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Thermo-chemical process associated with lithium cobalt oxide cathode in lithium ion batteries

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1. Introduction

The concept of galvanic couple and the development of battery and fuel cells made possible the direct current (DC) producing devices for practical applications. Even though, existing aqueous electrolyte based power sources such as lead acid, nickel metal-hydride, nickel-cadmium, alkaline/dry zinc based batteries and magnesium systems reached mature level of technology, the lithium based non-aqueous cell system (Plitcha et al., 1987) is able to penetrate and steadily expand its market share. Notwithstanding high cost, the lithium cells became the candidate of choice for miniature application and also for futuristic power pack for electric vehicle propulsion owing to its light weight, high voltage, high energy density and low self discharge characteristics. Present day lithium rechargeable cells are constructed usually by coupling a graphite anode and any one of the cathodes among lithium cobaltate (Li_xCoO_2), lithium manganese spinel ($\text{Li}_x\text{Mn}_2\text{O}_4$), Lithium iron phosphate Li_xFePO_4 (Olivine) and lithium Nickelate (Li_xNiO_2) in an air tight pouch or in a metal container. Assisted by potential difference between the anode and cathode electricity (electrons) flows from LiC_6 (lithium intercalated graphite) anode to the cathode through an external load accompanying simultaneously Li^+ ion de-intercalation from the anode and intercalation at the cathode, maintains charge neutrality in the electrodes for which the electrolyte plays the role of transporting Li^+ ions.

2. Problem description

Among the lithium batteries available in the market, one with Li_xCoO_2 cathode and graphite anode is acclaimed widely as a source of power for portable electronics. This cell system is considerably stable and provides acceptable calendar/cycle life at room temperature during normal operating conditions. However, under abuse conditions such as thermal (heating), mechanical (crushing) or electrical (overcharge), the temperature of the cell rises due to the chemical reactions between the organic solvent and electrode materials leading to cell

failure/explosion. The chemical reaction is prompted because of the coexistence of 1) combustible organic solvent with inorganic salt electrolyte 2) lithiated graphite anode and 3) partially delithiated Li_xCoO_2 cathode in the charged state. The graphite anode intercalate fairly well during the initial cycles. As the cycle proceeds, the available intercalating sites in the graphite slowly decreases and the lithium deposition over the surface of the anode increases during charging process. Such a situation prompts non-even lithium deposition or even dendrite growth over the graphite surface. When the battery is in the charged state the cathode remains in a delithiated state. Flow of current over and above the tolerable/standard charged state causes instability to the cathode which starts to release oxygen into the electrolyte. Thus released oxygen reacts exothermally with the lithium plated over the graphite anode and increases the temperature of the cell making the cathode to release oxygen further. The cell which was in the dormant state in the absence of oxygen and heat now becomes an explosive device in the event the cell is met with any abuse.

In the recent past the widespread recall of laptop batteries affected nearly 10 million products when it was found that some batteries in notebook computers got overheated and in some cases caught fire (ANSI News, 2006). There were also sporadic reports on the explosion of cell phones that contained lithium ion batteries. In consequence, safety became the password of lithium ion battery and it became mandatory for any particular company to evaluate and assure the quality of their product. In order to evaluate and improve the safety standards of lithium ion batteries, abuse tests procedures have been formulated by establishments such as Underwriter's Laboratories, UL-1642 (Under writer's Laboratories, 1995), United States Advanced Battery Consortium (USABC), Electrochemical Storage System Abuse Test Procedure Manual (Spotnitz & Franklin, 2003), and Japan Storage Battery Associations (JBA) (Tobishima & Yamaki, 1999).

This chapter presents reviews related to solid electrolyte interphase (SEI) film which provides stability to the electrode active materials, thermal study on electrode materials, on cell safety, additives to electrolyte, dopants & coatings to electro-active materials and coatings to electrodes. Also presents the contributions of the authors on the cell safety through experimental work, the mechanism underlying the cell safety, suggestions and conclusion for providing safe and long life Li-ion batteries.

3. Thermal stability–State of the art

3.1 Solid electrolyte interphase (SEI) film

In the ambient temperature, the charged battery exhibits phenomenal stability owing to solid electrolyte interphase film (SEI), a protective layer formed over the electrode particles during initial charging process (Aubach et al., 1997). This thin film is reported to be an electronically resistive, allows easy diffusion of lithium ions for providing cycle life characteristics (Ota et al., 2002). The stability of this film determines calendar life and risk free handling of the battery whereas its stability depends on operating temperature, charging current/voltages, electrolyte-solvent environment and extent of battery abuse.

Several researchers made in-depth study to understand the nature of the SEI film, electrode material properties, abuse test behavior of the batteries and also suggested precautionary measures to be followed for safe handling of the battery. The battery becomes hazardous when there arises flow of surge current into or out of the charged cell to cause SEI film break

down resulting in direct contact of the electrolyte with the electrode materials initiating exothermic chemical reactions ultimately leading to failure, bursting or bulging of the battery (Doh et al., 2008).

The authors in (Richard & Dahn, 1999) point out that at elevated temperatures, the SEI film is not stable which is why a rechargeable lithium battery with a lithium metal anode is unsafe. Present day primary lithium batteries use lithium foil anode while rechargeable batteries employ graphite anodes. In (Ota et al., 2003) the authors discuss on the nature of SEI layer in poly propylene carbonate(PC)-based electrolyte containing ethylene sulphite (ES) additive based on different sulphur oxidation states with sulfur K-edge X-ray absorption near-edge structure spectroscopy (S K-edge XANES), X-ray photo electron spectroscopy(XPS) and time-of-flight-secondary ion mass spectrometry(TOF-SIMS). The authors noted an inorganic film made of Li_2SiO_3 , organic film, ROSO_2Li on the graphite anode and also alkyl sulphide species over the cathode.

The main chemical species present in the interphase layer has been characterized through novel XPS combined with both core peaks and valance band analysis (Dedryvere et al., 2007). The authors noted cell potential dependent surface films on both positive and negative electrodes at different successive voltage ranges. In the negative electrode between 3 and 3.8 V the main species formed is Li_2CO_3 along with small but a significant quantity of $\text{CH}_3\text{OCO}_2\text{Li}$. Over the positive electrode a deposit of LiF is observed which upon interaction with proton (formed due to oxidation of the solvent with the cathode) forms H_2F_2 . The acidic species HF_2^- formed from H_2F_2 then reacts with Li_2CO_3 present in SEI film making it more fragile.

The authors in (Leroy et al., 2007) reported through XPS studies for the four lithium salts LiPF_6 , LiBF_4 , LiTFSI and LiBETI that are most preferred for Li-ion batteries. In all four cases the formation of carbonate species in the SEI film has been attributed to the reduction of solvents. At the first stage identified a large deposit of Li_2CO_3 and ROCO_2Li at 3.8 V. In comparison to other salts a high deposit of LiF is observed for LiPF_6 at the end of charging. An increase of acidity observed at the end of charging has been attributed to the formation of acid species like HF or HF_2^- which is supposed to react with Li_2CO_3 of the SEI film.

Through ^7Li NMR studies (Wang et al., 2001) monitored quantitatively the growth of the SEI over the surface of active materials of the positive electrode which consists mainly lithiated materials. The report in (Lin et al., 2001) states that for batteries operating at low temperature there is an increase of the impedance of SEI with state of charge of graphite electrode. Also the report by (Zheng et al., 1999) states that there is an increase in the instability of the SEI film for the cells operating at high temperature $\sim 70^\circ\text{C}$.

3.2 Electrode materials

In (MacNeil and Dahn, 2001) the thermal decomposition of $\text{Li}_{0.5}\text{CoO}_2$ by accelerated rate calorimetry(ARC) and X-ray diffraction(XRD) has been reported which states that the oxygen loss from the cathode remains above 200°C . However, the reaction of $\text{Li}_{0.5}\text{CoO}_2$ with ethylene carbonate: diethyl carbonate (EC: DEC) solvents starts at a temperature as low as 130°C which is much lower than the decomposition temperature of $\text{Li}_{0.5}\text{CoO}_2$. The reduction of $\text{Li}_{0.5}\text{CoO}_2$ to CoO or even to Co is found to be based on the reducing power of the solvent. The increase of LiPF_6 salt concentration seems to slow down the solvent combustion reaction, and the cathode-electrolyte reaction in practical Li-ion cells. The study shows that

more thermally stable cells based on LiCoO_2 cathode could be made using higher concentration of LiPF_6 salt (near 1.5M).

The authors (Richard and Dahn, 1999) report through ARC experiments that for MCMB with LiBF_4 the self heating begins early (50°C) compared to MCMB with LiPF_6 (70°C) for the same solvent composition (EC: DEC = 1:1). When MCMB sample containing LiPF_6 (EC:DEC=33:67) was heated directly to 150°C , the self-heating starts at a rate approximately equal to $100^\circ\text{C}/\text{min}$. The authors also stress the usefulness of knowledge on self-heating process for the understanding of the abuse behaviors of practical cells.

An important observation made by (McNeil and Dahn, 2002) is that when the electrode mass is low compared to the mass of the solvent a large exothermic reaction occurs above 300°C forming a large amount of Co metal as compared to other species. The amount of cobalt carbonate formed becomes less as most of CoO is reduced to Co. When the electrode mass is larger than the mass of the solvent, the solvent becomes insufficient to reduce fully the higher valent cobalt to Co metal.

