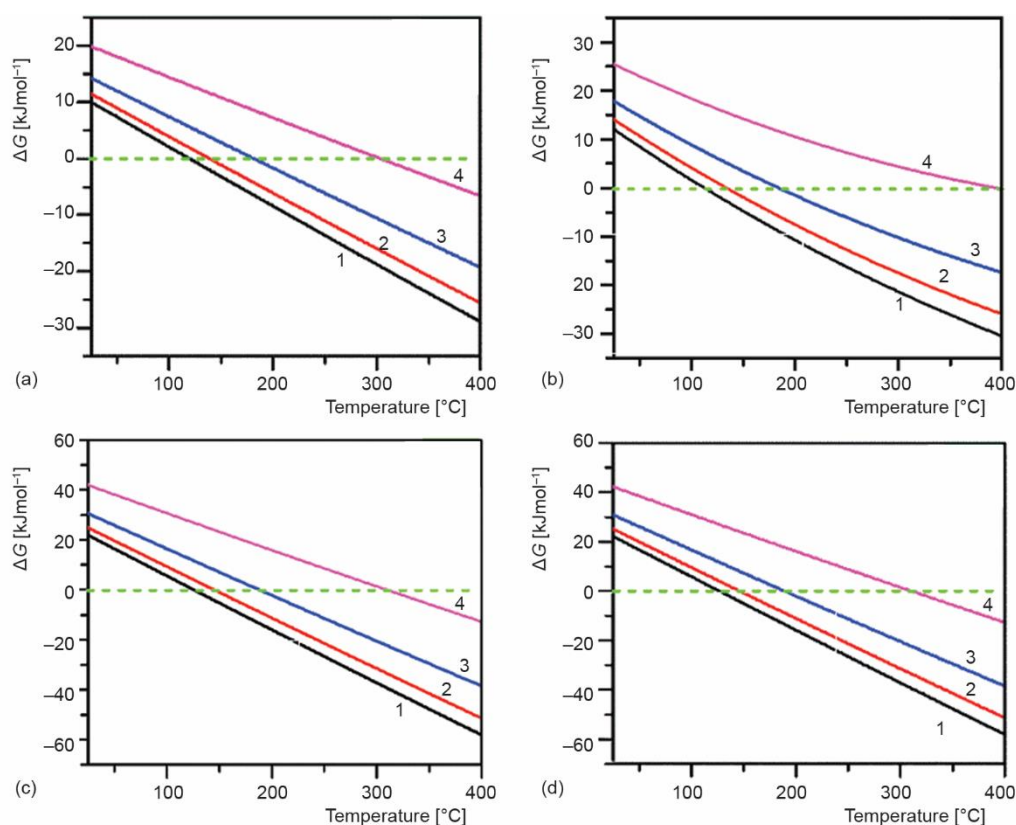
Figure 3. Diagrams of the relationship between the reaction free energy and temperature involved in the possible reaction of decomposition of lead carbonate: (a) R1, (b) R2, (c) R3, (d) R4; *1 – P = 30 Pa, 2 – P = 100 Pa, 3 – P = 1000 Pa, and 4 – P = 101325 Pa*
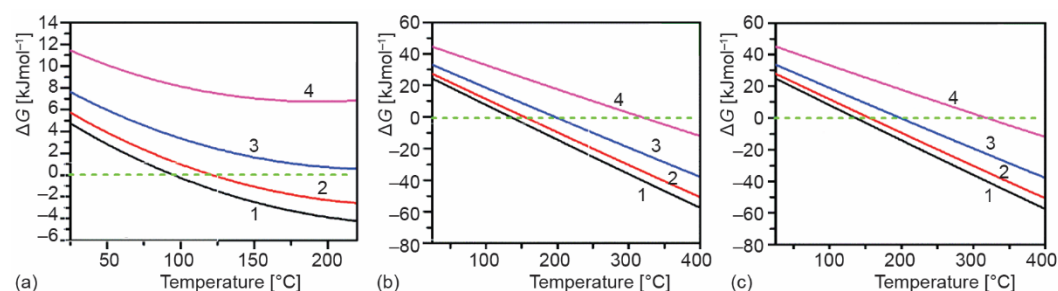
Figure 3 shows the relationship between the reaction free energy and temperature involved in the possible reaction of decomposition of lead carbonate, which indicated that the $\Delta_r G_m$ is dominated by vacuum pressure and temperature. With the decrease of the pressure, the

