

T.C.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE

**SYNTHESIS AND CHARACTERIZATION OF BINARY SOLID-
STATE ELECTROLYTES FOR ENERGY STORAGE DEVICES**

TUĞÇE PINAR ÖZTÜRK
A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY
PHYSICS DEPARTMENT

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SUMMARY

Supercapacitors (SCs) stand out among energy storage systems with long cycle life through ensuring the energy supply and demand with high-power. SCs are an alternative for fuel cells and batteries with a large surface area of highly porous electrode with the electrostatic charge accumulation. Electrolytes with liquid or solid-state types are a key factor to store the electrical charge. Solid electrolytes have high electrochemical performance with long life cycling times, light weight, good mechanical properties, flexibility and higher energy-storage capacity.

The aim of this thesis is to design binary solid gel-based electrolytes with different aqueous ion concentrations and compositions to increase the performance. Within the scope of the thesis; PVA based binary structural solid gel electrolytes were synthesized, and P₄ (1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt hydrate), TAAB (Tetra allil ammonium bromide) and KOH were used as ionic groups. The relationship between the massive host molecules P₄⁻⁴ and TAAB⁺¹ and their counter ions Na⁺, Br⁻ due to the mobility and the effect of conductive layer between binary electrolytes with doping agents including K⁺ and OH⁻ ions occurring additional charging were determined. In the first experiment; it was observed that, using binary electrolyte increases the performance of the SCs comparing to single electrolytes. Highly massive host molecules, which have low mobility comparing to their counter ions, decrease the amount of the charge stored while increasing the power density. In the second experiment; the conductive layer in binary electrolyte provides additional charge storing regions leading to an increased capacitance.

Key Words: Energy Storage Devices, Supercapacitors, Electrical Double Layer Capacitors, Ion Transport, Polymer Gel Electrolytes, Solid Gel Electrolytes, Binary Electrolytes.

ÖZET

Süperkapasitörler (SC), enerji arz ve talebinin sağlanmasında en az enerji üretimi kadar önemli olan enerji depolama sistemleri arasında yüksek güç yoğunlukları ve uzun çevrim ömürleri ile öne çıkmaktadır. SC'lerin performansına elektrot ve elektrolitlerinin kimyasal özelliklerinin yanı sıra konfigürasyon, gözenek yapısı, morfoloji, iç direnç ve iletkenlik gibi fiziksel özellikler de etki eder. SC'ler, elektrot-elektrolit ara yüzünde yüklerin elektrostatik birikimi yoluyla elektrik yükünü depolamak için geniş bir yüzey alanına sahip gözenekli elektrot ile iyonlarla katkılanmış yüksek iyonik iletkenliğe sahip elektrolit çözeltiden oluşur. Katı elektrolitler, uzun çevrim ömrü, hafifliği, iyi mekanik özellikleri, yüksek enerji depolama kapasitesi, esnekliği, düşük sızdırma (leakage) ve viskozite özellikleri gibi avantajlara sahiptir.

Tez çalışmasının amacı, polimer yapıdaki ikili katı hal jel bazlı elektrolitleri farklı konfigürasyonlarda sentezleyerek enerji depolama cihazlarında kullanımlarına yönelik karakterize etmektir. Bu kapsamında; polimer matris olarak PVA, P4, TAAB ve KOH sulu çözeltileri ile ikili katı hal jel elektrolitler sentezlenmiştir. İyonik yük transferi ve yük depolama performansına iyon konsantrasyonunun, ikili elektrolit konfigürasyonlarının ve elektrolitler arası iletken tabaka kullanımının etkileri incelenmiştir. Kütlece ağır (massive) konak (host) molekülleri P_4^{-4} ve $TAAB^+$ ile karşı (counter) iyonları Na^+ ve Br^- arası iyonik yük transfer ilişkisi, K^+ ve OH^- iyonları ile katkılanarak hazırlanmış ikili elektrolitler arası iletken tabakanın etkisi ile oluşan ilave şarj etkisi incelenmiştir. İlk deneyde; binary elektrolit kullanımının, SC'lerin performansını tekli elektrolitlere göre arttırdığı gözlenmiştir. Karşıt iyonlarına göre hareket kabiliyeti düşük olan yüksek kütleli konak molekülleri, sistemin güç yoğunluğunu artırırken depolanan yük miktarını azaltmıştır. İkinci deneyde; ikili elektrolit içindeki iletken tabaka, artan kapasitansa yol açarak ek yük depolama bölgesi oluşturmuştur.

Anahtar Kelimeler: Enerji Depolama Cihazları, Süperkapasitörler, Elektriksel Çift Katmanlı Kapasitörler, İyonik Taşınım, Polimer Jel Elektrolitler, Katıhal Jel Elektrolitler, İkili Elektrolitler.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations and Acronyms</u>	<u>Explanations</u>
Δt	: Discharge time
ΔV	: Potential Window
δV	: Voltage Drop
π	: Valance Bond
π^*	: Conduction Band
A	: The Surface Area of Electrode
AC	: Alternating Current
Ag ₂ S	: Silver Sulfide
BX	: Binary Electrolyte where X Stands for 1 to 4 Representing 0.5, 1, 1.5 and 2 M aqueous solution of KOH
BCX	: Binary Electrolyte with a Conductive Layer where X Stands for 1 to 4 Representing 0.5, 1, 1.5 and 2 M Aqueous Solution of KOH
C	: Capacitance
C _{DL}	: Capacitance of Double Layer
C _H	: The Helmholtz Capacitance
C _{INT}	: Capacitance of Interface
C _{ge@bin}	: Capacitance of Binary Electrolyte
C _{ge@mix}	: Capacitance of Mixture Electrolyte
C _{ge@P}	: Capacitance of P ₄ Based Electrolyte
C _{ge@T}	: Capacitance of TAAB ⁺ Based Electrolyte
C _s	: Specific Capacitance
C _T	: The Total Capacitance

°C	:	Centigrade
CV	:	Cyclic Voltammetry
d	:	The Distance Between Electrodes
DC	:	Direct Current
E	:	Energy
E _g	:	Energy Density
E _{INT}	:	Electric field at the Interface
ε ₀	:	Dielectric Constant, Vacuum Permittivity
ε _r	:	Relative Permittivity
EDLC	:	Electrical Double Layer Capacitance
EIS	:	Electrochemical Impedance Spectroscopy
ESR	:	Equivalent Series Resistance
F	:	Faraday Constant
ge@bin	:	Binary Gel Electrolyte
ge@KOH	:	KOH Based Gel Electrolyte
ge@P	:	P Based Gel Electrolyte
ge@T	:	T Based Gel Electrolyte
ge@mix	:	Mixture Gel Electrolyte
GCD	:	Galvanostatic Charge-Discharge
GTÜ	:	Gebze Teknik Üniversitesi
H ₂ SO ₄	:	Sulfuric Acid
HQ	:	Hydroquinone
I	:	Current, Ionic Strength
I _{cc}	:	Current of Galvanostatic Charge Discharge Analysis
KOH	:	Potassium Hydroxide
m	:	The Mass of the Active Material on the Electrode

M	:	Molarity
MB	:	Methylene Blue
Na ₂ MoO ₄	:	Sodium Molybdate
OH ⁻	:	Hydroxide
P _g	:	Power Density
P ₄	:	1,3,6,8-Pyrenetetrasulfonic Acid Tetrasodium Salt Hydrate
PbF ₂	:	Lead (II) Fluoride
PAN	:	Polyacrylonitrile
PC	:	Propylene Carbonate
PEDOT:PSS	:	Poly (3,4-ethylenedioxythiophene)-poly (styrene sulfonate)
PE	:	Polyethylene
PEO	:	Polyethylene Oxide
PMMA	:	Polymethyl Methacrylate
POIPC	:	Protic Organic Ionic Plastic Crystal
Ppy	:	Polypyrrole
PVA	:	Polyvinyl Alcohol
Q	:	Amount of Charge Accumulated on the Electrode
R	:	Resistance, Gas Constant, Solid Reactant
R _{CT}	:	Charge Transfer Resistance
R _{DL}	:	Double Layer Resistance
R _{ESR}	:	Equivalent Serial Resistance
R _{INT}	:	Interface Resistance
RC	:	Resistance-Capacitance
SC	:	Supercapacitor
SEM	:	Scanning Electron Microscopy

SX	:	Single electrolyte where X stands for 1 to 4 representing 0.5, 1, 1.5 and 2 M aqueous solution of KOH
TAAB	:	Tetra allil ammonium bromide
TEMABF ₄	:	Triethylmethylammonium Tetrafluoroborate
V	:	Potential Difference, Voltage
V ₀	:	Operating Voltage
v	:	voltage sweep rate
VOSO ₄	:	Vanadyl (IV) oxide sulfate
X _d	:	The Interactions of Electrolyte and The Whole System
W	:	Warburg Impedance

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1. INTRODUCTION

1.1. Supercapacitors

Supercapacitors (SCs) possess efficient energy storage with higher power density when compared with batteries. SCs can provide significant quantities of energy to the electric vehicle technologies in a short time and ensure the sustainability of resources such as solar and wind energy [1-2]. SCs offer variable and discontinuous energy storage according to the configurations of the renewable energy sources [3-4, 24].

The charging- discharging process occurs at the electrode and electrolyte interface. Electrostatic capacitors have micro- milli farad ranges of capacitance but SCs can reach even thousands of farads at the same physical dimensions. [5]. On the other hand, SCs can only offer operational voltages in the range of 1-3 V for both aqueous, solid and organic electrolytes, with the capacitance (C), in farads (F), as written in Equation 1.1 [1]. In order not to disrupt the chemical structure of the electrolyte, the reaction between the ions does not occur under limited operational voltages. Where the water breakdown approximately at 1.2 V potential window, the liquid component of the solvent does not electrolysis in an electrolyte, defined as the gap between the reduction and oxidation potentials.

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (1.1)$$

with the electrode surface area, A, the thickness of electrical double layer, d, the relative permittivity, ϵ_r , and vacuum permittivity, ϵ_0 .

The energy stored in a SC is calculated by Equation 1.2 with applied potential of V_0 [4].

$$E = \frac{1}{2} CV_0^2 \quad (1.2)$$

The performance comparison of energy storage devices is made with the Ragone graph shows the specific energy-power density relationship as given in Figure 1.1 [5].

It seems that SCs with a high power density - energy density fill the performance occupants between conventional (electrostatic) capacitors and batteries.

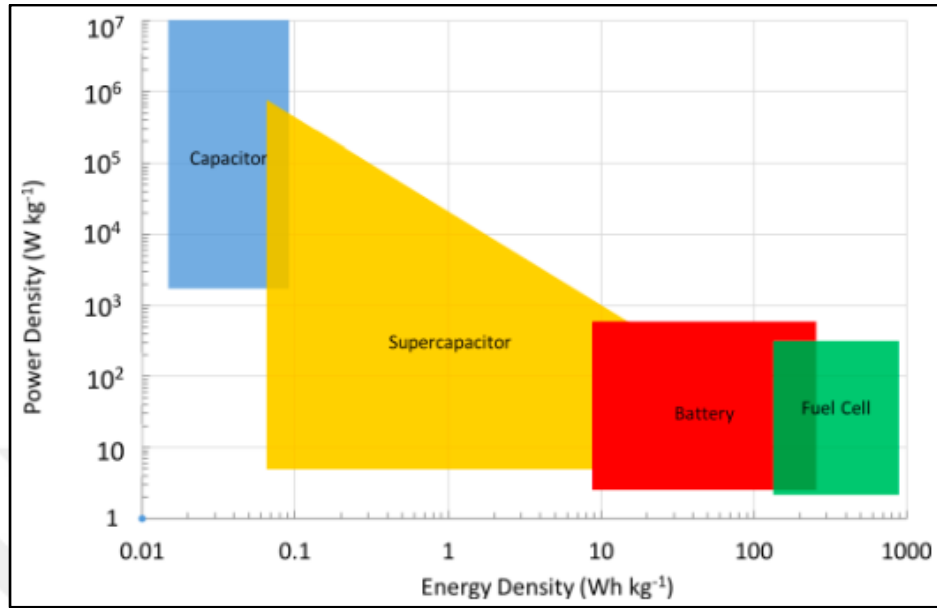


Figure 1.1: Ragone Graph.

