The Impact of Calendering Process Variables on the Impedance and Capacity Fade of Lithium-Ion Cells: An Explainable Machine Learning Approach

Mona Faraji Niri,* Geanina Apachitei, Michael Lain, Mark Copley, and James Marco

Determining the calendering process variables during electrode manufacturing is critical to guarantee lithium-ion battery cell’s performance; however, it is challenging due to the strong and unknown interdependencies. Herein, explainable machine learning (ML) techniques are used to uncover the impact of calendering process variables on the cells’ performance in terms of impedance and capacity fade. The study is based on experimental data from pilot-scale manufacturing line considering critical factors of calendering gap, calendering temperature, electrodes coating weight, and target porosity. It offers a hierarchical methodology based on the designed experiment, data-oriented modeling via ML techniques, and model explainability technologies. The study reveals the relative importance of calendering control variables for cell impedance and capacity fade and quantifies the contribution of factors and the predictability of the cell’s characteristics. The results show that the calendering factors affect cell’s performance differently and are dominated by electrode features.

1. Introduction

With an increasing demand for lithium-ion (Li-ion) cells to empower electric mobility in transition to a net-zero future, the energy density and power capability of the cells are becoming crucially important. The high-energy-density cells are particularly sought for applications such as portable devices, electric vehicles, and microrobots where packaging space is very limited. The energy density of a cell is its energy content per volume (or mass) which is closely related to the electrode porosity. The electrode porosity is usually defined as a ratio of void space to the whole volume and is determined by the compaction level that is experienced by electrodes during the calendering stage of cell manufacturing.\(^1\) Calendering is the fourth major step, after mixing, coating, and drying in the industry or the pilot-scale manufacturing process of Li-ion cells. It is the last step during electrode manufacturing that modifications and improvements can be done before electrode slitting and cell assembly. The compaction process of electrodes is performed via two calendering rolls at opposite directions, as shown on Figure 1. During the calendering process, the current collectors that are coated with the active material slurry mix during the coating process, are pushed into the calendering gap, and compressed by the two rolls in opposite directions. The amount of compression changes the coating density, plastic deformability, conductivity, as well as the porosity after a short elastic recovery experienced by the electrodes.\(^2\) Further details regarding the manufacturing stages can be found in the study by Li et al.\(^3\) The electrode porosity not only defines the electrode density, but also has a significant impact on cell performance, including lifetime, bearable charge or discharge rates and impedance.\(^4\) Although electrode calendering is usually aimed to increase energy density through reducing porosity, it is already well known that cells with very low porosities may have performance and stability limitations,\(^5\) and they have reduced power capabilities as increase impedance causes a large voltage fluctuation under load.

Therefore, ensuring an optimum or prescribed porosity is necessary to compromise the energy density and power capability of cells. This optimization requires the prediction of compaction load during calendering which is a very challenging task due to the large number of control factors in the calendering process and strong interdependencies.\(^6\)

The calendering roll gap size, the roll speed, and the roll temperatures are all among the control variables that need to be determined a priori to achieve a target porosity and thickness after the calendering process. To achieve this goal, recently, a number of studies have been dedicated to the calendering process and its impact on electrodes and cell characteristics in manufacturing.\(^7\) For example, the effect of calendering pressure on the electrochemical performance of the cathode has been shown for LiCoO\(_2\) (LCO) in the study by Westfahl et al.\(^12\)

---

M. Faraji Niri, G. Apachitei, M. Lain, M. Copley, J. Marco
WMG
University of Warwick
Coventry CV4 7AL, UK
E-mail: mona.faraji-niri@warwick.ac.uk
M. Faraji Niri, G. Apachitei, M. Lain, M. Copley, J. Marco
The Faraday Institution
Quad One
Harwell Science and Innovation Campus
Didcot OX11 0GD, UK

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/ente.202200893.

© 2022 The Authors. Energy Technology published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/ente.202200893
for LiFePO₄ (LFP) in the study by Gnanaraj et al. for LiNi₀.₅₀Co₀.₅₀Mn₀.₅₀O₂ (NCM) in other studies, and for LiNi₀.₅₀Co₀.₅₀Al₀.₅₀O₂ (NCA) in ref. [15] electrodes. The effect of mass loading of electrodes, the compaction ratio, and the temperature of calendering machine on the porosity of cells are investigated. The results confirm a linear relationship between the porosity and compaction ratio with slopes dependent on the temperature in specific regions. The linearity between the compaction ratio and the mass loading of the coating is also confirmed via this investigation. For high-nickel cathodes, the necessity of calendering for extending the cycle life is discussed in the study by Sim et al. The positive impact of compressing the conductive carbon, active material, and binder on the electrochemical conductivity of the electrodes is proven in other studies. It is shown in the study by Acharya that a higher discharge rate and a lower charge transfer resistance is obtained for calcined electrodes of LFP type compared with uncalendered electrodes. The decrease in ionic conductivity with compression during calendering is reported in the study by Lenze et al. The effect of dispersing and calendering on the structure of the carbon black binder matrix and electrode resistance is also discussed in the study by Dreger et al. and the impact of compaction density on the electrochemical performance of LFP cells is studied in ref. [23]. Here it is indicated that there is a reasonable range of compaction density, for an optimal performance. A theoretical study on the electrolyte imbibition through electrodes is conducted in ref. [24] considering the calendering pressure and temperature into account. The study shows that temperature is only significant for electrolytes with high salt concentrations. A calendering study with multiple compression levels is conducted in ref. [25] considering silicon-containing composites in electrodes. It shows that the silicon content directly affects the electrode degradation after calendering.

