Model for Voltage Hysteresis in Li-Ion Cells

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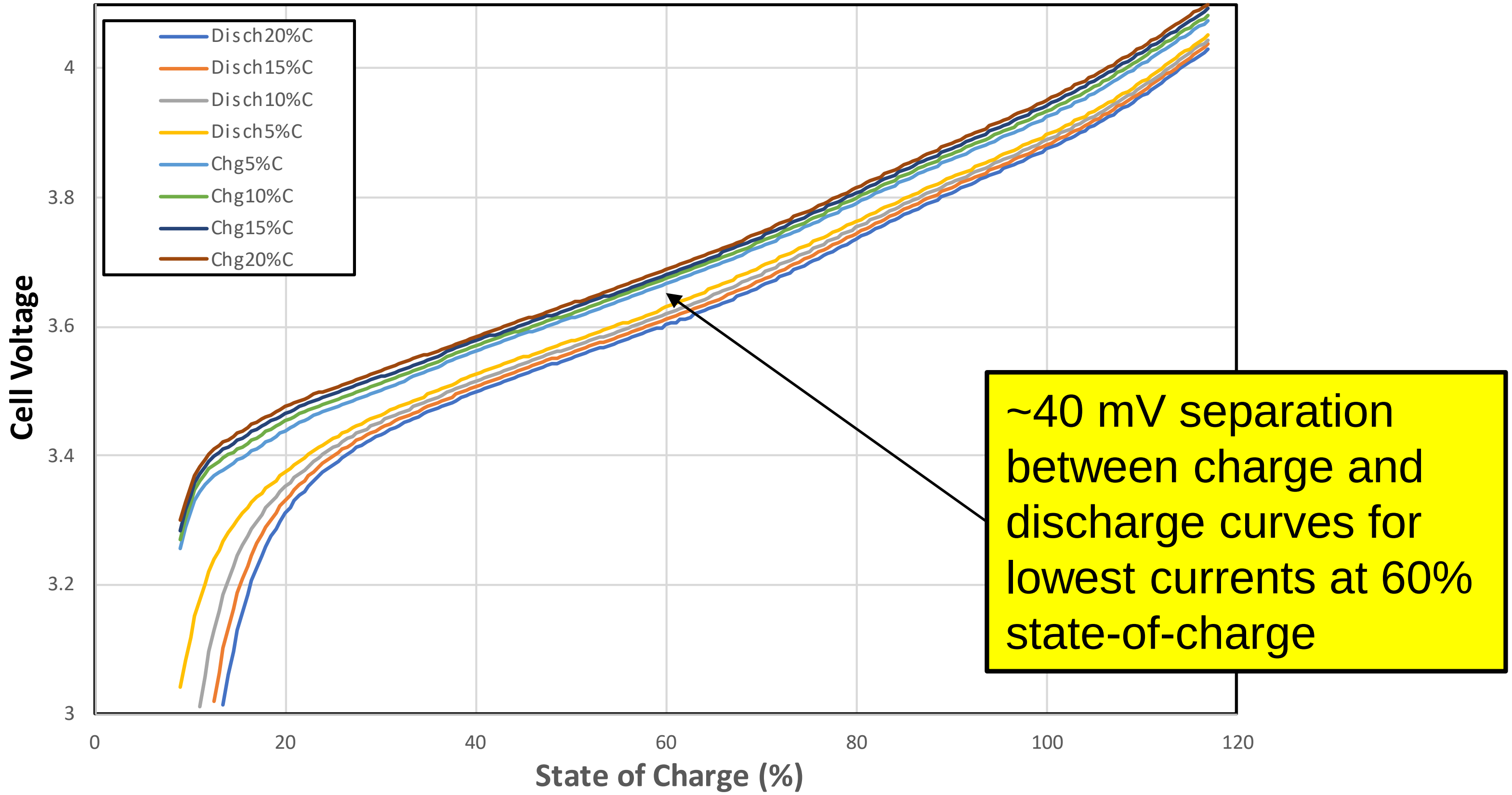
Note: Pictures, Graphs and Diagrams shown on the briefing charts are notional items, not exact.

