PyBaMM SPM: Beginning of Life Model

Building the SPM model: A Single Particle Model (SPM) was developed in PyBaMM based on the Prada et al. (2013) parameter set. This dataset corresponds to a lithium-ion cell with a nominal capacity of approximately 2.3 Ah and was selected due to its similarity in both electrochemical chemistry and capacity to the experimental beginning-of-life (BOL) data contained in the 95K dataset used for model development. To better align the model response with experimental observations, key parameters were calibrated, resulting in an adjusted model capacity of 2.5 Ah.

Data Availability: Voltage–capacity data from both charging and discharging experiments were used to calibrate the SPM voltage response, Figure1 and Figure 2.

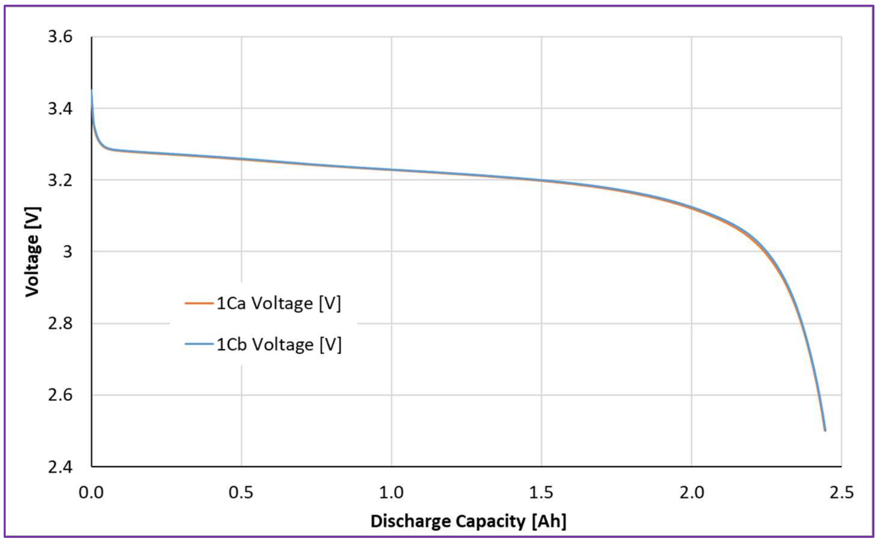

Figure 1: Discharge voltage Test data

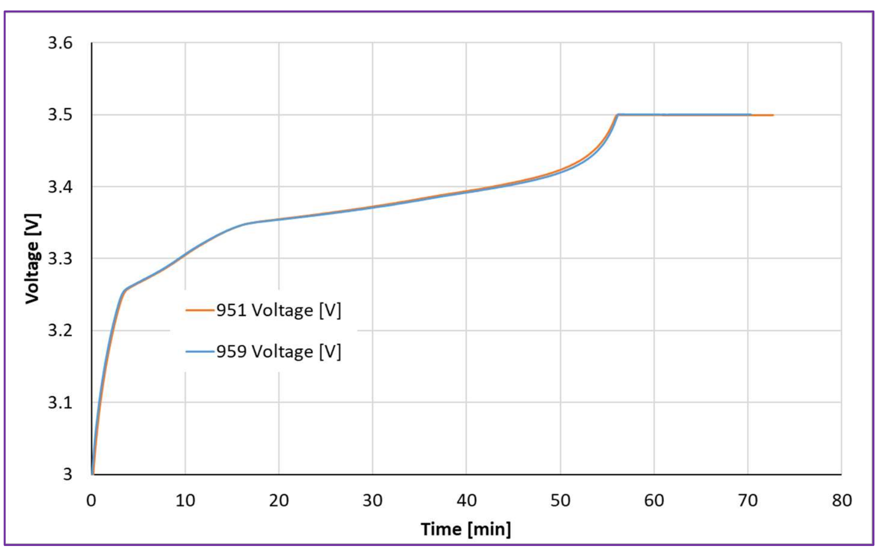

Figure 2: Charge voltage Test data

Model calibration was performed by optimizing a selected set of electrochemical and transport parameters to minimize the deviation between simulated and experimental voltage profiles, as detailed below.

```
params.update(
  {
       "Positive electrode delithiation OCP [V]":
pybamm.input.parameters.lithium_ion.Prada2013.LFP_ocp_Afshar2017_delithiation,
     "Positive electrode lithiation OCP [V]":
pybamm.input.parameters.lithium_ion.Prada2013.LFP_ocp_Afshar2017_lithiation,


    "Negative electrode lithiation OCP [V]":
pybamm.input.parameters.lithium_ion.Prada2013.graphite_LGM50_ocp_Chen2020_lith
iation,
     "Negative electrode delithiation OCP
[V]":pybamm.input.parameters.lithium_ion.Prada2013.graphite_LGM50_ocp_Chen202
0_delithiation,


     "Negative electrode thickness [m]": 3.4e-05*1.22,
     "Initial concentration in negative electrode [mol.m-3]": (0.81 * 30555*0.9),
     "Maximum concentration in negative electrode [mol.m-3]": 30555*1.1,
     "Negative particle diffusivity [m2.s-1]": 3e-13,
  }
)
```

The open-circuit potential (OCP) functions provided in the Prada et al. dataset are represented using polynomial fits. However, these polynomials do not accurately reproduce the OCP curves reported in the original Prada thesis. Consequently, the OCP polynomials were re-tuned to more closely match the reference OCP profiles, thereby improving the overall voltage prediction of the model.

In addition, separate lithiation and delithiation OCP functions were optimized to capture the intrinsic voltage hysteresis behavior characteristic of LFP chemistry. This approach is consistent with the PyBaMM framework, which allows independent charge and discharge OCP definitions as a pragmatic alternative to explicit hysteresis modeling. The use of distinct OCP curves enables improved agreement with experimental voltage profiles while avoiding the additional computational cost and parameter identifiability challenges associated with implementing a full hysteresis sub-model at this stage of the study.

Negative electrode thickness was optimized to simultaneously match the target cell capacity and ensure an N/P ratio greater than unity. In the calibrated model, an N/P ratio of approximately 1.18 was achieved, compared to a value of ~0.8 obtained using the default parameter set. An N/P ratio below unity is not recommended for practical LFP cells due to lithium plating and capacity-limitation concerns; therefore, maintaining an N/P ratio greater than one was assumed to be necessary for realistic cell representation.

Li^{+} concentration in negative electrode was optimized to ensure that the simulated cell voltage remains within experimentally observed operating limits.

The charge and discharge results are shown in Figures 3 and 4, respectively.

