IMPROVING SUPERCAPACITORS USING MACHINE LEARNING

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A capstone project submitted for Graduation with University Honors

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ABSTRACT

Energy storage devices are an important aspect of contemporary life. Lithium-ion batteries currently dominate the market, but the search for alternatives continues as improvements are desired. For this reason, research on supercapacitors is an option. While currently not being able to replace them, they serve a different purpose, for example, in train brakes and elevators. A lot of research has been done on carbon-based supercapacitors, but much less research about MXene-based supercapacitors is present. Moreover, the machine learning approach instead of a physical design approach had not been implemented. For this reason, four different machine learning models are tested: generalized linear regression, support vector machine, random forest, and artificial neural network. In the experiment, the artificial neural network model was the most efficient at predicting the specific capacitance of the supercapacitors. Furthermore, from this result, the artificial neural network model was used to test the accuracy of the prediction at different scan rates, which was successful. The training data of the machine learning model was also demonstrated. Finally, deep learning was applied to a larger scale MXene structure for quantum mechanics accuracy, which was able to predict the adsorption of water molecules. Ultimately, machine learning was shown to be a reliable method to predict the performance of MXene-based supercapacitors and lead to future optimizations to achieve higher efficiency in energy storage.

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1. INTRODUCTION

1.1 Energy Storage Devices

An energy storage device's objective is to convert electric power to another form of energy storage, which it can reconvert back to electricity when in demand. There are a variety of methods available for the conversion: thermal, mechanical, electrical, chemical, and electrochemical. From these methods, there are multiple energy storage devices available, some which are more efficient, others which have different usages, some which are outdated, and lastly, some which are still being researched and improved. Three of them will be focused on: Lithium-ion batteries, capacitors, and supercapacitors.

A lithium-ion battery is a type of rechargeable battery and is currently the most common type of battery used in smartphones and laptops due to their high capacity and reliable charging and discharging speeds. It consists of an anode, cathode, electrolyte, and separator. Lithium ions are stored and released from the electrode materials during charge and discharge. The ions move through the electrolyte, and the separator is a safety measure to prevent direct contact between the anode and the cathode, while still allowing ion movement. Some advantages of lithium-ion batteries include their reasonable durability. This is taking into consideration the battery degradation over time. The biggest advantage however is the capacity and charging speed, which will be further explained in the next section.

Capacitors operate differently from Li-ion batteries. They instead store energy through an electric field. They aid in the delivery of short amounts of energy to prevent an immediate shortage of energy. They consist of two conductive surfaces and a separator to avoid contact between them. Due to their extremely small capacity, capacitors have a much different usage

from lithium-ion batteries. Instead of powering devices, they can help power sections of the devices in case of power failure.

Supercapacitors are in a different category of energy storage devices. Due to their high reliability and discharge speed, they are essentially used when high bursts of power are demanded, for example in transportation devices ranging from cars, trains, and elevators. Supercapacitors are separated into different categories: electric double-layer capacitors, pseudocapacitors (PC), and hybrid supercapacitors (HSC). In this project, the main focus will be EDLCs. Similar to a lithium-ion battery, an EDLC is composed of an anode, cathode, electrolyte, and a separator, but with a few important distinctions. The electrodes are identical and as such, they are also known as symmetric supercapacitors. The electrolyte allows ions to move between the electrodes, while the separator insulates the system, but also allows ions to pass. Lastly, how energy is stored in between the interface of the electrode and electrolytes. By containing separated charge layers, while no chemical reaction occurs, the sole factor considering energy storage is the transport of ions in the electrolyte solution or electrons through the electrodes. This is the main reason for its reliability and longevity. The main advantage of EDLCs is the durability. Smartphone batteries degrade as they are constantly charging and discharging, lowering the total capacity of the battery. It is relatively good considering that the average consumer in the United States only uses their phone for 2 years before upgrading it. But EDLCs can sustain millions of cycles and still retain most of their capacity.