The temperature dependency of the heat generation between 283 and 333 K (Saito et al, 1997) shows an exothermic peak and an endothermic peak at around 4V caused by a phase transition of the positive electrode material Li_xCoO_2 between the hexagonal and monoclinic structures observed at around $x = 0.5$. At the point of phase change cathode also faces instability. Also the authors (Reimer & Dahn, 1992) describe that the temperature rise of battery is due mainly to two factors one the electrochemical reactions and the other associated polarization. The overcharges are the sign of cathode degradation and electrolyte decomposition at high voltages. As lithium is removed from Li_xCoO_2 , oxidation of Co^{3+} to an unstable oxidation state Co^{4+} follows. Large concentration of Co^{4+} is most likely to destroy the cathode crystallinity, finally the cell reversibility.

In (Yamaki et al., 2003) the authors made an in-depth study of the lithium battery electrodes. From high temperature XRD it was found that chemically delithiated $\text{Li}_{0.49}\text{CoO}_2$ exhibited exothermic peak at 190°C possibly caused by structural changes from a layered $R\bar{3}m$ to spinel ($Fd\bar{3}m$) unaccompanied by oxygen evolution. From DSC measurements for reaction of $\text{Li}_{0.49}\text{CoO}_2$ with electrolyte the authors reported two peaks, one at 190°C , due mainly to the decomposition of the solvent with the active cathode surface and the other at 230°C caused by oxygen release from $\text{Li}_{0.49}\text{CoO}_2$. The reaction of lithiated graphite with electrolyte showed several exothermic peaks. One small peak at 140°C for the reaction between PVdF binders coated lithiated graphite and electrolyte resulting in SEI film formation, another sharp peak at 280°C attributed to break down of SEI film followed by direct reaction between lithiated graphite and electrolyte.

In (Zhang et al., 1998) investigated through DSC the intrinsic reactivity of Li_xNiO_2 , Li_xCoO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, and Li_xC_6 , at different values of x . This experiment shows the reactivity between the active material and electrolyte as exothermic reaction. The amplitude of reaction depends on the availability of M^{4+} , particularly where $\text{M} = \text{Ni}$ or Co and that Mn^{4+} exhibits less oxidizing capability relative to others. Both Li_xNiO_2 and Li_xCoO_2 exhibited strong reactivity with the onset temperatures in the range 200 to 230°C as x was decreased, suggesting that control of stoichiometry is very important for achieving cell safety. Lithiated carbon in the presence of electrolyte produced DSC exotherms in two temperature ranges. The first was a low energy peak with onset temperatures at approximately 120 - 140°C which appeared to be due to surface passivation of the lithiated carbon materials. The second peak started at about 230°C and may have involved the PVDF binder materials of the electrode.

3.3 Abuse test behavior of the cells

The following passage presents an overview of the literature available on abuse behavior of lithium ion batteries. In (Wainwright, 1995) the author illustrated through spot weld tests for a cell with $\text{Li}_x\text{CoO}_2/\text{DME}$ combination a violent venting when $x = 0.4$ but could not vent for $x = 0.5$, even when the spot heating was sufficient to melt and breach the container. In (Fouchard et al., 1994) the authors bring out the response of AA size lithium ion cells on heating in an oven and reported that the thermal stability of the cathode increased with increasing lithiation of the cathode.

In (Kitoh & Nemoto, 1999) the authors noted that upon external short circuiting of the lithium ion cell the temperature reached $\sim 100^\circ\text{C}$ followed by a sudden drop in current. The drop in current was attributed to melting and shut down function of the separators. During nail penetration test (nail speed 1mm/s), the cell vented immediately. After the nail was inserted the cell did not ignite but reached a maximum temperature, 380°C .

In (Maleki et al., 1999), the thermal stability study of fully charged 550mAh prismatic lithium ion cell and the components inside the cell showed that the self-heating exothermic reactions starts at 123°C , and thermal runaway at 167°C . The report also brings out that the total exothermic heat generation of the NE and PE materials is 697 and 407 J/g respectively. The heat generation of NE and PE materials washed with diethyl carbonate, dried at $\sim 65^\circ\text{C}$ under vacuum are significantly lower than unwashed samples. Lithium plating increases the heat generation of the NE material at temperatures near lithium melting point. Comparison of heat generation profiles from DSC and ARC tests indicates the thermal runaway of the cell as close as to the decomposition temperature range of the unwashed PE materials. The authors conclude that the heat generation from the decomposition of PE materials and reaction of that with electrolyte initiates thermal runaway in a Li-ion cell subjected to thermal or other abuse exposures.

In (Biensan et al., 1999) all parameter identified from the DSC studies suggested that the reaction kinetics at the negative electrode, the binder nature (fluorinated or not), the state of charge of positive materials are the deciding ones for ascertaining the maximum safety voltage of the cell. Through nail tests on 4/5A size cells reported the safe voltage for a cell with cobalt oxide cathode is higher than that of nickel oxide cathode and with non fluorinated binder than with polyvinylidene fluoride binder.

(Tobishima and Yamaki, 1999) reported swelling on overcharge of 600mAh cells with aluminum can charged to 1C and 1.5C for which the safety vent did not open or smoke. On the other hand for a cell charged at 2C rate, the safety vent and anode cap housing welded ultrasonically opened simultaneously. The authors describe that as the overcharge current increases the heat output increases since joule heat output is proportional to i^2R (i = current, R = Resistance). Again if the graphite is not sufficiently porous to intercalate during charging then the lithium deposits on its surface, cause a drastic reduction in thermal stability. The thermal stability test on a commercial cell with 1270mAh capacity the cell smoked only at 155°C which led them to conclude that the thermal stability limit for lithium cells is not lower than 150°C . Upon nail penetration test a commercial prismatic cell does not smoke when charged at normal charging voltage to reach 835mAh. However, the cell smoked when charged 0.03V higher than the standard voltage to reach 863mAh. During crush test a cell charged to its standard capacity (720mAh) did not smoke but the same cell with 200% overcharged smoked, the possible reason presented being the deposition of lithium metal as fine particles on the graphite surface anode.

Dahn (Dahn, 2001), has reported that for a 18650-size cell embedded with thermo couple when pierced by a nail to the depth of <4.5 mm the cell temperature exceeded 600°C while for a fast, deep nail penetration (7.5 mm) the cell temperature did not exceed 140°C.

The overcharge and short circuit behavior of 1.5Ah prismatic lithium-ion cells presented in (Leising et al., 2001) showed that during short circuit test the inner temperature of the cell reached 132°C attributed for the shutdown temperature (132°C, melting point of polypropylene separator) and the outer surface of the cell measured was only 94°C. The salient features of their experiments are: (I), the thermal runaway not only depended on the state of charge of the cell but also on the amount of cathode material. (II), the battery rupture occurs when the cell temperature exceeds 190°C suggesting that the melting of the lithium metal may be the key factor responsible for rupture of the cells and (III), the cells assembled with lithium removed Li_xCoO_2 cathode and graphite anode upon overcharge tests (no lithium could plate on the anode) showed significantly higher temperature (~280°C) and (IV), the abused cell maintains a temperature difference of over 80°C between the interior and external surface.

The heat generated during overcharging was measured by a twin type heat conduction calorimeter at constant charging current at different charging rates (Saito et al, 2001) which gives values of heat flow especially the inner temperature difference between the sample vessel and reference vessel. The heat flow seems to be almost proportional to the current passed during the overcharge test for 18650-size cells. The authors measured the heat released for LiMn_2O_4 and LiCoO_2 cells at 0.2C rate for 160- 180% overcharging current.

Venugopal (Venugopal, 2001) showed that the vulnerability of battery is due to battery abuse which becomes less severe due to shutdown function of polyolefin separator membranes where the melting of the separator prevents the ionic flow through the pores, thereby minimizes the passage of current thus stopping the cell thermal runaway.

In (Spotnitz & Franklin, 2003) the abuse test on lithium-ion cells through modeling showed that the fluorinated binder plays relatively unimportant role in thermal runaway. In an overcharged cell even though the graphite is in well intercalated state the lithium prefers to react with solvent rather than the binder though there exists an intimate contact between lithium and the binder. Their result also shows that rapid and localized heat generation during nail test and crush test could activate well all the chemical reaction in the cell. In (Liu et al., 2001) it is observed that the gel polymer electrolyte provides less flammable environment within the cell

Wu et al., (2004) reported by soft-nail penetration on laminated aluminum packaged commercial lithium ion battery. The reports state that an internal short is more dangerous than an external short, because the former (soft-nail test) induces an enormous heat instantaneously and locally to cause thermal runaway of the electrolyte and electrode materials. Their experiment showed that all separators except polypropylene (PP) separator showed distinct shut down especially for batteries with more than 200 cycles, implying usage of PP may result in fire. The reported exothermic values for anode are 54 & 95.5 J/g and for the cathode 60 & 103 J/g for 10 and 200 cycles respectively. Changes in the cathode open circuit potential (OCP) reveals a decreasing amount of lithium content after cycling which is related to decreasing thermal stability. The decomposition temperature decreases for Li_xCoO_2 as the x value decreases. The decline in the thermal stability of the cell on overcharge is also due to both removal of lithium ions from the cathode and deposition over anode surface.

4. Abuse preventive measures

4.1 Gas evolution as Current Interrupter

In (Abe, 2006) reported the development of electro-conduction membrane (ECM), an alternative to solid electrolyte interphase (SEI) film. The electro-conductivity of ECM improves cathode cycleability, formerly known as overcharge protection proofs. For example, Benzene derivatives (biphenyl and o-terphenyl) and heterocyclic compounds (furon, thiophene, N-methyl pyrrole and 3, 4-ethylenedioxythiophene), by virtue of their lower oxidation potentials than those of electrolyte solvents, decompose on the cathode surface and form thin film. The author describes biphenyl compound could serve well as overcharge proof since the gas generated at higher voltage (decomposition at 4.5V verses Li/Li+) is released through the cell safety cap. Yoshino reports the use of cyclohexyl benzene which evolves hydrogen and activates current interrupter device (CID) and shuts off the cell current. The application of biphenyl (Moli/NEC) and pyrocarbonate (SONY – evolves CO₂) were also reported in (Yoshio, 2001, 2002).

