Eurasian Chemico-Technological Journal 15 (2013) 301-305

Charge and Discharge Behaviour of Li-Ion Batteries at Various Temperatures Containing $LiCoO_2$ Nanostructured Cathode Produced by CCSO

Y.Y. Mamyrbayeva[1,2], R.E. Beissenov[3], M.A. Hobosyan[1], S.E. Kumekov[2], and K.S. Martirosyan[1*]

[1]University of Texas at Brownsville, Department of Physics and Astronomy, Brownsville, TX, USA
[2]Kazakh National Technical University named after K.I. Satpaev, Almaty, Kazakhstan
[3]al-Farabi Kazakh National University, Almaty, Kazakhstan

Abstract

There are technical barriers for penetration market requesting rechargeable lithium-ion battery packs for portable devices that operate in extreme hot and cold environments. Many portable electronics are used in very cold (-40 °C) environments, and many medical devices need batteries that operate at high temperatures. Conventional Li-ion batteries start to suffer as the temperature drops below 0 °C and the internal impedance of the battery increases. Battery capacity also reduced during the higher/lower temperatures. The present work describes the laboratory made lithium ion battery behaviour features at different operation temperatures. The pouch-type battery was prepared by exploiting $LiCoO_2$ cathode material synthesized by novel synthetic approach referred as Carbon Combustion Synthesis of Oxides (CCSO). The main goal of this paper focuses on evaluation of the efficiency of positive electrode produced by CCSO method. Performance studies of battery showed that the capacity fade of pouch type battery increases with increase in temperature. The experimental results demonstrate the dramatic effects on cell self-heating upon electrochemical performance. The study involves an extensive analysis of discharge and charge characteristics of battery at each temperature following 30 cycles. After 10 cycles, the battery cycled at RT and 45 °C showed, the capacity fade of 20% and 25% respectively. The discharge capacity for the battery cycled at 25 °C was found to be higher when compared with the battery cycled at 0 °C and 45 °C. The capacity of the battery also decreases when cycling at low temperatures. It was important time to charge the battery was only 2.5 hours to obtain identical nominal capacity under the charging protocol. The decrease capability of battery cycled at high temperature can be explained with secondary active material loss dominating the other losses.

Introduction

Over the past 20 years, rechargeable (also known as secondary) lithium-ion battery technologies have evolved, providing increasingly greater energy density, greater energy per volume, longer cycle life, and improved reliability. Commercial lithium-ion batteries now are powering a wide range of electrical and electronic devices like as consumer electronics, telecommunication and biomedical devices, industrial equipment and automotive application. The worldwide market for lithium batteries is projected to reach nearly $10 billion (USD) in annual sales by 2014, with the market for lithium-ion batteries representing almost 86-percent of those sales ($8.6 billion) [1]. A large market penetration of hybrid electric vehicles and pure electric vehicles require overcoming number of technical barriers for Li-ion batteries.

One of the important issues is the significantly reduced energy and power capabilities of lithium-ion batteries due to unwanted chemical or physical changes during the battery operation. Another problem is the loss of the active materials when batteries operate at low or high temperatures [2]. These changes are usually irreversible and they affect the electrical performance of the electrochemical cells. Battery performance declines over the time whether the battery is used or not. As such, failure (in either performance or safety) can be caused by poor execution of a design, or an unexpected use or abuse of a product. Battery manufacturers of battery-powered products usually design and produce products to deliver specified performance characteristics in a safe manner under expected usage conditions.

Currently, the passive and active safeguards are used for batteries that give an opportunity to mitigate

* Corresponding author. E-mail: karen.martirosyan@utb.edu

some failures. However, major challenges in performance and safety still exist, including the thermal stability of active materials within the battery at high temperatures and the occurrence of internal short circuits that may lead to thermal runaway. Commercially rechargeable batteries operate under a realistically wide temperature range. This, however, does not automatically permit charge/discharge under these same temperature extremes. While operating batteries under hot or cold conditions cannot always be avoided, it is necessary to have some control over charge/discharge process [3]. Efforts must be made to charge and discharge the batteries at moderate temperatures. For safe use of Li-ion batteries in electronic devices, it is critical to study their performance at temperatures higher than room temperature. Increasing temperature accelerates the degradation of the battery materials, which causes a decline in capacity. Also, raising the temperature one might cause the onset of thermal runaway to occur, where the battery temperature increase dramatically as a result of reactions at the electrode interface that is exothermic in nature.

