Research Developments and Operating Principles of Lithium-Ion Batteries

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Abstract. Lithium-ion batteries are a type of rechargeable battery which is comprised of cells that employ lithium intercalation compounds as the anode and cathode materials. The high specific energy and energy density of commercial of lithium ion battery products makes them attractive for weight or volume sensitive applications. A survey of the research status for lithium-ion batteries was provided. The state-of-the-art materials and designs of lithium-ion batteries were introduced. Furthermore, lithium ion transport processes, battery charge/discharge behavior, effects of temperature on battery performance and capacity variation during battery operation were discussed.

Keywords: lithium-ion batteries; research developments; materials; designs; operating principles.

1. Introduction

Lithium-ion (Li-ion) batteries are a type of rechargeable battery which is comprised of cells that employ lithium intercalation compounds as the anode and cathode materials. The lithium ion moves from the anode to the cathode during discharge and from the cathode to the anode when charging.

The high specific energy and energy density of commercial of lithium ion battery products makes them attractive for weight or volume sensitive applications. Li-ion batteries allow a low self-discharge rate, long cycle life and a broad temperature range of operation [1], enable their utilization in a wide variety of applications. A wide array of sizes and shapes is now available from a variety of manufacturers. Single cells typically operate in the range of 2.5 to 4.2 V, approximately three times that of NiCad or NiMH cells, and thus require fewer cells for a battery of a given voltage. Li-ion batteries can offer high rate capability. In past decades, lithium ion batteries are one of the most popular types of battery for portable electronics with one of the best energy-to-weight ratios, no memory effect, and a slow loss of charge when not in use. Recently, lithium-ion batteries have been paid more and more attention to the popularity for electric vehicle (EV), hybrid electric vehicle (HEV), plug-in hybrid electric vehicle (PHEV) as well as aerospace applications, etc. due to their high input/output power, high energy density and large power capacity [1]. On all accounts, lithium-ion batteries are becoming the front-runner among rechargeable battery technologies. However, the massive commercialization of lithium-ion batteries for EV, HEV and PHEV applications has been hampered by high cell costs, safety concerns, limited cell life, and poor performance at low temperatures(e.g. below 0°C) [2]. Researches to overcome these limitations are being conducted on high-power lithium-ion cells where modeling is significantly important to assistant their advancement.

General analytical model for lithium ion battery power management are useful to select suitable batteries, to design products, to optimize battery management and operation when in researches in advanced EV, HEV, PHEV developments. It is valuable to incorporate actual battery state information into a power management model such as the effects of ambient temperature, self-temperature fluctuation, degradation as well as the instant variation of remain capacity, etc., which are usually requires a mathematical model could captures the battery nonlinearities.

2. State-of-the-art materials and designs

The lithium ion battery could be divided into three primary functional components, which are the anode, cathode, and electrolyte. Both the anode and cathode are materials into which and from which lithium ions can migrate. It should be noted that the anode is the electrode at which an oxidation reaction occurs. It means that the anode supplies electrons in reaction. Since the electron flow reverses between charging and discharging processes, the positive electrode is the anode during charging and the negative electrode is the cathode during discharging. Usually, we just define the anode of a battery during discharging, thus, the name “anode” commonly refer to the negative electrode. Similarly, the cathode is the electrode at which reduction reactions occur and is referred to as the positive electrode. In this study, to avoid the confusion, the names positive and negative are adopted in most cases.

The first Li-ion batteries marketed by Sony utilized petroleum coke at the negative electrode. Coke-based materials offer good capacity, and are stable in the presence of propylene carbonate (PC)-based electrolytes, in contrast to graphitic materials. The disorder in coke materials is thought to pin the layers inhibiting reaction or exfoliation in the presence of propylene carbonate. In the mid-1990s most Li-ion cells utilized electrodes employing graphitic spheres, in particular a Mesocarbon Micro bead (MCMB) carbon. MCMB carbon offers higher specific capacity, more than 300 mAh/g, and low surface area, thus providing low irreversible capacity and good safety properties. Recently, a wider variety of carbon types has been used in negative electrodes. Some cells utilize natural graphite, available at very low cost, while others utilize hard carbons that offer capacities higher than possible with graphitic materials. Up to now, many types of carbon materials are industrially available and the structure of the carbon greatly influences its electrochemical properties, including lithium intercalation capacity and potential [3].