All the aforementioned studies, although shed light on the impact of the calendering process variables on cell performance during manufacturing, they are largely based on simulation supported methods or classical data analysis techniques and less focused on a systematic analysis approach.

In the recent years, artificial intelligence (AI) and specially machine learning (ML) techniques have progressed as powerful tools to support the state estimation and performance analysis of batteries and control their manufacturing processes. Considering each individual process of Li-ion production chain, ML models are developed to relate the manufacturing variables and the physical characteristics of the cathode in studies. These studies build blackbox style ML models and investigate the predictability of the cell thickness, mass loading, and porosity at various settings of the coating process like coating gap, coating ratio, and line speed. The anode-coating process and the impact of its control variables on the structural features of electrodes as well as the discharge capacity of the cells is studied in ref. via gradient boosted tree models. The heterogeneity of the electrodes obtained at the end of the coating process is predicted via supervised models such as K-means clustering in ref. and unsupervised models such as random forest in ref. Similarly, the impact of mixing process variables such as solid-to-liquid ratio and mixture viscosity on the coating structure, such as thickness and mass loading, are addressed via Gaussian process ML models in ref. The same variables have been investigated in ref. via supervised ML techniques to predict the level of coating mass loading and porosity into one of the categories of low, medium, and high. Random forest and decision trees are developed in ref. to study the feature importance at different steps of cell manufacturing including laser cutting and cell assembly. ML-based models to predict the cell capacity given the electrode specifications are addressed via neural networks (NNs) in ref. and correlated with the electrolyte mass via NNs in ref. [41].

Evidently, most of the abovementioned ML-based and model-oriented studies to explain manufacturing processes of lithium-ion cells are dedicated to the coating process, and a limited number of research utilizing the powerful tools of ML have focused on the data-oriented modeling and investigation of calendering processes. To the best of the authors' knowledge, the reports are limited to. In ref. [42] experimental data are combined with electrode mesostructures generated by ML to correlate the calendering pressure and electrode properties. A similar study uses statistical methods such as principal component analysis to quantify the parameters of the cathode calendering, including pressure, roll temperature, and
line speed, on electrode conductivity. It is also worth highlighting that most of the previous studies have concentrated on the electrode structural features, including porosity and thickness, or electrochemical features such as energy capacity, against calendaring parameters, which has left other performance indicators such as impedance and capacity fade undocumented.

Obviously, impedance of Li-ion cells is an important characteristic of cells that not only contributes to their voltage response model such as equivalent circuit model with various resistances, capacitances, pseudocapacitances, and inductors, but also can serve as a predictor for the lifetime of cells as it has nonlinear dependency to battery age. The overall cell impedance is the sum of multiple components, with complicated interactions. There is the ionic resistance through the pores filled with liquid electrolyte, the electronic resistance through the solid phase, and the charge transfer resistance on the surface of the active particles. Solid-state diffusion in the active material particles can manifest as resistance. There is an interface resistance between the current collector and the coating, which can change with the calendaring conditions. However, it is assumed that the resistances attributed to the lithium metal counter electrode, the separator, the coin cell housing, and the leads are effectively constant in all the cells. The cell impedance generally relates to the reversible discharge current rate as well as the amount of heat generation and temperature change during an operating condition. The importance of this characteristic and the research gaps listed above have motivated the authors to conduct the present study. At an equivalent level of importance of impedance of cells, cells' capacity fade over time is an important factor to be considered and optimized during manufacturing processes. Consequently, studying both characteristics with respect to calendaring process variables is very critical and the main motivation for conducting this study.

There are two main objectives for this research. First, to quantify the impact of calendaring process variables on the cell's impedance and capacity via a systematic approach that is transferable from pilot scale to manufacturing scale. Second, to take the advantage of advanced artificial intelligent techniques, particularly ML, and adapt those to battery manufacturing. Here, the goal is not only to build a predictive model, but also to move toward a transparent representation of that model via explainable ML (XML) techniques.

To achieve the mentioned objectives, this study 1) conducts a systematic design of experiments (DoEs) to collect high-quality data from pilot-scale manufacturing line of electrodes and cells, 2) develops an explainable ML model considering the effect of calendaring parameters of roll gap, roll temperature, and post-calendared electrode characteristics on the performance of manufactured cells described by impedance and capacity, and 3) performs systematic analysis via XML methods. Notably, in here, impedance particularly refers to area-specific impedance (ASI) at various states of charge (SoCs), while capacity refers to cell's energy capacity after multiple cycles at different current rates (crates). For simplicity and to keep the focus on only one electrode, the study is dedicated to cathode half cells where the anode is lithium metal. This is because the characteristics such as impedance have very different ranges for anode and cathode and are affected by factors very differently. Figure 2 summarizes the framework of the XML for the calendaring process study of Li-ion half cells.

The proposed model and methodology are believed to support smart manufacturing of lithium-ion cells, where the conventional approaches of trial and error in determining the optimal calendaring process variables are replaced with data-centric approaches. Through this study, the relationship between calendaring control and response variables can be clarified where more than one factor has been altered in each single experiment. This is critical in customized DoEs or full factorial DoEs aimed to reduce the time and resource required for electrode design compared with the traditional way of investigations where usually only one variable changes at a time.

