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## Papers citing use of THT ARC

### Battery Papers

#### 2017

##### ***Preventing Li-ion cell explosion during thermal runaway with reduced pressure***

##### ***Applied Thermal Engineering 124 (2017) 539–544***

Andreas Hofmann, Nils Uhlmann, Carlos Ziebert, Olivia Wiegand, Alexander Schmidt, Thomas Hanemann  
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##### Abstract

Concerning Li-ion cells it is demonstrated by overcharging tests both on the shelf in a fume-hood and in an accelerating rate calorimeter that the application of reduced pressure in the moment of a thermal runaway accident can prevent a fire and in particular a cell explosion, caused by the electrolyte. Within the experiment, pouch-bag Li-ion cells (88 mAh and 264 mAh) composed of graphite and NMC (LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>) were overcharged by 10 C in order to induce a thermal runaway. In spite of a strong temperature increase, the cell remains tightly close during the thermal runaway without any fire or explosion in case of vacuum application.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S1359431116333609>

##### ***Roles of positive or negative electrodes in the thermal runaway of lithium-ion batteries: Accelerating rate calorimetry analyses with an all-inclusive microcell***

##### ***Electrochemistry Communications: In Press, Accepted Manuscript***

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##### Abstract

To improve the thermal stability of lithium-ion batteries (LIBs) at elevated temperatures, the roles of positive or negative electrode materials in thermal runaway should be clarified. In this paper, we performed accelerating rate calorimetry analyses on two types of LIBs by using an all-inclusive microcell (AIM) method, where the AIM consists of all LIB components. We found that the thermal runaway in LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA)|LiPF<sub>6</sub> dissolved in ethylene carbonate (EC)/diethyl carbonate solution (DEC) (EC/DEC = 1/1 by volume); LiPF<sub>6</sub>(EC/DEC)|artificial graphite (AG) and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NCM)|LiPF<sub>6</sub>(EC/DEC)|AG cells is brought about by different electrodes, i.e., NCA for the former, and AG for the latter. The above difference is attributed to the different oxidation temperature of the EC/DEC solvents, indicating that we first pay attention which electrodes govern the thermal runaway. Trials for improving the thermal stability of NCA are also reported.

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## ***Correlation of aging and thermal stability of commercial 18650-type lithium ion batteries***

***Journal of Power Sources: 342 (2017) 382-392***

M. Börnera, A. Friesena, M. Grützkea, Y.P. Stenzela, G. Brunklausa, J. Haetgea, S. Nowaka, F.M. Schappachera, , M. Wintera, b, c  
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### **Abstract**

Established safety of lithium ion batteries is key for the vast diversity of applications. The influence of aging on the thermal stability of individual cell components and complete cells is of particular interest. Commercial 18650-type lithium ion batteries based on LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub>/C are investigated after cycling at different temperatures. The variations in the electrochemical performance are mainly attributed to aging effects on the anode side considering the formation of an effective solid-electrolyte interphase (SEI) during cycling at 45 °C and a thick decomposition layer on the anode surface at 20 °C. The thermal stability of the anodes is investigated including the analysis of the evolving gases which confirmed the severe degradation of the electrolyte and active material during cycling at 20 °C. In addition, the presence of metallic lithium deposits could strongly affect the thermal stability. Thermal safety tests using quasi-adiabatic conditions show variations in the cells response to elevated temperatures according to the state-of-charge, i.e. a reduced reactivity in the discharged state. Furthermore, it is revealed that the onset of exothermic reactions correlates with the thermal stability of the SEI, while the thermal runaway is mainly attributed to the decomposition of the cathode and the subsequent reactions with the electrolyte.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775316317347>

## ***Effects of rest time after Li plating on safety behavior—ARC tests with commercial high-energy 18650 Li-ion cells***

***Electrochimica Acta 230 (2017) 454-460***

Thomas Waldmann, , Margret Wohlfahrt-Mehrens

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### **Abstract**

During charging at low temperatures, metallic Lithium can be deposited on the surface of graphite anodes of Li-ion cells. This Li plating does not only lead to fast capacity fade, it can also impair the safety behavior. The present study observes the effect of rest periods between Li plating and subsequent accelerated rate calorimetry (ARC) tests. As an example, commercial 3.25 Ah 18650-type cells with graphite anodes and NCA cathodes are cycled at 0 °C to provoke Li plating. It is found that the rest period at 25 °C between Li plating and the ARC tests has a significant influence on the onset temperature of exothermic reactions ( $T_{SH}$ ), the onset temperature of thermal runaway ( $T_{TR}$ ), the maximum temperature, the self-heating rate, and on damage patterns of 18650 cells. The results are discussed in terms of chemical intercalation of Li plating into adjacent graphite particles during the rest period. The exponential increase of capacity recovery and  $T_{SH}$  as a function of time suggests a reaction of 1st order for the relaxation process.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0013468617302979>

**2016**

***Impact of cycling at low temperatures on the safety behavior of 18650-type lithium ion cells: Combined study of mechanical and thermal abuse testing accompanied by post-mortem analysis***

***Journal of Power Sources 334 (2016) 1–11***

Alex Friesen , Fabian Horsthemke, Xaver Mönnighoff, Gunther Brunklaus,  
Roman Krafft , Markus Börner , Tim Risthaus , Martin Winter, Falko M. Schappacher  
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Abstract

The impact of cycling at low temperatures on the thermal and mechanical abuse behavior of commercial 18650-type lithium ion cells was compared to fresh cells. Post-mortem analyses revealed a deposition of high surface area lithium (HSAL) metal on the graphite surface accompanied by severe electrolyte decomposition. Heat wait search (HWS) tests in an accelerating rate calorimeter (ARC) were performed to investigate the thermal abuse behavior of aged and fresh cells under quasi-adiabatic conditions, showing a strong shift of the onset temperature for exothermic reactions. HSAL deposition promotes the reduction of the carbonate based electrolyte due to the high reactivity of lithium metal with high surface area, leading to a thermally induced decomposition of the electrolyte to produce volatile gaseous products. Nail penetration tests showed a change in the thermal runaway (TR) behavior affected by the decomposition reaction. This study indicates a greater thermal hazard for LIB cells at higher SOC and experiencing aging at low temperature.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775316313106>

***Thermal behavior and failure mechanism of lithium ion cells during overcharge under adiabatic conditions***

***Applied Energy 182 (2016) 464–474***

Jiana Ye <sup>a,d</sup>, Haodong Chen <sup>a</sup>, Qingsong Wanga,<sup>b,c</sup>, Peifeng Huang <sup>a</sup>, Jinhua Sun <sup>a,b</sup>, Siuming Lo <sup>d</sup>

