Abstract—This paper presents a novel battery modeling framework based on the enhanced single particle model (ESPM) to account for degradation mechanisms of second-life batteries. While accounting for the transport and electrochemical phenomena in the battery solid and electrolyte phases, the dominant anode-related aging mechanisms, namely, solid electrolyte interphase (SEI) layer growth and lithium plating, are modeled. For the first time, the loss of active material (LAM), which describes the tendency of anode and cathode, over time, to reduce the electrode material available for intercalation and deintercalation, is introduced in the ESPM. Moreover, the coupling of the aging modes with the LAM dynamics provides a comprehensive framework that can be employed for the prediction of both linear and non-linear capacity fade crucial to assess second-life battery. Thus, relying on data borrowed from [18], a model parameter identification and a comprehensive sensitivity analysis are performed to prove the effectiveness of the modeling approach.

I. INTRODUCTION

Lithium-ion battery (LIB) technology takes advantage of the high electrochemical potential of lithium (-3.040V vs. standard hydrogen electrode) while providing high specific power (300-1500W/kg) and specific energy density (100-250Wh/kg) against all the electrochemical battery devices available on the market [1]. For this reason, LIBs are considered the best means to store energy to support sustainable transportation systems and renewable grid applications. In 2019, the market of LIBs was valued at $36.7 billion and is expected to grow by an annual rate of 18.0% to reach $129.3 billion by 2027 [2].

Deployment of EVs has been growing rapidly over the past decade. It was estimated that 1.18 million EVs were present on the U.S. roads in 2019 [4]. Typically, EV batteries have a lifetime of 8-10 years, and they retire from the first life when their capacity and/or power capability decreases to 70-80 percent of their initial values [6]. The first large wave of retired EV batteries is expected by 2025, after the 15-year lifetime of the Tesla Model S and Nissan LEAF that first went to market [6]. In California, about 45,000 EV batteries are expected to retire by 2027 [7].

Potential end-of-life pathways for retired EV batteries include repurposing, remanufacturing, recycling, and disposal [8]. ‘Repurposing’, or reuse, is defined as the redeployment of retired EV batteries in a different application from the one they were first used. Retired EV batteries are postulated to be able to provide energy storage services in a stationary grid application. In the ‘Remanufacturing’ process, damaged battery cells/module are replaced within the battery module/pack and reused in EVs. The objective of ‘Remanufacturing’ is to extend the useful life of batteries with minimal additional cost. In ‘Recycling’ extraction and reprocessing of valuable metals (e.g., nickel and cobalt) are practiced. A sustainable life cycle would apply the ‘Recycling’ process after the batteries have been repurposed to provide a second-life. In the ‘Disposal’ pathway, the battery cells are moved to landfill and discarded under the assumption that they are no longer worth recycling.

Compared to other routes, the repurposing of EV batteries would maximize the total lifetime value and revenues of the device. The optimal deployment of repurposed retired EV batteries holds potential to reduce up-front costs and provides benefits to consumers and utilities, maximizing the usability and performance of the device.

To date, most second-life EV battery projects have been conducted by industrial vendors. In 2013, for example, ABB and General Motors built a 25kW energy storage system in San Francisco, California, USA by collecting retired EV batteries from the Chevrolet Volt plug in hybrid vehicle [10]. In 2015, BMW, Vattenfall, and Bosch obtained retired batteries from more than a hundred EVs and jointly constructed a 2 MW, 2800 kWh second-life battery energy storage system for grid support (Hamburg, Germany) [11]. In the same year, Toyota also built a stand-alone 10MW energy storage system with Prius retired batteries at the Lamar Buffalo Ranch in Yellowstone National Park, USA. This storage system supported a wind-battery microgrid system [12]. These early-stage research projects provided no systematic approach for the optimal battery deployment in grid applications; the original battery packs were just collected as they are and deployed in a microgrid or a building site to supply the needed power and energy.

Once retired EV batteries are collected, one should be able to group cells/modules into clusters of cells with similar performances.

A battery cell is a basic unit of a LIB whereas a battery module contains multiple battery cells, connected in series or in parallel. Finally, a battery pack involves multiple battery modules in parallel and/or series. For a given charging/discharging pattern, the position of batteries in a module/the location of battery modules in a pack level is one of the factors causing the different degradation trajectories of EV batteries. In a battery module, individual cells packed closely together interact with each other thermally, and heat is transferred through conduction between the surface of neighboring cells [30]. Not all the cells in the battery module will be at the same state of health (SOH).
A study conducted by National Renewable Energy Laboratory in 2015 found out, through the use of an in-house developed empirical aging model, that batteries can continue to operate for 10 years on second use, with a total service life of up to 25 years [13]. Empirical model-based research was also conducted in [14]. The effect of aging on commercial LiFePO₄ (LFP) batteries was studied. The battery cells were exposed to various aging tests under different temperatures and state of charges (SOCs). The highest capacity loss was observed in cells stored at high temperature (60°C from 35°C, 50 °C, and 60 °C) and fully charged (SOC 100%).

In [15], a three-stage cell screening procedure was proposed to classify retired EV batteries. The batteries were sorted in descending order from cells with a higher capacity to cells with a lower capacity. In the second step, batteries were grouped into the cells having a similar capacity. In the final stage, parameters (resistance, open-circuit voltage, capacitance) of empirical battery models were identified with the discharge voltage curve from each cell. These identified parameters were used to classify batteries with similar model parameter values. However, large amounts of retired EV batteries must be sorted out within a limited time framework. The aforementioned cell screening requires time-consuming protocols, including conventional capacity tests, which might be impractical in some cases.

