

MULTI-SCALE MODELLING OF SUPERCAPACITORS: A COMBINED
SIMULATION AND MACHINE LEARNING APPROACH

by

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ABSTRACT

MULTI-SCALE MODELLING OF SUPERCAPACITORS: A COMBINED SIMULATION AND MACHINE LEARNING APPROACH

Electrical double layer capacitors (EDLCs) store and release energy via reversible adsorption/desorption of ions at the electrode–electrolyte interface. Research on EDLCs mainly focus on improving their energy density while maintaining their attractive properties such as high power density and long cycle life. EDLC performance is a complex function of the properties of its components, as well as the interactions between them. Given the large number of parameter combinations make traditional experiments remain infeasible for parameter optimization. To address this problem, we use molecular dynamics simulation data for a set of room temperature ionic liquid/nanoporous carbon based EDLCs. By analyzing the charging kinetics and equilibrium behavior of EDLCs using a transmission line model, we construct a simple data-driven method that is capable of quantitatively predicting energy density and time-dependent charging profile as a function of electrode micropore size and electrolyte composition. In particular, linear and ridge regression, elastic networks, lasso, and neural network models are trained to predict gravimetric and volumetric capacitance (C_G and C_V), charging time (τ_M), and electrical resistance (R_l). The elastic network model yields the best performance with a root mean square error of 3.10 F/g (C_G), 0.15 s (τ_M), 1.09 F/cm³ (C_V), and 0.54 Ohm m (R_l). This model is then used to construct diagrams that show the dependence of the above-mentioned performance metrics to electrode pore size and electrolyte composition, and allow designing EDLCs with a set of predetermined performance criteria. This work can be extended to provide a framework that can quantify the effect of key factors on the EDLC performance.

ÖZET

SÜPER KAPASİTÖRLERİN ÇOK ÖLÇEKLİ MODELLENMESİ: MOLEKÜLER SİMÜLASYON VE VERİ TABANLI TASARIM

Elektrikli çift katmanlı kapasitörler (EDLC'ler) elektrolit ve yüksek yüzey alanlı elektrot arasındaki arayüzde iyonların tersinir adsorpsiyon/desorpsiyonu yoluyla enerjiyi depolar ve serbest bırakır. EDLC'ler üzerinde yapılan araştırmaların ana odağı mevcut güç yoğunluğunu ve işlem ömrünü korurken enerji yoğunluğunu artırmaya yöneliktir. EDLC performansı, bileşenlerinin özelliklerinin yanı sıra bunların arasındaki etkileşimlerden de etkilenen karmaşık bir sisteme bağlıdır. Bu parametreler ve kombinasyonlarından oluşan olasılıklar deneysel yöntemleri ya da simülasyonları optimizasyon için yetersiz ve etkisiz kılmaktadır. Bunu çözmek için, bir dizi oda sıcaklığında iyonik sıvı ve nanogözenekli karbon bazlı EDLC'ler için moleküler simülasyon verileri oluşturuldu. Bir iletim hattı modeli kullanarak EDLC'lerin şarj kinetiğini ve denge davranışını analiz ederek enerji yoğunluğunu ve karakteristik şarj/boşalım süresini elektrot gözenek boyutu ve elektrolit özelliklerinin fonksiyonu olarak tahmin edebilecek modeller oluşturuldu. Lineer regresyon, ridge regresyon, elastik ağlar, lasso regresyon ve yapay sinir ağları kullanarak ağırlıksal kapasitans (C_G), şarj süresi (τ_M), hacimsel kapasitans (C_V) ve direnç (R_l) tahminleri yapıldı. Elastik ağ modeli, 3,10 F/g (C_G), 0,15 s (τ_M), 1,09 F/cm³ (C_V) ve 0,54 Ohm m'lik (R_l) bir kök ortalama kare hatasıyla en iyi performansı verdi. Bu model performans ölçütlerinin elektrot gözenek boyutuna ve elektrolit bileşimine bağımlılığını gösteren ve seçilen performans kriteriyle EDLC'lerin tasarlanabileceği aralıkları gösteren tasarım haritaları oluşturmak için kullanıldı. Bu çalışma, diğer faktörlerin de performans parametreleri üzerlerindeki etkilerini gözlemlemek için genişletilebilir.

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LIST OF SYMBOLS

A	Area of the electrode
C	Capacitance
C_G	Gravimetric capacitance
C_{max}	Maximum capacitance
Co	Conductivity
C_T	Total capacitance
C_V	Volumetric capacitance
e	Electric charge
ED	Energy density
ED_G	Gravimetric energy density
ED_V	Volumetric energy density
I	Identity matrix
IF	Ion fraction
k_B	Boltzmann constant
l	Length
l_{macro}	Thickness of a macro scale electrode
l_{sim}	Thickness of electrodes in simulations
N	Number of observations
PD	Power density
Por	Porosity
PS	Pore size
R	Resistance
R_{bulk}	Bulk electrolyte resistance
R_l	Electrode side total resistance
R_s	Equivalent series resistance
Q	Charge
Q_i	Initial charging
Q_{max}	Maximum charging value obtained

Q_T	Total charge
T	Temperature
t	Time
V	Applied voltage
α	Regularization strength hyperparameter
β	Regression coefficient
ϵ	Error
κ	Conductivity
λ	Regularization parameter
ρ	Density
Δ	Difference or change
X^T	Transpose of a vector

LIST OF ACRONYMS/ABBREVIATIONS

ACN	Acetonitrile
ANN	Artificial Neural Network
CDC	Carbide-Derived Carbon
EDLC	Electrostatic Double-Layer Capacitance
HLS	Hidden Layer Size
R^2	Coefficient of Determination
RMSE	Root Mean Square Error
RTIL	Room Temperature Ionic Liquid
SVM	Support Vector Machines
TLM	Transmission Line Model

1. INTRODUCTION

Supercapacitors are electrochemical energy storage devices that store and release energy via reversible adsorption and desorption of ions at the interface between an electrolyte and a high surface area electrode material [1–4]. That ion exchange leads to high power density and long cycle lives [5–8]. Supercapacitors are able to store up to a hundred times more energy per unit volume or mass than their electrolytic counterparts. They accept and deliver charges much faster than batteries and used in various systems and applications that require fast charge and/or discharge [9]. Supercapacitors are able to tolerate significantly more cycles of charging and discharging. Energy is stored in the form of electrical charges in a supercapacitor, while a battery stores its energy in a chemical form. Electrochemical energy storage devices that store energy through redox reactions yield greater energy densities, in other words capable of storing more energy per weight, than supercapacitors. However, the power density of batteries is smaller than that of the supercapacitors because there is a latency stem from the chemical reaction to transfer the chemical energy into electrical energy [10].

Difference between batteries and supercapacitors can be investigated under five main categories, namely energy density, energy discharging rate, lifespan, energy changing time, and cost. Currently batteries have higher energy density and better leakage current than supercapacitors. But they have limited cycle life, there are harsher voltage and current limitations, and also they have lower power densities. Furthermore, supercapacitors can operate safely in a wider range of temperatures. But supercapacitors have higher self-discharge, and the cost is higher per watt. Although batteries have longer charging times, they cover this deficiency with their higher energy densities hence longer occupancies and less frequent charging requirements. Being less dependent on charging is an important factor for an active life which leads batteries domination over the marketplace. For delivering energy for extended periods of time, coupling supercapacitors with batteries or another energy storage device is still necessary [11].

Supercapacitors are also more expensive than conventional capacitors. While capacitors store energy in the form of electric field typically between two metal plates, supercapacitors store energy at the interface between electrode and electrolyte in a double layer of charge. As a medium activated carbon is used in supercapacitors while in conventional counterparts aluminum oxide, polymer films or ceramic are used.

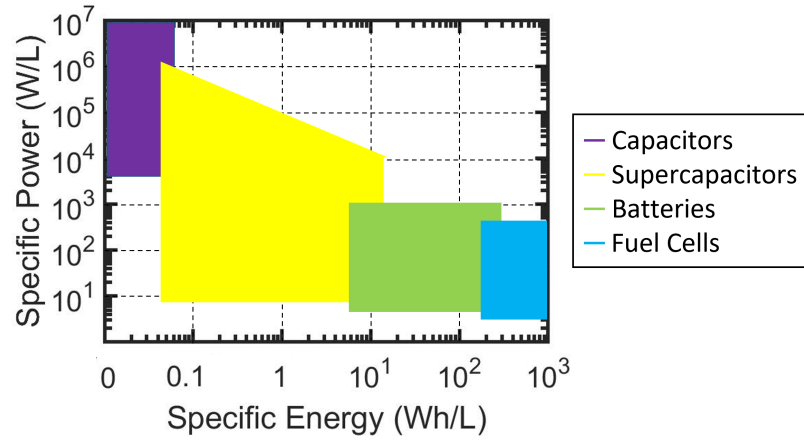


Figure 1.1. Energy density and power density comparison of energy storage systems.

Supercapacitors are mainly used in applications that require rapid charge and discharge cycles. Due to their high power density and long cycles lives they can be more advantageous than conventional batteries for niche applications that require bursts of energy in small amounts [12, 13]. Smaller supercapacitors can be used as a backup power supply for static random-access memory. But due to limited energy storage capacity, supercapacitors cannot be used in applications that require long-term compact energy storage like smartphones and consumer-grade devices. However, there are some consumer-grade applications that use supercapacitors because characteristics like quick recharge or prolonged life cycle are required. Examples of these include MP3 players and the flash for a professional-grade camera. Another common application for supercapacitors is smoothing out the intermittent power supply in wind turbines. [14].

1.1. The Working Principles of Supercapacitors

Supercapacitors are energy storage devices featuring high power delivery and rapid charge-discharge cycles. Supercapacitors are divided into three groups based on the mechanism of their energy storage, namely pseudocapacitors, hybrid capacitors, and electrical double layer capacitors (EDLCs) [15].

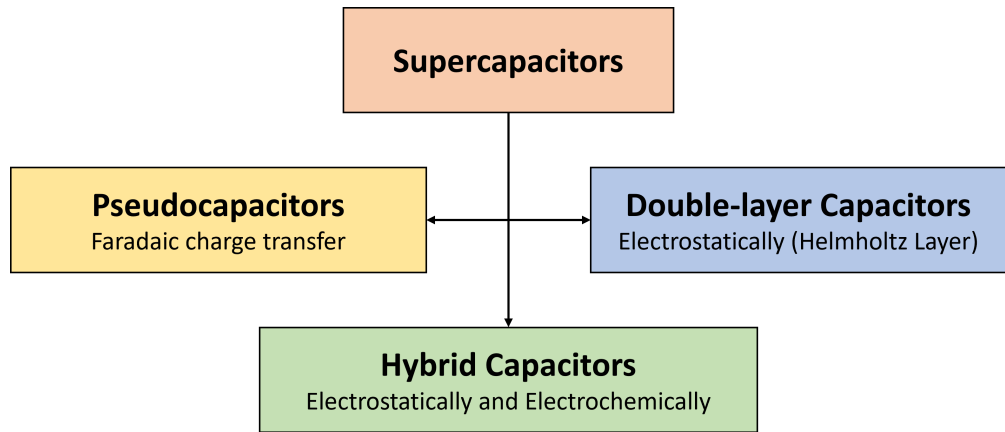


Figure 1.2. Supercapacitor types and their charging mechanisms.

Pseudocapacitors use faradaic mechanism for storing and/or exchanging charge which involves charge transfer between electrode and electrolyte similar to oxidation-reduction reactions. The applied potential leads oxidation and reduction on the electrode and charge passage over a double layer, resulting in the faradaic current passing through supercapacitor cell [16, 17].

EDLCs can either store the charges electrostatically or via a non-faradaic mechanism that does not need charge transfers between the electrode and electrolyte [18]. When voltage is applied, there is no charge buildup on the electrode surface since the potential difference causes opposing charge attraction. Hybrid capacitors are trying to combine the best features of pseudocapacitors and EDLCs via combining their storage mechanism and using electrochemical double layer ion adsorption/desorption and reversible faradaic reaction.

Hybrid capacitors are divided into three categories via their electrode combination, namely asymmetric, composite, and battery-type. The composite electrodes use carbon based materials with polymer conduction or metal oxides in a single electrode and have two mechanisms for storage, physical and chemical. Based on the amount of material types used, composites have two types namely binary and ternary composites [16]. Asymmetric hybrid capacitors use faradaic and non-faradaic processes via coupling pseudocapacitor electrode with EDLCs [16] while battery type tries to combine the supercapacitor recharging times with battery properties [19].

This work specifically focuses on EDLCs. EDLCs are comprised of two oppositely charged electrodes separated by an electrolyte. Typically, a metal current collector coated with carbon-based active electrode material is used in supercapacitors. The separator is sandwiched between these foils. The separator is an ion-permeable membrane, that provides insulation and allows the electrolyte's ions to pass between the electrodes. The interaction between the electrolyte and electrode ions leads to physical adsorption of counter-ions and desorption of co-ions at the interface. That leads charge accumulation and ion separation.

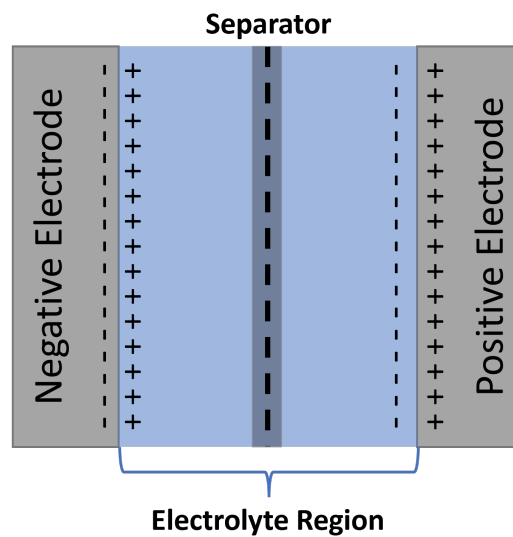


Figure 1.3. A schematic of an electrical double layer capacitor.

EDLC performance is a complex function of the physical properties and chemical properties of its components, as well as the interactions between them [20–22]. Electrode and electrolyte material features affect inherent properties such as capacitance and conductivity, and easy to control during device manufacturing. Hence the interaction between electrode and electrolyte needs to be optimized to enhance the overall device performance. Average electrode pore size, specific surface area, porosity, salt cation size, salt anion size, solvent size, solvent polarity, and electrolyte concentration are some of these factors that affect the performance of an EDLC.

Customizing electrode materials via changing pore geometry or/and size is one of the possible routes for performance optimization. Selected materials should be cheap and abundant, have large specific surface area and good conductivity, be easily processable and environmentally friendly. Therefore, nanoporous carbonaceous materials are among the most promising electrode materials [1, 6, 23, 24].

1.2. Performance Parameters of Supercapacitors

Energy storage performance depends on several interlinked parameters. The operating voltage, equivalent series resistance, cell capacitance, power density, energy density, and characteristic charging time are all important metrics to consider when evaluating the performance of a supercapacitor.

Supercapacitors are evaluated based on two predominant performance metrics namely energy density and power density. Energy density (ED) refers to the quantity of energy that is stored in a device and defined as follows [25, 26]

$$ED = \frac{C_{max}V^2}{2} \quad (1.1)$$

where C_{max} is the maximum capacitance and V is the applied potential difference. Power density (PD) describes how fast the device can be charged and discharged and can be calculated from the following relation [25, 26]

$$PD = \frac{V^2}{4R_s} \quad (1.2)$$

where V is the maximum cell voltage and R_s is the equivalent series resistance including all ohmic contributions.

The ultimate goal in supercapacitor optimization is to determine the design which will lead maximum energy and power densities. The performance of a supercapacitor is often evaluated based on gravimetric properties [27–30]. But the porous structure, electrode dimensions and compression ratio highly effect the performance, hence volumetric performance parameters should also be taken into account to make practical and compact devices [31–35]. To take into account both material properties and its packing and processing affects, gravimetric and volumetric performance should be investigated together. For that purpose, in this work gravimetric and volumetric specific capacitances and resistances are estimated. While capacitance is the reflection of electrical charge stored under a given voltage, resistance determines the duration of charging or discharging. For gravimetric investigation gravimetric energy density (Wh/kg) and characteristic charging time (s), for volumetric investigation volumetric energy density (Wh/l) and resistance (Ohm m) are used as performance parameters.

1.3. Optimization of Supercapacitor Performance

Performance evaluation of the supercapacitors are mainly based on two predominant performance metrics, namely energy density and power density [36]. The design criteria that control each of these performance measurements, on the other hand, are diametrically opposed. To increase power density, one might try to increase the pore sizes but that will lead lower energy densities hence the resulting device can no longer be as compact as it should be. On the other hand via maximizing the surface area one can try to achieve high energy densities but it will lead low power densities because ionic transport will be substantially limited by the exceedingly tiny pores [37].

Other than power and energy densities, capacitance, total resistances, characteristic charging duration can also be used to compare such devices. There are two main sides of that optimization; electrolyte side and electrode side. Both experimental and computational methods can be used for optimizing EDLC performance.

1.3.1. Properties of the Electrode Side

Carbons are the most preferred materials to date due to their high specific surface area, relative low cost, ease of processing, high electrical conductivity, non-toxicity, easiness of access, and stability [38]. Variety of carbon materials such as carbon nanofibres [39], carbon aerogels [40], template porous carbon [41–43], carbon nanotubes [44, 45], and activated carbon and composites [46–50] are used in various experimental studies.

Specific surface area is one of the key elements of the charge storage in supercapacitors. Higher surface area leads to more available sites for charge accumulation hence improved capacitances. Steam or CO₂ activation, heat treatment, alkaline treatment, and plasma surface treatment with NH₃ have all been tried to improve the specific area of carbon materials [47, 51–60].

Pore size also affects the performance as it is directly linked to ion diffusion resistance through electrodes. Pore size can be evaluated in three categories, namely micropores, which have less than 2 nm pore diameter, mesopores, which have between 2 and 50 nm pore diameter, and macropores, which have more than 50 nm pore diameter. Although micropores result in the largest surface area, presence of mesopores is essential for smooth and fast ion diffusion through electrodes. Hence, presence of mesopores on the surface increases the capacitance [61, 62]. Experimental studies have revealed an anomalous increase in gravimetric capacitance in micropores that cannot be readily explained solely by larger surface area, suggesting that pore structure affects the capacitance, hence selecting appropriate pore size according to the size of the ions can increase the overall performance compared to larger pore sizes [63, 64].

To reach the micropores, the existence of mesopores is required for the transportation of electrolyte ions into the bulk of the active material. Addressing this question through experiments alone is difficult due to the lack of techniques to examine the relationship between local structures of pores and local degree of charge separation. In that case, molecular simulations can provide more information yet previous research has been limited to simulations on flat surfaces of idealized geometries due to the challenges associated with representing the charge/discharge mechanisms accurately and computational cost of simulating such electrodes [20]. To investigate the performance of supercapacitors constant charge method, which distributes the charges uniformly, is used to approximate systems with open electrodes with planar, cylindrical, or spherical surface [65–67]. But that method does not give accurate results for nanoporous electrodes [68–71]. In modelling of nanoporous supercapacitors to get accurate charging dynamics and heat generation, constant potential method is preferred which maintains electrode atoms at constant potentials by self-adjusting electrode charges [71–74].

1.3.2. Properties of the Electrolyte Side

Room temperature ionic liquids (RTILs), salts that are liquid near room temperature, possess a unique combination of properties such as high charge density, electrochemical stability, low and negligible volatility, and tunable polarity. These properties make RTILs very attractive electrolytes for EDLCs [12,20,22]. Most importantly, their large electrochemical windows (up to 5 V) allows operation at high voltages that are inaccessible to conventional electrolytes [75].

Pure RTILs typically have lower ionic conductivity than conventional dilute electrolytes, which is detrimental to power density, but their conductivity can be altered through ion modifications or introducing an additive to the electrolyte [3,4,76]. RTILs' incorporation into EDLCs has been hindered, for the most part, due to the lack of fundamental knowledge on their structural and capacitive properties at the electrical double layer which differs markedly from that of conventional dilute electrolytes.

In the recent years, the interfacial properties of pure RTILs have begun to be unraveled using experimental, simulation and analytical techniques [20, 77–84]. Nevertheless, these studies have been limited to a narrow range of pure RTILs. Due to the large number of RTIL cations and anions, and easiness of mixing RTILs with each other and/or with other substances, there are an infinite number of solvent-free and/or solvent-enriched electrolytes with tunable properties. That makes the optimum RTIL selection of any selected application highly nontrivial, leaving the experimentalists with the only option of using heuristics [77, 80].

1.3.3. Data-driven Approaches for Energy Storage Device Design

To compare the systems hence find the optimum settings, physically meaningful performance outputs should be selected. For the supercapacitors, capacitances, energy densities, characteristic charging time, and total resistances can be used as performance parameters. In this project, gravimetric and volumetric energy densities, characteristic charging time, and internal resistance of electrode per unit length are selected as performance parameters. To calculate and predict these, various input parameters can be used such as electrolyte composition, electrical conductivity, equivalent series resistance, pore size and applied voltage. Some of these parameters and properties are related to operating conditions while some show the physical characteristics of the system. Due to high number of key parameter combinations, traditional experiments and computational modelling is not a feasible way to optimization as it requires significant amount of time and resources. Machine learning is a promising tool that can be used to understand and predict supercapacitor behavior without conducting extensive experiments and simulations. Zhang *et al.* shows the power and use of machine learning and deep learning tools in fault detection, diagnosis and prognosis in application domains including energy storage devices [85]. Hu *et al.* and Meng and Li reviewed the application of various model based, data-driven and hybrid approaches on the lifetime prognosis of energy storage devices [86, 87]. Gu *et al.* and Chen *et al.* reviewed the machine learning assisted design, development, and discovery of novel materials for rechargeable batteries, superconductors and solar cells [88, 89].