1.2 Ragone Plot

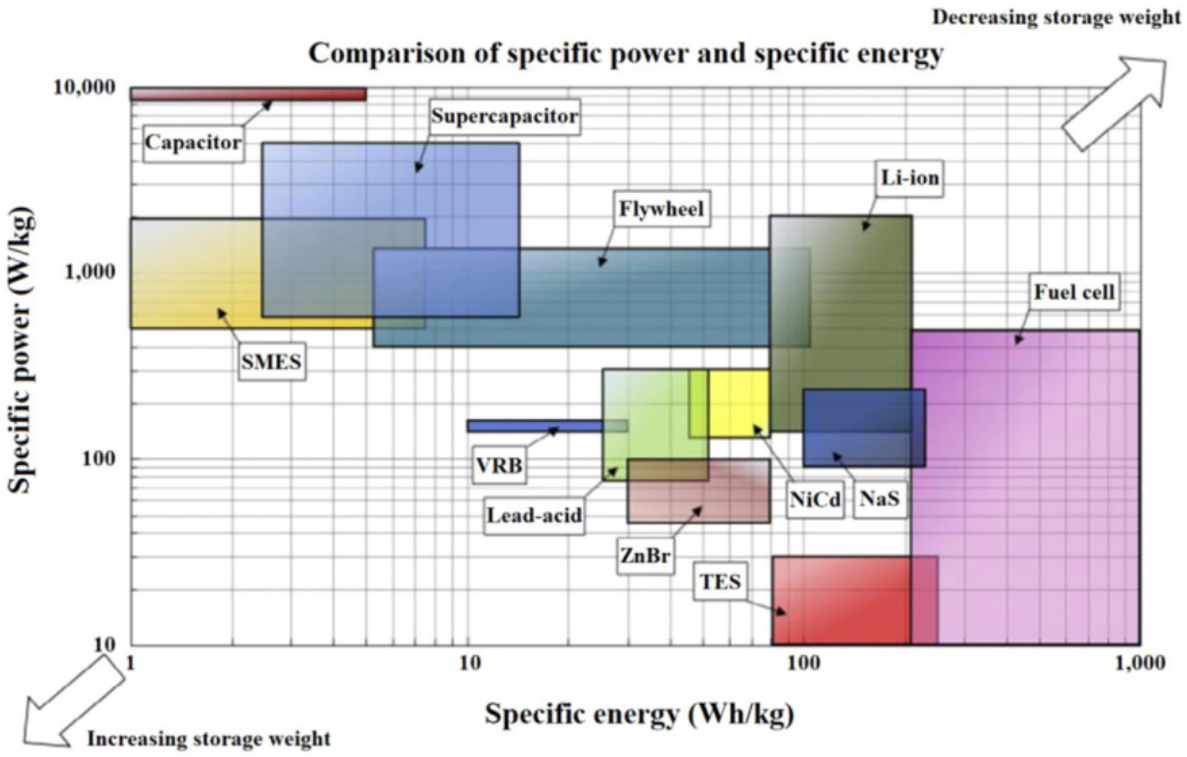

Figure 1: Ragone plot

Figure 1 contains a Ragone plot. It is used to compare the performance of different energy storage devices. In this Ragone plot, the y-axis is the power density (specific power), which is the power per cell mass or volume. The x-axis is the energy density (specific energy), which is the energy per cell weight or volume. The difference between them is that energy density is the amount of energy that can be stored in the device, while power density is the speed at which the energy can be delivered. Simply put, energy density is the capacity of a battery, and power density is how fast it can charge and discharge. An important aspect of the Ragone plot is that the axes are in logarithmic scale, therefore, comparisons are made with much larger differences than a standard scale. The three energy storage devices being compared are the lithium-ion batteries, the capacitors, and the supercapacitors. Lithium-ion batteries can have up

to 30 times higher energy density than EDLCs, while supercapacitors can have up to 1000 times higher power density. This means that lithium-ion batteries have higher capacities than supercapacitors, while supercapacitors can output their energy at a much higher rate, both while charging and discharging. Capacitors have the lowest energy density while having the highest power density. In this case, supercapacitors are a middle ground between a lithium-ion battery and a capacitor both in terms of energy and power density.

Currently, lithium-ion batteries are the best option in terms of a balance of energy density and power density. However, the research on alternatives is prevalent and improvements are always desired. In the field of energy sources, a large portion of renewable energy can't be used instantaneously and instead, has to be stored. Due to the lack of energy storage devices to store said energy, it is instead used to produce renewable fuels. This process is inefficient because of the secondary step. This is an example of the need for better energy storage devices.
The improvement of supercapacitors could potentially lead to better energy storage devices than lithium-ion batteries.