There are also safety concerns when using lithium-ion batteries at high temperatures, especially in cells containing cobalt or nickel electrodes [4]. Lithium ion batteries that utilize $LiCoO_2$ as the cathode material are widely used. However, there is a great deal of ongoing research with the aim of improving the performance of this material. The utilization of nano-structured cathode materials has become a very useful method to overcome the problem. It is not only enhancing the rate performance of the batteries but also usually extends the electrochemical activity. The utilization of nano-structured electrode materials leads to improvement of the performance of lithium-ion batteries by reducing diffusion path length for Li^+ ions and electron transport compared to micron-sized particles. There is an increased contact area between the electrode and the electrolyte that leads to better charge and discharge rates. The volume changes originating from Li^+ insertion/desertion will be better accommodated by nano-materials compared to bulk materials due to faster stress relaxation, which can extend the battery cycle life [4].

In this report we explore a novel method referred as Carbon Combustion Synthesis of Oxides (CCSO) to rapidly produce high-purity, nanoscale powders of lithium cobaltate ($LiCoO_2$). CCSO is a novel simple, economical, and energy-efficient technology for the production of micro- and nanostructured particles of complex oxides for advanced device applications and was recently patented by Martirosyan and Luss [5-10]. In CCSO, the exothermic oxidation of carbon nanoparticles generates a steep thermal reaction wave that propagates through the solid reactant mixture converting it to the desired complex oxide product. It is a modified form of Self-propagating High temperature Synthesis (SHS) [11] that uses nanostructured carbon as the fuel instead of a pure metal. In this method, the exothermic oxidation of carbon nanoparticles with an average size of 5 nm (surface area of 80 m^2/g) generates a self-propagating thermal wave with maximum temperatures of up to 900 ºC. The overriding objective of the present work is to estimate the permissible temperature limits to Li-ion battery consisting of positive electrode synthesized by CCSO.

Experimental

The crystalline $LiCoO_2$ nanoparticles were synthesized by carbon combustion synthesis of oxide according Ref [12]. Lithium cobalt oxide-based nano-composite positive electrodes were prepared consisting of the active powder material (93.5 wt.%), carbon black (4 wt.% as the conductor) and polyvinylidene fluoride (PVDF, <1 μm, Sigma Aldrich). The mixed powders were dissolved in N-methyl pyrrolidone (NMP, MTI Company) used as the binder agent (2.5 wt.%). After all components were mixed thoroughly, the cast was coated on an aluminium foil substrate. Afterward, the coating was followed by pressing and drying at 120 °C for 12 h under a vacuum. Then it was assembled in glove box (under nitrogen environment) using separator membrane with special type of polyethylene: thickness 16~25 μm, surface density 10~14 g/m^2, porosity 36-44%, pore size 0.03 μm, penetration strength 0.5~0.65 kg/mm, with shut-off temperature ~133 ºC. $LiPF_6$ with electrical conductivity of 10.5±0.5 ms/cm at 25 ºC (MTI Company) was used as electrolyte for electrochemical cell. Figure 1 shows the assembly steps of laboratory made Li-ion rechargeable battery.

The charge-discharge cycling studies were done for custom laboratory made Li-ion battery with esteemed capacity of 200 mA/h. For charging/discharging the battery, the conventional constant current – constant voltage (CC-CV) protocol was adopted. A direct current of 100 mA is used to charge the battery during constant current part and the cut off voltage was set to be 4.2 V. Subsequently the voltage was held constant at 4.2 V until the current dropped to 50 mA. Using this protocol, the battery could be completely charged to obtain nominal capacity. Charge-discharge studies were carried out in the potential range of 2.7-4.2 V. The 8- Channel Battery Analyzer for R&D Battery Materials - BST8-WA was used for all cycling studies. The battery was cycled at three different temperatures. The temperatures chosen were 0 ºC, room temperature (RT) 25 ºC and 45 ºC. The battery was cycled continuously up to 30 cycles. First 10 cycles were chosen to study the battery performance.