Voltage Hysteresis in Li-Ion Cells

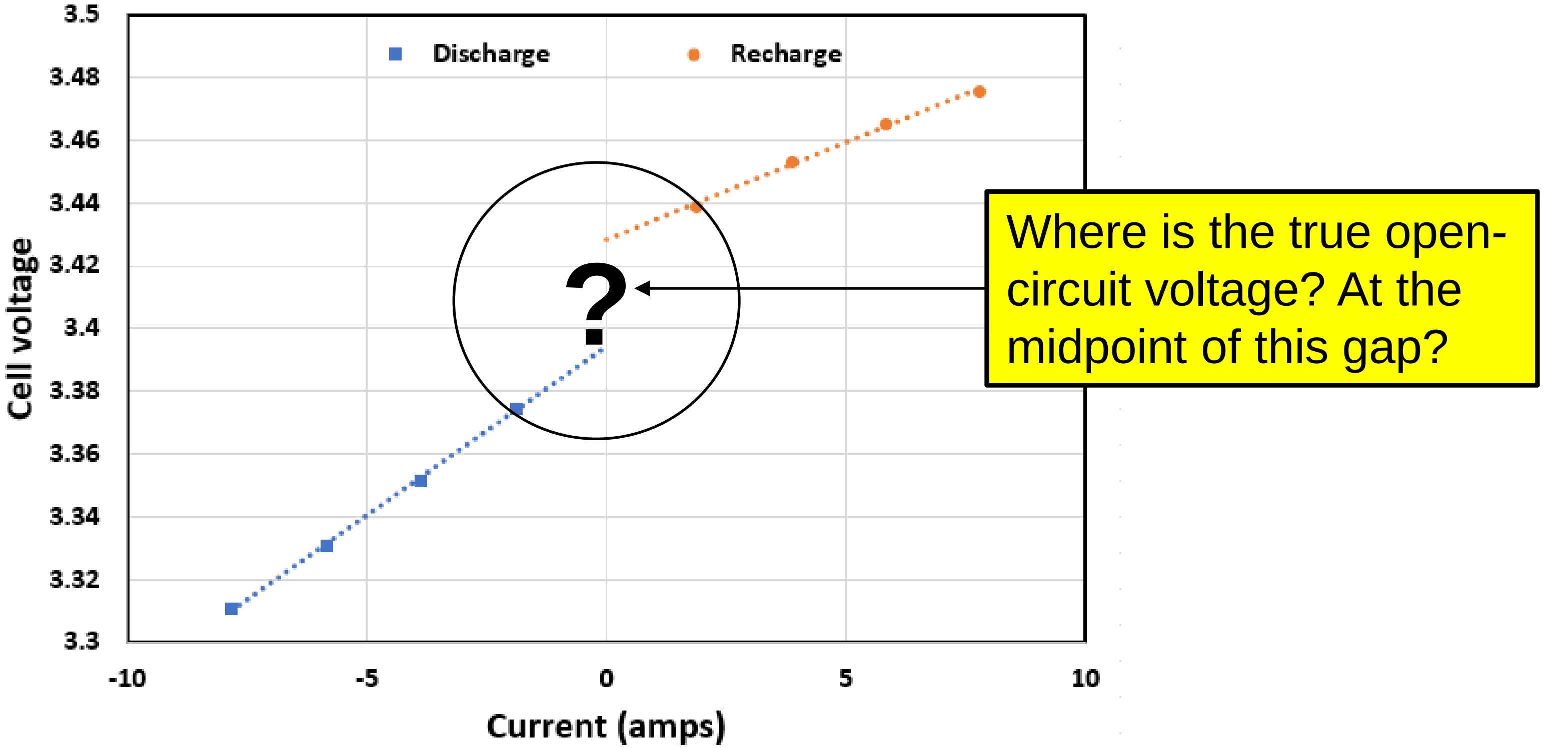
- **Li-ion cells generally exhibit a voltage hysteresis between charge and discharge, typically 10-40 mV in magnitude (data at 20°C temperature)**



- **Modeling cell voltage performance at very low charge or discharge rates cannot be accurately done by simple extrapolation.**
- **Complicates the determination of the reversible potential for the cell.**

