# Fractional Behaviour of Rechargeable Batteries

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***Abstract*—For decades authors have preferred to model batteries with either Thevenin-style models using RLC, or Randles-style by adding a Warburg element. These are claimed to model accurately. We present convincing empirical evidence suggesting that a fractional-derivative (constant-phase element) model is required. Our data shows that existing state-of-the-art models may be overly complicated, requiring numerical rather than physical considerations to find parameters.**

## I. Introduction

When subjected to a step change in current, batteries exhibit a step change in output voltage owing to their internal resistance. Following the step voltage change there additionally follows a gradual decay curve. This is usually attributed to chemical diffusion processes within the cell. Similarly, when the load current returns to zero, the terminal voltage does not immediately return to the steady-state, open-circuit voltage of the cell, but again exhibits a slow recovery.

Figure 1 shows such a recovery curve measured on a 900mAh nickel-metal hydride (NiMH) battery. The battery was cycled carefully to start in the 50-70 percent state of charge (SoC) range. The battery was connected to an E5270B and a constant current of 90mA was drawn for a period of 1 minute. This represents a discharge of only one-sixth of 1 percent of Q, the total capacity of the battery, drawn at the so-called 10C rate. In other words, only a small amount of the battery's capacity was drawn, and at a very modest rate. In spite of this, a significant change in terminal voltage is observed. As steady-state, open-circuit voltage is the most reliable indicator of a cell's state of charge, considerable effort has been put into understanding and modelling this recovery phenomenon.

The authors of [1], [2], [3], [4] modelled this characteristic using RC networks. These works were inspired by Randles original 1947 model [5], but disregard the fractional nature at which his work hints. Figure 2 shows a typical $2^{nd}$ order RC model where $U_{OC}$ and $U_t$ represent the open circuit and the terminal voltage respectively, and of course $R_o$ represents the Ohmic series resistance. It is claimed that the first RC network of $R_c$ and $C_c$ represents the effects due to mass transport and the second RC network of $R_d$ and $C_d$ represents the double layer effect, after [5]. In the next section we will demonstrate that this entire class of model is inappropriate.

## II. Application of Modified Swingler Method

In [6] Swingler proposed a modification of Gardener's method for resolving summed exponential functions. He observed that a function $f(x)$ made up by summing a number of exponential decay terms could be processed to yield a series of delta functions whose amplitudes and delays betrayed the amplitudes and decay time constants of the constituent exponential functions. The execution of Swingler's process proved to be less simple than promised, but a modified algorithm was put forward in [7] that gives good results. This technique can be applied to the recovery part of a battery voltage waveform, and ought to identify the multiplicity of reactive elements required in a battery equivalent-circuit model, as each will give rise to a single decay time constant. We applied this algorithm to the recovery

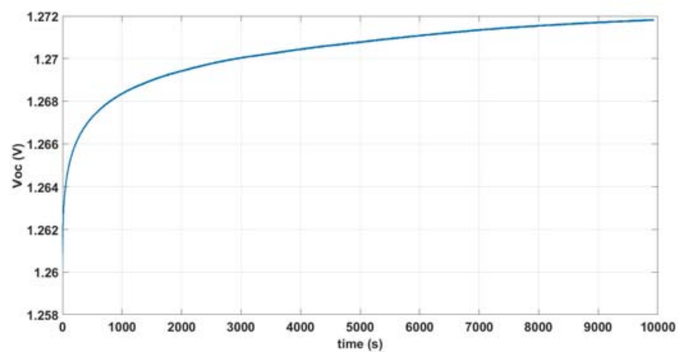


Fig. 1. The recovery curve of a 900mAh NiMH battery immediately after being subjected to a load of 90mA for 60 seconds beginning at a little over 50% SoC.

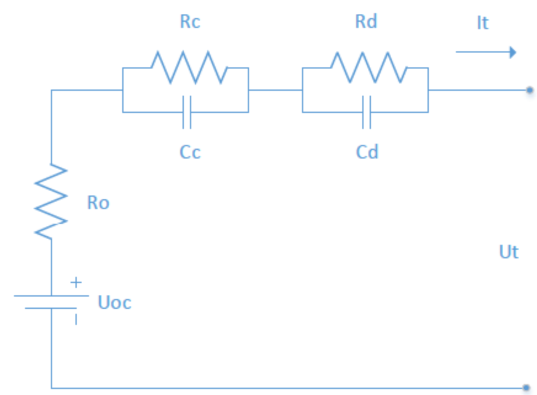


Fig. 2. A typical second-order RC battery equivalent-circuit model, reproduced from [3].