The electrode, electrolyte and the surface condition at the interface affect the equivalent series resistance (ESR) of the system which reduces the specific power as shown in Equation 1.3. and Equation 1.4 [12, 17].

$$R_{\text{ESR}} = \frac{\Delta V}{2I} \quad (1.3)$$

$$P_s = \frac{V^2}{4R_{\text{ESR}}} \quad (1.4)$$

$$E_s = \frac{1}{2} C_s \Delta V^2 \quad (1.5)$$

$$C_s = \frac{1}{2vm\Delta V} \int IdV \quad (1.6)$$

where P_s , I , E_s , ΔV , C_s , v and, m are power density, the current density, energy density, potential window, specific capacitance, voltage sweep rate, and the mass of the active material of the electrode, respectively. SCs store charges electrostatically as

conventional capacitors and maintain a low equivalent serial resistance R_{ESR} . Thus, it operates at high specific power in a reversible way, substantially higher than most batteries [6].

1.2. The Aim of the Thesis, Methods and Techniques

The aim of the thesis is to evaluate the effect of the binary solid gel-based electrolytes on the electrochemical properties of energy storage devices.

For this purpose, in the first part of the thesis, PVA based solid gel electrolytes were synthesized to prepare a binary electrolyte including P₄ (1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt hydrate), TAAB (Tetra allil ammonium bromide) and KOH as the ionic groups. Here, it was aimed to understand how the mobility of the ions affect the charge storage mechanism in the SCs.

It was observed that, using binary electrolyte increases the performance of the SCs comparing to single electrolytes in serially connected. Highly massive host molecules cause low mobility and decrease the charge stored while increasing the power density when compared to their counter ions. TAAB molecules agglomerate in PVA and cause a loose matrix structure, therefore they can trap their counter ions and their position does not change considerably in the charge-discharge process. Also, their effective masses and the internal resistances increases due to the agglomeration. In binary gels, some dense and mild regions occur, especially in the contact layer of two gels, some of the ions can pass to the other gel, a part of the ions does not change their position noteworthy. That causes an external charging process in the middle of the binary structure, then gains extra capacitance effect. As a conclusion; using binary gels is more effective than two serial connected capacitors due to the higher capacitances.

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) analysis were executed by using Gamry 1010 Potentiostat with 2 electrode configurations at 5, 10, 20 and 50 mV/s sweep rates and 0-0.8 V range. The GCD behaviors at 3.90, 7.81 and 15.62 mA g^{-1} current densities are analyzed. EIS analysis was performed by using a sinusoidal AC excitation signal with a 0.01 V amplitude in the 10^{-2} - 10^5 Hz frequency range [79].

In the second experiment; the Nickel conductive layer effect between the PVA-KOH based binary electrolytes were investigated. Binary solid gel-based electrolytes

were prepared with crosslinked PVA based polymer matrix and KOH as ionic solutions in different ionic concentrations with and without a conductive layer between the electrolytes. The ionic transport relation through the mobility and the charge storage properties that occur additional charging due to the conductive layer were investigated. The interaction of metal ions inside the binary electrolyte increased the electrochemical performance due to its quick electron relay, therefore, the binary SCs with a conductive Nickel layer have an increasing extra capacitance effect to the whole system. The ions which were located in the middle of the electrolyte gain mobility due to the conductive layer in the diffusion plate. That provides an external polarization between binary electrolytes to the interface of electrode and electrolyte.

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) analysis were used for electrochemical characterization by using PS Trace Potentiostat. CV analysis at 100, 50, 10 and 5 mV/s sweep rates and 0-1 V range were adjusted for the electrochemical performance tests. The GCD analysis were executed at 2.15 mA g^{-1} current density for time scale in second units. For EIS analysis, a sinusoidal AC excitation signal with a 0.01 V amplitude and 10^{-2} - 10^5 Hz of frequency range were adjusted. SEM images were taken by using Quanta FEG 250 Field Emission.

2. LITERATURE REVIEW

2.1. Energy Storage Models

Energy storage is a process of storing energy that can be released to use at a later stage. Energy storage devices convert the energy into electricity and return it back to the system. Electrical double layer capacitors are based on the separation of electronic and electrolytic charges between the contact surfaces between the electrode, which is a conductive structure, and the electrolyte solution as an energy storage mechanism. As a result of this phenomenon, which is an electrostatic deposition, some models have been proposed to explain the structure. This section aims to provide a brief description of most of the relevant energy storage models.

The first theoretical model was proposed by Helmholtz in 1879 on capacitor charge storage mechanism, to elucidate how the loaded binary sheet behaved. However, his model was not able to explain the electrolyte density, that neglects the interaction of the absorbed species with the electrode. Helmholtz model was formed by the combination of a charged electrode and a charged electrolyte layer as shown in Figure 2.1 a).

Helmholtz's model was later revised by Gouy and Chapman in 1913 with some corrections. According to this model, ions were influencing the capacitance of the EDLCs, both thermal and electrolyte solution concentrations. Gouy and Chapman argued with this study that, the size and free movement of ions (in which ions move freely) cannot be ignored. Gouy and Chapman's model in which ions move freely was shown in Figure 2.1 b).

The Gouy and Chapman model was later updated by Stern and emerged as the accepted model today. This model is a synthesis model created using both the Gouy Chapman and the Helmholtz model, called the Gouy Chapman Stern model. It reveals that ions can be of a certain size and that these ions can be in charge centers. The first part, the ions near the electrode surface are frequently found, then the second part, where the diffusion of ions continuing into the solution (electrolyte). The ions absorbed on the electrode surface are found more frequently in the inner Helmholtz plane, IHP, and the ions, where diffused from electrode-electrolyte surface area in the

outer Helmholtz plane, OHP. The absorbed ions and solvated ions take place in IHP and OHP plane and interact on the electrode surface as shown in Figure 2.1 c) [13].

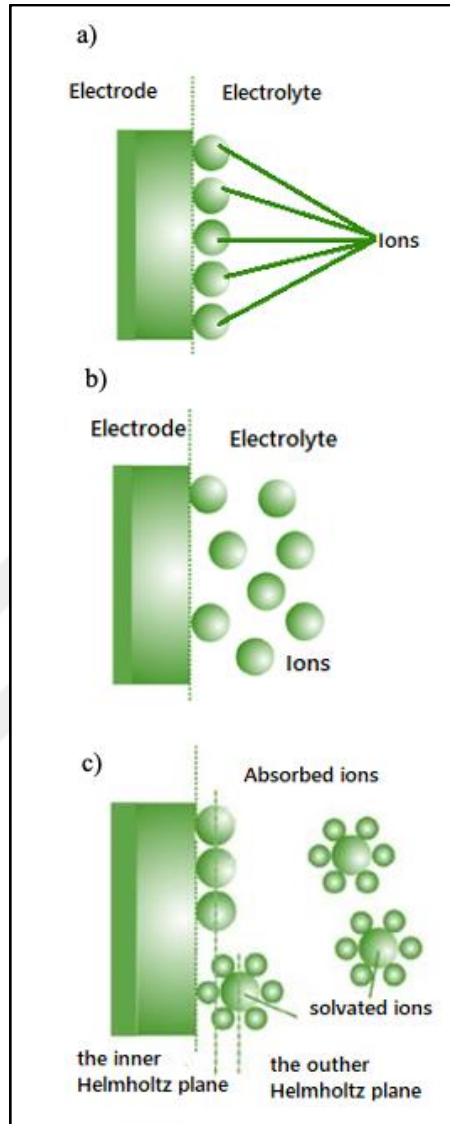


Figure 2.1: Energy Storage Models a) Helmholtz Model, b) Gouy-Chapman Model, c) Gouy-Chapman-Stern Model.

Stern model scope the nonlinear dynamics of diffusion and reproduce the change capacity of the SC. SCs have two capacity components such as, the Helmholtz capacity which is a constant component and the diffusion capacity. The Helmholtz capacity depends on the physical parameters of SCs. The diffusion capacity depends on the physicochemical processes such as, diffusion, electrostatic forces and the change of ion concentration in the electrolyte. The equations of Helmholtz and Stern models are represented in Equation 2.1, 2.2, where q , C_T and C_H , represents the charge of the

particles into electrolyte, the total capacitance, the Helmholtz capacitance. In Equation 2.3 the component of Stern model, X_d is given to represent the interactions of electrolyte and the whole system. The second term of C_T , represents the Gouy-Chapman effect, where R , T , F and I represents; gas constant, absolute temperature, Faraday constant and ionic strength [14].

$$C = \frac{dq}{dv} \quad (2.1)$$

$$C_T = C_H + \frac{\varepsilon \varepsilon_0}{X_d} \quad (2.2)$$

$$X_d = \frac{\varepsilon \varepsilon_0 RT}{F^2 I} \quad (2.3)$$

2.2. Supercapacitive Energy Storage Systems

Electrostatic, electrolytic and electrochemical capacitors are the general classification of the capacitors [18].

Electrostatic capacitors include two conductive plates to dispart the dielectric material and charges accumulate on the electrodes in an electrostatic way [15]. The dielectric substance located between the electrodes undergoes a polarization that occurs an increasing effect in the capacitance. [16-17].

When a capacitor is connected to a battery, electrons are pulled from one plate and accumulated on the other plates of the capacitor. As a result, while electrons are accumulated on one of the plates, an equivalent amount of electron deficiency occurs on the other plate. Initially, a relatively high current reached passes through the battery and as a result of the charge accumulation on the plates, a voltage starts to form between them. As the voltage increases, it begins to oppose the flow of electrons and then the current decreases. When the voltage in SC reaches to the same value of the initial voltage of the battery, the current stops flowing.

Electrolytic capacitors are similar in structure to electrostatic capacitors. However, these capacitors provide their conductivity by the connection of the electrolyte salts between the electrodes. Electrolytic capacitors have a large

capacitance per unit volume, high dielectric constant, a higher leakage current and less operating lifetime compared to other type of capacitors [19].

Electrochemical capacitors are also called as SCs or ultracapacitors. A SC is an energy storing device located between a battery and a electrostatic capacitor. They are electrochemical devices in which both physical reversible electrostatic charge and discharge process such as electrical double layer and a pseudo reversible electrochemical charge and discharge process can occur. Moreover, the charge-discharge curves are almost linear [4].

SCs occupy an extensive role, through appropriate design of the device, with both of energy and power ranges as a stand-alone and a combination of batteries for energy storage systems [6].

They are prepared by immersing a porous separator in an electrolyte solution and putting this material between porous electrodes. Since there is no phase change in the electrochemical process in SCs, such capacitors can be charged and discharged more than 1000000 times. SCs tend to have less energy density compared to batteries, since they only store an electric charge on the electrode surface, not the entire device. Since most SC materials are not involved in redox reactions, little degradation of the electrode takes place, giving it good cycling characteristics [20-21].

SCs have principles to store energy as, electrostatic double layered, electrochemical pseudo capacitance and a combination of EDLCs and pseudocapacitors as given in Figure 2.2 [25].

