Machine Learning Approach for Predicting the Discharging Capacities of Doped lithium Nickel-Cobalt-Manganese Cathode Materials in Li-ion Batteries

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1. Abstract

Understanding the governing dopant feature for cyclic discharge capacity is vital for the design and discovery of new doped lithium Nickel-Cobalt-Manganese (NCM) oxide cathodes for lithium-ion battery applications. We herein apply six machine learning regression algorithms to study the correlations of the structural, elemental features of 168 distinct doped NCM systems with their respective initial discharge capacity (IC) and 50^{th} cycle discharge capacity (EC). First, Pearson's correlation coefficient study suggests that the lithium content ratio is highly correlated to both discharge capacity variables. Among all six regression algorithms, gradient boosting models have demonstrated the best prediction power for both IC and EC, with the root-mean-square error calculated to be 16.66 $mAhg^{-1}$ and 18.59 $mAhg^{-1}$ respectively against a hold-out test set. Furthermore, a game-theory based variable importance analysis reveals that the doped NCM materials with higher lithium content, smaller dopant content and doped with lower electronegativity atoms, are more likely to possess higher IC and EC. This study has demonstrated the exciting potentials of applying cutting-edge machine learning techniques to accurately capture the complex structure-property relationship of doped NCM systems and the models can be used as fast screening tools for new doping NCM structures with more superior electrochemical discharging properties.

2. Introduction

The unprecedented increase in the demand for clean energy has accelerated the research for discovering new lithium-ion batteries with higher energy density, higher power density and more steady cyclic performance. Cathodes, in particular, have received a considerable amount of attention due to their current high cost, arising from the use of expensive cobalt metals, and the limited capacity that cannot fulfil the current demand.[1]

Among the various cathode candidates, layered cathodes have received tremendous market success owing to their high practical capacity and the wide operating voltage window. Quinary oxides (e.g. $LiNi_xCo_yMn_zO_2$) is currently the state-of-art layered cathode material as it integrates the superior properties of all three fundamental layered materials: $LiCoO_2$ (high kinetics), $LiNiO_2$ (high capacity), $LiMnO_2$ (high safety). The nature of its broad compositional space has enabled scientists to discover new and robust electrochemical compounds such as $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM333), $LiNi_{0.50}Co_{0.20}Mn_{0.30}O_2$ (NCM523), $LiNi_{0.60}Co_{0.20}Mn_{0.20}O_2$ (NCM622) and $LiNi_{0.80}Co_{0.10}Mn_{0.10}O_2$ (NCM811).[2–4] It is important to note that the different transition metals in these compounds play different roles during electrochemical reactions: nickel ion acts as the main active component during redox reactions, as it has the most diverse range of oxidation states among all. Manganese helps to stabilize the overall structure while cobalt can effectively prohibit the cation mixing effect between Li-ion and Ni-ion. Furthermore, the mixing ratio of each transition metal (TM) in the material can bring different benefits to the cathode's properties. A higher concentration of nickel can greatly improve the overall capacity as opposed to the benefits of higher kinetics and better safety from increasing the respective concentration of cobalt and manganese.[4]

A common bottleneck issue is encountered during the selection of the optimal mixing ratio of these TMs to reach all desirable cathode properties (i.e. high kinetics, high stability, high capacity). The underlying reasons are the compositional space being too broad to be explored experimentally and the unavoidable benefits trade-offs from TM substitution. A wide range of studies has been conducted in doping the quinary oxide system with a trace amount of cation atoms to enhance the cathode's electrochemical capability with minimal disturbance to the properties of the original crystal structure. Several successful cases have been made using various doping elements such as Al[5], Fe[5], Cu[6], Cr[78], Mg[9], Mo[10], K[11], Pb[12], Ti[13], Si[14], Sn[15]. In general, two major benefits can be attained through the doping method. The first benefit can be seen from the hindering of the migration of Ni^{2+} into the Li^+ layer to reduce the anionic

mixing during the intercalation reactions. The second benefit is to increase the strength of TM-O bond to improve the overall structural stability and reduce the oxygen release during charge-discharge cycling. Nevertheless, the diverse available doping sites (Li, Ni, Co, Mn) along with the large compositional space have inevitably increased the difficulty of identifying the most suitable dopant for each NCM -derived cathode material. The conventional approach to characterize the electrochemical properties of a new doped system is through conducting repetitive experiments which is costly and time-consuming. Another approach based on the first-principle computational modelling is also hindered by the expensive computing cost for studying very large supercell systems. To conquer these shortcomings, this paper reports the use of the robust data learning and analyzing features of machine learning to investigate the linkages among various doping factors and the experimental cyclic performance of doped NCM cathodes.

Machine learning (ML) methods have become increasingly popular across different fields of research nowadays. *Min et al* [16] implemented seven different algorithms to predict the cycling properties of Ni-rich NCM cathode from the corresponding synthesis parameters and reached an average prediction score of $R^2 = 0.833$. *Houchins et al* [17] implemented DFT-based neural network models to predict the structure energy and forces of various forms of NCM materials (e.g. 111,532,811,622) and achieved a promising prediction accuracy of 3.7meV/atom and 0.13 eV/ Å, respectively. *Allam et al* [18] constructed a deep learning model and attained a prediction error of 3.54% for predicting the redox potential of organic materials. From these works, data quality is frequently reported as an influential factor for model performance. Although databases like Inorganic Crystal Structure Database (ICSD)[19] and Material project[20] are widely accessible for ML training, there is still a lack of established large database in experimentally measured material properties, in particular, the measured discharging properties of various cathode materials in Li-ion batteries. From our previous work [21], we had successfully curated a dataset of 102 doped spinel cathodes containing the elemental, structural information and discharge

performance. In addition, small prediction errors of 11.90mAhg^{-1} and 11.77mAhg^{-1} were achieved by the gradient boosting machine models for the prediction of the initial and 20th cycle discharge capacity. These promising results had further encouraged us to curate a more high-quality discharge performance dataset for the layered NCM cathode and implement ML to reveal their complex structure-property relationship.

In this work, 168 distinctive NCM doped systems are collected carefully with strict selection rules as described in **Figure 1.** The dataset contains 3696 data entries which cover 20 variations of dopants for all doped NCM -derivate material classes (NCM -333, NCM -523, NCM -622, NCM -811). Firstly, Pearson's correlation coefficient study was performed to investigate the co-linearity of every variable pair. Furthermore, six non-linear algorithms, including gradient boosting machine, random forest, kernel ridge regression, feedforward deep learning, k-nearest neighbors and support vector machine was implemented with the design given in **Table 1** to predict the initial discharge capacities and 50th cycle discharge capacities of the doped NCMs based on twenty covariates (e.g. material characterization results, experimental parameters, elemental properties). By comparing their electrochemical performance against a held-out test set, the best models can be identified for each discharge capacity prediction task. Furthermore, a variable importance study was performed with the best performing model to reveal the key doping features that governed the accurate predictions of discharging performance of the doped NCM systems. These insights would greatly enhance the current understanding of the doping effects and facilitating the design of future experimental work (e.g. independent variable selection, the doping concentrations).