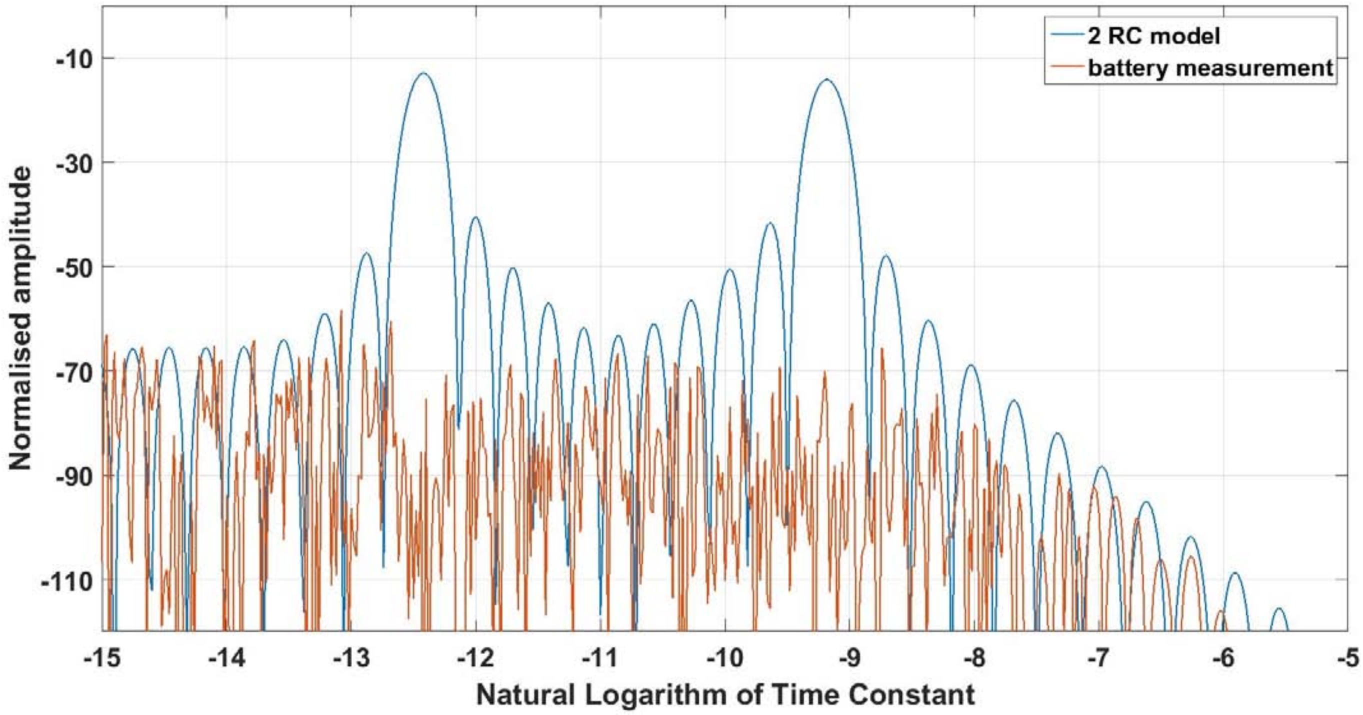


Fig. 3. Output of exponential-function analysis applied to the recovery curve of figure 1 and to a battery recovery curve generated using a two-RC battery model for comparison.

curve shown in figure 1. The result is shown in figure 3. The most important observation is that there is no evidence of any small number of exponential functions. Output of a two-RC model was analysed for comparison, and clearly shows 2 peaks 50dB above the noise floor. This observation suggests that RC models are not appropriate. A Constant-Phase Element (CPE) has a time-domain function that can only be approximated with an infinite series of exponentials, and is not expected to show any peaks on a Swingler-style analysis.

## III. Fractional-Order Models

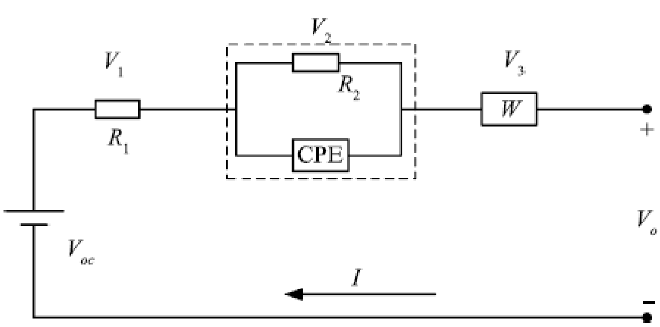


Fig. 4. Fractional equivalent circuit model reproduced from [12].