Wu *et al.* studied the effect of thickness, solid volume ratio, particle radius, electrolyte concentration and applied C-rate on capacitance with negligible computational cost and generate a design map that fulfills the requirements of both specific power and energy [90]. Machine learning algorithms are also used in life prediction of supercapacitors with aging experiments at different temperature and work voltage [91]. Ren *et al.* applied an artificial neural network (ANN) model to predict the life cycle with a data-set generated from 66 supercapacitors and it is seen that ANN can have a higher prediction accuracy than principal component analysis and logistic regression algorithms [92]. To be able to use machine learning methods, problem should be determined carefully first, then appropriate data should be collected. For that, some specifications and/or parameters should be selected to predict and evaluate performance parameters. To successfully predict the performance parameters, the related input parameters should be extracted from the models prepared. For our case, constant potential molecular dynamics simulation results will be used in an equivalent circuit model to create these parameters hence to understand the macroscopic behaviors.

To describe the charge/discharge kinetics and capacity of electrical double layer capacitors transmission line models can be used. In the transmission line model, charge penetrates progressively into the electrodes. Parallel slices that consist of a capacitor under constant potential solid surface creates the system. Pean *et al.* in 2014 used a small simulation system and divide their electrode into two slices of equal thicknesses and obtain a bi-exponential function which describes the charging kinetics of their system [73]. Later Sampaio *et al.* used that bi-exponential function to describe and investigate their simulation results [93]. In 2016, Pean *et al.* further simplified that model via taking the capacitance of each slice similar [94]. That model later used by various studies [95,96]. Once inputs are created, machine learning models will be used to predict the performance parameters which are energy density and charging time for gravimetric investigation and energy density and electrode inner resistance for volumetric investigation. After the investigation of the factors affecting the supercapacitor performance and selecting the key factors that affect the charge storage, the aim is to find the optimum settings of these factors.

2. MATERIALS & METHODS

2.1. Molecular Modelling of Supercapacitors

The physically accurate simulations of an EDLC’s charge and discharge mechanism requires maintaining a constant-potential difference between electrodes. Previously this description has been implemented in a few computer simulations [72, 82, 84, 97, 98]. but its use was limited to only primitive studies due to the computational cost of constant potential ensemble simulations. Instead, constant electrode charge simulations have been performed, but these do not correspond to experimental setups. This work used constant potential ensemble simulations to provide insights into the microscopic mechanisms that determine the electronic properties of the interface as a function of the molecular features of the electrolyte. An ideal model EDLC should be able to represent the actual device behavior while having the ability to tune many different experimental parameters independently.

The specific system considered here employs molecular simulation models of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) acetonitrile (ACN) mixtures confined by nanoporous carbon electrodes. The molecular simulation data used in this thesis is retrieved from Uralcan [99]. In particular, quenched molecular dynamics is performed to generate the nanoporous carbon electrodes using the molecular simulation software LAMMPS [100]. Constant potential ensemble simulations of the EDLCs are performed by applying a constant potential difference between the electrodes and letting the electrode charge fluctuate to reach equilibrium. Electrode charge is computed from summing up the individual charges of the electrode atoms. Self-diffusion coefficients are computed from the Einstein relation [101]. Electrode pore size distributions are obtained using the Zeo++ algorithm [102].

2.2. The Transmission Line Model

Transmission line model can be used to describe the charge/discharge kinetics and capacity of electrical double layer capacitors [73, 93, 94]. In the transmission line model an EDLC is represented by connected electrode slices and a bulk electrolyte, and charge penetrates progressively into the electrodes. Number of electrode slices is selected based on the size of the simulated system.

There are two types of transmission line models. The first one involves splitting the electrodes into slices with different capacitance values connected in parallel [73]. The second, simplified model assumes equal capacitance for each slice [94].

In the transmission line model with slices with different capacitance values, two slices of equal thickness are set. The mathematical model describing the total charge of the electrodes as a function of time is given by the following bi-exponential function

$$Q(t) = Q_{max} \left[1 - A_1 \exp\left(-\frac{t}{\tau_1}\right) - A_2 \exp\left(-\frac{t}{\tau_2}\right) \right] \quad (2.1)$$

where Q_{max} is the final charge and t is time. To be able to calculate the terms Q_{max} , A_1 , A_2 , τ_1 , and τ_2 , first following relations should be calculated

$$a = \frac{(R_{bulk} + 2R_l) C_1}{R_l (R_{bulk} + 2R_l) C_1 C_2} \quad (2.2)$$

$$b = \frac{2}{R_l (R_{bulk} + 2R_l) C_1 C_2} \quad (2.3)$$

$$c = \frac{C_1 + C_2}{R_l (R_{bulk} + 2R_l) C_1 C_2} \quad (2.4)$$

$$d = \frac{1}{R_{bulk} + 2R_l} \quad (2.5)$$

where R_{bulk} is the resistance of the electrolyte in the bulk region, R_l is the resistance of each electrode slice, C_1 and C_2 are the capacitance values of the inner and outer slices, respectively.

Once these terms calculated, terms of Equation (2.1), namely Q_{max} , A_1 , A_2 , τ_1 , and τ_2 , can be calculated using following relations

$$Q_{max} = \frac{C_1 + C_2}{2} V_0 \quad (2.6)$$

$$\tau_1 = \frac{2}{a + \sqrt{a^2 - 4b}} \quad (2.7)$$

$$\tau_2 = \frac{2}{a - \sqrt{a^2 - 4b}} \quad (2.8)$$

$$A_1 = \frac{1}{2} \left[1 + \frac{2bd - ac}{2c\sqrt{a^2 - 4b}} \right] \quad (2.9)$$

$$A_2 = \frac{1}{2} \left[1 - \frac{2bd - ac}{2c\sqrt{a^2 - 4b}} \right] \quad (2.10)$$

where C_1 and C_2 are the capacitance values of the inner and outer slices, and V_0 is the operating potential for which its maximum value is determined by the electrochemical stability of the device. This model is first used by Pean *et al.* in the context of molecular simulations of a model system composed of an ionic liquid electrolyte confined between a pair of nanoporous carbon electrodes [73]. The capacitances of inner and outer slices (C_1 and C_2) are given by the final total charge (Q_{max}). Bulk electrolyte conductivity (R_{bulk}) is computed from the electrical conductivity of the electrolyte (κ) using following relation

$$R_{Bulk} = \frac{1}{\kappa} \frac{l_z}{A} \quad (2.11)$$

where A is the cross-sectional area of the electrode, l_z is the bulk electrolyte region thickness, and κ is the conductivity. Conductivity of electrolyte with various ion fractions can be calculated via

$$\kappa = \frac{\rho e^2 (D^+ + D^-)}{k_B T} \quad (2.12)$$

where e is the electric charge unit, ρ is the density $\rho = n/V$ in which n is the number of cations (or anions), V is the volume of bulk electrolyte region, and T is the temperature of the system [103].

The only unknown left, R_l , is determined by fitting on charging data using a least-square method. To calculate the charge of the inner electrode slice, namely Q_1 , c in Equation (2.4) is replaced by

$$c_1 = \frac{1}{R_l (R_{bulk} + 2R_l) C_1} \quad (2.13)$$

which is used together with the other a , b and d values to calculate A and τ terms hence bi-exponential function in Equation (2.1) to obtain charge of the inner electrode slice. Then the charge of the outer electrode slice is calculated by

$$Q_2(t) = Q_T(t) - Q_1(t) \quad (2.14)$$

which is simply the difference between total charge and the inner slice charge. The transmission line model can be further simplified by assuming identical capacitance values for each electrode slice based on the idea that applied potential and pore size distribution is similar for each slice. Simplified model needs new set of equations for the terms a , b , c and d . The changes in these terms leads changes in τ and A calculations. The modified equations for Equation (2.6) through Equation (2.10) are given in Equation (2.15) through Equation (2.18)

$$a = \frac{2R_{bulk} + 6R_l}{R_l (R_{bulk} + 2R_l) C_l} \quad (2.15)$$

$$b = \frac{2}{R_l (R_{bulk} + 2R_l) C_l^2} \quad (2.16)$$

$$c = \frac{2}{R_l (R_{bulk} + 2R_l) C_l} \quad (2.17)$$

$$d = \frac{1}{R_{bulk} + 2R_l} \quad (2.18)$$

which can be obtained via equating C_1 to C_2 except Equation (2.15). Also Q_{max} equation is simplified since average capacitance of slices now become C_1 .

2.3. Machine Learning Methods

The first step of machine learning is to decide the target parameters. Target parameters here are gravimetric energy density and characteristic charging time for gravimetric investigation, and volumetric energy density and resistance for volumetric investigation.

For that purpose, gravimetric capacitance and volumetric capacitance values are predicted as step one. In the second step resistances are predicted via using various new feature sets. The effect of various initial charging data, namely initial slope (singular data) and 10-point initial charging data (extracted from 0.25 ns of the data) in both prediction steps and the effect of predicted capacitance in R_l prediction step is controlled. Predicted capacitance and resistance values together with physical properties provide information on the energy storage performance of the corresponding designs. Performance parameters, namely energy densities, characteristic charging time and resistance, will be explained in detail in section 2.4. Performance Parameters. In Figure 2.1 design steps through data generation to optimum design selection are given.

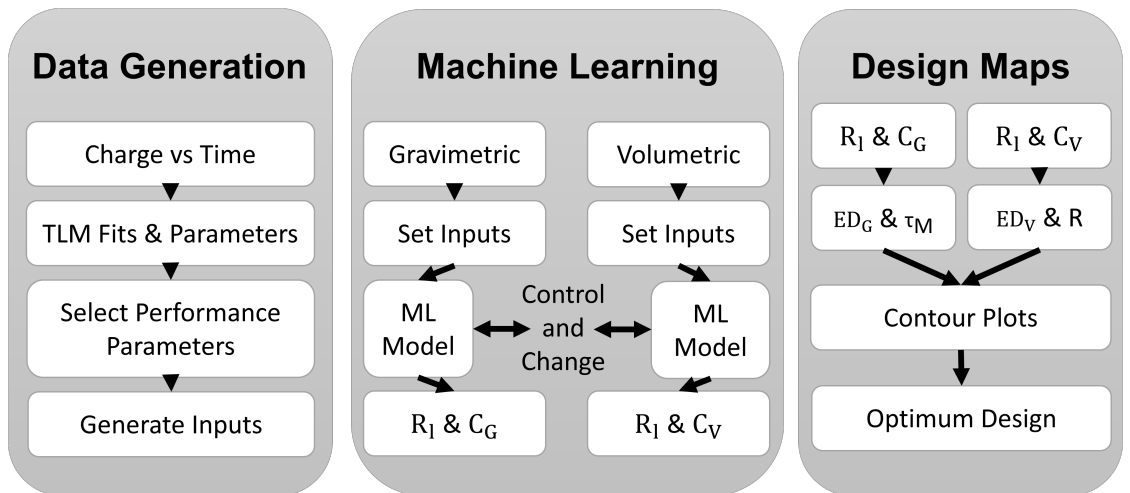


Figure 2.1. Design steps through data generation to design maps.

2.3.1. Linear Regression

Linear regression is used to fit a data model with linear coefficients. It depicts the relationship between the independent predictor variables x_i and the dependent input variable y . The following equation describes the relationship between one independent variable and one output variable in simple linear regression

$$y = \beta_0 + \beta_1 x + \epsilon \quad (2.19)$$

where β_0 is the intercept, β_1 is the regression coefficient (slope), and ϵ is the error. Then there is multiple linear regression which predicts the outcome using several input variables. The following is the multiple linear regression model

$$y = \beta_0 + \sum_{i=1}^N \beta_i x_i + \epsilon \quad (2.20)$$

where β_0 is the intercept, x_i values are the features, β_i values are the regression coefficients, and ϵ is the error. Negative coefficients imply a negative relationship between the characteristic and the goal value, whilst positive coefficients suggest a positive relationship between them [104].

2.3.2. Ridge Regression

Ridge regression is a type of linear regression that is used in scenarios where independent variables are highly correlated. The independence of the model terms is used to estimate coefficients in multiple linear regression models. The matrix $(X^T X)^{-1}$ is close to singular when terms are correlated, and the columns of the design matrix X exhibit an approximate linear relationship. Therefore, the least-squares estimate

$$\hat{\beta} = (X^T X)^{-1} X^T y \quad (2.21)$$

has a significant variation since it is highly sensitive to random errors in the observed response variable y . When data is collected without employing an experimental design, this type of multicollinearity might emerge. Ridge regression overcomes the problem of multicollinearity via using the equation below to estimate regression coefficients

$$\hat{\beta} = (X^T X + kI)^{-1} X^T y \quad (2.22)$$

where k is the ridge parameter and I is the identity matrix. Small, positive k values increase the problem's conditioning and reduce the variability of the estimates. When compared to least-squares estimates, the smaller variance of ridge estimates typically leads to a lower mean squared error. For a given value of λ , i , a non-negative parameter, ridge solves the following problem

$$\min_{\beta_0, \beta} \left(\frac{1}{2N} \sum_{i=1}^N (y_i - \beta_0 - x_i^T \beta)^2 + \lambda \sum_{j=1}^p \beta_j^2 \right) \quad (2.23)$$

where N is the number of observations, y_i is the response at observation i , x_i is the data, a vector of length p at observation i , λ is a non-negative regularization parameter corresponding to one value of λ , the parameter β_0 is a scalar, and the parameter β is a vector of length p [105].

2.3.3. Lasso Regression

Lasso is an abbreviation for the least absolute shrinkage and selection operator. It uses shrinkage meaning that the data values are shrinking towards a central. Additionally, it creates sparse models where feature selection occurs depending on the effect of the feature on the outcome. If a variable does not have a great impact on target value, lasso regression sets zero to its coefficient and as a result, it works with fewer parameters. In short, lasso creates simpler models hence leads faster solutions/predictions.

The lasso regression model is as the following

$$\min_{\beta_0, \beta} \left(\frac{1}{2N} \sum_{i=1}^N (y_i - \beta_0 - x_i^T \beta)^2 + \lambda \sum_{j=1}^p |\beta_j| \right) \quad (2.24)$$

where N is the number of observations, y_i is the response at observation i , x_i is data, a vector of length p at the observation i , λ is a nonnegative regularization parameter corresponding to one value of λ , the parameters β_0 and β are scalar and a vector of length p , respectively. As λ increases, the number of nonzero components of β decreases. The lasso problem involves the L^1 norm of β , as contrasted with the elastic net algorithm [105, 106].

2.3.4. Elastic Networks

Ridge regression and lasso regularization are combined in elastic networks. Elastic networks generate reduced models by producing zero-valued coefficients like lasso regression. For data-sets with strongly correlated variables, elastic networks outperforms lasso regularization [107]. For α strictly between 0 and 1, and non-negative λ , elastic net solves the following problem

$$\min_{\beta_0, \beta} \left(\frac{1}{2N} \sum_{i=1}^N (y_i - \beta_0 - x_i^T \beta)^2 + \lambda P_\alpha(\beta) \right) \quad (2.25)$$

where N is the number of observations, y_i is the response at observation i , x_i is data, a vector of length p at the observation i , λ is a nonnegative regularization parameter corresponding to one value of λ , the parameters β_0 and β are scalar and a vector of length p , respectively. P_α can be calculated using following relation

$$P_\alpha(\beta) = \frac{1-\alpha}{2} \|\beta\|_2^2 + \alpha \|\beta\|_1 = \sum_{j=1}^p \left(\frac{1-\alpha}{2} \beta_j^2 + \alpha |\beta_j| \right) \quad (2.26)$$

which shows that elastic net is the same as lasso when α is equal to unity. For other values of α , the penalty term $P_\alpha(\beta)$ interpolates between the L^1 norm of the β and the squared L^2 norm of β . As α shrinks toward 0, elastic net approaches ridge regression. In MATLAB lasso and elastic networks fit many values of λ simultaneously by an efficient procedure named coordinate descent, based on Friedman, Tibshirani, and Hastie [108, 109].

2.3.5. Support Vector Machines

In a high or infinite-dimensional space, a support-vector machine (SVM) creates a hyperplane (or hyperplanes) for regression. The hyperplane with the greatest distance to the nearest training-data point of any class, known as the functional margin, is used to create a decent separation, since the greater the margin, the lower the classifier's generalization error [110]. Even though the initial problem is expressed in a finite-dimensional space, the sets to discriminate are frequently not linearly separable in that space. As a result, the original finite-dimensional space was proposed to be mapped into a considerably higher-dimensional space. To keep the computational load reasonable, SVM systems utilize mappings that ensure that dot products of pairs of input data vectors can be readily computed in terms of the variables in the original space by defining them in terms of a kernel function selected to suit the problem. In a higher-dimensional space, hyperplanes are defined as a set of points whose dot product with a vector in that space is constant, where such a set of vectors is orthogonal, and so minimum, and forms a hyperplane. The hyperplanes' vectors can be chosen as linear combinations with parameters of images of feature vectors found in the data base. In this way, the sum of kernels can be used to calculate the distance between each test point and the data points originating in one of the discriminated sets. As a result, the set of mapped into any hyperplane can become rather complicated, allowing for far more intricate discriminating between sets which are not convex at all in the original space [110].

2.3.6. Artificial Neural Networks

An artificial neural network (ANN) is an adaptive system that uses a layered structure of interconnected nodes or neurons to learn using fed data. A neural network can be trained to identify patterns, to categorize data, and to predict future events using appropriate data. For training a data-set or creating a predictive model, neural network is a great way to perform machine learning [111].

ANNs consist of three main layers, namely an input layer, a hidden layer (or multiple hidden layers), and an output layer. The training set is introduced to the system through the input layer of the neural network. The independent parameters are specific in this part through neurons. The analysis of the relationships between data is done in hidden layers. Each node layer trains on distinct parameters dependent on the output of the preceding layer. Finally, in the output layer, target value is obtained from the input and hidden layers [111]. The neural network's primary concept is to evaluate, test, evaluate again, test again, and continue until the desired output is attained. The following equation represents the neural network model

$$y = f(b + \sum_{i=1}^n x_i w_i) \quad (2.27)$$

in which y , x values, w values, b and f stand for the output of the neuron, inputs, corresponding weights of the inputs, bias, and the activation function, respectively.

There are three properties one can select and change in ANNs. First one is the feed type. The positioning of each input can affect the output since that changes the interactions and interaction possibilities with other inputs. In this project, two step prediction is done. Output of the first step used as an additional input in second prediction step at some models. Also, initial charging data, which is actually an intermediate result, is used in some of the systems to obtain more accurate results. Feeding position of initial charging data also varies in neural network models. Schematic explanation for each model can be found in corresponding results and discussion section.

Second parameter one can change is number of hidden layers. With each layer, neural network will become a more powerful tool to find and show the interactions between the inputs and outputs yet it can also do over-fitting. Due to input size and parameter amount, one hidden layer is used in this project. The third parameter one can change is the size of these hidden layers, or in other words number of nodes. The number of unknowns and number of equations (input size) limits the hidden layer size. To avoid underestimating and/or overestimating, hidden layer size should be selected carefully. In Figure 2.2 a typical neural network architecture consists of three inputs, a corresponding input layer, two hidden layers with four nodes, and an output layer with two outputs can be seen.

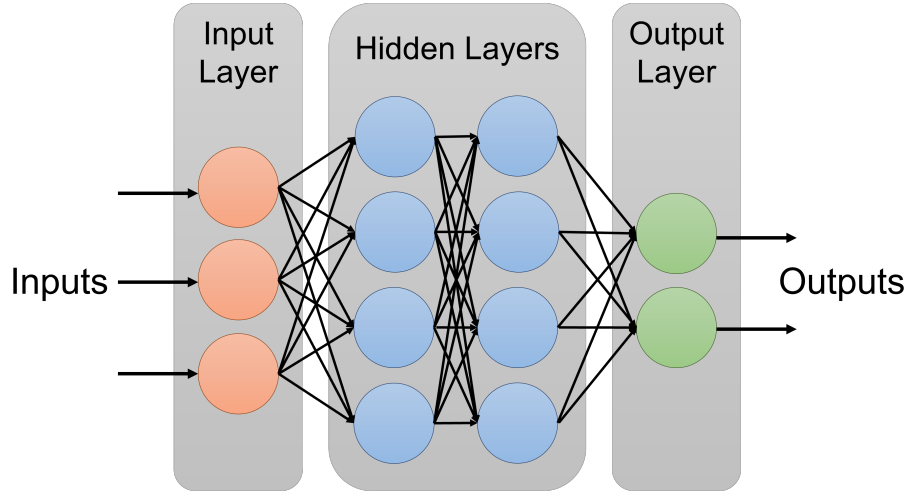


Figure 2.2. Typical neural network architecture.

2.4. Performance Parameters

To determine the goodness of the systems four performance parameters are selected, two for volumetric and two for gravimetric investigation. For gravimetric investigation, gravimetric energy density (ED_G) and characteristic charging time (τ_M) are selected as performance parameters while for volumetric investigation volumetric energy density (ED_V) and resistance (R) are selected. R_l , τ_1 and τ_2 from transmission line model fits are eliminated since they do not have direct physical meanings.

First performance parameter of the gravimetric investigation, gravimetric energy density can be calculated as follows

$$ED_G = \frac{1}{2}C_G V^2 \quad (2.28)$$

where C_G is the gravimetric capacitance of the system in F/g unit and V is the potential difference applied to the system in Volts. Final unit of the gravimetric energy density is chosen as Wh/kg, hence necessary conversions are done accordingly. To calculate gravimetric capacitance, C_1 values obtained from transmission line model, can be simply divided to weight of the electrode.