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Abstract

Cells in battery packs are easily overcharged when battery management system (BMS) is out of order, causing thermal runaway. However, the traditional calorimetry could not estimate dynamic overcharging heat release. In this study, commercial LiCoO<sub>2</sub> + Li(Ni<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>)O<sub>2</sub>/C + SiO<sub>x</sub> cells are employed to investigate the dynamic thermal behaviors during overcharge under adiabatic condition by combining a multichannel battery cyler with an accelerating rate calorimeter. The results indicate that overcharging with galvanostatic - potentiostatic - galvanostatic regime is more dangerous than that with galvanostatic way. Side reactions contribute 80% heat to thermal runaway in cases below 1.0 C charging rate. To prevent the thermal runaway, the effective methods should be taken within 2 min to cool down the batteries as soon as the cells pass inflection point voltage. Hereinto, the inflection and maximum voltages increase linearly with the increasing current rates. By scanning electron microscope and energy dispersive spectrometer, the decomposed products of cathode materials are suspected to be soluble with SiO<sub>x</sub>. The overcharge induced decomposition reaction of Li(Ni<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>)O<sub>2</sub> is also proposed. These results can provide support for the safety designs of lithium ion batteries and BMS.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0306261916312247>

***Heat loss distribution: Impedance and thermal loss analyses in LiFePO<sub>4</sub>/graphite 18650 electrochemical cell***

***Journal of Power Sources 328 (2016) 413–42***

Manikandan Balasundaram, Vishwanathan Ramar, Christopher Yap, Lu Li, Andrew A.O. Tay, Palani Balaya,  
Department of Mechanical Engineering, National University of Singapore, 117576, Singapore

We report here thermal behaviour and various components of heat loss of 18650-type LiFePO<sub>4</sub>/graphite cell at different testing conditions. In this regard, the total heat generated during charging and discharging processes at various current rates (C) has been quantified in an Accelerating Rate Calorimeter experiment. Irreversible heat generation, which depends on applied current and internal cell resistance, is measured under corresponding charge/discharge conditions using intermittent pulse techniques. On the other hand, reversible heat generation which depends on entropy changes of the electrode materials during the cell reaction is measured from the determination of entropic coefficient at various states of charge/discharge. The contributions of

irreversible and reversible heat generation to the total heat generation at both high and low current rates are evaluated. At every state of charge/discharge, the nature of the cell reaction is found to be either exothermic or endothermic which is especially evident at low C rates. In addition, electrochemical impedance spectroscopy measurements are performed on above 18650 cells at various states of charge to determine the components of internal resistance. The findings from the impedance and thermal loss analysis are helpful for understanding the favourable states of charge/discharge for battery operation, and designing better thermal management systems.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775316310448>

### ***Energy distributions exhibited during thermal runaway of commercial lithium ion batteries used for human spaceflight applications***

#### ***Journal of Power Sources Volume 329 (2016) 197–206***

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Lithium ion (Li-ion) batteries provide low mass and energy dense solutions necessary for space exploration, but thermal related safety concerns impede the utilization of Li-ion technology for human applications. Experimental characterization of thermal runaway energy release with accelerated rate calorimetry supports safer thermal management systems. ‘Standard’ accelerated rate calorimetry setup provides means to measure the addition of energy exhibited through the body of a Li-ion cell. This study considers the total energy generated during thermal runaway as distributions between cell body and hot gases via inclusion of a unique secondary enclosure inside the calorimeter; this closed system not only contains the cell body and gaseous species, but also captures energy release associated with rapid heat transfer to the system unobserved by measurements taken on the cell body. Experiments include Boston Power Swing 5300, Samsung 18650-26F and MoliCel 18650-J Li-ion cells at varied states-of-charge. An inverse relationship between state-of-charge and onset temperature is observed. Energy contained in the cell body and gaseous species are successfully characterized; gaseous energy is minimal. Significant additional energy is measured with the heating of the secondary enclosure. Improved calorimeter apparatus including a secondary enclosure provides essential capability to measuring total energy release distributions during thermal runaway.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775316310874>

### ***Computational fluid dynamic and thermal analysis of Lithium-ion battery pack with air cooling*** ***Applied Energy 177 (2016) 783–792***

Lip Huat Saw a, Yonghuang Ye c, <sup>†</sup>, Andrew A.O. Tay b, Wen Tong Chong d, Seng How Kuan a, Ming Chian Yewa

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A battery pack is produced by connecting the cells in series and/or in parallel to provide the necessary power for electric vehicles (EVs). Those parameters affecting cost and reliability of the EVs, including cycle life, capacity, durability and warranty are highly dependent on the thermal management system. In this work, computational fluid dynamic analysis is performed to investigate the air cooling system for a 38,120 cell battery pack. The battery pack contained 24 pieces of 38,120 cells, copper bus bars, intake and exhaust plenum and holding plates with venting holes. Heat generated by the cell during charging is measured using an accelerating rate calorimeter. Thermal performances of the battery pack were analyzed with various mass flow rates of cooling air using steady state simulation. The correlation between Nu number and Re number were deduced from the numerical modeling results and compared with literature. Additionally, an experimental testing of the battery pack at different charging rates is conducted to validate the correlation. This method provides a simple way to estimate thermal performance of the battery pack when the battery pack is large and full transient simulation is not viable.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0306261916307279>

### ***Performance assessment and optimization of a heat pipe thermal management system for fast charging lithium ion battery packs***

#### ***International Journal of Heat and Mass Transfer 92 (2016) 893–903***

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Thermal management system is critical for the electric vehicles and hybrid electric vehicles. This is due to the narrow operating temperature range for lithium ion batteries to achieve a good balance between performance and life. In this study, heat pipes are incorporated into a thermal management system for prismatic or pouch cells. Design optimizations focusing on increasing the cooling capacity and improving temperature uniformity of the system are undertaken through sensitivity studies. Subsequently, empirical study is carried out to assess the thermal performance of the optimized design integrated with prismatic cells at the unit level and the battery pack level. The results confirm that the optimized heat pipe thermal management system is feasible and effective for fast charging lithium ion battery packs. A delay quench cooling strategy is also proposed to enhance the performance of the thermal management system.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0017931015009825>

### ***The simulation on thermal stability of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/C electrochemical systems***

#### ***Journal of Power Sources 302 (2016) 1-6***

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A thermal model of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/C electrochemical system has been developed. The thermal model is based on the thermal characteristic and related calculation for full charged LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and full discharged carbon materials, respectively.