4.2 Flame retardant as additive to electrolyte

Blomgren (Blomgren, 2003) discusses on the additives which serves to lower the flammability (Flame retardants-FRs) of the electrolyte. The author points out that flames generally require the presence of materials which promote chain reactions for self-sustaining, hence majority of workers sought materials that can break the chain reactions (known as chain breakers) to avoid battery failures. It is reported (Wang et al., 2001) that the thermal stability is improved by the use of Trimethyl phosphate (TMP) containing electrolyte and for the one with 1 mol/dm³ LiPF₆/EC + PC + DEC +TMP (30 + 30 + 20 + 20) electrolyte composition the cell exhibited good thermal stability. They state that the use of a minimum of TMP in a disordered carbon negatives improves further the thermal behaviors. In several cases the FRs brings adverse impacts on the cell performances due to their extra weight fraction in the electrode. Comparatively costly FRs such as fluorinated alkyl phosphates and hexamethoxy cyclotriphosphazene are more promising with minimal impacts on cell performances. The report in (Xiang et al., 2007) states that a cost effective, highly efficient retardant additive dimethyl methylphosphonate (DMMP) to 1MLiPF₆/EC+DEC electrolyte system provides total non-flammability for a 10wt. %DMMP addition. The addition of DMMP causes little damage on the cell electrochemical performance and more promising for safety to lithium ion batteries.

4.3 Redox shuttle

The molecule which oxidizes to form a radical cation at high cell voltage at the positive electrode diffuse to the negative electrode where it reduces into neutral molecule and shuttles back to the positive electrode, a phenomenon called as redox shuttles. In (Chen et al., 2005) it is pointed out that a chemical redox shuttle additive to the electrolyte is shown to provide overcharge protection. The molecule 2, 5 diterbutyl-1, 4-dimethoxy benzene, provides overcharge and overdischarge protection for hundreds of charge-discharge cycles in both single cells and series connected cells. Yoshino (Yoshino, 2001, 2002) has described several of these materials for application in lower currents. The materials such as veratrole(Sony), difluoroanisole (LG chemical), bipyridyl(Sanyo) and biphenyl carbonate(Sanyo and Ube) were used beneficially in lithium ion batteries.

4.4 Dopants and coatings

The electro active particles or the electrodes are modified to achieve high cycle life and hazard free batteries. One way is doping a part of 'Co' in LiCoO_2 with some other metal (Needham et al., 2007 & Veluchamy et al., 2001) the other one is coating on the surface of LiCoO_2 particles (Kim et al., 2005; Nozaki, et al., 2009; Cho, 2004) and the third one is giving polymer coating (Oyama et al., 2009). Usually the electrode materials are modified by incorporating carbons, AlPO_4 , SnO_2 , Al_2O_3 , ZrO_2 and TiO_2 during or after the synthesis usually through heat treatment. For example, Lee et al., (2007) reported that Li-ion cells with olivine LiCoPO_4 grown over LiCoO_2 , showed only 10% swelling at 4.4V, whereas those containing bare sample showed 200% volume increase during storage at 90°C for 5h. In addition nail penetration test results of the cell containing Olivine, LiCoPO_4 , grown in LiCoO_2 at 4.4V, did not exhibit thermal runaway with a cell surface temperature of ~80°C. However, the cell containing bare LiCoO_2 showed a burnt-off of the pouch cell with a temperature reaching above 500°C. Cho described in (Cho, 2004) the dependence of thermal stability of LiCoO_2 cathode to the coating thickness of AlPO_4 over the cathode. As the thickness is increased the cell safety improved even for a 2C rate overcharged cell with no signs of thermal runaway. The author believed that the development of such coating acts as a replacement for protection circuit mode (PCM) for lithium ion battery (PCM consists of a material with a positive temperature coefficient and protective circuits that blocks overcharging above 4.35V, over discharging below 2V, and overcurrent above 1C)

4.5 Other physical devices

A patent by (Okutoh & Tadashi, 2001) describes that a flat sheet of lead taken out from a positive temperature coefficient (PTC) element incorporated inside the battery is connected to a protection circuit element for detecting any abnormality from overcharging, overdischarging, overcurrent, and unusual temperature to cut-off the current passing through the cell. Positive temperature coefficient (PTC) element installed inside the cell, whose resistance increases several fold in response to surge current during cell abuse, followed by this the cell temperature rises due to I^2R loss which causes sudden fall of current flow consequently preventing the cell failure. Contrary to (PTC) element, negative temperature coefficient (NTC) element decreases its resistance with temperature. This characteristic is used to monitor inside cell temperature and hence helps to understand any unwanted reactions inside the cell. Various companies incorporating protection circuit module (PCM/PCB) to keep safe Li-Ion/Polymer battery from overcharge, overdischarge, and accidental battery explosion due to its extra high energy density are available in the market (BATECH Korea INC. & Co., Ltd in Tokyo, Japan). During their discussion on safety mechanism in (Balakrishnan et al., 2006) the authors have described various devices including the use of thermostat or temperature cut-off (TCO) element, which serves to terminate current flow when the temperature reaches a preset value.

5. Experimental

5.1 Pouch cell construction

The cell used for safety tests is a commercial, rectangular, pouch cell (1000mAh) of dimensions 60mm x 33mm x 4mm. The data provided by the manufacturer reveals that the cathode constituents are LiCoO_2 , super p black (SPB) and polyvinylidene difluoride (PVDF)

coated over aluminum current collector in the wt ratio 94, 3, and 3 % respectively. The particle size of Li_xCoO_2 is 20 μm . The anode material constituents are coated over a copper current-collector and comprised a blend made up of mesocarbon microbeads and PVDF in a wt ratio 92 and 8%. The electrolyte (Techno Semichem.) is 1.12 M LiPF_6 with 2wt% vinylene carbonate (VC) dissolved in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) mixed in 1: 1(V/V)) ratio. The separator is a non-woven poly propylene separator. Electrodes and electrode materials removed from the cell were used for the obtaining thermal and structural data.

5.2 Instrumental procedures

The pouch cells were charged and/or overcharged to a set voltage using the current source from Digatron (Germany) either for heat-treatment experiments or for abuse tests. For measuring the temperature variation with time during abuse tests experiments an electronic digital recorder with a thermocouple probe was fixed tightly over the surface of the test cells. Designed and locally fabricated equipments (Fig. 1 & Fig. 2)) were employed for carrying out the nail penetration test and impact tests. To acquire data for 1C rate (Fig. 3) or 3C rate (Fig. 4) the batteries were overcharged by using current source from Digatron.



Fig. 1. Nail penetration Test equipment.

The nail penetration test (Fig.5) was performed on the cell noted as Cell-3 using a nail (50mm long, 5mm diameter) at a penetration rate of 5mm/s at the centre of the cell. The impact test (Fig. 6) was carried out by placing a rod (15.8mm diameter and 50mm. length) on the cell which was kept on a flat iron plate and over that an iron cylinder (~ 15 cm x 10 cm) weighing 9.1kg was allowed to fall from a height of ~ 610mm onto the cell named as Cell-4. The nail penetration and overcharge test chambers were provided with glass door to view the experiments. In order to have an insight into the materials formed during abuse tests, a pouch cell was charged to a cut-off voltage of 4.5V and then heated to 400°C in a furnace under argon atmosphere at a rate of 5°C/min. The heating was then switched off to cool the cell down spontaneously to room temperature. The heating temperature 400°C was chosen as this temperature is close to the cell temperature of pouch cell during/near explosion. Also, the observation (Cho et al., 2003) that the internal cell temperature of abused cell is always higher by 80°C over surface of the cell has also been taken into consideration.



Fig. 2. Impact test equipment

A Philips 1830 X-ray diffractometer with nickel filtered Cu K α radiation at a scan rate of 0.04°/s over 2 theta range 10°– 80° was used to analyze the cathode material heated to 400°C.

Differential scanning calorimetry (DSC-Q1000) and thermo-gravimetry (TGA-Q600) from TA Instrument USA which use data processing program universal analysis 2000 were used to carry out thermal behavior of the samples. The sample holders are made of alumina and aluminum for DGA and DSC, respectively. Electrode material weighing ~8 to 10mg was kept in open alumina holder and ~7 to 9mg was crimp sealed in aluminum holder; both experiments were carried out at a scan rate of 5°C/min in a nitrogen atmosphere. The cell opening and extraction of the cathode material for these experiments were carried out in a dry-room maintained at ~21°C with dew point temperature ~ 65°C.

A portion of the electrode cut in size 20mm x10mm washed first with dimethyl carbonate and then with acetone to remove any electrolyte in the electrode. It was then kept immersed in 50 ml of distilled water for 1h and the solution was subjected to identify presence of any carbonate ions in the cathode using Ion chromatography (IC). Ion chromatography was also carried out for a solution prepared by adding 1ml of the battery electrolyte (1.12 M LiPF₆ in VC/EC/EMC) in 9 ml of water giving a rest time of 30 minute in order to find out the presence of other ions in the electrolyte.

