Quality Decision for Overcharged Li Ion Battery from reliability and safety perspective

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Abstract

During charging of Lithium-ion battery (LiB), the charging cut-off voltage (COV) may exceed the manufacturers’ specification because of incorrect monitoring of the charging control circuit, either due to the ageing of the control circuit or the design/manufacturing errors of the control circuit. In fact, it is found that overcharging LiB cell is a common abuse. This work shows the effect of excessive COV on cell’s discharging ability, and the use of a novel non-destructive method to evaluate if the damage made in the cell by the excessive COV is rendering the cell from further safe usage or it is still acceptable with minor degradation in reliability and safety, thus providing a basis for quality consideration of the cell. The method also enables battery manufacturers to identify the internal components for their cells that are most vulnerable to the excessive COV so that quality improvement of their batteries can be designed and produced. This method also alerts electric vehicles user on the hidden safety issues of their battery pack, and enables battery management system to perform reliability balancing, a new patented technique to ensure the safe and reliable operation of battery pack.

Keywords
Lithium ion battery, Electrochemistry based electrical model, overcharge, battery safety, reliability balancing

1. Introduction

Rechargeable Lithium-ion battery (LiB) has been widely used in mobile phones, and notebook computers due to its high energy densities, high power densities, long cycle life and safe operation. It is also an enabler that makes pure electric and hybrid electric vehicles a reality [1].

However, several abusive conditions can happen to a LiB cell during its operation, and overcharge is considered as a common abuse that may lead to its severe degradation and even catastrophic failure via thermal runaway and subsequent fire hazard with possible explosion in extreme cases as reported [2]. This becomes a primary concern for battery users, and hence a non-destructive method is required to access the damaging effect of the overcharging in order to decide if one should change the cell from the reliability and safety perspective. From battery manufacturers point of view, if one can identify the internal components in a cell that are most vulnerable to excessive cut-off voltage COV, they can improve their cells so as to make the cell more robust against this abuse. Unfortunately, such a method is not available in the market.

With the recent development of electrochemistry based electrical (ECBE) model [3], the degradation of each individual components inside a cell can be determined through its discharging
curve (i.e. terminal voltage vs time during discharging) alone. In this work, we use the ECBE method to examine the effect of excessive COV on the degradation of each component experimentally.

Fig. 1a) shows the ECBE model and the physical meaning of each components as shown in Fig.1 b) where $R_e$ is the ohmic resistance of electrodes, $C_{dl}$ is the double layer capacitance, $R_{ct}$ is the total charge transfer resistances at the electrodes, $K$ is the charge transfer rate constant at the electrode embedded in the Butler-Volmer impedance ($Z_{BV}$), and $R_n$ and $C_w$ are the Warburg element in the electrolyte.

![ECBE model diagram](image1)

**Fig. 1 a) electrochemistry based electrical (ECBE) model [3]**

![Physical parts diagram](image2)

**Fig. 1 b) Real physical parts of the inner battery represented by ECBE model parameters**

### 2. Experiments

In this work, the discharging curves of LiB cells are obtained experimentally. LiB coin cells (LIR2032) rated ~44mAh as shown in Fig. 2 are used for experiments. The electrodes materials are graphite anode and lithium cobalt oxide (LCO) cathode, and it is the most commonly used cathode material in commercial LiB [4].
Fig. 2 the coin cell (LIR2032) used in this work.

Arbin Instruments battery cycler is used for the overcharging experiments, and the set-up for experiments in this work is programmed as follows [5]:

- All fresh battery cells are firstly discharged to a cut-off voltage of 2.75V.
- They are then charged abusively at C/4-rate (i.e. 11mA) to COV between 4.2V and 4.9V (specification of max COV is 4.2)
- They are rested for 160s after charging for the their overvoltage stabilization
- For the discharging experiments, they were discharged at a constant current of C/4 to a COV of 2.75V at constant room temperature of 23°C unless otherwise stated.
- The terminal voltages and charging/discharging currents of the entire tested cells are continuously monitored and recorded at every 20 seconds interval.

3. Results and analysis

Fig. 3 shows the discharging curves of the LiB cells after excessive COV. From the discharging curves, we can see that the higher the COV, the longer the discharging time to reach 2.75V, expect when the COV is above 4.7V. The rates of change of the terminal voltages for all cases are almost the same. Thus, this may indicated a benefit of having higher COV as cell can be used for longer time per charging.

Fig. 3 Discharging curves of LIR2032 cells subjected to different charge cut-off voltages (COV).

