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Impedance Diagnostic for Overcharged Lithium-Ion Batteries

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The impedance response of LiCoO₂/C battery cells is exploited to develop a single-frequency (500 Hz) diagnostic tool to detect overcharge abuse. The impedance data are reversible at all states-of-charge during normal charge/discharge operations (2.8–4.2 V), with little change in Z' or Z'' at 500 Hz even after 200 cycles. However, a single 4.6 V overcharge shows clear differentiation in the impedance values at 500 Hz, which is responsive to the cell passivation layers, with the Z' and Z'' first decreasing and then irreversibly increasing with cycling. Thus, this single-frequency impedance method provides a simple means of monitoring battery health.

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Preventing the overcharge of lithium-ion batteries is a significant challenge in battery safety. Lithium-ion batteries have voltage charging limits that are specific to the chemistry of the positive/negative electrode couple and electrolyte materials. The most common cathode material, LiCoO₂, has an upper limit of 4.2 V and a lower limit of 2.8 V vs. Li⁺/Li⁰. Charging above the voltage limit, or overcharging, destabilizes the cathode and causes thermal runaway and fires, thus presenting a significant challenge in battery safety. The path from overcharged Li_xCoO₂ to thermal runaway can comprise the following steps: Co³⁺ is oxidized to unstable Co⁴⁺ causing a loss of crystallinity, structural transformations^{1–3} and the release of oxygen, where the greatest quantities are evolved with voltage,⁴ temperature⁵ and the oxidation ability of the active material⁴ resulting in rapid exothermic reactions with the electrolyte solvent.⁵ Above 4.5 V organic electrolytes decompose forming insoluble products which block the pores of the electrode causing gas generation⁶ and the loss of ionic conduction.⁷ Once ionic transport ceases, the resistance of the cell becomes entirely ohmic resulting in heat generation through I^2R losses.⁷ The heat generation is greater than the heat dissipation of the cell resulting in an enormous increase in cell temperature⁸ leading to thermal runaway. Overcharge of a single cell is significant since failure resulting in explosion or fire can easily cascade to other cells in a battery pack.⁹

Here we use electrochemical impedance spectroscopy (EIS) to monitor the resistance increases associated with Li-ion batteries during and after overcharge. EIS is commonly used to measure the resistance within a Li-ion cell and can show changes in resistance behavior originating from chemical and electrochemical reactions occurring within bulk electrodes, electrolyte, and along electrode/electrolyte interfaces.¹⁰ The physical processes in electrochemical cells have different time constants or effective capacitances, which result in different frequency responses.¹¹ These processes can be differentiated using impedance measurements taken over a broad range of frequencies (i.e.: 100 kHz to 0.01 Hz).

We report the impedance characteristics for overcharged batteries are markedly different from those of the healthy batteries. We observe that at 500 Hz, the frequency responsive to the cell passivation layers, the results are independent of state of charge for healthy batteries, and grossly different for overcharged batteries. From the results, we recommend a single-point impedance-based diagnostic tool for monitoring battery health.

Experimental

Commercial Li-ion prismatic cells (Full River 30 mAh) were used, measuring approximately $1.98 \times 1.17 \times 0.4$ cm³ and weighing 1.1 g. X-ray diffraction (XRD, Bruker D8 Advance) of a disassembled cell confirmed that LiCoO₂ was the active material in

the positive electrode with a composite graphite/carbon negative electrode.

EIS measurements were collected using a Solartron SI 1260 impedance gain-phase analyzer driven by an EG&G PAR263A potentiostat. Impedance data were collected under open circuit conditions using a ± 10 mV amplitude perturbation between 50 kHz and 10 mHz at various voltages during charge, overcharge and discharge. The impedance data were also collected while the cell was under constant current (charging and discharging), however, the application of constant current for charge/discharge along with the impedance perturbation created a significant amount of noise in the data, thus motivating us to analyze the impedance from open circuit measurements. Measurements were also tested with a ± 10 mA perturbation, but the results were less stable than the ± 10 mV amplitude. The upper limit for the charge voltage ranged from 4.2 V to 5.0 V, while the discharge voltage cutoff was held constant at 2.8 V throughout all experiments. EIS data were collected and analyzed by ZPlot and ZView software packages (Scribner Associates Inc.) The batteries were charged and discharged at constant 1C rates (30 mA) at approximately 23°C. Repeated charge/discharge (2.8–4.2 V) and overcharge/discharge (2.8–4.4, 4.6, 4.8, 5.0 V) data were measured using a Maccor Series 4300 battery tester. After cycling, cells were disassembled in a glove box to visually observe changes to the electrodes.

