Study of Thermal and Electrochemical Characteristics of Li-ion Battery

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Abstract - Lithium-ion batteries are key components of portable, entertainment, computing, and telecommunication equipment because of their high-energy storage density, high voltage, long cycle life, high-power sources, and ambient temperature operation. Although lithium-ion batteries have many attractive features, a few key issues have to be investigated for the practical applications of hybrid electrical vehicles (HEVs) with large capacity of energy storage. Heat control and management is one of the most important issues in the lithium-ion batteries at high temperature or high charge/discharge rate will lower charge/discharge efficiency and lower the battery life, or even cause safety problem. The heat effects of lithium-ion battery cathode could substantially affect the safety and attenuate lifetime of lithium-ion battery. In order to disclose the thermo-electrochemical characteristics of LiFePO4 battery during charge discharge process at various rates at 30°C, electrochemical calorimetric measurements were employed in this study. The results showed that LiFePO4 battery had a smaller polarization and a better reversibility at low rate (0.1C, 0.2C, 0.5C). With the increasing of the rate structure of cathode material LiFePO4 was partially destroyed and impurities, like Li3PO4 and FeP2 appeared at rate 1.0C and 2.0C. Formation of these impurities resulted in electrochemical performance deterioration of battery. The charge-discharge process of LiFePO4 battery accompanied exothermic process and endothermic process at low rate (0.1C, 0.2C). When the rate increased to 1.0C, only exothermic phenomena existed. With the rate increasing heat production rate and the enthalpy change during charge-discharge process of LiFePO4 battery increased. These suggest that appropriate rate for battery should be choose in order to avoid safety problem, which initiated by internal heat accumulation of battery.

Keywords: Heat effect, thermo-electrochemistry, LiFePO4, lithium-ion battery, electrochemical calorimetry.

I. INTRODUCTION

Due to the increased demand for the limited availability of fossil fuels and increasing environmental concerns, there is great interest worldwide in the use of alternative energy and storage systems for electric or hybrid electric vehicles. At the moment, the most favoured technology for storing energy in electric or hybrid vehicles (EV/HEV) seems to be the lithium-ion or lithium-ion polymer chemistry. Currently there are different efforts to introduce EVs or HEVs into the market. The variety of both lithium chemistries and choice of packaging is wide. Many different cathode chemistries (LiNiCoAlO2, LiNiMnCoO2, LiMnO2, LiFePO4, etc), a variety of anode materials (graphite - natural or synthetic, soft or hard carbon, LTO, etc), the choice of electrolyte (e.g. LiPF6 based, lithium- oxalato borate, ionic liquids) and different cell structures (spirally wound cylindrical and elliptic, stacked plates and wound pouch cells) have to be considered when developing a battery system - initially disregarding safety requirements, costs and aging. Lithium ion cells are a promising technology for the use in hybrid vehicles due to their high energy and power densities. However, thermal management is necessary to prevent premature aging, and for safety reasons. The modelling and simulation of the temperature distribution in a lithium ion cell is therefore of high interest for the design of a cooling system. Heat sink for the cells is the automotive refrigeration cycle.

From the point of view of a developer of battery systems, it is difficult to decide which composition is the best for a given application. In this study, presents an approach to examine different types of lithium cells and to parameterize a coupled electrical-thermal simulation model. By means of the simulations the electrical performance and the thermal behaviour can be predicted and can be used as help selecting cells and designing battery systems. The extension of the cell model to the whole battery pack including thermal and battery management system, safety requirements, the implementation of aging effects and an analysis of lifetime costs is currently being carried out.

II. BASIC TERMS OF BATTERY PERFORMANCE AND CHARACTERIZATION

Various terms have defined for batteries to characterize their performance. Commonly used terms are summarized in the following as a quick reference [8].

Cell, Module, and Pack: A single cell is a complete battery with two current leads and separate compartment holding electrodes, separator, and electrolyte. A module is composed of a few cells either by physical attachment or by welding in between cells. A pack of batteries is composed of modules and placed in a single containing
for thermal management. An EV may have more than one pack of battery situated in a different location in the car.

