

Deliverable D2.7

Validation and analysis of physics-based and data-driven models for cells and recycling process



Feasible Recovery of critical raw materials through a new circular Ecosystem for a Li-Ion Battery cross-value chain in Europe

WP2 End-of-life LIBs Collection and Characterisation, Digital Tools and Battery Passports deployment

D2.7 - Validation and analysis of physics-based and data-driven models for cells and recycling process

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List of Abbreviations

ACRONYMS	DESCRIPTION
LIB	Lithium-Ion Battery
EoL	End-of-Life
LLE	Liquid-Liquid Extraction
NMC	Nickel Manganese Cobalt oxide
NCA	Lithium Nickel Cobalt Aluminum oxides
DES	Deep Eutectic Solvents
SEM	Scanning Electron Microscope
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
EIS	Electrochemical Impedance Spectroscopy
OCV	Open Circuit Voltage
PSD	Particle Size Distribution
EQMOM	Extended Quadrature Method of Moments
PBE	Population Balance Equation
SPM	Single Particle Model
DFN	Doyle-Fuller-Newman
RMSE	Root Mean Square Error
SSE	Sum of Squared Errors
SE	Stripping Efficiency
EE	Extraction Efficiency
SoH	State of Health
PBM	Population Balance Modelling
SCM	Shrinking Core Model
SoC	State of Charge

1. Introduction

1.1 Scope of the report

This report contains the results of different modelling activities performed in the FREE4LiB project under task T2.3, specifically Subtask 2.3.2. “Physics-based and data-driven models for cells and recycling process”. Modelling activities are of fundamental importance in the development and operation of recycling processes for LIBs. In one hand, cell models help predicting the battery behavior, allowing for predictive maintenance and efficient sorting between recycling and 2nd use or repurposing. On the other hand, modelling of recycling processes enables faster optimization of the process parameters, helping in understanding the physio-chemical limitations of the processes where further development work can be performed.

The scope of this report is to provide insight in the development, tuning and validation of both physics-based and data-driven models of recycling processes developed along the FREE4LiB project and physics-based models of the characterized cells.

The work here presented has strong connections with other tasks of the FREE4LiB project. Experimental data used as input for all the developed models comes from several tasks performed by different partners:

WP2 -- Cells characterization tests and measurements.

- ST2.2.1 Material Characterization (SEM measurements and recognition of cell chemistry NMC611, FBK, CARTIF).
- ST2.2.2 Electrochemical characterization (electrical tests on LIB cells, FBK).

WP3 -- Recycling processes and experimental acquisition.

- ST3.2.2 (Electrohydraulic fragmentation, Fraunhofer).
- T3.3 (Liquid-Liquid extraction, CSIC, Lurederra).
- ST3.4.2 (NADES leaching, EURECAT).

1.2 Overview of the battery recycling process

The end-of-life (EoL) management of lithium-ion batteries (LIBs) involves a sequence of mechanical, chemical, and sometimes thermal operations aimed at recovering valuable materials while minimizing environmental harm. A typical LIB recycling process can be segmented into three major stages [1]. The first stage includes pre-treatment and disassembly. This step involves sorting battery modules and physically separating the casing, electrolyte residues, and electrodes (anode, cathode). Crushing and sieving steps produce

a fine mixture known as black mass, rich in transition metals (Co, Ni, Mn), lithium salts, graphite, and binders [2]. Second stage is material generation, after the black mass generation, process diverge into Pyrometallurgical (high-temperature smelting), Hydrometallurgical (acid leaching, solvent extraction) and Direct recycling (material regeneration with minimal breakdown). In the FREE4LiB project, the hydrometallurgical route is emphasized, particularly leaching and liquid-liquid extraction (LLE), due to its high selectivity and lower energy demand [3]. The final stage is metal recovery and purification where purified solutions are used for metal precipitation, electrowinning, or regeneration into cathode precursors [1]. Selective recovery of critical metals such as cobalt (Co), nickel (Ni), lithium (Li), and manganese (Mn) is central to ensuring both economic viability and environmental sustainability of LiB recycling. Cobalt and nickel are essential for high-energy cathode chemistries (e.g., NMC, NCA).

Leaching is a solid-liquid separation process wherein valuable metals are extracted from solid waste (e.g., black mass from spent batteries) into a liquid solvent. In hydrometallurgical battery recycling, organic acids like citric acid or inorganic acids are commonly used to dissolve lithium, nickel, cobalt, manganese, and other metals from the cathode active material. The process is influenced by several physicochemical parameters, including diffusion rates, surface reactions, temperature, agitation, particle size, and acid concentration. From a modeling perspective, leaching is often represented using reaction-diffusion frameworks, where the rate of metal dissolution is governed either by surface chemical reactions or by mass transfer limitations. Among these, shrinking core models (SCM) have gained prominence for modeling the leaching of metal oxides from battery black mass due to their ability to represent the progressive reduction in particle size or reactive surface area during leaching [4].

1.3 Addressed recycling processes

This work analyzed three different processes, each one part of alternative route leading to complete recycling of the precious battery metals. Leaching and Liquid-Liquid Extraction processes have been modelled by FBK with physics-based approaches detailed in Chapter 2. Electrohydraulic fragmentation has been modelled by EURECAT with a data driven approach explained in Chapter 3.

Within the FREE4LiB project, Liquid-Liquid Extraction (LLE) is the process through which metals are selectively transferred from the aqueous phase into an organic solvent to achieve separation and purification. The experimental data was generated by CSIC and other consortium partners, aiming to improve

separation efficiency while minimizing chemical consumption. Leaching is the first key hydrometallurgical step, where valuable metals (Li, Ni, Co, Mn) are dissolved from black mass using green solvents such as citric acid or DES. The leaching experiments modelled in the report were conducted by EURECAT in WP3. Metal concentrations over time were measured via ICP-OES to evaluate extraction efficiency. The experimented results are presented in Deliverables D3.3 Development, testing and validation of recycling solutions for cathode and black mass at lab-scale. (First result version of LLE and Leaching).

The electrohydraulic fragmentation process is an alternative to the traditional shredding process for the separation of the different materials within a LIB cell. The process consists in inserting the entire cells into a water-filled pressurized vessel and exciting them with electrical pulses leading to strong mechanical and electrical shockwaves. This process has been developed and implemented by Fraunhofer in two different pilot lines within WP3 and WP4. The main experimental data used in this work results from the activities described in D3.3 Development, testing and validation of recycling solutions for cathode and black mass at lab-scale (first dataset).

These processes were chosen from among the ones developed in the project due to the availability of experimental data within the consortium. Nevertheless, the amount of data collected was often insufficient to implement highly detailed approaches. This issue has been addressed in different ways according to the model. In the case of the leaching process, a more complex model has been developed and successively simplified to adapt to the available data. For the electrohydraulic fragmentation, techniques on oversampling have been embedded in the model implementation. In the leaching-leaching extraction case, an empirical approach was chosen to adapt the model to the type of available data.

1.4 Overview of Cell Modeling

The second part of this report encompasses the development, implementation, and validation of electrochemical models for lithium-ion cells using a physics-based approach, with a particular emphasis on parameter estimation and model fidelity through experimental validation. This work focuses specifically on cell-level modeling using the PyBaMM framework. The goal is to simulate and analyze the performance of individual cells under a variety of operational scenarios, and to calibrate these models against real-world experimental data obtained in Subtask 2.2.1. These simulations aim to replicate key performance characteristics such as open-circuit voltage (OCV), dynamic response under pulse loading, energy capacity under constant current cycling, and impedance behavior under frequency perturbation.

This modeling effort is grounded in a physics-based methodology, relying on fundamental transport, kinetic, and thermodynamic equations that describe lithium-ion transport and interfacial reactions inside the cell. In parallel, experimental datasets collected through standardized battery testing protocols elaborated in T2.2 are used to fit, validate and refine the models. This includes integrating OCV curves, voltage-time profiles from charge/discharge tests, transient responses from pulse tests, and Nyquist plots from electrochemical impedance spectroscopy (EIS). The use of multi-parameter fitting and optimization allows for tailoring the model to match the specific behavior of the tested cells, enabling high accuracy in simulations. Thus, this section plays a central role in the deliverable by providing a validated, adaptable, and computation-ready representation of cell behavior across multiple testing dimensions. The content related to cell modelling is organized in Chapter 4.

2. Physics-Based Modeling of the Recycling Process

2.1 Model of leaching process

This chapter presents the work performed on modelling of leaching. First, a detailed model of the leaching process has been implemented and validated through literature data. In a second phase, this model was adapted and simplified to allow the application on the scarce amount of data available. Finally, fitting and validation was performed on data extracted from the deliverable “D3.3. Development, testing and validation of recycling solutions for cathode and black mass at lab-scale”.

2.1.1 Shrinking-core model

2.1.1.1 Model development

A comprehensive description of the leaching process requires a modelling tool capable to follow the evolution of particles when the particle size distribution (PSD) is not narrow enough to adopt mono-sized modelling approaches [5], [6]. In this context, a systematic approach for taking into account the PSD is population balance modelling (PBM) [7], [8], [9], [10], which essentially writes a population balance equation (PBE) in terms of the PSD. While the application of PBM to the leaching process is well established, the solution methods applied to the PBE for this process still have some limitations.

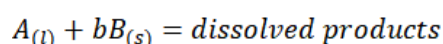
LeBlanc and Fogler [5] utilized the method of characteristics for dissolution under mass-transfer and surface-reaction controlling regimes, assuming a constant solvent concentration, which may not reflect real-world conditions. Hänchen et al. extended this method to olivine particle dissolution, neglecting the dependence of dissolution rate on solution concentration and particle size [11]. These methods are limited to surface-reaction rate-controlled scenarios.

Crundwell and Bryson [12] developed a steady-state PBE considering reactant concentration and reactor temperature, applicable beyond surface-reaction limitations. However, numerical integration poses challenges, especially for broad or rapidly changing size distributions, and isn't suitable for transient systems like batch reactors. The method of lines offers an alternative for transient cases but shares the same challenges of discretizing size space. Gbor and Jia proposed a PSD-based conversion calculation method, assuming constant reactant concentration [6]. The method requires discretization of PSD and struggles when inert-layer diffusion is significant.

The sectional method, adopted by Zhao et al. for reactive dissolution of particle agglomerate [13] and by Dale et al. for nanoparticle aggregation [14], suffers from the need for numerous classes to achieve accuracy. Additionally, no published work has combined this method with the shrinking-core kinetic model. Overall, these methods face limitations in accurately capturing complex dissolution processes.

To overcome the previously mentioned shortcomings, we propose a general approach to solve the PBE in transient leaching processes. In fact, it can be adopted to simulate the leaching process in spatially homogeneous batch reactors without making any assumption about the controlling regime or reactant concentration. The proposed approach is based on the extended quadrature method of moments (EQMOM) introduced by Yuan et al. [15], which is adapted to the shrinking-core model. This adaptation is indeed a novelty of this work as it allows us to consider both the (constant) distribution of the particle outer size and the (varying) distribution of the particle core size in the evaluation of the shrinking-core model.

In the leaching process, solid particles are brought into contact with a solution containing a leaching agent A (usually an acid), which dissolves a target compound B in the solid phase. The reaction can be written as:



where, the stoichiometric ratio b defines the number of moles of B dissolved by one mole of A. A widely adopted approach for the description of the leaching

process is the shrinking-core model that assumes the formation of an inert layer of a solid product around particles due to the reaction. Therefore, each solid particle is considered as an unreacted core rich in B surrounded by an inert layer. At the beginning of the process, solid particles are fully unreacted. As the reaction proceeds, the unreacted core shrinks and the thickness of the inert layer increases. Therefore, in general, the process can be viewed as three steps: 1) the diffusion of A in the liquid film around particles, i.e., from the bulk solution to the particle surface, 2) the diffusion of A in the inert layer, 3) the reaction between A and B at the surface of the unreacted core. The shrinking-core model is illustrated in Figure 2-1.

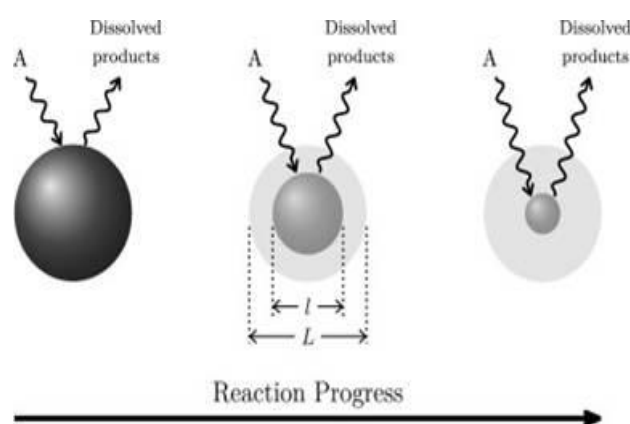


Figure 2-1 Shrinking-core model. Leaching agent, A diffuses from the bulk solution to the particle surface, where the reaction occurs between A and the active material in the particle.

As the reaction proceeds, an inert layer remains around the particle, and therefore, A needs to diffuse through this layer to reach the surface of the unreacted core of the particle, where the reaction can take place. l and L are the core and outer size of the particle, respectively. The proposed method is evaluated by performing several numerical tests for which some analytical or reference solutions can be obtained. In addition, the method is used to simulate a leaching process for which some experimental data is available. Finally, we show that the method can be applied to dissolution problems in which no inert layer forms around particles.

In all the following cases, the reaction is the one reported in the above equation. In addition, particles are assumed spherical. Moreover, the number of quadrature nodes is set to more than three following the suggestions by Yuan and co-workers who found that the EQMOM with three or four nodes provides accurate predictions for the moments of the NDF for evaporation, in which the growth rate is negative as in leaching. Regarding the ODE solver, a variant of Petzold's method [16] is used that switches automatically between (non-stiff)

Adams and (stiff) backward differentiation formulas. This method is available in Scipy package by selecting the LSODA option of solve_ivp solver. Furthermore, the relative and absolute tolerances of the ODE solver and the initial time step are set to 10^{-6} , 10^{-8} , and 0.001, respectively. These settings for the ODE solver led to fast simulations of the following test cases, except the last one, i.e., dissolution controlled by liquid-film mass-transfer, that takes a bit longer due to the stiffness of the equations. The results of this activity have been recently published in Chemical Engineering Science journal [17]. The paper presents a rigorous explanation of the proposed method and describes in detail five validation test cases and the results. Here below we present a summary of three validation cases that demonstrate the accuracy and effectiveness of the method.

2.1.1.2 Surface-reaction rate limited case

The first case is a leaching process controlled by the surface-reaction rate, in other words, negligible mass-transfer resistance in the inert layer and liquid film around particles. Here, no decaying factor is considered for negative-size particles because all particles shrink with the same rate. Moreover, we assume that the concentration of A in the bulk solution is constant, i.e., A is present in excess. In this extreme case, the expected behavior is that the PSD shifts with a constant rate to smaller values of particle size without changing its shape.

Figure 2-2 compares the results obtained by the EQMOM versus the analytical solutions at four selected times. As expected, the non-dimensional PSD shifts to the left without changing shape as the reaction proceeds. A very good agreement between the analytical solutions and EQMOM predictions at the selected times.

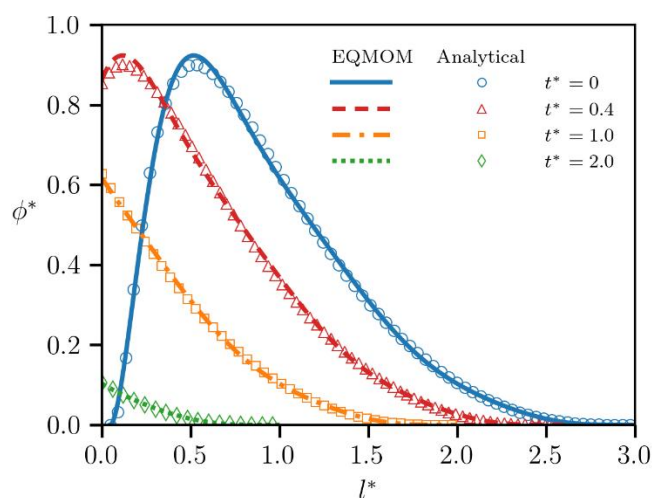


Figure 2-2 The comparison of the dimensionless PSD predicted by the EQMOM against the analytical solutions at four selected times for shrinking-core particles in the surface-reaction controlling regime.

2.1.1.3 Mixed controlling regimes

Here, we consider a problem similar to the previous case with the same initial NDF except that the mass-transfer resistance in the inert layer is not negligible. In this case, we assume an identical timescale for both the surface reaction and mass-transfer through the inert layer.

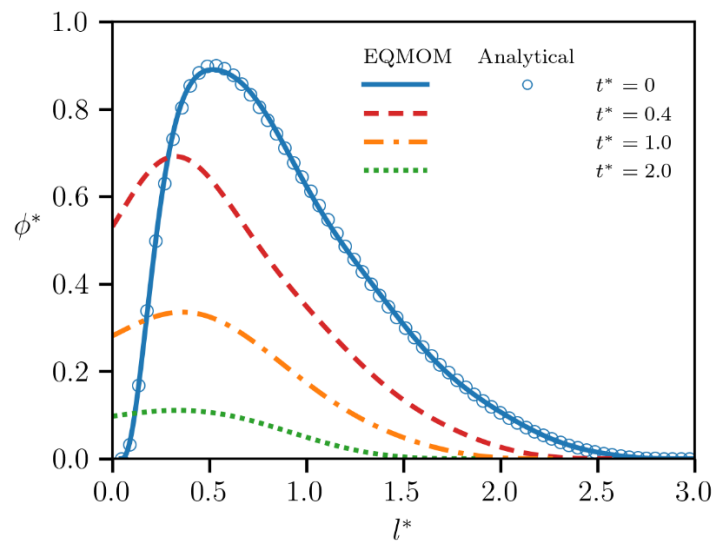


Figure 2-3 Time evolution of the dimensionless PSD predicted by the EQMOM for shrinking-core particles with a shrinkage rate that depends on the surface-reaction and mass-transfer in the inert layer.

