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Battery Papers 2024

Correlating lithium plating quantification with thermal safety characteristics of lithium-ion batteries Energy Storage Materials Volume 66, 25 February 2024, 103214

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Abstract

Lithium plating is one of the most safety-critical side reactions in lithium-ion (Li-ion) batteries. It is likely to occur under overcharge or fast-charge scenarios when the overwhelming Li-ion flux exceeds the intercalation or diffusion limits of the graphite host structure. Adverse lithium plating will cause the loss of lithium inventory to accelerate degradation and reduce the cell safety limits due to high thermal instability. Correlating lithium plating quantification with cell-level thermal safety characteristics remains a critical bottleneck. In this study, we derive correlations between the total plating energy and kinetic parameters of lithium plating induced exothermic reactions. Three-electrode electrochemical analytics of Li-ion pouch cells, under isothermal and thermal gradient conditions, are analyzed based on decoupled anode potential for lithium plating signatures. Post-mortem analysis reveals the distribution, morphology, and chemical state of lithium plating regimes. Accelerating rate calorimetry is employed to evaluate cell thermal hazards, followed by thermos-kinetic analysis to reveal correlations between the safety factor and plating energy. This work reveals the evolution of lithium plating induced early cell exotherm and total heat generation, promoting the development of real-time battery safety monitoring based on the online detection of lithium plating severity.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2405829724000424>

Needle penetration studies on automotive lithium-ion battery cells: Influence of resistance between can and positive terminal on thermal runaway

Journal of Power Sources Volume 592, 1 February 2024, 233902

Journal of Power Sources

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Abstract

Thermal runaway (TR) can be initiated by the heat dissipated from an internal short circuit (ISC). In prismatic cells, a crucial type of ISC is located between the cell can on positive potential and the first anode layer. To enhance the safety, the potential of the can could be adjusted by increasing the ISC resistance, i.e., realizing a floating can, whereas a universal automotive prismatic cell has a can on potential in contrast. This work demonstrates that the floating can mitigates the ISC current and possibly prevents ISC from leading to TR using an advanced needle penetration test. Moreover, the ISC current was quantitatively measured, proving that there is no significant ISC current between floating can and outmost anode, while the ISC with can on potential can

cause TR. To demonstrate that such difference originates only from the increased resistance, the equivalence in thermal behaviors between the two types of cans was analyzed by a heat-wait-see test in an accelerating rate calorimeter. This work provides not only a guidance on designing a safer prismatic cell but also a prospect how the optimized needle penetration test can bring a deeper insight into the internal processes of Lithium-ion cells during mechanical abuse.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0378775323012788>

Analysis of the thermal runaway phenomenon of Nickel-Manganese-Cobalt cells induced by nail penetration through high-speed infrared imaging

Journal of Energy Storage Volume 75, 1 January 2024, 109709

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Abstract

Gradual replacement of fossil fuels by clean and renewable energies is crucial to minimize the greenhouse effect from the transport sector. The electric vehicle is intended to be the leading technology for this purpose, for which clean and renewable energy must be stored as chemical energy in the battery. From the safety point of view, the main issue of this technology is related to the risk of thermal runaway. Among other factors, a collision can be one of the causes of a battery electric vehicle explosion, as damage to the surface of the battery can generate a short circuit, resulting in a battery thermal runaway. To replicate this situation at a system level, the nail penetration test is reproduced in laboratories. In this work, the effect of the nail penetration position, battery state of charge (SOC) and initial ambient temperature on the thermal runaway behavior of a Nickel-Manganese-Cobalt 811 cell is investigated. Infrared images were used to evaluate the temperature distribution in the battery surface, revealing the root causes for the scattering observed in the surface temperature when measured through thermocouples. Furthermore, a methodology to correct the thermographic images is described, abiding the main uncertainties related to the characteristics of the optical access. The results show that the battery state of charge has a strong effect on the heat release than nail position and initial ambient temperature, increasing in 20 % from SOC 50 % to SOC 100 %. Regarding the position, nail penetration tests at the top of the battery lead to lower temperatures when compared to the other positions, representing 10 % less heat release than middle and bottom nail position. Furthermore, the thermographic images showed a variability in the spatial distribution of temperature between the test cells of up to 40 °C, with case rupture being mainly responsible for the higher values.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2352152X23031079>

2023

Analysis of the aging effects on the thermal runaway characteristics of Lithium-Ion cells through stepwise reactions

Applied Thermal Engineering 230 (2023) 120685

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Abstract

The current political vision to drastically reduce carbon emissions pushes the electrified powertrain into an increasingly important role in the transport sector. However, concerns related to the battery's effectiveness as an energy source need to be overcome to make this technology widespread. One such concern is safety, catching attention as development races towards greater battery energy density. In this way, cathodic chemistry is important since exothermic reactions are unleashed from the components that originally formed the active material. Furthermore, the aging process reduces the battery capacity, reducing the amount of active material and thickening the solid electrolyte interface, which increases the joule effect. For these reasons, thermal runaway under aging conditions must be investigated to assess potential safety issues. Using an accelerating rate calorimeter, the heat-induced thermal runaway tests were performed with two-cathode chemistry (NMC and LFP) under pristine and aged battery conditions. For aging the batteries, the ARC was coupled with a bidirectional source. Two ambient temperatures, 20 °C and 50 °C, were used for the aging tests, being the batteries cycled up to 250 cycles with a determined protocol for charge and discharge. A numerical model was fed with experimental tests, targeting optimizing the battery output parameters and obtaining geometric aspects that are

difficult to measure. Unlike the single step model, a stepwise reactions model was created to assess the heat release from different battery components for pristine and aged conditions. The higher endothermic behavior from cathode decomposition and less oxygen released during this reaction make the LFP battery safer than the NMC. For aged batteries, the SEI growth consumes lithium and electrolyte, decreasing the quantity of both components in the anode. Thus, the anode and electrolyte reaction after SEI decomposition is lower, improving battery safety.

Link to paper (open access): <https://www.sciencedirect.com/science/article/pii/S1359431123007147>

A comparative analysis of lithium-ion batteries with different cathodes under overheating and nail penetration conditions

Applied Thermal Engineering

Volume 230, Part A, 25 July 2023, 120685

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Abstract

This work compares the thermal runaway characteristics and heat generation of LiCoO₂(LCO), Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O₂ (NMC622) and LiFePO₄ (LFP) batteries with the same capacity under thermal abuse, and provides an in-depth study of the electro-thermal behaviour and internal physical-chemical changes under mechanical abuse, forming basis for understanding thermal runaway and safe use of batteries. The overheating test shows that the LCO battery is the most dangerous during thermal runaway because of higher heat generation, followed by the NMC622 and LFP batteries. However, the LFP battery is more prone to thermal runaway than the NMC622 and LCO batteries under adiabatic environment due to the shortest time to trigger thermal runaway. The nail penetration test shows the NMC622 battery has the worst internal short circuit tolerance, followed by the LCO and LFP batteries. The LFP material is less affected by nail penetration and extrusion, and the LFP battery at 50% state of charge (SOC) has the lowest risk of thermal runaway. The particles and crystal structures of the LCO and NMC622 materials are obviously damaged due to nail penetration, especially the LCO, which produces a new phase LiAlCoO_{0.8}O₂. The risk of thermal runaway of the battery increases with the increase of SOC.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0360544223014214>

Comparative study on the influence of incident heat flux on thermal runaway fire development of large-format lithium-ion batteries

Process Safety and Environmental Protection

Volume 176, August 2023, Pages 831-840

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Abstract

In response to the growing demand for higher energy density in various applications, large-format batteries have gained popularity. However, the larger size of these batteries also increases their exposed area, which may lead to more severe thermal events. This study aims to understand the influence of incident heat flux on the occurrence and progression patterns of fires in large-format lithium-ion batteries. Two representative large-format lithium-ion batteries, 38 Ah LiNi_{0.3}Co_{0.3}Mn_{0.3}O₂ prismatic cell and 78 Ah LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ pouch cell, were investigated. To evaluate the thermal hazard to the environment, the heat release rates (HRR) of the lithium-ion battery fire were measured under incident heat fluxes ranging from 10 to 50 kW·m⁻², using the oxygen consumption principle. The results highlight significant differences in thermal runaway and fire development between

the 38 Ah and 78 Ah cells, attributable to variations in structure and materials, and scale effect. The 38 Ah cell exhibited an evident venting stage, characterized by an unignited jet on the verge of ignition, followed by a transition from momentum-driven jet fire to buoyancy-driven jet fire. In contrast, the 78 Ah cell experienced direct ignition, accompanied by strong air entrainment, overflow flame, and flame sinking phenomena as the fire progressed. Notably, unlike the 38 Ah cell, the peak HRR, THR, and burning time of the 78 Ah cell were minimally sensitive to the incident heat flux. Furthermore, a generalized relationship model between the incident heat flux and the ignition time was established and validated based on the energy conservation equation during the ignition stage of the cell. This model enhances our understanding of the interplay between incident heat flux and ignition time, contributing to the development of strategies for fire prevention and mitigation in large-format lithium-ion batteries.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0957582023005566>

Thermal and Mechanical Safety Assessment of Type 21700 Lithium-Ion Batteries with NMC, NCA and LFP Cathodes—Investigation of Cell Abuse by Means of Accelerating Rate Calorimetry (ARC) Batteries 2023, 9, 237

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Abstract

In this experimental investigation, we studied the safety and thermal runaway behavior of commercial lithium-ion batteries of type 21700. The different cathode materials NMC, NCA and LFP were compared, as well as high power and high energy cells. After characterization of all relevant components of the batteries to assure comparability, two abuse methods were applied: thermal abuse by the heat-wait-seek test and mechanical abuse by nail penetration, both in an accelerating rate calorimeter. Several critical temperatures and temperature rates, as well as exothermal data, were determined. Furthermore, the grade of destruction, mass loss and, for the thermal abuse scenario, activation energy and enthalpy, were calculated for critical points. It was found that NMC cells reacted first, but NCA cells went into thermal runaway a little earlier than NMC cells. LFP cells reacted, as expected, more slowly and at significantly higher temperatures, making the cell chemistry considerably safer. For mechanical abuse, no thermal runaway was observed for LFP cells, as well as at state of charge (SOC) zero for the other chemistries tested. For thermal abuse, at SOC 0 and SOC 30 for LFP cells and at SOC 0 for the other cell chemistries, no thermal runaway occurred until 350°C. In this study, the experimental data are provided for further simulation approaches and system safety design.

Link to open access paper: <https://www.mdpi.com/2313-0105/9/5/237>

Experimental study of three commercially available 18650 lithium ion batteries using multiple abuse methods

Journal of Energy Storage Volume 65, 15 August 2023, 107293

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Abstract

This study provides a comparative analysis of three commercially available and electrically similar lithium-ion batteries with a nominal capacity of 3 Ah, through a series of thermal, electrical, and mechanical abuse. Swab samples suggested that one cell type had an NMC [Li(Ni_xMn_yCo_{1-x-y})O₂] cathode, and the remaining two had an NCA [Li(Ni_xCo_yAl_{1-x-y})O₂] cathode. The precise nature of the chemical compositions and their ratios are not known. Repeated ARC tests showed that the three cells had comparable self-heating temperatures (~83 °C). Downward pressures of up to 41.5 kPa were recorded but were varied across all cells, and the furthest distance it travelled was over 40 m. Pressure vessel tests indicated that at least 20 L of air is required to ensure complete combustion, and higher molar concentrations in a nitrogen environment were witnessed for the NCA cells compared to the NMC cell, ~0.067 and ~0.052 mol Ah⁻¹, respectively. Overcharge tests at higher charging rates approached temperatures required for thermal runaway, and a variety of safety mechanisms were observed. Comparable LIBs on paper do not always fail in the same way and therefore the results from one test cannot be reliably extrapolated to different cells despite their similarities.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2352152X23006904>

Failure and hazard characterisation of high-power lithium-ion cells via coupling accelerating rate calorimetry with in-line mass spectrometry, statistical and post-mortem analyses

Journal of Energy Storage Volume 65, 15 August 2023, 107069

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Abstract

Lithium-ion battery safety continues to be an obstacle for electric vehicles and electrified aerospace. Cell failure must be studied in order to engineer improved cells, battery packs and management systems. In this work, the thermal runaway of commercially available, high-power cells is studied, to understand the optimal areas to develop mitigation strategies. Accelerating rate calorimetry is coupled with mass spectrometry to examine self-heating and the corresponding evolution of gases. A statistical analysis of cell failure is then conducted, combined with post-mortem examinations. The methodology forms a robust assessment of cell failure, including the expected worst- and best-cases, and the associated real-world hazards. Cells produce a highly flammable, toxic gas mixture which varies over the course of self-heating. Failure also produces particulate matter which poses a severe health hazard. Critically, the onset of self-heating is detectable more than a day in advance of full thermal runaway. Likewise, voltage drops and leaks are detectable prior to venting, highlighting the potential for highly effective early onset detection. Furthermore, the behaviour of the cap during thermal runaway indicates that ejection of material likely reduces the chance of thermal runaway propagation to neighbouring cells. These findings also emphasise that research must be conducted safely.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2352152X23004668#f0045>

Change of safety by main aging mechanism – A multi-sensor accelerating rate calorimetry study with commercial Li-ion pouch cells

Journal of Power Sources Volume 570, 30 June 2023, 233046

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Abstract

The safety of Li-ion batteries is the most critical of many important characteristics and must be carefully considered. However, depending on the aging conditions, safety of batteries can change drastically. We had recently introduced ARC-MS as a new tool for safety investigations, which is an updated accelerating rate calorimeter (ARC) combined with a mass spectrometer (MS). Additionally, our ARC-MS setup is equipped by seven more low cost sensors (temperature, voltage, resistance, audio, strain, and transmitted and reflected ultrasound). In this paper, the dependence of safety on the dominant aging mechanism as a function of aging temperature, and state-of-health (SOH) is investigated on the example of 3.3 Ah commercial pouch cells. The ambient temperature during aging has a strong influence on the dominant aging mechanism (Li plating or SEI growth) of this cell as shown by Arrhenius plots of the aging rate and Post-Mortem analyses (ICP-OES, SEM, EDX, Hg porosimetry, STA) of aged cells. Our in-depth evaluation shows that different sensors can provide indications of safety relevant events (onset of swelling, onset of self-heating, cell venting, stable exothermic reactions, separator melting, and thermal runaway) in the cells independently. Combining these low-cost sensors might be a solution for detection of unsafe cells in applications.

Link to open access paper: <https://www.sciencedirect.com/science/article/pii/S0378775323004214>

Comprehensive analysis on aging behavior and safety performance of LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂/graphite batteries after slight over-discharge cycle

Applied Thermal Engineering Volume 225, 5 May 2023, 120172

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Abstract

Over-discharge is one of the common abuse conditions for lithium-ion batteries (LIBs), while the safety hazard of over-discharged cell is still unclear. In this work, the aging behavior and safety performance of commercial Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O₂/graphite LIBs under 1.5, 1.0, 0.5, and 0.0 V over-discharge cycles are investigated. The cells experience capacity decay and structural damage during over-discharge cycle. Compare to the normal cycled cells, the increased impedance after over-discharge cycle leads to more heat generation during operating, which further accelerates the inconsistency of LIB module. Moreover, the thermal runaway behavior of the over-discharged cell was studied using Extended Volume Accelerating Rate Calorimeter. The kinetics of self-heating reaction is obtained, and the criticality of thermal runaway under different heat dissipation conditions was analyzed based on Semenov model. The thermal stability and maximum safe storage temperature of the LIB were decreased after over-discharge cycle, especially for the cell over-discharged to 0.0 V. Based on the electrochemical impedance spectroscopy, the loss of lithium inventory relate to the growth of solid electrolyte interphase (SEI) film is found to be the primary aging contribution. Moreover, the post-mortem test implied the dissolution of Cu initiated when over-discharged to 0.5–0.0 V.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S1359431123002016>

The suppression performance of fluorinated cooling agents on the Lithium-ion Batteries fire based on the Accelerating Rate Calorimeter (ARC)

Thermal Science and Engineering Progress Volume 42, 1 July 2023, 101877

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Abstract

Lithium-ion Batteries (LIB) fire has attracted a wide attention since it threatens the application limitation of LIB. The combustible gases are produced during the LIB thermal runaway. When the immersion cooling technology is used for LIB thermal management, the mixture of combustible gases and fluorinated cooling agents in a confined space could result in a big explosion due to the LIB thermal runaway. With an aim to have a deep understanding regarding the influence of fluorinated immersion cooling agents on the fire suppression performance, a series of tests were conducted to obtain the profile of critical temperature and pressure based on the accelerating rate calorimeter (ARC). During the tests, the cylindrical 18,650 LIB is heated under insulated environment firstly. Then several typical fluorinated cooling agents are selected to clarify the fire suppression performance of LIB thermal runaway. The results and discussion indicate that the utilization of HT (hexafluoropropene trimer) agent has a peak pressure 0.6 Mpa and a peak temperature 823 °C during LIB thermal runaway. The suppression results varying seven typical fluorinated cooling agents are discussed. BTP (2-Bromo-3,3,3-trifluoro propene) shows an obvious suppression effect because it results in a low pressure ratio. The suppression mechanism of agents on the LIB thermal runaway is discussed and presented. It could provide a insight into the development of new fluorinated agents for suppression.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2451904923002305>

Experimental investigation on thermal runaway suspension with battery health retention

Applied Thermal Engineering 225 (2023) 120239

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Abstract

With growing applications of Li-ion batteries in ground transportation and energy storage, thermal runaway of Li-ion batteries has become a major concern for energy and public safety. Existing studies on thermal runaway mitigation methods are largely passive, in that most of them focus on propagation mitigation and fire extinguish after thermal runaway has been triggered. In this work, we presented experimental results on thermal runaway suspension with battery health retention, for the first time. By analyzing the temperature and voltage evolution of commercial 18,650 cells with Lithium iron phosphate chemistry during step-heating thermal runaway test in an accelerating rate calorimeter, it is found that the voltage signal has a sudden drop corresponding to a similar temperature of 135 °C, before the occurrence of thermal runaway. Thermal runaway suspension experiments are then conducted by activating cooling when either the voltage drop or the target temperature signal is reached. It is observed that thermal runaway suspension from the target voltage drop signal fails to prevent the battery from further damage, even with fast liquid N₂ cooling. For thermal runaway suspension at the temperature signal 130 °C, batteries are successfully saved regardless of fast cooling with liquid N₂, or slow cooling using N₂ gas. Further electrical impedance spectrum testing shows that the batteries survived from thermal runaway suspension have increased bulk resistance while polarization resistance remains unchanged. The cycling performance of the saved batteries has demonstrated identical voltage but reduced capacity by around 20 %. This research can provide useful guidance on thermal runaway prevention and health retention of Li-ion batteries

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S1359431123002685>

Thermal and Electrochemical Analysis of Thermal Runaway Propagation of Samsung Cylindrical Cells in Lithium-ion Battery Modules

Journal of The Electrochemical Society, 2023 170 010515

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Abstract

Thermal runaway propagation analysis at the module and cell level was performed using the Samsung 30Q 18650 cylindrical cells. Measurements such as cell enthalpy, maximum thermal runaway temperature, and thermal runaway onset and initiation temperatures were collected and shown to be consistent by means of accelerated rate calorimetry (ARC). This study showed, using the module billet as a thermal runaway propagation mitigation strategy, the cell energy was successfully absorbed during a failure event and prevented thermal runaway propagation from between cells. However, the module level tests showed average maximum temperatures that were 229 °C higher than the average maximum temperatures in the cell level tests, showing the importance of evaluating both the cell level thermal runaway response and the module level response, as they can be different. This work shows the differences between cell TR and module level TR and an effective mitigation strategy based on effective spacing and thermal mass.