Ampere-hour Capacity: Ampere-hour (Ah) capacity is the total charge that can be discharged from a fully charged battery under specified conditions. The Rated Ah capacity is the nominal capacity of a fully charged new battery under the conditions predefined by the manufacturer. A nominal condition, for example, can be defined as 20°C and discharging at 1/20 C-rate. People also use Wh (or kWh) capacity to represent a battery capacity. The rated Wh capacity is defined as

\[
\text{Rated Wh Capacity} = \text{Rated Ah Capacity} \times \text{Rated Battery Voltage}
\]

C-rate: C (nominal C-rate) is used to represent a charge or discharge rate equal to the capacity of a battery in one hour. For a 1.6 Ah battery, C is equal to charge or discharge the battery at 1.6 A. Correspondingly, 0.1C is equivalent to 0.16 A, and 2C for charging or discharging the battery at 3.2 A.

Specific Energy: Specific energy, also called gravimetric energy density, is used to define how much energy a battery can store per unit mass. It is expressed in Watt-hours per kilogram (Wh/kg) as

\[
\text{Specific Energy} = \frac{\text{Rated Wh Capacity}}{\text{Battery Mass in kg}}
\]

Specific Power: Specific power, also called gravimetric power density of a battery, is the peak power per unit mass. It is expressed in W/kg as

\[
\text{Specific Power} = \frac{\text{Rated Peak Power}}{\text{Battery Mass in kg}}
\]

Energy Density: Energy density, also referred as the volumetric energy density, is the nominal battery energy per unit volume (Wh/l).

Power Density: Power density is the peak power per unit volume of a battery (W/l).

Internal Resistance: Internal resistance is the overall equivalent resistance within the battery. It is different for charging and discharging and may vary as the operating condition changes.

Peak Power: According to the U.S. Advanced Battery Consortium (USABC)’s definition, the peak power is defined as

\[
P = \frac{2V_{oc}^2}{9R}
\]

Where, \(V_{oc}\) is the open-circuit voltage and \(R\) is the internal resistance of battery. The peak power is actually defined at the condition when the terminal voltage is 2/3 of the open-circuit voltage.

Cut-off Voltage: Cut-off voltage is the minimum allowable voltage defined by the manufacturer. It can be interpreted as the “empty” state of the battery.

State of Charge (SOC): SOC is defined as the remaining capacity of a battery and it is affected by its operating conditions such as load current and temperature.

SOC = Remaining Capacity / Rated Capacity

SOC is a critical condition parameter for battery management. Accurate gauging of SOC is very challenging, but the key to the healthy and safe operation of batteries.

Depth of Discharge (DOD): DOD is used to indicate the percentage of the total battery capacity that has been discharged. For deep-cycle batteries, they can be discharged to 80% or higher of DOD.

\[
DOD = 1 - SOC
\]

State of Health (SOH): SOH can be defined as the ratio of the maximum charge capacity of an aged battery to the maximum charge capacity when the battery is new. SOH is an important parameter for indicating the degree of performance degradation of a battery and for estimating the battery remaining lifetime.

\[
\text{SOH} = \frac{\text{Aged Energy Capacity}}{\text{Rated Energy Capacity}}
\]

Calendar Life: Calendar life is the expected life span of the battery under storage or periodic cycling conditions. It can be strongly related to the temperature and SOC during storage.

Battery Reversal: Battery reversal happens when the battery is forced to operate under the negative voltage (voltage of positive electrode is lower than that in the negative electrode). It can happen on a relatively weak cell in a serially connected battery string. As the usable capacity of that particular weak cell runs out, the rest of batteries in the same string will still continue to supply the current and force the weak cell to reverse its voltage. The consequence of battery reversal is either a shortening cycle life or a complete failure.

Battery Management System (BMS): BMS is a combination of sensors, controller, communication, and computation hardware with software algorithms designed to decide the maximum charge/discharge current and duration from the estimation of SOC and SOH of the battery pack.

