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GRAPHENE AS AN ACTIVE MATERIAL FOR SUPERCAPACITORS: A MACHINE LEARNING APPROACH

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ABSTRACT

Graphene is a promising material for supercapacitors due to its unique properties, which influence supercapacitor devices. This study aimed to investigate the key factor of graphene properties in supercapacitors to improve their performance. This study applied Machine Learning (ML) to predict the capacitance of supercapacitors, involving four algorithms/models of Linear Regression (LR), Lazy IBK, Decision Table (DT), and Random Forest (RF). The results showed that the RF model demonstrated the best yield for predicting supercapacitors' capacitance with the highest correlation value of 0.745 with the lowest mean absolute error (MAE) and Read Mean Square Error (RMSE) values of 48.024 and 75.335, surpassing other models. Besides, the study also revealed that graphene with a high specific surface area and highly porous structure could induce a high capacitance value. Finally, these machine learning models can be applied in the materials sciences field to understand the materials' properties in supercapacitors.

Keywords: Graphene; Machine Learning; Surface area; Supercapacitors

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INTRODUCTION

The increasing energy demand necessitates the optimal utilization of renewable natural resources as an alternative to non-renewable ones. Energy storage technology, such as batteries and supercapacitors, can be used as a means to increase the utilization of alternative energy sources[1]. However, conventional batteries exhibit poor cycle stability and low power density compared to supercapacitors[2].

Supercapacitors are an efficient energy storage medium as their energy density is 10-100 times higher than that of conventional capacitors, and their power density is 1000 times higher than that of batteries[3]. Moreover, the high power density of supercapacitors enhances the optimal storage of energy[4]. The surface area of the electrode material plays a crucial role in improving the electrochemical performance of supercapacitors by providing accessible ion transport pathways[5]. Preparing porous carbon materials with a high surface area and mesopore fraction

can enhance energy capacitance in supercapacitors[6]. Among the various carbon materials used in supercapacitors, graphene is attractive and frequently exploited[7].

Graphene is a two-dimensional material with a regular arrangement of constituent atoms repeating periodically[7]. The superior properties of graphene, including high electrical, excellent surface area, and chemical equilibrium[8], make it a suitable candidate for various devices such as supercapacitors[9], transparent electrically conductive electrodes, conductive-polymer composites[10], transistors[11], solar cells, and energy storage materials[12]. Besides, the functionalized graphene has also been successfully applied as corrosion protection[13].

The performance of graphene supercapacitors is primarily influenced by the characteristics of their constituent materials, including specific surface area, pore volume, pore size, defect ratio, and the percentage of C, O, and N-doping on graphene[14]. The internal factors can cause changes in the surface characteristics of graphene materials for supercapacitors. Besides, there are contributions of experiment conditions for graphene supercapacitors, including the moles' number of electrolytes, voltage window, cyclic voltammetry, and current density.

In particular, the potential of the Machine Learning (ML) approach in optimizing energy storage performance has led to its application in various fields of physics, chemistry, biology, and engineering [15]. Remarkably, the use of machine learning in the development and management of energy storage devices and systems has shown promising results, significantly improving prediction accuracy and computational efficiency[16]. ML performance optimization has been conducted by previous samples or past experiences divided into three categories: supervised, unsupervised, and reinforcement learning[17]. Besides, regression analyses were employed to predict the continuous numerical values of graphene characteristics[9]. These focused on using ML to predict the capacitance of supercapacitors. Nevertheless, there are still limited studies observing graphene properties that influence supercapacitors' capacitance.