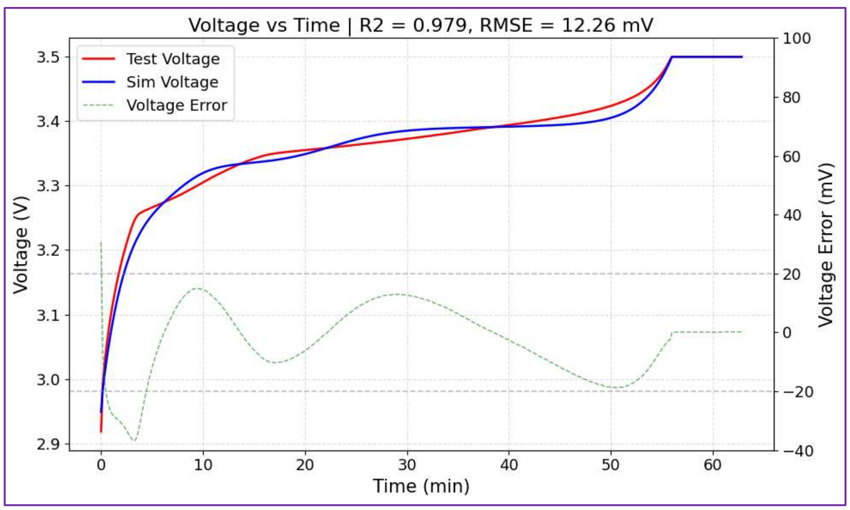

Figure 3: Charge Voltage at 1C

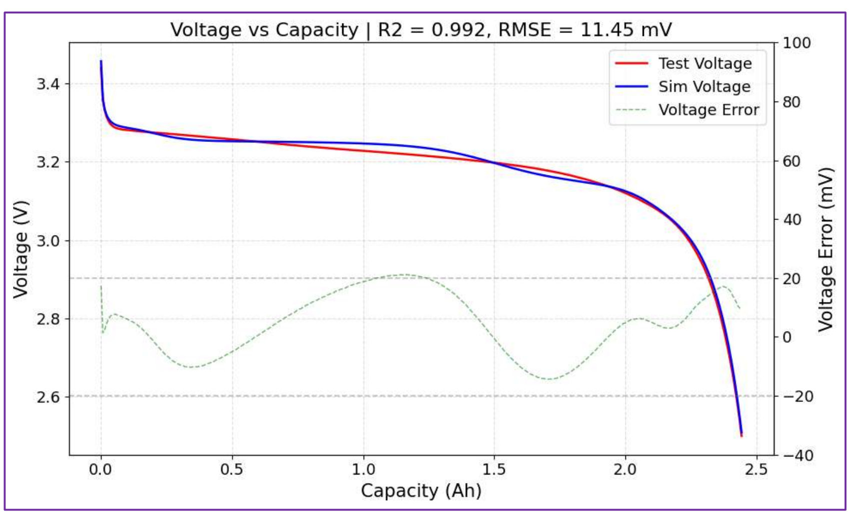

Figure 4: Discharge Voltage at 1C

The ***Negative particle diffusivity*** parameter was optimized to improve the model's C-rate capability. Due to the absence of experimental rate-capability data for validation, this parameter was calibrated based on physically reasonable behaviour and logical consistency with expected diffusion-limited performance. It is assumed that this preliminary optimization provides a reasonable approximation of rate capability at the studied operating conditions, while acknowledging that more accurate calibration can be achieved once experimental data across multiple C-rates become available, however as of now, Cell performance at various C-rates is shown in Figures 5 and 6