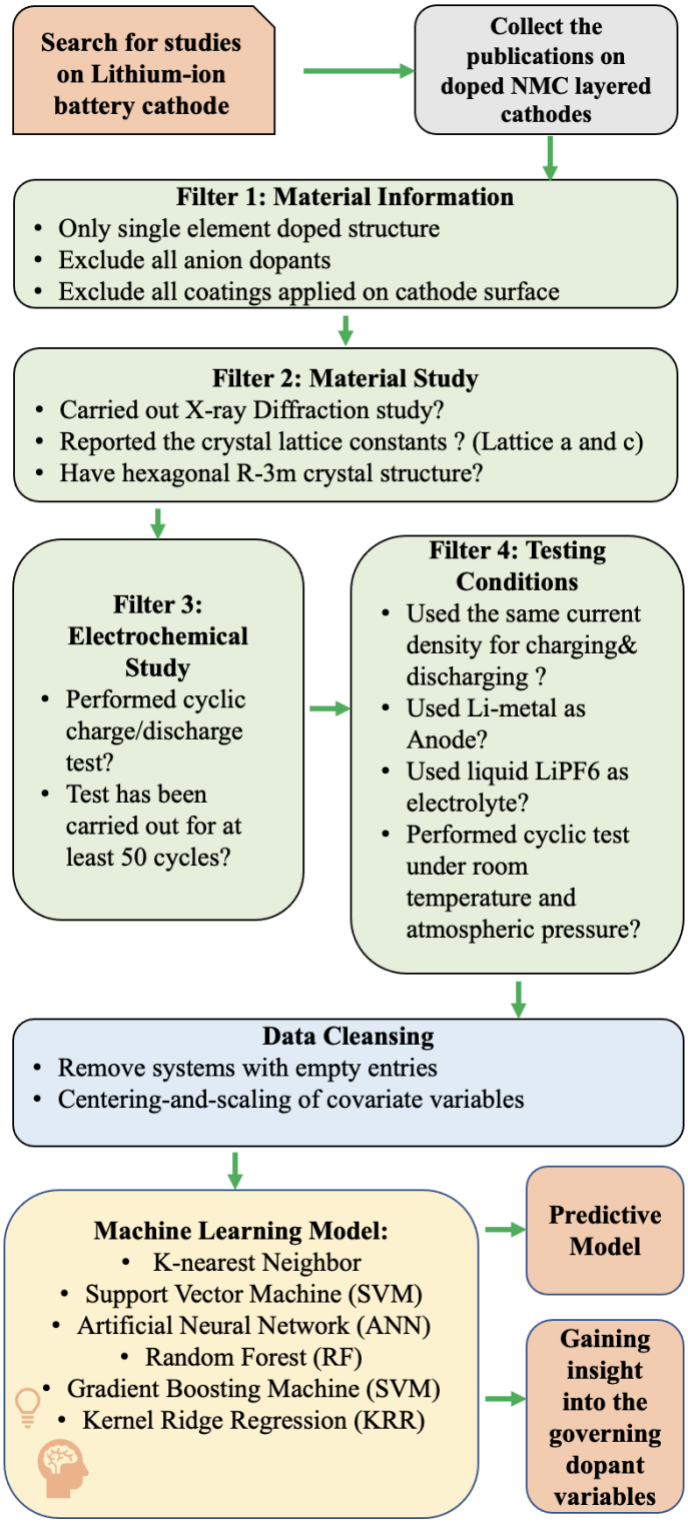


Figure 1. An overview of the data collection process with the demonstration of every filter applied in each publication selection stage.

Table 1. The proposed ML model architecture of this study including the name and abbreviations of the covariate variables, response variables.

Covariate Variables			
Publication Results		Elemental Properties	
Name	Abbreviation	Name	Abbreviation
The ratio of **lithium**, **nickel**, **cobalt**, **manganese**, **dopant** in the material formula	Li, Ni, Co, Mn, M - dopant	Material molar mass	Mr
Crystal lattice constants "*a*" and "*c*"	LC_a, LC_c	**Dopant**'s molar mass	Mr_dopant
Crystal Volume	CV	**Dopant**'s number of electrons	No_electron_dopant
Experimental current density	CD	**Dopant**'s electronegativity	EN_dopant
Minimum and maximum cyclic voltage	V_min, V_max	**Dopant**'s number of isotopes	No_iso_dopant
		Dopant's first ionization energy	E_ionisation_dopant
		Dopant's electron affinity	EA_dopant
		Dopant's atomic radius	AR_dopant
		Dopant's ionic radius	IR_dopant
Response Variables			
Name	Abbreviation	Name	Abbreviation
Initial discharge capacity	IC	50^{th} cycle end discharge capacity	EC

3. Methods

3.1 Data Collection of the doped NCM layered materials

The dataset consists of 168 different doped spinel systems with 20 dopant variations (e.g. Al, Ce, Cr, Cu, Cs, Eu, Fe, La, Mo, Mg, Nd, Na, Nb, Ru, Rb, Sn, Ti, V, Y, Zr) and was curated from over 59 reliable journals published from 1998 and 2020 (given as **Table S3** in Supporting Information). During the journal selection, strict rules were applied to ensure a high consistent standard of the collected data: NCM materials should be i) single-doped with cation ions since the multi-doped systems are hard to fabricate

and more costly, ii) be single-phase iii) have a space group of R-3m; and iv) have no surface coating. Furthermore, the electrochemical testing should also fulfil the following criteria to meet the data collection requirements: i) performed at least 50 cycles of charging/discharging cyclic test, ii) used lithium foil as anode and non-aqueous $LiPF_6$ as electrolyte iii) applied constant current density for charging and discharging the battery; iv) the cyclic tests are carried out under the atmospheric conditions (i.e. Temperature = 25±5 ℃, Pressure = 1atm). It is also important to note that the 50^{th} cycle discharge capacity has been chosen as it is the most performed test cycle among all studies.

Electrolyte plays a significant role in bridging the two contrasting electrodes and in facilitating the formation of a solid-electrolyte interface layer to protect the electrode from any unwanted side reactions. Electrolytes are often a mixture system with solvent and additives of which could lead to different performances if not standardised. The types of electrolyte systems from our collected studies are summarized in **Figure S3.** In our dataset, nearly 71% of the investigating electrochemical test were performed from either the mixture of ethylene carbonate/dimethyl carbonate (vol % 1:1) or the ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (vol% 1:1:1). These systems have similar dielectric constants (**Table S2**) which should result in similar electrochemical performance. Only seven of the material systems have been tested with the addition of fluoroethylene carbonates and these are used to improve the battery operation safety and hence should not influence the overall data quality by a considerate amount.

3.2 Model Training

The ML models used in this work were trained using Python programming language and with its relevant ML libraries (Sciki-learn, Pandas). Within the model, 20 covariate variables are selected to predict the initial and 50^{th} cycle discharge capacities of each material. These cover the experimental results such as the crystal lattice constants ("*a*" and "*c*"), the formula ratio of lithium, nickel, manganese, cobalt, dopant in the material formula (Li, Ni, Mn, Co, M), material molar mass, volume of the unit cell (CV) and cyclic

parameters such as the charge/discharge current density (CD) as well as the upper and lower operating voltage limit (V_min, V_max). In addition, seven dopant elemental properties are chosen as covariate variables to reveal their correlations with the discharging properties. These include: dopant's molar mass; the number of electrons; electronegativity; electron affinity; first ionization energy; atomic radius and ionic radius. In this work, six non-linear algorithms were implemented including artificial neural network (ANN), random forest (RF), gradient boosting machine (GBM), support vector machine (SVM), kernel ridge regression (KRR), k-nearest neighbors (KNN). The whole data space was randomly split into the ratio of 4:1 correspond to the model training set and test set, respectively. Model hyperparameters were optimised using 5-fold cross-validation during model training as there are 134 sets in the training set and the optimized hyperparameters are given in **Table S1**.

Model Evaluation Metrics: The model performance was evaluated through the calculation of the root mean square error (RMSE) and the coefficient of determination (R^2) from the predictions against the training and test set. The calculation methods are given as equation (1) and (2) below:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2} \quad (1)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y})^2} \quad (2)$$

Where n is the number of values, y_i is the observed variable, $\hat{y}_i$ is the predicted values and $\bar{y}$ is the average of the observed values.

The SHAP summary plots for the variable correlation and importance ranking are generated using the SHAP python package [22] and the further instruction are available in https://github.com/slundberg/shap.

3.3 Safety Statement

This work is performed wholly on the machine learning computational indicated and hence no unexpected or unusually high safety hazards were encountered

4. Results and Discussion

4.1 Pearson Coefficient Correlation Study

To gain initial insight into the underlying variable correlations, a Pearson's correlation coefficient study was performed for every pair of variables retrieved in the dataset. **Figure 2** shows the matrix of correlation values (R) calculated for the twenty covariates and the two response variables. The extent of correlation between every pair is color-coded with darker orange indicating a strong positive correlation and dark green strong negative correlations.