To our knowledge, no analytical solution exists for the evolution of the PSD in the case of mixed controlling regimes, and therefore, we can only discuss qualitatively the EQMOM predictions for the PSD. However, the conversion of B, can be calculated with the method used by Gbor and Jia [6], which we use as a reference solution for assessing the EQMOM predictions. As a quantitative evaluation, Figure 2-4 shows a perfect agreement between the conversion of B predicted by the EQMOM at four selected times with the reference solution. This agreement supports the PSD predictions by the EQMOM in Figure 25.

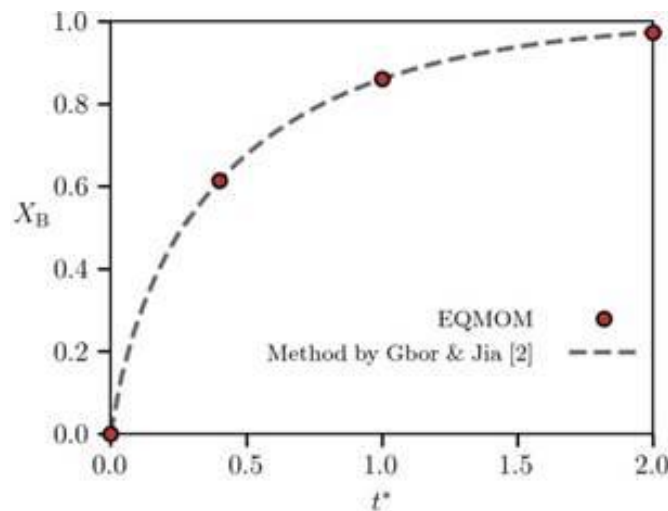
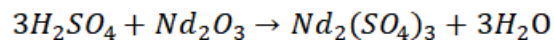


Figure 2-4 The comparison of the leaching conversion predicted by the EQMOM against the reference solution obtained by the method proposed by Gbor and Jia. The shrinkage rate of particle cores depends on the surface-reaction and mass-transfer in the inert layer.

2.1.1.4 Leaching example

After previous numerical analyses, we use the EQMOM to simulate a real leaching experiment conducted by Yoon et al.[17]. They studied the leaching of neodymium (Nd) from the oxidized E-scrap of NdFeB magnets in H₂SO₄ solutions according to the following reaction:



In the conducted experiments, they measured the conversion of Nd versus time at some selected H₂SO₄ concentrations and temperatures. Moreover, they used excess amounts of H₂SO₄, and therefore the concentration of A in the bulk solution, is assumed to be constant. According to their observations, the shrinking-core model can be used to describe the process because the initial particle size distribution differs only slightly from that measured after the completion of the leaching.

As shown in Figure 2-5, the agreement between the EQMOM predictions and the experimental data can be improved by modifying the mass-transfer timescale obtained by Yoon et al. via a mono-sized modelling approach. This fact highlights the significance of considering the PSD in the modelling of the leaching process, and the importance of methods that allow us to do this.

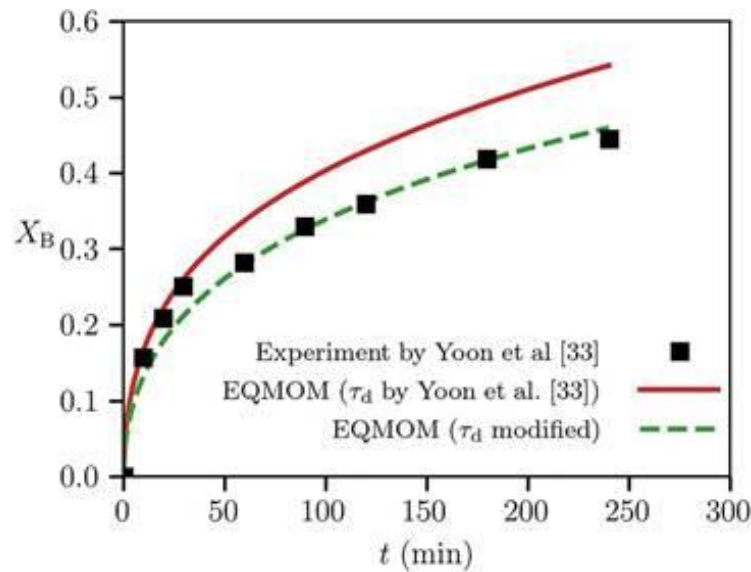


Figure 2-5 The conversion of the leaching process predicted by the EQMOM (solid red and dashed green curves) against the experimental values (black squares) reported by Yoon et al.

The main advantage of the proposed approach is that it requires no specific assumption on the limiting step or the operating conditions, as demonstrated by the different test cases studied. Another advantage is the superior performance with respect to the original EQMOM developed by Yuan et al. as exhibited in the case of a leaching process with an initial uniform particle size distribution (PSD). This superior performance is attributed to the fact that the proposed approach considers also particles with a negative core size, which has been implemented through the definition of the pseudo-NDF, the transformation of the internal coordinate (i.e., size) and the modification of the shrinking-core model.

2.1.2 Model adaptation

2.1.2.1 Governing Equation

The adapted leaching model is based on the foundational kinetic expression derived from the shrinking-core model (SCM), given as Equation (3) in the work by [17]. This equation quantifies the rate of core shrinkage during leaching and integrates three fundamental resistances: chemical reaction, internal diffusion through the inert layer, and external mass transfer across the liquid film.

$$G(l, t) = \frac{dl}{dt} = - \frac{2bC_A}{\rho_B} \left[\frac{1}{k_s} + \frac{1}{2D_e} \left(l - \frac{l^2}{L} \right) + \frac{1}{K_f} \left(\frac{l}{L} \right)^2 \right]$$

Here, l and L represent the time-varying unreacted core radius and constant outer particle radius, respectively; k_s , D_e , and k_f denote the surface reaction rate constant, effective diffusivity through the product layer, and mass transfer coefficient, respectively. C_A is the leachant concentration in the bulk fluid, and ρ_B is the molar density of the solid reactant. This formulation is a cornerstone for modern leaching models that aim to realistically capture transient behaviors in non-ideal systems where the particle size distribution (PSD) is broad or evolving. Unlike classical mono-sized particle models, which assume uniform reactivity and geometry, the SCM used here allows for simultaneous consideration of:

- Polydispersity in particle size (PSD),
- Temporal variation in leachant concentration, and
- Multi-step transport limitations that evolve as leaching proceeds.

To effectively solve the population balance equation (PBE) for such systems, the authors employ the Extended Quadrature Method of Moments (EQMOM). This approach reformulates the PBE into a set of moment-based ordinary differential equations and reconstructs the distribution using a weighted sum of beta distribution kernels. A key innovation is the introduction of pseudo-distributions that include "ghost" particles (negative-size domains) for numerical continuity, ensuring accurate conservation of particle number density.

The EQMOM framework permits dynamic mapping between the evolving core size and its corresponding initial outer size—critical for accurate evaluation of SCM kinetics where the total resistance depends on both. Furthermore, the formulation is general enough to accommodate reaction- and diffusion-controlled regimes as well as dissolution problems (where $l=L$).

The significance of Equation from [17] lies in its ability to unify all three limiting resistances within a single, dimensionally consistent term. It also sets the foundation for incorporating experimentally measured or estimated values of k_s , D_e , and k_f to validate against leaching data, such as that obtained for battery black mass recycling. This equation will serve as the launchpad for our modified SCM, which aims to account for time-varying mass transfer coefficients, non-uniform stirring effects, and temperature dependence through empirical correlations or mechanistic sub-models. The rest of the report will build upon this kinetic core by validating it against experimental datasets and extending it to hybrid or piecewise models in systems with multiple control regimes.

The motivation for this derivation arises from the availability of experimental data, where conversion (X) is measured with respect to time (t). Therefore,

deriving an analytical expression that relates to X and t is critical for fitting and validating the model with experimental leaching data.

Assuming surface reaction is the rate-controlling step, the resistances due to diffusion and film mass transfer can be neglected:

$$\frac{1}{k_s} \gg \frac{1}{2D_e} (...), \frac{1}{k_f} (...)$$

Thus, Equation (3) from Shiea et al. (2024) simplifies to:

$$\frac{dl}{dt} = - \frac{2bC_A}{\rho_B} \cdot \frac{1}{k_s} \rightarrow \frac{dl}{dt} = K \text{ (constant)}$$

Where K is constant. This means the core radius decreases linearly with time under surface-reaction controlled kinetics. Let X be the fraction of solid reacted (conversion). Assuming spherical particles:

$$X = 1 - \left(\frac{l}{L}\right)^3 \rightarrow \left(\frac{l}{L}\right) = (1 - X)^{\frac{1}{3}}$$

$$l = L(1 - X)^{\frac{1}{3}}$$

This equation allows conversion X to be linked to the shrinking radius $l(t)$. We now differentiate the expression for l with respect to time:

$$\frac{dl}{dt} = \frac{d}{dt} \left[L(1 - X)^{\frac{1}{3}} \right] = -\frac{L}{3} (1 - X)^{-\frac{2}{3}} \cdot \frac{dX}{dt}$$

But from earlier

$$\frac{dl}{dt} = K$$

Equating both expressions:

$$-K = -\frac{L}{3} (1 - X)^{-\frac{2}{3}} \cdot \frac{dX}{dt}$$

Solving of $\frac{dX}{dt}$

$$\frac{dX}{dt} = \frac{3K}{L} (1 - X)^{\frac{2}{3}}$$

We integrate the above differential equation,

$$\int_0^X \frac{1}{(1 - X)^{\frac{2}{3}}} dX = \frac{3K}{L} \int_0^t dt$$

The left-hand side is integral:

$$3 \left[1 - (1 - X)^{\frac{1}{3}} \right] = \frac{3K}{L} t$$

Divide both sides by 3

$$1 - (1 - X)^{\frac{1}{3}} = \frac{K}{L} t$$

Letting $k = \frac{K}{L}$, we obtain the final expression for the modified shrinking-core model

$$1 - (1 - X)^{\frac{1}{3}} = kt$$

The final equation enables direct fitting of experimental leaching data where conversion (X) is plotted over time (t) which will be implemented in the result section as Modified SCM. This form is advantageous for kinetic parameter estimation, process optimization and model validation with experiments. This equation now forms the core of our modified SCM, which will be extended further in the report to include stirring speed, temperature and parameter fitting based on battery recycling leaching data.

Now extend the shrinking-core model to incorporate transport effects via mass transfer coefficient k_f . The goal is to estimate k_f from empirical correlations and modify the leaching model to account for both surface reaction and external film diffusion resistances. With both surface reaction and film diffusion resistances acting in series, then the above equation becomes, - isolating cube root expression, cube both sides and solving for X

$$1 - (1 - k_{overall} \cdot t)^{\frac{1}{3}} = X(t)$$

Where $k_{overall}$ is

$$k_{overall} = \left(\frac{1}{k_s} + \frac{1}{k_f} \right)^{-1}$$

This expression is essential when diffusion resistance is not negligible (i.e., in viscous media or low stirring scenarios). It allows flexible simulation and better fitting with real data under different stirring speeds. This equation with the inclusion of mass transfer resistance, its estimation and fitting are implemented in the next section.

2.1.3 Experimental Setup and Data

The objective of the adapted model is to evaluate the leaching efficiency of recycled battery cathode materials using two types of leachants: Citric acid (a bio-based green leachant) and Deep Eutectic Solvent (DES). The experiment was conducted by EURECAT in the context of ST3.4.2. The first version of data was analyzed from “D3.3 Development, testing and validation of recycling solutions for cathode and black mass at lab-scale”. Two experiments were conducted, each one aiming to quantify metal dissolution over time under controlled stirring and temperature conditions.

The leaching experiments were conducted to evaluate the recovery efficiency of valuable metals from recycled lithium-ion battery cathode materials. The feedstock used was black mass obtained through direct cathode recycling, rich in lithium (Li), manganese (Mn), cobalt (Co), and nickel (Ni). The leaching process was performed in a standard 250 mL glass beaker placed on a magnetic stirrer with digital temperature control. To maintain homogeneity and maximize solid-liquid contact, the stirring speed was fixed at 500 rpm throughout the experiments. Temperature was held constant at 80°C (353 K) to simulate industrially relevant hydrometallurgical conditions.

Two separate leaching experiments were conducted using different solvents. In the first experiment, citric acid was employed as a green leachant due to its mild acidity and chelating properties. This experiment was designed with fine time resolution to observe the gradual leaching behavior over a period of 240 minutes. In the second experiment, a deep eutectic solvent (DES) system was used to investigate rapid leaching dynamics under similar physical conditions. Because of the stronger solvating power of DES, this experiment focused on shorter time intervals to capture the fast metal dissolution kinetics.

In both cases, small aliquots were sampled at pre-defined time points during the leaching process. These samples were then filtered and analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to determine the concentration of individual metals (Li, Mn, Co, and Ni) in the solution as a function of time. These datasets are crucial for modeling metal extraction kinetics. The metal concentration vs. time data will be directly used to compute the conversion $X(t)$ and fit kinetic models such as the Modified Shrinking Core Model (SCM) introduced in earlier sections.

2.1.4 Model fitting, estimation and validation

For quasi-spherical battery particles undergoing leaching in citric acid, we use the Ranz-Marshall correlation to estimate the external mass transfer coefficient:

$$Sh = 2 + 0.6 \cdot Re^{1/2} \cdot Sc^{1/3}$$

Where the correlation is combination of Sherwood number, Reynolds number and Schmidt number. It is defined as,

$$Sh = \frac{k_f \cdot d_p}{D}$$

$$Re = \frac{\rho \cdot N \cdot d_p^2}{\mu}$$

$$Sc = \frac{\mu}{\rho \cdot D}$$

The data we collected from experiments and literature are shown in Table 2-1.

Parameter	Symbol	Value	Units	Note
Stirring Speed	N	8.33	rev/s	Experimental (500 rpm)
Temperature	T	80	°C	Experimental
Particle Diameter	d _p	1×10 ⁻⁴	m	Typical
Density	ρ	1100	kg/m ³	Estimated at 80°C
Viscosity	μ	0.0015	Pa·s	Estimated at 80°C
Diffusivity	D	5×10 ⁻¹⁰	m ² /s	Estimated using Stokes-Einstein

Table 2-1 Experimental and Literature Value

Based on these values, the dimensionless number and mass transfer coefficient was calculated in the below,

Step	Formula / Expression	Substitution with Units	Result
1	$Re = \frac{\rho N d_p^2}{\mu}$	$\frac{1100 \cdot 8.33 \cdot (1 \times 10^{-4})^2}{0.0015}$	0.0611
2	$Sc = \frac{\mu}{\rho D}$	$\frac{0.0015}{1100.5 \times 10^{-10}}$	2727.27
3	$Sh = 2 + 0.6 \cdot Re^{1/2} \cdot Sc^{1/3}$	$2 + 0.6 \cdot (0.0611)^{1/2} \cdot (2727.27)^{1/3}$	4.07

4	$k_f = \frac{Sh \cdot D}{d_p}$	$\frac{4.07 \cdot 5 \times 10^{-10}}{1 \times 10^{-4}}$	$2.04 \times 10^{-5} \text{ m/s}$
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Table 2-2 Dimensionless number and mass transfer coefficient calculation

The low Reynolds number ($Re = 0.0611$) indicates that the system operates in a laminar regime, with minimal convective enhancement around the particles. The high Schmidt number ($Sc \approx 2727$) reflects strong viscous dominance and very limited ion diffusion in citric acid. The Sherwood number ($Sh = 4.07$) shows only mild improvement over pure diffusion ($Sh \approx 2$), confirming that mass transfer is still largely controlled by diffusion. As a result, the estimated mass transfer coefficient $k_f = 2.04 \times 10^{-5} \text{ m/s}$ is small but significant. These values demonstrate that film resistance plays an important role and must be included alongside surface reaction kinetics. Incorporating k_f in the model via the overall resistance expression ensures a more accurate and experimentally relevant prediction of conversion $X(t)$ over time.

To accurately estimate the kinetic rate constant from experimental data, a numerical optimization routine was implemented. The core idea is to find the best-fit value of the rate constant k_s such that the model-predicted conversion $X_{\text{model}}(t)$ closely matches the experimental conversion $X_{\text{exp}}(t)$ derived from ICP-OES concentration data. The optimization process was performed using the `curve_fit` function from the `scipy.optimize` library in Python. This method internally employs the Levenberg–Marquardt algorithm, which is a widely used approach for solving nonlinear least squares problems. The algorithm combines the fast convergence of gradient descent with the stability of the Gauss–Newton method, making it ideal for the kinetic fitting task at hand. The model predicts conversion as a function of time t , considering both surface reaction diffusion through the combined rate expression

$$X_{\text{model}}(t; k_s) = 1 - \left(1 - \frac{k_s \cdot k_f}{k_s + k_f} \cdot t \right)^{1/3}$$

Here:

- k_s is the surface reaction rate constant (fitted)
- k_f is the mass transfer coefficient (calculated from empirical correlation)
- t is time (experimental input)

The experimental conversion is computed as:

$$X_{\text{exp}}(t) = \frac{C(t)}{C_{\text{max}}}$$

Where:

- $C(t)$ is the metal concentration at time t
- $C_{\max}$ is the maximum concentration achieved in the experiment

The fitting process minimizes the sum of squared errors (SSE) between model and experimental values. For lithium, the model was applied to both the full experimental dataset of citric acid (0–240 minutes) and a focused early-time interval (0–10 minutes). The full-time fit showed Figure 2-6 excellent agreement with the experimental data, capturing the rapid initial leaching phase followed by a plateauing behavior as leaching approached completion. The high fitted value indicates an initially fast leaching rate with a quick transition to saturation, suggesting that lithium is predominantly present in readily accessible surface regions of the cathode material.