The structure of this article is as follows. In Experimental Section, the details regarding the calendaring experiments as well as the cell assembly are provided. The DoE settings, variables' range, and breakpoints are given here for clarity as well. In Modelling and Explainability Section, the ML model and the XML methodology is described. The main results and

Figure 2. The Framework of the XML-based study of the lithium-ion calendaring process.
2. Experimental Section

For electrode manufacturing, the mixing process was performed using 1% Eirich mixer, the cathodes were composed of three materials, 96% of active material NMC 622, 2% of C65 carbon black, and 2% of 5130 polyaniline nanofiber (PVDf). The solvent of N-methyl-2-pyrrolidone (NMP) was used to achieve the solid content of 67%. The current collector was aluminum foam for the cathode. The electrode coating was performed via a pilot-line coating machine (MegaJet), having a reverse comma bar coater assembly and three drying zones with the total length of 3.5 m.

In all cases, the coating thickness was controlled by the comma bar gap. The coating speed was fixed to 1 m min⁻¹ and the coating ratio (which is the ratio of the coating bump roll speed to the backing roll speed used to control the mass loading of the coating) was 130%. The drying temperature for cathode was 85°C in the first zone and 110°C in the second and 95°C at third zone. The drying air speed was set to 7.5 m s⁻¹ for all zones. These manufacturing parameters were defined based on the expert's recommendation.

The compaction of electrodes took place in a calendaring machine (Innovative Machine Corporation), with two rolls of 203 mm diameter. Different roll temperatures and roll gaps were set manually for each experiment according to the DoE.

Before the calendaring process, the coating was cut into sheets and then calendared at a speed of 0.8 m min⁻¹. During calendaring, the electrodes were held between two stainless steel shims with a total thickness of 500 μm. The added thickness helped with handling the electrodes and keeping the calendaring conditions the same for the two coating weights (as from observation, thin electrodes were more difficult to calender). The shims were heated on a hot plate to the calendaring temperature and used immediately. The electrodes were passed through the rolls in four different orientations to ensure uniformity. The process was repeated maximum thrice, as needed upon checking the calendared thickness being ±1 μm from the target.

In total, 18 different experiments were conducted to cover the range of different variables which were determined through the DoE plan. The experiments were designed for three main variables of cathode coating weight (2 levels, low and high), calendaring roll temperature (3 levels, low, medium, high), and target porosity (3 levels, porous, medium, dense). Table 1 summarizes the setting for each case. For simplicity, the two levels used for coating weight are noted as low coating weight (LCW) and high coating weight (HCW), which are LCW = 122.48 g m⁻² and high coating weight of HCW = 182.73 g m⁻² respectively. For each experiment, the pressure applied to coatings for target porosity was controlled by machine setting of roll gap. The settings were applied by the operator for the given line speed of 0.8 m min⁻¹ and a hydraulic pressure setpoint of 4000 psi for all cases. Coating weight was set during the coating process while the temperature and porosity were set during calendaring.

After calendering, the electrodes were cut to the discs of 14.8 mm diameter for 2032 half-coin cells. For each half cell, the anode was the lithium metal disc, and the assembly was completed inside the argon-filled glove box using H1609 separator (Celgard) and electrolyte of a composition of 1 mol L⁻¹ LiPF₆ in EC:EMC = 3:7 (by vol.), +1% wt% VC (where EC is ethylene carbonate, EMC-ethyl methyl carbonate, VC-vinylene carbonate). For each calendering experiment, three half-coin cells were made to ensure reproducibility. The cells were allowed to soak at 25°C for 12 h during a rest sequence before starting formation at C/20. The upper and lower cutoff voltage was 4.2 and 2.5 V, respectively. The formation was performed by five conditioning cycles, including charge and discharge at C/2.

The key characteristics of the electrode were quantified after calendaring. These include the thickness of each electrode used for cell assembly which was measured via a micrometer with 1 mm precision and the coating weight (coating mass) of each disc measured by a high-precision scale with an error range up to ±1 mg. The electrode density and porosity were calculated via Equations (1)–(2), where, TDensity (g cm⁻³) is the theoretical density at 0% porosity and CAM (mAh g⁻¹) is the capacity of active material in its powder form. Throughout this study, the TDensity was 4.458 (g cm⁻³).

\[
\text{Density (g cm}^{-3}\text{)} = \frac{\text{Coating Weight (g m}^{-2}\text{)}}{\text{Coating Thickness (μm)}} \tag{1}
\]

\[
\text{Porosity (%) = } \left(1 - \frac{\text{Density (g cm}^{-3}\text{)}}{\text{TDensity (g cm}^{-3}\text{)}}\right) \times 100 \tag{2}
\]

For electrochemical measurements, the cells were tested in a Binder chamber set at 25°C and connected to a Biologic cell cycler. At this step, the impedance of cells was obtained in the form of area ASI (Ω cm²) at various SOC between 90% and 20% with 10% intervals as it changed with SoC according to the previous research. ASI (Ω cm²) was quantified by Equation (3).

\[
\text{ASI (Ω cm}^2\text{)} = \text{Impedance (Ω) } \times \text{Cathode Area (cm}^2\text{)} \tag{3}
\]

The calculation of impedance was performed via the current and voltage values that were measured during the application of current pulses considering a method described in ref. [33]. The associated current (i) and voltage (E_cell) profiles are given in Figure 3 and the impedance follows Equation (4).