From the computed R values, it can be seen that there are more strong correlations ($R > 0.75$) being observed in-between covariates variables than for the covariate variables with either of the two response variables. However, some of these strong correlations observed between covariates might be misleading and do not provide any intuitive insights. For instance, the high correlations of lithium content ratio with minimum operating voltage ($R = -0.77$) and maximum operating voltage ($R = 0.68$) do not imply that any change in lithium content would influence the value of operating voltages. These voltage values are often preset for the experiments based on the specifications of the testing machine. In addition, a decrease in the lithium ratio seems to increase the molar mass of the material ($R = -0.93$) and this is because there are more available crystal lattice sites for the occupancies of heavier weighted TM and dopant elements. Similarly, the manganese molar ratio appears to have a correlation value of -0.95 with the nickel molar ratio in the formula, which is potentially due to the direct TM crystal site substitution. In addition, a high correlation ($R = 0.79$) is also identified for the pair of ionic radius of the dopant ion(IR_dopant) and the atomic radius of the dopant atom (AR_dopant). Both radii are the measurement of the distance away from the central nucleus despite one is under the neural state and the other is for the charged state and therefore their values might have a high linearity correlation with each other.For the model construction, it is important to find the linkage of covariate variables to the electrochemical properties. First, no strong correlations are being observed between covariate variable and response variables which might be due

to the presence of non-linear correlations. The maximum cyclic voltage is found to have a relatively high correlation with both IC and EC at 0.65 and 0.62, respectively. In addition, an increase in the Li content ratio in the formula seems to suggest a partial increase in both IC and EC as their correlation values are calculated to be positive 0.5 and 0.49 respectively. This seems to agree with the latest results on higher discharging performance are obtained from the lithium-rich layered cathode (~200mAhg^{-1}) than from the normal NCM-111 compounds (~165mAhg^{-1}).[23,24]

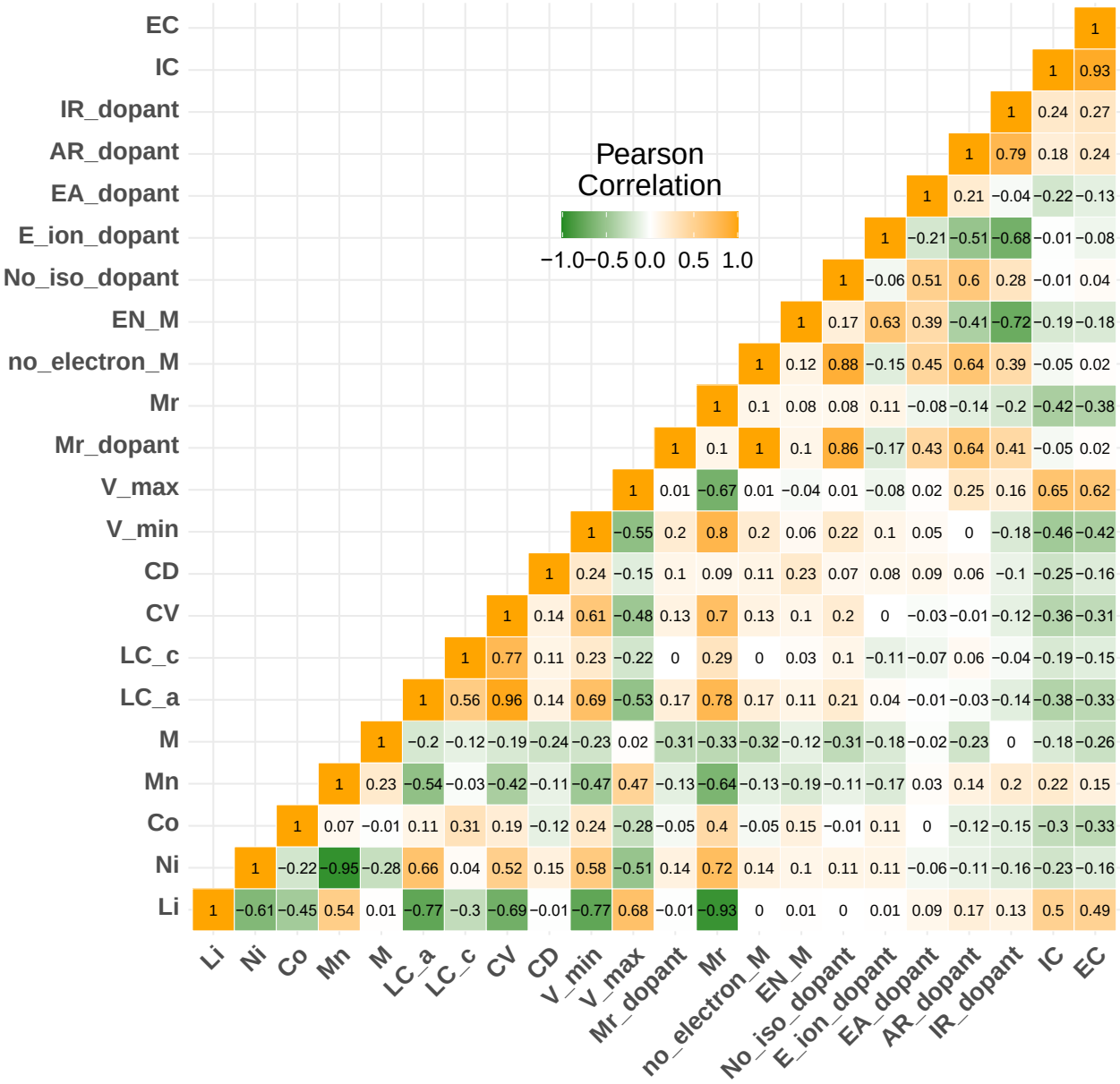


Figure 2. Results matrix of Pearson coefficient correlations for every pair of variables in the dataset, including covariate variables: Li, Ni, Co, Mn, M, LC_a, LC_c, CV, V_min, V_max, CD, Mr, Mr_dopant, No_electron_M, EA_dopant, No_iso_dopant, AR_dopant, IR_dopant, E_ionisation_dopant, EN_M and two response variables: IC, EC. The estimated correlation values are distributed within the range of -1 to 1, with the number reaching either end value implying a more perfect negative correlation and positive correlation, respectively.

4.2 Model Performance Comparisons:

To build accurate prediction models, six different non-linear regression algorithms have been trained and validated against a holdout test set for their prediction powers. **Table 2** shows the RMSE values computed during the training and for predicting the held-out test set. R^2 values are also calculated to demonstrate the proportion of variation in the test set being accurately captured by the model. In general, the validated test-set RMSE and R^2 values are more insightful for selecting the best performing model as the data are not involved in the training process and hence contains less prediction bias. Firstly, the ANN models are shown to have the worst performance with the lowest test-set RMSE among all. This is because both ANN models are embedded with many model parameters (**see Table S1**) and would require a much larger sample size to estimate these well. Furthermore, the tree-based ensemble methods generally have much lower test-set RMSE values than other nonlinear models such as SVM and KNN besides the KRR models. To help with visualizing the prediction mechanism of the tree-based ensemble methods, we have included diagrammatic illustrations for the random forest and gradient boosting algorithms and they are given in **Figure S1** and **Figure S2,** respectively in the supporting information. In addition, a plot of one decision tree generated from the random forest model for the prediction of 50^{th} cycle discharge capacity is given to illustrate the predicting process and this is given in **Figure S4**, in the supporting information. Overall, it is seen that the gradient boosting machine (GBM) has the best prediction performance for both tasks with their test set RMSE values being the lowest among all, at 16.66 $mAgh^{-1}$ and 18.59 $mAgh^{-1}$ respectively.

In the efforts to resolve the capacity fading issues faced by layered cathode material, a wide range of mathematical modelling-based studies has been conducted to understand the time series-based changes in NCM capacity with the loss of active materials.[25,26] Although several insights were gained in these studies, the inconsistent change in the capacity for different material compositions, as well as the influence of other essential testing conditions such as current density remains unresolved. It is estimated

that an experimental cyclic test of 25 cycles for a newly assembled Li-ion battery with the discharge rate of C/10 (1C denotes the discharge current density that would full discharge the battery within an hour) can take up to 20 days to complete.[27] Hence, the establishment of a highly accurate predictive model would greatly reduce the time duration required for the testing of electrochemical properties, and shorten the timespan for discovering new and robust cathode materials. The construction of a highly accurate model for predicting discharge capacities normally requires a large amount of experimental data with high diversity in material compositions and a good consistency in experimental factor controls. This has prompted us to implement strict selection rules for the journals and use high-quality data to train and build predictive models that would best describe the changes of discharging capacities for various NCM compounds at the initial and the 50th cycle.

