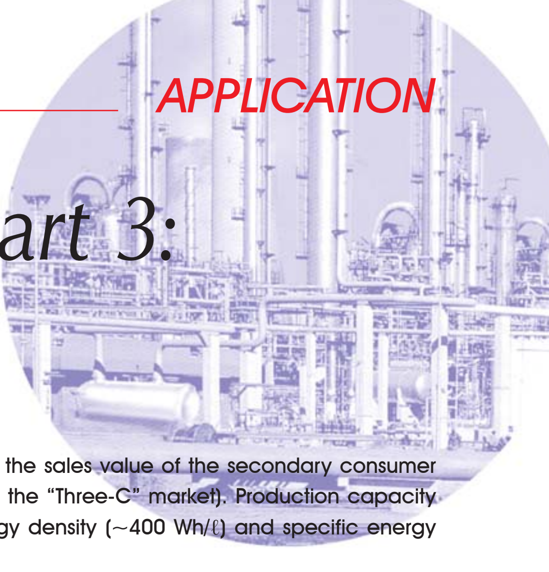

Rechargeable batteries – Part 3: Lithium-ion batteries

by Dr. Paul Lefley, Ayodele Soge, University of Leicester and Jonathan Starkey, Converteam

Lithium-ion batteries have emerged in the last one and half decades to capture over half of the sales value of the secondary consumer market, with applications such as laptop computers, cell phones and camcorders (known as the "Three-C" market). Production capacity has recently been estimated to be 75-million cells per month. These cells provide high energy density (~400 Wh/ℓ) and specific energy (~160 Wh/kg), and long life, typically greater than 1000 cycles at 80% depth of discharge.

Lithium-ion batteries (Fig. 10) are comprised of cells that employ lithium intercalation (or insertion) compounds as the positive and negative materials. As a battery is cycled, lithium ions (Li^+) exchange between the positive and negative electrodes. They are also referred to as "rocking-chair" batteries as the lithium ions "rock" back and forth between the positive and negative electrodes as the cell is charged and discharged. The positive electrode material is typically a metal oxide with a layered structure, such as lithium cobalt oxide ($LiCoO_2$), or a material with a tunneled structure, such as lithium manganese oxide ($LiMn_2O_4$), on a current collector of aluminium foil. The negative electrode material is typically a graphitic carbon, also a layered material, on a copper current collector. In the charge/discharge process, lithium ions are inserted or extracted from interstitial space between atomic layers within the active materials.

The major advantages and disadvantages of lithium-ion batteries, relative to other types of batteries, are summarised in Table 2.

Ageing effects in lithium-ion batteries

It is important to examine the ageing of Lithium-ion cells judging from the fact that this type of battery is increasingly used in many demanding applications. New applications such as satellites, electric vehicles and standby power require a very long life sometimes exceeding 15 years. A comprehensive knowledge of the ageing mechanisms will enhance correct predictions of the battery life.

Lithium-ion batteries are complex systems to understand, and the processes of their ageing are even more complicated. Capacity decrease and power fading do not originate from one single cause, but from a number of processes and their interactions. Two types of ageing processes can be identified; those occurring at anodes and those at cathodes. These two ageing processes differ significantly and are discussed separately.

Fig. 10: Lithiumion batteries [Panasonic].

Ageing of the negative electrode

Carbon, in particular graphite, has been the most important anode material in lithium-ion batteries, and thus, the greatest understanding of anode ageing has been accomplished with graphite-based cells. Changes at the electrode/electrolyte interface due to reactions of the anode with the electrolyte are considered by many researchers to be the major cause of anode ageing. Anodes generally operate at voltages that are outside the electrochemical stability window of the electrolyte components. Hence, reductive electrolyte decomposition accompanied by irreversible consumption of lithium ions takes place at the electrode/electrolyte interface when the electrode is in the charged state. The decomposition products build up "protective layers" (known as solid electrolyte interphase, SEI) that cover the electrode surface. This process occurs mainly (but not exclusively) at the beginning of cycling, especially during the first cycle. The properties of the SEI layers are unique since they are initially permeable for lithium cations but rather impermeable for other electrolyte components and electrons. Thus, normally the SEI reasonably protects:

- The electrolyte compounds from further reduction
- The charged electrode from corrosion

The amount of irreversible charge capacity that is lost during the formation of the SEI was found to be dependent on the specific surface area of the graphite electrode as well as on the conditions of the layer formation [15 – 17].