Link to open access paper: <https://iopscience.iop.org/article/10.1149/1945-7111/aca939>

Understanding of thermal runaway mechanism of LiFePO₄ battery in-depth by three-level analysis

Applied Energy

Volume 336, 15 April 2023, 120695

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Abstract

The complex chemical composition and material interactions of lithium-ion batteries challenge the in-depth understanding of thermal runaway reactions and failure mechanisms. In this study, detailed analysis and implementation have been made from three levels to further explain the thermal failure mechanism, from material interactions to cell-level experiments and applications. The LiFePO₄ thermal runaway mechanism is put forward to characterize exothermic peaks from differential analysis of differential scanning calorimetry (DSC) and Accelerating Rate Calorimetry (ARC) data. Furthermore, the development, parameterization, and application of the thermal runaway prediction model are also discussed. Multi-heating rate data is a prerequisite to kinetic analysis and modeling work and provides valuable data set for LiFePO₄ thermal failure. And the unraveled mechanism is believed to provide a profound understanding of the thermal failure mechanism, strengthening interactions between material characterization and thermal runaway modeling.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0306261923000594>

Understanding the failure mechanism towards developing high-voltage single-crystal Ni-rich Co-free cathodes.

Green Energy & Environment Available online 5 December 2022 In Press, Corrected Proof

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Abstract

Benefited from its high process feasibility and controllable costs, binary-metal layered structured $\text{LiNi}_{0.8}\text{Mn}_{0.2}\text{O}_2$ (NM) can effectively alleviate the cobalt supply crisis under the surge of global electric vehicles (EVs) sales, which is considered as the most promising next generation cathode material for lithium-ion batteries (LIBs). However, the lack of deep understanding on the failure mechanism of NM has seriously hindered its application, especially under the harsh condition of high-voltage without sacrifices of reversible capacity. Herein, single crystal $\text{LiNi}_{0.8}\text{Mn}_{0.2}\text{O}_2$ is selected and compared with traditional $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM), mainly focusing on the failure mechanism of Co-free cathode and illuminating the significant effect of Co element on the Li/Ni antisite defect and dynamic characteristic. Specifically, the presence of high Li/Ni antisite defect in NM cathode easily results in the extremely dramatic H2/H3 phase transition, which exacerbates the distortion of the lattice, mechanical strain changes and exhibits poor electrochemical performance, especially under the high cutoff voltage.

Furthermore, the reaction kinetic of NM is impaired due to the absence of Co element, especially at the single-crystal architecture. Whereas, the negative influence of Li/Ni antisite defect is controllable at low current densities, owing to the attenuated polarization. Notably, Co-free NM can exhibit better safety performance than that of NCM cathode. These findings are beneficial for understanding the fundamental reaction mechanism of single-crystal Ni-rich Co-free cathode materials, providing new insights and great encouragements to design and develop the next generation of LIBs with low-cost and high-safety performances.

Link to paper (open access): <https://www.sciencedirect.com/science/article/pii/S2468025722001777>

Investigation on step overcharge to self-heating behavior and mechanism analysis of lithium ion batteries **Journal of Energy Chemistry: Available online 3 January 2023 - In Press, Journal Pre-proof**

Fengling Yun^{a,c}, Shiyang Liu^b, Min Gao^{a,c}, Xuanxuan Bi^d et al

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Abstract

To obtain intrinsic overcharge boundary and investigate overcharge mechanism, here we propose an innovative method, the step overcharge test, to reduce the thermal crossover and distinguish the overcharge thermal behavior, including 5% state of charge (SOC) with small current overcharge and resting until the temperature equilibrium under adiabatic conditions. The intrinsic thermal response and the self-excitation behaviour are analysed through temperature and voltage changes during the step overcharge period. Experimental results show that the deintercalated state of the cathode is highly correlated to self-heating parasitic reactions. Before reaching the upper limit of Negative/Positive (N/P) ratio, the temperature changes little, the heat generation is significantly induced by the reversible heat (endothermic) and ohmic heat, which could balance each other. Following that the lithium metal is gradually deposited on the surface of the anode and reacts with electrolyte upon overcharge, inducing self-heating side reaction. However, this spontaneous thermal reaction could be "self-extinguished". When the lithium in cathode is completely deintercalated, the boundary point of overcharge is about 4.7 V (~148% SOC, >40 °C), and from this point, the self-heating behaviour could be continuously triggered until thermal runaway (TR) without additional overcharge. The whole static and spontaneous process lasts for 115 h and the side reaction heat is beyond 320,000 J. The continuous self-excitation behavior inside the battery is attributed to the interaction between the highly oxidized cathode and the solvent, which leads to the dissolution of metal ions. The dissolved metal ions destroy the SEI (solid electrolyte interphase) film on the surface of

the deposited Li of anode, which induces the thermal reaction between lithium metal and the solvent. The interaction between cathode, the deposited Li of anode, and solvent promotes the temperature of the battery to rise slowly. When the temperature of the battery reaches more than 60 °C, the reaction between lithium metal and solvent is accelerated. After the temperature rises rapidly to the melting point of the separator, it triggers the thermal runaway of the battery due to the short circuit of the battery.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2095495622007045>

Energy assessment of the ageing phenomenon in Li-Ion batteries and its impact on the vehicle range efficiency

Energy Conversion and Management 276 (2023) 116530

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Abstract

The 2035 European Union ban on internal combustion engines pushes the transport industry toward alternative propulsion technologies. One of the most potent alternatives to the 250 million passenger automobiles in Europe is the use of electric vehicles with lithium-ion batteries as a special energy storage system. To develop a sustainable, money-saving, and mature technology like today's internal combustion engines, however, issues including battery deterioration, charging times, and safety must be addressed. In this study, Lithium Ferrum Phosphate and Nickel Manganese Cobalt, two distinct cathode chemistries indicative of transport solutions, are compared for cell performance and ageing. It is possible to improve battery design to increase capacity and lower the risk of thermal runaway by using experimental and numerical methods to evaluate and predict the battery ageing effect. The calibrated ageing model may also forecast battery life and its effect on the vehicle's driving range. The findings indicate that the Lithium Ferrum Phosphate cathode chemistry has a lower energy density and ages more quickly than the Nickel Manganese Cobalt, resulting in a shorter driving range. In specifically, a brand-new Nickel Manganese Cobalt battery provides 84 km of additional city driving range and 50 km of highway driving range over a Lithium Ferrum Phosphate battery. The Nickel Manganese Cobalt battery offers 53 km more driving range on the interstate and 91 km more in urban driving at the end of its useful life (20 % capacity loss).

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0196890422013085>

An investigation on thermal runaway behaviour of a cylindrical lithium-ion battery under different states of charge based on thermal tests and a three-dimensional thermal runaway model

Journal of Cleaner Production: Volume 388, 15 February 2023, 135980

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Abstract

A significant risk for lithium-ion batteries (LIBs) is fire and explosions caused by thermal runaway (TR). A TR model for LIBs with various states of charge (SOCs) can help design safer battery modules. In this work, the TR mechanism of a commercial Li[Ni₅Co₂Mn₃]O₂/graphite 18650 type cylindrical battery with various SOCs has been investigated through differential scanning calorimetry (DSC) tests on the single and mixed components. Then, a three-dimensional (3D) TR model is developed to predict the battery TR behaviours under different SOCs. This model fits well with the accelerating rate calorimetry (ARC) test results of the batteries with various SOCs. Furthermore, the validated model and ARC experiment results are employed to investigate the TR mechanism of different SOC batteries. The results show that the reaction onset temperature for cathode-anode and anode-electrolyte roughly advances as the SOC increases and the reaction enthalpy of the cathode-anode, anode-electrolyte and cathode increases with the increase of SOC. Cathode-anode, anode-electrolyte are the main heat generation in the process of battery TR, and their proportion of heat generation will decrease with the decrease of SOC.

Link to purchase paper: <https://www.sciencedirect.com/science/undeararticle/abs/pii/S0959652623001385>

Effect of aging temperature on thermal stability of lithium-ion batteries: Part A – High-temperature aging **Author links open overlay**

Renewable Energy: Volume 203, February 2023, Pages 592-600

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Abstract

Aging and thermal runaway are two significant reasons why lithium-ion batteries are struggling to become more widely available. Aging at different temperatures causes differences in the aging mechanism and thermal runaway behaviour of lithium-ion batteries. In this paper, four sets of commercial lithium-ion batteries are aged at 25 °C, 40 °C, 60 °C and 80 °C respectively for 100 cycles. Then the morphology and composition of the electrodes and separators are analysed in order to reveal the mechanism of changes in electrical performance and thermal stability due to aging at different temperatures. The differences in the decomposition products of the solid electrolyte intermediate (SEI) layer are an important factor in inducing changes in thermal runaway behaviour. At 60 °C, the accumulation of SEI decomposition products results in thicker SEI layers and shorter thermal runaway times. At 80 °C, the SEI decomposition products are heavily transformed into particles with a loose structure, generating a large amount of gas in the process, which further leads to the rupture of the aluminium-plastic film and the evaporation of the electrolyte, with a longer duration of thermal runaway and a lower maximum temperature.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0960148122018882>

2022

Cell-to-cell variability in Li-ion battery thermal runaway: Experimental testing, statistical analysis, and kinetic modelling

Journal of Energy Storage 56 (2022) 106024

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Abstract

As one of the most promising energy storage mediums, Lithium-ion batteries (LIBs) have attracted extensive research interest. A major challenge associated with LIB application is thermal runaway, which can be triggered under abused conditions and impose direct threats to lives and properties. Here, we select Li-ion batteries with lithium cobalt oxide cathode and graphite anode (18650, Samsung), with relatively simple chemistry, to revisit thermal runaway. The experiment is conducted using an accelerating rate calorimeter (EV+ ARC, Thermal Hazard Technology) following the heat-wait-seek strategy, and is repeated for 9 similar new cells with 100 % state of charge (SOC). Key features such as onset temperature of self-heating, the onset temperature of thermal runaway, maximum heat release rate, thermal runaway delay time, and maximum temperature are measured experimentally. Although the cells are all brand new and have been initiated similarly, obvious cell-to-cell variability has been observed in the measured exothermic onset temperature, delay time, and mass losses. It is also shown that the widely used four-step thermal runaway model cannot quantitatively capture the activation energy from the heat release rate. To improve the kinetic modeling and accommodate the cell-to-cell variability, statistical analysis is conducted to process the experimental results. Mean and standard deviation of the frequency factor and activation energy has been acquired to determine the lower and upper bound of the kinetic modeling using a one-step global chemistry. The measured and simulated thermal runaway delay time has reached a reasonable agreement, with the uncertainty of the kinetic model considered. The role of reactant consumption during the heating process is also discussed. The identified cell-to-cell variability should not only be considered for cell-level safety evaluation and modeling, but also in the thermal runaway propagation of battery modules and packs.

Link to paper: <https://www.sciencedirect.com/science/article/pii/S2352152X22020126>

Experimental and modeling investigation on the gas generation dynamics of lithium-ion batteries during thermal runaway

eTransportation. Volume 15, January 2023, 100212

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Abstract

The gas generation and rupture are the special features of the thermal runaway (TR) of lithium-ion batteries (LIBs). The LIB's gas generation dynamics during TR are investigated using the extended-volume accelerating rate calorimeter and a gas-tight canister. The pressure within canister is measured, and the internal gas could be regarded as a lumped system before TR thanks to the adiabatic condition. The pressure increase is about 100 kPa at the safety valve opening, and the corresponding gas release is approximately 10 mmol. For 100% SOC cells, the peak pressure recorded before the canister pressure relief is 2.566 MPa. The gas generation rate is approximately proportional to the temperature increase rate, which facilitates the simulation on the gas generation because temperature is easier to measure. The gas generation process can be divided into different stages, and the multi-stage kinetics parameters (Frequency factor and activation energy) of the gas generation process are calculated, which predict the evolution of internal pressure and rupture behavior of LIB under external heating condition.

Link to paper: <https://www.sciencedirect.com/science/article/abs/pii/S2590116822000571>

Investigation on safety characteristics of high-nickel lithium-ion cells with anode partially doped by silicon oxide

Journal of Loss Prevention in the Process Industries. Volume 80, December 2022, 104924

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Abstract

Considering the prospect of lithium-ion cells with graphite + SiO_x anode and the fact that there is rare literature concerning the safety features of graphite + SiO_x based cells, this work performed an experimental investigation on the safety characteristics of Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂/(graphite+10%SiO_x) cells with different states of charge (50% SOC, 75% SOC and 100% SOC). Besides that, the impact of two well-known electrolyte additive components, i.e. 2% vinylene carbonate+1% ethylene sulfate (2VC1DTD) and 2% fluoroethylene carbonate+1% lithium difluorophosphate (2FEC1LFO) on the safety characteristics of cells was also revealed. The safety characteristics of Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂/(graphite+10%SiO_x) cells seem to be worse than Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂/graphite cells with the same capacity, the former illustrates larger the maximum temperature rise rate in accelerating rate calorimetry (ARC) tests (16,651 vs. ~6000 °C/min). Similar to the other types of lithium-ion cells, the safety features of the cells with graphite + SiO_x anode enhance with the decrease of cell SOC in typical safety tests. 2VC1DTD and 2FEC1LFO are unable to effectively improve the safety performance of cells under abusive conditions, which might result from the fact that the electrolytes addicted with 2VC1DTD and 2FEC1LFO are flammable as well, and 2VC1DTD and 2FEC1LFO cannot restrain the reactivity between anode materials and electrolytes

Link to paper: <https://www.sciencedirect.com/science/article/abs/pii/S0950423022002005>

Simulation, Set-Up, and Thermal Characterization of a Water-Cooled Li-Ion Battery System Batteries 2022, 8(10),

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Abstract

A constant and homogenous temperature control of Li-ion batteries is essential for a good performance, a safe operation, and a low aging rate. Especially when operating a battery with high loads in dense battery systems, a cooling system is required to keep the cell in a controlled temperature range. Therefore, an existing battery module is set up with a water-based liquid cooling system with aluminum cooling plates. A finite-element simulation is used to optimize the design and arrangement of the cooling plates regarding power consumption, cooling efficiency, and temperature homogeneity. The heat generation of an operating Li-ion battery is described by the lumped battery model, which is integrated into COMSOL Multiphysics. As the results show, a small set of nondestructively determined parameters of the lumped battery model is sufficient to estimate heat generation. The simulated temperature distribution within the battery pack confirmed adequate cooling and good temperature homogeneity as measured by an integrated temperature sensor array. Furthermore, the simulation reveals sufficient cooling of the batteries by using only one cooling plate per two pouch cells while continuously discharging at up to 3 C.

Link to paper: <https://www.mdpi.com/2313-0105/8/10/177>

Study on Thermal Runaway Behavior of Li-Ion Batteries Using Different Abuse Methods

Batteries 2022, 8, 201.

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Abstract

Thermal runaway (TR) and the thermal runaway propagation (TRP) of Li-ion batteries can lead to safety incidents and cause explosion or fire accidents. Therefore, TR is a critical issue for the thermal safety of Li-ion batteries. In this study, the TR and TRP behavior of Li-ion batteries using different abuse methods (nail penetration, side heating, and overcharge) was investigated experimentally. First, the Extended Volume Accelerating Rate Calorimetry (EV-ARC) test was performed using the cell with an internal implantation thermocouple for a comparative study. Three abuse methods were used to induce TR and TRP for the cells and modules. At the cell level, the maximum temperature inside the cell under the EV-ARC test, nail penetration, and side-heating abuse was 994.8 °C, 964.3 °C, and 1020 °C, respectively. The thermocouple inside the cell under the overcharge abuse test was broken, and the experimental phenomenon indicated that the cell was most severely damaged under the overcharging abuse test. At the module level, the TRP behavior using the three abuse methods was different than in the first two TR cells, while the behavior of the other cells was similar. It was evidenced that TRP triggered by the overcharge abuse was the most hazardous, followed by the side-heating abuse, and lastly, the nail-penetration abuse was the least.

Link to paper: <https://www.mdpi.com/2313-0105/8/11/201>

Non-uniform phase change material strategy for directional mitigation of battery thermal runaway propagation

Renewable Energy Volume 200, November 2022, Pages 1338-1351

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Abstract

Thermal runaway propagation of the power battery pack is an essential factor affecting the safety of electric vehicles. The commonly adopted propagation inhibition methods mainly include adding heat insulation materials and enlarging battery spacing, which could cause problematic heat dissipation and lower the system energy density. Herein, an innovative battery thermal management system composed of non-uniform thermal conductivity phase change materials and assisted liquid cooling is proposed. Combining the phase change materials with high and low thermal conductivity balances heat transfer and heat insulation requirements. The cooling performance and the ability of thermal runaway propagation mitigation of the proposed schemes are numerically studied. The results show that the proposed strategy can meet the heat dissipation requirements under normal operation and control the thermal runaway in a safe range by transferring the heat generated from the battery thermal runaway in the set direction. The maximum battery temperature and the temperature difference are 38.1 °C and 2.1 °C, respectively, under 3C discharge. Under thermal runaway conditions, the strategy successfully confines the thermal runaway propagation within the middle row. The maximum battery temperature in other rows can be controlled under the irreversible thermal runaway reaction temperature of 200 °C. Further study found that increased thermal conductivity benefits the battery heat dissipation and reduces the risk of thermal runaway. However, it propagates faster and broader once the thermal runaway is triggered. In comparison, the decrease of thermal conductivity is beneficial to the mitigation of propagation but may reduce the overall heat dissipation of the battery module. This study can provide a new way to solve the contradiction between battery temperature control and thermal runaway spread suppression.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0960148122015634>

Dendrite-accelerated thermal runaway mechanisms of lithium metal pouch batteries **SusMat.2022;2:435–444**

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Abstract

High-energy-density lithium metal batteries (LMBs) are widely accepted as promising next-generation energy storage systems. However, the safety features of practical LMBs are rarely explored quantitatively. Herein, the thermal runaway behaviors of a 3.26 Ah (343 Wh kg⁻¹) Li|LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ pouch cell in the whole life cycle are quantitatively investigated by extended volume-accelerating rate calorimetry and differential scanning calorimetry. By thermal failure analyses on pristine cell with fresh Li metal, activated cell with once plated dendrites, and 20-cycled cell with large quantities of dendrites and dead Li, dendrite-accelerated thermal runaway mechanisms including reaction sequence and heat release contribution are reached. Suppressing dendrite growth and reducing the reactivity between Li metal anode and electrolyte at high temperature are effective strategies to enhance the safety performance of LMBs. These findings can largely enhance the understanding on the thermal runaway behaviors of Li metal pouch cells in practical working conditions.