Gradient boosting machine (GBM) algorithms[28] have known to be robust in describing the non-linear correlations across the wide variable space. GBM have previously seen successful applications in the prediction of the bulk and shear moduli of zeolites[29], classification of metal and insulators of inorganic crystals[30], prediction of the bandgap of new hybrid (ogranic+inorganic) perovskites.[31]

Figure 3 shows scatter plots of the predicted and experimental values of the initial and 50th cycle end discharge capacities during the training and testing stages for the optimal GBM models and RF models. The values of the R^2 scores, RMSE values for the test set prediction are highlighted in the graph along with the mean train RMSE values which are averaged across the 5 folds of cross-validation. Firstly, all models have shown good ability in generalising the training set as all of the 134 training points are shown to be close to the red 45-degree line. For the given test dataset, the GBM models have much higher R^2 scores for both prediction tasks than the RF models and this suggests superior prediction power in capturing the variations in the new dataset. These high correlation scores are shown to be consistent with the low test-set RMSE for all GBM models. However, a few outliners can be identified from the training

and test sets at circa. near 225 $mAhg^{-1}$ and 250 $mAhg^{-1}$, respectively from the GBM-EC graph and this would potentially affect the R^2 scores.

Nevertheless, the correlation scores from both GBM-IC (R^2 = 0.76) and GBM-EC (R^2 = 0.64) model have exceeded the benchmark value of R^2 >0.6 for a model to be considered as predictive.[32] These high correlation values have indicated that structural and elemental parameters such as the crystal lattice dimension and dopant's ionic radius can predict the discharge capacity of layered doped NCM cathode as accurately as the synthesis parameters variables used in *Min et al's work*.[16] Based on the above results, both GBM models for the IC and EC predictions are chosen for further analysis.

Table 2. Comparisons of the mean RMSE values during the 5-fold cross-validation and for testing against holdout test and the R^2 test score computed by six non-linear models, for the prediction of initial discharge capacity and end discharge capacity.

ML techniques	Initial Discharge Capacity ($mAhg^{-1}$)			50th Cycle End Discharge Capacity ($mAhg^{-1}$)		
	Cross-validated RMSE mean	RMSE on the test set	R^2 scores on the Test Set	Cross-validated RMSE mean	RMSE on the test set	R^2 scores on the Test Set
GBM	20.26	16.66	0.76	21.53	18.59	0.64
RF	21.98	17.00	0.59	21.86	19.25	0.42
SVM	22.94	21.11	0.37	22.00	19.38	0.41
KRR	20.65	17.28	0.58	21.77	19.13	0.43
KNN	23.57	18.98	0.49	25.03	21.51	0.28
ANN	34.15	22.39	0.29	33.93	24.58	0.05

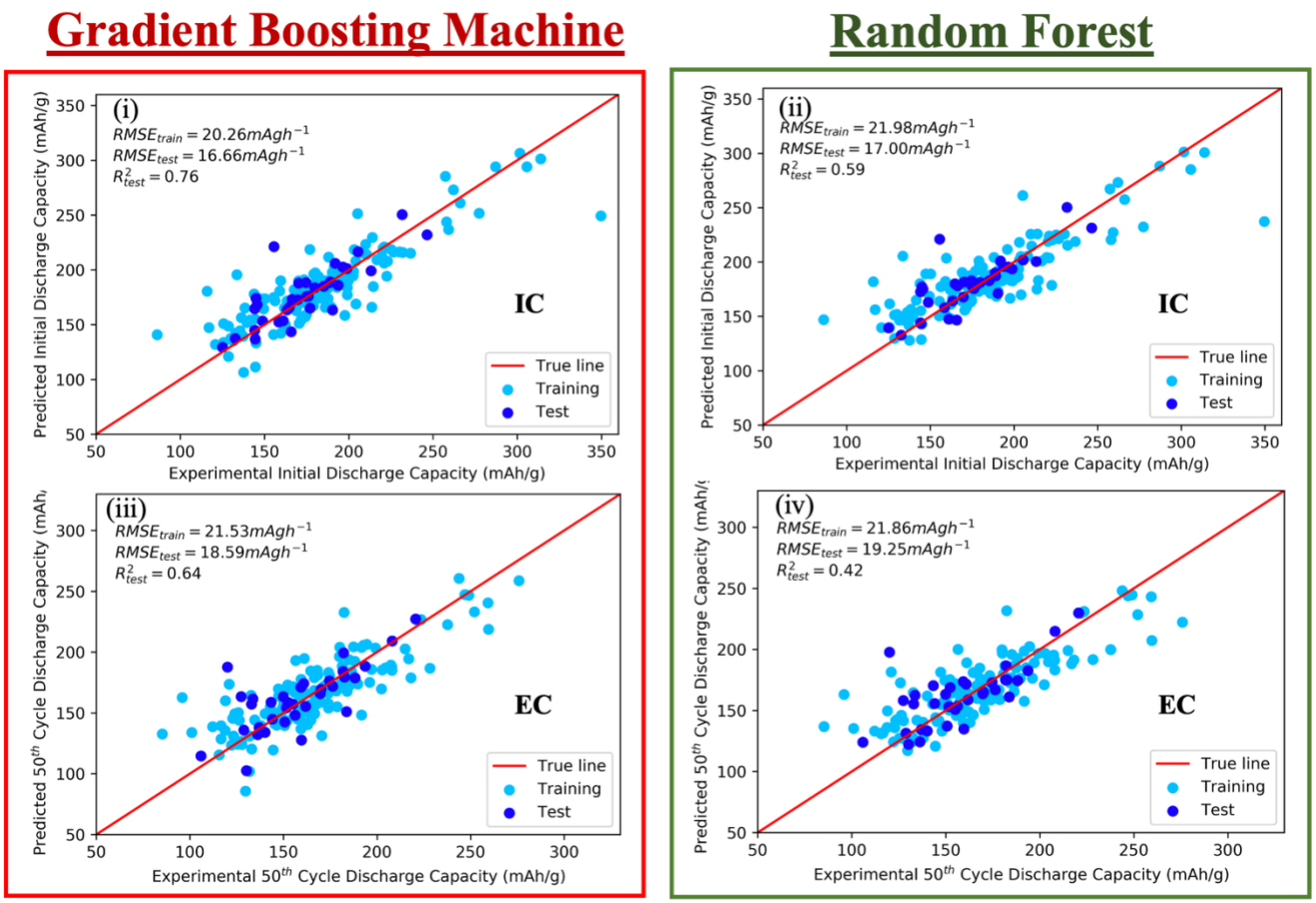


Figure 3. Scatter plots of the experiment values against the predicted values for the prediction of initial discharge capacity and 50th cycle end discharge capacity computed by gradient boosting models [ie. (i) and (iii), respectively], and random forest [i.e. (ii) and (iv), respectively].

4.3. Variable Importance Studies

The covariate variable importance can be estimated through the calculation of the Shapley values from the best performing models' predictions of the hold-out test set. Sharpley values come from the coalitional game theory where each of the covariate variables is treated as the individual "player" and the values estimate the covariate variables' contribution to the final prediction of a response variable instance. It is more desirable than the traditional permutation method for the easier interpretation of the variable correlation with the response variable. In this project, the treeSHAP (Shapley Additive exPlanations) method proposed by Lundberg et al[33], is used to gain insight into the importance of all

covariate variables and their feature effect on the prediction. **Figure 4-a and b** show the summarized Sharpley values for all 20 covariate variables during the predictions of IC and EC in the test-set through the GBM-IC model and the GBM-EC model, respectively. The Sharpley values measure the impact of that covariate variable on the model prediction with the more positive or negative value implying a larger overall influence. The y-axis of each graph gives the list of covariates in the order of their contribution to the overall prediction with the most important one being at the top and less important ones at the lower ranks.

To begin with, the minimum cut-off voltage, maximum cut-off voltage and the current density are ranked within the top 10 important variables. These covariate variables are all the experimental conditions for cycling and thereby are expected to have great influences on the material's discharging performance as a cathode.[34] After excluding these experimental setting variables, one can see that the dopant content ratio and the lithium content ratio are being ranked as the third and the fifth most important features, respectively for the IC test-set prediction from **Figure 4-a**.