According to simulations on the thermal stability of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/C electrochemical system, there is one exothermic process for the full charged LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and two for the full discharged carbon. The first exothermic reaction for carbon material should be the best explanation for the initially self-heating of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/C electrochemical system. It is the reactions between LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and the electrolyte that make the LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>/C cell going into thermal runaway. The simulated result shows a good consistency with the testing result, so this simulation method can provide a significant basis for the thermal and safety design of batteries.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S037877531530433X>

### ***Thermal hazards and kinetic analysis of salicyl hydroxamic acid under isothermal and adiabatic conditions***

#### ***Thermochimica Acta 623 (2016) 43–49***

Gui-bin Lu, Cai-xing Zhang, Wang-hua Chen\*, Li-ping Chen, Yi-shan Zhou Department of Safety Engineering, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094 Jiangsu, China

Kinetic study and thermal hazards analysis on the thermal decomposition of salicyl hydroxamic acid (SHA) was carried out using differential scanning calorimetry (DSC). The isothermal and dynamic differential scanning calorimetric curves were recorded, respectively. The temperature dependence of the observed induction periods suggests an autocatalytic decomposition mechanism, which was supported by the conversion-reduced time plots. The differential and integral isoconversional methods were used to obtain the kinetic parameters. The decomposition mechanism model of the first peak was  $f_c = 1.49(1 - \alpha)^{1.59}$ . Moreover, the isothermal temperature induction period were studied to obtain the activation energy, which was close to that obtained by the isoconversional integral method. The adiabatic accelerating calorimetry (ARC) was also employed to evaluate the thermal hazards. The adiabatic activation parameters were also obtained based on the autocatalytic reaction model

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## **2015**

### ***Novel Ethylene Carbonate Based Electrolyte Mixtures for Li-Ion Batteries with Improved Safety Characteristics***

#### ***ChemSusChem 8 (2015) 1892-1900***

A. Hofmann\*, M. Migeot, E. Thißen, M. Schulz, R. Heinzmann, S. Indris, Th. Bergfeldt, B. Lei, C. Ziebert, Th. Hanemann

In this study, novel electrolyte mixtures for Li-ion cells are presented with highly improved safety features. The electrolyte formulations are composed of ethylene carbonate/dimethyl sulfone (80:20 wt/wt) as the solvent mixture and LiBF<sub>4</sub>, lithium bis(trifluoromethanesulfonyl)azanide, and lithium bis(oxalato)-borate as the conducting salts. Initially, the electrolytes are characterized with regard to their physical properties, their lithium transport properties, and their electrochemical stability. The key advantages of the electrolytes are high flash points of > 140 °C, which enhance significantly the intrinsic safety of Li-ion cells containing these electrolytes. This has been quantified by measurements in an accelerating rate calorimeter. By using the newly developed electrolytes, which are liquid down to T = -10 °C, it is possible to achieve C-rates of up to 1.5 C with > 80% of the initial specific capacity. During 100 cycles in cell tests (graphite | LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>), it is proven that the retention of the specific

capacity is > 98% of the third discharge cycle with dependence on the conducting salt. The best electrolyte mixture yields a capacity retention of > 96% after 200 cycles in coin cells.

Link to purchase paper: <http://onlinelibrary.wiley.com/doi/10.1002/cssc.201500263/epdf>

### ***Thermal runaway propagation model for designing a safer battery pack with 25 Ah LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> large format lithium ion battery***

Xuning Feng <sup>a</sup>, Xiangming He <sup>b</sup>, Mingguo Ouyang <sup>a,†</sup>, Languang Lu <sup>a</sup>, Peng Wuc, Christian Kulp <sup>c</sup>, Stefan Prasser <sup>c</sup>

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Abstract

Thermal runaway (TR) propagation in a large format lithium ion battery pack can cause disastrous consequences and thus deserves study on preventing it. A lumped thermal model that can predict and help prevent TR propagation in a battery module using 25 Ah LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> large format lithium ion batteries has been built in this paper. The TR propagation model consists of 6 fully-charged single batteries connected through thermal resistances and can fit experiment data well. The modeling analysis focuses on discussing the influences on the TR propagation process caused by changes in different critical modelling parameters. The modeling analysis suggests possible solutions to postpone and prevent TR propagation. The simulation shows that it might be better to choose proper parameters that help prevent TR propagation rather than just postpone it, because a delay in the TR propagation process leads to a higher level of heat gathering which may cause severer thermal hazards. To prevent TR propagation, the model provides some substantial quantified solutions: (1) raise the TR triggering temperature to higher than 469 °C; (2) reduce the total electric energy released during massive internal short circuit to 75% or less of its original value; (3) enhance the heat dissipation by increasing the heat dissipation coefficient to higher than 70 Wm<sup>-2</sup> K<sup>-1</sup>; (4) add extra thermal resistant layers between adjacent batteries with a thickness of 1 mm and a thermal conductivity less than 0.2 Wm<sup>-1</sup> K<sup>-1</sup>. One implementation, which is verified by experiment, is to insert thermal resistant layer between adjacent batteries to prevent TR propagation in the battery module.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0306261915005814>

### ***Interaction of cyclic ageing at high-rate and low temperatures and safety in lithium-ion batteries*** ***Journal of Power Sources 274 (2015)***

Meike Fleischhammer\*, Thomas Waldmann, Gunther Bisle, Bjeorn-Ingo Hogg, Margret Wohlfahrt-Mehrens

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Abstract

The differences in the safety behaviour between un-aged and aged high-power 18650 lithium-ion cells were investigated at the cell and material level by Accelerating Rate Calorimetry (ARC) and Simultaneous Thermal Analysis (STA). Commercial cells containing a Li<sub>x</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>/Li<sub>y</sub>Mn<sub>2</sub>O<sub>4</sub> blend cathode, a carbon/graphite anode and a PP/PE/PP trilayer separator were aged by high-rate and low temperature cycling, leading to (i) mechanical deformation of the jelly roll and (ii) lithium plating on the anode. The results show a strong influence of the ageing history on the safety behaviour. While cycling at high current does not have a strong influence on the cell safety, lithium plating leads to a significant increase of heat formation during thermal runaway and thus to a higher hazard of safety.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S037877531401489X>



**2014**

***Heat evolution and temperature increase in lithium ion cells studied by combined electrochemical-calorimetric measurements on lithium ion cells***

***CEEES Conference Environmental Testing and Safety of Batteries and Fuel Cells, Pfinztal, Germany, 18-09-2014***

Magnus Rohde\*, Boxia Lei, Carlos Ziebert, Andreas Melcher, Hans Jürgen Seifert

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The performance of a lithium ion cell is strongly related to the temperature. Therefore it is important to understand the process of heat generation and dissipation inside a single cell but also in battery packs since this is also closely coupled to safety issues. In this study, commercial 18650 lithium ion cells with  $\text{LiMn}_2\text{O}_4$  cathodes as well as 20 Ah pouch cells with  $\text{LiFePO}_4$  cathodes were tested under isoperibolic and adiabatic conditions in an accelerating rate calorimeter (THT Company) to investigate the heat effects during cycling. Isoperibolic investigations in the range from 25 to 60°C show that the applied environmental temperature does not largely influence the battery thermal behavior. At 1C rate the maximum temperature increase over three cycles was 4°C almost independent of the environmental temperature. Additionally, the heat capacity and calorimeter constant were measured after calibration using cylindrical dummy cells made of  $\text{AlMgSi}_{0.5}$  with the cell dimensions. By integrating over the heat dissipation rate and the enthalpy accumulation rate the total generated heat was determined in dependence of discharge C-rate. Tests under adiabatic conditions, i.e. under negligible heat loss, more accurately simulate a battery pack where several cells are closely packed and the neighboring cells prevent the heat transfer to the ambient. The cell temperature was largely increasing at 1C rate over three cycles by more than 40°C rate before reaching the safety limit temperature of 75°C. This work presents also a short overview of some ECMs followed by a first implementation of an extended ECM with a simplified thermal model in Matlab®/Simulink®/Simscape™. The identification problem of the structure and the parameters of an ECM are discussed in terms of the Current Interruption Technique (CIT). In addition to the calorimetric measurements the distribution of the surface temperature was determined on the pouch cell during charging and discharging using a thermographic camera system (FLIR, X6540sc) which allows temperature measurements with spatial resolution. The resulting information from the IR images could be correlated to the results of measurements with the calorimeter. It could be also used to identify temperature gradients and “hot spots” on the surface of the cell.