However, it is reported that when cell is overcharged at excessive COV, it is indeed stressed, and its life will be reduced, and both the cell reliability and safety are compromised [6]. As LiB cells use volatile and flammable organic electrolytes, irreversible decomposition of the electrolyte may occur and this will trigger the gas evolution reaction at high COV, and leads the continuously swell and rupture of the cells eventually. The overcharged cell behaves as a resistor at high voltages, dissipating excess energy as heat. The locally accumulated heat due to increasing of cell resistance as a result of
degradation at electrodes, leading to the catastrophic failure such as fire hazard and possible explosion of battery by thermal runaway at extreme conditions [5, 7-9]. These accidents resulted from the extreme COV as shown in Fig. 4. This is attributed to the following degradation of the internal components in the LiB cells as revealed by our ECBE method as follows.

![Accidents caused by extreme overcharging abuse](image)

**Fig. 4** The accidents caused by extreme overcharging abuse

Fig. 5 shows that the maximum initial capacity of a cell increase with COV, and this explains the observed “enhanced” runtime of the discharging curves with higher COV as observed in Fig. 3. This increase is a result of more lithium ions are extracted from electrode due to overcharging.

![Graph showing maximum initial capacity vs. excessive COV](image)

**Fig. 5** Maximum initial capacity vs. excessive COV.

The \( m_1 \) and \( m_2 \) represent efficiencies of anode and cathode in providing their stored Li ion for discharging respectively. The decrease in \( m_1 \) with excessive COV can be seen in Fig. 6, and this implies that anode electrode is degraded when COV is excessive. However, the performance of the graphite electrode is insignificant against excessive COV as seen in Fig. 7. Here we have to take note that graphite electrode is anode during charging, and as our results are extracted from discharging curve, the anode mentioned from the extraction using ECBE is referred to the LCO electrode.
The sum of ohmic resistance of electrode and charge transfer resistance decreases with COV and then increases for COV above 4.3 as shown in Fig. 8. While the chemical kinetic explanation of the phenomena is beyond the scope of this work, the increase of Re+Rct increases the localized heating of the anode due to Joule heating. Thus the localized temperature of anode is expected to be higher for higher COV above 4.3 V, and this could explain the degradation observed in anode as in Fig. 6. This localized high temperature at anode could also be one of the reasons for higher Qm as the chemical reaction rate is going to be higher at higher temperature according to the Arrhenius relation.

As COV is further increased to beyond 4.5V, the localized high temperature can become so high that dissociation of the electrolyte next to electrode occurs, and the formation of solid electrolyte interface (SEI) is enhanced (this is also reflected as an increase in Rct). The much higher localized temperature at the electrode is also evidenced by the higher rate of increase in Qm with respect to COV when COV is above 4.5V. With formation of thicker SEI, the charge transfer at the electrode will be retarded, and hence one can see a sharp decrease in K values as shown in Fig. 9 when COV is above 4.5V. This thick SEI also tends to protect the anode from the electrolyte and thus its degradation stop when COV is above 4.5V as shown in Fig. 6. However, with thicker SEI, most part of the charging voltage will be dropped across the SEI, and the electric field in the SEI can become too high at COV above 4.5V which causes it to breakdown, trigger the full cell thermal runaway [10]. It is to be noted that the above degradation happen with only one excessive COV charging. One could expect that with continuous excessive COV charging, the electrode resistance will increase continuously, and the localized temperature at anode will continue to increase. While we enjoy the seemingly longer runtime with higher COV, the cell reliability is degrading, and at some point in time, the high localized temperature can trigger some safety issue. In a mild case, we will see a swelling of the Li Ion cell in our hand phones due to larger thermal expansion, but in a severe case, fire and explosion can occur as have been observed in electric vehicles incident [11].

As our method can provide real time on-line non-destructive assessment of the internal components in a Li Ion cell, battery manufacturers can identify the weakest components that are most vulnerable to the excessive COV. This method can also be incorporated into battery management.
system (BMS) and once a cell is in an unsafe situation as defined by the Re+Rct, a bypass of the cell can be initiated according to the new technology of reliability balancing developed recently [12]. Thus our method enables both battery manufacturers and BMS producers to improve their products quality over time and safety.

![Graph showing Re+Rct vs. Overcharging Terminal Voltage](image1)

**Fig. 8** The sum of ohmic resistance of electrode and charge transfer resistance vs. excessive COV.

![Graph showing k vs. Overcharging Terminal Voltage](image2)

**Fig. 9** Charge transfer rate constant vs. excessive COV.

**4. Conclusion**

**4.1 Achievement**

We have successful identify the seeming gain of Li Ion cell by having it to charge with high COV, and reveal the hidden issues associated with charging the cell with high COV, with the use of recently developed ECBE battery model. Therefore the misconception of higher COV to enhance the runtime is clarified. With our method, we are able to provide real time on-line non-destructive assessment of the internal components in a Li Ion cell to evaluate its reliability and safety with respect to this overcharging abuse. We are able to characterize the degradation level of each internal electrochemical component in LiB and consequently identify the weakest material that is most vulnerable to the excessive COV. This will be beneficial for battery manufacturers to design and produce more robust cells against overcharging. Our method can also be incorporated into existing battery management system so that a more advanced safety technology to ensure safe operation of the battery pack with enhanced system reliability can be possible.
4.2 Acknowledgement

The authors would like to acknowledge the support from Nanyang Technological University, School of Materials Science and Engineering and Research Institute at Nanyang (ERIAN) in providing testing facilities.