A negative correlation is identified for the dopant content ratio and the IC as an increase in the corresponding Shapley values lead to the decrease in the IC feature values (shown in the sequence of red to blue). On the contrary, the Shapley values of lithium content ratio are shown to be positively correlated to the IC value, with the colour of the data plot shown to be blue to red. **Figure 4-c** shows the 3D plot of the dopant content ratio, Li content ratio correlating to the respective IC values for the entire dataset (train+ test). Firstly, two clusters of data can be identified with one characterized for having a lower Li content ratio with different dopant content ratios and the other having a higher Li content ratio and lower dopant content ratio. Observations can be made such that the IC values increase (Change from blue to green) as the dopant content ratio reduces in the first cluster. Moreover, the latter cluster has much higher average IC values than the first one which implies that a higher Li content is generally more desirable for obtaining a high IC value. This concludes that a higher Li content ratio ($x > 1.20$) coupled with a

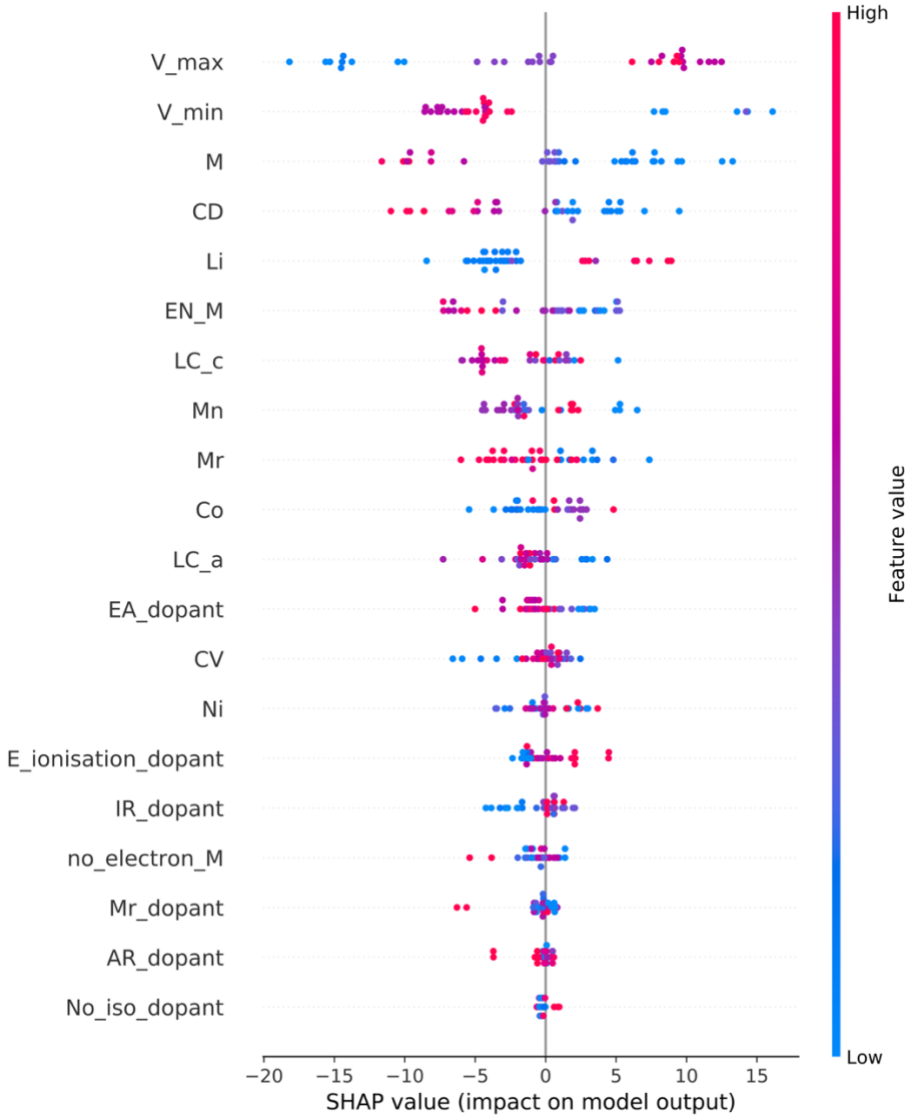
lower dopant content ratio ($y < 0.02$) can reach a higher IC. Further key insights can be also gained from **Figure 4-a** on that a doped NCM cathode material formula with lower dopant's electronegativity (EN_M), the shorter lattice constant "*a*" (LC_a) and "*c*"(LC_c), smaller formula molar mass, less manganese content and more cobalt content, can lead to higher IC values.

Figure 4-b shows that the dopant content ratio and its electronegativity value are ranked as the second and the fourth important for the predictions of EC. Electronegativity measures the dopant element's ability to attract electron pairs toward itself. Dopant's EN controls the bonding strength with the surrounding TMs and oxygen atoms and influences structural stability as well as the overall crystal structure density. During long cyclic charging and discharging performance, the overall crystal structure often becomes unstable which then triggers significant lattice collapses and leads to severe capacity fading.[35] The involvement of dopant content can greatly improve the structure stability by forming stronger bonds whilst the strategy with doping with a small amount can ensure that no second material phase is formed and also the whole crystal structure is not modified significantly to disturb the Li-ion intercalation/deintercalation mechanisms. Both the content ratio and the electronegativity of dopant are demonstrated to be negatively correlated to the EC feature value as the colour of the trend are changing blue to red (left to right). **Figure 4-d** displays the 3D intercorrelation of the two dopant-related covariate variables with the respective EC in the whole dataset. A clear trend is observed for EC decreasing with the decrease in the dopant content ratio (from blue to red). In addition, high EC data are observed to be at the lower range between 1.25 and 1.5 for the dopant's electronegativity for when the dopant content ratio is kept low ($x > 0.02$) and this corresponds to the magnesium(1.31) and zirconium (1.33) dopant in the collected dataset. From these phenomena, it is suggested that doping the atom with the electronegativity closer to 1.5 and with less amount can lead to higher EC values. Other observations can be made from **Figure 4-b** that a smaller material molar mass with lower manganese and higher nickel content can lead to a higher EC value for using doped NCM materials as the cathode, which shares a lot

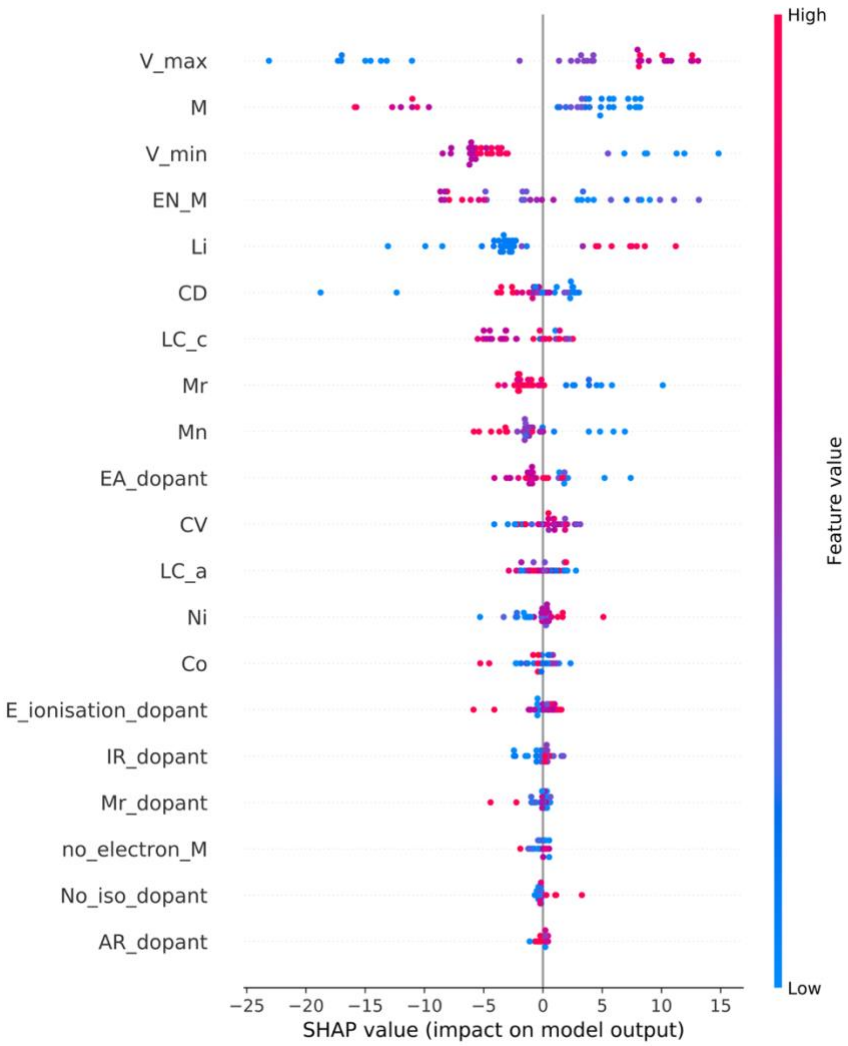
of similarities with the previous findings in the IC variable correlations. Interestingly, the dopant ratio in the material formulas has shown to be the most influential factor as it is ranked the third and the second for IC and EC, respectively and this is much higher than other material properties such as the dopant's electronegativity value and the lithium content ratio in the material formula. This suggests that the doping amount might play a much more important role in influencing the discharge capacities than other material systematic properties.