1.3 Objective and Decisions

With the main objective of maximizing energy and power density, the components of supercapacitors can be analyzed to understand the effects of changes. As previously mentioned, electrolytes affect how ions move between electrodes. One of the reasons that the energy density in supercapacitors is low is due to the possible decomposition of the electrolyte at higher voltages. A better electrolyte would allow higher operating voltages and thus, increase energy density. As for the electrodes, by containing separated charge layers, while no chemical reaction occurs, the sole factor considering energy storage is the transport of ions in the electrolyte

solution or electrons through the electrodes. This defines the high power density of EDLCs. Also, for this reason, they require electrode materials with a high specific surface area, high capacitance, and high electrical conductivity to maximize power density.

For these highly intricate designs of supercapacitors with very specific properties, a physical design for testing purposes would not be appropriate. Other models that are commonly used for the charging and discharging of energy storage devices, but due to the intrinsic properties of the electrodes, the models are not a good application. Machine learning (ML) methods can be used as an alternative to physics-based approaches. As the name suggests, ML is the usage of machines, coding, and algorithms to learn about a topic. With enough training data, ML methods can establish connections between material properties and performances without the need for physical details. As ML is not a physics-based model, it uses computer algorithms to improve automatically and narrow down the results, extracting correlations between the input and output variables from existing data.

Currently, a lot of research has been done on carbon-based supercapacitors and other electrolytes. However, there are other possibilities of materials to be used for the electrodes. MXene-based electrodes have been researched but not to the same extent as carbon-based ones. For the machine learning approach to this problem, MXene is one of the materials that has yet to be researched. MXenes are two-dimensional ceramics made of transition metals and a nonmetal. Theoretically, MXene based supercapacitors have the potential to have a much higher energy density than the traditional electrode due to the physical properties of the material.

2. METHODS AND MODELS

2.1 Machine Learning Models

Many different machine learning models lead to different results and for this reason, a variety of them will be used to check which gives the most reliable and accurate results. To start, the data will be gathered. As no practical experiment will be made and just machine learning models will be created, the data acquired will be from other papers.

Generalized linear regression (GLR) is a generalization of linear regression. It creates a connection between the linear model with a function to allow the succeeding variables to be a function of a predicted value. Therefore, with an input, the output will be predicted and produce a curve fitted based on the function.

A support vector machine (SVM) is a machine learning model that uses an algorithm to predict based on a training example, with two different categorical variables. The algorithm then assigns new inputs into the categories and finalizes the results.

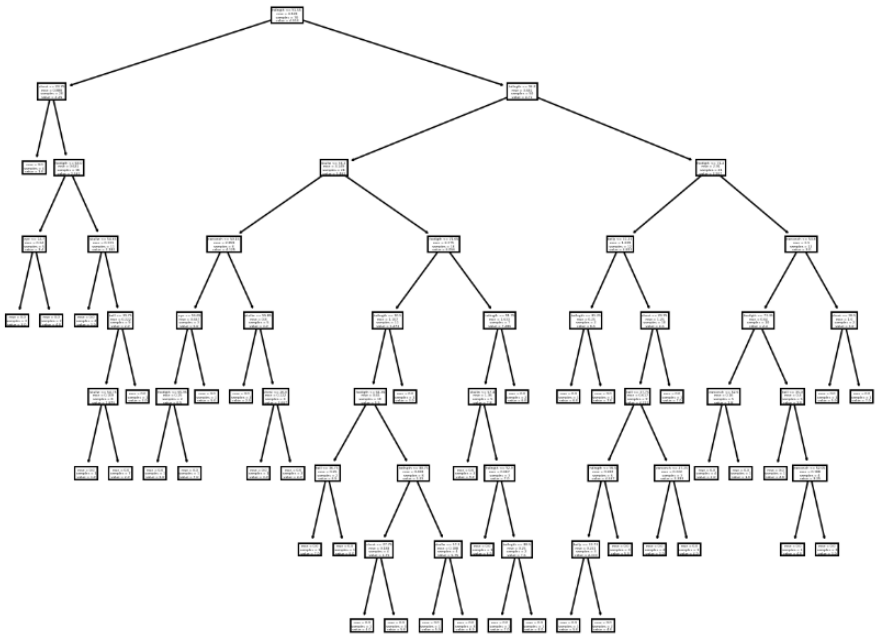

Figure 2: Decision Tree Example

The regression tree (decision tree) is another machine learning model based on tree branches. The branches being the observations and the leaves being the result. In a regression tree, it is simpler to view the parameters compared to other machine learning models. Starting from certain inputs, the data will follow the branches to reach an output. In this experiment, the random forest model will be used, which are multiple trees that provide multiple outputs, with the final result being the average between them.