6. Results and discussion

6.1 Over charge behavior

6.1.1 Overcharge at 1C rate

The overcharge behaviors of a pouch cell designated as Cell-1 at 1C rate for 2.5h is presented in Fig. 3 along with photograph of the abused cell. During the first hour, the cell voltage shifts from 4.2 to 4.5V. Consequently, the electrode gets polarized giving rise to the following processes. As the potential of Li_xCoO₂ electrode shifts to more positive value, the deintercalation of lithium ions proceeds along with the oxidation of Co³⁺ into unstable Co⁴⁺, which dissolves in the electrolyte. The dissolution of Co⁴⁺ accelerates with time as the potential shifts to a more positive value and results in damage to Li_xCoO₂ crystal, a process which is related to fading of cell capacity (Oh et al., 2004). This polarization process is followed by a thermal process. As the x in Li_xCoO₂ shifts from 0.45 to 0.3, a large anisotropic volume change of 3% occurs due to the phase transition between hexagonal and monoclinic

H1-3 phases (Jang et al., 2002 & Amatucci et al., 1996). Such crystal-phase change is also presumed to induce thermal stability of the positive electrode (Saito et al., 1997).

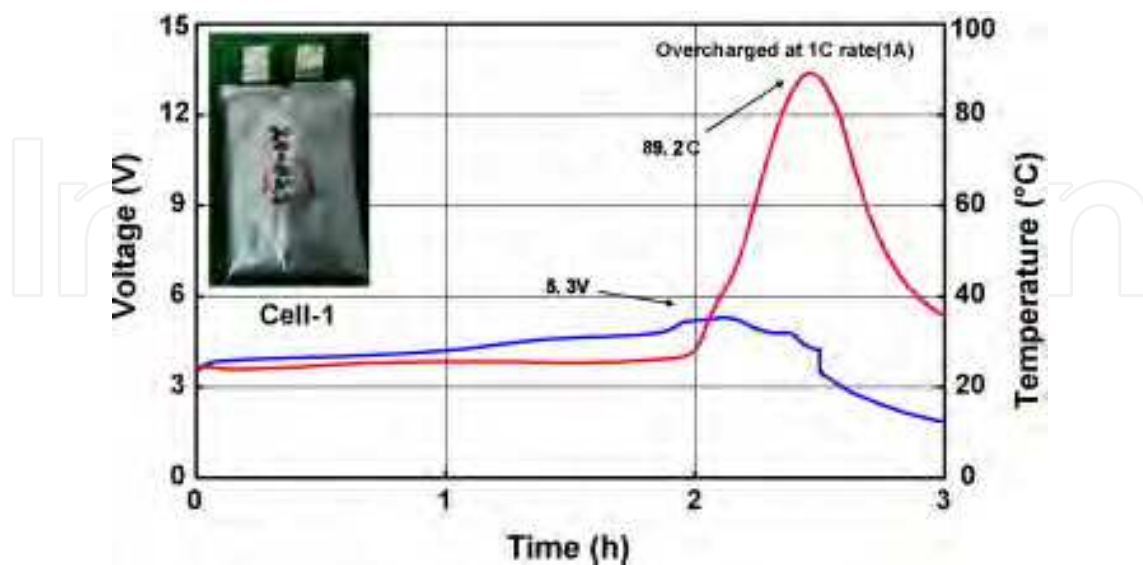


Fig. 3. Voltage and thermal behaviour of Cell-1 on overcharge at 1 C rate, (Doh et al, 2008)

As the cathode is completely de-lithiated, the cell voltage moves above 4.5V, the ionic conduction completely ceases, and the passage of current through the cell becomes purely ohmic resulting in heat generation due to I^2R loss. The poor heat dissipation of the cell components causes an exponential increase in cell temperature (Saito et al., 1997), which induces decomposition of Li_xCoO_2 according to equation. (1). As discussed in section 6.15 the overcharged cathode Li_xCoO_2 , as $x \rightarrow 0$, decomposes into Co_3O_4 and oxygen, (Dahn et al., 1994). At higher temperatures, the liberated oxygen and Co_3O_4 promotes combustion of carbonaceous materials. Since the electrolyte contains organic solvent, Co_3O_4 will be reduced to CoO (Mac Neil, 2001). The extent of conversion depends on the probability of contact between Co_3O_4 and the reductive organic species available during the combustion process. The Fig. 3 also shows an abrupt triggering of heat after 2h of charging is possibly be due to meltdown of the separator ($\sim 125^\circ\text{C}$ for polyethylene and $\sim 155^\circ\text{C}$ for polypropylene) (Tobishima et al., 1999) leading to a cell short-circuit. As the passage of overcharge current ends at 2.5h, the joule heating also ceases. Finally both cell voltage and temperature start decline from the peak values 5.3V and 89°C , respectively. As reported in (Cho., 2003) the inner cell temperature will be 169°C . The disconnected battery from the abuse tests was subjected to charge but found the cell could not be recharged and has undergone thermal runaway.

6.1.2 Overcharge at 3C rate

The overcharge behaviors of the pouch cell designated as Cell-2 recorded at 3C rate (current-3A) and a photograph of cell used for the tests are presented in Fig. 4. After 0.7h, there appears to be a change in voltage and temperature behavior of the cell. At the $\sim 0.8\text{h}$, the cell temperature and voltage move above 300°C and 12V respectively. The sudden drop of cell voltage after reaching 12V implies perfect short circuiting of the electrodes, possibly due to melt down of the separator. The temperature and the cell voltage are so high to cause

all the erroneous process (described for the Cell-1) for the cell destruction. Meltdown of the separator and combustion of the organic electrolyte with the released oxygen would have been instantaneous to cause volume expansion and violent explosion. The maximum dc power attained is $\sim 39\text{W}$ and the cell surface temperature reaches 300°C .

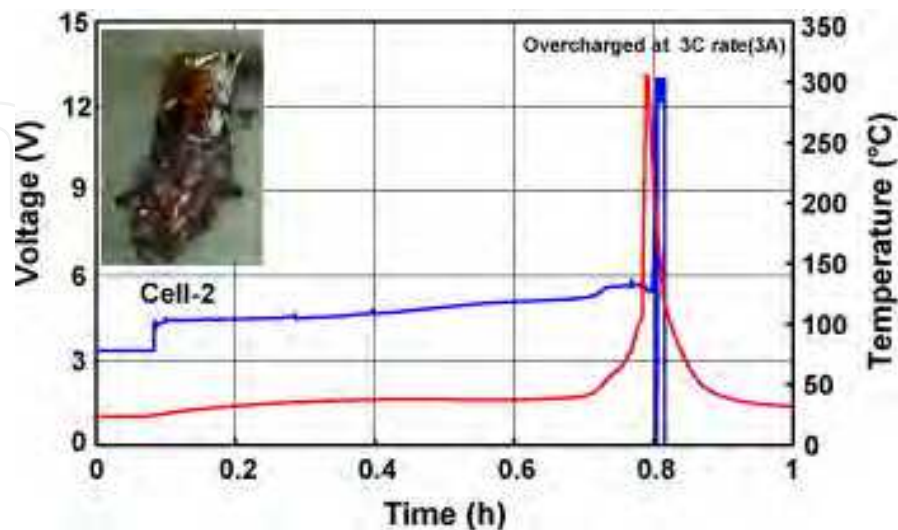


Fig. 4 Voltage and thermal behavior of cell Cell-2 on overcharge at 3C rate, (Doh et al, 2008).

6.1.3 Nail penetration test

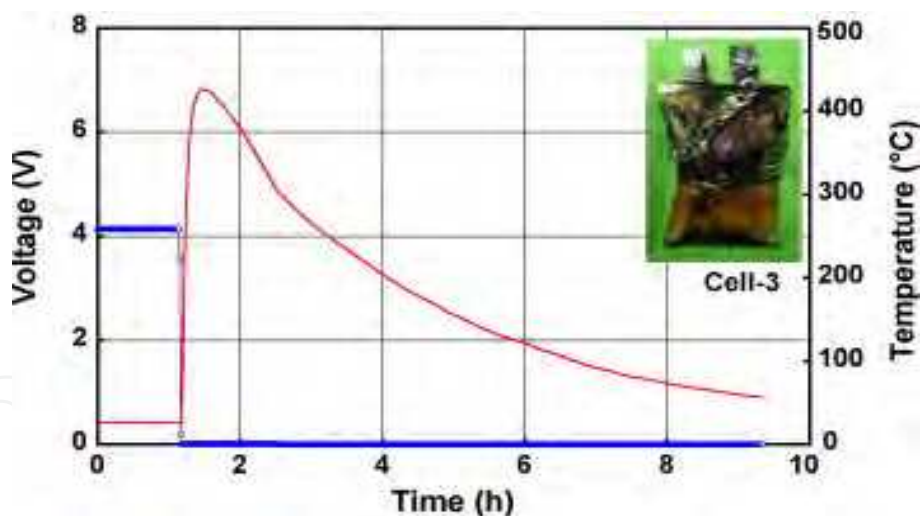


Fig. 5. Voltage and thermal behaviour of Cell-3 on nail penetration test, (Doh et al, 2008).

The cell designated as Cell-3 was subjected to nail penetration and a photograph of the cell taken after the test is presented in Fig.5. The Figure shows a constant voltage and temperature before the test is conducted. At the instant the experiment is started, the voltage falls to zero and the surface temperature of the cell shoots up to 420°C which could only be attributed to a high surge of discharge current resulting in a high joule heat followed by separator meltdown and contact of the anode and cathode. In the case of overcharge tests, the electrodes are charged at a known current, whereas, in nail penetration tests the quantity of the discharge current flowing through the nail is not known. The temperature of the cell

reaching 420°C shows the intensity of the discharge current in the nail penetration test which could have been much higher than that in overcharge test. The current flowing through nail can be compared with well-known dendrite shorting. The usual discharge product LiCoO_2 along with Co_3O_4 and O_2 from the decomposition of de-lithiated cathode Li_xCoO_2 could be expected, after combustion process. In addition, a trace quantity of CoO could be expected (section 6.15). The cell does not explode violently as the nail has made a partial way for the release of gaseous materials and the cell appears to have expanded as evident from the figure (Fig.5).