To conclude, our results have demonstrated that the materials that both constitute high IC and EC share the common characteristics of high Li content ratio, small dopant ratio, small manganese ratio and being doped with atoms of low to middle range electronegativity and low electron affinity. In addition, it is also encouraged to design a doped NCM material with low formula molar mass as it is inversely related to both discharge capacities.

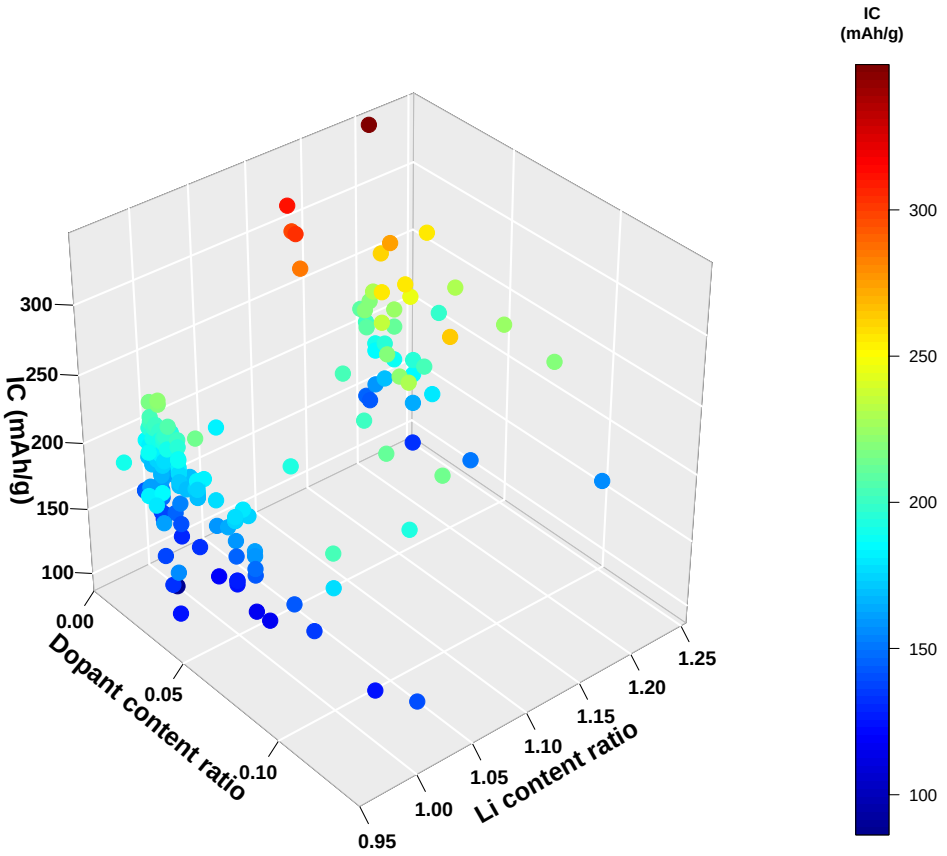
(a)


V_max
V_min
M
CD
Li
EN_M
LC_c
Mn
Mr
Co
LC_a
EA_dopant
CV
Ni
E_ionisation_dopant
IR_dopant
no_electron_M
Mr_dopant
AR_dopant
No_iso_dopant
−20
−15
−10
−5
0
5
10
15
SHAP value (impact on model output)
High
Feature value
Low

(b)


V_max
M
V_min
EN_M
Li
CD
LC_c
Mr
Mn
EA_dopant
CV
LC_a
Ni
Co
E_ionisation_dopant
IR_dopant
Mr_dopant
no_electron_M
No_iso_dopant
AR_dopant
−25
−20
−15
−10
−5
0
5
10
15
SHAP value (impact on model output)
High
Feature value
Low

(c)


IC
(mAh/g)
300
250
200
150
100
IC (mAh/g)
300
250
200
150
100
0.00
0.05
0.10
Dopant content ratio
0.95
1.00
1.05
1.10
1.15
1.20
1.25
Li content ratio

(d)

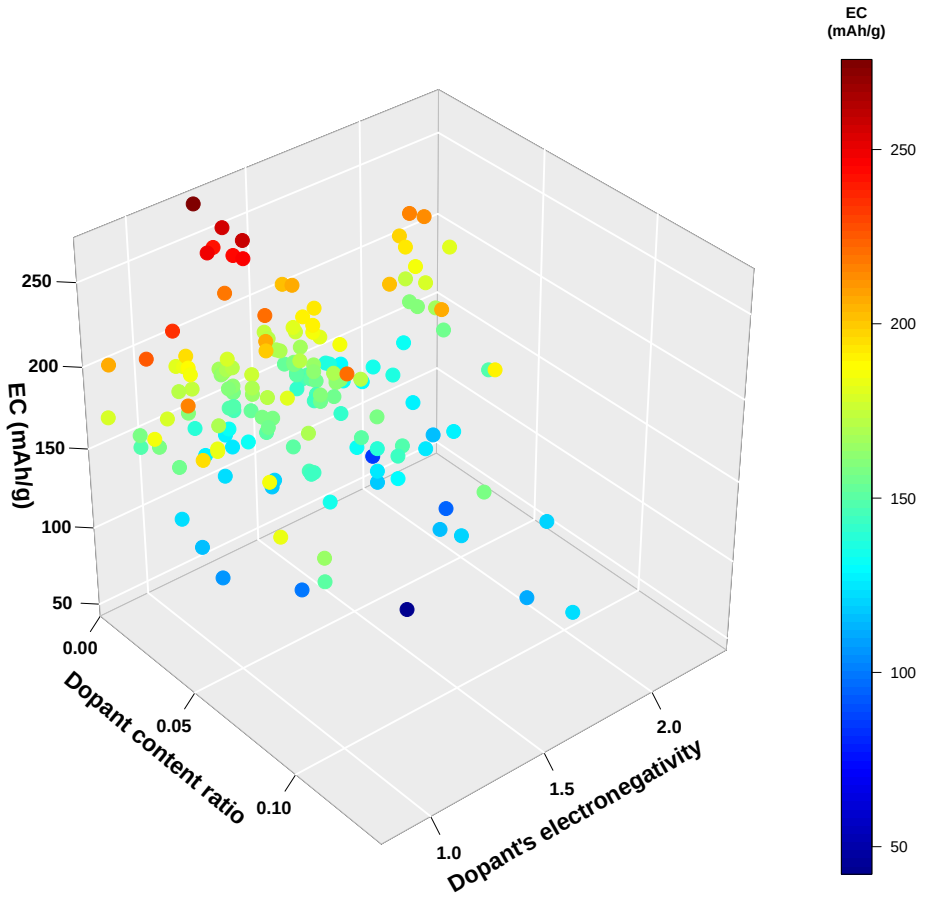


Figure 4. The summary plots for the feature contribution of twenty covariate variables in the test-set prediction of (a) IC generated based on GBM-IC model and (b) EC generated based on GBM-EC model. The y-axis indicates the feature importance of variables ranked in descending order. The x-axis shows the scale of the Shapley values for every feature and indicates their contribution to the prediction. The figure legends are given as heat-map showing the values of the respective response feature variable. The 3D plots give insights into the intercorrelations of (c) IC with two most important variables (Li content ratio, dopant content ratio) and (d) EC with the two most important variables (Dopant content ratio and dopant's electronegativity) in the whole dataset.

