

Thermal study of organic electrolytes with fully charged cathodic materials of lithium-ion batteries

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Received: 20 April 2007 / Revised: 13 June 2007 / Accepted: 23 July 2007 / Published online: 9 September 2007
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Abstract We systematically investigated thermal effects of organic electrolytes/organic solvents with fully charged cathodic materials ($\text{Li}_{0.5}\text{CoO}_2$) of Li-ion battery under rupture conditions by using oxygen bomb calorimeter. In the six studied systems, both the amount of combustion heat and heat release rates showed a pronounced increase with the increase in mass ratios of cathodic materials to electrolytes/solvents. More importantly, synergistic effects not simply physical mixtures have firstly been observed between cathodic materials and electrolytes/solvents in the complete combustion reactions. The results have been further analyzed by X-ray diffraction spectra, which revealed that Co_3O_4 , CoO , and LiCoO_2 were the main solid products for the combustion reactions of studied systems. And there are more CoO and less LiCoO_2 products for the higher ratio of cathodic materials system and more amount of heat generated. It means that the combustion reaction, which produced CoO , generated more amount of heat than LiCoO_2 .

Keywords Lithium-ion battery · Thermal effect · Combustion reaction · Fully charged cathode · Organic electrolyte

Introduction

When the environmental pollution and the crisis of energy become a hot topic, the development of hybrid vehicles has been paid more and more attentions. Lithium-ion battery systems, with large power and energy density as a best candidate for the power source of hybrid vehicles, have not been widely utilized because of safety issues. The heat will be accumulated inside of the batteries, probably accompanied by thermal runaway and even cell burning, if they are kept running under thermal or abusive conditions (e.g., at elevated temperature or high charge/discharge rates). Recently, the cases of cell burning in Dell, Sony, and Apple notebooks have come to public attention on the further application of lithium-ion batteries due to safety concerns.

Various abuse tests (e.g., oven-heating, short-circuit, overcharge, nail, and crush) [1–6] are used to characterize the abuse tolerance of lithium-ion batteries. Furthermore, direct analyses on thermal stabilities of battery materials have been carried out by accelerating rate calorimetry (ARC) [7–12], differential scanning calorimetry (DSC) [12–24], and thermogravimetric analysis (TGA) [14, 15, 17] techniques.

However, most thermal research of lithium-ion batteries just focused on the sealed cell. Analytical techniques such as ARC and DSC are also performed in the sealed testing system. In practice, abusive operations and the consequent thermal runaway may break the sealed cell. Then high temperature inside of the cell combined with up-rushed oxygen from the air will cause the burning of active cell components. This situation is especially dangerous for the fully charged or even overcharged cell, whose active material of cathode is a strong oxidizing agent and more exothermically reactive with electrolyte. The instantaneous

Electronic supplementary material The online version of this article (doi:10.1007/s10008-007-0400-7) contains supplementary material, which is available to authorized users.

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release of combustion heat is probably large enough to become an original motivation of cell explosion. Therefore, it is indispensable to study the complete combustion reactions of organic electrolytes with fully charged cathodic materials, which helps to better understand the heat-generated mechanism of a ruptured lithium-ion battery. In our work, the heat for the combustion of organic electrolytes, organic solvents combined with fully charged cathodes were respectively investigated by using oxygen bomb calorimeter. And the solid products of these combustion reactions were determined by using X-ray diffraction analysis.

Materials and methods

Preparation for fully charged cathode

The cathodic material used in the testing was taken from a fully charged Li-ion cell ($\text{Li}_x\text{C}_6/\text{1M LiPF}_6/\text{Li}_{1-x}\text{CoO}_2$, with the capacity of 400 mAh) in a dry glove box. The cathodic electrode contained 90 wt.% LiCoO_2 , 5 wt.% carbon black, and 5 wt.% poly(vinyl difluoride) (PVdF) binder, coated on an Al foil substrate. The battery was fully charged as following: firstly charged to 4.20 V and then cycled twice between 2.75 V and 4.20 V with a constant current of 40 mA (0.1 C) at room temperature of 20 °C. After charged to 4.20 V again and kept at constant 4.20 V for 3 h (SOC=1), the fully charged battery was opened in the glove box. The positive electrode powder was scraped out from the Al foil substrate and washed with dimethyl carbonate (DMC) to remove the electrolyte. At last, the testing powder was under vacuum for 2 h to remove the DMC solvent. The crystal structure of prepared cathode sample was identified by X-ray diffraction analysis, and $\text{Li}_{0.5}\text{CoO}_2$ was considered as the main active material.

Heat measurement of combustion

The heat measurement of combustion for electrolyte (or solvent) with cathodic material was carried out by using oxygen bomb calorimeter (Julius Peters Berlin). The calorimeter and the related calculation were detailedly described in the supplemental information.