6.1.4 Impact tests

In nail penetration tests, the nail makes a direct contact between the anode and cathode. But in the impact tests the cylindrical rod is kept horizontally over the cell which crushes the cell at the centre. Since the action is expected to expand and tear the separator that makes contact between positive and negative electrodes. A high discharge current will flow between the anode and cathode of the cell. The highest surface temperature noted is 161°C (the internal temperature will be around 241°C). As the internal portion of the cell is opened the gaseous products formed will be easily released from the cell and there will be less severe effect on the environment. The thermal behavior along with a photograph of the impact tested cell designated as Cell-4 is presented in Fig. 6.

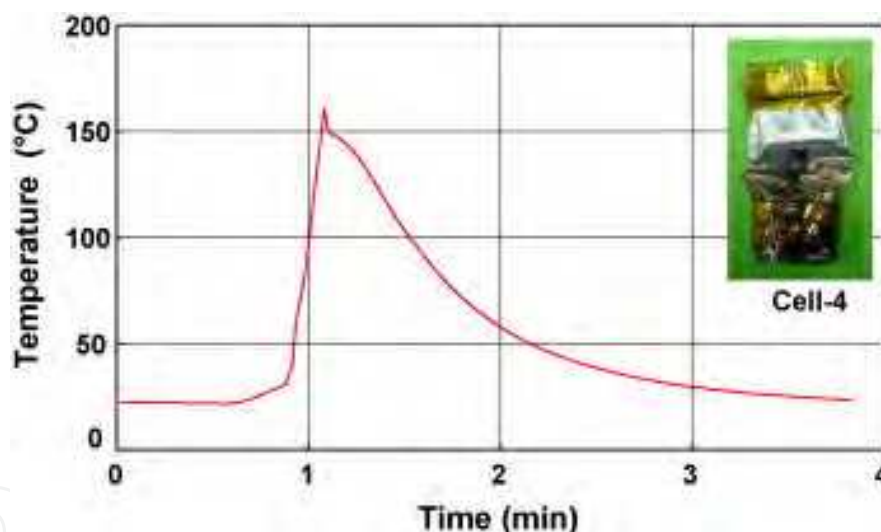
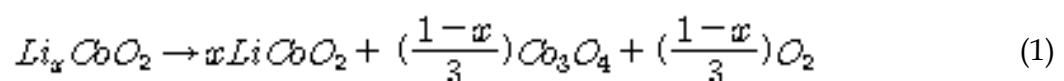


Fig. 6. Thermal behavior of Cell-4 on impact test; (Doh et al, 2008).

6.1.5 XRD analysis of the cathode material exposed to high temperature.

The general equation that govern the decomposition of Li_xCoO_2 may be represented by the equation



This shows that during overcharging, highly de-lithiated cathode material Li_xCoO_2 , as $x \rightarrow 0$, decomposes into Co_3O_4 and O_2 gas. In a partially delithiated cathode, of $\text{Li}_{0.5}\text{CoO}_2$ (4.2V cells), the possible products are LiCoO_2 , Co_3O_4 and O_2 gas. The XRD patterns of cathode

material Li_xCoO_2 , unheated (4.5V cell), heated (4.5V cell) and LiCoO_2 (3V cell for comparison) are presented in Fig. 7. The Bragg peaks appearing for the unheated cathode of 4.5V cell show a change in the crystal parameters for LiCoO_2 , which can possibly be attributed to a de-lithiated state. After heat treatment, the XRD pattern shows disappearance of many peaks corresponding to the parent sample. The resultant material after heat treatment has lost its crystallinity, as evident from the XRD pattern. The Bragg peaks of LiCoO_2 , Co_3O_4 overlap in many cases, except in the region of Co_3O_4 (220) peak near 31.1° . The appearance of this peak in the heat treated sample confirms the formation of Co_3O_4 upon decomposition of Li_xCoO_2 (MacNeil., 2001). The effective conversion of Co_3O_4

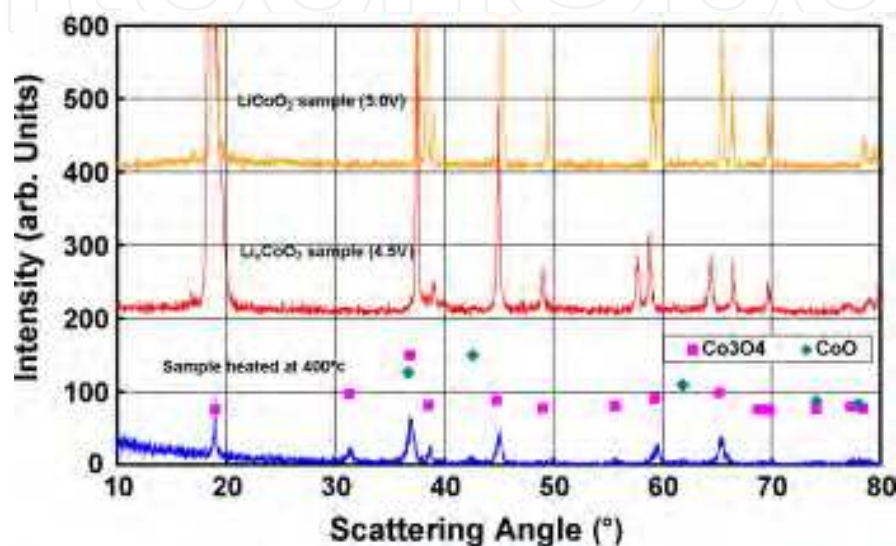


Fig. 7. XRD patterns of cathodes LiCoO_2 (3V cell), Li_xCoO_2 (4.5V cell) and heat-treated cathode (4.5V cell) at 400°C , (Doh et al, 2008).

into CoO by the reductive action of organic solvent becomes likely. On the other hand, the probability of the formation of a trace quantity of CoO from the reduction of Co_3O_4 by the carbonaceous residues present in the cathode material may be attributed to the weak peak appearing in the XRD pattern. The formation of LiCoO_2 , Co_3O_4 and CoO has been reported in (MacNeil & Dahn, 2001, 2002) from a thermal study of $\text{Li}_{0.5}\text{CoO}_2$ with electrolyte. Since all the abuse tested cells contains electrolyte, the formation of a small quantity of CoO from the reduction of Co_3O_4 is expected by virtue of reducing power of solvent. In (Dahn et al., 1994) reported the thermal behavior of Li_xCoO_2 , Li_xNiO_2 , and $\text{Li}_x\text{Mn}_2\text{O}_4$ materials and found that the amount of oxygen released into the electrolyte increases with decrease of x value. Hence a highly oxidized cathode could explode violently as the amount of oxygen released from the combustion reaction is enormous.

6.1.6 Thermogravimetric analysis

The TGA curves obtained for electrodes charged to different temperature are presented as Fig. 8. The figure shows the extent of weight loss at three different regions. In the region around 100°C where the weight loss may either be due to evaporation of the electrolyte solvent or combination of evaporation of the solvent and weight loss due to oxidation reaction. If there is exothermic energy release in any region that will be understood from the DSC data. In the region between 200 and 400°C the weight loss is attributed to

decomposition of Li_xCoO_2 into LiCoO_2 , Co_3O_4 and oxygen. The reduction of Co_3O_4 into lower cobalt oxide or to cobalt depends on the extent of electrolyte solvent present in the sample. The liberated oxygen oxidizes the carbonaceous materials releasing carbon dioxide and energy. In (MacNeil & Dahn, 2001) the authors analyzed the XRD pattern of $\text{Li}_{0.5}\text{CoO}_2$ sample heated with and without organic solvent using ARC and demonstrated that the former one even at lower temperature (275°C), not only produces LiCoO_2 and Co_3O_4 but also shows the presence of $\text{Li}_x\text{Co}_{(1-x)}\text{O}$. Since the amount of lithium (Li) is very small, the authors refer $\text{Li}_x\text{Co}_{(1-x)}\text{O}$ as CoO . Fig. 8 shows that the highly charged electrode materials of 4.20 and 4.35V cells to undergo pronounced weight loss compared to electrode materials of cells charged to lower voltage cells (3.85 and 3.95V). The highly charged material with low value of lithium could behave well like an oxidizing agent towards the electrolyte which may lead to the formation of less quantity of LiCoO_2 and Co_3O_4 , but with larger proportion of CoO .

