

Towards Optimal Production of Graphene by Electrolysis in Molten Salts Using Machine Learning

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Abstract

Graphene is very exciting and one of the best materials in the last decade. The interest in producing non-expensive and high-quality graphene is of great interest to many Departments of materials and researchers worldwide. The main goal of this research considers the design, development, and optimisation of new technology for producing graphene by electrolysis in molten salts using constant cell voltage, reversing cell voltage, and constant overpotential and reversing overpotential methods. Compared to other processes, the electrolysis process is simple, ecological, and economical. Furthermore, it offers possibilities to control various parameters: type of electrolyte, applied voltage, current density, temperature and type of graphite used as a raw material for synthesis of graphene. The underlying relationship between the parameters and the quality of the graphene is obtained through an explainable tree-based Machine Learning (ML) model. We trained the model by using the production process parameters as input attributes and the quality of the produced graphene as a target variable. Domain experts provide labels regarding the quality of each experimental instance in our data set. We propose using the extracted rules from the model to serve as a blueprint for optimal graphene production by electrolysis in molten salts and choosing the correct values for the process parameters results in high-yield graphene production, up to ten times cheaper than the one produced with other existing technologies.

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Introduction

Modern scientific research in nanotechnologies and nanomaterials has focused on carbon nanostructures due to their exceptional properties and potential applications in various fields (Andonovic, Azemi, Andonovic, & Dimitrov, 2022) (Andonovic, Ademi, Grozdanov, Paunovic, & Dimitrov, 2015). The two most well-known allotropic modifications of carbon are diamond and graphite, both characterised as three-dimensional (3-D) structures. However, in the past 30 years, new allotropic modifications of carbon were discovered, such as fullerenes (0-D) and carbon nanotubes (1-D), which are derived from graphite. The missing piece in this sequence was the two-dimensional (2-D) form of carbon.

In 2003, Andre Geim and Costa Novoselov (Novoselov, Geim, Morozov, Zhang, & Dubons, 2004) (Geim & Novoselov, *The rise of graphene*, 2007) (Geim, Nobel Lecture: *Random walk to graphene*, 2011) were able to isolate graphene sheets, disproving the claims of other scientists that the two-dimensional structure of graphene is thermodynamically unstable and proving that graphene is a two-dimensional material that is environmentally stable. This began the study of the properties of this material. Those two scientists, in the 2010s, were awarded the Nobel Prize for Physics. Due to its superior properties, scientists call graphene the material of the future or magical material. Therefore, graphene was considered one of the leading discoveries of the 21st century.

The two-dimensional structure of graphene consists of interconnected sp^2 carbon atoms in a plane reminiscent of a honeycomb. The dimensions of this atomic plane are 0.142 nm, which means graphene is as thick as one carbon atom. Graphene, the youngest member (last obtained) of the nanocarbon family, is the basic building block of which graphite is composed, and the other allotropic modifications of carbon are formed by graphene, too: fullerenes and carbon nanotubes.

From the two-dimensional structure of graphene, the thinnest material known to humankind derives its superior properties compared to other materials. Graphene possesses outstanding electrical, thermal, optical, mechanical, surface, and other properties. Because of these superior properties, the fields of its application in both science and everyday life are huge. It can be used in electronics when making transistors, integrated electric circuits, LEDs, and LCD screens; as a sensor material with high resistance to the change of electric current and with multi-purpose applications; as a membrane for ultra-purification of liquid media; solar cells, bio-devices in medicine; electrocatalysis; as a high-capacitance material for energy storage and photocatalysis.

In (Kamali & Fray, 2013) the authors studied the structural and microstructural changes in graphite when heating a mixture of synthetic polycrystalline graphite and lithium chloride at 1250°C. The results of thermal analysis, XRD, Raman spectroscopy, and electron microscopy showed that the average size of graphite crystallites increases significantly after thermal treatment, although the oxidation of graphite is largely inhibited. Various forms of corrosion attack on graphite were observed. Consequently, this allowed the creation of various microstructures composed of exfoliated carbon sheets and nanosheets, hollow particles, and carbon nanowires.