Thermal Management System (TMS): TMS is designed to protect the battery pack from overheating and to extend its calendar life. Simple forced-air cooling TMS is adopted for the NiMH battery, while more sophisticated and powerful liquid cooling is required by most of the Li-ion batteries in EV applications.
III. COMPONENTS OF BATTERY

The heart of the battery is the cell, which is composed of four main features: cathode, anode, electrolyte and separator along with a fifth category, safety structures. Each of these five components is described below [9].

Cathode: Cathodes are made of cathode materials pasted on aluminum foil. Cathode paste contains cathode materials, including lithium metal oxide, a binder (poly vinylidene fluoride (PVDF)), carbon material (carbon black, graphite powder, and carbon fiber, etc.) and solvent (Ninethyl-2-pyrollidone (NMP)). The paste is coated on aluminum foil, then dried and pressed into the appropriate thickness. Four types of cathodes are used in lithium-ion batteries for vehicles. LMO (lithium manganese oxide) is the most commonly used as a cathode for HEVs, PHEVs, and EVs. Originally, LCO (lithium cobalt oxide) is commonly used in lithium-ion batteries for consumer electronics such as laptop PCs, cell phones, and cameras, due to its high energy density. However, because of recent price increases in cobalt metal and safety issues related to LCO cathodes, battery makers have opted for cheaper and safer alternatives, including LMO (lithium manganese oxide) and LFP (lithium iron phosphate) for vehicle use. NCA (nickel cobalt aluminum) and NMC (nickel manganese cobalt) are being aggressively developed because of their relatively high energy density.

Anode: Anodes are made of anode materials pasted on copper foil. Anode active materials, such as graphite, are kneaded with binder (PVDF or styrene butadiene rubber (SBR)), solvent (NMP or water), and carbon (carbon tubes and carbon black). After coating, the anode is dried and pressed. Two types of anode active material are primarily used: highly crystallized natural graphite and randomly crystallized artificial carbon.

Electrolyte: Electrolyte used in lithium-ion batteries is a mixture of lithium salt and organic solvent. Several organic solvents are mixed to decrease the electrolyte’s viscosity and increase solubility of lithium salts. This increases the mobility of lithium ions in the electrolyte, resulting in higher battery performance. Lithium polymer batteries use gel electrolyte to prevent electrolyte from leaking from the laminate pouch. Gel electrolyte is composed of electrolyte with an added gel precursor. The materials below are used for making electrolyte.

Materials used as lithium salts:
• Lithium hexafluorophosphate (LiPF6)
• Lithium perchlorate (LiClO4)
• Lithium hexafluororesenate (LiAsF6)

Organic solvents:
• Ethyl methyl carbonate (EMC)
• Dimethyl carbonate (DMC)
• Diethyl carbonate (DEC)
• Propylene carbonate (PC)
• Ethylene carbonate (EC)

Materials used to create gel electrolyte (for lithium polymer battery):
• Polyethylene oxide (PEO)
• Polyacrylonitrile (PAN)
• Poly vinylidene fluoride (PVDF)

Separator: The separator is a micro-porous membrane, which prevents contact between the anode and cathode. The separator is made of either polyethylene or polypropylene. In addition, the separator has a safety function called a “shutdown.” If the cell heats up accidentally, the separator melts due to the high temperature and fills its micro pores to stop lithium-ion flow between anode and cathode.

Safety structures: Lithium-ion batteries have internal safety structures, such as tear away tabs to reduce internal pressure, safety vents for air pressure relief, and thermal interrupters called positive temperature coefficient (PTC) thermistors, for over current protection. Some battery companies insert a metal center pin as a pillar to strengthen against bending force and put insulators on the edge of the electrode where short circuit accidents are likely to generate.

IV. BASIC OPERATION OF A RECHARGEABLE BATTERY

A battery is composed of a positive electrode (holding a higher potential) and a negative electrode (holding a lower potential) with an ion-conductive but electrically insulating electrolyte in between. During charging, the positive electrode is the anode with the reduction reaction, and the negative electrode is the cathode with the oxidation reaction. During discharge, the reaction is reversed, and so the positive and negative electrodes become cathode and anode electrodes, respectively. As a side-note, the positive and negative electrode active materials are also conventionally referred to as cathode and anode material, respectively. In a sealed cell, the liquid electrolyte is held in a separator to prevent the direct short between the two electrodes. The separator also serves as a reservoir for extra electrolyte, a space saver allowing for electrode expansion, an ammonia trap (in NiMH battery), and a safety device for preventing shortage due to Li-dendrite formation (in Li-ion battery) [8].