In this work, three organic electrolytes and their corresponding solvents (without salt LiPF_6) are extensively investigated: (a) 1 M LiPF_6 /ethylene carbonate (EC): DMC: diethyl carbonate (DEC)=1:1:1, (b) EC:DMC:DEC=1:1:1, (c) 1M LiPF_6 /EC:DMC=1:1, (d) EC:DMC=1:1, (e) 1 M LiPF_6 /EC:DEC=1:1, and (f) EC:DEC=1:1 (all in volume ratios). Each testing sample for the heat measurement of combustion is composed of two parts: organic electrolyte (or organic solvent) with a fixed mass of 1.50 g and fully

charged cathodic materials whose mass varied from 0 to 0.50 g (0, 0.10, 0.20, 0.30, 0.40, and 0.50 g).

X-ray diffraction analysis

After the heat measurement of every testing sample by oxygen bomb calorimeter, the solid remains of combustion were taken out from the bomb and analyzed by X-ray diffraction (XRD). A Bruker D8 Advance X-ray Diffractometer was used at a scan rate of $7.5^\circ \text{ min}^{-1}$ with $\text{CuK}\alpha$ radiation.

Results and discussion

Combustion heat of organic electrolyte with fully charged cathodic material

Figure 1 shows the changes of bulk water temperature relative to the starting temperature ($T-T_0$) as a function of time for the combustion of organic electrolyte 1 M LiPF_6 /EC: DMC:DEC=1:1:1 (in volume ratios, $V/V/V$) ($m_{\text{ele}}=1.50$ g) with different mass of fully charged cathodic materials ($m_{\text{cat}}=0-0.50$ g). A series of combustion reactions completely occur owing to the existence of enough oxygen. And all the curves present some similar characteristics: (1) $t=0-12$ min, the system temperature increases slightly and becomes relatively stable with a low starting value (1 °C below the room temperature), the same in different test samples; (2) $t=12-15$ min, the temperature of bulk water rises sharply once

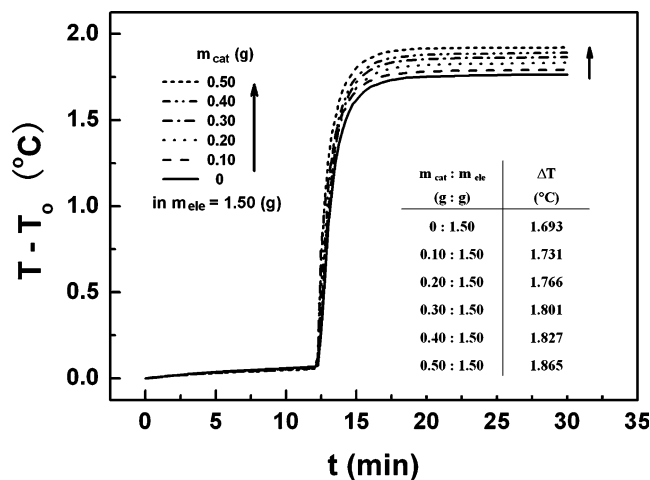


Fig. 1 Changes of bulk water temperature in oxygen bomb calorimeter relative to the starting temperature ($T-T_0$) as a function of time (t) for the combustion of organic electrolyte 1 M LiPF_6 /EC: DEC:DMC=1:1:1 ($V/V/V$; $m_{\text{ele}}=1.50$ g) with different mass of fully charged cathodic material ($m_{\text{cat}}=0, 0.10, 0.20, 0.30, 0.40,$ and 0.50 g). *Inset table*: temperature rise (ΔT) corresponding to the mass ratio of cathodic material to electrolyte ($m_{\text{cat}}:m_{\text{ele}}$) for every combustion curves

the testing sample is ignited (at $t=12$ min) in each sample. The fully charged cathode can notably benefit the heat generation of electrolyte combustion reactions in lithium-ion batteries; (3) $t=15$ – 30 min, the temperature reaches the plateau after the reactions are completely finished. During the whole process, the heat transfer between the bomb calorimeter and the corresponding surroundings cannot be fully avoided. The variation in temperature caused by this effect can be calibrated by the Reynolds temperature correction curve [25]. This correction was carried out in each combustion curves to avoid the agitation of the system and obtain the real temperature rise (ΔT) for each testing samples.

The combustion curves indicate that all the testing samples instantaneously release all the heat from combustion reactions. The exothermic effects in oxygen bomb are more violent and prompt than in the sealed system at elevated temperature by ARC or DSC analysis. The phenomenon suggests that it is much more dangerous/explosive for the fully charged Li-ion battery even with a tiny aperture opened to the air than a sealed cell at high temperature.