A multilayer perceptron is a type of feedforward artificial neural network. In other terms, instead of achieving results based on the inputs, the outputs are predetermined and the inner parameters guide the input.

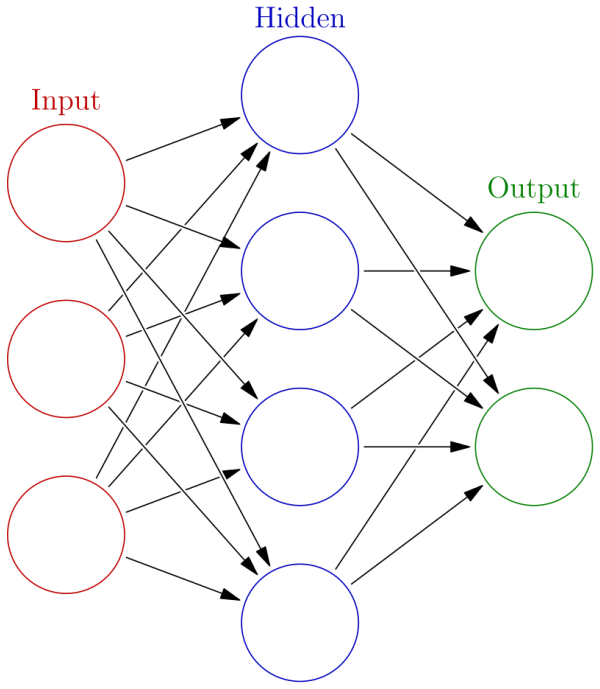

Figure 3: Artificial Neural Network basic schematic

An artificial neural network (ANN) is a type of machine learning model based on algorithms and it simulates a brain. Starting with the inputs, they are connected to nodes, also

known as hidden layers, which continuously emit signals to other nodes to reach an output. Training is done by providing inputs and changing the nodes to achieve a known output.

DeePMD is a python package written to simplify the usage of machine learning of interatomic potential energy and force fields for molecular dynamics (MD). It is similar to the artificial neural network, but instead of only having one hidden layer, DeePMD contains more than one hidden layer. The main difference between deep learning and machine learning is that while deep learning is still a machine learning method, instead of being built around structured data (in this case the database), deep learning is instead using more of the hidden layers to generate the output.

2.2 Database Construction

The machine learning database was constructed using information from other research papers. Not any paper about supercapacitors could be used. For the experimental values, the information needed includes BET surface area, which is a measure of the adsorption of gas molecules to the surface of the material. With the surface area being one of the most important factors regarding the power density of the supercapacitor, a factor that maximizes it is the pore size. Mesopore size was another value needed from the research papers. It is a pore in the material with a size between 2 nm and 50 nm. Micropore size was also needed, which is a pore in the material with a size lower than 2 nm. Lastly, the cyclic voltammetry (CV) curves at different scan rates were needed. A CV curve is created from the cycling of potential of an electrode and measuring the current. Different scan rates produce different CV curves. The graph then can be used to calculate the capacitance of the electrode. Finally, the scan rate is the rate of

potential change over time. With all this information in a research paper, the data could be used to calculate the specific capacitance and it was added to the database.

A crucial concept to understand before moving into the results is how machine learning is able to correlate the electrodes with their performance. Starting with the inputs, which are the BET surface area of the micropores and mesopores, and the scan rate, they are recorded for each of the electrode specifications and used for one input set. Using the database to train the machine learning algorithms, each of the machine learning models will provide a different output for each input. The predicted outputs of each model are then compared to experimental data from other papers.