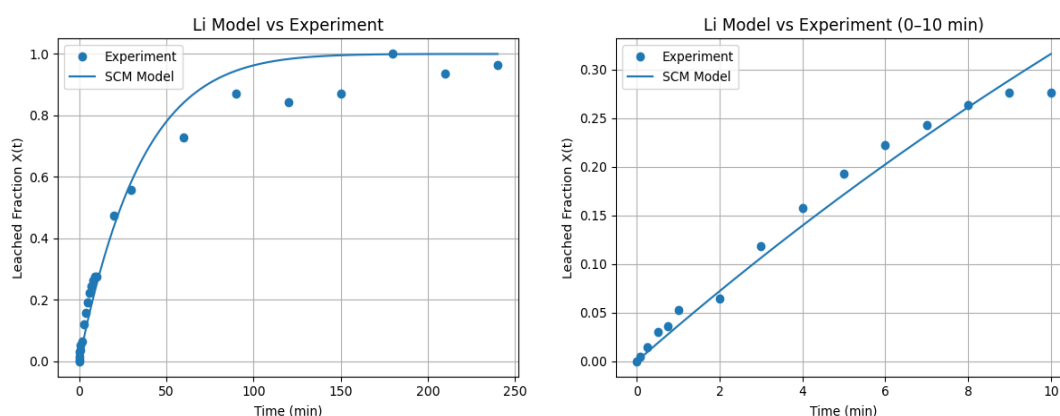


Figure 2-6 Experimental vs. SCM model fit for lithium leaching using Citric acid. (Left) Full-time leaching fit using SCM; (Right) Early-stage leaching fit (0–10 min).

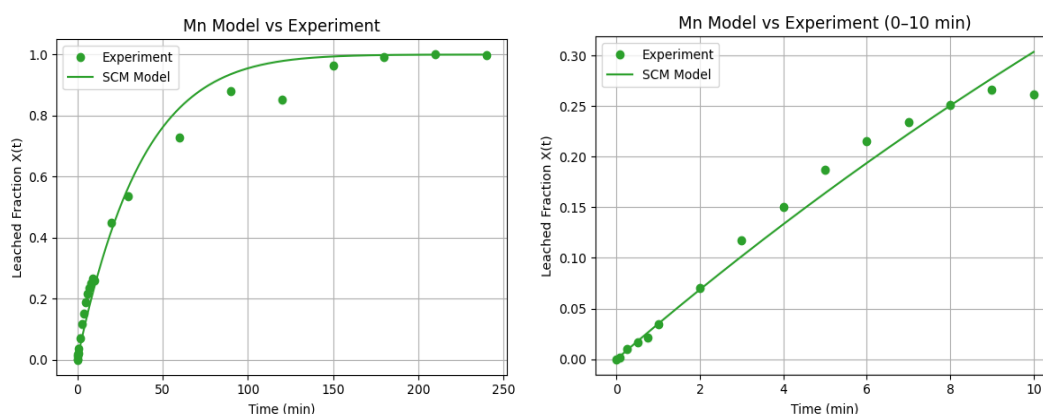


Figure 2-7 Experimental vs. SCM model fit for Mn leaching using Citric acid. (Left) Full-time leaching fit using SCM; (Right) Early-stage leaching fit (0–10 min)

The full-time model fit (Figure 2-7) for Manganese revealed a rapid leaching phase that saturated toward 100% Mn extraction, with the fitted parameter. This combination indicates a highly curved profile, suggesting fast initial kinetics followed by stabilization. The high value of fitted parameter reflects accelerated leaching in the early phase, consistent with manganese being easily released from exposed surfaces, possibly due to its weak bonding in the oxide matrix under acidic conditions. This early-stage behavior aligns well with the characteristics of a surface-reaction-controlled mechanism, where Mn dissolution occurs rapidly before transitioning into a slower stage.

Cobalt showed a similar leaching profile to manganese, though with subtle differences in kinetics. The full-time SCM fit (Figure 2-8) reflecting rapid initial extraction followed by saturation. This behavior suggests that cobalt, like manganese, is predominantly leached from surface-accessible regions of the cathode material. The curvature of the model accurately captured the experimental data across the entire 240-minute duration, reinforcing the suitability of the SCM framework for Co. Nickel leaching behavior followed a similar overall trend to cobalt and manganese but exhibited slightly slower kinetics. The full-time SCM fit (Figure 2-9) yielded again, indicating a sharp rise in leached fraction followed by a gradual plateau. The SCM model closely followed the experimental curve over the full-time range, suggesting that nickel, while slower than Li and Mn, also undergoes rapid early dissolution followed by saturation.

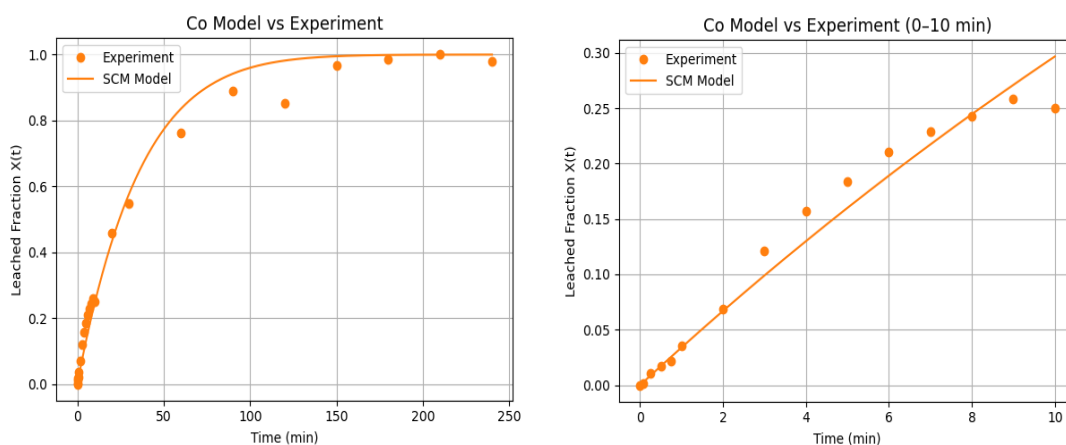


Figure 2-8 Experimental vs. SCM model fit for Co leaching using Citric acid. (Left) Full-time leaching fit using SCM; (Right) Early-stage leaching fit (0–10 min)

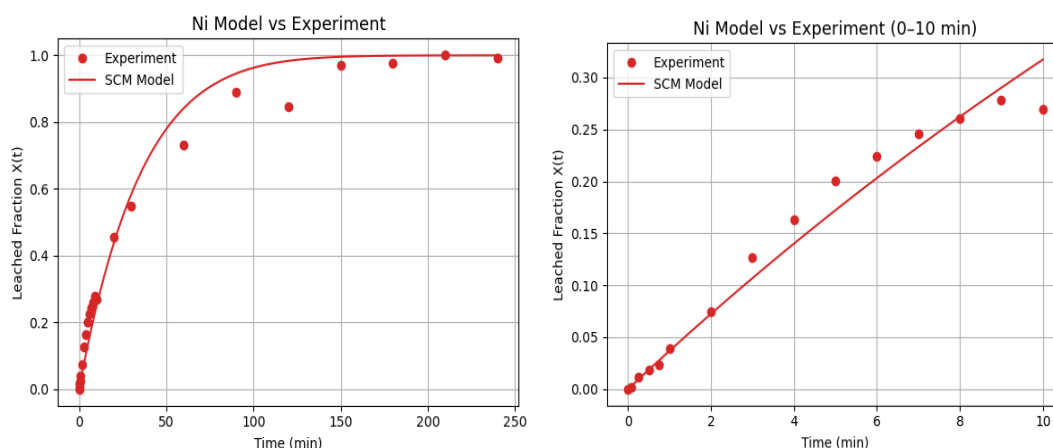


Figure 2-9 Experimental vs. SCM model fit for Ni leaching using Citric acid. (Left) Full-time leaching fit using SCM; (Right) Early-stage leaching fit (0–10 min)

The experimental leaching kinetics of lithium (Li), manganese (Mn), cobalt (Co), and nickel (Ni) using deep eutectic solvent (DES) reveal rapid extraction behavior, particularly within the initial 10 minutes of the leaching process. As observed from the plots (Figure 2-10), all four metals display a steep rise in concentration during the early stages, followed by a plateau phase, indicating near-complete leaching within a short timeframe. This behavior is characteristic of diffusion-limited or surface-reaction-limited systems, where leaching reaches saturation quickly. However, discrepancies are visible at early time points, where the experimental values exhibit a steeper slope than the SCM predictions. This may suggest the presence of initial pore diffusion enhancement or surface complexation kinetics not fully captured by conventional models. Overall, the SCM offers a reliable approximation of the leaching behavior, particularly beyond the initial burst phase, reinforcing its relevance in modeling solid-liquid leaching systems using DES.

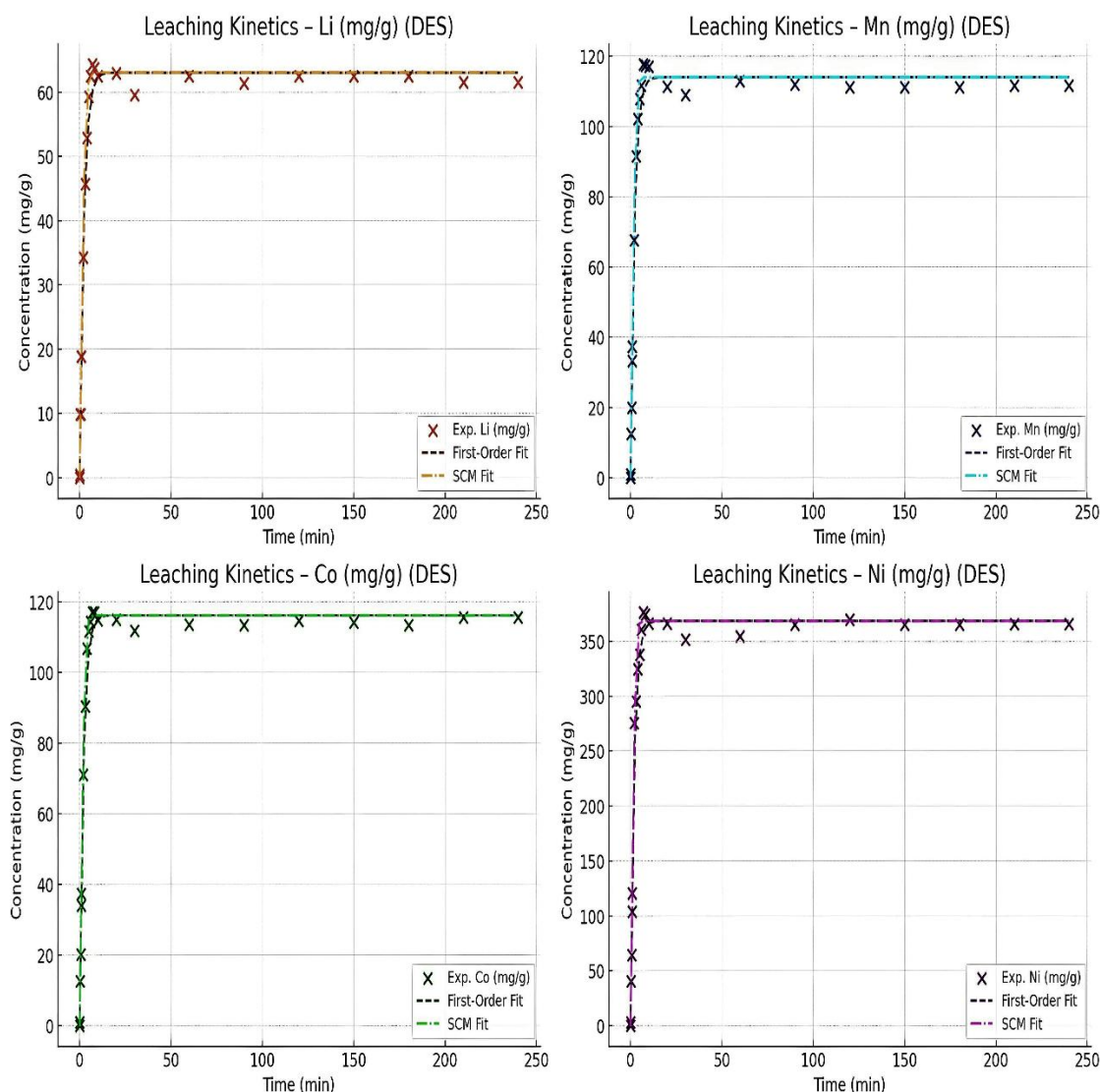


Figure 2-10 Experimental vs. SCM model fit for using DES. (Top Left) Lithium; (Top Right) Manganese; (Bottom Left) Cobalt; (Bottom Right) Nickel

2.1.5 Result Interpretation

From the SCM fits, it is evident that the rate constant values for all four metals are relatively low in the case of citric acid (on the order of 10^{-3}min^{-1}), suggesting a slower reaction-diffusion process. This aligns with the nature of citric acid—a mild, biodegradable organic acid that complexes slowly with transition metals due to its relatively lower acidity ($\text{pK}_a \approx 3.1, 4.7, 6.4$) and lower reactivity compared to mineral acids.

Metals	K – SCM	k _{overall}	Absolute Difference

Li	0.00617	0.03177	0.02560
Mn	0.00647	0.00832	0.00185
Co	0.00621	0.03162	0.02540
Ni	0.00624	0.00832	0.00208

Table 2-3 Fitted K values for different Metals

The experimental curves for early times (0–10 min) reveal that the SCM model slightly underestimates the leached fraction, indicating that initial leaching could be influenced by external mass transfer or surface reaction—not purely diffusion-controlled as the SCM assumes. Nevertheless, the model captures the general sigmoidal behavior well, particularly after ~10 min, when diffusion through the product layer becomes dominant. The leaching behavior of Li, Mn, Co, and Ni in Deep Eutectic Solvent (DES) medium is markedly different. As observed from the plots, the experimental concentration rapidly reaches saturation within the first 10–20 minutes for all metals. SCM offers a more realistic description of gradual saturation. The fitted k values for DES are much higher, indicating significantly faster leaching kinetics. This can be attributed to:

- Stronger complexation between DES components and metal ions, enhancing solubility.
- Better penetration and wetting of DES into the cathode structure.
- Possible partial breakdown of surface barriers by DES, allowing faster internal diffusion.

The rapid saturation observed also suggests that external diffusion and surface reaction steps are no longer rate-limiting, and equilibrium is reached quickly. Unlike citric acid, the assumptions of the SCM model (uniform core shrinking, constant diffusivity) may hold more robustly here due to the faster transport properties of DES.

2.2 Model of liquid-liquid extraction process

2.2.1 Experimental Setup and Data

The experiments described in this report were conducted by CSIC as part of the validation efforts under the deliverable D3.3 “Development, testing and validation of recycling solutions for cathode and black mass at lab scale” of the

FREE4LIB project. The primary objective of the LLE experiments was to evaluate the extraction and stripping efficiency of transition metals, especially cobalt, using a deep eutectic solvent (DES) system and mineral acids. The work serves both as a benchmark for empirical observations and as foundational data for model-based simulation. The process begins with black mass samples (e.g., BM01–BM10) derived from spent Li-ion batteries.

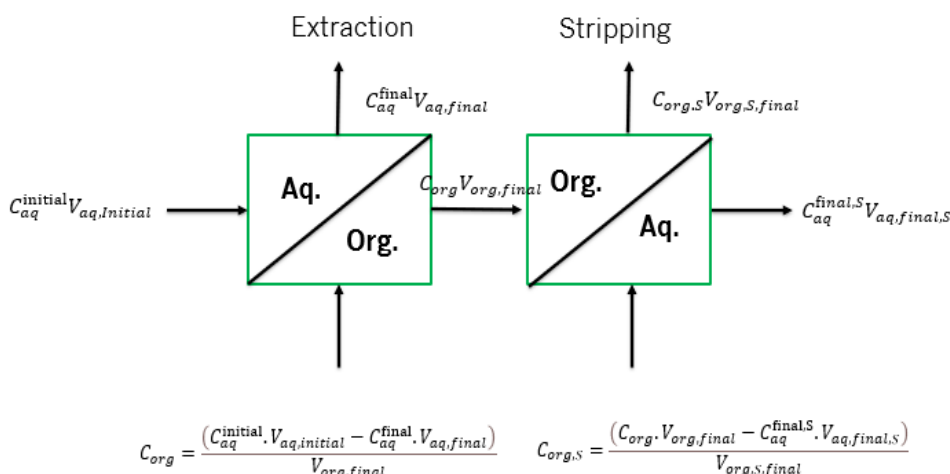


Figure 2-11 Mass Balance between extraction and stripping process [18], [19]

These samples undergo a preliminary acid leaching process to obtain a mixed-metal solution containing Co, Ni, and Mn. The leachate is then subjected to a sequence of liquid-liquid extraction and re-extraction (stripping) steps described in the following.

Extraction Phase:

- The aqueous leachate containing dissolved metal salts is brought into contact with a DES-based organic phase.
- Metal ions selectively partition into the organic phase based on their affinity toward the DES components.
- After equilibration, the phases are separated, and the Co-loaded organic phase is collected.

Stripping Phase:

- The Co-rich organic phase is re-contacted with an aqueous solution of 0.5 M H₂SO₄.
- A reverse mass transfer occurs, releasing cobalt back into the aqueous phase (stripping).
- The resulting aqueous cobalt solution is evaporated, yielding solid CoSO₄.

This procedure was carefully tracked for each black mass sample. Mass flows were recorded for each phase before and after extraction and stripping while a schematic mass balance diagram helps to contextualize performance. Some variations in final volumes were observed due to DES–water interactions. This was acknowledged by the research team as likely resulting from the absorption of water by DES, which cannot be fully saturated prior to extraction. (Reference: personal communication from CSIC).

