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The effect of charging rate on the graphite electrode of commercial lithium-ion cells: A post-mortem study

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HIGHLIGHTS

- Higher charging currents increase the quantity of negative electrode surface film.
- Degradation preferentially occurs along the center of the electrode roll.
- This degradation is related to insufficient electrode wetting.
- The center of the electrode roll delaminates at rates of 6-C.
- Delamination is caused by binder degradation from increased temperature.

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ABSTRACT

Increased charging rates negatively affect the lifetime of lithium-ion cells by increasing cell resistance and reducing capacity. This work is a post-mortem study of 18650-type cells subjected to charge rates of 0.7-, 2-, 4-, and 6-C. For cells charged at 0.7-C to 4-C, this performance degradation is primarily related to surface film thickness with no observable change in surface film chemical composition. However, at charge rates of 6-C, the chemical composition of the surface film changes significantly, suggesting that this change is the reason for the sharper increase in cell resistance compared to the lower charge rates. In addition, we found that surface film formation was not uniform across the electrode. Surface film was thicker and chemically different along the central band of the electrode “jelly roll”. This result is most likely attributable to an increase in temperature that results from non-uniform electrode wetting during manufacture. This non-uniform change further resulted in active material delamination from the current collector owing to chemical changes to the binder for the cell charged at 6-C.

1. Introduction

A common criticism of electric vehicles is that they have a much smaller range compared to those with a traditional internal combustion engine (ICE). Electric vehicles typically have a range of 100–300 km between charges, whereas ICE vehicles have a range of 800–1000 km. In addition, it takes approximately five minutes to refill an ICE vehicle's tank, whereas recharging electric vehicles can take up to eight hours. This difference in charge/refill time presents a significant barrier to consumer acceptance of electric vehicles.

The reason electric vehicles take longer to charge is because the lifetime (capacity and power) of the cell is significantly reduced as the charging rate increases. Previous work into this area has shown the negative impact of charge rate on cell performance [1].

When a cell is being charged, lithium-ions transfer out of the positive electrode; pass through the electrolyte; and intercalate into the negative electrode. Charging rate is the speed at which this transfer takes place. Increased current rate increases the amount of lithium plating onto the negative electrode surface [2,3]. Lithium plating is accelerated by three conditions, these are low temperature [4], increased current rates during charge [3] and high state of charge [5]. Smart and Ratnakumar explain that lithium plating occurs because of two competing mechanisms [6]. These are

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intercalation into the electrode and plating onto the electrode surface. At low temperatures the kinetics of intercalation are hindered and as a consequence lithium plates onto the surface of the electrode. At increased current rates the negative electrode is polarised to a lower potential and the mechanism of intercalation is superseded by lithium plating. This is because at below 0.0 V (vs Li/Li$^+$) lithium preferentially plates onto the negative electrode [7] instead of intercalating into the graphite.

Increased charge rate has also been related to thickening surface film [8,9] and blocking electrode pores [10]. Both of these are outcomes of lithium plating at the negative electrode. By increasing the concentration of lithium at the surface of the electrode, reduction of the electrolyte will occur more rapidly because the concentration of reactants has increased. Zhang postulates that when the Li$^+$ ion intercalation paths become blocked, it increases the concentration at other paths [3]; this finding further increases the localized current rate at the other pores, which, in turn, increases the rate of lithium plating.

There is some ambiguity because these conclusions are based on models, electrical data, and/or theoretical calculations alone. Plus, the behavior of commercial cylindrical format cells can often differ from that of laboratory coin cells. If we knew which chemical mechanisms were responsible for the cell's degradation in commercial cells, it may be possible to mitigate them and increase battery life through better cell control or material design. This work utilizes analytical methods to study the internal materials of commercial 18650-type cells after the cells were subjected to varied rates of charge to determine the location, extent, and cause of damage. This study is the first of its type to quantify the relationship between electrical performance and internal chemical changes from commercial cells subjected to different rates of charge.

2. Experimental

2.1. Materials

Twelve commercially available 1.25Ah NiMnCo/graphite 18650-type cells were charged between 0 and 100% state of charge at rates of 0.7-, 2-, 4-, and 6-C, respectively (three cells at each charge rate). All cells were discharged at a rate of C/3. The cells were cycled in temperature-controlled environmental chambers at 25 °C and allowed to rest for 30 min after each charge and discharge [11].

