Optimal Selection of Parameters for Production of Multiwall Carbon Nanotubes (MWCNTs) by Electrolysis in Molten Salts using Machine Learning

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Abstract

The production and use of carbon nanotubes (CNTs) have become extremely wide within the last decade. Hence, the high interest in producing non-expensive and quality CNTs has motivated many research projects. This research considers the design and development of new technology for producing MWCNTs by electrolysis in molten salts using non-stationary and stationary current regimes. The electrolysis is simple, ecological, economical, and flexible, and it offers possibilities for accurate control of various parameters, such as applied voltage, current density, or temperature. We infer the underlying relationship between the parameters and the quality of the experimentally produced MWCNTs by using explainable tree-based Machine Learning (ML) models. We train several models in a supervised manner, whereas in model covariates, we use the parameters of the MCWNTs, and as a target variable, the quality of the produced MWCNT. Domain experts label all the experimental examples in our data set. Controlling these parameters enables high-yield production and, particularly important, obtaining MWCNTs, which are up to ten times cheaper than other existing technologies.

Keywords: CNT; electrolysis; graphite; molten salts; machine learning
JEL classification: C61, O31, L61
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Introduction

Carbon nanotubes (CNTs) discovered by Lijima (1991) are promising materials because of their unique and superior electrical, mechanical, and chemical properties. The field of their application has been rapidly growing for the last decade. There is a wide range of applications: energy storage (hydrogen), electrode material in electrochemical capacitors, support component of electrocatalytic materials for fuel cells/hydrogen electrolysers, field emission electron source, fillers in polymer composites, etc.

One of the most promising ways to produce carbon nanotubes is the electrolysis of alkali molten salts. Hsu and co-workers (Hsu et al., 1995) electrolysed molten lithium chloride on a graphite cathode. The cathode erodes during the electrolysis; hence nano-scaled products, including multiwalled nanotubes, were found in the electrolyte. This was the first attempt to produce CNTs in the molten liquid phase. Chen et al. (Kamali et al., 2011) have related cathode erosion and the formation of such products to the intercalation of alkali metals into graphite. This statement was further extended by Fray (Dimitrov 2009) (Schwandt et al., 2010), who realised that the cathodic (carbon/graphite) erosion was similar to the one found in the Hall-Heroult cell (Schwandt et al., 2012). Dimitrov et al. (Dimitrov et al., 2002) reported that the electrolysis at constant voltage, instead of the constant current electrolysis, could improve the process and increase the yield of produced CNTs. Some of such produced carbon nanomaterials, containing about 30 vol. % CNTs, were tested as an electrode in a lithium-ion battery. A charge-discharge capacity was 15% higher related to the standard carbon materials, but the life of the charge-discharge cycle needs to be improved.

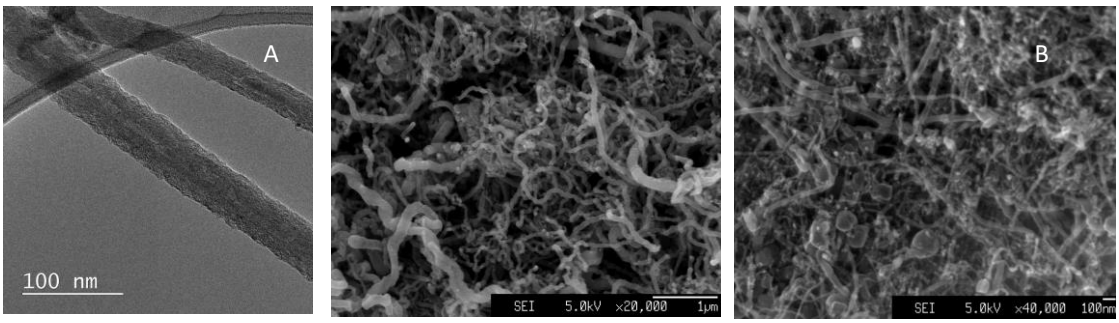
The relationship between the quality of an experimentally produced CNT using the electrolysis in molten salts method and the experiment parameters are hard to model. A growing number of experimentally produced CNTs under different conditions opens possibilities for a data-driven modeling approach. Data science and machine learning techniques have been widely used to model certain phenomena while bridging the need for an exact physical model that completely describes the relationship between different parameters and the target variable. Examples of applications of machine learning algorithms on scientific problems come from different fields – ecology (Ghannam & Techtmann, 2021), biology (Xu & Jackson, 2019), civil engineering (Vadyala et al., 2022), labor market modeling (Andonovikj et al., 2021), etc. In the literature, there is also a wide range of applications of Deep Learning (DL) approaches to solve this problem end-to-end. Still, usually, these models require a large amount of data (rough estimation is more than 100 000 experimental data) which is too expensive to obtain.