To address these issues, incremental capacity (IC) analysis on a partial voltage range was proposed to quickly screen retired EV batteries in [16] and a data-driven approach was employed to screen retired EV batteries in [17].

Despite these initial encouraging results, the SOH estimation and cell screening approaches for second-life batteries found in the literature lack of electrochemical dynamics information. In LIBs, for example, capacity fade and impedance increase occur due to SEI layer formation, lithium plating, electrolyte oxidation, and electrolyte decomposition processes. To date, the SEI layer growth has been regarded as the main cause of capacity fade and impedance increase of the battery system [18]. Accurate estimation of lithium plating dynamics is essential to assess future and safe usability of retired EV batteries. Lithium plating is defined as the formation of metallic lithium on the anode of LIBs during charging (Li⁺+e⁻ → Li). Lithium plating not only causes capacity/power fade but also poses significant safety concerns. Lithium plating can lead to irregular dendrite-shaped growth that could cause thermal runaway inside the device. Once EV batteries are retired, one critical question is whether lithium plating has developed inside of LIBs even under normal operating conditions. Typically, lithium plating is known to occur under extreme operating charging conditions, such as fast charging and low temperature [29]. In order to study the second-life of retired EV batteries, it is deemed important necessary to investigate whether lithium plating is generated under normal operating conditions. Several nondestructive lithium plating detection methods have been proposed for online battery characterization.

In [19], differential voltage analysis to detect the high voltage plateau was introduced to provide quantitative results concerning the lithium stripping reaction. Lithium stripping, which is the opposite reaction (Li → Li⁺+e⁻) to lithium plating, can occur during discharge after lithium plating forms during charge. During discharge, if lithium plating already exists on the anode, the metallic lithium favors the conversion to lithium ions rather than deintercalation of lithium ions inside solid particles. In addition, the electrochemical potential of lithium is higher (stripping), compared to the potential of lithium deintercalation from the negative electrode. For this reason, the voltage plateau can be observed at the initial stage of SOC during discharging from a fully charged battery. In [19], a cylindrical 26650-type commercial Li-ion battery (LiFePO₄) with 2.5 Ah capacity was investigated under various low temperatures (-20°C, -22°C, -24°C, -26°C), SOC (1.0-0.1) with charge currents (1C, C/2). This study showed that the differential voltage and capacity discharge curves can be used to calculate lithium plating quantitatively. In this paper, however, extreme operating conditions have been used to detect lithium plating (low temperature). In [20], the analysis to identify and quantify lithium plating on a commercial graphite LiFePO₄ (LFP) cell was proposed. This study indicated that lithium plating can also occur at mild charging conditions after extended cycling, leading to rapid aging of the cell. This is a fundamental breakthrough in the field of SOH estimation. In addition, several papers indicate the loss of active material (LAM) can be one of the causes leading to lithium plating after extended cycles (LAM is defined when active mass of the electrodes is no longer available for the insertion of lithium) [20-21]. The amount of lithium ions can exceed the accommodation of anode capacity due to the LAM of the electrode. Excess lithium ions can plate on the surface of the graphite. To the best of the authors’ knowledge, there are no detailed studies providing a physical insight including relationships between lithium plating and LAM dynamics. Mathematical battery models can be used to understand, operate, and optimize LIBs’ performance. Among many other models, physics-based battery models deliver internal physics dynamics such as transport and kinetic phenomena. Moreover, physics-based battery models can incorporate transport phenomena, chemical/electrochemical kinetics, side reactions, and thermal/stress/mechanical effects. Physics-based models offer the SOC and SOH along with internal electrochemical information that can be used to maximize safety, usability, and lifetime of the battery.

In this paper, we formulate a physics-based modeling framework that integrates LAM, lithium plating, and SEI dynamics, using the enhanced single particle model (ESPM). This paper consists of four sections: ESPM, Parameter identification, Results, and Conclusion. In the ESPM section, governing equations including the SEI layer growth, lithium plating, and LAM are presented. In the Parameter Identification section, the particle swarm optimization (PSO) algorithm is used to identify the kinetic/transport parameters. The experimental discharging voltage profiles at constant C-rate obtained from [18] are used to identify the model parameters. In the Results section, we show the model performance over experimental data from [18].
II. ENHANCED SINGLE PARTICLE MODEL

The ESPM is formulated upon the assumption that each electrode can be represented by a single spherical particle, which implies that all solid particles are uniform and have the same chemical properties (see Figure 1) [23].

In the ESPM framework, solid particle concentration is described along with the r dimension. The variation of electrochemical potential in the solid particles along with x-axis is ignored (see Figure 1) whereas the electrolyte concentration and potential are considered. According to [25], ESPM maintains only a few mV errors up to 5C for the discharging voltage profile with constant C-rates (compared to the DFN model). For this reason, in this paper, the ESPM is selected as a modeling tool to include SEI layer growth, lithium plating, and LAM. It is worth mentioning that, in accordance with [18], the anode SEI growth and lithium plating side reactions are considered the dominant aging mechanisms.