Results and Discussion

EIS data during normal operation between 2.8–4.2 V are shown in Figures 1a–1c. The electrolyte resistance, R_{el} , at the high-frequency, $Z' = 0$ intercept, is the combined resistance of the electrolyte, current collectors, separator and the electrical contacts,^{12,13} and remains nearly constant from the initial open circuit voltage (3.8 V) to 4.0 V and 4.2 V (Figure 1a). At low frequency, the Warburg line slope increases illustrating the impedance associated with solid-state Li⁺ diffusion into porous electrodes.

The resistance intercepts of the high- and medium-frequency arcs decrease with increasing battery voltage (Figure 1a) likely due to the increased conductivity of the passivation layer surrounding both the positive and negative electrodes at high state-of-charge (SOC).^{14–17} Upon discharge the opposite trend is observed where the two arcs increase in diameter (Figure 1b) until they combine to form a single arc at 3.4 V (Figure 1c). The growth of this single arc indicates the progressive increase of the slow charge transfer kinetics of the cathode with increased lithiation.^{12,14,18,19} The arc is therefore largest at 2.8 V.

The shape of the impedance data is reversible with voltage when cycled within the 2.8–4.2 V limits. For instance, the impedance spectrum at 3.8 V during charging (Figure 1a) mirrors the impedance spectrum at 3.8 V during discharge (Figure 1b). When cycled between 4.2 and 2.8 V, the impedance behavior is reproducible with only minimal resistance increases after 200 cycles and no capacity loss (Table I).

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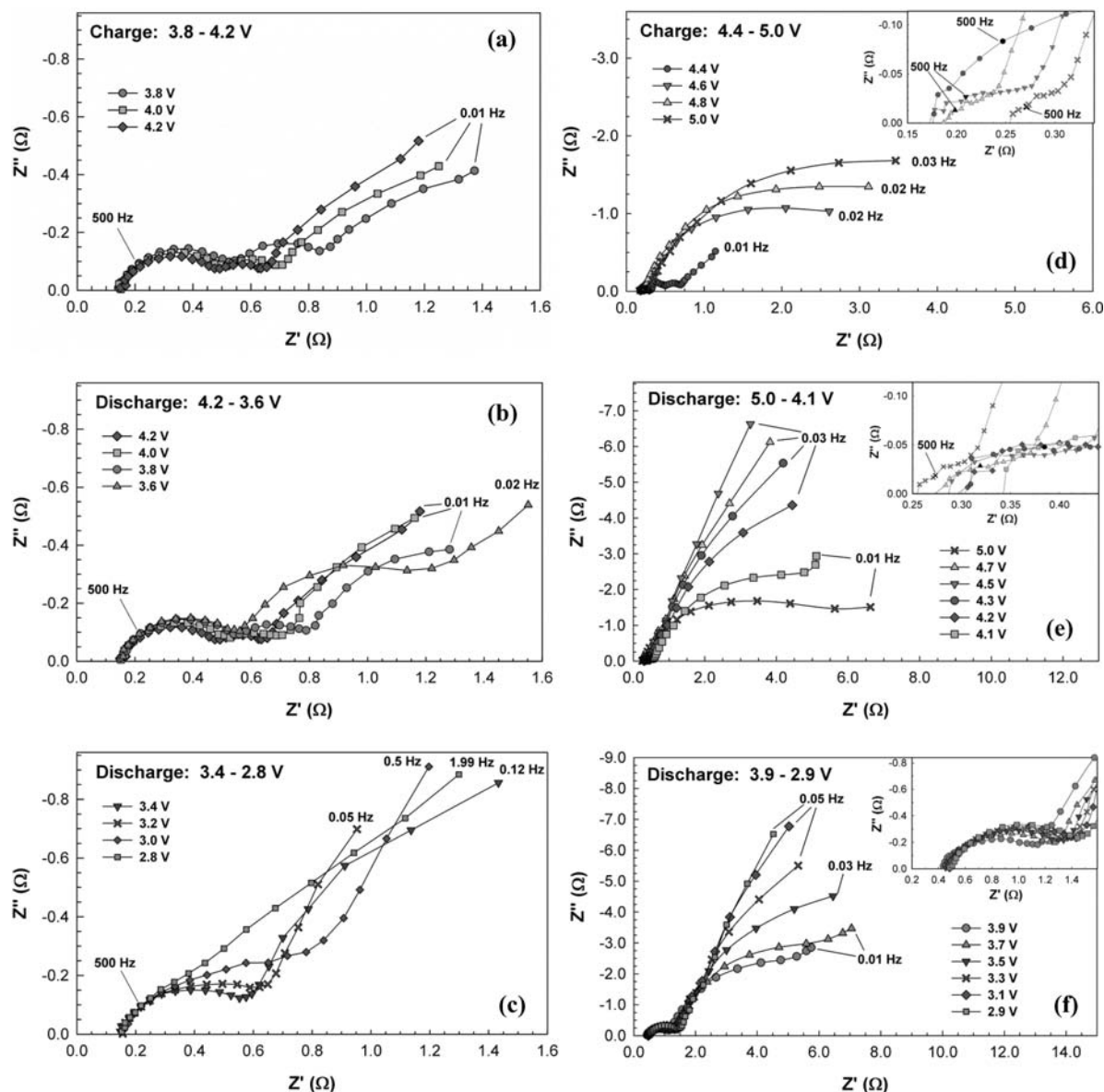


