

# Measuring Electrical Properties of Batteries at Ultra-long Timescales

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**Abstract:** Quantifying battery behavior is critical to development of new battery technologies and energy storage systems. While it is straightforward to measure properties such as impedance at short timescales (i.e. frequencies larger than  $\sim 1$  Hz) the relevance of this is questionable since rechargeable batteries in normal usage are often cycled on timescales of hours or days. Making measurements at these timescales, for example impedance measurements below  $\sim 1$  mHz, is more challenging. In this paper we discuss approaches to quantifying battery behavior at timescales from hours to weeks (frequency scales of  $\sim 0.1$  mHz down to  $\sim 1$   $\mu$ Hz). We present frequency domain measurements and time domain measurements, achieved through four-point measurements with a Keysight 66332A at around 100 mA RMS. At low frequencies significant charge is shifted in a measurement cycle, complicating interpretation. The digitization of a sine-wave may introduce errors such as constant current offsets that build in significance with time. The operating point (DC voltage level) of the battery should be controlled since it influences impedance at the lowest frequencies as a result of the voltage-dependent nature of different electrochemical processes. We relate the voltage-dependent effects to time-domain measurements such as cyclic voltammetry and incremental capacity analysis.

## 1. Introduction

Rechargeable batteries are becoming increasingly important in energy storage applications, such as electric cars. Reliably measuring battery performance parameters such as state-of-charge and state-of-health is critical. Failing to identify state-of-health reliably results in waste as batteries are disposed of when they still have useful life remaining, or ugly surprises for a user when a battery fails unexpectedly. In the case of medical implants, replacing a battery involves risky surgery – knowing exactly when to do this would save many surgical procedures.

Batteries are frequently described by equivalent circuit models (ECMs) [1, 2, 3]. A variety of electronic circuit elements, typically capacitors and resistors but also constant-phase elements, are put together to form an equivalent circuit. These are useful for modeling battery response in different situations, but have limitations. It is difficult to distinguish one circuit model from another, particularly when data have been measured over a limited frequency range [3]. While laboratory-based measurements might be carried out using frequencies of order hertz (timescales of order seconds), batteries in practice operate at much longer timescales – often days between charging periods.

In this paper we discuss ways in which battery performance over long timescales may be characterized, in both the frequency domain and time-domain. We first discuss some general principles of rechargeable batteries. We then discuss the process of measuring battery impedance, highlighting some subtleties. Then we move

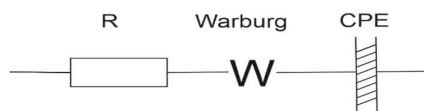
to considering time-domain measurements, specifically charge-discharge cycles and their relationship to cyclic voltammetry. Finally, we put our findings into a broader context for battery measurement.

## 2. General Principles

### 2.1 Equivalent Circuit Models

Numerous ECMs have been proposed in the literature [1]. ECMs allow prediction of the voltage response to different current profiles, facilitating investigation of battery properties such as state-of-charge (the charge held by the battery relative to its maximum charge capacity) and state-of-health (often defined as the charge capacity relative to its capacity when first manufactured).

Numerous ECMs have been proposed for batteries, including the historical model of Randles [5], the physical model of Westerhoff [2] with 16 elements to describe explicitly various battery electrochemical processes, and the phenomenological model proposed in reference [4], Figure 1.



**Figure 1.** One of the battery ECMs proposed in [4], consisting of a resistor, Warburg element and constant-phase element (CPE).

### 2.2 Fractional Elements

The CPE and Warburg are components whose impedance  $Z$  is a non-integer power of frequency, and whose phase

is a constant,  $Z = 1/(j\omega)^\alpha C_F$ , where  $\omega$  is the angular frequency,  $2\pi$  times frequency,  $\alpha$  is a constant between 0 and 1, and  $C_F$  is a constant known as the fractional capacitance. A pure capacitor has  $\alpha=1$ ; a pure resistor has  $\alpha=0$ . The special case of  $\alpha=1/2$  gives a ‘Warburg’ element, often associated with ion-diffusion mechanisms.

An unpleasant feature of fractional elements is that their behavior is non-local – their voltage depends not just on their state now but on how they reached that state. Their behavior may be modeled mathematically in the time domain through fractional calculus [6].

### 2.3 Frequency Domain and Time Domain

Typically electrical measurements are carried out (a) in the frequency domain, using sine-wave currents of constant frequency, or (b) in the time domain using controlled pulses of current. For linear systems, the two are connected via Fourier or Laplace transforms. For realistic systems, there is often discrepancy between the two forms of measurement, e.g. [7, 8], due to nonlinearities.

