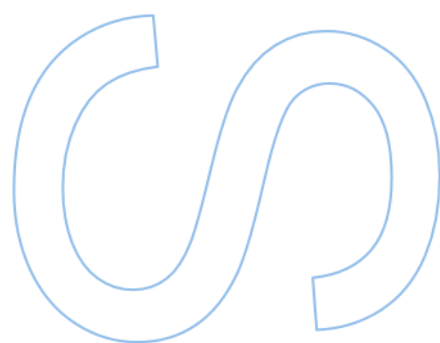
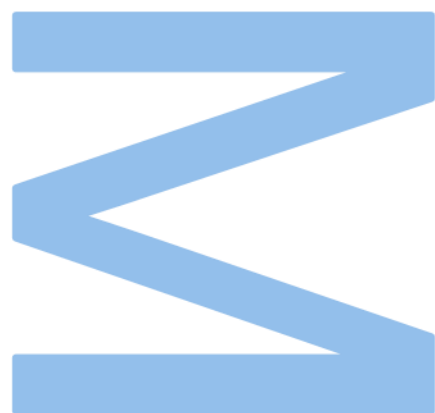


Chargeable thermoionic supercapacitor: from design to applications

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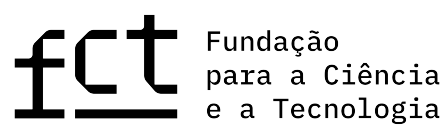
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Resumo

Supercondensadores (SCs) e Supercondensadores termicamente carregáveis (TCSCs) são componentes essenciais nos sistemas modernos de armazenamento de energia, conhecidos pela sua alta densidade de potência e longevidade. Esta tese detalha o desenvolvimento e a validação de um modelo de simulação do programa COMSOL, capaz de replicar com precisão os comportamentos eletroquímicos e termiônicos desses dispositivos. O modelo foi rigorosamente testado contra dados experimentais, especificamente utilizando nanotubos de carbono de paredes múltiplas em combinação com um eletrólito de PVA em gel sólido dopado com H_3PO_4 . As simulações revelaram que um dispositivo com espaçamento de eletrodos de 0,5 cm apresentou um aumento de 11% na capacitância simulada em comparação com os dados experimentais, enquanto um dispositivo com espaçamento de 1 cm mostrou um aumento de 5%. Os resultados confirmaram a precisão do modelo na simulação de comportamentos de voltametria cíclica e de carga-descarga galvanostática, demonstrando uma forte correlação com os resultados experimentais.

Uma análise aprofundada no estudo identificou vários parâmetros críticos que influenciam diretamente o desempenho dos SCs. Esses parâmetros incluem coeficientes de difusão de íons do eletrólito, área de superfície do eletrodo por unidade de volume e distância entre os eletrodos. Ao otimizar esses fatores na simulação, o modelo conseguiu otimizar as densidades de energia e potência previstas para os dispositivos, fornecendo informações valiosas sobre os mecanismos que regem o desempenho dos SCs. Os resultados mostraram que o aumento do coeficiente de difusão por uma ordem de grandeza pode mais que dobrar a capacitância do dispositivo, enquanto um aumento na área de superfície do eletrodo por unidade de volume pode triplicar esse valor, assumindo que os poros do eletrodo sejam de tamanho ideal. Além disso, a redução da distância entre eletrodos resultou num aumento exponencial significativo na capacitância. Esse processo de otimização destacou a importância de ajustar detalhadamente as configurações dos dispositivos para alcançar métricas de desempenho superiores.

Investigações adicionais sobre os TCSCs, particularmente aqueles com eletrodos de platina, revelaram que o modelo de simulação poderia replicar de forma confiável o comportamento eletroquímico de dispositivos com espaçamentos entre eletrodos de 1 cm ou mais. Observou-se que há uma distância ideal, com uma correlação mais forte entre os dados experimentais e simulados quando o espaçamento entre eletrodos está mais próximo de 1 cm, apresentando uma incerteza relativa mínima de 22%. No entanto, a

simulação enfrentou desafios ao ser aplicada a TCSCs com espaçamentos entre elétrodos menores (0,3 cm e 0,5 cm), onde efeitos de borda e campos elétricos não lineares se tornaram proeminentes.

O comportamento termiônico dos dispositivos TCSC foi analisado sob diferentes gradientes de temperatura e distâncias entre os elétrodos, revelando importantes detalhes sobre seu desempenho. A simulação replicou com sucesso a diferença de potencial gerada por um gradiente de temperatura, que se estabilizou quando o TCSC atingiu um estado de carga completa, semelhante às observações experimentais. No entanto, a simulação não mostrou variações significativas com diferentes distâncias entre os elétrodos, refletindo as condições idealizadas sem perdas resistivas. O coeficiente de Soret simulado foi obtido, com um máximo de $3,18 \text{ mV K}^{-1}$, mostrando um aumento com a distância entre os elétrodos, embora menos pronunciado do que nos dados experimentais. Análises adicionais identificaram que um aumento de uma ordem de grandeza no valor da termodifusão levou a um aumento proporcional no coeficiente de Soret, enquanto um aumento de uma ordem de grandeza no coeficiente de difusão dos cátions aumentou o coeficiente de Soret em 9%. Por outro lado, o mesmo aumento no coeficiente de difusão dos ânions resultou numa redução de 15 vezes na capacitância. Além disso, estudos sobre ciclos consecutivos de carga-descarga indicaram que gradientes de temperatura mais altos e maiores distâncias entre os elétrodos exigiam tempos de estabilização mais longos, enfatizando a necessidade de tempos de carga e descarga otimizados para simular com precisão o comportamento dos TCSCs.

O trabalho alcançou um marco significativo no avanço da modelagem de SCs e TCSCs, fornecendo uma estrutura confiável para prever o comportamento dos dispositivos sob várias configurações.

Palavras-chave: Supercondensador; Supercondensador termicamente carregável; Armazenamento de energia eletroquímica; Captação de energia térmica; Simulação COMSOL.

Abstract

Supercapacitors (SCs) and thermally-chargeable supercapacitors (TCSCs) are essential components in modern energy storage systems, known for their high power density and longevity. This thesis details the development and validation of a COMSOL simulation model capable of accurately replicating the electrochemical and thermionic behaviors of these devices. The model was rigorously tested against experimental data, specifically using multi-walled carbon nanotubes in combination with a solid-gel PVA (Poly(vinyl alcohol)) electrolyte doped with H_3PO_4 . Simulations revealed that a device with 0.5 cm electrode spacing exhibited an 11% increase in simulated capacitance compared to experimental data, while a device with 1 cm spacing showed a 5% increase. The outcomes confirmed the model's accuracy in simulating cyclic voltammetry and galvanostatic charge-discharge behaviors, demonstrating a strong correlation with experimental results.

An in-depth analysis within the study identified several critical parameters that directly influence the performance of SCs. These parameters include electrolyte ions diffusion coefficients, electrode surface area per unit volume, potential scan rate, and electrodes distance. By optimizing these factors within the simulation, the model was able to improve the predicted energy and power densities of the devices, providing valuable insights into the mechanisms that govern SC performance. The findings showed that increasing the diffusion coefficient by one order of magnitude could more than double the device's capacitance, while an increase in the electrode surface area per unit volume could triple that value, assuming the electrode pores were optimally sized. Additionally, reducing the electrode distance resulted in a significant exponential boost in capacitance. This optimization process underscored the importance of finely tuning device configurations to achieve superior performance metrics.

Further investigation into TCSCs, particularly those with platinum electrodes, revealed that the simulation model could reliably replicate the electrochemical behavior of devices with electrodes spacing of 1 cm or greater. It was observed that there was an ideal distance, with a stronger correlation between experimental and simulated data when the electrode spacing was closer to 1 cm, showing a minimum relative uncertainty of 22%. However, the simulation encountered challenges when tested against TCSCs with smaller electrodes spacing (0.3 cm and 0.5 cm), where edge effects and non-linear electric fields became prominent.

The thermionic behavior of TCSC devices was analyzed under varying temperature gradients and electrodes distances, revealing key insights into their performance. The simulation successfully replicated the potential difference generated by a temperature gradient, which stabilized when the supercapacitor reached a fully charged state, similar to experimental observations. However, the simulation did not show significant variations with different electrodes distances, reflecting the idealized conditions without resistive losses. The simulated Soret coefficient was obtained, with a maximum of 3.18 mV K^{-1} , showing an increase with electrodes distance, although less pronounced than in experiments. Further analysis identified that an increase of one order of magnitude in the thermodiffusion value led to a proportional increase in the Soret coefficient, while a one-order of magnitude increase in the cation diffusion coefficient raised the Soret coefficient by 9%. Conversely, the same increase in the anion diffusion coefficient resulted in a 15-times reduction in capacitance. Studies on consecutive charge-discharge cycles also indicated that higher temperature gradients and larger electrode distances required longer stabilization times, emphasizing the need for optimized charging and discharging times to accurately simulate TCSC behavior.

The work achieved a significant milestone in advancing the modeling of supercapacitors and TCSCs, providing a reliable framework for predicting device behavior under various configurations.

Keywords: Supercapacitor; Thermally Chargeable Supercapacitor; Electrochemical energy storage; Thermal energy harvesting; COMSOL Simulation.

Table of Contents

Acknowledgements	i
Resumo	iii
Abstract	v
Table of Contents	vii
List of Figures	ix
List of Abbreviations	xi
1. Supercapacitors	5
1.1. History and Evolution	5
1.2. Structure and Types of Supercapacitors	6
1.2.1. EDLC	10
1.2.2. Pseudocapacitors	12
1.2.3. Hybrid capacitors	13
1.3. Thermally-Chargeable Supercapacitors	14
1.4. Supercapacitor Simulation	16
1.4.1. Molecular Dynamics	17
1.4.2. Density Functional Theory	18
1.4.3. Finite Element Method	19
1.5. Objective	20
2. Eletrochemical Analysis: Numerical Simulation vs Experimental Methods	21
2.1. Simulation Models	21
2.2. Supercapacitor Fabrication	22
2.3. Electrochemical performance of SCs	24
2.4. Simulation of Planar SCs based on MWCNT Electrodes	26
3. SCs Tuning Properties: Influence of geometric, electrolyte and electrode parameters	31
3.1. Diffusion Coefficient	31
3.2. Surface Area per Unit Volume	34
3.3. Potential Scan Rate in CV Studies	39
3.4. Electrodes Distance	40
4. Electrochemical and Thermoionic Numerical Simulation of a TCSC	41
4.1. TCSC Fabrication	41
4.2. TCSC Eletrochemical Analysis	43
4.3. Thermoionic Simulation Models	49
4.4. Thermoionic performance of TCSCs	50
4.5. Thermoionic Analysis: Simulation vs Experimental	51

5. Conclusion.....	61
Bibliography	64

List of Figures

1.	Diagram illustrating the process and steps taken to adjust the SC models, including the sequence of actions and the incorporation of experimental data for refinement. ...	3
1.1.	Ragone plot comparing the energy storage performance of various energy-storing devices in terms of power density, energy density, and typical charging times [18]. ...	8
1.2.	Illustration of a supercapacitor structure and its elements, as well as, a representation of the role that each part has in the SC's charging process [19].	9
1.3.	Illustration of the three SC classes: (a) EDLC, (b) PC, and (c) HC, as well as a basic representation of their respective charge storage mechanism [20].	9
1.4.	GCS model description of the double layer. Adapted from [24].	11
1.5.	Different pseudocapacitive electrochemical mechanisms: (a) underpotential deposition, (b) redox pseudocapacitance, and (c) intercalation pseudocapacitance [30].	13
1.6.	Operation principle of a TCSC: a) and b) describe the charging process, while c) and d) represent the discharging process [5].	15
2.1.	In-plane CNT-based SC with PVA/H_3PO_4 electrolyte deposited in Kapton by: a) screen printing; b) coating using a 3D printed box.	23
2.2.	Illustration of a SC GCD curve and its key features (Adapted from [4]).	25
2.3.	Comparison of CV curves between simulated and experimental data for SC devices with electrode distances: A) 0.5 cm and B) 1 cm.	27
2.4.	Representation of the typical i-V cycles of the different types of supercapacitors (Adapted from [4]).	28
2.5.	Comparison of GCD measurements between simulated and experimental data for device A.	29
2.6.	Representation of the typical GCD cycles of the different types of supercapacitors (Adapted from [4]).	30
3.1.	A) CV curves for different diffusion coefficients of the electrolyte ions. B) Capacitance of device A as a function of the diffusion coefficients.	31
3.2.	A) CV curves for different anion's diffusion coefficients. B) Capacitance as a function of the ratio between the anion's and cation's diffusion coefficients.	32
3.3.	A) GCD curves for different diffusion coefficients of the electrolyte ions. B) Discharge time as a function of the diffusion coefficients.	33
3.4.	A) Capacitance derived from GCD measurements as a function of the diffusion coefficients. B) Energy density plot as a function of the power density for different diffusion coefficients (right).	34
3.5.	A) CV curves for different surface areas per unit volume. B) Capacitance as a function of the surface area.	35
3.6.	Simulated capacitance values for different surface areas per unit volume (left). Areal capacitance as a function of the electrode's pore size (right) [49].	36
3.7.	A) CGD curves for different surface areas per unit volume. B) Discharge time as a function of the surface area.	37
3.8.	A) Capacitance derived from GCD measurements as a function of the surface area per unit volume. B) Energy density plot as a function of the power density for different surface areas.	39
3.9.	Capacitance as a function of the scan rate for different diffusion coefficients.	40
3.10.	A) CV curves for different distances between electrodes. B) Capacitance as a function of the electrode distance.	40

4.1. Five different configurations of an in-plane TCSC composed of Pt electrodes and PVA/H_3PO_4 electrolyte deposited in a glass substrate.	42
4.2. Illustration of the TCSCs geometry and their dimensions, where d represents the distance between the electrodes: 0.3 cm, 0.5 cm, 1.0 cm, 1.5 cm, or 2.0 cm.	42
4.3. CV curves at different scan rates for the device with a 0.3 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.	43
4.4. CV curves at different scan rates for the device with a 0.5 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.	44
4.5. CV curves at different scan rates for the device with a 1 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.	45
4.6. CV curves at different scan rates for the device with a 1.5 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.	46
4.7. CV curves at different scan rates for the device with a 2 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.	47
4.8. Mean relative uncertainty calculation between experimental and simulation results for each TCSC device.	47
4.9. Capacitance as a function of the distance between the electrodes.	48
4.10. Scheme of the TCSC setup used to determine experimentally the Soret coefficient in planar-type devices.	50
4.11. Thermal charging process of the TCSCs for different applied temperature gradients and electrode distances.	51
4.12. Initial simulation of the TCSC's charging process for a temperature gradient of 15 K and a distance between the electrodes of 1 cm.	52
4.13. Simulation of the experimental thermal charging process of the TCSCs for different applied temperature gradients and distances between electrodes.	53
4.14. Maximum charging potential values as a function of the temperature gradient for each electrode spacing.	54
4.15. Soret coefficient as a function of the distance between the electrodes: experimental results (left) and simulated results (right).	55
4.16. A) Thermal charging process for different thermodiffusion coefficients. B) Soret coefficient as a function of the thermodiffusion coefficient.	56
4.17. A) Thermal charging process for different cation diffusion coefficients. B) Soret coefficient as a function of the cation diffusion coefficient (right).	57
4.18. A) Thermal charging process for different anion diffusion coefficients. B) Soret coefficient as a function of the anion diffusion coefficient.	57
4.19. Thermal charging process for different surface areas per unit volume.	58
4.20. Thermal charging and discharging processes for different temperature gradients and electrodes distances: 0.3cm and 1 cm.	59

List of Abbreviations

CV Cyclic Voltammetry

DFT Density Functional Theory

EC Electrochemical Capacitor

EDL Electric Double Layer

EDLC Electric Double Layer Capacitor

FEM Finite Element Method

GCD Galvanostatic Charge/Discharge

GCS Gouy-Chapman-Stern

HC Hybridcapacitor

IHP Inner Helmholtz Plane

IoT Internet of Things

MD Molecular Dynamics

MWCNT Multi-Walled Carbon Nanotube

MXenes Transition metal carbides and carbonitrides

OHP Outer Helmholtz Plane

PC Pseudocapacitor

PVA Poly(vinyl alcohol)

SC Supercapacitor

TCSC Thermally Chargeable Supercapacitor

Thesis Outline

For thousands of years, Planet Earth has served as the backbone of Humanity's growth. Today, this same planet bears the scars of a selfish society driven by convenience and disregard for the surrounding environment. It's our generation's duty to reverse the damage caused in the past and give our successors a place to call Home.

In recent years, ambitious long-term targets have been set by the United Nations and the European Commission to prevent global warming. The most important plan of action comes from the Paris Agreement, signed by countries all over the world, to limit global warming to well below 2 °C above pre-industrial levels, with efforts to limit the increase to 1.5 °C. The European Commission also revealed its aim of reducing Europe's net emissions by at least 55 % by 2030 compared to 1990 and to be the first climate neutral continent by 2050 [1]. Innovations and initiatives are more than ever, crucial elements for the emergence of sustainable solutions and the neutralization of carbon.

The integration and expansion of renewable energy sources is the most fundamental part of reducing the reliance on fossil fuels. Thereby, numerous research fields have been constructed to develop the tools to fulfill that purpose, among which is the area of energy storage. Nowadays, batteries are the predominant and most reliable storage device due to their higher energy density and capacity. However, as a consequence of chemical degradation, batteries display structural changes over repeated charge and discharge cycles, thus failing to have a long cycle-life [2]. Additionally, many batteries contain toxic materials, which can pose environmental and health hazards if not properly managed. As an alternative, supercapacitors (SCs) provide higher power density, longer cycle life, faster charging and discharging, as well as, environmental security. From consumer electronics to Formula 1 and electric cars, these attributes have already shown the value and potential of SCs as a trustworthy energy storage choice in the most diverse areas [3]. Unfortunately, the reason that prevents SCs from being as successful as batteries is their low energy density. As such, new SC designs and materials need to be tested as a way to optimize the specific surface area, porosity, and ion adsorption sites of the electrodes [4]. The final goal of such a study is to improve the energy density, as well as the charge and discharge rates of the device without compromising its high power density and cycle life.

Every single day, huge amounts of waste thermal energy, provided by low-grade heat sources, such as the human body or industry and electronic equipment, are released into the atmosphere. With the abundant wasted energy, it's essential to find technologies that harness and make the most out of these free sources of energy. As a solution, thermally chargeable supercapacitors (TCSCs) are a subset of SCs able to efficiently harvest and storage dissipated heat and convert it into electrical energy. This cutting-edge device exploits the different responses of distinct size particles induced by a temperature gradient, thus generating an electric potential difference. The above-mentioned phenomenon, regarded as ion thermophoresis or the Soret effect, is still far off from being totally comprehended. Although some advances have already been reached experimentally, a complete theoretical description is still missing. Moreover, it is still necessary to enhance the efficiency of TCSCs for their integration into practical applications.

Following their bendable structure and self-powering characteristics, TCSCs exhibit an undeniable appeal for the flexible wearable electronics market. By enabling the harvesting of waste thermal energy from low-grade heat sources, TCSCs may even continuously store energy from the human body [5]. These versatile applications serve as motivation to continue developing TCSCs and reduce reliance on batteries.

The present thesis aims to push forward the development and optimization of SCs by exploring optimal geometries, as well as the ideal properties of electrode and electrolyte materials that contribute to achieving the highest energy density. Furthermore, a thorough investigation was performed on the Soret effect, with the ambition of finding a coherent description of ion thermophoresis, along with establishing a strong groundwork for new TCSCs. To fulfill these goals, extensive comparisons were conducted between experimental findings and numerical simulations using COMSOL Multiphysics, a finite element software employed to model the SCs. This method was applied in both electrochemical and thermionic studies as follows: first, a base model of the supercapacitor was built in the simulation. Then, using a small experimental dataset, the model was refined through a trial-and-error approach. With a solid understanding of the model established, a parameter analysis was conducted to study the fundamental parameters influencing the model, aiming to gain insight into how to further improve it. Finally, the model was adjusted to accommodate a larger experimental dataset to achieve a more accurate refinement. This train of thought was followed throughout the entire thesis and is represented in Figure 1.

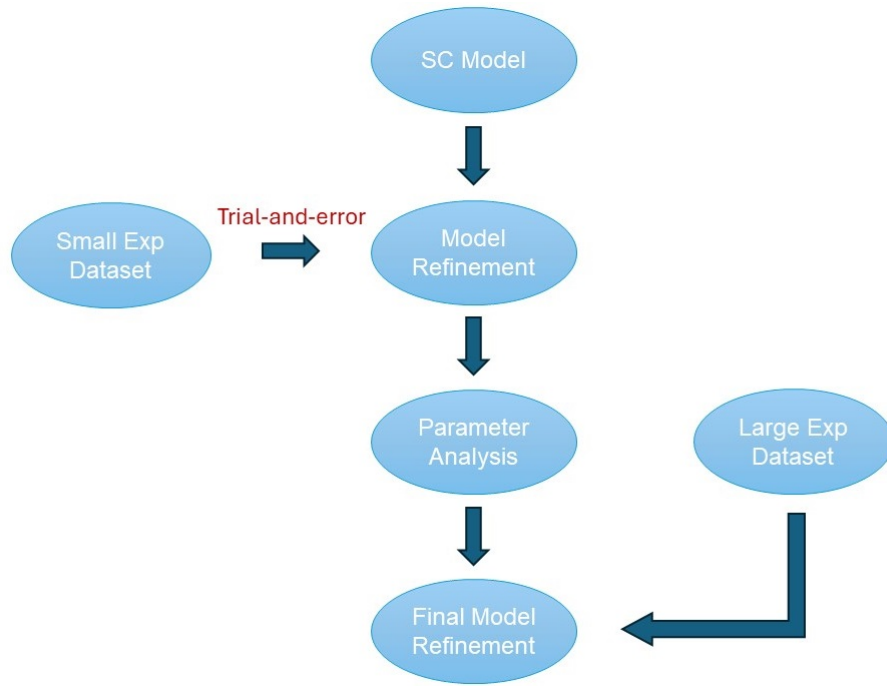


Figure 1: Diagram illustrating the process and steps taken to adjust the SC models, including the sequence of actions and the incorporation of experimental data for refinement.