A similar schematic with two half-cell reactions for the Li-ion battery in charging mode is shown in Fig.1

Figure1. Schematic of the charging operation of a Li-ion battery [8].
The most commonly used active material in the negative electrode is graphite. During charging, Li ions, driven by the potential difference supplied by the charging unit, intercalate into the interlayer region of graphite. The arrangement of Li\(^+\) in graphite is coordinated by the surface–electrolyte–interface (SEI) layer, which is formed during the initial activation process. The active material in the positive electrode is a Li-containing metal oxide, which is similar to Ni(OH)\(_2\) in the NiMH battery but replaces the hydrogen with lithium. During charging, the Li\(^+\) (similar to the H\(^+\) in NiMH) hops onto the surface, moves through the electrolyte, and finally arrives at the negative electrode. The oxidation state of the host metal will increase and return electrons to the outside circuitry. During discharge, the process is reversed. Li ions now move from the intercalation sites in the negative electrode to the electrolyte and then to the original site in the LiMO\(_2\) crystal. The commonly used electrolyte is a mixture of organic carbonates such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate containing hexafluorophosphate (LiPF\(_6\)). The separator is a multilayer structure from PP, which provides oxidation resistance, and PE, which provides a high-speed shutdown in the case of a short.

V. BATTERY CHARGING METHODS

The safety, durability, and performance of batteries are highly dependent on how they are charged or discharged. Abuse of a battery can significantly reduce its life and can be dangerous. A current BMS includes both charging and discharging control on-board. In the future, it will be integrated into the grid energy distribution system [8].

**Constant Voltage:** Constant voltage method charges battery at a constant voltage. This method is suitable for all kinds of batteries and probably the simplest charging scheme. The battery charging current varies along the charging process. The charging current can be large at the initial stage and gradually decreases to zero when the battery is fully charged. The drawback in this method is the requirement of very high power in the early stage of charging, which is not available for most residential and parking structures.

**Constant Current:** In this charging scheme, the charging voltage applied to the battery is controlled to maintain a constant current to the battery. The SOC will increase linearly versus time for a constant current method. The challenge of this method is how to determine the completeness of a charge with SOC = 100%. The cut-off can be determined by the combination of temperature raise, temperature gradient raise, voltage increase, minus voltage change, and charging time.

**The Combination of Constant Voltage and Constant Current Methods:** During the charging process of a battery, normally both the methods will be used. Fig.2 shows a charging profile of a Li-ion cell. At the initial stage, the battery can be pre-charged at a low, constant current if the cell is not pre-charged before. Then, it is switched to charge the battery with constant current at a higher value. When the battery voltage (or SOC) reaches a certain threshold point, the charging is changed to constant voltage charge. Constant voltage charge can be used to maintain the battery voltage afterward if the DC charging supply is still available.

VI. THERMO-ELECTROCHEMICAL STUDY OF LITHIUM-ION BATTERY DURING CHARGE-DISCHARGE PROCESS

Olivine-type LiFePO\(_4\) is regarded as the most promising alternative cathode material for Lithium-ion batteries because of its advantages of higher theoretic capacity (170 mAh·g\(^{-1}\)), lower cost, higher safety, and environmental friendliness. However, LiFePO\(_4\) has low electronic and ion conductivities, low tap density, and poor low-temperature character. A large number of efforts have been made to overcome the electronic and ionic transport limitations by doping with super-valent cations, incorporating nanostructure designs, or coating electronically conductive agents. Much has been reported about the electrochemistry and structures of LiFePO\(_4\) material, but little has been reported on such thermal behaviour of this material as this paper.