## 3. Measuring Impedance

### 3.1 General Principles

Impedance of a component is often measured using a four-point impedance meter. This equipment sets a controlled current through the device under test (DUT) and then monitors the voltage over the DUT. Often impedance meters will produce AC signals of frequencies of the order 1 Hz at the low end, though some will go much lower. For example, the Solartron 1260A will measure down to 10  $\mu$ Hz. But to work at still lower frequencies, programmable supplies are required, such as a Keysight 66332A.

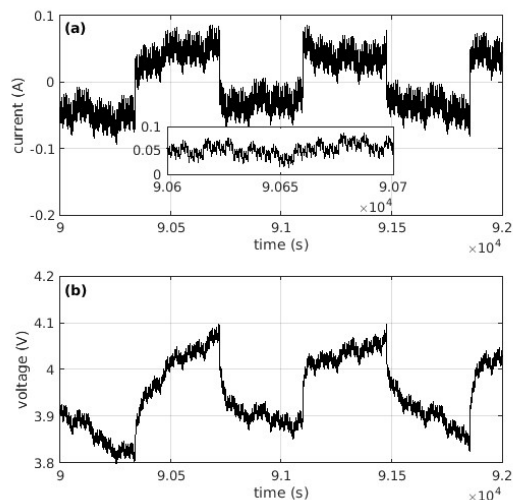
Low frequency measurements demand long timescales and are slow to make. Impedance measurements are often non-repeatable unless carried out carefully. Battery impedance decreases after cycling and takes many days to re-equilibrate [9]. Several periods are required to acquire a good quality measurement. This long timescale means that the battery’s operating point (state-of-charge) might change during the course of the measurement, complicating the interpretation of the result.

### 3.2 Measuring at Multiple Frequencies

If a DUT behaves linearly, it is practicable to measure impedance at several frequencies simultaneously. This superposition will speed up measurement of an impedance spectrum considerably, by constructing a current waveform that exhibits multiple frequencies, carried on a lower frequency that ensures the battery is always actively working [9]. The amplitude of the carrier waveform should be kept low in order that the battery does not charge or discharge significantly during the measurements. Spectral windowing (e.g. Hann

windowing) should be applied to the collected data before a discrete Fourier transform is applied to recover a spectral response. Linearity should be checked by repeating with a different current amplitude.

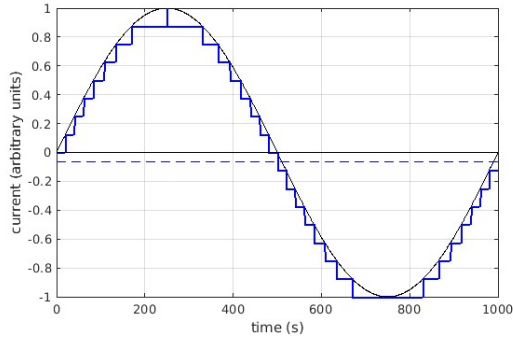
Alternatively, multiple frequencies may be applied on top of a square carrier wave of several-milliampere current; the carrier wave ensures that the battery is always in a ‘working’ condition when measured [9, 10]. Figure 2 shows a section of the voltage and current in an example measurement on a Li-ion battery.



**Figure 2.** Using a square wave of 0.00132 Hz to ensure a battery is continually working (charging or discharging) during an impedance measurement using several frequencies. (a) The current against time, as set by the measurement machine. The inset is a close-up of one section showing multiple frequencies in the time domain. (b) The voltage against time, as measured.

### 3.3 Analogue-to-Digital Conversion

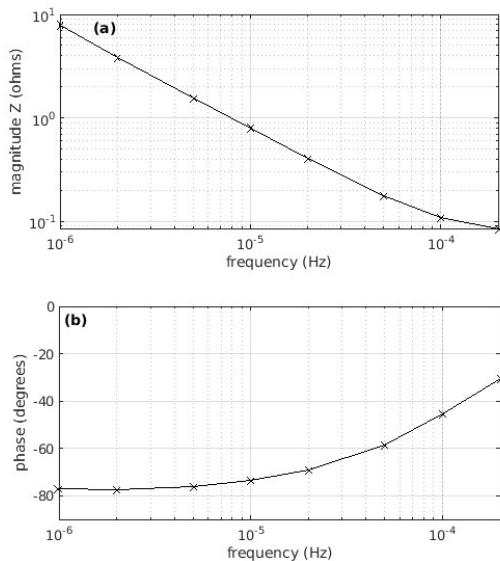
Impedance meters will construct sine-wave signals digitally. Some analogue-to-digital converters (ADCs) will round towards zero, but others may round up or round down. This rounding may cause difficulties. Figure 3 illustrates the error when an ADC rounds down. The solid black line shows a sine wave. The solid blue line shows this wave converted (four-bit ADC) into a digital form. The dashed blue line is the average of the digitally constructed sine wave – this average is not zero. A consequence of this non-zero average is that the battery will slowly discharge during the measurement period. For short periods this is unlikely to be problematic, but at ultra-long periods this will result in a significant movement in charge during the measurement period even with 12-bit resolution – meaning that the battery’s operating point is different by the end of the measurement period. This error may be corrected by monitoring and adjusting charge drift throughout a measurement.