<table>
<thead>
<tr>
<th>Table 1. Experimental matrix with the calendaring process control variables.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment number</strong></td>
</tr>
<tr>
<td><strong>Roll temperature [°C]</strong></td>
</tr>
<tr>
<td><strong>Cathode coating weight [g m⁻²]</strong></td>
</tr>
<tr>
<td><strong>Target porosity [%]</strong></td>
</tr>
<tr>
<td><strong>Roll gap [μm]</strong></td>
</tr>
</tbody>
</table>

© 2022 The Authors. Energy Technology published by Wiley-VCH GmbH
$V_1$ and $I_1$ refer to the voltage and current of the half cells at the end of each pulse and $V_2$ and $I_2$ are related to the voltage and current measured immediately after the applied pulse.

\[
\text{Impedance (Ω)} = \left( V_1(V) - V_2(V) \right) / (I_1(A) - I_2(A))
\]  

During the ASI quantification, first, the capacity of the cells was determined using a battery capacity determination program during the final C/5 discharge and the value was used for impedance testing. Identical current pulses with 10 s width were applied for each SoC from 90% to 20%, in 10% steps. Starting with fully charged state, the first target SoC, 90%, was reached by discharging the cell at C/2 rate for the suitable amount of time (12 min for the 10% SoC step). Then, the pulse sequence was applied (negative and positive current pulses, corresponding to discharge at 1.8C and charge at 1.2C rates), and again the cell was discharged to the next target SoC. Following this sequence, the ASI determination was repeated at 50% SoC with shorter pulse (2 s) and at 20% SoC with a longer one (30 s) to ensure stability of the results.

In order to investigate how the physical properties of the electrodes might influence the electrode degradation and impact performance, the cycling life of the cathode half cells was briefly investigated. The cells went through 50 cycles at 25 °C, charging at C/5 and discharging at C/2. The testing protocol included measuring the capacity before and after cycling at a lower C rate: C/10 charge and discharge. Figure 4 shows the flowchart of the manufacturing and experimental processes. The experiments described earlier led to a total of 54 cells with associated data ready for modeling and analysis.

3. Modeling and Explainability

The modeling framework used in this study is described in Figure 5. It relates the calendering settings and calendured electrode characteristics to the cell’s impedance and capacity. In both cases, impedance at each SoC and capacity at each cycle number, the model is a multi-input, single-output structure with the full list of inputs and outputs given in Table 2.

The models are extremely randomized trees or so called extra-trees (ETs). Extra-trees are totally randomized trees whose structures are not dependent to the output values of the learning samples. The reason that the ET is preferred here is that it can be tuned according to the randomization level and is computationally efficient compared with other ensemble methods such as random
Figure 5. Calendering model details.

<table>
<thead>
<tr>
<th>Coating Weight</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>Thickness</td>
</tr>
<tr>
<td>Roll Temperature</td>
<td>Roll Gap</td>
</tr>
<tr>
<td>Calendered Electrode Features</td>
<td>Calender settings</td>
</tr>
<tr>
<td>Model</td>
<td>Area Specific Impedance</td>
</tr>
<tr>
<td>@ 90% to 20% SoC Capacity</td>
<td>50 cycles at C/10 and C/2</td>
</tr>
</tbody>
</table>

Table 2. List of input and output variable names and definitions for the model.

| Inputs                                      | ASI [2 cm²] outputs | Capacity [mAh] outputs
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating weight [g m⁻²]</td>
<td>ASI_5000</td>
<td>10th C/10 Cap: 10th C/10 cycle</td>
</tr>
<tr>
<td>Roll gap [µm]</td>
<td>90% SoC, 10 s pulse</td>
<td>1st C/2 Cap: 1st C/2 cycle</td>
</tr>
<tr>
<td>Roll temperature [°C]</td>
<td>ASI_5000</td>
<td>10th C/2 Cap: 10th C/2 cycle</td>
</tr>
<tr>
<td>Porosity [%]</td>
<td>50% SoC, 10 s pulse</td>
<td>20th C/2 Cap: 20th C/2 cycle</td>
</tr>
<tr>
<td>Thickness [µm]</td>
<td>ASI_5000</td>
<td>30th C/2 Cap: 30th C/2 cycle</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>20% SoC, 10 s pulse</td>
<td>40th C/2 Cap: 40th C/2 cycle</td>
</tr>
<tr>
<td></td>
<td>ASI_2000</td>
<td>50th C/2 Cap: 50th C/2 cycle</td>
</tr>
<tr>
<td></td>
<td>50% SoC, 0.2 s pulse</td>
<td>Last C/2 Cap: Last C/10 cycle</td>
</tr>
<tr>
<td></td>
<td>ASI_2000</td>
<td>20% SoC, 0.2 s pulse</td>
</tr>
</tbody>
</table>

forest. It is a type of ensemble model, which means that it is built via an ensemble of unpruned regression trees following the classical top-down procedure. Compared with other tree-based ensemble models, ET splits nodes by choosing the cut-points randomly and utilizes all sample points during growing each tree. The randomization of cutpoints and features as well as the ensemble averaging help to limit the variability of prediction. Furthermore, the use of all samples at each grow rather than bootstrap replicas contributing to minimum bias.

The pseudocode for randomized node splitting for nonconstant features (a) (which are input variables listed in Table 2) is given in Table 3. Here S is the local sample subset, K is the number of features, a, is the cut point, and r_mins refers to the minimum number of samples for splitting a node. A complete pseudocode and algorithm can be traced in ref. [34]. The splitting procedure is repeated multiple times for all samples to create an ensemble model with M trees. The final prediction is an arithmetic average of each individual prediction.