Conversely, classical machine learning algorithms, especially the ones whose base is a tree model, have proven successful in many applications with a small dataset (less than 100 experimental data). One big advantage of the tree-based methods over the DL approaches is that they are easily interpretable. One can easily extract separate rules guiding a final decision based on the input parameters. This is quite an important factor considering the nature of the problem since, through these rules, one can understand the importance of the parameters and the way they influence the quality of the CNT.

The aim of this work is the optimisation of the production process of MWCNTs by electrolysis in molten alkali salt by applying machine learning algorithms on laboratory data, such as applied voltage, current density, temperature, and morphology of starting material. This opens a direction for further research in

characterising obtained CNTs by SEM (scanning electron microscopy), TEM (transmission electron microscopy), and Raman spectroscopy.

Figure 1
A. TEM images; and B. SEM images of MWCNTs produced at the Faculty of Technology and Metallurgy in Skopje, North Macedonia



Source: Author´s work

In Fig. 1 (A, B), one may observe TEM and SEM images of MWCNTs of undetermined diameter and/or chirality produced in the Lab for Nanomaterials and Nanotechnologies at the Department of Extractive Metallurgy, Faculty of Technology and Metallurgy in Skopje via electrolysis in molten salts. Due to the consideration that the electrochemical route offers a possibility for accurate control of the mentioned various parameters, it is expected that performing such optimisation provides that the yield and quality of CNTs could be improved.

Methodology

Multi-wall carbon nanotubes are produced by electrolysis in molten salts applying stationary and non-stationary current regimes, and a corresponding machine learning algorithm analyses the obtained data.
The decision Tree (D.T.) model is trained to classify the experimentally produced CNTs into one of three possible classes: *1,2,*3. The classes estimate the quality of the CNTs, such that a higher class number represents better quality in terms of higher yield and decreased defects. The rules derived from the trained D.T. model are used to optimise the production of low-cost, high-quality CNTs at a large scale.

Before training the model, several data preprocessing steps were performed to make the data suitable as input to the D.T. model. The preprocessing of data and modeling were performed in Python by making use of its modules like pandas, NumPy and sci-kit learn.

First, normalisation of the features' values was applied to scale the attributes so that their mean value is zero, and their variance is retained with their standard deviation. It allows equality of opportunity for each attribute. By this, no feature gives more value to itself regarding the range of values it has. Several normalisation techniques are commonly used; in our case, we used the Standard Scaler, defined as:

$$z = \frac{x - \mu}{s} \tag{1}$$

where x is the actual value of the feature, μ is the mean, and s is the standard deviation.

Most of the machine learning algorithms implemented in Python require all the features to be in numerical form. The encoding technique must be applied to convert the absolute values into approximative numeric form. One-hot-encoding (Potdar et al., 2017) was applied, where each label (categorical value) of the feature is converted into a new categorical column with a binary value (1 or 0) assigned to it.

The modeling procedure begins by splitting the dataset D into X and Y, where $X = \{X_1, X_2, \dots, X_n\}$ is the feature matrix representing the values for the parameters of the CNT, and $Y = \{y_1, y_2, \dots, y_n\}$ is the vector containing the classes for the respective CNTs. A pair of the form (X_i, y_i), where $i = 1, \dots, N$, describes a single instance of a CNT used for model training.