Understanding the thermal behaviour of these heat generation sources would offer much valuable information to develop the battery thermal management strategies as well as cell design, optimization and operation. In the battery operation, the heat generation is mainly ascribed to the electrochemical reactions, the active polarization and the electric conductive resistance. In addition, high rates greatly increase the rate of heat generation in a battery. If the rate of heat generation is faster than heat dissipation, the battery temperature increases. This may bring the battery to a thermal runaway condition.

Calorimetry is an effective method to characterize the thermal behaviour of batteries, various materials have been tested to evaluate their performance and to study their thermal behaviour using electrochemical-calorimetric methods with commercial Li-ion cells. However, researches are rarely focused on the point of analysis of thermodynamics parameters from button
cells with microscale active material. These parameters from pocket-size cell are very important in optimizing battery design, fabrication, thermal management for the applications and model building through which the thermal characteristics of lithium-ion batteries can be studied conveniently.

In this study, focus is on the characterization of heat generation occurring during charge and discharge, especially cycling at various rates, by calorimetric measurement. And the emphasis of this is to analyze different heat generation sources a button cell.

**Experimental:**

**Materials:**

Commercially available LiFePO$_4$ powders and N-methyl-2-pyrrolidone (NMP) are provided by Hunan Shanshan Toda Advanced Material Co., Ltd. Acetylene black is obtained from ZhuHai TaiYi Battery Co., Ltd. Polyvinylidene fluoride (PVDF) is supported by Guangdong Jiejin Chemical Co., Ltd. All other chemicals are of analytical grade and the experimental water is grade II desalted water.

**Battery Preparation:**

Active material LiFePO$_4$ is mixed with acetylene black, PVDF binder (mass ratio of LiFePO$_4$ : acetylene black and PVDF is 80:10:10) in NMP onto an aluminum foil current-collector. The electrodes are dried at 120°C under vacuum for 6 h and pressed using a hydraulic press. CR2025 button cells are assembled using lithium metal foil as anode and the above prepared electrode as cathodes, Celgard 2300 microporous membrane is used as separator. LiPF$_6$ (1.0M) in a 1:1:1 (v/v/v) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) is used as electrolyte. The cells are assembled in an argon-filled glove box.

**Electrochemical-Calorimetric Measurements:**

The electrochemical and thermodynamic properties of LiFePO$_4$ are measured by using CR2025 button cell. Charge-discharge performances are evaluated using a Land automatic battery test system (CT2001A, China). The charge/discharge voltage region is 2.2–3.8V, and the current is 0.1C, 0.2C, 0.5C, 1.0C and 2.0C rate. Heat generation occurring during charge and discharge is recorded by an eight-channel micro-calorimeter (3114/3236 TAM Air, Swiss). The calorimeter is electrical calibrated at 303.15K before experiment. As shown in Fig.3, LiFePO$_4$/Li CR2025 button cell is put into the ampoule bottle, which is hanging up in the channel of micro-calorimeter. The calorimeter is then stabilized at constant temperature (303.15K) for 12 h. The positive and negative terminals of the button cell are connected to the external land automatic battery test system with the aid of 2 copper wires, and then the charge/discharge studies at 0.1C, 0.2C, 0.5C, 1.0C and 2.0C rate are carried out. The thermal spectra are recorded after electrode reaction started.

**Results and Discussion**

**Electrochemical Performances of LiFePO$_4$:**

The initial charge-discharge curves of LiFePO$_4$ at different charge-discharge rate are shown in Fig.4. It can be shown from Fig.4 that the lower rate, the greater charge-discharge capacity, the flatter charge-discharge platform, and the smaller voltage difference between the charge platform and discharge platform. Therefore, the battery had a smaller polarization and a better reversibility during low range charging and discharging process. Structure and morphology of cathode material is partially destroyed in the charge-discharge process with high current density. So with the increasing of charge-discharge rates, charge-discharge capacity of battery reduced. For example, the discharge capacity of LiFePO$_4$ at 0.1C rate is 151.3mAh g$^{-1}$, and at 2.0C rate is 144.5 mAh g$^{-1}$ [4].