3. RESULTS AND DISCUSSION

3.1 Comparison of Four Machine Learning Models

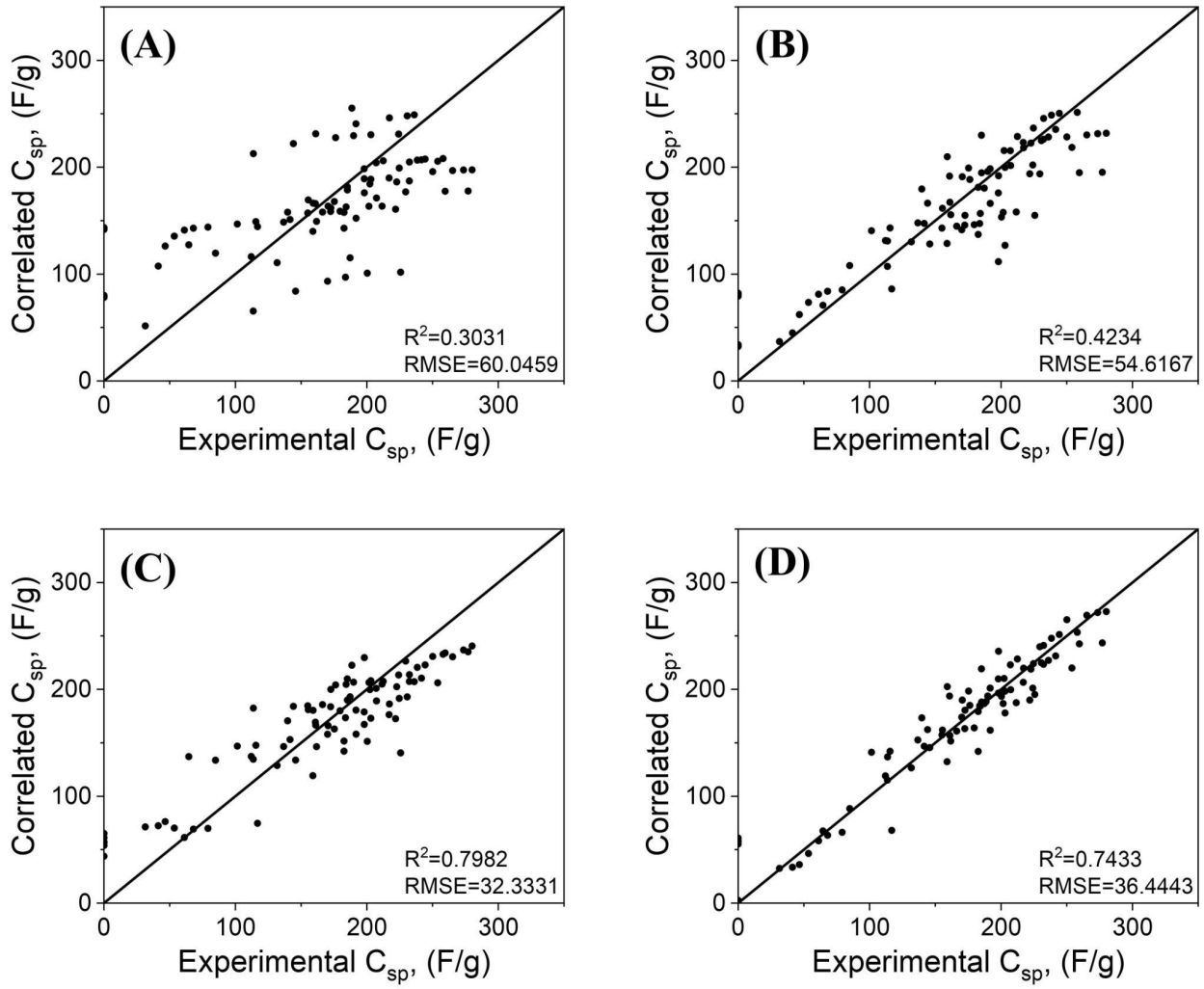

Figure 4: Graphs of experimental specific capacitance (C_{sp}) compared with results from machine learning models: (A) Generalized linear regression (GLR), (B) Support vector machine (SVM), (C) Random forest (RF), (D) Artificial neural network (ANN). The diagonal line represents a perfect correlation between the experimental result and the machine learning result.