The idea of modelling batteries with fractional system was first introduced by the authors of [8] in 2006. The authors

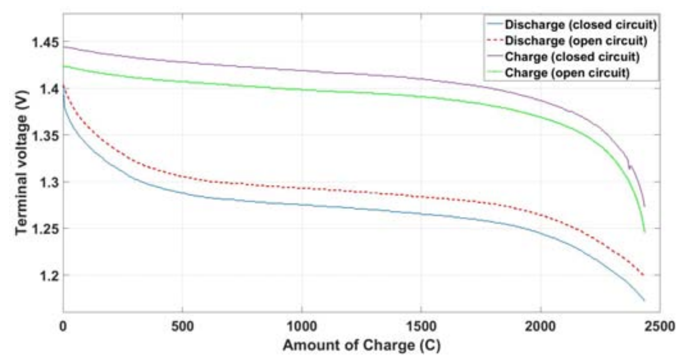


Fig. 5. Cycle test of 900mAh NiMH battery

claimed to be able to estimate the state of charge of lead-acid batteries within 5% error using a mathematical model based on limited frequency band of 2mHz-200Hz. One of the main drawbacks of this model is that it does not have any physical justification or any compact equivalent circuit. It is purely mathematical model with no clear electronic equivalent. A similar mathematical model involving complex algorithm was later proposed in [9] in 2010. This algorithm is specific to the cranking capability of a lead-acid battery. The best that can be said about this work is that it tends to confirm that batteries are fractional in their nature.

Other authors employed Randles battery model with varying degrees of success [10], [11]. In both papers, the authors measured impedance of a lead-acid battery over a certain

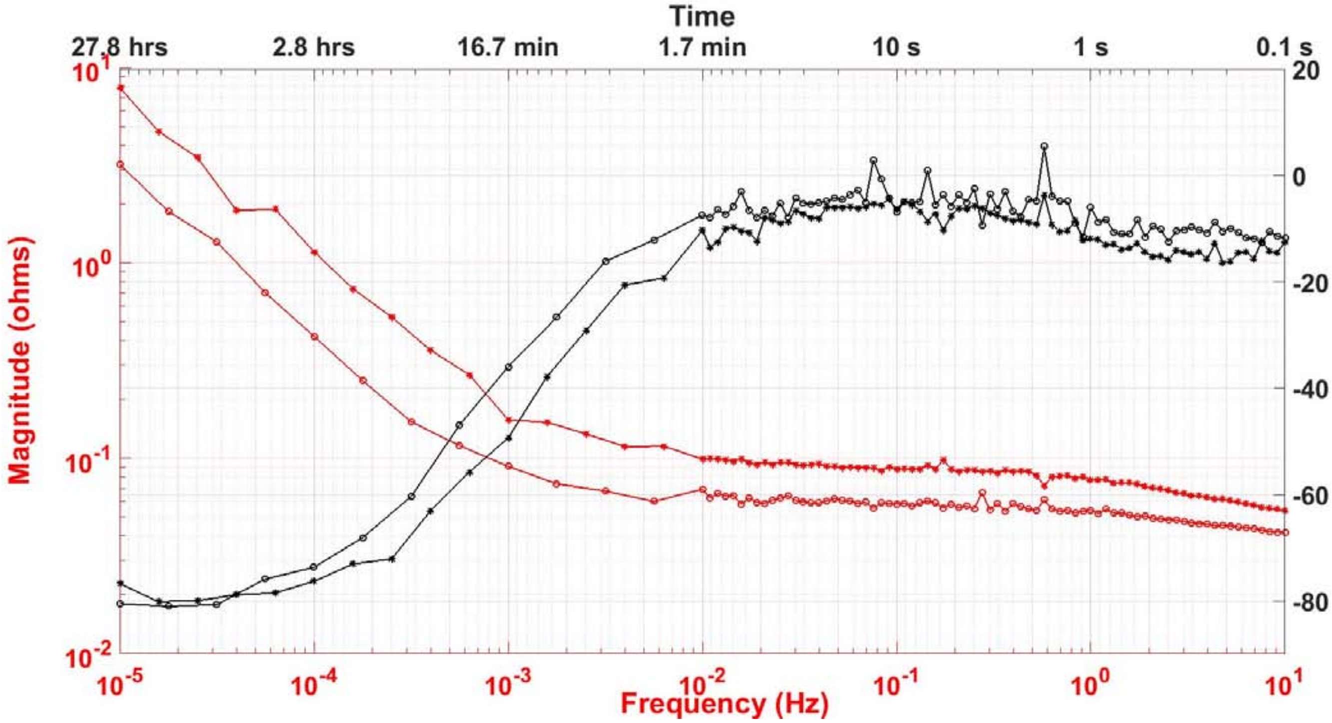


Fig. 6. The bode plot of the magnitude and phase of impedance of two NiMH batteries of 900mAh and 2400mAh capacity.

band of frequencies and used the frequency response to fit the parameters of a first-order Randles model.