**Thermal Behaviours of LiFePO$_4$:**

Fig.5 shows the variation in the heat flow of LiFePO$_4$ battery, as a function of time at different charge-discharge rates (0.1C, 0.2C, 0.5C, 1.0C, 2.0C). It can be shown from Fig.5 that two obvious exothermic peaks appeared at all the curves of heat flow and voltage of LiFePO$_4$ with time at different charge-discharge rates. The heat flow slowly increased at the initial stage of charge-discharge process at 0.1C and 0.2C rate, but increased rapidly at 0.5C, 1.0C and 2.0C rate. With the increasing of the rate, the heat flow increased during the
charge-discharge process, and that’s because irreversible heat production rate of the battery increased with the increasing of the charge-discharge rate. The whole charge-discharge stage of LiFePO₄ battery accompanied exothermic process and endothermic process at 0.1C and 0.2C rate. It follows that exothermic and endothermic phenomena of the battery will be determined together by reversible heat and irreversible heat. When the rate increased to 1.0C, only exothermic phenomena existed in the whole charge-discharge process of battery. Because irreversible heat played a dominant part in the charge-discharge process when its’ current is large. Heat effect during charge-discharge process of battery came mainly from irreversible heat, which produced by overcoming battery internal resistance. When the battery is in maximum discharge degree, great irreversible heat produced due to the electrodes reached at serious polarization state. Irreversible heat showed an exothermic effect no matter the charge process or the discharge process [4].

The enthalpy change for LiFePO₄ at various charge-discharge rates (0.1C, 0.2C, 0.5C, 1.0C and 2.0C) are shown in Fig.6. Heat production rate is linearly related to the rate, and decreased with the rate decreasing. The smaller the rate, the less the total heat production rate, the less the total enthalpy change in the reaction and the higher the safety performance of the battery.

\[ \Delta H = h + \Delta H \]

where \( h \) is total heat production rate in the reaction, \( h(t) \) is the heat flow at time \( t \), \( n \) is the number of electrons passed in the reaction, \( Q \) is quantity of electricity in the reaction, \( F \) is the Faraday’s constant, and \( i(t) \) is the current at time \( t \). Table 1 summarizes detailed information about heat generations for LiFePO₄/Li CR2025 button cell.

Figure 5. Change curves of heat flow and voltage of LiFePO₄ with time at different charge-discharge rates [4].

Figure 6. Enthalpy change against charge-discharge rate of LiFePO₄ [4].
The data listed in Table 1 show that exothermic phenomenon played a dominant role in total heat effects during the charge-discharge process of the battery. With the rate increasing, the enthalpy change (ΔH) in the reaction increased from 5.100 kJ·mol⁻¹ (0.1C) to 34.731 kJ·mol⁻¹ (2.0C). Heat production rate during the charge-discharge process of battery increased with the rate increasing. The reason is that with the rate increasing, current increased, battery polarization effect increased, and quantity of heat increased.

Table 1. Heat generation parameters for LiFePO₄/Li CR2025 button cell [4].

![Table 1](image)

Summary

The thermal stability of cathode materials plays a key role in lithium-ion battery safety, and the electrochemical-calorimetric measurements show good performance in studying the thermo-electrochemical behaviours of LiFePO₄.

(1) The lower rate, the greater charge-discharge capacity, the flatter charge-discharge platform, and the smaller voltage difference between the charge platform and discharge platform. Therefore, the LiFePO₄ battery had a smaller polarization and a better reversibility at low rate. With the increasing of the rate structure of cathode material LiFePO₄ was partially destroyed, electrochemical performance deteriorated.

(2) The whole charge-discharge stage of LiFePO₄ battery accompanied exothermic process and endothermic process at low charge-discharge rate (0.1C, 0.2C). When the rate increased to 1.0C, only exothermic phenomena existed. With the rate increasing heat production rate and the enthalpy change during the charge-discharge process of LiFePO₄ battery increased.

Based on the experiment results obtained in this study, conclude that appropriate charge-discharge rate for battery should be choose in order to avoid safety problem, which initiated by internal heat accumulation of battery.

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