Liquid electrolytes in Li-ion batteries consist of lithium salts, such as $LiPF_6$, $LiBF_4$, or $LiClO_4$, in an organic solvent [1-2]. A liquid electrolyte conducts Li ions, acting as a carrier between the positive and the negative when a battery passes an electric current through an external circuit. Unfortunately, organic solvents are easily decomposed on negatives during charging. When appropriate organic solvents are used as the electrolyte, the solvent is decomposed and forms a solid layer called the solid electrolyte interphase (SEI) at first charge that is electrically insulating yet sufficiently conductive to lithium ions. The interphase prevents decomposition of the electrolyte after the second charge. For example, ethylene carbonate is decomposed at a relatively high voltage, 0.7 V vs. Li, and forms a dense and stable interface [4].

Negative electrode materials in commercially available Li-ion batteries utilize a litigated metal oxide as the active materials. Some typical positive electrode materials are listed in Table 1 [5].

Table 1 Typical positive electrode materials for lithium ion batteries

Material	Average Voltage	Gravimetric Capacity
LiCoO2	3.7 V	140 mAh/g
LiMnO2	4.0 V	115 mAh/g
LiFePO4	3.3 V	160 mAh/g

As for utilization for EV/HEV/PHEV, the $LiFePO_4$ batteries may offer greater range, power and safety. The special advantages of $LiFePO_4$ are summarized as following [6]:

Safe technology — will not catch fire or explode with overcharge.

Over 2000 discharge cycles life compared to typically around 300 for lead acid.

Double the usable capacity of similar amp hour over lead acid batteries.

Virtually flat discharge curve means maximum power available until fully discharged (no “voltage sag” as with lead acid batteries).

High discharge rate capability, 10C continuous, 20C pulse discharge.

Unlike lead acid batteries, can be left in a partially discharged state for extended periods without causing permanent damage.

Extremely low self-discharge rate (unlike lead acid which will go flat quite quickly if left sitting for long periods).

Does not suffer from “thermal runaway”.

Can be used safely in high ambient temperatures of up to 60C without any degradation in performance.

Maintenance free for the life of the battery.

Can be operated in any orientation.

Does not contain any toxic heavy metals such as lead, cadmium, nor any corrosive acids or alkali thus making $LiFePO_4$ batteries the most environmentally friendly battery chemistry available.

Solid construction — there are no fragile/brittle plates made of lead which can be prone to failure over time as a result of vibration.

Can be safely rapidly recharged — when fully discharged can be brought to a state of over 90% fully charged in 15 minutes.

The basic electrochemical unit to generate electrical energy from the stored chemical energy or to store electrical energy in the form of chemical energy is called cell. The battery is consisted of cells to obtain the required operating voltage and capacity for using a certain load.

3. Operating principles

3.1. Lithium ion transport processes.

During the discharging process, the lithium ions are moved out of the negative electrode and flow into the positive electrode. When the cell is charging, the reverse process occurs: lithium ions are extracted from the positive electrode and flow into the negative electrode.

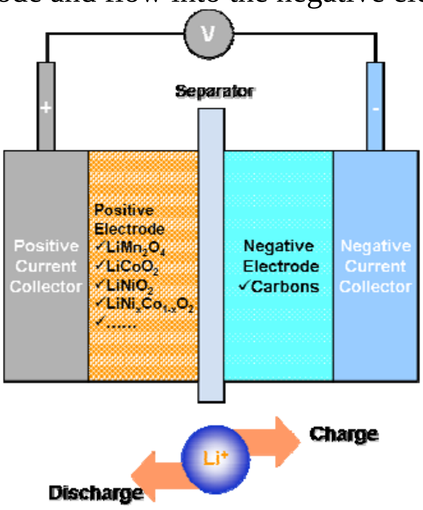

Figure 1 Schematic of the lithium ion battery operation

Electricity can be produced when electrons flow through an external circuit. The following equations are written in units of moles to use the coefficient x. The reaction formulas are based on an example of $LiCoO_2$ positive electrode material. The positive electrode half reaction is:

$$LiCoO_2 \rightleftharpoons Li_{1\text{-}x}CoO_2 + xLi^+ + xe^-$$

The negative electrode half reaction is:

$$xLi^+ + xe^- + 6C \rightleftharpoons Li_xC_6$$

It also should be noted that lithium ions themselves are not being oxidized in the battery and are only transported between the anode and cathode. The transition metal, e.g. Co, in $LixCoO_2$ is oxidized from Co3+ to Co4+ during charging, and reduced from Co_4+ to Co_3+ during discharge.

Both composite electrodes contain binder and filler to enhance electron transport across the solid matrix.

3.2. Battery charge/discharge behavior.

In a practical utilization of lithium ion battery, charge and discharge are both limited mainly by lithium ion diffusion in the solid phase and electrolyte depletion in positive electrode. The energy drawn from or supplement into a battery is not always equal to the consumed or charged energy in the device circuits, thus, the understanding of discharge/charge processes is important to model development.

