

## Managua lithium-iron-phosphate batteries lfp

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LFP batteries are notoriously cheaper and offer better cycle life compared to the NCA or NMC cathode LIBs (approximately 4-5x longer) and withstand high rates of charge and discharge (up to 20C<sup>7</sup>). Major LIB manufacturers are investing in this technology. In 2020, the Chinese automaker and battery company BYD unveiled a new generation of LFP batteries, called "Blade"<sup>8,9</sup>, followed by Tesla who in 2020 first announced the use of iron phosphate in LIBs manufactured for the Chinese electric vehicle market<sup>9</sup>, and later in 2021 extended to LIBs manufactured globally<sup>10,11</sup>.

Lithium-ion batteries are electrochemical energy storage devices in which lithium is exchanged between the positive and the negative electrode. During discharging (positive current), lithium leaves the negative electrode (deintercalation) and enters the positive one (intercalation). During charging (negative current), the positive electrode experiences deintercalation, and lithium intercalates into the negative electrode.

The presence of a two-phase transition in the positive electrode results in a flat OCV curve, which makes the task of estimating the state of charge (SOC) challenging as it causes a lack of observability of the system's states from the voltage output measurements<sup>21</sup>. Moreover, a pronounced hysteresis<sup>22</sup>, and path dependence behavior, i.e., for the same SOC the battery relaxes to different OCV values depending on whether it was charging or discharging, pose additional challenges in the design of battery management system (BMS) strategies.

Hysteresis results from thermodynamic effects, mechanical stress, and microscopic distortions within the active material particles caused by dopants<sup>23</sup>. Thermodynamic effects are related to the electrodes being composed of multiple particles and to the heterogeneity of the lithium insertion rate. Mechanical hysteresis is associated with the different lattice constants of lithiated and delithiated phases that cause mechanical stress at the phase barrier.

In ref. 30, the formulation of a core-shell enhanced single particle model (ESPM), blending the predictive capabilities of ESPM with the core-shell modeling paradigm in the positive electrode, is proposed and experimentally validated. In ref. 31, this model is further enhanced through an average core-shell ESPM formulation, where the bulk-normalized concentration is used to prevent discontinuity of the positive particle lithium surface concentration arising from the transition between one-phase to two-phase regions<sup>32</sup>.

The flat OCV-SOC relationship and the prominent hysteresis challenge the status quo in lithium-ion battery modeling. Similar to what was done in ref. 36 to improve battery safety, in this paper, we combine the strengths of physics-based and machine-learning approaches by leveraging the aptness of the average core-shell ESPM model<sup>31</sup> (to track the cathode lithium concentration) integrated with a machine-learning hysteresis model (Fig. 1).

a Starting from field data (electric vehicles, grid, or home stationary storage), the proposed hybrid model merges the strengths of physics-based and machine-learning approaches for improved prediction performance. In this paper, we use EV driving data to train the machine-learning hysteresis model. b The hybrid model can be employed in battery performance analysis, synthetic data generation, and as the basis for reduced-order models.

This model copes with both static and dynamic hysteresis. The static hysteresis is associated with the battery equilibrium potentials being different whether coming from charge or discharge. Instead, dynamic hysteresis arises from the switching between charge and discharge conditions and is a function of the battery history, and local and instantaneous operating conditions (SOC and C-rate).

The hybrid model proposed in this paper can increase the predictive capabilities of traditional battery models<sup>39</sup>. The physical understanding of lithium intercalation and deintercalation is preserved in all the stages of the model development, which reaffirms the key role of physics. Moreover, the pseudo-hysteresis machine-learning model pursued in this work is not constrained within a fixed model structure, like semi-empirical approaches.

As shown in Fig. 2a, b, the average core-shell ESPM approximates the battery positive and negative electrodes as two, spherical, single particles where transport of lithium ions in the solid (the single particle) and electrolyte phase is expressed by mass conservation equations, charge conservation is used in the electrolyte phase, and phase transitions in the positive particle are modeled with a mass balance equation and a moving boundary<sup>31</sup>.

The use of the bulk-normalized concentration in the average core-shell ESPM was introduced to remove the positive particle surface concentration discontinuity arising in the traditional core-shell modeling paradigm during the transition from one-phase to two-phase region<sup>31</sup>. Model equations for the core-shell ESPM are summarized in Supplementary Tables 1, 2, and 3.

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