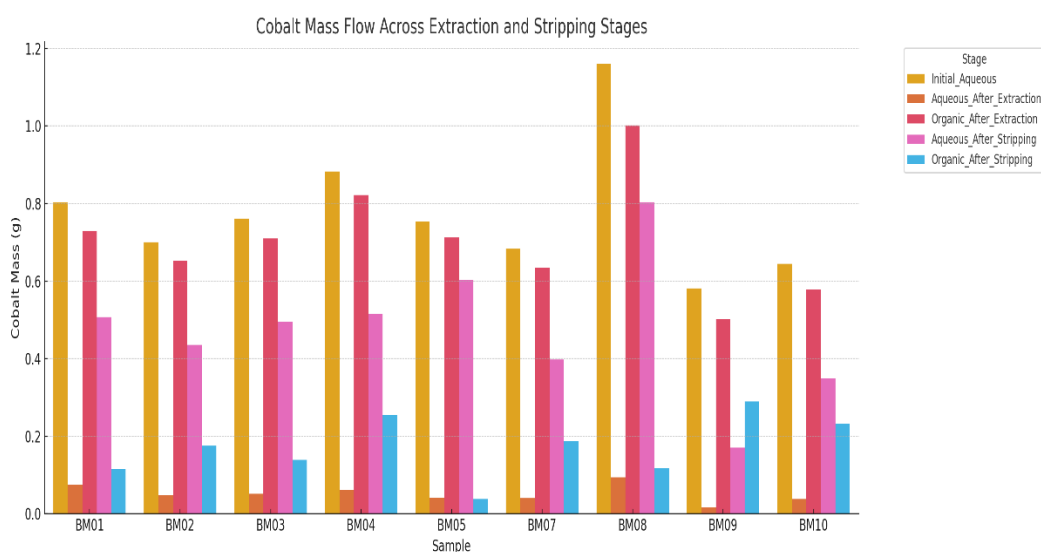


Figure 2-12 Cobalt mass flow across extraction and stripping stages

- Initial Aqueous: Total Co present before any processing.
- Aqueous After Extraction: What remains in aqueous after extraction.
- Organic After Extraction: Amount transferred to organic phase.
- Aqueous After Stripping: Co recovered back into aqueous.
- Organic After Stripping: Co still stuck in organic phase

As shown in the above figure, a significant portion of cobalt is recovered during the stripping step, though a residual amount remains in the organic phase. This highlights the potential for process optimization, especially in enhancing the cobalt and its stripping efficiency. By quantifying efficiency gaps, the data provides a pathway for RMSE-based optimization of stripping performance, where models can be trained and tuned to predict outcomes under varying process conditions. In the case of this work, the experimental work provided a very limited number of tests, that is one experiment per sample, where each sample came from different pre-processing steps. This amount of data did not allow the development of a model based on diffusion or kinetics phenomena.

Instead, different approaches have been tried with Empirical and Semi-Empirical models.

2.2.2 Governing equations

The liquid–liquid extraction process is fundamentally governed by mass transfer principles and equilibrium partitioning between two immiscible phases: aqueous and organic. A key parameter describing this equilibrium is the distribution coefficient (D), which is defined as the ratio of metal concentration in the organic phase to that in the aqueous phase at equilibrium. Mathematically, it is expressed as:

$$D = \frac{C_{\text{organic}}}{C_{\text{aqueous}}}$$

where C_{organic} is the concentration of the metal ion in the organic phase and C_{aqueous} is its concentration in the aqueous phase. A higher value of D indicates a stronger preference of the metal for the organic phase, thus signifying a more effective extraction process. To quantify the extraction performance, the extraction efficiency (%) is calculated using the difference in metal concentration in the aqueous phase before and after extraction. The general form is:

$$\text{Extraction Efficiency} = \frac{C_{\text{aq}}^{\text{initial}} - C_{\text{aq}}^{\text{final}}}{C_{\text{aq}}^{\text{initial}}} \times 100$$

This equation gives the percentage of the metal that has been transferred from the aqueous phase to the organic phase. Alternatively, for systems where both phase volumes and distribution coefficients are known, the efficiency can be estimated as:

$$\text{Extraction Efficiency} = \frac{D \cdot V_{\text{org}}}{D \cdot V_{\text{org}} + V_{\text{aq}}} \times 100$$

The design of mass transfer experiments further necessitates a mass balance approach, ensuring that the total amount of metal is accounted for across both phases. The concentration of metal in the organic phase after extraction can be calculated using:

$$C_{\text{org}} = \frac{(C_{\text{aq}}^{\text{initial}} V_{\text{aq}}^{\text{initial}} - C_{\text{aq}}^{\text{final}} V_{\text{aq}}^{\text{final}})}{V_{\text{org}}^{\text{final}}}$$

Here, the difference in metal content between the initial and final aqueous phase is attributed to the amount transferred to the organic phase. Following the extraction stage, the organic phase enriched in metal ions undergoes a

stripping process where metal is transferred back into an aqueous phase using a strong acid such as $0.5\text{MH}_2\text{SO}_4$. A similar mass balance is used to quantify the remaining metal in the organic phase post-stripping:

$$C_{\text{org},S} = \frac{(C_{\text{org}}V_{\text{org}}^{\text{final}} - C_{\text{aq}}^{\text{final},S}V_{\text{aq}}^{\text{final},S})}{V_{\text{org},S}^{\text{final}}}$$

Correspondingly, the stripping efficiency can be expressed as:

$$\text{Stripping Efficiency} = \frac{C_{\text{aq}}^{\text{final},S} \cdot V_{\text{aq}}^{\text{final},S}}{C_{\text{org}} \cdot V_{\text{org}}^{\text{final}}} \times 100$$

Together, these governing equations offer a robust framework for modeling the extraction–stripping behavior of metal ions and evaluating the effectiveness of the liquid–liquid extraction process. They also serve as foundational components for fitting experimental data and performing custom optimization using techniques such as RMSE minimization.

2.2.3 Model fitting, estimation and validation

We explored multiple alternative models to understand how well they could capture the trends in extraction (EE) and stripping (SE) efficiencies. These include two widely used empirical models—Power Law and Exponential, a multivariable regression model incorporating known process parameters and, finally, a semi-empirical non-linear model. The rationale, mathematical formulations, and their observed performance are discussed below.

The first model analyzed is the power law model, which consists in a common empirical relationship used in chemical and process engineering to model non-linear trends based on concentration or operating variables. It assumes that the response (efficiency) is a power function of the input variable.

The functional form used in our case is:

$$E = a \cdot C^b$$

Where:

- E is the extraction or stripping efficiency (%)
- C is the initial metal concentration in the aqueous phase (g/L)
- a, b are empirical fitting constants:
 - a scale the magnitude
 - b controls the curvature (non-linearity)

The second attempt was done with an exponential model, which is another empirical formulation that assumes an exponential decay or growth in response with respect to the predictor variable. It is commonly used in systems with saturation behavior or attenuation.

The model form is:

$$E = a \cdot e^{bC}$$

Where:

- E is the efficiency
- C is the initial concentration (g/L)
- a and b are fitting parameters:
 - a represents the base scale
 - b represents the exponential rate (growth or decay)

In the third attempt, a multivariable linear model was used. To incorporate known physical parameters from the LLE process, we applied a multivariable regression model using the following predictors: Initial aqueous concentration (C_{aq}), Distribution coefficient (D) and Volume ratio of organic to aqueous phase (V_R).

The simplest model takes the following linear form:

$$E = \beta_0 + \beta_1 \cdot C_{aq,0} + \beta_2 \cdot D + \beta_3 \cdot V_R$$

Where β_0 is the intercept and $\beta_1, \beta_2, \beta_3$ are regression coefficient. This approach introduces theoretical grounding by explicitly using physical process variables. It assumes linear dependence between efficiency and each parameter, which is a simplification, but useful for initial modeling and interpretation.

The last approach used to describe and predict the behavior of the liquid-liquid extraction (LLE) process is a semi-empirical model. This modeling approach serves as a practical bridge between fully mechanistic models and purely statistical curve-fitting techniques, making it highly suitable when the underlying physical and chemical mechanisms are only partially known or too complex to fully describe. The semi-empirical model enables us to incorporate experimental observations, while maintaining a functional dependence on key process parameters such as the distribution coefficient (D) and phase volume ratio (V_R).

The experimental data for both extraction efficiency (EE) and stripping efficiency (SE) consists of a limited number of samples ($n = 9$), each of which involves known operational parameters such as Initial concentration in the aqueous phase ($C_{aq,0}$), Distribution coefficient (D), Organic-to-aqueous volume ratio (V_R), Extraction and stripping times (held constant), Stirring speed ($V = 940$ rpm) and Temperature (25°C , isothermal). Given the small dataset size and moderate experimental variability, fully mechanistic models (e.g., based on diffusion, interfacial kinetics) would be overly complex and difficult to validate. Therefore, the last fit was performed using a semi-empirical formulation, which allows us to incorporate non-linear behavior using a compact analytical form with interpretable parameters.

The semi-empirical equation used is a non-linear rational expression that behaves similarly to Michaelis-Menten or Langmuir-type kinetics [20], [21]. This function is of the form

$$EE = a \cdot \ln(C_{initial}) + b \cdot D + c$$

Where:

- $C_{initial}$ is the initial cobalt concentration in the aqueous phase (g/L),
- D is the distribution coefficient (metal partitioning between organic and aqueous phases),
- a, b, c are fitting coefficients,
- EE is the predicted extraction efficiency (%).

This hybrid formulation blends empirical flexibility (logarithmic and linear terms) with physically meaningful parameters ($C_{initial}$, D). It allows the model to capture nonlinear saturation effects of concentration while still maintaining sensitivity to the distribution ratio. Finally, we performed non-linear optimization of the parameters a , b , and c by minimizing the root mean square error (RMSE) between predicted and experimental values using the Nelder-Mead algorithm. The fitting was applied separately for extraction and stripping efficiency.

The model fitting of Nickel (Figure 2-13) extraction efficiency against the initial concentration reveals a weak correlation across the first three models. While the power law and exponential models attempt to capture slight decreasing trends, they fail to align with the scattered experimental data. The multivariable linear regression model shows a slightly less curved but still diverges significantly from experimental data, especially at high concentrations. This mismatch indicates that Nickel's extraction behavior is likely governed by more complex interactions not captured by simple empirical models.

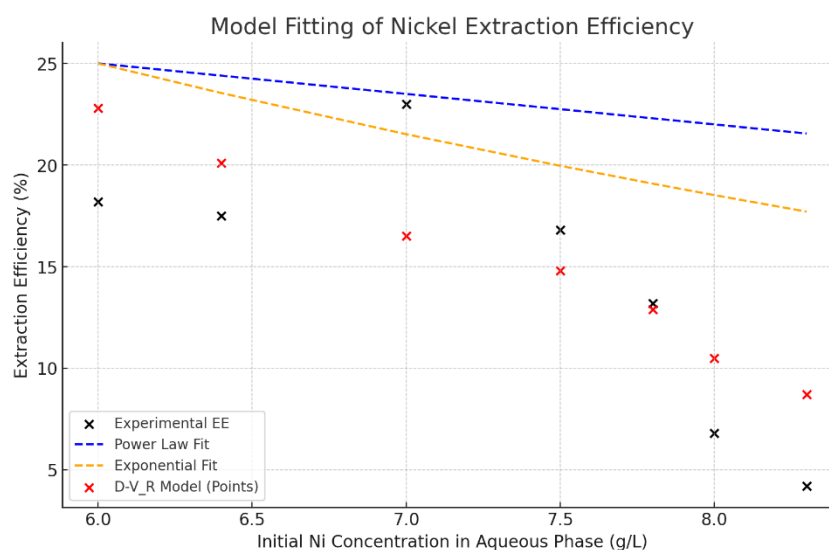


Figure 2-13 Empirical Model Fitting for Ni through extraction process. Black dots indicate experimental points, X marker is D-V_R (multivariable linear regression model), blue and red dotted lines are power and exponential law

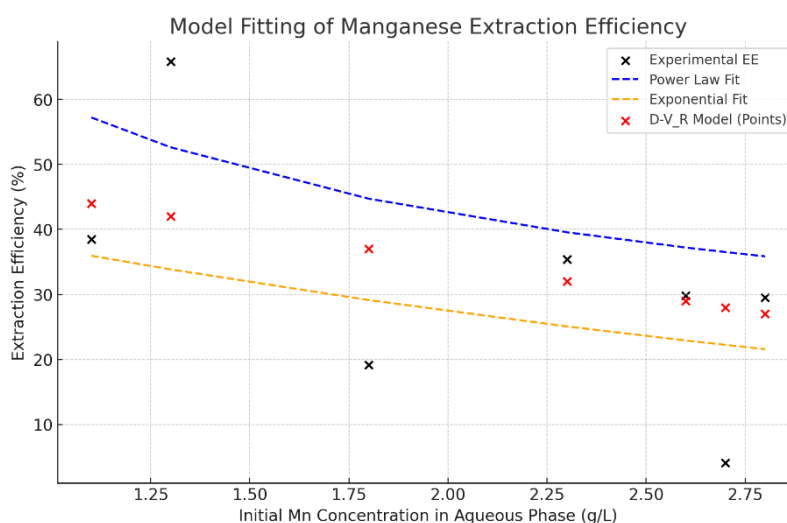


Figure 2-14 Empirical Model Fitting of Mn through extraction process. Black dots indicate experimental points, X marker is D-V_R (multivariable linear regression model), blue and red dotted lines are power and exponential law

For Manganese (Figure 2-14), the experimental extraction efficiency displays a high degree of variability across samples. Although all three models (power law, exponential, and multivariable linear regression model) suggest a declining efficiency with increasing initial concentration, none of them fit closely due to inconsistent experimental behavior. This suggests that manganese extraction may be influenced by additional kinetic or phase equilibrium factors beyond what the tested models can represent.

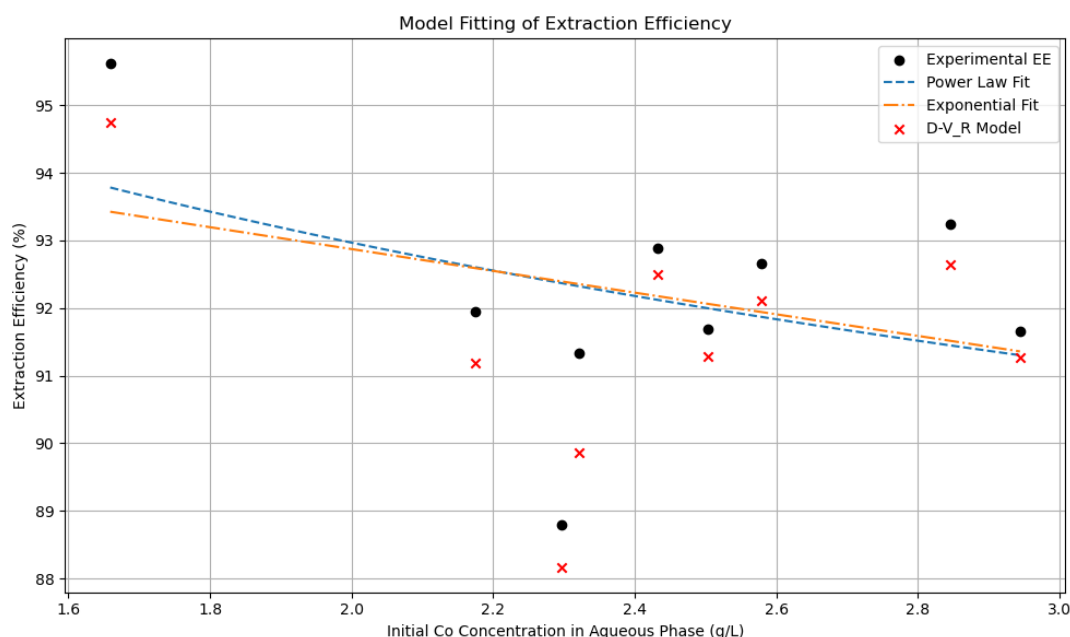


Figure 2-15 Fitting of different empirical models through extraction process. Black dots indicate experimental points, X marker is D-V_R (multivariable linear regression model), blue and red dotted lines are power and exponential law

Black circles represent experimental extraction efficiency (EE) values obtained from ICP measurements (CSIC). Dashed blue line corresponds to the Power Law Model fit. Dash-dot orange line shows the Exponential Model fit. Red crosses denote predictions from the multivariable linear regression model based on known process parameters (Figure 2-15).

Both empirical models attempt to capture the overall trend of extraction efficiency as a function of initial metal concentration in the aqueous phase. However, the fits appear visibly poor when compared to the experimental scatter. The Power Law model assumes a monotonic relationship where efficiency changes smoothly with concentration, but it fails to capture the non-linear fluctuations observed in experimental data. Specifically, it underpredicts the highest EE values and overpredicts some mid-range values, indicating that the curvature imposed by the power term is not flexible enough for this system. The Exponential model, while slightly smoother, also struggles to reflect the observed experimental behavior, especially at lower and higher concentration ends. The model assumes an exponential decay or growth, which leads to underfitting where data points deviate above and below the predicted trend line with no consistent pattern. multivariable linear regression model (Theoretical Regression with Multiple Inputs) incorporates theoretically relevant parameters but still displays inconsistent alignment with experimental EE. Some points

show decent alignment (especially mid-range samples), while others show large discrepancies (particularly at low and high ends of the concentration range).

The below Figure 2-16 illustrates the performance of three models in predicting stripping efficiency (SE) from a liquid–liquid extraction system used in battery recycling.