This thesis is organized into five chapters. In Chapter 1, an overview of supercapacitors is presented, beginning with a discussion of their historical development and evolution. The chapter then describes the typical structure and types of supercapacitors, including electric double-layer capacitors, pseudocapacitors, and hybrid capacitors. Following this, the focus shifts to thermally chargeable supercapacitors, explaining their theoretical concept and working principle. The chapter concludes with an examination of various simulation software used in the study of supercapacitors, such as molecular dynamics, density functional theory, and finite element methods.

In Chapter 2, the focus is on the experimental fabrication of a supercapacitor utilizing multi-walled carbon nanotube electrodes and a PVA doped with H_3PO_4 solid gel electrolyte. The chapter also covers the experimental measurement techniques employed, as well as the equations that govern the simulation model and the foundational elements used to build it. Following this, the chapter presents the initial electrochemical results, comparing experimental data with simulation measurements through a trial-and-error approach to refine the initial model.

Chapter 3 is dedicated to parameter analysis, where various factors influencing the electrochemical behavior of the simulation are examined. This chapter presents the results

of the analysis and discusses how each factor impacts the simulation outcomes. The goal is to identify key parameters that affect performance and to understand their roles in optimizing the supercapacitor model.

Chapter 4 focuses on thermally chargeable supercapacitors. Building on the knowledge from previous chapters, this chapter compares the electrochemical behavior of various thermally chargeable supercapacitors with platinum electrodes and PVA doped with H_3PO_4 solid gel electrolyte, contrasting simulation results with experimental data. It then presents the experimental measurement techniques and the simulation equations used to model thermoionic behavior. Following this, the chapter investigates the thermal charging processes under different temperature gradients and device distances. The chapter concludes with a parameter analysis of the main factors influencing the thermoionic behavior of the TCSCs and an examination of consecutive charging and discharging processes.

To conclude, Chapter 5 presents the main findings and conclusions of the thesis, along with future perspectives for continued research and development in this area.

1. Supercapacitors

Regarded as the evolution of the electrolytic capacitor, supercapacitors (SCs) utilize high surface area electrode materials with high conductivity, and thin electrolytes to obtain higher capacitance values. Through electrostatic charge separation in the electrode/electrolyte interface and/or electrochemical pseudocapacitance [6], SCs enable the bridge between the high energy density rechargeable batteries and the high power density capacitors while maintaining a very long cycle life as well as fast charge and discharge cycles [7].

This chapter provides a review of the path that led to the origin and evolution of SCs and discloses the different categories of SCs. Following a more general description of the SCs, we will delve into the comprehension of Thermally Chargeable Supercapacitors and their importance in the world of low-power electronics. To conclude, we will assess the role of numerical simulations in the development of SCs, along with a detailed analysis of the main software used for that purpose.

1.1. History and Evolution

To understand the origin of the SCs, it is necessary to put into perspective the concept that gave rise to it. The notion of using an electric double layer as a means of storing electrical energy was settled around the late 1800s, by Hermann von Helmholtz. Helmholtz discovered that charged electrodes in electrolyte solutions repel ions of the same charge while attracting ions of the opposite charge to their surfaces. Despite the early discovery, its practical purpose in a cell was only accomplished in 1957 by H. I. Becker at General Electric Company (USA). As in any other technology, the final step is to commercialize it, and for the electrochemical capacitors (ECs) it happened in the 1970s when a Japanese multinational tech company, Nippon, introduced the first Electric Double Layer Capacitor (EDLC) (see section 1.2.1) of porous carbon and aqueous electrolyte by the name of "supercapacitor", revolutionizing the industry of energy storage and establishing the renowned designation still in use today [8–11].

Following the EDLC's impact, ECs suffered a drought in their development in the succeeding years that culminated with the unveiling of pseudocapacitors (PCs) (see section

1.2.2). This discovery, achieved by Brian Conway in the early 1990s, gave the first applicability to the concept, started in 1971 by Trasatti, of pseudocapacitance in ruthenium oxide films [12].

After Conway's breakthrough, the study of EDLCs and PCs intensified as scientists tried to reduce the gap in energy density. The product of that research was the hybrid supercapacitor that coupled the concept of an electric double layer in one electrode and the notion of pseudocapacitance or battery in the other [13].

In recent years, SCs have gained particular interest due to the rise of the Internet of Things (IoT) and their applicability in the market of wearable electronics. Major companies are each day more willing to invest in this field, as is the case of Maxwell Technologies, Panasonic, and even Tesla [8]. To address the rising demand for such devices and keep expediting scientific knowledge, new designs and materials have been introduced into the realm of SCs. For instance, advanced carbon-based (activated carbon, carbon nanotubes, graphene) and MXene* materials are captivating researchers as promising electrode compounds because of their high surface area, electrical conductivity, and flexibility [15]. Furthermore, 3D architectures allied with new advanced printing techniques pave the way for new interdigital geometries. These 3D electrode configurations allow for strictly designed porosity, wettability, and flexibility that offer high surface area accessibility with excellent ion transport [16]. Finally, to complement the clean solution that SCs embody within energy storage and drive the manufacturing of these devices to a greener future, biodegradable materials represent an innovative prospect in reducing electronic waste, contributing to a more eco-friendly answer to the state-of-the-art development of SCs. As the base for this sustainable alternative are natural biopolymers and small biological molecules that show efficient storage of electrochemical energy, semiconductor behavior, and have demonstrated superior performance in SC operation when combined with carbon electrode materials, surpassing that of pure carbon-based SCs. In this case, the SC electrode is composed of self-organizing peptides, while the electrolyte is a green amino acid ionic liquid [17].

1.2. Structure and Types of Supercapacitors

To understand the different types of SCs, it is essential first to examine the operational principles of a basic electrolytic capacitor. An electrolytic capacitor is based on a metal

*MXenes are 2D materials composed of layers of transition metal carbides, nitrides, or carbonitrides. MXene is formed through selective etching using chemical $M_{n+1}X_nT_x$, where M represents an early transition metal, X is nitrogen or carbon, and T denotes functional groups (e.g., OH, F, O, Cl) [14]

anode, an insulating oxide layer that acts as the dielectric, and a solid, liquid, or gel electrolyte which acts as the cathode. The oxide layer is formed at the anode's surface through an anodization process and is completely covered by the electrolyte. Typically, the insulating dielectric material formed is Aluminium oxide (Al_2O_3), Tantalum pentoxide (Ta_2O_5), or Niobium pentoxide (Nb_2O_5), depending on the anode material. Due to the thin dielectric and enlarged anode surface, electrolytic capacitors have a much higher capacitance than ceramic or film capacitors. They store electric energy statically by ionic charge separation in the dielectric oxide layer between the metal and the electrolyte. Unlike SCs, which use the electrolyte as an ionic conductive connection for storage through double-layer capacitance and electrochemical pseudocapacitance, the electrolyte in electrolytic capacitors serves as the second electrode.

The capacitance (C) of a capacitor is defined as the ratio of the charge stored (Q) on one electrode to the potential difference (V) between the electrodes ($C = \frac{Q}{V}$). To enhance the capacitance, the surface area (A) of each electrode, as well as the distance (d) between the electrodes, must be optimized, due to their proportionality ($C = \epsilon_0 \epsilon_r \frac{A}{d}$, where ϵ_0 is the vacuum permittivity and ϵ_r is the relative permittivity of the dielectric material).

The principal properties of a capacitor are its energy and power values, which can be derived from the following equations:

$$E = \frac{1}{2}CV^2 \quad (1.1)$$

$$P = \frac{V^2}{4R_{ES}} \quad (1.2)$$

where R_{ES} represents the equivalent series resistance [7].

The slow discharge rate inherent to the concept of battery is opposed by the conventional capacitor, which shows a very high power density. However, its low energy density makes the capacitor an inadequate device for day-lasting instruments that require high amounts of energy for long periods. The Ragone plot, shown in Figure 1.1, demonstrates the versatility of the SC and how it differentiates itself from capacitors, batteries, and even fuel cells.

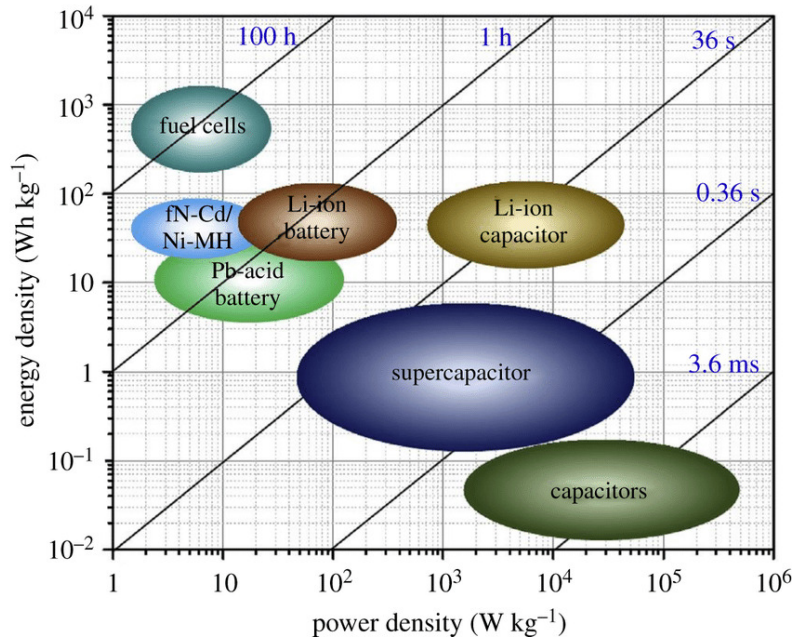


Figure 1.1: Ragone plot comparing the energy storage performance of various energy-storing devices in terms of power density, energy density, and typical charging times [18].

Born from the capacitor's limited energy storage capacity, the supercapacitor emerged as the battery's closest competitor for small electronics powering. The pillars of its structure are two highly porous and electrically conductive electrodes, which provide a large surface area for electrical ion adsorption. The electrode material determines the type and behavior of the SC, which will be explained in more detail in the following sections.

SCs employ a solid, liquid, or gel electrolyte between the electrodes. The electrolyte facilitates the movement and diffusion of ions, enabling efficient charge and discharge processes. The separator, positioned between the positive and negative electrodes, prevents physical contact between the two electrodes while allowing electrolyte ions to pass through.

Current collectors, typically made of aluminum due to its high electrical conductivity and good corrosion resistance, are connected to the electrodes to enable the external flow of electrons from the negative electrode to the positive electrode. Figure 1.2 illustrates an example of a supercapacitor structure, encased in a plastic insulating material to protect the internal components from environmental factors.

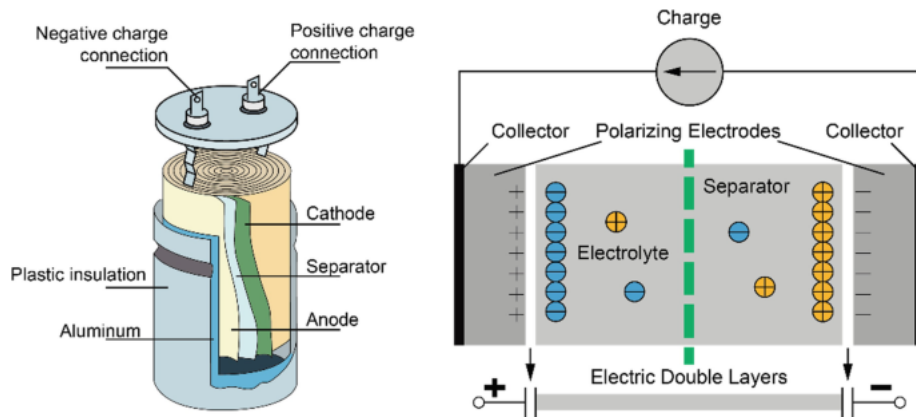


Figure 1.2: Illustration of a supercapacitor structure and its elements, as well as, a representation of the role that each part has in the SC's charging process [19].

Alongside the SC structure, it's also possible to visualize the ion separation between the two electrodes, depicting the charging process of the supercapacitor. This charge storage typically results from one of the three following mechanisms: non-Faradaic, Faradaic, or a combination of both. The non-Faradaic method is associated with the adsorption of the electrolyte ions at the electrode/electrolyte interface, hence no chemical mechanism is involved. Contrarily, the Faradaic mechanism is grounded on redox reactions, thus involving charge transfer between electrode and electrolyte. Ascribed to this clear storage process distinction, SCs can be divided into three major classes, as depicted in Figure 1.3. These are, respectively, electrochemical double-layer capacitors (EDLCs), pseudo-capacitors (PCs), and hybrid capacitors (HCs) [4, 7, 8].

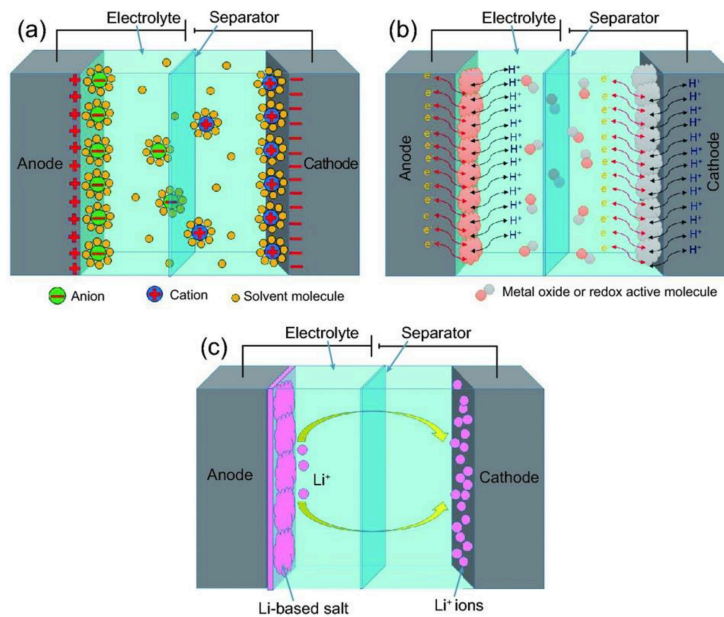


Figure 1.3: Illustration of the three SC classes: (a) EDLC, (b) PC, and (c) HC, as well as a basic representation of their respective charge storage mechanism [20].

1.2.1 EDLC

As the name suggests, the operation principle of EDLCs is intrinsically linked to the electric double-layer phenomenon. When a voltage is applied, electrons flow from the negative electrode to the positive electrode, which induces the movement of cations toward the positive electrode and anions toward the negative electrode. This results in the formation of two oppositely charged layers at each electrode/electrolyte interface: one layer of charge accumulates on the surface of the solid electrode, while the corresponding counter-charge forms in the adjacent liquid electrolyte, as demonstrated in example (a) of Figure 1.3. The separation between these two layers occurs on the nanometer scale, leading to high capacitance due to the extremely small distance over which the electric field operates [20, 21].

Over the last couple of centuries, large advancements have been achieved regarding the description of the electric double-layer (EDL). Amongst the many theories, the Gouy-Chapman-Stern (GCS) model stands out as the most widely used, capable of explaining the majority of the experimental behavior [22]. Two crucial approaches preceded and laid the groundwork for the GCS model. The first was Helmholtz's model (1853), which represented a similar behavior to a conventional capacitor, where the potential decreased linearly with the double-layer thickness. The other concept was developed by Gouy and Chapman who came up with a diffuse charge model (1913). Both scientists proposed that the cations/anions distribution was not uniform due to thermal agitation and the free movement of ions present in the solution. Instead, the EDL was formed by a fixed layer at the electrode joined by a diffuse layer on the electrolyte. According to this concept, the electric potential decreases exponentially with the distance from the electrode surface [23].

Whilst both theories reflect some of the EDL's behavior, they either fail to consider ion size and thermal motion (Helmholtz model) or neglect specific ion adsorption and don't succeed for highly charged EDLCs (Gouy-Chapman model). As a result, Otto Stern, in 1924, merged both theories and established a new approach to obtain a more accurate description of the EDL.

The GCS model (Figure 1.4) proposes the existence of two different regions with distinct ion distributions, a compact layer, and a diffuse layer. The compact or Stern layer is composed of the inner Helmholtz plane (IHP) together with the outer Helmholtz plane (OHP), which delimit the region associated with a strong adsorption of the electrolyte ions to the

electrode surface. The IHP contains mostly solvent molecules and specifically adsorbed ions. The thickness of this layer matches the size of the adsorbed ions. The OHP has also a nanometric length and includes the solvated counterions. Due to the highly adsorbed ions, the electric potential behaves similarly to the Helmholtz model description; however, in this case, the potential decreases with different slopes in each Helmholtz plane. As the distance from the electrode surface increases the ion distribution starts to follow the Gouy-Chapman model, giving rise to the diffuse layer. In this region, the charges are thought to be freely movable along the electrolyte solvent, suffering the combined effect of electrostatic attraction, as well as, thermal agitation. As a consequence, the electric potential decreases exponentially away from the electrode surface. Finally, at the bulk solution, the potential reaches a plateau with a constant potential [24, 25].

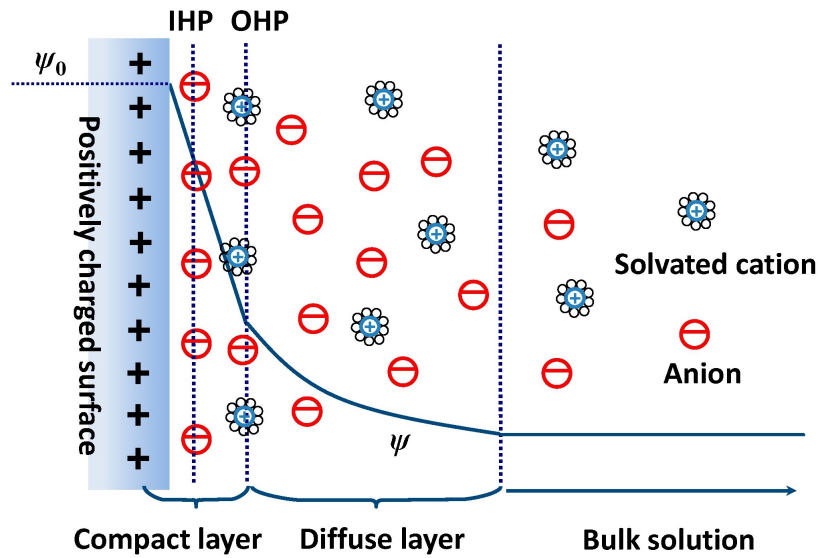


Figure 1.4: GCS model description of the double layer. Adapted from [24].

The performance and efficiency of EDLCs heavily depend on the characteristics of both the electrodes and the electrolyte. For the electrodes, a high surface area is fundamental to increase the charge accumulation space and maximize the SC capacitance. Furthermore, the electrodes need high electrical conductivity, to ensure efficient charge transfer, along with strong compatibility with the electrolyte to prevent any chemical reaction and guarantee high durability through multiple cycles of operation. On this premise, carbon-based materials are to this date the most reliable electrode material choice. Activated carbon, carbon aerogels, carbon nanotubes, and even graphene show the most promise of the back off their large specific surface area, excellent electrical conductivity, high porosity, availability, and chemical stability [7, 20, 26, 27].

The significant gap in surface area between carbon-based electrodes and their peers is primarily due to the porosity and the precise control over their porosity. The intricate network of these pores provides numerous sites for ion adsorption. The high density of these adsorption sites is what contributes to the large surface area and, consequently, to the high capacitance of the material. While pore density is closely linked to the capacitance of SCs, it's also crucial to consider the size of the pores and their accessibility. The mobility of ions within the pores differs from their mobility in the bulk electrolyte solution and is significantly influenced by pore size. If the pores are too small for the electrolyte ions to enter easily, they won't contribute effectively to double-layer capacitance. Therefore, the pore size must be selected to match the electrolyte, ensuring that the pore size distribution is optimized based on the size of the ions [27].

The electrolyte choice is coupled with the selected electrode material. Besides the coherence between ionic and pore size, numerous parameters influence the electrolyte selection such as ionic conductivity, intrinsic resistance, electrochemical stability, and ionic concentration. Such details can heavily influence the capacitance, operating potential window, cycle stability, working temperature range, and equivalent series resistance [20]. With this in regard, most electrolytes are either aqueous (e.g., sulfuric acid - H_2SO_4), non-aqueous (e.g., tetraethylammonium tetrafluoroborate - $TEABF_4$), or gel (e.g., polyvinyl alcohol - PVA doped with H_3PO_4) [7, 20, 28].

1.2.2 Pseudocapacitors

Unlike the physical process of electrostatic charge separation associated with the EDLCs, pseudocapacitors rely on Faradaic electrochemical mechanisms for charge storage, originating the pseudocapacitance. This generated capacitance is either derived by underpotential deposition, redox pseudocapacitance, or intercalation pseudocapacitance. Firstly, the underpotential deposition pseudocapacitance appears when metal ions form an adsorbed monolayer at another metal's surface above their redox potential, typically lead (Pb) is adsorbed in gold (Au) electrodes (Fig 1.5 (a)). The second pseudocapacitance mechanism resembles the operation principle of a battery, where ions are electrochemically adsorbed onto the electrode surface and undergo oxidation/reduction reactions at the electrode/electrolyte interface (Fig 1.5 (b)). Transition metal oxides such as manganese oxide (MnO_2) and, especially, ruthenium oxide (RuO_2), as well as conducting polymers are well-known examples of pseudocapacitive materials used for these redox reactions. Finally, intercalation pseudocapacitance, unlike the other processes, occurs

when electrolyte ions intercalate into the tunnels or layers of a redox-active material, such as vanadium pentoxide (V_2O_5) or niobium pentoxide (Nb_2O_5), accompanied by a Faradaic charge transfer (Fig 1.5 (c)) [4, 29, 30]. The main difference between pseudocapacitors and EDLCs comes in the capacitance value, where a pseudocapacitor can reach 10 to 100 times the capacitance of an EDLC, as well as, a superior energy density. However, due to the slower faradaic nature of the charging process, pseudocapacitors exhibit lower power density and lower cycle life [31, 32].