The model training aims to find the optimal partitioning of the input variable space, which in our case, is defined by the parameters of the CNTs, to minimise a predefined cost function. The splitting starts at the tree's root node, where all of the instances of the dataset are present. Then, at each internal node, the inference method for the tree splits the training set pertinent to the node to maximise a splitting criterion. The split uses a single feature (CNT parameter) from the training set and forms a condition on the value of this feature that evaluates to true or false. The condition splits the data D into two data sets, each pertinent to one of the two siblings of the node. This procedure results in a binary tree. The node splitting criteria are related to a predefined cost function or estimated error. The cost of splitting is estimated for each of the resulting sibling nodes and then weighted according to the probability that the data instance will fall in one of the two constructed regions.

$$cost(node, criterion) = \frac{|D_L|}{|D|} cost(D_L) + \frac{|D_R|}{|D|} cost(D_R) \tag{2}$$

There are several different splitting criteria used in classification problems. In our procedure, Gini Index (G.I.) (Daniya et al., 2020) is used, given by the following relation:

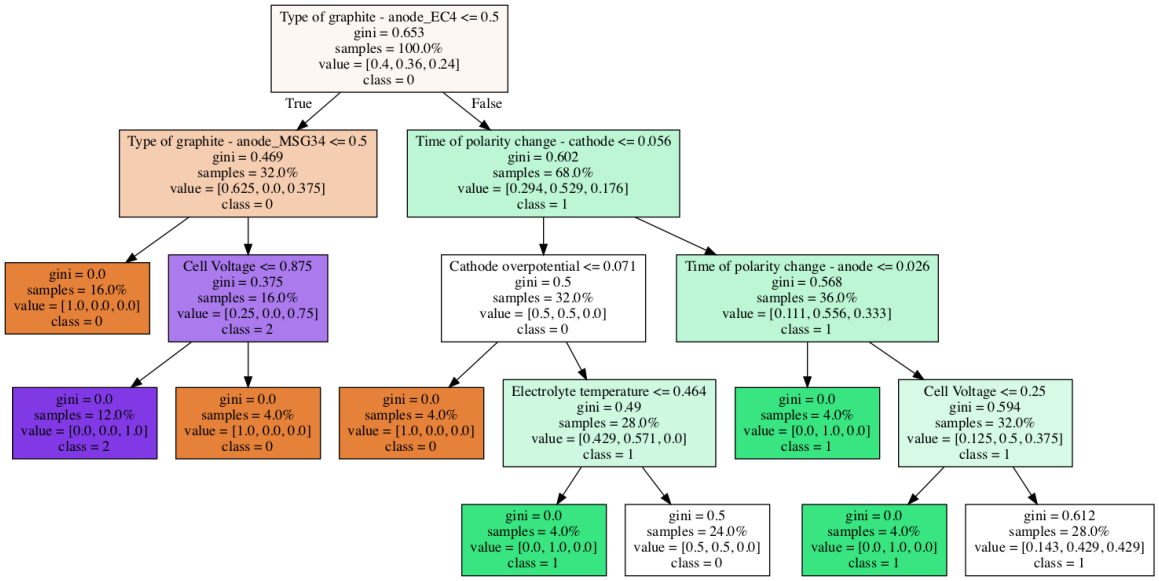
$$\sum_{c=1}^{C} P_c(1 - P_c) = \sum_{c} P_c - \sum_{c} {P_c}^2 = 1 - \sum_{c} {P_c}^2 \tag{3}$$

where P_c is the probability a random entry in the leaf belongs to class c, and $1 - P_c$ is the probability for this entry to be misclassified. In each node, the objective is to minimise the G.I., ending with the optimal split for that node.

Results and discussion

The model's performance was tested on a fraction of the original dataset, called a test set. The test set contains randomly chosen 30% of the data instances of the original dataset, while the other part, called a training set, was used for training the model. Classification accuracy was used as a performance metric. The resulting D.T. obtained by training the model on the training set is given in Figure 2.