Link to view paper:

[https://www.researchgate.net/publication/272021037\\_Heat\\_evolution\\_and\\_temperature\\_increase\\_in\\_lithium\\_ion\\_cells\\_studied\\_by\\_combined\\_electrochemical-calorimetric\\_measurements\\_on\\_lithium\\_ion\\_cells](https://www.researchgate.net/publication/272021037_Heat_evolution_and_temperature_increase_in_lithium_ion_cells_studied_by_combined_electrochemical-calorimetric_measurements_on_lithium_ion_cells)

***Electro-thermal analysis and integration issues of lithium ion battery for electric vehicles***

***Applied Energy 131 (2014) 97–107***

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Abstract

Electrical and thermal characteristics of lithium-ion battery packs in electric vehicles in different operating conditions are important in order to design the battery pack thermal management system. In this work, electrical and thermal behaviors of different size of  $\text{LiFePO}_4$  cylindrical cells are investigated under various operating conditions. The simulation results show good agreement with the experimental data under various operating modes. Due to the large thermal resistance of layered active material in a Li-ion cell, the temperature difference in the radial direction is significantly correlated with a diameter of cell and It-rates. Compared with natural convection, strong forced convection will reduce the temperature uniformity in the cell and accelerate the thermal aging rate. Lastly, integration issues of the cells into a battery pack are discussed from mechanical, electrical, thermal, control and monitoring, manufacturing and maintenance aspects. These issues could impact the performance, cost, driving range and life cycle of the battery pack in electric vehicles.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0306261914005984>

***Thermal and overcharge abuse analysis of a redox shuttle for overcharge protection of LiFePO<sub>4</sub>***  
***Journal of Power Sources 247 (2014)***

Joshua Lamb <sup>a,\*</sup>, Christopher J. Orendorff <sup>a</sup>, Khalil Amine <sup>b</sup>, Gregory Krumdick <sup>b</sup>, Zhengcheng Zhang <sup>b</sup>, Lu Zhang <sup>b</sup>, Antoni S. Gozdz <sup>c</sup>

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**Abstract**

This work investigated the performance and abuse tolerance of cells protected using the redox shuttle 1,4-bis(2-methoxyethoxy)-2,5-di-tert-butylbenzene. The thermal efficiencies were evaluated using isothermal battery calorimetry. Cells containing the overcharge shuttle were observed to reach a steady state value of approximately 3.8 V, with a small variance in direct proportion to the applied current. In all cases the heat output from the cells was measured to reach ~90% of the total input power. The heat output was also measured using isothermal calorimetry. At higher rates of overcharge, the data shows that the cell containing the shuttle rapidly reaches a steady state voltage, while the temperature increases until a moderately high steady state temperature is reached. The control cell meanwhile rapidly increases in both applied voltage and cell temperature until cell failure. Two cells in series were taken deliberately out of balance individually, then charged as a single pack to observe the time needed to bring the cells into balance with one another.

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***Thermal runaway features of large format prismatic lithium ion battery using extended volume accelerating rate Calorimetry***  
***Journal of Power Sources 255 (2014)***

Xuning Feng <sup>a</sup>, Mou Fang <sup>b</sup>, Xiangming He <sup>a,b</sup>, Minggao Ouyang <sup>a</sup>, Languang Lu <sup>a</sup>, Hao Wang <sup>b</sup>, Mingxuan Zhang <sup>a</sup>

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<sup>b</sup> Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

**Abstract**

In this paper, the thermal runaway features of a 25 Ah large format prismatic lithium ion battery with Li(NixCoyMnz)O<sub>2</sub> (NCM) cathode are evaluated using the extended volume-accelerating rate calorimetry (EV-ARC). 4 thermocouples are set at different positions of the battery. The temperature inside the battery is 870 °C or so, much higher than that outside the battery. The temperature difference is calculated from the recorded data. The temperature difference within the battery stays lower than 1 °C for 97% of the test period, while it rises to its highest, approximately 520 °C, when thermal runaway happens. The voltage of the battery is also measured during the test. It takes 15–40 s from the sharp drop of voltage to the instantaneous rise of temperature. Such a time interval is beneficial for early warning of the thermal runaway. Using a pulse charge/discharge profile, the internal resistance is derived from the quotient of the pulse voltage and the current during the ARC test. The internal resistance of the battery increases slowly from 20 mΩ to 60 mΩ before thermal runaway, while it rises to 370 mΩ when thermal runaway happens indicating the loss of the integrity of the separator or the battery swell.

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## **Simultaneous estimation of thermal parameters for large-format laminated lithium-ion batteries** **Journal of Power Sources 259 (2014)**

Jianbo Zhang, Bin Wu, Zhe Li\*, Jun Huang

State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, China

### Abstract

In-situ determination of the battery thermal parameters is important to provide accurate inputs for battery thermal models. This paper develops a method to estimate the multiple thermal parameters of large-format laminated lithium-ion batteries both simultaneously and in-situ. The central area of one battery surface is heated with a circular planar heater, while the temperature responses on the opposite surface at multiple strategically-chosen locations are recorded with the attached thermocouples. This thermal system is modeled in COMSOL v4.2 using a two-dimensional axially-symmetric thermal conduction equation containing thermal parameters such as the thermal capacity, anisotropic thermal conductivities, and thermal interfacial conductance between the Al-plastic film package and the electrode core. Using optimization techniques, these thermal parameters are adjusted step by step till the difference between the simulated and the experimental temperature responses at the corresponding locations reaches a minimum. As one validation of the developed method, the estimated specific heat capacity agreed with the value measured with an accelerating rate calorimeter within 10%. The proposed method can be applied to simultaneously determine the thermal parameters of generic objects consisting of anisotropic internal materials and an outer packaging made of different material.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775314002729>

## **Characterization of large format lithium ion battery exposed to extremely high temperature** **Journal of Power Sources 272 (2014)**

Xuning Feng <sup>a, b</sup>, Jing Sun <sup>b</sup>, Minggao Ouyang <sup>a</sup>, Xiangming He <sup>a, c</sup>, Languang Lu <sup>a</sup>,  
Xuebing Han <sup>a</sup>, Mou Fang <sup>c</sup>, Hwei Peng <sup>d</sup>

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### Abstract

This paper provides a study on the characterizations of large format lithium ion battery cells exposed to extreme high temperature but without thermal runaway. A unique test is set up: an extended volume-accelerating rate calorimetry (EV-ARC) test is terminated at a specific temperature before thermal runaway happens in the battery. The battery was cooled down after an EV-ARC test with early termination. The performances of the battery before and after the EV-ARC test are investigated in detail. The results show that (a) the melting point of the separator dictates the reusability of the 25 Ah NCM battery after a near-runaway event. The battery cannot be reused after being heated to 140 °C or higher because of the exponential rise in ohmic resistance; (b) a battery can lose up to 20% of its capacity after being heated to 120 °C just one time; (c) if a battery is cycled after a thermal event, its lost capacity may be recovered partially. Furthermore, the fading and recovery mechanisms are analyzed by incremental capacity analysis (ICA) and a prognostic/mechanistic model. Model analysis confirms that the capacity loss at extremely high temperature is caused by the increase of the resistance, the loss of lithium ion (LLI) at the anode and the loss of active material (LAM) at the cathode.