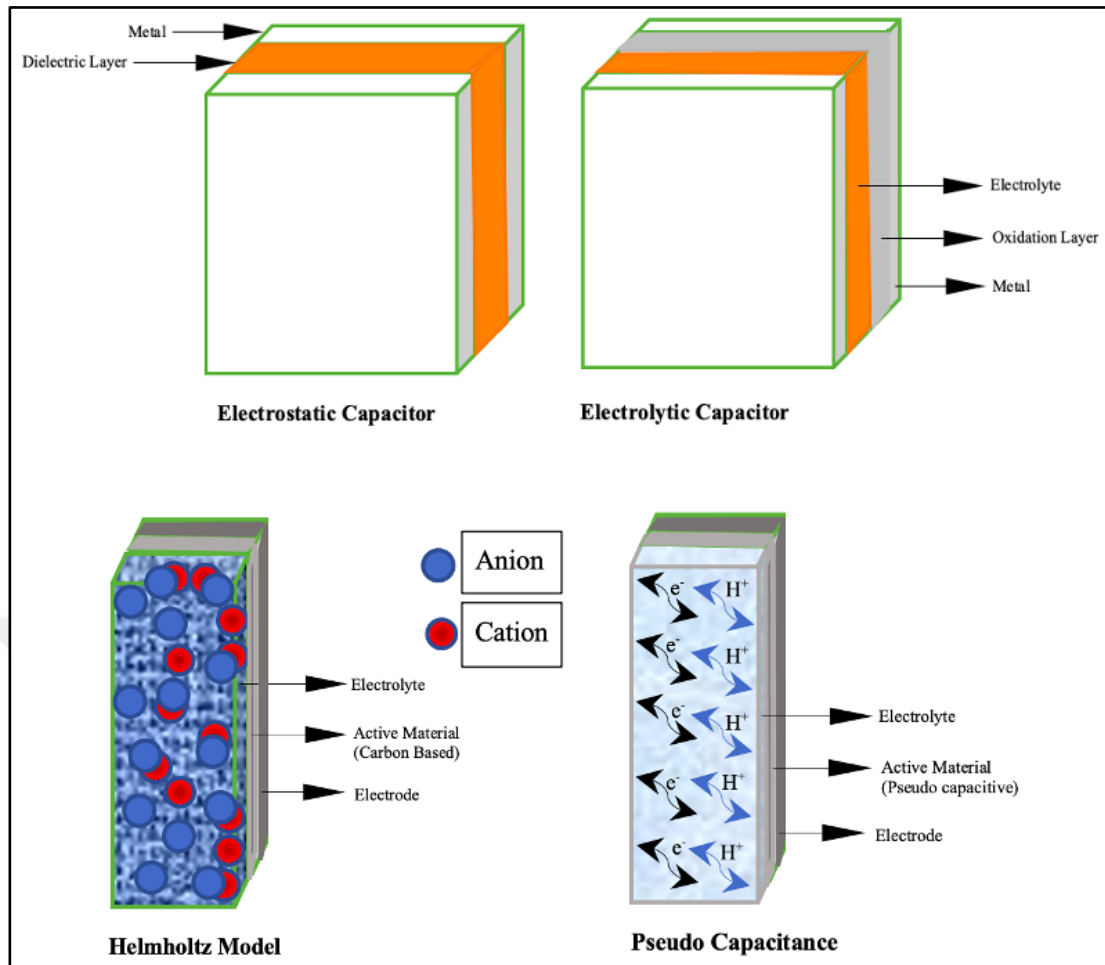


Figure 2.2: Historical Development of Capacitors.

SCs are divided into two main groups through the energy storage mechanisms as shown in Figure 2.3 [17] and expressed in section 2.2.1 and 2.2.2: Electric double layer capacitors and pseudocapacitors. Electrical double layer capacitors store the charges electrostatically on the electrode-electrolyte interface with generating a double Helmholtz layer. The carbon-based electrodes like activated carbon and derivatives are chosen to construct EDLC. Pseudocapacitors store energy electrochemically via Faradaic charge transfer between the electrode-electrolyte interface and include conductive polymers and metal oxides as electrode material. Hybrid capacitors store energy both electrostatically and electrochemically and include asymmetric electrodes with EDLC and pseudocapacitor type electrode materials.

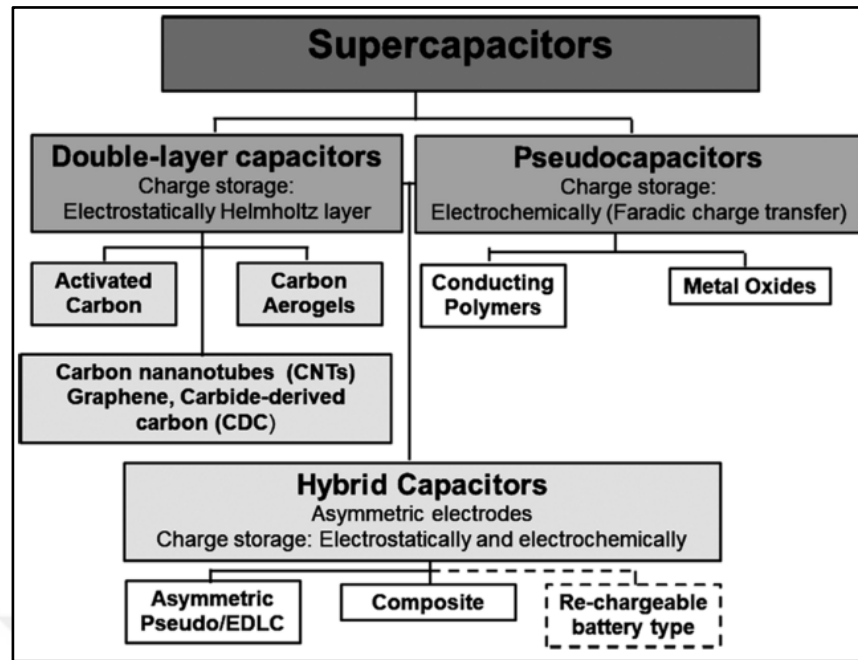


Figure 2.3: Supercapacitors Through the Energy Storage Mechanism.

2.2.1. Electrical Double Layer Capacitors

EDLC is consisted of two polarizable and porous electrodes. The energy storage process in EDLC is accomplished by dividing the charge between the two electrodes with a sufficient potential difference. The electrode material has no electrochemical reactions in EDLC. Electrons are transferred from the positive to the negative electrodes in the charging process, via external current source. Ions in the electrolyte move between the electrodes.

Charge density and electrolyte concentration at the interface change during both charging-discharging process and accumulate on the electrode–electrolyte interface [19]. In EDLCs, there is a non-Faradaic, electrostatic charging mechanism, depend on the charge separation, without electron transfer in the electrode-electrolyte interface [26].

In EDLCs, electric double-layer capacitance depends on the factors such as; electrode material, the surface area between electrode-electrolyte, the properties of electrode-electrolyte material and the interaction between electron and dipole moments [22]. EDLCs have effective electrodes with highly porous surface, where the dimension of the diffuse and double layer result redistribution as given in Figure 2.4

[27]. The carbon derivatives such as activated carbon have larger electrostatic double layer capacitance more than the electrochemical pseudocapacitance [23, 28].

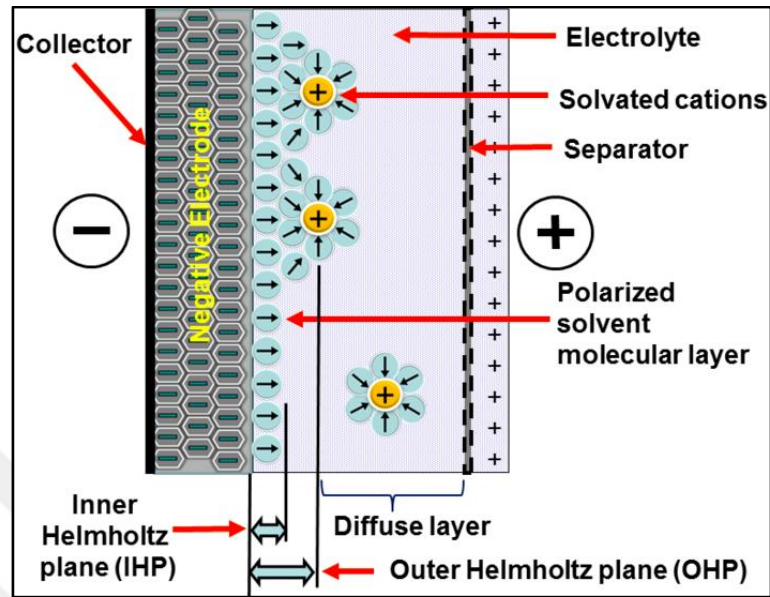


Figure 2.4: IHP and OHP of Stern Model.

The Inner Helmholtz Plate (IHP) where diffuse layer begins addresses to the nearest adsorbed ions (mostly anions). In the Outer Helmholtz Plate (OHP) the diffusion of ions still accumulates. The double-layer distance which is represented with d , and the potentials with V_0 and V on the electrode and the electrode-electrode interface, respectively as shown in Figure 2.5 [30-31].

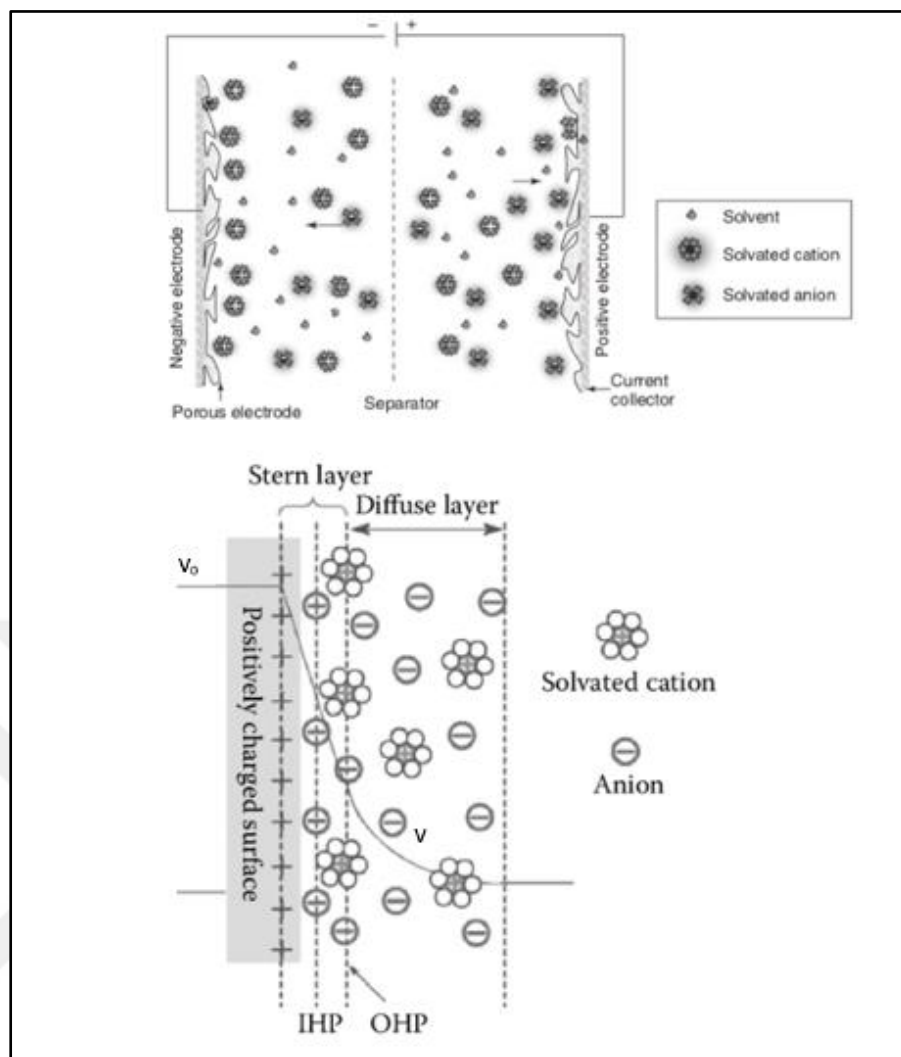


Figure 2.5: The Representation of Solvated Ions into Electrolyte.

2.2.2. Pseudocapacitors

Pseudocapacitors (PCs) have electrochemically active electrode material, which are different from EDLCs, where the capacitance increases with fast faradaic (redox) reactions on the surface of electrode. PCs store the electric charge with redox reactions which induce a faradaic current from reactions such as reduction-oxidation of electroactive materials or electro absorption and EDL capacitance. [21-22].