A. Model governing equations

The ESPM model is in the form of partial differential equations (PDEs), including multivariable functions and their partial derivatives. The model predicts the dynamics of lithium concentration in the solid phase \(\mathcal{C}_\text{solid} (\mathbf{x},r,t)\) at the anode and cathode \((i=p, n)\), electrolyte concentration \(\mathcal{C}(\mathbf{x},t)\), and electrolyte potential \(\Phi_e(\mathbf{x},t)\) [23]. All equations, variables, and parameters are described in Table I, II, and III. Equations T.1 ~ T.25 in Table II and III describe the ESPM model dynamics. Variables and parameters are shown in Table I. Equations T.1, T.4, and T.6 in Table II represent electrolyte dynamics in the positive electrode, separator, and negative electrode. Equations T.2, T.5, and T.7 in Table II represent electrolyte potential in macro-scale systems. Equations T.3 and T.8 in Table II represent solid particle concentrations in micro-scale systems. Additional equations describing diffusivity, conductivity, porosity, cell voltage, overpotential, SEI layer growth, lithium plating, LAM dynamics, and capacity loss are also given in Table III.

### Table I. Nomenclature (p: positive electrode, s: separator, n: negative electrode)

| Symbol | Variables | Units |
|--------|-----------|-------|
| \(t_s\) | Transfer number | - |
| \(\alpha\) | Transfer coefficient | - |
| \(\text{brugg}\) | Bruggeman coefficient | - |
| \(\varepsilon_i\) | Porosity \((i=p,n)\) | - |
| \(\varepsilon_{i0}\) | Initial porosity \((i=p,n)\) | - |
| \(V_i\) | Active volume fraction of the solid phase \((i=p,n)\) | - |
| \(V_{i_filler}\) | Active volume fraction of filler \((i=p,n)\) | - |
| \(\beta\) | Fraction of lithium plating converted into SEI | - |
| \(\beta_i^\prime\) | Inactive area evolution coefficient \((i=p,n)\) | - |
| \(k_i^\prime\) | Fracture evolution coefficient \((i=p,n)\) | - |
| \(\text{SOC}_i\) | State of charge \((i=p,n)\) | - |
| \(\theta_i\) | Bulk normalized lithium concentration | - |
| \(\theta_i_{0\%}\) | Reference stoichiometry ratio @0% SOC \((i=p,n)\) | - |
| \(\theta_i_{100\%}\) | Reference stoichiometry ratio @100% SOC \((i=p,n)\) | - |
| \(t\) | Time | s |
| \(x\) | Cartesian coordinate | m |
| \(r\) | Radial coordinate | m |
| \(L_i\) | Region thickness \((i=p,s,n)\) | m |
| \(L_{film}\) | Thickness of surface film | m |
| \(L_{SEI}\) | Fraction of \(\delta_{SEI}\) related to SEI growth | m |
| \(A_{cell}\) | Cell cross sectional area | m² |
| \(a_{s}\) | Specific surface area \((i=p,n)\) | m²/m³ |
| \(a_{f}\) | Specific fracture surface area \((i=p,n)\) | m²/m³ |
| \(a_{ina}\) | Specific inactive surface area \((i=p,n)\) | m²/m³ |
| \(k_f\) | SEI side reaction kinetic constant | m/s |
| \(D_i\) | Electrolyte phase diffusion coefficient | m²/s |
| \(D_{eff,i}\) | Effective electrolyte phase diffusion coefficient \((i=p,s,n)\) | m²/s |
| \(D_{sol}\) | Solid phase diffusion coefficient | m²/s |
| \(D_{ref,i}\) | Reference solid phase diffusion coefficient \((i=p,n)\) | m²/s |
| \(c_{avg}\) | Average electrolyte concentration | mol/m³ |
| \(c_{eff,i}\) | Solid phase concentration \((i=p,n)\) | mol/m³ |
| \(c_{surf,i}\) | Surface solid phase concentration \((i=p,n)\) | mol/m³ |
| \(c_{max,i}\) | Maximum solid phase concentration \((i=p,n)\) | mol/m³ |
| \(c_{sol}\) | Solvent concentration | mol/m³ |
| \(c_{bulk}\) | Effective solvent bulk concentration | mol/m³ |
| \(c_{sol,bulk}\) | (function of the film porosity [27]) | mol/m³ |
| \(c_{avg}\) | Average solid phase concentration | mol/m³ |
| \(c_{SEI}\) | Solid phase concentration at surface | mol/m³ |
| \(k_i\) | Reaction rate \((i=p,n)\) | mol/(m²·s) |
| \(I_i\) | Pore wall flux \((i=p,n)\) | mol/m²/s |
| \(Q\) | Applied current | A |
| \(Q\) | Capacity loss due to side reactions | A/s |
| \(I_{eq}\) | Exchange current \((i=p,n)\) | A/m² |
| \(J_{pl,SEI}\) | Intercalation and side current densities \((SEI, Li\text{-plating})\) | A/m² |
| \(V_{lq,i}\) | Liquid phase conductivity \((i=p,s,n)\) | S/m |
| \(V_{eff,i}\) | Effective liquid phase conductivity \((i=p,s,n)\) | S/m |
| \(K_{SEI}\) | SEI layer solid conductivity | S/m |
| \(R_{film}\) | Film resistance | Ω |
| \(R_i\) | Lumped contact resistance | Ω |
| \(R_{el}\) | Electrolyte resistance | Ω |
| \(\Phi_{i}\) | Solid phase potential | V |
| \(\Phi_{lq}\) | Liquid phase potential | V |
| \(U_i\) | Open circuit potential at positive and negative electrode \((i=p,n)\) | V |
In Equations T.9, Bruggeman coefficients are used to describe effective diffusivity and conductivity in the porous electrodes. The specific particle area–particle surface to volume (see Equation T.10) is driven under the assumption that all solid particles have idealized spherical shape and uniform size. Equation T.13 shows the porosity change due to aging phenomena. Equation T.12 describes the cell voltage as a function of the open-circuit voltage, overpotential and liquid phase potential difference between the positive and negative electrodes, respectively. Ohmic losses due to internal resistance and SEI layer growth are also included. Equation T.13 describes the electrochemical overpotential, and Equations T.14, T.15, and T.20 adopt the Butler–Volmer (BV) kinetic expression for the mole flux of intercalation/deintercalation of lithium ions, SEI layer growth, and lithium plating. The BV expression describes the charge transfer processes, which occur at the surface of solid particles–electrolyte interfaces (for SEI layer growth and lithium plating). The SEI layer growth dynamics was successfully implemented in our previous study [23, 28] within the ESPM framework following the approach proposed by [27]. In this paper, the SEI layer growth dynamics in [21] is adopted as shown in Equations T.15–T.19 in Table III. For modeling of lithium plating, the BV kinetic expression is adopted to describe the charge transfer processes occurring across both the electrode–electrolyte interfaces (see Equation T.20). The BV equation is linked to lithium plating’s mass balance dynamics, as shown in Equation T.21.