Link to paper: <https://onlinelibrary.wiley.com/doi/full/10.1002/sus2.74>

Combined Thermal Runaway Investigation of Coin Cells with an Accelerating Rate Calorimeter and a Tian-Calvet Calorimeter Batteries 2022, 8, 15

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Abstract

Commercial coin cells with LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ positive electrode material were investigated using an accelerating rate calorimeter and a Tian-Calvet calorimeter. After cycling and charging to the selected states of charge (SOCs), the cells were studied under thermal abuse conditions using the heat-wait-see (HWS) method with the heating step of 5 K and a threshold for self-heating detection of 0.02 K/min. The onset temperature and the rate of the temperature rise, i.e., the self-heating rate for thermal runaway events, were determined. The morphology of the positive electrode, negative electrode and the separator of fresh and tested cells were compared and investigated with scanning electron microscopy (SEM). Furthermore, the microstructure and the chemical compositions of the individual components were investigated by X-ray diffraction (XRD) and inductively coupled plasma with optical emission spectrometry (ICP-OES), respectively. In the Tian-Calvet calorimeter, the coin cells with the selected SOC and the individual components (positive electrode, negative electrode and separator) were heated up with a constant heating rate of 0.1 °C/min (ramp heating mode). Simultaneously, the heat flow signals were recorded to analyze the heat generation. The combination of the three different methods—the HWS method using the ES-ARC, ramp heating mode on both cells and the individual components using the Tian-Calvet calorimeter—together with a post-mortem analysis, give us a complete picture of the processes leading to thermal runaway.

Link to paper: <https://doi.org/10.3390/batteries8020015>

Laser irradiation illuminates uncertain degradation, leading to thermal runaway of 18650 cells charged/discharged at low temperatures

Journal of Power Sources Volume 542, 15 September 2022, 231767

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Abstract

The safety of Li-ion secondary cells decreases during charging and discharging at low temperatures due to the deposition of Li metal that reduces the cell thermal stability. Generally, the thermal stability of Li-ion cells is evaluated by an accelerating rate calorimeter (ARC). Therefore, in this study, degraded cells with low capacities have been prepared by charge/discharge cycling at a low temperature. After confirming the decrease in thermal stability by ARC heating, the degraded cells are charged at room temperature, and a thermal runaway is initiated by both ARC heating and laser irradiation. During ARC heating, the exothermic behavior of the degraded cell is identical to that of a new cell; however, the degraded cell undergoes a thermal runaway after laser irradiation at an input energy 100 times lower than that required to induce the runaway of a new cell. Therefore, the degradation of cells due to charge/discharge cycling at low temperatures can be detected by the laser irradiation method despite the decreased thermal stability undetectable by the ARC.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775322007595>

An online temperature estimation for cylindrical lithium-ion batteries based on simplified distribution electrical-thermal model

Journal of Energy Storage Volume 55, Part A, 1 November 2022, 105326

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Abstract

Accurate modeling of electrical-thermal properties is essential for safe use and efficient and reliable thermal management of Lithium-ion batteries. However, online estimation of the internal temperatures of the battery is very difficult due to the limitations of sensor testing methods. To address this issue, this paper proposes a simplified distributed electrical-thermal model of the cylindrical lithium-ion battery to realize the online temperature estimation. First, the cylindrical battery is divided into microcells according to its actual internal Archimedean spiral winding structure and established the electrical-thermal model for each microcell. Then, these microcells are then connected in parallel to form a multilayer electrical-thermal model to better capture the core and surface temperature evolution of the battery. Extensive experiments are conducted and illustrated that this method can estimate the core and surface temperature of the battery accurately under different current rates and dynamic test conditions at wider temperature ranges (from 0 °C to 55 °C). And the estimation maximum root mean square error is 0.9384 K. Moreover, a comparison with other models shows that this model can not only realize online internal and external temperature estimation but also have high accuracy.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2352152X22013238>

Combined numerical and experimental studies of 21700 lithium-ion battery thermal runaway induced by different thermal abuse

International Journal of Heat and Mass Transfer 194 (2022) 123099

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Abstract

Combined numerical and experimental studies have been carried out to investigate thermal runaway (TR) of large format 21700 cylindrical lithium-ion battery (LIB) induced by different thermal abuse. Experiments were firstly conducted with the Extend Volume Accelerating Calorimetry (EV-ARC) using both the heat-wait-see (HWS) protocol and under isothermal conditions. The

kinetic parameters were derived from one of the HWS EV-ARC tests and implemented in the in-house modified computational fluid dynamics (CFD) code OpenFOAM. For the subsequent CFD simulations, the cell was treated as a 3-D block with anisotropic thermal conductivities. The model was verified by the remaining two HWS tests not used in the derivation of the kinetic parameters and validated with newly conducted isothermal EV-ARC tests. Further laboratory tests and model validation were also subsequently conducted using Kanthal wire heaters. The validated model was also used to fill the experimental gaps by predicting the onset temperature for TR in simulated EV-ARC environment, heat generation rate due to different abuse reactions, the influence of heating power and heating arrangement as well as the effect of heat dissipation on TR evolution and the implications for battery thermal management. The present study has identified the TR onset temperature of the considered 21700 LIB to be between 131 and 132 °C. The predicted heat generation rate due to the decompositions of SEI and anode were found to follow similar patterns while that from cathode increase sharply near the maximum cell surface temperature, indicating the possibility of delaying TR onset temperature by optimising the cathode material. The time to maximum cell surface temperature decreases rapidly with the increase of the heating power.

Link to paper: <https://www.sciencedirect.com/science/article/pii/S0017931022005713>

Characterizing and predicting 21700 NMC lithium-ion battery thermal runaway induced by nail penetration

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Abstract

Combined numerical and experimental studies are conducted to characterise 21,700 cylindrical lithium-ion battery (LIB) thermal runaway (TR) induced by nail penetration. Both radial and axial penetrations are considered for 4.8 Ah 21,700 NMC cell under 100% state of charge. Heat generation from the decomposition of the cell component materials are analysed. The maximum cell surface temperature rise and time to reach it in both types of penetration tests are compared. Snapshots from the video footages captured by three high definition and one high speed cameras shed light on the dynamic processes of spark ejection and flame evolution. A generic predictive tool is developed within the frame of the in-house version of open-source computational fluid dynamics code OpenFOAM for nail induced TR. The code treats the cell as a lumped block with anisotropic thermal conductivities and considers heat generation due to nail induced internal short circuit resistance, exothermic decomposition reactions and heat dissipation through convective and radiative heat transfer. Validation with the current measurements shows promising agreement. The predictions also provide insight on the magnitudes of heat generation due to internal short circuit resistance, decompositions of solid electrolyte interphase layer (SEI), anode, cathode and electrolyte. Parametric studies further quantify the effects of cell internal short circuit resistance, contact resistance between the nail and cell, convective heat transfer coefficient and cell surface emissivity on TR evolution.

Link to paper: <https://www.sciencedirect.com/science/article/pii/S135943112200237>

Thermal behavior and failure mechanisms of 18650 lithium ion battery induced by overcharging cycling **Energy Reports: Volume 8, November 2022, Pages 7286-7296**

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Abstract

Overcharging is one of the most serious safety problems in large-scale application of lithium ion battery (LIB). An in-depth understanding of the failure mechanism of battery overcharge is necessary to guide the safe design of battery system. In this paper, the electrochemical performance of commercial 18650-type cylindrical battery with Li(NiCoMn)O₂ cathode and graphite anode as the background is evaluated with different state of charge (SOC). The dynamic thermal behavior of overcharge in adiabatic conditions is studied, and the cathode materials, separator and anode materials after long-term overcharge cycle are characterized to identify the side reactions in battery. The results show that the battery impedance increases with the increase of SOC, and thereby greatly accelerating the attenuation of battery capacity. When LIB is charged and discharged in adiabatic

conditions, the battery surface temperature of 116% SOC is about 10.03 °C higher than that of 100% SOC. Therefore, the battery with higher SOC has higher heating and is easy to induce the thermal runaway reactions. During the overcharge cycle, electrolyte decomposition, transition metal dissolution and phase transformation occur at the cathode, and serious lithium plating occur at the anode, as a result, increasing battery impedance, accelerating aging and increasing heat production. These results provide feasible support for understanding the overcharge mechanism and battery management system.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2352484722010307>

Targeted masking enables stable cycling of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ at 4.6V

Nano Energy. Volume 96, 1 June 2022, 107123

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Abstract

Layered $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM, or $\text{NCM}_{xy}(1-x-y)$) is a dominant family of cathode materials for lithium-ion batteries (LIBs) due to its high energy density. Among all NCM cathode materials, NCM622 possess the optimal energy density at high potential (≥ 4.6 V vs. Li/Li^+). However, the practical application of NCM622 at high voltage (≥ 4.6 V) is limited by its parasitic reactions and associated safety concerns. Completely physical isolation has been considered as the main approach to mitigate the parasitic reaction. It has also been previously demonstrated that the interface reaction has active site selectivity, and that the reactivity of the active sites can effectively suppressed by blocking the chemically active sites. Herein, a targeted masking by LiFePO_4 @C nanoplates is reported to unlock the stable performance of NCM622 up to 4.6 V vs. Li/Li^+ . The (targeted masked-NCM622)|graphite pouch cell shows 86.5% capacity retention after 1000 cycles and its maximum temperature during thermal runaway is dramatically reduced from 570 °C to 415 °C. Systematic in/ex situ characterizations, first-principles calculations and half/pouch targeted LiFePO_4 @C covers the surface of NCM partcell evaluation prove that PO_4^{3-} is preferentially adsorbed on transition metal sites, stabilizing both the transition metal ions and oxygen ions on the surface against the ethylene carbonate-containing traditional electrolyte even under high voltage (≥ 4.6 V vs. Li/Li^+). This work opens up new venue for rational design of high-performance cathode materials through a low-cost and scalable decoration process, and reveal a new understanding of interfacial activity of materials.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S221128552200204X>

An experimental analysis on thermal runaway and its propagation in Cell-to-Pack lithium-ion batteries

Applied Thermal Engineering - Available online 26 March 2022, 118418 In Press, Journal Pre-proof

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Abstract

Thermal runaway and its propagation are the technological barriers for the large-scale promotion of new energy vehicles and energy storage. This paper investigates the temperature characteristics between jelly rolls, influence of heating power on internal propagation time and energy flow during thermal runaway propagation through experiments and models. Results indicated that

the maximum temperature between jelly rolls has a maximum temperature difference up to 487°C compared to the surface temperature during thermal runaway. The distribution of energy flow showed that approximately 60% of total energy was used to self-heat and approximately 31% was emitted through venting. Experimental results and model calculation shows that the time it takes for thermal runaway to propagate within the Cell-to-Pack battery is affected by heating power. This study provides a reference for creating safe cell designs, developing mitigation strategies for addressing thermal runaway propagation in system, and investigating battery-related accidents in new energy vehicles and energy storage.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S1359431122003738>

Comparison of thermal runaway pressures within sealed enclosures for nickel manganese cobalt and iron phosphate cathode lithium-ion cells

Journal of Loss Prevention in the Process Industries Volume 76, May 2022, 104739

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Abstract

Mining vehicle manufacturers are developing lithium-ion (Li-ion) battery electric vehicles as an alternative to diesel-powered vehicles. In gassy underground mines, explosion-proof (XP) enclosures are commonly used to enclose electrical ignition sources to prevent propagation of an internal methane-air explosion to a surrounding explosive atmosphere. Li-ion batteries can create pressurized explosions within sealed enclosures due to thermal runaway (TR). NIOSH researchers measured TR pressures of nickel manganese cobalt (NMC) cathode type 18650 Li-ion cells, model MH1, as a function of free space within sealed enclosures and observed an inverse power relationship. TR pressure-rise rates, gas quantities, and temperatures were also measured. A confined NMC cell with 92.5 mL of free space produced 232 bar of pressure, far exceeding minimum pressure containment specifications for conventional XP enclosures. Approximately 287 times the cell volume of free space would be needed to reduce the TR pressure of these cells to 8.62 barg (125 psig) per U.S. Code of Federal Regulations, Title 30, Part 18. The NMC cell TR pressures were significantly higher than those measured previously for iron phosphate cathode Li-ion cells under comparable confinement conditions.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S095042302200016X>

Numerical and experimental characterisation of high energy density 21700 lithium-ion battery fires **Process Safety and Environmental Protection 160 (2022) 153–165**

Chandra M.R. Vendra^a, Ashish V. Shelke^a, Jonathan E.H. Buston^b, Jason Gill^b, Daniel Howard^b, Elliott Read^b, Ahmed Abaza^c, Brian Cooper^c, Jennifer X. Wen^a,

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Abstract

High energy density lithium-ion batteries (LIBs) are well suited for electrical vehicle applications to facilitate extended driving range. However, the associated fire hazards are of concern. Insight is required to aid the development of protective and mitigation measures. The present study is focused on 4.8 Ah 21700 cylindrical LiNi_xCo_yMn_zO (NMC) LIBs at 100% state of charge (SOC) with the aim to develop a viable predictive tool for simulating LIB fires, quantifying the heat release rate and temperature evolution during LIB thermal runaway (TR). To aid the model development and provide input parameters, thermal abuse tests were conducted in extended volume accelerating rate calorimetry (EV-ARC) and cone calorimetry. Some cells were instrumented with inserted temperature probe to facilitate in-situ measurements of both cell internal and surface temperatures. The mean peak values of the heat release rate, cell surface and internal temperatures were experimentally found to be 3.6 kW, 753 °C and 1080 °C, respectively. An analytical model has been developed to predict cell LIB internal pressure evolution following vent opening. The model uses the measured cell internal temperature and EV-ARC canister pressure as input data. Its predictions serve as boundary condition in the three-dimensional computational fluid dynamics (CFD) simulation of TR induced fire using open-source code OpenFOAM. The predicted transient heat release rate compares favourably with the measurements in the cone calorimetry tests. Predictions have also been conducted for an open cluster to assess the likelihood of TR propagation in the absence of cell side rupture. The present modelling approach can serve as a useful tool to assess the thermal and environment hazards of TR induced fires and aid design optimisation of mitigation measures in enclosed cell clusters/modules.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0957582022001082>

Fundamental Insights into Battery Thermal Management and Safety

CS Energy Letters 2022, 7, 3, 1103–1111

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Abstract

To break away from the trilemma among safety, energy density, and lifetime, we present a new perspective on battery thermal management and safety for electric vehicles. We give a quantitative analysis of the fundamental principles governing each and identify high-temperature battery operation and heat-resistant materials as important directions for future battery research and development to improve safety, reduce degradation, and simplify thermal management systems. We find that heat-resistant batteries are indispensable toward resistance to thermal runaway and therefore ultimately battery safety. Concurrently, heat-resistant batteries give rise to long calendar life when idling at ambient temperatures and greatly simplify thermal management while working, owing to much enlarged temperature difference driving cooling. The fundamentals illustrated here reveal an unconventional approach to the development of current and future battery technologies as society moves toward ubiquitous electrified transportation.

