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Short Communication Effect of Humidity on Properties of Lithium-ion Batteries

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A study was performed to determine the cause of abnormal direct current resistance (DCR) during hightemperature storage of a commercialized lithium-ion battery (1C=50 Ah) designed for an electrical vehicle. Scanning electron microscopy, energy-dispersive X-ray spectroscopy, inductively coupled plasma atomic emission spectroscopy, air permeability measurements and electrochemical impedance spectroscopy were used to analyze batteries with abnormal and normal DCRs. The results of these analyses show that imperfect solid electrolyte interface formation increases the direct current resistance. This imperfection results from the presence of excessive moisture during battery production.

Keywords: Excess moisture; Lithium-ion battery; Imperfect solid electrolyte interface; Direct current resistance

1. INTRODUCTION

Lithium-ion batteries (LIBs) are highly efficient energy storage devices that have been used with considerable success over the past decade and are considered one of the most promising candidates for electric vehicles and portable electronic devices. The rapid development of electric vehicles over recent years has placed higher demands on the electrical performance of LIBs [1-5]. As electrochemical properties depend directly on the electrode materials used, considerable effort has been expended to achieve high-performance electrode materials, including those with high energy density and power capability, robust cycling life and superior rate retention. Significant results have been achieved for many potential LIB electrode materials at the laboratory scale. A combination of a nickel cobalt lithium manganate cathode (NCM) and an artificial graphite (A. G) anode has been shown to be a very successful candidate for commercial lithium batteries [6-10].

Although NCM+AG chemistry exhibits high performance in general, but sometimes parasitic side reactions intrinsic can easily cause rapid performance degradation. The capacity and power of LIBs always fade during usage or storage [11, 12]. The capacity fade is attributed to lithium inventory loss

and active material loss. Power fade results from a rise in the impedance, namely, increased voltage polarization, where the direct current resistance (DCR) is the best indicator of the battery impedance. The materials used for the separator, cathode and anode are the main factors, among a multitude of causes, for DCR rise [13-16].

Batches of batteries that exhibited a high direct current resistance (HCR) after storage in a hightemperature environment (HTS) for a commercial LIB (1C=50 Ah) research project were analyzed in this study. As the environmental conditions were confirmed as the cause of battery failure, these batteries are referred to as HTS failure batteries (HTS-FBs). Most of the batteries used for the high-temperature storage tests exhibited normal DCRs and are referred to as high-temperature storage normal batteries (HTS-NBs). The analysis performed in this study show that imperfections in the anode solid electrolyte interface (SEI) and the cathode electrolyte interphase (CEI) layer cause HCR. The imperfections in the SEI and CEI films occur in the presence of excessive moisture during battery production.

2. EXPERIMENTS

2.1. Sample preparation

Commercialized LIBs designed for electric vehicles with normal and excessive moisture levels were disassembled and analyzed. Each pouch battery was assembled using a lamination process. Each battery contained a 36-layer cathode and a 37-layer anode filled with 145±1 g of electrolyte. The cathode electrode was fabricated from Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O₂, with poly(vinylidene fluoride) as a binder, acetylene black as a conductive additive and aluminum foil (thickness: 12 µm) as a current collector. A graphite anode was fabricated using 95.2 wt% commercialized artificial graphite (BTR New Energy Materials Co., Ltd.), 0.8 wt% C65 (Timcal) as a conductive additive and 4.0 wt% styrene butadiene rubber (Showa Denki Co., Ltd.) with carboxymethyl batteryulose (Nappon Paper Co., Ltd.) as a binder. Copper foil (thickness: 6 µm) was used as an anode current collector, and 16-µm-thick polyethylene was used as a separator (Shanghai Enjie New Material Technology Co., Ltd.). The electrolyte solution (Guangzhou Tinci Materials Technology Co., Ltd.) consisted of salt (LiPF₆) dissolved in a solvent blend (ethyl methyl carbonate, ethylene carbonate, etc.) with proprietary additives. All the chemicals used in this study were obtained from commercial sources as guaranteed-grade reagents and used without further purification. Cathode and anode films were prepared using a series of industry-standard processes, including mixing, coating, calendering, cutting, stamping, etc. The LIBs were assembled using the abovementioned anode, cathode, separator, and electrolyte. The electrodes were placed in a baking oven for different periods of time and temperatures to control the moisture content.

The battery formation process consisted of two charging steps, where the CEI and SEI mainly formed during the 1st charging step. During the 1st charging step, the batteries were charged at 0.01 C for 50 minutes, 0.05 C for 70 minutes and 0.1 C for 120 minutes until the voltage reached 3.6 V (at room temperature). The LIBs were aged for several days and then subjected to the 2nd charging step at currents ranging from 0.33 C to 4.25 C, followed by a constant-voltage step at 4.25 V with a 0.05 C cutoff. The batteries were degassed in a temperature- and humility-controlled room by cutting open the battery

pouch packages, followed by resealing with a vacuum sealer. The LIBs were stored at 60°C for 28 days in a constant temperature oven; the increase in DCR was evaluated by performing a hybrid pulse power characterization (HPPC) test to measure the DCR of the LIBs at a 50% state-of-charge (SOC) every 7 days at a 2-C current.