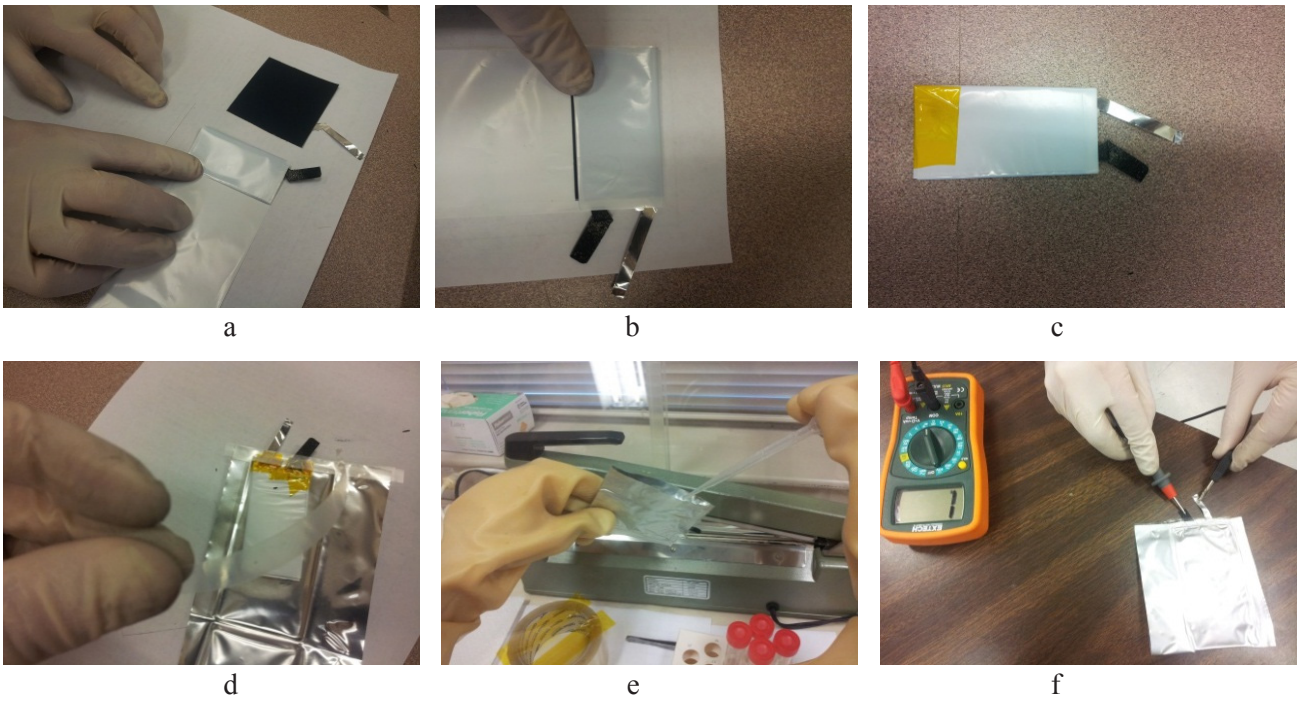

Fig. 1. The assembly of laboratory made Li-ion rechargeable battery: (a) separating the anode and cathode substrates by separator film; (b) firmly stacking the anode and cathode substrates between separator film; (c) the inner working cell of battery; (d) isolating the inner cell by laminated aluminum foil; (e) injecting the electrolyte under inert atmosphere in glove-box; (f) testing the battery for inner circuits before sending for electro-chemical charge-discharge characterization.

Results and Discussion

Figure 2a illustrates the pouch-type battery consisting the $LiCoO_2$ nano-composite powder producing by CCSO process. In the first stage, the battery was charged with 150 mA constant current mode until the voltage raised to 4.2 V. At this point, the charging mode shifted to 4.2 V constant voltage charging mode and charging continued until the current dropped to the 10% of initial value (15 mA). After charging, the battery was relaxated for 1 min and then the constant current discharge with 50 mA was applied until the voltage dropped to the cutoff value of 2.7 V. The decreasing tendency of charge-dischgarge time of one cycle is indicating that the battery capacitance is also decreasing because initially more Li ions could pass from cathode to anode and vice versa, but after several cycles not all ions are returning to their initial positions and therefore the capacitance is dropping over many cycles, which is a known factor for the rechargeable batteries.

The efficiency of battery is indicating how complete was performed the current cycle run compared to the previous cycle. Thus, the efficiency of less than 100% is indicating that the cycle under consideration showed less capacity compared to previous cycle, whereas efficiency more than 100% is showing that the current run was demonstrating better capacity value than the previous cycle. The small deviations around 100% of efficiency is showing that the cycles showed substantial consistency over 30 cycles. The specific capacity had initial value of 200 mAh/g and after 30 cycles the capacity dropped to almost 180 mAh/g showing that over 90% of initial capacity is preserved over continuous charge-discharge series as can see from Fig. 2b. This result is confirming that CCSO synthesized ultrafine $LiCoO_2$ has stable structure and gives opportunity to extract more than 66% of theoretical capacitance (200 mAh/g form theoretical value of 300 mAh/g).