In 2019, Narayna Rao et al. modeled LAM by decreasing the specific surface area of solid particles from active surface area at the initial stage ($a_i$) [26]. This LAM model is established in two steps (see Figure 1): solid particles fracture ($a_{i,f}$) occurs first, resulting in a larger overall active surface area. The wider surface area at this stage is still active material, but as the surface area increases, the SEI layer is formed over a wider area, and the capacity loss phenomenon becomes more pronounced. The first step assumes that the ratio between the area created through the fracture to the total initial area of the electrode particles is a linearly increasing function of time as shown below:

$$\frac{d(a_{i,f})}{dt} = k_i' \rightarrow a_{i,f} = a_i k_i'$$  \hspace{1cm} (1)

where $a_i$ is the active surface area at the initial stage, $a_{i,f}$ is the fracture surface area, and $k_i'$ is the fracture rate constant.

In the second step, inactive surface area or isolation ($a_{i,ina}$) occurs under the assumption that the rate of increase of inactive area is to be proportional to the total surface area as following:

$$\frac{d(a_{i,ina})}{dt} = \beta'_i a_{i,f} = \beta'_i (a_i + a_{i,f} - a_{i,ina})$$  \hspace{1cm} (2)

where $a_{i,ina}$ is the inactive surface area and $\beta'_i$ is the inactive area evolution constant. The inactive surface area dynamics.

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| Positive | Governing equations |
| --- | --- |
| $\varepsilon_p \frac{dc}{dt} = \frac{1}{r^2 \theta r} \left( r^2 D_{\phi, p}(T) \frac{dc}{dr} \right)$ | Boundary condition |
| $\varepsilon_p \frac{dc}{dt} = \frac{1}{r^2 \theta r} \left( r^2 D_{\phi, p}(T) \frac{dc}{dr} \right)$ | $\frac{dc}{dt} \mid_{r=r_p} = 0$ (T.1) |
| $\varepsilon_n \frac{dc}{dt} = \frac{1}{r^2 \theta r} \left( r^2 D_{\phi, n}(T) \frac{dc}{dr} \right)$ | $-D_{\phi, p}(c, T) \frac{dc}{dr} \mid_{x=x_{i,n}} = -D_{\phi, n}(c, T) \frac{dc}{dr} \mid_{x=x_{i,n}}$ |
| $\varepsilon_n \frac{dc}{dt} = \frac{1}{r^2 \theta r} \left( r^2 D_{\phi, n}(T) \frac{dc}{dr} \right)$ | $\frac{dc}{dr} \mid_{x=x_{i,n}} = 0$ (T.2) |
| $\kappa_{eff, p}(c, T) \frac{dc}{dr} + 2 \kappa_{eff, p}(c, T) R T F (1 - t_i) \frac{dc}{dx}^2 = 0$ | $c \mid_{x=x_{i,n}} = c \mid_{x=x_{i,n}}$ |
| $\kappa_{eff, n}(c, T) \frac{dc}{dr} + 2 \kappa_{eff, c}(c, T) R T F (1 - t_i) \frac{dc}{dx}^2 = 0$ | $c \mid_{x=x_{i,n}} = c \mid_{x=x_{i,n}}$ |
| $\frac{dc}{dr} \mid_{r=r_p} = \beta'_i a_{i,f} \mid_e = \beta'_i (a_i + a_{i,f} - a_{i,ina})$ | $\frac{dc}{dr} \mid_{r=r_p} = \beta'_i a_{i,f} \mid_e = \beta'_i (a_i + a_{i,f} - a_{i,ina})$ |

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**Table II. Governing equations for ESPM model.**

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**Governing equations**

**Positive**

$$\varepsilon_p \frac{dc}{dt} = \frac{1}{r^2 \theta r} \left( r^2 D_{\phi, p}(T) \frac{dc}{dr} \right) + (1 - t_i) \frac{dc}{dr}$$

**Separator**

$$\varepsilon_s \frac{dc}{dt} = \frac{1}{r^2 \theta r} \left( r^2 D_{\phi, s}(T) \frac{dc}{dr} \right)$$