When the battery is connected to a load, the oxidation-reduction reaction transfers electrons between anode and cathode. The transfer process converts the chemical energy stored into the battery to electrical energy. The cell voltage increase with the charging and decrease with the discharging.

The charge/discharge behaviors are governed by thermodynamic laws, electrode kinetics and transport phenomena. The equilibrium potential (open circuit voltage) depends on the temperature, the amount of active material available in the electrode. The overall cell potential could be divided into three types: osmic over potential, activation over potential and the concentration over potential [7]. The equilibrium potential is the internal driving force of a battery for providing the energy to an external load. The osmic over potential is caused by the internal osmic resistance. The activation over potential is the potential which makes the electrode reaction happed at certain reaction rates. The concentration over potential is due to the concentration variations near the electrode surface.

3.3 Effects of temperature on battery performance.

Temperature strongly affects battery charge and discharge behavior. When the cell is working at a relative low temperature, the chemical activity will decrease and internal resistance will increase, and the full charge capacity will decrease while the slope of the charge/discharge curves will increase. When the cell is working at a higher temperature, the internal resistance will decrease and the full charge capacity and voltage will increase. However, the relative higher chemical activity will also lead to higher self-discharge rate, which will reduce the usable capacity. In addition, not only the ambient temperature have significant effects on battery performance, but also the temperature fluctuation due to self-heat generation will also affect the cell performance much. It suggests that the temperature control is one of the key issues in lithium ion battery power management.

3.4 Capacity variation during battery operation.

Battery capacity decreases as the discharge rate increases. To avoid confusion, the following definitions related to charge and discharge capacity are defined:

State of Charge (SOC) is the charge which is present inside the battery.

Remaining capacity is the charge which is available to the external load under the valid discharge conditions.

Full charge capacity is the remaining capacity of a fully charged battery at the beginning of a discharge cycle.

Theoretical capacity is the maximum amount of charge which could be drawn from a battery.

In a fully charged cell, the electrode contains the maximum amount of active species. When the cell is connected to a load, current flows through the external circuit; active species are consumed during the oxidation and reduction reactions with the diffusion processes. Since the diffusion process will lead to the concentration gradient between the electrode bulk and the reaction active sites. A higher load current results in a higher concentration gradient and thus a lower concentration of active species at the electrode surface. When this concentration falls below a certain value, the electrochemical reaction could not react at the electrode surface. Thus, the charge that was unavailable at the electrode surface due to the gradient remains unusable and is responsible for the reduction in capacity. Decreasing the discharge rate effectively reduces could save this part of the active species and could decrease the concentration gradient.

From above, it could be seen that the charging and discharging methodology should be carefully chosen and optimized to obtain maximum battery lifetime through power management under certain performance conditions.

4. Conclusion

Lithium-ion batteries are a type of rechargeable battery which is comprised of cells that employ lithium intercalation compounds as the anode and cathode materials. The high specific energy and energy density of commercial of lithium ion battery products makes them attractive for weight or volume sensitive applications. In this paper, the research developments of lithium-ion batteries was provided. The Tate-of-the-art materials and designs of lithium-ion batteries were introduced. Finally, the opirating principles, such as lithium ion transport processes, bartery charge/discharge behavior, effects of temperature on battery performance and capacity variation during battery operation, were described.

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Li-ion batteries have a voltage and capacity rating. The nominal voltage rating for all lithium cells will be 3.6V, so you need higher voltage specification you have to combine two or more cells in series to attain it.Â Unless some Tony Stark steps in and invents the Arc reactor or the research in Solar Power Satellites (SPS) for wireless Energy transfer gets through, we humans have to depend on Batteries for powering our portable or remote electronic devices. The most common type of rechargeable batteries that you find in consumer electronics is either Lithium ion or of Lithium Polymer type.Â As the name obviously indicates, the Lithium Ion batteries use the Lithium ions to get the job done. Lithium-ion batteries are the most commonly used source of power for modern electronic devices. However, their safety became a topic of concern after reports of the devices catching fire due to battery failure. Making safer batteries is of utmost importance, and several researchers are trying to modify various aspects in the battery to make it safe Recent papers in Lithium-Ion Battery. Papers. People.Â It outlines the development of a train performance model and associated computer simulation software for a design of hybrid multiple unit, powered by a combination of hydrogen fuel cells and batteries. Assumptions underlying the model are discussed in detail. The chosen mode of operation involves steady state conditions for the fuel cells, with the batteries being used to provide additional stored energy for use on gradients and when the train is accelerating. The simulation techniques involve a mix of conventional â€œforwardâ€ simulation and an approach based on an â€œinverseâ€ simulation method.Â Several lithium-ion chemistries are employed, but the relative environmental impacts of manufacturing them is poorly understood.