Link to purchase paper: <https://pubs.acs.org/doi/10.1021/acsenergylett.2c00077>

Effect of electrode crosstalk on heat release in lithium-ion batteries under thermal abuse scenarios **Energy Storage Materials Volume 44, January 2022, Pages 326-341**

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Abstract

Predicting thermal safety events of lithium-ion (Li-ion) batteries is significant in optimizing electrochemical systems with high thermal tolerance. The safety performances of Li-ion batteries are dictated by the thermal stability of their component materials both individually and collectively due to intricate exothermic reactions. Although the heat release of individual battery material has been thoroughly investigated, the safety hazards of inter-electrode chemical crosstalk under thermal abuse scenarios remain elusive and thus need a fundamental understanding. This study carries out a comprehensive thermal analysis of various material samples harvested from a commercial Li-ion cell using differential scanning calorimetry (DSC), complemented with full-cell accelerating rate calorimetry (ARC) and computational modeling. Reaction kinetics of electrolyte, wet cathode, wet anode and DSC-full cell samples imitating cell layered architectures are delineated to reveal substantial thermal interactions between electrodes. High-resolution kinetic parameters of reaction mechanisms are estimated using a synergy of Kissinger's method and mechanism-driven non-linear optimization strategies. A thermal abuse model is built based on the extracted kinetic parameters to simulate the cell-level thermal runaway phenomenon and compared with experimental observations, indicating how interlayer crosstalk effects significantly impact the thermal safety characteristics of Li-ion cell chemistries.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2405829721004943>

Thermal runaway modeling of large format high-nickel/silicon-graphite lithium-ion batteries based on reaction sequence and kinetics

Applied Energy Volume 306, Part A, 15 January 2022, 117943

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Abstract

Commercial large format high-nickel/silicon-graphite (NCM811/SiC) lithium-ion batteries have been applied in long range electric vehicles for their exceptional high energy density. However, fire and explosions caused by these high-energy batteries arouse safety concerns. Mathematical model is a powerful method to study and predict the hazardous thermal behaviors but have not been well established due to lack of the detailed side reaction sequence and kinetics of the NCM811/SiC chemistry. This paper reveals that the thermal interactions between the high energy materials dominate the heat generation process and determines the detailed side reaction sequence and thermal kinetics based on experiments. A cell thermal runaway model considering the reaction sequence is then established based on the kinetics and achieves accurate prediction of the cell thermal behaviors. The validated model is further employed to investigate the thermal deterioration originated from high-energy NCM811/SiC chemistry. According to the simulations, the thermal interactions between SiC-electrolyte, NCM811-electrolyte and NCM811-SiC can lead to maximum temperature increase by 318 °C, 222 °C and 174 °C, respectively, with total heat rising by 29%, 20% and 17%, when compared with the conventional Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂/graphite chemistry.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0306261921012538>

Battery eruption triggered by plated lithium on an anode during thermal runaway after fast charging Energy Volume 239, Part B, 15 January 2022, 122097

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Abstract

Lithium-ion batteries (LIBs) are suffering from severe thermal runaway risks in the use of their whole lifespans. The heat release characteristics of thermal runaway after fast charging have been proven to be highly related to lithium plating, yet whose impacts on the eruption behaviors are rarely investigated. In this study, the changes in the battery eruption temperature during thermal runaway after fast charging are thoroughly analyzed, and the effects of lithium plating on gas production are revealed. Accelerating Rate Calorimetry tests of pouch cells and prismatic cells are performed to investigate the eruption temperature of LIBs charged at different rates, confirming the advanced eruption of thermal runaway on batteries with plated lithium. To reveal the root cause of early eruptions, reactions between plated lithium and electrolytes are characterized by Synchronous Thermogravimetry Analysis and Mass Spectrometry, observing the fierce gas production process. Afterwards, and the gas and solid products of the reaction are further obtained using partially reactive systems in hot-box tests, and their compositions are analyzed. Overall, this study contributes to a more profound understanding of the characteristics of thermal runaway after fast charging, providing valuable insights on the rational design and management for LIB safety.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0360544221023458>

2021

A comparative study on the reactivity of charged Ni-rich and Ni-poor positive electrodes with electrolyte at elevated temperatures using accelerating rate calorimetry

Journal of Energy Chemistry

Volume 60, September 2021, Pages 523-530

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Abstract

The reactivity between charged Li(Li_{0.115}Mn_{0.529}Ni_{0.339}Al_{0.017})O₂ (Li-rich), single crystal Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂ (SC-NMC811), LiFePO₄ (LFP) and LiMn_{0.8}Fe_{0.2}PO₄ (LMFP) positive electrodes at different states of charge (SOCs) and traditional carbonate-based electrolyte at elevated temperatures is systematically studied using accelerating rate calorimetry (ARC). The results show that the SOC greatly affects the thermal stability of the Li-rich and SC-NMC811 when traditional carbonate-based electrolyte is used. Although an increase in the SOC increases the energy density of lithium-ion cells, it also increases the

reactivity between charged Li-rich and SC-NMC811 samples with electrolyte at elevated temperatures. In comparison with SC-NMC811, the Li-rich samples are much more stable at elevated temperatures, and the latter have higher specific capacity. SC-NMC811 samples are less reactive than traditional polycrystalline NMC811. Both LFP and LMFP samples show excellent thermal stability at elevated temperatures. The substitution of Fe by Mn in the olivine series positive materials does not impact the reactivity with electrolyte.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2095495621000656>

An experimental-based Domino prediction model of thermal runaway propagation in 18,650 lithium-ion battery modules

International Journal of Heat and Mass Transfer Volume 181, December 2021, 122024

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Abstract

Currently, the thermal safety issue of lithium-ion battery (LIB) has become a major challenge to restrict its development. In this work, the thermal runaway propagation (TRP) process of the 18,650-type LIB module is studied by experimental and modeling methods. A novel experimental-based Domino prediction model is proposed, which can predict the TRP path and its probability. The calculation part of the model is realized with the Matlab software. This model for the first time proposes that whether the battery thermal runaway (TR) is a probability event, and the probability is a function of its temperature. To verify the feasibility of the model, the TRP process in a 4 × 4 arrangement battery module with three different first TR battery locations is detailed analyzed. The results show that the dangerous level ranking of cell locations from low to high is the corner location, the edge location, and the location near the module center. Higher dangerous level means more maximum probability TRP paths and higher probability. Moreover, it was found that the whole TRP process can be divided into four stages: the TRP trigger stage, the heat accumulation stage, the Domino effect stage, and the TRP stop stage. The proposed model can effectively predict the TRP process in modules, and the results have important reference value for the design of the battery thermal management system and the research on the method of blocking TRP.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0017931021011303>

Thermal hazard evaluation of styrene-methyl methacrylate bulk copolymerization by differential scanning calorimetry and accelerating rate calorimetry

Thermochimica Acta Volume 706, December 2021, 179052

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Abstract

Thermal runaway primarily occurs during the course of copolymerization due to the release of large amounts of heat. In this paper, the thermal risk associated with styrene-methyl methacrylate bulk copolymerization was firstly investigated by differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC). The result found that the exothermic behavior was greatly affected by the initiator concentration, in contrast the exothermic enthalpy was not. This exothermic behavior was firstly illustrated via polymerization mechanism. The temperature and pressure have changed dramatically during the adiabatic runaway copolymerization, which demonstrated a great potential risk of thermal runaway. Kinetic parameters, such as TNR, TSADT was calculated accordingly, which provided guidance for the safety of storage and transportation. This study will provide a helpful safety assessment for the styrene-methyl methacrylate bulk copolymerization, which is widely used in industry.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0040603121001933>

Characterisation of thermal runaway behaviour of cylindrical lithium-ion battery using Accelerating Rate Calorimeter and oven heating

Case Studies in Thermal Engineering Volume 28, December 2021, 101474

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Abstract

In this work, thermal runaway of lithium-ion battery was characterised under adiabatic and non-adiabatic conditions using Accelerating Rate Calorimeter (ARC) and oven respectively. Battery with higher electrical capacity demonstrated a higher tendency to experience thermal runaway with shorter induction time and resulted with a more energetic response, as indicated by higher maximum temperature rise. Oven tests at 190 °C were able to capture thermal runaway characteristics in batteries with 100% state-of-charge (SOC) only and resulted in a maximum temperature of 738–783 °C. Two batteries were more inclined to suffer thermal runaway as the induction time was reduced by 8.6% to 115.98 min, compared to 126.92 min for single cell. A further inclined by 15% to 107.72 min was recorded for two batteries with parallel electrical connection. Meanwhile, ARC was able to induce thermal runaway in 50% SOC battery and instigated exothermic thermal decomposition in 0% SOC battery due to the longer heating process. The maximum temperatures recorded from ARC tests were between 404 and 522 °C, lower than oven tests since some of the battery energy content was released slowly during the long self-heating period, leaving the battery with less energy for rapid release during thermal runaway.

Link to paper (open access) <https://www.sciencedirect.com/science/article/pii/S2214157X21006377>

Long cycle-life prototype lithium-metal all-solid-state pouch cells employing garnet-rich composite electrolyte

Electrochimica Acta Volume 397, 20 November 2021, 139249

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Abstract

All-solid-state batteries (SSB) emerge as a promising candidate to exceed the performance of conventional lithium ion batteries (LIB) due to their improved energy density, durability and safety. However, very few reports have demonstrated a long-term stable cycling and safety of pouch SSB. Herein, solid state pouch cell with nominal capacity of 0.3 Ah is successfully developed employing current-collector-free thin Li metal anode, double-sided composite LiFePO₄ cathode, and garnet-rich composite solid electrolyte (CSE) containing a doping of Li₇La₃Zr_{1.75}Nb_{0.25}O₁₂ garnet in a ratio 1:1 relative to poly(ethylene oxide) (PEO) host polymer, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt. All-solid-state Li/CSE/LiFePO₄ prototype pouch cells tested under 0.2C/0.5C protocol at 60°C exhibit long cycle life (>4,100 cycles) and excellent safety attributed to the improved electrochemical properties, thermal and mechanical stability of the garnet-rich CSE. To the best of our knowledge, this is the longest lifetime up to date reported for bulk Li metal SSB. These outstanding results may pave the way for industrial development of advanced Li metal SSB towards practical application.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0013468621015395>

Investigating the critical characteristics of thermal runaway process for LiFePO₄/graphite batteries by a ceased segmented method

iScience Volume 24, Issue 10, 22 October 2021

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Abstract

Lithium-ion batteries (LIBs) are widely used as the energy carrier in our daily life. However, the higher energy density of LIBs results in poor safety performance. Thermal runaway (TR) is the critical problem which hinders the further application of LIBs. Clarifying the mechanism of TR evolution is beneficial to safer cell design and safety management. In this paper, liquid nitrogen spray is proved to be an effective way to stop the violent reaction of LIBs during the TR process. Based on extended-volume accelerating rate calorimetry, the liquid nitrogen ceasing combined with non-atmospheric exposure analysis is used to investigate the TR evolution about LiFePO₄/graphite batteries at critical temperature. Specifically, the geometrical shape, voltage, and impedance change are monitored during the TR process on the cell level. The morphologies/constitution of electrodes and separators are presented on the component level. Utilizing the gas analysis, the failure mechanism of the prismatic LiFePO₄/graphite battery is studied comprehensively.

Link to paper (open-access) <https://www.sciencedirect.com/science/article/pii/S2589004221010567>

Thermal runaway characteristics of a LiFePO₄-based lithium-ion secondary battery using the laser-irradiation method

Journal of Energy Storage Volume 40, August 2021, 102715

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Abstract

The establishment of a test method is a prerequisite to ensure the safety of lithium-ion secondary batteries. In context, laser irradiation is a heating technique that causes explosion of the batteries and is deemed as a safety test according to international standards. In this study, we elucidate the characteristics of laser irradiation heating by subjecting a 18650-type battery with LiFePO₄ as the cathode material to laser irradiation to cause thermal runaway. Subsequently, we estimated the thermal runaway process and compared the heating method with those of an accelerating rate calorimeter furnace and a ceramic heater. The experimental results revealed that the thermal runaway was activated at the laser-irradiated small area by immediate heating. Initially, the separator shrink occurs, which was followed by an internal short circuit caused by the subsequent heating, and further heating resulted in thermal runaway. The findings of this study indicate that an extremely high power per unit area is generated by laser irradiation heating, and the battery heat generation rate during thermal runaway is equivalent to that obtained by a ceramic heater.

Link to paper (open access) <https://www.sciencedirect.com/science/article/pii/S2352152X21004503>

Thermal Runaway Suppression of High-Energy Lithium-Ion Batteries by Designing the Stable Interphase

Journal of The Electrochemical Society, 2021 168 090563

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Abstract

Battery thermal runaway (TR) hinders the safe application of high-energy lithium-ion batteries with high-nickel cathodes. The use of non-flammable perfluorinated electrolytes is a promising alternative for enhancing the thermal stability of the battery and inhibiting the occurrence of TR. Herein, the electrochemical and thermal performances of single-crystal LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (SCNCM811) cathode cells based on a perfluorinated electrolyte were investigated. A conventional electrolyte was selected for comparison. It was found that the capacity of the battery cycling in the perfluorinated electrolyte was as high as 110.12% after 200 cycles. In addition, the test results demonstrate that the perfluorinated electrolyte can increase the trigger temperature of TR by 12.5 °C, decrease the highest temperature of TR by 41.2 °C, and reduce the oxygen release and crack formation. After characterizing the single-crystal cathode in a fully charged state, it can be confirmed that a uniform F, B-rich cathode electrolyte

interphase can enhance the battery performance to some extent. This study provides a novel direction for addressing the thermal safety issues of high-nickel lithium-ion batteries.

Link to paper (open access): <https://iopscience.iop.org/article/10.1149/1945-7111/ac285f>

Investigating the thermal runaway features of lithium-ion batteries using a thermal resistance network model

Applied Energy Volume 295, 1 August 2021, 117038

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Abstract

Accurate measurement of the characteristic temperatures of thermal runaway, which are affected by many factors, is important for battery safety evaluation. A one-dimensional thermal resistance network model is built in this study to investigate the influences of various factors on the thermal runaway features of lithium-ion batteries. In the model, the battery is divided into four independent components in the thickness direction, with thermal resistances connecting different nodes. The gas thermal resistance is added to simulate swelling and rupture of the battery. The model can effectively fit the battery thermal runaway behavior under both adiabatic thermal runaway and oven test conditions. Model-based analyses show that the thermal runaway features and characteristic temperatures are significantly affected by the test conditions, thermocouple positions, and battery thickness. The onset temperature of thermal runaway (T_2) obtained in the oven test is 48.1 °C lower than that obtained in the adiabatic thermal runaway test. The measured T_2 varies at different positions, and the difference can exceed 20% when the battery thickness increases to 10 cm. Moreover, the maximum thermal runaway temperature (T_3) at the surface is approximately half that at the other positions. Finally, several suggestions for reasonable thermocouple placement are proposed, which can provide useful guidance for accurately evaluating battery thermal runaway performance.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0306261921004980>

Reliable and Early Warning of Lithium-Ion Battery Thermal Runaway Based on Electrochemical Impedance Spectrum

Journal of The Electrochemical Society, Volume 168, Number 9

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Abstract

Lithium ion battery thermal runaway constitutes a severe inhibitor for the spread and application of electric vehicles and widespread adoption of renewable energy. Reliable and early warning of thermal runaway calls for a technique capable of detecting abnormal response well in advance of the critical event and being effective to the module when a single cell in it has safety issues. In this study, electrochemical impedance spectrum (EIS) dependence on cell temperature and deformation is exploited to generate a two-staged warning method with three indicators in three frequency ranges. Specifically, the first stage utilizes the high sensitivity of EIS at the intermediate-frequency range to abnormal cell internal temperature rise, which is before self-heating temperature, as an early indicator for safety issues. The second stage utilizes the abrupt changes in EIS behaviors due to cell deformation in high- and low-frequency ranges, which are more sensitive than cell voltage change, as indicators for the thermal runaway onset temperature. The potential and issues of such an EIS-based method for both reliable and early warning of thermal runaway in field application, including measurement feasibility, versatility in various scenarios and the difference between the experimental and actual situation, are discussed.

Link to purchase paper: <https://iopscience.iop.org/article/10.1149/1945-7111/ac239b>

Evaluation of Heat Generation and Thermal Degradation of Lithium Ion Batteries by a Calorimetry Method

Journal of The Electrochemical Society, Volume 168, Number 6

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Abstract

With the wide application of lithium-ion batteries (LIBs), it is important to understand the internal heating effects and thermal runaway behavior of such batteries to evaluate their thermal safety and improving thermal management systems. The heat generation of LiCoO₂/graphite LIBs under various conditions was compared using calorimetry and electrochemical methods. The heat generation results of the two methods in the process of charging/discharging at different current rates were consistent, but the calorimetry method is simple, convenient, and more feasible. The greater the working current, the greater the irreversible heat generation. Through the identification of the thermal runaway behavior, it was found that the change of the onset temperature of self-heating reactions fluctuates in a narrow range. Thermal runaway after battery degradation is more likely to be triggered by the degradation of thermal stability.

Link to purchase paper: <https://iopscience.iop.org/article/10.1149/1945-7111/ac0b59>

Investigating the Role of Energy Density in Thermal Runaway of Lithium-Ion Batteries with Accelerating Rate Calorimetry

Journal of The Electrochemical Society, Volume 168, Number 6

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Abstract

This work uses accelerating rate calorimetry to evaluate the impact of cell chemistry, state of charge, cell capacity, and ultimately cell energy density on the total energy release and peak heating rates observed during thermal runaway of Li-ion batteries. While the traditional focus has been using calorimetry to compare different chemistries in cells of similar sizes, this work seeks to better understand how applicable small cell data is to understand the thermal runaway behavior of large cells as well as determine if thermal runaway behaviors can be more generally tied to aspects of lithium-ion cells such as total stored energy and specific energy. We have found a strong linear correlation between the total enthalpy of the thermal runaway process and the stored energy of the cell, apparently independent of cell size and state of charge. We have also shown that peak heating rates and peak temperatures reached during thermal runaway events are more closely tied to specific energy, increasing exponentially in the case of peak heating rates.

Link to paper (open access) <https://iopscience.iop.org/article/10.1149/1945-7111/ac0699>

Comprehensive Electrochemical, Calorimetric Heat Generation and Safety Analysis of Na0.53MnO₂ Cathode Material in Coin Cells

Journal of The Electrochemical Society, Volume 168, Number 5

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Abstract

The sodium ion cells were assembled by using Na0.53MnO₂ as cathode material, pure sodium metal as anode in case of half coin cells and coconut shell-derived hard carbon in case of full coin cells. Cyclic voltammetry, galvanostatic charge-discharge, and self-discharge analysis were conducted. A good rate capability, capacity retention, coulombic efficiency (99.5%), reproducibility and reversible Na-ion intercalation revealed a satisfactory performance of this cathode material. The safety related parameters

including the heat generation during charging-discharging and thermal abuse tests have been executed by the means of sophisticated calorimetry instruments. It was observed that during the charging process less heat was generated than during discharging process. The exothermic reactions during thermal runaway were identified by using an accelerating rate calorimeter and pressure measurements during this thermal abuse test were performed as well. The thermal runaway of full coin cells occurred beyond 190 °C with a temperature rate (dT/dt) of 2.5 °C min⁻¹. Such detailed analysis of heat generation and thermal abuse helps finding new and quantitative correlations between different critical thermal and safety related issues in future post Li batteries that are a prerequisite for the design of safer batteries, the safe upscaling and for the adaptation of the thermal management system.