In (Rao, Senthilnathan, Liu, & Yoshimura, 2014) the authors demonstrated a simple, easy, and environmentally friendly approach for efficient electrochemical exfoliation of graphite using a sodium hydroxide/hydrogen peroxide/water ($\text{NaOH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) system, which can obtain high-quality anodic few-layer graphene (AFLG), with a yield of 95% under ambient conditions. Controlled experiments have shown that hydrogen peroxide plays a key role in graphite exfoliation. The reaction of hydrogen peroxide (H_2O_2) with hydroxyl ions (OH^-) leads to the creation of highly nucleophilic peroxide

ions (O_2^{2-}), which play a key role in graphite exfoliation by electrochemical intercalation and strong expansion of graphite sheets.

Since the discovery of graphene using mechanical exfoliation, numerous procedures for its production have been developed, including chemical vapor deposition (CVD), plasma-enhanced CVD, liquid-phase exfoliation, laser ablation, and more (Alanyalıoğlu, Segura, Oró-Solé, & Casañ-Pastor, 2012) (Vlassioug, Fulvio, III, & Lavrik, 2013) (Schwandt, Dimitrov, & Fray, 2010).

Production of graphene by electrolysis in molten salts

Experimental

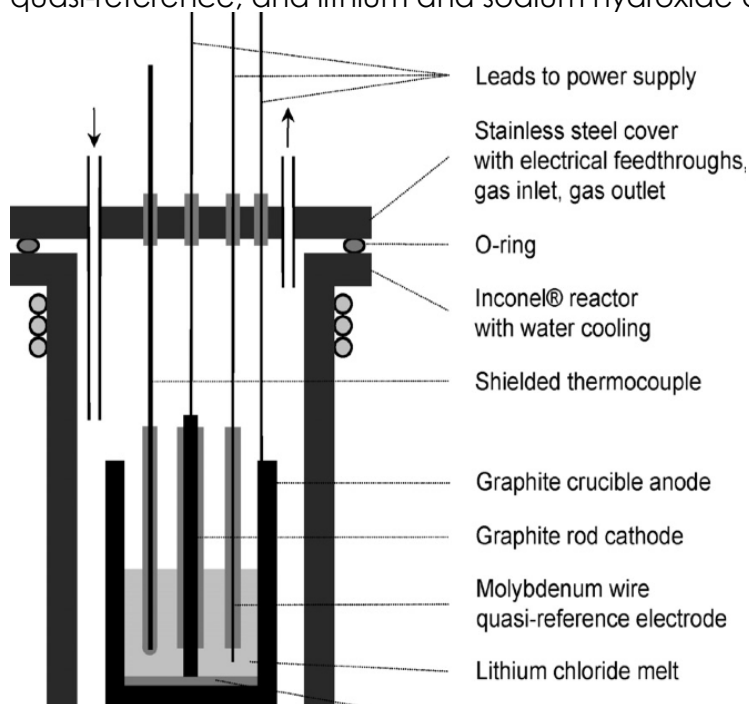
The electrochemical measurements were carried out in a graphite crucible (external dimensions: 150 mm in height and 90 mm in diameter; internal dimensions: 140 mm in height and 70 mm in diameter, see Fig. 1), which served as the container for the molten salt electrolyte. The cell was used inside a sealable Inconel tube reactor with a water-cooled jacket and was heated by a vertical Lenton furnace capable of reaching 1600°C, equipped with a programmable controller (Fig. 1). The electrolyte used was a chloride salt, specifically LiCl. The salts were thermally pre-dried in an argon atmosphere inside an Inconel tube at 250°C for at least 6 hours before being melted in the same atmosphere.

The working electrode was either a graphite rod with a diameter of 10 mm, shielded in an alumina tube and connected to a molybdenum lead, or a molybdenum wire with a diameter of 0.5 mm, shielded in an alumina tube. A molybdenum wire was used as a quasi-reference electrode, and the carbon crucible served as the counter electrode.

The characterisation was performed using SEM, TEM, and Raman spectroscopy.