In figure 4, the results show the comparison between experimental values and the machine-learning counterparts of the specific capacitance. The R^2 value is the coefficient of

determination and it expresses the variance of one variable compared to the other. For example, a value of 1 means that all the values can be explained using the model, and a value of 0 means that none of the values can be explained using the model. The RMSE value is the root-mean-square error, which takes into account the standard deviation of the prediction errors. In figure 4A, the clear worst performing machine learning method is the generalized linear regression, both seen in the low R^2 and high RMSE values, and in the graph itself, with the scattering of the data points. At first glance, it might seem that the random forest model is the most accurate. However, due to a few inherent problems with the model, such as random forest having problems with extrapolations, or values that are not within the dataset. This is the case when the capacitance approaches zero, which has most of the data points further from the line. As such, the final result is not a smooth prediction as it contains many irregularities. For this reason, an artificial neural network is used as the machine learning model for this experiment. From the results of this experiment, an artificial neural network is further used for the following experiments.

3.2 Machine Learning Prediction at Different Scan Rates

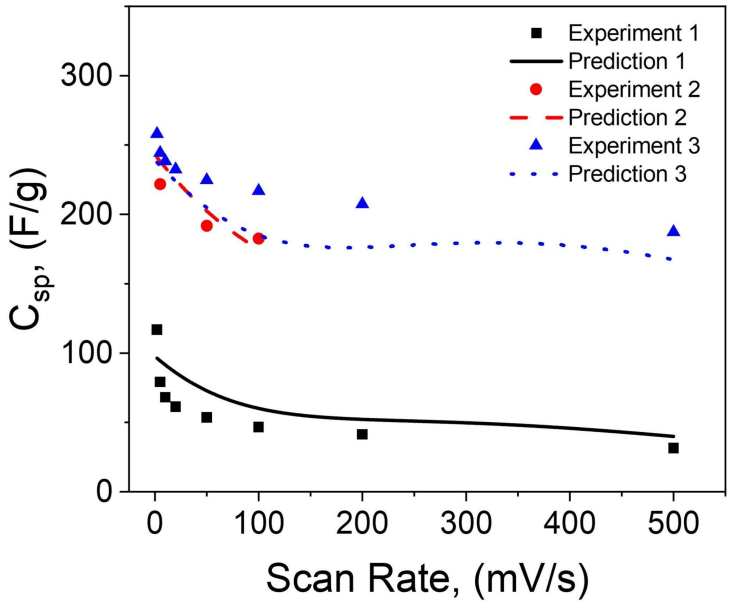

Figure 5: Experimental and machine learning model (ANN) specific capacitance (C_{sp}) over different scan rates. Three different datasets are tested.

For figure 5, the experimental and predicted specific capacitances are compared at different scan rates. The electrodes have different physical properties in each case, with the difference being the surface area of the pores. The most important factor in this figure is the change in specific capacitance as the scan rate increases. The scan rate dictates the duration of charging and discharging of the supercapacitor, which is inversely proportional to the capacitance measured. Thus at lower scan rates, the capacitance is higher than at higher scan rates. This is seen in all three experiments. One thing to note is that in physics-based models of energy storage devices, the experiments are done at the scan rate in equilibrium conditions, while the energy storage device is operating at non-equilibrium. This causes a discrepancy between the values from the model and the experimental value. An example of where this problem occurs is at lower scan rates, where a physics-based model would not provide a good prediction of the

result. This is not the case for the artificial neural network model, which is able to predict the values regardless of the physical condition. Despite the prediction not being completely accurate, as in overshooting the capacitance in experiment 1 and undershooting the value in experiment 3, the prediction follows the trend of the experimental capacitance. The artificial neural network model was successfully able to predict the specific capacitance.