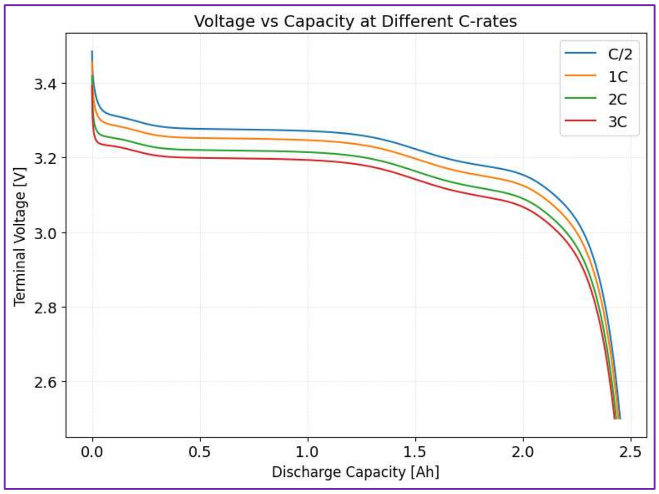

Figure 5: Voltage vs Capacity at different C-rates

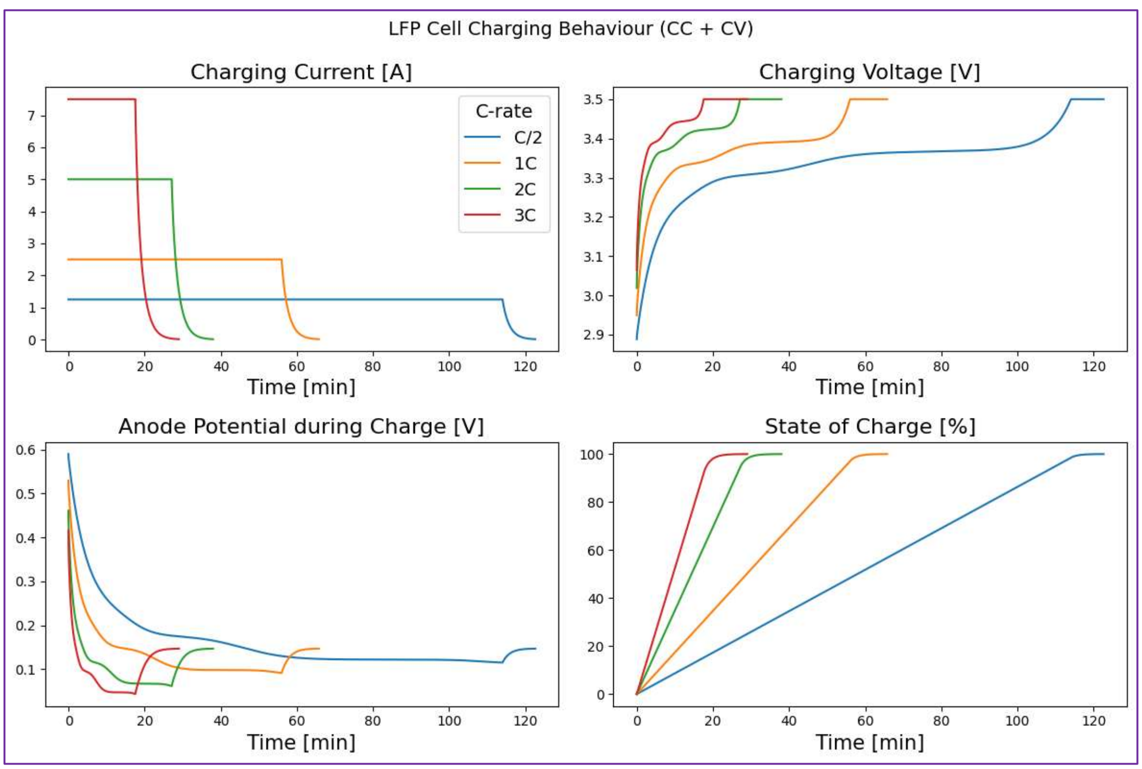

Figure 6: Cell Charging behaviour

HPPC test data current profile is shown in Figure 7.

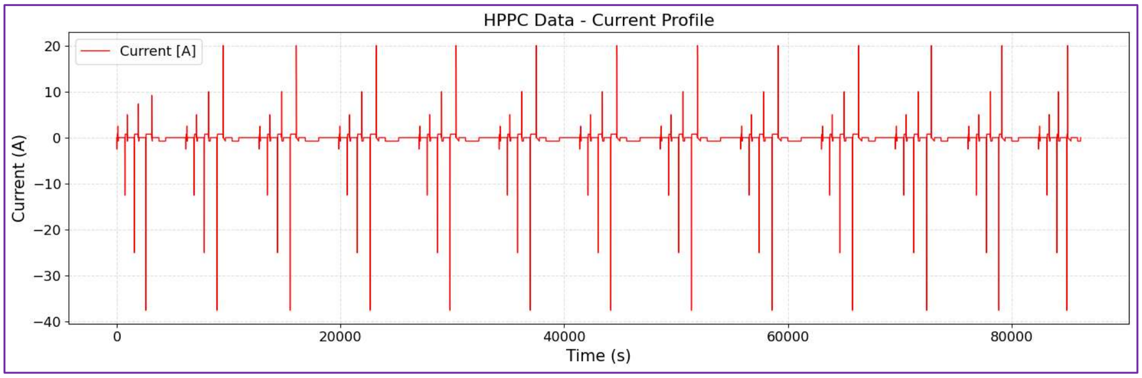

Figure 7: HPPC Current Profile (HPPC_951.csv)

A retracted HPPC profile compatible with the PyBaMM Experiment framework is shown in Figure 8. However, the profile could not be accurately reconstructed from the available test data in the HPPC_951.csv file, as several discharge pulses are defined for only a single time step. This limitation complicates the reconstruction process and prevents accurate execution of the HPPC experiment; therefore, the HPPC simulation could not be performed with high fidelity.