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decomposition temperature decreases. Figure 3(a) exhibits $PbCO_3$ will decompose into the $PbCO_3 \cdot PbO$ under the pressure of 101325 Pa with the temperature of 304 °C, under the pressure of 30 Pa with the temperature of 121 °C. Figure 3(b) presents the products of R2 were converted into $PbCO_3 \cdot 2PbO$ at 114 °C with the pressure of 30 Pa. As shown in fig. 3(c), the temperatures for the onset of α-PbO formation at approximately 128-311 °C conversion of $PbCO_3$ to α-PbO for system pressures of 30 to 101325 Pa. In fig. 3(d), when lowering the system pressure from 101325 Pa to 30 Pa not only shifts the formation of β-PbO to much lower temperatures but it also frees the CO_2 gas from the lead carbonate already at more lower temperatures corresponding to the decomposition law of Mo_2S_3 under vacuum [18].

It is observed in fig. 3 that the lower vacuum pressure condition, it is facilitating to the decomposition of lead carbonate. For decomposing lead carbonate with lower temperature, the lower the vacuum pressure is, the smaller $\Delta_r G_m$ of decomposition process is in thermodynamics calculation. Within 30-100 Pa system pressure, on the basis of lower reaction temperature, reaction occurs, the priority is reaction R2 generated $PbCO_3 \cdot 2PbO$ priority, second reaction R1, R3, and R4 are in turn, and the corresponding product $PbCO_3 \cdot PbO$, α-PbO, β-PbO.

Thermodynamic analysis of thermal
decomposition of $PbCO_3 \cdot PbO$

The thermodynamics calculation results of thermal decomposition R5, R6, and R7 of $PbCO_3$ are shown in fig. 4.

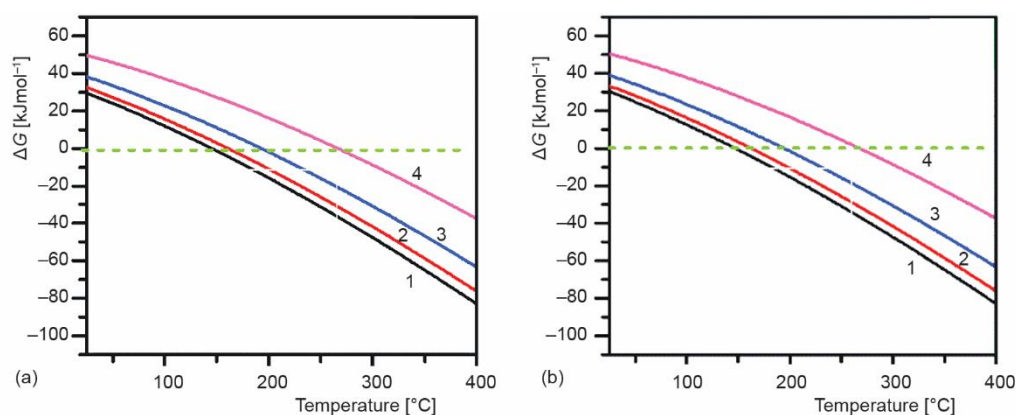**Figure 4. Diagrams of the relationship between the reaction free energy and temperature involved in the possible reaction of decomposition of $PbCO_3 \cdot PbO$: (a) R5, (b) R6, (c) R7;** *1 – P = 30 Pa, 2 – P = 100 Pa, 3 – P = 1000 Pa, and 4 – P = 101325 Pa*

As can be seen in fig. 4 that the determination of $PbCO_3 \cdot PbO$ stability depends on the vacuum pressure and the temperature. Figure 4(a) shows the $PbCO_3 \cdot PbO$ cannot be decomposed as the temperature evaluated from 25 °C to 230 °C and the vacuum pressure extended from 1000 Pa to 101325 Pa. But when the vacuum pressure drop to 100 Pa or more less helped to accelerate the reaction R5, which can occur. The thermodynamics calculation for analyzing the reaction of R6 were showed according to results of fig. 4(b). The lines of reaction free energy indicated that $PbCO_3 \cdot PbO$ would be decomposed into α-PbO when the temperature was greater than 136 °C under vacuum pressure of 30 Pa. However, when the vacuum pressure is 101325 Pa, only the reaction of R6, reached 319 °C, began to be decomposed. According to fig. 4(c), the temperatures in vacuum pressures of 30-101325 Pa, calculated by thermodynamics, ranged from 136 °C to 318 °C, which also can obtain β-PbO.