**Figure 3.** An illustration of an error introduced by an ADC. The black line is a sine wave; the blue line a digitally-reconstructed sine wave where the ADC has rounded down. The average of the digital reconstruction is not zero (blue dashed line).

### 3.4 Example Impedance Plot

An example impedance plot is shown in Figure 4. These data were collected with a Keysight 66332A four-point dynamic measurement source with a current of up to 100 mA (lower at lower frequencies), with 12 bits of ADC. Current waveforms were digitally constructed at single frequencies and the resulting voltage measured over three periods. Waveforms were then Hann-windowed and a discrete Fourier transform applied and  $Z$  recovered at the applied frequency [3].



**Figure 4.** A plot of (a) magnitude and (b) phase of impedance against frequency for a 4.8 A h NCA battery, for sub-millihertz frequencies. The lowest and highest frequencies shown correspond to periods of 11.6 d and 1.4 h respectively.

## 4. Time-Domain Measurements at Constant Current

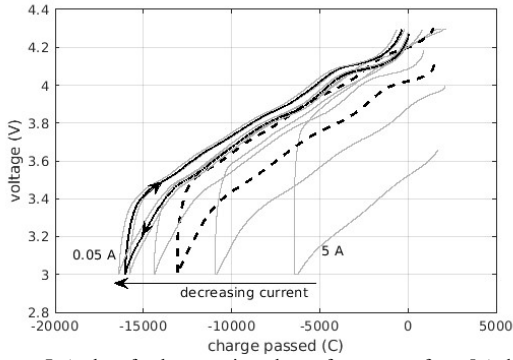
One may also analyze time-domain measurements. Here, one may cycle a battery (charge and discharge) several times. One option is a constant current (CC) protocol:

here we charge at a constant current until the voltage reaches a defined upper limit, then discharge at a constant current, which is often same as the charge current, until the voltage reaches a defined lower limit, and then repeat. The voltage response  $V(t)$  then contains information about the battery in a complementary manner to the impedance measurements. Another well-used alternative, which is more akin to battery charging protocols used in practice, is constant current – constant voltage (CC-CV). Here one begins by charging at constant current until the voltage reaches a defined upper limit, then holding the voltage constant, which means that the current reduces, before applying a constant discharge current.

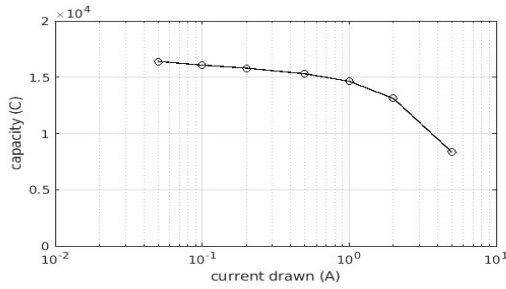
With time domain data we may typically analyze (a) the *charge capacity*, that is how much charge the battery takes during a charge cycle, equal to  $I_0T$  for a constant current  $I_0$  charge over a time  $T$ , (b) the *discharge capacity*, how much charge the battery gives out in a discharge cycle (which might not equal the charge capacity [11]), and (c) the shape of the voltage response  $V(t)$ . For a battery, the charge-discharge capacities vary with timescale (longer periods give higher capacities), a phenomenon labeled *capacity offset*.

Practically, CC or CC-CV measurements at long timescales require careful consideration. A programmable supply such as the Keysight 66332A or Keithley 2400-series Source Measurement Unit will put out a current at the requested level subject to an analogue to digital conversion. Thus the actual current applied will differ from the requested current. With a resolution of around 1 mA this will result in a significant error in calculated charge passed over timescales of hundreds of days. E.g. for an eight-day charge period this error results in 0.2 A h of extra charge, a significant fraction of the capacity of a 4 A h battery. It is important to use the actual applied current in calculations of charge capacity.

We have performed CC measurements for a lithium nickel-cobalt-aluminium-oxide (NCA) battery, rated at 4.8 A h charge capacity and 17.1 Wh energy capacity [7]. Specifically, we have charged and discharged the battery at currents of 5 A, 2 A, 1 A, 0.5 A, 0.2 A, 0.1 A and 0.05 A in that order. Charging is considered complete when the voltage reaches 4.30 V; discharging is considered complete when the voltage drops to 3.00 V. The lowest current gives a charging period of about 4 days. Figure 5 shows  $V$  against  $q$  plots for selected currents. Figure 6 shows the discharge capacity as a function of current drawn.



