

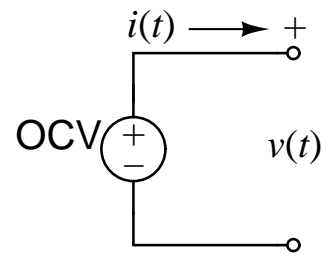
Equivalent-Circuit Cell Models

2.1: Open-circuit voltage and state of charge

- We begin our study of battery models by building up behavioral/phenomenological analogs using common circuit elements.
- The resulting “equivalent circuit” models will be helpful in getting a feel for how cells respond to different usage scenarios, and are adequate for some application design as well.
- Ultimately, however, we will need a deeper physical understanding of how the cells work. The rest of the course will focus on that.

Open-circuit voltage (OCV)

- We start with the simplest possible model. An ideal battery is modeled as an ideal voltage source. In this model,
 - Voltage is not a function of current,
 - Voltage is not a function of past usage,
 - Voltage is constant. Period.
- This model is inadequate, but provides a starting point.
 - Batteries **do** supply a voltage to a load.
 - And, when the cell is unloaded and in complete equilibrium (*i.e.*, “open circuit”), the voltage is fairly predictable.
 - An ideal voltage source will be part of our equivalent-circuit model.



State of Charge

- When a cell is fully charged, its open-circuit voltage is higher than when it is discharged.
- So, we can improve our model by including a dependence on the charge status of the cell.
- We define the state of charge (SOC) $z(t)$ of a cell to be:¹
 - When the cell is fully charged, $z = 100\%$;
 - Also, $z = 0\%$ when the cell is fully discharged.
- We define the total capacity Q of a cell to be the total amount of charge removed when discharging a cell from $z = 100\%$ to $z = 0\%$.
 - Q is usually measured in Ah or mAh.
- We can model SOC as (where $\dot{z} = dz/dt$)

$$\dot{z}(t) = -i(t)/Q$$

$$z(t) = z(t_0) - \frac{1}{Q} \int_{t_0}^t i(\tau) d\tau,$$

where the sign of $i(t)$ is positive on discharge.

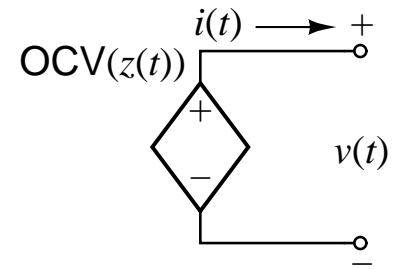
- In discrete time, if we assume that current is constant over sampling interval Δt ,

$$z[k + 1] = z[k] - i[k]\Delta t/Q.$$

- Note that cells are not perfectly efficient. We can accommodate this fact by including an efficiency factor $\eta(t)$

$$\dot{z}(t) = -i(t)\eta(t)/Q$$

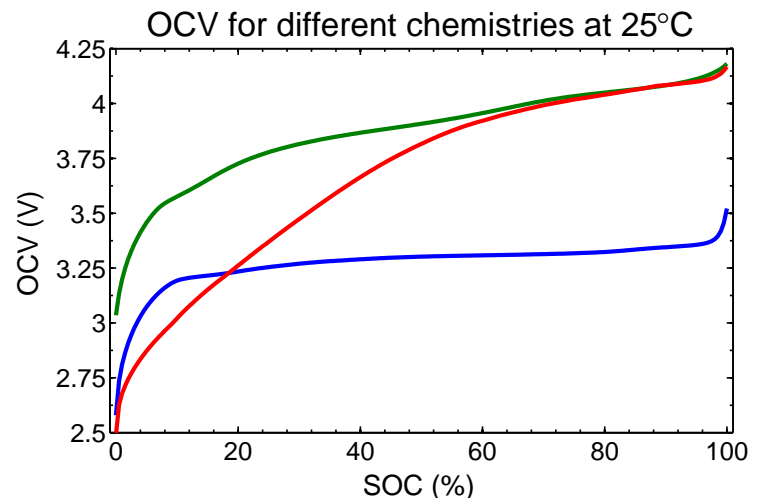
$$z[k + 1] = z[k] - i[k]\eta[k]\Delta t/Q.$$



¹ We will be more precise in our definitions later. But, these will suffice for now.

- The term $\eta[k]$ is called “coulombic efficiency.”
 - We model $\eta[k] \leq 1$ on charge, as some charge is typically lost due to unwanted side reactions.
 - We usually model $\eta[k] = 1$ on discharge.
- Don't confuse coulombic (or charge) efficiency with energy efficiency.
- Coulombic efficiency in a typical lithium-ion cell is around 99 % and is equal to (charge out)/(charge in).
 - Energy efficiency is closer to 95 %, and is equal to (energy out)/(energy in).
 - ◆ Energy is lost in resistive heating, but charge is not lost.

- OCV is plotted as a function of SOC for several lithium-ion chemistries.
- Note that OCV is also a function of temperature—we can include that in the model as $OCV(z(t), T(t))$.



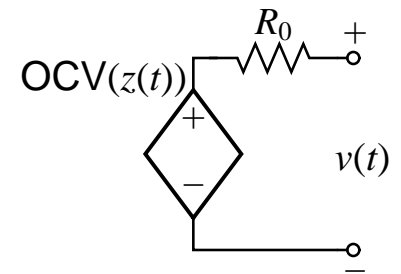
- Also note that “depth of discharge” or DOD is the inverse of SOC:
- $DOD = 1 - SOC$ if it is being expressed as a fraction.
 - DOD is sometimes expressed in Ah: $DOD = Q(1 - SOC)$.
- So, it's possible to plot OCV curves versus DOD as well as SOC.

2.2: Linear polarization

Equivalent series resistance

- A cell's voltage drops when it is under load.
- This can be modeled, in part, as a resistance in series with the ideal voltage source

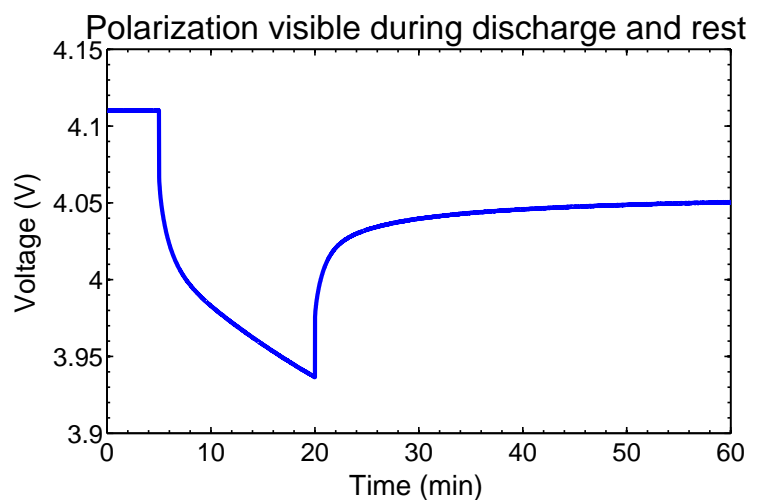
$$v(t) = \text{OCV}(z(t)) - i(t)R_0.$$



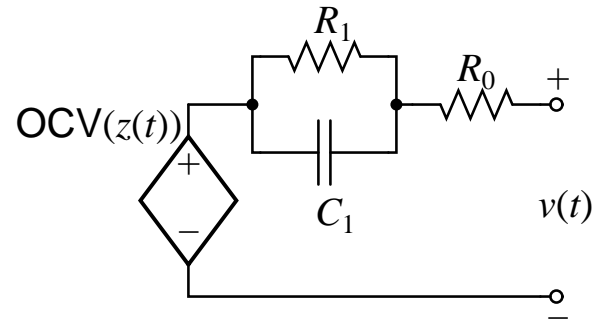
- Note that $v(t) > \text{OCV}(z(t))$ on charge, and $v(t) < \text{OCV}(z(t))$ on discharge.
- This implies that power is dissipated by the resistor R as heat, and therefore that energy efficiency is not perfect.
- This model is sufficient for many simple electronic circuit designs, but not for advanced consumer electronics and xEV applications.

Diffusion voltages

- Polarization refers to any departure of the cell's terminal voltage away from open-circuit voltage due to a passage of current.
- $i(t) \times R_0$ is one example of polarization, modeling an instantaneous response to a change in input current.
- In practice, we also observe a dynamic (non-instantaneous) response to a current step.



- Similarly, when a cell is allowed to rest, its voltage does not immediately return to OCV, but decays gradually (sometimes taking an hour or more to approach OCV).
- We will find out later that this phenomena is caused by slow diffusion processes in the cell, so we will refer to this slowly-changing voltage as a diffusion voltage.
- Its effect can be closely approximated in a circuit using one or more parallel resistor-capacitor sub-circuits.