In PCs, the electron charge transfer between electrode-electrolyte surface is provided faradaically to store the electrical energy in a fast and reversible way on the electrode active material. Like batteries, PCs involve the charge in double layer and through the faradaic current. Materials used in PCs are generally metal oxides and conducting polymers that possess large electrochemical pseudocapacitance where

redox reactions take place [25, 30]. Electrical energy is stored and executed by electrochemical process, achieving redox reactions on electrode surface by specifically absorbed ions [31-32].

The Stern model of PCs which includes solvent ions, polarized solvent molecules and adsorbed ions into electrolyte system was shown in Figure 2.6 [28].

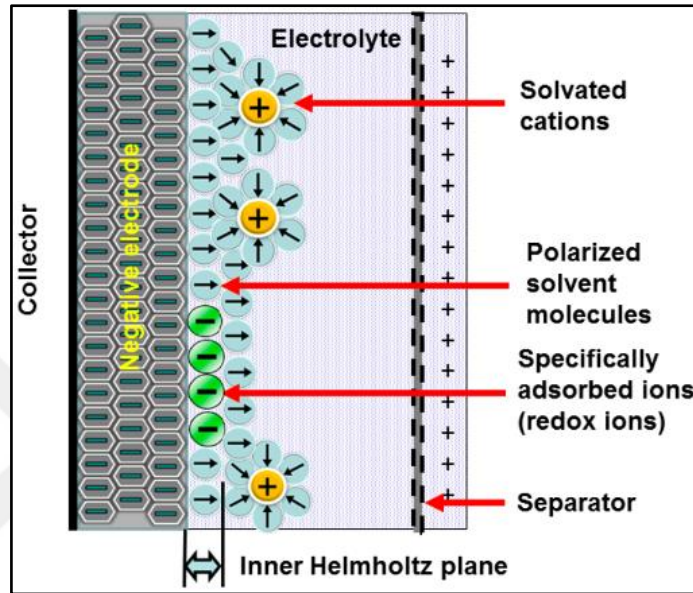


Figure 2.6: The Stern Model of the Pseudocapacitor.

There are several Faradaic process types that occur on the surface of electrode. The first is fast and reversible process such as hydrogen (H_2) adsorption on the electrode surface. The second is the redox reactions of pseudocapacitive electrode. The third one is the reversible process of doped electrochemical electrodes based on conductive polymer [4]. The Faradaic reactions in pseudocapacitors is given in Equation 2.4 and 2.5, where ne , R , a_R , a_0 , c_R are represented as; the charge stored, the solid reactant, the distance between particles and, the concentration of species, respectively [127].

$$\Delta V = V_c - V = \Delta V^0 \frac{kT}{ne} \ln \left(\frac{a_R}{a_0} \right) \quad (2.4)$$

$$a_R(c_R) = a_0 e^{\frac{(\Delta V^0 - \Delta V)ne}{kT}} \quad (2.5)$$

2.3. Electrode

Electrode, electrolyte and device configuration specify the performance of SCs. SCs are basically an electrochemical double-layer structure in which consisting superficial electrodes. The physical contact between the electrodes via electrolyte allows the ions pass through the pores of the electrode.

Electrodes are divided into 3 main groups such as; conductive polymer-based electrodes, metal oxide electrodes and carbon-based electrodes [30].

2.3.1. Conductive Polymer Based Electrodes

Polymers were generally considered as insulators and their electrical conductivity was considered undesirable, after all, researches are carried out to give the properties of inorganic metals or semiconductors to polymeric materials or some synthetic organic materials.

The electronic conductivity of polymers allows the chains to be transported and depends on the lattice of the polymers. This condition is provided by conjugated double bonds in the main chain [29]. In order to make the polymers highly conductive, the polymer must be doped in addition to conjugation. By doping, the conductivity of conjugated double bonded polymers can be changed by chemical and electrochemical means [7].

With the doping process, electrons that provide conductivity of the polymer structure are taken to form polymer lattice. How conductivity is provided in conductive polymers can be explained with a very simple approach through these gaps. An electron that jumps to a positively charged space from another place will create a positively charged space where it came from. These processes are repeated along the chain or between the chains, transmitting electricity.

Conducting polymers are conjugated systems with a π -orbital system. Doped conductive polymers; firstly, through the injection of π -electron system of charge carriers are achieved by oxidation or reduction of the polymer. Since each monomer is a redox site, the mobility of charge carriers is expanded to transition by electron transfer and delocalization of π -electrons along the polymer chain [32, 35].

PEDOT:PSS (Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) is an electrode material which is not at a sufficient level, first of all, some materials were

doped in order and the conductivity amount was aimed to reach the desired level. The doped materials can be carbon based materials, with addition of PEDOT:PSS achieves desired high conductivity. PEDOT:PSS is composed of long chains of carbon-based molecules that can conduct electricity as shown in Figure 2.7 [25]. It is known for its flexibility, lightweight, and ability to conduct electricity, which makes it an attractive material for use in SCs [31, 33]. It is a versatile material that has many hierarchical structures as shown in Figure 2.6 [31].

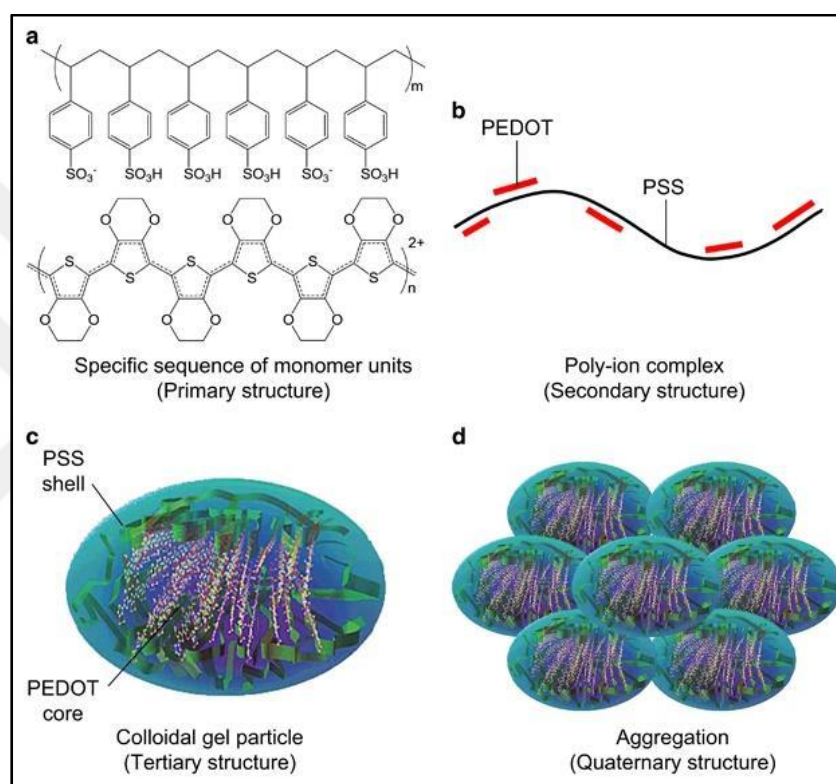


Figure 2.7: PEDOT:PSS a) Primary Structure as Monomer, b) Secondary Structure as Complex Poly-ion, c) Tertiary Structure as Colloidal Gel Particle, d) Quarternary Structure as Aggregation.

The most known and studied conductive polymers with the wide range of applications are PEDOT:PSS, polyethylene (PE), polyethylene oxide (PEO), polyaniline (PANI), and polypyrrole (Ppy); which are given in Table 2.1 [128-132]. Conductive polymers can be combined with carbon-based materials in order to increase the conductivity.

Table 2.1: Conductive Polymers Used in Electrodes of SCs.

Conductive Polymers	Conductivity (S cm ⁻¹)
PEDOT:PSS	10 ⁻¹ -1.5×10 ⁰
PE/Graphite	2.4×10 ⁻⁴ -8.0×10 ⁻²
PEO	10 ⁻⁹ -10 ⁻⁸
PANI	10 ⁻¹⁰ -10 ⁻¹
PPy	2×10 ⁰ -10 ²

2.3.2. Metal Oxide Electrodes

In pseudocapacitors, charge storage is rapid on the surfaces of electroactive materials, depends on reversible redox reactions. Ruthenium as a typical pseudocapacitive metal oxide material, also, (IV) oxide, iron oxide (magnetite), nickel (II) oxide and manganese (IV) oxide can be given as examples of metal oxide materials [32]. Metal oxide SC electrodes are generally more stable and with high energy density compared to electrodes of carbon derivatives and with additives such as carbon based and nano-structural materials to increase conductivity, electrochemical properties and the specific capacitance. The metal oxide-based SC electrodes have high surface area which are causing multiple redox reactions of metal centers and the degree of crystallinity [22, 32, 34, 36-37].

2.3.3. Carbon Based Electrodes

Carbon-based electrodes allow working in a wide voltage range, have rich surface chemistry, cheapness, chemical inertness, low residual current, high sensitivity and high surface activity. Depending on the fact that the aromatic rings in the graphite powder contain active oxygen groups and various functional groups of hydrogen to bond on the surface of carbon. [21].

Carbon materials, as shown in Figure 2.8 [17] have a longer cycle life than conductive polymers. However, its specific capacitance and electrical conductivity are lower than that of conductive polymers. The fact that conductive polymers have higher capacitance than carbon materials is due to the fact that both capacitive and Faradaic current contribute to charge storage. The reason why it shows a lower cycle life than

carbon materials is that the redox regions in the polymer structure are not stable enough to meet the repeated redox processes [10, 18-19].

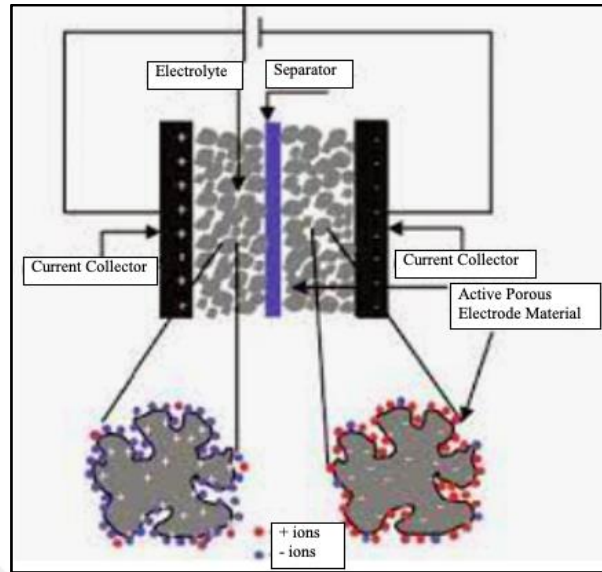


Figure 2.8: The Carbon-Based Electrodes.

Graphene is a crystalline allotrope of carbon, which has properties like honeycomb design. Also, graphene can reshape into different dimensions such as 0, 1, 2 and 3D. Two-dimensional graphene has attracted attention with its charging properties and mobility, light absorption ability, elasticity, high surface area. The hexagonal lattice of graphene consists of two equivalent carbon sublattices linked by σ bonds [19].

The properties of graphene are similar to those of graphite, of which it is a constituent with sp^2 hybridized in a hexagonal lattice that becomes delocalized in valence band (π) and conduction band (π^*) [39]. In condensed matter physics, it has been stated that while electrons of all other known materials behave according to the Schrödinger equation, electrons in graphene behave as relative particles [32].

The appearance of quasi-particles, i.e., electrons are represented without mass at rest. In SCs, graphene provides a variety of benefits. It can store a lot of electrical charge because of its high conductivity and huge surface area and because of its flexibility and lightweight, it may be used in a variety of settings. In addition, graphene is a material that is appealing for use in SCs since it is very simple to produce and is anticipated to have a long lifespan [37-38].

Graphene may be employed in SCs in a variety of ways. It may either be used alone to create the electrodes or mixed with other substances, such as metal oxides or carbon nanotubes, to create hybrid electrodes. Additionally available in several sizes and configurations, graphene-based SCs are appropriate for usage in a wide range of applications [18-19, 21].