Figure 1. Impedance spectroscopy data at various cell voltages illustrating the reversibility during initial (a) charge cycle from original OCV to an upper voltage limit of 4.2 V and (b) discharge cycle from 4.2 V to 3.6 V and (c) to the low voltage limit of 2.8 V; and impedance spectroscopy data at various cell voltages illustrating the destructive nature of overcharging during (d) the initial overcharge from 4.4 V to 5.0 V; (e) discharge from 5.0 V to 4.1 V; and (f) discharge from 3.9 V to 2.9 V. Impedance data were collected at specific cell voltages under open circuit current conditions. The impedance perturbation was ± 10 mV over a 50 kHz to 10 mHz frequency range. The imaginary impedance due to inductance has been omitted.

Table I. Li-ion cell capacity during the 1st, 12th and 200th discharge cycles following charging cycles to 4.2 to 5.0 V. The lower cutoff discharge voltage was held constant at 2.8 V. The number of discharge cycles above 80% nominal capacity (24 mAh) shows the long term capacity performance degradation following overcharge.

Charge Voltage Upper Limit, V	Discharge Capacity, mAh (± 0.2 mAh)			Number of Cycles Reaching 80% Discharge Capacity
	1 st Cycle	12 th Cycle	200 th Cycle	
4.2	29	31	27	200+
4.4	38	33	12	53
4.6	40	25	0.4	15
4.8	45	22	0.4	6
5.0	17	0.6	-	0

Overcharge causes battery swelling and delamination of the electrode materials from the aluminum and copper current collectors. The degree of physical failure and capacity loss corresponds to the severity of the overcharge voltage. Discharge capacity decreases from about 30 mAh (normal voltage conditions) to as low as 0.4 mAh after overcharging to 5.0 V.

Figure 1d shows the impedance for a battery overcharged above 4.2 V to 4.4, 4.6, 4.8, and 5.0 V. A soft overcharge to 4.4 V results in small changes in the impedance spectrum compared to the 4.2 V upper limit. When overcharged above 4.4 V, the impedance characteristics change dramatically. Increases in cell impedance during overcharge are often ascribed to an insulating layer forming on the surface of the positive electrode.²⁰

The second arc, attributed to charge transfer, appears to merge with a greatly increased Warburg impedance, as previously reported by Belov.²¹ The electrolyte resistance remains nearly constant ($R_{el} \approx 0.15 \Omega$) until 5.0 V, where R_{el} increases to 0.26Ω , signifying

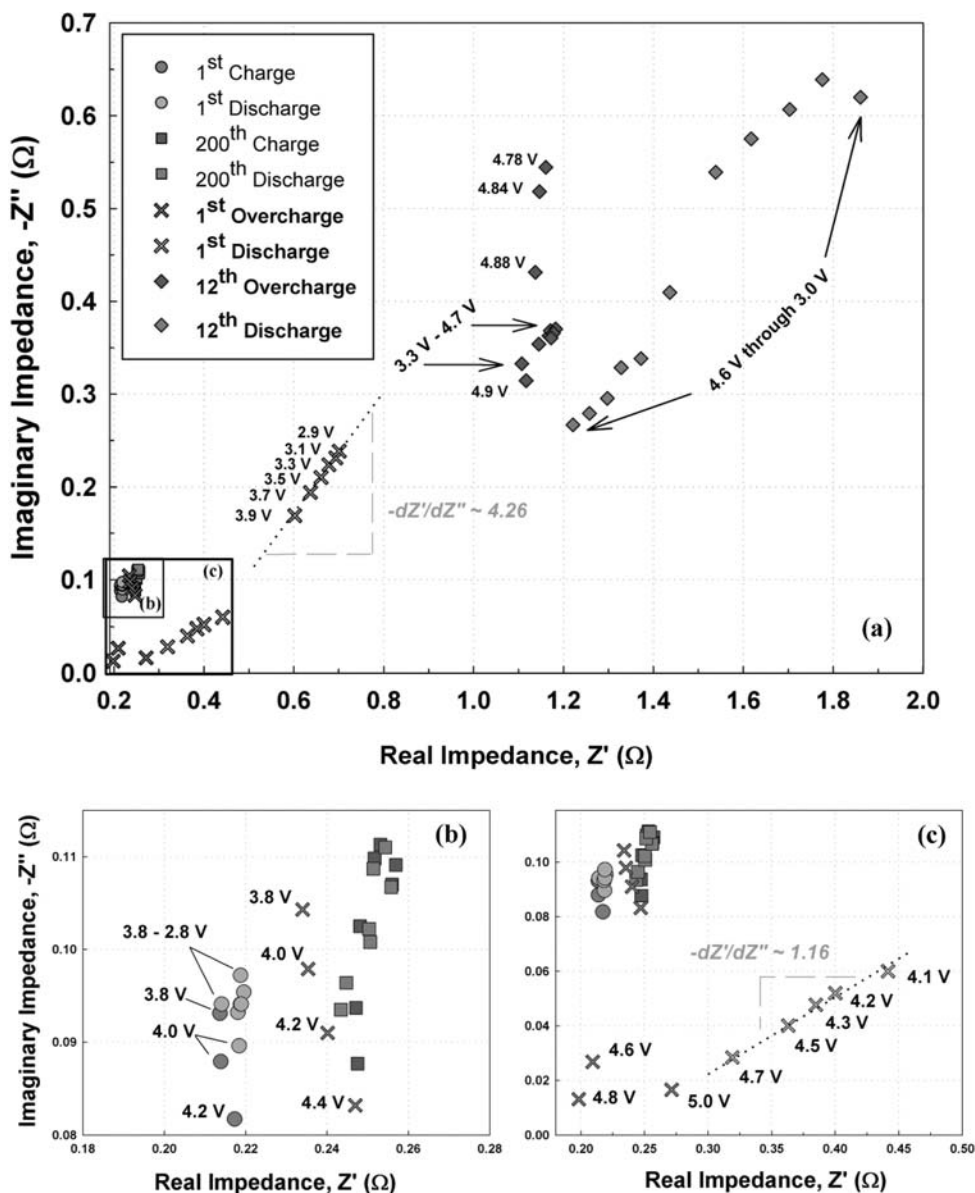


Figure 2. Single point impedance data identifying irreversible impedance behavior with repeated overcharge. All impedance values were collected at 500 Hz perturbation frequency at various charge and discharge voltages during the 1st and 200th charge/discharge cycles (2.8–4.2 V) and the 1st and 12th overcharge/discharge cycles (2.8–5.0 V). (b) smaller inset from Figure 2a, illustrating tight grouping of impedance data collected during 1st charge to 4.2V (red circles), 1st discharged to 2.8 V (green circles), 200th charge to 4.2 V (blue square), and 200th discharge to 2.8 V (pink squares). The impedance data for an overcharged cell to 4.4 V are also given by the red X's. (c) larger inset from Figure 1a, showing the effect of 1st severe overcharge to 5.0 V (red X's) and 1st discharge after initial overcharge (green X's).

electrolyte decomposition. At high voltages, organic carbonate electrolyte solvents are unstable and begin to degrade² drastically impeding the ability of the electrolyte salt to facilitate ionic mobility between the electrodes, increasing impedance.

The shapes of the impedance spectra irreversibly change upon discharge after a severe 5.0 V overcharge (Figures 1e and 1f) and no longer resemble the impedance spectra measured for the battery charged to 4.2 V (Figures 1b and 1c). Increased impedance due to ionic diffusion is evident in the overcharged battery by the steep slope in the Warburg (low frequency) region of the curves between 4.7 – 4.1 V. Below 4.1 V a single large diameter arc is observed in the overcharged cell while two distinct arcs remain for the cell charged to normal voltage cutoff. This transition in impedance profile was not observed in cells cycled within the 2.8–4.2 V voltage range, and is clearly the result of overcharge. The diameter of the single arc increases with decreasing voltage. Electrolyte resistance, the result of

degradation at high voltage steadily increases throughout discharge to 2.9 V.

This irreversibility in the impedance response for overcharged Li-ion cells is exploited here to develop a diagnostic to detect overcharge abuse. The resulting diagnostic technique is naïve to the source of cell impedance, but is intelligent to detect cell damage due to overcharge. We track the impedance data collected at a single point within the high frequency arc (500 Hz). The 500 Hz frequency response is generally attributed to the resistance and capacitance of the cell passivation layers. Not surprisingly, the impedance features are highly dependent upon overcharging, when the passivation layer on the LiCoO₂ changes drastically. In comparison, the impedance response is unchanged during normal charge/discharge operations when the LiCoO₂ surface is stable. The 500 Hz impedance values for cells cycled between 2.8–4.2 V are grouped tightly with little change in Z' or Z'' even after 200 cycles (Figure 2a and 2b).

During a single overcharge >4.6 V (Figure 2c) the imaginary impedance decreases. A two-stage linear increase in impedance arises during discharge following a 5.0 V overcharge. Between 5.0–4.1 V the imaginary impedance changes slowly with respect to the real impedance ($dZ''/dZ' \approx -1.16$). This is most likely due to impedance associated with electrolyte breakdown, increasing R_{el} . The imaginary impedance changes sharply with respect to real impedance ($dZ''/dZ' \approx -4.26$) during discharge between 3.9 V–2.9 V. This distinction is seen in the differing impedance profiles shown in the insets in Figure 1e and 1f. The 12th overcharge shows a large grouping of impedance data above the values after the 1st overcharge and well outside the tight grouping for cells cycled between 2.8 – 4.2 V. The impedance values continue to increase and scatter into the 12th discharge.

An arbitrary radius is drawn in Figure 2 at 3σ the standard deviation at the 500 Hz single-point impedance to show the region to be monitored for overcharge abuse. The impedance data presented for batteries with repeated 5.0 V overcharges are presented as the most severe scenario to illustrate the effect of overcharge and the irreversibility in impedance taken at the 500 Hz single-point frequency. However, deviation in the impedance from the assigned radius is observed even after a single overcharge to 4.6 V.

The impedance of multiple sizes of LiCoO_2/C batteries show the same trends (not shown). The temperature dependence of the single-point impedance method will be studied further as well as the applicability of the diagnostic to detect overdischarge.

Conclusions

A single frequency impedance measurement at 500 Hz may be a simple means of monitoring battery health and predict safety issues that may occur due to overcharge abuse. Overcharged LiCoO_2/C cells have drastically different impedance spectra as compared to properly operated ones (charged between 2.8–4.2 V). At 500 Hz, a frequency responsive to the passivation layers on the electrodes, the drastic changes in the impedance of the overcharged batteries can be detected most clearly. The imaginary impedance drops sharply after a single overcharge to 4.6 V, and then increases significantly at voltage >4.6 V. Preliminary results show that these trends are independent of battery size (10–300 mAh) but more work is needed to determine these trends

across different chemistries (i.e. LiFePO_4 cathodes) and for cells operating at different temperatures.

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