Thermodynamics analysis results were exhibited in fig. 4, the $PbCO_3 \cdot PbO$ tend to decomposing into $PbCO_3 \cdot 2PbO$ compared to the formation of α-PbO and β-PbO. And the corresponding formation temperature of α-PbO and β-PbO was basically the same.

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Thermodynamic analysis of thermal
decomposition of PbCO₃·2PbO

The results of thermal decomposition R8 and R9 of $PbCO_3 \cdot 2PbO$ under different pressures are shown in fig. 5. Thermodynamics calculation of $PbCO_3 \cdot 2PbO$ was finished and the results were presented in fig. 5, the $PbCO_3 \cdot PbO$ can decompose to get α-PbO and β-PbO, and the temperature has a little difference under the same vacuum pressures. But the decomposition reaction was affected by vacuum pressures. Obviously, in figs. 5(a) and 5(b), when the vacuum pressure is 30 Pa, corresponding reaction temperature is about 146 °C. As the vacuum pressure is raised from 30 Pa to 101325 Pa, corresponding reaction temperature is increased to 269 °C.

Figure 5. Diagrams of the relationship between the reaction free energy and temperature involved in the possible reaction of decomposition of PbCO₃·2PbO: (a) R8, (b) R9; *1 – P = 30 Pa, 2 – P = 100 Pa, 3 – P = 1000 Pa, and 4 – P = 101325 Pa*
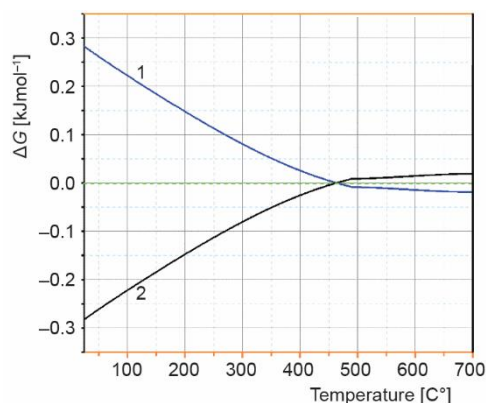
Figure 6. Diagrams of the relationship between the reaction free energy and temperature involved in the possible reaction of transformation phase of: *1 – α-PbO = β-PbO, and 2 – β-PbO = α-PbO; R10, R11*

Thermodynamic analysis of phase
transition process

As observed in fig. 6, the phase transformation process of α-PbO and β-PbO can occur. It is thermodynamically favorable process of α-PbO to β-PbO when the temperature is above 466 °C. Instead β-PbO also can transform into α-PbO when the temperature is below 461 °C.

Based on the previous thermodynamics calculation results of thermal decomposition of $PbCO_3$, $PbCO_3 \cdot PbO$, $PbCO_3 \cdot 2PbO$ and phase transition process of α-PbO and β-PbO, the values of reaction free energy are effected by the reaction temperature and pressures, the lower the vacuum pressure, the lower the theoretical thermal decomposition temperature, and the more conducive to thermal decomposition. The thermal decomposition of lead carbonate tend to synthesize $PbCO_3 \cdot 2PbO$ and the reaction starting temperature is lower. The $PbCO_3 \cdot 2PbO$ can decompose to produce α-PbO and β-PbO. As the temperature increases, α-PbO can further transform into β-PbO.

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Thermal decomposition equilibrium of
1 kmol PbCO₃ using HSC software

The decomposition equilibrium of 1 kmol PbCO$_3$ in defined system was also obtained by HSC chemistry®6, as shown in fig. 7.