2.4. Electrolyte

Electrolytes specify the performance of SCs with long cycling life, high ionic concentration and high-power density which are composed of the solvents and the dissolved cations and anions to gain electrical conductivity [9, 40]. Electrolytes must have low resistivity, low viscosity, low volatility, low toxicity and high purity [34-36]. The electrolyte should not chemically affect the capacitor as other materials to ensure that the electrical parameters of the capacitor are stable for a long time. Electrode and electrolyte interaction should be wet to reach the pores with a low viscosity [6, 49]. The representation of mobile and solvated ions is given in Figure 2.9 [42]

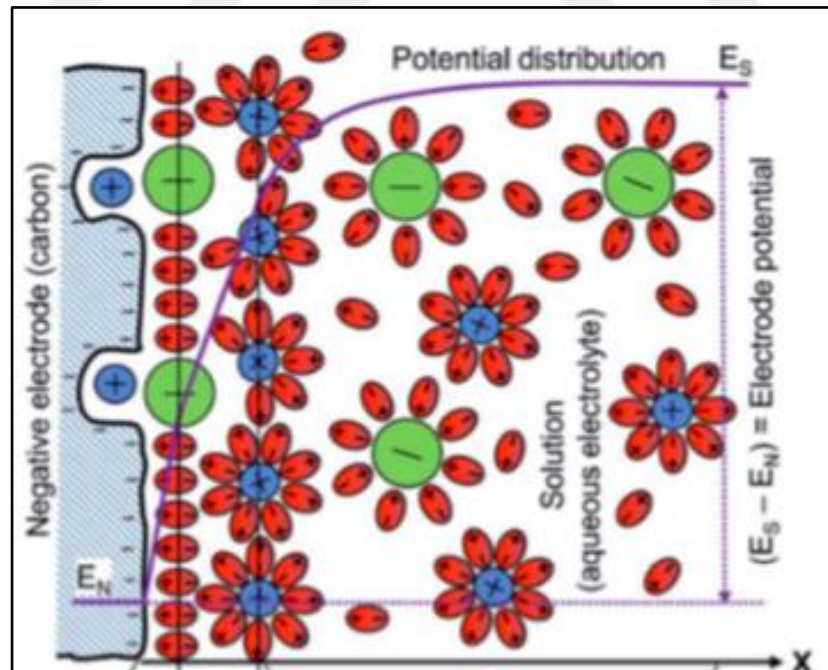


Figure 2.9: Mobile and Solvated Ions into EDLC.

Electrolytes contain mobile and solvated ions and divided into liquid, redox active and solid electrolytes as shown in Figure 2.10 [63].

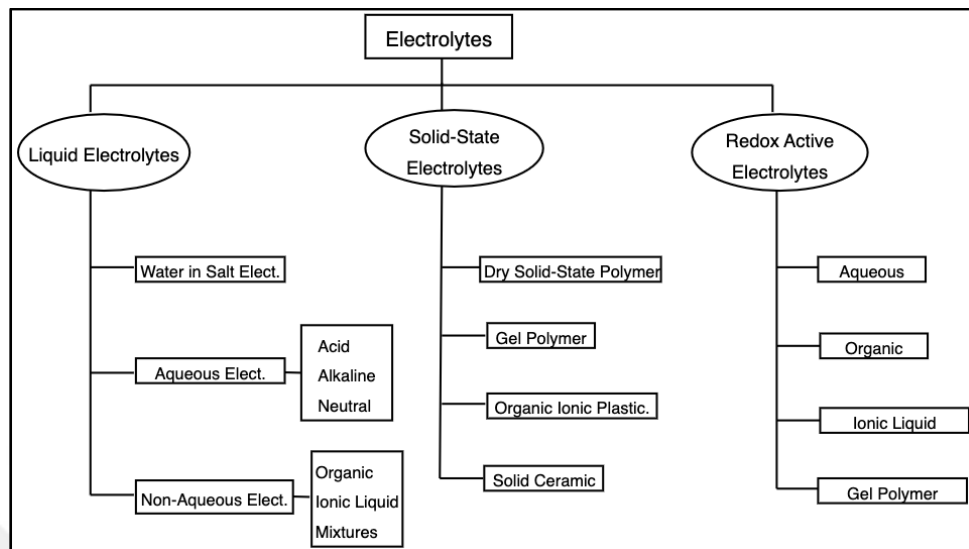


Figure 2.10: Classification of Electrolytes for Electrochemical SCs.

The self-leakage of electrolytes decreases the electrochemical performance of SCs and therefore the solid gel electrolytes are more advantageous. The next generation solid-state SCs have flexible and rigid container, and a lightweight, printable, self-healing and wearable structure with a mechanical and thermal stability. [37-38, 40].

2.4.1. Liquid Electrolytes

Liquid electrolytes are divided, aqueous electrolytes and non-aqueous electrolytes. Liquid electrolytes have benefits, such as solubility, a higher conductivity and power density due to the radius of ions.

Organic electrolytes are classified under non-aqueous, liquid electrolytes. Over liquid electrolytes, the advantages of organic electrolytes are having a large voltage window, approximately 2.7 V and energy density as given in Equation 1.5. The voltage window can increase to 3.2 V for some of the applications. In organic electrolytes, such; acetonitrile, propylene carbonate and TEMABF₄ (Triethylmethylammonium tetrafluoroborate), resistivity is between 20-60 Ω , and purification are higher than liquid electrolytes [41, 47].

Ionic liquids have advantages such as non-flammability, non-corrosivity, thermal and hydrolytic stability, wide liquid phase range and high ionic conductivity $\sim 10^{-2} \text{ Scm}^{-1}$. They are synthesized with a combination of anions and cations. The ionic liquid electrolytes with a wide potential window can enhance electrochemical potential. Other type of electrolyte additives is cheaper than ionic liquids and have higher voltage window, than 1.2 V which is typical for ionic liquids, in SC applications as a disadvantage [11, 16].

2.4.2. Redox-Active Electrolytes

Redox-active electrolytes are compatible with electro-active electrode materials and also have a significant effect on improving the Faradaic capacitance value with the help of reversible charge transfer reactions [48]. Analysis of the electrodes revealed that the crystal-like structures which are the product of side reactions with the electrolyte cause low ion diffusion. High surface area and homogeneous pore electrolytes are compatible with electrode materials [50]. The ions into electrolyte with oxidation reactions are transported in polymer chains and reduction reactions is released during reversible redox reactions which only takes place across the entire polymer, not on its surfaces [42, 51]. It has been suggested in the studies that the electrolytes with redox additives are an inexpensive tool to improve the electrochemical properties of SCs, and to encourage the performance compared with liquid water included electrolytes [43]. When the negative ions of the electrolyte are attracted by the positive charges distributed on the high surface area of the electrode, which is composed of porous carbon materials, an electrical attraction force is created between the opposite charges [52]. This allows the greatest possible ion diffusion [30]. The opposite ions in the double layer with a high charge increase on the surface, the active states acting on the surface and the short distance between the electrodes allow to reach high energy density. Thanks to this charge storage mechanism, energy can be transferred very quickly.

Redox active electrolytes are usually composed of iodide species such as potassium iodide (KI). Although the use of these electrolytes is simple and economical to achieve high capacitance, there are still some problems to be solved. Among them

some types of redox are irreversible and redox types go back and forth between the electrodes [44].

Redox active materials in aqueous electrolytes are divided into acidic, alkaline, and neutral solution types [17]. Most preferred redox organic electrolytes are consisted of Propylene carbonate and acetonitrile, $C_8H_2OBF_4N$ (Tetraethyl ammonium tetrafluoroborate) and $LiPF_6$ (Lithium hexafluorophosphate) salts. Ionic liquid electrolytes with redox additives mostly include organic bulk material of anion and cation. Hydroquinone (HQ), benzoquinone (BQ), $[FcEIm][NTf_2]$ (1-(methylferrocenyl)-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide) and $[EMIm][FcNTf]$ (1-ethyl-3-methylimidazolium ferrocenylsulfonyl-(trifluoromethylsulfonyl)-imide) are most preferred types of redox additives [53], [54]. Redox additives of electrolytes in a gel form exhibit high ionic conductivity than solid electrolytes [55].

2.4.3. Solid-State Electrolytes

Solid-state electrolytes are a newer type of electrolyte material that is gaining popularity for use in SCs [56]. They are composed of solid materials, like ceramics or polymers, and they offer several potential advantages over liquid electrolytes such as; high operating temperature, and easy packaging [58], [59]. For example, solid-state electrolytes are non-flammable and non-volatile, which makes them safer to use in certain applications [57]. M. Faraday discovered the first inorganic solid electrolytes (Ag_2S (Silver sulfide) and PbF_2 (Lead(II) fluoride)) and V. Wrigth discovered PEO (Polyethylene glycol), the first material of polymer-based electrolytes which leads conductivity to solid-state ions [30].

They are also more mechanically stable than liquid electrolytes, which can improve the performance and durability of SCs. However, solid-state electrolytes are typically less conductive than liquid electrolytes, which can limit their effectiveness in some applications and avoid the ion diffusion limitation [49].

Solid state gel polymer electrolytes are included a polymer matrix with mobile ions [60, 61]. They are outstanding in terms of flexibility when compared with inorganic solids. Ionically conductive polymers have received significant attention for versatile electrochemical devices [82-83]. Polymer electrolytes indicate enriched polar

groups of NH_2 and OH within the chains as conjunction sites, and they are prevalent sorbents for transition metal ions with high affinity. The construction of solid gel electrolyte is shown in Figure 2.11 [36].

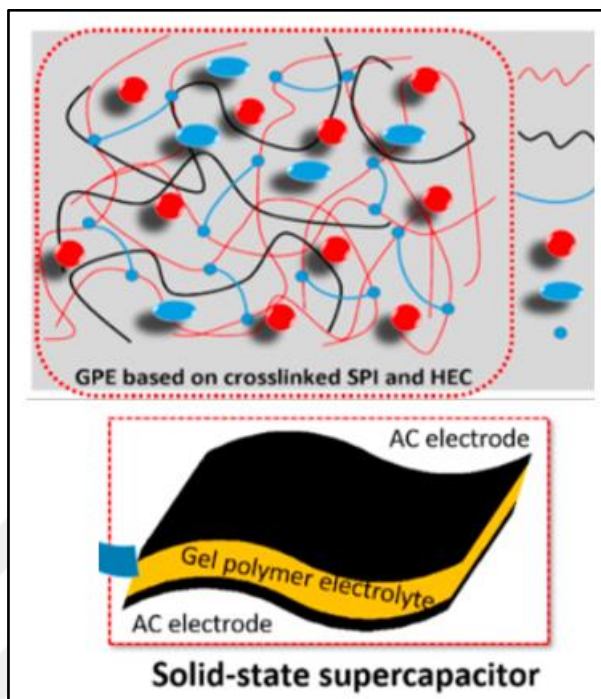


Figure 2.11: Solid-State Electrolytes.

Polymer gel electrolytes have high ionic conductivity which is related with amorphous phase and chemistry mechanism. They also have the capability to accommodate a various range of ionic dopants, desirable electrode-electrolyte connection, favorable ionic conductivity, and the ease of forming it into thin films that could deliver high energy density [42, 84].

These requirements must be considered such as dimensional stability, high chemical and mechanical strength and stability [62-63].

The ionic diffusion is related with the motion of the flexible polymer chains, and the amorphous structure degree in solid electrolytes [65].

Until now many works have been reported on both solid and quasi solid gel electrolytes [35]. SC with sulfonated poly (ether ketone) as electrolyte, polyaniline as electrode, also, PEO and alkaline based polymer electrolytes [50-51].

Solid gel electrolytes are mostly classified in; dry polymer, gel, solid ceramic and organic ionic plastic crystals as shown in Figure 1.4 [43-45]

Solid gel electrolytes also eliminate the use of separators (also when prepared in gel forms) with low melting point and mobile ions [41]. Solid gel electrolytes are closely resembled as liquid electrolytes, increase the conductivity of such systems. The most known examples are; proton conducting, lithium-ion, gel polymer and alkaline electrolytes [45-46].