Characteristic charging time is the second performance parameter of gravimetric investigation, and it can be calculated as follows

$$\tau_M = R_l \left(\frac{l_{macro}}{l_{sim}} \right) C_T \quad (2.29)$$

in which C_T is the total capacitance of the system, R_l is the resistance inside the electrode, l_{sim} is the thickness of these electrodes and l_{macro} is the thickness of a typical commercial supercapacitor which is around 100 μm .

For volumetric investigation, volumetric energy density (ED_G) and resistance (R) are used. Volumetric energy density can be calculated from the following equation

$$ED_V = \frac{1}{2}C_V V^2 \quad (2.30)$$

where C_V is the volumetric capacitance in F/cm³ and V is the potential difference applied to the system in Volts. Resulting volumetric density should have the units of Wh/L, hence necessary conversions are done accordingly. To calculate volumetric capacitance, C_1 values obtained from transmission line model, can be simply divided to volume of the electrode.

R_l value calculated via transmission line is an extensive property, which means it depends on the size and/or amount of the system. To be able to analyze systems, intensive properties should be used. In volumetric investigation section following relation is used as resistance

$$R = \frac{R_l A}{l_{sim}} \quad (2.31)$$

where R_l is the resistance calculated from transmission line model in units of Ohm, A is the cross sectional area of the electrode and l_{sim} is the thickness of the electrode. Resulting resistance will have the units of Ohm meter.

3. RESULTS & DISCUSSION

3.1. Dataset Preparation

3.1.1. Molecular Simulations

The molecular simulation data used in this work is comprised of 23 molecular simulation models of 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) acetonitrile (ACN) mixtures confined by nanoporous carbon electrodes. The molecular simulations of the charging process start near the potential of zero charge after applying a potential difference of 1 V, and the charging process is monitored as shown in Figure 3.1. In particular, these simulations investigate the effect of electrode pore size and electrolyte composition on energy storage performance.

The simulations used in this work differ from previous approaches as two key features were implemented: a) realistic atomistic structures for microporous carbon electrodes corresponding to nanoporous carbon synthesized from crystalline SiC at high chlorination temperatures, and (b) realistic modelling of the charging process by allowing charge fluctuations [103]. This approach allows us to perform simulations under constant applied electrical potential, analogous to experiments [112]. These simulations provide a training set that contains the relationship between electrode micro-structure, electrolyte composition and energy storage performance.

Charging data throughout the simulation and distribution of the charging data are investigated first. To reduce the noise moving averages are taken and the the following total charge as a function of time graphs are generated. The first figure, Figure 3.1, shows the processed data of the training set and the second figure, Figure 3.2, shows the distribution of the charges in systems with various pore sizes at 0.03 M, 0.12 M, 0.47 M, 0.63 M, and 0.89 M electrolytes via histograms.

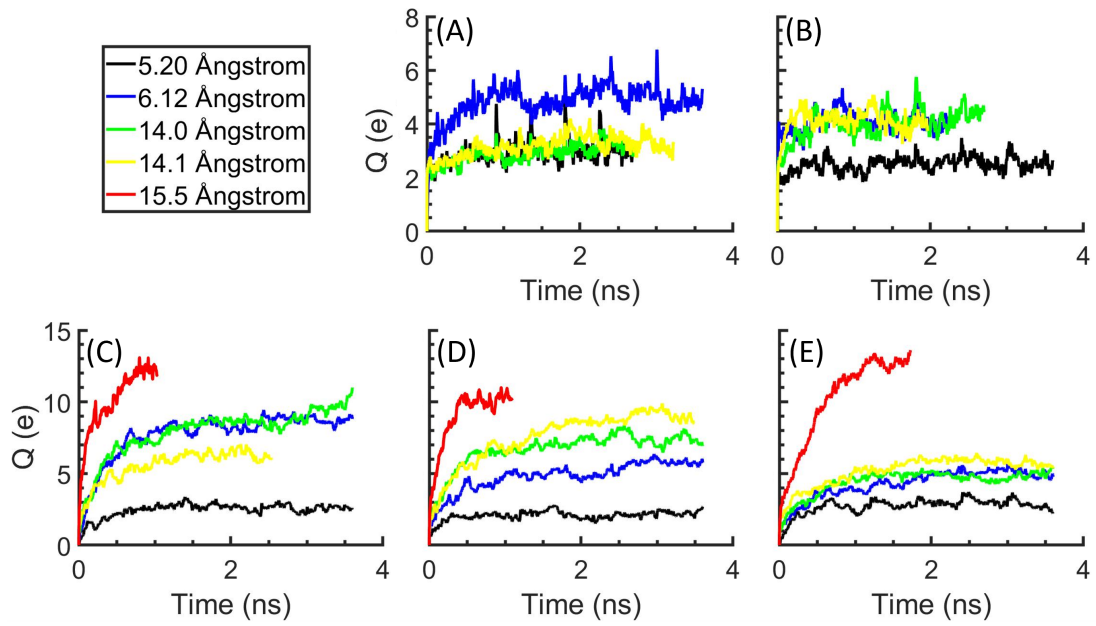


Figure 3.1. Total charge as a function of time a) 0.03 M, b) 0.12 M, c) 0.47 M, d) 0.63 M, and e) 0.89 M.

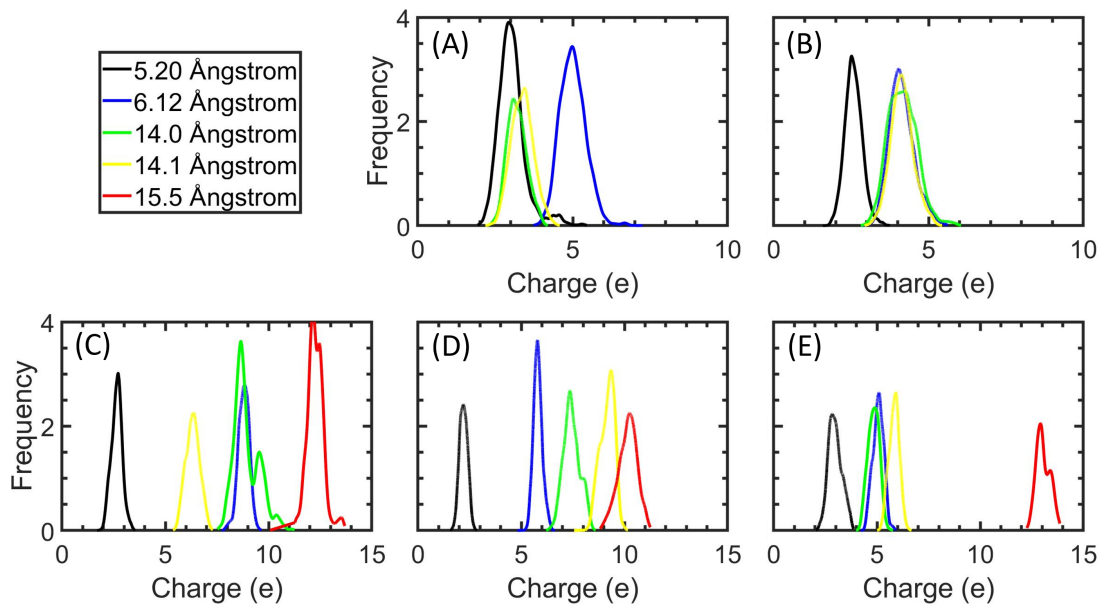


Figure 3.2. Charge distribution histograms of a) 0.03 M, b) 0.12 M, c) 0.47 M, d) 0.63 M, and e) 0.89 M.

It is seen from the Figure 3.1 that, there is a fast increase in initial charging period and then they reach a plateau value which is taken as equilibration. Systems with lower pore sizes reach equilibrium faster especially in systems with higher ion fractions. The difference became unclear in systems with lower ion fractions.

Figure 3.2 shows the distribution in data and as expected, systems with higher pore sizes generally have higher average charges. The difference became unclear in lower ion fractions since the process is faster and the decision of beginning of the equilibrium is problematic.

In the next section, after the validation of the transmission line model, TLM fits of these systems will be done and extracted model parameters will be used in Section 3.2. Machine Learning Methods.

3.1.2. Transmission Line Model

3.1.2.1. Validation of Transmission Line Model. Demonstrating the applicability of the transmission line model using data from the literature is the first step in validating the generalizability of the transmission line model to different electrode and electrolytes of interest. Both models are tested in this section yet second model, model with equal capacitances for each electrode slice, is selected for further investigation since the parameter estimation is more straightforward for the second model due to the capacitance estimation step. To validate the models, molecular simulation data of a variety of electrode and electrolyte materials from the literature are used.

The room temperature ionic liquid electrolyte 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) confined between a pair of carbide-derived carbon electrodes structures (CDC-800, CDC-950 and CDC-1200) are used as the model system in Pean *et al.* [73]. The charging simulations are carried out at 1 V. Other than electrolyte region thickness l_z which is 10 nm for all three systems, parameters used in Pean *et al.* are tabulated in Table 3.1.

Table 3.1. Parameters used in Pean, 2014 [73].

	κ	l_x	R_{bulk}	R_l	C_1	C_2
CDC	(S m ⁻¹)	(nm)	(10 ⁸ Ohm)	(10 ⁸ Ohm)	(10 ⁻¹⁸ F)	(10 ⁻¹⁸ F)
800	4.5	4.33	1.2	4.9	3.9	2.6
900	5.0	4.36	1.1	0.7	3.6	3.2
1200	5.3	4.37	1.0	1.2	4.3	2.7

Using the parameters in Table 3.1, together with l_z and V infoelectrode charging profiles for the two slices Q_1 and Q_2 , inner and outer slices respectively, and the total charge (Q_T) as a function of time are plotted in Figure 3.3.

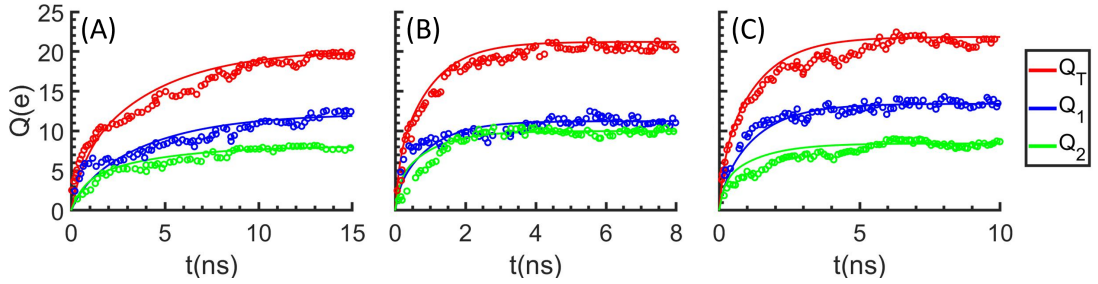


Figure 3.3. Charge as a function of time for a) CDC-800, b) CDC-950, and c) CDC-1200.

In Sampaio *et al.* sulfonium and phosphonium ionic liquids electrolytes are used as electrolytes for simulating the charging of carbide-derived carbon electrodes [93]. In particular, (2-methoxy-ethyl)-ethyl-methyl sulfonium bis (trifluoro methane sulfonyl) imide (P_{222,201}-NTf₂) (IL-1) and (2-methoxy-ethyl)- triethyl-phosphonium bis (trifluoromethanesulfonyl) imide (S_{12G1}-NTf₂) (IL-2) are the tested ionic liquids. Both systems are tested under two different potential difference, namely 2.5 V and 4 V. [93]. Bulk electrolyte resistances are calculated as 1.71 x 10⁸ Ohm for IL-1 and 1.80 x 10⁸ Ohm for IL-2. Rest of the TLM parameters together with τ_1 and τ_2 values, and corresponding applied potentials are tabulated in Table 3.2.

Table 3.2. Parameters used in Sampaio, 2020 [93].

	$Q_{\max}$ (e)	τ_1 (ps)	τ_2 (ps)	R_1 (10^8 Ohm)	C_1 (10^{-18} F)	C_2 (10^{-18} F)	ΔV (V)
IL-1	22.0	348	2250	6.04	1.73	1.09	2.5
IL-2	26.0	210	1500	3.00	1.92	1.41	2.5
IL-1	36.5	383	2460	6.42	1.80	1.12	4.0
IL-2	42.8	270	1840	3.89	2.08	1.28	4.0

Using the parameters in Table 3.2, and R_{bulk} values mentioned above with equations explained in Materials & Methods section, electrode charging profiles for the two slices Q_1 and Q_2 , inner and outer slices respectively, and the total charge (Q_T) as a function of time are evaluated. Figure 3.4 demonstrates the excellent fits obtained by using the transmission line model on the simulations of CDC electrodes ($P_{222,201}$ -NTf₂) (IL-1) and (S_{12G1} -NTf₂) (IL-2) electrolytes at 2.5 V and 4.0 V.

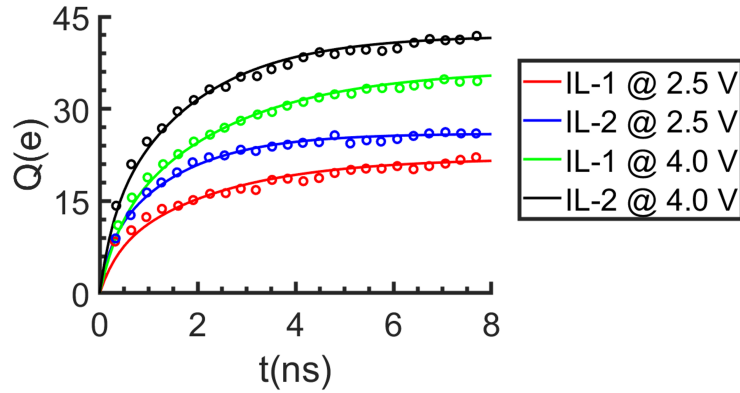


Figure 3.4. Charge as a function of time for Sampaio, 2020.

Figure 3.5 shows the electrode charging profiles Q_1 and Q_2 , inner and outer slices respectively, and the total charge (Q_T) as a function of time for these four systems separately. The initial charging period and the equilibrium point for each slice and for the whole system can be investigated from these graphs.

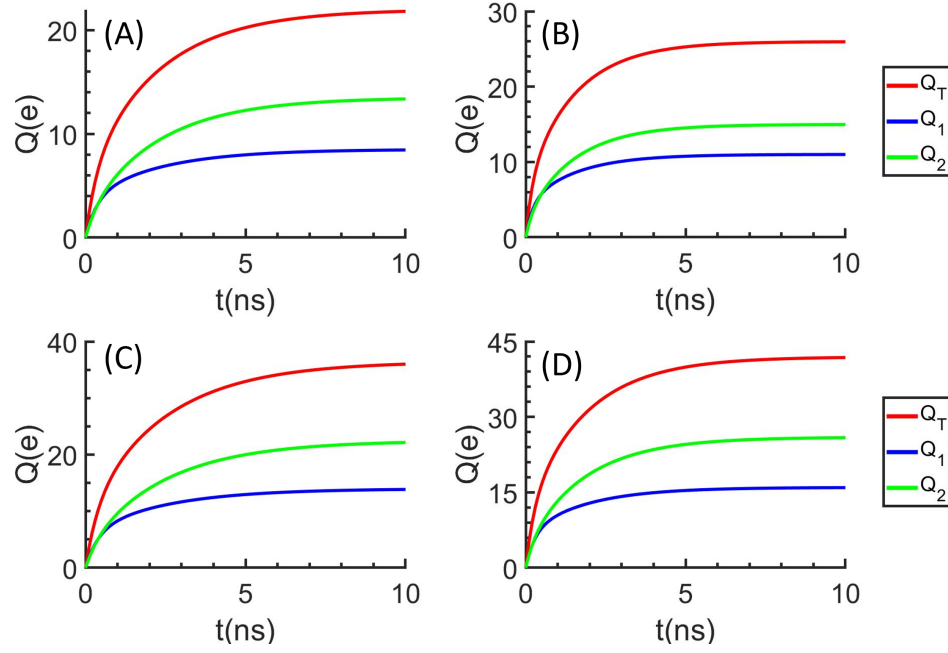


Figure 3.5. Charge as a function of time a) IL-1 at 2.5 V, b) IL-2 at 2.5 V, c) IL-1 at 4.0 V, and d) IL-2 at 4.0 V.

The work of Pean *et al.*, Noh *et al.*, and Liu *et al.* have used the simplified version of transmission line models which assume similar capacitances for electrode slices [94–96]. In Pean *et al.*, the room temperature ionic liquid electrolyte 1-ethyl-3-methylimidazolium hexafluorophosphate ($C_4mim-PF_6$) confined between a pair of carbide-derived carbon electrodes structure (CDC-1200) is used as the model system [94]. The charging simulations are carried out at 1 V potential difference. Transmission line model parameters of that study together with κ , l_x and l_z values are tabulated in Table 3.3.

Table 3.3. Parameters used in Pean, 2016 [94].

	κ	l_x	l_z	R_{Bulk}	R_l	C_1	ΔV
CDC	($S\ m^{-1}$)	(nm)	(nm)	($10^8\ Ohm$)	($10^8\ Ohm$)	($10^{-18}\ F$)	(V)
1200	5.3	4.37	10	1.0	1.2	3.5	1.0

In Figure 3.6 experimental results of that system is plotted together with total charge obtained from transmission line model. Result shows that the simplified version is quite successful to describe the charging of the supercapacitor.

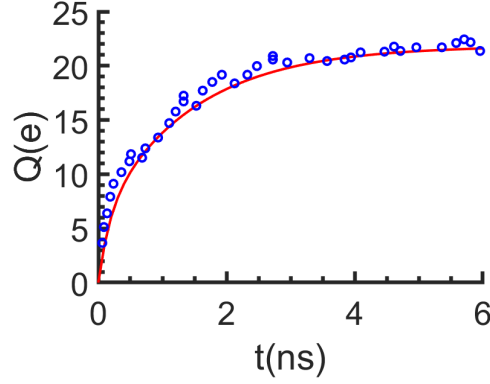


Figure 3.6. Charge as a function of time for Pean, 2016.

In Noh *et al.*, 1-ethyl-3-methylimidazolium thiocyanate (EMIM-SCN) ionic liquid is confined between graphene walls for the simulations [95]. Parameters of the [EMIM] cation were taken from the study on the imidazolium-based ionic liquids, and the [SCN] anion parameters were taken from a previous study of cyano-anion ionic liquids. Various electrical potentials (0.5 V to 4 V with 0.5 V increments) are tested [95]. Dimensions of the whole model and electrolyte concentration are the same for each test. Cross-sectional area of the electrode is taken as $1.165 \times 10^{-17} \text{ m}^2$, while electrolyte section length is taken as $6.3 \times 10^{-9} \text{ m}$. Using Equation (2.1) R_{bulk} of each system is calculated as 10^8 Ohm .

Table 3.4. Parameters used in Noh, 2019 [95].

Potential (V)	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
$Q_{\max}$ (e)	0.701	1.467	2.538	3.705	4.479	5.508	6.397	7.041
C_1 (10^{-19} F)	2.248	2.350	2.711	2.968	2.870	2.941	2.928	2.820
R_1 (10^8 Ohm)	0.94	1.96	2.37	2.90	2.45	2.08	1.74	9.74

Using these TLM parameters in Table 3.4, and R_{bulk} values mentioned above with equations explained in Materials & Methods section, electrode total charging profiles are plotted together with their corresponding experimental values in Figure 3.7.

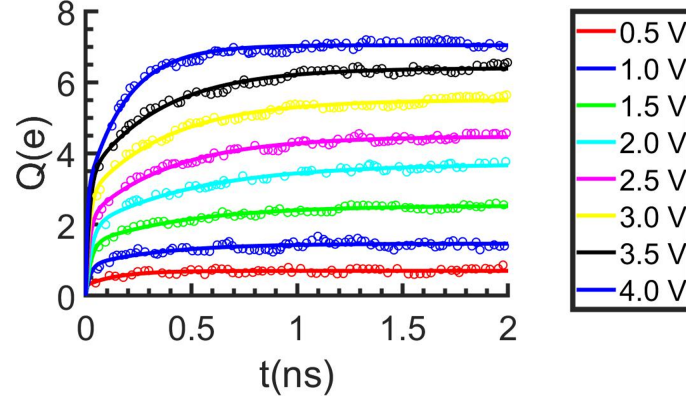


Figure 3.7. Charge as a function of time for Noh, 2019.

In Liu *et al.*, molecular dynamics simulations are used to screen the zeolite-templated carbon materials of Braun *et al.* as electrode materials, namely FAU_1, BEA and EMT [113], and 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄) and acetonitrile (ACN) with the concentration of ions equal to 1 M is used as electrolyte [96]. Conductivity is 10.2 S/m for each system while surface area is $1.056 \times 10^{-17} \text{ m}^2$, and electrolyte region thickness is 10.66 nm hence R_{bulk} is calculated as $9.9 \times 10^7 \text{ Ohm}$. Rest of the TLM parameters, namely Q_{max} , C_1 , and R_l can be found in Table 3.5.

Table 3.5. Parameters used in Liu, 2019 [96].

	Q_{max} (e)	C_1 (10^{-19} F)	R_l (10^8 Ohm)
FAU_1	2.36	3.79	0.715
BEA	1.70	2.72	6.510
EMT	2.41	3.86	1.360

Using the parameters in Table 3.5, and R_{bulk} values mentioned above electrode total charging profiles of FAU_1, BEA and EMT are plotted together with their corresponding experimental values in Figure 3.8.