**Figure 5.** A plot of voltage against charge for currents from 5 A down to 50 mA for a 4.8 Ah NCA battery cycled under CC.



**Figure 6** A plot of discharge capacity against time for a 4.8 Ah NCA battery.

Figure 5 shows that, at lower discharge currents, the charge capacity is greater and the hysteresis is reduced (less area in a charge-discharge loop, meaning less energy is dissipated as heat). Also, there are pronounced ‘wiggles’ in the  $V(q)$  curves at the higher voltages, for the lower discharge currents, where  $dV/dq$  fluctuates significantly from low (a ‘plateau’) to high, as the battery approaches fully charged. Figure 6 demonstrates the phenomenon of ‘capacity offset’, where charge capacity increases as the rate of charge-discharge (current drawn) reduces.

## 5. Relationship to Cyclic Voltammetry and Incremental Capacity Analysis

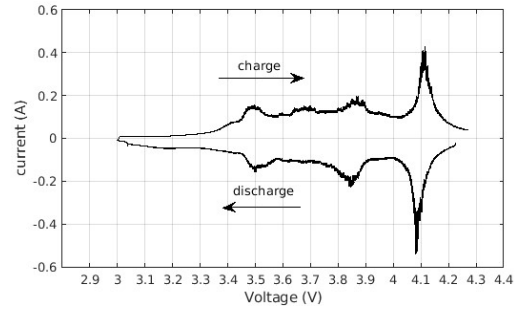
The wiggles of Figure 5 may be related to cyclic voltammetry (CV), an experimental method commonly used to characterize and identify electrochemical reactions [12]. In CV, the voltage across a cell is swept up (increasing  $V$ ) at a constant rate and the resulting current is recorded; the voltage is then swept down at the same rate to complete the cycle. A plot of  $i$  against  $V$  typically shows a series of peaks which correspond to various electrochemical reactions and phase transitions.

If we assume for a battery voltage is a function of charge,  $V=V(q)$ , then the relationship between Figure 5 and CV becomes clear. Differentiating with respect to time gives:

$$\frac{dV}{dt} = \frac{dV}{dq} \frac{dq}{dt} = \left(\frac{dV}{dq}\right) i \quad (1)$$

and hence  $i = V_{\text{rate}}/(dV/dq)$  where  $V_{\text{rate}}=dV/dt$  is the voltage slew rate. The peaks of current in CV thus correspond to regions of low  $dV/dq$ . That is, broadly the plateaus of Figure 5 correspond to the peaks in CV. This is a simplistic assessment, since for a battery,  $V$  is not a strict function of  $q$ , since it has memory effects. However, it is reasonable to assume that the plateaus (wiggles) of the  $V$  against  $q$  plot are associated with specific electrochemical processes in the battery.

One may reconstruct a pseudo-CV from the time-domain data via Eq. (1); for example, the CV reconstructed from the 0.1 A data of Figure 5 (the solid black line) is shown in Figure 7 below.



**Figure 7.** A reconstruction of a CV from constant-current data for a NCA battery cycled at 0.1 A (corresponding to the solid black line in Figure 5).

A study of a cyclic voltammogram suggests why electrical impedance spectroscopy (EIS) will sometimes produce highly variable results. If the battery is operating near a peak, voltage will vary little with a given change in current (thus impedance is low), but away from a peak the same change in current requires a much greater change in voltage and thus a higher impedance measurement. Operating point is thus significant, for example Figure 7 suggests that at around 4.05 V a small change in operating point would give a significant change in measured impedance. Using a square carrier wave for impedance measurements (Figure 2) may help reduce these fluctuations by varying the operating point during measurement.

A related experimental technique is incremental capacity analysis (ICA) [13]. During ICA, voltage is increased in small steps  $\Delta V$  and a measurement of the charge  $\Delta Q$  passed in order for the battery to re-equilibrate is made. A plot of  $\Delta Q/\Delta V$  against  $V$  then yields similar information to Figure 7.

## 6. Discussion and Conclusion

We have presented frequency and time domain measurements of batteries, at ultra-long timescales (several days). At such scales, battery behavior may be modeled through fractional calculus, using ECMs containing fractional elements. These elements lead to measurable phenomena such as capacity offset. Measurements should be made carefully since errors in current, e.g. due to ADC, will accumulate into a considerable error in charge over a long time period.

Batteries have nonlinear  $V(q)$  characteristics at high and low states of charge and it is advisable to make impedance measurements away from these regions to ensure repeatability. Even so, reconciling time-domain and frequency-domain measurements is difficult. If done well, frequency and time domain measurements allow identification of plausible ECMs and component values, thus allowing a battery to be described with meaningful, and measurable parameters. At long timescales, the complexities of battery electrochemistry become evident and plots of  $V(q)$  demonstrate patterns that link with cyclic voltammetry.

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