Figure 1

Schematic of the experimental set-up used for conventional electrolysis. The cell consists of a graphite rod cathode, a graphite crucible anode, a molybdenum wire quasi-reference, and lithium and sodium hydroxide as electrolytes.



Source: Author's illustration

Production of graphene

In recent times, graphene has been produced using various methods that are usually expensive and provide low yields. Graphene production methods are based on dispersing the basic carbon raw material and redistributing it into graphene. Based on the extensive literature search, it can be concluded that the number of published scientific papers or studies on the production of graphene by means of electrolysis from molten salts using nonstationary current regimes is small.

Hence, one of the goals of this research is to obtain graphene by electrolysis from molten salts using nonstationary current regimes and optimisation using machine learning.

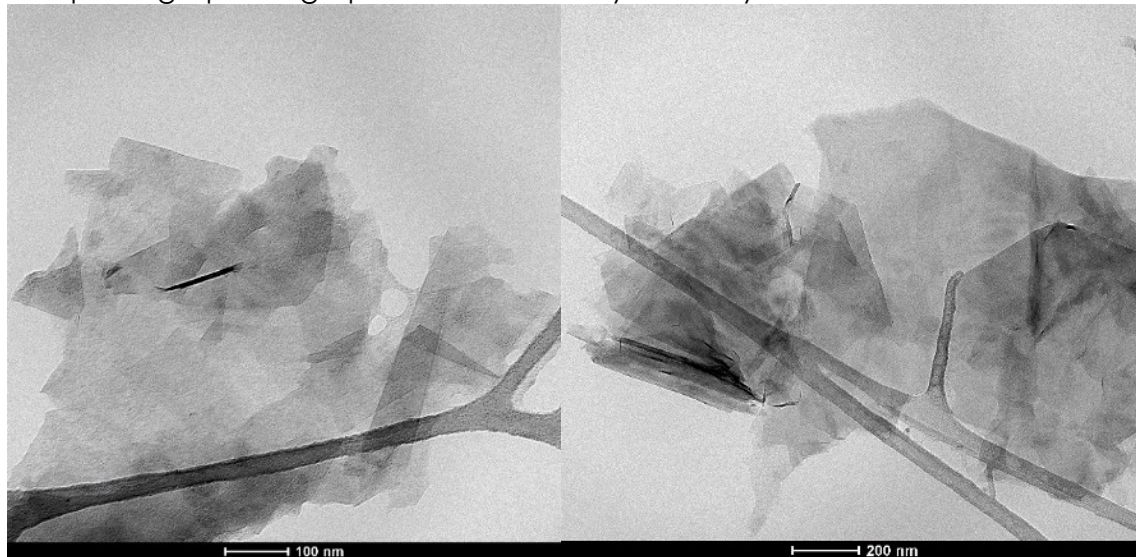
The electrochemical method offers great possibilities for controlling the various parameters of the process: the reversible overvoltage, current density, alternating current frequency, the temperature of the electrolyte and the type and morphology of the starting material. Controlling these parameters can ensure the obtaining of high-quality graphene, high production yield, and the selection of the best graphite for graphene production and a product with low prices.

The graphene in this research is produced as a result of ion intercalation during the process of electrolysis. The cation reduces at the cathode and intercalates at the electrode surface, generating a high mechanical stress that causes exfoliation. This process of intercalation and exfoliation enables the electrochemical synthesis of graphene to be performed.

Figures 2 and 3 presented TEM photographs of graphene obtained produced by electrolysis in molten salt using nonstationary current regimes.