Transport of solvated lithium cations and other electrolyte components can occur in the latter stages of cycling, as irreversible charge capacities and self-discharge reaction can still be observed after prolonged cycling. Consequently, corrosion of the lithiated carbon anode (and thus capacity loss) and electrolyte decomposition (resulting in electrolyte loss and further SEI formation) are ongoing throughout the entire battery life. The increase in electrode impedance, which is directly linked to the power fade of the cell, is considered to be caused by the growth of the SEI layer.

Moreover, it is widely believed that the morphology and composition of the SEI changes at elevated temperatures. In the

Advantages	Disadvantages
Sealed cells; no maintenance required	Moderate initial cost
Long cycle life	Degrades at high temperature
Broad temperature range of operation	Need for protective circuitry
Long shelf life	Capacity loss or thermal runaway when overcharged
Rapid charge capability	Venting and possible thermal runaway when crushed
High rate and high power discharge capability	Cylindrical designs typically offer lower density than NiCd or NiMH
High coulombic and energy efficiency	
High specific energy and energy density	
No memory effect	

Table 2: Advantages and disadvantages of lithium-ion batteries.

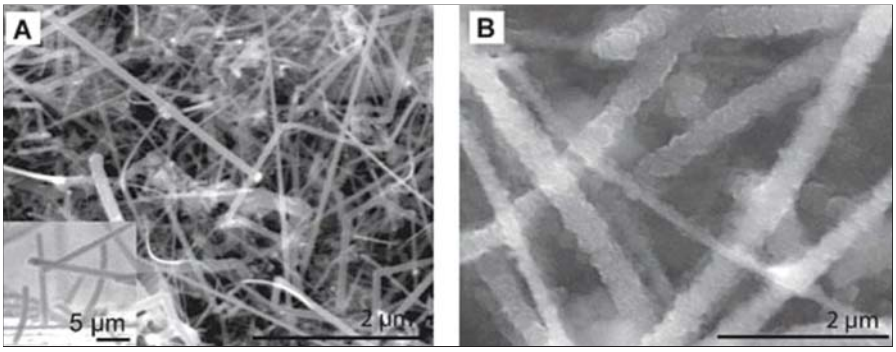

Fig. 11: Scanning electron microscope photos of silicon nanowires (a) before, and (b) after absorbing lithium.

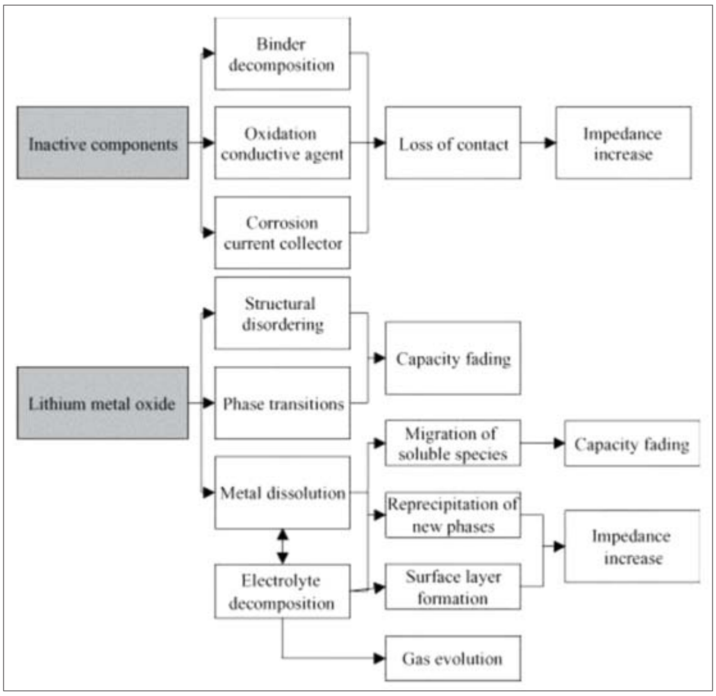

Fig. 12: Causes and effects of ageing mechanisms of cathode materials in Li-ion cells.

worst case, thermal runaway may cause the cell to catch fire or to explode. Lithium-ion cell behaviour at elevated temperatures has been investigated by different battery researchers. Research results revealed that exothermic side reactions of the anode (lithiated carbon) can cause self-heating, which starts typically at temperatures of approximately 80°C in various electrolytes. The onset temperature depends on the electrolyte salt and can be as low as 60°C for electrolytes containing $LiBF_4$. There seems to be significant influence of the cell temperature on Lithium-ion battery capacity, as the results of electrochemical cycling studies indicate that Li/graphite half-cells (i.e. the anodes) show a significant capacity fade when they are stored at elevated temperatures even below 60°C. The negative impact of elevated temperatures on cell ageing is mainly attributed to an increased degradation rate of the SEI, as the SEI film starts to break down or dissolve.