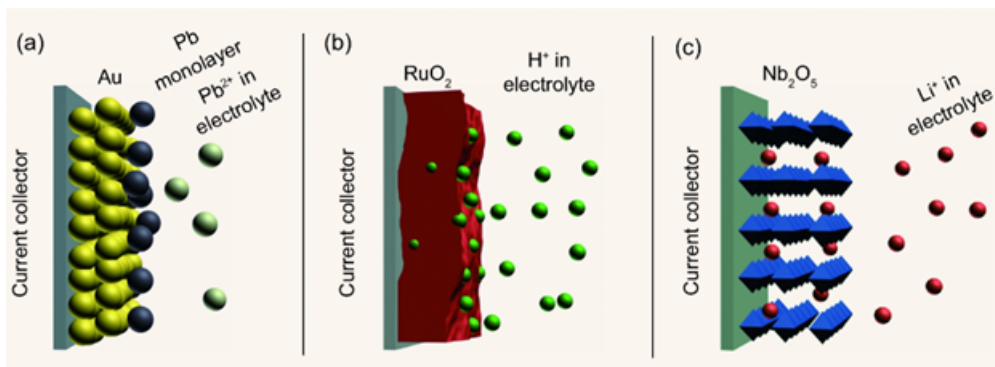


Figure 1.5: Different pseudocapacitive electrochemical mechanisms: (a) underpotential deposition, (b) redox pseudocapacitance, and (c) intercalation pseudocapacitance [30].

1.2.3 Hybrid capacitors

The final type of supercapacitor combines the best of both worlds by highlighting the strengths of EDLC and PC, while also mitigating their flaws. In detail, hybrid capacitors offer the enhanced capacitance properties of faradaic mechanisms, coupled with the superior power density and improved cycle stability characteristic of EDLCs [8, 26].

To bridge these two concepts, hybrid supercapacitors can be formed by one of three electrode configurations: Asymmetric, Composite, and Battery-type. The asymmetric structure, as the name suggests, merges an EDLC electrode with a PC electrode (e.g., activated carbon as the negative electrode with manganese dioxide as the positive electrode), the second configuration uses a composite electrode material* that amalgamates the characteristics of both PCs and EDLCs (e.g., composite electrode consisting, for example, of $Li_4Ti_5O_{12}$ /carbon nanofibers) [33]. Finally, the battery-type, couples an EDLC electrode, generally a carbon-based material, to a battery electrode (e.g., lead dioxide (PbO_2), nickel oxyhydroxide ($NiO(OH)$), lithiated graphite (Li_xC_6)) [7, 20, 34].

*Composite electrodes integrate carbon-based materials with either conducting polymer or metal oxide materials [7].

1.3. Thermally-Chargeable Supercapacitors

As awareness of global warming increases, the demand for new environmentally friendly advancements grows stronger. From the dispersed solar radiation, passing through huge industry byproducts dissipation, to small-scale energy generation from everyday activities, there are numerous opportunities to harness the almost infinite amount of waste heat that flees from the Earth's surface daily, contributing to the greenhouse effect.

To this day, the most common heat-to-electricity conversion comes from the Seebeck effect where a temperature gradient across a thermoelectric material generates an electrical voltage. This occurs in an electrical conductor or semiconductor because the charge carriers at the hot end have more kinetic energy than those at the cold end, leading to charge diffusion from the hot region to the cold region [35]. Although thermoelectric materials lead the way in energy harvesting for powering low-consumption electronic devices, they face several limitations, including low power generation, mechanical rigidity that limits their use in portable and wearable devices, high material costs, and challenges in scalability [35]. As a promising solution to all of these drawbacks, thermally-chargeable supercapacitors (TCSCs) integrate the principles of thermoelectric energy conversion with the high power density, rapid charging, and extended lifespan of supercapacitors.

A TCSC makes use of a Seebeck-like effect known as the Soret effect to convert a temperature gradient, which is induced along an ionic electrolyte, into an electric voltage between the electrodes. The Soret effect is evidenced in a fluid mixture of two or more compounds when the presence of a temperature gradient leads to a thermodiffusion* of the distinct species at different diffusion rates [36]. This disparity in the migration speed of ions in the electrolyte is due to differences in size, activation energy, and Coulomb forces. As cations and anions diffuse at different rates through the electrolyte, a concentration imbalance is created, resulting in a potential difference [35].

In the presence of the Soret effect, the net mass flow rate (J^i) of a particular species i is governed by two terms, one related to Fick's law of diffusion and the other to thermal diffusion. The former is described by the ion's mass diffusion coefficient (D) while the mass transfer driven by the temperature gradient is described by a characteristic thermal diffusion coefficient (D_T), resulting in equation 1.3 [36].

$$J^i = -D\nabla c - D_T\nabla T \quad (1.3)$$

*Thermodiffusion is regarded as the flow of matter caused by a macroscopic temperature gradient.

where c is the species concentration and T is the temperature. The Soret effect is characterized by the Soret coefficient (S_i), which can be positive if the ion migrates from the hot to the cold side or negative if the ion travels in the opposite direction.

The Soret coefficient is given by the following formula:

$$S_i = \frac{D_T}{D} \quad (1.4)$$

With a general understanding of the Soret effect, it's easy to partition the four phases of the TCSC working mechanism, represented in Figure 1.6A and schematized in Figure 1.6C: (1) thermal energy harvesting; (2) electric charging; (3) energy storage process; and (4) discharging of the TCSC [5].

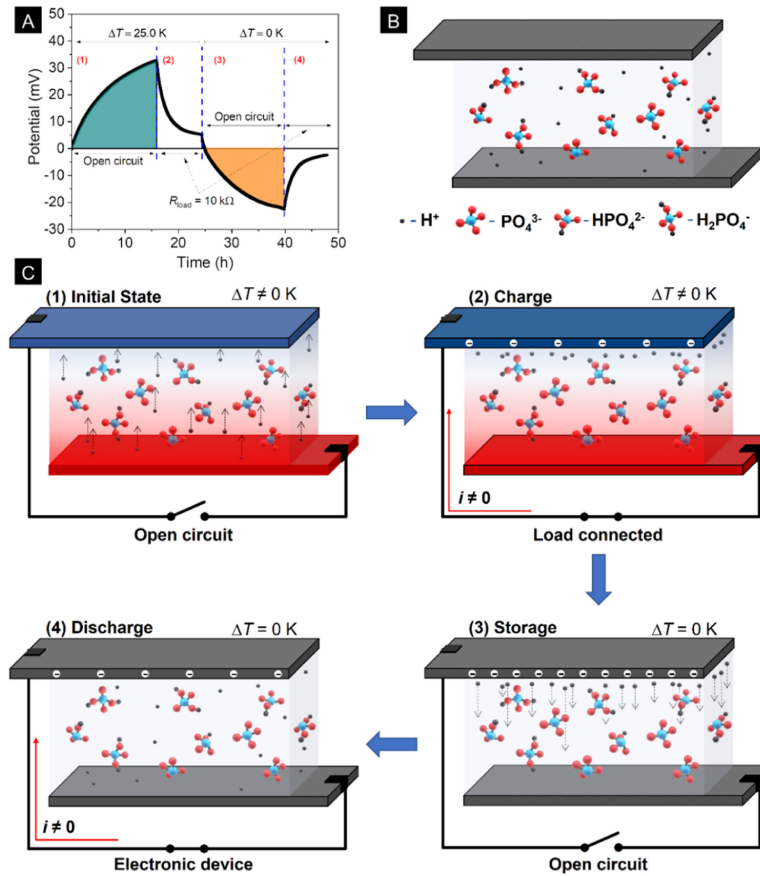


Figure 1.6: Operation principle of a TCSC: a) and b) describe the charging process, while c) and d) represent the discharging process [5].

This illustrative example describes a TCSC composed of an ionic electrolyte mixture of PVA doped with H_3PO_4 sandwiched between two carbon nanotube electrodes, with copper current collectors and a cotton substrate. In the equilibrium state (Figure 1.6B), both

cations (H^+) and anions (PO_4^{3-} , HPO_4^{2-} , $H_2PO_4^-$) flow arbitrarily through the electrolyte medium (PVA), nullifying each other's effect and keeping the TCSC at zero voltage. Once a temperature gradient is applied between the two TCSC electrodes, a thermodiffusion of the cations occurs from the hot to the cold electrode (scheme (1) of Figure 1.6). Although the temperature gradient also influences the anions, they don't show any significant movement due to their larger size and weight. Afterwards, the thermovoltage of the device reaches a plateau and an external load is connected, marking the end of the thermal energy harvesting.

As cations accumulate at the cold surface, a charge imbalance is created between the electrodes that force electrons, from the hot to the cold side through an external circuit, to compensate for the ionic charges, resulting in the charging of the supercapacitor (scheme (2) of Figure 1.6). As soon as electroneutrality is reached, the energy storage process occurs by removing the temperature gradient, which causes the ionic charges to diffuse back to the bulk of the electrolyte and revert to their original state (scheme (3) Figure of 1.6). By establishing a closed external circuit with an electrical device, electrons then flow in the reverse direction of the charging process. This final discharge current, represented in the scheme (4) of Figure 1.6, is what allows the powering of low-consumption electronic devices [37].

Although the working mechanism of TCSCs can be easily understood from a macro point of view, complex interactions rule the motion of ions under a temperature gradient. From hydrostatic pressure in the double-layer to solvent-ion dispersion forces in the electrolyte many factors may interfere with the charging of the TCSC [36]. Moreover, because this research field is still new, there is also room to explore the many materials and designs that haven't already been tested [38]. This thesis aims to contribute to the recent progress and development made in this regard.

1.4. Supercapacitor Simulation

In today's world, we live in an era dominated by computational technology. The rapid advancements in computing power, data processing, and algorithm development have transformed nearly every aspect of our lives. This computational revolution enables us to process vast amounts of data quickly, solve complex problems that were once thought impossible, and create sophisticated models that simulate real-world phenomena with remarkable accuracy. In this context, the integration of computational tools in research

and development processes is not just beneficial but essential for driving innovation and progress.

Supercapacitors clearly exemplify the need to leverage computational tools for technology development. Optimizing their performance requires a deep understanding of materials science, electrochemistry, and, in the case of TCSCs, the thermal motion of ions. Traditional experimental approaches, while valuable, are often limited by time, cost, and complexity. By coupling computational simulations with experimental methods, a vast number of designs can be explored, different hypotheses may be tested efficiently, and new materials and device configurations can be predicted before they are physically realized. At present, significant steps are being taken to develop and construct robust simulation models. The most common methods to investigate the physical and chemical phenomena of SCs are Molecular Dynamics (MD), Density Functional Theory (DFT), and Finite Element Methods (FEM) [39].

1.4.1 Molecular Dynamics

MD provides an analysis of particle movement and interaction at the atomic level. In this computational method, Newton's equations of motion are solved for an initial set of N particles with specified initial conditions and thermodynamic assumptions. Once the model system reaches equilibrium, the desired measurements are performed over a defined period [40]. MD is particularly useful in supercapacitor research given its precision in representing the diffusion and interaction of ions with the electrode surface. This allows for a detailed analysis of the materials composing the supercapacitor and a thorough simulation of the electric double layer.

By tracing the trajectories of ions in different electrode materials, Bo et al. [39] demonstrated the significance of MD in understanding electrode design and morphology. The precise capabilities of MD at the atomic level have enabled numerous studies on pore size and electrode structure. This paper specifically demonstrates how MD is currently being used for energy density optimization and power density enhancement *via* fine-tuning the porous structure of carbon-based electrodes. In addition, MD was also used as a powerful tool for the comprehension of complex quantum interactions and effects happening in 2D nanostructures, such as graphene electrodes. Similarly, Eyvazi et al. [41] employed MD in supercapacitor development. However, unlike the previously mentioned work that

focused primarily on electrode improvement, the authors used MD to examine the electrolyte. That study compared polymer-based electrolytes and the more common ionic liquid ones, helping determine their viability as alternatives.

1.4.2 Density Functional Theory

DFT provides a distinct approach for supercapacitor simulation by focusing on the electronic structure and quantum mechanical behavior of the particles involved in the system. This is achieved by approximating a solution to the Schrödinger equation using electron density instead of the wavefunction. In short, a set of theorems (Hohenberg-Kohn theorems) explain the relation between the ground state of a quantum mechanical system and its energy density. DFT makes use of this relation, along with the Kohn-Sham equations, to achieve a close estimate of realistic models of bulk materials and their surfaces. The exchange interactions and the correlation effects between electrons are defined by the exchange-correlation functional, making it a crucial component in the accuracy of DFT calculations [42].

With the exponential progress of supercapacitor simulation in the last decade, several researchers have adopted DFT simulations for detailed studies of the electronic structure and behavior, as well as, chemical bonding in the supercapacitor components. Besides allowing for the analysis of fundamental processes governing energy storage and charge transfer, DFT also grants the possibility of examining unique quantum mechanical effects that would be impossible to investigate in most simulation software. This capability is essential for understanding how quantum effects influence the performance of materials at the nanoscale, as demonstrated by the work of Song et al. [43]. This paper highlights DFT's distinct capabilities in studying graphene oxide as a supercapacitor electrode. In this case, DFT allowed for complex calculations of quantum capacitance and electronic properties when different oxygen-containing groups were added to the graphene sheet structure.

Aside from investigating the quantum mechanical behavior and chemical bonds in 2D electrodes, DFT also facilitates a broader study of various supercapacitor materials and the influence of different geometries. In their research, Lian et al. [44] examined how pore size and electrode curvature affect supercapacitor capacitance by developing a novel pore representation model. This model offered a new approach to characterizing nanoporous materials and quantifying their performance. Their initial findings revealed that maximum

capacitance occurs when the pore size closely matches the ion diameter. The study also explored the ionophobicity of electrode pores (tendency to repel the infiltration of ions) and found that increasing this resistive behavior could enhance the energy stored in an EDLC at a specific electrode voltage. To complement the electrode surface analysis, an electrolyte study was conducted to guide future researchers in the selection of ionic liquids. This involved determining an optimal value for the dipole moment of the solvent and examining the impact of impurities in the electrolyte. Additionally, the authors investigated how ion dispersion interactions influence the charging process of supercapacitors.

1.4.3 Finite Element Method

The FEM is the most popular numerical technique for physics and engineering problem-solving. Its objective lies in obtaining an approximate solution to partial differential equations that describe the laws of physics for space and time-dependent problems that cannot be solved with analytical methods. To achieve this goal, the FEM subdivides the geometry of a specific system into smaller and simpler parts called finite elements. This discretization results in an algebraic equation system that provides an approximate value for the unknown variables over each finite element. The simple equations that model these finite elements are then assembled into a larger system of equations that models the entire problem [45].

Although MD and DFT have shown remarkable capabilities in expressing and simulating the interactions and effects that regulate a supercapacitor capacitance at the atomic level, the FEM offers unique advantages over them. The first main advantage is FEM's ability to easily handle complex and large geometries, which often exceed the nanometric scale of MD and DFT simulations. This allows FEM to model real-world supercapacitor designs more effectively. Additionally, FEM can integrate multiple physical phenomena into a single simulation, including electrical, chemical, thermal, and mechanical behaviors, for example. The most common FEM software used for simulations are COMSOL Multiphysics and ANSYS.

The work developed by Pierfrancesco Ombrini in his thesis [46] demonstrates the versatility of COMSOL in the study of TCSCs. A combination of the electrochemical and thermal components allowed for the research and investigation of the effects that a temperature gradient inflicts on SC performance. To begin with, Ombrini analytically solved the Poisson-Nernst-Planck equations, which represent the electrochemical behavior, and

found a novel solution to represent the effect of a temperature gradient for his specific system and proved his results through FEM simulations. Then a general solution for an n-electrodes system was found and tested in COMSOL. Cases of high-temperature gradients, together with high concentrations, and the case of electrodes with small pores were all also verified and compared with his model. His work contributed to the expanding research in TCSC and the effect that the Soret coefficient inflicts on these devices.

1.5. Objective

The present work aims to develop a FEM model in COMSOL that accurately simulates the electrochemical and thermophoretic behavior of a supercapacitor. Additionally, this thesis seeks to deepen the understanding of the physical and chemical properties of the supercapacitor's ions and materials. To achieve this, a strong connection between experimental results and simulation tests will be initially established. The experimental work will be conducted in a laboratory, where various geometries will be fabricated using different methods to identify which designs provide the most consistent results for comparison with simulations.

Following this, a comprehensive analysis of each main parameter that influences the electrochemical response will be undertaken to investigate strategies for enhancing the supercapacitor's capacitance. Finally, the Soret effect will be described, tested, and compared between simulation and experimental findings, aiming to improve the output voltage of a TCSC. In summary, the ultimate goal of this thesis is to contribute to the emerging field of TCSC simulation and support ongoing research efforts to find innovative ways to harvest and storage waste energy.

2. Eletrochemical Analysis: Numerical Simulation vs Experimental Methods

This chapter is devoted to the development of an electrochemical simulation model of a supercapacitor (SC). To establish a foundation for the simulation model, SC devices were experimentally fabricated and measured to gain an initial understanding of their electrochemical characteristics. This approach allowed for the identification of key parameters and factors that influenced the SC's simulation. By leveraging cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements, this study examines the proximity between the simulation model and the experimental results, with the objective of tailoring the simulation model for greater accuracy.

2.1. Simulation Models

Supercapacitor simulation requires a large set of differential equations to describe the distinct physicochemical interactions occurring in the electrodes, electrolyte, and their interfaces. In COMSOL, such equations can be integrated in one of two ways: manually, describing with detail all the variables and physical phenomena, or utilizing the diverse collections of pre-built models given by the software, which provide a solid foundation for simulating most fundamental physics laws.

For this work, the Tertiary Current Distribution (TCD) model, built for generic electrochemical cell modeling, was used as a basis for the study of the supercapacitor's electrochemical behavior. The TCD interface describes the current and potential distribution in a SC taking into account the individual transport of charged and uncharged species in the electrolyte using the Nernst-Planck equations. The general mass balance for species i in the electrolyte is described by the following continuity equation:

$$\frac{\partial c_i}{\partial t} + \nabla N_i = 0 \quad (2.1)$$

where c_i represents the concentration of the ion i (in mol m^{-3}), and N_i is the total flux of species i (in $\text{mol m}^{-2} \text{s}^{-1}$). The total flux accounts for the flux of charged solute species by diffusion, migration, and convection, which are respectively the first, second, and third terms of the following equation:

$$N_i = -D_i \nabla c_i - z_i u_{m,i} F c_i \nabla \phi_i + c_i \mathbf{u} \quad (2.2)$$

where D_i is the diffusion coefficient of species i (in $m^2 s^{-1}$), z_i is the ion's valence, $u_{m,i}$ is the ion's mobility (in $s mol kg^{-1}$), F represents the Faraday constant (in $C mol^{-1}$), $\nabla \phi_i$ the electrolyte potential, and $\mathbf{u}$ is the convection velocity vector (in $m s^{-1}$).

The electrolyte's current density (i_l , in $A m^{-2}$) can be described using the sum of all species fluxes, while the electrode's current density (i_s , in $A m^{-2}$) arises from Ohm's law:

$$i_l = F \sum_i z_i N_i \quad (2.3)$$

$$i_s = -\sigma_s \nabla \phi_s \quad (2.4)$$

where σ_s denotes the electrical conductivity and ϕ_s the electric potential. To obtain the overall current in the electrode for electrochemical studies an integration across the electrode area was calculated.

Besides Ohm's law, a charge balance condition is needed to completely describe the flow of current in the electrodes, which is given by the following electroneutrality equation:

$$\sum_i z_i c_i = 0 \quad (2.5)$$

This set of equations, along with well-defined initial and boundary conditions, provides all the necessary tools to determine the fundamental dependent variables of the model, which are the concentration of the species, the electrolyte potential, and the electric potential. To accurately model supercapacitors and differentiate them from other electrochemical cells, specific adjustments were also made. In particular, porous electrodes were defined in every tested device. Additionally, to create an ideal EDLC, possible chemical reactions on the electrode/electrolyte interfaces were disregarded, focusing solely on the EDL phenomena. The developed model was the centerpiece in cyclic voltammetry and charge-discharge cycle studies.

2.2. Supercapacitor Fabrication

To validate the accuracy of the computational model, various in-plane devices were fabricated and measured to obtain comparable experimental results. The first geometry was

based on two thin electrode rectangles and an electrolyte that covered most of the electrodes, both deposited in a Kapton substrate. The electrodes were composed of multi-walled carbon nanotube (MWCNT), while the electrolyte was solid-gel *PVA* doped with H_3PO_4 . The electrode dimensions were 3.8 cm in length, 0.5 cm in width, and 40 μm in thickness.

In a first approach, the electrolyte was deposited by screen printing, in the same manner as the electrodes. In this case, the electrolyte dimensions were 4 cm in length, 3 cm in width, and 210 μm in thickness. Cyclic voltammetry and charge-discharge tests were then made and revealed promising results for the comparison with the simulation method. However, due to the formation of bubbles and the time consumption associated with the screen-printing technique, the deposition method was replaced by a 3D box drop coating technique. Although this change led to some improvements in electrolyte deposition, the cyclic voltammetry results exhibited significant deficiencies in charge storage, resulting in insufficient capacitance compared to the previous method. Therefore, only the results obtained from the screen printing method were analyzed and compared against the simulation model.