In order to study the multiple charging-discharging influence on the performance of Li-ion battery made with the synthesized $LiCoO_2$ as cathode material, the battery was tested over 30 cycles at different temperatures and the current, voltage, capacity and charging-discharging efficiency curves were monitored during the measurement process. The battery was discharged using a constant current of 100 mA until the battery potential reached the cut-off value of 2.7 V. The constant current 100 mA was used to charge the battery until the battery voltage reached 4.2 V followed by constant voltage charging until the charging current decrease to 50 mA.

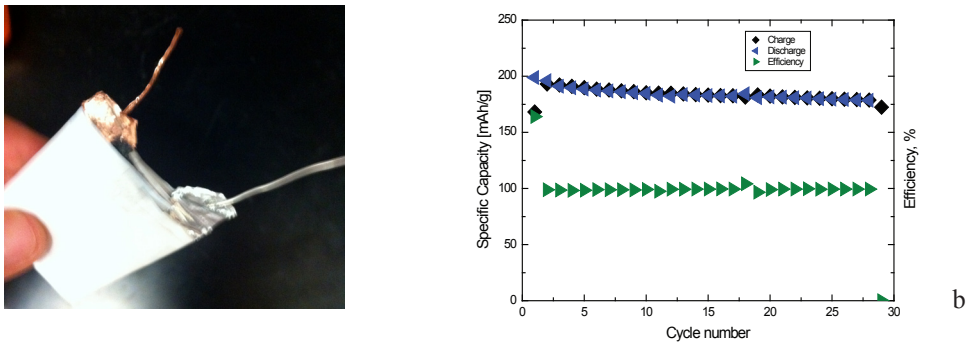

Fig. 2. (a) Laboratory made pouch-type battery; and (b) Galvanostatic cycle life of the $LiCoO_2$ positive electrode.

Figure 3a presents the capacity fade of the battery when cycled at different temperatures. The discharge capacity for the battery cycled at 25 °C was found to be higher when compared with the battery cycled at 0 °C and 45 °C. For the first 10 cycles, the battery cycled at 0 °C and 45 °C showed similar variation in capacity loss with cycling. The battery cycled at RT and 45 °C showed after 10 cycles, a capacity fade of 20% and 25% respectively. From first cycle the voltage plateau remains almost identical for all temperatures. The drop in the battery voltage during the beginning of discharge was found to be slightly higher for the battery at RT, whereas for all other temperatures this initial drop was almost the same.

As shown in Fig. 3b after 10 cycles a large voltage drop observed for battery discharged at 0 °C. The voltage drop during discharge decreases the energy of the battery drastically. To cycle the battery at RT the duration of the total charging time during 2 cycles was approximately 2 hours. For battery cycled at 0 °C the total charging time during first 2 cycling was significantly lower when compared to the total time estimating for battery cycled at other temperatures. It is generally believed that the poor performance of Li-ion cells at low temperatures are associated with reduced electrolyte conductivity, sluggish kinetics of charge transfer, increased resistance of solid electrolyte interphase, and slow Li diffusion through the surface layers and through the bulk of active material particles. It was necessary to charge the battery only 2.5 hours to obtain identical nominal capacity under the same charging protocol.