- The cell voltage is modeled as

$$v(t) = \text{OCV}(z(t)) - v_{C_1}(t) - i(t)R_0.$$
- When using data to identify model parameters, it becomes simpler if we write this expression in terms of element currents instead:

$$v(t) = \text{OCV}(z(t)) - R_1 i_{R_1}(t) - R_0 i(t).$$

- To find an expression for the $i_{R_1}(t)$, we recognize that the current through R_1 plus the current through C_1 must be equal to $i(t)$.
- Further, $i_{C_1}(t) = C_1 \dot{v}_{C_1}(t)$, which gives

$$i_{R_1}(t) + C_1 \dot{v}_{C_1}(t) = i(t).$$

- Then, since $v_{C_1}(t) = R_1 i_{R_1}(t)$,

$$i_{R_1}(t) + R_1 C_1 \frac{di_{R_1}(t)}{dt} = i(t)$$

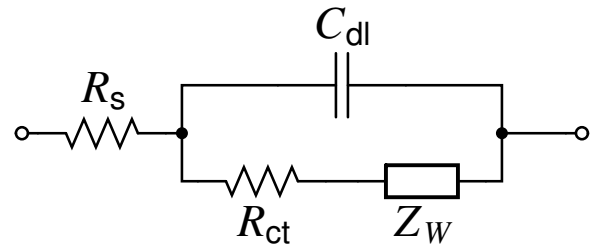
$$\frac{di_{R_1}(t)}{dt} = -\frac{1}{R_1 C_1} i_{R_1}(t) + \frac{1}{R_1 C_1} i(t).$$

- This differential equation can be simulated as-is to determine $i_{R_1}(t)$. We'll see how to convert to discrete-time, shortly.

Warburg impedance

- In the literature, it is not uncommon to see equivalent-circuit models containing a so-called “Warburg impedance” element, Z_W .

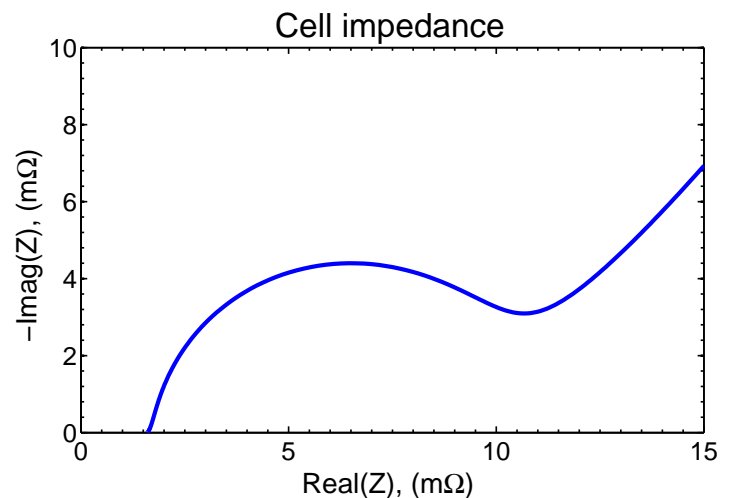
- For example, the *Randles circuit* (shown without OCV) is based on electrochemical principles, a bit like we will see in later chapters.



- In the circuit,

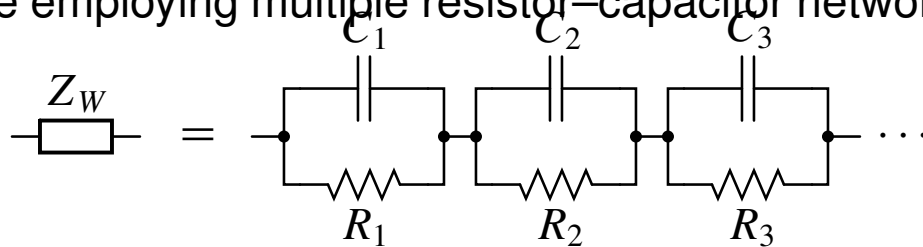
- R_s models the electrolyte resistance,
 - R_{ct} is the *charge-transfer resistance* that models the voltage drop over the electrode–electrolyte interface due to a load,
 - C_{dl} is the *double-layer capacitance* that models the effect of charges building up in the electrolyte at the electrode surface, and
 - Z_W is the Warburg impedance.
- The frequency-dependent Warburg impedance $Z_W = A_W/\sqrt{j\omega}$ models diffusion of lithium ions in the electrodes.

- The phase contributed to the circuit by this element is 45° , which is most easily observed in a Nyquist plot of a cell’s electrochemical impedance spectrum as a straight line at 45° at low frequency.



- The figure shows a simulated electrochemical impedance spectrum representing a realistic cell.

- The equivalent series resistance R_0 for this cell is about $1.5 \text{ m}\Omega$, found as the infinite-frequency impedance.
- The low-frequency impedance is represented by the straight line at 45° , and models lithium diffusion in the solid particles.
- At mid-range frequencies, the semi-circular loop is caused by charge-transfer dynamics, which can be modeled as a single R–C pair.
- There is no simple differential-equation representation of a Warburg impedance, which makes precise circuit simulation intractable.
- However, it is possible to reproduce the effect of a Warburg impedance employing multiple resistor–capacitor networks in series.



- For an exact equivalence, an infinite number of resistor–capacitor networks are needed; but, the circuit can often be modeled very well over some frequency range using a small number of R–C pairs.
- The double-layer capacitance is often omitted as it has little impact on the Randles circuit performance except at very high frequencies.
- With C_{dl} removed from the circuit, and the Warburg impedance replaced by a small finite number of R–C circuits, the cell model collapses to the one we have already seen, with additional R–C pairs.
- When we discuss implementation of physics-based models that have this type of impedance relationship intrinsically built in, we will see how to automatically create ODEs that accurately model the diffusion.

2.3: Converting to discrete time

- The R–C models we have seen to date are expressed in continuous time as ordinary differential equations.
- We wish to convert them to discrete-time ordinary difference equations (ODEs) for easier use in a final application.
- We start by deriving a generic process, which we will then apply to the equation we've seen. Consider

$$\dot{x}(t) = ax(t) + bu(t)$$

$$x(t) = e^{at}x(0) + \underbrace{\int_0^t e^{a(t-\tau)}bu(\tau) d\tau}_{\text{convolution}}.$$

- How did we get this result?

1. $\dot{x}(t) - ax(t) = bu(t).$

2. $e^{-at}[\dot{x}(t) - ax(t)] = \frac{d}{dt}[e^{-at}x(t)] = e^{-at}bu(t).$

3. $\int_0^t \frac{d}{d\tau}[e^{-a\tau}x(\tau)] d\tau = e^{-at}x(t) - x(0) = \int_0^t e^{-a\tau}bu(\tau) d\tau.$

- We wish to evaluate $x(t)$ at discrete times $x[k] \triangleq x(k\Delta t)$. So then,

$$x[k+1] = x((k+1)\Delta t)$$

$$= e^{a(k+1)\Delta t}x(0) + \int_0^{(k+1)\Delta t} e^{a((k+1)\Delta t-\tau)}bu(\tau) d\tau.$$

- With malice aforethought, break up the integral into two pieces.

$$x[k+1] = e^{a\Delta t}e^{ak\Delta t}x(0) + \int_0^{k\Delta t} e^{a((k+1)\Delta t-\tau)}bu(\tau) d\tau$$

$$+ \int_{k\Delta t}^{(k+1)\Delta t} e^{a((k+1)\Delta t-\tau)}bu(\tau) d\tau$$

$$\begin{aligned}
&= e^{a\Delta t} e^{ak\Delta t} x(0) + \int_0^{k\Delta t} e^{a\Delta t} e^{a(k\Delta t-\tau)} bu(\tau) d\tau \\
&\quad + \int_{k\Delta t}^{(k+1)\Delta t} e^{a((k+1)\Delta t-\tau)} bu(\tau) d\tau \\
&= e^{a\Delta t} x(k\Delta t) + \int_{k\Delta t}^{(k+1)\Delta t} e^{a((k+1)\Delta t-\tau)} bu(\tau) d\tau \\
&= e^{a\Delta t} x[k] + \int_{k\Delta t}^{(k+1)\Delta t} e^{a((k+1)\Delta t-\tau)} bu(\tau) d\tau.
\end{aligned}$$

- Assume $u(\tau)$ is constant from $k\Delta t$ to $(k+1)\Delta t$ and equal to $u(k\Delta t)$

$$\begin{aligned}
x[k+1] &= e^{a\Delta t} x[k] + e^{a(k+1)\Delta t} \left(\int_{k\Delta t}^{(k+1)\Delta t} e^{-a\tau} d\tau \right) bu[k] \\
&= e^{a\Delta t} x[k] + e^{a(k+1)\Delta t} \left(-\frac{1}{a} e^{-a\tau} \Big|_{k\Delta t}^{(k+1)\Delta t} \right) bu[k] \\
&= e^{a\Delta t} x[k] + \frac{1}{a} e^{a(k+1)\Delta t} (e^{-ak\Delta t} - e^{-a(k+1)\Delta t}) bu[k] \\
&= e^{a\Delta t} x[k] + \frac{1}{a} (e^{a\Delta t} - 1) bu[k].
\end{aligned}$$