Hence, in this study, we promoted four machine learning algorithms, including linear regression (LR), decision table (DT), Lazy IBK, and random forest (RF), to classify the best algorithm for predicting the graphene supercapacitor. The RF model achieved the best correlation coefficient (R) up to 0.745 and MEA 48.024. Also, this research identified the contribution of the properties of graphene materials and experimental conditions that most influenced the capacitance of supercapacitors. The graphene properties comprised surface area (SSA), Pore Volume (PV), Pore size (sz), defect properties (Id/Ig), and chemical surface (carbon, oxygen, and nitrogen content). Besides, the experimental conditions observed were voltage window, current density, and electrolyte concentration. Finally, this study contributes to improving the performance of energy storage devices and the utilization of renewable natural resources in the global era. The findings of this study may have significant implications for the development of more efficient and sustainable energy storage solutions.

METHOD

The research procedure is illustrated in Figure 1. This study had three main stages: data collection, dataset processing, and data analysis. The flowchart of this work is shown in Figure 1 (supporting information). This research employed the Waikato Environment for Knowledge Analysis (WEKA) for dataset processing in ML. WEKA is a software that uses ML algorithms to process data mining[18].

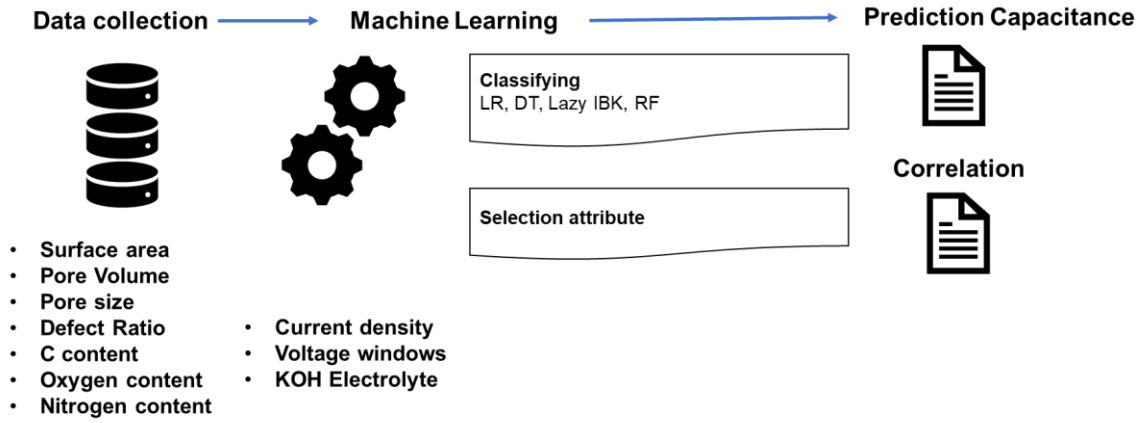

Figure 1. The process of machine learning for graphene

Dataset Collection

The datasets were collected from the journals concerning graphene supercapacitors indexed by Scopus, which were 213 datasets in total. Furthermore, the datasets were grouped based on graphene properties and experimental conditions. The graphene properties included surface area (SSA), Pore Volume (PV), Pore size (sz), defect properties (Id/Ig), carbon content (C), oxygen (O), and nitrogen (N). Besides, the experimental conditions were current density (Density), electrolyte concentration (KOH electrolyte), and voltage windows (VW). The group of datasets is presented in Table 1 (Supporting Information).

Data Processing

There were two datasets processes with different purposes by ML, including the classification for supercapacitor prediction and the selection attribute. Datasets processing by the classification applied the four machine learning models: LR, DT, lazy IBK, and RF. Furthermore, the k-fold cross-validation method was used for the process with a 10-fold value, whereby the 213 datasets were separated into 10 subsets, with 9 subsets used for training and 1 subset for testing. The selection attribute was applied to determine the key factors influencing capacitors' capacitance, including material properties and experimental conditions.

Data Analysis

Further, the machine learning model prediction also resulted in the Correlation Coefficient (R), Mean Absolute Error (MAE), and Root Mean Square (RMSE). Equations 1 and 2 present the formulas of MAE and RMSE.

$$\text{MAE} = \frac{1}{n}\sum_{i=1}^{n}|f_i - y_i| \quad (1)$$

where :

$f_i =$ predicted value

$y_i =$ true value

n = amount of data

$$\text{RMSE} = \sqrt{\sum_{i=1}^{n}\frac{(y_1 - \hat{y}_1)^2}{n}} \quad (2)$$

where :

$\hat{y}_1, \hat{y}_2, \ldots\ldots, \hat{y}_n = predicted\ value$

$y_1, y_2, \ldots\ldots, y_n = observed\ value$

n = amount of data[19].