The decomposition of PbCO$_3$ can form PbCO$_3$·PbO, PbCO$_3$·2PbO, α-PbO, and β-PbO, successively. Particularly, PbCO$_3$·PbO and PbCO$_3$·2PbO have a trend of increase before 300 °C, and a decrease trend after 300 °C. Then, PbCO$_3$·2PbO has a faster trend of decrease after 300 °C than PbCO$_3$·PbO. Compared to the possible reactions comprehensive analysis, and the decomposition equilibrium of 1 kmol PbCO$_3$ was consistent. Combined with the decomposition process for PbCO$_3$, the intermediate solid products PbCO$_3$·PbO and PbCO$_3$·2PbO, and final products α-PbO and β-PbO all can exist. Once the PbCO$_3$ was

Figure 7. Decomposition equilibrium of 1 kmol PbCO₃ in defined system

fully decomposed into PbO, the amount of carbon dioxide and lead oxide is essentially unchanged, but which must ensure the temperature was more than 300 °C and also provided the basis of temperature for preparing lead oxide.
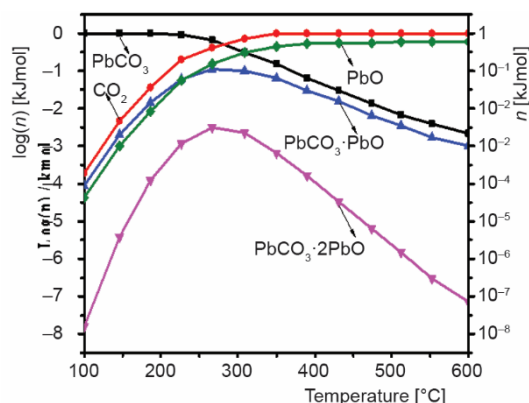
The TG/DSC analysis of recycled lead carbonate
from waste lead acid battery

For verifying the possible results of the thermodynamic calculation reaction R1-R11, the TG/DSC analysis under vacuum conditions was completed. Simultaneous TG/DSC results was shown in fig. 8. The total thermal decomposition process of recycled lead carbonate (10 mg raw materials) was divided into two mass loss stages at the different heating rate of 1, 5, and 10 K per minute in a vacuum system pressure of 0.2 atmosphere, respectively. In order to
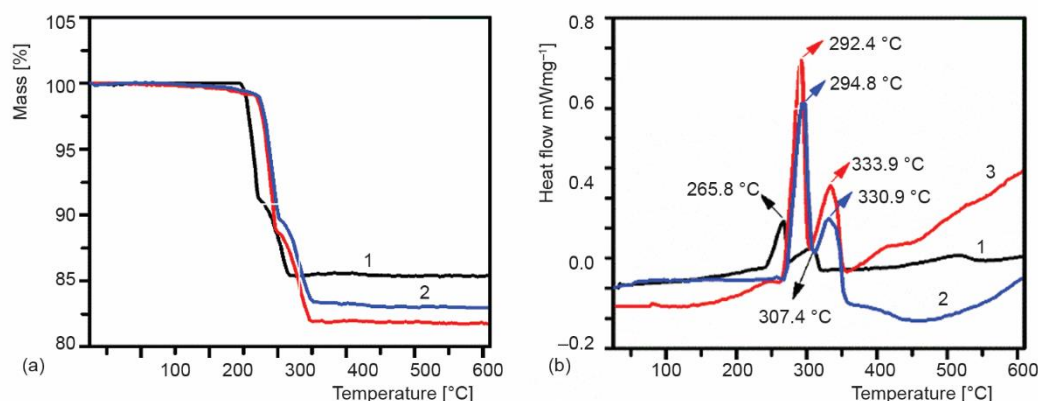

Figure 8. Thermogravimetric and heat flow analysis of 10 mg raw materials in a vacuum system pressure of 0.2 atmosphere; *1 – 1 K per minute, 2 – 5 K per minute, 3 – 10 K per minute*

clearly obtain the decomposition process of lead carbonate detailed, different heating rate was employed to complete the decomposition of recycled lead carbonate in vacuum. It is noteworthy to employ that different heating rate play an important role in the decomposition process. Low heating rate can ensure that the any tiny intermediate information can be hold. On the contrary, high heating rate can make the some tiny intermediate information lost. According to fig. 8 involved the decomposition of lead carbonate, the different heating rate of 1, 5, and 10 K per minute have the similar shape of peaks. With the increase of heating rate from 1 K per minute to 10 K per minute, thermal weightlessness loss curve gradually move to high temperature, and the location of the highest mountain in the DSC curve also shift to the right, the peak height increases, the maximum weight loss rate increased obviously. The onset reaction temperature for the process increased from approximately 260 °C to 310 °C, and the final reaction temperature increased from or so 325 °C to 350 °C. However, when the heating rate was increased from 5 K per minute to 10 K per minute, the corresponding weight loss and heat flow curve tends to be consistent. That is, the final weight loss of lead carbonate is almost unchanged, indicating that when the decomposition temperature reaches 350 °C, the final weight loss of lead carbonate decomposition does not change with the change of heating rate.

