Development of Novel Charging Protocols for Li-ion Cells

by

Godfrey Sikha, P. Ramadass, Bala S. Haran, Ralph E. White, Branko N. Popov
Center for Electrochemical Engineering,
Department of Chemical Engineering,
University of South Carolina Columbia, SC 29208
Objectives

- To develop new protocols for charging Li-ion cells.
- To reduce the total charging time.
- To reduce capacity fade due to over-charging.
- To develop a smart charger after optimizing the cell capacity, charging time and capacity decay.
Development of Current Decay Protocol
Need for a New Protocol…

- The charging time for CC-CV protocol is higher.
- Using higher DC currents during CC charge keeps the cell in most part of the time in CV mode, but still there is no considerable decrease in total charging time.
- Usage of CV mode for the entire charging time could decrease the total charging time.
- But the CV charging needs a very high current during the earlier stages of charging that makes the cost of the charger high. In addition, its capacity fade is more.
- Thus, a new protocol that may be similar to CV charging, but not using very high currents, could be ideal for a smart charger that could reduce the charging time to a great extent.
Our Approach...

- Charging the Li-ion cell with linearly descending current with time reduces the charging time as compared to constant current charging.

- Similar mode of charging was tested with commercial Sony 18650 cells.

- Based on the preliminary results of LCD charging, the protocol was modified to avoid over charging and to decrease the charging time further.

- A new protocol was developed that consists of initial high current DC charging (~3C rate) followed by exponential current decay with the fixed total charging time.

- Cycling studies were carried out with the new protocol and the performance was compared with conventional CC-CV and CV mode of charging.

**Development of New protocol**

**Linear Current Decay Protocol (LCD)**

\[ I = I_0 - k_1 t \]

**Modified Linear Current Decay Protocol (MLCD)**

\[ I = I_0 - k_1 t - k_2 \sqrt{t} \]

**The New Protocol**

High Current DC charging followed by exponential current decay
LCD & MLCD Protocols…

**LCD-Protocol**

\[ I = I_0 - k_1 t \]

**MLCD-Protocol**

\[ I = I_0 - k_1 t - k_2 \sqrt{t} \]
Variation of Charging Current and Cell Voltage for the New Protocol

![Graph showing variation of charging current and cell voltage over time.](image-url)
The following studies were made for both fresh and for the cells cycled with conventional CC-CV, CV protocol and the newly developed protocol.

- Rate Capability Studies were done after 150 cycles, where all cells are charged using CC-CV protocol with 1A DC and discharged at different rates namely C/10, C/2, 1C, 3C/2 and 2C.

- CV's were obtained at the scan rate of 0.1 mV/s within the voltage range of 2.5-4.2 V at the end of 150cycles.

- Impedance measurements were done at fully charged and fully discharged states. (100 SOC & 0 SOC) for fresh and cycled cells
Comparison of Utilization of CV-charging, CC-CV charging and new protocol (cycle 1)
## Comparison of utilization times for the charging protocols (first cycle)

<table>
<thead>
<tr>
<th>Protocol</th>
<th>Time for 80% Utilization (sec)</th>
<th>Time for 97% Utilization (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-CV</td>
<td>4476</td>
<td>6625</td>
</tr>
<tr>
<td>CV</td>
<td>2461</td>
<td>5400</td>
</tr>
<tr>
<td>New Protocol</td>
<td>2125</td>
<td>5400</td>
</tr>
</tbody>
</table>
Charge Curves of the CC-CV Protocol
Charge Curves of the CV Protocol

![Graph showing charge curves for different cycles.](image-url)
Charge Curves of the New Protocol
Variation of Charge Capacity with Cycling

![Chart showing variation of charge capacity with cycling]

- CC-CV Protocol
- New Protocol
- CV Protocol
Charge Utilization for CC-CV Protocol

![Graph showing charge utilization over time for different cycles (cycle1, cycle50, cycle100, cycle150).]
Charge Utilization for CV Protocol

- Cycle 1
- Cycle 50
- Cycle 100
- Cycle 150

% Utilization vs. Time (sec)
Charge Utilization for the New Protocol

![Graph showing charge utilization over time for different cycles. The x-axis represents time in seconds, ranging from 0 to 6000, and the y-axis represents percent utilization, ranging from 0 to 100. There are multiple curves, each labeled as cycle 1, cycle 50, cycle 100, and cycle 150, showing the charge utilization over time.]
Variation of Charge Utilization

![Graph showing variation of charge utilization over cycle number for different protocols: CC-CV Protocol, New Protocol, CV Protocol. The graph illustrates the utilization percentage against cycle number, with data points indicating the performance of each protocol.]
Discharge Curves for CC-CV Protocol

![Discharge Curves Graph]

- Voltage (V) vs. Discharge Capacity (Ah)
- Lines represent different cycles: cycle 1, cycle 50, cycle 100, cycle 150
Discharge Curves for CV Protocol
Discharge Curves for the New Protocol

![Graph showing discharge curves for different cycles](image_url)
Variation of Discharge Capacity with Cycling

![Graph showing variation of discharge capacity with cycling. The graph compares three protocols: CC-CV protocol, New Protocol, and CV Protocol. The y-axis represents discharge capacity (Ah) ranging from 1.0 to 1.4, while the x-axis represents cycle number ranging from 0 to 200. Each protocol has a distinct line indicating its performance over cycles.](image-url)
# Capacity Fade Comparison after 150 Cycles

<table>
<thead>
<tr>
<th>Mode of Charging</th>
<th>% Capacity Fade after…</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 cycles</td>
</tr>
<tr>
<td>CC-CV</td>
<td>5.244</td>
</tr>
<tr>
<td>CV</td>
<td>2.849</td>
</tr>
<tr>
<td>New Protocol</td>
<td>2.253</td>
</tr>
</tbody>
</table>
Rate Capability after 150 cycles

Discharge capacity (Ah)

Discharge Current (A)

- CC-CV charging (red dashed line)
- CV charging (blue dashed line)
- Fresh Cell (magenta line)
- New Protocol (green dotted line)
Cyclic Voltammetry of Full Cell at the end of 150 cycles

Scan Rate-0.1mVs

CC-CV protocol
CV Protocol
Fresh Cell
New Protocol

Current (A)
Voltage (V)

Scan Rate-0.1mVs
Nyquist Plots of Fresh Sony 18650 cell

Fresh (0 and 100 SOCs)
Nyquist Plots of Fresh and Cycled Sony 18650 cell

After 150 cycles (0 SOC)
Nyquist Plots of Fresh and Cycled Sony 18650 cell

After 150 cycles (100 SOC)
Conclusions

- New charging protocols were developed for charging commercial 18650 Li-ion cells.
- New protocol shows better performance when compared with CC-CV and CV mode of charging. (Results based on first 150 cycles)
- Cycling studies past 200 cycles are in progress
Acknowledgements

This work was carried out under a contract with the National Reconnaissance Office for

*Hybrid Advanced Power Sources # NRO-00-C-1034.*