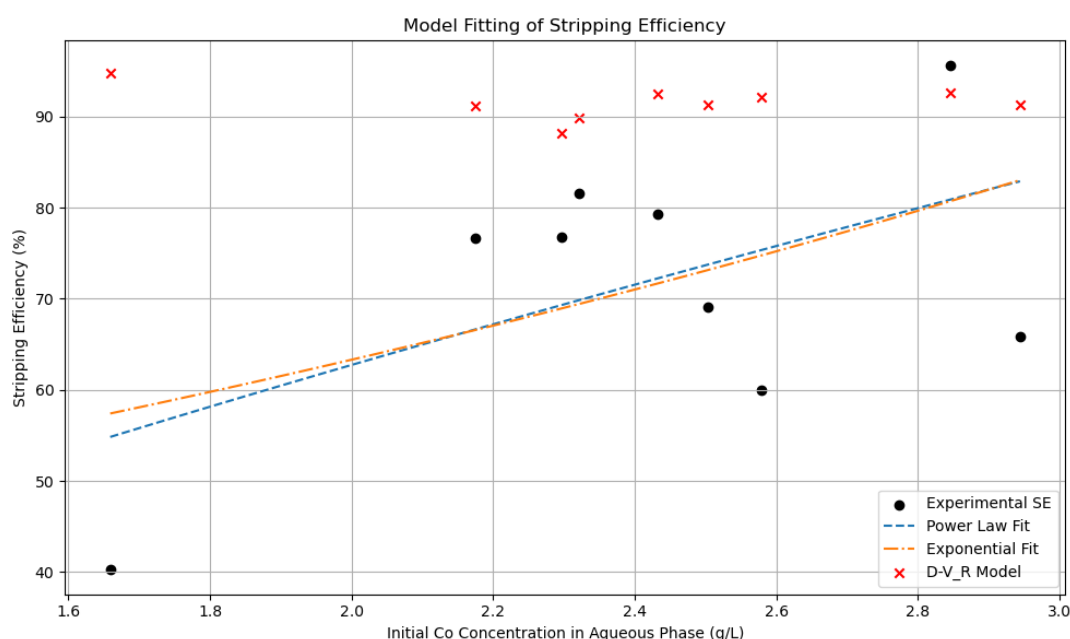


Figure 2-16 Fitting of different empirical models through stripping process. Black dots indicate experimental points, X marker is D-V_R (multivariable linear regression model), blue and red dotted lines are power and exponential law

Both empirical models attempt to express SE as a function of the initial Co concentration in the organic phase, assuming a one-dimensional functional relationship. However, the fit quality is visibly inadequate. The Power Law model displays a steadily increasing trend with concentration, but this is inconsistent with the scattered experimental results. It underestimates SE at both low and high concentration extremes and cannot replicate the non-monotonic behavior evident in the data. The Exponential model, which assumes an exponential rise or decay in SE, performs similarly poorly. While slightly smoother in trend, it still significantly deviates from many experimental points—suggesting that the underlying physics of stripping cannot be captured via a simple single-variable exponential relationship. For multivariable linear regression model, despite using three inputs, the predicted SE values are clustered at the upper end (near 90–95%), failing to replicate the strong variation seen in experimental SE (which ranges from ~40% to ~95%). This likely indicates that the model is overfitted or biased by a limited number of parameters and cannot adequately capture the dynamic complexities involved

in stripping, such as back-extraction kinetics, equilibrium limits, or solvent saturation.

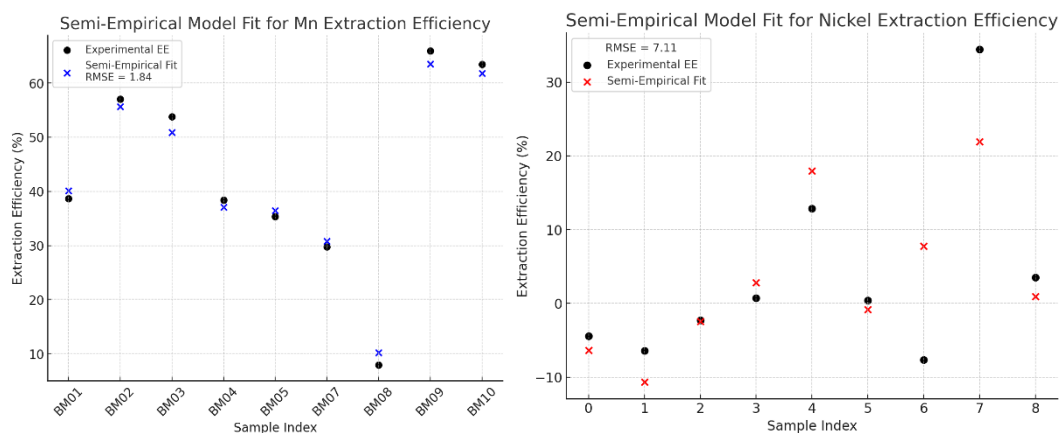


Figure 2-17 Semi-Empirical fit for Mn (left) and Ni (Right) through extraction process

The semi-empirical model fitting results (Figure 2-17) for manganese (Mn) and nickel (Ni) extraction efficiencies reveal distinct trends in predictive performance. For Mn, the semi-empirical fit closely follows the experimental extraction efficiencies across all samples, with minimal deviation. The low RMSE value (1.84) indicates excellent agreement, confirming that the model successfully captures the relationship between initial concentration and extraction performance.

In contrast, the Ni dataset presents challenges. Several samples yielded negative or unrealistic fitted values, which were excluded to focus on positive fits. Even after this adjustment, the Ni fit shows larger deviations from experimental points, reflected in a higher RMSE (7.11). This discrepancy suggests greater variability in Ni extraction efficiency, possibly due to factors not fully represented in the semi-empirical equation, such as stronger sensitivity to operational conditions, competitive metal interactions, or kinetic limitations. The big difference in RMSE arises because Mn data is smoother and fits the semi-empirical assumptions well, while Ni data shows high scatter and possible experimental or process-related inconsistencies. This mismatch between the model's functional form and Ni's irregular behavior inflates RMSE significantly.

The Figure 2-18 displays the comparison between experimental extraction efficiency (black markers) and the predicted values from a semi-empirical model (markers). This model was constructed using optimized parameters derived from nonlinear curve fitting, minimizing the RMSE between model prediction and actual experimental data.

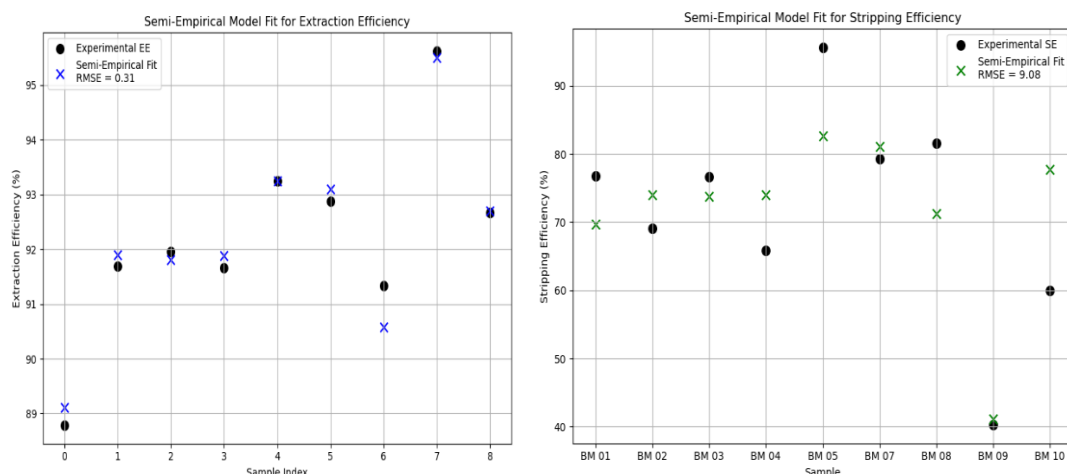


Figure 2-18 Semi-Empirical model fit for Co through extraction (Left) and stripping (Right) process

This model successfully captures the non-linear dependency of extraction efficiency on both concentration and distribution behavior, which are critical factors in the liquid-liquid extraction process. Using nonlinear optimization, the following parameters were identified as $a=10.5835$, $b=0.2684$ and $c=62.8179$. The Root Mean Square Error (RMSE) of the fit was found to be 0.31, indicating excellent agreement between the model and experimental data. Unlike purely empirical models (e.g., power law or exponential), this semi-empirical formulation incorporates logarithmic term for concentration, consistent with solute-solvent interaction behavior and thermodynamic activity coefficients and a linear dependency on D . The Figure 2-18 illustrates the comparison between the experimental stripping efficiency (black dots) and the predictions from a semi-empirical model (blue marker). The optimized coefficients obtained through nonlinear least squares fitting were $a=0.2386$, $b=-0.0649$ and $c=66.2317$. The model yielded a Root Mean Square Error (RMSE) of 9.08, which is notably higher than in the case of extraction efficiency modeling, indicating a moderate deviation from experimental points. However, the model shows clear deviation from certain experimental points (e.g., Sample 7), which likely represent outliers or uncontrolled variability in the stripping process (e.g., mixing inefficiencies, local saturation, or phase imbalance). The low RMSE in extraction arises from stable equilibrium-dominated behavior and narrow efficiency range, while the high RMSE in stripping reflects process instability, nonlinear deviations, and wider experimental scatter that the semi-empirical model cannot fully capture.

2.2.4 Result Interpretation

For extraction efficiency, the Power Law model and Exponential model both demonstrated limited capability in capturing the data trend. As seen in the

corresponding plot and the Table 2-5 Combined table of RMSE and R^2 values for all the models and metals, including the semi-empirical values., both fitted lines showed a declining trend with increasing initial cobalt concentration, whereas the experimental points displayed nonlinear scatter and deviations, particularly at mid and high concentration ranges. The D-V_R model, derived from theoretical mass balance, offered slightly better alignment but still failed to match local fluctuations, indicating that a single-variable dependency might be insufficient for accurate prediction. To overcome these limitations, a semi-empirical model was introduced, incorporating key experimental variables and fitted using nonlinear optimization.

Model	Nature	Input Variable(s)	Key Advantage	Limitation
Power Law	Empirical	Initial Concentration	Simple, interpretable	Weak fit in plateau regions
Exponential	Empirical	Initial Concentration	Good for exponential decay or growth	Poor fit for non-monotonic trends
Regression	Theoretical	$C_a q_0$, D, V _R	Uses known process parameters	Cannot capture non-linear coupling
Semi-Empirical	Hybrid	$D \times V_R$ (composite term)	Non-linear, interpretable, flexible	Needs optimization of parameters

Table 2-4 Summarizes the characteristics of the different models applied for extraction and stripping efficiency prediction

A similar pattern was observed for stripping efficiency modeling. Both the empirical Power Law and Exponential models showed increasing trends with initial concentration in the aqueous phase. However, they exhibited notable deviation from experimental values, particularly for mid-range concentrations.

Metal / Process	Model Type	RMSE	R^2
Ni Extraction	Power Law	2.94	0.78
	Exponential	3.56	0.72

	Multi Variable Linear regression	4.84	0.61
	Semi-Empirical	7.11	0.48
Mn Extraction	Power Law	7.32	0.84
	Exponential	9.25	0.76
	Multi Variable Linear regression	5.18	0.89
	Semi-Empirical	1.84	0.97
Co Extraction	Power Law	0.52	0.97
	Exponential	0.48	0.98
	Multi Variable Linear regression	1.29	0.90
	Semi-Empirical	0.31	0.98
Co Stripping	Power Law	8.05	0.34
	Exponential	7.91	0.35
	Multi Variable Linear regression	6.72	0.45
	Semi-Empirical	9.08	0.33

Table 2-5 Combined table of RMSE and R^2 values for all the models and metals, including the semi-empirical values.

The multi-variable linear regression model, based on theoretical mass balance provides a good fit for the extraction process. The multi-variable linear regression model systematically overestimated stripping efficiency, indicating a lack of sensitivity to operational deviations. In contrast, the semi-empirical model provided a more nuanced fit, using a function that included the final organic concentration and aqueous volume. Despite a higher RMSE (~9.08), the model captured the general curvature of the experimental data. However, larger deviations at specific points—such as Sample 7—suggest the presence of process outliers or unmodeled disturbances.

3. Data-Driven Modeling of the Recycling Process

3.1 Introduction

3.1.1 Context

A digital twin modeling of Fraunhofer's Electrohydraulic Fragmentation recycling plant was selected as the target of this task due to the recycling process being one of the ones with the most potential data available and being more advanced than other recycling processes at the time.

Electrohydraulic fragmentation is a method used to recycle electric vehicle (EV) batteries by breaking them apart using powerful electrical pulses in water. The process begins after the battery has been safely discharged and dismantled. Instead of cutting or grinding the battery like traditional mechanical methods, this technique relies on high-voltage electrical discharges between two electrodes submerged in water. These discharges generate intense shockwaves that travel through the water and into battery materials.

When these shockwaves hit the battery, they naturally cause it to fracture along the boundaries where different materials meet—such as between metal foils and the active coating materials. This results in the battery breaking apart cleanly, allowing valuable materials like lithium, cobalt, copper, and aluminum to be more easily separated from one another.

One of the major benefits of electrohydraulic fragmentation is that it happens underwater, making it much safer by greatly reducing the risk of fire or explosion. It also produces less dust and contamination than traditional shredding methods, which means the recovered materials are usually of higher purity and need less chemical treatment afterward.

The objective of the Data-Driven Modeling of the Recycling Process is that the developed digital representation of the process can predict the outputs of the process given the input parameters.

3.1.2 Analysis of data availability

During the duration of the development three datasets have been received from Fraunhofer.

First dataset: *fraunhofer_data_template_v2.xlsx*

Process Inputs:

Column	Description
process_id	Unique identifier of the process
voltage [kV]	Voltage used during the process
number_of_pulses	Total number of electrohydraulic pulses during the process
frequency [Hz]	Frequency of the pulses.
energy [kWh]	Total energy used in kWh
cell_type	Type of EV battery cell. Can be 'round' or 'pouch'
cell_size [mm]	Cell size in AxBxC format
total_cell_weight [g]	Total cell weight in grams
tap_water_weight [l]	Tap water weight used in process
flushing_water_weight [l]	Flushing water weight used in process

Process Outputs:

Column	Description
black_mass_percentage [%]	Percentage of black mass in the output
black_mass_purity percentage [%]	Purity percentage of the black mass
wet_black_mass_weight [g]	Weight of the wet black mass
wet_metal_fraction_weight [g]	Weight of the wet metal fractions
wet_plastic_weight [g]	Weight of the wet plastic
dry_black_mass_weight [g]	Weight of the dry black mass
dry_metal_fraction_weight [g]	Weight of the dry metal fractions
dry_plastic_weight [g]	Weight of the dry plastic

This dataset contains 31 rows of which 6 contain missing values in the wet_black_mass_weight, wet_plastic_weight and wet_metal_fraction_weight columns.

Some other columns like Voltage of Frequency contain the same or almost the same value for every row. With repeated values for 27 of more of the 31 rows.

Second Dataset: *fraunhofer_data_template-2_v6.xlsx*

Process Inputs:

Column	Description
process_id	Unique identifier of the process
voltage [kV]	Voltage used during the process
number_of_pulses	Total number of electrohydraulic pulses during the process
frequency [Hz]	Frequency of the pulses.
energy [kWh]	Total energy used in kWh
cell_type	Type of EV battery cell. Can be 'round' or 'pouch'
cell_size [mm]	Cell size in AxBxC format
total_cell_weight [g]	Total cell weight in grams
tap_water_weight [l]	Tap water weight used in process
flushing_water_weight [l]	Flushing water weight used in process

Process Outputs:

Column	Description
total_time [s]	Total process time
quality_check	Quality check evaluation. Can be good or medium.
throughput [kg/h] (optional)	Kg/h of output in the continuous process.

This dataset contains data from the newer fragmentation plant at Fraunhofer, where the recycling process is semi-continuous. It contains 30 rows of data.

Unfortunately, this dataset does not contain values for the output weights of percentages. It contains a general quality assessment and the production rates of the process.

Third Dataset: *fraunhofer_data_template-2_v7.xlsx*

Process Inputs:

Column	Description
process_id	Unique identifier of the process
voltage [kV]	Voltage used during the process
number_of_pulses	Total number of electrohydraulic pulses during the process
frequency [Hz]	Frequency of the pulses.
energy [kWh]	Total energy used in kWh
cell_type	Type of EV battery cell. Can be 'round' or 'pouch'
cell_size [mm]	Cell size in AxBxC format
total_cell_weight [g]	Total cell weight in grams
tap_water_weight [l]	Tap water weight used in process
flushing_water_weight [l]	Flushing water weight used in process

Process Outputs:

Column	Description
black_mass_percentage [%]	Percentage of black mass in the output
black_mass_purity percentage [%]	Purity percentage of the black mass
wet_black_mass_weight [g]	Weight of the wet black mass
dry_black_mass_weight [g]	Weight of the dry black mass

dry_metal_fraction+plastic_weight [g]	Weight of the dry metal fractions plus the weight of the dry plastic
total_time [s]	Total process time
quality_check	Quality check evaluation. Can be good or medium.
throughput [kg/h] (optional)	Kg/h of output in the continuous process.

The third dataset is a mix of the previous two, containing weight values in the outputs but also process time and quality checks. However, some of the weights are missing or contain mostly missing values. The dataset is 30 rows long.

Due to the low amounts of data available for the project, data augmentation and oversampling methods have been employed to try to solve or mitigate the issues that arise from the limited datasets.

3.1.3 Data Oversampling

Synthetic Data Vault's CTGANSynthesizer is based on a type of generative model called a Conditional Tabular GAN, or CTGAN. Unlike traditional oversampling methods such as SMOTE, which interpolate between existing data points, CTGAN learns a deep generative model that can produce entirely new, realistic samples. It does this by training a generator and a discriminator in tandem, where the generator tries to create realistic data and the discriminator tries to tell real from fake. Over time, the generator learns to produce highly realistic synthetic rows. CTGAN is especially powerful for tabular data as its ability to handle both continuous and categorical variables effectively.

After processing the first and third datasets to generate new features and clean up missing data. The processed datasets are fed into the CTGANSynthesizer to generate a parametrized number of new rows.

The second dataset is not used in the data oversampling process due to the lack of most of the output features.

The generated data fits logically the rest of the datasets but does not add new information. Making the lack of variance in the previous datasets more visible in the new larger datasets.

In the next figure we can see the data correlation of the enlarged dataset.