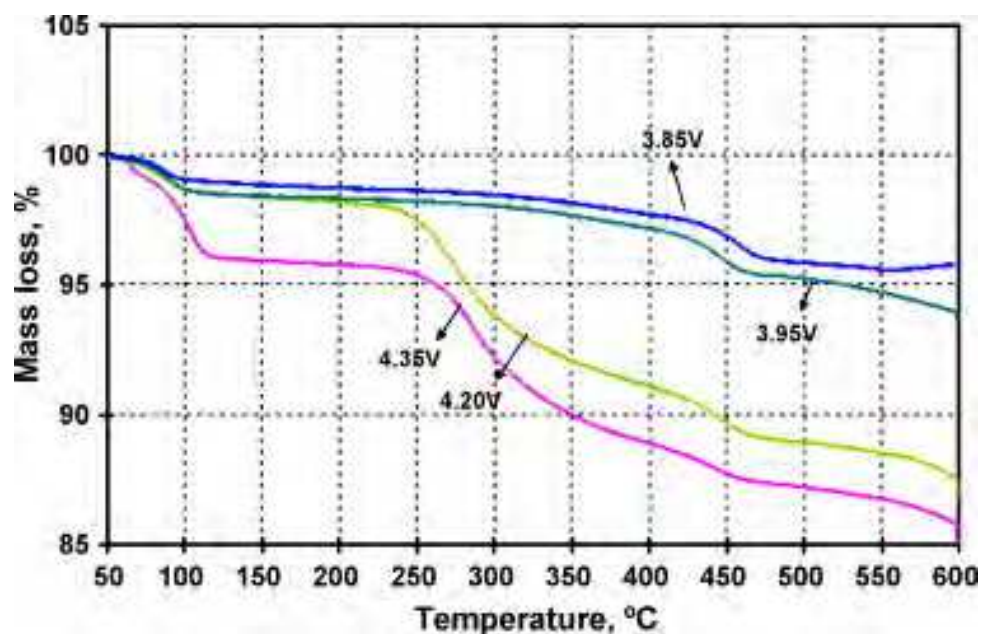


Fig. 8. TGA curves for the different cathode materials; (veluchamy et al., 2008).

6.1.7 Differential Scanning calorimetry

The DSC spectrums representing the heat flow with temperature for the charged cathode are presented as Fig.9. The figure shows that the cathodes of cells charged to 3.85 and 3.95V have no thermal peaks in the low temperature region whereas the cells charged to 4.20 and 4.35V have well defined exothermic peaks of the order of 4.9 and 7.0 J/g respectively below 100°C . Even though the intensity of these peaks is low, they arouse more curiosity as no such peaks in this temperature region have so far been reported. In (MacNeil and Dahn, 2001) the authors made in-depth thermal study of the cathode materials with calculated quantity of organic solvents. In this present study the cathode material containing electrolyte was used as such for obtaining thermal data. The exothermic energy released is assumed to be due to the reaction between the oxide cathode material and the organic electrolyte present in it. The heat energy calculated from DSC spectrum for the two cathodes materials are 83 and 80 J/g between 125 and 250°C and above 250°C the values are 81 and 17 J/g for the respective cathode materials of 4.20 and 4.35V cells. The lower exothermic energy

release of cathode material of 4.35V cells at higher temperature region may be associated with early history of the sample such as decomposition of the cathode material/electrolyte during overcharging and decomposition at low temperature region in DSC itself.

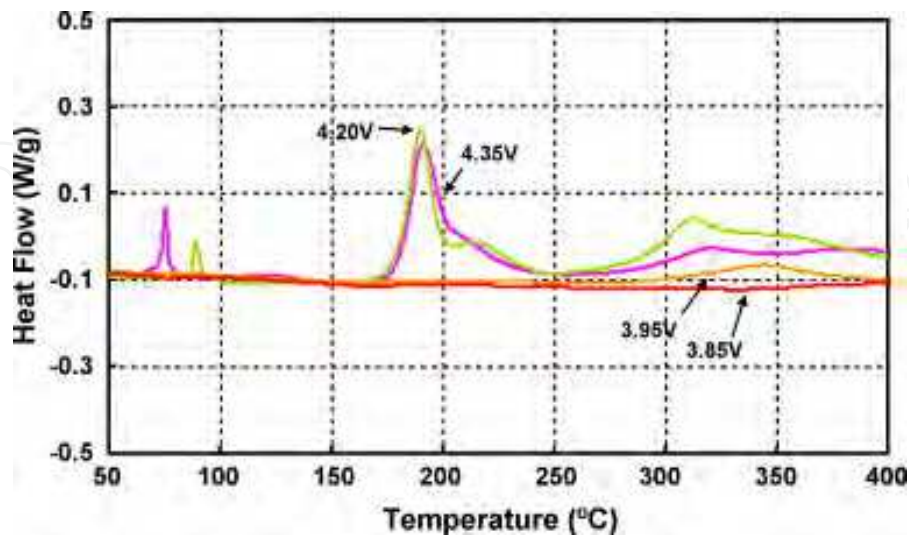


Fig. 9. DSC scans for the cathodes of 3.85, 3.95, 4.20, and 4.35 V cells, (veluchamy et al., 2008).

6.1.8. Ion Chromatography

Through XPS spectra the authors in (Dedryvère et al, 2007) identified a passivation film of LiF on the surface of positive electrode material Li_xCoO_2 of the cell LiCoO_2/C charged to different cell voltages, which increased progressively from ~10% at 3V up to 18% at 4.2V. In our experiment the electrode is washed first with organic solvent to remove the organic electrolyte along with dissolved inorganic salt present in the electrolyte.

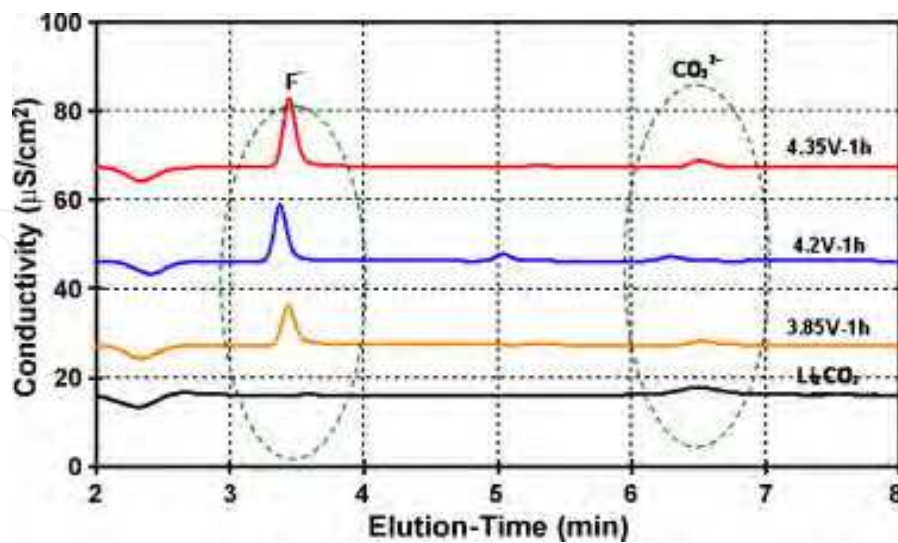


Fig. 10. Ion chromatography of the solution: the electrodes dipped in distilled water; Li_2CO_3 dissolved in distilled water. (veluchamy et al., 2008).

Then the electrode is immersed in distilled water for 1 hour so that the ionic materials present in SEI film could be dissolved in water and identified using Ion

Chromatography(IC) technique (Fig. 10).The curves show the presence of ionic carbonates and ionic fluoride. Again 1ml of fresh battery electrolyte (1.12 M LiPF_6 in VC/EC/EMC) added to 9 ml of distilled water with a 30 minute rest time was analyzed and presented in Fig.11.The figure shows the probable ionic species which may get incorporated in the electrode materials. Comparison of Fig.10 and Fig 11 shows the peak at 5 minute elution time in the IC of 4.2V, electrode immersed in distilled water for 1 h is due to the presence of chloride impurities present in the electrolyte. Hence it may be concluded that the possible materials present over the surface of the electrode material are LiF , Li_2CO_3 and trace quantity of LiCl . Even though LiCl could have same role as LiF , only LiF is considered for discussion as the contribution of LiF will be greater compared to LiCl .

6.1.9 Mechanism of SEI film break-down

During overcharge process the x value of the cathode steadily changes from 0.45 to 0.3. The electrode faces an instability and passes through a phase change from hexagonal structure to monoclinic H1-3 accompanying a large anisotropic volume change ($\sim 3\%$) (Jang et al., 2002 & Amatucci and Tarascon, 1996). Over the highly positive unstable electrode during the phase change process protons are generated due to oxidation of the solvent by the cathode. This proton interacts with LiF deposit present in the SEI film and forms H_2F_2 . The acidic species HF_2^- formed from H_2F_2 then reacts with Li_2CO_3 present in SEI film making it more fragile (Lorey et al, Doh et al., 2008 & Saito et al., 1997). The reactions are presented as equation (2) and (3).

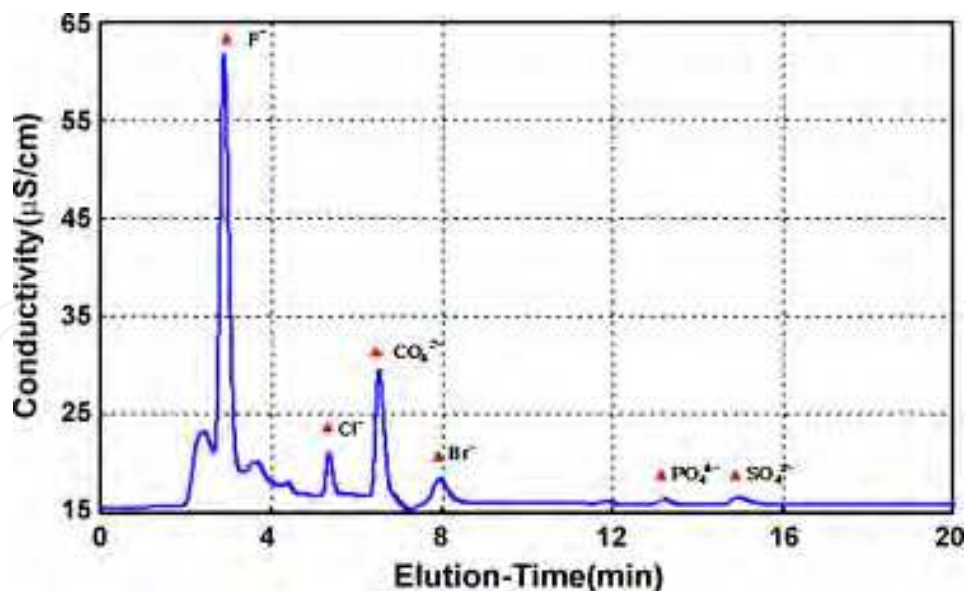
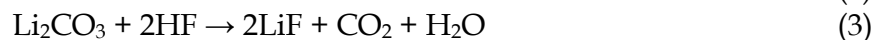


Fig. 11. Ion chromatography of the electrolyte added to distilled water, (Veluchamy et al., 2008).