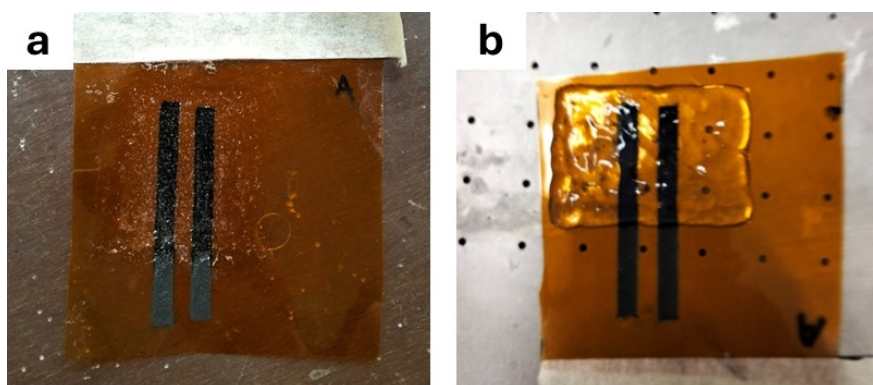


Figure 2.1: In-plane CNT-based SC with *PVA*/ H_3PO_4 electrolyte deposited in Kapton by: a) screen printing; b) coating using a 3D printed box.

The electrode ink used for screen printing was composed of sodium dodecylbenzene-sulfonate (SDBS), Polyvinylpyrrolidone (PVP), commercial MWCNTs, commercial Denka Black, and ultrapure water, in a 1:4:4:2:114 mass ratio. The procedure began with the dissolution of SDBS and PVP in water with the help of a mechanical stirrer. Afterward, the Denka Black and MWCNTs were added and kept under stirring for 7 hours. Finally, the deposition of the electrodes was done by printing a layer, taking it to the oven at 100 $^{\circ}\text{C}$, and repeating it twice for each fabricated electrode.

The solid gel electrolyte was made up of polyvinyl alcohol (PVA), phosphoric acid (H_3PO_4), and ultrapure water, in a 1:1:9 mass ratio. The preparation began by adding the phosphoric acid to the ultrapure water. The obtained mixture was then placed on a stirring plate at 35 °C. Once the acid and water were thoroughly mixed, the PVA was gradually introduced into the solution under continuous stirring. The solution, contained in a round-bottom flask, was then subjected to a controlled heating process. The temperature was incrementally increased through a series of heating stages: 35 °C, 45 °C, 55 °C, 65 °C, 75 °C, and, finally, 85 °C. This heating ramp was maintained for 24 hours to allow complete dissolution and proper gel formation.

The electrolyte's deposition by screen printing was carried out similarly to the process used for the electrodes, with the key difference being the oven temperature, which was set to 60 °C for 10 minutes. Due to the thinness of each deposited layer, which was approximately 10 μm in height, the process was repeated 15 times for each device. In the case of the 3D box printing, the electrolyte was deposited with a pipette in a box with a 3 mm height, and taken into the oven for 8 hours.

The Kapton substrates underwent a specific treatment to ensure surface cleaning and to enhance the adhesion of the electrodes and electrolyte layers. The preparation process began by cutting the substrates to the desired dimensions. Following this, the substrates were placed in an aqueous solution of KOH and stirred for 1 hour. After the potassium hydroxide treatment, the substrates were rinsed with water to remove any residual KOH and dried up. Subsequently, the substrates were submerged in an aqueous solution of HCl and stirred for 5 minutes. The treatment concluded with another water wash and drying process to ensure all traces of acid were removed.

2.3. Electrochemical performance of SCs

The electrochemical performance of the fabricated SCs was evaluated at room temperature by cyclic voltammetry (CV) and galvanostatic charge-discharge experiments (GCD) in a standard two-electrode cell configuration. The cyclic voltammograms were acquired on an AutoLab PGSTAT 20 over the potential window of $[-0.5, 0.5]$ V or $[-1.0, 1.0]$ V at 1, 5, 10, 25, 50, 75 and 100 mV s^{-1} scan rates. The specific capacitance (C_s , in F cm^{-2}) values of all SC cells, at different scan rates, were determined through the i-V curves, using the following equation [47]:

$$C_s = \frac{\int_{-V}^V I(V) dV}{2vX\Delta V} \quad (2.6)$$

where I denotes the electrical current intensity (in A), ΔV the applied potential window (in V), v the scan rate (in $V s^{-1}$), and X the total area of the electrodes active material (in cm^2). The energy density and power density of each device were obtained by equations 1.1 and 1.2, respectively.

The GCD experiments were performed using the same equipment, by applying a constant current density until a potential of 0.5 V or 1 V was reached and then reversing the current intensity to discharge the device back to its original potential, -0.5 V or -1 V. The value for the constant current density was the maximum value measured for each device in the respective cyclic voltammogram [47].

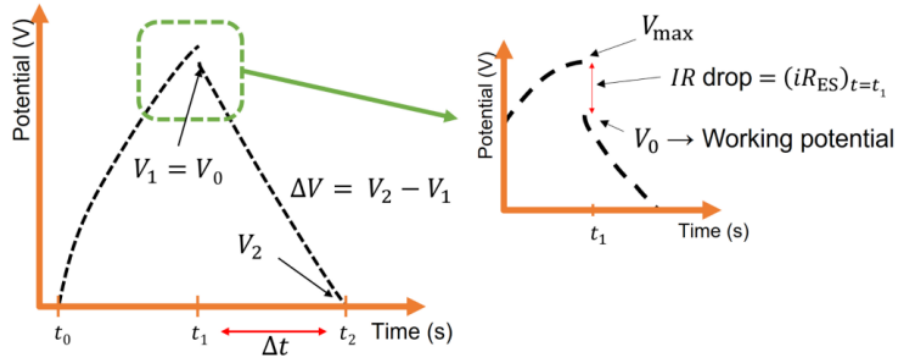


Figure 2.2: Illustration of a SC GCD curve and its key features (Adapted from [4]).

GCD measurements are essential to determine the working potential (V_0) of the SC, as well as the potential drop value (V_{drop} or IR drop), as demonstrated in Figure 2.2. The working potential represents the effective potential stored in the device after the charging process, while the IR drop is linked to the internal resistance of the SC. The equivalent series resistance (R_{ES} , in Ω) can be calculated by the following equation:

$$V_{max} - V_0 = (iR_{ES})_{t=t_1} \quad (2.7)$$

where V_{max} and V_0 are obtained through the GCD curve, as illustrated in Figure 2.2, and i (in A) is the applied current intensity. Additionally, the specific capacitance can be derived from the slope of the discharge curve using the following equation [4]:

$$C_s = \frac{i\Delta t}{\Pi\Delta V} \quad (2.8)$$

where i (in A) is the discharging current intensity, Δt (in s) is the discharging period corresponding to the potential difference ΔV (in V) and Π (in cm^2) is the area of the SC.

The energy density per area (E_D , in Wh cm^{-2}) and power density per area (P_D , in W cm^{-2}) can also be obtained from GCD measurements using expressions similar to equations 1.1 and 1.2 [48]:

$$E_D = \frac{C_s V_0^2}{2} \quad (2.9)$$

$$P_D = \frac{V_0^2}{4R_{ES}\Pi} \quad (2.10)$$

2.4. Simulation of Planar SCs based on MWCNT Electrodes

Five experimental SC devices were fabricated, all with varying distances between the electrodes: 0.5 cm, 1 cm, 1.5 cm, 2 cm, and 2.5 cm. Each device was composed of an MWCNT ink as electrodes material and PVA doped with H_3PO_4 as the solid-gel electrolyte. The geometry used is displayed in Figure 2.1a and the utilized procedure can be seen in Section 2.2. The electrodes distance variation between the devices was intended to test the versatility of the simulation model for different geometries. However, only the first two devices, with electrode distances of 0.5 cm and 1 cm, demonstrated capacitive behavior. The main issue with the fabrication of the latter three devices was related to difficulties in applying the electrolyte accurately to a defined area. During the preparation, the electrolyte inadvertently soaked all of the electrodes, leaving no space for proper electrical connections necessary for CV measurements and preventing reliable data collection.

Although a significant portion of the data collected from the last three devices proved to be unreliable, the primary objective of this study was successfully achieved with the first two devices. The CV measurements for devices A and B, which featured electrode distances of 0.5 cm and 1 cm, respectively, enabled the configuration and refinement of the simulation model. To achieve the most accurate simulation possible, a trial-and-error approach was employed. This method involved iteratively adjusting the model parameters to minimize the discrepancy between the simulated and experimental results.

The same computational model and parameters were used for both devices to replicate the respective experimental data. The CV curves were measured for a scan rate of 10

mV s^{-1} and an ionic concentration of 1000 mol m^{-3} . Successive tests conducted with varying parameters revealed that the primary influence on the SC's performance came from the diffusion coefficient (D , in $\text{m}^2 \text{ s}^{-1}$) of the electrolyte ions (positive and negative) and the surface area per unit volume (a_v , in m^{-1}). The values utilized for the model were $2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $8 \times 10^6 \text{ m}^{-1}$, respectively. Another factor with a significant impact on the CV measurements was the EDL capacitance (C_{dl} , in F m^{-2}), and its defined value was 0.5 F m^{-2} . However, this value remained constant throughout the studies due to its dependence on a_v :

$$i_{v,dl} = a_v \left(\frac{\partial(\phi_s - \phi_l)}{\partial t} \right) C_{dl} \quad (2.11)$$

The chosen value for C_{dl} was a default setting, unrelated to the specific capacitance value of the device. Therefore, without a trustworthy method to define either a_v or C_{dl} , only the surface area value was analyzed. This uncertainty restricted the study to drawing conclusions about the general influence of the surface area parameter, rather than establishing its precise value.

The areal capacitance values of the prepared and simulated SCs were determined using Equation 2.6. From Figure 2.3, it is possible to observe a significant reduction in capacitance from Device A to Device B. Specifically, the capacitance value is approximately halved when the distance between the electrodes (d) is doubled. This behavior aligns with the theoretical expectation, as capacitance is inversely proportional to d .

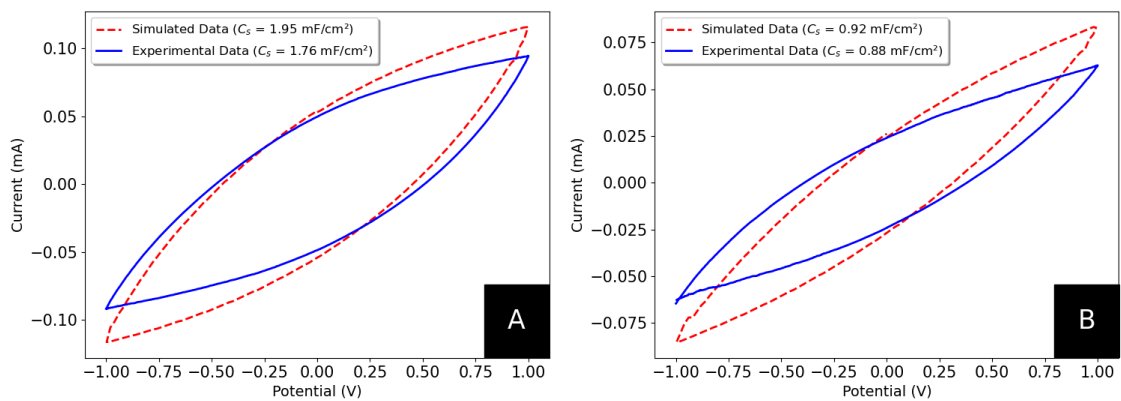


Figure 2.3: Comparison of CV curves between simulated and experimental data for SC devices with electrode distances: A) 0.5 cm and B) 1 cm.

In comparison with the characteristic i-V curves shown in Figure 2.4, it is evident that both the experimental and simulated devices exhibit an EDLC-type behavior, with no observable peaks or non-linearities that would indicate the presence of pseudocapacitance, which is consistent with expectations given that the devices contain only CNT electrode material. Although two devices are not enough to definitively establish the overall reliability of the simulation model, the consistent capacitance results, as well as the similar behavior, provide a promising indication of its potential effectiveness.

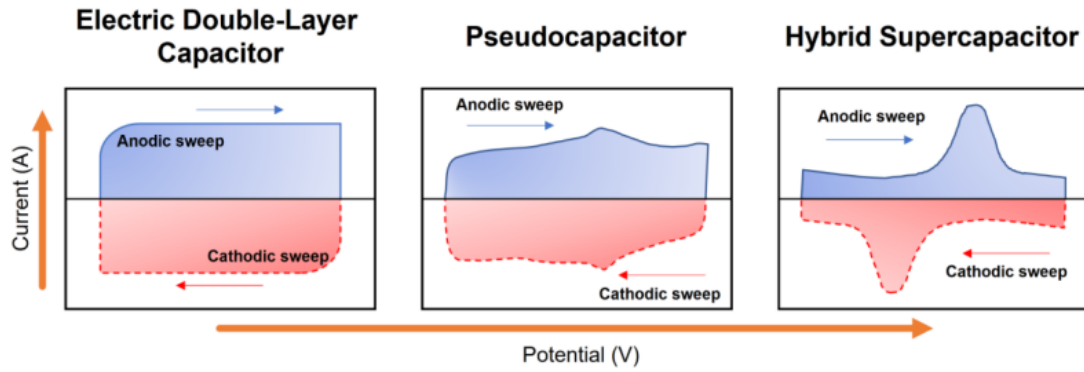


Figure 2.4: Representation of the typical i-V cycles of the different types of supercapacitors (Adapted from [4]).

GCD measurements were also conducted for devices A and B to determine the working voltage, the IR drop, and consequently the capacitance, energy density, and power density of the fabricated SCs. However, only device A provided suitable results for simulation comparison, as experimental data acquisition issues affected the results for device B. The constant current intensity applied was the maximum current value obtained in the previous CV measurement, with $i_{sim} = 1.15 \times 10^{-4} A$ for the simulated data and $i_{exp} = 9.55 \times 10^{-5} A$ for the experimental data. The measurement was performed within a potential window of $[-1.0, 1.0]$ V, using the same simulation parameters as those employed for the CV data acquisition.

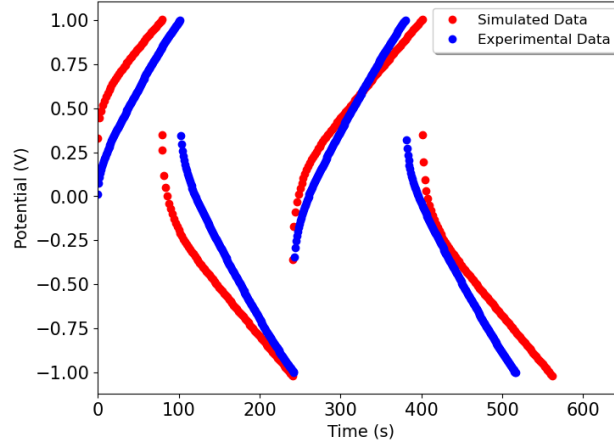


Figure 2.5: Comparison of GCD measurements between simulated and experimental data for device A.

The working potential of the SC is defined as the first potential value measured after the current reversal. Figure 2.5 shows the similarity between the working potentials in the experimental and simulated data, with $V_{0,exp} = 0.346$ V and $V_{0,sim} = 0.347$ V, respectively. The IR drop, which is the difference between the maximum voltage and the working potential, was found to be $IR_{drop,exp} = 0.657$ V and $IR_{drop,sim} = 0.653$ V. This voltage drop is associated with the internal resistance of the SCs, which arises from the limited diffusion mobility of the electrolyte ions within the electrodes structure, the contact resistance and the electrical conductivity of the electrode material [4]. The simulated GCD data indicate a lower equivalent series resistance value of $R_{ES,sim} = 5701$ Ω compared to $R_{ES,exp} = 6876$ Ω in the experimental results. The difference in resistance is not of great concern, because a small variance in the diffusion coefficient can easily alter the outcome. It is therefore expected that the experimental results show a larger voltage drop and consequent resistance, as simulations tend to idealize conditions, whereas experimental measurements must deal with various practical factors that contribute to internal resistance.

The areal capacitance values were also calculated from the GCD curves using Equation 2.8. For the experimental measurements, a value of $C_{T,exp} = 3.45$ mF cm^{-2} was obtained, while the simulated GCD led to an areal capacitance of $C_{T,sim} = 4.78$ mF cm^{-2} . Although the simulated capacitance is higher than the experimental one, similar to the CV results, both their values are more than double when compared with the CV capacitance. One possible explanation for the discrepancy in capacitance values could be attributed to the

differences in measurement methodologies between GCD and CV. The GCD measurements are performed at a constant current, which allows the capture of slower electrochemical processes that may not be fully reflected in the CV results, especially at higher scan rates. The disparity between the experimental and simulated capacitance values likely arises from the higher charge and discharge currents used in the simulations.

By evaluating the working potential, IR drop, and capacitance, the energy and power densities can be calculated using Equations 2.9 and 2.10, respectively. The SC measurements resulted in an energy density of $E_{D,exp} = 5.73 \times 10^{-2} \mu W h cm^{-2}$ for the experimental device and $E_{D,sim} = 8.00 \times 10^{-2} \mu W h cm^{-2}$ for the simulated data. The experimental SC showed a power density of $P_{D,exp} = 2.25 \mu W cm^{-2}$, while the simulated value was $P_{D,sim} = 2.73 \mu W cm^{-2}$. Although the results are not identical, the simulations consistently afford higher energy and power densities compared to the experimental measurements, under similar conditions. This trend aligns with the idealized nature of the simulations, where reduced internal losses and optimized conditions result in superior performance metrics compared to real-world measurements.

The characteristic GCD curves shown in Figure 2.6, reveal the ideal triangular shape associated with an EDLC-type behavior, suggesting the lack of faradaic reactions during charge and discharge processes. The close alignment between the experimental and simulated GCD results underscores the accuracy of the simulation model in replicating the real device's performance. These initial experimental results were crucial in not only developing a reliable simulation model but also in deepening the understanding of the foundational principles and main parameters on which the model is based.

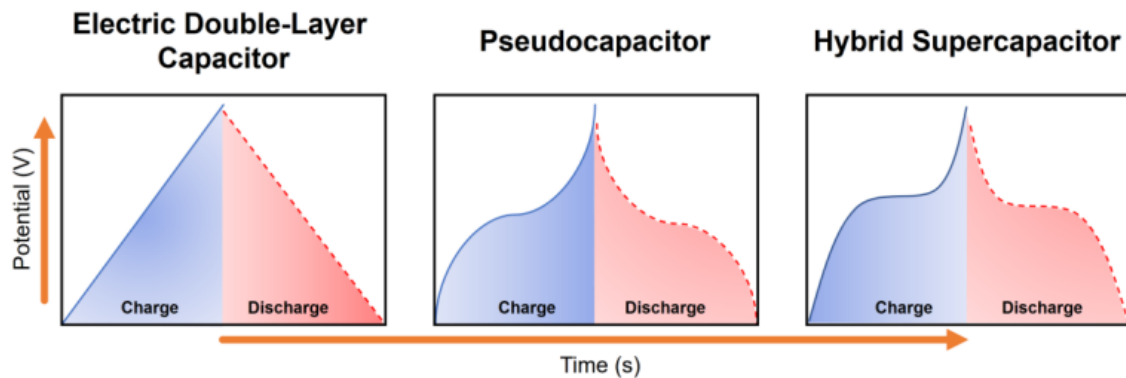


Figure 2.6: Representation of the typical GCD cycles of the different types of supercapacitors (Adapted from [4]).

3. SCs Tuning Properties: Influence of geometric, electrolyte and electrode parameters

With a reliable simulation model in place, the next step involved studying the various parameters, such as the diffusion coefficient of the electrolyte ions, the electrode surface area per unit volume, scan rate, and electrode spacing, to understand their influence on CV and GCD measurements. This analysis provided insights into how these parameters affect the SC's capacitance, charging/discharging times, energy density, and power density. The previous study showed a large influence of the diffusion coefficient and the surface area per unit volume on the electrochemical measurements. These factors were the initial focus of the investigation, followed by a study of the influence of the potential scan rate and the distance between the electrodes, in CV measurements.

3.1. Diffusion Coefficient

To investigate the impact of the diffusion coefficient on CV measurements, a series of simulations were performed where the diffusion coefficient was varied across an order of magnitude, while other key parameters were held constant, as shown in Figure 3.1. Specifically, a surface area per unit volume of $5 \times 10^6 \text{ m}^{-1}$ was used, with the potential window set from -1.00 V to 1.00 V and a scan rate of 10 mV s^{-1} . Device A served as the geometry model for all the chapter simulations.

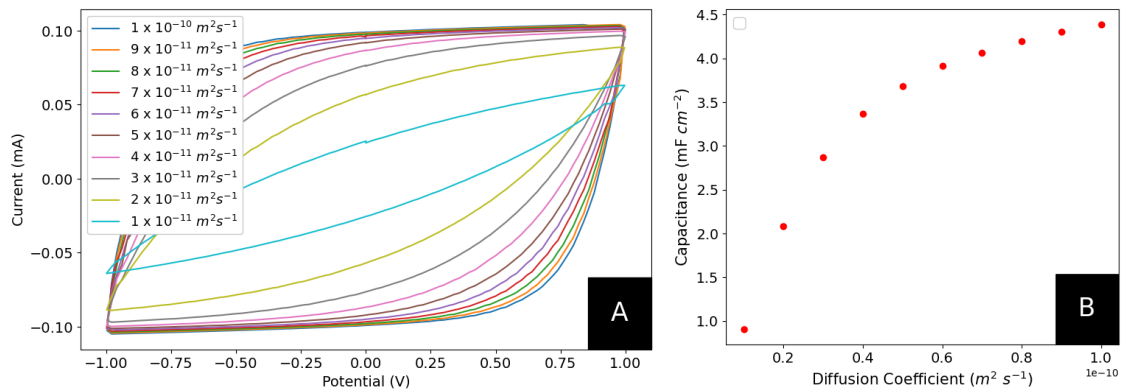


Figure 3.1: A) CV curves for different diffusion coefficients of the electrolyte ions. B) Capacitance of device A as a function of the diffusion coefficients.

In this initial study, the diffusion coefficient was set equally for both positive and negative ions. The simulated CV results exhibit more capacitive behavior at higher diffusion coefficients. This observed relationship aligns with the Nernst-Planck equation (Equation

2.2), which indicates that an increase in the diffusion coefficient leads to a higher absolute value of the total flux of charged species. However, the increase in the capacitance becomes less pronounced as the diffusion coefficient rises because the SC reaches a saturation point, where the number of available adsorption spots limits the maximum current intensity value. Consequently, the capacitance exhibits a logarithmic dependence on the diffusion coefficient, as illustrated in Figure 3.1B. This behavior not only highlights the way in which the SC is affected by the diffusion coefficient but also how surface and EDL properties can limit its performance.