Proton conducting gel polymer electrolytes prepared in a proton donor solution with the highest ionic conductivity and narrow potential window [47, 49]. Alkaline gel polymer electrolytes, especially multifarious types, have higher potential in batteries and SCs [8, 59, 65].

Dry polymer gel electrolytes have high dielectric constant and low lattice structure and high electrochemical potential such as; PEO, PMMA, PAN, etc. to increase the mechanical strength and conductivity [45, 48-50]. Solid ceramic electrolytes have interstitials lattice structure. The mobile ions of the organic ionic plastic crystals rotate around their centers orientationally located in the crystal structure [66-67, 50-53].

2.5. Binary Gel Electrolytes

The implication of ion-ion interactions into electrolyte must be considered for the performance of SCs as much as the electrodes. This is a novel method to increase the power of the SCs with the developments of both electrode and electrolyte, hereby using binary electrolytes that consist of two different electrolyte system in a sandwich-type configuration is an effective way [79].

Binary electrolytes act as two electrolytes with positive-negative electrode sides where ionic species are mobile, therefore the electrode kinetics get faster, through the electrode-electrolyte surface. Interaction between two gels occurs a layer with an extra capacitance effect and the whole system behaves like serially connected capacitor system with an additional charging mechanism. Therefore, the performance of SCs is enhanced via electrochemically interactions with pseudo typed electrolytes and electrostatically with EDLC type electrolytes. The interaction of the different anions and cations with each other exhibits high power densities [92].

The ionization degree of the binary solid electrolytes is related with the distribution of the ions in the diffusion plate. The ionization rate of the reactions is

depended on the difference of valency from the multispecies of electrolytes. Therefore, using non-identical electrolytes is necessary to obtain higher performance. The ion size differences provide considerable effect in binary fully ionized electrolytes. Low ion valence of anion and cation invents effective potential and higher power in the capacitors [79].

Li, Shaohui, et al. studied of the ionic liquid additives with EMIMBF₄ and TEP based binary electrolytes. The solubility in organic solvent with such redox additives increases the performance of the system [67].

Wong, Shao Ing, et al. also studied on the ionic liquid binary electrolytes, the common anion [NTf₂]⁻ and different cations [EMIM]⁺, [N1114]⁺ in different ionic concentrations [75].

Zhong, Ji, et al. studied with HQ and M additives of PVA in binary configuration, such as; the combination of PVA with H₂SO₄-HQ and H₂SO₄-MB. The ionic conductivity, aggregation and crystallization of the redox additives in PVA-based SCs were investigated in this study [92].

Fan, Le-Qing, et al. studied with the VOSO₄ and Na₂MoO₄ redox additives to obtain H₂SO₄-VOSO₄ and H₂SO₄-Na₂MoO₄ included PVA based binary electrolytes. The reversible Faradaic reactions obtained with the ionic conductivity and increment of molarities to compare capacitances [93-94].

Binary electrolyte combinations of different redox additives are studied to increase the capacitance in the literature. In this thesis studies, gel polymer based binary electrolytes are investigated comprehensively without redox additives. Gel polymer electrolytes generally consist elastomeric phases of a macromolecular components. The anions and cations into the ions of electrolyte interact electrostatically and occurs a mixture layer to gain additional capacitance to the system. Gel polymer electrolytes are classified under solid electrolytes with fast ion conductivity [92].

This is an impressive method instead of using two independent serial connected SC in a system. The performance of the system can be enhanced via the ingredients of the binary electrolytes, the properties of solvated ions and the interactions of ions in different mobilities and ionic conductivities. Sandwich design can prohibit the chemical interchange between electrolytes and reduce the interface resistance [93].

Sandwich-type binary solid gel electrolytes have a big amount of ionic conduction, and the structure improves Coulombic efficiency, cycle life and rate capability of the SC device [102].

In the positive direction of the electrode, between the first gel and the positive electrode surface, takes place where hydrogen desorption takes place an anodic polarization consists, in the negative direction, between the second gel and the negative electrode surface, where hydrogen adsorption takes place, a cathodic polarization consists.

The structure of binary electrolyte and the mixture layer which is consisted of the interface between electrolytes are represented in Figure 2.12 [76].

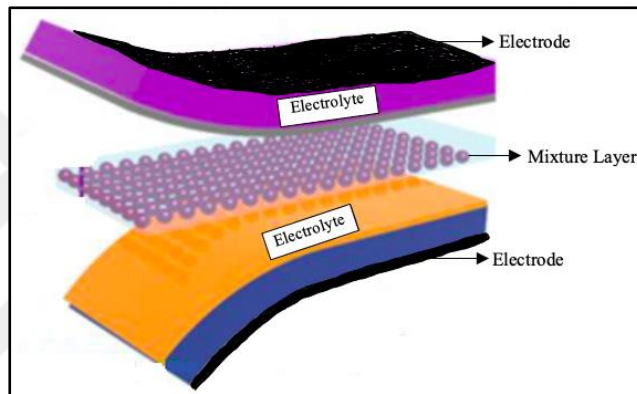


Figure 2.12: The Structure of Binary Electrolyte Included SCs.

3. ELECTROCHEMICAL PERFORMANCE ANALYSIS OF SUPERCAPACITORS

Electrochemical stability is connected with the life cycle and the redox interactions of SCs which is expressed of operational voltage and the compatibility of the electrode and electrolyte [68]. The capacitance, energy and power values of SCs can be measured by the electrochemical analysis. Cyclic voltammetry (CV), The Galvanostatic charge-discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) analysis are the main methods to recognize the energy storage mechanism of the SCs, such as, EDLC or pseudocapacitive type [15], [30]. These analysis methods are considered in this section in detail. CV is a technique on stability and detection of the reactions between the electrode and the ions in the electrolyte [69]. Pseudocapacitive behaviors, the optimum potential window and the performance of the SCs can be evaluated by CV analysis.

GCD analysis is another technique to measure capacitance, energy and power of the SCs. Equivalent serial resistance values can be extracted from the charge-discharge curves. The charge-discharge time of a SC is a main component to measure power of the device. The movement of separated charges near the interface of the porous electrode and charge storage properties can be observed by redox peaks through the electrochemical analysis occurring by oxidation and reduction reactions. [28, 34].

EIS is a sign of capacitive and diffusion characteristic of SCs. The ESR of the system and the charge transfer resistance can be obtained from the EIS graphs.

3.1. Cyclic Voltammetry

Cyclic Voltammetry (CV) method is based on current and potential relation at the interface of electrode and electrolyte.

The CV curve of a conventional capacitors are shown in Figure 3.1 [64]. The electron transfer at a constant rate between the electrode and electrolyte indicates quite a mirror effect between charging and discharging process [64].

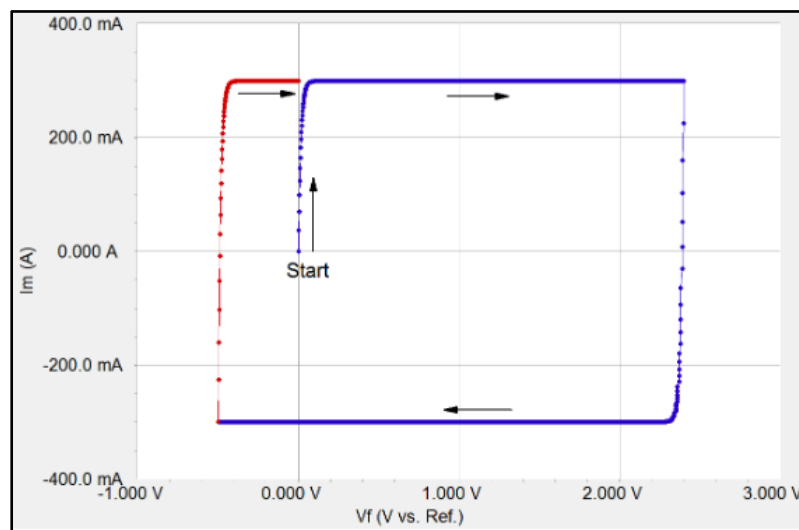


Figure 3.1: The CV Graph of Capacitors.

In this test, the voltage first increases up to a specific value, then returns to its initial value linearly and it is repeated many times [55-56]. Here, the forward and the reverse scanning speeds can be kept the same as well as different scanning speeds can be used. Multi-cycle alternating voltammograms are obtained when the forward and reverse scanning is repeated without stopping [69]. By examining the cyclic voltammograms in detail, it is possible to easily understand at what voltages the system can be reduced and oxidized, whether it is electrochemically reversible, whether there is a solution reaction following the electrode reaction, whether the products formed are stable, whether the substances or products that enter the electrode reaction are attached to the electrode surface [58].

The measurement techniques to determine the characteristics of EDLCs, with capacitance, equivalent serial resistance, energy and power, in contrast with conventional capacitors, as a conventional charging mechanism. The performance and the voltage-current relationship of an EDLC, which is composed of carbon-based electrodes with a high surface area, is subjected by linear voltage sweep rate. The outstanding charging properties are principally the result of the porous surface area between the electrode and electrolyte. Sub-nanometric pore size of carbon-based electrode such with electrical double layer capacitance is smaller than the solvated ions that increase the stored energy in EDLCs, by the electronic and ionic charge transport [14]. The CV diagram of ELDCs is shown in Figure 3.2 [78] as nearly an ideal EDLC with rectangular shape.

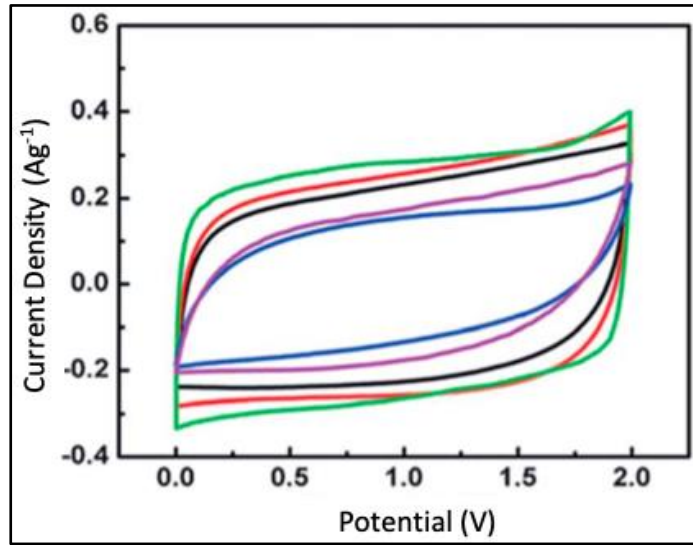


Figure 3.2: The CV Graph of EDLCs.

CV experiment with the linear changing mechanism, the current-voltage relation between the two metallic electrode layers gives a specific information about the system. The integral of the CV graph, gives the capacitance (C) value, as shown in Equation 3.1, with dV/dt as the sweep rate of the current-time curve and ΔV as the potential window.

$$C = \frac{1}{\Delta V \left(\frac{dV}{dt} \right)} \int IdV \quad (3.1)$$

Capacitance is depended on the viscosity of the electrolyte that can be explained by Columbic charge–discharge efficiency [74]. The charge storage nature of the CV analysis of EDLCs provides information of the anodic and cathodic regions. The leaf-shaped pattern means the same characteristics with an approximately rectangular shape with an exact internal resistance. The electrical double layer with high internal resistance causes fast build-up as the reason for the shape of CV curve as non-rectangular [73]. The CV diagram is lack of redox peaks and has no reversible humps concluding a Faradaic reaction as shown in Figure 3.3 [72].