As observed in fig. 8(a), when the temperature range is 230-310 °C, the raw material has major mass loss with an enormous heat needing. When the temperature range is 310-400 °C, the mass loss decreased slightly, which is caused by intermediate product further decomposition accompanied by a weak absorption peak. The original mass loss of the raw material is about 10.95 wt.% when the temperature reach 310 °C. As the temperature rises to 400 °C further, the second stage mass loss of the raw material is approximately 5.46 wt.%. The lead carbonate has poor thermal stability, it is possible to decompose in vacuum. Combined with fig. 8(b), the obvious endothermic peak of the raw material indicate that the lead carbonate decomposed into intermediate compounds in the temperature range of 230-310 °C. After 400 °C, TG curves were smooth and the mass loss equal to 0, which meant that the raw material had been decomposed totally, but heat flow of the absorption peak existed indicate a phase transition process appeared in vacuum atmosphere.

The detailed decomposition mechanism of lead carbonate was simple and was affected by the heating rate, the temperature of the corresponding maximum absorption peak and mass loss stage obtained by the heating rate of 5 K per minute and 10 K per minute is similar, and can be seen that decomposition temperature increased as the heating rate increased and higher heating rate helped to accelerate the reaction accomplishment. Also, based on the above comprehensive analysis, we considered that the temperature rise is slow about the real vacuum furnace conditions and the experiments was time-consuming. Thus, thermal decomposition experiments, the heating rate of 10 K per minute was suggested in the following.

Analysis of vacuum thermal decomposition products

On the basis of thermodynamics calculation and TG/DSC analysis, the decomposing process conditions are set to 230, 250, 280, 310, 340, 370, 400, 430, 460, 490, 520, 550, 580, and 610 °C for 30 minutes in vacuum atmosphere of 30-100 Pa, respectively. To clarify the process of decomposing, about 20 g recycled lead carbonate powder was fed into the crucible placed simultaneously into vacuum furnace (fig. 2). The XRD detections of decomposing products after decomposing are shown in fig. 9. As shown in fig. 9(a), there is the only kind of stable compound, $PbCO_3 \cdot 2PbO$, ranging from 230-310 °C. When the temperature is set to 230 °C, one kind of white solid product is detected from the decomposing product; it is $PbCO_3$. When the temperature reached 250 °C, two kinds of solids product are detected from the