Traditionally graphite is used as a good current collecting material at the negative terminal, but clearly has undesirable effects at elevated temperatures. Other materials have been tried such as silicon and various oxides, nitrides and recently various nano-particles. Silicon though is an attractive anode material for lithium-ion batteries because it has a low discharge potential and the highest known theoretical charge capacity (4200 mAh/g) which is more than ten times higher than existing graphite anodes.

However, using silicon as the anode material for lithium-ion batteries suffers from pulverisation (or fracture) due to the expansion and contraction of silicon during a charge/ discharge cycle. A silicon anode expands by 400% as it absorbs positively charge lithium atoms during charging, and then contracts during discharge as the lithium is drawn out of the silicon. This consequently causes the silicon anode (mostly in the form of particles or a thin film) to pulverise and thereby degrading the performance of the battery.

The shortcoming associated with the silicon anode was solved by a group of researchers at Stanford University using nanotechnology to develop silicon nanowires for high performance lithium battery anodes [20]. In this new lithium-ion battery, lithium is stored in a "forest" of tiny silicon nanowires, each with a diameter one-thousandth the thickness of a sheet of paper, as shown in Fig. 11a. The nanowires inflate four times their normal size as they soak up lithium (Fig. 11b:). But, unlike other silicon shapes, they do not fracture.

This new lithium-ion battery is able to store up to ten times more charge than existing lithium-ion batteries. Therefore, this increase in storage capacity should make these batteries more attractive to electric car manufacturers in the future.

Ageing of the positive electrode

Lithium manganese oxides ($LiMn_2O_4$) and lithium nickel cobalt mixed oxides [$Li(Ni,Co)O_2$] have been extensively studied in the last few years for use in high energy and high power batteries in order to replace lithium cobalt oxide ($LiCoO_2$) as a cathode material in terms of cost, abundance and performance [13]. Manganese-based cathodes continue to receive industrial and commercial interest because of their low cost, benign environmental qualities, good electrochemical properties, and excellent safety properties, despite the higher capacity and improved high temperature stability possible with cobalt or nickel-based cathodes. A number of changes on the cathode may influence the life-time of a lithium-ion cell. These changes include:

- Ageing of the cathode active material;
- Degradation of electrode components e.g. conducting materials, binder and current collector;
- Oxidation of electrolyte components and surface film formation;
- Interaction of the cathode ageing products with the anode.

These effects do not occur separately and cannot be discussed independently from each other. They depend extensively on the cathode composition and are influenced by cycling and storage conditions. The ageing (or charge capacity fading) of the cathode active material is governed by three major principles:

- Structural changes during cycling;
- Chemical decomposition/dissolution reaction;
- Surface film modification.

Fig. 12 schematically shows how these three phenomena collectively induce the ageing of lithium-ion cathode materials.

In conclusion, ageing in lithium-ion batteries originate from multiple and complex mechanisms which lead to

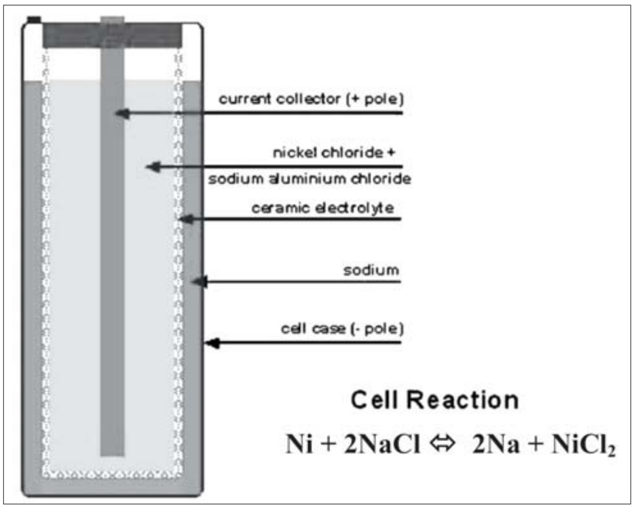

Fig. 13: Schematic diagram of a Zebra cell.

Fig. 14: Z5C standard Zebra battery with a battery management interface.