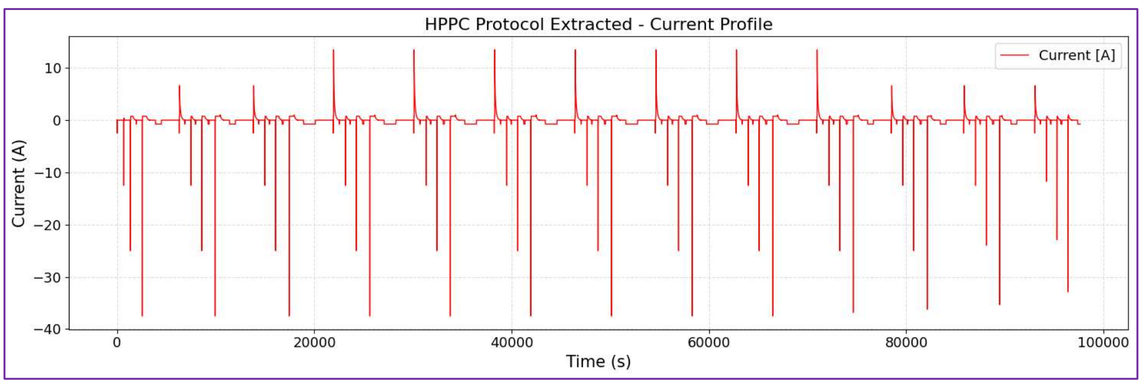

Figure 8: Retracted HPPC Profile

Figure 9 presents the simulated HPPC profile in comparison with the experimental test data. As observed, the results exhibit a degree of uncertainty. The primary sources of this uncertainty are summarized below:

i) The HPPC protocol could not be reconstructed accurately, with several repeating discharge pulses missing from the available data.
ii) The constant-voltage (CV) operating mode is not accurately represented in the current model implementation.
iii) The model has not been validated across multiple C-rates due to the

unavailability of experimental data; consequently, the voltage response is expected to improve once such validation is performed.