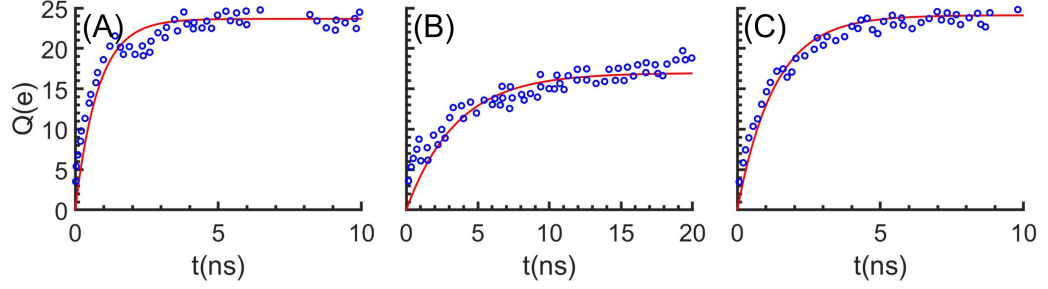


Figure 3.8. Total charge as a function of time for a) FAU_1, b) BEA, and c) EMT.

3.1.2.2. Application of the Transmission Line Model to Simulation Data. The validation tests demonstrate the applicability of the transmission line model to such systems. Next step is to use TLM on our own molecular simulation data.

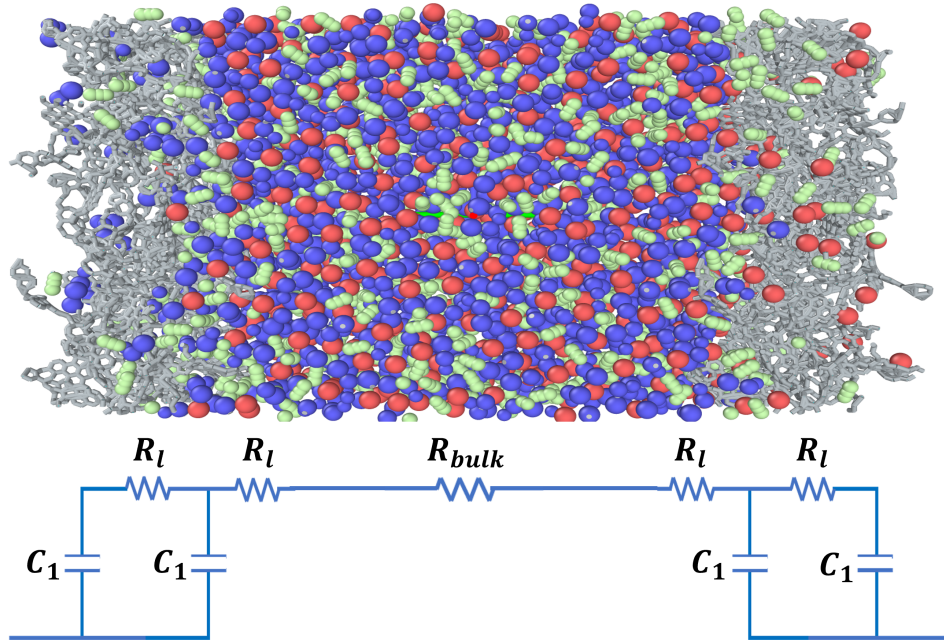


Figure 3.9. Simulation cell and equivalent circuit of transmission line model.

To be able use the charge versus time data of 23 simulations created, noise should be reduced first. After the pre-processing step we start to obtain required data for TLM fits. As it is implied earlier TLM fit has three different parameters in it. R_{bulk} is the resistance of the electrolyte in the bulk region, R_l is the resistance of each electrode slice, and C_1 is the capacitance of the electrode slices. Equivalent circuit in the transmission line model can be seen in Figure 3.9.

Due to noise in data, estimation of Q_{max} is a bit problematic since the decision of equilibrium point is harder in noisy data. To overcome this problem, moving average of the raw data is generated and starting points of the equilibrium are selected. Q_{max} values are obtained via averaging the rest of the data. Once Q_{max} values are found, and used for root mean square of error (RMSE) calculation for verification then C_1 values are calculated using Equation (2.6) and charging data.

For the R_{bulk} calculation together with the dimensions of the electrolyte, conductivity of the ionic liquid is required. Using Equation (2.12) five different conductivity values for our five different ion fractions at room temperature are found.

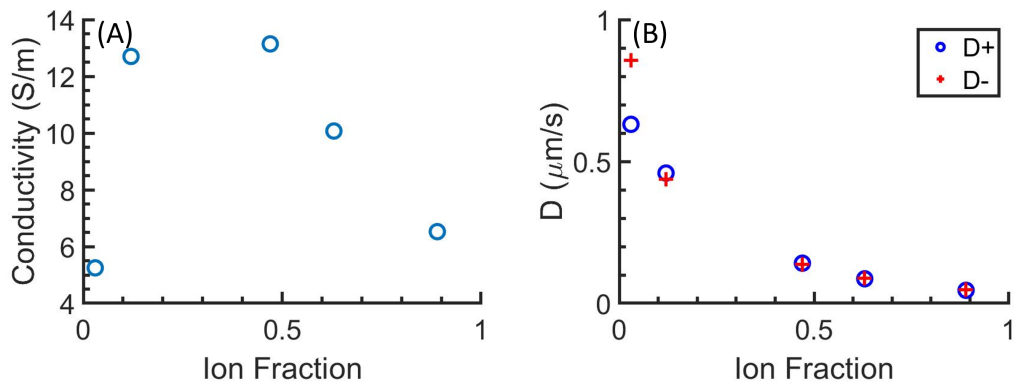


Figure 3.10. a) bulk conductivity, b) D^+ and D^- as a function of ion fraction.

In Figure 3.10 for each ion fraction, D^+ , D^- values and bulk conductivity results are plotted. Then using these conductivity values and dimensions of the systems 23 different R_{bulk} values are calculated via Equation (2.11).

With the calculation of C_1 and R_{bulk} , since potential difference is already set, only unknown of the TLM will become R_l , the resistance of each electrode slice. R_l is back calculated via minimizing the error sum of the initial charging part of the data using MATLAB cftool then controlled via solver plug-in of the Microsoft Excel.

Table 3.6. TLM parameters of the molecular simulations.

Model No	Q_{max} (e)	C_1 (10^{-19} F)	R_{bulk} (10^7 Ohm)	R_l (10^8 Ohm)	τ_M (s)
1	2.97	4.758	6.584	2.453	0.811
2	5.10	8.171	4.392	3.537	1.374
3	5.14	8.235	4.103	2.277	0.833
4	5.93	9.501	3.812	2.195	0.815
5	13.41	21.485	2.225	1.002	0.538
6	2.17	3.477	4.192	1.735	0.419
7	5.78	9.261	2.919	2.763	1.217
8	7.44	11.920	2.726	1.339	0.709
9	9.17	14.692	2.554	2.095	1.202
10	10.35	16.583	1.478	0.398	0.165
11	2.64	4.230	3.269	3.083	0.906
12	8.80	14.099	2.274	1.367	0.916
13	8.82	14.131	2.142	1.390	0.873
14	6.33	10.142	1.990	1.433	0.568
15	12.32	19.739	1.123	0.452	0.223
16	2.58	4.134	3.493	0.456	0.131
17	4.11	6.585	2.587	0.053	0.017
18	4.16	6.665	2.414	0.625	0.185
19	4.19	6.713	2.260	0.177	0.046
22	3.18	5.095	5.972	0.945	0.214
23	3.36	5.383	5.670	0.989	0.208

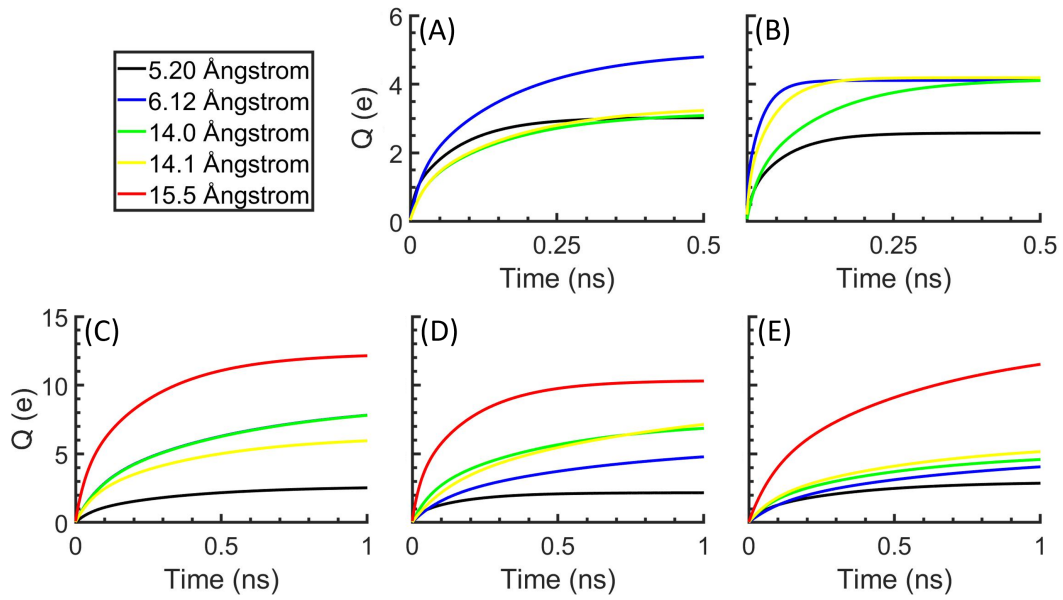


Figure 3.11. TLM charging as a function of time a) 0.03 M, b) 0.12 M, c) 0.47 M, d) 0.63 M, and e) 0.89 M.

3.2. Machine Learning Methods

There are various parameters that affect the performance of the supercapacitors which can be considered as input parameters such as molarity of the electrolyte solution, ion fraction of electrolyte, conductivity of the electrolyte, bulk electrolyte resistance, electrode dimensions, electrolyte dimensions, pore size, porosity, applied voltage, and initial slope of the charge data. In this particular work, features that represent physical meanings and adequate variances namely pore size, ion fraction, conductivity, porosity, initial slope of the charging data, and bulk electrolyte resistance, selected as input parameters and fed to machine learning models.

Performance parameters with respect to pore size, ion fraction, conductivity, porosity, initial slope of the charging data, and bulk electrolyte resistance are plotted in Figure 3.12 and Figure 3.13 for gravimetric investigation, and Figure 3.14 and Figure 3.15 for volumetric investigation.

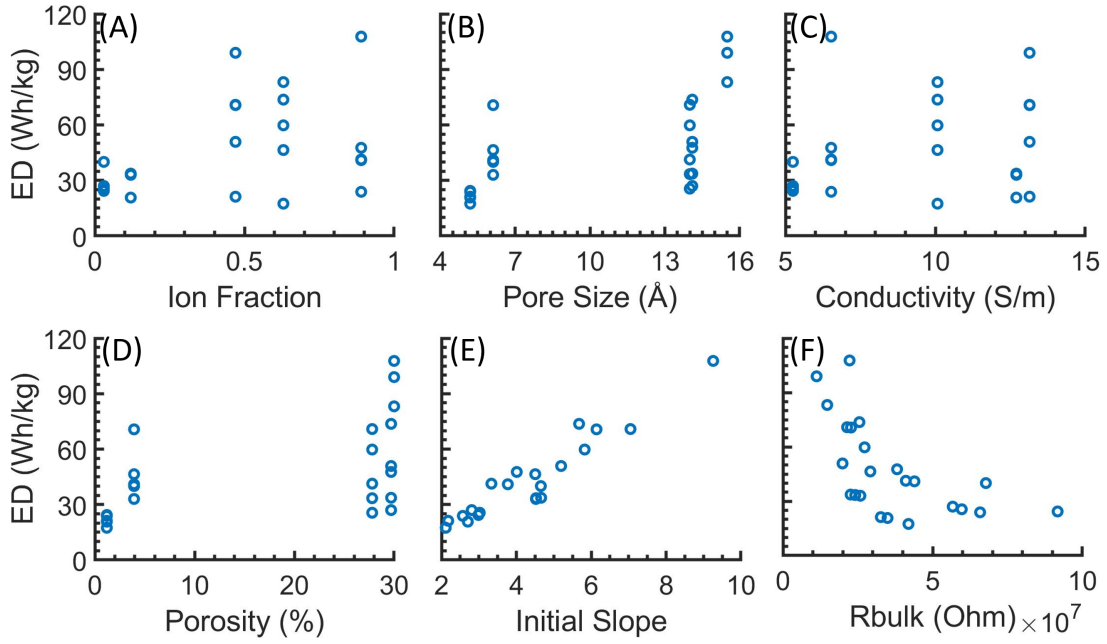


Figure 3.12. Gravimetric energy density as a function of a) ion fraction, b) pore size, c) conductivity, d) porosity, e) initial slope, and f) bulk electrolyte resistance.

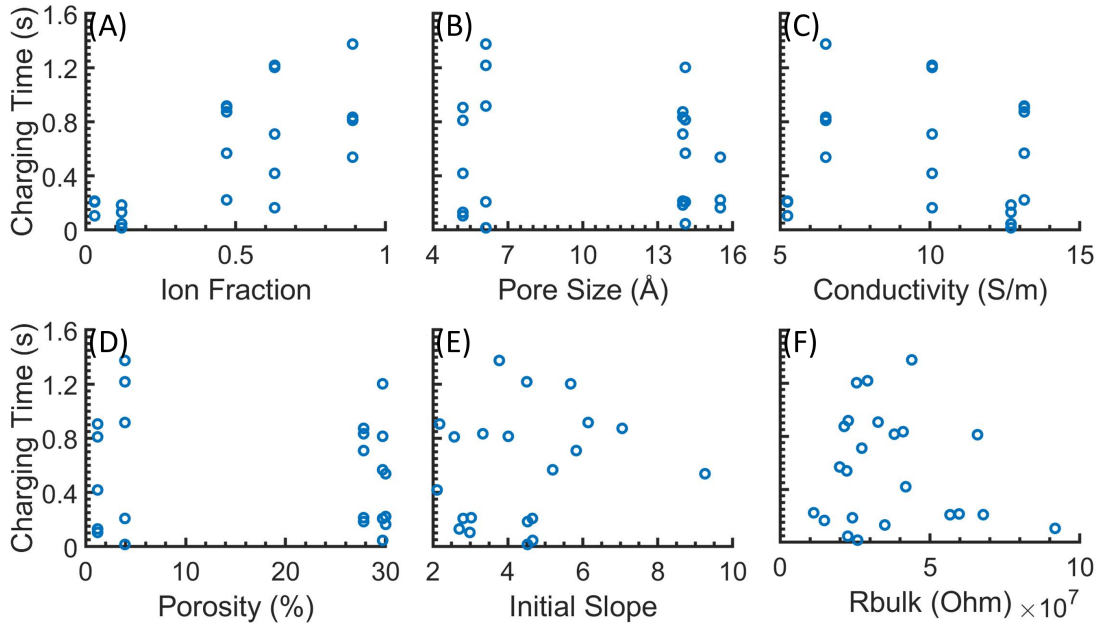


Figure 3.13. Characteristic charging time as a function of a) ion fraction, b) pore size, c) conductivity, d) porosity, e) initial slope, and f) bulk electrolyte resistance.

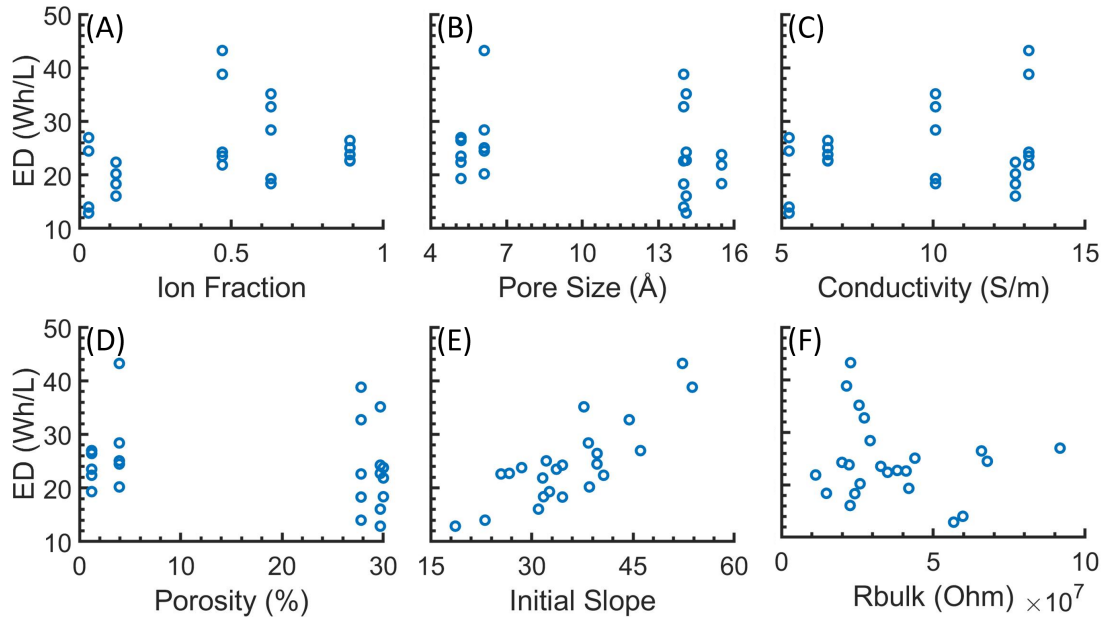


Figure 3.14. Volumetric energy density as a function of a) ion fraction, b) pore size, c) conductivity, d) porosity, e) initial slope, and f) bulk electrolyte resistance.

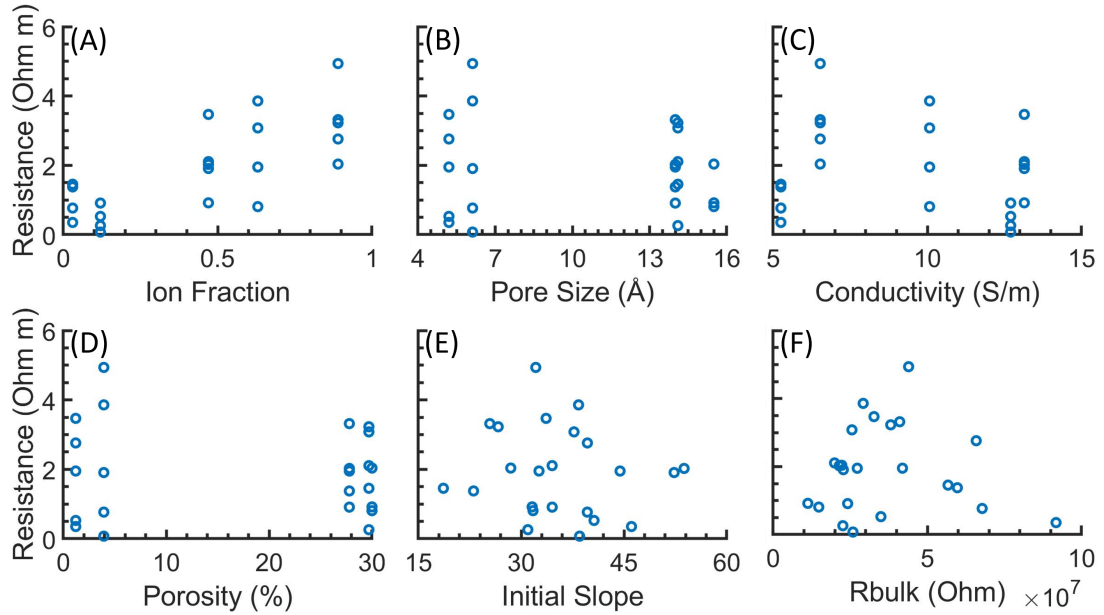


Figure 3.15. Resistance as a function of a) ion fraction, b) pore size, c) conductivity, d) porosity, e) initial slope, and f) bulk electrolyte resistance.

Feature selection is an important part of machine learning. Features with a higher variance contain more useful information since the effect can be trained with data. If there is no variance in a parameter that parameter should be excluded from the model. Since simulations have no variance in voltage, these values are eliminated but will be used in calculation of performance parameters. Correlations are the second thing one should consider, since highly correlated data increase the weight of these variables in prediction. For example, R_{bulk} and κ is related via Equation (2.11), hence using them both in a model can make their weight significantly higher in prediction which can lead over-fitting. In addition to that, after investigating the effect of each via adding them one by one to a linear regression model, parameters related to the geometry of the systems will be eliminated. Some machine learning methods include parameter elimination in them, for example LASSO regularization add penalty terms to different features to reduce the freedom of the model to avoid over-fitting. The feature selection leads simplification of models hence shorter training duration.

The optimization here is a two-step process. In the first step, capacitance values are predicted using various set of inputs. In the second step, various set of features are generated and tried to predict R_l . Some of these sets include predicted capacitance values as well to control the effect that additional feature. The reasoning comes from the R_l calculation method of transmission line model. In TLM, R_l is estimated using the charging data and the rest of the TLM parameters. Therefore, the effect of capacitance in prediction might be significant hence should be controlled. To control and compare the goodness of the fits RMSE and R^2 values are used. That give the required information about the importance of each parameter. But for that method some of the simulation results must be eliminated to make that parameter the only variable. Since the effect of each can also be seen directly from data, some combinations of the features are selected, and R^2 and RMSE are controlled again. Via observing the effect of parameters, possible sets of inputs are selected. Since our systems have the similar electrode weight, gravimetric capacitance can be directly predicted using predetermined transmission line model parameters. Also in the volumetric capacitance calculation, porosity gave us the similar freedom together with the similar carbon volume in electrodes.

3.2.1. Gravimetric Investigation

For the gravimetric investigation, as a first step, capacitance values are predicted in units of farad per gram. In the second step, R_l values are predicted in units of ohm with new set of inputs. The effect of addition of predicted capacitance is also controlled in that step. Once R_l and capacitance values are predicted, energy densities are calculated using Equation (2.28) and characteristic charging time values are calculated using Equation (2.29). Below the simulation results of gravimetric capacitance and characteristic charging time values for the simulation data can be seen. Since the results show that system with 0.03 ion fraction and 5.2 Å and 6.12 Å pore sizes have not reached equilibrium yet, these results are eliminated from the data-set used to train the machine learning models.