When an ET model is created following the steps given in Table 3, it is necessary to validate its performance against new data to ensure its generalizability. As Figure 6 shows, the data is first divided into K equal portions, K–1 portions are used for training and the last remaining one is utilized for validation. The model's performance is then evaluated by prediction accuracy metrics. The model performance and generalizability metrics are only calculated for the validation portion of the data at each iteration. The whole process is then repeated for K times with different portions of training and test data.

This is to ensure that each data point is used at least once for validation. The accuracy metrics of all iterations are then averaged arithmetically for the final prediction performance indication. Remarkably, cross validation is very suitable to deal with small-to-medium-size datasets, when the traditional train test split faces challenges due to a small number of samples.

In order to quantify the ability of model in capturing the relationship between inputs and outputs of the calendering process in the validation step, three metrics are considered here. The metrics are given in Equation (S)-(7).

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (Y_{\text{exp}} - Y_{\text{p}})^2}$$

$$\text{MAE} = \frac{1}{N} \sum_{i=1}^{N} |Y_{\text{exp}} - Y_{\text{p}}|$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (Y_{\text{exp}} - Y_{\text{p}})^2}{\sum_{i=1}^{N} (Y_{\text{exp}} - \text{Mean} Y_{\text{exp}})^2}$$

Y_{exp} and Y_{p} refer to the measured values of output during experiments and after prediction, respectively. Mean Y_{exp} is the mean value of all the measured targets. Here, RMSE refers to root mean squared error, which is an average of squared errors between all predicted and actual values. MAE is the mean value of the absolute errors in the whole range. R^2 is the coefficient of
determination which shows the proportionate amount of variation in the response that is explained by the control factors through models. While a good model is expected to have lower values of the RMSE and MAE, there should be a balance between those two with $R^2$. Closer values of $R^2$ to 1 shows that the more variability of data is captured by the model.

Although the ET model and in the broader sense the ML models can strongly support the analysis of complex manufacturing processes of lithium-ion batteries, they are regarded as "blackbox" structures difficult to be explained. The XML techniques help to clarify why a model makes a decision and this explainability is as important as the accuracy of that decision. In fact, XML provides a greater level of insight into the possible causality between the input and output variables. The explanations increase the trust of the manufacturer on the models and offer transparency during the decision-making process. In this study two explanation methods are utilized, Shapley values and accumulated local effects (ALEs). Both methods are essential in revealing the impact of the input (control) variables on the impedance and energy capacity of the cells due to the size of the data set and as the spread of data points in the space of the calendering process variables. Considering the fact that during each experiment more than one factor is changing, showing the impact of each individual control factor on the outputs is not achievable via traditional analysis as they can only handle the variation of only one factor at a time. On the contrary, Shapley values and ALEs help performing analysis efficiently via the models including multiple factors changing simultaneously.

Specifically, the Shapley values help to quantify the impact and contribution of each input variable in the prediction of the response. They also provide a feature importance analysis based on the magnitude of the contribution. Here the particular version of Shapley values, the Shapley additive explanations (SHAP), is utilized. SHAP is equal to the classical Shapley values of a conditional expectation function of the model but easier and more efficient in terms of calculation. The full formulation of SHAP is spared here to save the space and suggested to be traced in ref. [61]. It is worth noting that while Shapley analysis seems similar to a conventional correlation analysis, the main difference is that the correlation analysis, such as Pearson product-moment correlation analysis, is only able to reveal linear correlations, while SHAP is able to uncover nonlinear correlations as well.

Similar to SHAP, ALEs help to quantify how each control variable is related to the response variable independent of other control variables. Such analysis is very insightful specially where the control factors are coupled or dependent to each other, which is exactly the case for the calendering processes where factors such as thickness is highly correlated mass loading and porosity. It is also much more suitable when the impact of the inputs on the responses does not have a uniform trend across the range. To save space, the details of this method are spared and they can be traced in ref. [50].

4. Main Results and Discussions

In what follows, the main results of this calendering study are reported and discussed. The results are in three main categories, i) the predictability of the responses given the calendering process settings and electrode characteristics, 2) the importance of each factor in the predictability of cells' performance, and 3) the direction of the impact of each input feature on the cells' performance as a response and the essence of the factor response dependency.

4.1. Predictability

The model's estimation of the cell's ASI compared with actual values is given in Figure 7 for various SoC and pulse durations (the labels are defined in Table 2). This figure is a representation of the real versus predicted outputs in comparison with a perfect prediction which is the solid black line. The perfect prediction line is related to $R^2$ of 1. The performance of the model for predicting the responses is summarized in Table 4 in the form of numerical accuracy indices. The metrics have been presented in their mean and standard deviation (STD) of multiple runs. In fact, the results are related to 50 runs of the models by shuffling the data after each attempt to achieve more trustable results. Notably, the number of runs is a compromise between the total run time and the stability of values.

According to the table, the prediction of ASI values at 90% SoC has RMSE of 11.098 ($\Omega$ cm$^2$) and 82.5% of the variability in the data has been captured successfully. For ASI at 50% SoC and a 10 s pulse, this error is 15.814 ($\Omega$ cm$^2$) and 74.8% of the data has been represented by the model. For ASI at lower SoC values, this representation is at the same range between 78.1% and 86.1% which is acceptable. Based on the results of Table 4, it can be concluded that an ML model of the ET type can help estimating the cell impedance given the calendering setting and electrode charaterizations with an accuracy of average of 80.38% for all cases. It is believed that the uncertainties imposed during the intermediate processes of electrode and cell manufacturing, such as cell assembly, have a considerable impact on the achieved
accuracy, but they have not been quantified in here due to resource limitations.