The smaller RMSE value indicates a higher accuracy[20].

RESULTS AND DISCUSSION

In this study, the dataset consisting of 213 data was collected by searching for the most influential graphene as supercapacitor material. Several properties of graphene studied in this research included specific surface area, pore volume, pore size, defect ratio, carbon, oxygen, and nitrogen content. Besides, the experimental condition comprised the electrolyte (KOH) concentration, voltage window, and current density. The dataset summary is shown in Table 1, displaying the minimum, maximum, mean, and standard deviation of 213 data. The highest supercapacitor capacity was reported at 571 F/g, while the lowest was 0.84 F/g, with an average value of 186.884 F/g. Based on the analysis, the characteristics of graphene materials and experiment conditions that most affected the supercapacitors' capacitance are depicted in Figure 1.

Table 1. Summary of dataset distribution

NO	Variable	Min	Max	Mean	Stdev
1	SA (m^2/g)	6	1754	425.225	314.363
2	PV (cm^3/g)	0.02	7.98	1.643	1.707
3	PZ (nm)	0.39	450	41.284	91.028
4	ID/IG	0.03	1.99	0.901	0.394
5	Carbon (at. %)	52.94	98.47	83.863	9.349
6	Nitrogen (at. %)	0	18.5	3.226	5.077
7	Oxygen (at. %)	0	40.27	10.819	8.799
8	KOH electrolyte (M)	2	6	5.678	0.942
9	VW (V)	1	3.5	0.857	0.85
10	Current density (A/g)	0	100	7.525	16.435
11	Capacitance (F/g)	0.84	571	186.884	108.499

Further, from the data analysis, the supercapacitors' capacitance would increase with the application of graphene material as the electrode material. The machine learning with selection attribute model was applied to observe the key factor of supercapacitors, which is presented in Figure 2. Three graphene properties strongly impacted the supercapacitor, including the surface area, oxygen, and carbon content. Graphene material with a large specific surface area can facilitate the formation of duplicate electrical layers on the electrode surface, thereby enhancing the capacitance[21-22]. This is because graphene surface area is determined based on the amount of micropore surface area, mesoporous surface area, and outer pore surface area[23]. A high surface area also provides a high capacitance value if all pores are accessible to ions and the carbon material has a good wetness level[24]. The correlation contribution between graphene properties and the supercapacitors' capacitance obtained from the ML approach is presented in Figure 2.

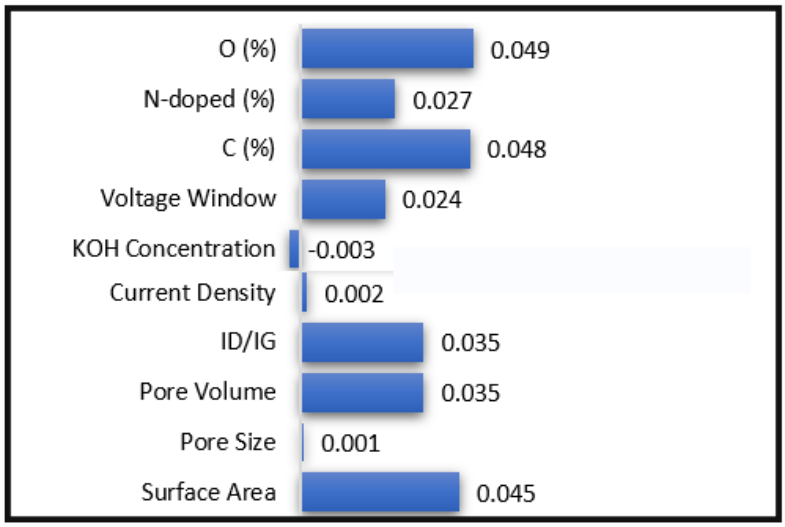

Figure 2. The correlation contribution of graphene properties on the capacitance of supercapacitor.