On the other hand, the heat release for the combustion reactions of organic electrolyte with fully charged cathodic material is much faster than without cathodic materials, as shown in Fig. 1. The peaks corresponding to exothermic reactions shift to the left with the increase in mass ratio of cathodic material to electrolyte and the slopes of the curves become steeper. To further understand the instantaneous processes of combustion reactions, the differential curves of combustion from Fig. 1 are plotted in Fig. 2. Figure 2 shows the temperature rise rate (dT/dt) as a function of time during the period of combustion reactions for each sample.

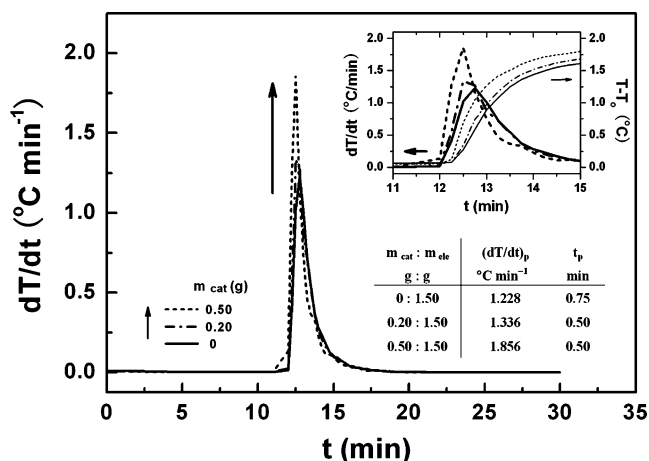


Fig. 2 Temperature rise rate (dT/dt) as a function of time (t) during the period of combustion reactions for organic electrolyte 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}:\text{DMC}=1:1:1$ ($V/V/V$; $m_{ele}=1.50$ g) with fully charged cathodic material ($m_{cat}=0, 0.20$, and 0.50 g). *Inset table*: peak value of temperature rise rate ($dT/dt)_p$ and the time for reaching the peak value since ignition t_p corresponding to the mass ratio of cathodic material to electrolyte ($m_{cat}:m_{ele}$) for every differential combustion curves

The temperature rise rate of bulk water in oxygen bomb calorimeter should be closely associated with the heat release rate of combustion reaction. The curves in Fig. 2 indicate a higher heat release rate for a higher mass ratio of cathodic material to electrolyte. The inserted table of Fig. 2 lists the peak value of temperature rise rate ($dT/dt)_p$ and the time for reaching the peak value since ignition t_p . It reveals that the value of $(dT/dt)_p$ for blank electrolyte system is 1.228 $^{\circ}\text{C min}^{-1}$, and when the mass ratio of cathodic material to electrolyte rises to 0.50 g/ 1.50 g, the peak value reaches 1.856 $^{\circ}\text{C min}^{-1}$. Thus, even with the addition of 25.0 wt.% cathodic materials, the testing sample is ca. 1.5 times of the temperature rise rate in comparison with the single electrolyte system. Then considering the corresponding time of peak (t_p), it has been shortened from 0.75 min for the blank system to 0.50 min for the cathode-added system. In this study, the temperature rise is not too high (less than 2 $^{\circ}\text{C}$) because of the huge volume of bulk water as the heat receiver compared to that of samples (less than 2 g). But in a real Li-ion battery, the heat is more than enough to cause the battery explosion.

Combining with the exothermic effects in the preceding description, both the heat and heat release rate of the electrolyte combustion are markedly increased due to the addition of fully charged cathodic material. It implies that the fully charged cathode, whose active material is known as a strong oxidizing agent ($\text{Li}_{0.5}\text{CoO}_2$), can greatly promote the positive electrode/electrolyte combustion reaction, in which much more heat is released at a much higher speed during a very short time compared with the combustion reaction of electrolyte alone.

In this study, the quantitative analysis is achieved for the exothermic heats in combustion reactions. The inserted table in Fig. 1 lists the temperature rise ΔT for every combustion curve. Then the combustion heat (q_v) corresponding to the temperature rise (ΔT) for every testing sample is respectively calculated (the detailed calculation present in the supplements). The amount of combustion heat vs the mass of cathodic materials is plotted in Fig. 3. A linear relationship has been well determined in curve (a), with the linear correlation: $q_v(\text{kJ}) = (-23.24) + (-4.64) \times m_{cat}(\text{g})$. The intercept of fitted line (-23.24 kJ) is the combustion heat of blank electrolyte (1.50 g 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}:\text{DEC}=1:1:1$), by which the heat of combustion can be calculated: $q_{ele}^{\circ} = -23.24$ kJ/ 1.50 g = -15.49 kJ g_{ele}^{-1} . And the value of slope represents the heat rise per gram of fully charged cathodic material added to electrolyte: $\Delta q_{cat} = -4.64$ kJ g_{cat}^{-1} . They are both listed in the inserted table of Fig. 3.