Similar to impedance prediction case, the results for predicting the cell’s capacity at various cycles are given in Figure 8. The data at almost all cases are clustered in two as they depend on the electrodes’ coating weight. Quantified predictability metrics are summarized in Table 5 for 50 consecutive runs. According to this table, the predictability is highest at cases with fewer cycles. For example, the first C/2 capacity is predicted with an $R^2$ accuracy level of 99.6%, given the calendering settings and electrode features. This accuracy is about 99.4%, 97.8%, and 95.2% for the 10th, 20th, and 30th cycles. The model performance slightly diminishes for higher cycles of 40 and 50 but is still very acceptable. This performance loss compared with initial cycles is believed to be due to larger impact of unquantified factors that affect the cell’s performance at the higher number of cycles.

This confirms that the cell’s energy capacity and its fade are highly predictable given the calendering process variables and control settings. The same analysis applies to the C/10 case. The predictability at the first and last C/10 cycling is higher than 98.9% and it is believed to be due to the slow rate of cycling and the ability of a model relating the input and output variables successfully.

5. Explanation by XML

The level of accuracy achieved by the ML models shows that the input–output relationships in between the data points have been identified well and therefore, the model can be used for XML-based explanations. In the next step, the importance of input (control) factors on the predicted responses is obtained.
via SHAP and visualized in Figure 8 for ASI. This figure is the ranking of the contribution of features in the prediction of ASI values by models, and the x-axis is the SHAP value (Ω cm²), which is an output of the XML model in the framework of Figure 2. Each bar belongs to one feature and the length of it shows the average impact it has on the ASI magnitude at a particular SoC. As the graphs show, for all ASI values at all considered SoCs, the density and porosity of calendared electrodes are the most important and contributing features. It is worth mentioning that the top contributing factors, density, porosity, roll gap, and thickness, are related to each other and to the thickness reduction occurring during calendering. While the rank of each feature is slightly different from one to another ASI at a specific SoC, calendering settings have less importance compared with electrode features at all cases. Roll gap is the feature with medium-level importance and the results show that the roll temperature contributes minorly to the response values compared with the other features. The results show the relative importance of the features individually, and one of the opportunities they create is to decide whether a feature is worth to be measured during the manufacturing process and to what precision. Considering the calendering setting, it is fair to further focus on roll gap than temperature by increasing the measurement precision or the number of break points for further studies. It is also worth mentioning that the importance of the electrode characteristics on the cell impedance is matched with the empirical expectations reported in other studies. However, the quantifications are only achievable via the proposed methodology of this study.

The ranking and importance of each feature on the cells' capacity at various cycles of C/2 and C/10 are shown in Figure 10. For capacity at C/2, during the first cycle, the
contribution of coating mass and thickness is very considerable compared with the other electrode characteristics and the calendering settings. For C/2 capacity at cycles 10, 20, and 30, the contribution of other features (porosity, density, calendering roll gap, and temperature) slightly increases compared with the very first C/2 cycle. At C/2 cycles of 40 and 50, the effect of all electrode features becomes much more noticeable, but still the calendering features are dominated by electrode features. A similar thing is witnessed for C/10 cycling according to Figure 10.h. When the cell is fresh, the electrode characteristics are very important in determining its capacity and after its aged due to 50 cycles of C/2, the contribution of other factors becomes more significant. It is also worth noting the contribution of porosity to the responses, which is minor at up to 20 cycles and gradually increases after that.

While Figure 9 and 10 shows the bar charts of the average SHAP values for ASI and capacity at a particular condition, Figure 11 and 12 show a set of bee swarm plots. These graphs not only rank the importance of the features on the model prediction, but also show the direction of the relationship. They show whether an increase in a feature would have a positive or a negative impact on the response variable. In these figures, each dot corresponds to an individual data of the study. The color bars represent the range of each feature. Yellow means larger values of the feature and red means lower values of it.

In each graph, the x-axis is the centered SHAP value and shows the direction of the impact, positive values mean positive impact and negative values mean inverse impact on the model’s prediction. In all cases, the larger the gap between the positive and negative values, the clearer the impact of the feature on the response. Such a case means that the larger and smaller values of each feature have quite different effects on the responses. As the graphs show, for all ASI values, (Figure 11a–e), the first three influential factors show a similar impact on all SoC cases. In fact, larger porosity and thickness values have a positive impact on the ASI. For density, it is the opposite, meaning that an increase in density reduces the ASI values. The roll gap has also a positive impact on the ASI at all SoC conditions. According to figures, an increase in the calendering roll gap increases the ASI and this is consistent for all SoC breakpoints. The same applies to the coating weight as a feature for the model.

An important consideration regarding Figure 11 is that the six factors are not independent of each other. For a fixed coating weight, a larger roll gap during calendering will give an increased coating thickness and hence a higher porosity and a lower density. It also leads to an increased ASI for all the five of the measurements shown at SoC breakpoints. Typically, the increased calendering force would be expected to reduce the electronic resistance of the electrode, through improved particle to particle contact, but increase the ionic resistance, due to lower porosity. Therefore, the implication is that the electronic resistance is more important in these measurements, which use relatively short current pulses.

As mentioned earlier, according to Figure 11, coating weight is a less influential factor, but there is a consistent trend of higher ASI with higher coating weight. The greatest effect is probably for the 30 s pulses at 20% state of charge. According to the standard ASI theory, the electrode resistance is inversely proportional to the coating thickness, but the difference is greatest when comparing thin and very thin coatings. As the coating weight increases, it becomes increasingly difficult to achieve uniform utilization of the active material throughout the electrode, which
Figure 10. The importance of control factors of calendering process on capacity: a–f) C/2 cycling and g–h) C/10 cycling.