Table 3.7. Gravimetric capacitance and characteristic charging time values.

IF	Capacitance (F/g)					Charging Time (s)				
0.89	13.25	22.76	22.94	26.47	59.85	0.81	1.37	0.83	0.81	0.54
0.63	9.68	25.80	33.20	40.93	46.19	0.42	1.22	0.71	1.20	0.17
0.47	11.78	11.78	39.36	28.25	54.98	0.91	0.92	0.87	0.57	0.22
0.12	11.51	18.34	18.57	18.70	-	0.13	0.02	0.19	0.05	-
0.03	-	-	14.19	15.00	-	-	-	0.21	0.21	-
PS (Å)	5.2	6.12	14	14.1	15.5	5.2	6.12	14	14.1	15.5

3.2.1.1. Linear Regression. The simplest way to find the relation between input parameters and design parameters are to use linear regression. First the simplest model is created to predict the capacitance.

$$C_1 = \beta_0 + \beta_1 PS + \beta_2 IF + \beta_3 Co \quad (3.1)$$

in which pore size, ion fraction, and conductivity are used to predict gravimetric capacitance of the system.

To test the goodness of the fits R^2 and p-values are used as performance metrics. R^2 needs to be close to unity while p-value needs to be less than the significance level which is generally set to 0.05. That shows a significant linear regression relationship exists between the response variables and the predictor variables. To investigate the effect of each parameter test input sets are generated and R^2 and p-values are monitored. This guides us in determining the appropriate feature set for further evaluation.

The simplest model (T-1) which uses pore size, conductivity, and ion fraction to predict the capacitance has 0.577 R^2 and 0.0018 p-value. To increase the accuracy of the system additional parameters and interaction terms should be added to the model. Four interaction terms added to the T-1 model which are combinations of two parameters. That new model, namely T-2, has a higher R^2 value and lower p-value. R^2 for the T-2 is found as 0.760 while p-value is found as 0.0010 which is again below the required amount. Since the effect of some parameters can also be seen directly from data, some combination of these are selected. Also, for each system the effect of interaction terms are controlled. Via that method possible sets of inputs are selected and total of eight models created.

Table 3.8. Gravimetric parameter set control results.

Model	Input	Interactions	R^2	P-Value
T-1	PS, IF, Conductivity	-	0.577	0.0018
T-2	PS, IF, Conductivity	Included	0.760	0.0010
T-3	T-1 & Electrode Dimensions	-	0.841	<0.0001
T-4	T-1 & Electrode Dimensions	Included	0.885	0.0001
T-5	T-3 & Electrolyte Dimensions	-	0.845	0.0001
T-6	T-3 & Electrolyte Dimensions	Included	0.873	0.0008
T-7	T-5 & Initial Slope	-	0.944	<0.0001
T-8	T-7 & Porosity	-	0.945	<0.0001
T-9	T-7 & Porosity	Included	0.960	0.0001

In Table 3.8 the set of inputs of each model, together with R^2 and p-values are tabulated. Among these test models, it is seen that the model which includes information on pore size, ion fraction, conductivity, porosity, dimensions of the electrolyte region, initial slope of the charging data, interactions of pore size, ion fraction, and conductivity as independent variables leads the best results. This result shows that the dimensions of the electrode and electrolyte should be considered in prediction.

To be able to understand the effect of pore size and ion fraction better, the parameter selection step is important. To create meaningful contour plots, most of the parameters should change for each point of that plot accordingly. Keeping them as constants reduces the explanation power of the contour plots, hence additional sets are made accordingly. Porosity is related to pore size and conductivity is related to ion fraction. Hence these are chosen as the main set of inputs and four models are created. First model uses ion fraction, pore size, conductivity, and porosity as inputs. In second model interaction terms are added to the system to increase the accuracy of the prediction. Third model uses initial slope data in addition to the parameters used in first model. And finally, the fourth model include the terms of the third model together with interaction terms for prediction.

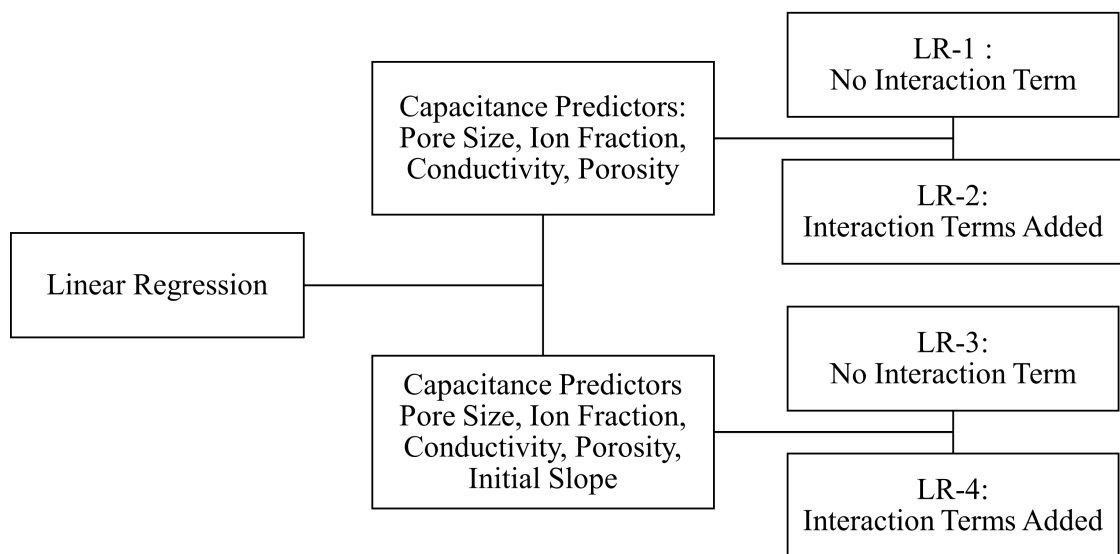


Figure 3.16. Gravimetric linear regression models created.

First model (LR-1) has $R^2 = 0.753$ and RMSE = 8.049 F/g. Second model (LR-2) with the addition of interaction terms R^2 decreases to 0.706 and RMSE increases to 9.5639 F/g. Third model (LR-3) has $R^2 = 0.908$ and RMSE = 5.5834 F/g. The fourth model (LR-4) with the addition of interaction terms of ion fraction, pore size, porosity, and conductivity R^2 increases to 0.9421 while RMSE decreases to 3.9769 F/g. In R_l prediction step, similar setups are used. In first model ion fraction, pore size, conductivity, and porosity are used as input features. In second model interaction terms are added to the system to increase the accuracy of the prediction. Third model uses initial slope data in addition to the parameters used in first model and finally, the fourth model interaction terms in addition to the input set of the third model. Predicted R_l values are used to compute characteristic charging times with Equation (2.29) and resulting τ_M values are used for comparison.

First model has $R^2 = 0.576$ and RMSE = 0.301 s while second model has $R^2 = 0.772$ and RMSE = 0.251 s. Third model has $R^2 = 0.671$ and RMSE = 0.249 s while fourth model has $R^2 = 0.737$ and RMSE = 0.194 s. The best model is found as LR-3. Related capacitance and charging time graphs are plotted in Figure 3.17. Results are tabulated in Table 3.9. Both cross validation average and overall RMSE values are given for each model in Table 3.9.

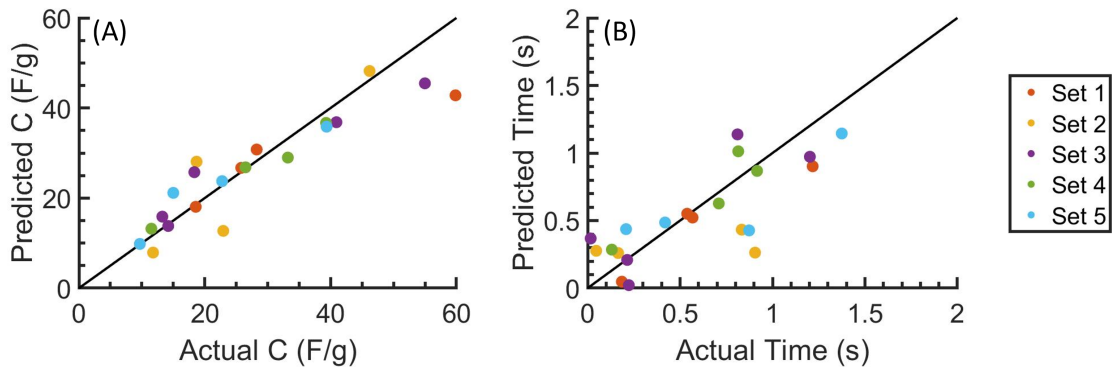


Figure 3.17. Linear regression (LR-3) comparison graphs a) gravimetric capacitance, b) characteristic charging time.

Table 3.9. Gravimetric linear regression model results.

	C_G (F/g)			τ_M (s)		
Model	R^2	RMSE		R^2	RMSE	
LR-1	0.7353	8.0491	8.0845	0.5760	0.3013	0.3241
LR-2	0.7057	9.5639	9.9661	0.7725	0.2507	0.2792
LR-3	0.9075	5.5834	6.0050	0.6709	0.2493	0.2655
LR-4	0.9421	3.9769	5.5214	0.7372	0.1937	0.2261

3.2.1.2. Ridge Regression. First model, namely R-1, uses ion fraction, pore size, conductivity, and porosity alone. R-2 added interaction terms to the model to increase R^2 and to decrease RMSE. The third model R-3 uses initial slope data together with pore size, porosity, ion fraction, and conductivity. The fourth and final model added interaction terms to the third model. Predicted R_i values are used to compute characteristic charging times with Equation (2.29). Ridge parameter (k) values are tried with 0.1 increments for each model. Both cross validation average and overall RMSE values are given for each model in Table 3.10 together with the selected ridge parameters.

Table 3.10. Gravimetric ridge regression model results.

	C_G (F/g)				τ_M (s)			
Model	k	R^2	RMSE		k	R^2	RMSE	
R-1	0.01	0.7526	7.4015	7.4440	0.01	0.5980	0.2827	0.2927
R-2	0.01	0.7488	7.7637	7.9173	0.01	0.7656	0.2188	0.2419
R-3	0.01	0.9675	3.5418	3.7639	0.01	0.7356	0.2210	0.2316
R-4	0.01	0.9754	3.1244	3.3484	0.01	0.8491	0.1700	0.1748

Considering the R^2 and RMSE values of both gravimetric capacitance and characteristic charging time, the best predictive model is selected as R-4. Related gravimetric capacitance and characteristic charging time comparison graphs are plotted.

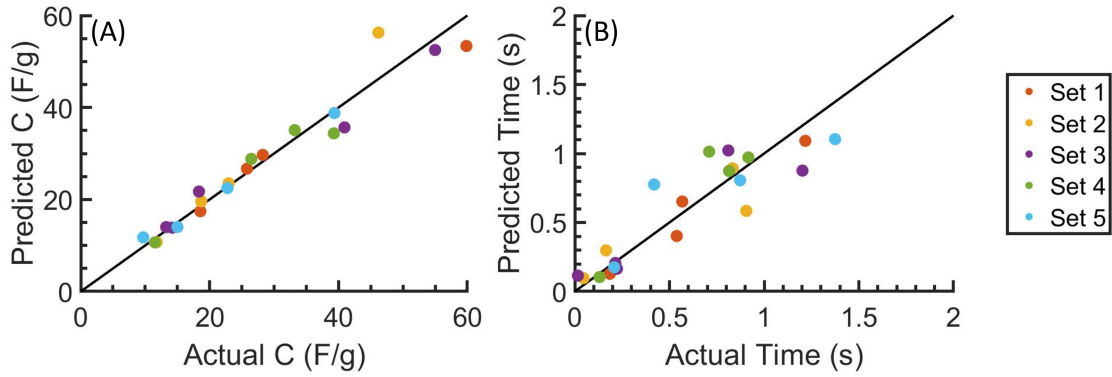


Figure 3.18. Ridge regression (R-4) comparison graphs a) gravimetric capacitance, b) characteristic charging time.

3.2.1.3. Lasso Regression & Elastic Networks. In MATLAB, elastic network solution and lasso regression use same build-in function. While alpha (α) set to unity solution gives the lasso regression, the change in α values leads scanning through elastic network. For all models, λ values that gave minimum deviance and error summation is selected. Figure 3.19 shows the models created for gravimetric investigation with their corresponding R_l prediction inputs. Total of six systems are created.

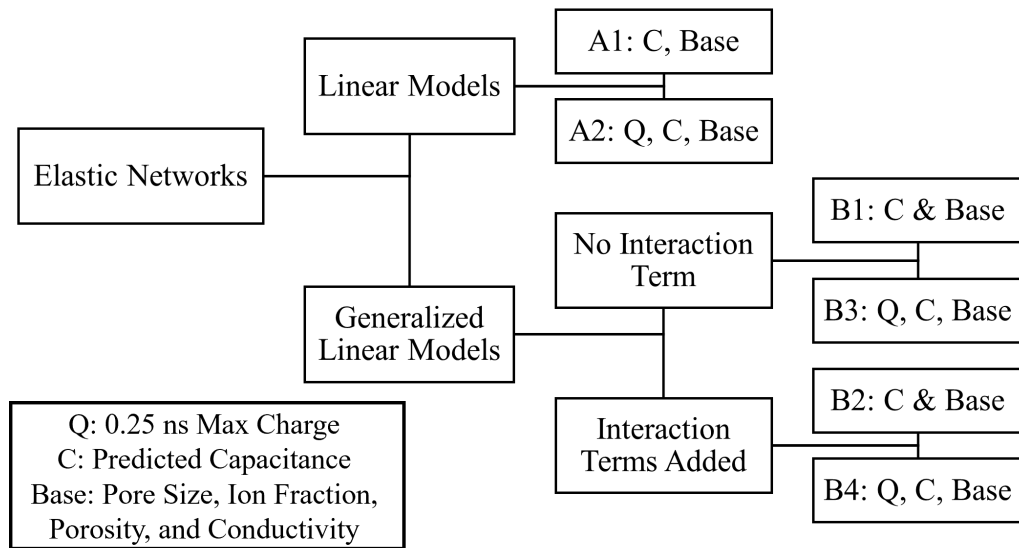


Figure 3.19. Elastic network models created.

A1 and A2 have elastic network solutions. B1 to B4 use generalized linear models, particularly normal distribution. Initial slope, pore size, porosity, ion fraction, and conductivity data are used to predict capacitance. A1, A2, B1, and B2 use interaction terms in addition to these parameters. In R_l prediction all models uses pore size, porosity, ion fraction, conductivity, and predicted capacitance as input parameters. A2, B3, and B4 use initial slope in addition to these. Also B1 and B3 use interaction terms in R_l prediction. Predicted R_l values are used to compute characteristic charging times with Equation (2.29). Best model is found as B2.

Table 3.11. Gravimetric elastic network model results.

Model	Capacitance (F/g)					Charging Time (s)				
	α	λ	R^2	RMSE		α	λ	R^2	RMSE	
A1	0.11	0.0152	0.980	3.127	3.362	0.54	0.0215	0.870	0.161	0.172
A2	0.11	0.0152	0.980	3.127	3.362	1.00	0.0185	0.861	0.165	0.174
B1	0.07	0.0015	0.966	3.623	3.824	0.01	0.0110	0.699	0.231	0.243
B2	0.11	0.0115	0.980	3.103	3.350	0.58	0.0166	0.875	0.159	1.170
B3	0.07	0.0015	0.966	3.623	3.824	0.01	0.0306	0.704	0.230	0.242
B4	0.11	0.0115	0.980	3.103	3.350	1.00	0.0154	0.868	0.161	0.171

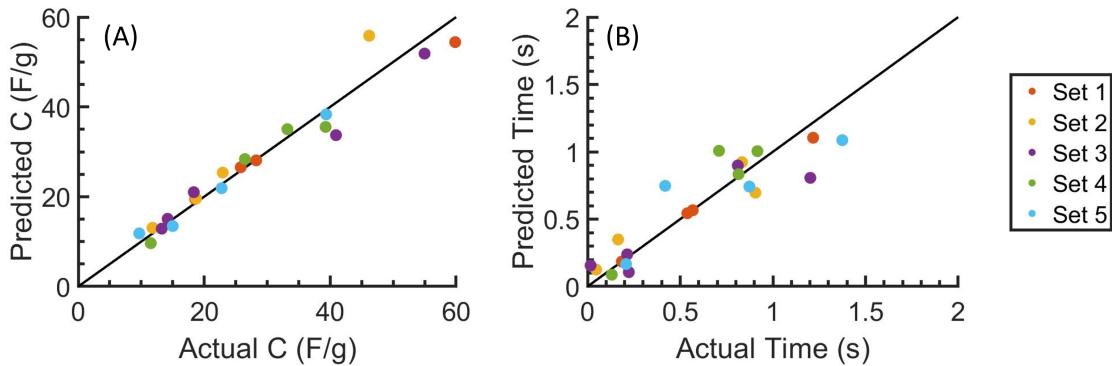


Figure 3.20. Elastic network (B2) comparison graphs a) gravimetric capacitance, b) characteristic charging time.

3.2.1.4. Support Vector Machines. For the capacitance prediction, initial slope data, pore size, porosity, ion fraction, and conductivity data are used. R^2 is found as 0.960 and RMSE is found as 3.703 F/g. In R_l prediction in addition to pore size, porosity, ion fraction, and conductivity, predicted capacitance values are used. Predicted R_l values are used to compute characteristic charging times with Equation (2.29). R^2 is found as 0.734 and RMSE is found as 0.250 s for charging time prediction. Related gravimetric capacitance and characteristic charging time comparison graphs are plotted.

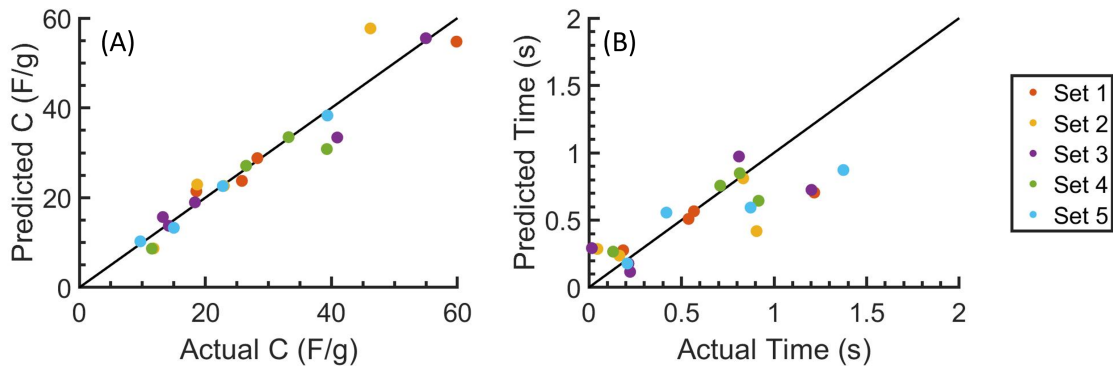


Figure 3.21. Support vector machines comparison graphs a) gravimetric capacitance, b) characteristic charging time.

3.2.1.5. Artificial Neural Network. Total of 17 models are created for gravimetric investigation. Models have different input types and positions yet can be grouped. Unless otherwise explicitly stated, in capacitance prediction pore size, porosity, ion fraction, and conductivity are used. There are four types of systems related to feeding positions and input types. First, matrix type input is used in two models, namely G1 and G2. Then there are separated feeds which enters the system via various positions.

In type NN1, all the inputs entered to the first hidden layer including initial charging data. In type NN2, initial charging data fed to both layers hence has an additional direct effect on the outcome and prediction. In type NN3, initial charging data only fed to the second layer. In Figure 3.22 whole set of models created for gravimetric investigation can be seen.

