Double Layer Capacitance in a Lithium Ion Battery

Problem Statement

Double layer effect has been largely ignored in most numerical simulations for lithium batteries due to very small characteristic time scale. However for applications with current pulses and rest periods in the order of millisecond, double layer capacitance plays an important role in lithium ion battery. Here using AutoLion 1D™/AutoLion ST™, the effects of double layer capacitance is investigated under the condition of short current pulse. It is shown that the double layer capacitor smooths out the effects of sudden current change under short times.

Setup

- An 2.2Ah NCM/Graphite 18650 cell is set up in AutoLion 1D™. The initial SOC of the cell is set to be 100%.
- 0.2 ms 1C current discharge is applied through user defined load profile (UDLP).

Result

The incorporation of double layer affects the solid and electrolyte charge balance equations alone [1].

\[
0 = \frac{\partial}{\partial x} (\sigma_r \frac{\partial \phi}{\partial x}) - j^{\mu} - a_d C \frac{\partial (\phi - \phi_e)}{\partial t}
\]

\[
0 = \frac{\partial}{\partial x} (k^{\theta} \frac{\partial \phi_e}{\partial x}) + \frac{\partial}{\partial x} (k^{\theta} \frac{\partial \ln c}{\partial x}) + j^{\mu} + a_d C \frac{\partial (\phi - \phi_e)}{\partial t}
\]

The double layer current is calculated using

\[
l_{dl} = a_d C \frac{\partial (\phi - \phi_e)}{\partial t}
\]

where \(a_d\) [m²/m³] is the specific interfacial area and the \(C\) [F/m²] is the specific capacitance. The time constants for the electrodes can be approximated using

\[
\tau = \frac{1}{\kappa a_d C} \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right)
\]

For the simulated 18650 cell, estimated characteristic time is 0.11 ms for negative electrode and 0.26 ms for positive electrode with a specific capacitance \(C\) of 0.2F/m² for both electrodes. Within these time constants, the double layer effects could be extremely important under dynamic operation.

In order to observe the double layer effect, the cell is subjected to a short time 1C constant current pulse. The period of the pulse is chosen to be 0.2 ms, in the range where double layer effects are significant. After the pulse, the current is interrupted.

Figure 1 shows voltage response during the current interrupt test. Comparison between curves with and without double layer effect clearly shows the importance of incorporating the effect of double layer. Gradual and smooth change in the voltage response is observed with inclusion of double layer effect. The time required for the voltage response to reach a steady state is around 0.2ms, which is close to the estimated characteristic time scale.

![Figure 1 Voltage responses for 1C current discharge for 0.2ms](image)

Figure 2, 3 and 4 shows the electrolyte potential, reaction current and double layer current across the cell thickness after the interruption respectively. Just before the interruption (time = 0.2 ms), the potential of the cell does not change noticeably, as seen in Figure 1. The double layer current is very small as seen in 0.0 ms curve in Figure 3. Right after the current interruption, the current transfer through the separator is stopped. The electrolyte potential drop across the separator goes to zero (Figure 2). After the interruption, the discharging of charged double layer onto the electrochemical reaction leads to the local reaction current. Both double layer current and
reaction current change dramatically within the characteristic time scale and go to zero as the rest period continues. With time, the double layer current profile moves into the electrodes and become more uniform as seen in Figure 3.

Figure 2 Electrolyte potential across the cell after the interruption.

Figure 3 Double layer current across the cell after the interruption

**Summary**

- The characteristic time scale for double layer effect is very short, less than millisecond for typical lithium batteries. The inclusion of double layer capacitance is extremely important for application with pulses within this very short time range.
- With activation of double layer model, AutoLion 1D™/AutoLion ST™ is able to capture the dynamic response of the cell voltage and reaction current cause by the effect of double layer capacitance.
- AutoLion™ is a versatile software package that can readily be used for rapid analysis of cell performance under dynamic operations with minimal effort and cost.

**Reference**