decomposing product; They are $PbCO_3$ and $PbCO_3 \cdot 2PbO$ and the peak height of $PbCO_3 \cdot 2PbO$ is weak, which corresponded to the theoretical decomposition temperature of 230 °C. When the temperature increased from 250 °C to 280 °C or 310 °C, the color of product was deepen to red and $PbCO_3$ and $PbCO_3 \cdot 2PbO$ are detected from the decomposing red product and the peak height of $PbCO_3 \cdot 2PbO$ improves clearly, and this temperature range for decomposing was consistent with the equilibrium diagram of thermal decomposition of lead carbonate in fig. 7. When the temperature is raised to 340 °C, $PbCO_3$, α-PbO, and $PbCO_3 \cdot 2PbO$ are detected from the decomposing product and the peak height of $PbCO_3$ decreases strongly. When the temperature is elevated to 370 °C, the color of product was red, $PbCO_3$ is not detected from the decomposing product and the peak height of α-PbO and $PbCO_3 \cdot 2PbO$ improves further strongly. As shown in fig. 9(b), then the process of reaction of lead carbonate is more fully under 400 °C and 430 °C while $PbCO_3 \cdot 2PbO$ is used up. Also red product α-PbO is the only phase after decomposing at 400 °C and 430 °C for 30 minutes. The peak height of α-PbO at 430 °C was much higher than 400 °C was, which also confirmed the temperature of TG/DSC results with 400 °C for decomposing completely. As shown in fig. 9(c), the peak of β-PbO in the decomposing products was originally found the color of product was still red, and XRD results of decomposing products shown the peak of α-PbO and β-PbO was hold and the peak height of α-PbO was decreasing gradually, when the temperature is increased from 460 °C to 550 °C,
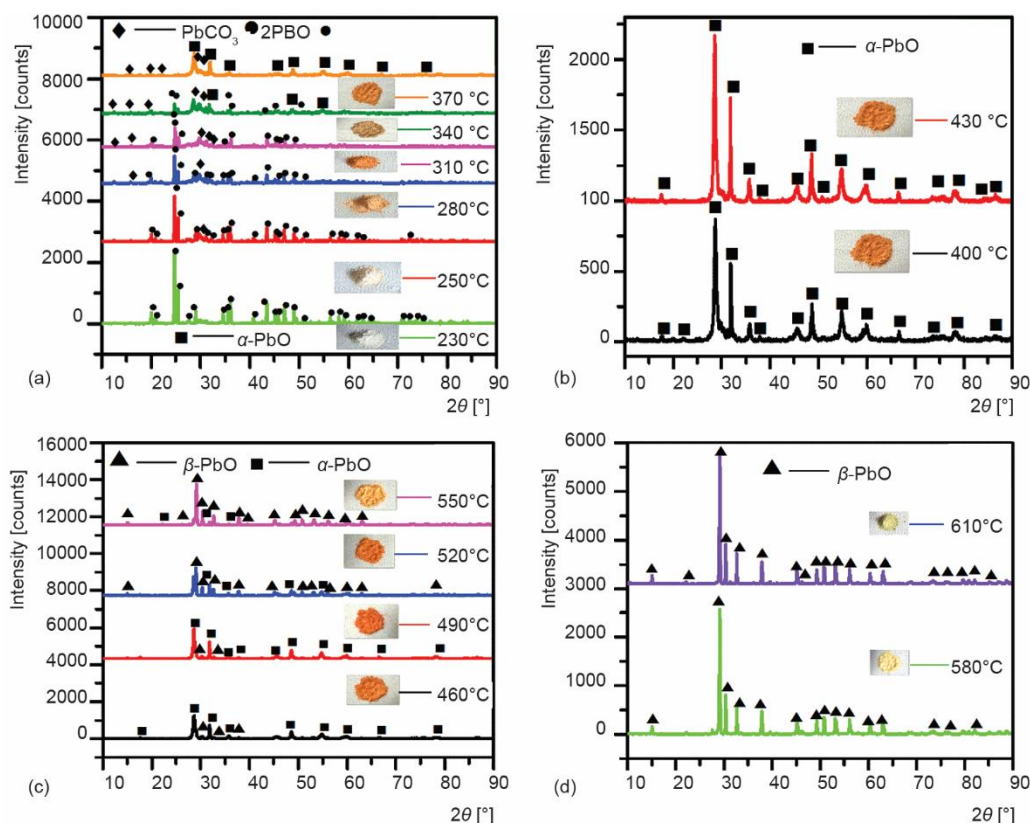
**Figure 9. The XRD detection of decomposing products after decomposing at different temperature for 30 minutes in vacuum atmosphere**

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and the color of product was becoming gradually yellow, which corresponded to the calculated transformation temperature of 460 °C. In fig. 9(d), when the temperature is increased from 580 °C to 610 °C, XRD results of decomposed yellow products only found the peaks of β-PbO.

The obtained results for decomposing the recycled lead carbonate from fig. 9, the vacuum thermal decomposition furnace were compared with the results of vacuum thermodynamics calculations and TG/DSC analysis. The product results decomposed indicated that phase composition $PbCO_3 \cdot PbO$ was not detected in this process, but the thermal decomposition phase $PbCO_3 \cdot 2PbO$, α-PbO, and β-PbO was consistent with the thermodynamics theoretical calculation results. Further research will focus on the vacuum thermal decomposition kinetics of recycled lead carbonate in this process because lead carbonate does not decompose completely. This study provides a theoretical basis of recycled lead carbonate from waste lead acid battery thermal decomposition in vacuum atmosphere.