Hysteresis in I/V Curves at Fixed State of Charge

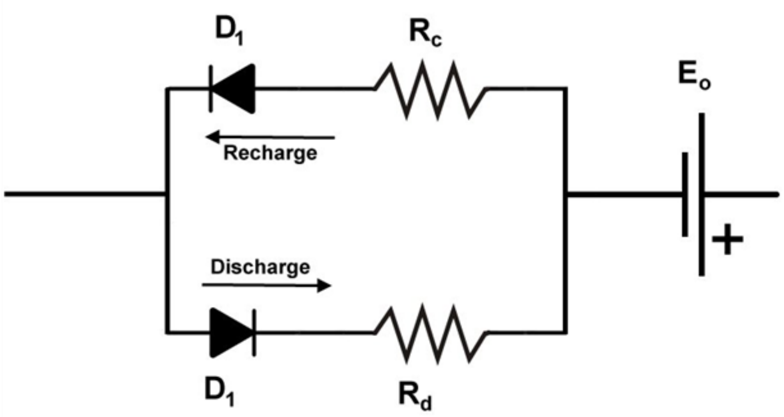
- Hysteresis can be seen as a gap between linear charge and discharge I/V curves at zero current. Data shown is at 20% state of charge.



- Suggests that resistance becomes non-linear near zero current.
- Is there a better way to model the voltage behavior of a cell at very low discharge and recharge currents?
- Can we accurately determine where the reversible potential lies?

Li-Ion Cell Model

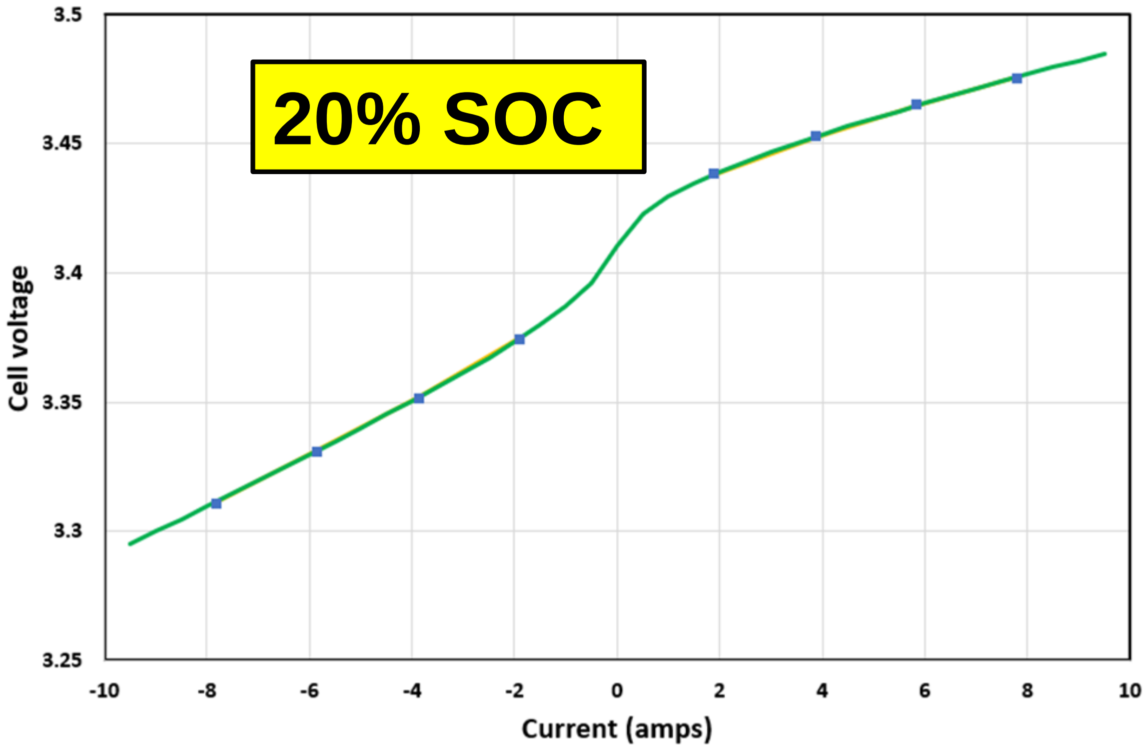
- **Defined by an equivalent circuit that includes an open circuit voltage and different charge and discharge resistances**
- **Similar Schottky diodes inserted into charge and discharge pathways**
  - $I_d = I_s\left(e^{V_d/V_t} - 1\right)$ *where I_d is diode current and V_d is voltage across diode*
  - *V_t is the diode turn-on voltage, and I_s is the diode saturation current*



- **All parameters are dependent on state of charge in this model**
- **Diode parameters I_d and V_d , resistances R_c and R_d, and E_o varied to give best fit to data at each state of charge**
- **Schottky diodes have been previously used to model interesting cell performance features (2^{nd} plateau discharge in nickel electrodes)**