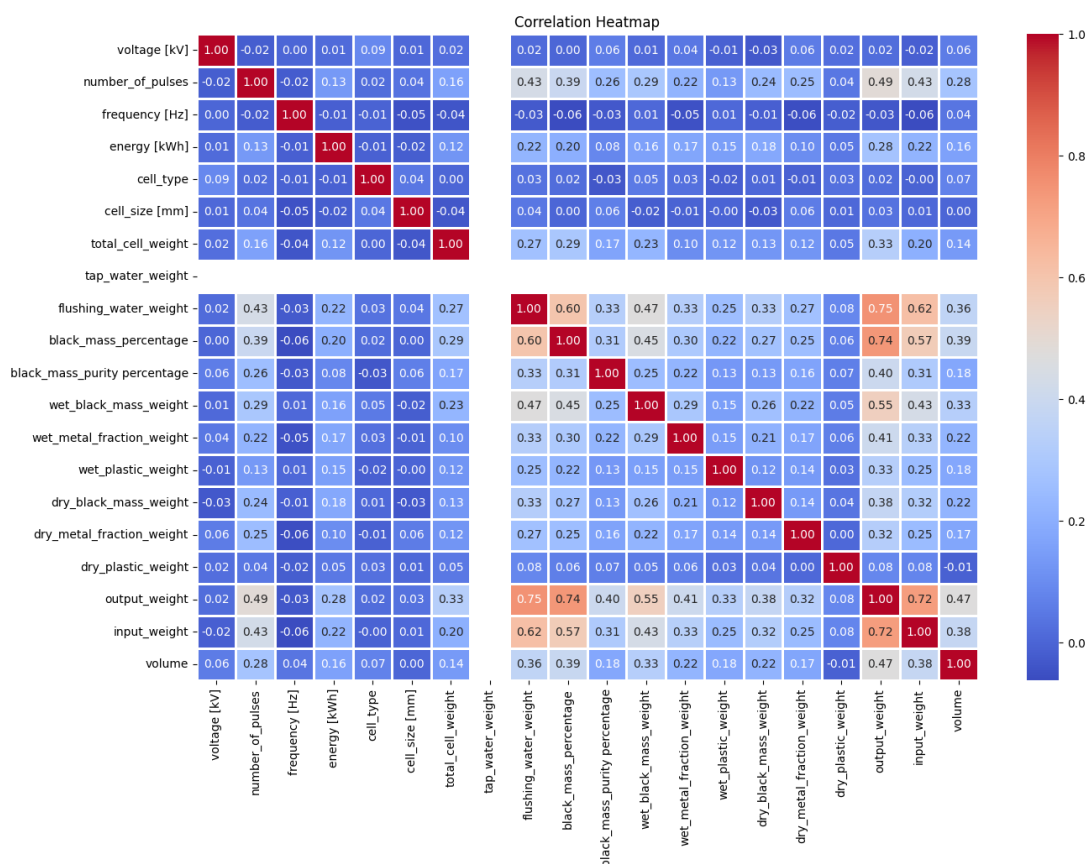


Figure 3-1 Feature Correlation of Oversampled Dataset

3.2 Data-driven models

Two implementations have been developed to simulate digitally the electrohydraulic process. First Categorical Boosting (CatBoost) a machine learning implementation based on decision trees and extreme gradient boosting with categorical and numerical data. Next a neural network implementation using Multi-Layer Perceptron that using deep learning methodologies might capture complexities in the data that other machine learning methods could not.

3.2.1 Governing equations and theory

3.2.1.1 Categorical Boosting

CatBoost is an **ensemble method** based on **gradient boosting over decision trees**. The prediction of a CatBoost regression model can be expressed as:

Where:

$$\hat{y}(X) = \sum_{m=1}^M \eta \cdot f_m(X)$$

- $\hat{y}(x)$ is the predicted output for input vector x ,
- M is the number of trees in the ensemble,
- η is the learning rate
- $f_m(x)$ is the prediction made by the m -th regression tree.

When using CatBoost regression for this purpose, the algorithm is trained on historical process data to learn how process inputs (such as Voltage, frequency, cell weight, etc.) influence outputs (such as black mass purity, black mass percentage, etc.). Once trained, it can predict process behavior in real time and very quickly return expected outputs.

CatBoost introduces several key innovations that improve performance, especially for categorical features and small datasets:

Ordered Boosting:

Standard gradient boosting methods can suffer from target leakage when computing statistics (like means) from the full dataset. CatBoost solves this with ordered boosting, where data is processed in a way that mimics online learning. It only uses past data to compute statistics for each example, avoiding information leakage from future data.

Handling of Categorical Features:

CatBoost can process categorical variables directly without one-hot encoding. It uses a target encoding method, computing a smoothed mean of the target variable for each category.

Symmetric Trees:

Unlike other gradient boosting frameworks, CatBoost uses symmetric (oblivious) trees, where the same decision rule is applied at each level across all branches. This leads to faster training, more compact models, better compatibility with GPU acceleration (if available).

3.2.1.2 Multi-Layer Perceptron

MLP uses the typical Neural Network architecture of Input layers, Hidden layers and Output layers to capture complex relations within the data. Artificial neural networks, particularly Multilayer Perceptrons (MLPs), are commonly employed due to their universal function approximation capabilities.

Therefore, the process of Electrohydraulic Fragmentation can be modeled within the hidden layers of a neural network with enough data.

Using MLP will allow the model to capture highly complex interactions within the data, making sure that predicted outputs are a product of a deep understanding of all possible connections and interactions in the dataset.

Neural network models have no problem with multi-output regression which makes them also a good candidate to handle a process with up to 9 output variables.

3.2.2 Training CatBoost

The training of the CatBoost model is done over a wrapper implementation that handles multiple models, one for each of the target variables. The architecture handles the preprocessing, creation and training of the models as well as saving the trained models along with all configurable parameters used.

3.2.2.1 Data Acquisition and Preprocessing

The training process begins by invoking a custom data extraction routine (`extract.read_dataframe`), which ingests a dataset from a location and format specified under the `settings["extract"]` configuration. The dataset must include the full set of predictor variables and target columns as defined in the `global_settings` dictionary. If the data cannot be loaded or specified variables are missing, the pipeline raises appropriate exceptions (`FileNotFoundError`, `ValueError`).

3.2.2.2 Model Initialization and Output Management

A CatBoost model manager is instantiated, encapsulating functionality for model training and storage. A timestamped execution directory is then created, using the current system time in the format `YYYY-MM-DD_HH:MM:SS`. This directory serves as the centralized location for saving trained model artifacts and corresponding configuration files, ensuring traceability and version control.

3.2.2.3 3. Target-Specific Model Training with Grid Search

The core of the pipeline is a loop that iterates over all target variables listed in `global_settings["targets_cb"]`. For each target:

- The `grid_train` method is invoked, which constructs a `cb.Pool` object from the specified feature columns and target values.

- A CatBoostRegressor instance is initialized using the loss function and logging preferences defined in `settings["train_grid"]`.
- Hyperparameter optimization is conducted via `model.grid_search(...)`, which searches over the user-defined parameter grid using the training dataset.
- The trained model is stored internally and subsequently saved to disk via `models.load(...)`, with a naming convention of `catboost_<target>.pkl`.

This per-target model training approach allows independent optimization of each regression model, accommodating potential differences in data distribution and model complexity across targets.

3.2.2.4 Configuration Archival

To support auditability and experimental reproducibility, the pipeline serializes and saves all runtime configuration parameters (`settings` and `global_settings`) to a YAML file within the execution directory. This practice ensures that each experiment is fully documented and can be reconstructed or analyzed post hoc.

3.2.2.5 Output and Deliverables

Upon successful execution, the pipeline produces the following artifacts:

- One serialized CatBoost model file per target variable (e.g., `catboost_price.pkl`, `catboost_demand.pkl`).
- A YAML file storing all configuration parameters used during the run.

This pipeline provides a systematic and scalable solution for multi-target regression modeling using CatBoost, with built-in support for hyperparameter tuning, model persistence, and configuration management.

3.2.3 Training MLP

The MLP Train pipeline performs sequential data preparation, model optimization, and artifact persistence using PyTorch. It is designed to support multi-target regression tasks where input features are mapped to multiple continuous output variables.

3.2.3.1 Data Loading and Column Selection

The process begins with data ingestion via a parameterized extraction function (`extract.read_dataframe`). From the retrieved dataset, the relevant feature and target columns are selected using the keys `features_mlp` and `targets_mlp` in

global_settings. A validation routine ensures that all specified columns exist, raising a ValueError otherwise.

3.2.3.2 Feature Scaling and Data Splitting

Feature standardization is conducted separately on the input and output variables using StandardScaler, transforming both predictors (X_data) and response variables (y_data) to have zero mean and unit variance. Following this, the dataset is partitioned into training and validation subsets using a stratified random split based on the val_size parameter in settings.

3.2.3.3 Tensor Conversion and DataLoader Preparation

The training and validation subsets are encapsulated in a custom dataset class (transform.ProcessDataset), which applies further tensor transformations via transform_tensor(). These are then passed into PyTorch DataLoader objects, enabling efficient batch-wise iteration over the data during model training. The DataLoaders are configured using user-defined parameters (e.g., batch size, number of workers) provided in settings["data_loader"].

3.2.3.4 Model Initialization and Configuration Management

A feedforward neural network (DigitalTwin) is instantiated, where the input and output dimensions correspond to the number of selected features and targets, respectively. The model is managed within a time-stamped execution directory (YYYY-MM-DD_HH:MM:SS), which serves as a central repository for saving model weights, scalers, and configuration files.

3.2.3.5 Training and Early Stopping

The model is trained using the Transmap() function, which employs the Adam optimizer and Mean Squared Error (MSE) loss. The training loop runs for a maximum number of epochs defined in settings["train"]["epochs"], with early stopping based on validation loss of the first target variable only (e.g., black_mass_percentage). The early stopping mechanism:

- Monitors the validation loss of output index 0 across epochs.
- Saves the best-performing model weights to disk (best_model.pt).
- Halts training if no improvement is observed after a user-specified number of epochs (patience parameter).

After training, the model reloads the best weights to ensure optimal performance based on the validation criterion.

3.2.3.6 Artifact Serialization

Upon training completion, the pipeline performs the following serialization steps:

- Trained model weights are saved to MLP.pkl via a dedicated load() method.
- The fitted feature and target scalers are serialized using joblib and stored as X_scaler.joblib and Y_scaler.joblib, respectively.
- All pipeline configurations (including data processing, model training, and global feature/target selection) are persisted in a YAML format.

3.2.3.7 7. Output and Deliverables

The execution of the pipeline yields:

- A fully trained and optimized PyTorch MLP model saved to disk.
- StandardScaler objects for reproducible inference.
- A configuration YAML file documenting the experimental setup.

This pipeline offers a systematic and reproducible approach for training neural digital twin models, incorporating best practices such as modularization, early stopping, and configuration logging.

3.2.4 Validation

Given that the nature of the outputs is fully numeric and that the training uses regression methodology, the evaluation and validation of the models is done with regression metrics, specifically Root Mean Square Error (RMSE), Mean Absolute Error (MAE) or R^2 Score.

CatBoost Results:

Output	RMSE	R^2
black_mass_percentage [%]	8.14	-0.01
black_mass_purity percentage [%]	1.92	0.01
wet_black_mass_weight [g]	2588.95	0.05
wet_metal_fraction_weight [g]	263.92	-0.05

wet_plastic_weight [g]	78.71	-0.01
dry_black_mass_weight [g]	90.33	0.03
dry_metal_fraction_weight [g]	87.25	-0.1
dry_plastic_weight [g]	6.53	0.04
output_weight [g]	2583.61	0.01

MLP Results:

Output	MAE	RMSE	R2
black_mass_percentage [%]	8.9346	10.3252	0.0055
black_mass_purity percentage [%]	1.6501	1.9828	0.0005
wet_black_mass_weight [g]	507.6648	627.4132	- 0.0013
wet_metal_fraction_weight [g]	183.4304	222.6495	- 0.0072
wet_plastic_weight [g]	147.5732	168.0928	- 0.0009
dry_black_mass_weight [g]	123.8851	146.0620	0.0017
dry_metal_fraction_weight [g]	70.7712	92.0201	0.0087
dry_plastic_weight [g]	9.0610	11.2833	0.0023
output_weight [g]	2223.1635	2576.3177	0.0010

3.3 Conclusions

The models seem to perform good when looking at the RMSE or MAE, but the low values of the R2 score metrics indicate that the models are learning to predict within a range of expected data but not fully adapting to the possible

behaviors of the real process. Most likely this is due to the lack of data specifically due to the lack of diversity in the inputs and outputs of the datasets, which cannot be easily offset with data oversampling due to all possible ranges of behaviors seen in the original dataset being exhausted very quickly.

However, the implementation of the modeling system is highly parametrizable, with configurable settings for almost any possible future dataset, it's expected that with more data in the future the current implementation would be able to handle and use the models to better fit the datasets and generate more accurate and real predictions.

4. Physics-Based Modeling of the cells (Lithium Ion)

4.1 Role of PyBaMM framework

PyBaMM (Python Battery Mathematical Modelling) is an open-source simulation tool for modeling lithium-ion batteries, offering a flexible and modular framework that supports models from basic equivalent circuits to physics-based DFN and SPM. Its design enables rapid prototyping, parameter customization, and integration with experimental data for model validation.

4.1.1 Key Features and their role

PyBaMM's modular architecture allows independent control over sub models—such as electrodes, electrolytes, and thermal effects, making it suitable for both detailed and simplified simulations. It supports incorporation of various degradation mechanisms and thermal effects and allows switching between different physical models with ease. Model parameters can be loaded from literature, defined by users, or fitted to experimental data. In this project, data from OCV, capacity, pulse, and EIS tests were used to calibrate electrochemical and kinetic parameters. PyBaMM supports visual and numerical validation, along with gradient-based optimization and sensitivity analysis using tools like CasADi.

Given the flexibility, available features and wide use in the community, PyBaMM was chosen as the core cell simulation tool to fit and validate the battery model against experimental results. It enabled multi-parameter optimization for matching discharge curves, OCV profiles, and impedance spectra. The framework provided a robust platform for simulating and comparing voltage

vs. capacity trends at various C-rates and temperatures, ensuring a physics-informed and data-driven model fit.

4.2 Experimental Dataset and Analysis

The experimental validation and parameter optimization conducted throughout this work are grounded on a series of high-fidelity datasets generated by Fondazione Bruno Kessler (FBK). These experiments were systematically designed and executed to evaluate the electrochemical behavior of both new and recycled lithium-ion cells under controlled conditions. The complete experimental methodology, test procedures, and instrumentation details are thoroughly documented in the Deliverable D2.3 – Report on Electrochemical Testing of New, Spent, and Recycled Cells. Several datasets were utilized across different stages of modeling and validation, categorized as follows:

Open Circuit Voltage (OCV) Data:

The OCV dataset—based on low-rate charge-discharge cycles (0.05C)—was used to calibrate the equilibrium behavior of the cell and to optimize key parameters such as the maximum and initial lithium concentrations in the electrodes (C_{n_max} , C_{p_max} , c_{n_init} , c_{p_init}). This calibration served as the foundation for defining accurate State-of-Charge (SoC) vs. voltage relationships.

Energy and Capacity Tests:

Experimental discharge data at multiple C-rates (0.3C, 0.5C, and 1C) were used to validate the dynamic behavior of the battery. These tests were performed under different ambient temperatures, including 5°C, 25°C, and 40°C, enabling temperature-dependent parameter identification. This allowed us to fit critical parameters such as exchange current densities (i_{0n} , i_{0p}) and electronic conductivities (σ_n , σ_p) under realistic thermal conditions. Temperature effects were also considered during model validation, ensuring that the fitted parameters remained physically meaningful across different thermal environments.

Pulse Discharge and EIS Tests:

High-current pulse test data, recorded at different SoC levels (20%, 50%, 80%), was leveraged to isolate and validate the ohmic loss components of the battery, thereby enabling the separate evaluation of resistive and kinetic overpotentials. This data was particularly effective in assessing the suitability of the fitted dynamic parameters under transient load conditions.

Although primarily used as a qualitative reference, EIS measurements were collected to compare the frequency-dependent behavior of the cells with the internal resistance components captured in the model. This offered an additional layer of validation for the fitted ohmic resistance and charge transfer parameters.

All datasets were preprocessed and aligned with PyBaMM-compatible formats to facilitate smooth integration into simulation and optimization workflows. The inclusion of temperature-dependent experimental data played a vital role in ensuring the robustness and generalizability of the fitted model parameters.

4.3 Electrochemical model and its equations

To simulate the electrochemical behavior of lithium-ion cells and validate experimental datasets, several parameters were used in the Single Particle Model (SPM) framework. These parameters fall into two main categories: equilibrium parameters (used to define the initial state and open-circuit voltage behavior) and dynamic parameters (which govern the kinetics, transport, and ohmic behavior of the cell). Below is a detailed explanation of these parameters in the context of the governing equations and how they are implemented in PyBaMM.

Solid-Phase Lithium Diffusion (in particle):

Describes lithium concentration $c_s(r, t)$ within each spherical electrode particle:

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s r^2 \frac{\partial c_s}{\partial r} \right)$$

Boundary conditions:

- At $r = 0$: $\frac{\partial c_s}{\partial r} = 0$ (symmetry),
- At $r = R_s$: $-D_s \frac{\partial c_s}{\partial r} = \frac{j}{aF}$

The key parameter here is the solid-phase diffusion coefficient D_s [m^2/s], which determines how quickly lithium redistributes within the active material during charging or discharging. In the current model, this parameter was assumed constant but can also be made SoC- or temperature-dependent in future refinements. It was not directly fitted in with this study due to the limited sensitivity of the voltage profile at low to moderate C-rates.

Electrochemical Reaction Kinetics (Butler-Volmer equation):

Govern the interfacial current density j :

$$j = 2i_0 \sinh\left(\frac{F\eta}{2RT}\right)$$

Where:

- i_0 is the exchange current density, often expressed as:

$$i_0 = k \cdot c_e^\alpha \cdot c_s^\alpha \cdot (c_{s,\max} - c_s)^\alpha$$

- $\eta = \phi_s - \phi_e - U(c_s)$ is the overpotential

The exchange current density governs how fast the intercalation reaction can proceed at the electrode/electrolyte interface. It is strongly dependent on temperature and concentration. The value obtained through fitting experimental voltage-capacity curves for each temperature case (5°C, 25°C, and 40°C). A lower value of i_0 indicates higher kinetic resistance, especially observable at higher C-rates.

Charge Conservation (Ohm's Law):

In solid phase (electrodes):

$$\nabla \cdot (\sigma_{\text{eff}} \nabla \phi)_s = aj$$

Though not explicitly modeled in SPM, ohmic drop due to separators and current collectors can be represented using an effective resistance Rohmic. This was accounted for indirectly during pulse test fitting by analyzing the instantaneous voltage drop under high-current conditions. The electronic conductivity of the electrodes, σ_n and σ_p [S/m], controls the voltage drop within the solid phase due to resistance. These values were fitted using experimental discharge data at various C-rates and temperatures. While graphite generally shows high conductivity, the conductivity of NMC materials (particularly for polycrystalline structures) can be limited and highly sensitive to temperature and degradation. In PyBaMM, these equations are automatically defined based on the model class selected.