**Negative electrode**

$$\varepsilon_n \frac{dc}{dt} = \frac{1}{r^2 \theta r} \left( r^2 D_{\phi, n}(T) \frac{dc}{dr} \right) + (1 - t_i) \frac{dc}{dr}$$

$$J_n = \frac{A_{cell} F L_p}{A}$$

$$\kappa_{eff, n}(c, T) \frac{dc}{dr} + 2 \kappa_{eff, c}(c, T) R T F (1 - t_i) \frac{dc}{dx}^2 = 0$$

$$\frac{dc}{dr} \mid_{r=r_p} = \beta'_i a_{i,f} \mid_e = \beta'_i (a_i + a_{i,f} - a_{i,ina})$$

---

**Boundary conditions**

$$\frac{dc}{dr} \mid_{r=r_p} = 0$$ (T.1)

$$-D_{\phi, p}(c, T) \frac{dc}{dr} \mid_{x=x_{i,n}} = -D_{\phi, n}(c, T) \frac{dc}{dr} \mid_{x=x_{i,n}}$$ (T.2)

$$\frac{dc}{dr} \mid_{x=x_{i,n}} = 0$$ (T.3)

$$c \mid_{x=x_{i,n}} = c \mid_{x=x_{i,n}}$$ (T.4)

$$c \mid_{x=x_{i,n}} = c \mid_{x=x_{i,n}}$$ (T.5)

$$\Phi \mid_{x=x_{i,n}} = \Phi \mid_{x=x_{i,n}}$$ (T.6)

$$\frac{dc}{dr} \mid_{x=x_{i,n}} = 0$$ (T.7)

$$-D_{\phi, p}(c, T) \frac{dc}{dr} \mid_{x=x_{i,n}} = -D_{\phi, n}(c, T) \frac{dc}{dr} \mid_{x=x_{i,n}}$$ (T.8)
(Equations T.22 and T.23 in Table III) can be obtained by combining Equations 1 and 2. This paper couples the inactive surface dynamics with related terms presented in Table III. In detail, Porosity (Equation T.11), electrochemical overpotential (Equation T.13), and mole fluxes for lithium intercalation/deintercalation, the SEI layer growth, and lithium plating are a function of the active surface area. As the total active surface area changes with cycles, the aforementioned electrochemical states vary with time. The total mole flux is a function of active mole fluxes for lithium intercalation/deintercalation, SEI layer growth, and lithium plating. As the total active area is reduced, the relative ratio of mole fluxes for lithium intercalation/deintercalation and SEI layer growth are decreased, while the relative ratio of mole flux for the lithium plating is increased.

III. PARAMETER IDENTIFICATION

In this paper, the identification of the model parameters is carried out relying on the particle swarm optimization (PSO) algorithm. To this aim, voltage vs capacity data for a 12.4Ah pouch cell discharged at C/3 (at 25°C) are borrowed from [18]. In this scenario, the identification process is divided into two phases. In the first phase, the parameter vector Θ1 is identified over a fresh cell. Later, for the aged cell the parameter vector Θ2 is identified. For the aged cell, experimental data at the 1000th and 3300th cycle are employed. Data at the 1000th cycle are related to aging conditions dominated by SEI growth. Conversely, the measurements at the 3300th cycle are characterized by the superposition of two aging modes, namely, SEI growth and lithium plating. For both the fresh and aged cell, it is assumed that LAM is not occurring.

The identification aims at minimizing a cost function defined as follows:

\[
J(\theta) = \frac{1}{N} \sum_{k=1}^{N} \left( V_{\text{cell}}^\text{exp}(k; \theta) - V_{\text{cell}}^\text{eff}(k) \right)^2 + \frac{1}{P} \sum_{k=1}^{N} \left( SOC_{\text{p}}(k; \theta) - SOC_{\text{exp}}(k) \right)^2 + \frac{1}{N} \sum_{k=1}^{N} \left( SOC_{\text{f}}(k; \theta) - SOC_{\text{exp}}(k) \right)^2 \tag{7}
\]

where θ is a generic vector collecting the parameters to be identified (Θ1 and Θ2 for the fresh and aged cell, respectively), \(SOC_{\text{p}}\) and \(SOC_{\text{f}}\) are the simulated state of charge at the cathode and anode (computed as in Equation T.24), \(V_{\text{cell}}\) is the simulated voltage profile (Equation T.12), k is the time instant, N the number of samples, \(V_{\text{cell}}^\text{exp}\) and \(SOC_{\text{exp}}\) are the experimental cell voltage and state of charge from Coulomb counting, respectively.

Starting from the fresh cell, the vector Θ1 is defined to contain the following parameters: the electrode area \(A_{\text{cell}}\), the lumped contact resistance \(R_c\), the volume fraction at the negative electrode \(V_n\), the solid particle radius at the positive and negative electrode \(R_p\) and \(R_n\), the reference diffusion coefficients at the positive and negative electrode \(D_{\text{Lam, eff}}^p\) and \(D_{\text{Lam, eff}}^n\), and the stoichiometry ratios at \(SOC = 100\%\) for the open circuit potential at the positive and negative electrode \((\theta_p, 100\%)\) and \((\theta_n, 100\%)\). Under this scenario, the SEI growth and lithium plating side reaction paths are inactive (no aging is happening on a fresh cell), the identification is performed minimizing the objective function (7), with lower and upper