4.4 .Overall Discussions

Although some of the obtained correlations were known qualitatively, our model gives new insights by providing a quantitative prediction of IC and EC using these features for any new cathode materials that practitioners want to experiment on. These quantitative correlations were identified through the use of the Shapley value method developed from the coalitional game theory, of which based on the author's

knowledge, our study was the first in the field to implement this theory into analysing the contribution of the doping features for the predictions of the LIB discharge capacities.

In addition, the results of our research are novel in that it gives an estimation of the importance of each of the material property related features for each capacity property. For instance, despite that the higher lithium content is more favourable for achieving higher IC and EC as identified in the manuscript, its importance as given in **Figure 4-a** and **Figure 4-b** are shown to be much less than than the dopant content feature. This could of a suggestion for the experimentalist to consider the factor of optimal dopant ratio first before considering the lithium content ratio in the formula in the design of experiments.

During the selection of covariate variables (input variables) for the machine learning model, two major criteria have been used to guide this process: i) the relevance of the feature towards reflecting on the material properties and the performance properties ii) whether such data is widely reported or collectable. We selected the variables that can best describe the properties of synthesised materials to reflect wholly on the differences in synthesis methods, raw materials used across different research groups. For example, these properties include the crystal volume, crystal structure lattice constant of the materials can reflect on the conditions of the cathode materials as the host for the Li-ions. These properties are completely dependent on what the authors have reported in the publication and therefore we have not introduced any bias in the selection of these. In addition, we included the elemental properties related to the dopant atoms used in the studies from the NCM material dataset. As indicated in the initial results of the Pearson correlation coefficient matrix, no strong linear correlations have been identified for the pair of covariate and response variables of which indicate that the correlations between the selected covariates variables are not possibly explained by a simple linear model. This suggests that the selection process of the covariate variables in our project contain little bias.

Simple correlations of the structure and property for NCM material could be observed if the investigating material system is fixed. For example, the researcher could be investigating the effects of one dopant

with a different concentration on the discharge performance of the NCM material. On the other hand, The interpretation of a large dataset containing different doped NCM material systems is extremely hard to be achieved through simple human intuition. The novelty of our work focus on investigating a much wider range of doped NCM materials with 168 different compositions and 20 different dopant elements. We introduce this machine learning method to gain much broader insights into the overall variable correlations of different types of doped NCM materials to promote a much broader understanding of the doping effects on the NCM materials' electrochemical performance and the relevant governing variables in each case.

4.5. Remaining Challenges and Future Improvements

Data quality is essential for building highly predictive ML models. In this section, the data collection challenges for this work are highlighted and discussed along with the recommendation made for future potential research. Firstly, the doped NCM materials involved in this project all composite materials with the variations seen in the mixing ratio of the remaining two components, namely, conductive additive and binder. The lack of standardization in which conductive additive and binder to be used has led to a large variation in material usage across different research teams. The roles of these materials are to stabilize the overall cathode structure and to promote the Li-ion mobility within the structure which are considered essential for long cycle discharging. Furthermore, considering that the active material is the major component (75% ~ 90%) of this composite, the information of conductive additives and binder are assumed to be standardized for all collected data and further research could be done in investigating their effects. Secondly, the effects of materials' microstructural properties (etc. particle sizes) and the morphological features on the material discharging properties have been extensively studied.[36–40] Such information, however, is very difficult to collect owing to the reporting in various particle reporting scales (e.g. D10, D50, D90) as well as the general lack of conducting cathode surface study. For the electrochemical test, information such as the surface area of the cathode material and volume of the

electrolyte is often misreported and since the elemental composition might be unevenly distributed in the whole of the cathode composite system, this could lead to unreasonable fluctuations in the capacity loading.

Despite a great amount of efforts being devoted to establishing strict journal filters and selecting suitable journals (**Figure 1)** in this work, there are still rooms for improvement to be made as discussed above. To fully unleash the power of ML for the application of predicting the futuristic discharge performances of NCM cathode, the following points are worthy of considerations for future experimental and modelling research in NCM cathode:

1. Fully report the cathode material information such as the surface compositions, primary and secondary particle size, pore size.
2. For the full cell electrochemical test, report key information such as the surface area of cathode and anode materials.
3. Conduct comparative studies on the changes in microstructure and crystal structures for the cathode material after long cycle discharging.
4. For a small dataset (less than 500 rows), implement tree-based algorithms such as random forest and gradient boosting first before constructing an artificial neural network as it is shown to be time-consuming and less efficient in predicting capacities.

5. Conclusions

Analyzing the past experimental results is a crucial step to better understand the complex correlations of the NCM system properties and their discharging performance and additionally, the outcome of this project demonstrated the feasibility of using machine learning techniques in doing so. Six various non-linear machine learning algorithms have been trained and validated with the manually curated 2197 experimental results of 168 doped NCM materials. The models are built on using thirteen material

physical properties and seven dopant's elemental properties as covariate variables to predict the initial (IC) and 50^{th} cycle (EC) discharge capacities of each material structure. First, the Pearson coefficient correlation study has indicated that no strong linear correlations are captured for any pairs of covariate variables and two response variables. In addition, gradient boosting models are proven to hold the best prediction power against the holdout test set for having the lowest root-mean-square error at 16.66 $mAhg^{-1}$, 18.59 $mAhg^{-1}$ and highest R^2 scores at 0.76, 0.64 during IC and EC prediction respectively. Further insights are gained into the governing material features for each discharging property. NCM materials with higher lithium content, smaller dopant content and doped with the lower electronegativity value atom seem to bring higher values in both IC and EC. From these promising results, we expect that these machine learning models can be used as a guide tool to estimate the discharging properties of any single doped NCM material and potentially discover new cathode materials with more advanced electrochemical properties.

Keywords

Machine-learning, Lithium-ion Batteries, Doped Cathodes, lithium Nickel-Cobalt-Manganese (NCM) oxides

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. The dataset used for constructing these machine learning algorithms is available on the GitHub page (https://github.com/thepowerligand/NCM-ML/blob/main/NMC_numerical_new.csv) and the references for these selected journals are given as **Table-S4** in supporting information. The codes used for creating the machine learning models in this manuscript are given in https://github.com/thepowerligand/NCM-ML.

Conflict of Interest
The authors declare no conflict of interest.

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References:

1. Manthiram, A. A reflection on lithium-ion battery cathode chemistry. *Nature Communications* **11**, 1–9 (2020).

2. Xu, J., Lin, F., Doeff, M. M. & Tong, W. A review of Ni-based layered oxides for rechargeable Li-ion batteries. *J. Mater. Chem. A* **5**, 874–901 (2017).

3. Schipper, F. *et al.* Review—Recent Advances and Remaining Challenges for Lithium Ion Battery Cathodes. *J. Electrochem. Soc.* **164**, A6220–A6228 (2017).

4. Chakraborty, A. *et al.* Layered Cathode Materials for Lithium-Ion Batteries: Review of Computational Studies on LiNi1- x- yCoxMnyO2 and LiNi1- x- yCoxAlyO2. *Chem. Mater.* **32**, 915–952 (2020).

5. Lee, K. K., Yoon, W. S., Kim, K. B., Lee, K. Y. & Hong, S. T. Characterization of LiNi0.85Co0.10M0.05O2 (M = Al, Fe) as a cathode material for lithium secondary batteries. in *Journal of Power Sources* **97**–**98**, 308–312 (2001).

6. Sa, Q., Heelan, J. A., Lu, Y., Apelian, D. & Wang, Y. Copper Impurity Effects on LiNi1/3Mn1/3Co1/3O2 Cathode Material. *ACS Appl. Mater. Interfaces* **7**, 20585–20590 (2015).

7. Nisar, U. *et al.* Synthesis and electrochemical characterization of Cr-doped lithium-rich

Li1.2Ni0.16Mn0.56Co0.08-xCrxO2 cathodes. *Emergent Mater.* **1**, 155–164 (2018).

8. Sun, Y., Xia, Y. & Noguchi, H. The improved physical and electrochemical performance of LiNi0.35Co0.3-xCrxMn0.35 O2 cathode materials by the Cr doping for lithium ion batteries. *J. Power Sources* **159**, 1377–1382 (2006).

9. Jin, Y., Xu, Y., Ren, F. & Ren, P. Mg-doped Li 1.133 Ni 0.2 Co 0.2 Mn 0.467 O 2 in Li site as high-performance cathode material for Li-ion batteries. *Solid State Ionics* **336**, 87–94 (2019).