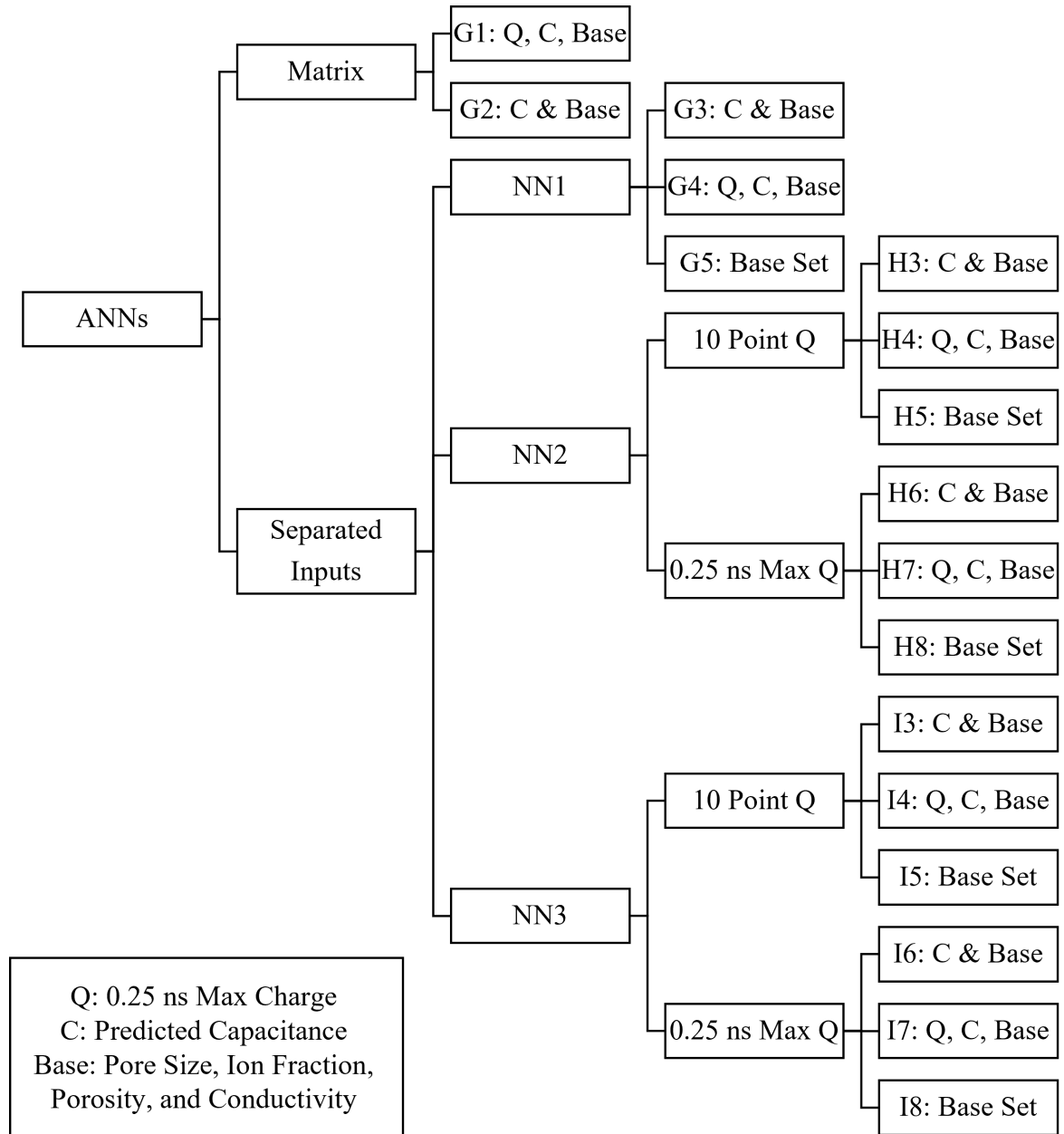


Figure 3.22. Gravimetric neural network models created.

Hidden layers are controlled via various sizes, namely one to five since the optimal size of the hidden layer is usually between the size of the input and size of the output layers. The layer size which gave the best R^2 and RMSE values selected for each model for further calculations. In Table 3.12 selected hidden layer sizes (HLS), input types (Matrix, NN1, NN2, or NN3), and terms used in R_t prediction in addition to pore size, ion fraction, porosity, and conductivity are given for each system.

Table 3.12. Gravimetric neural network model details.

Model	Type	Hidden Layer Sizes		R_i Prediction		
		C_G Prediction	R_i Prediction	Q_i Type	C_G	Q_i
G1	Matrix	3 Nodes	4 Nodes	Initial Slope	+	-
G2	Matrix	3 Nodes	3 Nodes	Initial Slope	+	+
G3	NN1	3 Nodes	2 Nodes	10-Point	+	-
G4	NN1	3 Nodes	3 Nodes	10-Point	+	+
G5	NN1	3 Nodes	Failed	10-Point	-	-
H3	NN2	1 Nodes	3 Nodes	10-Point	+	-
H4	NN2	1 Nodes	3 Nodes	10-Point	+	+
H5	NN2	1 Nodes	Failed	10-Point	-	-
H6	NN2	3 Nodes	2 Nodes	Initial Slope	+	-
H7	NN2	3 Nodes	3 Nodes	Initial Slope	+	+
H8	NN2	3 Nodes	4 Nodes	Initial Slope	-	-
I3	NN3	1 Nodes	4 Nodes	10-Point	+	-
I4	NN3	1 Nodes	3 Nodes	10-Point	+	+
I5	NN3	1 Nodes	Failed	10-Point	-	-
I6	NN3	3 Nodes	3 Nodes	Initial Slope	+	-
I7	NN3	3 Nodes	3 Nodes	Initial Slope	+	+
I8	NN3	3 Nodes	3 Nodes	Initial Slope	-	-

Both G1 and G2 have pore size, porosity, ion fraction, conductivity, and initial slope data to predict capacitance. Initial slope is defined as the maximum charge in the first 0.25 ns of the simulation trajectory. Matrix type feeds use maximum charge of 0.25 ns of the data. G1 and G2 have $R^2 = 0.987$ and $RMSE = 2.583$ F/g in capacitance prediction. In R_i prediction G1 uses predicted capacitance, pore size, porosity, ion fraction, and conductivity while G2 also uses initial slope. Predicted R_i values are used to compute characteristic charging times with Equation (2.29). G1 has $R^2 = 0.796$ and $RMSE = 0.211$ s while G2 has $R^2 = 0.836$ and $RMSE = 0.196$ s.

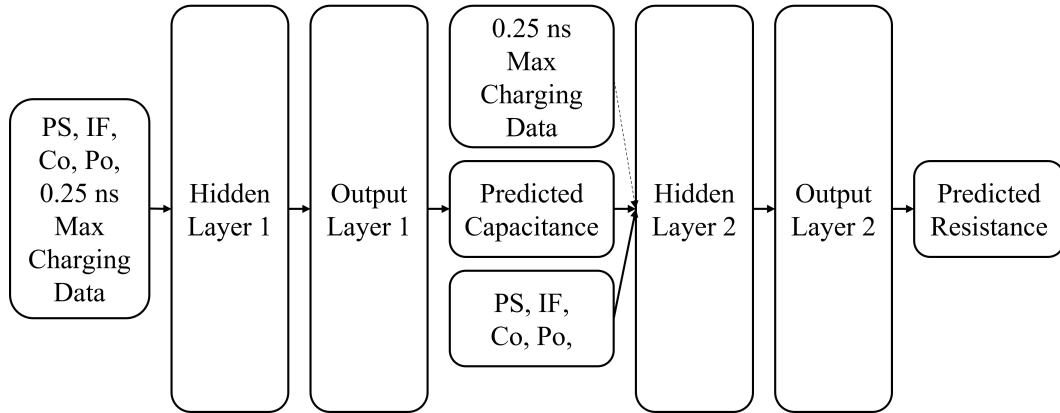


Figure 3.23. Matrix type ANN design for G1 and G2.

G3, G4, and G5 uses NN1 type of feeding. In capacitance prediction pore size, porosity, ion fraction, conductivity, and 10-point initial charging data entered the first layer together. Capacitance prediction has $R^2 = 0.951$ and RMSE = 3.763 F/g. In R_l prediction G3 uses predicted capacitance, while G4 also uses initial charging data. G5 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute characteristic charging times with Equation (2.29). G3 has $R^2 = 0.770$ and RMSE = 0.216 s while G4 has $R^2 = 0.732$ and RMSE = 0.232 s. G5 is failed to predict R_l hence eliminated.

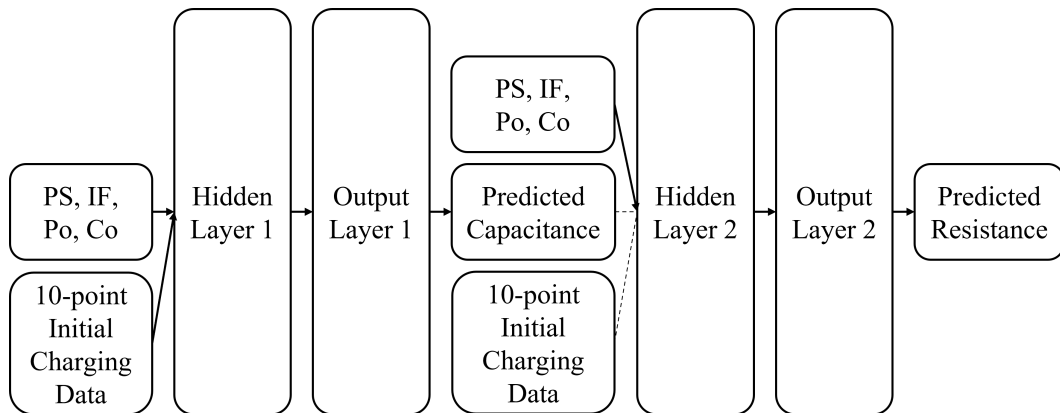


Figure 3.24. NN1 type ANN design for G3, G4, and G5.

H3, H4, and H5 uses NN2 type of feeding. Predictors entered to first layer together. Initial charging data added to both first and second layer. In capacitance prediction pore size, porosity, ion fraction, conductivity, and 10-point initial charging data are used. Visual explanation of the models can be seen in Figure 3.25. Capacitance prediction has $R^2 = 0.898$ and RMSE = 5.949 F/g. In R_l prediction H3 uses predicted capacitance, while H4 also uses 10-point initial charging data. H5 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute characteristic charging times with Equation (2.29). H3 has $R^2 = 0.680$ and RMSE = 0.255 s while H4 has $R^2 = 0.686$ and RMSE = 0.254 s. H5 is failed to predict R_l hence characteristic charging time.

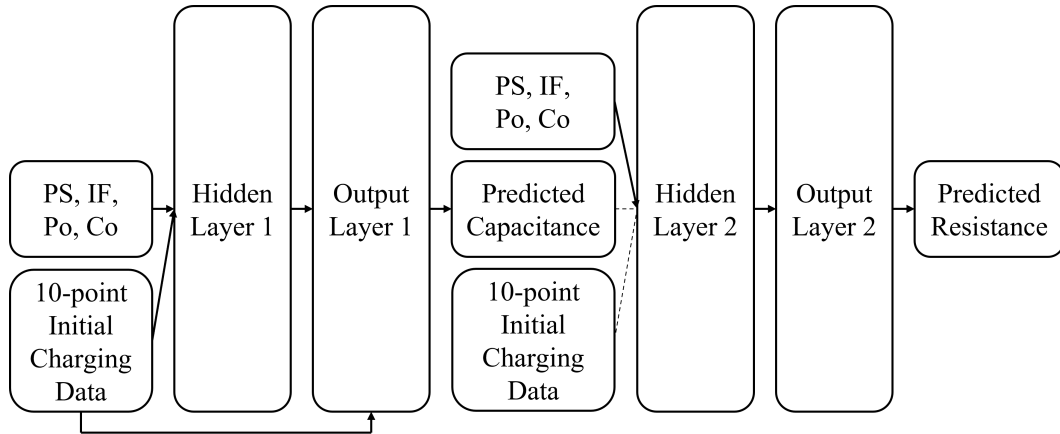


Figure 3.25. NN2 type ANN design for H3, H4, and H5.

H6, H7, and H8 uses NN2 type of feeding. Predictors entered to first layer together. initial slope data added to both first and second layer. In capacitance prediction pore size, porosity, ion fraction, conductivity, and initial slope data is used. Capacitance prediction has $R^2 = 0.973$ and RMSE = 3.296 F/g. In R_l prediction H6 uses predicted capacitance, while H7 also uses initial slope data. H8 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute characteristic charging times with Equation (2.29). H6 has $R^2 = 0.785$ and RMSE = 0.211 s while H7 has $R^2 = 0.811$ and RMSE = 0.186 s. H8 has $R^2 = 0.633$ and RMSE = 0.242 s.

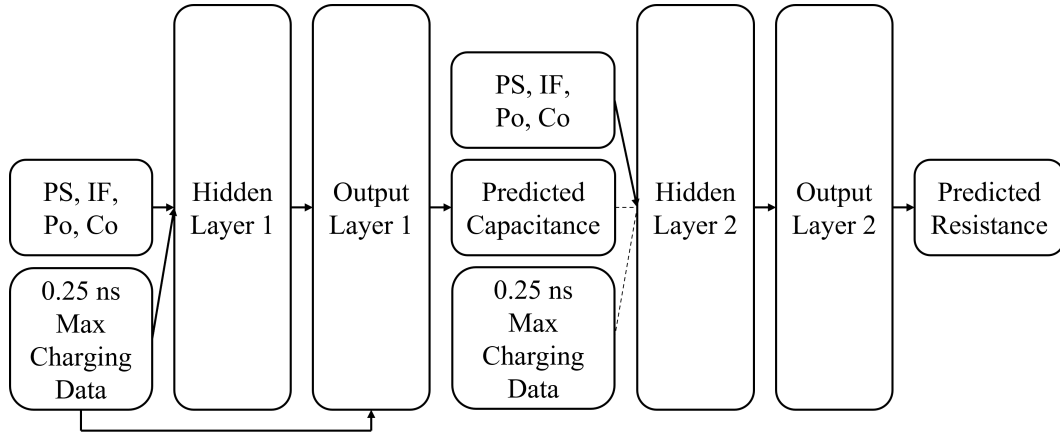


Figure 3.26. NN2 type ANN design for H6, H7, and H8.

I3, I4, and I5 uses NN3 type of feeding. In capacitance prediction pore size, ion fraction, porosity, and conductivity entered the first layer together. 10-point initial charging data added to the second layer only. In R_l prediction step, I3 uses predicted capacitance, while I4 also uses 10-point initial charging data to increase accuracy of the prediction. I5 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute characteristic charging times with Equation (2.29). Visual explanation of the models I3, I4, and I5 can be seen in Figure 3.27.

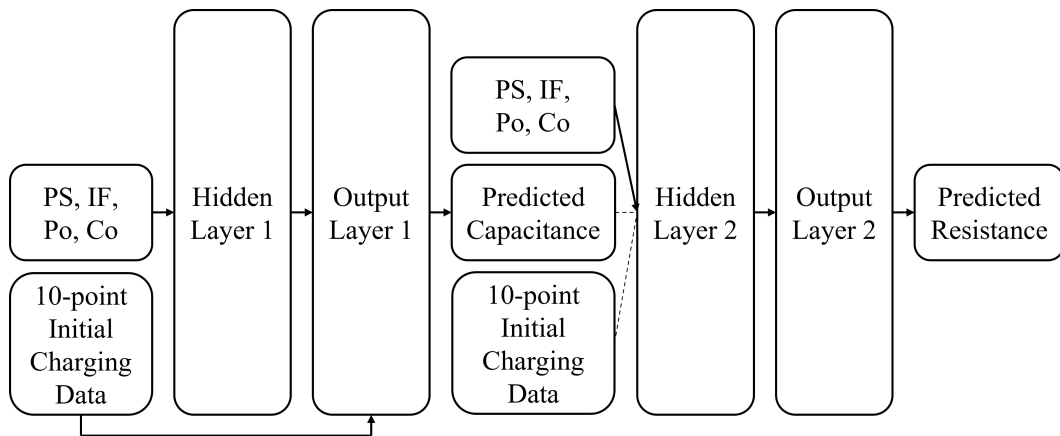


Figure 3.27. NN3 type ANN design for I3, I4, and I5.

Capacitance prediction has $R^2 = 0.903$ and RMSE = 6.018 F/g. I3 has $R^2 = 0.690$ and RMSE = 0.245 s while I4 has $R^2 = 0.700$ and RMSE = 0.557 s. I5 is failed to predict R_l hence characteristic charging time.

I6, I7, and I8 uses NN3 type of feeding. Predictors entered to first layer together. Initial slope data added to second layer only. In capacitance prediction pore size, porosity, ion fraction, conductivity, and initial slope data is used. Visual explanation of the models can be seen in Figure 3.28. Capacitance prediction has $R^2 = 0.964$ and RMSE = 3.708 F/g. In R_l prediction I6 uses predicted capacitance, while I7 also uses 0.25 ns initial slope data. I8 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute characteristic charging times with Equation (2.29). I6 has $R^2 = 0.795$ and RMSE = 0.207 s while I7 has $R^2 = 0.777$ and RMSE = 0.213 s. I8, the simplest model of these three, has $R^2 = 0.601$ and RMSE = 0.251 s.

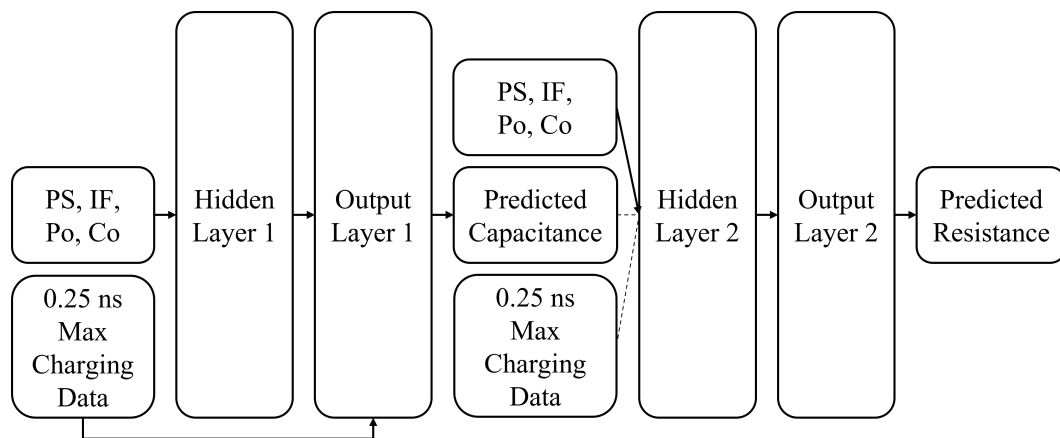


Figure 3.28. NN3 type ANN design for I6, I7, and I8.

In Table 3.13 whole set of neural network models can be found. Lines with no hidden layer size or R^2 and/or RMSE values are failed predictions which have below 0.6 R^2 values. 5-Fold cross validation is applied to each system and pre-selected sets are used in calculation. Both cross validation average and overall RMSE values are given for each model.

Table 3.13. Gravimetric neural network model results.

	Capacitance (F/g)			τ_M (s)		
Model	R^2	RMSE		R^2	RMSE	
G1	0.9871	2.5829	2.8091	0.7961	0.2110	0.2207
G2	0.9871	2.5829	2.8091	0.8360	0.1964	0.2029
G3	0.9508	3.7634	3.8699	0.7696	0.2157	0.2255
G4	0.9508	3.7634	3.8699	0.7324	0.2319	0.2407
G5	0.9508	3.7634	3.8699	-	-	-
H3	0.8981	5.9493	6.1567	0.6795	0.2551	0.2711
H4	0.8981	5.9493	6.1567	0.6859	0.2537	0.2685
H5	0.8981	5.9493	6.1567	-	-	-
H6	0.9732	3.2964	3.4709	0.7852	0.2110	0.2203
H7	0.9732	3.2964	3.4709	0.8110	0.1862	0.1972
H8	0.9732	3.2964	3.4709	0.6330	0.2416	0.2610
I3	0.9026	6.0183	6.2461	0.6896	0.2451	0.2711
I4	0.9026	6.0183	6.2461	0.7000	2.5570	0.2687
I5	0.9026	6.0183	6.2461	-	-	-
I6	0.9640	3.7085	3.8707	0.7948	0.2066	0.2173
I7	0.9640	3.7085	3.8707	0.7771	0.2126	0.2218
I8	0.9640	3.7085	3.8707	0.6094	0.2512	0.2708

According to these values in Table 3.13, G2 is found as the most accurate predictive ANN model of the gravimetric investigation. None of the models is eliminated in capacitance prediction step. Models using 10-point initial charging data as an input in first step yet predicting R_l without such data failed to predict R_l hence characteristic charging time. Although there are models that gave quite close results in capacitance prediction step, in R_l prediction they became far worse than the G2. Comparison graphs of G2 for gravimetric capacitance and characteristic charging time values can be seen in Figure 3.29.

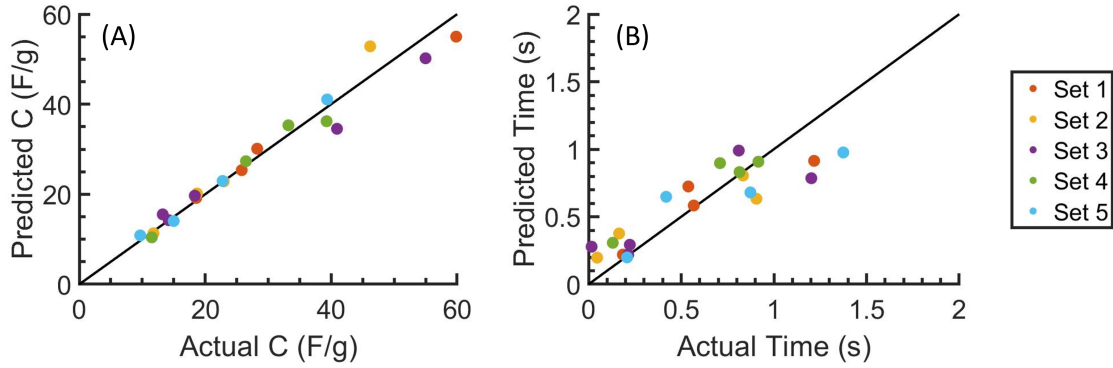


Figure 3.29. Neural network (G2) comparison graphs a) gravimetric capacitance, b) characteristic charging time.

3.2.2. Volumetric Investigation

For the volumetric investigation, as a first step capacitance values are predicted in units of farad per cubic centimeter. In the second step, R_l values are predicted in units of ohm with new set of inputs. The effect of addition of predicted capacitance is also controlled in that step. Once R_l and capacitance values are predicted volumetric energy densities are calculated using Equation (2.30) and resistances are calculated using Equation (2.31). In Table 3.14 the simulation results of volumetric capacitances and resistances can be found.

Table 3.14. Volumetric capacitance and resistance values.