Based on the obtained results, the shape of the cyclic voltammogram can be predicted for both very low and very high diffusion coefficients. For very low diffusion coefficients (lower than $1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$), the restricted ion movement would result in minimal charge storage at the electrode/electrolyte interfaces, causing the CV curve to approach a flat line near zero current intensity. Conversely, at very high diffusion coefficients (greater than $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), the rapid ion movement would lead to a nearly rectangular CV curve, reflecting the ideal capacitive behavior seen in Figure 2.4.

To complement the analysis of the diffusion coefficient parameter, a similar study was conducted with the variation applied solely to the diffusion coefficient of the negative ions, as depicted in Figure 3.2. The objective of this test was to determine whether differences in the diffusion coefficients of the two ions would lead to a comparable increase in capacitance, or if the diffusion coefficient of one ion would overlap the other. The cation's diffusion coefficient (D_{c_1}) was set at $3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, while the anion's value was varied between 0.5 and 1.5 times D_{c_1} .

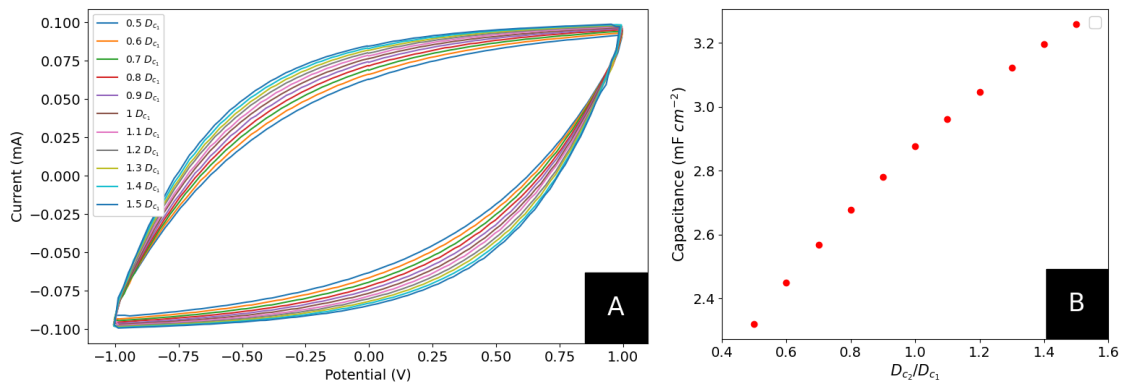


Figure 3.2: A) CV curves for different anion's diffusion coefficients. B) Capacitance as a function of the ratio between the anion's and cation's diffusion coefficients.

The variation in capacitance resulting from changes in the negative ion's diffusion coefficient exhibited a similar pattern to that observed when both ion diffusion coefficients were varied. However, the change was more subtle, likely due to the smaller range of variation applied in this study compared to the previous one (Figure 3.1). Despite this, the findings demonstrate that altering the diffusion coefficient of even a single ion can significantly impact the CV measurements, and consequently, the capacitance values. This effect is particularly important in systems where cations, such as H^+ , diffuse much faster than anions like PO_4^{3-} , HPO_4^{2-} , and $H_2PO_4^-$. Therefore, the divergence in their diffusion coefficients must be carefully considered in the analysis of electrochemical behavior.

The diffusion coefficient was further investigated using GCD measurements, with the results shown in the graphs of Figure 3.3. In this study a constant current intensity of $70 \mu A$ was applied, alternating between $-1.00 V$ and $1.00 V$. All other parameters were kept consistent with those used in the CV measurements, and the diffusion coefficient was varied across an order of magnitude. The choice of the variation range was based on the experimentally determined value of the diffusion coefficient ($2 \times 10^{-11} m^2 s^{-1}$), with the range selected to cover an order of magnitude relative to the obtained experimental value.

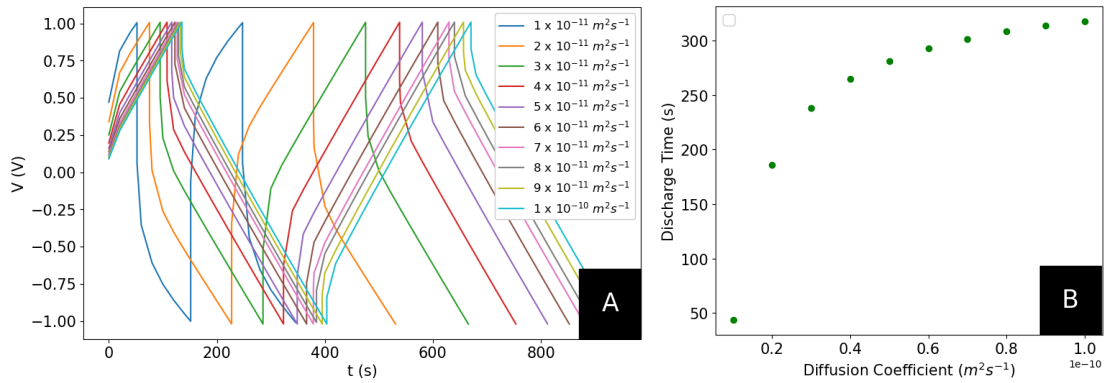


Figure 3.3: A) GCD curves for different diffusion coefficients of the electrolyte ions. B) Discharge time as a function of the diffusion coefficients.

The simulation results revealed that an increased anion's and cation's diffusion coefficient results in a longer discharge time. While it may seem counterintuitive that higher ion diffusion results in longer discharge times, this behavior aligns with the linear relationship between capacitance and discharge time, as shown in equation 2.8. Since the capacitance has been observed to rise with the diffusion coefficient (Figure 3.1), it naturally follows that the discharge time would also increase, given that all other parameters, such as discharge current, potential window, and the SC's surface area, remain constant.

A more detailed analysis of the GCD curves indicates a reduction in the IR drop, accompanied by an increase in the device's working potential with higher diffusion coefficients. This observation is consistent as enhanced ion mobility leads to a decrease in the SC's internal resistance, minimizing its energy losses and allowing the device to operate more efficiently at an elevated working potential.

The capacitance derived from this analysis exhibited an increase with higher diffusion coefficients, consistent with the results observed in the CV measurements. However, while the overall behavior is similar, there are notable differences in the capacitance values obtained from these two methods. This discrepancy arises because, in GCD measurements, capacitance is determined based on the total discharge time, whereas in CV measurements, it is calculated from the integral of the current intensity over the potential range.

To further validate the performance enhancements associated with higher diffusion coefficients, an energy density plot was generated as a function of power density, illustrated in Figure 3.4. This plot clearly demonstrates an increase in both parameters with rising diffusion coefficients, reinforcing the conclusion that higher electrolyte ion mobility contributes to the overall improvement in SC performance.

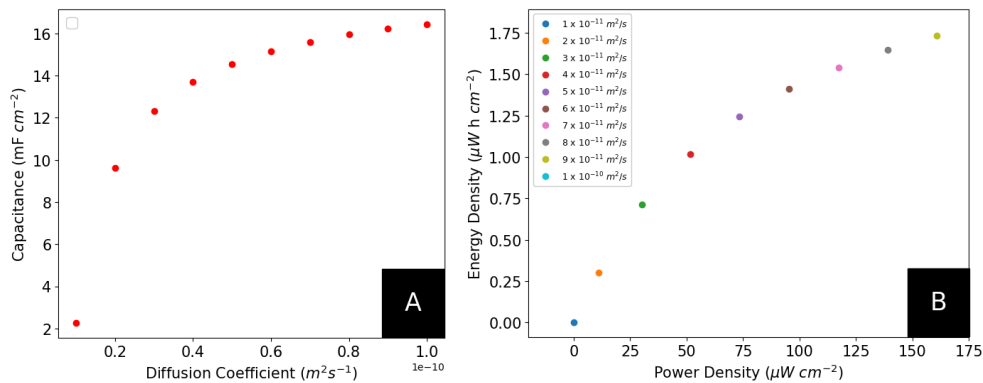


Figure 3.4: A) Capacitance derived from GCD measurements as a function of the diffusion coefficients. B) Energy density plot as a function of the power density for different diffusion coefficients (right).

3.2. Surface Area per Unit Volume

The diffusion coefficient analysis evidenced that the current intensity was constrained by surface properties. Therefore, it was necessary to investigate how the electrode's surface area influences and limits the supercapacitor's performance. CV studies were conducted, varying the surface area per unit volume by an order of magnitude, within a potential window of -1.00 V to 1.00 V at a scan rate of 10 mV s^{-1} . The results are presented in Figure 3.5. The diffusion coefficient used in these studies was $3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, chosen

for its proximity to the value obtained in the analysis of the experimental device and due to its ideal capacitive behavior observed in the diffusion coefficient parameter analysis.

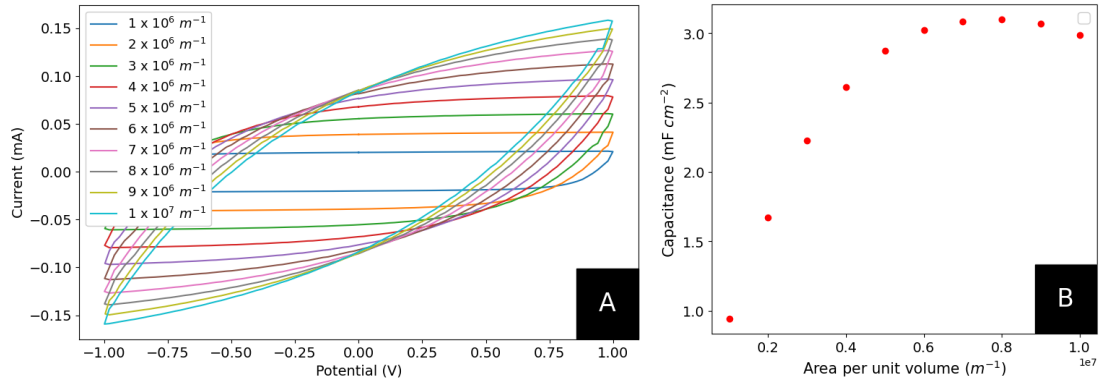


Figure 3.5: A) CV curves for different surface areas per unit volume. B) Capacitance as a function of the surface area.

As expected, increasing the device's surface area led to a significant rise in the maximum current intensity. This outcome is due to the increased number of active sites on the electrode surface for ion adsorption provided by the larger surface area, which, in turn, enhances the overall charge storage capacity, resulting in higher current densities during the CV measurements. The increased current intensity reflects the improved capacitive performance, as shown in Figure 3.5, as the device can store and release more electrolyte ions due to the enhanced interaction between the ions and the electrodes. However, within the chosen interval of surface area values, a slight decrease in the capacitance is observed for the i-V cycles corresponding to the highest area per unit volume, interrupting the upward trajectory seen in the other capacitance values. This suggests that beyond a certain point, increasing the surface area may not continue to enhance performance. For that reason, an additional study was conducted using a larger dataset of surface area values. The data was retrieved under the same conditions as the previous study between $1 \times 10^6 \text{ m}^{-1}$ and $1 \times 10^9 \text{ m}^{-1}$, and is represented in Figure 3.6. It is important to reinforce that the specific capacitance analysis focused solely on the influence of surface area on the capacitance trend, rather than the actual capacitance values. As a result, any further comparison with other studies is limited to analyzing the trends and behavior observed, rather than directly comparing absolute capacitance values.

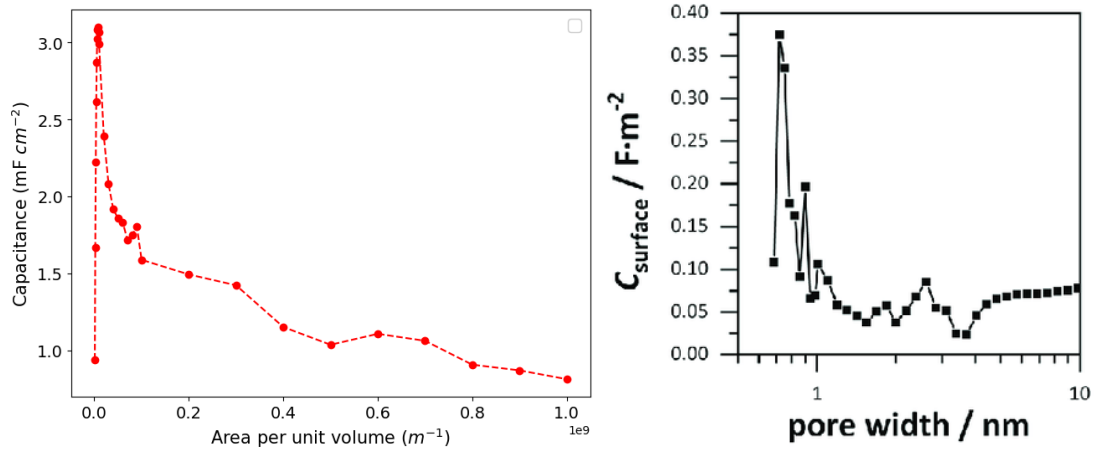


Figure 3.6: Simulated capacitance values for different surface areas per unit volume (left). Areal capacitance as a function of the electrode's pore size (right) [49].

The additional simulation measurements revealed a decrease in the supercapacitor's capacitance for surface area per unit volume values exceeding $8 \times 10^6 \text{ m}^{-1}$. This observed decline aligns with the behavior described by the Stern model, illustrated in Figure 1.4. In the simulated data, a more pronounced drop in capacitance occurs immediately after the maximum capacitance is reached, exhibiting a linear tendency similar to that seen in the inner and outer Helmholtz planes, between $8 \times 10^6 \text{ m}^{-1}$ and $3 \times 10^7 \text{ m}^{-1}$. Furthermore, as the surface area approaches $1 \times 10^8 \text{ m}^{-1}$, the rate of capacitance reduction begins to smoothen, which can be attributed to the exponential decay of the diffuse layer.

To better understand how capacitance responds to increasing surface area, Heimböcke et al. [49] examined the impact of pore size and surface area of activated carbons on the energy storage of the resulting EDLCs. Two main conclusions from this work are relevant to the simulation results. First, as depicted on the right-hand side of Figure 3.6, an increase in pore volume due to larger pores generally leads to a decrease in surface capacitance. This occurs because larger pores can reduce the effective surface area available for ion adsorption. Second, the article highlighted that synthesis parameters resulting in higher specific surface areas often lead to larger pore sizes, which can diminish the benefits of increased surface area. This observation aligns with the simulation results, where capacitance decreased with increasing surface area due to the associated increase in pore size.

The authors of the article thoroughly investigated the non-linear behavior of capacitance. They found that the capacitance peak for pore widths between 0.72 nm and 0.75 nm closely aligned with the simulated results. This peak is attributed to the electrolyte ion

size, as maximum capacitance is achieved when the pore width matches the size of the desolvated ions, enabling greater surface interaction. As pore sizes increased beyond this range, the capacitance declined due to the increased distance between the ions and the pore walls. Luo et al. [50] confirmed that high specific surface areas often result in a large pore volume driven by micropores, which in turn decreases the specific capacitance of porous carbon. Moreover, the authors emphasized that the optimal pore size matches the size of the desolvated ions, thereby providing the maximum capacitance. This conclusion was reached through a study conducted with carbide-derived carbon electrodes and an EMITFSI ionic liquid electrolyte.

In the right-hand side of Figure 3.6 it is also notable that for specific pore sizes, such as around 0.90 nm and 1.0 nm, the capacitance increases. Heimböcke et al. [49] attributed these capacitance peaks to improved ion accessibility due to partial or full solvation of the electrolyte ions. The simulation results similarly show a slight enhancement of capacitance around $1 \times 10^8 \text{ m}^{-1}$, which may reflect this behavior. However, a more detailed study would be required to confirm this conclusion. Nonetheless, this work highlights the importance of ensuring that the electrode surface has a high ion-accessible surface area, providing abundant active sites for ion storage, along with an appropriate pore structure to facilitate ion transport and storage, thereby enhancing specific capacitance and the overall performance of the supercapacitor.

GCD measurements were also performed for different surface area values, as demonstrated in Figure 3.7. Due to the current intensity increase in the CV comparison, the applied constant current intensity was increased to 200 μA . The potential window of -1.00 V to 1.00 V and the diffusion coefficient of $3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ were kept from the previous study.

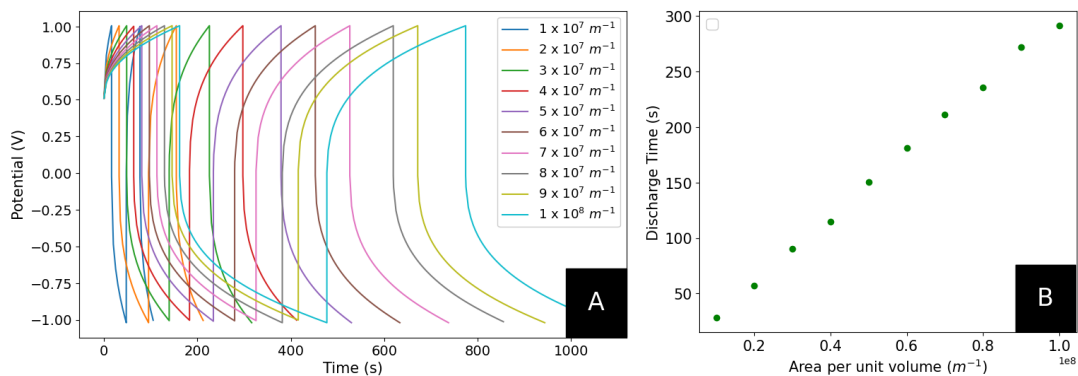


Figure 3.7: A) CGD curves for different surface areas per unit volume. B) Discharge time as a function of the surface area.

An increased surface area per unit volume led to a linear rise in the discharging time of the supercapacitor. This is due to the larger surface area allowing for greater interaction between the electrolyte ions and the electrode material, which enhances the charge storage capacity. As a result, the supercapacitor requires more time to fully discharge the stored energy.

In contrast to the diffusion coefficient results, varying surface area values led to similar *IR* drops and working potentials. This is because the internal resistance of a supercapacitor is more significantly influenced by factors such as electrical conductivity and electrolyte composition, rather than surface area alone. As a result, changes in surface area do not substantially impact the *IR* drop or working potential, resulting in comparable performance across different surface area values.

A linear relationship was also observed between capacitance and surface area, analogous to the relationship found with discharge time. This correlation arises because capacitance is directly related to the amount of stored charge, which affects the discharge time. As the surface area increases, more charge can be stored, resulting in both higher capacitance and a longer discharge time.

The plot of energy density as a function of power density (Figure 3.8) demonstrated that as the surface area increased, the power density initially decreased and then stabilized at $5 \times 10^7 \text{ m}^{-1}$. This decline in power density was accompanied by a corresponding increase in energy density. This outcome can be attributed to the trade-off between energy storage and delivery speed. Higher surface areas allow for more extensive charge storage, thereby enhancing the energy density. However, the increased surface area also leads to greater internal resistance and slower ion movement, which in turn reduces the rate at which energy can be delivered, thus lowering the power density. This inverse relationship highlights the inherent balance between maximizing energy density and maintaining high power density in the design and optimization of SCs.

The power and energy density values experienced a significant reduction compared to those observed in the diffusion coefficient study. This discrepancy is likely due to the increased surface area and, more importantly, the elevated charge and discharge current densities employed during the measurements. For example, at higher current densities, the rate at which ions move and adsorb onto the electrode surfaces might not keep up

with the current demand, leading to increased local resistance and voltage drops. Furthermore, the larger surface area could result in longer ion diffusion paths, potentially exacerbating internal resistance. This situation underscores the relationship between electrode surface area, current density, and internal resistance, emphasizing the need to carefully optimize these parameters to improve the simulation model and, consequently, the SC performance.

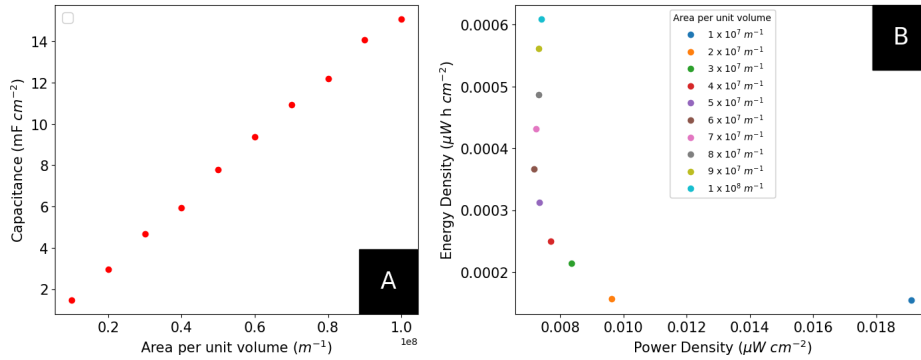


Figure 3.8: A) Capacitance derived from GCD measurements as a function of the surface area per unit volume. B) Energy density plot as a function of the power density for different surface areas.

3.3. Potential Scan Rate in CV Studies

To explore the potential scan rate effects on the capacitance of the SCs, CV measurements at different scan rates were performed. Figure 3.9 presents the variation of the capacitance as a function of the scan rate (1, 5, 10, 25, 50, 75, 100 mV s⁻¹) for different diffusion coefficient values of the electrolyte ions. Regardless of the SC's diffusion coefficient, the specific capacitance is higher at lower scan rates because the electrolyte ions have more time to penetrate and reside within the available pores of the electrode material and thus form the EDL which is necessary to generate high capacitance. The increase in the diffusion coefficient merely reinforces the previously established conclusion that higher diffusion coefficients lead to an increase in capacitance.

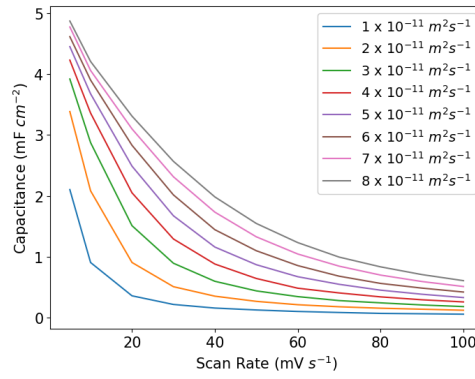


Figure 3.9: Capacitance as a function of the scan rate for different diffusion coefficients.

