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Factors responsible for impedance rise in high power lithium ion batteries

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Abstract

High-power, 18,650 lithium-ion cells have been designed and fabricated in order to understand the factors limiting the calendar life of the lithium-ion system. Each cell consisted of a $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive electrode, a blend of MCMB-6 and SFG-6 carbon negative electrode, and a LiPF_6 in EC:DEC (1:1) electrolyte. These cells, which initially meet the power requirement set by the partnership for a new generation of vehicles (PNGV), were subjected to accelerated calendar life and cycle life testing. After testing at elevated temperatures, the cells experienced a significant impedance rise and loss of power. The fade rate of power in these cells was dependent of the state of charge and the temperature of testing. Micro-reference electrode and ac-impedance studies on symmetrical cells have confirmed that the interfacial resistance at the positive electrode was the main reason behind the impedance rise in the high power cell. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: High power cell; ac-Impedance; Charge-transfer resistance; Reference electrode; Symmetrical cell

1. Introduction

Lithium-ion batteries have been proven to meet and even exceed the high power goals set by the partnership for a new generation of vehicles (PNGV). However, one of the major challenges, which prevents this technology from being used as an energy storage system for hybrid vehicles, is its short calendar life. At the moment, the lithium-ion technology has a 3- to 5-year calendar life, which is far shorter than the 10 years required by the PNGV. To support the PNGV's industrial partners, the US Department of Energy has created a program referred to as the "Advanced Technology Development Program". The Argonne National Laboratory (ANL) is leading this program with participation from four other national laboratories, Lawrence Berkeley National Laboratory, Brookhaven National Laboratory, Sandia National Laboratories, and Idaho National Engineering and Environmental Laboratory. One of the main goals of this program is to utilize a variety of diagnostic tool to identify the main causes responsible for calendar life limitation in the high power lithium ion system; and to propose potential solutions that can lead to meeting the 10-year life requirement. The end-of-life of the high-power cell is caused by power fade associated with an impedance rise [1–3]

rather than a capacity fade. The latter is the typical cause of end-of-life for high-energy cells [4]. Two related and complementary techniques, micro-reference electrode and ac-impedance using symmetrical cells [5], were used to determine which cell component is mainly responsible for the cell impedance rise during accelerated calendar life testing.

2. Experimental

Several hundred 18,650 high power cells, were fabricated by a battery manufacturer using a high power design with multi-tab configuration. These cells are based on a conventional lithium-ion chemistry using $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive electrode, a blend of MCMB-6 and SFG-6 as a negative electrode and 1 M LiPF_6 in EC:DEC (1:1) electrolyte. Both the positive and the negative electrodes were engineered to reduce initial cell resistance and enhance power. The high power 18,650-cells (36 W) were used to identify the causes limiting the calendar life for this lithium-ion cell chemistry. These cells were first characterized at 25°C in terms of ac impedance (at 0 and 100% SOC at 1 kHz), C/1 capacity and hybrid pulse power ability (HPPC test at 8–12 C rate) [6]. These cells were then subjected to extensive accelerated calendar and cycle life testing. The cells were brought to a fixed SOC (40 and 60%) and their voltages were allowed to

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equilibrate for at least 3 h. After equilibrating, the cells were heated to a soak temperature (40, 50, 60 and 70°C). At the soak temperature, the cells were potentiostated at the new equilibrium voltage. At the end of a month (2 weeks for 70°C) soak time, the cells were periodically cooled to room temperature and an HPPC test was carried out to check their pulse power and impedance rise. The hybrid pulse power characterization test (HPPC) consists of a series of C/1 discharges to remove 10% of the cell's capacity, after which the HPPC profile (18 s at 8–2 C rate discharge and “trapezoidal” regenerative-charge) is applied. The discharge and regenerative braking pulse power capability are calculated at each discharged capacity increment. If the cell can not perform the 40% SOC pulse, it has reached the end-of-test criteria.

After the cells failed the HPPC test, they were disassembled and their electrodes were investigated using a 32 cm² laboratory cell, that employs a reference electrode, and ac-impedance spectroscopy on symmetrical cells. The micro-reference electrode used in this case was made of 25 μm copper wire, insulated by a 3 μm layer of polyurethane enamel. The role of the insulation layer is to prevent any mixed potential along the wire during the study. The insulation layer was stripped from the tip of the wire, using stripping solution, and a tin layer (1 μm thick) was electroplated onto the exposed copper. This micro-reference electrode was placed between two layers of separator to be insulated from both electrodes. After cell assembly, the tin plated layer on the tip of the wire was charged slightly with lithium from the positive electrode, using negligible quantities of active lithium.