Table III. Additional equations for the ESPM model.2

| Equation | Description |
|----------|-------------|
| \(D_{\text{Lam, eff}}(z, T) = D_{\text{Lam, eff}}^p \exp \left( - \frac{E_{\text{Lam, eff}}^p}{R_T \left( 1 + \frac{1}{T_{\text{ref}}} \right)} \right)\) | Diffusion and conduction coefficients |
| \(\kappa_{\text{eff}} = \kappa(z, T) \cdot e^{\text{bragg}}\) \(i = p, s, n\) | |
| \(\Delta_f(T) = \Delta_f^\text{ref} \exp \left( - \frac{E_{\text{Lam, eff}}^p}{R_T \left( 1 + \frac{1}{T_{\text{ref}}} \right)} \right)\) | |
| \(a_i = \frac{1}{n_i} v_i\) \(i = p, n\) | Active area |
| \(\epsilon_{i0} = 1 - v_i - v_i \text{ filler}\) \(i = p, n\) | Porosity |
| \(\epsilon_p = a_p + \frac{a_{i0}}{3} \) | |
| \(\epsilon_n = a_n + \frac{a_{i0}}{3} \) | |
| \(V_{\text{cell}} = U_p - U_n + \eta_p - \eta_n + A \Phi_s - \left( \Phi_p + \Phi_n + R_{\text{cell}} \right)\) | Cell voltage |
| \(R_{\text{cell}} = \frac{1}{2A_{\text{cell}}} \left( \frac{1}{\kappa_{\text{eff}}(z, T)} + \frac{1}{\kappa_{\text{eff}}(z, T)} + L_p \right)\) | Electrochemical overpotential |
| \(\eta_p = \frac{RT}{F} \ln \left( \frac{1}{2A_{\text{cell}}} \epsilon_{i0} \right)\) | |
| \(\eta_n = \frac{RT}{F} \ln \left( \frac{1}{2A_{\text{cell}}} \epsilon_{i0} \right)\) | |
| \(i_{b,i} = k_f(T) F \left( \omega_{i}\epsilon_{\text{surf}}(\epsilon_{i} - \epsilon_{surf}) \right)\) | Total mole flux |
| \(A_{\text{cell}} = f_{\text{cell}} + f_{\text{se}} + f_{\text{ip}}\) | SEI layer growth |
| \(f_{\text{se}} = -2F a_n k_f(\epsilon_i, T) \epsilon_{\text{surf}} \exp \left( \frac{-a_z F}{RT} \Phi_s - \Phi_z R_{\text{film}} \right)\) | |
| \(\frac{\partial \Delta_{\text{se}}}{\partial t} = \left( \frac{f_{\text{se}} + f_{\text{ip}}}{2} \right)\) | |
| \(\frac{\partial \Delta_{\text{film}}}{\partial t} = \frac{1}{\epsilon_{\text{surf}}^2} \left( \frac{\partial \Delta_{\text{se}}}{\partial t} + \frac{\partial \Delta_{\text{film}}}{\partial t} \right)\) | |
| \(\frac{\partial \Delta_{\text{film}}}{\partial t} = \frac{\partial \Delta_{\text{film}}}{\partial t} \epsilon_{\text{surf}} \exp \left( - \frac{a_z F}{RT} \Phi_s - \Phi_z R_{\text{film}} \right)\) | |
| \(D_{\text{film}}(z, T) = \frac{\partial \Delta_{\text{film}}}{\partial t} \frac{\partial \Delta_{\text{film}}}{\partial t} \epsilon_{\text{surf}} \exp \left( - \frac{a_z F}{RT} \Phi_s - \Phi_z R_{\text{film}} \right)\) | |
| \(D_{\text{film}}(T) = D_{\text{film}}^\text{ref} \exp \left( - \frac{E_{\text{Lam, eff}}^p}{R_T \left( 1 + \frac{1}{T_{\text{ref}}} \right)} \right)\) | |
| Li plating |
| \(J_{\text{flux}} = -2a_n \epsilon_{\text{surf}} \exp \left( \frac{-a_z F}{RT} \Phi_s - \Phi_z R_{\text{film}} \right)\) | |
| \(\frac{\partial \Delta_{\text{flux}}}{\partial t} = \frac{J_{\text{flux}}}{RT} (1 - \beta)\) | Loss of active material |
| \(\frac{d(\theta_{\text{inol}})}{dt} = \beta_i (\theta_{\text{inol}} + \theta_{\text{inol}} - \theta_{\text{inol}})\) \(i = p, n\) | |
| Total active area |
| \(\epsilon_{\text{surf}} = \epsilon_{\text{surf}}(\epsilon_{i} - \epsilon_{\text{surf}})\) | State of charge (SOC) |
| \(\theta_p = \theta_p(\%\% \text{ SOC}_{\text{p}})\) | |
| \(\theta_n = \theta_n(\%\% \text{ SOC}_{\text{p}})\) | |
| \(\theta_{\text{ip}} = \theta_{\text{ip}}(\%\% \text{ SOC}_{\text{ip}})\) | |
| \(\theta_{\text{ip}} = \theta_{\text{ip}}(\%\% \text{ SOC}_{\text{ip}})\) | Capacity loss due to side currents |
| \(\frac{dQ}{dt} = (f_{\text{se}} + f_{\text{ip}}) A_{\text{cell}} l_n\) | |

Notes

The variable T is the cell core temperature modeled as in [28]. The parameters \(D_i(z, T), \kappa(z, T), \kappa_f(T), \) and \(D_{\text{Lam, eff}}(T)\) are computed according to [23]. Eventually, a comprehensive description of \(k_f(\epsilon_i, T)\) and \(D_{\text{Lam, eff}}(T)\) is provided in [27].
bounds of the parameters defined in Table IV. The bounds are computed as ± 50% of the initial guesses, with some exceptions: for the diffusion coefficients a larger range is analyzed, for \( c_n \), ±20% is employed (as a matter of fact, values for the solid phase volume fraction lie around 0.5). Values for the initial guesses are obtained from [23] and [27]. The first column of Table IV shows the identified parameters. Also, in Figure 3, simulated voltage and SOC profiles are compared with experimental data (data at the 0th cycle correspond to the fresh cell condition).