Typical Model Fit to Li-Ion Cell Data

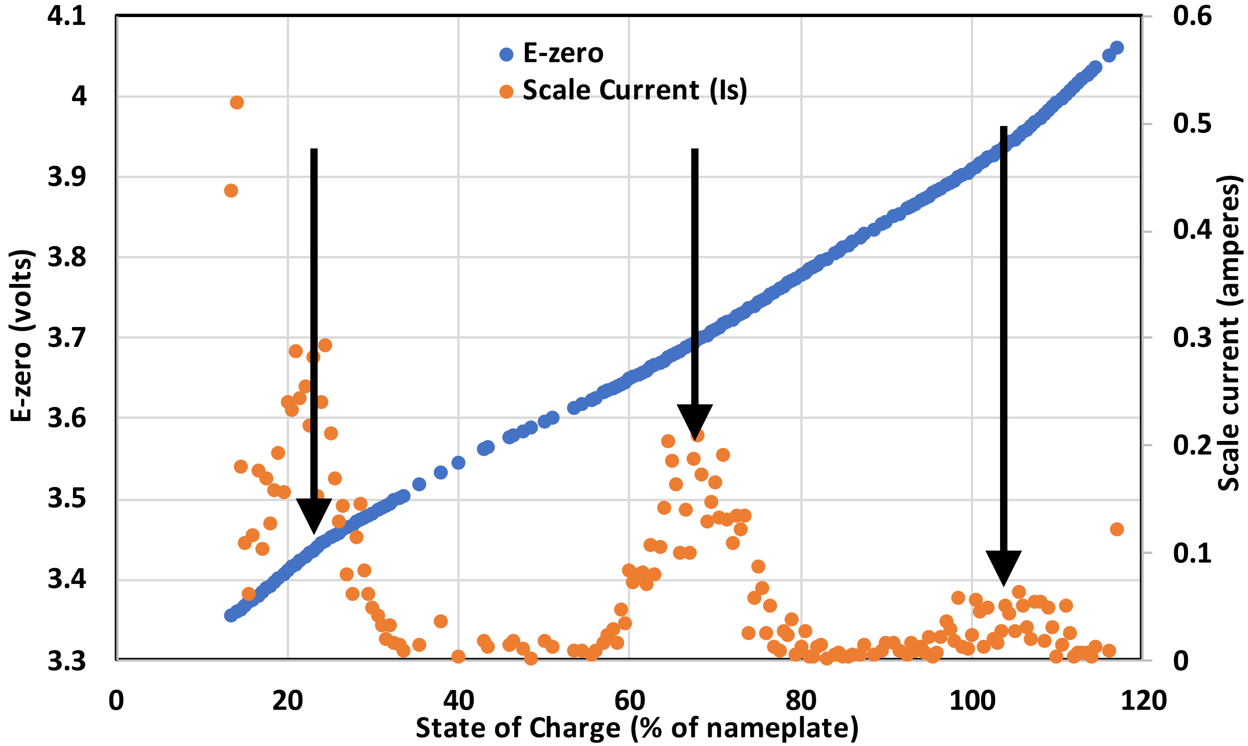
- Model fit to dataset shown on first chart, fit shown here at 20% SOC
- The model typically fits the data points to <0.0001-volt average deviation



- Fitting process performed at each desired state of charge, providing each model parameter as a function of state of charge