Link to paper (open access) <https://iopscience.iop.org/article/10.1149/1945-7111/ac0176>

Thermal and gas characteristics of large-format LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ pouch power cell during thermal runaway

***Journal of Energy Storage* 39 (2021) 102609**

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Abstract

With the widespread use of lithium-ion batteries as a power source, higher and higher energy density has been required. This study focused on a promising battery with representative high energy density. The thermal and gas characteristics of large-format LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ pouch power cell during thermal runaway were investigated using Extended Volume+ Accelerating Rate Calorimetry (EV+ ARC). Differing from previous studies, the characterization of large-format pouch cells cannot be studied by the lumped parameter method, while the multipoint measurement was adopted to visualize the variation of temperature distribution. The calorimetry that has been commonly used for evaluating thermal runaway of batteries was discussed whether it is also applicable to the large-format pouch cell. And the distributed parameter method was utilized to explore the heat production of the large-format cell. Also, the gas generated by the thermal runaway cell was analyzed by gas chromatography, and the gas generation mechanism of the LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cell was traced based on the results. This work also confirmed the thermal runaway hazard of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ pouch power cell and could provide a reference for the evaluation of thermal runaway and application safety of large-format batteries.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2352152X21003510>

Internal short circuit evaluation and corresponding failure mode analysis for lithium-ion batteries

***Journal of Energy Chemistry* 61 (2021) 269–280**

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Abstract

Internal short circuit (ISC) is the major failure problem for the safe application of lithium-ion batteries, especially for the batteries with high energy density. However, how to quantify the hazard aroused by the ISC, and what kinds of ISC will lead to thermal runaway are still unclear. This paper investigates the thermal-electrical coupled behaviors of ISC, using batteries with Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ cathode and composite separator. The electrochemical impedance spectroscopy of customized battery that has no LiPF₆ salt is utilized to standardize the resistance of ISC. Furthermore, this paper compares the thermal-electrical coupled behaviors of the above four types of ISC at different states-of-charge. There is an area expansion phenomenon for the aluminum-anode type of ISC. The expansion effect of the failure area directly links to the melting and collapse of separator, and plays an important role in further evolution of thermal runaway. This work provides guidance to the development of the ISC models, detection algorithms, and correlated countermeasures.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2095495621001522>

Experimental study on thermal runaway of fully charged and overcharged lithium-ion batteries under adiabatic and side-heating test

Journal of Energy Storage. Volume 38, June 2021, 102519

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Abstract

In this work, the thermal runaway (TR) hazards of a 4.5 Ah 21,700 cylindrical lithium-ion battery (LIB) are investigated at 100%, 110% and 120% stage of charge (SOC). The TR behavior of the sample at elevated temperature is characterized using an extended volume accelerating rate calorimetry and a customized battery test canister. The results show that the time interval from the LIB voltage drop to the initial of TR increases with the increase of SOC. The time interval for the LIB with 120% SOC is significantly greater than 100% and 110% SOC, which is meaningful for the early warning of TR. In adiabatic or side-heating test, the initial temperature of TR of LIBs at different SOC is almost the same, but the temperature at voltage drop shows a downward trend as the adding SOC. The separator thermal stability of slightly overcharged LIB is lower than fully charged LIB according to the SEM and DSC tests. Besides, the TR hazards of the LIB are recommended to be determined by multiple factors, including pressure, ambient temperature and battery surface temperature.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2352152X2100267X>

Thermal runaway features of lithium sulfur pouch cells at various states of charge evaluated by extended volume-accelerating rate calorimetry

Journal of Power Sources 489 (2021) 229503

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Abstract

High energy density lithium–sulfur (Li–S) batteries are regarded as the promising next-generation energy storage devices. The thermal runaway (TR) issues posed by Li–S batteries have been less investigated, while they are critical for the practical application of Li–S batteries. Herein, we first evaluate the TR features of the 1.5 Ah Li–S pouch cell (LSPC) at various states of charge (SOC) using extended volume-accelerating rate calorimetry (EVARC). The specific heat capacity and thermodynamic parameters have been calculated from the recorded data. An intermittent pulse technique has been used to quantify the internal resistance of LSPC during the EV-ARC test. The heat sources in the TR processes of LSPC composed of different chemistries have been probed using EV-ARC and differential thermal analysis (DTA). Moreover, it takes as long as 15.7 min for LSPC with 100% SOC from the sharp drop of voltage to the instantaneous rise of temperature, while it takes 16 s for lithium ion pouch cell (LIPC). The experiment results indicate that the major heat source during TR may not be the internal short circuit but the redox reaction between cathode and anode, which can provide an important insight into the rational design of safe Li–S battery system.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0378775321000525>

Heat generation quantification of high-specific-energy 21700 battery cell using average and variable specific heat capacities

Applied Thermal Engineering 184 (2021) 116215

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Abstract

The electrical performance, safety and life of a battery are closely related to its operating temperature; therefore, a thermal management system is necessary to ensure that the battery operates within its most suitable temperature range. Accurately testing the heat generation of a battery is necessary for the design of a thermal management system. Specific heat capacity is one of the most important parameters of thermophysical properties, and its accurate measurement is a prerequisite for the quantitative analysis of battery heat generation. In the literature on battery heat generation tests, the average specific heat capacity is usually used to calculate the battery heat generation. Thus, the change in the specific heat capacity of the battery is not considered. Considering the high-specific-energy 21700 battery made with a nickel-cobalt-manganese (NCM)/graphite material system, this paper compares for the first time the difference between using the average specific heat capacity and variable specific heat capacity to calculate the instantaneous heat generation of a battery. The experimental results showed that the specific heat capacity in the target temperature range during the actual use of power batteries (i.e., a low temperature range of 25–35 °C) had a more significant impact on the heat generation power calculation error, and the relative error could reach 30%. In addition, based on the obtained variable specific heat capacity, the heat generation characteristics of the 21700 battery under different operating conditions were analysed. The results showed that this battery has a higher specific volume heat generation power compared with the pouch-type batteries reported in the literature. This article provides guidance for battery cell thermal simulation, more accurate quantitative measurement of battery heat generation and thermal management system design.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S1359431120336942>

Effect of Li plating during formation of lithium ion batteries on their cycling performance and thermal safety

Journal of Power Sources 484 (2021) 229306

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Abstract

The presented work focuses on the effect of different applied C-rates within the formation procedure on the performance and the thermal safety of lithium ion battery cells. The formation procedure is based on constant-current constant-voltage charging and constant-current discharging. Here, two different formation procedures were used characterized by the applied current rate of either 0.2C or 2C. The cells were investigated via electrochemical, microscopic and spectroscopic methods. Applying a C-rate of 2C shortens the formation to 1.5 h compared to 10.5 h at 0.2C for one formation cycle. However, also the occurrence of Li plating with an amount corresponding to (7.8 ± 0.3) mAh g⁻¹NMC was observed. Based on those results, thermal safety properties of cells after 0.2C or 2C formation was analyzed under quasi-adiabatic conditions in an accelerated rate calorimeter. Within the margin of error, no influence of the C-rate during formation on the thermal safety could be detected. In addition, no difference in cell cycling performance could be observed. Therefore, the here determined amount of Li plating originating solely from the formation process does not lead to significant differences in cycling performance and thermal safety behavior for the here considered lithium ion battery cells.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775320315949>

Enhancing thermal safety in lithium-ion battery packs through parallel cell ‘current dumping’ mitigation ***Applied Energy 286 (2021) 116495***

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Abstract

This paper presents the first comprehensive study of a propagation mechanism referred to as ‘current dumping’, which has been

identified as a dominant cause for thermal runaway in Lithium-ion battery packs. Baseline nail penetration tests were performed on commercial, fully charged lithium-ion battery packs with 18650 nickel-manganese-cobalt cells and Phase Change Composite to study the propagation of thermal runaway in packs with both electrically connected and disconnected cells. This study showed that packs with electrically connected cells experience thermal runaway propagation due to neighboring cell current dumping. Packs with electrically disconnected cells did not propagate and maximum neighboring cell temperatures were less than 85 °C, below the cell thermal runaway threshold temperatures characterized by accelerating rate calorimetry tests. Cell-to-cell current dumping tests were performed on 18650 and 21700 cells at 60, 80 and 100% state-of-charge. These tests demonstrated that cell current interrupt device activation times vary over several minutes, and trigger cell short resistance vary between 17 and 62 mΩ. Along with neighboring cell internal resistance data obtained from hybrid pulse power characterization testing, the current dumping study allowed accurate prediction of the magnitude of current dumping for various battery designs. This enabled the first battery design with individual cell fusing integrated into battery current collectors. Nail penetration tests performed on commercial 18650 battery packs incorporating the engineered fuse did not propagate and current dumping was prevented. Practical insights from this study can play a critical role in solving the thermal runaway propagation problem plaguing lithium-ion battery manufacturers globally.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0306261921000568>

2020

Thermal runaway of Lithium-ion batteries employing $\text{LiN}(\text{SO}_2\text{F})_2$ -based concentrated electrolytes

Nature Communications 11, 5100 (2020)

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Abstract

Concentrated electrolytes usually demonstrate good electrochemical performance and thermal stability, and are also supposed to be promising when it comes to improving the safety of lithium-ion batteries due to their low flammability. Here, we show that $\text{LiN}(\text{SO}_2\text{F})_2$ -based concentrated electrolytes are incapable of solving the safety issues of lithium-ion batteries. To illustrate, a mechanism based on battery material and characterizations reveals that the tremendous heat in lithium-ion batteries is released due to the reaction between the lithiated graphite and $\text{LiN}(\text{SO}_2\text{F})_2$ triggered thermal runaway of batteries, even if the concentrated electrolyte is non-flammable or low-flammable. Generally, the flammability of an electrolyte represents its behaviors when oxidized by oxygen, while it is the electrolyte reduction that triggers the chain of exothermic reactions in a battery. Thus, this study lights the way to a deeper understanding of the thermal runaway mechanism in batteries as well as the design philosophy of electrolytes for safer lithium-ion batteries.

Link to purchase paper: <https://www.nature.com/articles/s41467-020-18868-w>

Estimation of the critical external heat leading to the failure of lithium-ion batteries

Applied Thermal Engineering 179 (2020) 115665

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Abstract

A detailed experimental investigation on the critical external heat leading to the failure of lithium-ion (Li-ion) batteries was conducted using an Accelerating Rate Calorimeter (ARC) at the National Institute for Occupational Safety and Health (NIOSH). Several types of commercial Li-ion batteries were selected for the study, including an iron phosphate Li-ion battery (LFP), a lithium-titanate battery (LTO), and a lithium-nickel-manganese-cobalt oxide battery (NMC). Each battery was placed in a specially designed sealed steel canister and heated in the ARC.

Battery voltage throughout the test was monitored and used to indicate the time to a battery failure. Three thermocouples, one attached to the battery surface, one measuring air temperature inside the canister, and one attached to the canister's internal surface, were used to record temperature changes during the heating tests. Different thermal behaviors were observed for the various battery types. An analytical model was developed to estimate the total external heat received by the battery using the measured temperatures. Experimental data ranked the batteries tested in terms of the heat to failure as: LFP 26,650 (11 kJ) > LFP 18650 (4.3 kJ) > NMC 18650 MH1 (3.6 kJ) \approx LTO 18650 (3.6 kJ) > NMC 18650 HG2 (3 kJ). Total heat normalized to the battery nominal energy capacity was also calculated and ranked as: LTO 18650 \approx LFP 26650 \approx LFP 18650 > NMC 18650 MH1 \approx NMC 18650 HG2. The test and analysis method developed can be extended to other types of batteries with a cylindrical shape. Results from this work provide insights to the thermal safety of Li-ion batteries and can help enhance battery thermal design and management.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S1359431120331471>

Thermal Runaway Pressures Of Iron Phosphate Lithium-Ion Cells As A Function Of Free Space Within Sealed Enclosures

SME Annual Meeting Feb. 23 - 26, 2020, Phoenix, AZ

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Abstract

Mining vehicle manufacturers are developing lithium-ion (Li-ion) battery electric vehicles as an alternative to diesel-powered vehicles. In gassy underground mines, explosion-proof (XP) enclosures are commonly used to enclose electrical ignition sources to prevent propagation of an internal methane (CH₄)-air explosion to a surrounding explosive atmosphere. Li-ion batteries can create pressurized explosions within sealed enclosures due to thermal runaway (TR). Researchers at the National Institute for Occupational Safety and Health (NIOSH) measured TR pressures of lithium iron phosphate (LFP) cells as a function of free space within sealed enclosures and observed an inverse power relationship. A well-confined cell produced 294 bar (4,260 psia) of pressure during a TR, far exceeding minimum pressure containment specifications for conventional XP enclosures. Results indicate that enough free space surrounding LFP cells can reduce TR pressures to levels below that expected for CH₄-air mixtures.

Link to purchase paper: <https://www.researchgate.net/scientific-contributions/T-H-Dubaniewicz-2174259250>

Experimental study on thermal runaway and vented gases of lithium-ion cells ***Process Safety and Environmental Protection 144, (2020), 186-192***

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Abstract

Lithium-ion (Li-ion) batteries have become more prevalent in mining to power a wide range of devices from handheld tools to mobile mining equipment. However, the benefits associated with using Li-ion batteries may come with a higher risk of a fire or an explosion. The major cause for a Li-ion battery fire is thermal runaway. If unmitigated, a thermal runaway can lead to cell rupture and the venting of toxic and highly flammable gases. Those flammable gases can cause a fire or explosion if ignited. In this study, researchers from the National Institute for Occupational Safety and Health (NIOSH) conducted experiments to monitor the heating of a Li-ion cell with different battery chemistries using an accelerating rate calorimeter (ARC). Inside the ARC, the cell was exposed to increasing temperatures until it reached a thermal runaway. Samples of vented gases after the thermal runaway were collected and analyzed using a gas chromatograph. Major gas components were identified, and their concentrations were measured. The results of this study can be useful in reducing the hazard of Li-ion battery fires.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0957582020316360>

4.2 V poly(ethylene oxide)-based all-solid-state lithium batteries with superior cycle and safety performance

Energy Storage Materials 32 (2020) 191–198

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Abstract

All-solid-state batteries have been considered as the ultimate solution for energy storage systems with high energy density and high safety. However, the obvious solid-solid contact and the interface stability issues pose great challenges to the construction of all-solid-state batteries with practically usable performances. Here, we discover that the heat-initiated polymerization of vinylene carbonate (VC) and the simultaneous incorporation of cathode electrolyte interphase (CEI) forming additive lithium difluoro(oxalato)borate (LiDFOB) can synergistically promote the formation of a high-voltage stable and low resistant interface layer between the cathode and solid electrolyte. A poly(ethylene oxide) PEO-based all-solid-state lithium battery (ASSLB) employing the LiCoO₂ cathode electrode modified through such an in-situ CEI strategy demonstrates superior 4.2 V cycle stability, with a discharge capacity retention of 71.5% after 500 cycles. Besides, the accelerating rate calorimetry (ARC) test reveals that the cell displays extraordinary safety performance with no distinct thermal runaway below 350 °C. This work demonstrates an effective interface engineering strategy that can promise the formation of electrochemically and thermally stable cathode/solid electrolyte interface which is essential for the stable and safe operation of ASSLBs. Moreover, the validation of stable cycling of PEO-based ASSLBs at high voltages may encourage the efforts on further optimizations of interface engineering processes as well as large-scale fabrication, as the improvement of the energy-densities of PEO-based ASSLBs will be of paramount significance for practical applications.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2405829720302919>

Internal temperature detection of thermal runaway in lithium-ion cells tested by extended-volume accelerating rate calorimetry

Journal of Energy Storage 31 (2020) 101670

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Abstract

This paper presents a method of internal temperature detection of thermal runaway in lithium-ion cells during extended-volume accelerating rate calorimetry (EV-ARC) tests. Thermocouples were inserted into pouch, prismatic, and cylindrical cell samples with only moderate breakage of the cell packages. The temperatures measured at cell surface were compared with the internal temperatures. And for the pouch and prismatic cell samples, a common alternative method of simulating internal temperature by measuring the temperature between two identical cells was also evaluated for comparison. The results demonstrate that the surface measurements can be used to investigate the mild side reactions from the onset temperature, where the rate of temperature increase is slow enough to allow equilibration, to the triggering temperature, beyond which thermal runaway cannot be arrested. However, after the triggering temperature, the internal temperature detection is the

most accurate for evaluating the maximum temperature and rate of increase. For the pouch cell, the simulated internal temperature detection method was sufficiently accurate, whereas for the prismatic and cylindrical cells, the simulated temperatures were inaccurate.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S2352152X20315073>

A polyethylene microsphere-coated separator with rapid thermal shutdown function for lithium-ion batteries

Journal of Energy Chemistry 44 (2020) 33–40

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Abstract

Thermal runaway is the main factor contributing to the unsafe behaviors of lithium-ion batteries (LIBs) in practical applications. The application of separators for the thermal shutdown has been proven as an effective approach to protecting LIBs from thermal runaway. In this work, we developed a thermal shutdown separator by coating a thin layer of low-density polyethylene microspheres (PM) onto a commercial porous polypropylene (PP) membrane and investigated the thermal response behaviors of the as-prepared PM/PP separator in LIBs. The structural and thermal analysis results revealed that the coated PM layer had a porous structure, which facilitated the occurrence of normal charge-discharge reactions at ambient temperature, although it could melt completely and fuse together within very short time periods: 3 s at 110 °C and 1 s at 120 °C, to block off the pores of the PP substrate, thereby cutting off the ion transportation between the electrodes and interrupting the battery reaction. Consequently, the PM/PP separator exhibits very similar electrochemical performance to that of a conventional separator at ambient temperature. However, it performs a rapid thermal shutdown at an elevated temperature of ~110 °C, thus controlling the temperature rise and maintaining the cell in a safe status. Due to its synthetic simplicity and low cost, this separator shows promise for possible application in building safe LIBs.

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Nano LiFePO₄ coated Ni rich composite as cathode for lithium ion batteries with high thermal ability and excellent cycling performance

Journal of Power Sources 464 (2020) 228235

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Abstract

Ni-rich LiNi_{0.82}Co_{0.12}Mn_{0.06}O₂ (denoted as NCM) is successfully coated by LFP nanoparticles (denoted as NCM@LFP) through physical mechanical fusion in industrial level. The 18650 full cells are assembled with NCM@LFP as cathode, which exhibits quite excellent cycling performance and thermal stability. After 500 cycles, NCM@LFP || Graphite full cell still delivers a discharge capacity of 165.3 mA h g⁻¹ (capacity retention with 91.65%) at 1 C in voltage range from 3.0 to 4.2 V at room temperature. Besides, according to Accelerating rate calorimeter (ARC) test, the onset thermal runaway temperature T_c and self-heating interval time Δt of NCM@LFP || Graphite are much higher than that of NCM || Graphite, respectively, indicating an improved security performance of LFP-coated NCM@LFP || Graphite cell.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S0378775320305383?via%3Dihub>

Low temperature performance enhancement of high-safety Lithium-Sulfur battery enabled by synergetic adsorption and catalysis

Electrochimica Acta 353 (2020) 136470

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Abstract

The application of lithium-sulfur battery (LSB) is limited by shuttle effect and performance at low temperature. This work investigates the catalytic effect and mechanism for polysulfides conversion by cobalt sulfides/carbon nanotubes (Co₃S₄@CNT) at low temperature of -25°C. In order to find out whether the use of catalysts has an impact on safety, thermal runaway behaviors are also explored. For electrochemical performances at -25°C, the capacity of 1275.6 mAh g⁻¹ is achieved at 0.1 C and the capacity decay rate can be as low as 0.06% at 0.5 C when running 500 cycles. The capacity reaches 941.7 mAh g⁻¹ at 1 C and 858 mAh g⁻¹ even at 2 C. The self-discharge in battery is also relieved. The superior low-temperature performances illustrate the crucial role of catalyst to accelerate reaction kinetics and alleviate shuttle effect. From the perspective of safety, the temperature of thermal runaway occurred in Co₃S₄@CNT-S button battery is higher than CeS battery. It means Co₃S₄@CNT can not only accelerate the polysulfides conversion rate and improve the reaction dynamics even at low temperature, but also will not accelerate the occurrence of thermal runaway. These results illustrate that the Co₃S₄@CNT as sulfur carrier and catalyst play an important role in enhancing the electrochemical performance even at low temperature and improving safety of LSB.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S001346862030863>

Study about thermal runaway behavior of high specific energy density Li-ion batteries in a low state of charge

Journal of Energy Chemistry 52 (2021) 20–27

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Abstract

Lithium-ion batteries are widely used in electric vehicles and electronics, and their thermal safety receives widespread attention from consumers. In our study, thermal runaway testing was conducted on the thermal stability of commercial lithium-ion batteries, and the internal structure of the battery was analyzed with an in-depth focus on the key factors of the thermal runaway. Through the study of the structure and thermal stability of the cathode, anode, and separator, the results showed that the phase transition reaction of the separator was the key factor affecting the thermal runaway of the battery for the condition of a low state of charge.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2095495620301613>

Comparative study of thermal runaway and cell failure of lab-scale Li-ion batteries using accelerating rate calorimetry

Journal of Industrial and Engineering Chemistry Volume 83, 25 March 2020, Pages 247–251

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Abstract

The safety of Li-ion batteries (LIBs) has long been a critical issue for their widespread application. The ever-increasing requirements for large-scale applications such as electric vehicles and stationary energy storage systems have spurred great interest in ensuring high standards of safety, which requires an understanding of the thermal runaway features of cells and modules. In this study, we evaluated the thermal runaway of pouch-type LIB cells with cell capacities of 33–3300 mA h by using accelerated rate calorimetry (ARC) and lab-made hotbox ramping measurements. The large-capacity cells (1000 and 3300 mA h) exhibited distinct stage behaviors of the self-heating rate in the ARC profiles and large exothermic reactions accompanied by an abrupt open-circuit voltage drop (internal short circuit) in the ramping test. The small-capacity cell (33 mA h) showed an incomplete thermal runaway feature. These findings were attributed to the large proportion of inactive components relative to the active components, which is discussed in terms of the heat capacity. The data sensitivity factor is also suggested as a reliable measure of thermal runaway evaluation of LIB cells.