Figure 2
Visual representation of the final Decision Tree model



Source: Author´s Work

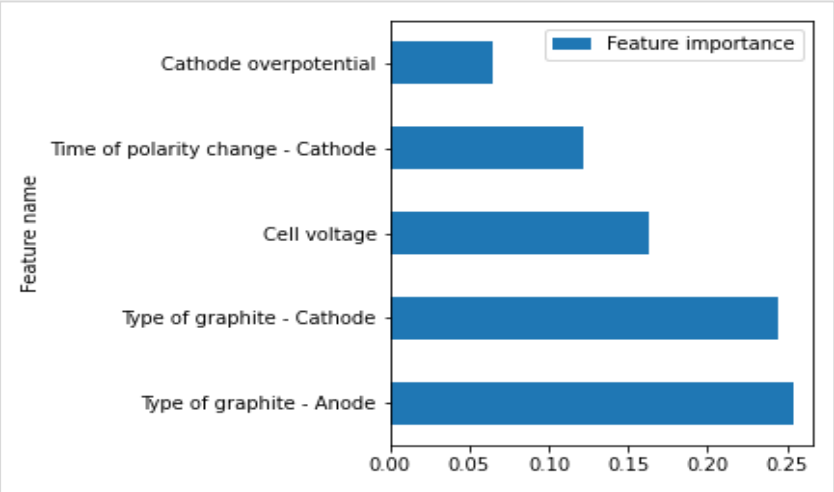
All paths, starting from the root and leading to a tree leaf, represent a single rule. The rules can be extracted by logically following the path from the root to a certain leaf ANDing the splitting criteria. By looking at those rules, one can see how the model reaches the final prediction. The following are an example of rules extracted from the model. They are aligned with the theoretical foundations of nanomaterials and the knowledge of experts in the field. There is at least one rule that characterises each of the possible quality labels of the CNT:

- If the type of the graphite of the anode is not EC4 and the type of graphite of the cathode is not MSG34 => the yield of the CNT is low (quality = 1)
- If the overpotential of the cathode is lower than 4,5V => the yield of CNT is highest (quality = 3)
- If the time of polarity change of the cathode is lower than 35s and the cell potential is lower than 2,8V => the quality of the CNT is estimated as 1 (quality = 2)

Analysing those rules with domain expertise in nanomaterials can lead to either acceptance or rejection of the rule. This may lead to the generation of generally applicable guidelines for the optimal production of CNTs. This is important since one can use those rules to produce quality CNTs for different purposes without needing expert knowledge or significant expenses on consulting, supervision, and support by experts in the field.

Besides the extraction of rules, it is possible to calculate the feature importance of the model. The feature importance allows us to rank the parameters of the CNT according to their influence on the model to make a final decision on the quality of the CNT. Feature importance is calculated as the decrease in node impurity weighted by the probability of reaching that node. The node probability is calculated as the number of examples that reach that node divided by the total number of examples. A higher value means higher feature importance. Figure 3 lists the five most important features of the model.

Figure 3
List of the five most important features of the model



Source: Author´s work

Having the feature ranking for the model offers the possibility to produce higher-quality CNTs 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 CNT 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 CNT 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 CNT.

Conclusion

The electrochemical method is a cheap and reliable method of obtaining MWCNTs. It is hard to control the parameters that influence the quality of the MWCNTs without expensive equipment or constant supervision by experts in the field. By leveraging the datasets gathered from experimentally produced CNTs, it is possible to learn a model which can guide and optimise the process of production of CNTs. The aim of obtaining high-yield MWCNTs with improved quality and highly decreased defects is reached by leveraging the explanatory power of symbolic machine learning algorithms. Performing the latter, a leaned decision tree model is produced, which can characterise CNTs, while also providing information about the relationship between the quality of the CNT and the input parameters. The experimental results from the model highly correlate to the theoretical basis from the experts in the field. Thus, by following the descriptive rules from the model, which achieves 80% accuracy in characterising, it is possible to obtain more optimal CNTs by electrolysis in molten salts.

Furthermore, the rules from the model can assist in producing CNTs from the quality level which is least present in the dataset. This can further enlarge and improve the dataset to retrain and improve the current model's performance. Therefore, this model gives us a valuable novel tool in producing certain quality high-yield MWCNTs, which can be later used and widely applied.

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