AN EXPLORATION OF LI-ION CELL RELAXATION USING EIS

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KEYWORDS
EIS, impedance, Li-ion battery, relaxation, testing

ABSTRACT

This paper describes a systematic study of the effect of cell relaxation after a charge or discharge event. The EIS technique was used to investigate how the properties of the cells changed with time after charge or discharge up to a maximum of 15 hours. It was found that different chemistries show different relaxation rates and frequency dependence of $R_o$ and $R_d$. The cells still showed a relaxation at 15 hours after a charge/discharge event. A suggested compromise of measurement accuracy and test length is to measure the properties of cells 4 hours after a charge/discharge event.

I. INTRODUCTION

Lithium-ion batteries have been common in portable consumer electronics since the early 1990. They have high energy density, high power density, long cycle life, low self-discharge and are also environmentally friendly compared to other type of batteries [1-3]. In recent years, lithium-ion batteries have become the main interest for high power and high energy storage systems like battery electric vehicles (BEV) [1, 4-8], power distribution grids [8-12], wind & solar battery systems [8, 9, 13]. Power and energy density plays a significant role in selecting a battery system for these types of applications.

The maximum power and energy that a battery can deliver are directly related to the impedance of the battery. The impedance of a battery cell defines how quickly the cell voltage will reduce during discharge and how fast it will increase during charge. To maximize the lifetime of a cell it needs to operate within a defined voltage window. Operating beyond this voltage window also poses safety risks.

The impedance of a battery cell is highly dependent on the chemistry, temperature, state of charge (SoC), age and amplitude of charge/discharge current. Extensive of work has been done to study cell impedance; the relationship between impedance and SoC has been developed by researchers [14-18]. Another group of researchers have presented temperature dependency of impedance [17-24]. In contrast to the SoC and temperature effect, age and charge-discharge current amplitude have received less attention. Ratankumar et al. and Buller et al. gave an indication of the effect of the current amplitude on cell impedance [25, 26]. Vetter et al. explained the root cause of the impedance rise of a cell with ageing [27]. It is also reflected by the results presented by other researchers [17, 28-31].

Despite several studies investigating the use of EIS to estimate SoC and SoH in electric vehicles and electrode properties, limited attention has been given towards understanding the effect of relaxation time prior to performing an EIS measurement. To ensure its repeatability and reproducibility in a vehicle or laboratory environment, it is crucial to develop suitable experimental protocols which minimise uncertainties. In this study, the authors investigated, what is believed to be the first study of the effect of relaxation time on EIS measurement of several cell chemistries and several cell formats.

II. EXPERIMENTAL METHOD

A. Cell details

EIS tests were carried out on commercially available lithium-ion cells of different chemistries and different cell format. Seven cells were selected for this study with capacity ranging from 2.2Ah to 40Ah. All cell details are listed in Table 1.
Table 1 Cell details

<table>
<thead>
<tr>
<th>Cell Manufacturer</th>
<th>Chemistry</th>
<th>Capacity (Ah)</th>
<th>Nominal Voltage (V)</th>
<th>Format</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NMC</td>
<td>40</td>
<td>3.70</td>
<td>Pouch</td>
</tr>
<tr>
<td>2</td>
<td>Li-Titanate</td>
<td>13</td>
<td>2.26</td>
<td>Pouch</td>
</tr>
<tr>
<td>3</td>
<td>Mixed Oxide</td>
<td>17.5</td>
<td>3.60</td>
<td>Pouch</td>
</tr>
<tr>
<td>4</td>
<td>NMC/LCO</td>
<td>2.2</td>
<td>3.70</td>
<td>Cylindrical</td>
</tr>
<tr>
<td>5</td>
<td>LMO</td>
<td>3.4</td>
<td>3.60</td>
<td>Cylindrical</td>
</tr>
</tbody>
</table>

B. Test matrix and EIS test details

EIS tests were performed in galvanostatic mode at a frequency range of 100 mHz to 10 kHz and ten frequency points per decade. The amplitude of the current applied was adjusted for individual cell type within the range of C/25 to C/13 Root Mean Square (RMS) value. The spectra were obtained without any superimposed DC current. EIS tests were performed on each cell every 10 min for 15 h after adjusting to 50% state of charge (SoC) using 1C charge/discharge current, at 25°C unless otherwise specified. The SoC, charge/discharge rate and temperature are selected to represent normal operating condition of the cell. The entire experiment was performed within a temperature controlled chamber using a battery cell cycler to adjust SoC. The EIS test was performed using a potentiostat outfitted with a 2A booster card.