For post-mortem analysis, the cells were discharged to 0.5 V. They were dismantled in an argon-filled glove box. The cathode/separator/anode roll was unwound, and samples were cut from the bulk of the electrode material using stainless steel scissors. Care was taken to handle the samples with tweezers by the edges, and samples were stored separately in individual re-sealable plastic bags.

2.2. Characterization

After unwinding and harvesting the electrodes in a glove box, samples were transferred to an adjoining glove box via a common antechamber for analysis. During this transfer, samples were exposed to pressures of around 1.0×10^{-4} kPa for 15 min but were not exposed to air.

Scanning electron microscope (SEM) samples were transferred to the microscope using a custom-made, air-tight sample holder, which was adapted from that used by Howe et al. [12]. Micrographs were collected on a JEOL JSM 6610LV scanning electron microscope using an accelerating voltage of 10 kV and a working distance of 15 mm with a secondary electron detector.

X-ray photoelectron spectroscopy (XPS) samples (10 × 10 mm) were mounted on a sample holder by means of double-sided tape. Spectroscopy was performed using a Physical Electronics 5000 VersaProbe II with a monochromatic aluminum Kα (15 kV) X-ray source. The excitation beam size employed was 100 μm, and the power was 25 W. Pressures of the system were between 2×10^{-10} kPa before sample insertion and 2×10^{-9} kPa immediately after. Ar$^+$ ion sputtering was performed at 500 V over an area of 3 × 3 mm F1s spectra were recorded in Fixed Analyzer Transmission mode, using a pass energy value of 11.75 eV, step size of 0.1 eV, and acquisition time of 2.7 s/step. Binding energy correction was carried out assuming that the main component of the C1s region after sputtering corresponds to C—C (graphite) environments at 284.4 eV.

High performance liquid chromatography (HPLC) was performed with an Agilent Technologies 1260 infinity series liquid chromatograph containing a 6120 Quadrupole mass spectrometer. The stationary phase was three Agilent Technologies oligopore 5 μm columns, with HPLC quality methanol (MeOH) (90%) and water (10%) as the mobile phase; the tests were performed at 25 °C. HPLC samples were created by washing the electrode in the glove box with 5 mL of dimethyl carbonate (DMC), and ~0.1 g of calcium carbonate ($CaCO_3$) was added afterward. The samples were then transferred out of the glove box and mixed vigorously with 5 mL of water. The organic phase was then extracted by syringe and filtered twice with grade 5 Whatman filter paper soaked in DMC. The sample was desiccated overnight and then re-solvated with 2 mL of dichloromethane (DCM).

3. Results

The electrical performance of these cells was presented in an earlier paper by Prezas et al. [11]. Briefly, as the charge rate increased, the cell resistance increased and the capacity reduced. In this work, these cells were dismantled to understand the underlying changes that caused the performance decline.

Fig. 1 depicts the negative electrodes at each charge rate based on a photograph in Ref. [11]. The electrodes in an 18650-type cell are stacked on top of one another with a separator between them. This is then rolled up like a scroll to form the jelly roll that sits inside the can. The illustration of the electrodes in Fig. 1 is a cross section of that jelly roll. The electrodes, as illustrated in this figure by the cell can, align with the top and bottom of the 18650 can as they are positioned within the can during use. The middle refers to the part of the electrode furthest from both the bottom and top of the can. The 0.7- and 2-C electrodes look identical in color, shading, and appearance. The 4-C electrode is mostly similar in color and appearance but has a single grey band covering approximately one-third of the middle of the electrode roll. The electrode from the cell subjected to a charge rate of 6-C also has a band; however, it covers only one-quarter of the electrode, and the active material is delaminated from the current collector so that the copper is visible in places within this band. The presence of the grey-colored band in the center of the 4-C charged electrode and the delamination along the center of the 6-C charged electrode indicates that the increased charge rate is affecting the middle sections at the 4- and 6-C rates of charge differently. This difference is highlighted further by Fig. 1 inset, which is a magnified photograph of the 6-C electrode and shows that the electrode changes in color across the electrode surface. It is multicolored with white patches in the middle (far right), and moving from the middle to the outside of the electrode (far left), the color changes from greenish to blue to lighter blue to grey. Although chemical changes in surface film do not always present themselves visually, changes in color always indicate a change in the thickness or chemistry of the material under study.

Delamination of the 6-C electrode had a uniform pattern in the center and across the length of the electrode roll. This pattern of