The previous DSC analysis revealed that the charged cathodic material (Li_xCoO_2 , $0.5 \leq x < 1$) released the heat of 60 – 146 J g^{-1} during its thermal decomposition at about 200 $^{\circ}\text{C}$ [6, 15, 19]. So here the much larger heat rise

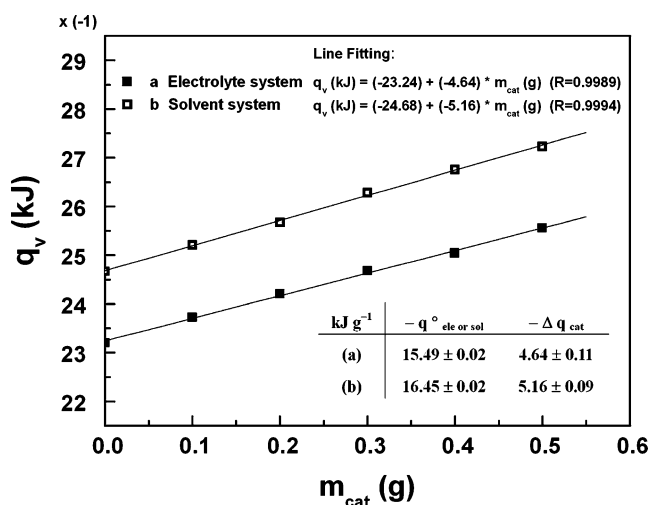


Fig. 3 Heat of combustion (q_v) as a function of the mass of fully charged cathodic material (m_{cat}) added to: (a) 1 M $\text{LiPF}_6/\text{EC}:\text{DEC}:\text{DMC}=1:1:1$ ($V/V/V$) organic electrolyte, and (b) $\text{EC}:\text{DEC}:\text{DMC}=1:1:1$ ($V/V/V$) organic solvent test system ($m_{\text{ele or sol}}=1.50$ g). *Inset table:* heat of combustion for single electrolyte or solvent ($q^{\circ}_{\text{ele or sol}}$; kJ g^{-1}) and heat rise per gram of fully charged cathodic material added to electrolyte or solvent (Δq_{cat} ; kJ g^{-1}) respectively for (a) organic electrolyte and (b) organic solvent test systems (based on the intercept and slope of both fitted lines)

($-4.64 \text{ kJ g}_{\text{cat}}^{-1}$) should not be attributed to the heat generation from charged cathode itself. It indicates a pronounced synergistic relationship between electrolytes and fully charged cathodic materials in the complete combustion reactions. Thus, in an actual cell with the common mass ratio of cathodic material to electrolyte (1:0.3), the combustion heat of electrolyte with fully charged cathode should be two times of the electrolyte alone. So the synergistic effect of fully charged cathode is very significant on the combustion heat of electrolyte in a real lithium-ion battery.

In a sealed system without oxygen, a complex synergistic relationship was also reported among the electrolyte and delithiated Li_xCoO_2 and/or its decomposition products that created a large exothermic reaction by DSC or ARC analysis. The combination of these materials probably catalyzed the electrolyte/oxygen reaction. The heat of reaction for charged cathode decomposition was coupled with that of solvent oxidation [6, 15, 19]. However, the mechanism has not been clearly explained up to now. In this work by using oxygen bomb calorimeter, the exothermic effect of a rupture cell is initially investigated. In this study, with the existence of sufficient oxygen, the organic electrolyte with fully charged cathode might completely react in a direct way, accompanied by the instantaneous release of huge combustion heat. This rather violent exothermic reaction probably induces a more pronounced synergistic effect than the sealed system. The exact explanation needs to be further investigated in our future work.

Combustion heat of organic solvent with fully charged cathodic material

Fully charged cathodic material can increase the heat and heat release rate of combustion reactions for the electrolyte. Organic electrolyte is important to the whole heat effect of combustion reaction. To further disclose the contribution of every component to the combustion heat in a real battery, the corresponding solvent system $\text{EC}:\text{DEC}:\text{DMC}=1:1:1$ ($V/V/V$) is also investigated in our studies. The heat measurements follow the same procedure as aforementioned in the electrolyte system.

The curve (b) in Fig. 3 shows the accurate values of combustion heat q_v for 1.50 g solvent combined with 0–0.50 g fully charged cathodic material. It again presents a good linear relationship between the heat value and the mass of cathodic material. And the linear correlation for curve (b) is also shown in Fig. 3: $q_v(\text{kJ}) = (-24.68) + (-5.16) \times m_{\text{cat}}(\text{g})$. The value of intercept (-24.68 kJ) is the combustion heat of blank solvent (1.50 g $\text{EC}:\text{DEC}:\text{DMC}=1:1:1$), by which the heat of combustion can be calculated: $q^{\circ}_{\text{sol}} = -24.68 \text{ kJ}/1.50 \text{ g} = -16.45 \text{ kJ g}_{\text{sol}}^{-1}$. And the value of slope represents the heat rise per gram of fully charged cathodic material added to solvent: $\Delta q_{\text{cat}} = -5.16 \text{ kJ g}_{\text{cat}}^{-1}$. They are also listed in the inserted table of Fig. 3.