Link to purchase paper: <https://www.sciencedirect.com/science/article/abs/pii/S1226086X1930629>

Thermal runaway hazards investigation on 18650 lithium-ion battery using extended volume accelerating rate calorimeter

Journal of Energy Storage 28 (2020) 101232

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Abstract:

With the increase of lithium-ion batteries energy density and capacity, the thermal runaway (TR) is becoming a significant issue that can't be ignored. In this work, one kind of commercial 18650 lithium-ion battery with different states of charge (SOCs) and cycling times is used to evaluate the TR hazards by a ramp heating method in an extended volume accelerating rate calorimeter. Some thermal characteristic parameters are selected and analyzed from the experiment trails, such as the cell surface temperature, temperature rise rate, canister internal pressure and average canister surface temperature. The experiment results show that the maximum surface temperature of the battery and the maximum canister internal pressure increase with the increase of SOC when the TR occurs. The thermal energy released from the battery during TR is calculated using the initial and the maximum temperature on the battery and the canister surface. A fully charged fresh battery can release 61.72 kJ energy when it gets into TR, which could be converted to an explosion equivalent of 5.57 g TNT-equivalent. Compared with fresh batteries, aged batteries are more prone to get into TR and the TR hazards increase

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2352152X19311077>

Toward a high-voltage fast-charging pouch cell with TiO₂ cathode coating and enhanced battery safety

Nano Energy 71 (2020) 104643

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Abstract:

Nickel-rich layered lithium transition metal oxides, LiNi_xCo_yMn_{1-x-y}O₂, are key cathode materials for high-energy lithium-ion batteries owing to their high specific capacity. However, the commercial deployment of nickel-rich oxides has been hampered by their poor thermostability and insufficient cycle life. Here full batteries with uncoated and TiO₂-coated LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathodes and graphite anodes are compared in terms of electrochemical performance and safety behavior. The battery using a TiO₂-coated LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode exhibited better cyclic performance at high cutoff voltage. Electrochemical impedance spectroscopy analysis indicated that the TiO₂-coated LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode gave the battery a more stable charge transfer resistance. Transmission electron microscopy demonstrated that TiO₂ coating reduced accumulation of the cathode electrolyte interface layer on the particle surface. Time-of-flight secondary ion mass spectrometry demonstrated that TiO₂ coating markedly enhanced the interface stability of the cathode particle and protected the particle from serious etching by the electrolyte. Accelerating rate calorimetry revealed that the trigger temperature of thermal runaway for the battery using TiO₂-coated LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ as cathode material was 257°C, which was higher than that of the battery with the uncoated LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode (251°C). In situ X-ray diffraction during heating demonstrated that this enhanced safety can be attributed to the suppressed phase evolution of the coated cathode material.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2211285520302007>

Three-dimensional layered electrochemical-thermal model for a lithium-ion pouch cell Part II. The effect of units number on the performance under adiabatic condition during the discharge

Abstract

Recently, lithium-ion battery system appears to be an effective approach for energy storage due to their excellent performances. The internal structure of the lithium-ion pouch cell is laminated and is composed of several repeated units, and the unit includes five parts of positive current collector, positive electrode, separator, negative electrode and negative current collector. This structure brings great difficulties for simulator to develop full-scale model of the battery due to the complex calculation. In this paper, three kinds of three-dimensional layered electrochemical-thermal models with different unit numbers, one unit model (OUM), two unit model (TUM), and half-scale model (HSM) are established to study the effect of number of units on lithium-ion battery thermal behavior and electrochemical characteristics under adiabatic condition. The corresponding experimental procedure is performed for model validation, the simulation and experiment are in good agreement with temperature and discharge curves at four different discharge rates (0.5 C, 1 C, 1.5 C and 2 C). The results show that the temperature distribution and heat generation rate per volume as well as the representative electrochemical properties are almost the same of the three models; it is also found that each unit of the TUM and HSM is uniform and symmetrical distributed. Therefore, the HSM and full-scale model can be replaced by the OUM for lithium-ion pouch cell under adiabatic condition. The OUM can save 1/140 of computing time and greatly reduce the computational resources compared to HSM, which can facilitate the related research under adiabatic.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0017931019331989>

Journal of Energy Chemistry 44 (2020) 33–40

A polyethylene microsphere-coated separator with rapid thermal shutdown function for lithium-ion batteries

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Abstract:

Thermal runaway is the main factor contributing to the unsafe behaviors of lithium-ion batteries (LIBs) in practical applications. The application of separators for the thermal shutdown has been proven as an effective approach to protecting LIBs from thermal runaway. In this work, we developed a thermal shutdown separator by coating a thin layer of low-density polyethylene microspheres (PM) onto a commercial porous polypropylene (PP) membrane and investigated the thermal response behaviors of the as-prepared PM/PP separator in LIBs. The structural and thermal analysis results revealed that the coated PM layer had a porous structure, which facilitated the occurrence of normal charge-discharge reactions at ambient temperature, although it could melt completely and fuse together within very short time periods: 3 s at 110 °C and 1 s at 120 °C, to block off the pores of the PP substrate, thereby cutting off the ion transportation between the electrodes and interrupting the battery reaction. Consequently, the PM/PP separator exhibits very similar electrochemical performance to that of a conventional separator at ambient temperature. However, it performs a rapid thermal shutdown at an elevated temperature of ~110 °C, thus controlling the temperature rise and maintaining the cell in a safe status. Due to its synthetic simplicity and low cost, this separator shows promise for possible application in building safe LIBs.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2095495619308216>

Journal of Power Sources 445 (2020) 227263

Aging mechanisms and thermal stability of aged commercial 18650 lithium ion battery induced by slight overcharging cycling

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Abstract:

Because of the inconsistency in battery pack and failure of charging device, slight overcharging of lithium ion batteries appears and even causes to thermal runaway. The aging behavior and mechanisms of lithium ion battery under slight overcharging cycling are studied qualitatively and quantitatively based on incremental capacity analysis and electrochemical impedance spectroscopy in this work. The results show that slight overcharging accelerates battery aging because of the loss of active material. While, conductive loss influences capacity fading less. The effect of lithium density loss is in the middle level. So it is suggested that incremental capacity analysis and impedance estimation are used to detect overcharging cycling on-line. Furthermore, the thermal stability of aged batteries are studied using Extended Volume Accelerating Rate Calorimeter. The results show that the stability of aged batteries become worse. The anode plays a key role in the thermal stability changes because of lithium plating under overcharging. The cathode dominates the stability after 70% SOH because of structure damage of cathode.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S037877531931256X>

International Journal of Heat and Mass Transfer 149 (2020) 119178

Self-heating reaction and thermal runaway criticality of the lithium ion battery

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Abstract

Thermal runaway of lithium ion batteries (LIBs) attracts more and more attentions. In this paper, the self-heating reaction of LIBs with different states of charge (SOCs) is investigated by the standard accelerating rate calorimeter (ARC). The onset temperature of self-heating and trigger temperature of thermal runaway are measured. The kinetics of self-heating reaction is obtained, and the self-accelerating decomposition temperatures (SADTs, i.e. the maximum safe storage temperature) are calculated based on thermal explosion model (Semenov model and Thomas model). The results show that the fully-charged LIB (18650-type, Li(Ni 0.5 Co 0.2 Mn 0.3)O₂/graphite) self-ignites if the storage temperature exceeds 149.6 °C under the natural convection condition (the battery surface heat transfer coefficient is 10 W m⁻² K⁻¹). The logarithmic relationship between SADT and heat dissipation condition suggests that it is effective to reduce the fire risk of LIB by modifying the heat dissipation at low heat transfer coefficient (U), while it becomes inefficient when U is high.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0017931019338670>

Renewable Energy 145 (2020) 2046-2055

Experimental investigation on a novel phase change material composites coupled with graphite film used for thermal management of lithium-ion batteries

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Abstract:

Thermal management system is a key component to maintain the performance of lithium-ion batteries in electric vehicles. Cooling technology based on phase change materials with single-phase transition range has been proposed by many researchers but the temperature control of batteries is not ideal for high charge/discharge rates and cycle tests. Herein, we designed a novel phase change material consisting of paraffin with dual-phase transition ranges (around 34 °C and 48 °C), expanded graphite (thermal conductivity ¼ 40 W/m K), and epoxy resin with a mass ratio of 5:2:3. This material was combined with graphite film (in-plane thermal conductivity of 1400 W/m K) to prepare a thermal management module. Graphite film and expanded graphite form an excellent heat conduction structure. Epoxy resin endows this composite with satisfactory mechanical properties, even at 70°C. The paraffin provides a double buffer effect that minimizes the temperature increase of the batteries and the temperature differences between the batteries in the pack due to the broad phase transition range. As a result, the maximum temperature of the batteries is 33°C and the maximum temperature difference between the batteries is only 1.4°C, even at the highest 4C discharge rate. In addition, the maximum temperature of the batteries is only 44.8°C after six extreme cycles.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0960148119311322>

2019

Journal of Power Sources 412 (2019) 204–223

Modeling and simulation of inhomogeneities in a 18650 nickel-rich, silicongraphite lithium-ion cell during fast charging

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Abstract

Recent high-energy lithium-ion batteries contain highly densified electrodes, but they are expected to endure fast charging without safety compromises or accelerated aging. To investigate fast charging strategies, we use a multi-dimensional model consisting of several newman-type electrochemical models (p2D) coupled to an electrical- thermal cell domain model. Open-circuit potential, infrared thermography and calorimetry experiments of a high-energy 18650 NMC-811/SiC lithium-ion cell are used for model parameterization and validation. First, a single p2D model is used to compare the charging rate capabilities of NMC-811/SiC and NMC-111/graphite cells. We assess the modeling error of the single p2D model relative to the multi-dimensional model as a function of tab design. The multi-dimensional model is then used to study different tab and electrode designs regarding their susceptibility to lithium plating, which is evaluated based on local anode overpotential and local temperature. High-rate charging current profiles that minimize the risk of lithium plating are derived by implementing an anode potential threshold. We show that a state of charge beyond 60% can be reached in less than 18 min.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775318312849>

Journal of Power Sources 435 (2019) 226777

Multi-scale thermal stability study of commercial lithium-ion batteries as a function of cathode chemistry and state-of-charge

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Abstract

This paper takes a critical look at the materials aspects of thermal runaway of lithium-ion batteries and correlates contributions from individual cell components to thermal runaway trends. An accelerating rate calorimeter (ARC) was used to evaluate commercial lithium-ion cells based on LiCoO₂ (LCO), LiFePO₄ (LFP), and LiNixCoyAl_{1-x-y}O₂ (NCA) at various states of charge (SOC). Cells were disassembled and the component properties were evaluated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and temperature-resolved X-ray diffraction (TR-XRD). The whole cell thermal runaway onset temperature decreases and peak heating rate increases with SOC due to cathode destabilization. LCO and NCA cathodes are metastable, with NCA cells exhibiting the highest thermal runaway rates. By contrast, the LFP cathode is stable to >500°C, even when charged. For anodes, the decomposition and whole cell self-heating onset temperature is generally independent of SOC. DSC exotherm onset temperatures of the anodes were generally within 10°C of the onset of self-heating in whole cell ARC. However, onset temperatures of the cathodes were typically observed above the ARC onset of whole cell runaway. This systematic evaluation of component to whole cell degradation provides a scientific basis for future thermal modeling and design of safer cells.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775319307487>

Applied Thermal Engineering 153 (2019) 39–50

Inhibition effect of different interstitial materials on thermal runaway propagation in the cylindrical lithium-ion battery module

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Abstract

With the growing demand for high specific energy density of lithium-ion battery pack in electric vehicle to relieve range anxiety, thermal stability in abused conditions is becoming increasingly important in battery pack safety design. Most of the fire accidents are resulted from the thermal runaway (TR) of a single cell and then propagate to the battery modules and entire pack. This study focuses on the safety enhancement methods for battery module, which is filled with different interstitial materials. The basic safety unit is composed of 11 commercial 18650 cylindrical cells, which is isolated from the electric vehicle pack as the test module. The test modules were intentionally triggered into TR by heating wire to evaluate the TR propagation resistance. A model based on finite volume method was established to simulate the TR propagation. The results of both simulation and experiments show that the protection of neighbouring cells from different interstitial materials varies significantly. Graphite composite sheet and Al extrusion as interstitial materials could effectively suppress TR propagation. The results also indicate that for safety design of battery pack, thermal path should be effectively controlled, and particularly the combustion of expelled electrolyte must be directed away from adjacent cells.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S1359431118356783>

Journal of Hazardous Materials 375 (2019) 241–254

Experimental investigation on the thermal runaway and its propagation in the large format battery module with $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ as cathode

Huang Li, Qiangling Duan, Chunpeng Zhao, Zonghou Huang, Qingsong Wang

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Abstract

Thermal runaway (TR) and its propagation behavior in the large format lithium-ion battery (LIB) with various states of charge (SOC) are experimentally investigated in this work. Thermal runaway feature of the cell under thermal abuse condition is characterized using extended volume accelerating rate calorimeter. Based on the experimental results, the modules with five LIBs are built to analyze TR propagation mechanism and further discuss the impact of SOC on TR propagation behavior. It is found that the TR is firstly triggered on the layer near the front surface of the LIB, and then spread to the whole battery. The average propagation time inside the single LIB is 10 s in the module with 100% SOC while 39 s in the module with 50% SOC. Moreover, the module with 100% SOC shows intense combustion behavior, which is replaced by a considerable amount of smoke in the module with 50% SOC. Besides, the average propagation time between adjacent LIBs is significantly delayed from 87 s in 100% SOC module to 307 s in 50% SOC module. This work details TR propagation feature in large format LIB pack, and can provide the guidelines for the safety design of lithium-ion battery module.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S030438941930398X>

Electrochimica Acta 309 (2019) 382–391

Entropy measurement of a large format lithium ion battery and its application to calculate heat generation

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Abstract:

As large format lithium ion batteries are used in EV and ESS applications, the temperature control of a battery is important to achieve a safe and long cycle life operation. To control the temperature properly, we need to know the heat generation characteristics. Heat generation of a battery mainly depends on the applied current, internal resistance, temperature and entropy of the battery. However, it is not easy to measure the entropy, because they depend on SOC and temperature simultaneously. Here, we suggested a new way to measure the entropy, on the assumption of adiabatic condition and calculate the heat generation. Internal resistance, specific heat capacity, OCCP values are also measured experimentally. The entropy ($F\delta E_{oc} \delta T^{-1}$) at a given SOC were measured from the variation of OCCP with temperature and expressed via a polynomial equation. The temperature dependence of the internal resistance were also expressed in the same procedure. The battery temperature variations calculated from the above parameters showed a good agreement with those from experiments. This suggested method provides a simple and reliable temperature estimation of lithium ion batteries.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0013468619307017>

Journal of Energy Storage 23 (2019) 29–36

Lithium-ion capacitor safety assessment under electrical abuse tests based on ultrasound characterization and cell opening

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Abstract:

Safety issues related to lithium-ion batteries are a driving force in the search for new energy storage systems. Lithium-ion capacitors are becoming recognised as promising devices to address the question of safety. These products are a combination of lithium-ion batteries and electric double-layer capacitors in terms of energy and power density. The aim of this work is to assess lithium-ion capacitor safety under over-charge and underdischarge processes for pouch and prismatic cells. In the course of performing abuse tests, no evidence was found of severe hazard (explosion, fire or flame, rupture or major leakage). Quantitative external parameters (thickness, resistance and mass) and electro-thermal measurements showed an increase of swelling and internal resistance, which caused a decrease of capacity and energy efficiency in all cases. The ultrasound characterization technique confirmed that there were irreversible physical modifications of the materials under abuse conditions on prismatic cells, which could not be seen with the commonly used magnitudes (U, I, T). This technique was also used for the identification of the start of cell degradation. In post-mortem analysis, were observed different degradation phenomena such as melting of the separator and delamination in the electrodes.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2352152X19300210>

Solid State Ionics 337 (2019) 7–11

Safety optimization enabled by tris(2,2,2-trifluoroethyl) phosphite additive for advanced pouch lithium ion batteries

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^b School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

Abstract:

The safety issue challenges the application of lithium ion batteries. To solve this problem, organophosphorus additives are applied to construct a non-inflammable electrolyte. Herein an enhanced performance is obtained with tris(2,2,2-trifluoroethyl)phosphite (TTFP) additive for pouch lithium ion batteries. With comparable electrochemical performance, cells with optimized electrolyte come to thermal runaway at higher temperature, which indicates more stable thermal stability. On the other hand, cells with optimized electrolyte exhibit low self-discharge performance. XPS results confirm a better SEI layer, which contributes to the enhancements of the thermal stability and self-discharge. All these results show that TTFP will bring better safety performance and will be a strong candidate for applicable electrolyte.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0167273819301286>