Results from Li-Ion Cell Model

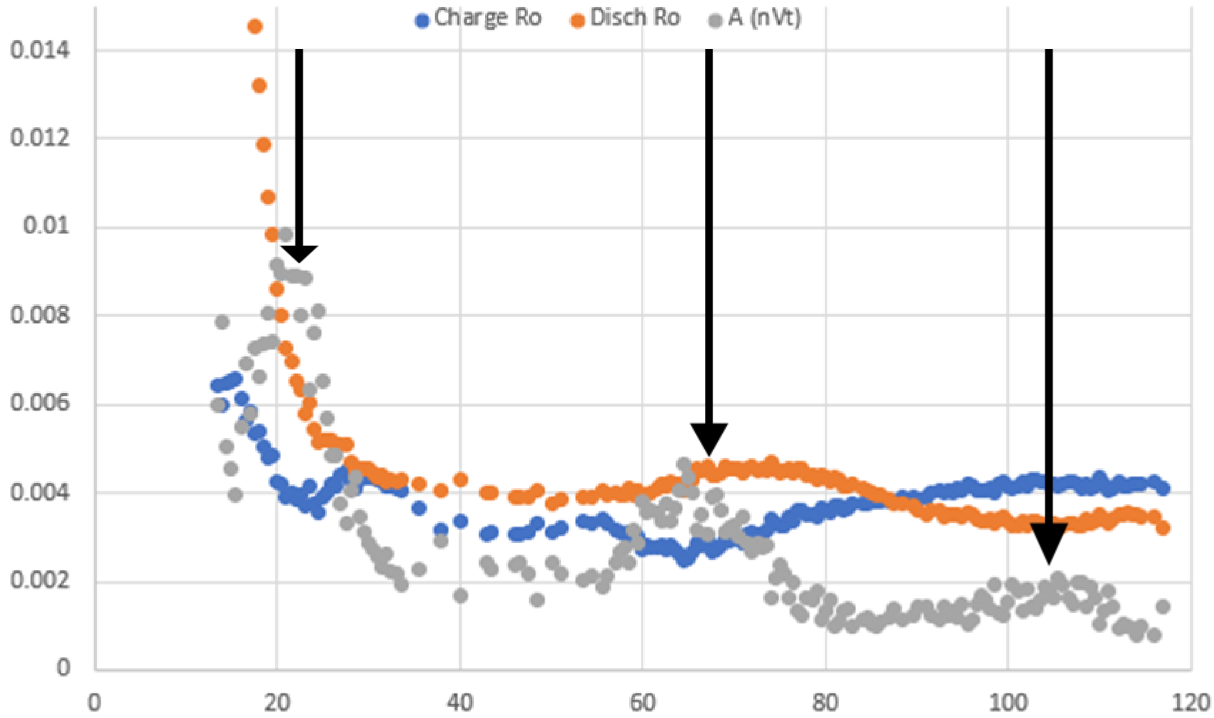
- **Open circuit voltage and diode saturation current parameters**



- **E_o varies monotonically with state of charge**
  - *Arrows show slope changes typically associated with Li intercalation states in carbon*
- **Diode saturation current is only a few ma, but increases significantly in regions where new Li intercalation stages start to fill**