10. Breuer, O. *et al.* Understanding the Role of Minor Molybdenum Doping in LiNi $_{0.5}$ Co $_{0.2}$ Mn $_{0.3}$ O $_{2}$ Electrodes: from Structural and Surface Analyses and Theoretical Modeling to Practical Electrochemical Cells. *ACS Appl. Mater. Interfaces* **10**, 29608–29621 (2018).

11. Yang, Z. *et al.* K-doped layered LiNi0.5Co0.2Mn0.3O2 cathode material: Towards the superior rate capability and cycling performance. *J. Alloys Compd.* **699**, 358–365 (2017).

12. Zhang, X., Xiong, Y., Dong, M. & Hou, Z. Pb-Doped Lithium-Rich Cathode Material for High Energy Density Lithium-Ion Full Batteries. *J. Electrochem. Soc.* **166**, A2960–A2965 (2019).

13. Markus, I. M., Lin, F., Kam, K. C., Asta, M. & Doeff, M. M. Computational and experimental investigation of Ti substitution in Li1(NixMnxCo1-2x-yTiy)O2 for lithium ion batteries. *J. Phys. Chem. Lett.* **5**, 3649–3655 (2014).

14. Na, S. H., Kim, H. S. & Moon, S. I. The effect of Si doping on the electrochemical characteristics of LiNi xMnyCO(1-x-y)O2. *Solid State Ionics* **176**, 313–317 (2005).

15. Qiao, Q. Q., Qin, L., Li, G. R., Wang, Y. L. & Gao, X. P. Sn-stabilized Li-rich layered Li(Li0.17Ni0.25Mn0.58)O2 oxide as a cathode for advanced lithium-ion batteries. *J. Mater. Chem. A* **3**, 17627–17634 (2015).

16. Min, K., Choi, B., Park, K. & Cho, E. Machine learning assisted optimization of electrochemical properties for Ni-rich cathode materials. *Sci. Rep.* **8**, 1–7 (2018).

17. Houchins, G. & Viswanathan, V. An accurate machine-learning calculator for optimization of Li-ion battery cathodes. *J. Chem. Phys.* **153**, 054124 (2020).

18. Allam, O., Cho, B. W., Kim, K. C. & Jang, S. S. Application of DFT-based machine learning for developing molecular electrode materials in Li-ion batteries. *RSC Adv.* **8**, 39414–39420 (2018).

19. Zagorac, D., Muller, H., Ruehl, S., Zagorac, J. & Rehme, S. Recent developments in the Inorganic Crystal Structure Database: Theoretical crystal structure data and related features. *J. Appl. Crystallogr.* **52**, 918–925 (2019).

20. Jain, A. *et al.* Commentary: The materials project: A materials genome approach to accelerating materials innovation. *APL Materials* **1**, (2013).

21. Wang, G., Fearn, T., Wang, T. & Choy, K.-L. Insight Gained from Using Machine Learning Techniques to Predict the Discharge Capacities of Doped Spinel Cathode Materials for Lithium-Ion Batteries Applications. *Energy Technol.* 2100053 (2021). doi:10.1002/ente.202100053

22. Lundberg, S. & Lee, S.-I. A Unified Approach to Interpreting Model Predictions. *Adv. Neural Inf. Process. Syst.* **2017-December**, 4766–4775 (2017).

23. Toney, M. F. Li gradients for Li-rich cathodes. *Nature Energy* **4**, 1014–1015 (2019).

24. Xu, L. *et al.* A Li-rich layered-spinel cathode material for high capacity and high rate lithium-ion batteries fabricated via a gas-solid reaction. *Sci. China Mater.* **63**, 2435–2442 (2020).

25. Carnovale, A. & Li, X. A modeling and experimental study of capacity fade for lithium-ion batteries. *Energy AI* **2**, 100032 (2020).

26. Plattard, T., Barnel, N., Assaud, L., Franger, S. & Duffault, J.-M. Combining a Fatigue Model and an Incremental Capacity Analysis on a Commercial NMC/Graphite Cell under Constant Current Cycling with and without Calendar Aging. *Batteries* **5**, 36 (2019).

27. Kauwe, S., Rhone, T. & Sparks, T. Data-Driven Studies of Li-Ion-Battery Materials. *Crystals* **9**, 54 (2019).

28. Friedman, J. H. Greedy function approximation: A gradient boosting machine. *Ann. Stat.* **29**, 1189–1232 (2001).

29. Evans, J. D. & Coudert, F. X. Predicting the Mechanical Properties of Zeolite Frameworks by Machine Learning. *Chem. Mater.* **29**, 7833–7839 (2017).

30. Isayev, O. *et al.* Universal fragment descriptors for predicting properties of inorganic crystals. *Nature Communications* **8**, (2017).

31. Lu, S. *et al.* Accelerated discovery of stable lead-free hybrid organic-inorganic perovskites via machine learning. *Nat. Commun.* **9**, 1–8 (2018).

32. Tropsha, A., Gramatica, P. & Gombar, V. K. The importance of being earnest: Validation is the absolute essential for successful application and interpretation of QSPR models. in *QSAR and Combinatorial Science* **22**, 69–77 (Wiley-VCH Verlag, 2003).

33. Lundberg, S. M., Erion, G. G. & Lee, S.-I. Consistent Individualized Feature Attribution for Tree Ensembles. *arXiv* (2018).

34. Wu, Y., Keil, P., Schuster, S. F. & Jossen, A. Impact of Temperature and Discharge Rate on the Aging of a LiCoO 2 /LiNi 0.8 Co 0.15 Al 0.05 O 2 Lithium-Ion Pouch Cell . *J. Electrochem. Soc.* **164**, A1438–A1445 (2017).

35. Li, W., Asl, H. Y., Xie, Q. & Manthiram, A. Collapse of LiNi1- x- yCoxMnyO2 Lattice at Deep Charge Irrespective of Nickel Content in Lithium-Ion Batteries. *J. Am. Chem. Soc.* **141**, 5097–5101 (2019).

36. Tang, T. & Zhang, H. L. Synthesis and electrochemical performance of lithium-rich cathode material Li[Li0.2Ni0.15Mn0.55Co0.1-xAlx]O2. *Electrochim. Acta* **191**, 263–269 (2016).

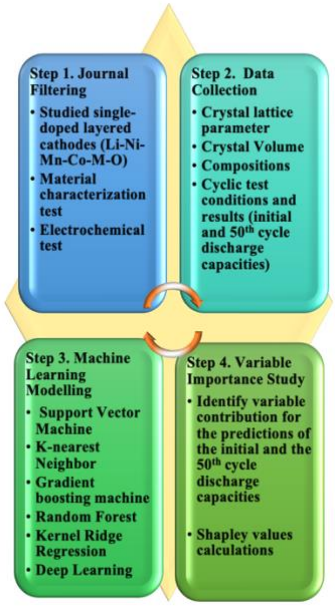
37. Gao, S., Zhan, X. & Cheng, Y.-T. Structural, electrochemical and Li-ion transport properties of Zr-modified LiNi0.8Co0.1Mn0.1O2 positive electrode materials for Li-ion batteries. *J. Power Sources* **410**–**411**, 45–52 (2019).

38. Xue, L. *et al.* Effect of Mo doping on the structure and electrochemical performances of LiNi0.6Co0.2Mn0.2O2 cathode material at high cut-off voltage. *J. Alloys Compd.* **748**, 561–568 (2018).

39. Lim, S. N. *et al.* Rate capability for Na-doped Li1.167Ni0.18Mn0.548Co0.105O2 cathode material and characterization of Li-ion diffusion using galvanostatic intermittent titration technique. *J. Alloys Compd.* **623**, 55–61 (2015).

40. Kim, U. H., Myung, S. T., Yoon, C. S. & Sun, Y. K. Extending the Battery Life Using an Al-Doped Li[Ni0.76Co0.09Mn0.15]O2 Cathode with Concentration Gradients for Lithium Ion Batteries. *ACS Energy Lett.* **2**, 1848–1854 (2017).

Table of Content (TOC) Figure:



Synopsis:

Six machine learning methods are used to predict the initial and the 50^{th} cycle discharge capacities (EC) for 168 doped lithium-nickel-manganese-cobalt-oxide systems based on the material structural and element properties. Among all models, gradient boosting machine has demonstrated the best prediction power in both tasks and the additional contributions of each input material variables for the capacity prediction are estimated.