Next, the quality of graphene could be seen from the crystallinity and defect coefficient observed by Raman spectroscopy. The I_D/I_G ratio value represents the magnitude of the defect in the sample[25]. Defects can originate from voids in carbon bonds. The thinner sample leads to higher 2D peaks[26]. The intensity of Raman spectroscopy produced depends on the increasing size and thickness of the particles[27]. Raman spectroscopic characterization is carried out to determine the number of layers of carbon atoms on graphite that is reduced to graphene[28]. Graphene materials have a variety of derivative compounds. This type of derived material also dramatically affects the capacitance of supercapacitors.

Furthermore, electrolytes play an essential role in supercapacitors by achieving the power and current density desired[29]. Thus, the performance of supercapacitors can be adjusted by changing the type of electrolyte[30]. This study observed KOH electrolytes with concentration variation as one of the experimental conditions affecting the supercapacitors' capacitance. Hence, it is logical that using the ML approach, it was found that the concentration of KOH affected the supercapacitors' capacitance. The higher concentration produced greater capacitance[31]. The correlation between the experimental conditions and the capacitance of graphene supercapacitors is displayed in Figure 3.

The capacitance prediction of supercapacitors was performed with the ML model through a classification model by trying the four ML algorithms (LR, DT, Lazy BK, and RF). This classification model describes the feature data used in machine learning models, the selection of optimal parameters to apply to machine learning models, and the results of capacitance predictions for optimal supercapacitors. The difference between the four algorithms lies in the coefficient correlation, MEA, and RMSE for the feature data. Figure 3 demonstrates the prediction of the graphene supercapacitors using the ML approach with the four algorithms.

The LR model has the advantage of combining removing non-essential features from Lasso and reducing feature coefficients from the Ridge model to improve predictive results. Although LR has the benefit of the Lasso and Ridge models as resampling feature data used when the capacitance of the supercapacitor is below 100 F/g and above 300 F/g, the predicted capacitance results stay away from the actual capacitance value. The experiment of predicting the capacitance of supercapacitors with ML models that feature input data with a test model (using cross-validation) has a more accurate correlation level. Thus, the performance of ML models as a prediction of supercapacitors' capacitance is compared based on the full data input feature used.

The RF model has the benefit of improving accuracy results if there is missing data and resisting outliers, as well as being efficient for storing data. In addition, it has a bagging algorithm that is bootstrap used to resample feature data to estimate population statistics by sampling datasets with replacement and can reduce overfitting on predicted capacitance. Meanwhile, Lazy-IBK has the benefit of working better with a large number of datasets and can find an approach between new data and old data to improve prediction results.