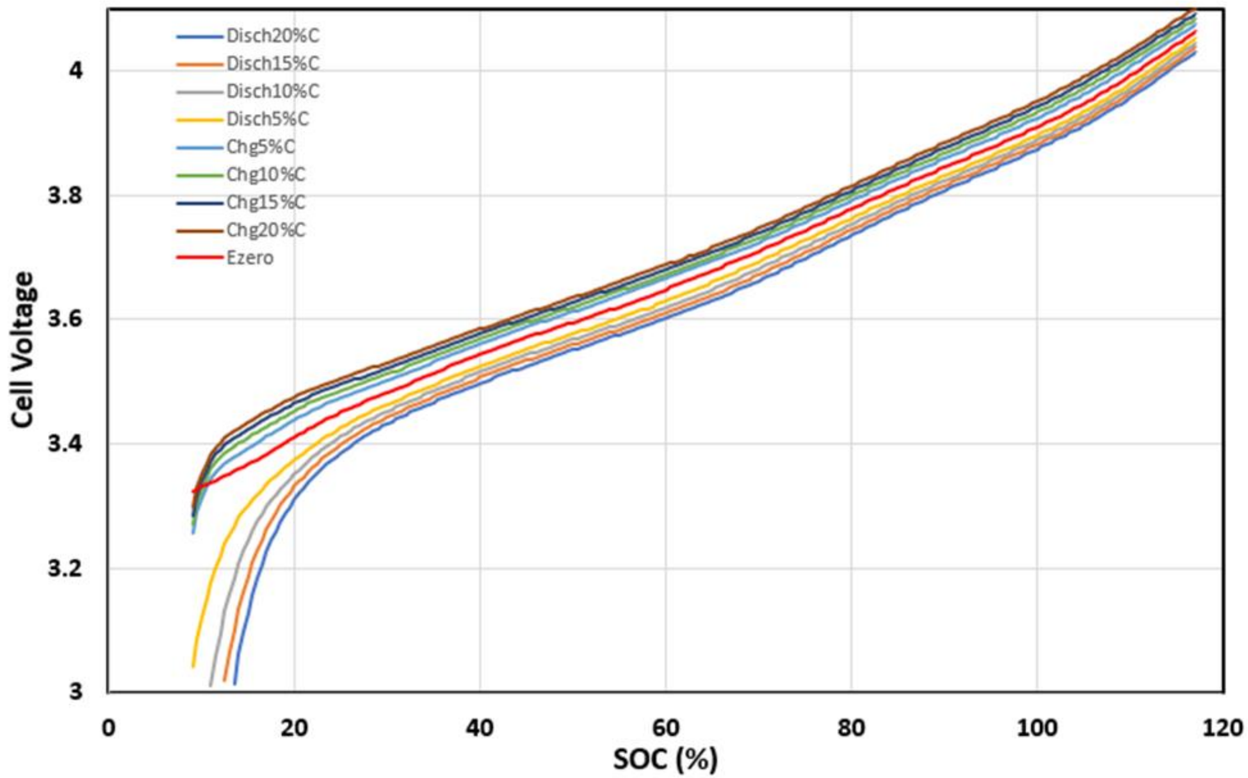
Results from Li-Ion Cell Model

- **Charge and discharge resistance, diode turn-on voltage parameters**



- **Diode turn-on voltage is low, but peaks occur where new stages form**
- **Resistances vary out of phase with each other, likely due to changing surface areas of each stage during charge or discharge**

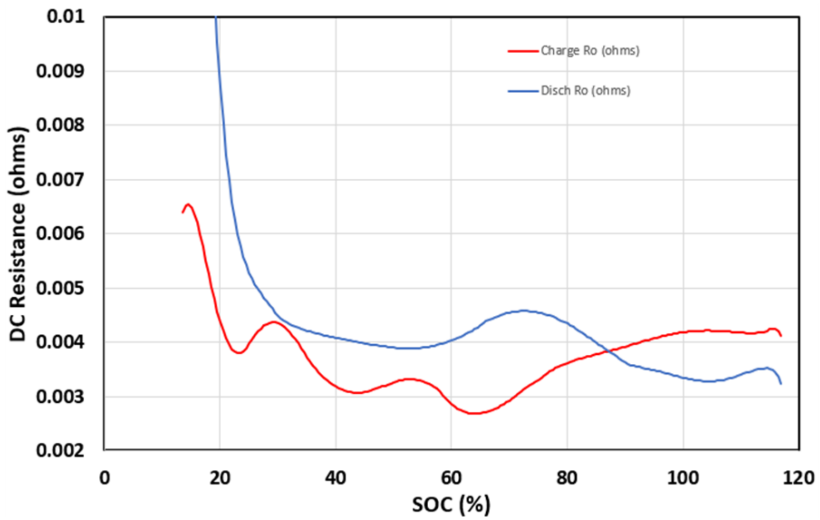
Extraction of Reversible Potential from Data

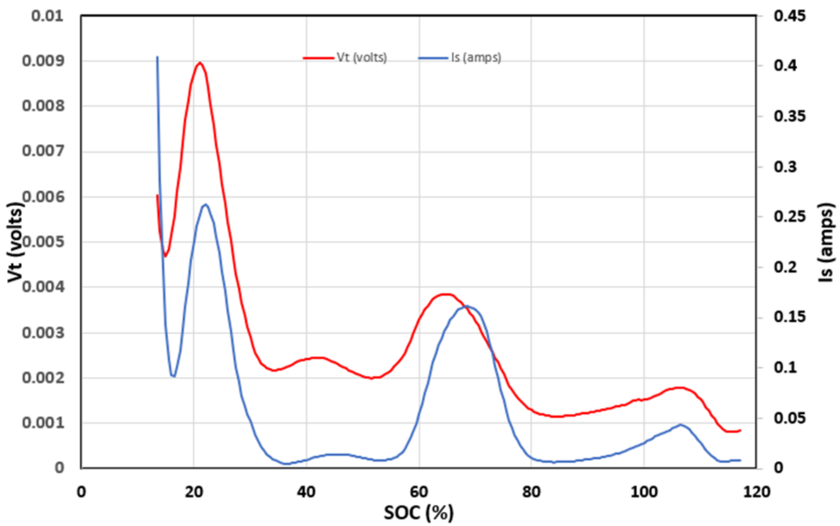


- **Model provides the reversible potential as a function of SOC**
- **Reversible potential falls close to middle of gap between lowest charge and lowest discharge currents, except at low SOC during discharge**
- **Consistent with time-consuming open-circuit stand voltage measurements**