Energy Storage Materials 23 (2019) 646–652

Lithium metal batteries capable of stable operation at elevated temperature

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Abstract:

Rechargeable lithium metal batteries have attracted wide attention due to high theoretical energy density. For practical applications, high-temperature performance of lithium batteries is essential due to complex application environments, in terms of safety and cycle life. However, it's difficult for normal operation of lithium metal batteries at high temperature above 55–60°C using current lithium hexafluorophosphate (LiPF₆) electrolyte systems. Herein, a kind of new electrolyte system is designed by adding two thermal-stable lithium salts together (i.e. lithium bis(trifluoromethanesulfonimide) (LiTFSI) and lithium difluoro(oxalato)borate (LiDFOB)) into carbonate solvents with high boiling/flash point (i.e. ethylene carbonate (EC) and propylene carbonate(PC)). Small amount of LiPF₆ is also added to prevent the corrosion of aluminum current collector. The results indicate that the new electrolyte possesses superior high-temperature performance, meanwhile, it effectively suppresses the formation of lithium dendrite by synergy effects of salts and solvents. Li/LiCoO₂ cells with high LiCoO₂ real capacity (2.4 mAh/cm²) using this kind of new electrolyte shows excellent cycling performance at elevated temperature up to 80°C. Such performance is achieved for the first time for rechargeable Li metal battery using liquid organic electrolytes. It overcomes the operation temperature upper limit of traditional Li-ion batteries (i.e. 55–60°C), which would effectively reduce thermal runaway risk and simplify the thermal management of Li metal batteries in reality.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2405829718313072>

Mechanical collapse as primary degradation mode in mandrel-free 18650 Li-ion cells operated at 0°C

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Abstract

Low temperature charging of Li-ion batteries threatens undesired deposition of lithium dendrites which are often blamed for catastrophic, thermal runaway failures. This work identifies three distinct degradation modes experienced by 0°C operated 18650 Li-ion batteries, revealing safety and performance risks beyond lithium plating. Two equivalently rated (2.6Ah) commercial cells from different vendors, one possessing a mandrel and one lacking, were cycled at 0°C. Through a combination of techniques, it is identified that the first degradation mode is dominated by cell polarization at low temperature, causing lower coulombic efficiency and undesired side reactions. Next, mechanical deformation or jellyroll collapse occurs, followed by accelerated metal plating. However, in the mandrel-containing cell, physical constraint of the electrodes prevents both the deformation and metal plating modes. These degradation modes, difficult to isolate with electrochemistry alone, were diagnosed with non-destructive micro X-ray computed tomography and destructive physical analysis and confirmed with differential capacity assessment. The implication of the physical conditions induced by 0°C operation on cell safety was assessed with accelerated rate calorimetry. Our observations emphasize the presence of thermomechano- electrochemical interplay in commercial cells operated in extreme conditions and assesses the safety implications of their coupling.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775319308134>

Applied Energy 246 (2019) 53–64

Investigating the thermal runaway mechanisms of lithium-ion batteries based on thermal analysis database

Xuning Feng^{a,b}, Siqi Zheng^a, Dongsheng Ren^b, Xiangming He^a, Li Wang^a, Hao Cui^a, Xiang Liu^{b,c}, Changyong Jin^{b,d}, Fangshu Zhang^{b,e}, Chengshan Xu^e, Hungjen Hsu^b, Shang Gao^b, Tianyu Chen^b, Yalun Li^b, Tianze Wang^{b,f}, Hao Wang^g, Maogang Li^g, Minggao Ouyang^b

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^g China Office, Thermal Hazard Technology, Shanghai 200029, China Energy Procedia 158 (2019) 4684–4689

Abstract

The cause of the thermal runaway problem in lithium-ion batteries problem is still unclear. This bottle neck has prevented increases in the energy density of lithium-ion batteries, of which the technology may stagnate for many years. The diversity of cell chemistries makes this problem more difficult to analyze. This paper reports work conducted by Tsinghua University and its collaborators into the establishment of a thermal analysis database. The database contains comparable data for different kinds of cells using accelerating rate calorimetry and differential scanning calorimetry. Three characteristic temperatures are summarized based on the common features of the cells in the database. In attempting to explain the mechanisms that are responsible for the characteristic temperature phenomena, we have gained new insight into the thermal runaway mechanisms of lithium-ion batteries. The results of specially designed tests show that the major heat source during thermal runaway for cells with Li(NixCoyMnz)O2 cathode and carbon-based anode is the redox reaction between the cathode and anode at high temperature. In contrast to what is commonly thought, internal short circuits are responsible for very little of the total heat generated during thermal runaway, although they contribute to triggering the redox reactions after the separator collapses. The characteristic temperatures provide comparable parameters that are useful in judging the safety of a newly designed battery cell. Moreover, the novel interpretation of the thermal runaway mechanism provide guidance for the safety modelling and design of lithiumion batteries.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0306261919306348>

Applied Energy 250 (2019) 323–332

Overcharge behaviors and failure mechanism of lithium-ion batteries under different test conditions

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Abstract

Overcharge is one of the most severe safety problems for the large-scale application of lithium-ion batteries, and in-depth understanding of battery overcharge failure mechanism is required to guide the safety design of battery systems. In this paper, the overcharge performance of a commercial pouch lithium-ion battery with Liy(NiCoMn)1/3O2-LiyMn2O4 composite cathode and graphite anode is evaluated under various test conditions, considering the effects of charging current, restraining plate and heat dissipation. Charging current is found to have only minor influences on battery overcharge behaviors, whereas the battery overcharged with pressure relief design (restraining plate and cuts on pouches) and good heat dissipation shows significantly improved overcharge performance and can endure larger amount of overcharge capacity and higher temperature before thermal runaway. Characterizations on cathode and anode materials at different overcharge states are carried out to identify the side reactions inside the battery. The overcharged cathode suffers from electrolyte decomposition, transition metal dissolution and phase transition, but still exhibits no obvious exothermic behaviors before thermal runaway occurs. Severe lithium plating happens on the anode, and would accelerate the overcharge-induced thermal runaway process. Further analysis on the onset temperature of thermal runaway helps to reveal the overcharge-induced thermal runaway mechanism of lithium-ion batteries. The result shows that rupture of the pouch and separator melting are the two key factors for the initiation of thermal runaway during overcharge process.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0306261919308566>

Solid State Ionics 337 (2019) 7–11

Safety optimization enabled by tris(2,2,2-trifluoroethyl)phosphite additive for advanced pouch lithium ion batteries

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The safety issue challenges the application of lithium ion batteries. To solve this problem, organophosphorus additives are applied to construct a non-inflammable electrolyte. Herein an enhanced performance is obtained with tris(2,2,2-trifluoroethyl)phosphite (TTFP) additive for pouch lithium ion batteries. With comparable electrochemical performance, cells with optimized electrolyte come to thermal runaway at higher temperature, which indicates more stable thermal stability. On the other hand, cells with optimized electrolyte exhibit low self-discharge performance. XPS results confirm a better SEI layer, which contributes to the enhancements of the thermal stability and self-discharge. All these results show that TTFP will bring better safety performance and will be a strong candidate for applicable electrolyte.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0167273819301286>

Energy Procedia 158 (2019) 4684-4689

Key Characteristics for Thermal Runaway of Li-ion Batteries

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Abstract

The lithium ion batteries are having increasing energy densities, meeting the requirement from industry, especially for the electric vehicles. However, a cell with a higher energy density is more prone to thermal runaway. We analyze the key characteristics during thermal runaway to help better define battery thermal runaway. Three characteristic temperatures are regarded as the common features of thermal runaway for all kinds of lithium ion batteries. The underlying mechanisms for the three characteristic temperatures have been investigated by thermal analysis. The conclusion of the analysis set benchmarks for evaluating the thermal runaway behaviors of commercial lithium-ion batteries, and the proposed methodologies benefits further research and development of battery safety design for electric vehicles.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S187661021930774X>

Energy Procedia 158 (2019) 4921-4926

Comparison of the overcharge behaviours of Lithium-ion Batteries Under Different Test Conditions

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Abstract

Overcharge is one of the most severe safety issues of lithium-ion batteries. In this paper, the overcharge performance of a commercial lithium-ion battery is evaluated under different test conditions, considering the effects of charging current, restraining plate and heat dissipation. Charging current and heat dissipation are found to have only minor influence on the battery overcharge behaviors, while batteries with restraining plate and cuts on the pouches show improved overcharge performance, as SOCTR and TTR both increase significantly. Further analysis on TTR helps to identify the overcharge-induced thermal runaway mechanism for the batteries with different configurations.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S1876610219307362>

Journal of Energy Storage 23 (2019) 29–36

Lithium-ion capacitor safety assessment under electrical abuse tests based on ultrasound characterization and cell opening

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Abstract

Safety issues related to lithium-ion batteries are a driving force in the search for new energy storage systems. Lithium-ion capacitors are becoming recognised as promising devices to address the question of safety. These products are a combination of lithium-ion batteries and electric double-layer capacitors in terms of energy and power density. The aim of this work is to assess lithium-ion capacitor safety under over-charge and underdischarge processes for pouch and prismatic cells. In the course of performing abuse tests, no evidence was found of severe hazard (explosion, fire or flame, rupture or major leakage). Quantitative external parameters (thickness, resistance and mass) and electro-thermal measurements showed an increase of swelling and internal resistance, which caused a decrease of capacity and energy efficiency in all cases. The ultrasound characterization technique confirmed that there were irreversible physical modifications of the materials under abuse conditions on prismatic cells, which could not be seen with the commonly used magnitudes (U, I, T). This technique was also used for the identification of

the start of cell degradation. In post-mortem analysis, were observed different degradation phenomena such as melting of the separator and delamination in the electrodes.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S2352152X19300210>

Journal of Power Sources 412 (2019) 204–223

Modeling and simulation of inhomogeneities in a 18650 nickel-rich, silicon-graphite lithium-ion cell during fast charging

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Abstract

Recent high-energy lithium-ion batteries contain highly densified electrodes, but they are expected to endure fast charging without safety compromises or accelerated aging. To investigate fast charging strategies, we use a multi-dimensional model consisting of several newman-type electrochemical models (p2D) coupled to an electrical-thermal cell domain model. Open-circuit potential, infrared thermography and calorimetry experiments of a high-energy 18650 NMC-811/SiC lithium-ion cell are used for model parameterization and validation. First, a single p2D model is used to compare the charging rate capabilities of NMC-811/SiC and NMC-111/graphite cells. We assess the modeling error of the single p2D model relative to the multi-dimensional model as a function of tab design. The multi-dimensional model is then used to study different tab and electrode designs regarding their susceptibility to lithium plating, which is evaluated based on local anode overpotential and local temperature. High-rate charging current profiles that minimize the risk of lithium plating are derived by implementing an anode potential threshold. We show that a state of charge beyond 60% can be reached in less than 18 min.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775318312849>

Thermochimica Acta 674 (2019) 44–51

Kinetic model of thermal decomposition of CL-20/HMX co-crystal for thermal safety prediction

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Abstract

To promote the practical application of CL-20/HMX co-crystal, the understanding of its thermal decomposition kinetics and thermal hazard prediction are highly required. In this study, the kinetic model was evaluated based on the non-isothermal DSC data by using non-linear optimization method, which was identified as a complicated reaction comprising two parallel autocatalytic paths, and the contribution of the two reaction paths was revealed to vary depending on the heating rate. Based on the kinetic model, the thermal hazard simulation indicates that the temperature when the occurrence of thermal decomposition after 24 h ($T_{d,24}$) of CL-20/HMX co-crystal is 151.64 °C, and the critical temperature of 1000th second explosion is determined as ~196 °C. Besides, simulation results of self-accelerating decomposition temperature demonstrate that the package mass of CL-20/HMX cocrystal, rather than the package material, has a remarkable effect on the thermal safety of CL-20/HMX co-crystal.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S004060311831164X>

Applied Thermal Engineering 153 (2019) 39–50

Inhibition effect of different interstitial materials on thermal runaway propagation in the cylindrical lithium-ion battery module

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Abstract

With the growing demand for high specific energy density of lithium-ion battery pack in electric vehicle to relieve range anxiety, thermal stability in abused conditions is becoming increasingly important in battery pack safety design. Most of the fire accidents are resulted from the thermal runaway (TR) of a single cell and then propagate to the battery modules and entire pack. This study focuses on the safety enhancement methods for battery module, which is filled with different interstitial materials. The basic safety unit is composed of 11 commercial 18,650 cylindrical cells, which is isolated from the electric vehicle pack as the test module. The test modules were intentionally triggered into TR by heating wire to evaluate the TR propagation resistance. A model based on finite volume method was established to simulate the TR propagation. The results of both simulation and experiments show that the protection of neighboring cells from different interstitial materials varies significantly. Graphite composite sheet and Al extrusion as interstitial materials could effectively suppress TR propagation. The results also indicate that for safety design of battery pack, thermal path should be effectively controlled, and particularly the combustion of expelled electrolyte must be directed away from adjacent cells.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S1359431118356783>

Int. J. Electrochem. Sci., 14 (2019) 44 – 58,

Influence of aging paths on the thermal runaway features of lithium-ion batteries in accelerating rate calorimetry tests

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Abstract

Aging is inevitable during the use of lithium-ion batteries. However, the influence of aging paths on the safety of the lithium-ion batteries remains unclear, leaving uncertainties about safe operation throughout their full life cycle. This paper studies the influence of aging paths on the thermal runaway features in lithium-ion batteries using ARC. Characteristic temperatures are defined to quantify the thermal stability of lithium-ion batteries. Two kinds of aging tests are designed, high-temperature storage and low-temperature cycling. The effects of aging on the change in the characteristic temperatures have been investigated, providing a quantified analysis of the evolution of battery safety performance during aging. The thermal stability of the cells after low-temperature cycling is worse than that of the fresh cells and less than that of the cells that are treated by high-temperature exposure. Although the capacity retention rates of the cells aged by high-temperature exposure and low-temperature cycling can be similar, their thermal stabilities are quite different. The consumption of active lithium at the anode surface to generate a new SEI layer will result in a better thermal stability in the cells that are treated by high-temperature exposure. However, if there is lithium deposition on the surface of the anode, the thermal stability of the lithium-ion battery will become worse. The quantitative discussions and conclusions of this paper can provide guidance on evaluating the safety throughout the full life cycle.

Link to download paper: <http://www.electrochemsci.org/papers/vol14/140100044.pdf>

Modeling and simulation of inhomogeneities in a 18650 nickel-rich, silicongraphite lithium-ion cell during fast charging

Journal of Power Sources 412 (2019) 204–223

J. Sturm^{a,*}, A. Rheinfeld^a, I. Zilberman^a, F.B. Spingler^a, S. Kosch^a, F. Frie^{b,c}, A. Jossen^a

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Abstract

Recent high-energy lithium-ion batteries contain highly densified electrodes, but they are expected to endure fast charging without safety compromises or accelerated aging. To investigate fast charging strategies, we use a multi-dimensional model consisting of several newman-type electrochemical models (p2D) coupled to an electrical-thermal cell domain model. Open-circuit potential, infrared thermography and calorimetry experiments of a high-energy 18650 NMC-811/SiC lithium-ion cell are used for model parameterization and validation. First, a single p2D model is used to compare the charging rate capabilities of NMC-811/SiC and NMC-111/graphite cells. We assess the modeling error of the single p2D model relative to the multi-dimensional model as a function of tab design. The multi-dimensional model is then used to study different tab and electrode designs regarding their susceptibility to lithium plating, which is evaluated based on local anode overpotential and local temperature. High-rate charging current profiles that minimize the risk of lithium plating are derived by implementing an anode potential threshold. We show that a state of charge beyond 60% can be reached in less than 18 min.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775318312849>

2018

Time Sequence Map for Interpreting the Thermal Runaway Mechanism of Lithium-Ion Batteries With LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ Cathode

Frontiers in Energy Research

Xuning Feng¹, Siqi Zheng¹, Xiangming He^{1*}, Li Wang¹, Yu Wang², Dongsheng Ren² and Minggao Ouyang^{2*}

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Abstract

Thermal runaway is one of the key failure reasons for the lithium-ion batteries. The potential of thermal runaway in applications increases when the industry starts to use high energy LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode. The thermal runaway mechanism is still unclear, because the side reactions are complex. Heat generation during thermal runaway can be caused by the decomposition of individual cell components, or by interactive reactions between multiple components. This paper tries to comb the heat sources during thermal runaway using a novel method named the “Time Sequence Map” (TSM). The TSM tracks the heat sources according to the notion of thermodynamic systems. The thermodynamic system means a combination of materials that stay and react together, and generate heat independently without interruptions from other thermodynamic systems. With the help of the defined thermodynamic systems, researchers will be rescued from being trapped in the complex reactions, and the heat sources during thermal runaway can be clearly explained from bottom up. The thermal runaway results for two battery samples demonstrate the validity of the TSM. The TSM shows the heat sources including that: (1) fire, (2) internal short circuit, (3) oxidation-reduction reaction between the cathode and anode, etc. The contributions for the heat sources to the thermal runaway are further discussed. Conclusions come to: (1) the major heat source is the oxidation-reduction reaction; (2) the fire releases lots of heat, but most of the heat is not to heat the cell itself; (3) the internal short circuit is critical to trigger the oxidation-reduction reaction; (4) the internal short circuit is not the major heat source that heat the cell to 800°C or higher; (5) the oxidation-reduction reaction is triggered when the temperature reaches a critical temperature. The TSM helps depict the frontiers in the researches of battery thermal runaway. It suggests that we focus on: (1) the relationship between internal short circuit and thermal runaway; (2) the mechanism of the oxidation-reduction reaction between the cathode and anode; (3) the detailed reaction mechanisms for a specific thermodynamic system within the cell

Link to download paper: <https://www.frontiersin.org/articles/10.3389/fenrg.2018.00126/full>

Thermal Analysis of $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ /Mesocarbon Microbeads Cells and Electrodes: State-of-Charge and State-of-Health Influences on Reaction Kinetics

Journal of The Electrochemical Society, 165 (2) A104-A117 (2018)

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Abstract

The thermal stability of lithium ion batteries was studied by means of Accelerating Rate Calorimetry in Heat-Wait-Search operation on both electrode and cell level. Fresh and aged samples were investigated depending on the state-of-charge (SoC) of a 5 Ah pouch cell comprising mesocarbon microbeads and $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ as the anode and cathode materials. 1 M LiPF₆ in EC:DEC 3:7 (by weight) containing 2 wt% VC and 0.5 wt% LiBOB was chosen as the electrolyte. Measurements on the electrode level revealed a higher self-heating rate (SHR) of the cathode compared to the anode for all SoC and state-of-health (SoH) combinations in the temperature range where a self-sustaining decomposition reaction could be detected. A lower SoC showed a lower SHR of the electrode/electrolyte mixture with no reaction detected on the anode side $\leq 50\%$ cell SoC. Cyclic aging led to a decrease in thermal stability of the cathode at lower SoC values with no significant influence on the anode implying a larger safety threat on the cell level. Avrami-Erofeev and autocatalytic reaction models were used to quantify the influences of SoC and SoH on reaction kinetics. Full cell measurements confirmed the observations at a higher SHR.