In addition, after the decomposition, the relationship between temperature and decomposition rate also was provided in fig. 10.
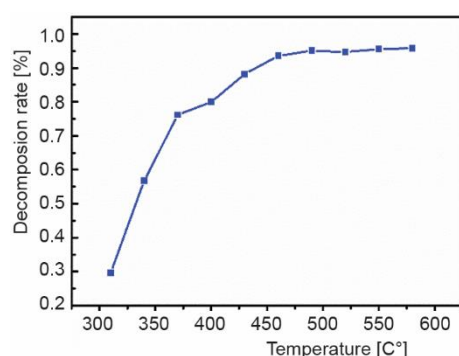
Figure 10. Relationship of temperature between decomposition rate

Figure 10 showed while the temperature rose from 310 °C to 580 °C, the decomposition rate gradually increased from 29.62% to 95.76%. The color of solid products had an apparent difference along with temperature variation, which confirmed that the temperature contributed to decompose to lead oxide. Meanwhile, the decomposition rate increased from 29.62% to 95.10%, while the temperature rose from 310 °C to 490 °C, and the color of solid products deepened because more lead carbonate decomposed. When the temperature increased from 490 °C to 580 °C, the solid products only contained α-PbO and β-PbO. When the temperature changed from 490 °C to 580 °C, α-PbO converted into β-PbO.

According to the previous analysis, the decomposition process of lead carbonate under vacuum was confirmed: $PbCO_3 \rightarrow PbCO_3 \cdot 2PbO \rightarrow \alpha$-PbO. Thus, the enthalpy results for thermal decomposition reactions with different temperatures were calculated by HSC software and listed in tab. 2.

**Table 2. The enthalpy results for thermal decomposition reactions with different temperatures**

Reaction	T [°C]	100	200	300	400	500	600
$3PbCO_3 = PbCO_3 \cdot 2PbO + 2CO_2(g)$	ΔH [kJ]	153.208	130.933	105.686	77.364	45.887	11.184
$PbCO_3 \cdot 2PbO = \alpha$-PbO + $CO_2(g)$		106.478	125.462	145.393	166.201	188.356	210.054

Table 2 found that the reaction $3PbCO_3 = PbCO_3 \cdot 2PbO + 2CO_2(g)$ and the reaction $PbCO_3 \cdot 2PbO = \alpha$-PbO + $CO_2(g)$, all were endothermic, so the higher temperatures supported the decomposition. When the temperature was beyond 300 °C, the decomposition of $PbCO_3 \cdot 2PbO$ needed more heat to convert into α-PbO corresponding to higher decomposition rate.

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Conclusions

In order to improve the recycling of lead carbonate in waste lead acid batteries, the thermal decomposition under vacuum was used to study it. The conclusions obtained are as follows.

- Thermal decomposition reaction of recycled lead carbonate from waste lead acid battery under vacuum atmosphere. The reaction equation can be described:

$$3PbCO_3 = PbCO_3 \cdot 2PbO + 2CO_2(g)$$

$$PbCO_3 \cdot 2PbO = 3\alpha\text{-PbO} + CO_2(g)$$

$$\alpha\text{-PbO} = \beta\text{-PbO}$$
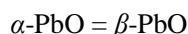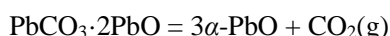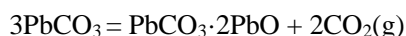
- The vacuum thermal decomposition reaction process of recycled lead carbonate has the only intermediate phase $PbCO_3 \cdot 2PbO$ from 250 °C to 370 °C, preservation time 30 minutes. The reaction of vacuum thermal decomposition process of recycled lead carbonate is more fully under 400 °C and 430 °C, 30 minutes, the decomposing red product is α-PbO; The vacuum thermal decomposition reaction process of recycled lead carbonate is more fully under 580 °C and 610 °C, 30 minutes, the yellow product is β-PbO.
- This process is an exploratory investigation at laboratory scale. It gave the clear relationship between the products and temperatures of decomposition process. It will contribute to control the accurate decomposition temperature for directional decomposition to obtain pure product or avoid intermediates such as $PbCO_3 \cdot PbO$, $PbCO_3 \cdot 2PbO$ or others. It also provided the researcher sight for the more waste solid materials by "transform-recycle-regeneration".

Acknowledgment

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