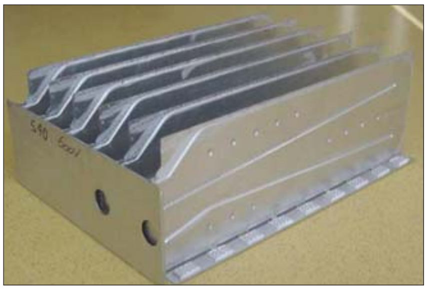

Fig. 15: Cooling plate of the Zebra battery.

increasing cell impedance, power fading, and capacity decay material parameters, as well as storage and cycling conditions, have an impact on battery life-time and performance. Depending on the cell chemistry, both high and low state of charge may deteriorate performance and shorten battery life. At high temperatures, the decay is accelerated, but low temperatures, especially during charging, can also have a negative impact. Amongst the material parameters, surface chemistry plays a major role for both anode and cathode materials. On the cathode, phase transitions and structural changes in the bulk material strongly influence ageing, while changes in the bulk anode material are considered of minor importance only.

The Zebra battery: An alternative to lithium-ion?

The principle of the Zebra battery was invented in South Africa by a group led by Dr. Johan Coetzer at the CSIR in Pretoria, hence the name Zebra battery (for the Zeolite Battery Research Africa Project). The first patent was applied in 1978. The Zebra battery, which utilises only freely available and environmentally friendly materials (plain salt and ceramic) for its functioning, has been highly successful in numerous electric vehicle and related tests conducted throughout Europe over more than a decade. It has an attractive specific energy of 120 Wh/kg and a specific power of 180 W/kg. With this data the battery is well designed for all types of electric vehicles and hybrid electric buses.

The zebra battery is a member of molten salt batteries, which use molten salts as an electrolyte. Molten salt batteries generally offer both a higher density through the proper selection of reactant pairs as well as a higher power density by means of a high conductivity molten salt electrolyte. Operating temperatures of 400 – 700°C for some molten salt batteries, however, bring problems of thermal management and safety, and places more stringent requirements on the rest of the battery components.

Zebra technology

The Zebra cell has a central positive electrode consisting mainly of nickel and sodium chloride together with a liquid electrolyte sodium chloro aluminate (NaAlCl4) contained within a sodium-conducting beta-alumina ceramic (β-Al2O3), also known as a ceramic electrolyte. The β-Al2O3 separates the positive electrode from a molten sodium negative electrode. The liquid electrolyte facilitates rapid transport of sodium ions from the solid nickel chloride electrode (i.e. the positive electrode in the charged state) to and from the ceramic electrolyte. Furthermore, the melting point of the NaAlCl4 electrolyte (157°C) determines the minimum operating temperature of the zebra cell but optimum performance is obtained in the temperature range 270 – 350°C. At these temperatures, the ceramic electrolyte contributes only a minor component to the cell resistance. A schematic of the cell is shown in Fig. 13. The main cell reaction involves chlorination of nickel to form nickel chloride and sodium:

This reaction is coulombically efficient as there are no side reactions i.e., the charging ampere-hour equals the discharge ampere-hour. Also, the discharge capacity is independent of the rate of discharge and, there is no overcharge gassing reaction like, for example, with a lead acid battery. Cells can also be cycled to full nameplate capacity and at high rates. They are not limited to 70 – 80% capacity compared with some rechargeable batteries.

Furthermore, there is also no evidence of self discharge and thus series combinations of cells are unlikely to get out of step when being cycled. However, the cells will eventually fail, but the electrical resistance of a failed cell is similar to a good cell. Therefore, chains of cells can continue to operate with apparently several failed cells.

Zebra battery design

Zebra cells can be connected in parallel and in series. Different battery types have been made with one to five parallel strings, up to 220 cells in series and 100 – 500 cells in one battery pack. The standard battery type Z5C (Fig. 13) contains 216 cells and is available in two voltages 278 V and 557 V. It has a specific energy of 91,2 Wh/kg and a specific power of 164 W/kg; the height of the battery is 300 mm. Between every other cell there is a cooling plate through which ambient air is circulated (Fig. 14) providing a cooling power of 1,6 – 2 kW. For thermal insulation and mechanical support the cells are surrounded by a double walled vacuum insulation typically 25 mm thick.

Light plates made out of foamed silicon oxide take the atmospheric pressure load. This configuration has a heat conductivity of only 0,006 W/mK and is stable for up to 1000°C.

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Contact Dr. Paul Lefley,
University of Leicester,
pwl3@leicester.ac.uk ❖