3. Results and discussion

Fig. 1 represents an example of the pulse power characteristics of one high-power cell. The results show the 18 s pulse power discharge capability and 2 s pulse power

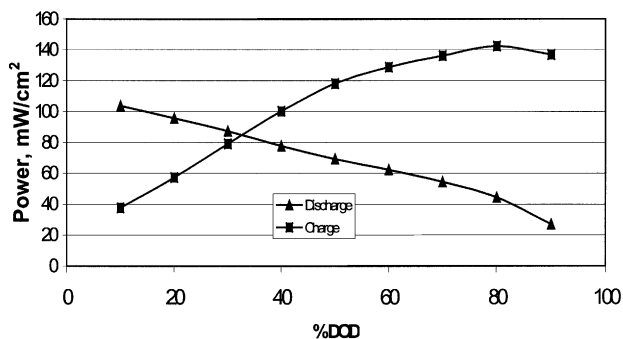


Fig. 1. High power pulse characteristic (HPPC) test of a high power cell made of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive electrode, a blend of MCMB-6 and SFG-6 negative electrode and $\text{LiPF}_6/\text{EC}:\text{DEC}$ (1:1) electrolyte. The marker squares and triangles are for 2 s pulse charge and 18 s pulse discharge at 11 C rate, respectively.

regen-charge at different depths of discharge (DOD). In this case, the pulse rate was about 11 C rate. The pulse power at each DOD is calculated from the area specific impedance and the cell open circuit voltage. These values are used to determine the total available state-of-charge and energy swings that can be utilized (within the PNGV operating voltage limits) for specified discharge and regen power levels. The cell pulse power capability during both charge and discharge was found to meet the PNGV power requirement, especially in the “sweet spot” of 30–70% DOD. The PNGV power requirement limit, calculated from ANL's battery design spreadsheet model for a 40 kW battery pack is 66 mW/cm² for the 2 s regen charge, which can be reached starting from 30% DOD, and 55 mW/cm² for the 18 s pulse discharge, which can be reached up to 70% DOD. This calculation was made using an ANL spreadsheet model for a full battery pack; injecting the power requirement set by the PNGV into the model; and then calculating the power in mW/cm² for cell electrodes. This result clearly indicates that a conventional lithium-ion chemistry with proper design and electrode engineering can meet and exceed the power requirements set by PNGV to level the load on the main engine in a hybrid vehicle.

Fig. 2 shows the average percent power fade rates of these 18,650 high power cells when stocked at 40 and 60% SOC at elevated temperature. The power fade is greater at 60% SOC than at 40% SOC because both the delithiated $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ and the lithiated graphite are less stable at high SOC. The fade process is too fast at 70°C to extract any useful kinetic information. As the temperature decreases, the life of the cell increases and more kinetic information is available from the power fade data; the curves show more and more parabolic behavior. By plotting the data, after the first soak period, on an Arrhenius plot, a straight line is obtained. This indicates that power fade is a thermally-activated and perhaps diffusion-controlled process. At 40°C, the life of the cell is extended to over 6 months, because of reduced reactivity between the electrode and

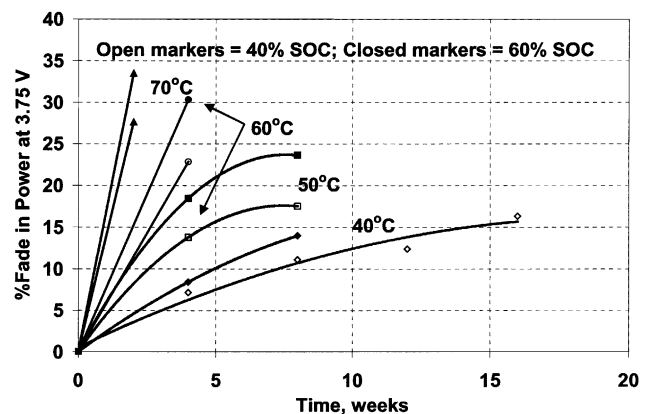


Fig. 2. Fade (%) vs. time and temperature for two states of charge. The fade (%) was calculated at a fixed cell potential of 3.75 V (60% SOC). The markers indicate at which SOC the cell was stored.

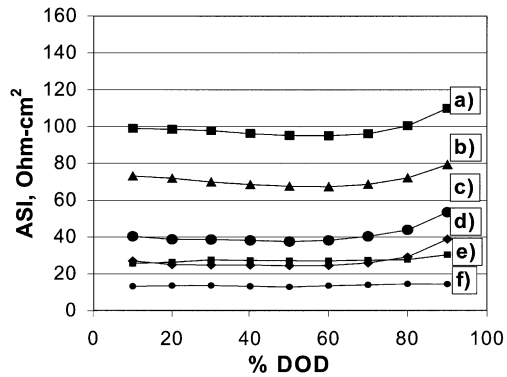


Fig. 3. Area specific impedance of (a) aged cell, (b) aged positive electrode, (c) fresh cell, (d) fresh positive electrode, (e) aged negative electrode and (f) fresh negative electrode.