Figure 11. The contribution of each control factor on the predicted ASI by ET model; a) ASI_9010, b) ASI_5010, c) ASI_2010, d) ASI_5002, and e) ASI_2010.
This leads to variations in the local current density and an increased resistance.

The temperature of the calendering rolls was the least significant factor for the ASI, indicating that all three temperatures were within the acceptable operating range. Furthermore, for roll temperature, the impact is mixed, and the direction is not clear by the swarm plots and the red and yellow dots are not distinguishably distributed. In order to show the effect of the roll temperature on the predicted ASI, another analysis is conducted by the ALEs in Figure 13 and 14.

The swarm bee plots of Figure 12 are given to show the impact direction of calendering process inputs as well as calendared electrodes on the capacity at various cycles. The impact of electrode coating weight, thickness, and the calendering roll gap is quite similar at all cycles and Crates. While an increase in the first two inputs leads to an increase in the capacity value, an increase in roll gap is associated with smaller capacities. Roll temperature has a negative impact on the cell's capacity at the first cycle of C/2 and C/10 (Figure 9a,g). It has the same trend for up to 40 cycles at C/2, but the direction changes to the opposite at cycles 40 and 50, which means that an increase in the roll temperature reduces the cell capacity at higher cycles, as shown in Figure 9e,f.

In general, based on what is given in Figure 12, the most important factor for determining the cell capacity is coating weight, which is entirely expected; more active material means a higher capacity. Heavier coatings are also by and large thicker, so coating thickness is the second ranking factor. Again, the temperature of the calendering rolls has minimal impact. For the other three factors, the greatest influence was seen in the capacities for the 50th cycle at C/2. The cell capacities were lower with a higher roll gap and hence a higher porosity and lower density. There are numerous possible degradation mechanisms that can cause capacity fade during cycling, either by loss of active lithium, or due to an increase in the cell resistance, or both.\[5\] 50 cycle degradation is a relatively short test duration, but the cycle life of half cells is often limited by the lithium metal counter electrode. Surface layers with a higher resistance can form on cathode particles, but this would not be expected for the studied NMC-622 charged up to 4.2 V and discharged down to 2.5 V. The counter electrode provides an excess of lithium, but the isolation
of active material particles can reduce the number of lithium intercalation sites. Since heavier calendering reduces the capacity fade rate, the implication is that particle isolation is caused by electronic isolation, rather than ion or mechanical.

Figure 13 and 14 show ALE plots to clarify the exact impact of each input on the response. At each ALE plot, the x-axis refers to the feature under study, and the y-axis is the response variable. The faded bars at the ALE plots show the distribution of the feature values. The roll temperature graph is discrete as it only includes three temperatures, and the roll gap and porosity are continuous variables as they have multiple values within a range. For better understanding of a positive and negative impact, the x-axis variables have been centered to their mean value.

According to Figure 13a–e, an increase in the temperature from 85 to 120 reduces the ASI values at all conditions; on the contrary, an increase from 120 to 145 increases the ASI. Therefore, the impact of temperature is not uniform nor monotone and there is an optimum temperature of 120 detected within the range. It is also worth noting that the smaller scale of Y axis for roll temperature plots compared with porosity and roll gap plots confirms the finding by SHAP graphs of Figure 11, which has roll temperature as a less significant factor.
For roll gap in Figure 13f–j, and porosity (Figure 13k–o), the impact is monotonic; while the roll gap effect is shown in Figure 11, the impact of porosity is only detectable via ALE plots in here. Generally, an increase in roll gap has a minor impact on ASI until the gap of about 440 μm, and after that an increase in the gap size increases the ASI considerably and linearly. For porosity, the trend is also similar for all ASI at all SoCs, and the existence of a threshold is evident. In fact, while an increase in the porosity till about 32% has a minor effect on ASI, an increase beyond that till the end of the range increases the ASI linearly and considerably.

Figure 14, shows the local effects of roll temperature, roll gap, and porosity on the cell’s capacity at selected cycles. According to these graphs, the C/2 capacity up to 30th cycle shows an increase with the temperature rising from 85 to 120 °C and then a slight decrease after 120 till 145 °C. The impacts of roll temperature on cells’ capacity after 40th and 50th cycles are different from what is witnessed for up 30th cycle. The capacity drop with temperature is much harsher after 120–145 °C, Figure 14d, and for 50th cycle it has a completely different trend. In this case, a temperature rise decreases the cell capacity monotonically, as shown in Figure 14e.

According to Figure 14f–j, an increase in roll gap has a minor impact on the capacity up to about 460 μm and then leads to a decrease in its value till the end of the range which is about 500 μm. Considering both Figure 13 and 14, a threshold of roll gap of about 460 is necessary for low resistance and minimized capacity fade. The impact of porosity on capacity fade is more complicated, as shown in Figure 14k–o. Porosity increase from 30% to about 37% leads to a slight increase in capacity at all cycles, while after that it causes a drop in capacity value.