3.3 Training and Validation of Artificial Neural Network Model

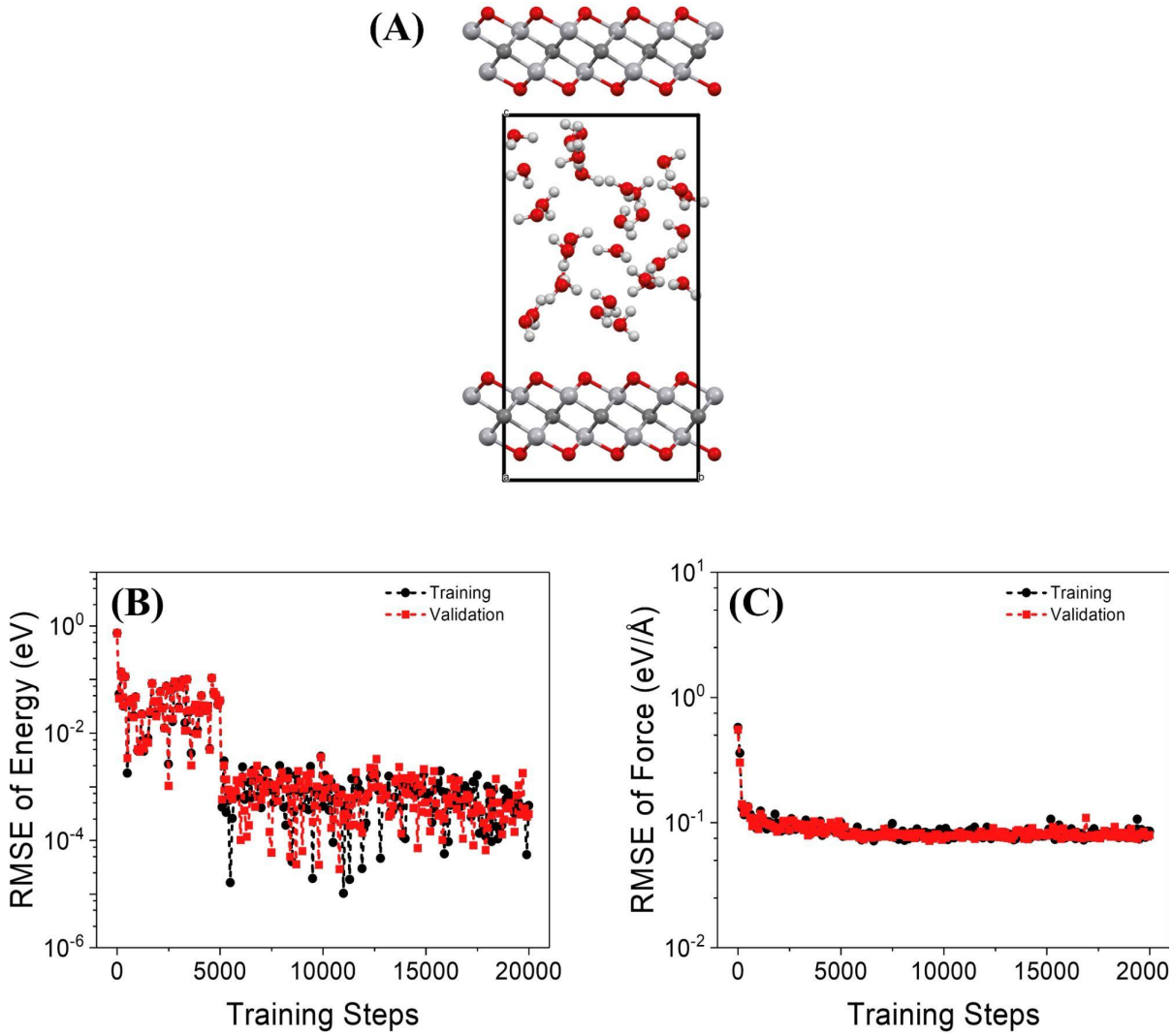

Figure 6: (A) Schematic structure of the MXene molecule, (B) Root-mean-square error of energy (eV) of the training and validation steps. (C) Root-mean-square error of force (eV/Å) of the training and validation step.

Figure 6A shows the structure of the MXene molecule being tested. For this, the training and validation steps are shown. Starting with training, a dataset is used to train the artificial neural network model to learn the trend and output unbiased and predictable results. The validation step takes into account the general trend of the output and validates whether there is an impossible output. For example, if a test result expects a value below 100 and someone scores 105, the validation step would take into account and fix the mistake. The training data was obtained from Ab Initio Molecular Dynamics (AIMD), a simulation of complex molecular systems. In figures 6B and 6C, it might seem that the force values are much more accurate than the energy, however, it is important to take into account the scale of both results. The y-axis of the force graph has a magnitude ranging from 10^{1} to 10^{-2}. Comparatively, the y-axis of the energy graph has a magnitude ranging from 10^{0} to 10^{-6}. This large difference makes results seem less accurate, but both graphs have similar results over the data training and validation.