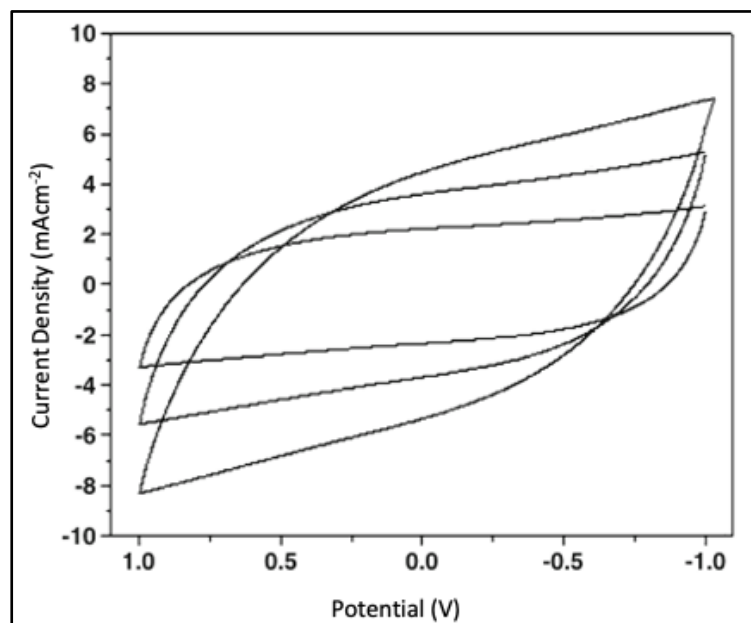


Figure 3.3: The Leaf-Shaped CV Circles of EDLCs.

The electrochemical characteristics through faradic reactions of Pseudocapacitors are like batteries that gather the energy in chemical bonds of electrode and electrolyte materials with increasing the scan rate, the redox peak currents increase. When the applied voltage reaches the oxidation (or reduction) voltage of the electroactive material, the very rapid consumption of diffusion layer surrounding the surface of electrode causes a rapid increase in current [70]. As a result, mass transfer begins by diffusion between electrode and electrolyte. Since the mass transfer rate by diffusion cannot compete with the electron transfer rate, an exponential decrease in the current is observed after the peak and a peak is obtained. When the voltage sweep is reversed, a back peak is observed due to the reoxidation or reduction of the product formed during the forward voltage sweep [57].

The redox peaks towards different potential ranges imply diffusion control of the system. The separation between the redox peaks which means potential overrates is required. With the increasing scan rates, CV profiles increase in a linear charging mechanism, to demonstrate the fast charge and discharge regimes as shown in Figure 3.4 [69].

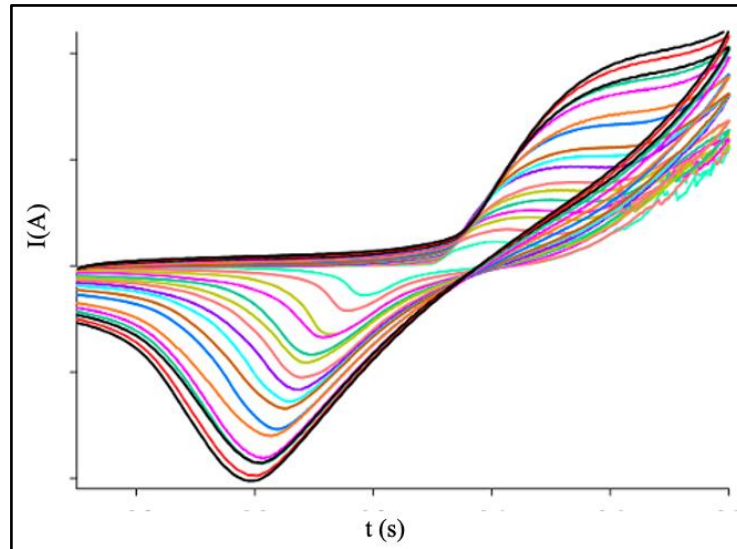


Figure 3.4: The CV Circles of Pseudocapacitors.

3.2. Galvanostatic Charge-Discharge

The Galvanostatic Charge-Discharge method can be used to measure capacitance, energy, power and equivalent serial resistance (R_{ESR}), (or internal resistance). The drop of the voltage in GCD curves, the current values and the discharge time can be used to calculate the capacitance values. The voltage drop (IR drop) gives the (R_{ESR}) from the charge-discharge curves, which is the main component to measure power of the device as given in Equation 1.3 and 1.4. The voltage drop which is at the beginning of the discharge curve is a measure of serial resistance which is proportional to the current [71]. The voltage-drop obtain to find the value of R_{ESR} is used in connection of Ohm's law as given in Figure 3.5 [72, 110].

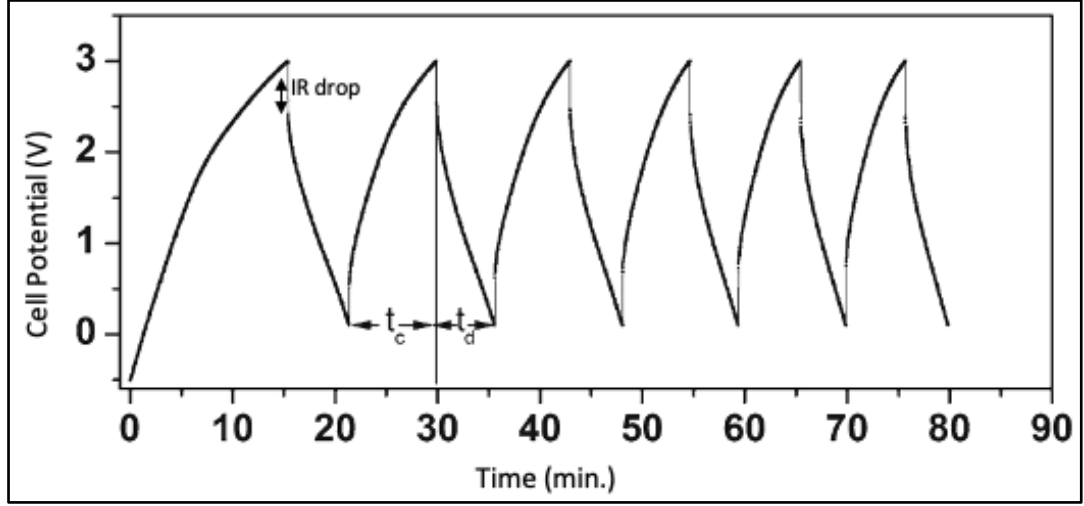


Figure 3.5: The GCD Curves to Represent IR Drop.

Theoretical analysis and simulations avail to find R_{ESR} with canonic circuit model, by a factor of two with normalization as given in Equation 1.3 [57, 72]. The integral of GCD area with adding the constant current gives the energy of the energy storage systems.

The capacitance with the increasing degree of voltage is obtained through GCD curves by using Equation 3.2. The constant current is used in terms of simulating the galvanostatic curve properties. [73, 74].

$$C = \frac{I_{cc}}{\left(\frac{dV}{dt}\right)} \quad (3.2)$$

The power is calculated from the ohmic drop given in Equation 1.4 by assuming a capacitive behavior. The shape of GCD curves and charge-discharge time depends on the drop in voltage across the R_{ESR} , which is the combination of electronic properties of the electrode and electrolyte [91].

The GCD curve of an ideal capacitor is as shown in Figure 3.6 [75]. The potential increases and decreases under a constant current value by the function of the time. The slope reflects the instant capacitance. The instant discharging capacitance at different potentials reflected by the slope of the GCD curve.

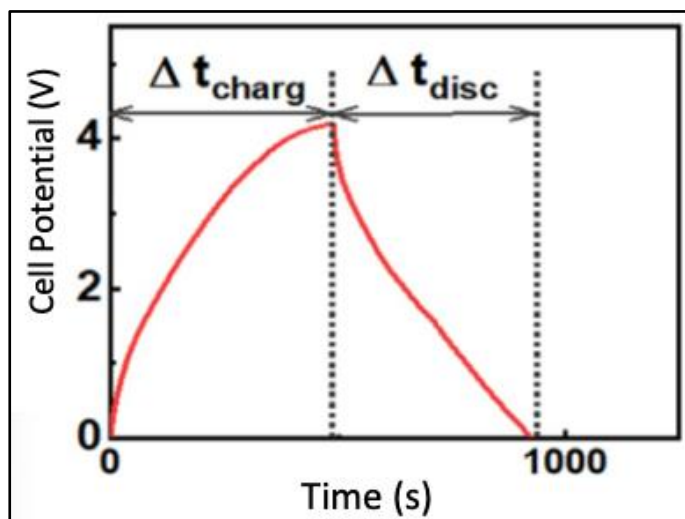


Figure 3.6: The GCD Graph of Capacitors.

GCD curves are divided into two regions; the first one is the pseudocapacitance and the other one is double layer capacitance. The fast electron transfer and the aggregation of electrode contributes to the total capacitance for pseudocapacitors. The first step is the increasing voltage due to the dissipation of the linear charging mechanism. The second quasi-linear stage of the pseudocapacitive charging mechanism is nonlinear exhibited by a quick voltage drop. Discharge curve shows a linear characteristic for EDLCs, a non-faradic capacitive charge-storage mechanism, and a small ohmic drop for pseudocapacitors. The capacitance of the EDLCs is linked in a discharging time and IR drop as shown in Figure 3.5, above.

The nonlinear voltage-time curves through the electrical behavior of porous electrode are not proper from a RC model [73-74]. The Fourier transform analysis demonstrate the obtained decomposition of current waveforms as shown in Figure 3.7 [70].

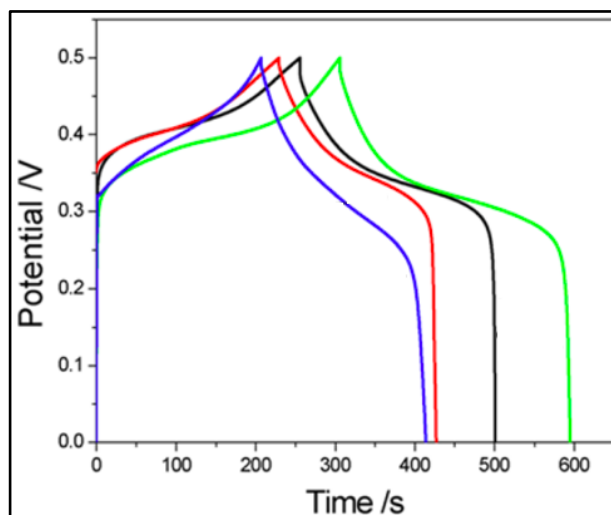


Figure 3.7: The GCD Curves of Pseudocapacitors.

3.3. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is based on the disruption of amplitude signal for a linear response through the stationary state in electrode [66].

Impedance spectroscopy is used to determine the charging properties of the energy storage device by a specified perturbation voltage which is applied with a frequency interval. The impedance is consisted of real and imaginary component, as two vectors which are combined to produce the impedance. The angle between real and imaginary components gives the phase angle, and the phase angle changes over the frequency. The current is depended on the frequency; therefore, the phase difference shows that the impedance must have a real and an imaginary part. The real component is a measure of the active part (i.e.; resistance), and the imaginary component is a measure of the reactive part of the impedance which is also called reactance (i.e.; capacitance) in the EIS analysis. At high frequencies, the real part gives the resistance of solution, near the origin. At low frequencies the real part gives the resistance of polarization and solution [68].