Despite these limitations, a good agreement between the simulated and experimental responses is observed for the initial pulse, as shown in Figure 10. With access to complete HPPC test data and additional electrochemical measurements, the full protocol can be reproduced more accurately, and further optimization of model parameters can be performed.

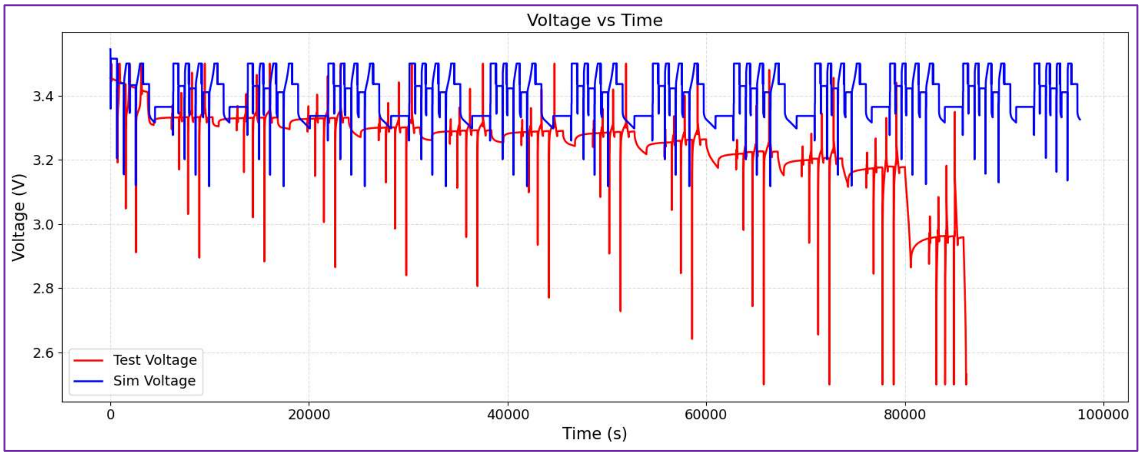

Figure 9: HPPC Voltage Profile

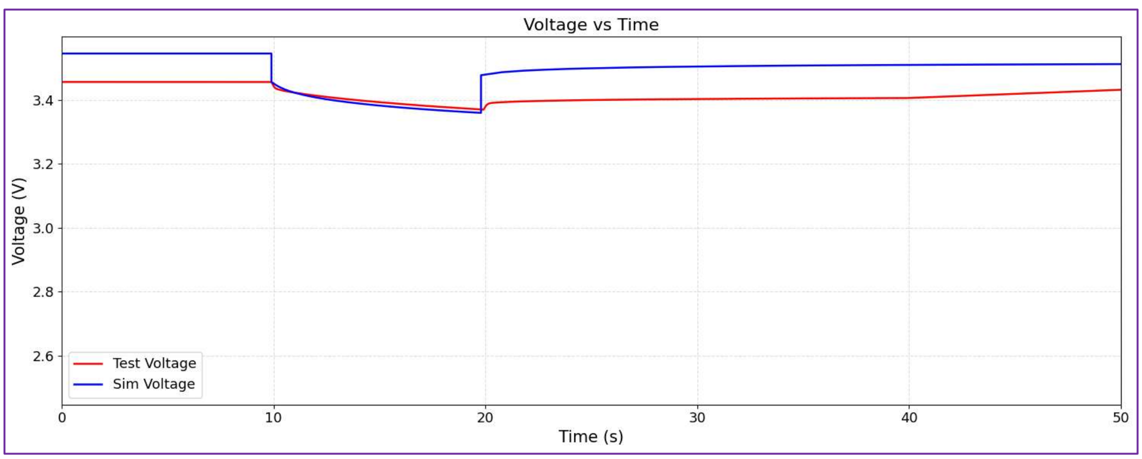

Figure 10: HPPC Initial pulse

Due to my system limitations, the WLTP data could not be processed and a parameter optimizer could not be implemented. As an alternative, a parameter sensitivity analysis code was developed to investigate the influence of key electrochemical parameters, providing a practical basis for model calibration under the given constraints (can be found in the last cell of the *LFP_2.5Ah_V1.ipynb* file).

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