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**2013**

***Lithium-ion capacitors: Electrochemical performance and thermal behavior***

***Journal of Power Sources Volume 243, 1 December 2013, Pages 982–992***

Patricia H. Smith<sup>a,\*</sup>, Thanh N. Tran<sup>a</sup>, Thomas L. Jiang<sup>a</sup>, Jaesik Chung<sup>b</sup>

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<sup>b</sup> PCTEST Engineering Laboratory, Inc., 9017 Mendenhall Ct., Columbia, MD 21045, USA

Abstract

We report on the electrochemical performance of 500 F, 1100 F, and 2200 F lithium-ion capacitors containing carbonate-based electrolytes. First and second generation lithium-ion capacitors were cycled at temperatures ranging from –30 °C to 65 °C, with rates from 5 C to 200 C. Unlike acetonitrile-based electric double-layer capacitors, whose performance has been reported to be relatively insensitive to temperatures between –30 °C and 40 °C, lithium-ion capacitor performance degrades at low temperatures and displays characteristics typical of a lithium-ion battery. Three-electrode lithium-ion capacitor cycling tests revealed that reduced capacity at low temperatures is due to the polarization of the lithiated, negative electrode. The self-discharge of cells at the various temperatures was studied and compared to an electric double-layer capacitor and a lithium-ion battery cell. Lithium-ion capacitors and batteries were observed to have significantly lower self-discharge rates than electric double-layer capacitors. Accelerating rate calorimetry and differential scanning calorimetry were used to assess the thermal runaway behavior of full cells along with the thermal properties of the cell components. Our study showed that the thermal behavior of the lithium-ion capacitor is in between those of an electric double-layer capacitor and a lithium-ion battery.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775313010033>

***Thermal characterization of a high-power lithium-ion battery: Potentiometric and calorimetric measurement of entropy changes***

***Energy Volume 61, 1 November 2013, Pages 432–439***

Akram Eddahech\*, Olivier Briat, Jean-Michel Vinassa

Univ. Bordeaux, IMS, UMR 5218 CNRS, F-33400 Talence, France

Abstract

This paper focuses on the thermal behaviour of high-power lithium-ion cells during charge-discharge at several current rates. A series of tests are conducted using an accelerating rate calorimeter to promote an adiabatic environment. Cell heat capacity is identified and the overall heat generated is quantified. Cell entropy is measured, using both potentiometric and calorimetric methods. The part of reversible reaction in the overall thermal behaviour is determined during charge-discharge tests and compared to joule losses. The influence of the state-of-charge variation and the impact of charge-discharge current rate on battery heat generation are highlighted. Experimental results for two lithium-ion technologies are presented and discussed.

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## Presentations citing use THT ARC

### Battery Presentations

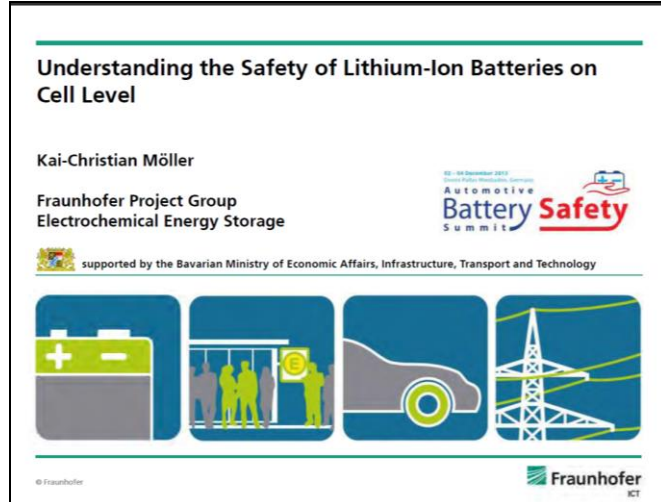
2013

#### [Understanding the Safety of Lithium-Ion Batteries on Cell Level](#)

**Presented at Automotive Battery Safety Summit, Wiesbaden, Germany**

Kai-Christian Möller

Fraunhofer ICT Project Group Electrochemical Energy Storage



#### [Electrochemical-calorimetric studies for the determination of heat data of 40 Ah lithium ion pouch cells](#)

**Presented at Automotive Battery Safety Summit, Wiesbaden, Germany**

C. Ziebert, E. Schuster, H. J. Seifert

Karlsruhe Institute of Technology (KIT)



**Multiscale electrochemical-thermal modeling of cylindrical Li-ion cells and comparison with electrochemical-calorimetric studies**

**Presented at 17<sup>th</sup> Topical Meeting of the International Society of Electrochemistry, St. Malo, France, 31.05-03.06.2015.**

C. Ziebert, A. Melcher, B. Lei, A. Ossipova, M. Rohde, H.J. Seifert

Karlsruhe Institute of Technology, Institute for Applied Materials - IAM-AWP, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

**Combination of electrochemical-calorimetric studies on cylindrical lithium ion cells and thermal modelling by COMSOL Multiphysics software**

**Presented at 225<sup>th</sup> ECS Meeting, Orlando, USA, 11.-16.05.2014.**

C. Ziebert, A. Ossipova, M. Rohde, H.J. Seifert

Karlsruhe Institute of Technology, Institute for Applied Materials - IAM-AWP, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

**Thermal runaway of lithium ion batteries**

**Presented at 7<sup>th</sup> Asian Conference on Electrochemical Power Sources (ACEPS - 7), Osaka, Japan**

Xiangming He

Tsinghua University

The poster features a title box at the top with the text "Thermal runaway of lithium ion batteries". Below the title, it specifies the event: "the 7th Asian Conference on Electrochemical Power Sources (ACEPS - 7)", the dates "November 24 to 27, 2013", and the location "Osaka, Japan". A photograph of a traditional Chinese building is shown on the left. On the right, the text reads "Lithium Ion Battery Lab", "Tsinghua University", and "Xiangming He". At the bottom, there is a contact email "hexm@tsinghua.edu.cn" and the date and time "Nov. 27, Tues., 2013, Life hall, 16 : 00—16 : 15".