Here's how they are implemented: The process begins with selecting the model (e.g., SPM), followed by loading parameters from literature or custom files. The default geometry is defined and processed, and a mesh is generated to discretize the spatial domains. PyBaMM's symbolic engine then processes both the model and geometry using the provided parameters. The simulation is executed using a solver (e.g., CasadiSolver), and relevant outputs such as terminal voltage are extracted from the solution for comparison with experimental data. This modular workflow enables rapid testing of different parameter sets and ensures consistency with the governing equations of battery physics.

4.4 Input parameterization

To enable accurate and scientifically justified parameter fitting, several input values were obtained directly from experimental measurements, while others were taken from literature sources and used as constants. This ensured the model was grounded in both experimental evidence and validated electrochemical theory.

4.4.1 Experimental Inputs

Key experimental inputs included the open-circuit voltage (OCV) profile, obtained from low-rate (0.05C) charge–discharge cycles, and voltage–capacity curves at varying C-rates (0.3C, 0.5C, and 1C), recorded under controlled temperature conditions. The OCV data was used to determine equilibrium-related parameters such as maximum and initial lithium concentrations in the electrodes, while the dynamic discharge data enabled the identification of kinetic parameters like exchange current densities and electrode conductivities. These datasets offered direct insight into the cell's electrochemical behavior and were essential for accurately capturing both the equilibrium and transient responses of the model.

Parameter	Symbol	Formula	Value	Units
Electrode area	A	0.090 m×0.260 m	0.0234	m ²
Total number of electrodes	N	-	62	-
Total electrode area	A _{tot}	A×N	1.4508	m ²
Cathode Thickness	L _p	Given (SEM)	50×10 ⁻⁶	m
Anode thickness	L _n	Given (SEM)	100×10 ⁻⁶	m
Cathode Volume	V _p	A _{tot} × L _p	7.254×10 ⁻⁵	m ³
Anode Volume	V _n	A _{tot} × L _n	1.450×10 ⁻⁴	m ³
Cathode Energy Density	E _p	Reference	3600	Wh/L
Separator Thickness		Given	1×10 ⁻⁵	m

Table 4-1 Experimental cell geometry dataset generated by FBK

In this work, the physical geometry parameters (Table 4-1)—such as electrode thickness, surface area, and number of electrode layers—were treated as fixed

inputs and not subject to optimization. These values were derived from direct experimental characterization performed by Fondazione Bruno Kessler (FBK). Specifically, the electrode thicknesses of both the positive and negative electrodes were determined using Scanning Electron Microscopy (SEM) imaging of the cross-sections of fresh and recycled cells. These high-resolution SEM measurements provided accurate estimates of the cathode and anode layer thicknesses, which were then used in the model to compute the total active material volume. Furthermore, the electrode area per layer and number of electrode layers were extracted from the design specifications of the pouch cell under test. By using these experimentally determined geometric parameters as constants in the model, we ensured that the simulation results remained physically meaningful and aligned with the actual cell architecture. This approach also reduces the degrees of freedom in parameter fitting, helping to isolate the effects of electrochemical kinetics and transport processes.

4.4.2 Referenced Inputs and Constants

To reduce complexity and avoid overfitting, several physical and electrochemical parameters were held constant during the fitting process. These constants (Table 4-2) —such as transference number, electrode porosity, electrolyte diffusivity, and particle radius—were selected based on values reported in reputable literature sources, including works by Chen [4], Mohtat [22], and Verbrugge & Baker [23].

Parameter	Symbol	Value	Unit	Source / Notes
Universal Gas Constant	R	8.314	J/mol·K	Physical constant
Faraday's Constant	F	96485	C/mol	Physical constant
Charge transfer coeff.	α	0.5	—	Assumed symmetric
Temperature (varied)	T	278, 298, 313	K	Measured at 5°C, 25°C, 40°C
Electrolyte transference number	t^+	0.4	—	Chen2020 [4]
Electrolyte conductivity function	$\kappa(c,T)$	—	S/m	Chen2020, PyBaMM default

Electrolyte diffusion coefficient	D_e	function	m^2/s	Chen2020
Electrode OCP functions	$U_n(x), U_p(x)$	function	V	Chen2020, fitted curves
Electrode porosity	ϵ_n, ϵ_p	0.3–0.35	—	Chen2020 estimates
Electrode active material fraction	ϕ	0.6–0.8	—	Chen2020
Particle radius (graphite)	R_n	1e-6	m	Chen2020
Particle radius (NMC)	R_p	2e-6	m	Chen2020
Solid-phase diffusion coefficient	D_s	1e-14	m^2/s	Assumed constant for diff. C rates

Table 4-2 Reference values and constants used in cell modelling

These references represent widely accepted baselines for lithium-ion cell modeling and are integrated by default in the PyBaMM framework. By anchoring the model in experimentally measured inputs and validated literature constants, we ensured both the physical realism and scientific robustness of the fitted parameters.

4.5 Parameter Optimization Strategy

To calibrate the electrochemical model and ensure consistency with experimental data, two distinct optimization processes were carried out. The first optimization focused on equilibrium parameters, using open-circuit voltage (OCV) data collected under low C-rate conditions. The objective of this step was to identify values for the maximum and initial lithium concentrations in both electrodes that best replicated the experimentally observed SoC–voltage relationship. This was achieved using a Bayesian optimization routine with a defined objective function that minimized the root-mean-square error (RMSE) between the simulated and experimental OCV curves. The output of this step provided a well-aligned equilibrium profile, which served as the foundation for further dynamic simulations.

A multi-parameter fitting strategy was employed in both the equilibrium and dynamic stages of model calibration to ensure accurate replication of the experimental voltage behavior. Instead of treating parameters independently,

key groups of interdependent variables were optimized simultaneously to capture coupled electrochemical effects and avoid artificial parameter compensation.

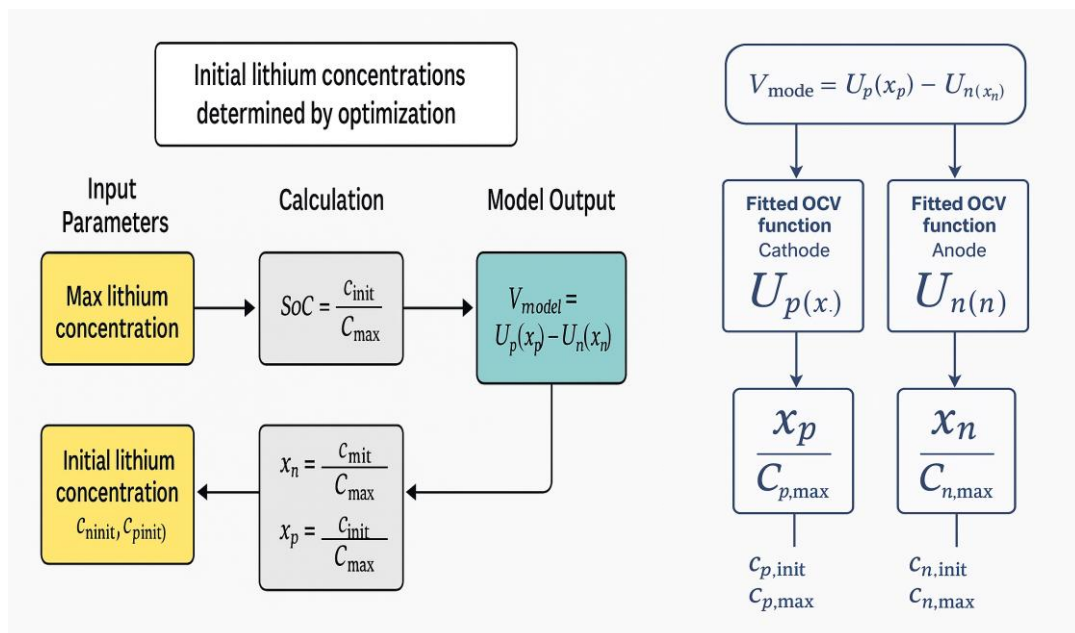


Figure 4-1 OCV (Left) and Dynamic (Right) optimization strategies

The Figure 4-1 corresponds to the OCV-based optimization, where the objective was to fit equilibrium parameters—specifically the maximum and initial lithium concentrations in the electrodes. The total lithium content in the system was either fixed or adjusted iteratively to ensure mass balance. The model computes stoichiometries and uses them in open-circuit voltage functions $U_n(x_n)$ and $U_p(x_p)$ to simulate the terminal voltage. The optimization aimed to minimize the difference between simulated and experimental OCV curves, providing a strong foundation for initializing dynamic simulations.

In the equilibrium fitting stage, the optimization targeted four key parameters: the maximum and initial lithium concentrations in both the negative and positive electrodes ($c_n^{max}, c_p^{max}, c_n^{init}, c_p^{init}$). These parameters are coupled through mass conservation constraints and directly affect the computed stoichiometry and resulting OCV.

Optimization procedure was adapted for fitting dynamic parameters such as exchange current density (i_0) and electronic conductivity (σ) across multiple C-rates (0.3C, 0.5C, 1C) and temperatures (5°C, 25°C, 40°C). Unlike the OCV fitting where equilibrium conditions apply, this dynamic fitting accounts for the effects of kinetics, overpotentials, and ohmic losses during high-current operation. The model outputs voltage–capacity curves which are then compared to experimental data. The optimization algorithm minimizes the

RMSE across all C-rates and thermal conditions, with equilibrium parameters fixed from the previous step. Although the computational graph structure remains similar, the physical interpretation, input-output relationships, and optimization objective differ significantly. The dynamic fitting stage involved optimizing kinetic and transport parameters, specifically the exchange current densities ($i_{o,n}$, $i_{o,p}$) and electronic conductivities (σ_n, σ_p) of the electrodes. These parameters were tuned based on experimental discharge data at different C-rates (0.3C, 0.5C, and 1C) and temperatures (5°C, 25°C, and 40°C).

To ensure scientific validity and reduce overfitting, the parameter fitting process was guided using well-established electrochemical equations from the literature. Rather than relying solely on numerical optimization, functional forms and baseline values were drawn from prior studies such as Chen et al. [4], Mohtat et al. [22], and Verbrugge & Baker [23]. These equations were either directly implemented in PyBaMM and adapted within our custom parameter files. Below is a summary of the key equations used during the fitting process:

$$i_0(T) = i_{0, \text{ref}} \cdot \exp\left(\frac{E_{a,i_0}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right) \cdot c_e^{0.5} c_{s, \text{surf}}^{0.5} (c_{s, \text{max}} - c_{s, \text{surf}})^{0.5}$$

Explanation:

- $i_{0, \text{ref}}$: Reference exchange current density
- E_{a,i_0} : Activation energy for charge-transfer kinetics
- c_e : Electrolyte concentration
- $c_{s, \text{surf}}$: Surface concentration in electrode
- $c_{s, \text{max}}$: Max concentration in electrode

$$k(T) = \kappa_{\text{ref}} \cdot \exp\left(\frac{E_{a,\kappa}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right)$$

Explanation:

- κ_{ref} : Reference electrolyte conductivity
- $E_{a,\kappa}$: Activation energy for ionic conduction
- Conductivity increases with temperature, improving ionic transport.

$$D_s(T) = D_{s, \text{ref}} \cdot \exp\left(\frac{E_{a,D}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right)$$

- $D_{s, \text{ref}}$: Reference diffusivity at T_{ref}

- $E_{a,D}$: Activation energy for diffusion (J/mol.K)

By embedding literature-based equations into the parameter fitting workflow, we ensured that the fitted parameters remain scientifically justified, physically consistent, and reproducible. This approach reduces the risk of overfitting while maintaining fidelity to the underlying electrochemical physics of the system.

4.6 Validation and Analysis

The OCV fitting for Cell 04 at 25°C using NMC622 chemistry was carried out by optimizing key equilibrium parameters in the PyBaMM single particle model. The OCV is calculated using the equilibrium potential of the cathode minus the one of the anode. Both equilibrium potentials are modelled with an empirical polynomial equation [4], and defined with respect to local Li concentration over maximum Li concentration. These include the maximum lithium concentrations and initial lithium concentrations in the negative and positive electrodes. The fitted values were compared against reference values from literature to ensure physical validity and consistency with real-world material properties.

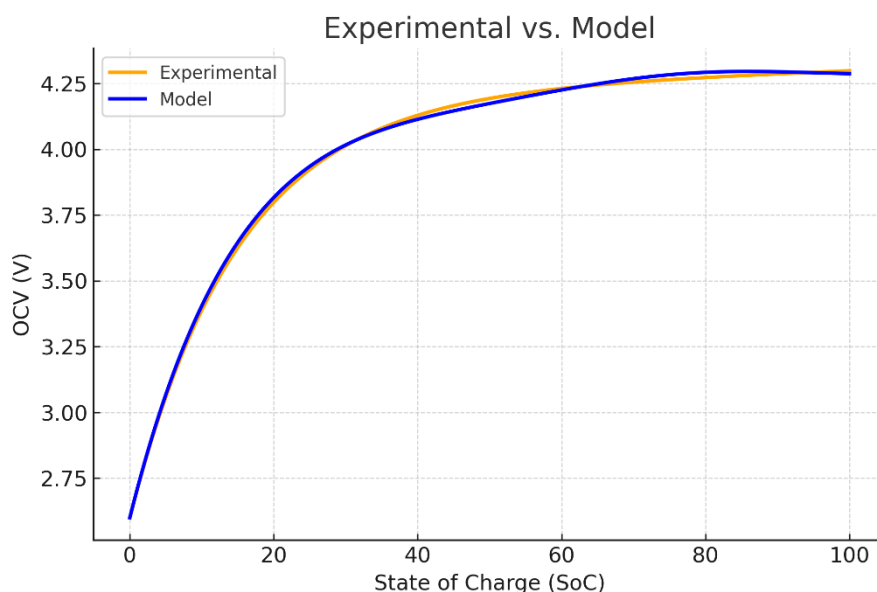


Figure 4-2 Fitted OCV model vs experiment

The Figure 4-2 shows a strong agreement between the simulated OCV curve (orange line) and the experimental data (green dots) across the full SoC range (0%–100%). Key points of validation include: The model captures the steep voltage rise near full charge (SoC $\approx$ 90–100%), associated with the sharp increase in lithium intercalation in the cathode. It also matches the mid-plateau regions (SoC $\approx$ 30–80%) where both electrodes operate within their stable

stoichiometry windows. The low SoC region (0–20%) shows proper curvature, indicating the model has captured the anode's staging behavior, although slight deviation may be due to hysteresis or relaxation effects not captured in the model. Overall, the low RMSE between curves (visually observed) confirms that the chosen values for $C_{\max}$ and C_{init} yield a highly accurate voltage profile, validating the effectiveness of the multi-parameter fitting strategy.

Maximum Concentration in Anode value is lower than the commonly reported range for graphite electrodes, which is typically as reported by Chen et al. [4] and Safari & Delacourt [24]. However, in this case, the lower value may be justified by the specific morphology, porosity, or partial utilization of the active material in the tested recycled cell. Given the high alignment with experimental OCV curves, the effective usable lithium storage may be lower than the theoretical maximum. Maximum Concentration in Cathode value is also below the expected range of typically reported for NMC622 materials (e.g., Mohat et al., 2020; Chen et al., 2020 [4], [22]). This again suggests either underutilization of the active material or reduced volumetric capacity due to degradation, particle cracking, or binder loss in the cathode layer. It is also possible that the calibration matches only the accessible lithium fraction, which is common in practical cells.

Parameter	Description	Fit Value	Ref. Literature
$C_{n_{\max}}$	Max Li conc. in anode [mol/m ³]	14110	30,000 – 35,000
$C_{p_{\max}}$	Max Li conc. in cathode [mol/m ³]	28200	49,000 – 52,000
$c_{n_{\text{init}}}$	Initial conc. in anode [mol/m ³]	9800	6500 – 1300
$c_{p_{\text{init}}}$	Initial conc. in cathode [mol/m ³]	11000	10000 – 20000
n_{Li}	Total Li moles in system	2.3	~2 - 3 mol

Table 4-3 Equilibrium parameter fitted values with referenced literature values

Initial concentration values define the stoichiometric window at full charge and align with realistic assumptions for cells operating near 100% SoC. The values fall within the estimated operating range for these materials and are consistent with prior optimization studies where OCV curves are matched empirically through voltage plateaus. Total Lithium in system value is within the physically

reasonable range of 2 to 3 mol, assuming a nominal capacity of ~60 Ah and 62 electrode layers, each contributing ~1.45 m² of active area. The calculation matches with the theoretical lithium requirement to deliver the measured nominal capacity $Q_{\text{exp}} = 61.59\text{Ah}$ confirming a physically meaningful optimization result.

Following the successful fitting of equilibrium parameters using OCV data, dynamic parameter optimization was performed using voltage–capacity discharge data collected at three different C-rates: 0.3C, 0.5C, and 1C, at a fixed temperature of 25°C. The goal of this optimization was to accurately capture the battery's overpotential behavior by adjusting key parameters governing electrochemical kinetics and transport.