- To use this result for the ODE describing the R-C circuit,

$$a = -\frac{1}{R_1 C_1}, \quad b = \frac{1}{R_1 C_1}, \quad x[k] = i_{R_1}[k], \quad \text{and} \quad u[k] = i[k].$$

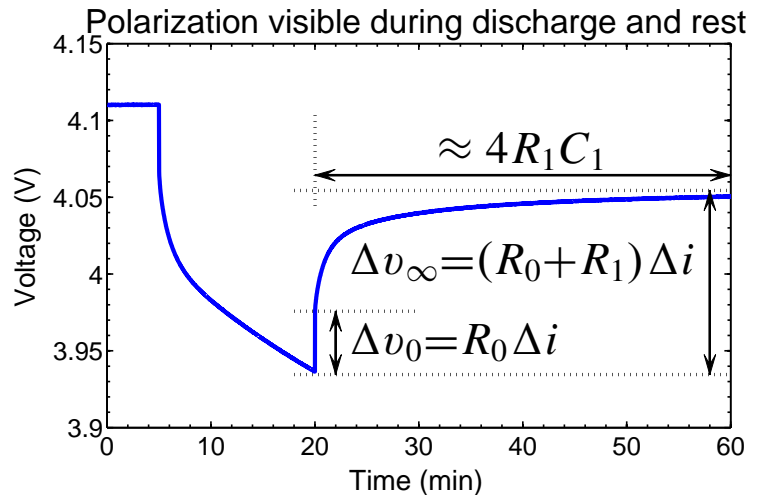
- Substituting these values into the generic result, we get

$$\begin{aligned}
i_{R_1}[k+1] &= \exp\left(-\frac{\Delta t}{R_1 C_1}\right) i_{R_1}[k] \\
&\quad + (-R_1 C_1) \left(\exp\left(-\frac{\Delta t}{R_1 C_1}\right) - 1 \right) \left(\frac{1}{R_1 C_1} \right) i[k] \\
&= \exp\left(-\frac{\Delta t}{R_1 C_1}\right) i_{R_1}[k] + \left(1 - \exp\left(-\frac{\Delta t}{R_1 C_1}\right) \right) i[k].
\end{aligned}$$

Ballparking parameters

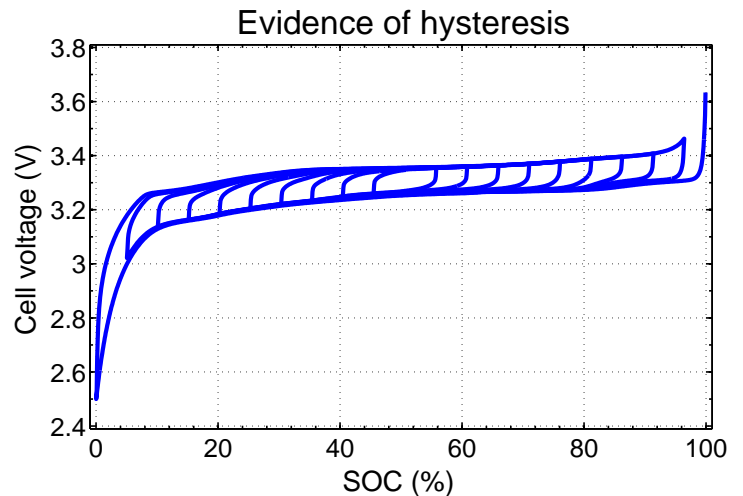
- Note that if a single parallel R–C branch is in the model, it is quite simple to get a ballpark idea of the parameter values.
- First, conduct a pulse test on the cell, similar to the one shown at the beginning of Topic 2.2.
- The immediate jump in voltage at the application of the current pulse is $\Delta v_0 = R_0 \Delta i$, from which we can deduce R_0 .
- The steady-state voltage change, is $\Delta v_\infty = (R_0 + R_1) \Delta i$, from which we can deduce R_1 .
- The pulse response converges to steady state in about four or five time constants, $\Delta t = 4R_1C_1$, from which we can deduce the product of R_1 and C_1 , and therefore C_1 .
- For the cell test conducted to gather the plotted data, $\Delta i = 5 \text{ A}$, $|\Delta v_0| = 41 \text{ mV}$, and $|\Delta v_\infty| = 120 \text{ mV}$.
 - From these values, we compute $R_0 \approx 8.2 \text{ m}\Omega$ and $R_1 \approx 15.8 \text{ m}\Omega$.
- The time to convergence is about $60 \text{ min} - 20 \text{ min} = 40 \text{ min} = 2400 \text{ s}$. So, we might estimate

$$4R_1C_1 \approx 2400 \text{ s} \quad \text{and} \quad C_1 \approx \frac{2400}{4R_1}.$$
 - Using our prior result for R_1 , we can compute $C_1 \approx 38 \text{ kF}$.
- If the model uses multiple parallel R–C branches in series, this simple approach will not work—we'll look at another approach later.



2.4: Hysteresis voltages

- If a cell is allowed to rest for long enough time, diffusion voltages decay to zero, so the prior model voltage decays to OCV.
- In reality, this doesn't occur. For every SOC, there is a range of possible stable "OCV" values.
- Plot shows C/30 (approximate equilibrium) test.
- Evidence of hysteresis: Ignoring it causes large prediction errors.
- Note the distinction between hysteresis and diffusion voltages: Diffusion voltages change with time but hysteresis voltages change when SOC changes. They are not directly a function of time.



SOC-varying hysteresis

- Let $h(z, t)$ be the hysteresis voltage as a function of SOC and time, and let $\dot{z} = dz/dt$. Then, one (not too great) model of hysteresis is

$$\frac{dh(z, t)}{dz} = \gamma \operatorname{sgn}(\dot{z}) (M(z, \dot{z}) - h(z, t)),$$

where $M(z, \dot{z})$ is a function that gives the maximum polarization due to hysteresis as a function of SOC and the rate-of-change of SOC.

- Specifically, $M(z, \dot{z})$ is positive for charge ($\dot{z} > 0$) and is negative for discharge ($\dot{z} < 0$).
- The $M(z, \dot{z}) - h(z, t)$ term in the differential equation states that the rate-of-change of hysteresis voltage is proportional to the distance

away from the major hysteresis loop, leading to a kind of exponential decay of voltage to the major loop.

- The term in front of this has a positive constant γ , which tunes the rate of decay, and $\text{sgn}(\dot{z})$, which forces the equation to be stable for both charge and discharge.
- In order to fit the differential equation for $h(z, t)$ into our model, we must manipulate it to be a differential equation in time, not in SOC.
- We accomplish this by multiplying both sides of the equation by dz/dt .

$$\frac{dh(z, t)}{dz} \frac{dz}{dt} = \gamma \text{sgn}(\dot{z}) (M(z, \dot{z}) - h(z, t)) \frac{dz}{dt}.$$

- Note that $dz/dt = -\eta(t)i(t)/Q$, and that $\dot{z} \text{sgn}(\dot{z}) = |\dot{z}|$. Thus,

$$\dot{h}(t) = - \left| \frac{\eta(t)i(t)\gamma}{Q} \right| h(t) + \left| \frac{\eta(t)i(t)\gamma}{Q} \right| M(z, \dot{z}).$$

- This may be converted into a difference equation for our discrete-time application using the above techniques (assuming that $i(t)$ and $M(z, \dot{z})$ are constant over the sample period):

$$h[k + 1] = \exp \left(- \left| \frac{\eta[k]i[k]\gamma \Delta t}{Q} \right| \right) h[k] + \left(1 - \exp \left(- \left| \frac{\eta[k]i[k]\gamma \Delta t}{Q} \right| \right) \right) M(z, \dot{z}).$$

- Note that this is a linear-time-varying system as the factors multiplying the state and input change with $i[k]$ and hence with time.
- The simplest representation is when $M(z, \dot{z}) = -M \text{sgn}(i[k])$, when

$$h[k + 1] = \exp \left(- \left| \frac{\eta[k]i[k]\gamma \Delta t}{Q} \right| \right) h[k] - \left(1 - \exp \left(- \left| \frac{\eta[k]i[k]\gamma \Delta t}{Q} \right| \right) \right) M \text{sgn}(i[k]).$$

- With this representation $-M \leq h[k] \leq M$ at all times, and $h[k]$ has units of volts.
- When attempting to find the model parameters, we will find it valuable to re-write this in an equivalent but slightly different representation, which has unitless hysteresis state $-1 \leq h[k] \leq 1$,

$$h[k + 1] = \exp\left(-\left|\frac{\eta[k]i[k]\gamma \Delta t}{Q}\right|\right) h[k] - \left(1 - \exp\left(-\left|\frac{\eta[k]i[k]\gamma \Delta t}{Q}\right|\right)\right) \text{sgn}(i[k])$$

Hysteresis voltage = $Mh[k]$.

- This makes the output equation linear in M , which will make estimating M from lab-test data easier.