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## Papers citing use of THT ARC

### Chemical Papers 2017

#### ***Estimation of kinetic parameters from adiabatic calorimetric data by a hybrid Particle Swarm Optimization method***

***Chemical Engineering Research and Design Volume 122, June 2017, Pages 273–279***

Zi-Chao Guo, Li-Ping Chen, Wang-Hua Chen, Department of Safety Engineering, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China

#### Abstract

Due to the intense non-linear behavior in the task of estimation of the kinetic parameters from the experimental adiabatic data, a hybrid Particle Swarm Optimization (PSO) is proposed to estimate the kinetic parameters. This method is applied to two real cases: decomposition of DTBP and a nitro-compound under adiabatic conditions. By comparing the experimental and calculated temperature rise rate curve, the accuracy of the fitted parameters is verified. These two cases reasonably prove the validation of this hybrid PSO algorithm in the estimation of kinetic model parameters of adiabatic data.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0263876217302502>

#### ***Thermoanalytical investigation of the reactions causing the transuranic waste drum breach that occurred in the Waste Isolation Pilot Plant Thermochimica Acta 650 (2017) 76-87***

Randall D. Scheele<sup>a,\*</sup>, Bruce K. McNamara<sup>a</sup>, Jon M. Schwantesa, David T. Hobbsb, Michael J. Minettea, Christopher A. Barretta

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<sup>b</sup>Savannah River National Laboratory, Savannah River Site, Aiken, SC 29808, United States

#### Abstract

In February 2014, an energetic gas-producing chemical reaction occurred in remediated plutonium processing waste emplaced in the Waste Isolation Pilot Plant causing the drum's seal to fail and release radioactive material into and outside of the plant. This article provides results of our probative study using simultaneous thermogravimetric and differential thermal analysis and accelerating rate calorimetry to determine the thermal sensitivities of selected simulated characteristic remediated wastes such as hydrogen- and hydrogen, metal-triethanolamine nitrates and nitric acid solidified and stabilized with wheat-based pet litter. These studies found that these nitrate wastes were chemically unstable and susceptible to gas-producing thermal runaway reactions. If undried or partially dried, self-sustaining or accelerating-exothermic reactions were delayed in nitrate- and organic-containing materials to above 100 °C while air-dried nitric acid and pet litter began self-heating exothermic reactions near 30 °C that led to thermal runaway. Caution must be exercised when managing nitrate-containing wastes.

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## 2016

### ***Evaluation of thermal hazards and thermo-kinetic parameters of N,N'-dinitro-4,4'-azo-Bis(1,2,4 triazolone) (DNZTO)***

***Thermochimica Acta 623 (2016) 58-64***

Jiaping Zhu, Shaohua Jin, Yuehai Yu, Chunyuan Zhang, Lilijie Li, Shusen Chen, Qinghai Shu  
School of Materials Science & Engineering, Beijing Institute of Technology, Beijing, China

#### Abstract

Thermogravimetric–differential thermal analysis (TG–DTA) and accelerating rate calorimetry (ARC) were performed to understand thermal characteristics and kinetics of energetic N,N'-dinitro-4,4'-azo-Bis(1,2,4-triazolone) (DNZTO). A single sharp and narrow exothermic decomposition occurred at 143.3, 150.3, 156.4, 157.4, 159.8 and 160.3 °C at different heating rates (0.5, 1, 2, 3, 4, and 5 °C min<sup>-1</sup>) suggesting that DNZTO composition was vulnerable to thermal hazard. The FTIR–TGA–MS results revealed that the decomposition product was made up of H<sub>2</sub>O, NO<sub>2</sub>, NO, CO<sub>2</sub>, CO, HCN, and N<sub>2</sub>O. ARC studies depicted onset temperature at 116.6 °C with temperature step of 5 °C and phi factor of 41.46, and a sharp rise in exothermic reaction at 127.69 °C within the time span of 49.04 min with the maximum heat release rate of 0.47 °C min<sup>-1</sup>. The exothermic activity resulted in adiabatic pressure rise of the sample up to 300 kPa by the sample pyrolysis into gas. In addition, the kinetic parameters of DNZTO were estimated for the thermal process by TG–DTA and ARC.

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## 2015

### ***Thermal hazards and kinetic analysis of salicyl hydroxamic acid under isothermal and adiabatic conditions*** ***Thermochimica Acta 623 (2016) 58-64***

Gui-bin Lu, Cai-xing, Zhang, Wang-hua Chen\*, Li-ping Chen, Yi-shan Zhou  
Department of Safety Engineering, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094 Jiangsu, China

#### Abstract

Kinetic study and thermal hazards analysis on the thermal decomposition of salicyl hydroxamic acid (SHA) was carried out using differential scanning calorimetry (DSC). The isothermal and dynamic differential scanning calorimetric curves were recorded, respectively. The temperature dependence of the observed induction periods suggests an autocatalytic decomposition mechanism, which was supported by the conversion-reduced time plots. The differential and integral isoconversional methods were used to obtain the kinetic parameters. The decomposition mechanism model of the first peak was  $f(\alpha) = \alpha^{1.49}(1 - \alpha)^{1.59}$ . Moreover, the isothermal temperature induction period were studied to obtain the activation energy, which was close to that obtained by the iso conversional integral method. The adiabatic accelerating calorimetry (ARC) was also employed to evaluate the thermal hazards. The adiabatic activation parameters were also obtained based on the autocatalytic reaction model

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***Research on the critical temperature of thermal decomposition for large cartridge emulsion explosives***  
***Journal of Loss Prevention in the Process Industries 38 (2015) 199-203***

Kai Wang, Sen Xu\*, Dabin Liu, Gaowen Cai

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, China

**Abstract**

Emulsion explosives are one type of main industrial explosives. The emergence of the large cartridge emulsion explosives has brought new security incidents. The differential scanning calorimeter (DSC) and the accelerating rate calorimeter (ARC) were selected for the preliminary investigation of the thermal stability of emulsion explosives. The results showed that the initial thermal decomposition temperatures were in the range of 232-239°C in nitrogen atmosphere (220e232 °C in oxygen atmosphere) in DSC measurements and 216 °C in ARC measurements. The slow cook-off experiments were carried out to investigate the critical temperature of the thermal decomposition ( $T_c$ ) of the large cartridge emulsion explosives. The results indicated that the larger the diameter of the emulsion explosives, the smaller the  $T_c$  is. For the large cartridge emulsion explosives with diameter of 70 mm, the  $T_c$  was 170 °C at the heating rate of 3°C h<sup>-1</sup>. It is a dangerous temperature for the production of the large cartridge emulsion explosives and it should cause our attention.