3.4 Deep Learning (DeePMD) for Larger Structure of MXene

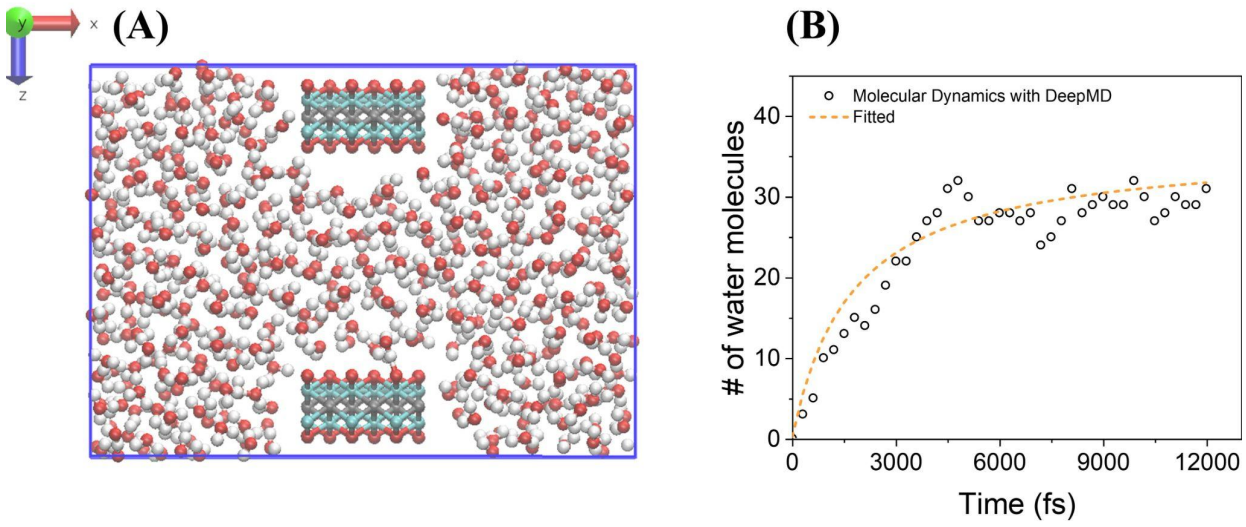

Figure 7: (A) Schematic structure of MXene ($Ti_3C_2O_2$) on a larger scale, (B) DeePMD prediction of adsorption of water molecules over time.

Lastly, figure 7A contains another schematic with a much larger scale of MXene molecules. This experiment is done for quantum mechanics accuracy. In general, quantum mechanics is used to calculate the properties and behavior of physical systems. This is required in this case because it is dealing with extremely small structures, in this case, for the molecules of MXene. Moreover, since the surface area and pore sizes is an integral part of the calculations, calculations for the microscopic structure is needed. Figure 6A had a much smaller scale compared to figure 7A, which leads to different results. As such, the deep learning (DeePMD) machine learning model is used to accurately predict the adsorption of water molecules onto the surface of the electrode. Figure 7B shows how the number of water molecules adsorbed increases over time, with a more rapid increase at first and plateaus at the end. The deep learning model is able to correctly predict the trend of the adsorption for a highly specific system.

4. CONCLUSION

From the four different experiments carried out, a few conclusions can be drawn. Firstly, the comparison between four machine learning models: generalized linear regression, support vector machine, random forest, and artificial neural network. Despite higher R^2 and lower RMSE values for the random forest model, due to inaccuracies, the best model to predict the specific capacitance of the electrodes is the artificial neural network. Following this decision, the artificial neural network model was used to compare experimental results with the predicted results at different scan rates. The model was successfully able to predict even the specific capacitance at low scan rates, which is a problem for physics-based models. The training and validation steps of the artificial neural network model are also provided. A deep learning model is used for the larger schematic of the MXene structure, which was able to predict the trend of the adsorption of water molecules onto the surface. With all this information, a correlation between the physical properties of MXene and the supercapacitor performance was drawn using machine learning. This can help inverse-design MXene as an electrode material for supercapacitors, and be used to further improve the efficiency of supercapacitors.

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