These reactions will convert the rigid SEI layer into fragile one especially as liquid phase which could allow easy diffusion of the available organic solvent from the bulk into the surface of the oxide cathode. Now the oxidative reaction between the reactive cathode and

the solvent causes release of exothermic heat flow of low magnitude even at low temperature region near 100°C. This low heat pulse acts as a prelude for the large scale release of oxygen from the cathode to an eventual catastrophic exothermic reaction which accentuates damage to the cell, even causes explosion. This explanation may be compared with the experimental findings reported earlier that only highly charged batteries are prone to explosion during battery abuses (Doh et al 2008).

7. Conclusion

A. Results from abuse analysis

- I) The extent of cell deterioration or the resultant explosion depends on the quantity of charge/discharge current passing through the charged cell.
- II) At the instant the battery is abused the processes such as rise of joule heat, break down of SEI film, release of oxygen from cathode, oxidation of plated lithium over graphite anode takes place consecutively leading to combustion of organic molecule resulting in cell failure or explosion.
- III) The internal shorts such as nail penetration, impact and dendrite short could cause catastrophic damage to the cell compared to external short.
- IV) The extent of exothermic reaction is greater for (a) when $x \rightarrow 0$, in Li_xCoO_2 , (b) amount lithium plated over the graphite anode and (c) the quantity of organic electrolyte present in the cell.
- V) At higher cycles the lithium plated over graphite anode is higher than the intercalated lithium which causes the cell to experience greater heat energy released during battery abuse.
- VI) Even though binders are in close contact with lithium metal, lithium prefers to react with solvent rather than with binder.

B. State of the art

- I) The search for electrolyte additives to arrive non-degradable electrode-electrolyte interface film with cycling is to serve as an alternative one to SEI film for providing stability to the electrode materials.
- II) Additives to the electrolytes such as low resistant flame retardants, current interrupter materials and redox shuttles are expected to further reinforce safety of lithium ion batteries.
- III) Dopants to cathode materials and coatings to electrodes and electrode materials of cathodes and anodes are a noteworthy development and are expected to contribute further for the stability of electrodes.
- IV) Physical devices such as Positive temperature coefficient(PTC) and Negative temperature coefficient (NTC), developed may further has scope for improvement to check/monitor battery condition.
- V) Present activity on the development of non flammable electrolyte is expected to reach a mile-stone which will be a final solution for making electric vehicle a more safe.

C. Need of the Future

Heat dissipating pouch/metal container, state of charge monitor, thermally more stable cathodes, anode without dendrite or plating with cycles, non flammable electrolytes are some of the areas wherein the researchers will continue, to arrive a safe and ultimate lithium ion battery for use in electric vehicles, domestic utilities and also in emerging non-conventional energy sectors.

8. References

- Abe, K.; Ushigoe, Y.; Yoshitake, H & Yoshio, M. (2006). Functional Electrolytes: Novel type additives for cathode materials, providing high cycleability, *Journal of Power Sources*. Vol. 153, (July 2006) 328-335.
- Abraham, K. M.; Pasquariello, D. M. & Willstaedt, E. B. (1990). N-butylferrocene for overcharge protection of secondary lithium batteries, *Journal of The Electrochemical Society*, Vol. 137, No. 6, (June 1990) 1856-1857.
- Amatucci, G. G.; Tarascon, J. M. & Klein, L. C. (1996). Cobalt dissolution in LiCoO₂-based non-aqueous rechargeable batteries, *Solid State Ionics*, Vol. 83, No.1-2, (January 1996) 167-173.
- ANSI News and publications. New York, November 20, 2006.
- Aurbach, D.; Levi, M. D.; Levi, E.; Markovsky, B.; Salitra, G. & Teller. H. (1997). Batteries for Portable Applications and Electric vehicles, in: Holms, C. F.; Landgrebe, A. R.(Eds.),*The Electrochemical Society Proceedings Series*, PV 97-18, Pennington, NJ, 1997, P.941.
- Balakrishnan, P. G.; Ramesh, R. & Prem Kumar, T. (2006), Safety mechanisms in lithium ion battery, 15) *Journal of Power Sources*, 155 (February, 2006) 401- 414.
- Biensan, P.; Simson, B.; Peres, J. P.; Guibert, A. D.; Broussely, M.; Bodet, J. M.& Perton, F.(1999). On safety of lithium-ion cells, *Journal of Power Sources*, Vol. 81-82, (September 1999) 906-912.
- Blomgren, G. E.(2003). Liquid electrolytes for lithium and lithium-ion batteries. *Journal of Power Sources*, Vol. 119-121, (June 2003) 326-329.
- Cho, J. (2003). Improved thermal stability of LiCoO₂ by nanoparticle AlPO₄ coating with respect to spinel Li_{1.05}Mn_{1.95}O₄, *Electrochemistry Communications*, Vol. 5, No. 2, (February 2003) 146-148.
- Cho, J. (2004). Dependence of AlPO₄ coating thickness on overcharge behavior of LiCoO₂ cathode material at 1 and 2 C rates, *Journal of Power source*, Vol. 126, Issues 1-2, 16 (February 2004) 186-189.
- Chen, J.; Buhrmester, C. & Dahn. J. R (2005). Chemical Overcharge and Overdischarge Protection for Lithium ion Batteries, *Electrochem. Solid state letters*, Vol. 8, issue 1 (2005)A 59-A 62.
- Dahn, J. R. (2001) Lithium ion battery Tutorial and update: *Power 2001*, Anaheim, CA, September 30, 2001
- Dahn, J.R.; Fuller, E.W.; Obrovac, M. & Sacken, U. V. (1994). Thermal stability of Li_xCoO₂, Li_xNiO₂ and λ-MnO₂ and consequences for the safety of Li-ion cells, *Solid State Ionics*, Vol. 69, No. 3-4, (August, 1994) 265-270.

- Dedryvère, R.; Martinez, H.; Leroy, S.; Lemordant, D.; Bonhomme, F.; Biensan, P. & Gonbeau, D.(2007). Surface film formation on electrodes in a LiCoO₂/graphite cell, A step by step XPS study, *Journal of Power Sources*, Vol. 174, Issue 2, 6 (December 2007) 462-468.
- Doh, C. H.; Kim, D. H.; Kim, H. S.; Shin, H. M.; Jeong, Y.D.; Moon, S. I.; Jin, B. S.; Eom S. W.; Kim, H.S.; Kim, K.W.; Oh, D. H. & Veluchamy, A.(2008). Thermal and electrochemical behaviour of C/Li_xCoO₂ cell during safety test. *Journal of Power Sources*, Vol. 175, Issue 2, 10 (January 2008) 881-885
- Fouchard, D.; Xie,L.; Ebner,W.& Megahed,S. A.(1994). Rechargeable lithium and lithium ion (RCT) batteries in: Megahed, S. A. (Ed), *Electrochemical Society*. PV 94-28 Miami Beach, Florida, October 1994.
- Jang, Y-I.; Dudney, N.J.; Blom, D.A. & Allard, L. F. (2002). High-Voltage Cycling Behavior of Thin-Film LiCoO₂ Cathodes. *Journal of The Electrochemical Society*, 149 (2002) A1442-1447.
- Kim, J.; Kim, B.; Lee, J-G; Cho, J. & Park. B. (2005). Direct carbon-black coating on LiCoO₂ cathode using surfactant for high-density Li-ion cell, *Journal of Power Sources*, Vol. 139, No. 1-2, 4 (January 2005) 289-294
- Kim, J.; Noh, M.; Cho, J.; Kim, H. & Kim, K.B. (2005). Controlled Nanoparticle Metal Phosphate (Metal = Al, Fe, Ce, and Sr) coating on LiCoO₂ cathode materials. *Journal of The electrochemical society*, Vol. 152, No 6(2005) A1142- A1148.
- Kitoh, K. & Nemoto,H. (1999). 100 Wh Large size Li-ion batteries and safety tests, *Journal of Power Sources*. Vol. 81-82, (September 1999) 887-890.
- Lee, H.; Kim, M. G & Cho. J.(2007). Olivine LiCoPO₄ phase grown LiCoO₄ cathode material for high density Li batteries. *Electrochemistry communications*, Vol. 9, Issue 1, (January 2007), 149-154
- Leising, R. A.; Palazzo, M. J.; Takeuchi, E. S. & Takeuchi, K.J. (2001). Abuse testing of lithium-ion batteries characterization of the overcharge reaction of LiCoO₂/graphite cells, *Journal of The Electrochemical Society* (2001), 148(8), A838-A844.
- Leroy, S.; Martinez, H.; Dedryvère, R.; Lemordant, D.& Gonbeau, D. (2007). Influence of the lithium salt nature over the surface film formation on a graphite electrode in Li-ion batteries: An XPS study, *Applied surface science*, 253(2007) 4895-4905.
- Lin, H.-P.; Chua, D.; Salomon, M.; Shiao, H. C.; Hendrickson, M.; Plichta, E.& Slane, S. (2001), Low-Temperature Behavior of Li-Ion Cells, *Electrochemical and solid state letters*, Vol. 4, Issue 6, (April, 2001) A71-A73.
- Liu, X.; Kusawake, H. & Kuwajima, S. (2001). Preparation of a PVdF-HFP/polyethylene composite gel electrolyte with shutdown function for lithium-ion secondary battery, *Journal of Power Sources*, Vol. 97-98, (July 2001), 661-663.
- MacNeil, D. D. & Dahn, J. R. (2002). The reactions of Li_{0.5} CoO₂ with non aqueous Solvents at elevated temperature, *Journal of The electrochemical society*, Vol. 149, No. 7 (2002) A912-A919.
- MacNeil, D. D. & Dahn J.R. (2001). The Reaction of Charged Cathodes with Nonaqueous Solvents and Electrolytes, *Journal of The Electrochemical Society* 148 (11) A1205-A1210 (2001).