In this study, the large heat rise ($-5.16 \text{ kJ g}_{\text{cat}}^{-1}$) indicates a synergistic relationship between the cathodic material and solvent in their combustion reactions, the same as the foregoing electrolyte system. On the other hand, the solvent system (without salt LiPF_6) shows a more significant effect on the heat (q°) and the heat rise rate (Δq_{cat}) compared with the foregoing electrolyte system (with LiPF_6). It suggests that the exothermic effect of the combustion reactions can be effectively reduced with the existence of salt LiPF_6 in electrolyte. The similar phenomena were observed in the sealed testing system. MacNeil and Dahn [10] studied the thermal reactions of fully charged cathodes with x M $\text{LiPF}_6/\text{EC}, \text{DEC}$ ($0 < x < 1.5$) electrolyte by using ARC measurement and found that the solvent combustion reaction was depressed as the LiPF_6 concentration was increased. Baba et al. [19] also found the more exothermic reaction in the cathode and solvent system than in the cathode and electrolyte (with LiPF_6) system by DSC analysis. The results reveal that no matter in the sealed system or for the rupture case: the thermal effects of lithium-ion batteries can be effectively reduced with the addition of lithium salt LiPF_6 , which should be taken into consideration when optimizing the thermal design of Li-ion battery especially with large capacity.

Combustion heat of other electrolyte/solvent systems

The above studies on the organic electrolyte and its solvent systems have disclosed the effects of lithium salt LiPF_6 on

the exothermic heat during the period of combustion reactions. To systematically explore the thermal effects of different solvents, the dual solvents systems (EC, DMC, or DEC) are further investigated. The combustion heats for four testing systems: EC/DMC and EC/DEC with and without 1 M LiPF₆ are respectively studied following the same procedures as aforementioned in the tri-solvent testing system. Figure 4 shows an overall view of the heat effect of fully charged cathodic material on the combustion of di-solvent systems: circle and triangle marks, respectively, for the (EC, DMC) and (EC, DEC) testing systems; as well as square marks for the foregoing tri-solvent (EC, DMC, DEC) system by comparison. Linear relationships between the combustion heat and the mass of cathodic material are well determined in all six studied systems when the electrolytes or solvents keep a fixed mass. It clearly reveals that owing to the existence of fully charged cathode, the changes happen during the period of combustion reactions (under sufficient oxygen atmosphere). And cathodic materials show the prominent synergistic effects on the exothermic reactions, which also depends on the mass ratios of cathodic material to electrolyte/solvent in the testing samples.

The heat of combustion for electrolyte or solvent ($q^{\circ}_{\text{ele or sol}}$) and the heat rise per gram of cathodic material added to electrolyte or solvent (Δq_{cat}) were respectively calculated from the intercepts and slopes of their fitted lines, as shown in Fig. 5.

Each electrolyte systems have the less exothermic heat compared with their corresponding solvent systems. This effects by the existence of salt LiPF₆ in electrolytes are

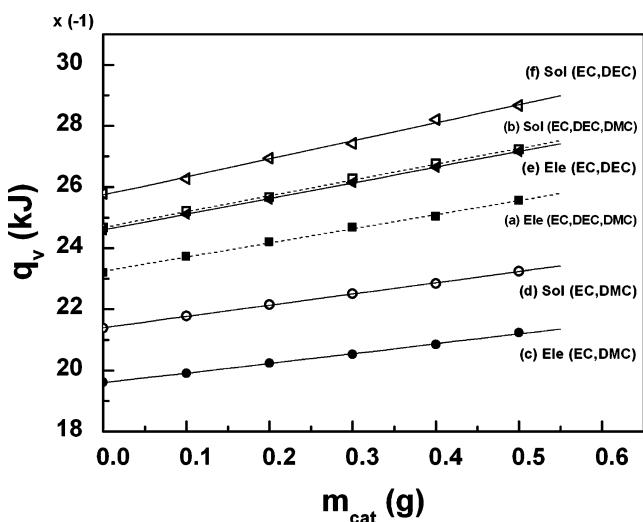


Fig. 4 Combustion heat q_v (kJ) as a function of the mass of fully charged cathodic material m_{cat} (g) for different electrolyte or solvent test systems: (a) 1 M LiPF₆/EC:DMC:DEC=1:1:1; (b) EC:DMC:DEC=1:1:1; (c) 1 M LiPF₆/EC:DMC=1:1; (d) EC:DMC=1:1; (e) 1 M LiPF₆/EC:DEC=1:1; and (f) EC:DEC=1:1 (all in volume ratio). In every test system, electrolyte or solvent keeps a fixed mass of 1.50 g

