Evaluate Impact of Different Carbon-based Anode Active Materials on Cell Performance

Introduction

For majority of commercial application, Li-ion batteries rely on carbon-based active material for anode with Graphite as the most commonly used material. However, other forms of carbon such as hard carbon are also considered for commercial applications. For instance, hard carbon owing to its non-stacked carbon layers offer better Li transport than in graphite. Also, due to almost no change in hard carbon volume with intercalation, as compared to approx. 10% change in graphite particle volume, render better cycle life than for graphite electrodes. But hard carbon suffers from lower material density and significantly higher irreversible capacity loss during formation. Therefore, many a times cell developers prefer mixing small amount of hard carbon to graphite electrode. In this case study, we showcase AutoLion™ capabilities in simulating behavior of hard carbon and its mixture with graphite. Users can change the mixture composition easily and the resulting change in electrode properties and its effect on performance is automatically captured with AutoLion™

Technology Used

- AutoLion-1D™ Version 4.1.3 (or later) for performance simulation
- Hard carbon is NOT a part of material database in AutoLion-1D™ Version 4.1.3, but will be made available in our database in the next version.
- Hard carbon is incorporated in this case study via user-defined functions (UDF).
- The same can be achieved with AutoLion-ST™

Setup

- Three types of cells all with NMC111 (LiNi_{0.3}Co_{0.3}Mn_{0.3}O_2) cathode active material but different anode active material composition (Graphite-only, hard carbon-only, and 85%-15% by weight mixture of graphite and hard carbon) are simulated. Active material properties shown in Table 1 are used for this case study. Open circuit potential of graphite and hard carbon at 25°C is shown in Figure 1.
- We have measured electrochemical properties of hard carbon over wide range of temperature. That database will be made available in the next version of AutoLion-1D™ and AutoLion-ST™. For this case study, we have collected hard carbon electrochemical properties through literature survey and inputted in AutoLion-1D™ through relevant UDFs.
- To showcase user-friendliness of our UDFs, we have taken electrochemical properties of graphite from reference [1] and inputted through relevant UDFs. For NMC 111, properties are taken from database.
- All the negative electrodes irrespective of active material composition have same thickness (80 µm single side coating) and loading. Positive electrode design (thickness, loading) is same for all the cells. All cells have N/P ratio of 1.15.
- Reversible cell capacity and Li stoichiometry range in full cell operation (after cell formation) is dictated by irreversible capacity losses of hard carbon and graphite, and is accounted for in this case study.
- 1.2M LiPF₆ in EC:EMC:DMC solvent is used as solvent

Table 1. Material properties for anode and cathode active materials used in this case study

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial capacity* (mAh/gm)</th>
<th>Reversible capacity* (mAh/gm)</th>
<th>Material density (gm/cm³)</th>
<th>Particle diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>372</td>
<td>342</td>
<td>2.24</td>
<td>15</td>
</tr>
<tr>
<td>Hard Carbon</td>
<td>500</td>
<td>410</td>
<td>1.76</td>
<td>10</td>
</tr>
<tr>
<td>NMC111</td>
<td>163</td>
<td>163</td>
<td>4.8</td>
<td>10</td>
</tr>
</tbody>
</table>

*values taken from half-cell experiments
Results

Figure 2. Simulated voltage response of Li-ion cells with NMC111 cathode and anode with three different active material compositions. Simulation carried out at 1C rate and 25°C

Analysis and User Benefits

- For commercially-available Li-ion batteries, mixing of hard carbon and graphite is a very common practice to optimize performance and life. AutoLion™ enables users to easily simulate behavior of any desired mixture of anode active materials.
- Mixing small amount of hard carbon (in this case 15% by weight of active material) to graphite renders a sloping voltage profile which is characteristics of hard carbon. This, in contrast to graphite only anode which gives very sharp drop in voltage towards the end of discharge, helps in reliably estimating cell state of charge.
- Although users can add any new material to AutoLion through UDFs, we are continuously increasing our database for ease of AutoLion use for our users. As mentioned before, hard carbon and other anode and cathode active materials will be included in AutoLion™ database (properties as a function of SOC and temperature) in the next version of AutoLion-1D™ and ST™.

References