3.4. Electrodes Distance

The relationship between the capacitance of a SC and the distance between its electrodes is well understood, with capacitance decreasing as the distance increases. This is because the higher the distance the ions in the electrolyte must travel to form the electric double-layer, the higher the resistance becomes, which in turn reduces the efficiency of charge storage. This behavior was confirmed in a simulation study designed to investigate this effect, where capacitance was measured across various electrode distances (0.5 cm, 1 cm, 1.5 cm, 2 cm, 2.5 cm, 3 cm, 3.5 cm, 4 cm, 4.5 cm, 5 cm). The results, depicted in Figure 3.10, clearly illustrate the inverse relationship between capacitance and electrodes distance. The predictable outcome of this study serves to validate the accuracy and reliability of the model used, further solidifying our understanding of the factors influencing SC performance.

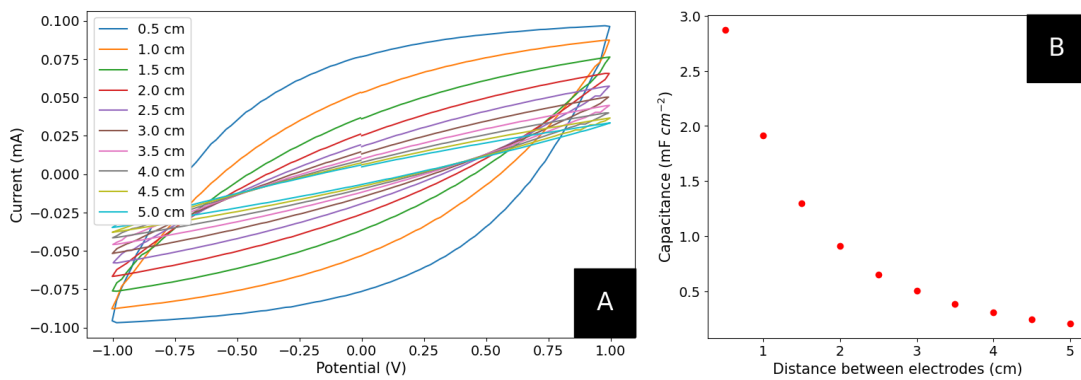


Figure 3.10: A) CV curves for different distances between electrodes. B) Capacitance as a function of the electrode distance.

4. Electrochemical and Thermoionic Numerical Simulation of a TCSC

The previous chapter provided a comprehensive understanding of the physical factors and parameters that can significantly influence the electrochemical performance of SCs. By examining these variables, we gained insight into their influence on critical performance metrics such as capacitance, energy density, power density, and charge/discharge behavior. This foundational understanding paves the way for the present chapter, where these insights will be applied to the simulation of TCSC behavior.

This chapter demonstrates how the identified parameters can be effectively incorporated into a simulated model to predict the TCSC electrochemical performance. The accuracy and reliability of the simulation model will be validated by comparing the simulated CV results with those obtained from various experimental devices. This comparison not only highlights the strengths of the simulation but also identifies potential areas for further refinement and optimization. Through this approach, the gap between theoretical predictions and experimental outcomes can be bridged, ultimately advancing the design and optimization of SCs. In addition, to explore the thermal energy harvesting capabilities, the simulation model was specifically adapted to represent the Soret effect and the operation of a TCSC under a temperature gradient. The primary goal is to leverage this simulation to enhance the performance of TCSCs, thereby enabling the harvesting of a higher amount of waste energy. Specifically, by optimizing the Soret coefficient, we aim to maximize the voltage difference generated for a given temperature gradient.

4.1. TCSC Fabrication

The TCSC geometry was based on two thin electrode squares and an electrolyte that covered almost half of the electrodes, both deposited in a glass substrate. The electrodes were mostly composed of platinum (Pt), while the electrolyte was the same solid-gel PVA doped with H_3PO_4 . Five 25 mm × 15 mm size and 1 mm thickness glass substrates were used. Their cleaning and preparation steps for the fabrication of the TCSCs were based on previous work [51]. Firstly, the glass substrates were cleaned using a three-step sonication process, with each step lasting 15 min: (i) using a soap/water solution (1:10 v/v); (ii) using distilled water for the removal of excess soap, and (iii) using isopropanol

medium. After the cleaning process, each substrate was dried under a compressed air flow and treated in a UV ozone cleaner (Ossila, L2002A2-UK) for 20 min.



Figure 4.1: Five different configurations of an in-plane TCSC composed of Pt electrodes and PVA/H_3PO_4 electrolyte deposited in a glass substrate.

For the preparation of the electrodes, five different configurations were used, as shown in Figure 4.1. Each contact region had dimensions of $0.8\text{ cm} \times 0.8\text{ cm}$, and the distances between the electrodes varied: 0.3 cm, 0.5 cm, 1.0 cm, 1.5 cm, and 2.0 cm. The electrode materials were deposited by sputtering (Quorum, Q300T D Plus) at the Thermal and Electrical Systems Laboratory (TESLab) at Universitat Jaume I (Castelló, Spain). Initially, a chromium (Cr) seeding layer was deposited in glass substrates for 15 s, followed by a Pt layer (100 nm of thickness) deposited by the same method for 60 s. To complete the preparation of the planar devices, the solid-gel electrolyte was cooled and then deposited by drop-casting onto the glass substrates and dried overnight. The COMSOL geometry used to describe the TCSCs is illustrated in Figure 4.2.

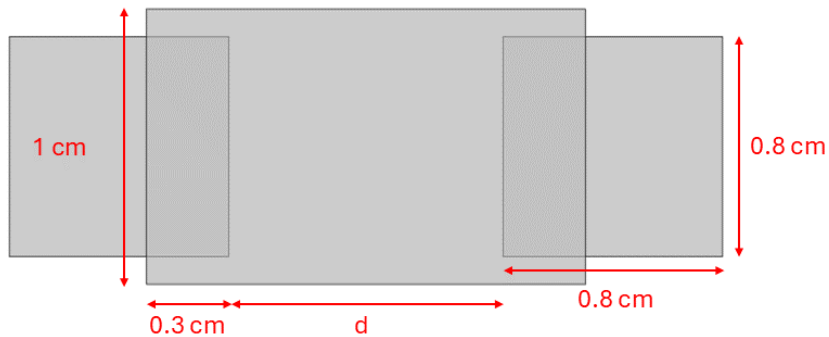


Figure 4.2: Illustration of the TCSCs geometry and their dimensions, where d represents the distance between the electrodes: 0.3 cm, 0.5 cm, 1.0 cm, 1.5 cm, or 2.0 cm.

4.2. TCSC Electrochemical Analysis

The CV measurements were acquired for each device over a potential window of $[-0.5, 0.5]$ V at scan rates of 1, 5, 10, 25, 50, 75, and 100 mV s^{-1} . A trial-and-error approach was again used to determine the optimal electrode surface area per unit volume and the value of the diffusion coefficient of the electrolyte ions. These parameter values were kept consistent across all simulations, with the surface area per unit volume set at $5 \times 10^7 \text{ m}^{-1}$ and the diffusion coefficient set at $6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The ionic concentration was 1000 mol m^{-3} , a value calculated based on the molar mass of the orthophosphoric acid (85% purity) used. Figure 4.3 represents the experimental and simulated results obtained and their respective comparison for the TCSC with a 0.3 cm distance between the electrodes.

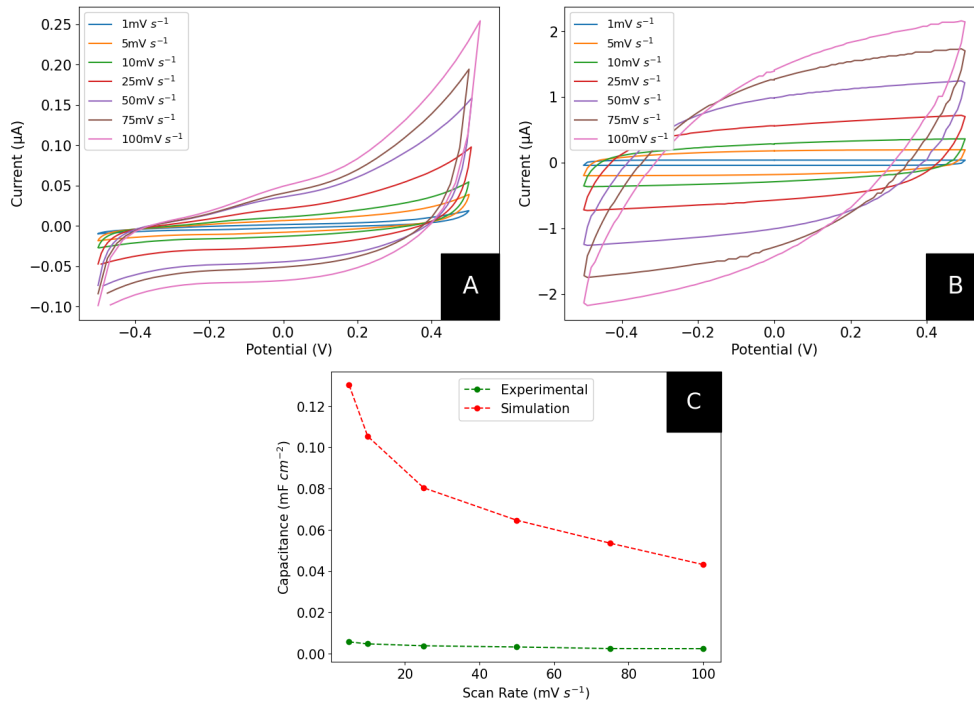


Figure 4.3: CV curves at different scan rates for the device with a 0.3 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.

The experimental and simulation CV measurements for 1 mV s^{-1} were excluded for most of the studied devices, as they led to significantly higher capacitance values compared to other scan rates and were not comparable with the experimental results for any of the devices. This discrepancy likely arises because, at very low scan rates, factors such as slow ion diffusion and the extended time required for ions to move and redistribute within the supercapacitor influence the experimental measurements. However, this prolonged process may not be fully accounted for in the simulation, leading to an overestimation of

capacitance values. The experimental CVs show a noticeable increase in the slope of the i-V curve at the maximum potential, with a pronounced deviation at the upper right side, rather than exhibiting the rectangular shape typical of an ideal EDLC. This behavior is indicative of water decomposition phenomena, suggesting that using lower potential windows could help mitigate this issue. These effects, linked to the use of aqueous electrolytes, are not fully captured by the EDLC model employed in the simulations.

Figures 4.3 and 4.4 show that for smaller electrode distances (0.3 cm and 0.5 cm), the simulation fails to accurately replicate the current intensity and capacitance values observed experimentally, particularly when compared to the SCs with higher electrodes distance. This discrepancy suggests that the present simulation model may not be sufficient to account for the effects of reduced electrode spacing. To address this, it may be necessary to develop a modified or entirely different model tailored to smaller electrode distances. For example, by analyzing the resistance within the supercapacitor across various electrode distances, the EDLC capacitance and diffusion coefficient values could be adjusted for each distance, leading to a more accurate and comprehensive model.

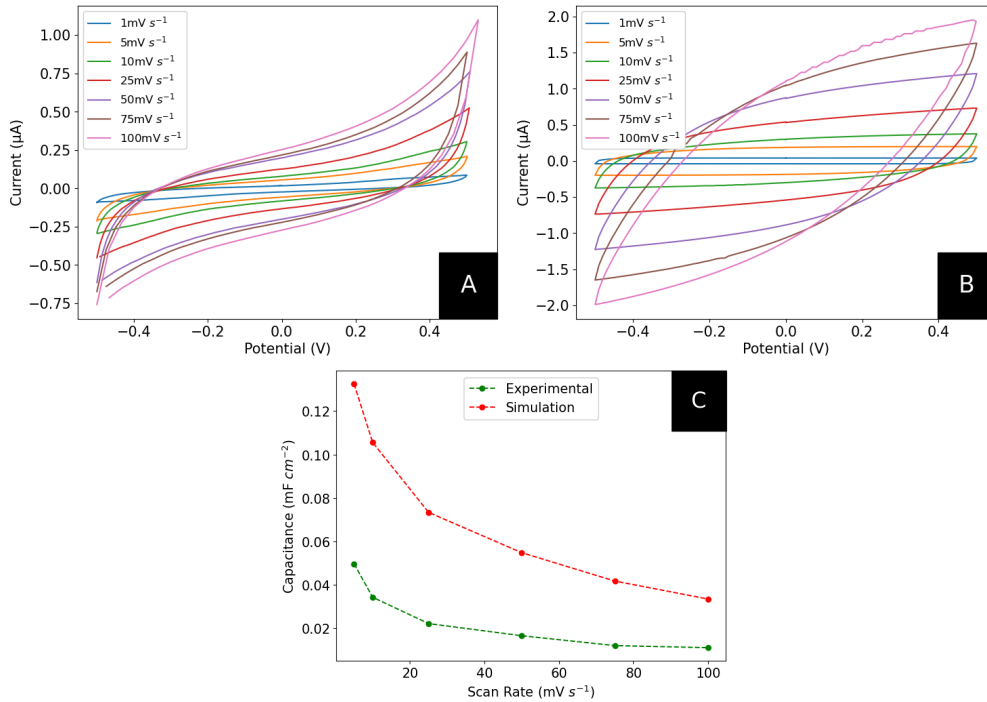


Figure 4.4: CV curves at different scan rates for the device with a 0.5 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.

Alternatively, a systematic analysis could be conducted to establish a relationship between capacitance and electrodes distance in the experimental data. This approach would help

to explain why the experimental results deviate from theoretical predictions and identify the factors contributing to this variation. Understanding these factors could refine the simulation model and enhance its accuracy across different electrode spacings.

As the distance between the electrodes reaches 1 cm (Figure 4.5) and beyond (Figures 4.6 and 4.7), a closer alignment between the experimental data and the simulation results begins to emerge. Additionally, the experimental behavior starts to resemble that of an ideal EDLC. While the simulation results demonstrate a dependence on the inverse of the scan rate, which is characteristic of ideal EDLC behavior, the experimental data show a similar but not perfectly matching behavior. This discrepancy suggests that the experimental system may involve additional complexities in the electrode or electrolyte behavior, which are not fully captured by the simulation.

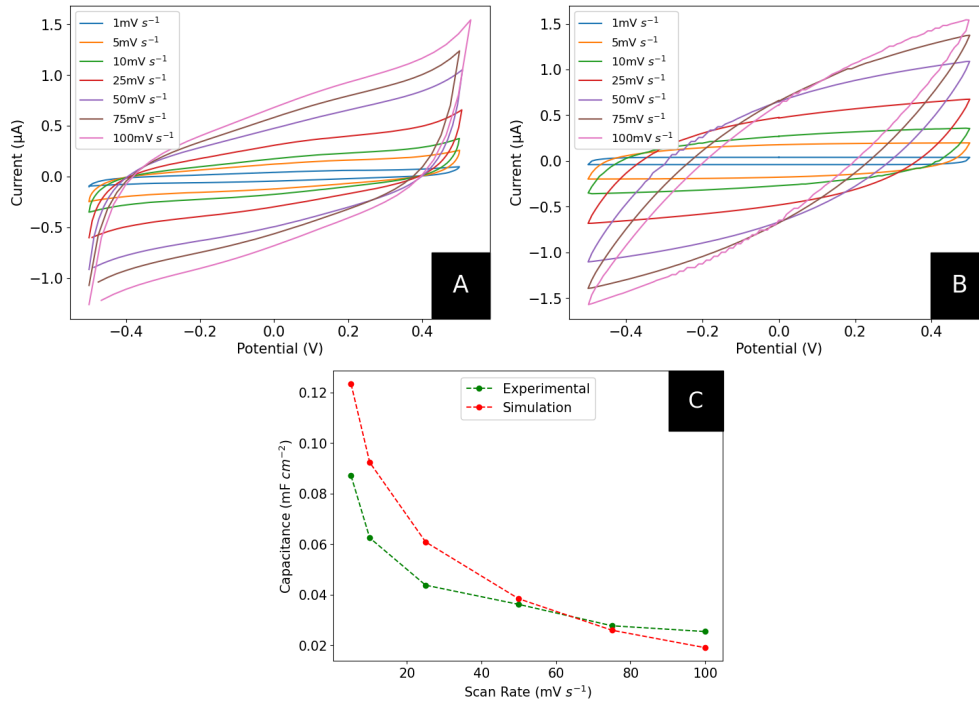


Figure 4.5: CV curves at different scan rates for the device with a 1 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.

In the simulation, increasing the electrode distance shows only a minor effect on capacitance, with a slight reduction observed. This limited impact on capacitance is likely related to the significant scale difference between the nanometer-thick electrodes (100 nm) and the millimeter-thick electrolyte (116 μm). The thick electrolyte provides ample space for ions to move and redistribute, so variations in electrode distance have minimal impact on ion conduction pathways. This stability in ion movement helps maintain a relatively

constant capacitance, even with small increases in electrode spacing. In the experimental case, the expected reduction in capacitance with increased electrode spacing was not observed. This suggests that kinetic constraints, particularly due to the use of a gel electrolyte instead of a liquid one, may have influenced the results. The gel electrolyte's restricted ion movement likely caused slower capacitance variations, making the experimental behavior less responsive compared to the idealized conditions in the simulation. Therefore, further investigation needs to be conducted to better understand the factors affecting capacitance in the experimental system.

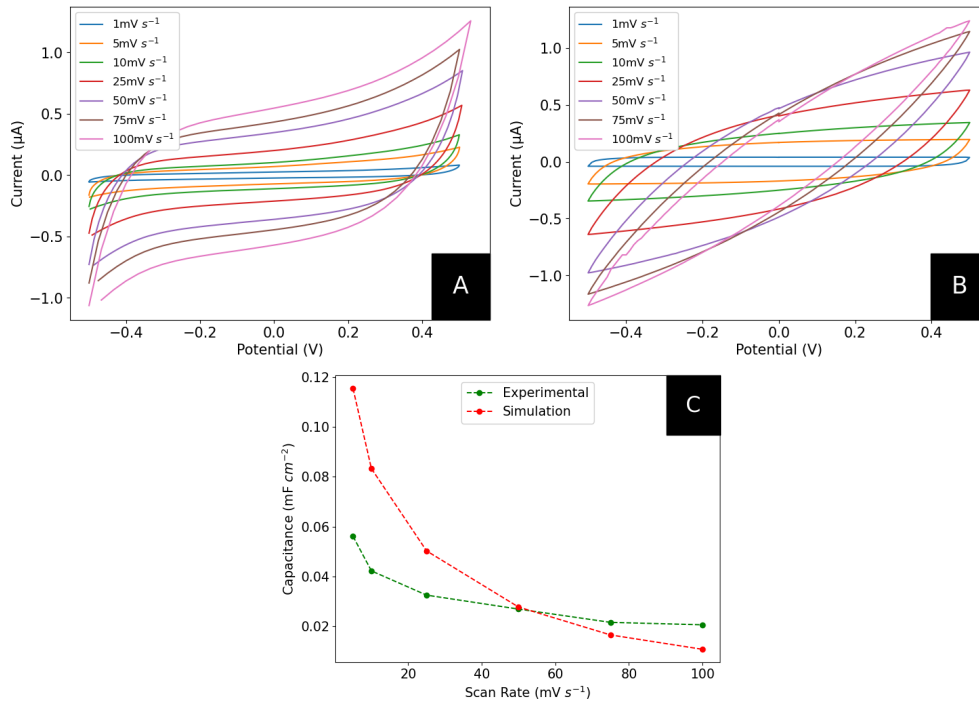


Figure 4.6: CV curves at different scan rates for the device with a 1.5 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.

For electrode spacings exceeding 1 cm, the experimental data begins to show a stronger correlation with the simulation, particularly when compared to shorter distances. However, this alignment is more accurate at the 1 cm electrode distance compared to the 1.5 cm and 2 cm distances. In the latter two cases, the experimental results show more constant capacitance values for scan rates above 25 mV s⁻¹, deviating from the ideal inverse scan rate behavior that is more accurately represented in the 1 cm device and in the simulation curves. This suggests that there may be an optimal electrode distance for this system, likely close to 1 cm.

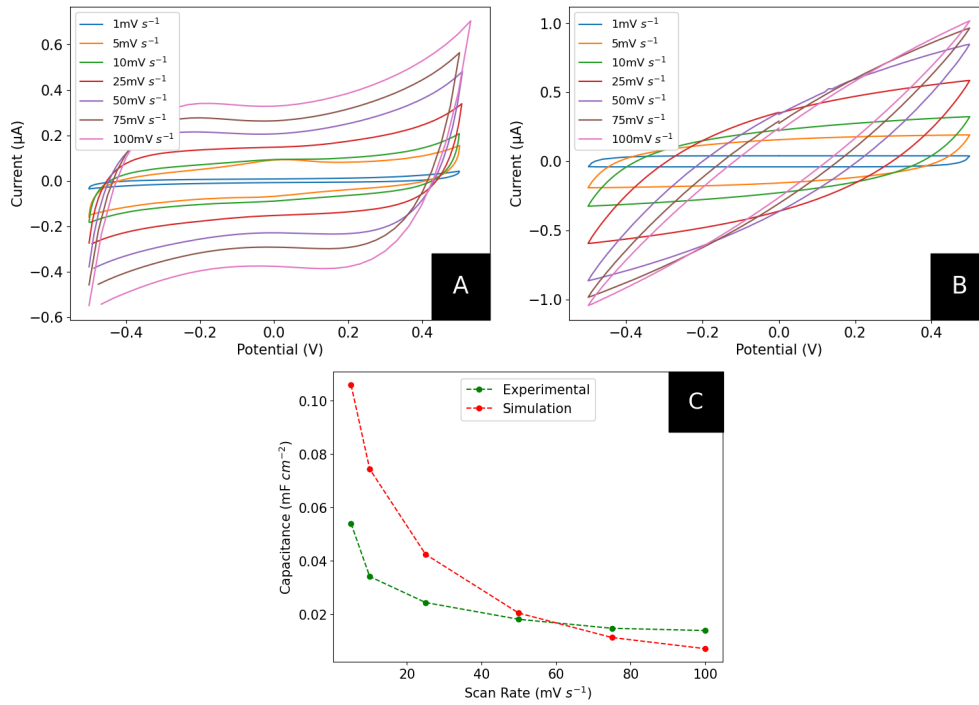


Figure 4.7: CV curves at different scan rates for the device with a 2 cm electrode spacing: A) experimental results and B) simulated results. C) The comparison of capacitance derived from CV measurements as a function of scan rate for both experimental and simulated data.