2.2. Material characterization

Material samples were obtained from the fully discharged batteries (0% SOC). An argonatmosphere glove box was employed for the experimental analysis. Field-emission scanning electron microscopy (SEM) was performed using a ZEISS Sigma 500 to observe the morphology and structure of the samples. Elemental qualitative analysis was performed by energy-dispersive X-ray spectroscopy (EDX, OXFORD INCA). Electrode film moisture data were obtained using a Metrohm 885 compact oven SC and an 831 KF coulometer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Optima 8000) was used to detect minor or trace quantities of elements. A permeability measuring instrument (ULTRAPYC 1200e, Quantachrome Instruments) was used to measure the separator permeability. Electrochemical impedance spectroscopy (EIS) was performed using an AMETEK PARSTAT4000 electrochemical workstation. The parameters were set as follows: starting frequency, 5000 Hz; ending frequency 0.01 Hz; and amplitude, 4600000 (uA RMS). The HPPC test was performed using a Neware parameter measuring instrument (CT-8008-5 V200A-NTFA, Shenzhen Neware Electronics Co. LTD). The following conditions were maintained for the DCR test: the test temperature was controlled at 23-27°C, the voltage ranged from 2.5-4.2 V, and the pulse time was 18 seconds.

3. RESULTS AND DISCUSSION

The impact of an elevated moisture level on the pouch batteries was analyzed. The two types of batteries were broken down in preparation for analysis.

Fig. 1 shows SEM images for the HTS-NB and HTS-FB sample cathodes. The low-magnification SEM images (Fig. 1a and 1b) do not show any difference between the morphologies of the two sample cathodes. The cathode particles obtained from the two samples exhibited similar sizes and distributions. The high-magnification SEM images for the two samples show that all the cathode particles in Fig. 1c (the normal electrode) and Fig. 1d (the failed electrode) have typical single crystal structures, without discernable morphological differences (no cracking and pulverization of the secondary structure). The uniform dispersion of conductive materials, including carbon black and carbon nanotubes, among the cathode particles indicates no abnormality for the manufacturing process [17-19].

The compositions of the normal and failed samples were investigated by EDX (Fig. 1e and 1f). There is no difference in the elemental Ni, Co, or Mn contents (that derive from the cathode active material NCM) for the two samples. C is mainly composed of carbon black and carbon nanotubes, for which the contents are consistent for both samples [20, 21]. However, the F and P contents of the failed battery cathode are slightly higher than those of the normal group: as these two elements mainly occur

in the electrolyte and CEI, this difference indicates a change in the composition of the CEI films on the cathode surface. Apparently, the increase in the DCR is caused by the continuously growth of the CEI on the NCM surface, which increases the impedance and may produce adverse effects. The CEI covers the surface of the single crystal structure particles, and the dense CEI affects the electrochemical performance by hindering the lithiation/delithiation reaction and increasing the charge transfer impedance, hence increasing the internal impedance [22,23].

(a) 5 μm			(b) 5 μm		
/(¢) 7 1 µm					
e Elements	Weight percent (%)	Atomic percent (%)	(1) Elements	Weight percent (%)	Atomic percent (%)
С	11.70	24.81	С	11.70	24.40
0	27.34	43.51	0	27.34	43.01
Mn	10.40	4.82	Mn	10.40	4.71
Со	5.90	2.55	Со	5.90	2.57
Ni	38.12	16.53	Ni	38.12	16.15
F	5.15	6.90	F	5.15	7.88
Р	0.34	0.28	Р	0.34	0.41
S	0.25	0.20	S	0.25	0.19
Al	0.35	0.33	Al	0.35	0.61
W	0.45	0.06	W	0.45	0.07
Total	100.00	100.00	Total	100.00	100.00

Figure 1. SEM/EDX characterization of cathode for (a, c, and e) HTS-NB and (b, d, and f) HTS-FB



Figure 2. (a) Permeability of HTS-NB and HTS-FB separators; SEM images of (b) HTS-NB separator and (c) HTS-FB separator

Abnormal separators can also cause abnormal increases in the DCR. Therefore, SEM and porosity tests were conducted on the separators to determine whether the septum was disabled. Fig. 2 shows generally similar permeabilities for the two samples, indicating no abnormality in the HTS-FB permeability. There is also no discernable difference in the separator morphology shown by the SEM images of the two samples, which both maintain good permeability [24, 25]. The permeability and SEM test results show no pore blocks in the separator; thus, the separator could not have affected the DCR of the battery stored at high temperature.

Fig. 3b and 3d are SEM images of the HTS-FB graphite anode. The graphite laminar structure of the sample is well-maintained without peeling, and no collapse of the structure can be observed, which is consistent with the graphite structure of the HTS-NB anode (Fig. 3a and 3c). The conductive agent is evenly dispersed on the graphite surface, indicating no abnormality during the electrode manufacturing process. However, the EDX results show high contents of O and F, which mainly exist in the SEI of the HTS-FB anode, which indicates that increasing the thickness of the SEI film on the HTS-FB anode produces abnormal changes in the internal resistance of the LIBs [26-28].