Link to purchase paper: <http://jes.ecsdl.org/content/165/2/A104.abstract>

Mechanism of Thermal Runaway in Lithium-Ion Cells

Journal of The Electrochemical Society, 165 (7) A1303-A1308 (2018)

N. E. Galushkin, *,z N. N. Yazvinskaya, and D. N. Galushkin

Don State Technical University, Laboratory of Electrochemical and Hydrogen Energy, Town of Shakhty, Rostov Region 346500, Russia

Abstract

In this investigation, it was shown that a probability of thermal runaway in commercial lithium-ion cells of the type 18650 grows with number increase of charge/discharge cycles and increase of cells state of charge (SOC). Notably, experiments in an accelerating rate calorimeter (ARC) showed that with the number growth of cells charge/discharge cycles, it is observed a considerable decline of an initiation temperature of exothermic reactions of thermal runaway and increase of released energy. Additional ARC-experiments with the following analysis of the gas released showed that in a course of cells cycling in anode graphite, hydrogen is accumulated. It was proven in experiments that a recombination of released-from-graphite-anode atomic hydrogen is exactly that powerful exothermic reaction, which increases the released energy in the beginning of the thermal runaway and decreases the temperature of its initiation. Thus, the reason for the initiation of thermal runaway in lithium-ion cells is a powerful exothermic reaction of recombination of atomic hydrogen accumulated in anode graphite in a during of cells cycling. The possible mechanism of initiation thermal runaway has been proposed corresponding to all the experimental results obtained.

Link to download paper: <http://jes.ecsdl.org/content/165/7/A1303.full>

State of charge influence on thermal reactions and abuse tests in commercial lithium-ion cells

Journal of Power Sources 399 (2018) 392–397

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Abstract

Cycling stability and thermal runaway characteristics of four commercially available cylindrical cells based on LiFePO_4 (LFP) and $\text{Li}_x(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ (NCA) cathode materials were investigated. The cells with different formats were cycled to three states of charge (SOC): 0, 50 and 100%, before adiabatic thermal analysis using an accelerating rate calorimeter (ARC). The charged cells experienced thermal runaway; the first rise in temperature due to the exothermic reaction and maximum cell temperature are discussed in detail for the different cells. Abuse testing (crush and nail penetration tests) was also performed at 100% SOC; the videos of the tests are available online as supplementary data. The LFP cathode exhibited superior cycling and thermal stability compared to NCA.

Link to purchase paper: <https://www.sciencedirect.com/science/article/pii/S0378775318308450>

Novel thermal management system using mist cooling for lithium-ion battery packs ***Applied Energy 223 (2018) 146–158***

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Abstract

Thermal management system is crucial for a Lithium-ion battery pack as cycle life, driving range of electric vehicle, usable capacity and safety are heavily dependent on the operating temperature. Optimum operating temperature of Lithium-ion battery pack is about 25–40 °C. Power availability of the battery pack may differ according to the operating temperature. Although air cooling is the simplest and cheapest cooling solution, the cooling capacity is still limited by the low specific heat capacity. This will cause large variation of temperature of cells across the battery pack. In this study, mist cooling is proposed for battery pack thermal management system. Experiments and numerical simulations are conducted to investigate the thermal performance of conventional dry air cooling and mist cooling. Simulation results are then validated with the experimental data. The simulation results show that mist cooling can offer lower and more uniform temperature distribution compared to dry air cooling. Mist cooling with mass flow rate of 5 gs⁻¹ and 3% mist loading fraction is sufficient to ensure the surface temperature of the battery module maintained to below 40 °C. Therefore, mist cooling is a potential solution for the thermal management system of Lithium-ion battery pack.

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Electrochemical performance and thermal stability analysis of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ cathode based on a composite safety electrolyte

Journal of Hazardous Materials 351 (2018) 260–269

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Abstract

$\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) cathode material with high energy density is one of the best choices for power batteries. But the safety issue also becomes more prominent with higher nickel content. The improvement of thermal stability by material modification is often complex and limited. In this study, a composite safety electrolyte additive consisting of perfluoro-2-methyl-3-pentanone, N, N-Dimethylacetamide (and fluorocarbon surfactant is proved to be effective and simple in improving the thermal stability of NCM materials. Electrochemical compatibility of composite safety electrolyte with various NCM materials is investigated. Uniform interface film, lower impedance and polarization for NCM (622) cycled in composite safety electrolyte are proved to be the main reasons to ensure good cycle performance. Homemade pouch cells (NCM (622)/C) are used to verify the effectiveness for practical application, accelerating rate calorimeter and nail penetration test shows a slower temperature rise and delay of thermal runaway. For heating experiment, no fire appears for pouch cell with composite safety electrolyte. Thus, this composite safety electrolyte is effective to improve the safety of lithium ion batteries with NCM materials.

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Probing the heat sources during thermal runaway process by thermal analysis of different battery chemistries

Journal of Power Sources 378 (2018) 527–536

Siqi Zheng, Li Wang, Xuning Feng, Xiangming He. Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing, 100084, China

Abstract

Safety issue is very important for the lithium ion battery used in electric vehicle or other applications. This paper probes the heat sources in the thermal runaway processes of lithium ion batteries composed of different chemistries using accelerating rate calorimetry (ARC) and differential scanning calorimetry (DSC). The adiabatic thermal runaway features for the 4 types of commercial lithium ion batteries are tested using ARC, whereas the reaction characteristics of the component materials, including the cathode, the anode and the separator, inside the 4 types of batteries are measured using DSC. The peaks and valleys of the critical component reactions measured by DSC can match the fluctuations in the temperature rise rate measured by ARC, therefore the relevance between the DSC curves and the ARC curves is utilized to probe the heat source in the thermal runaway process and reveal the thermal runaway mechanisms. The results and analysis indicate that internal short circuit is not the only way to thermal runaway, but can lead to extra electrical heat, which is comparable with the heat released by chemical reactions. The analytical approach of the thermal runaway mechanisms in this paper can guide the safety design of commercial lithium ion batteries

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2017

Experimental Analysis of Thermal Runaway in 18650 Cylindrical Li-Ion Cells Using an Accelerating Rate Calorimeter

Batteries 2017 Vol 3, Issue 2, 14

Boxia Lei, Wenjiao Zhao *, Carlos Ziebert, Nils Uhlmann, Magnus Rohde and Hans Jürgen Seifert Institute of Applied Materials-Applied Materials Physics, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany.

Abstract

In this work, commercial 18650 lithium-ion cells with LiMn₂O₄, LiFePO₄, and Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O₂ cathodes were exposed to external heating in an accelerating rate calorimeter (es-ARC, Thermal Hazard Technology (THT), Bletchley, UK), to investigate the thermal behaviour under abuse conditions. New procedures for measuring the external and internal pressure change of cells were developed. The external pressure was measured utilizing a gas-tight cylinder inside the calorimeter chamber, in order to detect the venting of the cells. For internal pressure measurements, a pressure line connected to a pressure transducer was directly inserted into the cell. During the thermal runaway experiments, three stages (low rate, medium rate, and high rate reactions) were observed. Both the pressure and temperature change indicated different stages of exothermic reactions, which produced gases or/and heat. The onset temperature of the thermal runaway was estimated according to the temperature and pressure changes. Moreover, the different activation energies for the exothermic reactions could be derived from Arrhenius plots.

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Al₂O₃ coating on anode surface in lithium ion batteries: Impact on low temperature cycling and safety behaviour

Journal of Power Sources 363 (2017) 70-77

Alex Friesen, Stephan Hildebrand, Fabian Horsthemke, Markus Boerner, Richard Kloepsch a, Philip Niehoff, Falko M. Schappacher, Martin Winter

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Commercial 18650-type lithium ion cells employing an Al₂O₃ coating on the anode surface as a safety feature are investigated regarding cycling behavior at low temperatures and related safety. Due to irreversible lithium metal deposition, the cells show a pronounced capacity fading, especially in the first cycles, leading to a shortened lifetime. The amount of reversibly strippable lithium metal decreases with every cycle. Post-mortem analysis of electrochemically aged anodes reveals a thick layer of lithium

metal deposited beneath the coating. The Al₂O₃ coating on the electrode surface is mostly intact. The lithium metal deposition and dissolution mechanisms were determined combining electrochemical and post-mortem methods. Moreover, the cell response to mechanical and thermal abuse was determined in an open and adiabatic system, revealing a similar behavior of fresh and aged cells, thus, demonstrating no deterioration in the safety behavior despite the presence of a thick lithium metal layer on the anode surface.

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***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 (LiNi₁/3Mn₁/3Co₁/3O₂) 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.

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***Chapter Six – Electrochemical–Thermal Characterization and Thermal Modeling for Batteries
Emerging Nanotechnologies in Rechargeable Energy Storage Systems: A volume in Micro and Nano
Technologies. 2017, Pages 195–229***

Ziebert, A. Melcher, B. Lei, W. Zhao, M. Rohde, H.J. Seifert. Karlsruhe Institute of Technology, Institute of Applied Materials—Applied Materials Physics, Eggenstein-Leopoldshafen, Germany

Abstract

Calorimetry of the electrochemical cells, batteries, and their individual active materials is required to obtain quantitative thermal and thermodynamic data. The two most important experimental calorimetric devices, namely the isothermal heat conduction calorimeter (IHC) and the accelerating rate calorimeter (ARC), will be introduced and examples for the measurements that are possible with these devices will be shown. Moreover, it will be demonstrated how thermal runaway behavior and the related reaction mechanisms of the cells and materials can be investigated quantitatively using an ARC.

To gain additional information for lithium-ion batteries (LIBs) beyond the experiments, mathematical modeling and simulations are used. With respect to the thermal issues of a thermal runaway in a LIB, the coupled electrochemical thermal model based on porous electrode theory of Newman has been extended with a simple combustion model coming from reaction kinetics including various types of heat sources based on an Arrhenius law. This model was realized using the commercial finite element (FEM) package COMSOL Multiphysics. Finally simulation results for an oven test and simple electrical current loads will be presented.

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***Modelling electro-thermal response of lithium-ion batteries from normal to abuse conditions
Applied Energy 205 (2017) 1327–1344***

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Abstract

Insight of thermal behaviour of lithium-ion batteries under various operating conditions is crucial for the development of battery management system (BMS). Although battery thermal behaviour has been studied by published models, the reported modelling normally addresses either normal operation or thermal runaway condition. A comprehensive electro-thermal model which can capture heat generation, voltage and current variation during the whole process from normal cycling to thermal runaway should be of benefit for BMS by evaluating critical factors influencing potential transition to thermal runaway and investigating the evolution process under different cooling and environment conditions. In this study, such a three-dimensional model has been developed within the frame of open source computational fluid dynamics (CFD) code OpenFOAM to study the electrical and thermal behaviour of lithium-ion batteries (LIBs). The equations governing the electric conduction are coupled with heat transfer and energy balance within the cell. Published and new laboratory data for $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2/\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$ (LNCMO/LTO) cells from normal cycling to thermal runaway have been used to provide input parameters as well as model validation. The model has well captured the evolution process of a cell from normal cycling to abnormal behaviour until thermal runaway and achieved reasonably good agreement with the measurements. The validated model has then been used to conduct parametric studies of this particular type of LIB by evaluating the effects of discharging current rates, airflow quantities, ambient temperatures and thickness of airflow channel on the response of the cell. Faster function losses, earlier thermal runaway and higher extreme temperatures were found when cells were discharged under higher current rates. The airflow with specific velocity was found to provide effective mitigation against over-heating when the ambient temperature was below 370 K but less effective when the ambient temperature was higher than the critical value of 425 K. The thickness of airflow channel was also found to have critical influence on the cell tolerance to elevated temperatures. These parametric studies demonstrate that the model can be used to predict potential LIB transition to thermal runaway under various conditions and aid BMS.

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An electrochemical-thermal coupled overcharge-to-thermal-runaway model for lithium ion battery
Journal of Power Sources 364 (2017) 328-340

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Abstract

This paper presents an electrochemical-thermal coupled overcharge-to-thermal-runaway (TR) model to predict the highly interactive electrochemical and thermal behaviors of lithium ion battery under the overcharge conditions. In this model, the battery voltage equals the difference between the cathode potential and the anode potential, whereas the temperature is predicted by modeling the combined heat generations, including joule heat, thermal runaway reactions and internal short circuit. The model can fit well with the adiabatic overcharge tests results at 0.33C, 0.5C and 1C, indicating a good capture of the overcharge-to-TR mechanism. The modeling analysis based on the validated model helps to quantify the heat generation rates of each heat sources during the overcharge-to-TR process. And the two thermal runaway reactions including the electrolyte oxidation reaction and the reaction between deposited lithium and electrolyte are found to contribute most to the heat generations during the overcharge process. Further modeling analysis on the critical parameters is performed to find possible solutions for the overcharge problem of lithium ion battery. The result shows that increasing the oxidation potential of the electrolyte, and increasing the onset temperature of thermal runaway are the two effective ways to improve the overcharge performance of lithium ion battery.

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Safety of solid-state Li metal battery: Solid polymer versus liquid
Electrolyte

Journal of Power Sources 359 (2017) 182-185

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Abstract

In this article we present the difference in thermal stability of Li/LiFePO₄ half cells with liquid and solid polymer electrolytes. After two initial cycles, the cells were charged to two different state of charge (SOC) of 50 and 100%. The thermal stability of the half cells is assessed with an accelerating rate calorimeter, and the thermal runaway parameters are discussed for each

experiment: dependence of self-heating rate on temperature, temperature of a first-detected exothermic reaction, and maximum cell temperature. The dependence of those parameters with respect to the SOC is also presented.

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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_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA)|LiPF₆ dissolved in ethylene carbonate (EC)/diethyl carbonate solution (DEC) (EC/DEC = 1/1 by volume); LiPF₆(EC/DEC)|artificial graphite (AG) and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM)|LiPF₆(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_{0.5}Co_{0.2}Mn_{0.3}O₂/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.

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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

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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.

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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.

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

Applied Energy 182 (2016) 464–474

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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 $\text{LiCoO}_2 + \text{Li}(\text{Ni}_0.5\text{Co}_0.2\text{Mn}_0.3)\text{O}_2/\text{C} + \text{SiO}_x$ 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_x . The overcharge induced decomposition reaction of $\text{Li}(\text{Ni}_0.5\text{Co}_0.2\text{Mn}_0.3)\text{O}_2$ is also proposed. These results can provide support for the safety designs of lithium ion batteries and BMS.

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Heat loss distribution: Impedance and thermal loss analyses in LiFePO_4 /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,
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We report here thermal behaviour and various components of heat loss of 18650-type LiFePO₄/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, [†], 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.

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The simulation on thermal stability of LiNi0.5Mn1.5O4/C electrochemical systems

Journal of Power Sources 302 (2016) 1–6

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A thermal model of LiNi0.5Mn1.5O4/C electrochemical system has been developed. The thermal model is based on the thermal characteristic and related calculation for full charged LiNi0.5Mn1.5O4 and full discharged carbon materials, respectively.

According to simulations on the thermal stability of LiNi0.5Mn1.5O4/C electrochemical system, there is one exothermic process for the full charged LiNi0.5Mn1.5O4 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 LiNi0.5Mn1.5O4/C electrochemical system. It is the reactions between LiNi0.5Mn1.5O4 and the electrolyte that make the LiNi0.5Mn1.5O4/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.

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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

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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 $f(\alpha) = 1.49(1 - \alpha)^{1.59}$. 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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Novel Ethylene Carbonate Based Electrolyte Mixtures for Li-Ion Batteries with Improved Safety Characteristics

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

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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 LiBF₄, lithium bis(trifluoromethanesulfonyl)azanide, and lithiumbis(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_{1/3}Co_{1/3}Mn_{1/3}O₂), 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.

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Thermal runaway propagation model for designing a safer battery pack with 25 Ah LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ large format lithium ion battery

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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_{1/3}Co_{1/3}Mn_{1/3}O₂ 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⁻² K⁻¹; (4) add extra thermal resistant layers between adjacent batteries with a thickness of 1 mm and a thermal conductivity less than 0.2 Wm⁻¹ K⁻¹. One implementation, which is verified by experiment, is to insert thermal resistant layer between adjacent batteries to prevent TR propagation in the battery module.

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

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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_xNi_{1/3}Mn_{1/3}Co_{1/3}O₂/Li_yMn₂O₄ 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.

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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

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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 LiMn_2O_4 cathodes as well as 20 Ah pouch cells with 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

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 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 LiFePO₄
Journal of Power Sources 247 (2014)

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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)

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Abstract

In this paper, the thermal runaway features of a 25 Ah large format prismatic lithium ion battery with Li(NixCoyMnz)O₂ (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.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775314000159>

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

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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.

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

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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***

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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.

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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

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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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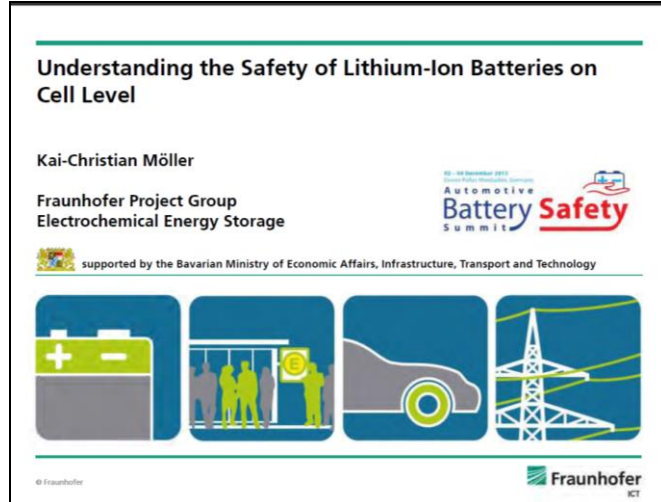
2013

[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

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

Presented at 17th 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

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

Presented at 225th ECS Meeting, Orlando, USA, 11.-16.05.2014.

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Thermal runaway of lithium ion batteries

Presented at 7th Asian Conference on Electrochemical Power Sources (ACEPS - 7), Osaka, Japan

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