To numerically confirm the existence of an optimal electrode distance, a relative uncertainty calculation was performed on the experimental data, assuming the theoretical value was derived from the simulation. A graph was then generated, plotting the mean relative uncertainty for each tested SC configuration. As shown in Figure 4.8, the minimum uncertainty value corresponds to the device with a 1 cm electrode distance, suggesting that this particular geometry is closer to the ideal behavior or value, thereby indicating the presence of an optimal electrode spacing.

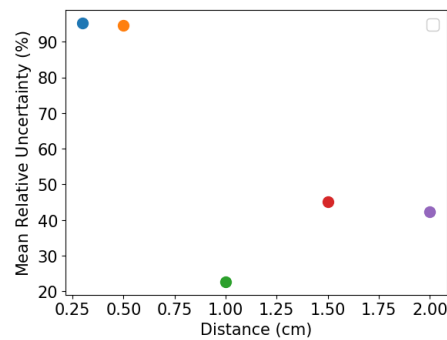


Figure 4.8: Mean relative uncertainty calculation between experimental and simulation results for each TCSC device.

A final study on capacitance was carried out, focusing on electrode spacing within the simulation framework, with the results shown in Figure 4.9. The data reveal that the expected d^{-1} dependence of capacitance becomes noticeable only for electrode spacings greater than 0.8 cm, which is approximately the width of the electrodes. For distances smaller than 0.8 cm, the capacitance appears to remain relatively constant.

This observation can be explained by the fact that when the electrode spacing is very small compared to the electrode dimensions, the system no longer behaves as an ideal infinite capacitor. Consequently, the capacitance deviates from the expected d^{-1} relationship and displays more complex behavior. At spacings smaller than the electrode width, edge effects and non-uniform field distributions become significant, leading to deviations from the ideal dependence.

Barrachina et al. [52] and Yariv [53] highlight the critical role of edge effects in capacitance calculations for cylindrical and parallel-plate capacitors, respectively. Barrachina et al. note that when the length of the cylinders is comparable to their radius, edge effects cannot be ignored, complicating the analysis significantly. Yariv similarly emphasizes that for parallel-plate capacitors, edge effects necessitate corrections to the capacitance formulas to accurately represent these phenomena.

These findings underscore the importance of accounting for edge effects in simulations and practical designs of supercapacitors, particularly when dealing with dimensions that approach or are smaller than the electrode width. Understanding these deviations helps refine our simulation models and improve the accuracy of theoretical predictions. To further understand this phenomenon, future work should explore different electrode sizes and investigate the most effective ways to explain and account for these edge effects in simulations and practical applications.

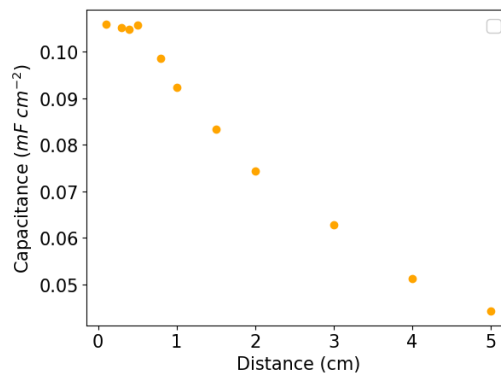


Figure 4.9: Capacitance as a function of the distance between the electrodes.

4.3. Thermoionic Simulation Models

With a solid electrochemical simulation framework in place, the focus of the work shifted towards finding a physical description of the Soret effect. To investigate this phenomenon, a temperature gradient was introduced into the simulation using COMSOL's Heat Transfer (HT) interface. This interface is designed to model heat transfer processes in the supercapacitor through conduction, convection, and radiation. The HT model in COMSOL solves for the temperature distribution as the single dependent variable, using the following heat transfer equation:

$$\rho C_p \left(\frac{\partial T}{\partial t} + \mathbf{u}_{trans} \cdot \nabla T \right) + \nabla \cdot (q + q_r) = Q_{ted} + Q \quad (4.1)$$

where ρ is the material's density (in $kg\ m^{-3}$), C_p is the specific heat capacity at constant stress of the material (in $J\ kg^{-1}\ K^{-1}$), T is the absolute temperature (in K), $\mathbf{u}_{trans}$ denotes the velocity vector of translation motion (in $m\ s^{-1}$), q and q_r are the heat flux by conduction and radiation, respectively (both in $W\ m^{-2}$), Q represents the additional heat sources (in $W\ m^{-3}$), and Q_{ted} accounts for the thermoelastic effects (in $W\ m^{-3}$). Because in all simulations there was no radiation, heat sources, or thermoelastic effects, these terms presented null values. The heat flux by conduction was given by the negative of the product between the temperature gradient and the thermal conductivity (k , in $W\ m^{-1}\ K^{-1}$).

Although the HT interface offers a solid framework in the temperature behavior and heat transfer between the materials, it still lacks a component related to the Soret effect. Therefore, the mass separation induced by a temperature gradient description was withdrawn from Jean K. Platten's paper [54]. The mass flux of the reference chemical compound in a binary mixture along the x -axis is given by the following equation:

$$J_x = -\rho D \frac{\partial c}{\partial x} - \rho D_T c_0 (1 - c_0) \frac{\partial T}{\partial x} \quad (4.2)$$

The first term on the right-hand side of the equation is Fick's law, while the second term describes the Soret effect, which is governed by the thermodiffusion coefficient (D_T , in $m^{-2}\ s^{-1}\ K^{-1}$). For a mixture containing 50 wt% of each chemical component $c_0 = \frac{1}{2}$ and $1 - c_0 = \frac{1}{2}$. Assuming a steady-state condition ($J_x = 0$), it is possible to rewrite Equation 4.2 and obtain an expression for the mass variation of a specific species along the x -axis:

$$\frac{\partial c}{\partial x} = -\frac{D_T}{D} c_0 (1 - c_0) \frac{\partial T}{\partial x} \quad (4.3)$$

By connecting this equation to the concentration gradient expression, for each spatial component, in COMSOL, a novel Soret effect model was established. This work allowed us to calculate the electric potential formed with the thermodiffusion effect and perform numerous studies involving different temperature gradients, electrode distances, and TCSC charging tests.

4.4. Thermoionic performance of TCSCs

For the analysis of the thermoionic performance of the TCSCs, an experimental setup, developed on a previous work [4], was used. The experimental system was composed of two Peltier stages (TEC1-12706, size: 40×40 mm, maximum applied current intensity of 1 A) used as cold and hot sources, two k-type thermocouples connected to a TC-08 thermocouple datalogger (Pico Technology) to measure the applied temperature gradient established between the electrodes, and a 34420A HP nanovoltmeter to obtain the generated voltage. The planar device is positioned on top of the Peltier stages, which are positioned in the same plane, in such a way that each electrode is only in contact with one Peltier, as is demonstrated in Figure 4.10.

The temperature difference (ΔT) generated between the two electrodes results in the formation of a thermovoltage, which increases and then stabilizes over time. This stabilized voltage (V_{thermo}), together with the measured ΔT , allows for the experimental determination of the Soret coefficient using the following equation:

$$V_{thermo} = S_i \Delta T \quad (4.4)$$

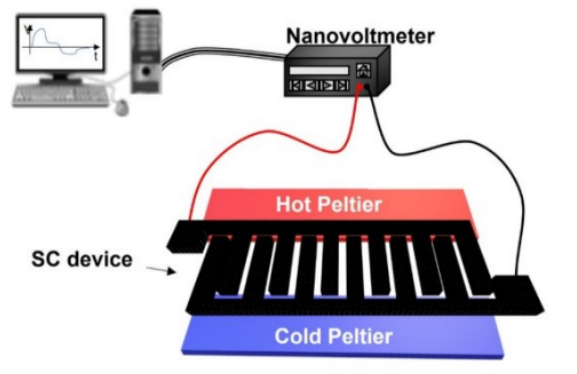


Figure 4.10: Scheme of the TCSC setup used to determine experimentally the Soret coefficient in planar-type devices.

4.5. Thermoionic Analysis: Simulation vs Experimental

To analyze and test the developed simulation model, thermal charging measurements were conducted on the same TCSC devices. Different temperature gradients were applied to five different devices with varying electrode distances (0.3 cm, 0.5 cm, 1 cm, 1.5 cm, and 2 cm), to assess the maximum voltage achieved by each device and the time required to reach it.

The experimental results, shown in Figure 4.11, demonstrated that applying different temperature gradients to the devices resulted in the generation of different potential differences. The stabilization of the potential indicated that the TCSC had reached a fully charged state. Devices with larger electrode separations exhibited higher voltage outputs for comparable temperature gradients. This increase in voltage was accompanied by longer charging times, which aligns with the expected behavior that a larger distance between electrodes requires more time for charge accumulation. Additionally, as expected, higher temperature gradients produced higher voltage values across the devices, confirming the direct relationship between the magnitude of the temperature gradient and the generated potential.

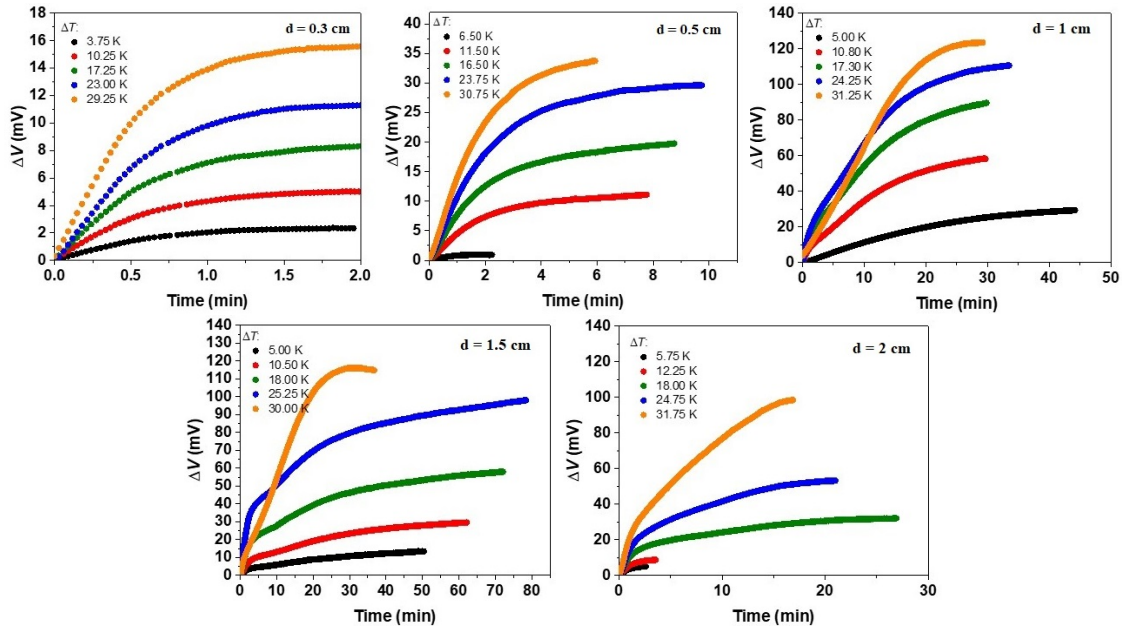


Figure 4.11: Thermal charging process of the TCSCs for different applied temperature gradients and electrode distances.

To replicate the behavior observed in the TCSCs, a test was performed on the TCSC with an electrode separation of 1 cm and a temperature gradient of 15 K, which is demonstrated in Figure 4.12. In this test, distinct diffusion coefficient values were assigned for

cations and anions to reflect the necessity for the cations to respond more quickly to the temperature gradient. Specifically, the diffusion coefficient for cations was set to $6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, while for anions it was $1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. Additionally, the area per unit volume was maintained at $5 \times 10^7 \text{ m}^{-1}$. These values were chosen to be consistent with those reported in the previous electrochemical study. The thermodiffusion coefficient was set to $1 \times 10^{-12} \text{ m}^2 \text{ K}^{-1} \text{ s}^{-1}$, a value referenced from existing literature [54]. Although this value is not directly related to the specific materials used in this study, it served as a preliminary benchmark for initial investigations.

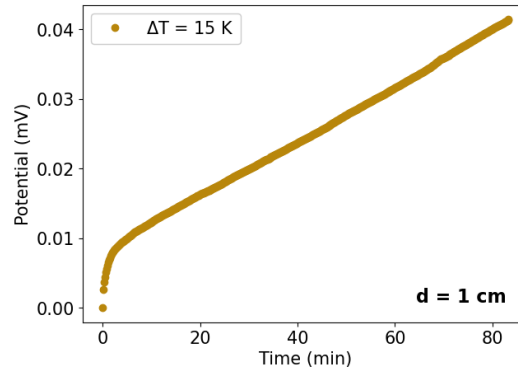


Figure 4.12: Initial simulation of the TCSC's charging process for a temperature gradient of 15 K and a distance between the electrodes of 1 cm.

The initial simulation reflected a similar trend in voltage increase as observed in the experimental results. However, the charging process was significantly slower, and the potential did not reach a stable value. This discrepancy suggested that the selected parameters did not accurately represent the experimental behavior. To better replicate the experimental charging dynamics, the diffusion coefficients for both cations and anions, as well as the thermodiffusion coefficient, were systematically increased. These adjustments were made to enhance the ion mobility and, consequently, the charging rate, thereby aiming to achieve a more accurate and representative simulation of the observed experimental phenomena. Specifically, the diffusion coefficient for the anion was adjusted to $1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, while for the cation, it was set to $5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. Additionally, the thermodiffusion coefficient was updated to $1 \times 10^{-7} \text{ m}^2 \text{ K}^{-1} \text{ s}^{-1}$. The obtained results are illustrated in Figure 4.13.

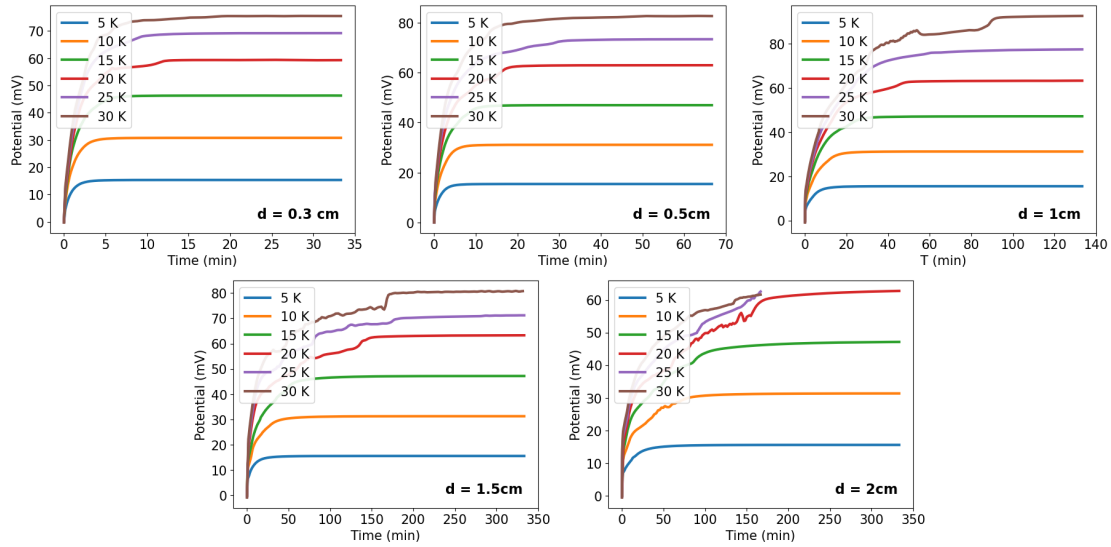


Figure 4.13: Simulation of the experimental thermal charging process of the TCSCs for different applied temperature gradients and distances between electrodes.

With the adjusted parameters, the output potential in the simulation stabilized at a value within the same order of magnitude as observed in the experimental results, indicating a closer alignment between the simulation and experimental data. However, it is notable that in the simulation, variations in electrode distance do not result in significant changes in the maximum output potential, unlike the experimental observations where the voltage varied considerably. This outcome reflects the fact that the simulation models an idealized condition where there are no resistive losses, causing the maximum voltage to remain constant and independent of inter-electrodes distance, depending instead on the temperature gradient and the electrode and electrolyte material properties.

The simulation results also indicate that the time required to charge the device increases with both the electrode distance and the temperature gradient. This is because a higher electrode distance leads to a longer path for electrolyte ion migration, thereby extending the charging time. Additionally, a higher temperature gradient drives a stronger thermodiffusion effect, resulting in more charge accumulation, which similarly requires more time to reach a fully charged state.

For the three largest electrode distances, the simulation data begins to exhibit anomalies, manifested as a form of noise where the expected linear relationship was disrupted, leading to erratic fluctuations. This issue was particularly pronounced at higher temperature gradients. The source of this problem can be traced to the computational limitations of the system used for the simulations. Simulations involving larger electrodes distances

and higher temperature gradients demanded more computational power than the available hardware could provide. Moreover, the mesh created for the device was relatively large and lacked sufficient detail, which was a compromise made to reduce computation time, further degrading the quality of the data. As a result, some data points were excluded from the analysis due to their lack of reliability, underscoring the need for more robust computational resources and finer mesh resolution in future simulations to ensure the accuracy and consistency of the results.

The data presented in Figure 4.13 enabled the calculation of the Soret coefficient for each device. To achieve this, the stabilized potential corresponding to each temperature gradient was extracted and plotted as a function of the temperature gradient. The results represented in Figure 4.14 exhibited the expected linear behavior, which allowed for the extraction of the Soret coefficient via linear regression, following the relationship described in equation 4.4. Any deviations from the expected linearity or the presence of irregularities in the data can be attributed to the computational limitations encountered during the simulations.

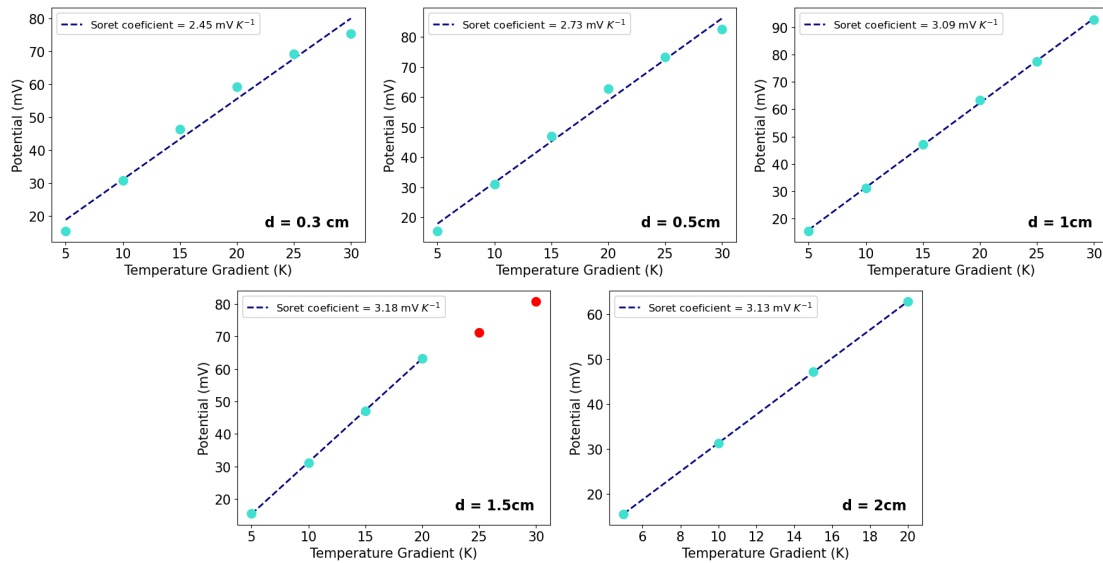


Figure 4.14: Maximum charging potential values as a function of the temperature gradient for each electrode spacing.

Besides demonstrating the linear relationship between the temperature gradient and the charging potential of the TCSC, the results also indicate that increasing the distance between the electrodes leads to an increase in the Soret coefficient. This increase occurs because a larger separation of the electrodes can lead to a more pronounced temperature gradient across the device, which, in turn, enhances the thermal diffusion effects. However, the data indicates that the Soret coefficient appears to increase more significantly at

shorter distances and then potentially approaches a saturation point, beyond which further increases in electrode distance may result in minimal changes to the coefficient. This observation raises the possibility of an optimal electrode distance: at shorter distances, the device's capacitance is maximized, and since larger distances do not seem to significantly enhance the Soret coefficient, there could be a specific distance that optimizes both the capacitance and the Soret coefficient of the TCSC.

The experimental results presented in Figure 4.15 similarly demonstrate this tendency, further suggesting the potential existence of a saturation point and an optimized electrode distance. Additionally, the results indicate that for the same distance values, the variation in the Soret coefficient is significantly higher in the experimental data compared to the simulations. This discrepancy reinforces the notion that additional factors may be influencing the experimental measurements, contributing to the observed variability.