- Maleki, H.; Deng, G.; Anani, A. & Howard. (1999). Thermal stability studies of Li-ion cells and components. *Journal of The electrochemical society*, Vol. 146, Issue 9, (September, 1999) 3224-3229.
- Needham, S.A.; Wang, G.X.; Liu, H.K.; Drozd, V.A. & Liu, R.S. (2007). Synthesis and electrochemical performance of doped LiCoO₂ materials, *Journal of Power Sources*, Vol. 174, No. 2, 6 (December 2007) 828-831.
- Nozaki, H.; Nagaoka, K.; Hoshi, K.; Ohta, N. & Inagaki, M. (2009). Carbon-coated graphite for anode of lithium ion rechargeable batteries: Carbon coating conditions and precursors, *Journal of Power Sources*, Vol. 194, No. 1, (October 2009) 486-493.
- Oh, S.; Lee, J. K.; Byun, D.; Cho, W. & Cho, B. W. (2004). Effect of Al₂O₃ coating on electrochemical performance of LiCoO₂ as cathode materials for secondary lithium batteries. *Journal of Power Sources*, Vol. 132, No 1-2, 20 (May 2004) 249-255.
- Okutoh and Tadashi (2001). Battery protector having a positive temperature coefficient element, American patent No: 6177209. Publication on 01/23/2001.
- Ota, H.; Kominato, A.; Chun, W.; Yasukawa, E. & Kasuya, S. (2002) Extended abstract no. 201, in: Proceedings of the 11th International Meeting on Lithium batteries, Monterey, CA, 2002.
- Ota, H.; Akai, T.; Namita, H.; Yamaguchi, S. & Nomura, M. (2003). XAFS and TOF-SIMS analysis of SEI layers on electrodes, *Journal of Power Sources*, Vol. 119-121, 1 (June 2003) 567-571.
- Ota, H.; Kominato, A.; Chun, W.J.; Yasukawa, E.; Kasuya, S. (2003) Effect of cyclic phosphate additive in non-flammable electrolyte, *Journal of Power Sources*, Vol. 119-121, 1 (June 2003) 393-398.
- Oyama, N.; Fujimoto, Y.; Hatozaki, O.; Nakano, K.; Maruyama, K.; Yamaguchi, S.; Nishijima, K.; Iwase, Y.; Yoshikazu Kutsuwa (2009). New gel-type polyolefin electrolyte film for rechargeable lithium batteries, *Journal of Power Sources*, Volume 189, Issue 1, 1 (April 2009) 315-32.
- Plichta, E.; Salomon, M.; Slane, S.; Uchiyama, M.; Chua, D.; Ebner, W.B. & Lin, H.W. (1987). A rechargeable Li/Li_xCoO₂ Cell, *Journal of Power Sources*, Vol. 21, No. 1, (August 1987) 25-31.
- Richard, M. N. & Dahn, J.R. (1999). Accelerating rate Calorimetry Study on the Thermal Stability of Lithium Intercalated Graphite in Electrolyte, I Experimental, *J. Electrochemical Society*, Vol. 146, No. 6. (January, 1999) 2068-2077.
- Reimers, J. N. & Dahn, J. R. (1992) Electrochemical and *in situ* X-ray Diffraction Studies of Lithium intercalation in Li_xCoO₂, *Journal of The Electrochemical Society* Vol. 139, No. 8 (August 1992) 2091-2097.
- Saito, Y.; Kanari, K. & Takano, K. (2001). Thermal studies of a lithium-ion battery, *Journal of Power Sources*, Vol. 68, No. 2, (October 1997), 451-454.
- Saito, Y.; Takano, K. & Negishi, A. (2001). Thermal behaviors of lithium-ion cells during overcharge, *Journal of Power Sources*, Vol. 97-98, (July 2001) 693-696.
- Spotnitz, R. & Franklin. (2003). Abuse behavior of high-power, lithium-ion cells, *Journal of Power Sources*, Vol. 113, No. 1, 1 (January 2003) 81-100.

- Tobishima, S.; Takei, K.; Sakurai, Y. & Yamaki, J. (2000). Lithium ion cell safety, *Journal of Power Sources*, Vol. 90, No. 2, 1 (October 2000) 188-195.
- Tobishima, S.; Yamaki, J. (1999). A consideration of lithium cell safety, *Journal of Power Sources*, Vol. 81-82, (September 1999) 882-886.
- Underwriters laboratories, Inc., standard for Safety 1642- Lithium batteries (April 1995).
- Veluchamy, A.; Ikuta, H. & Wakihara, M. (2001). Boron-substituted manganese spinel oxide cathode for lithium ion battery, *Solid State Ionics*, Vol. 143, No. 2, 2 (June 2001) 161-171.
- Veluchamy, A.; Doh, C. H.; Kim, D. H.; Lee, J. H.; Shin, H. M.; Jin, B. S.; Kim, H. S.; Moon, S. I. (2009), Thermal analysis of Li_xCoO_2 cathode material of lithium ion battery, *Journal of Power Sources*, Vol. 189, No.1, 1 (April 2009) 855-858.
- Venugopal, G. (2001). Characterization of thermal cut-off mechanisms in prismatic lithium-ion batteries, *Journal of Power Sources*, Vol. 101, No 2, 15 (October 2001) 231-237.
- Venugopal, G; Moore, J.; Howard, J. & Pendalwar, S. (1999) Characterization of microporous separators for lithium-ion batteries, *Journal of Power Sources*, Vol. 77, No. 1, 1 (January 1999), 34-41.
- Wainwright, D. (1995) Method of evaluating relative safety of porous electrode/electrolyte combinations to spot heating, *Journal of Power Sources*, Vol. 54, Issue 2, (April 1995) 192-197
- Wang, Y.; Guo, X.; Greenbaum, S.; Liu, J.; & Amine, K. (2001). Solid Electrolyte Interphase Formation on Lithium-Ion Electrodes: A ^7Li Nuclear Magnetic Resonance Study. *Electrochem. Solid-State Lett.*, Vol. 4, No. 6, (April, 2001) A68-A70..
- Wang, X.; Yasukuwa, E & Kasuya, S. (2001). Nonflammable Trimethyl Phosphate Solvent-Containing Electrolytes for lithium ion batteries-I. Fundamental Properties. *Journal of The Electrochemical Society*, Vol. 148. No. 10, (October 2001), A1058-41065.
- Wu, M. S.; Chiang, P.J.; Lin, J. C. & Jan. Y. S. (2004), Correlation between electrochemical characteristics and thermal stability of advanced lithium-ion batteries in abuse tests – short-circuit tests, *Electrochimica Acta*, Vol 49, No. 11, 30 (April 2004), 1803-1812
- Xiang, H.F.; Jin, Q.Y.; Chen, C.H.; Ge, X.W.; Guo, S. & Sun, J. H. (2007). Dimethyl methylphosphonate-based nonflammable electrolyte and high safety lithium-ion batteries, *Journal Power Sources*, 174(1) (2007) 335-341.
- Xiang, H.F.; Xu, H.Y.; Wang, Z.Z. & Chen C.H. (2007). Dimethyl methyl phosphonate (DMMP) as an efficient flame retardant additive for the lithium-ion battery electrolytes, *Journal of Power Sources*, 173(1) (2007) 562-564.
- Yamaki, J.; Baba, Y.; Katayama, N.; Takatsuji, H.; Egashira, M & Okada, S. (2003). Thermal stability of electrolytes with Li_xCoO_2 cathode or lithiated carbon anode. *Journal of Power Sources*, Vol. 119-121, 1 (June 2003), 789-793.
- Yoshino, A. (2001), in: *Proceedings of the 3th Hawaii battery conference*, ARAD Enterprises, Hilo, HI, 3 January 2001, p. 449.
- Yoshino, A. (2002) in: *Proceedings of the 4th Hawaii battery conference*, ARAD Enterprises, Hilo, HI 8 January 2002, p. 102.
- Zhang, Z.; Fouchard, D & Rea, J.R. (1998), Differential scanning calorimetry material studies: Implications for the safety of lithium-ion cells. *Journal of Power Sources*, Vol. 70, No. 1, 30 (January 1998), 16-20
- Zheng, T.; Gozdz, A.S. & Amatucci, G.G. (1999) Reactivity of the solid electrolyte interface on carbon electrodes at elevated temperatures, *Journal of The Electrochemical Society*, 146(11) (1999) 4014-4018.



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