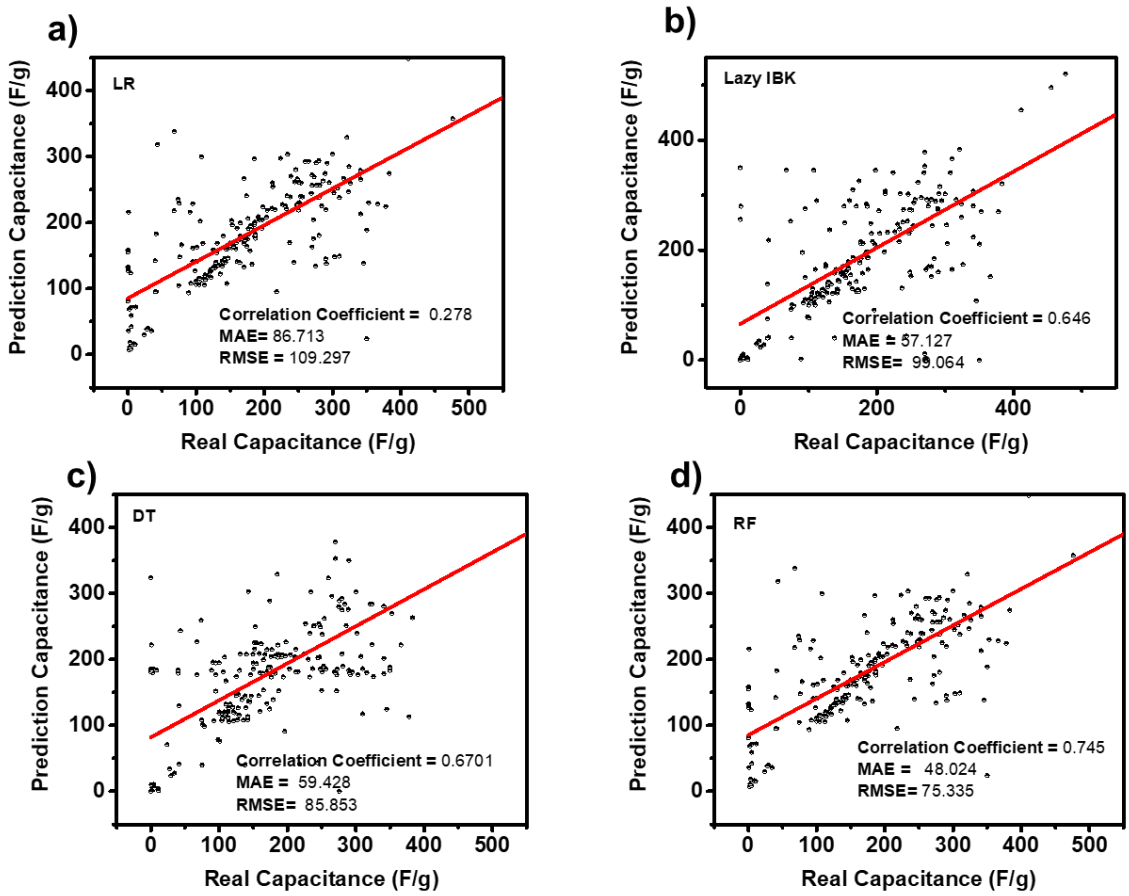

Figure 3. Prediction results of Supercapacitor Capacitance using ML approach with algorithms of a) Linear Regression (LR); b) Lazy IBK; c) Decision Tree (DT) ; d) Random Forest (RF)

Based on the advantages, the optimal ML model for supercapacitor capacitance prediction was still uncertain. Therefore, it was necessary to evaluate the test results by estimating the MEA and RMSE values to compare the performance of optimal prediction results. As seen in Figure 3, the RF model had the smallest MAE and RMSE values of 48.024 and 75.335, respectively. Meanwhile, the LR model achieved the highest MAE and RMSE values of 86.173 and 109.297, respectively. Accordingly, the RF was the optimal model for predicting supercapacitor capacitance with full data input features. Moreover, it also revealed a high accuracy level with the highest correlation coefficient of 0.745.

Finally, the ML algorithms are suitable to be applied in materials science, especially for predicting the capacitance of graphene supercapacitors. Besides, the model correlation in ML could predict the key factors of supercapacitor capacitance, including material properties and experimental conditions.

CONCLUSION

ML approach has been employed to demonstrate the correlation contribution of graphene properties and experimental conditions to supercapacitors' capacitance. The results revealed that the surface area and oxygen content were the key factors of graphene properties to achieve high supercapacitor capacitance, while the experimental condition was the voltage window. Besides, the ML approach with the four models of LR, DT, Lazy BK, and RF has also been used to predict the capacitance of supercapacitors. Further, the RF was the best model to predict the supercapacitors' capacitance with the lowest MAE and RMSE values of 48.024 and 75.335, respectively, and the highest accuracy level.

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