Figure 3. SEM/EDX characterization of anodes from (a and c) HTS-NB and (b and d) HTS-FB



Figure 4. (a) ICP analysis of Li content of HTS-NB and HTS-FB anodes; (b) charge-discharge curves for LIB formation stage at 1/3 C within 2.5–4.2 V range; (c) electrochemical impedance spectra (EIS) of HTS-NB and HTS-FB; and (d) corresponding equivalent circuit used to fit impedance spectra

The HTS-FB anode exhibits a significantly higher measured Li content than the HTS-NB anode (Fig. 4a). A higher Li content indicates a thicker SEI layer, because the detected Li is present in the SEI layer (LiF, Li₂CO₃, Li₂O, ROCO₂Li). Fig. 4b shows the battery charge-discharge curves within the 2.5-4.2 V range. The potential increases sharply up to approximately 3.67 V during initial charging and then decreases in slope because of delithiation of ternary materials over the 3.67 V to 4.2 V range; the ~3.67-V charge-discharge voltage plateau of the NCM corresponds to a sequential phase transition process (Ni²⁺/Ni³⁺/Ni⁴⁺) [29]. The plateau at 4.2 V results from changing the charging mode to constant voltage charging. Fig. 4c shows the evolution of the impedance spectra of HTS-NB and HTS-FB batteries (which is fit using the equivalent circuit shown in Fig. 4d). The EIS spectra consist of a compressed semicircle in the high- to medium-frequency region, which corresponds to the charge transfer resistance (R_{ct}) of the electrode, and an approximately 45° inclined line in the low-frequency range, which represents the Warburg impedance (Z_w) . The intercept before the start of the semicircle of the equivalent circuit can be ascribed to the bulk electrolyte resistance (R_{Ω}), and the difference between the intercepts of the two samples indicates that HTS-FB consumes more electrolyte to form SEI/CEI films than HTS-NB. R_{SEI} and R_{ct} represent the resistance for the SEI and charge transfer, respectively. The X-intercept of the semicircle corresponds to R_{SEI}+R_{ct}, which is higher for an HTS-FB than an HTS-NB. CPE1 and CPE2 denote the capacitances of the SEI and the double layer, respectively, and Zw denotes the Warburg impedance [30-32].



Figure 5. Mechanistic analysis showing how SEI/CEI film affects DCR

As mentioned above, a high temperature and SOC shift the anode energy level, inducing violent side reactions between H₂O and the electrolyte. Lithium salt (LiPF₆) spontaneously decomposes into LiF and PF₅, which reacts with H₂O to form POF₃ and HF (Fig. 5a). LiF and POF₃ have poor electronic and Li⁺ conductivity and deposit on the surfaces of the NCM and graphite, thus hindering the lithiation/delithiation reaction and increasing the charge transfer impedance, which affects the electrochemical performance and produces an abnormal increase in the DCR. At the same time, HF corrodes the NCM material and the CEI film, as indicated by the results of the cathode analysis (Fig. 5b). The newly rebuilt SEI repairs the broken SEIs with high thickness and poor conductivity and induces DCR growth. Therefore, excessive moisture accelerates side reactions and thickens the SEI, which are highly detrimental to the entire battery system [33-35]. A mechanical analysis shows that the change in the SEI/CEI composition at 60°C and 100% SOC promoted the DCR, and excessive moisture was a determining factor for the abnormal DCR.



Figure 6. Influence of moisture content on DCR of batteries stored at 60°C

A reproduction experiment was performed with different controlled electrode moisture contents to verify the aforementioned hypothesis that excessive moisture was the underlying cause of the abnormal DCR. We used 3 packs of batteries with strictly controlled moisture contents (cathode: 198 ppm; anode: 154 ppm) and high moisture contents (cathode: 244 ppm; anode: 285 ppm) in a 28-day high-temperature storage experiment, where DCR tests were conducted at 7-day intervals. Fig. 6 presents the increase in DCR results. During the first 7 days of storage, the controlled-moisture group exhibits a lower increase in DCR (by 1.33% on average) than the high-moisture group. This difference becomes increasingly noticeable as the storage time increases. The average difference is 4.34% by 28 days of storage. The average increase in DCR for high moisture group is 10.67% which significantly exceeds the original design allowance. The initial high-temperature storage result indicates that the moisture content significantly affects the DCR increase. The controlled-moisture group exhibits a lower increase in DCR during the high-temperature storage test than the high-moisture group.

4. CONCLUSIONS

We systematically analyzed the main contributions to the rapid increase of the DCR of selected batches of batteries during high-temperature storage. The data analysis presented above shows that inadequate moisture control and specifications are the main causes of abnormal DCR. The main factors that deteriorate battery HTS performance are SEI/CEI destruction and regeneration, which are induced by excessive moisture [36]. Therefore, the humidity during battery production must be strictly controlled, especially for an NCM + A. G system. The methodology in our study provides insight into the failure of high-performance LIBs.

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