Figure 2

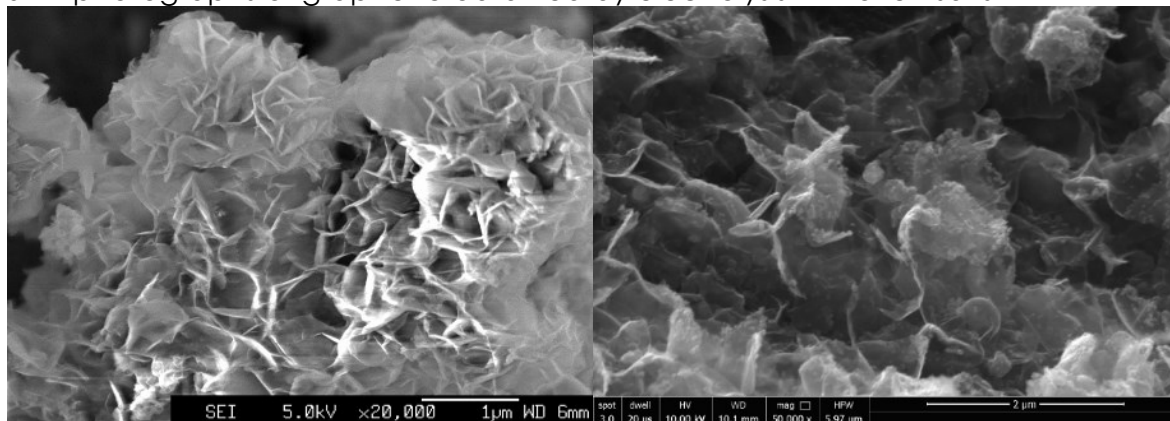
TEM photographs of graphene obtained by electrolysis in molten salts



Source: Author's illustration

Figure 3

SEM photographs of graphene obtained by electrolysis in molten salts



Source: Author's illustration

Methodology

Graphene is synthesised through electrolysis in molten salts, utilising both stationary and nonstationary current regimes. To optimise production at a large scale, a decision tree model was trained to classify experimentally produced graphene into three quality classes based on factors such as yield and defect rates. The descriptive power of the decision tree model is utilised to optimise the production of high-quality graphene by using the rules derived from the trained model. Prior to model training, data preprocessing was conducted using Python modules such as pandas, NumPy, and sci-kit learn. This involved normalising feature values to ensure equal opportunity for each attribute, with the Standard Scaler technique (Raju, Lakshmi, Jain, Kalidindi, & Padma, 2020) being used in this case. By scaling the attributes so that their mean value is zero and their variance is retained with their standard deviation, no feature receives undue preference based on the range of values it possesses.

In order to apply most machine learning algorithms in Python, all features must be converted into numerical form using an encoding technique. For this purpose, one-hot encoding (Potdar, Pardawala, & Pai, 2017) is commonly used, whereby each categorical value of a feature is converted into a new categorical column with a binary value (1 or 0) assigned to it.

To initiate the modelling procedure, the dataset D is split into X and Y , where $X = \{X_1, X_2, \dots, X_N\}$ represents the feature matrix containing the CNT parameters, and $Y = \{Y_1, Y_2, \dots, Y_N\}$ is the vector of classes for the respective graphene samples. A pair of the form $\{X_i, Y_i\}$, where $i = 1, \dots, N$, describes a single instance of graphene used for model training.

Model training aims to find the optimal partitioning of the input variable space, which in our case is defined by the graphene parameters, to minimise a predefined cost function. Starting at the root node, the inference method for the decision tree model splits the training set pertinent to the node to maximise a splitting criterion. The split uses a single feature (graphene parameter) from the training set to form a condition on the feature's value, which evaluates to true or false, thereby dividing the data into two sets that correspond to the two siblings of the node. This procedure continues recursively, resulting in a binary tree.

The splitting criteria for each node are related to a predefined cost function or estimated error. In our procedure, we used the Gini Index (G.I.) (Daniya, Geetha, & Kumar, 2020) as the splitting criterion. The cost of splitting is estimated for each resulting