Equivalent Circuit Cell Performance Model

- E_o, I_s, V_t, R_c, and R_d parameters fit to smoothed functions of SOC

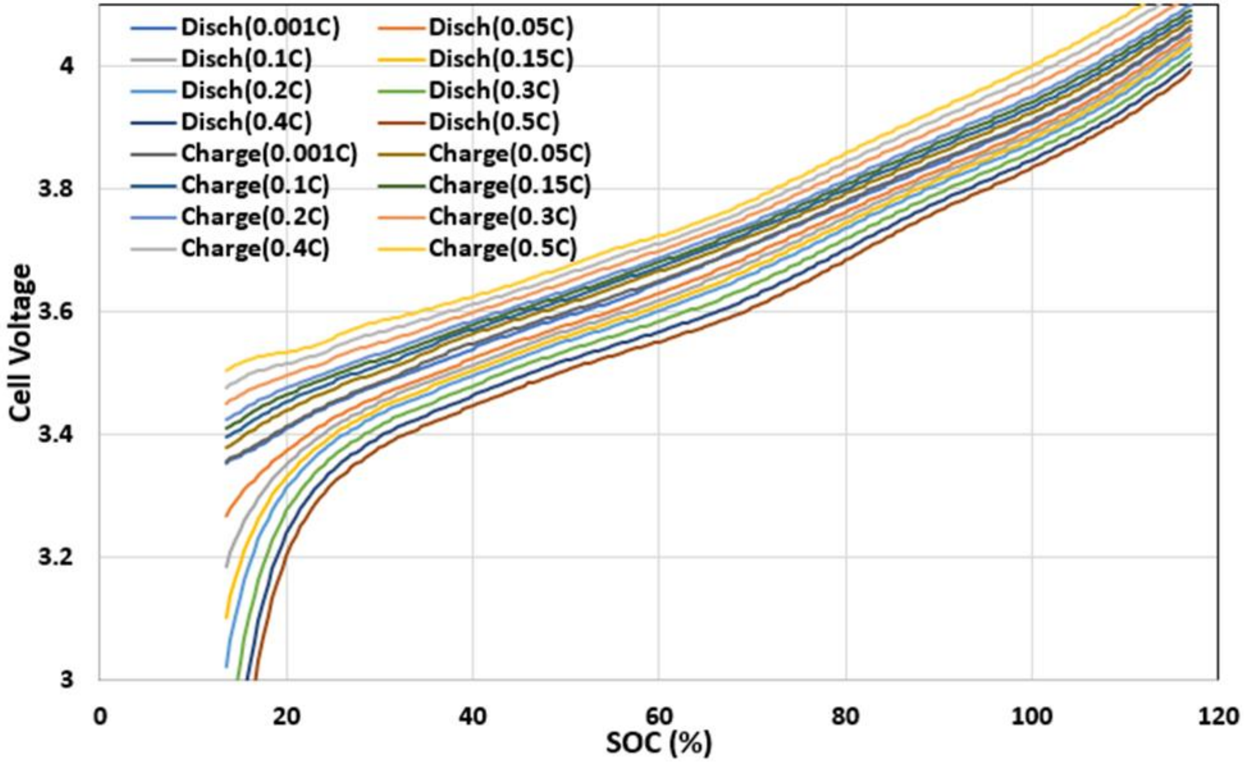




- Equivalent circuit model with smoothed parameters enables cell voltage accurate prediction of cell voltage at any current or SOC
- Model parameters can be determined at other temperatures, or as cells age, to develop a more complete model

Results from Cell Performance Model

- **Model was used to predict cell voltages at currents as low as C/1000**



- **Deviations from measured voltages were within 0.0004 volts over a 13% to 117% SOC range**
- **Even at C/1000 charge or discharge current, predicted voltage still differed from E_o by ~2 mv**

Conclusions

- **A model capable of accurately predicting Li-ion cell voltages, including within the low-current voltage hysteresis gap has been demonstrated**
  - A Schottky diode function can accurately model the non-linear behavior seen in Li-ion cell I/V curves at low overpotentials
  - Improved method to determine reversible potential
- **Model parameters can be identified with physics of electrode charge and discharge**
  - Resistances appear to vary with changing surface area of charged and discharged intercalation stages
  - Peaks occur in diode turn-on voltage and saturation current at states of charge where new intercalation stages start to form
- **Approach can be expanded to develop a more complete battery power/thermal model**
  - Behavior at other temperatures
  - Charge and discharge path dependences