For the aged cell, the parameter vector \( \Theta_2 \) is defined as a collection of the following quantities: the ratio between the SEI thickness and ion conductivity \( (L_{SEI}/k_{SEI}) \), and the stoichiometry values \( \theta_{p,00}, \theta_{n,100} \). \( L_{SEI}/k_{SEI} \) is identified under the assumption of constant SEI layer during the discharge experiment, which is reasonable since \( L_{SEI} \) is a slow varying variable. Generally speaking, the anode and cathode open circuit potentials are a function of the normalized lithium concentration \( \theta_i \), defined as in Equation T.24. As SEI layer and lithium plating start growing, lithium ions participating in these side reactions are lost, leading to a reduction of the cyclable lithium and, consequently, to a modification of the solid phase normalized concentrations. Therefore, as the battery cycles, the stoichiometry values \( \theta_{i,00} \) and \( \theta_{i,100} \) are expected to change. Among the four stoichiometry values, \( \theta_{p,00} \) and \( \theta_{n,100} \) are expected to vary more because of the SEI layer growth and lithium plating. As a matter of fact, if cyclable lithium is lost, during the discharge of the cell the anode open circuit potential increases more rapidly (with respect to the fresh condition) and \( \theta_{n,00} \) is reached quickly, limiting the intercalation in the cathode. This leads to a reduction of the cathode solid phase lithium concentration (with respect to the fresh condition) or, equivalently, to a decreased \( \theta_{p,00} \). Conversely, while charging, the cathode open circuit potential increases more rapidly (with respect to the fresh condition) and \( \theta_{p,100} \) is quickly reached, limiting the intercalation in the anode. This brings to a decrease of the anode solid phase lithium concentration (with respect to the fresh condition) or, equivalently, to a decreased \( \theta_{n,100} \). Therefore, \( \theta_{p,00} \) and \( \theta_{n,100} \) are the chosen parameters to be identified. Further details regarding this choice can be found in [21].

From experimental data at the 1000th cycle, the vector \( \Theta_2 \) is identified minimizing the cost function (7), with suitable upper and lower bounds for the parameters considered (Table V) and assuming the lithium plating side reaction to be inactive. A meaningful initial guess for \( L_{SEI}/k_{SEI} \) is obtained from [27]. Moreover, except for \( \theta_{n,100} \), parameters in Table IV are not identified again. The outcome of the identification is summarized in the first column of Table V, also, a comparison between experimental data and simulation results is shown in Figure 3. To reflect the increase in battery aging, \( L_{SEI}/k_{SEI}, \theta_{p,00}, \theta_{n,100} \) have to be updated with battery cycles. The parameter vector \( \Theta_2 \) is identified from experimental data at the 3300th cycle. It is worth mentioning that, at this stage of the life, the lithium plating reaction path is active, with the parameter \( t_{p,plt} \) retrieved from [18]. Results are shown in Figure 3 and Table VI.

**Table IV. Fresh cell identified parameters \( \Theta_2 \).**

| Parameter       | Lower bound | Upper bound | Initial guess | Identified value | Unit |
|-----------------|-------------|-------------|---------------|-----------------|------|
| \( A_{cell} \)  | 0.28        | 0.83        | 0.55          | 0.57            | m²   |
| \( R_t \)       | 0.02        | 0.07        | 0.045         | 0.04            | Ω    |
| \( v_n \)       | 0.45        | 0.65        | 0.5           | 0.54            |      |
| \( R_p \)       | 0.6×10⁶     | 1.9×10⁶     | 1.25×10⁶      | 10⁶             | m    |
| \( R_n \)       | 5×10⁶       | 15×10⁶      | 10×10⁶        | 5.16×10⁶        | m    |
| \( D_{SEI}^{pl} \) | 10⁻¹⁴      | 3.4×10⁻¹⁳  | 2.25×10⁻¹³   | 2×10⁻¹³         | m²/s |
| \( D_{SEI}^{fr} \) | 10⁻¹⁴      | 3.4×10⁻¹³  | 2.25×10⁻¹³   | 10⁻¹³           | m²/s |
| \( \theta_{p,100} \) | 0.14        | 0.41        | 0.28          | 0.30            |      |
| \( \theta_{n,100} \) | 0.43        | 1           | 0.85          | 0.99            |      |

Cost function value: \( J(\Theta_2) = 0.03 \)

**Table V. Aged cell identified parameters \( \Theta_2 \) (after 1000 charge/discharge cycles).**

| Parameter       | Lower bound | Upper bound | Initial guess | Identified value | Unit |
|-----------------|-------------|-------------|---------------|-----------------|------|
| \( L_{SEI}/k_{SEI} \) | 0.0015      | 0.15        | 0.076         | 0.085           | Ωm² |
| \( \theta_{p,00} \) | 0.7         | 1           | 0.85          | 0.92            |      |
| \( \theta_{n,100} \) | 0.7         | 1           | 0.85          | 0.88            |      |

Cost function value: \( J(\Theta_2) = 0.03 \)


Table VI. Aged cell identified parameters $\Theta_2$ (after 3300 charge/discharge cycles).