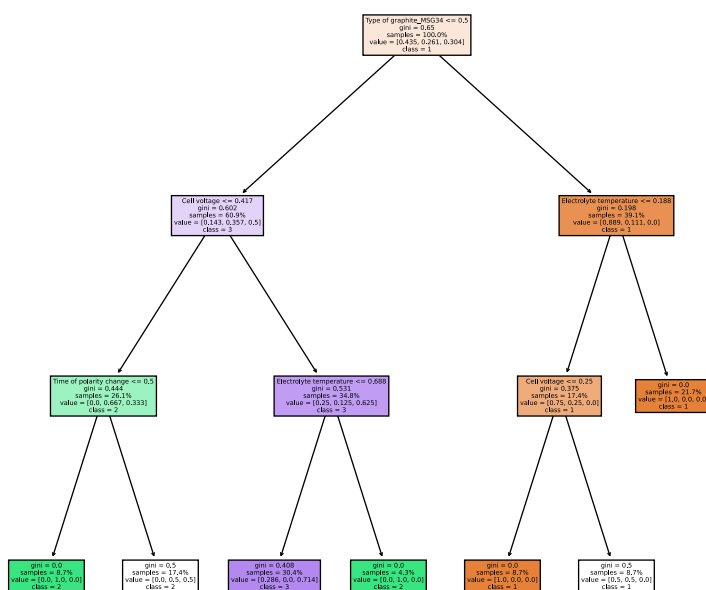
sibling node and then weighted according to the probability that the data instance will fall into one of the two constructed regions.

Results

The study aimed to determine the optimal parameters for the production of graphene using decision tree (D.T.) modelling. We used k-fold cross-validation for performance estimation instead of a single test set, which allowed us to obtain a more accurate and reliable estimation of the performance of the model. Classification accuracy was used as a performance metric, and the resulting D.T. obtained by training the model on the training set was analysed to extract rules and calculate feature importance.

Figure 4

Visual representation of the decision tree model providing general guidelines for optimal parameters



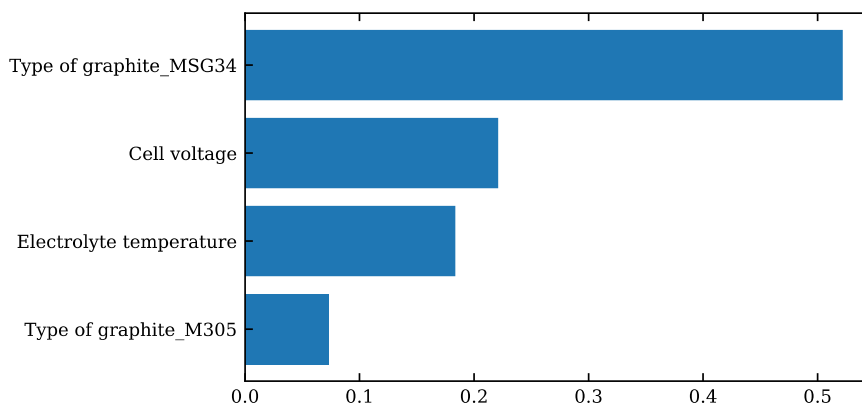
Source: Author's illustration

The D.T. model generated in this study provides valuable insights into the optimal parameters for graphene production. By analysing the rules extracted from the model with domain expertise in nanomaterials, we were able to generate generally applicable guidelines for the optimal production of graphene. These guidelines can be used to produce high-quality graphene for different purposes without requiring expert knowledge or significant expenses on consulting, supervision, and support by experts in the field.

In addition to the extraction of rules, we also calculated the importance of the feature of the model. The feature importance allowed us to rank the parameters of the graphene production process according to their influence on the model and make a final decision on the quality of the graphene. The top four most important features of the model are listed in Figure 5.

Figure 5

Feature ranking: top 4 most influential features on the model's decisions



Source: Author's illustration

Having the feature ranking for the model offers the possibility of producing higher-quality graphene by looking at the tree nodes where a split is done based on some of these features. At each node, a threshold value for the feature is defined based on which, if the value of that feature of the particular graphene is higher or lower than the threshold, a different path (left or right) is taken respectively. By looking at the value in the leaf of that path (where a decision for the graphene quality has been made), one can get a good sense of the range of values of that parameter that result in high (or low) quality graphene.

Discussion

The experimental results demonstrate that the D.T. model is an efficient tool for providing valuable insights into the optimal parameters for graphene production. This is particularly important given the complexity of the process and the need for expert knowledge in nanomaterials.

By combining the results of the D.T. model with domain expertise in nanomaterials, we were able to generate generally applicable guidelines for the optimal production of graphene. These guidelines could be used to produce high-quality graphene for various purposes without requiring expert knowledge or significant expenses on consulting, supervision, and support by experts in the field. This represents a significant advantage, as it could streamline the production process, reduce costs, and increase the accessibility of high-quality graphene for different applications.

