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Battery Papers

2017

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.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S0378775317310595>

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.

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

2016

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

Journal of Power Sources 334 (2016) 1–11

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Roman Krafft , Markus Börner , Tim Risthaus , Martin Winter, Falko M. Schappacher
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Abstract

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

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

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

Applied Energy 182 (2016) 464–474

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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 LiCoO₂ + Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O₂/C + 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 Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O₂ is also proposed. These results can provide support for the safety designs of lithium ion batteries and BMS.

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

Heat loss distribution: Impedance and thermal loss analyses in LiFePO₄/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***

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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 LiNi_{0.5}Mn_{1.5}O₄/C electrochemical systems

Journal of Power Sources 302 (2016) 1-6

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A thermal model of LiNi_{0.5}Mn_{1.5}O₄/C electrochemical system has been developed. The thermal model is based on the thermal characteristic and related calculation for full charged LiNi_{0.5}Mn_{1.5}O₄ and full discharged carbon materials, respectively.

According to simulations on the thermal stability of LiNi_{0.5}Mn_{1.5}O₄/C electrochemical system, there is one exothermic process for the full charged LiNi_{0.5}Mn_{1.5}O₄ and two for the full discharged carbon. The first exothermic reaction for carbon material should be the best explanation for the initially self-heating of LiNi_{0.5}Mn_{1.5}O₄/C electrochemical system. It is the reactions between LiNi_{0.5}Mn_{1.5}O₄ and the electrolyte that make the LiNi_{0.5}Mn_{1.5}O₄/C cell going into thermal runaway. The simulated result shows a good consistency with the testing result, so this simulation method can provide a significant basis for the thermal and safety design of batteries.

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

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

Thermochimica Acta 623 (2016) 43–49

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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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2015

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

ChemSusChem 8 (2015) 1892-1900

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

In this study, novel electrolyte mixtures for Li-ion cells are presented with highly improved safety features. The electrolyte formulations are composed of ethylene carbonate/dimethyl sulfone (80:20 wt/wt) as the solvent mixture and LiBF₄, lithium bis(trifluoromethanesulfonyl)azanide, and lithium bis(oxalato)-borate as the conducting salts. Initially, the electrolytes are characterized with regard to their physical properties, their lithium transport properties, and their electrochemical stability. The key advantages of the electrolytes are high flash points of > 140 °C, which enhance significantly the intrinsic safety of Li-ion cells containing these electrolytes. This has been quantified by measurements in an accelerating rate calorimeter. By using the newly

developed electrolytes, which are liquid down to $T = -10\text{ }^{\circ}\text{C}$, 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 | $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$), it is proven that the retention of the specific capacity is > 98% of the third discharge cycle with dependence on the conducting salt. The best electrolyte mixture yields a capacity retention of > 96% after 200 cycles in coin cells.

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

Thermal runaway propagation model for designing a safer battery pack with 25 Ah LiNixCoyMnzO2 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 LiNixCoyMnzO2 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 $70\text{Wm}^{-2}\text{K}^{-1}$; (4) add extra thermal resistant layers between adjacent batteries with a thickness of 1 mm and a thermal conductivity less than $0.2\text{Wm}^{-1}\text{K}^{-1}$. One implementation, which is verified by experiment, is to insert thermal resistant layer between adjacent batteries to prevent TR propagation in the battery module.

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

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

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

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Abstract

The differences in the safety behaviour between un-aged and aged high-power 18650 lithium-ion cells were investigated at the cell and material level by Accelerating Rate Calorimetry (ARC) and Simultaneous Thermal Analysis (STA). Commercial cells containing a $\text{Li}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{Li}_y\text{Mn}_2\text{O}_4$ blend cathode, a carbon/graphite anode and a PP/PE/PP trilayer separator were aged by high-rate and low temperature cycling, leading to (i) mechanical deformation of the jelly roll and (ii) lithium plating on the anode. The results show a strong influence of the ageing history on the safety behaviour. While cycling at high current does not have a strong influence on the cell safety, lithium plating leads to a significant increase of heat formation during thermal runaway and thus to a higher hazard of safety.

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

2014

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

CEES Conference Environmental Testing and Safety of Batteries and Fuel Cells, Pfalz, Germany, 18-09-2014

Magnus Rohde*, Boxia Lei, Carlos Ziebert, Andreas Melcher, Hans Jürgen Seifert
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The performance of a lithium ion cell is strongly related to the temperature. Therefore it is important to understand the process of heat generation and dissipation inside a single cell but also in battery packs since this is also closely coupled to safety issues. In this study, commercial 18650 lithium ion cells with 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 LiFePO_4
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.

Link to Purchase Paper: <http://www.sciencedirect.com/science/article/pii/S037877531301392X>

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.

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Simultaneous estimation of thermal parameters for large-format laminated lithium-ion batteries

Journal of Power Sources 259 (2014)

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

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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)

Xuning Feng ^{a, b}, Jing Sun ^b, Minggao Ouyang ^a, Xiangming He ^{a, c}, Languang Lu ^a,
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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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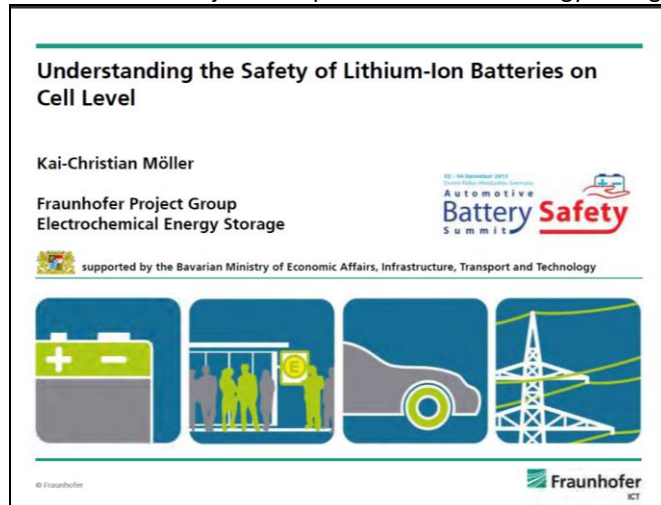
2013

[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

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

Karlsruhe Institute of Technology (KIT)



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

Presented at 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.

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

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Thermal runaway of lithium ion batteries

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

Xiangming He

Tsinghua University

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