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Authors’ Biographical Notes

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Prof. Cher Ming Tan (M’83–SM’06) received his Ph.D in Electrical Engineering from the University of Toronto in 1992. He has 10 years of working experiences in reliability in electronic industry (both Singapore and Taiwan) before joining Nanyang Technological University (NTU) as faculty member in
1996 till now. He has published more than 260 International Journal and Conference papers, and holding 8 patents and 1 copyright for reliability software. He has given more than 20 invited talks in International Conferences. He has written 3 books and 3 book chapters in the field of reliability. He is also the Series Editor of SpringerBrief in Reliability. He is the past chair of IEEE Singapore Section, Senior member of IEEE and ASQ, Distinguish Lecturer of IEEE Electronic Device Society on reliability, Founding Chair of IEEE Nanotechnology Chapter - Singapore Section, Fellow of Institute of Engineers, Singapore, Fellow of Singapore Quality Institute, Education Chair of Singapore Quality Institute, Director of SIMTech-NTU Reliability Lab, and Senior Scientist in SIMTech. He is an Editor of IEEE TDMR. Editorial Advisory Board of Microelectronics Reliability, Associated Editor of International Journal on Computing, and Guest Editor of International J. of Nanotechnology, Nano-research letter etc. His research interests include reliability and failure physics modeling of electronic components and systems, finite element modeling of materials degradation, statistical modeling of engineering systems, nano-materials and devices reliability, and prognosis & health management of engineering system.

Prof. Rachid Yazami is a Professor in the School of Materials Science & Engineering at the Nanyang Technological University, Singapore, on leave from the French National Center for Scientific Research (CNRS) where he has held a Research Director position since 1985. Prof. Yazami spent 10 years at the California Institute of Technology (Caltech) where he co-founded a CNRS-Caltech joint laboratory on materials science for energy storage applications, including in lithium ion batteries and in hydrogen storage. Prof. Yazami is the author of over 200 published scientific papers, book chapters and reports. He is the inventor involved in over 50 patents related to battery technology. In 1980 while starting his Ph. D. research at the Grenoble National Polytechnic Institute (INPG), Prof. Yazami invented the graphite anode (negative electrode) used in the 3-billion lithium ion batteries produced in 2010. This discovery was the turning point in rechargeable lithium battery technology. In the mid-80s Prof. Yazami contributed to a new graphite fluoride cathode invention, which after further research led him to start a company (Contour Energy Systems, Inc.) in Azusa, California. The company commercializes high performance primary lithium batteries and carries out R&D on rechargeable fluoride ion batteries discovered by Prof. Yazami. In addition to materials science research, Prof. Yazami’s interest focused recently on battery safety and life extension. He developed a technology based on thermodynamics measurements being used to accurately assess the state of health and the state of charge of batteries. This technology is licensed by Caltech to a new start up company founded by Prof. Yazami in Singapore, KVI LTP, LTD and addresses mobile electronics and electric vehicles markets for the most.

Dr. Kenza Maher is Research Fellow and Project Leader at Joint Future Mobility Research Lab with BMW Group and Nanyang University, and TUM CREATE Center for Electromobility, Singapore. Dr Kenza Maher received her PhD from Cadi Ayyad University (Marrakech, Morocco) in January 2011. Her PhD focused on development of new phosphates for high energy lithium-ion batteries. After her PhD, she joined the Energy Research Institute @ Nanyang Technological University (ERI@N, Singapore) as Research Fellow for 1year and 4months; she worked on the development of a new method to analyze the commercial Li-ion batteries to determine their state of health (SOH) based on the entropy and enthalpy profiles. Her research focuses on Electrochemistry, Thermodynamics and Safety of Li-ion Batteries using Electrochemical Thermodynamic Measurement System (ETMS), Electrochemical Impedance Spectroscopy (EIS) and Accelerating rate calorimetry (ARC). She is working on determination of Li-ion batteries SOC, SOH and SOS.

Mr. Robert Wang is software engineer ShowBox Pte.Ltd and CTO of Innovation and Reliability Solution Pte.Ltd. He graduated from NTU with M. Science Degree. His interest is mainly in web development, mobile apps development, computational methods and large server operation.