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## **2014**

***Thermal risk evaluation on decomposition processes for four organic peroxides***  
***Thermochimica Acta 589 (2014) 11–18***

Jiayu Lv, Wanghua Chen, Liping Chen, Yintao Tian, Jiaojiao Yan

Department of Safety Engineering, Nanjing University of Science and Technology, Xiao Ling Wei Street 200, Nanjing, Jiangsu 210094, China

**Abstract**

Four widely used organic peroxides, namely DTBP, DTAP, BTDH and TBPB, were investigated for hazards caused by their thermal instabilities. Chemically pure materials without diluents were adopted to reveal their thermal decomposition and associated kinetic processes. DSC was employed to carry out experimental thermal study and the Friedman isoconversional method, the Kissinger method, as well as AKTS software were used for kinetic calculations and numerical simulations. Experimental results showed TBPB had the lowest detected “onset temperature”, and unlike DTBP, DTAP and BTDH, all of which showed a two-stage decomposition, TBPB decomposition occurred in a single stage. Heats of reactions measured by ARC were between ca. 37 and 54% of the heats of reaction measured by DSC and reported elsewhere by both, DSC and ARC. The obtained values are compared and discussed. Then, a risk diagram was established to determine the conditionally acceptable conditions of use for the OPs. Furthermore, pressure evaluation results by TSu indicated the generation of non-condensable gas during runaway reactions should be seriously considered.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0040603114002184>

***Water induced thermal decomposition of pyrotechnic mixtures: Thermo kinetics and explosion pathway***  
***Journal of Loss Prevention in the Process Industries 30 (2014)***

Sridhar Vethathiri Pakkirisamy <sup>a</sup>, Surianarayanan Mahadevan <sup>a</sup>, Sivapirakasam Suthangathan Paramashivan <sup>b</sup>, Mandal Asit Baran <sup>a</sup>

<sup>a</sup> Cell for Industrial Safety and Risk Analysis, Chemical Engineering Department, Central Leather Research Institute (CLRI), Adyar, Chennai 600 020, Tamil Nadu, India

<sup>b</sup> Mechanical Engineering Department, National Institute of Technology, Tiruchirapalli 620 015, India

**Abstract**

Pyrotechnic mixtures are susceptible to explosive decompositions. The aim of this paper is to generate thermal decomposition data for flowerpot tip, which is a mixture used in the tip of flowerpot fireworks for easy ignition. Several accidents were reported by using this mixture. The mixture is prepared by mixing barium nitrate, potassium nitrate, aluminum (666) and dextrin in a slurry manner with water. In the manufacturing process 40% water wt/wt is added to the mixture. The thermal characteristics of pure sample and water added sample were studied. Differential Scanning Calorimeter is used for screening tests and Accelerating Rate Calorimeter is used for detailed studies in adiabatic and isothermal mode. The self heat rate data obtained showed onset temperature for pure sample at 170.62 °C and the sample with water showed a much earlier onset at 95.71 °C in adiabatic mode. Also it gets decomposes even at 40 °C and starts exothermic characteristics with a substantial rise in system pressure of 32 bar in isothermal mode. The heats of exothermic decomposition and Arrhenius kinetics were computed.

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## 2013

***Effects of incompatible substances on the thermal stability of dimethyl sulfoxide***  
***Thermochimica Acta 559 (2013) 76– 81***

Xiao-Wu Yang, Xiang-Yang Zhang, Zi-Chao Guo, Wen-Shuai Bai, Lin Hao, Hong-Yuan Wei

School of Chemical Engineering and Technology, Tianjin University, Tianjin, PR China

**Abstract**

Thermal decomposition of pure dimethyl sulfoxide (DMSO) and DMSO in the presence of different incompatible substances including N,N-dimethyl formylamine, NaOH, KBr and FeCl<sub>3</sub> were investigated using accelerating rate calorimeter. Hazard indicators such as onset temperature Tonset, adiabatic temperature rise ΔT<sub>ad</sub>, maximum pressure P<sub>max</sub> at T<sub>final</sub>, residual pressure P<sub>residual</sub> at 50 °C, maximum rate of pressure-rise (dP/dt)<sub>max</sub> and self-heating rate (dT/dt)<sub>max</sub> have been determined directly. Activation energy E<sub>a</sub> of decomposition reaction and time to maximum rate TMR<sub>ad</sub> of pure and impure DMSO have been studied from the measured self-heating rate data by assuming a zero-order reaction. Moreover, the decomposition mechanisms of pure and impure DMSO have also been discussed.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0040603113001044>

***Evaluation of thermal hazards and thermo-kinetic parameters of a matchhead composition by DSC & ARC***  
***Thermochimica Acta 557 (2013) 13– 19***

S.P. Sivapirakasama\*, M. Nalla Mohameda, M. Surianarayananb, V.P. Sridharb

<sup>a</sup> Safety Engineering Lab, Department of Mechanical Engineering, National Institute of Technology, Tiruchirappalli 620 015, India

<sup>b</sup> Cell for Industrial Safety and Risk Analysis, Central Leather Research Institute, Adyar, Chennai 600 020, India

**Abstract**

From the process safety point of view, irrespective of the kind of stimulus (friction, impact, heat), the final event is “thermal” in nature. Differential Scanning Calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) were performed to understand thermal characteristics and kinetics of a matchhead composition. A single sharp and narrow exothermic transition occurred at 200, 210, 215 and 220 °C at different heating rates (5, 10, 15 and 20 °C min<sup>-1</sup>) suggesting that the matchhead composition was vulnerable to thermal hazard. ARC studies depicted onset temperature at 115.5 °C and a sharp rise in exothermic reaction at 127.64 °C within the time span of 14 s with the maximum heat release rate of 598.4 °C min<sup>-1</sup>. The exothermic activity resulted in rapid pressure rise (50.45 bar) confirming the vulnerability of this mixture to undergo catastrophic explosion. Kinetic parameters were estimated for the thermal process observed in DSC and ARC. Such data were validated.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0040603113000646>

## **Thermal stability evaluation of $\beta$ -artemether by DSC and ARC**

***Thermochimica Acta 569 (2013) 134– 138***

Haisu Gao, Liping Chen\*, Wanghua Chen, Shilong Bao

Department of Safety Engineering, School of Chemical and Environment, Nanjing University of Science and Technology, Nanjing, China

### Abstract

The thermal stability of  $\beta$ -artemether under dynamic, isothermal and adiabatic conditions were investigated by differential scanning calorimeter (DSC) and accelerating rate calorimeter (ARC), respectively. The dynamic DSC measurements at various heating rates (1, 2, 4 and 8 °C min<sup>-1</sup>) displayed that  $\beta$ -artemether experienced polymorph transformation in the melting process. According to the isothermal DSC results at different temperatures 86, 88, 90 and 92 °C,  $\beta$ -artemether decomposed after the completion of the melting and the polymorph transformation, and the thermal decomposition of  $\beta$ -artemether is hazardous for its characteristic of autocatalytic decomposition. The kinetics analysis dynamically and isothermally described by Friedman method indicated the thermal decomposition of  $\beta$ -artemether did not comply with a single mechanism. The ARC results showed that the pressure increased with the increase of temperature, and indicated obvious linear relationship. Based on the ARC data, the value of SADT of  $\beta$ -artemether in 50 kg package was obtained.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0040603113003869>

## ***Accelerating rate calorimeter studies of water-induced thermal hazards of fireworks tip mixture***

***Journal of Thermal Analysis and Calorimetry June 2013, Volume 112, Issue 3, pp 1335-1341***

Thermochemical Laboratory, Department of Chemical

Vethathiri Pakkirisamy Sridhar, Mahadevan Surianarayanan, Suthangathan Paramashivan Sivapirakasam, Asit Baran Mandal Engineering, Central Leather Research Institute (CLRI), Adyar, Chennai 600020, Tamilnadu, India

### Abstract

The objective of this article is to generate thermal decomposition data on fireworks tip mixture, a mixture used to coat the tip of fireworks, for easy ignition. This mixture has reportedly involved in triggering many accidents in fireworks industry. Different quantities of water were added to the mixture and its thermal characteristics were studied. Differential scanning calorimeter was used for screening tests and accelerating rate calorimeter was used for detailed studies in adiabatic and isothermal modes. The self-heat rate data obtained showed onset temperature for different quantity of water, at a range of 80–170 °C. The mixture with 40 % water wt/wt had onset at 80 °C in adiabatic mode. The same mixture on isoaging at 40 °C exhibited exothermic characteristics with a substantial rise in system pressure (57 bar). The heats of exothermic decomposition and Arrhenius kinetics were also computed.