Instantaneous hysteresis

- In addition to the type of dynamic hysteresis that changes as SOC changes, we also often see benefit in modeling an instantaneous change in hysteresis voltage when the sign of current changes.
- Define

$$s[k] = \begin{cases} \text{sgn}(i[k]), & |i[k]| > 0; \\ s[k - 1], & \text{otherwise.} \end{cases}$$

- Then, the instantaneous hysteresis is modeled as

$$\text{Instantaneous hysteresis voltage} = M_0s[k],$$

and overall hysteresis is

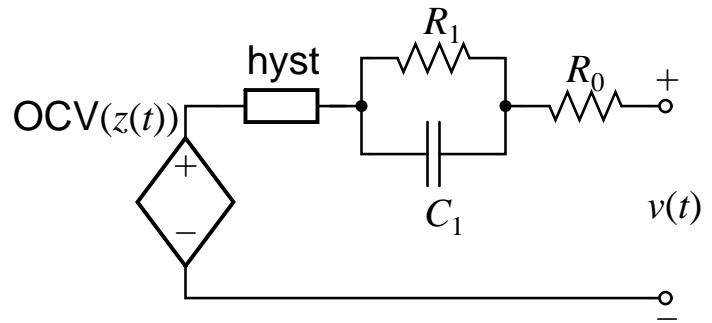
$$\text{Hysteresis voltage} = M_0s[k] + Mh[k].$$

2.5: The Enhanced Self-Correcting (ESC) cell model; OCV testing

- The “enhanced self-correcting” (ESC) cell model combines all the aforementioned elements.

- **Enhanced:** Model includes a (poor) description of hysteresis (which is still better than not including it at all).

- **Self correcting:** Model voltage converges to OCV + hysteresis on rest, and to OCV + hysteresis $- i \sum R$ on constant current event.
- The circuit can contain more than a single parallel resistor-capacitor pair. We can define vector valued



$$i_R[k + 1] = \underbrace{\begin{bmatrix} \exp\left(\frac{-\Delta t}{R_1 C_1}\right) & 0 & \dots \\ 0 & \exp\left(\frac{-\Delta t}{R_2 C_2}\right) & \\ \vdots & & \ddots \end{bmatrix}}_{A_{RC}} i_R[k] + \underbrace{\begin{bmatrix} \left(1 - \exp\left(\frac{-\Delta t}{R_1 C_1}\right)\right) \\ \left(1 - \exp\left(\frac{-\Delta t}{R_2 C_2}\right)\right) \\ \vdots \end{bmatrix}}_{B_{RC}} i[k].$$

- Then, if we define $A_H[k] = \exp\left(-\left|\frac{\eta[k]i[k]\gamma \Delta t}{Q}\right|\right)$,

$$\begin{bmatrix} z[k+1] \\ i_R[k+1] \\ h[k+1] \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & A_{RC} & 0 \\ 0 & 0 & A_H[k] \end{bmatrix} \begin{bmatrix} z[k] \\ i_R[k] \\ h[k] \end{bmatrix} + \begin{bmatrix} -\frac{\eta[k]\Delta t}{Q} & 0 \\ B_{RC} & 0 \\ 0 & (A_H[k] - 1) \end{bmatrix} \begin{bmatrix} i[k] \\ \text{sgn}(i[k]) \end{bmatrix}.$$

- This is the ESC “state equation”, and describes all dynamic effects.
- The “output equation” is

$$v[k] = \text{OCV}(z[k], T[k]) + M_0 s[k] + M h[k] - \sum_j R_j i_{R_j}[k] - R_0 i[k].$$

- These two equations, with associated parameter values filled in, comprise the ESC model.
- Note that all model parameters must be non-negative.

Cell testing to determine the OCV relationship

- To find specific numeric values for the ESC model parameters, we must perform experiments on the cells of interest.
- A cell’s OCV is a static function of SOC and temperature; all other aspects of a cell’s performance are dynamic in some sense. Separate cell tests are performed to collect data for the OCV versus SOC relationship and for the dynamic relationship.
- We first discuss experiments to determine the OCV relationship.
 - The cell is very slowly discharged, then very slowly charged while measuring cell voltage and accumulated ampere hours.

- Tests are run at a number of temperatures spread over the operational range of the cell.
- The following procedure is conducted for each temperature. (v_{\min} and v_{\max} are cutoff voltages, specified by the cell manufacturer.)

OCV test script #1 (at test temperature)

1. Soak the fully charged cell at the test temperature for at least two hours to ensure a uniform temperature throughout the cell.
2. Discharge the cell at a constant-current rate of C/30 until cell terminal voltage equals manufacturer-specified v_{\min} .

OCV test script #2 (at 25 °C)

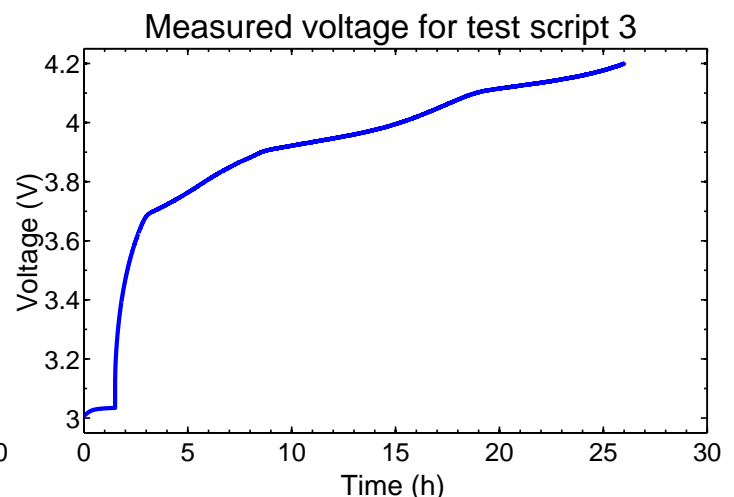
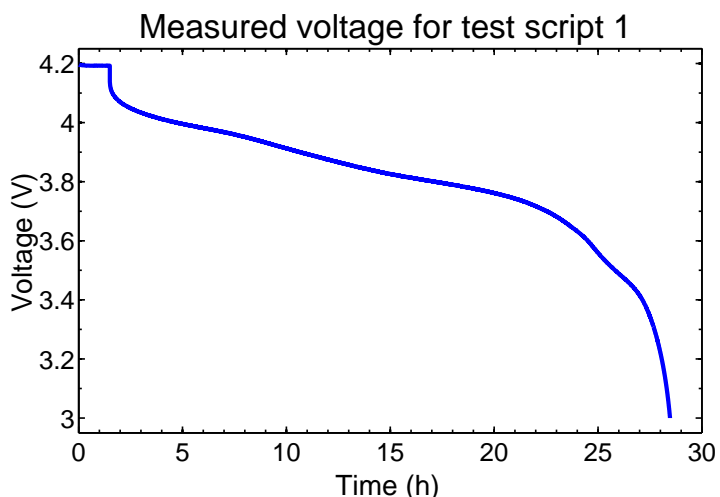
3. Soak the cell at 25 °C for at least two hours to ensure a uniform temperature throughout the cell.
4. If the cell voltage is below v_{\min} , then charge the cell at a C/30 rate until the voltage is equal to v_{\min} . If the cell voltage is above v_{\min} , then discharge the cell at a C/30 rate until the voltage is equal to v_{\min} .

OCV test script #3 (at test temperature)

5. Soak the cell at the test temperature for at least two hours to ensure a uniform temperature throughout the cell.
6. Charge the cell at a constant-current rate of C/30 until the cell terminal voltage equals v_{\max} .

OCV test script #4 (at 25 °C)

7. Soak the cell at 25 °C for at least two hours to ensure a uniform temperature throughout the cell.
8. If the cell voltage is below v_{\max} , then charge the cell at a C/30 rate until the voltage is equal to v_{\max} . If the cell voltage is above v_{\max} , then discharge the cell at a C/30 rate until the voltage is equal to v_{\max} .
 - Voltage, accumulated ampere-hours discharged, and accumulated ampere-hours charged are recorded periodically (e.g., once per second) during every step.
 - Because a very low current rate is used, there is negligible heat generation in the cell, and we can consider all data points to be collected at the ambient test temperature for every script (but, temperature data can be measured as well to verify this assumption).
 - Raw test output for scripts 1 and 3 are shown.



2.6: Determining Coulombic efficiency

- There are some subtle points if the test temperature is not 25 °C.
- Prior to step 2, the cell is still at 100 % state of charge, but its voltage is no longer v_{\max} because OCV is temperature-dependent.
- At the end of step 2, the cell will be at 0 % state of charge *only* if the test temperature is 25 °C because, again, OCV is temperature-dependent, and the v_{\min} specification defines 0 % SOC only for 25 °C.
 - At other temperatures, the actual state of charge may be above or below 0 % at the end of step 2.
- Similarly, at the end of step 6, the cell will be at 100 % state of charge *only* if the test temperature is 25 °C.
 - At other temperatures, the actual state of charge may be above or below 100 % at the end of step 6.
- This is why we must execute test scripts 2 and 4, to ensure that the cell is fully discharged and charged, respectively, before starting test scripts 3 and 1 (for the next temperature to be tested).
- These considerations require some careful processing of the data.
- Let's consider processing data for test temperature 25 °C first.
 - This is the easiest case because all four scripts are then executed at 25 °C—no other temperatures are involved.
 - And, since voltages v_{\max} and v_{\min} are calibrated to 25 °C, the net ampere-hours discharged over all steps equals total capacity Q .
- The net ampere-hours charged over all steps turns out to be slightly higher than Q since the coulombic efficiency of the cell is not perfect.