The information regarding the feature importance of the model is critical for optimising the graphene production process, as it enables producers to focus on the parameters that have the most significant impact on the quality of the graphene, ultimately leading to more efficient and effective production processes.

Conclusion

In this research, we analysed a machine learning approach to find the optimal values of the key parameters for the production of graphene by electrolysis in molten salts. The electrolysis in molten salts is a simple, ecological, and economical method for producing graphene, and various parameters such as the type of electrolyte, applied voltage, current density, temperature, and type of graphite used as a raw material can be controlled to optimise the production process.

Through the use of an explainable tree-based machine learning model, we were able to extract rules that serve as a blueprint for the optimal production of graphene by electrolysis in molten salts. These rules were obtained by training the model using the production process parameters as input attributes and the quality of the produced graphene as the target variable. Domain experts provided labels regarding the quality of each experimental instance in our data set.

Our proposed method offers a cost-effective alternative to existing technologies, with yields of high-quality graphene up to ten times cheaper than other methods. By following the rules extracted from the machine learning model, one can produce high-quality graphene without the need for expert knowledge or significant expenses on consulting, supervision, and support by experts in the field.

In summary, this research provides valuable insights into the production of high-quality graphene using electrolysis in molten salts and offers a practical solution for achieving optimal production parameters. It is hoped that this work will contribute to the ongoing efforts to develop graphene-based materials for a wide range of applications, including electronics, energy storage, and biomedical devices.

References

1. Alanyalıoğlu, M., Segura, J. J., Oró-Solé, J., & Casañ-Pastor, N. (2012). The synthesis of graphene sheets with controlled thickness and order using surfactant-assisted electrochemical processes. Elsevier (BV).
2. Andonovic, V., Azemi, M. K., Andonovic, B., & Dimitrov, A. (2022). Optimal Selection of Parameters for Production of Multiwall Carbon Nanotubes (MWCNTs) by Electrolysis in Molten Salts using Machine Learning. Association for Advancing Innovation and Research in Economy.
3. Andonovic, B., Ademi, A., Grozdanov, A., Paunovic, P., & Dimitrov, A. T. (2015). Enhanced model for determining the number of graphene layers and their distribution from X-ray diffraction data. Beilstein Institut.
4. Daniya, T., Geetha, M., & Kumar, K. S. (2020). Classification and regression trees with gini index. Union of Researchers of Macedonia.
5. Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene . Springer Science and Business Media (LLC).
6. Geim, A. K. (2011). Nobel Lecture: Random walk to graphene. American Physical Society (APS).
7. Kamali, A. R., & Fray, D. (2013). Molten salt corrosion of graphite as a possible way to make carbon nanostructures. Elsevier (BV).
8. Novoselov, K. S., Geim, A., Morozov, S., Zhang, Y., & Dubons, S. (2004). Electric field effect in atomically thin carbon films. American Association for the Advancement of Science (AAAS).
9. Potdar, K., Pardawala, T., & Pai, C. (2017). A Comparative Study of Categorical Variable Encoding Techniques for Neural Network Classifiers. Foundation of Computer Science.
10. Rao, K. S., Senthilnathan, J., Liu, Y.-F., & Yoshimura, M. (2014). Role of Peroxide Ions in Formation of Graphene Nanosheets by Electrochemical Exfoliation of Graphite. Springer Science and Business Media (LLC).
11. Raju, V. N., Lakshmi, K. P., Jain, V. M., Kalidindi, A., & Padma, V. (2020). Study the Influence of Normalisation/Transformation process on the Accuracy of Supervised Classification. IEEE.
12. Schwandt, C., Dimitrov, A. T., & Fray, D. (2010). The preparation of nano-structured carbon materials by electrolysis of molten lithium chloride at graphite electrodes . Elsevier (BV).
13. Vlassioux, I., Fulvio, P. F., III, H. M., & Lavrik, N. (2013). Large scale atmospheric pressure chemical vapor deposition of graphene. Elsevier (BV).

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