electrolyte. This situation is more favorable at low SOC (40%) because of the enhanced stability of both positive and negative electrodes. To identify the cell component responsible for the impedance rise during the accelerated calendar life testing of these high power 18,650 cells, micro-reference electrodes were used. The aged cells were disassembled after their power could no longer meet the HPPC test criteria set by the PNGV. Fig. 3 compares the area specific impedances (ASI), during the 18 s pulse discharge of the cell, for the positive and the negative electrodes of fresh and aged cells. The aged cell was subjected to accelerated calendar life at 60% SOC and 70°C. The ASI's of the cathode and anode were calculated based on the potential change at each electrode, versus the LiSn reference electrode, during the current pulses. The reference electrode potential was very stable and did not drift during extensive HPPC pulse cycling (over 4000 cycles). From these results, it is clear that initially for cell that was subjected to only room temperature formation process, the bulk of the impedance comes from the positive electrode (Fig. 3d). After the cell was subjected to accelerated calendar life testing, the ASI of the cell increased significantly from 40 $\Omega \text{ cm}^2$ in the fresh cell (Fig. 3c) to 100 $\Omega \text{ cm}^2$ after 2 weeks of testing at 70°C (Fig. 3a). The bulk of the impedance rise in this case, is due mainly to the positive electrode, as clearly indicated from the comparison of the ASI's of the fresh (Fig. 3d) and aged (Fig. 3b) positive electrodes. The increase in the ASI of the aged negative electrode (Fig. 3e) is not significant when compared to the ASI of the fresh negative electrode (Fig. 3f). To understand the cause of the impedance rise at the positive electrode, we compared the ac impedance of two symmetrical electrode cells made using two positive electrodes from either fresh or aged cells. The positive electrode symmetrical cells were built by taking electrodes from two identical normal cells that were cycled. The two cells were stored at the same 60% SOC and 70°C, disassembled, and then the positive electrodes of both regular cells were reassembled into one symmetrical positive electrode cell. Fig. 4 compares the ac impedance of symmetrical positive electrode cells, made using electrodes from a fresh cell after

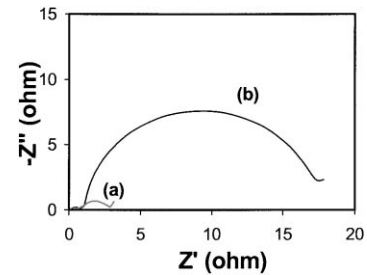


Fig. 4. The ac impedance spectra of symmetrical positive cells made of (a) fresh electrodes and (b) aged electrodes subjected to calendar life testing at 70°C.

only one cycle (Fig. 4a), and electrodes from cells that underwent accelerated calendar life testing (Fig. 4b). The semi circle at medium frequency, which corresponds to lithium transport at the interface between the liquid electrolyte and the positive electrode surface, i.e. a charge transfer resistance [7,8], increases significantly after accelerated calendar life testing. Therefore, the impedance rise of these high power 18650 cells is mainly due to an increase in the charge transfer resistance at the positive electrode. Initial work using high resolution transmission electron microscopy (HRTEM) on a cross sectioned positive-electrode particle, indicated the formation of a thick amorphous film at the surface of the positive electrode particle. The presence of this thick film at the surface of the particle could be responsible for the increase in the interfacial resistance at the surface of the positive electrode.

4. Conclusions

Conventional lithium-ion cell chemistry with proper design and electrode engineering was found to deliver more than enough power to level the load on the main engine in the hybrid electric vehicle. However, after accelerated calendar life testing, by soaking 18,650 cells at different elevated temperatures, the power of the cell fades and the fade rate was found to be dependent on both the SOC and the storage temperature. Micro-reference electrode and ac impedance studies, using a symmetrical cell approach, identified that the impedance rise of these high power 18,650 lithium-ion cells, was primarily due to a significant increase in the charge transfer resistance at the positive electrode. To obtain a stable lithium-ion cell chemistry that can provide a 10-year calendar life, we are focussing on improving the stability of the positive electrode by preventing surface reactions with the non-aqueous electrolyte solvent.

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References

- [1] K. Amine, J. Liu, *ITE Lett.* 1 (1) (2000) 59–63.
- [2] J. Liu, A.N. Jansen, D. Simon, A.E. Newman, G.L. Henriksen, K. Amine, in: *Proceedings of the 195th Electrochem. Soc. Meeting*, Seattle, WA, 4 May 1999, p. 52.
- [3] K. Amine, J. Liu, A.N. Jansen, A.E. Newman, D.R. Simon, G.L. Henriksen, in: *Proceedings of the 196th Electrochem. Soc. Meeting*, Honolulu, HI, 17–22 October, 1999, p. 117.
- [4] P. Arora, R.E. White, M. Doyle, *J. Electrochem. Soc.* 145 (1998) 3647.
- [5] C.H. Chen, J. Liu, K. Amine, *Electrochem. Commun.* 3 (2001) 44–47.
- [6] PNGV Battery Test Manual, Revision 2, DOE/ID-10597, August 1999.
- [7] M.D. Levi, G. Salitra, B. Markovsky, H. Teller, D. Aurbach, U. Heider, L. Heider, *J. Electrochem. Soc.* 146 (1999) 1279.
- [8] M.G.S.R. Thomas, P.O. Bruce, J.B. Goodenough, *J. Electrochem. Soc.* 132 (1985) 1521.