IF	Capacitance (F/cm ³)					Resistance (Ohm m)				
0.89	14.69	13.92	12.56	12.62	13.22	2.76	4.94	3.32	3.23	2.04
0.63	10.73	15.78	18.18	19.52	10.20	1.95	3.86	1.95	3.08	0.81
0.47	13.05	13.05	21.56	13.47	12.14	3.47	1.91	2.03	2.11	0.92
0.12	12.43	11.22	10.17	8.92	-	0.53	0.07	0.91	0.26	-
0.03	-	-	7.77	7.15	-	-	-	1.38	1.45	-
PS (Å)	5.2	6.12	14	14.1	15.5	5.2	6.12	14	14.1	15.5

Since the results show that system with 0.03 ion fraction and 5.2 Å and 6.12 Å pore sizes have not reached equilibrium yet, these results are eliminated from the data-set used to train the machine learning models

3.2.2.1. Linear Regression. Pore size, porosity, ion fraction, and conductivity are chosen as the main inputs and four models are created for volumetric investigation.

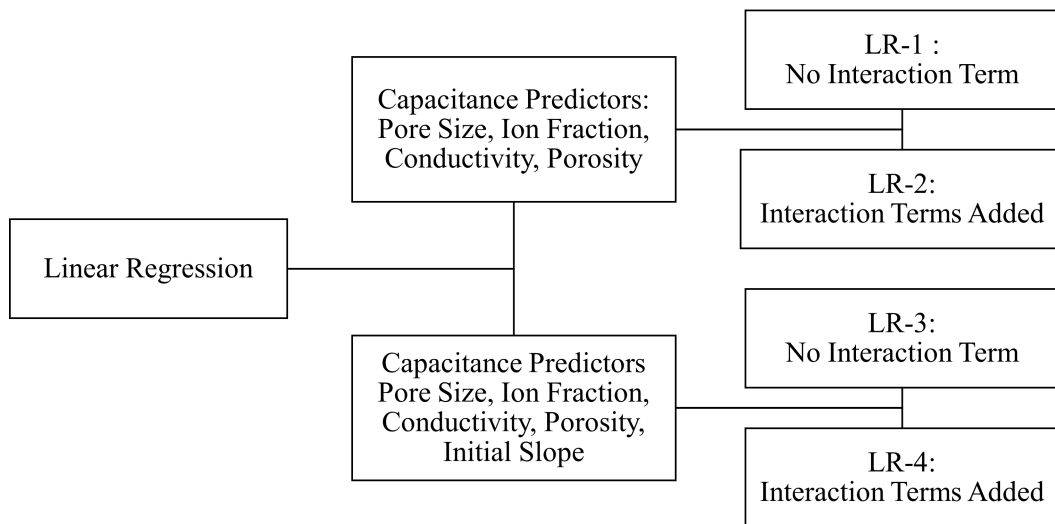


Figure 3.30. Volumetric linear regression models created.

First model uses ion fraction, pore size, conductivity, and porosity alone. That leads $R^2 = 0.489$ and $\text{RMSE} = 3.871 \text{ F/cm}^3$. In second model, interaction terms are added to the system and R^2 value increases to 0.631 and RMSE value increases to 4.173 F/cm^3 . In third model in addition to the parameters used in first model, volumetric initial slope data is also used. That increases the R^2 to 0.687 and reduces the RMSE to 1.580 F/cm^3 . The fourth model uses interaction terms of ion fraction, pore size, porosity, and conductivity, and further increases the R^2 to 0.718 while increases RMSE to 3.442 F/cm^3 . In R_l prediction step, similar setups are used. First model gives 0.730 R^2 with 0.726 Ohm m RMSE while second model gives 0.622 R^2 and 0.787 Ohm m RMSE. Third model gives 0.746 R^2 and 0.735 Ohm m RMSE while fourth model gives 0.775 R^2 and 0.976 Ohm m RMSE. Results are tabulated in Table 3.15.

Table 3.15. Volumetric linear regression model results.

	C_v (F/cm ³)			R_l (Ohm m)		
Model	R^2	RMSE		R^2	RMSE	
LR-1	0.4893	3.8712	3.8856	0.7303	0.7259	0.7456
LR-2	0.6310	4.1734	4.5856	0.6224	0.7866	0.8756
LR-3	0.6867	1.5803	1.6149	0.7462	0.7351	0.7589
LR-4	0.7183	3.4417	3.9097	0.7753	0.9763	1.2431

According to the results in Table 3.15 the best predictive linear regression model is selected as LR-3 via considering R^2 and RMSE values. Related volumetric capacitance and resistance comparison graphs are plotted in Figure 3.31.

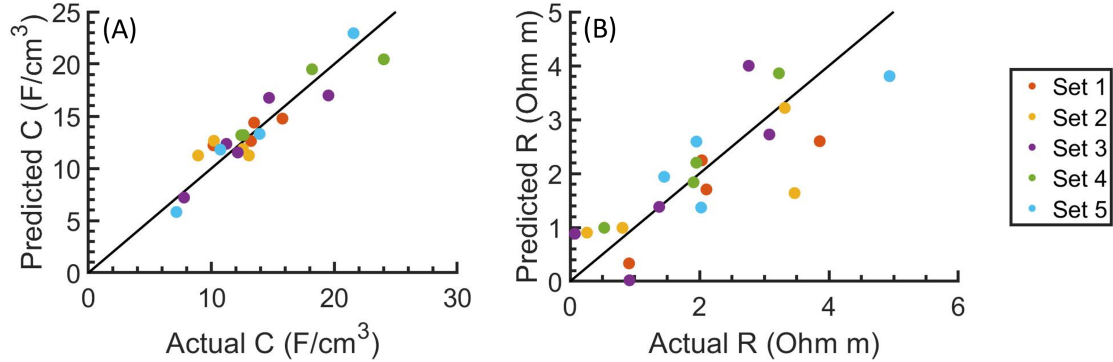


Figure 3.31. Linear regression (LR-3) comparison graphs a) volumetric capacitance, b) resistance.

3.2.2.2. Ridge Regression. R-1 uses ion fraction, pore size, conductivity, and porosity alone. R-2 added interaction terms to the model to increase R^2 and to decrease RMSE. The third model uses initial slope data together with pore size, porosity, ion fraction, and conductivity. The fourth uses additional interaction terms for prediction. Ridge parameter (k) values are tried with 0.1 increments for each model. Below together with the results, the selected ridge parameter values are tabulated in Table 3.16.

Table 3.16. Volumetric ridge regression model results.

	C_v (F/cm ³)				R_l (Ohm m)			
Model	k	R^2	RMSE		k	R^2	RMSE	
R-1	0.02	0.5817	3.0932	3.2166	0.02	0.7641	0.6758	0.6947
R-2	0.02	0.6852	2.8017	2.9577	0.02	0.7219	0.6822	0.7140
R-3	0.02	0.7262	1.4926	1.5722	0.02	0.7582	0.6734	0.6930
R-4	0.02	0.8246	1.2421	1.2781	0.02	0.8579	0.5096	0.5360

According to the results in Table 3.16 the best ridge regression model is as selected R-4, and volumetric capacitance and resistance comparison graphs are plotted.

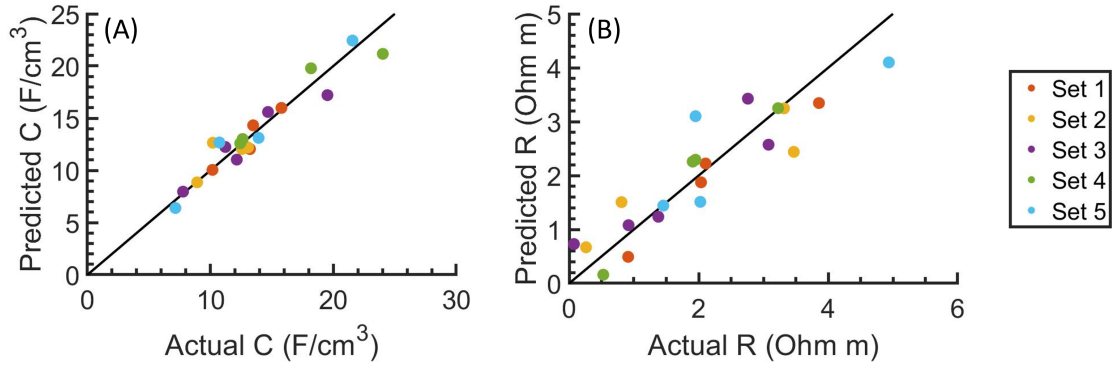


Figure 3.32. Ridge regression (R-4) comparison graphs a) volumetric capacitance, b) resistance.

3.2.2.3. Lasso Regression & Elastic Networks. For volumetric investigation total of six systems are created and tested. First two, namely A1 and A1, have elastic network solutions. B1 to B4 use generalized linear models, particularly normal distribution. All six models use initial slope together with pore size, porosity, ion fraction, and conductivity to predict capacitance. A1, A2, B1, and B2 use interaction terms in addition to these parameters.

In R_l prediction all models use pore size, porosity, ion fraction, conductivity, and predicted capacitance as input parameters. A2, B3, and B4 use initial slope in addition to these. Also B1 and B3 use interaction terms in R_l prediction. Predicted R_l values are used to compute resistance with Equation (2.31). Results of all six models together with their corresponding α and λ values can be seen in Table 3.17. According to the results in Table 3.17 the best predictive elastic network model is found as B4. Related volumetric capacitance and resistance comparison graphs are plotted in Figure 3.33. Both cross validation average and overall RMSE values are given for each model.

Table 3.17. Volumetric elastic network model results.

Model	Capacitance (F/cm ³)					Resistance (Ohm m)				
	α	λ	R^2	RMSE		α	λ	R^2	RMSE	
A1	0.08	0.0113	0.888	1.097	1.181	0.28	0.0503	0.831	0.555	0.571
A2	0.08	0.0113	0.888	1.097	1.181	0.33	0.0514	0.841	0.534	0.561
B1	0.06	0.0553	0.728	1.610	1.701	0.38	0.0003	0.767	0.671	0.689
B2	0.09	0.0083	0.890	1.090	0.172	0.26	0.0450	0.835	0.545	0.562
B3	0.06	0.0553	0.728	1.610	1.701	0.22	0.0002	0.767	0.671	0.689
B4	0.09	0.0083	0.890	1.090	0.172	0.27	0.0522	0.844	0.527	0.553

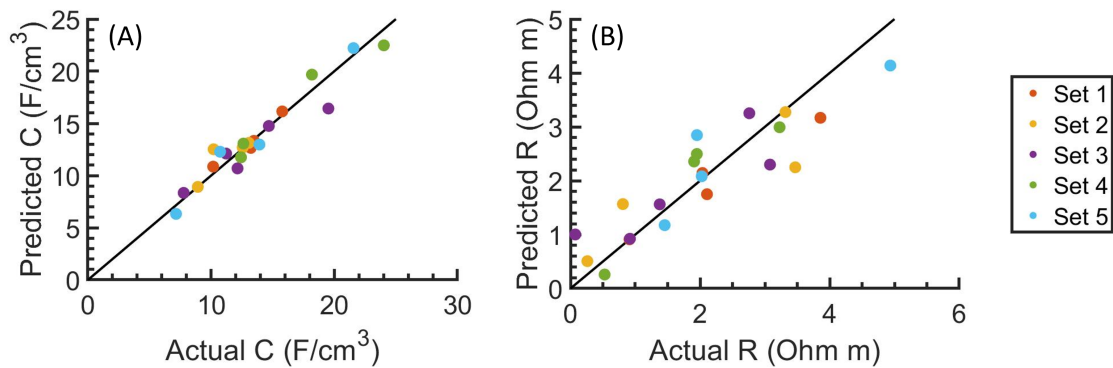


Figure 3.33. Elastic network (B4) comparison graphs a) volumetric capacitance, b) resistance.

3.2.2.4. Support Vector Machines. For the capacitance prediction, initial slope data, pore size, porosity, ion fraction, and conductivity are used. R^2 is found as 0.859 and RMSE is found as 1.640 F/cm³ in volumetric capacitance prediction. In R_l prediction in addition to pore size, porosity, ion fraction, and conductivity, predicted capacitance values are used. Predicted R_l values are used to compute resistance with Equation (2.31). R^2 is found as 0.672 and RMSE is found as 0.779 Ohm m in resistance prediction. Volumetric capacitance and resistance comparison graphs are plotted.

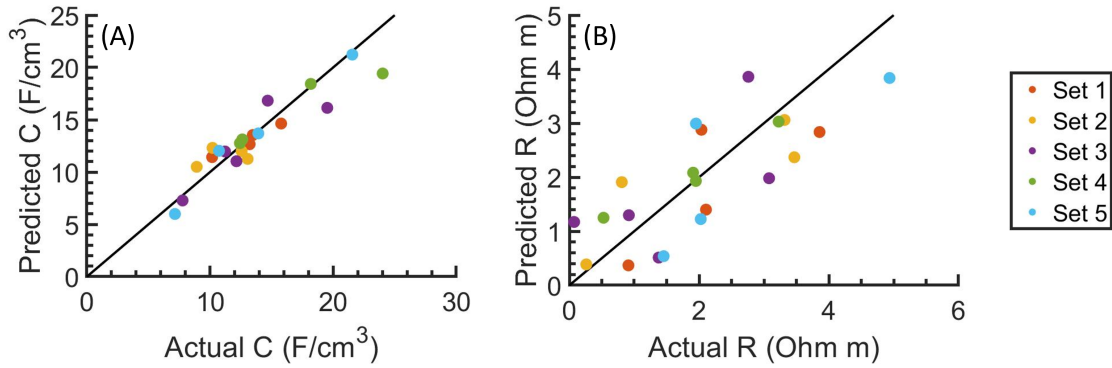


Figure 3.34. Support vector machine comparison graphs a) volumetric capacitance, b) resistance.

3.2.2.5. Artificial Neural Network. Total of 17 models are created for volumetric investigation. Models have different input types and positions yet can be grouped. Unless otherwise explicitly stated, in capacitance prediction pore size, porosity, ion fraction, and conductivity are used in all systems. There are four types of systems related to feeding positions and input types. First, matrix type input is used in two models, namely G1 and G2. Then there are separated feeds which enters the system via various positions. In type NN1, all the input parameters entered to the first hidden layer including selected type of initial charging data. In type NN2, initial charging data fed to both of the layers, namely hidden layer and output layer, hence have a more direct effect on the outcome. In type NN3, selected type of initial charging data only fed to the output layer.

Layers are controlled via various sizes, namely one to five since the optimal size of the hidden layer is generally between the size of the input and size of the output layers. The layer size which gave the best R^2 and RMSE values are selected for the corresponding model and used in further studies.

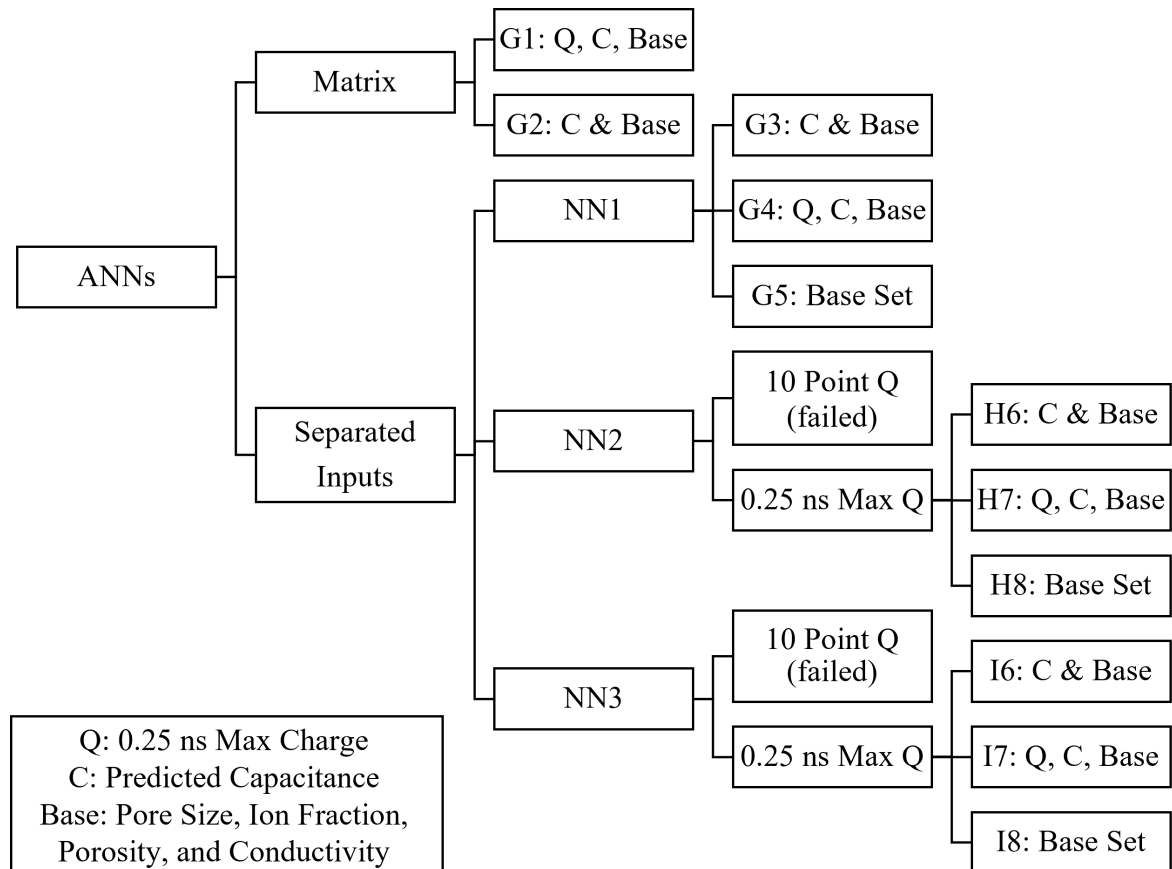


Figure 3.35. Volumetric neural network models created.

As it can be seen from the Figure 3.35, NN2 and NN3 type of models are failed while using 10 point initial charging data. They cannot give consistent above 0.6 R^2 values, hence eliminated in capacitance prediction step. Selected hidden layer sizes (HLS), input types (Matrix, NN1, NN2, or NN3), and features used in R_i prediction (predicted capacitance and initial charging data with its corresponding type) in addition to pore size, porosity, ion fraction, and conductivity are tabulated for each in Table 3.18.

Table 3.18. Volumetric neural network model details.

Model Name	Input Type	Hidden Layer Sizes		R_l Prediction		
		C_G Prediction	R_l Prediction	Q_i Type	C_G	Q_i
G1	Matrix	3 Nodes	2 Nodes	Initial Slope	+	-
G2	Matrix	3 Nodes	3 Nodes	Initial Slope	+	+
G3	NN1	3 Nodes	3 Nodes	10-Point	+	-
G4	NN1	3 Nodes	4 Nodes	10-Point	+	+
G5	NN1	3 Nodes	4 Nodes	10-Point	-	-
H6	NN2	4 Nodes	5 Nodes	Initial Slope	+	-
H7	NN2	4 Nodes	3 Nodes	Initial Slope	+	+
H8	NN2	4 Nodes	2 Nodes	Initial Slope	-	-
I6	NN3	3 Nodes	3 Nodes	Initial Slope	+	-
I7	NN3	3 Nodes	2 Nodes	Initial Slope	+	+
I8	NN3	3 Nodes	3 Nodes	Initial Slope	-	-

Both G1 and G2 have pore size, porosity, ion fraction, conductivity, and initial slope data to predict capacitance. initial slope is defined as the maximum charge obtained in the first 0.25 ns of the simulation. The design of the G1 and G2 can be seen from the Figure 3.23. G1 and G2 have $R^2 = 0.898$ and $RMSE = 1.295$ F/cm³ in capacitance prediction. In R_l prediction G1 uses predicted capacitance, pore size, porosity, ion fraction, and conductivity while G2 also uses initial slope. Predicted R_l values are used to compute resistance with Equation (2.31). G1 has $R^2 = 0.691$ and $RMSE = 0.889$ Ohm m while G2 has $R^2 = 0.861$ and $RMSE = 0.680$ Ohm m.

G3, G4, and G5 uses NN1 type of feeding. Selected set of features entered to first layer together. In capacitance prediction pore size, porosity, ion fraction, conductivity, and 10-point initial charging data is selected as input parameters. The design of the G3, G4, and G5 can be seen from the Figure 3.24. Capacitance prediction has $R^2 = 0.667$ and $RMSE = 2.732$ F/cm³.

In R_l prediction G3 uses predicted capacitance, while G4 also uses 10-point initial charging data. G5 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute resistance with Equation (2.31). G3 has $R^2 = 0.670$ and RMSE = 0.905 Ohm m while G4 has $R^2 = 0.667$ and RMSE = 0.778 Ohm m. G5 has $R^2 = 0.672$ and RMSE = 0.766 Ohm m.

H3, H4, and H5 uses NN2 type of feeding. Predictors entered to first layer together. Initial charging data added to both first and second layer. The design of the H3, H4, and H5 can be seen from the Figure 3.25. In capacitance prediction pore size, porosity, ion fraction, conductivity, and 10-point initial charging data is used. Capacitance predictions have failed hence these systems are eliminated.

H6, H7, and H8 uses NN2 type of feeding. Predictors entered to first layer together. initial slope data added to both first and second layer. In capacitance prediction pore size, porosity, ion fraction, conductivity, and initial slope is used. The design of the H6, H7, and H8 can be seen from the Figure 3.26. Capacitance prediction has $R^2 = 0.864$ and RMSE = 1.064 F/cm³.

In R_l prediction H6 uses predicted capacitance, while H7 also uses 0.25 ns maximum initial slope data. H8 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute resistance with Equation (2.31). H6 has $R^2 = 0.683$ and RMSE = 0.818 Ohm m while H7 has $R^2 = 0.692$ and RMSE = 0.884 Ohm m. H8 has $R^2 = 0.680$ and RMSE = 0.816 Ohm m.