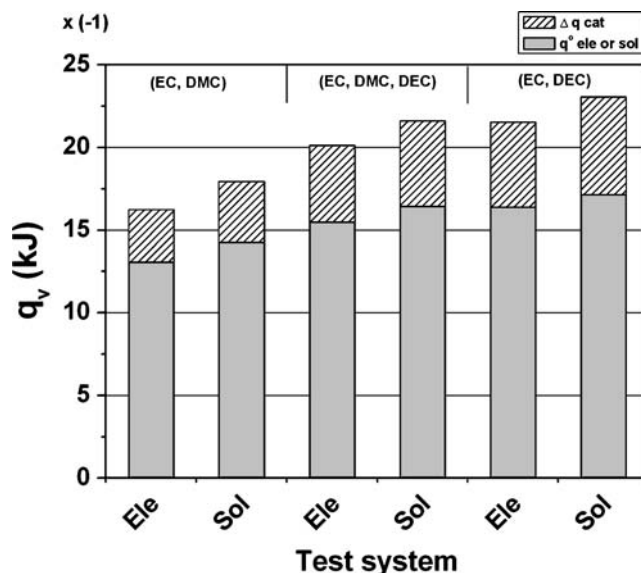


Fig. 5 Heat of combustion for single electrolyte or solvent ($q^{\circ}_{\text{ele or sol}}$, kJ g⁻¹) and heat rise per gram of fully charged cathodic material added to electrolyte or solvent (Δq_{cat} , kJ g⁻¹) respectively for every test system (based on the intercept and slope of each line in Fig. 4)

absolutely independent on the types of organic solvents and lead to the overall decreases both in the heat of combustion of electrolytes (q° , bottom columns in the histogram) and in the heat rise rate with the addition of fully charged cathodic materials (Δq_{cat} , top columns). Roughly, electrolyte systems have the decrease ratios of 4.5–8.4% and 10.0–13.1% for q°_{ele} and Δq_{cat} , respectively, compared with their corresponding solvent systems. Therefore, the safety of lithium-ion batteries can be effectively improved by the addition of lithium salt LiPF₆.

In an overall view of the histogram, (EC, DEC)-based solvent system (without LiPF₆) has the largest values of q°_{sol} (–17.16 kJ g⁻¹) and Δq_{cat} (–5.89 kJ g⁻¹); (EC, DMC)-based electrolyte system (with LiPF₆) has the smallest exothermic heats of q°_{ele} (–13.06 kJ g⁻¹) and Δq_{cat} (–3.19 kJ g⁻¹); and (EC, DEC, DMC)-based systems are located in the middle region. The phenomenon suggests that the solvent DEC would be rather exothermically active during combustion, consequently with the more heat release. This should be dominantly attributed to the much larger heat of combustion for the pure solvent DEC (–2,710.8 kJ mol⁻¹, 20 °C, at 1 atm.) [26] than that of DMC (–1,425.9 kJ mol⁻¹, 20 °C, at 1 atm.) [26] and EC (–1,161.4 kJ mol⁻¹) [27]. Therefore, the use of solvent DEC in electrolyte is unfavorable for a safe lithium-ion battery.

As a result of above quantitative analysis, both the heat of electrolyte/solvent (–13.06 to –17.16 kJ g⁻¹) and the heat rise owing to the charged cathodic materials added to the electrolyte/solvent (–3.19 to –5.89 kJ g⁻¹) are much larger than the corresponding heat effects reported by ARC

or DSC measurement. In ARC or DSC analysis, the thermal stabilities of active cell components were studied in a sealed and inert gas-filled testing system at elevated temperature. The results revealed that electrolytes/solvents released the heat in a main range of 370–530 J g⁻¹ at about 230–280 °C [6, 12, 23]. Furthermore, for the charged cathode with electrolyte/solvent system, the exothermic effect was reported in a range of 420–1,200 J g⁻¹ based on the cathode weight, which was considered from the oxidation of electrolyte/solvent by the oxygen liberated during the thermal decomposition of cathodic material at ca. 130 °C [10, 18, 19]. Thus, for a sealed Li-ion cell at high temperature, fully charged cathode may exothermically react with electrolyte/solvent in an indirect way, potentially inducing thermal runaway.

In this study, the testing samples are kept under sufficient oxygen atmosphere with the aim to simulate the thermal behavior of a ruptured battery for the first time. In this case, the complete combustion reactions of organic electrolyte/solvent with fully charged cathode can promptly happen in a direct way once they are ignited, accompanied by a much more exothermic and short-lived heat release compared with the sealed system. The rather huge combustion heat might result in the cell explosion eventually.