- We compute the coulombic efficiency at 25 °C as

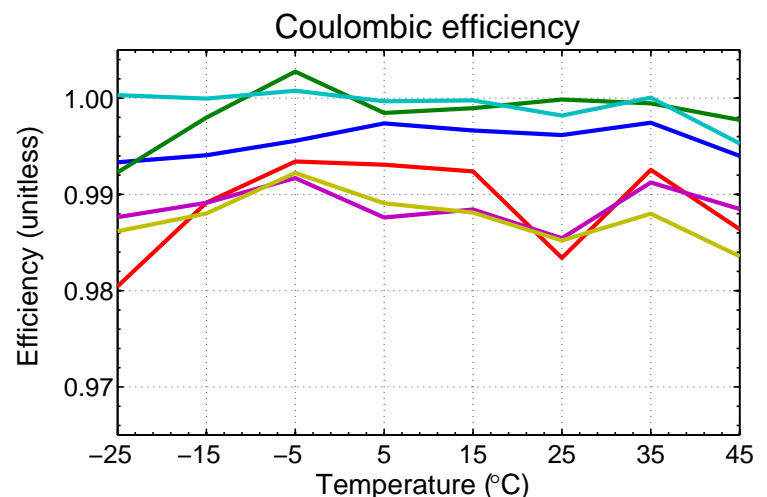
$$\eta(25\text{ }^\circ\text{C}) = \frac{\text{total ampere-hours discharged in all steps at } 25\text{ }^\circ\text{C}}{\text{total ampere-hours charged in all steps at } 25\text{ }^\circ\text{C}}.$$

- At a test temperature T different from 25 °C, we must follow a somewhat different approach.
- We don't know *a priori* the cell state of charge at the end of steps 2 and 6.
- However, we do know that the cell is at 0 % SOC at the end of step 4 and is 100 % at the end of step 8.
- We use this information to compute first the coulombic efficiency at test temperature T :

$$\eta(T) = \frac{\text{total ampere-hours discharged}}{\text{total ampere-hours charged at temperature } T} - \eta(25\text{ }^\circ\text{C}) \frac{\text{total ampere-hours charged at } 25\text{ }^\circ\text{C}}{\text{total ampere-hours charged at temperature } T}.$$

- The figure shows coulombic efficiency calculations for six different lithium-ion cells as a function of temperature.

- The efficiency *should* always be less than one, but experimental accuracy of accumulated ampere hours is inexact, and these calculations are reasonable, to within experimental error.



2.7: Determining temperature-dependent OCV

- We now compute an SOC corresponding to every data sample.
- The depth-of-discharge (in Ah) at every point in time is calculated as

$$\text{DOD}(t) = \text{total Ah discharged until } t$$

$$- \eta(25^\circ\text{C}) \times \text{total Ah charged at } 25^\circ\text{C until } t$$

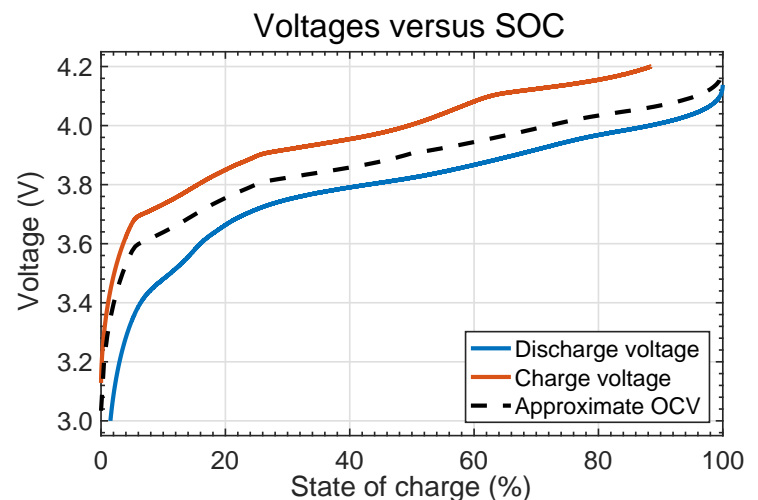
$$- \eta(T) \times \text{total Ah charged at temperature } T \text{ until } t.$$

- Using this metric, the cell capacity Q (measured at temperature T) is equal to the depth-of-discharge at the end of step 4.
- Likewise, the SOC corresponding to every data sample is then

$$\text{state of charge}(t) = 1 - \frac{\text{depth of discharge}(t)}{Q}.$$

- As a check, the state of charge at the end of step 4 must be 0 %, and the state of charge at the end of step 8 must be 100 %.

- The figure plots discharge voltage from step 2 versus state of charge (lower solid curve) and charge voltage from step 6 versus state of charge (upper solid curve).



- These are the same data as shown before, but now presented as a function of state of charge rather than test time.
- This example shows that there is a challenge in determining the open-circuit-voltage relationship at all states-of-charge:

- Missing discharge voltages at low SOC because test encountered cutoff voltage v_{\min} in step 2 before 0 % SOC was reached;
 - Missing charge voltages at high SOC because test encountered cutoff voltage v_{\max} in step 6 before 100 % SOC was reached.
- We can estimate the cell's ohmic resistance R_0 at high SOC via instantaneous voltage change when test moves from step 1 to step 2.
 - We can estimate the ohmic resistance at low SOC by looking at voltage change when the test moves from step 5 to step 6.
 - Also, we can approximate the steady-state resistance at 50 % SOC by considering the voltage change between the discharge voltage curve and the charge voltage curve at the 50 % SOC point.
 - Then, we can assume that the resistance changes linearly from its 0 % SOC value to its 50 % SOC value, and then linearly again from its 50 % SOC value to its 100 % SOC value.
 - At SOC's lower than 50 %, the OCV is estimated as the *charge* voltage plus *charge* current times resistance at that SOC;
 - At SOC's higher than 50 %, the OCV is estimated as the *discharge* voltage plus *discharge* current times resistance at that SOC.
 - The figure shows this approximate OCV estimate as a dashed line.
 - We combine these individual approximate single-temperature OCV results to make a final model of the form

$$\text{OCV}(z(t), T(t)) = \text{OCV}_0(z(t)) + T(t) \times \text{OCVrel}(z(t)),$$

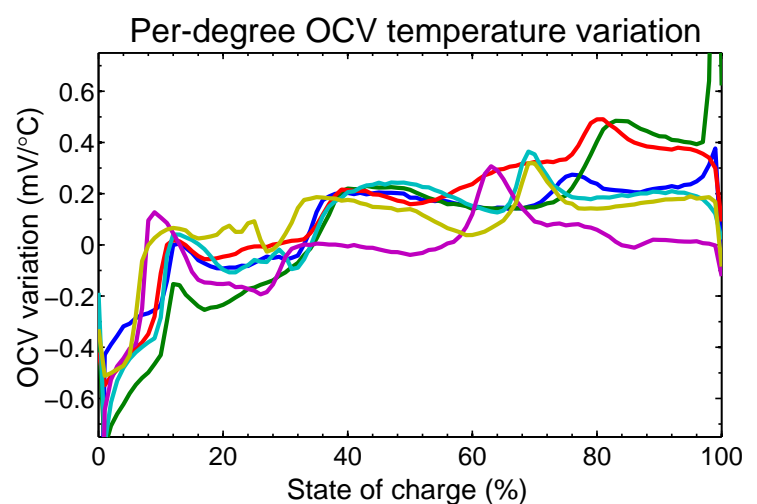
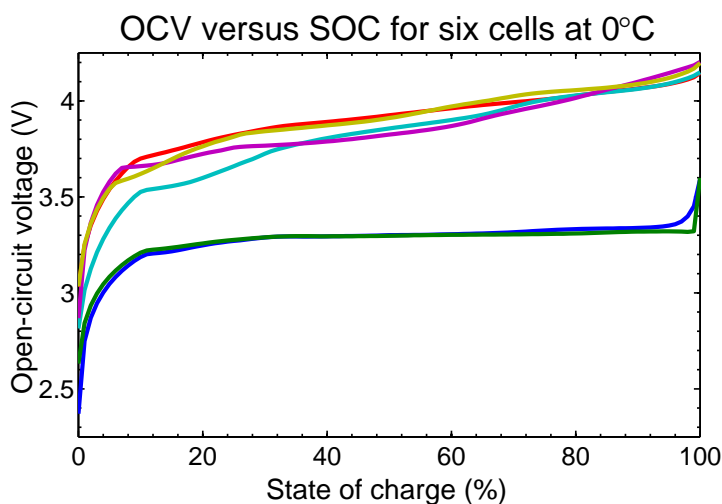
where $\text{OCV}_0(z(t))$ is the OCV relationship at 0 °C , and $\text{OCVrel}(z(t))$ (V/°C) is the linear temperature correction factor at each SOC.