The four fitted key parameters optimized were:

- i_0 : Exchange current density of the negative electrode
- i_0 : Exchange current density of the positive electrode
- σ_n : Electronic conductivity of the negative electrode
- σ_p : Electronic conductivity of the positive electrode

These parameters were jointly fitted using a multi-parameter optimization strategy, minimizing the root mean square error (RMSE) between simulated and experimental voltage curves across all three C-rates

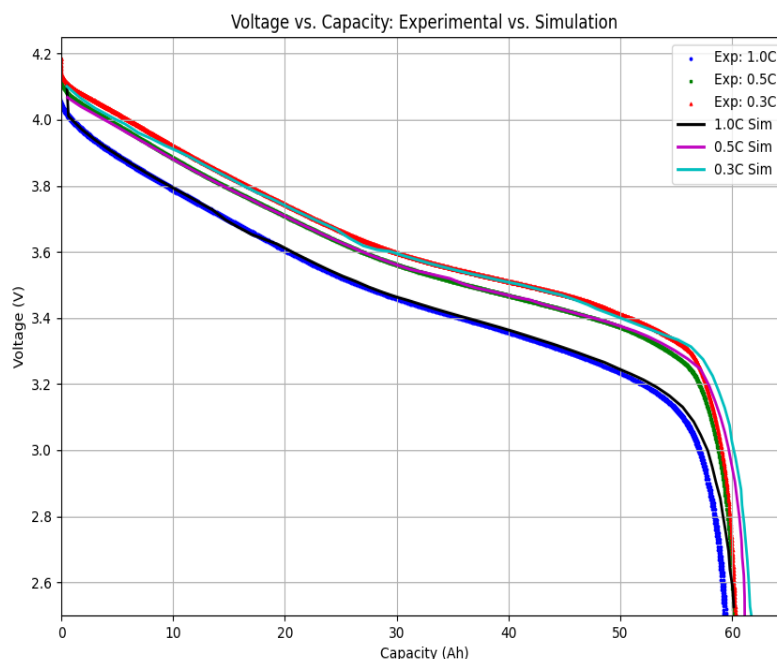


Figure 4-3 voltage vs. capacity plot comparing experimental and simulated data for the 3 C-rates (1.0C, 0.5C and 0.3C)

The Figure 4-3 comparing simulated and experimental voltage vs. capacity shows strong agreement across the three discharge conditions: 0.3C (cyan curve): The model closely tracks the experimental data throughout the entire discharge range, reflecting minimal overpotential and almost ideal behavior. The 0.5C (magenta): The simulation maintains a close match with the experimental profile, especially in the mid-capacity region (20–50 Ah). Slight deviation appears near end-of-discharge, which is common due to increasing concentration gradients and cell resistance. Finally, 1C (black curve): This case introduces higher overpotentials due to faster reaction and transport limitations. The model captures the downward voltage shift with reasonable accuracy, validating the combined role of i_0 and σ in replicating real cell behavior under dynamic loading.

Parameter	Fitted Value	Physical Range Justification
$i_{0,n}$	7.97e-02 A/m ²	Higher value consistent with graphite's fast kinetics
$i_{0,p}$	1.84e-04 A/m ²	Lower kinetics in NMC622 cathodes, as reported in Mohtat et al. [22]
σ_n	390.07 S/m	Matches typical conductivity of graphite in porous form (Safari et al., [24])
σ_p	6.01 S/m	Within reported range for polycrystalline NMC622 electrodes (Chen et al., [4])

Table 4-4 Dynamic parameter fitted values for different C rates at 25deg.C

To characterize the electrochemical behavior of the NMC622-based cell under different thermal conditions, a detailed parameter fitting procedure was carried out using experimental discharge data at 0.5C across three temperatures: 5°C, 25°C, and 40°C. The aim was to identify how core dynamic parameters such as reaction kinetics and transport properties vary with temperature, enabling robust model behavior over a wide range of operational scenarios. Eight key parameters were estimated such as exchange current density at negative and positive electrodes, solid-phase electronic conductivity of the electrodes, electrolyte conductivity, electrolyte diffusivity and solid-phase diffusivity.

A strong temperature dependence was observed for most parameters, in line with theoretical expectations and literature findings: Exchange Current Densities (i_0): Both $i_{0,n}$ and $i_{0,p}$ showed a significant increase with temperature. This follows the Arrhenius relationship $i_0 \propto \exp(-E_a/RT)$, confirming that the

charge transfer kinetics are thermally activated. For instance, i_{op} increased from 0.00018 A/m² at 5°C to 0.00063 A/m² at 40°C. Similar values and trends have been reported by Mohtat et al. [22] for NMC-based cells. Electrode Conductivity (σ_n , σ_p): While the anode (graphite) conductivity σ_n remained nearly constant (~390 S/m), the cathode conductivity σ_p decreased slightly with temperature. This may reflect microstructural changes or contact resistances compensating for the model fit. Chen et al. (2020) noted similar variability in effective conductivity based on particle size and binder effects. Electrolyte Conductivity and Diffusivity (κ , D_e): Both increased steadily with temperature, as expected for liquid-phase ionic transport. At 40°C, κ and D_e were nearly 1.5× higher than at 5°C. These trends are consistent with data from Safari and Delacourt (2011), who modeled electrolyte transport properties across wide thermal windows. Solid Diffusivity in Electrodes (D_s): The diffusivity increased from 2×10^{-14} m²/s to 4.25×10^{-14} m²/s. This supports improved lithium intercalation kinetics at higher temperatures and matches the order of magnitude values reported by Torchio et al. [25] and Prada et al. [26].

Parameter	Unit	5°C	25°C (Ref)	40°C
Graphite Diffusivity (D_{sn})	m ² /s	1.446×10^{-15}	5.00×10^{-15}	1.14×10^{-14}
NMC Diffusivity (D_{sp})	m ² /s	4.670×10^{-15}	8.00×10^{-15}	1.14×10^{-14}
Graphite Exchange Current Density (i_{on})	A/m ²	3.58×10^{-7}	1.06×10^{-6}	2.19×10^{-6}
NMC Exchange Current Density (i_{op})	A/m ²	1.90×10^{-6}	4.82×10^{-6}	9.95×10^{-6}
Electrolyte Conductivity (κ)	S/m	0.475	1.300	2.542
Electrolyte Diffusivity (D_e)	m ² /s	1.83×10^{-10}	5.35×10^{-10}	1.09×10^{-9}
Graphite Conductivity (σ_n)	S/m	227.84	215.00	206.85
NMC Conductivity (σ_p)	S/m	0.170	0.180	0.187

Table 4-5 Dynamic Fitted parameter values for different temperatures

The simulation results were validated using voltage vs. capacity plots at 0.5C across all temperatures. As shown in the figure, the model accurately reproduced the observed behavior:

- At 5°C, both the experimental and simulated curves show pronounced overpotential and voltage drop, reflecting slower kinetics and transport.
- At 25°C, the fitness is excellent, with the model capturing the nominal behavior of the cell.
- At 40°C, the model captures the increased reaction rates and reduced overpotential, closely matching the experimental curve.

This validation confirms that the fitted parameters not only follow expected physical trends but also reliably reproduce full-cell behavior across thermal conditions.

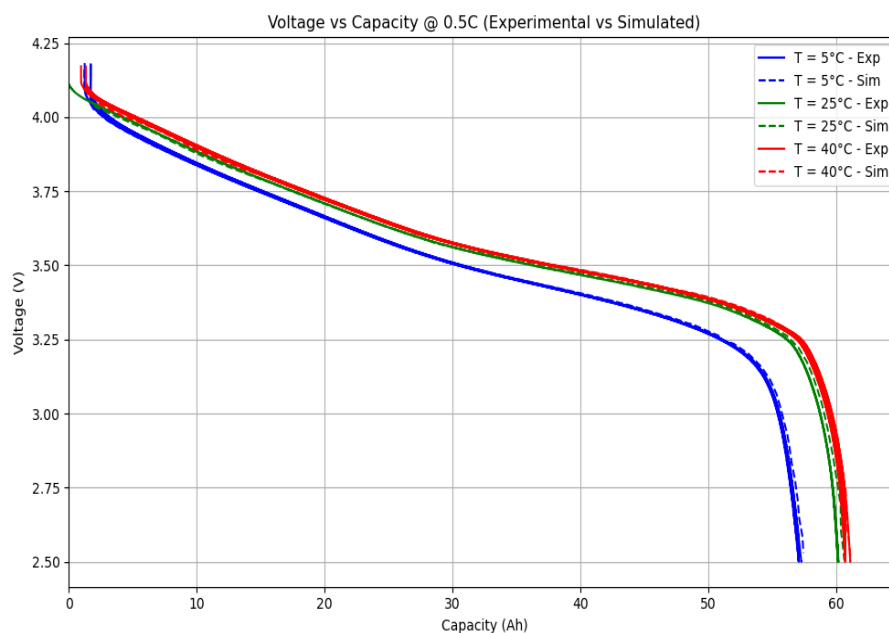


Figure 4-4 voltage vs. capacity plot comparing experimental and simulated data for 3 temperatures at 0.5C

A more generalized and physically meaningful prediction model across different temperatures, the temperature dependence of electrochemical parameters was incorporated using the Arrhenius equation:

$$P(T) = P_{ref} \cdot \exp\left(\frac{E}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right)$$

- $P(T)$ is the temperature-dependent parameter (e.g., diffusivity D , exchange current density i_0 , or electrolyte conductivity κ).
- P_{ref} is the reference parameter value (fitting parameter).
- E is the activation energy (fitting parameter).
- R is the universal gas constant.

In earlier analyses, dynamic parameter values (diffusivity, exchange current density, and conductivity) were independently optimized at each temperature (5°C, 25°C, and 40°C) to match the experimental discharge profiles. This approach helped observe trends but lacked physical generality and was impractical for predictive simulation at unseen temperatures. To overcome this, six dynamic parameters (solid phase diffusivity of graphite & NMC, exchange current density, electrolyte conductivity and diffusivity) were fitted using the Arrhenius formulation.

For both graphite and NMC electrode conductivity, it was observed from prior fitting trials that their values did not change significantly with temperature. Hence, they were assumed constant across all temperatures. This assumption not only reduces fitting complexity but also agrees with literature reports suggesting a weaker temperature dependence for electronic conductivity in electrode materials compared to electrochemical processes like diffusion or charge transfer.

Parameter	Unit	5°C	25°C (Ref)	40°C
Graphite Diffusivity (D_{sn})	m ² /s	1.770×10^{-15}	7.24×10^{-15}	1.839×10^{-14}
NMC Diffusivity (D_{sp})	m ² /s	5.430×10^{-15}	9.50×10^{-15}	1.510×10^{-14}
Graphite Exchange Current Density (i_{on})	A/m ²	3.58×10^{-7}	1.06×10^{-6}	1.143×10^{-6}
NMC Exchange Current Density (i_{op})	A/m ²	1.70×10^{-6}	2.90×10^{-6}	6.912×10^{-5}
Electrolyte Conductivity (κ)	S/m	0.456	1.4	2.974
Electrolyte Diffusivity (D_e)	m ² /s	2.54×10^{-10}	6.78×10^{-10}	8.76×10^{-9}
Graphite Conductivity (σ_n)	S/m	216.56		
NMC Conductivity (σ_p)	S/m	0.179		

Table 4-6 Temperature-dependent dynamic parameter for different temperatures

The experimental and simulated discharge voltage vs. capacity profiles at 0.5 C across 5°C, 25°C, and 40°C show a strong match (Figure 4-5). Incorporating

the Arrhenius term leads to a more physically grounded representation, capturing the non-linear thermal effects on electrochemical kinetics and transport.

- At low temperature (5°C), reduced diffusivity and lower exchange current densities lead to higher overpotentials and earlier voltage drop-off. The model accurately mimics this trend.
- At higher temperature (40°C), faster lithium transport and reaction kinetics reduce losses, resulting in extended flat voltage profiles and higher capacity—well replicated by the model.
- The middle range (25°C) serves as the reference and matches both in magnitude and shape, validating the selected P_{ref} values.

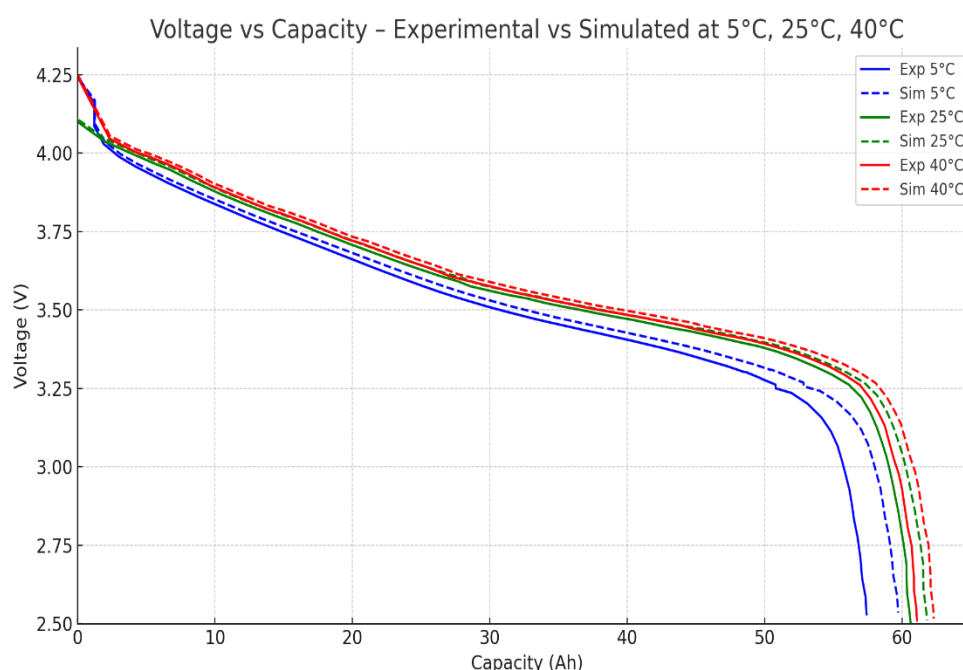


Figure 4-5 Experimental and simulated discharge voltage vs. capacity profiles at 0.5 C across 5°C, 25°C, and 40°C

The fitted activation energies are also in agreement with literature:

- Exchange current density typically exhibits activation energies in the range of 20–40 kJ/mol [4], [22].
- Solid diffusivity values also fall within the accepted 15–30 kJ/mol range for graphite and NMC electrodes.

The electrolyte properties (κ and D_e) show a relatively weaker temperature dependence, as expected due to the ionic nature of liquid electrolytes, which aligns with their smaller activation energies (~4–5 kJ/mol). The comparison of

simulated and experimental voltage–capacity profiles across 5 °C, 25 °C, and 40 °C highlights the effectiveness of incorporating Arrhenius-type temperature dependence into the dynamic parameter fitting. The RMSE and mean percentage error values (5 °C: 1.523 V, 3.94 %; 25 °C: 0.834 V, 2.00 %; 40 °C: 0.836 V, 2.00 %) indicate that the model achieves excellent agreement with experimental data at moderate and elevated temperatures, while deviations are more pronounced at low temperature. This performance trend is consistent with electrochemical theory: at low temperatures, the Arrhenius relation captures the general decrease in reaction kinetics and transport properties, but additional physical phenomena—such as lithium plating, electrolyte viscosity changes, and solid-state diffusion limitations—become significant and are not fully accounted for by a simple activation energy adjustment. The close match at 25 °C and 40 °C suggests that the fitted activation energies (E) and reference values (P_{ref}) for key parameters such as the exchange current density (i_0) and diffusion coefficient (D_s) successfully generalize the model to a wide temperature range without overfitting to a single condition. The decision to fix electrode conductivities while fitting six temperature-sensitive parameters also supports stability and avoids unrealistic conductivity trends. Overall, the results confirm that the Arrhenius-based parameterization within the PyBaMM framework provides a robust, physics-consistent method for temperature generalization of lithium-ion cell models, with primary limitations arising under sub-ambient conditions where non-Arrhenius processes dominate.

5. Conclusion

This deliverable presents a comprehensive validation and analysis of both physics-based and data-driven models applied to lithium-ion battery (LiB) recycling processes and cell-level electrochemical behavior within the framework of the FREE4LiB project. Through a systematic combination of experimental insights, mathematical modeling, and digital tools, we have addressed the core processes of leaching, liquid–liquid extraction (LLE), electrohydraulic fragmentation, and battery cell modeling to enable predictive simulations and optimization capabilities in support of circular battery value chains.

In the recycling domain, the report detailed a physics-based approach to leaching using a modified Shrinking Core Model (SCM), enhanced with particle size distribution via the Extended Quadrature Method of Moments (EQMOM). This adaptation enabled dynamic modeling under real-world conditions, including temperature and stirring effects, validated against experimental datasets for both citric acid and deep eutectic solvents (DES). The model accurately captured the metal extraction kinetics for Li, Mn, Co, and Ni, highlighting the slower, diffusion-limited behavior of citric acid and the rapid

surface-controlled leaching in DES. The incorporation of calculated mass transfer coefficients provided a scientific basis for matching experimental profiles and estimating kinetic parameters, demonstrating the robustness and flexibility of the SCM framework.

The liquid–liquid extraction process, modeled empirically and semi-empirically, aimed to simulate cobalt separation and stripping efficiency. Despite limited data availability, the developed semi-empirical model, incorporating distribution coefficients and phase ratios, showed strong agreement with experimental outcomes, outperforming simpler power-law and exponential models. These results validate the feasibility of simplified predictive models for optimizing solvent extraction conditions under constrained datasets, offering practical tools for process design and upscaling in hydrometallurgical workflows.

In the data-driven modeling of electrohydraulic fragmentation, the implementation of both CatBoost and MLP-based digital twins marked a significant advancement in representing real process behaviors. While model performance was hindered by limited data variance, especially in the input–output range, the modular and highly parametrized code structure ensures future scalability as more diverse datasets become available. These models establish a foundational layer for integration into a broader decision-support platform for end-of-life battery recycling.

In the cell modeling section, PyBaMM was leveraged to construct and validate a detailed electrochemical model of NMC622 lithium-ion cells. A dual-stage parameter optimization strategy was employed: equilibrium parameters were fitted using OCV data to ensure SoC-voltage accuracy, while dynamic parameters—such as exchange current density, conductivity, and diffusivity—were optimized against multi-rate discharge data across different temperatures. Arrhenius-type expressions were used to embed temperature dependencies, enabling robust model extrapolation. The resulting model effectively replicated experimental behavior under various C-rates and thermal environments, affirming its suitability for integration into recycling workflows where cell characterization, SoH estimation, or reuse assessments are required.

Overall, this deliverable demonstrates how physics-based and data-driven models—anchored by experimental validation—can complement one another to simulate and optimize critical recycling and cell processes. The methodologies presented herein contribute directly to the objectives of FREE4LIB WP2 and WP3, supporting the transition toward a closed-loop battery ecosystem. Future work will focus on integrating these models into

digital twins and battery passports, enabling real-time decision-making and adaptive process control in LiB recycling infrastructure across Europe.

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