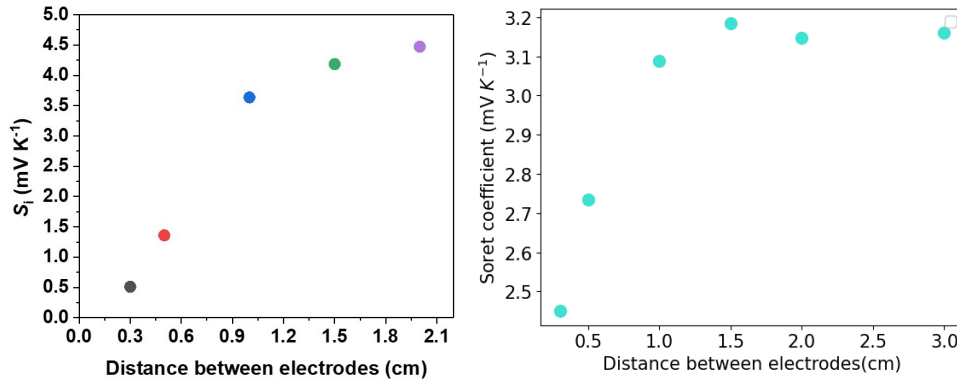


Figure 4.15: Soret coefficient as a function of the distance between the electrodes: experimental results (left) and simulated results (right).

Similar to the electrochemical study conducted in the previous chapter, after the initial comparison between the simulated and experimental results, a series of studies were performed to investigate the influence of different parameters on the simulation outcomes. In this case, the examined parameters included the thermodiffusion coefficient, the diffusion coefficient of cations, the diffusion coefficient of anions, and the electrode area. For consistency, the ion diffusion coefficients and the thermodiffusion coefficient were kept the same as in the previous study, while the surface area per unit volume was set at $9.5 \times 10^7 \text{ m}^{-1}$. The temperature gradient applied in these simulations was 15 K, with an electrode distance of 1 cm. These studies aimed to identify how variations in these parameters impact the simulated behavior of the TCSC, providing deeper insights into the factors that govern the system's performance and aiding in the refinement of the simulation model.

By analyzing the results in Figure 4.16, it is evident that an increase in the thermodiffusion coefficient leads to a corresponding increase in the maximum thermovoltage, with this relationship exhibiting a linear trend. This behavior aligns with Equation 4.3 employed in the simulation, where the ions concentration gradient is linearly dependent on the thermodiffusion coefficient. As a result, a similar linear relationship is observed for the Soret coefficient. The thermodiffusion coefficient quantifies the extent to which particles or ions migrate in response to a temperature gradient. Therefore, a higher thermodiffusion coefficient indicates a stronger tendency for ions to move from the hot to the cold regions of the TCSC, leading to a greater accumulation of charge and, consequently, a higher stabilized potential. However, this increase in the thermodiffusion coefficient also results in a longer charging time for the TCSC. The enhanced ion migration causes a more substantial buildup of charge, which requires additional time to fully stabilize.

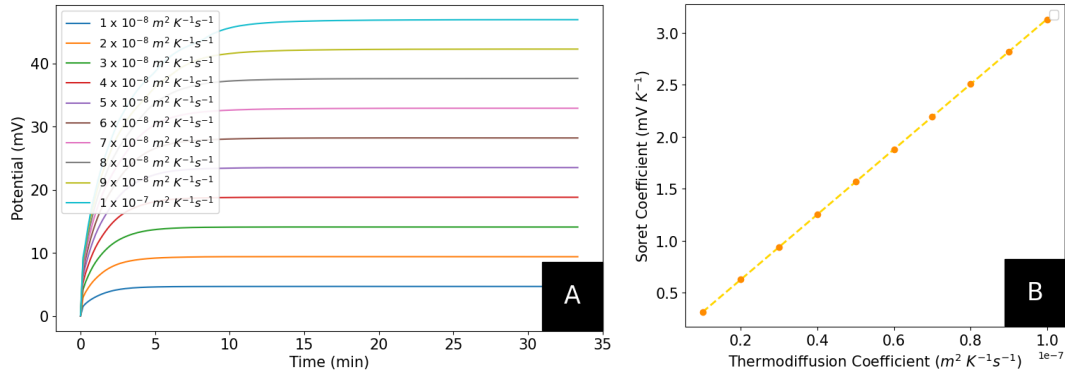


Figure 4.16: A) Thermal charging process for different thermodiffusion coefficients. B) Soret coefficient as a function of the thermodiffusion coefficient.

The study of the cation diffusion coefficient (Figure 4.17) revealed that an increase in its value resulted in an increase in both the thermovoltage and the Soret coefficient. However, this increase is more pronounced at lower diffusion coefficients, with the rate of increase diminishing as the diffusion coefficient rises, suggesting that the Soret coefficient may be approaching a saturation point. This behavior comes from the relationship between the cation and anion diffusion coefficients. With the anion diffusion coefficient held constant, increasing the cation diffusion coefficient creates a larger gap between the diffusion rates of cations and anions. This disparity enhances the concentration gradient, leading to a higher stabilized potential and a more significant Soret effect.

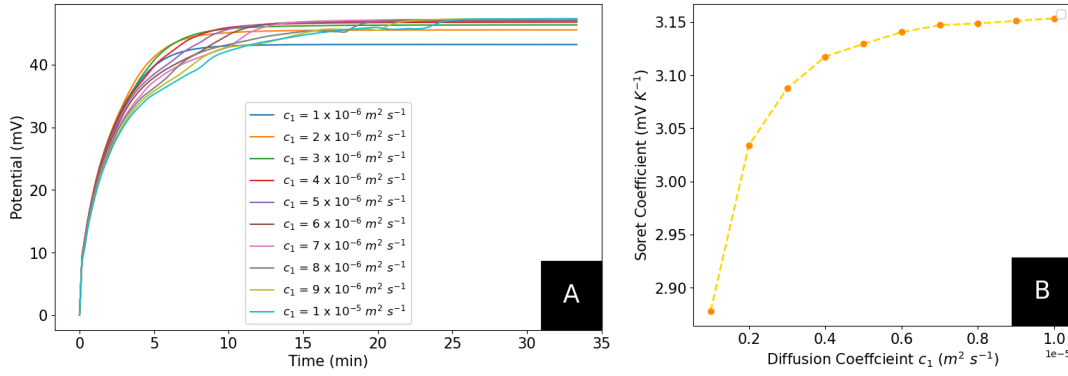


Figure 4.17: A) Thermal charging process for different cation diffusion coefficients. B) Soret coefficient as a function of the cation diffusion coefficient (right).

Furthermore, as the cation diffusion coefficient increases, the time required for the TCSC to reach its fully charged state also increases. This is due to the higher thermoelectric response, which results in a greater maximum output voltage and a larger concentration gradient. Consequently, more ions must accumulate to achieve equilibrium, extending the charging process. Therefore, identifying the ideal diffusion coefficient involves balancing the benefits of increased performance, in terms of both the Soret coefficient and capacitance, with the practical limitations posed by the longer charging time.

In contrast to the previous findings regarding cation diffusion, an increase in the diffusion coefficient of the anion results in a decrease in both the thermovoltage and the Soret coefficient, as shown in Figure 4.18. This inverse relationship can be attributed to the same underlying mechanism: as the anion diffusion coefficient increases, the disparity between the diffusion rates of cations and anions decreases. This reduction in the diffusion rate gap leads to a less pronounced concentration gradient, thereby diminishing the Soret effect and lowering the resultant thermovoltage.

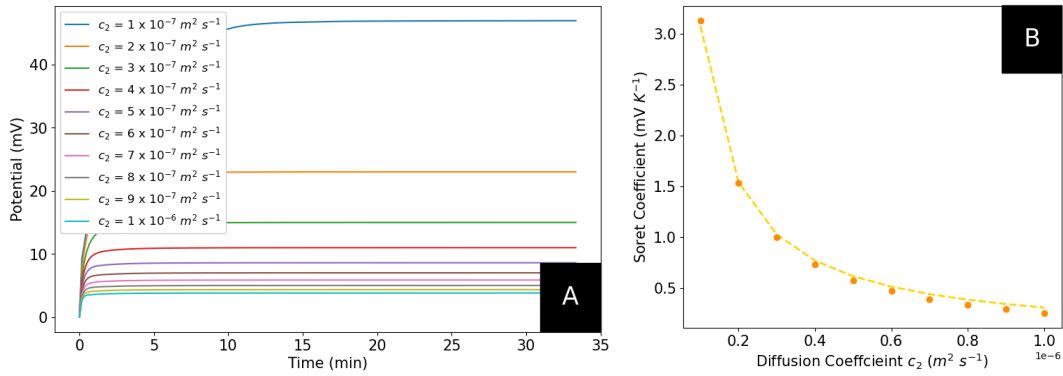


Figure 4.18: A) Thermal charging process for different anion diffusion coefficients. B) Soret coefficient as a function of the anion diffusion coefficient.

Contrary to the behavior observed with cations, increasing the anion diffusion coefficient also shortens the time required for the TCSC to reach its fully charged state. This reduction in charging time occurs because the smaller concentration gradient, resulting from the reduced gap between diffusion rates, leads to a lower accumulation of charges. Consequently, the system requires less time to reach equilibrium. Thus, while a higher anion diffusion coefficient may enhance the capacitance of the TCSC by facilitating faster ion migration, it simultaneously results in a lower Soret coefficient and a quicker charging process. This suggests that there is likely an optimal value for the anion diffusion coefficient, where the trade-off between maximizing capacitance and minimizing the Soret effect is balanced to achieve the best overall performance of the TCSC.

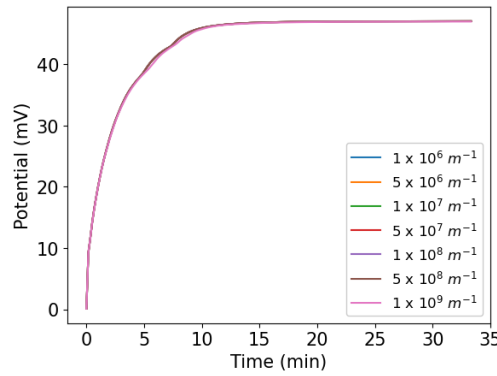


Figure 4.19: Thermal charging process for different surface areas per unit volume.

The final parameter analyzed in this study was the surface area per unit volume. The results indicated that increasing this parameter had no discernible effect on either the Soret coefficient or the time required to fully charge the TCSC. This lack of variation can be attributed to the fact that the Soret effect and the charging dynamics are primarily governed by the diffusion processes and the applied temperature gradient, which are not directly influenced by changes in surface area. Therefore, surface area per unit volume does not influence the thermionic performance metrics, such as the Soret coefficient or charging time, but it does play a crucial role in the electrochemical performance of the device. Thus, selecting the optimal surface area is primarily a matter of electrochemical considerations, where maximizing capacitance and ion interaction are key factors.

The final study was conducted under conditions identical to the previous simulations but focused on a thermal charging process followed by a discharging process. In this experiment, the temperature gradient was applied and then removed after 200 seconds, followed by a 200-second discharge period, simulating the working principle of a TCSC

under open circuit. Five different temperature gradients (5 K, 10 K, 15 K, 20 K, and 25 K) were applied, as depicted in Figure 4.20, to two different devices: one with an electrode spacing of 0.3 cm and the other with a spacing of 1 cm. The results of this study corroborate the trends observed in earlier experiments: increasing the temperature gradient leads to an increase in the thermovoltage, while decreasing the electrode spacing results in faster charging rates, as ions diffuse more quickly to the electrode/electrolyte interfaces.

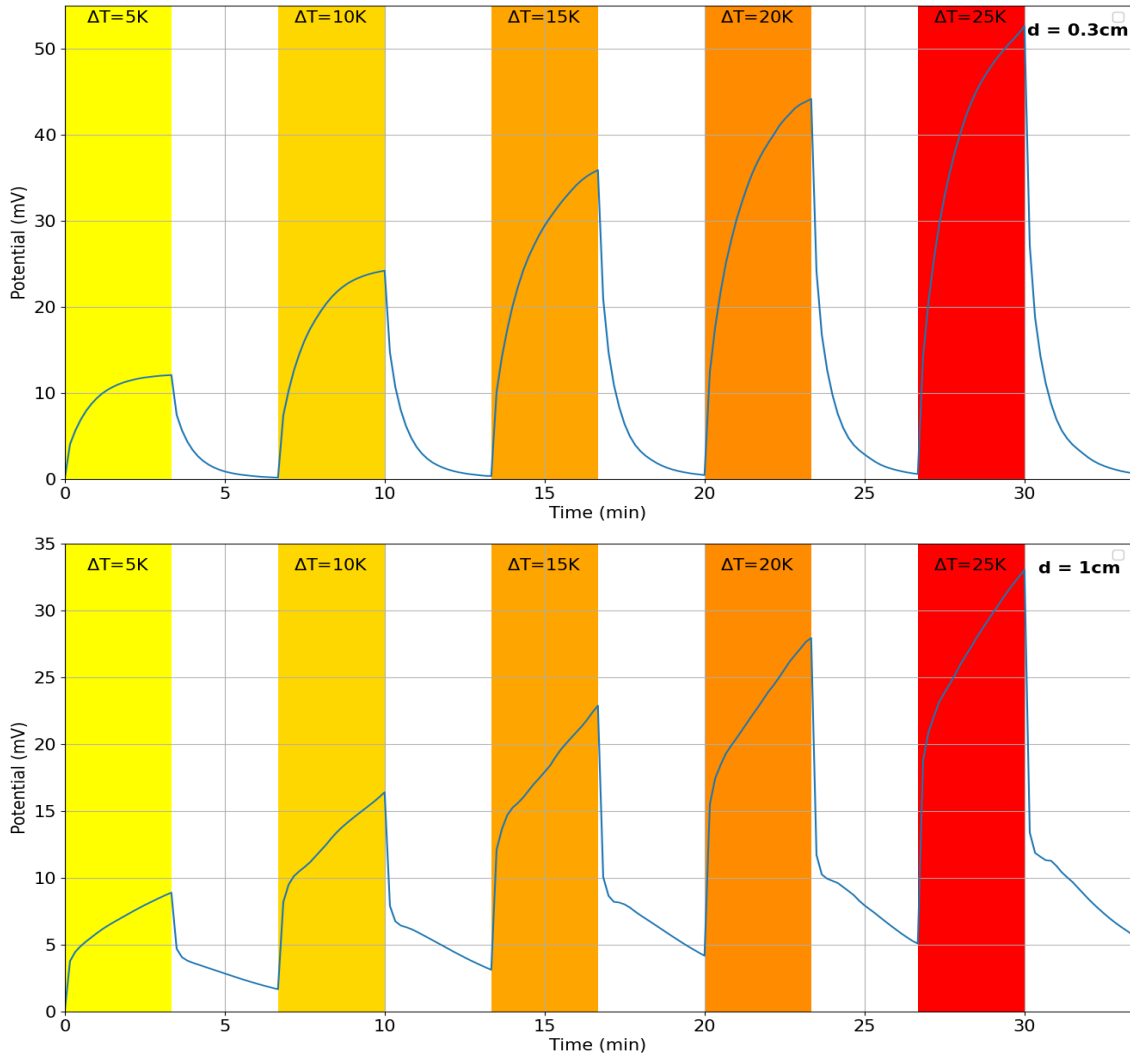


Figure 4.20: Thermal charging and discharging processes for different temperature gradients and electrodes distances: 0.3cm and 1 cm.

It is evident that for the device with a smaller electrode spacing (0.3 cm), the 200-second charging period for a 5 K temperature gradient was nearly sufficient to reach a plateau in the thermovoltage, with the device fully discharging in the subsequent 200 seconds. However, for higher temperature gradients, it becomes clear that the time required to fully

stabilize and maximize the potential exceeds the 200-second charging period. This is further supported by observations from the device with a 1 cm electrode spacing, where the charging process did not conclude within 200 seconds, and the discharge was incomplete, leaving a residual potential after the 200-second discharge period.

These findings suggest that to accurately simulate the behavior of the TCSC, it is necessary to determine optimal charging and discharging times based on the specific temperature gradient and electrode distance. The incomplete charging and discharging processes observed in this study indicate that a more tailored approach is required, where the charging time is adjusted according to the specific operational conditions to fully capture the performance characteristics of the TCSC.

5. Conclusion

SCs are crucial energy storage devices in contemporary technology due to their ability to deliver high power density, rapid charge and discharge cycles, and extended cycle life. These characteristics render SCs highly valuable for applications that require efficient and reliable energy storage, such as in portable electronics and renewable energy systems. This thesis primarily focused on the computational simulation of SCs with the objective of exploring methods to enhance their performance.

A simulation model was developed and rigorously validated against experimental data to enable the accurate simulation of both the electrochemical behavior of SCs and the thermionic behavior of TCSCs. Initial simulations were conducted on devices experimentally fabricated using multi-walled carbon nanotubes and a solid-gel PVA electrolyte doped with H_3PO_4 . The CV and GCD measurements were successfully replicated, demonstrating a strong resemblance to the idealized behavior of EDLCs. In particular, for a device with a 0.5 cm electrodes spacing (Device A), the simulated capacitance exhibited an 11% increase compared to the experimental data, while the device with a 1 cm electrodes spacing (Device B) showed a 5% increase. The GCD data revealed a notable difference in energy density (40%) and power density (21%) between the simulated and experimental data. These initial findings were instrumental in identifying key parameters in the simulation, including the electrolyte ions diffusion coefficient, electrode surface area per unit volume, potential scan rate in CV measurements, system geometry, and electrolyte ions concentration. These insights provided critical information regarding the order-of-magnitude variations in these values.

Building upon this initial study, an in-depth analysis was conducted on each of these parameters to understand their impact on SC performance. It was found that increasing the electrolyte ions diffusion coefficient significantly enhanced the device capacitance, as well as power and energy densities. Analysis of the electrode surface area revealed that increasing the surface area up to a certain threshold—where the pore size matches the ion size—resulted in increased capacitance; beyond this point, however, capacitance began to decrease. These findings were corroborated by similar studies. Furthermore, it was observed that while an increased surface area improved energy density, it reduced power density, highlighting the necessity of balancing both parameters to achieve optimal performance. Additionally, studies on scan rate and electrode distance indicated that

capacitance was higher at lower scan rates and smaller electrode distances. This detailed study allowed greater control over parameter optimization, demonstrating that selecting electrolytes with ions exhibiting higher diffusion coefficients, alongside electrodes designed with pore sizes matching ion dimensions, could markedly improve the energy storage performance. This underscores the importance of selecting the appropriate combination of electrode and electrolyte materials.

With a robust understanding and validation of the simulation model's accuracy, further electrochemical tests were performed, this time on a TCSC composed of platinum electrodes and the same solid-gel PVA doped with H_3PO_4 electrolyte. The results highlighted the model's limitations for devices with 0.3 cm and 0.5 cm electrode spacings, indicating the need for either a modified model or a more detailed study to assess the influence of smaller electrode distances on capacitance. In contrast, for devices with electrode spacings of 1 cm, 1.5 cm, and 2 cm, the model demonstrated a strong correlation with experimental data (0.992 correlation coefficient for the 1 cm electrodes spacing device), increasing the model's reliability. Moreover, a detailed analysis of mean relative uncertainty confirmed that the lowest uncertainty (22%) was observed for the device with a 1 cm spacing, suggesting this distance is close to the ideal value. A study of capacitance as a function of electrode spacing elucidated the reason for the discrepancies in the data for 0.3 cm and 0.5 cm distances: for distances below 0.8 cm (corresponding to the electrode length), capacitance calculations become influenced by edge effects and non-linearities in the electric field, introducing complexity that necessitates further investigation.

Subsequently, the thermionic behavior of the TCSC devices was analyzed. After initial tests to understand the contributing factors and to achieve comparable results, simulations were conducted under varying temperature gradients and electrode distances. The behavior of the TCSCs under a temperature gradient closely mirrored that of experimental devices, where a potential difference was generated and stabilized when the TCSC device reached a fully charged state. However, the simulation results showed no significant variation with differing electrode distances, in contrast to experimental findings. This outcome reflects the idealized conditions modeled in the simulation, where resistive losses are absent, leading to a constant maximum voltage independent of electrode spacing. The simulated Soret coefficient was obtained, with a maximum of 3.18 mV K^{-1} , and it was observed that increasing the electrode distance resulted in a higher Soret coefficient, though this increase was less pronounced than in experimental results. Further parameter analysis identified that the Soret coefficient increased with higher cation diffusion coefficients

and decreased with higher anion diffusion coefficients, with no impact from the electrode surface area per unit volume. Finally, studies on consecutive charge-discharge cycles with varying temperature gradients revealed that higher temperature gradients required longer times to fully stabilize and maximize the potential. Additionally, it was found that the 1 cm spaced TCSC could not fully charge within the timeframe used, indicating that to accurately simulate TCSC behavior, charging and discharging times must be optimized based on the specific temperature gradient and electrode distance.

In conclusion, this work has successfully demonstrated the development and validation of a simulation model capable of replicating both the electrochemical and thermionic behaviors of supercapacitors and TCSCs. The model has proven to be reliable for various device configurations, providing valuable insights into the key parameters that influence supercapacitor performance. However, the limitations encountered when simulating devices with smaller electrode spacings and the discrepancies in thermionic behavior indicate that further refinement of the model is necessary. Future work should focus on addressing these limitations by expanding experimental and simulation studies to include new materials and configurations, thereby further enhancing the predictive power of these models.

Future perspectives:

- **Refinement of Simulation Models:** Further improvements are needed to address the limitations observed in devices with smaller electrode spacings and complex thermionic behaviors.
- **Expansion of Experimental Comparisons:** Future work should include additional experimental comparisons with new materials and device configurations to enhance the model's predictive capabilities.
- **Incorporation of Additional Factors:** Factors such as substrate effects, resistive losses, and non-linear electric field should be integrated into the simulation to provide a more comprehensive understanding of device performance.
- **Optimization for Emerging Applications:** Further research should focus on tailoring supercapacitor and TCSC designs for emerging applications such as wearable electronics and renewable energy systems.

- **Advancement in Understanding Electrolyte Ion Dynamics:** A deeper investigation into electrolyte ions diffusion dynamics and their impact on device performance will be crucial for optimizing SCs and TCSCs.
- **Development of More Accurate Simulation Tools:** Continued efforts should be made to refine and develop more accurate simulation tools that can simulate a broader range of device behaviors under different conditions.
- **Sustainable Energy Storage Solutions:** Focus should be placed on advancing materials and designs that contribute to more efficient and sustainable energy storage solutions, aligning with environmental goals.

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