As this manuscript was being prepared, Yan Ma et alia in [12] proposed a fractional battery model with a constant phase element (CPE) and a Warburg element as shown in figure 4. $V_{oc}$ represents the open circuit voltage, $V_o$ is the battery terminal voltage, $R_1$ represents the ohmic series resistance and W denotes the Warburg element. At first this work seems very powerful. In figures 1 and 5 of [12], the authors plot EIS data measured on a 26650 Lithium-ion battery on real/imaginary axes, but nowhere do they state the range of frequencies used in the measurement, nor do the plots show data points or variations with noise. In extracting their model parameters they eventually resort to a numerical fitting process. The model is then tested by having it predict very similar time-voltage data as that to which it was fitted. Finally, they note that the model predicts with “most errors below 20mV” which is claimed to represent only about 1% error in SoC, yet publically-available plots show in the linear region that Li-ion batteries have more like 3mV per percent of SoC.

We contend that any model of the complexity proposed in [12] can be fitted to a set of data and subsequently used to predict similar data. This does *not* suffice to verify the appropriateness of the model, especially if that model is overly complex, perhaps with too many degrees of freedom. We will now show measurement that suggest a simpler fractional-order model is appropriate.

## IV. Cycle test

A 900mAh NiMH battery was cycled in order to determine the full capacity of the battery. This is important as we want to be certain that the range of the SoC stays within 50% during impedance measurement. The steps followed to obtain figure 5 are listed below:

- A current pulse of 0.18A (0.2 C) was generated to charge or discharge the battery for a period of 1 minute using Agilent E5270. Agilent E5270B Precision IV Analyzer contains SMUs (Source/Monitor Units) for voltage/current sourcing and voltage/current measurement as low as 0.1 fA.
- The battery was then allowed to rest for 2 minutes for the recovery voltage to settle down after every 0.3% SOC charging and discharging.
- The battery was idled for 12 hours in between charge and discharge.
- Open circuit and under-load terminal voltages of the battery were measured..

## V. Impedance measurement

We measured the impedance of two NiMH batteries against frequency from 10$\mu$Hz to 10Hz using a Solartron 1260A analyser with a fixed dc offset corresponding to 50% SoC. The batteries were rated at 900mAh and 2400mAh. Stimulus levels were chosen to ensure that cells did not deviate more than 10% from 50% SoC for even the lowest stimulus frequencies, where current flowed in one direction for periods approaching 14 hours. Figure 6 depicts the results.

For both cells, the magnitude of impedance is relatively flat at higher frequency, but increases below 10mHz, while phase shifts from about 0 degrees to settle at about -80 degrees. Such a Bode plot is characteristic of a single CPE corresponding to a derivative of order 0.89.

The phase traces in figure 6 show a deviation of 10–15 degrees as frequency increases above 1Hz. We have not conducted any analysis as to what might cause this so far, chiefly as we are interested in modelling SoC, and the response in this frequency range is not really of interest.

The frequency responses of NiMH obtained at higher frequencies are noisy. In order to confirm that the noise were not generated from the measurement system, a resistor of value comparable to the magnitude of battery impedance was measured using Solartron 1260. The results reproduced shown in figure 7 concludes that the noise in the impedance measurement data for batteries were not generated from Solartron 1260.

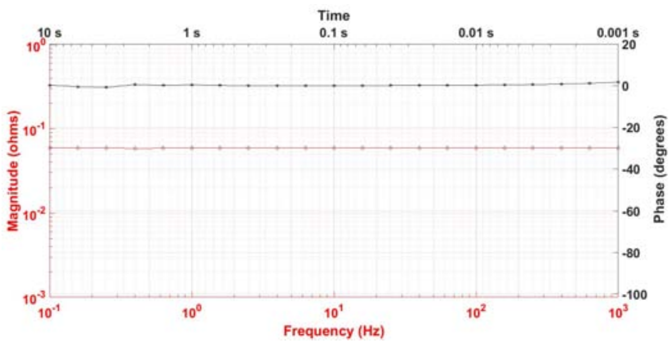


Fig. 7. The bode plot of the magnitude and phase of impedance of a pure resistor in the Solarton measurement setup.

## VI. Discussion and Conclusion

We have shown that the impedance characteristic of NiMH batteries corresponds to that of a single CPE in series with a fixed resistor. The authors of [13] and [14] have adopted a similar approach to model the impedance characteristics of electrode-electrolyte interface and implantable electrode respectively with CPE. Since a CPE is defined by two parameters, its magnitude and the order of the derivative function relating current and voltage, this should lead to a battery model with greatly reduced parameter set.

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