- Once $OCV_0(z(t))$ and $OCV_{rel}(z(t))$ are determined, $OCV(z(t), T(t))$ can be computed via two computationally efficient 1D table lookups.
- To make $OCV_0(z(t))$ and $OCV_{rel}(z(t))$, note that we can write

$$\underbrace{\begin{bmatrix} \text{Approx. OCV at SOC } z, \text{ temp. } T_1 \\ \text{Approx. OCV at SOC } z, \text{ temp. } T_2 \\ \vdots \\ \text{Approx. OCV at SOC } z, \text{ temp. } T_n \end{bmatrix}}_Y = \underbrace{\begin{bmatrix} 1 & T_1 \\ 1 & T_2 \\ \vdots & \vdots \\ 1 & T_n \end{bmatrix}}_A \underbrace{\begin{bmatrix} OCV_0(z) \\ OCV_{rel}(z) \end{bmatrix}}_X$$

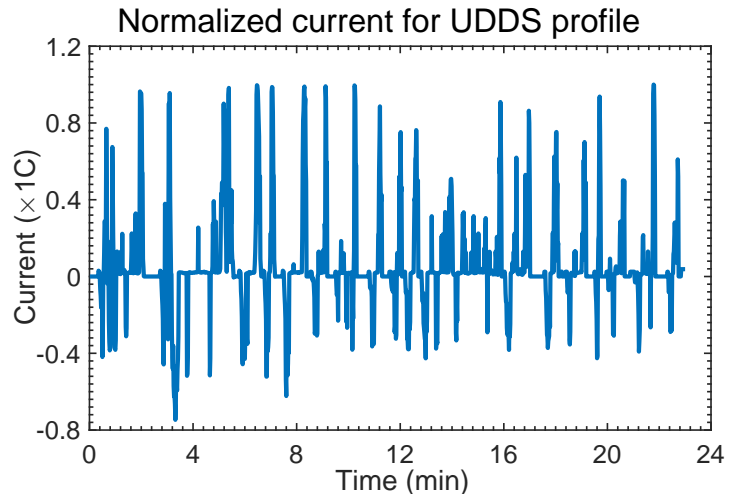
at every state of charge z .

- One way to compute X from A and Y is to use the least-squares solution, which is written mathematically as $X = A^\dagger Y$, where the dagger symbol (\dagger) represents a matrix pseudo-inverse, and is computed in MATLAB as $X=A \setminus Y$;
 - We tend to use data only from tests above 0°C because accuracy degrades at low temperatures due to high cell resistances.
- The figures plot the outcome of this overall process for six different lithium-ion cells.



2.8: Cell testing to determine the dynamic relationship

- Dynamic data is captured while exercising the cell with a profile of current versus time that is representative of the final application.
- The figure shows a sample profile for an automotive application, the “urban dynamometer drive schedule” (UDDS) profile.
- This current profile is repeated over the entire SOC and temperature range of the cell.



Dynamic test script #1 (at test temperature)

1. Soak the fully charged cell at the test temperature for at least two hours to ensure a uniform temperature throughout the cell.
2. the cell using a constant current at a C/1 rate long enough to deplete about 10 % of capacity (helping ensure we avoid over-voltage conditions during charging portions of the profile).
3. Execute dynamic profiles over the SOC range of interest, nominally from 90 % SOC down to 10 % SOC.

Dynamic test script #2 (at 25 °C)

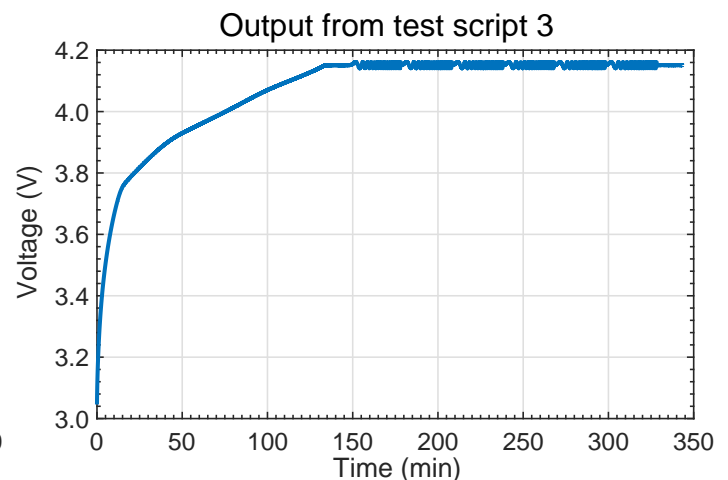
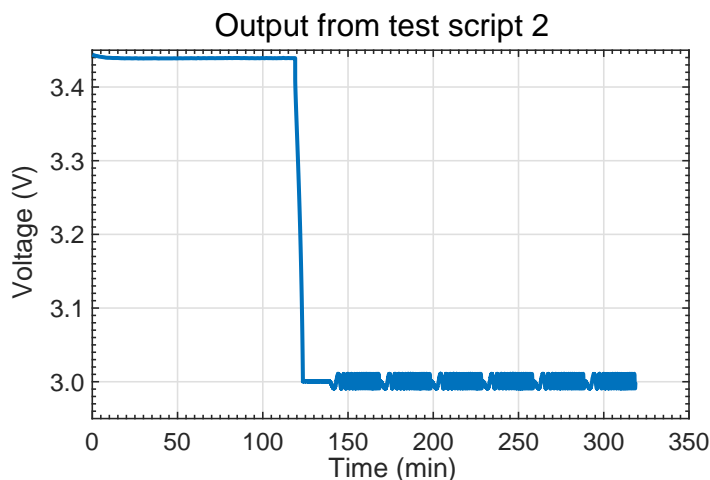
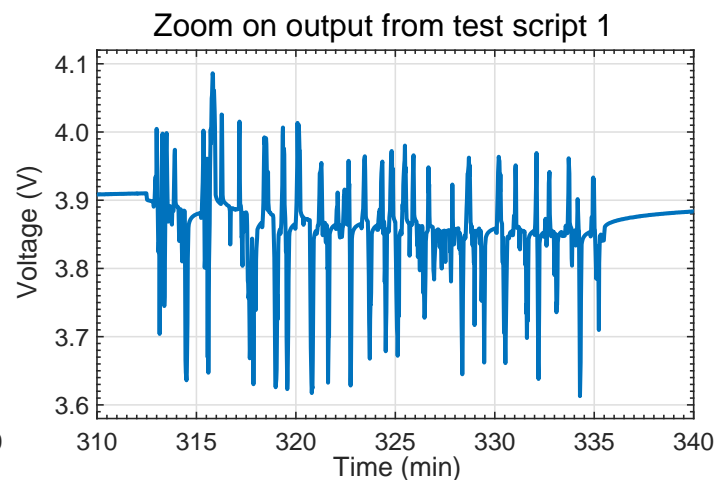
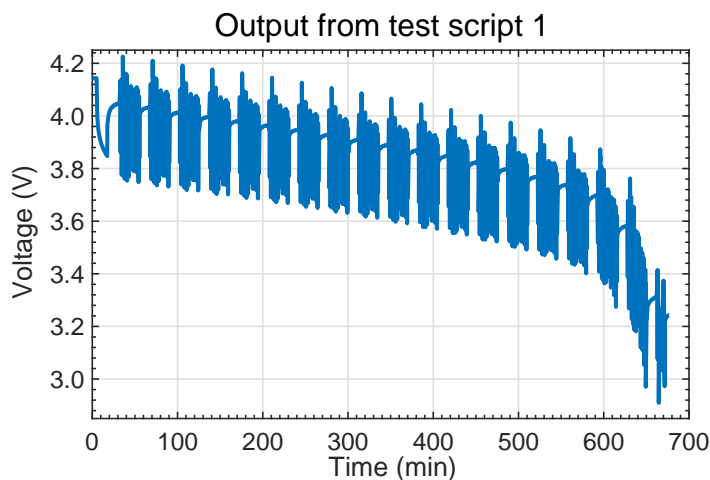
4. Soak the cell at 25 °C for at least two hours to ensure a uniform temperature throughout the cell.
5. If the cell voltage is below v_{\min} , then charge the cell at a C/30 rate until the voltage is equal to v_{\min} . If the cell voltage is above v_{\min} , then

discharge the cell at a C/30 rate until the voltage is equal to v_{\min} . A follow-on dither profile can be used to eliminate hysteresis to the greatest degree possible.

Dynamic test script #3 (at 25 °C)

6. Charge the cell using a constant current at a C/1 rate until voltage is equal to v_{\max} . Then, maintain voltage constant at v_{\max} until current drops below C/30. A follow-on dither profile at the end can be used to help eliminate hysteresis.

- Voltage and current are recorded every second. Cell temperature data may also be collected.