Solid products analysis of cathodic materials

In pursuit of a further study on the combustion reactions of electrolyte or solvent with charged cathodic material, X-ray diffraction is used to analyze the solid remains in oxygen bomb calorimeter after the combustion for each testing samples. The curves in Fig. 6 show the XRD profiles of solid products after combustion reactions: 1.50 g organic electrolyte (1 M LiPF₆/EC:DMC:DEC=1:1:1 (V/V/V)) respectively with (a) 0.10, (b) 0.30, and (c) 0.50 g of fully charged cathodic material (Li_{0.5}CoO₂) in the bottom figure and 1.50 g organic solvent (EC:DMC:DEC=1:1:1), respectively, with (d) 0.10 g, and (e) 0.50 g fully charged cathodic material in the top figure.

In curve (a) for the lowest mass ratio of cathodic material to electrolyte (0.10/1.50 g), the peaks assigned to face-centered cubic Co₃O₄ (Fd3m; at around 19.0°, 31.3°, 36.8°, 38.5°, 44.8°, 59.4°, and 65.2°) and rhombohedral LiCoO₂ (R-3m; chiefly at about 18.9°, 45.3°, and 69.7°) were respectively indexed in comparison with a series of standard XRD patterns. Therefore, Co₃O₄ and LiCoO₂ are considered as the main solid products in the complete combustion reaction of organic electrolyte with a rather low concentration of cathodic materials (main active material Li_{0.5}CoO₂). Then when increasing the mass ratio up to 0.30/1.50 g ($m_{\text{cat}}/m_{\text{ele}}$), two new peaks at around 42.6° and 77.5° come up in curve (b), both attributed to the face-centered cubic CoO (Fm3m). And for the highest mass of

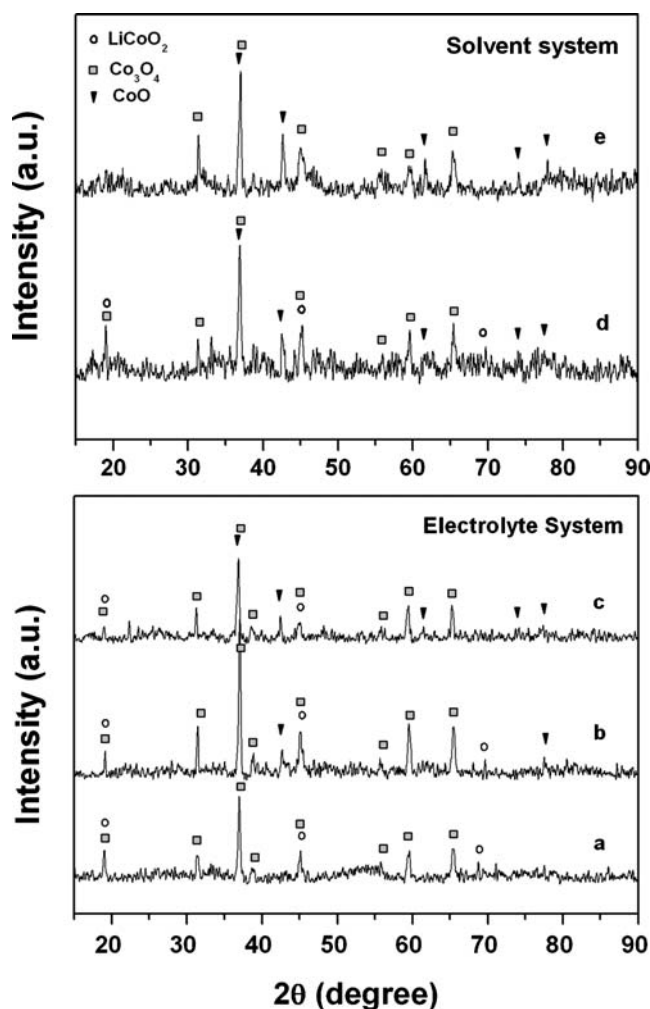


Fig. 6 XRD profiles of solid products for the combustion of different test systems: 1.50 g organic electrolyte (1 M LiPF₆/EC:DMC:DEC=1:1:1 (V/V/V)) respectively with (a) 0.10, (b) 0.30, and (c) 0.50 g of fully charged cathodic material (Li_{0.5}CoO₂) in the bottom figure; and 1.50 g organic solvent (EC:DMC:DEC=1:1:1 (V/V/V)) respectively with (d) 0.10, and (e) 0.50 g of fully charged cathodic material (Li_{0.5}CoO₂) in the top figure

cathodic material ($m_{\text{cat}}=0.50$ g), another three new CoO (Fm3m) peaks at 36.7°, 61.8°, and 74.0° emerge in curve (c). All the above phenomena reveal that with the increasing addition of cathodic material to electrolyte, CoO is proved to act as a more prominent component in the solid products of combustion reaction. Thus the products for the combustion reaction consist of three components: Co₃O₄, LiCoO₂, and CoO when an adequate amount of cathodic material is added to electrolyte. It should be mentioned that in curve (b) and (c), the LiCoO₂ (R-3m) peaks (at about 18.9°, 45.3°, and 69.7°) are pronouncedly weakened while the Co₃O₄ (Fd3m) peaks have little changes. So, in a higher mass ratio of cathodic material to electrolyte, LiCoO₂ plays a less important role in the combustion products, just the reverse to CoO.