I3, I4, and I5 uses NN3 type of feeding. Predictors entered to first layer together. Initial charging data added to second layer only. In capacitance prediction pore size, porosity, ion fraction, conductivity, and 10-point initial charging data is used. The design of the I3, I4, and I5 can be seen from the Figure 3.27. Capacitance predictions have failed hence systems are eliminated.

I6, I7, and I8 uses NN3 type of feeding. Predictors entered to first layer together. initial slope data added to second layer only. In capacitance prediction pore size, porosity, ion fraction, conductivity, and initial slope is used. The design of the I6, I7, and I8 can be seen from the Figure 3.28. Capacitance prediction has $R^2 = 0.784$ and $RMSE = 1.396 \text{ F/cm}^3$. In R_l prediction I6 uses predicted capacitance, while I7 also uses initial slope. I8 uses the base predictors only which consist of pore size, porosity, ion fraction, and conductivity. Predicted R_l values are used to compute resistance with Equation (2.31). I6 has $R^2 = 0.680$ and $RMSE = 0.901 \text{ Ohm m}$ while I7 has $R^2 = 0.676$ and $RMSE = 0.998 \text{ Ohm m}$. I8 has $R^2 = 0.679$ and $RMSE = 0.890 \text{ Ohm m}$.

Below full table of neural network set results can be found. Models with failed capacitance predictions are eliminated. Predictions with R^2 values below 0.6 are considered as failed. Both cross validation average and overall RMSE values are given for each model in Table 3.19.

Table 3.19. Volumetric neural network model results.

	Capacitance (F/cm³)			Resistance (Ohm m)		
Model	R²	RMSE		R²	RMSE	
G1	0.8980	1.2949	1.3908	0.6912	0.8890	0.8989
G2	0.8980	1.2949	1.3908	0.8611	0.6805	0.6826
G3	0.6674	2.7322	2.8672	0.6700	0.9051	0.9181
G4	0.6674	2.7322	2.8672	0.6669	0.7782	0.7970
G5	0.6674	2.7322	2.8672	0.6724	0.7662	0.7870
H6	0.8643	1.0636	1.1921	0.6844	0.8183	0.8306
H7	0.8643	1.0636	1.1921	0.6919	0.8839	0.8950
H8	0.8643	1.0636	1.1921	0.6805	0.8158	0.8309
I6	0.7841	1.3965	1.5065	0.6803	0.9007	0.9123
I7	0.7841	1.3965	1.5065	0.6755	0.9975	1.0103
I8	0.7841	1.3965	1.5065	0.6794	0.8895	0.9035

Overall, neural networks with matrix type feed, namely G1 and G2, gave better R^2 and RMSE values. All the models using 10-point initial charging data as an input failed to predict capacitance. Since capacitance prediction is the first step of the optimization, these models are eliminated. Although models with NN2 type feeding, namely H6, H7, and H8, have quite close R^2 values and RMSE, their R_i prediction results are worse than that of G2. Since the overall accuracy of the models are considered here, G2 is selected as the best predictive ANN model in volumetric investigation. Below corresponding comparison graphs can be seen.

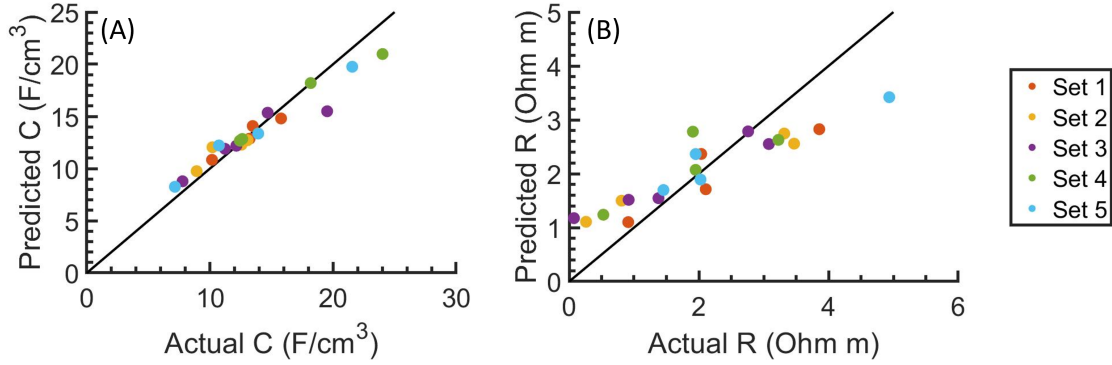


Figure 3.36. Neural network (G2) comparison graphs a) volumetric capacitance, b) resistance.

3.3. Optimum Design Selection & Contour Plots

To determine the optimum design selection, in addition to R^2 and RMSE values calculated, detailed data/error investigation are done to avoid over-fitting. Relation between pore size and porosity, and relation between ion fraction and conductivity are formulated and used in generation of contour plots. In Figure 3.37 the resulting equations together with the related data points can be seen. With the addition of these relations each data other than initial charging data (initial slope) changes accordingly. Since initial slope can be adjusted via changing potential difference applied, contour plots can give useful information about these systems.

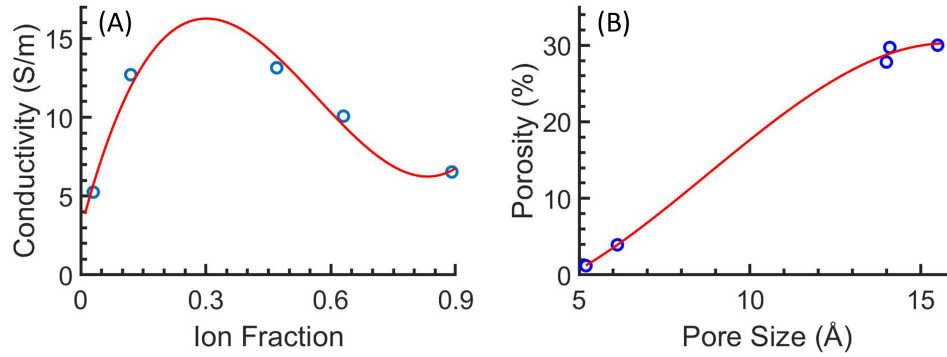


Figure 3.37. Relation graphs a) conductivity as a function of ion fraction, b) porosity as a function of pore size.

3.3.1. Gravimetric Contour Plots

As it is mentioned in previous section, A1, B2, and G2 are found as the best models in gravimetric investigation. A1 is the elastic network solution with 0.11α and 0.0152λ for capacitance prediction and 0.54α and 0.0215λ for R_l prediction. B2 is the normal distribution elastic network solution with 0.11α and 0.0115λ for capacitance prediction and 0.58α and 0.0166λ for R_l prediction. And G2 is the neural network model with matrix type input which has 3 hidden layers in both capacitance prediction part and R_l prediction part. Among these three the minimum error and fluctuations are seen in B2, hence it is selected as the best predictive model.

Throughout the Section 3.2.1 and Section 3.2.2, namely gravimetric and volumetric investigation, capacitances and R_l values are predicted yet to understand the effect of parameters, in our case especially the effect of pore size and ion fraction, and to optimize design parameters for improved energy density and fast charging, contour plots are generated. For that purpose, pore size and ion fraction are selected as axis parameters, using the relation between pore size and porosity and relation between ion fraction and conductivity, these values are also changed accordingly for each point in the map. The only constant in these graphs are initial charging data which is taken from an average system, namely the system with 0.47 ion fraction and $6.12 \text{ \AA}$ pore size.

Figure 3.38 shows the contour plots of gravimetric energy density and characteristic charging time of the selected elastic network model, B2.

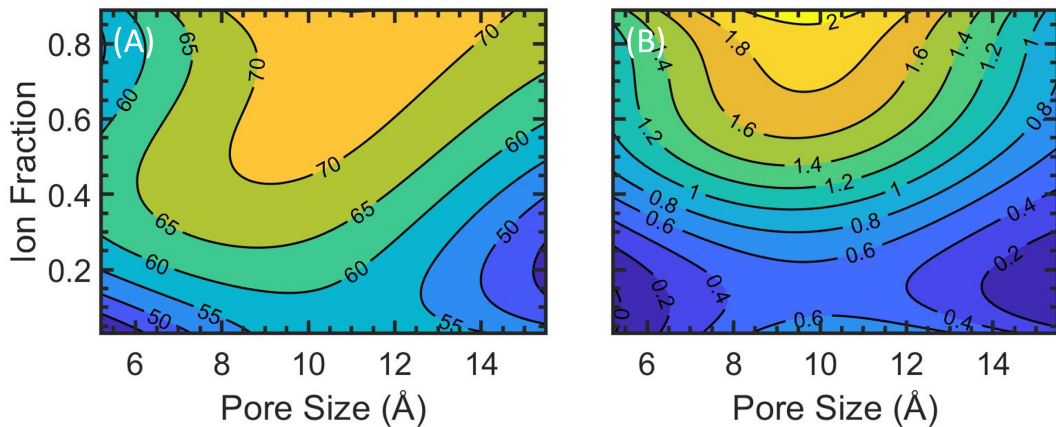


Figure 3.38. Contour plots of selected model (B2) a) gravimetric energy density (Wh/kg), b) characteristic charging time (s).

It is seen that, higher energy densities are seen at medium pore sizes and generally at higher ion fractions. At low ion fractions, both end of pore sizes resulted in lower energy densities, while at higher ion fractions the decrease in higher pore sizes are lower. In general, at pore sizes smaller than or equal to size of ions, capacitance hence energy density show a maximum at intermediate dilution. Capacitance enhancement weakens with further increase in pore size and eventually disappears. In dilute regime, ion saturation by increasing ion fraction enhances capacitance while in concentrated solutions solvent improves capacitance by decreasing charge overscreening. Competition of two forces leads to capacitance max in mid-section.

The characteristic charging time graph indicates a similar trend which is actually the opposite of what we want at the beginning. Lower charging times, which also shows smaller resistances or higher power densities, are more preferable for supercapacitors. Characteristic charging time has its preferable lower values at the areas where energy density is also low.

According to the data at hand, various energy density and characteristic charging time values are set as design limits, namely top ten, twenty, and thirty percentages according to highest energy density and lowest characteristic charging time obtained from these contour plots. But it is seen that there is no such intersection areas. Therefore a decision should be made for either sacrificing energy density or charging time. According to the data at hand, characteristic charging times are increased up to 60% of its range which is 1.25 second and energy densities are decreased down to 75 and 70% of their maximum value, namely 66.165 and 64.37 Wh/kg respectively. Two isolines are generated and their intersection areas which are above the limiting energy densities and below the limiting characteristic charging time are shaded.

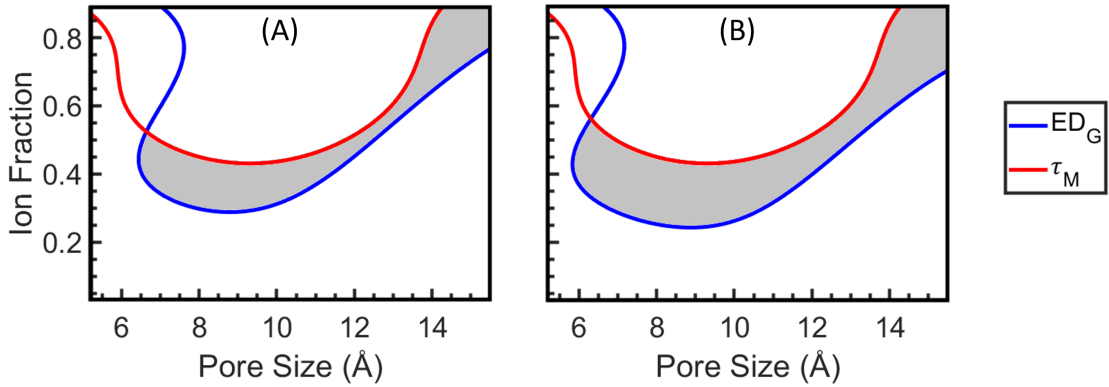


Figure 3.39. Gravimetric isolines (B2) a) 75% gravimetric energy density and 60% characteristic charging time, b) 70% gravimetric energy density and 60% characteristic charging time.

3.3.2. Volumetric Contour Plots

A2, B4, and G2 are found as the best models in volumetric investigation. Using capacitance values and R_l values found, contour plots of volumetric energy density and resistance are generated. In the generation of these graphs, relation between pore size and porosity and relation between ion fraction and conductivity are used.

A2 is the elastic network solution with 0.08 α and 0.0113 λ for capacitance prediction and 0.33 α and 0.0503 λ for R_l prediction. B4 is the normal distribution elastic network solution with 0.09 α and 0.0083 λ for capacitance prediction and 0.27 α and 0.0522 λ for R_l prediction. And G2 is the neural network model with matrix type input which has 3 hidden layers in both capacitance prediction part and R_l prediction part.

Among these three, the minimum error and minimum fluctuations are seen in B4, hence it is selected as the best predictive model. To understand the effect of parameters, in our case especially the effect of pore size and ion fraction, and to optimize design parameters for improved energy density and fast charging, contour plots are generated.

For that purpose, pore size and ion fraction are selected as axis parameters, using the relation between pore size and porosity, and relation between ion fraction and conductivity, these values are also changed accordingly for each point in the map. The only constant in these graphs are initial charging data which is taken from an average system, namely the system with 0.47 ion fraction and 6.12 Å pore size. Figure 3.40 shows the contour plots of volumetric energy density and resistance of the selected elastic network model, B4.

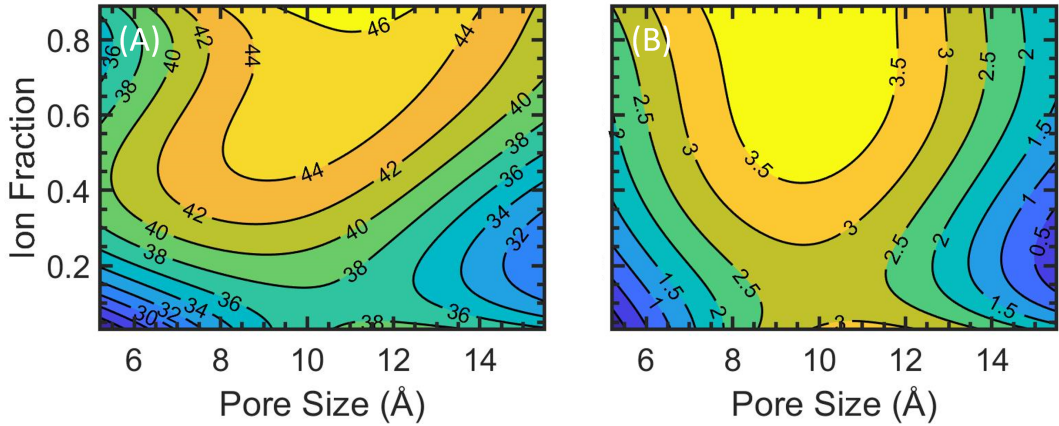


Figure 3.40. Contour plots of selected model (B4) a) volumetric energy density (Wh/L), b) resistance (Ohm m).

It is seen that, higher energy densities are seen at medium pore sizes and generally at higher ion fractions. Pore sizes lower or equal to the solvated ion size capacitance hence energy density shows a maximum at intermediate dilution. Capacitance enhancement diminishes with further increase in pore size and eventually disappears. At low ion fractions, both end of pore sizes resulted in lower energy densities, while at higher ion fractions the decrease in higher pore sizes are lower. Resistance graph indicates a similar trend which is actually the opposite of what we want at the beginning since lower resistances are more preferable for supercapacitors. Therefore a decision should be made for either sacrificing energy density or resistance. According to the contour plots seen in Figure 3.40, various energy density and resistance values are set and tried as design limits, namely top ten percentages, top twenty percentages and top thirty percentages according to the highest energy density and lowest resistance obtained. But it is seen that, there is no such intersection areas. Therefore a decision should be made for either sacrificing energy density or resistance hence charging time. According to the data at hand, resistances are increased up to 60% of its range, which is 2.23 Ohm m, and energy densities are decreased down to 75 and 70% of their maximum value, namely 41.15 and 40.0 Wh/L respectively. Two isolines are generated and their intersection areas which are above the limiting energy densities and below the limiting resistance are shaded.

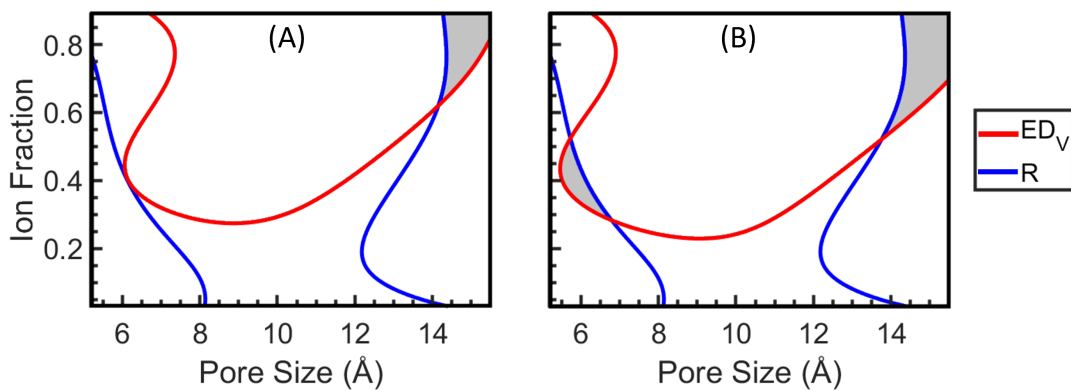


Figure 3.41. Volumetric isolines (B4) a) 75% volumetric energy density and 60% resistance , b) 70% volumetric energy density and 60% resistance.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

To overcome the challenges associated with the high costs of experiments and molecular simulations, this work combines machine learning tools with molecular simulations to provide guidelines for tuning material properties for supercapacitors. Transmission line models are fitted to molecular simulation data to link microscopic material properties to macro-scale performance metrics. Using the transmission line model, sets of input and performance parameters are generated. Various machine learning methods, namely linear regression, ridge regression, lasso regression, elastic networks, support vector machines, and neural networks are applied to the simulation data for performance prediction. Among the microscopic material properties, pore size, porosity, conductivity, and ion fraction data are determined as the most important features for capacitance prediction. In addition, information on charging kinetics at the initial stage of the charging process is also integrated into the model in several forms including, i) slope of the initial charging data with respect to time, ii) the maximum charge obtained from the 0.25 ns simulations, and iii) 10-point charge data from the same simulations. The most accurate predictions are obtained using the maximum charge data of the first 0.25 ns trajectories. In R_l prediction step, predicted capacitance values from the first section of the ML model are integrated into the model. Among the machine learning methods applied to the data, elastic net gives the best results in predicting both the gravimetric (C_G and τ_M) and volumetric (C_V and R_l) properties.

In predicting the gravimetric performance metrics, the elastic net model B2 yields the best performance with $\alpha = 0.11$ and $\lambda = 0.115$ in capacitance, and $\alpha = 0.58$ and $\lambda = 0.0166$ in R_l prediction. That model has a high coefficient of determination ($R^2 = 0.98$) and an impressively low RMSE (3.1 F/g) for gravimetric capacitance. The model gives $R^2 = 0.88$ with RMSE = 0.16 s for characteristic charging time prediction.

In volumetric investigation B4 is the selected as the optimum model. It has 0.09 α and 0.0083 λ in capacitance prediction and 0.27 α and 0.0522 λ in R_l prediction. That model has 0.89 R^2 with 1.09 F/cm³ RMSE for volumetric capacitance, and 0.84 R^2 with 0.53 Ohm m RMSE for resistance prediction.

After the investigation of capacitance and ion transfer resistance inside the electrodes, for a better understanding of the dependence of gravimetric energy density, volumetric energy density, characteristic charging time and ion transfer resistance on microscopic material properties, we generate contour plots of these performance metrics as a function of two variables used in the predictive models. In particular, the pore size and ion fraction dependence of the above-mentioned performance metrics are evaluated. For energy density, both gravimetric and volumetric investigation yield similar results in which energy density exhibits a maximum at intermediate dilution levels for pore sizes smaller than or equal to the size of a solvated ion. Enhancement in energy density weakens with further increase in pore size and eventually disappears for both gravimetric and volumetric investigation. In the dilute regime, ion saturation with increasing ion content enhances energy density while in concentrated solutions, solvent improves energy density by decreasing charge over screening. Combining the contour plots for energy density and τ_M (or R_l for volumetric investigation) yields design maps that identify the feasible regions satisfying preset requirements both for energy density and charging kinetics. These results show optimum design parameters can be identified for given design requirements for further investigations.

4.2. Recommendations

This work currently considers the micropore structure of the electrodes via using average pore size and porosity. Yet, these global parameters may fall short in describing the effect of micropore structure on energy storage performance as detailed individual pore level information is lost in these parameters. That effect is seen when set of systems whose average pore sizes are 9.8 Å but have narrowed down pore size distribution introduced to the machine learning models.

Incorporating the effect of pore size distribution into the feature set can improve the accuracy and generalizability of the model to a diverse class of carbon-based electrode materials. Furthermore, the precise effect of pore size can be investigated more accurately by simulating pores of fixed pore size, such as slit pores or cylindrical pores.

Expanding the data-set with new molecular simulations is also crucial in increasing the accuracy and generalizability of the models. In particular, the present simulations investigate electrodes with average pore size 5.2, 6.12, 14, 14.1, and 15.5 Å, respectively. Although training data has good enough amount of data for higher and lower values, conducting simulations in the pore size range 6.12 to 14 Å can enrich the data-set and lead better prediction especially in that mid-section.

The third thing that can be improved for further studies is incorporating the effect of applied potential to energy storage performance. Sampaio *et al.* and Noh *et al.* showed that applied potential and Q_{max} do not have a direct relation in between. Therefore the relation between them can be examined via applying various potential differences to set simulation models.

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