- The dynamic data is used to identify all ESC parameters, except for the OCV versus SOC relationship, which has already been described.
 - We first compute η and Q from the data, directly, as we did for the OCV test results.
 - We use a technique called *subspace system identification* to find the R–C time constants.
 - We then guess a value for γ .
 - Using γ , we compute $h[k]$; we also compute $z[k]$, $s[k]$, $i_{R_j}[k]$ and $\text{OCV}(z[k])$.
 - This leaves the following unexplained part of the measured cell voltage

$$\begin{aligned}\tilde{v}[k] &= v[k] - \text{OCV}(z[k], T[k]) \\ &= Mh[k] + M_0s[k] - \sum_j R_j i_{R_j}[k] - R_0 i[k].\end{aligned}$$

- We can solve this for the unknowns

$$\underbrace{[\tilde{v}[k]]}_Y = \underbrace{\left[h[k] \quad s[k] \quad -i[k] \quad -i_{R_j}[k] \right]}_A \underbrace{\begin{bmatrix} M \\ M_0 \\ R_0 \\ R_j \end{bmatrix}}_X,$$

via least-squares solution $X = A^\dagger Y$.

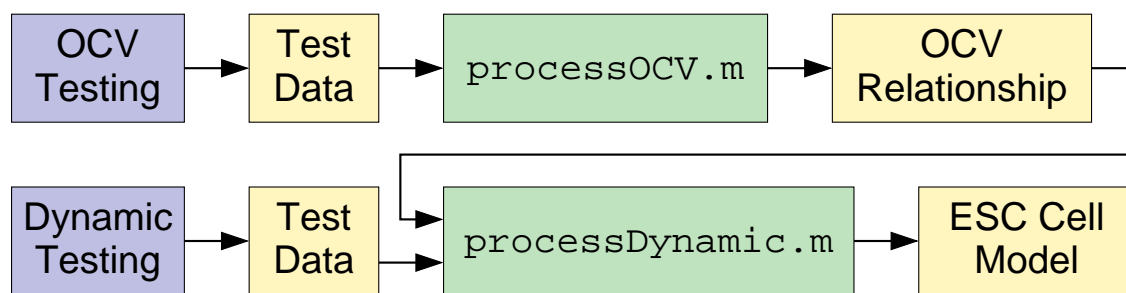
- We then compute the RMS error and update γ to minimize this error.

2.9: Matlab code to create models from data and to simulate

- A MATLAB toolbox and data set comprising code implementing these steps and companion cell-test data collected from a number of cells is available on the book web site.
- Here, we quickly introduce the main code components. A great deal of learning is possible if this discussion is coupled with a diligent examination of the code itself, to see how the steps are implemented.

Creating the model

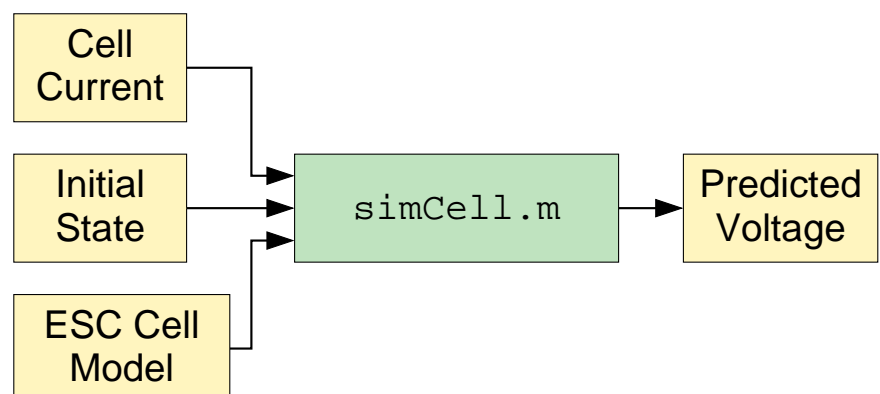
- The figure below depicts the overall process for creating an enhanced self-correcting (ESC) cell model.



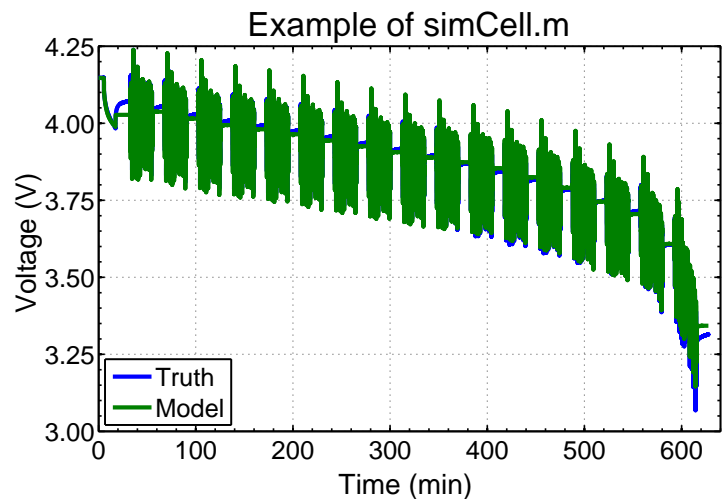
- The blue boxes = laboratory processes; the yellow boxes = data files; and the green boxes = processing by MATLAB functions.

Using the model

- Once the model is created, it is ready to be used.
- The figure depicts the process.



- The following code illustrates how to use the `simCell.m` function.
- Output is displayed to the right.



```
load DYN_Files/E2_DYN/E2_DYN_35_P25.mat % load data file
load DYN_Files/E2model.mat % load model file

time      = DYNDData.script1.time; % make variables easier to access
voltage   = DYNDData.script1.voltage;
current   = DYNDData.script1.current;

ind = find(diff(time)<=0); % get rid of duplicate time steps
time(ind+1)=[]; voltage(ind+1)=[]; current(ind+1)=[];

t1=time(1); t2=time(end); % make sure evenly sampled in time
deltaT = 1; t = (t1:deltaT:t2) - t1; % one-second sampling
current = interp1(time,current,t1:deltaT:t2);
voltage = interp1(time,voltage,t1:deltaT:t2);

vest = simCell(current,25,deltaT,model,1,0,0); % simulate cell

figure(1); clf; % plot some results
plot(t/60,voltage,t/60,vest);
legend('Truth','Model','location','southwest');
xlabel('Time (min)'); ylabel('Voltage (V)');
title('Example of simCell.m');
```

Model internals

- Sometimes, it may be important to query the model parameters.
 - This may be done by directly accessing fields in “`model`”.
 - But, this is generally not considered good programming practice.

- Instead, the toolbox provides data accessor functions.
- In order to determine OCV at one or more SOCs, the `OCVfromSOCTemp.m` function may be used. For example,

```
load DYN_Files/E2model.mat % load model file
z = 0:0.01:1; % make SOC input vector
T = 25; % set temperature value
plot(z,OCVfromSOCTemp(z,T,model));
```

- In order to determine SOC from one or more at-rest OCVs, the `SOCfromOCVtemp.m` function may be used. For example,

```
load DYN_Files/E2model.mat % load model file
v = 2.5:0.01:4.2; % make voltage input vector
T = 25; % set temperature value
plot(v,SOCfromOCVtemp(v,T,model));
```

- Finally, in order to determine a model dynamic parameter value, the `getParamESC.m` function may be used. For example,

```
load DYN_Files/E2model.mat % load model file
T = 25; % set temperature value
gamma = getParamESC('GParam',T,model); % hysteresis rate factor
```

- This requires that the user have some knowledge of the internal structure of the `model` data structure. (Again, it is not recommended that the user access the fields of this data structure directly. However, the field name is required as input to the `getParamESC.m` function.)
- See table on next page.