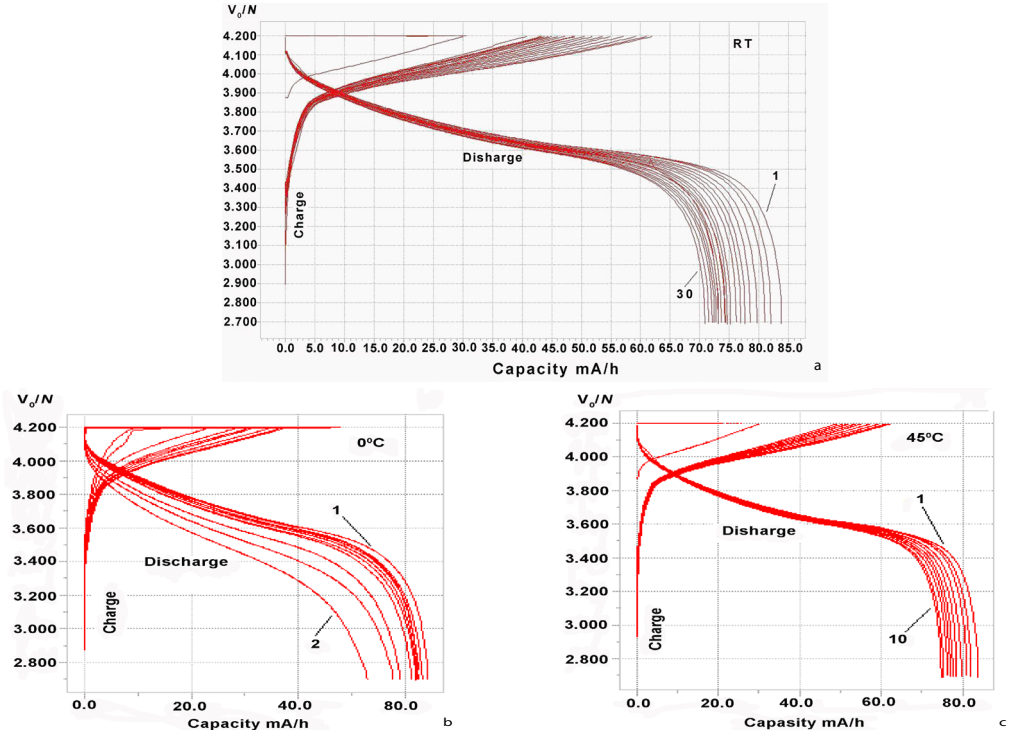

Fig. 3. Charge-discharge curves of Li-ion battery $LiCoO_2$ based of positive electrode synthesised by carbon combustion synthesis measured at different temperatures: a – room temperature; b – 0 °C; and c – 45 °C.

The battery cycled at higher temperature 45 °C (Fig. 3c) showed better performance for the first 10 cycles. The total energy of a battery during complete charge or complete discharge can be estimated by summation of the product of the battery voltage, current (during charge or discharge) and the time of charge/discharge. The charge-dischgarge time during the cycling decreases that indicating that the battery capacitance is also decreasing because initially more Li ions could pass from cathode to anode and vice versa, but after several cycles not all ions are returning to their initial positions and therefore the capacitance is dropping over many cycles, which is a known factor for the rechargeable batteries.

Conclusion

CCSO is an attractive method to produce $LiCoO_2$ based materials that can be used as Li-ion battery positive electrode with improved electrochemical performance. The custom-build pouch type Li-ion battery was made with rated capacity of 200 mA/h and tested up to 12 months period. After along preserving time the battery was showing capacity fade upon cycling at the different temperatures (RT, 0 °C, 45 °C). It was found that efficiency of battery is decreasing with increasing the temperature. The capacity of the battery also decreases when cycling at low temperatures.

Acknowledgments

We would like to acknowledge the financial support of this research by the NSF, grant 0933140, USA.

References

1. Lithium Ion Batteries Outlook and Alternative Energy Vehicles (Hevs, Phevs, Evs)-Technologies, Markets, Competitors and Opportunities: 2010-2020 Analysis and Forecasts Market-Research.com, Rockville, MD (2010).
2. Yan Ji, Yancheng Zhang, and Chao-Yang Wang, J. Electrochem. Soc. 160 (4) (2013) A636-A649.
3. D. Linden, Handbook of Batteries, McGraw-Hill, New York, (1995).
4. Y. Abu-Lebdeh, Nanotechnology for Li-ion batteries, Springer, (2013).
5. K.S. Martirosyan and D. Luss, AIChE J., 51 (10) (2005) 2801-2810.
6. K.S. Martirosyan and D. Luss, Carbon combustion synthesis of oxides, US Patent # 7,897,135, (2011).
7. A. Markov, I. Filimonov, and K.S. Martirosyan, J. of Computational Physics, 231 (2012) 6714-6724.
8. K.S. Martirosyan and D. Luss, Ind. Eng. Chem. Res., 46 (2007)1492-1499.
9. K.S. Martirosyan, M. Iliev, and D. Luss, Int. J. SHS, 16 (2007) 36-45.
10. K.S. Martirosyan, L. Chang, J. Rantschler, S. Khizroev, D. Luss and D. Litvinov, IEEE Transactions on Magnetics, 43 (6) (2007) 3118-3120.
11. A.G. Merzhanov, J. Mater. Chem. 14 (12) (2004) 1979-1791.
12. Y. Mamyrbaeva, M.A. Hobosyan, S.E. Kumekov, K.S. Martirosyan, Carbon Combustion Synthesis of Lithium Cobaltate, NSTI-Nano-Tech, 2 (2013) 657-659.

Received 23 July 2013