The analysis based on SHAP and ALEs given in the abovementioned figures all confirms that the impact of calendering variables and electrode features on cell performance is very different and, in some cases, conflicting between ASI and cell capacity fade at various conditions. It is clear that the minimum ASI is related to middle-range calendering roll temperature of 120 °C at all SoCs, and while the most favorable capacity behavior at lower cycles is witnessed at the same temperate, the capacity loss is considerable at this temperature in long-term cycling (50th cycle). While it seems that the roll gap is not a conflicting factor for ASI and capacity, there are definitely different thresholds for desired values of each response. In fact, whereas less than 32% was required for low resistance, the optimum porosity to minimize capacity fade was around 34%.

Although Figure 9–12 help to rank the features for the predictability of the ASI and capacity responses, it is worth investigating the model sensitivity to less important features. For both ASI and capacity, the electrode features are retained, and the rest of the features are left aside. This means that the calendering settings of temperature and gap have been eliminated from the feature pool and then the model has been retrained and validated. The R² accuracy metric of a model with full features is compared with the reduced-feature one in Table 6 and 7.

According to the results in Table 6, although calendering features are at the lower ranks for model’s predictability, removing them completely from the pool of features reduces the prediction accuracy. This performance loss for ASI prediction is by average 0.0308 (equal to 3.08%).

According to Table 7 for capacity, eliminating the calendering features from the pool leads to slight performance loss, up to the 50th cycle, which was expected due to the very minor contribution of those features, as shown in Figure 10. However, the performance loss up at the 50th cycle is more than the previous cases and is about 4.3%. This analysis helps with decision-making regarding the calendering features. In fact, the feature reduction should only be performed if the model’s performance is still acceptable.

<table>
<thead>
<tr>
<th>Table 6. R² for full versus reduced features for ASI prediction.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Response</strong></td>
</tr>
<tr>
<td>SoC [%]</td>
</tr>
<tr>
<td>Pulse length [s]</td>
</tr>
<tr>
<td>Full feature mean (std)</td>
</tr>
<tr>
<td>Reduced feature mean (std)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 7. R² for full versus reduced features for capacity prediction.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Response [mAh]</strong></td>
</tr>
<tr>
<td><strong>Cycle number</strong></td>
</tr>
<tr>
<td>Full feature mean (std)</td>
</tr>
<tr>
<td>Reduced feature mean (std)</td>
</tr>
<tr>
<td><strong>Condition</strong></td>
</tr>
<tr>
<td><strong>Full feature mean (std)</strong></td>
</tr>
<tr>
<td>Reduced feature mean (std)</td>
</tr>
</tbody>
</table>
6. Summary and Conclusions

ML techniques have been developed as powerful tools for decision-making for the energy storage systems and particularly lithium-ion batteries. While they offer an opportunity to model lithium-ion battery manufacturing processes, there is still a necessity to extend them via XML methods to better explain those processes. This study proposes a methodology based on XML to study the calendaring step of cell manufacturing and how it affects the characteristics of cells in terms of impedance and energy capacity across various conditions. In fact, the XML methods utilized in this study help to uncover quantitative, rather than qualitative, dependencies between the calendering control variables and the cell performance. It is worth noting that while in general the term impedance can refer to ohmic and ionic resistance, this study only considers the impedance based on voltage drops and therefore is focused on ohmic resistance in particular.

The analysis shows that the calendering control variables are strongly dominated by the electrode’s physical characteristics. In fact, while the roll gap and roll temperature both contribute to the ASI and capacity prediction through the model, they are less important than the electrode physical characteristics such as porosity, density, and thickness. This highlights that for a deeper understanding of the impact of calendering control variables on the cell’s performance, the electrode features should be effectively managed through a suitable DoE plan.

Considering the ASI as a performance index, the SHAP and ALE analysis revealed that an increase in porosity, thickness, and calendering roll gap contributes to the cells with larger ASI values but a local optimum and a threshold for each variable is necessary. This threshold can be identified via the proposed methodology. Unlike the mentioned features that have almost a piecewise linear impact on ASI, the roll temperature does not show uniform contribution and a medium value of temperature during calendering is observed to result in the lowest ASI in the manufactured cells. For capacity at various cycles, the results are slightly different and conflicting in some cases and cycles. While an increase in cathode’s coating weight and thickness leads to cells with higher capacity and smaller fade at higher cycles, the impact of roll gap is the opposite and has a local optimum. Furthermore, the impact of the roll temperature on the cell’s capacity is quite different between early and late cycles, with midrange temperature being more favorable for up to 40 cycles and lower temperatures are more desirable for capacity fade minimization at 50 cycles. These findings all confirm why an optimization of the calendering process variables for a desirable range of ASI at various SoCs and capacities at early and late cycles are necessary and what the role of XML is in this regard.

The XML-based methodology developed in here is believed to not only shed light on the effect of the control variables on the ASI and cell capacity fade, but also helps to gain the trust of the manufacturer when using a model-based representation of manufacturing processes. It is showing how the ML-based findings can be compatible with the expectations or empirical observations and how it can help quantifying some of those understandings. The application of XML for battery manufacturing is still at its beginning stage, and creating a comprehensive model which is able to capture the cross-process interactions still needs to be addressed. The authors aim to address a number of items in future works, including the impact of anode calendering control variables on the cell’s performance especially its ASI and cycle life, investigation of the impact of other material such as LFP on cell performance during the calendering processes, and the extension of models to other performance characteristics such as charge ASI, charge capacity, and energy density.

Acknowledgements

This research was undertaken as part of the NEXTRODE project, funded by the Faraday Institution, UK. [Grant Number: F1RG015]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

calendering, electrode manufacturing, explainable machine learning, impedance, lithium-ion batteries

Received: August 5, 2022
Revised: September 28, 2022
Published online:
