Measurement for fractional characteristic of Lithium batteries

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Abstract—It is shown that RC circuits are inappropriate for modelling the transient runtime characteristics of battery voltage. In contrast, impedance-frequency measurements suggest that a fractional capacitor or “constant phase element” (CPE) can represent battery impedance over a wide frequency range. In this paper, we present evidence that shows RC models of rechargeable batteries to be theoretically inappropriate. We then propose a fractional mathematical model which uses 3 parameters to predict charge-voltage characteristics or steady-state Q-V function of a Li-ion cell.

I. INTRODUCTION

In recent years, various models have been proposed which attempts to estimate the state-of-charge (SoC) and state-of-health (SoH). [1]–[3] A number of authors model these characteristic using Thevenin-style second-order RC battery model consisting of two RC networks with a series resistor. [4]–[6]. Employing capacitors, such circuits must predict transients that are exponential decays, or the sum of a small number of exponentials. We will next show that these models are inherently incorrect.

Figure 1 shows the voltage-time characteristic measured on a small rechargeable battery subjected to a rectangular current pulse. The battery is a 800mAH 14500 Lithium-ion single cell. The measurements were made with an Agilent E5270 Precision IV Analyzer and an Agilent 34401A DMM. Figure 2 depicts the connection. All measurements were made with the battery held at a constant environmental temperature of 25 Celsius using a Contherm Polar 1000.

It turns out that the recovery curve is not an exponential decay at all. A neat method is presented in [7] that analyses a decay curve to identify the magnitudes and time constants of exponential functions that may have been summed to produce the composite decay curve. In other words, it permits the identification of exponential components within a multi-exponential function. Applying this to the recovery portion of the battery characteristic presented in figure 1 yields the result in figure 3. If the recovery transient was to be exponential, or the sum of a small number of exponentials, figure 3 would evidence this by showing distinct peaks in the analysis of the measured data, just as it does for the data generated from a 2-RC model, also shown in the figure. Instead the result is essentially noise.

In this manuscript, we present a mathematical model based on impedance-frequency plot and predict the charge-voltage characteristic of 800mAH 14500 Lithium-ion single cell. Section II derives a mathematical equation from the measured impedance of the cell. Section III describes the fitting of the mathematical model to the charge-voltage characteristic of the cell. Section IV provides valuable discussion and section V presents our conclusion.

II. MATHEMATICAL MODEL DERIVATION

We previously measured the impedance of a 800mAH 14500 Lithium-ion cell. [8] Some authors conducted similar
Fig. 3. Plot of the analysis output for the measured recovery curve presented in figure 1 (noisy trace) along with the same analysis applied to a similar magnitude recovery transient simulated using a second-order RC battery model (scalloped, dashed trace).

Fig. 4. Impedance and phase measurement of a single 800mAh Li-ion cell reproduced from [8].

Measurement which only extends to 100Hz. [9], [10] However, a Li-ion cell only reveals fractional behaviour at frequencies as low as 100µHz. This is shown in figure 4. From this simple curve we can deduce that a Li-ion cell can be represented with a single resistor and a Constant Phase Element (CPE). Therefore, the equivalent impedance equation in frequency domain is

$$Z = R + \frac{1}{C_F s^\alpha}$$

Where $R$ is the series resistance, $C_F$ is the capacitance of the CPE and $\alpha$ is a slope parameter which varies between 0 and 1. The terminal voltage of the cell can then be expressed as follows

$$\frac{V}{s} = \frac{I}{s} \left(R + \frac{1}{C_F s^\alpha}\right)$$

(2)

Applying Inverse Laplace Transform to equation 2 yields

$$V = IR + \frac{I t^\alpha}{C_F \Gamma(\alpha + 1)}$$

(3)

Since the second term (voltage across the CPE) only contributes to the Q-V function, it can be written as

$$V(Q) = \frac{I t^\alpha}{C_F \Gamma(\alpha + 1)}$$

(4)

Substituting $t = Q/I$ in equation 4 leads to

$$V(Q) = \frac{I^{(1-\alpha)} \times Q^\alpha}{C_F \Gamma(\alpha + 1)}$$

(5)

Where $I$ is the charging/discharging current and $Q$ is the amount of charge drawn. In the next section, we derive the values for the 3 parameters in equation 5 and fit the model to the measured Q-V characteristic.

III. MODEL FITTING

A. Measuring the Q-V characteristic

The problem with measuring a battery charge voltage characteristic is that this is a dynamic measurement. When charging a cell, the terminal voltage will be higher than would be the steady-state voltage perceived if the battery were completely at rest. A common response to this is to measure the voltage of the cell under constant-current charging and then to discharge at the same constant current, relying on the impedance characteristic to be linear and symmetrical. The steady-state characteristic is then approximated by averaging...
the two data sets point by point to yield the average characteristic. A very similar, but more informative, variant is used here. The battery was charged at 100mA for 60 seconds using the ES270. Then the voltage was measured, the current set to zero for 60 seconds, and the voltage measured again. Reference to the measured data trace in figure 1 will indicate that 60 seconds should allow the battery to settle only some of the way towards its asymptotic value, owing to the exceptionally slow decay of the fractional tail. This cycle was repeated until the battery reached full charge. At the end of a sweep the battery was rested for 12 hours to allow complete equalisation. Next the current was set for discharge, and the same minute-off, minute on scenario used to discharge the battery. Figure 5 shows four traces, being the charge and discharge characteristics during current flow (“closed circuit”) and after the 60-second rest (“open circuit”). The steady-state characteristic is calculated by averaging the traces point by point. This is shown in figure 6.

B. Fitting the mathematical model

We next calculated the three parameters of equation 5. As previously stated in III-A, the charging/discharging current, \( I \) is 100mA. Using figure 4 the slope parameter, \( \alpha \) is calculated from the CPE phase settled to 80 degrees at 20\( \mu \)Hz yielding

\[
\alpha = \frac{80}{90} = 0.889
\]

(6)

The CPE capacitance is obtained from the measured impedance of the cell which was taken as 0.75\( \Omega \) at 55.7\( \mu \)Hz giving

\[
C_F = \frac{1}{Z(2\pi f)^\alpha} = 1587.6 S \alpha
\]

(7)

The mathematical model was then fitted to predict the relationship between terminal voltage and SoC. The calculated terminal voltage trace shown in figure 6 was obtained using Matlab with appropriate initial condition. To understand the validity of the model, we calculated the accuracy of the fitted data. Figure 7 portrays this.

### IV. Discussion

Most battery manufacturers recommend to stay within the linear region of the Q-V curve in order to extend the lifetime of a cell. However, in a Prius hybrid, the SoC is maintained between 40% and 80% to make the battery last longer. Existing mathematical model can predict this to an accuracy of 5% using a complex algorithm containing 6 parameters. [11], [12]

Some authors adopt a different model which achieves a better accuracy (0.5%) with the same number of parameters. [13], [14]

Our mathematical model predicts the 20%-80% SoC region of the charge-voltage characteristic with a similar accuracy but uses only 3 parameters. There exists a possibility to extend this model to the non-linear region of the Q-V function by incorporating with a non-linear function.

### V. Conclusion

We presented a revolutionary mathematical model consisting of only 3 parameters. All parameters can be easily identified from a simple impedance-frequency curve of the cell under test. The model predicts the linear of the Q-V characteristic which an extraordinary accuracy of 0.5%. It
is possible to stretch the model to the non-linear region by including a polynomial based function.

REFERENCES