Table of model fields

Identifier field

name An identifying string storing a name for the cell type

Fields pertaining to the OCV versus SOC relationship

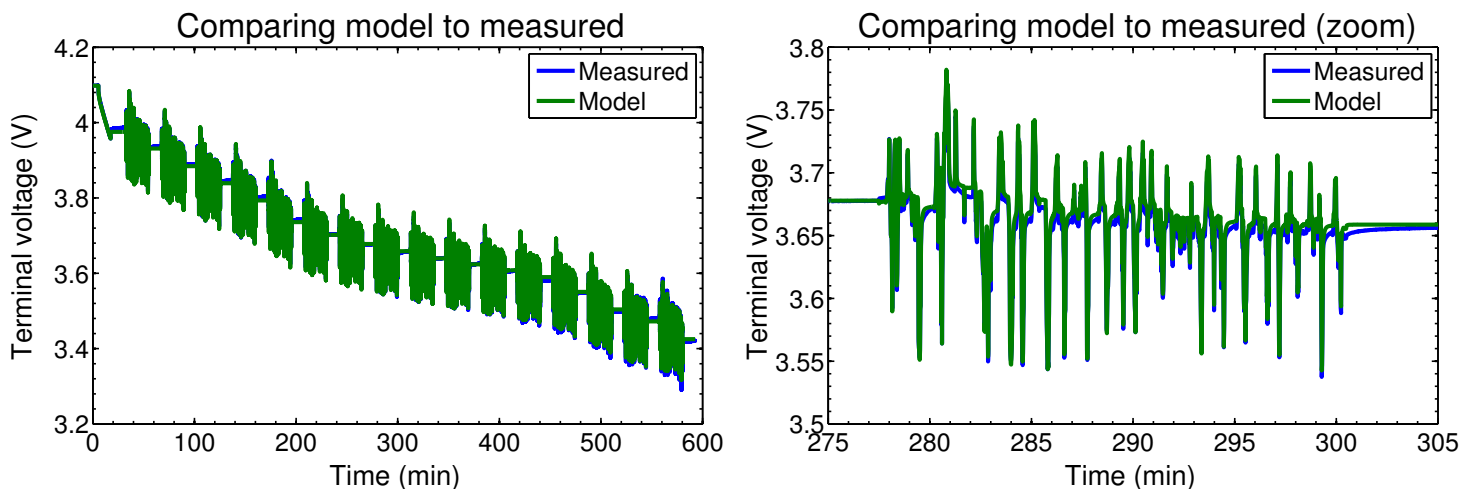
OCV0 Vector of OCV versus SOC at 0 °C [V]
 OCVrel Vector of change in OCV versus SOC per °C [V/°C]
 SOC SOC vector at which OCV0 and OCVrel are stored
 SOC0 Vector of SOC versus OCV at 0 °C (unitless)
 SOCrel Vector of change in SOC versus OCV per °C [1/°C]
 OCV OCV vector at which SOC0 and SOCrel are stored

Fields pertaining to the dynamic relationship

temps Temperatures at which dynamic parameters stored [°C]
 QParam Capacity Q at each temperature [Ah]
 etaParam Coulombic efficiency η at each temperature (unitless)
 GParam Hysteresis “gamma” parameter γ (unitless)
 MParam Hysteresis M parameter [V]
 M0Param Hysteresis M_0 parameter [V]
 R0Param Series resistance parameter R_0 [Ω]
 RCParm The R–C time constant parameter $R_j C_j$ [s]
 RParam Resistance R_j of the R–C parameter [Ω]

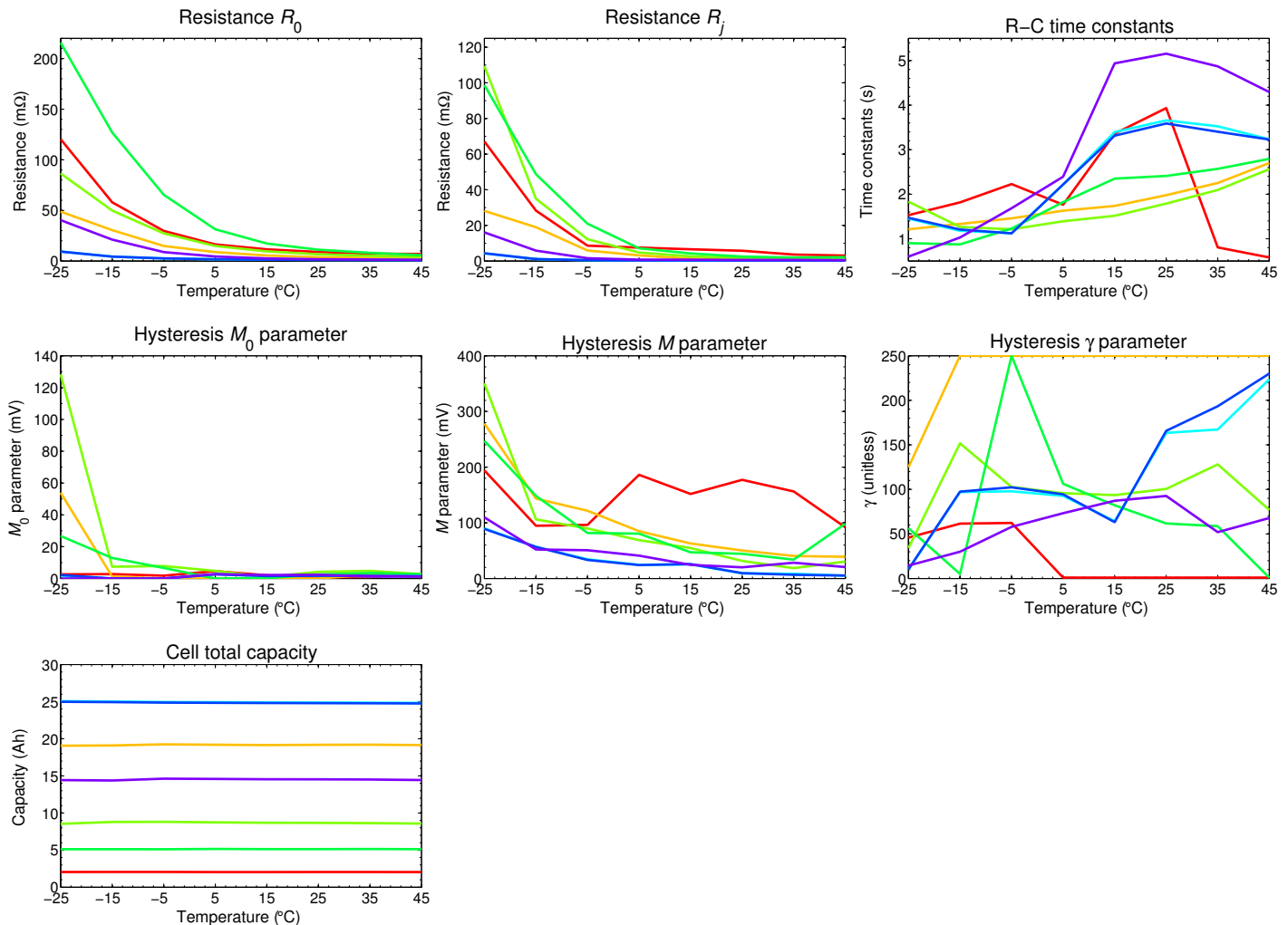
2.10: Example results

- To give a better feel for the capabilities of an equivalent-circuit type model, we present some modeling results in this section.
- Data were collected from a 25 Ah automotive battery cell using the procedures outlined in this chapter, and open-circuit-voltage and dynamic modeling parameters were estimated from the data (using one R–C sub-circuit in the model).
- Here, we concentrate on simulating the optimized model open-loop, and comparing its predictions against the measured voltage data for a test conducted at 25 °C.
- The figure shows an overlay of true and model-predicted voltage over the entire 10 h test.



- The root-mean-squared difference between the true and model results was 5.37 mV in this case.
- The right frame of the figure zooms in to one UDDS cycle, more clearly showing that the circuit model captures the cell performance quite well.

- Optimized temperature-dependent parameter values for seven different cells are shown below (tests were conducted from $-25\text{ }^{\circ}\text{C}$ to $45\text{ }^{\circ}\text{C}$ in $10\text{ }^{\circ}\text{C}$ steps).



- These particular results are characteristic of results obtained from other cells as well, in a variety of ways.
 - ESR R_0 decreases exponentially as temperature increases. This is a near-universal result. Any model lacking this feature is suspect.
 - Resistor–capacitor resistances R_j also decrease (roughly) exponentially as temperature increases. This is also expected.
 - Resistor–capacitor time constants tend to increase with temperature.

- ◆ This might actually seem a surprising result, as we would expect the cell dynamics to speed up at warmer temperatures.
- ◆ However, results in Chap. 7 (based on physics models) show that at some states of charge the cell speeds up while at other states of charge the cell slows down overall.
- ◆ The result in the figure shows a single optimized time constant over all SOC, so it is not necessarily a surprising result.
- ◆ Moreover, the results in Chap. 7 lead us to realize that this relationship should not be expected to be monotonic.
- Hysteresis is generally “speeding up” (that is, a smaller change in SOC is required to effect a large change in the hysteresis state) and decreasing in magnitude as temperature increases. Hysteresis levels generally decrease as temperature increases.
- The measured capacity is very nearly constant across temperature (as it should be).
- In practice, the model will need to be evaluated at temperatures not included in the testing protocol.
 - Linear interpolation is used to approximate parameter values from tables made via the system-identification process.
 - This assumes a smoothness in the functions as temperature varies. We don’t always (*i.e.*, rarely) see this from the initial system-identification output.
 - Some hand smoothing of parameter relationships is usually necessary to make models that match measured data nearly as well as the automatically tuned versions, but which work better at intermediate temperatures.

Where from here?

- Equivalent circuit models of battery cells are very powerful and sufficient for many circuit designs and control algorithm development.
- So, are we done? (No.)
- Circuit models lack predictive power over the long term.
 - How will a cell behave if it is subjected to stimuli not used during training of the model?
 - How will a cell behave as it ages?
 - How can we control a cell to maximize its utility while maximizing its life?
- So, we now start to look at physics-based models of cells, which enable us to increase the predictive power of our models.
- These physics-based models are originally very complex, but ultimately we will be able to reduce them to models of similar complexity to the equivalent circuit models we have studied in this chapter.