Link to Purchase Paper: <http://link.springer.com/article/10.1007%2Fs10973-012-2716-5>

## ***Thermal behavior pattern of tributyl phosphate under adiabatic conditions***

***Journal of Thermal Analysis and Calorimetry January 2013, Volume 111, Issue 1, pp 849-856***

V. S. Smitha, M. Surianarayanan, H. Seshadri, A. B. Mandal Thermo Chemical Lab, Chemical Engineering Department, Central Leather Research Institute (CLRI), Adyar, Chennai 600 020, Tamilnadu, India

### Abstract

Violent decomposition of Tributyl Phosphate (TBP), a widely employed extractant in the Plutonium Uranium Extraction process of nuclear fueling reprocessing plants in the presence of Nitric acid at temperatures in excess of 130 °C is a matter of concern in serious accidents including in the Savannah River (USA) and Tomsk (Russia). The thermal behavior of TBP under adiabatic conditions employing the world's benchmark adiabatic calorimeter, the Accelerating Rate Calorimeter is examined. TBP shows multiple self heating exothermic activities with the onset of primary exotherm at 250 °C. The exothermic activity is accompanied by considerable pressure rise. The thermal decomposition of TBP is found to follow first order Arrhenius kinetic model. TBP loses about 70% of its chemical moieties as volatile matter during the exothermic decomposition. Spectroscopic methods are used to elucidate the degradation pathway.

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***Thermal hazard analysis of cyclohexanone peroxide and its solutions***  
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Abstract

Cyclohexanone peroxide (CYHPO) is widely used in the chemical industry, but unfortunately, as an organic peroxide, it has been involved in many serious fires and explosions in daily manufacturing, storage, and transportation. We present an advanced methodology of application of thermal analysis for thermal hazard investigation of complex chemical reactions. The applied method is based on a differential isoconversional approach and involves the combination of non-isothermal differential scanning calorimetry (DSC) and adiabatic measurements by accelerating rate calorimeter (ARC) for kinetic analysis and prediction. The kinetic parameters and heat balance were analyzed and used for a simulation of the adiabatic behavior: time to maximum rate under adiabatic conditions (TMRad) and self-accelerating decomposition temperature (SADT). Applications of finite element analysis (FEA) for heat balance and accurate kinetic description allowed us to determine the effect of scale, geometry, heat transfer, thermal conductivity, and ambient temperature on the heat accumulation process. The presented explosion simulations of the thermal behavior of 100 kg storage tank at different temperatures, related to the possible storage scenarios, may help in the elucidation of a real accident which occurred in Beijing during CYHPO storage.

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## 2012

***Study on thermal properties and kinetics of benzoyl peroxide by ARC and C80 methods***  
***Journal of Thermal Analysis and Calorimetry March 2012, Volume 107, Issue 3, pp 943-948***

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Abstract

Benzoyl peroxide (BPO) has been widely used in the industrial and food field, it is sensitive to shock, heat and friction, and causes thermal explosion incidents easily. Therefore, it is important to understand its thermal behaviors and kinetics for loss prevention and safety management. Two kinds of experimental methods (C80 calorimetry and accelerating rate calorimetry) were used to study the hazardous characteristics of BPO, and idea kinetic parameters, such as the pre-exponential factor and the activation energy were obtained. These results contribute to improve the safety in the reaction, transportation, and storage processes and help to the stability criterion of decomposition reaction of BPO

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### ***Thermal hazard research of smokeless fireworks***

***Journal of Thermal Analysis and Calorimetry September 2012, Volume 109, Issue 3, pp 1151-1156***

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#### Abstract

The problem of dealing with expired military propellant is paid wide attention throughout the world. Currently, destruction is adopted as the main disposal route; however, the process is cumbersome, dangerous, costly, and even more non-environment-friendly. As a result, it is absolutely necessary to find out an appropriate recycling method. Nowadays a feasible method, by which the expired military powders are used to make smokeless fireworks, has already been proposed. However, the security of expired military propellant is still making all those concerned anxious on account of the stabilizer's volatilization during long-term storage. In this article, waste single base propellant (named powder 128, one of expired military propellants) and waste single base propellant/potassium perchlorate mixed powder are analyzed by differential scanning calorimeter (DSC) and accelerating rate calorimeter (ARC). The mixtures of these two are considered as the ideal raw materials of smokeless fireworks. DSC results show onset temperature, peak temperature, and normalized heat release of thermal decomposition under the condition of linear heating. Based on DSC data, activation energy and pre-exponential factor of the test samples are calculated according to Kissinger method, Ozawa method, and Friedman method. Furthermore, TD24 is derived by means of AKTS-Thermokinetics software using DSC data. ARC results reveal onset temperature, adiabatic temperature rise, self-heat rate, time to maximum rate and pressure-temperature profile. TD24, which can be applied for the evaluation of thermal and pressure hazards, can be obtained in two ways from the data measured by ARC. One is calculated directly from the experiment, and the other indirectly from the fit-calculations. Based on these results, the thermal hazards of these two mixtures were analyzed preliminarily

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### ***Adiabatic thermokinetics and process safety of pyrotechnic mixtures***

***Journal of Thermal Analysis and Calorimetry September 2012, Volume 109, Issue 3, pp 1387-1395***

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#### Abstract

Pyrotechnic mixtures are susceptible to explosive decompositions. The aim of this paper is to generate thermal decomposition data under adiabatic conditions for fireworks mixtures containing potassium nitrate, barium nitrate, sulfur, and aluminum which are manufactured on a commercial scale. Differential scanning calorimeter is used for screening tests and accelerating rate calorimeter is used for other studies. The self heat rate data obtained showed onset temperature in the range of 275–295 °C for the fireworks atom bomb, Chinese cracker and palm leaf cracker. Of the three mixtures studied, atom bomb mixture had an early onset at 275 °C. The mixtures in general showed vigor exothermic decompositions. Palm leaf mixture exhibits multiple exotherm and reached a final temperature of 414 °C. The thermal decomposition contributes to substantial rise in system pressure. The heats of exothermic decomposition and Arrhenius kinetics were computed. The kinetic data are validated by comparing the predicted self heat rates with the experimental data

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