III. RESULTS AND DISCUSSION

The Nyquist plots obtained from cells 1 to 5 at 25°C with SoC of 50%, adjusted with a discharge rate of 1C are shown in Fig. 1. Based on the observations in Fig. 1, it is noticeable that relaxation process changes the total impedance of the cell. It is also evident that the pure resistance of the cell $R_o$ does not change nor has a minor change with diffusion process except cell 3. This can be explained from the origin of pure ohmic resistance of the cell. Pure ohmic resistance mainly originate from resistance of electrolyte, electrode-electrolyte interface and current collectors of the cell [17, 18, 22, 41, 42].

The total resistance of the cell $R_d$ which incorporates pure ohmic resistance and electrochemical impedances of the cell defines the energy and power behaviour of an application. $R_d$ is plotted against relaxation period in Fig. 2. Depending on the cell, $R_d$ was found at different frequencies; which is listed in Table 2. This variation can originate from cell chemistry, capacity, size, shape and temperature. Trend lines had been added to the graphs showing in Fig. 2. The trend has a generalized equation as shown in equation 1:

$$y = a \ln(x) + b$$ Equation 1

Values of $a$ and $b$ of this equation for different cells are presented in Table 2. The $R^2$ value of trend lines varies from 0.9581 to 0.9948, indicating good fit with data.
Fig. 1 Nyquist plots obtained after adjusting SoC to 50%, at 25°C using 1C discharge current (note: scale varies from graph to graph but the ratio between ‘X’ and ‘Y’ axis value remains same to show the change of shape).
Fig. 2 Relaxation of $R_d$ for different cell (a) for cell 1 $R_d$ is at 0.63 Hz, (b) for cell 2 it is at 0.63Hz, (c) for cell 3 it is at 2 Hz, (d) for cell 4 it is at 1 Hz.

Table 2 Logarithmic parameters, value and associated frequency of $R_d$ of the cells and value of $R_o$ are listed.

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Coefficient $\alpha$</th>
<th>Constant b</th>
<th>$R_d$ value at 15 h (mΩ)</th>
<th>Frequency of $R_d$ (Hz)</th>
<th>$R_o$ value at 15 h (mΩ)</th>
<th>Frequency of $R_o$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3E-05</td>
<td>0.0014</td>
<td>1.64</td>
<td>0.63</td>
<td>1.00</td>
<td>251.2</td>
</tr>
<tr>
<td>2</td>
<td>1E-05</td>
<td>0.0012</td>
<td>1.25</td>
<td>2.00</td>
<td>0.95</td>
<td>158.5</td>
</tr>
<tr>
<td>3</td>
<td>2E-05</td>
<td>0.0021</td>
<td>2.26</td>
<td>2.51</td>
<td>2.07</td>
<td>79.43</td>
</tr>
<tr>
<td>4</td>
<td>5E-04</td>
<td>0.0617</td>
<td>65.05</td>
<td>1.00</td>
<td>50.15</td>
<td>794.33</td>
</tr>
<tr>
<td>5</td>
<td>8E-04</td>
<td>0.0473</td>
<td>52.63</td>
<td>0.63</td>
<td>36.41</td>
<td>1584.89</td>
</tr>
</tbody>
</table>
IV. CONCLUSION

Findings
- Different chemistries show different relaxation rates.
- 4 h is the suggested minimum waiting time before an EIS measurement should be taken.
- The relaxation process continues even after 15 h.
- The frequency of $R_d$ and $R_o$ depends on chemistry and capacity.

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REFERENCES

35. Institution, B.S., Electrically propelled road vehicles - Test specification for lithium-ion traction battery packs and systems, in Part 2: High-energy applications2012, British Standards Institution
38. SAC, Cycle Life requirements and test methods of traction battery for electric vehicles, 2012, Standardization Administration of China: China.