| Parameter     | Lower bound | Upper bound | Initial guess | Identified value | Unit |
|---------------|-------------|-------------|---------------|------------------|------|
| $L_{SEI}/k_{SEI}$ | 0.003       | 0.3         | 2             | 0.25             | Ωm²  |
| $\theta_{p,0\%}$ | 0.6         | 1           | 0.8           | 0.79             | -    |
| $\theta_{n,100\%}$ | 0.6         | 1           | 0.8           | 0.72             | -    |

Cost function value: $J(\Theta_2) = 0.04$

Table VII. Fracture and inactive area evolution coefficients. Minimum and maximum values are retrieved from [26] and remapped from cycle to time domain relying on the following expressions: $\beta'_i = \beta_i\text{cycle} / T\text{cycle}$, $k'_i = k_i\text{cycle} / T\text{cycle}$, with $T\text{cycle}$ the time to perform a charge/discharge cycle.

### Cathode

| $k_i\text{cycle}$ | $k'_i$ | $\beta_i\text{cycle}$ | $\beta'_i$ |
|-------------------|--------|------------------------|------------|
| 1.65e-7           | 3.06e-11 | 1.07e-8               | 0.198e-11  |
| 5e-7              | 9.26e-11 | 1e-7                  | 1.85e-11   |

### Anode

| $k_i\text{cycle}$ | $k'_i$ | $\beta_i\text{cycle}$ | $\beta'_i$ |
|-------------------|--------|------------------------|------------|
| 7.57e-7           | 1.40e-10 | 4e-6                   | 0.741e-9   |
| 3.40e-6           | 6.30e-10 | 5.18e-5               | 9.59e-9    |

IV. RESULTS

In this section, a comprehensive sensitivity analysis for the LAM dynamics (Equation 2) is proposed. Firstly, the influence of fracture and inactive area evolution coefficients is analyzed. Secondly, the impact of LAM dynamics on the cell behavior is analyzed in simulation. From Equation 2, the behavior of LAM is classified into three cases. Case (i): $k'_i$ and $\beta'_i$ are greater than zero and comparable in magnitude, i.e., $(1 - k'_i/\beta'_i)$ is close to zero. Case (ii): $k'_i$ dominates over the inactive area evolution, i.e., $(1 - k'_i/\beta'_i) < 0$. Case (iii): the inactive area evolution coefficient $\beta'_i$ dominates and $0 < (1 - k'_i/\beta'_i) < 1$. Starting from values proposed in [26] and summarized in Table VII, the evolution of the total active area $\alpha_{t,t}$ is analyzed for both the positive and negative electrodes. Given these parameter configurations, shown in maps (a) and (b) of Figure 4, the simulated values for $\alpha_{t,t}$, normalized with respect to $\alpha_{t}$, at the 3300th charge/discharge cycle are shown in maps (c) and (d), respectively. It is clear that, for the proposed combination of parameters, the cathode is experiencing fracture dominated mechanisms, with the total active area $\alpha_{p,t}$ increasing over time (Figure 4, (c)). Conversely, for the anode, the inactive area component is dominating and a decrease of the active surface is shown (Figure 4, (d)). In other words, the cathode is mostly experiencing mechanical fractures, which increase the surface area available for intercalation/deintercalation reactions.

Instead of the anode experiencing LAM, which reduces the area available for both intercalation/deintercalation phenomena and side reactions.

Focusing on the anode only, where SEI growth and lithium plating develop, the impact of LAM dynamics on the cell behavior is analyzed. Map (d) of Figure 4 is used to obtain the initial conditions for Equation 2. Then, for each combination of parameters, the model is simulated and results are compared to experimental data (Figure 6, (a)). The reduction of the active area, related to an increment of the parameter $\beta''_n$, leads to a reduced discharged capacity. This phenomenon is mainly caused by the increment in the film resistance (Equation T.18 and Figure 5, (b)), caused by the reduced total active surface $\alpha_{n,t}$, and by the modification of the solid phase porosity (Equation T.11). Eventually, the decreased discharged capacity is a symptom of the reduced capability of the anode of accepting lithium ions during the intercalation process. Thus, the negative electrode limits the charging capability of the cell, reducing the available capacity during the discharge process.

V. CONCLUSION

This paper proposed a physics-based battery modeling framework to study and replicate battery degradation trajectory to use in SOH estimation of second-life battery.

In this paper, the ESPM was formulated to include SEI growth, lithium plating, and LAM dynamics. LAM dynamics is composed by mechanical fractures, which lead to an increment of the active surface, and isolation, which brings to a decrement of the active surface. Coupling LAM dynamics with lithium plating can help to accurately predict the electrochemical state of retired EV batteries. The accurate prediction is directly related to the safety issues of battery use, which is a concern from a users’ point of view.
Figure 5. (a) Comparison of voltage profiles between experimental data and outputs from the ESPM model at the 3300th cycle (Experimental data: yellow; Model outputs: from black to gray according to the values taken by $\beta_n^t$) (b) The film resistance at the end of the discharge, over different combinations of the parameters $k_n^t$ and $\beta_n^t$.

Model identification results show the predictability of the proposed modeling strategy for 1) fresh cell scenario, aged conditions at 2) 1000th and 3) 3300th cycle). Also, a sensitivity analysis for LAM was performed considering different configurations for the fracture and inactive area evolution parameters. This model, a first to the authors’ knowledge, will offer the opportunity to tackle the SOH evaluation issues in retired batteries.

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