XRD profiles for electrolyte systems (curve a–c) suggest that the solid components and their relative contents in combustion products are closely associated with the mass ratio of fully charged cathodic material to electrolyte. As discussed above, when increasing the mass ratio of cathodic material to electrolyte gradually, both the heat and heat release rate of combustion reactions can notably go up step by step. So a violent exothermic reaction to produce CoO occurs in the high mass ratio of cathodic material to electrolyte and generates more amount of heat.

This result can be further confirmed by the following XRD profiles for solvent systems (curve d–e). Even with the lowest mass ratio of cathodic material to solvent (0.10/1.50 g), curve (d) has already showed the CoO (Fm3m) peaks, besides the Co₃O₄ (Fd3m) and LiCoO₂ (R-3m) peaks. And when the mass ratio reaches 0.50/1.50 g ($m_{\text{cat}}/m_{\text{sol}}$), the chief peak of LiCoO₂ (R-3m) at about 18.9° even disappears in curve (e), implying the solid products of combustion reaction are composed of Co₃O₄ and CoO in this instance. As aforementioned, the solvent system (without salt LiPF₆) is proved to have a much larger exothermic effects during the period of combustion reactions compared to the corresponding electrolyte system. Thus a more violent combustion reaction in the LiPF₆-free system presents the variation of solid products: the earlier generation of CoO even for the lowest mass ratio 0.1/1.5 g and the disappearance of LiCoO₂ when its ratio increases to 0.5/1.5 g ($m_{\text{cat}}/m_{\text{sol}}$).

In the sealed system, the solid products after ARC or DSC measurement were also studied by XRD. MacNeil and Dahn [10] supposed that the thermal decomposition of fully charged cathode (Li_{0.5}CoO₂) resulted in the formation of LiCoO₂ and Co₃O₄ at temperature above 200 °C, and further in the presence of solvent (EC, DEC), the reaction proceeded to another new products CoO even at temperature as low as 130 °C. Therefore, similar solid products (LiCoO₂, Co₃O₄, and CoO) are well-determined in the thermal reactions of fully charged cathodic material combined with electrolyte/solvent whether by previous ARC and DSC [10, 15, 19], or by oxygen bomb calorimeter here.

The combustion products for the other four testing systems are also analyzed, as studied in the combustion heat. The similar results prove that the solid products might be correlated with the exothermic effect in combustion reactions. Generally, a more violent combustion reaction (high concentrations of charged cathodic material or/and lower concentration of salt LiPF₆ in electrolyte) would cause more CoO and less LiCoO₂ products and more amount of heat generated. It means that the combustion reaction, which produced CoO, generated more amount of heat than LiCoO₂. And this needs to be exactly confirmed in the further study.

As a whole, the complete combustion reactions of organic electrolytes (or solvents) with fully charged cathodic materials for the rupture case of lithium-ion batteries (under sufficient oxygen conditions) can be roughly described as follows:

Fully charged cathode (Li_{0.5}CoO₂) + Solvents (EC, DEC or/and DMC) + Salt (LiPF₆ or free) → CoO + LiCoO₂ + Co₃O₄ + CO₂ + H₂O (condition: O₂, ignited).

Conclusions

This study showed that the combustion reactions of organic electrolytes/solvents with fully charged cathodes had very pronounced exothermic effects under rupture conditions of Li-ion battery. The results revealed that the existence of fully charged cathodic materials in the electrolyte accelerated the heat release and increased the heat amount of combustion reactions. The heat release rate and the amount of heat were dependent on the mass ratios of cathodic materials to electrolyte/solvents. More heat was generated for the higher ratio of cathodic material system. And synergistic effects not simply physical mixtures have firstly been observed between cathodic materials and electrolytes/solvents in the complete combustion reactions.

Linear relationships between the amount of combustion heat and the mass of cathodic materials are well determined in all six studied systems: EC:DEC=1:1, EC:DMC:DEC=1:1:1, and EC:DMC=1:1 (all in volume ratios) with or without 1 M LiPF₆. Furthermore, the electrolyte systems (with salt LiPF₆) exhibit the less exothermic effects in combustion reactions than the corresponding solvent systems (without salt LiPF₆).

X-ray diffraction analysis revealed that Co₃O₄, CoO, and LiCoO₂ were the main solid products of combustion reactions. And there are more CoO and less LiCoO₂ products for the higher mass ratio of cathodic materials to electrolyte/solvent system and more amount of heat generated. It means that the combustion reaction, which produced CoO, generated more amount of heat than LiCoO₂.

Much more combustion heat was generated under sufficient oxygen atmosphere in a ruptured Li-ion cell than in a sealed cell, which probably led to the explosion of battery eventually.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China.

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