An equivalent circuit consists of the electrolyte resistance, the charge transfer resistance (R_{ct}) and the relaxation time (τ) demonstrated in the Nyquist plot. The phase angle between these capacitive and resistive components becomes 0° in systems consisting of resistors only, and 90° in systems consisting only of capacitors. In systems where the resistor and capacitor present together, the phase angle takes the

values between these two values [100]. Nyquist Chart includes Z_{im} and Z_{real} can also be represented as Z'' and Z' , Bode Plot includes $\log |Z|$ (θ) and $\log |Z|$ ($\log w$) (frequency), respectively. The impedance results of an ideal capacitor are linear along the Z_{im} axis of the impedance diagram. However, in SCs, a curved line appears due to the diffusion resistance of the electrolyte in the electroactive layer as shown in Equation 3.3, 3.4 and 3.5 [66, 68].

$$Z(w) = Z_{real} - jZ_{im}. \quad (3.3)$$

$$|Z|^2 = R^2 = (Z_{real})^2 - (Z_{im})^2. \quad (3.4)$$

$$\tan \theta = Z_{real} / Z_{im}. \quad (3.5)$$

The real part, C' is the capacitance, C'' is the imaginary part as shown in Equation 3.6 and 3.7 [68].

$$C' = \frac{C(w)}{1 + R^2(w) \times C^2(w) \times W^2} \quad (3.6)$$

$$C'' = \frac{C^2(w) \times R(w) \times w}{1 + R^2(w) \times C^2(w) \times w^2} \quad (3.7)$$

The size of semi-circle in the EIS spectrum shows a significant increase due to the charge transfer reactions where the branch of the capacitive term remains unchanged in low frequencies. The size of the semi-circle is attributed to a decrease with an increasing DC voltage. A semi-circle indicates contact point in high frequencies, and the resistance between current collector-electrode. The charge-transfer resistance overlaps for the redox active electrolyte, and a quasi-vertical line indicates after the semi-circle, represents the diffusion resistance [68].

Nyquist plots, including Z'' (Z_{im}) and Z' (Z_{real}), represents the increases in the impedance of the capacitive retention as shown in Figure 3.8 [70].

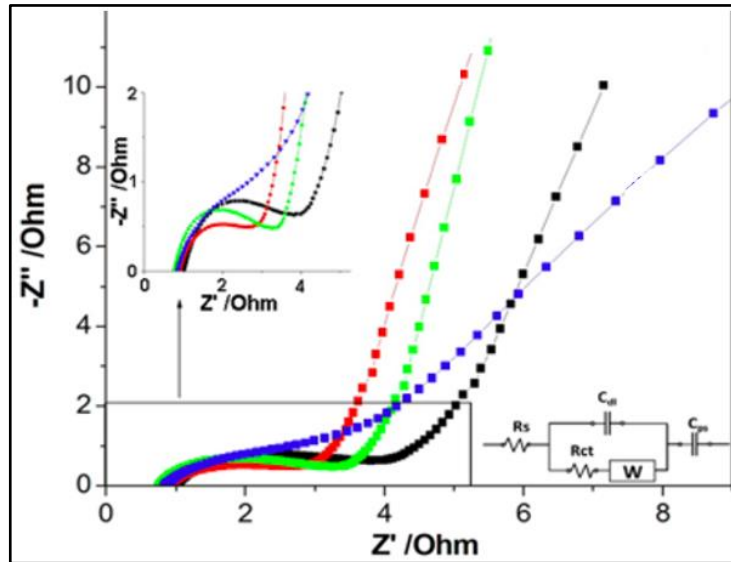


Figure 3.8: The EIS Graph of EDLCs.

The network frequency is independent from the impedance of resistance, and the capacitive element as given in Figure 3.9 a), b) [100]. The Nyquist plane is vertical to the imaginary axis in a line and Warburg impedance (W) is a straight slope with approximately 45° and changes through the resistance, as shown in Figure 3.9 c) [100]

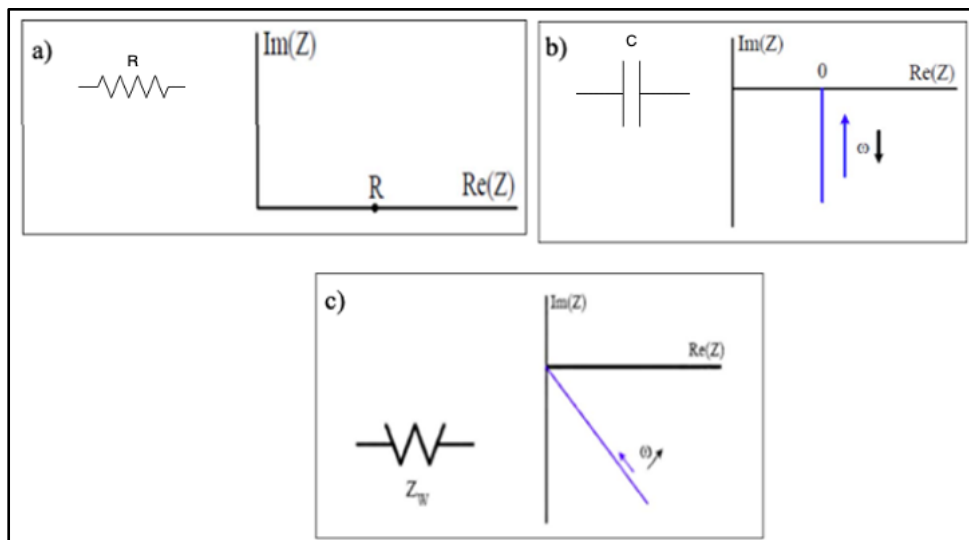


Figure 3.9: a) Resistive Element, b) Capacitive Element c) Warburg Element.

The scheme of faradic impedance of EDLC is represented with a reducing charge transfer resistance. The conductivity is depended on the transportation of ions. The simplest representation of SC, EIS model is given in Figure 3.10 a) and d) [100].

Two semi-circles in the nyquist plot represents that, the first one is at higher frequency indicating the solid electrolyte resistance, and the other indicate the resistance of electrode as given in Figure 3.10 b) and e) [100].

Impedance of a SC with warburg term of the randle model with oxidation-reduction reactions and R_{ct} with a diffusion layer is given in Figure 3.10 c) and f) [100].

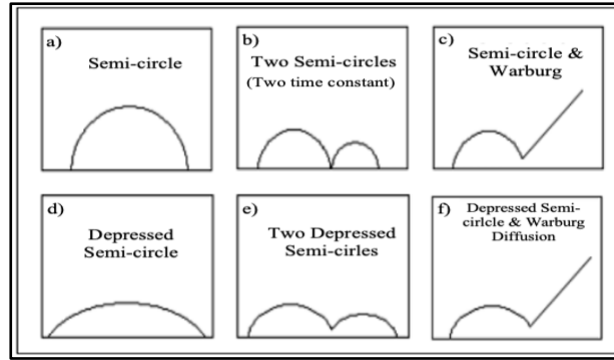


Figure 3.10: Typical Nyquist Plots of SCs.

EDLCs exhibit fractional or constant phase representing energy characteristics which is not similar with capacitors. The solid properties of electrolytes and the charge transfer mechanism between electrode and electrolyte are represented in EIS graphs. EDLCs can be evaluated of the real axis of impedance response. Randle's circuit gives the nyquist plot of EDLC. The semi-circle region the electrolyte resistance represented by R_b , starts with high frequency. The semi-circle midfrequency region is in a parallel combination for R_{ct} and EDLC capacitance, C_{DL} . In an intermediary frequency region, SC shows resistance with the decreasing capacitance. EDLCs provide constant phase behavior in the frequency domain. [68].

In solid polymer electrolytes, determining the dominant charge carrier species is significant due to the characteristic of the material which is different from the capacitor behavior. First, the semicircle region of the solid electrolyte for high frequency, then the low frequency region with electrode polarization that blocks the electrodes. [68]. The degradation of the layer of solid electrolyte interphase contributes an increase to the size of semi-circle.

In pseudocapacitors, specific capacitances can be calculated from the knee frequency in EIS plot, as shown in Figure 3.11 [72].

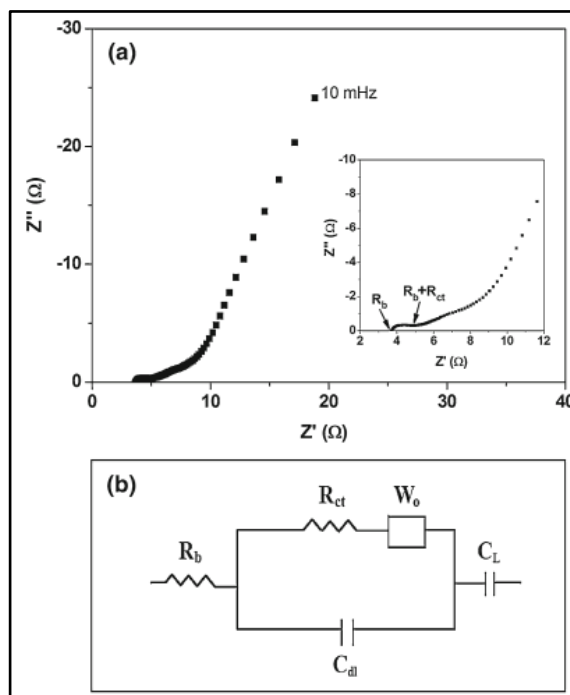


Figure 3.11: The EIS Graph of Pseudocapacitors.

4. SYNTHESIS AND CHARACTERIZATION OF PVA-BASED BINARY-GEL ELECTROLYTES INCLUDING MASSIVE IONS

4.1. Introduction

The mobility of the ion pairs is significant in the charging mechanism of the energy devices. Although the ion diffusion in solid electrolytes is not high as much as the liquid electrolytes, in combination with energy storage devices they can be used for a sufficient energy storage component [77-80]. The charge carriers and the electrolyte matrix properties directly affect the charge transport in SCs [99-100], through the mobility and the functional ionic groups [81, 85]. In addition, the interaction of the charge carriers into gel electrolytes, affects the ionic transport mechanism [86, 88].

Vargas-Barbosa et.al. studied on the ion correlations in gel and aqueous electrolytes of single cation, the self-correlations and distinct-cation correlations. The transport properties directly depend on the ion interactions [89].

Margulis et.al. demonstrated the conductivity and the charge transport process relation in the ionic liquids, which decreases the correlated motion of ions in electrolyte solutions [90].

Braun et.al. studied the non-symmetric boundaries in solid electrolytes due to the limited ionic mobility [91]. Different ion mass resulting in asymmetric charge layers at the electrodes is also investigated this study.

The researches in literature are evaluated to pointed out the correlations of ion pairs through the type of the ions in electrolytes [95-96]. Thought out the studies, it is considered that, the charge transport properties, the thickness and massive ions in electrolytes, agglomeration of the host molecules and the binary configurations were not studied extensively.

P₄ and TAAB have lower mobility than their counter ions; Na⁺ with Br⁻, with the masses of 23 and 80 g/mole, respectively. The masses of counter ions are very small than their host molecules P₄⁻⁴ and TAAB⁺¹ with the masses of 524 and 322 g/mole, respectively. PVA included electrolyte with P₄, and TAAB, and mixture of

ionic groups were synthesized and characterized to investigate the effect of massive ions to the charging mechanism in the electrolyte. The binary electrolyte system was obtained with P₄ and TAAB based electrolytes by putting over the one on another. The characterizations were executed by using CV and GCD techniques.

The binary gel polymer electrolyte included SC was analyzed and compared with single and mixture electrolyte included SCs where massive P₄ and TAAB host molecules and counter ions with decreasing in the charge stored. TAAB molecules trapped their counter ions in the dense regions and are aggregated in the polymer structure. The agglomeration of the TAAB molecules increased the internal resistance and their effective mass.

4.2. Materials and Methods

PVA was supplied by Zag Kimya, the ionic groups; 1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt hydrate (P₄) was supplied by Acros Organics, Tetra allil ammonium bromide (TAAB) and KOH was supplied by Merck. In addition, the graphene sheets as electrodes (cut in a circular shape of 2.0 cm² surface area) and coin cell cases as current collectors were supplied by Nanografi Nano Technology.

PVA based electrolytes were synthesized by 1 g of PVA in 10 ml distilled water and stirred continuously for 4 h at 60 °C. Single electrolytes of ge@P, ge@T, ge@KOH and, ge@mix were prepared with 20 mM of P₄, 80 mM of TAAB and KOH with PVA solutions and 20 mM P₄+80 mM TAAB for mixture configuration. The obtained gels were annealed in the oven at 60 °C for a while, then cut in 1 mm of diameters.

Graphene sheets in circular shape (2.01 cm² of surface area and 35 μm of thickness) are used as electrodes with 2 electrode configurations and the gel electrolytes were put on electrodes as shown in Figure 4.1.

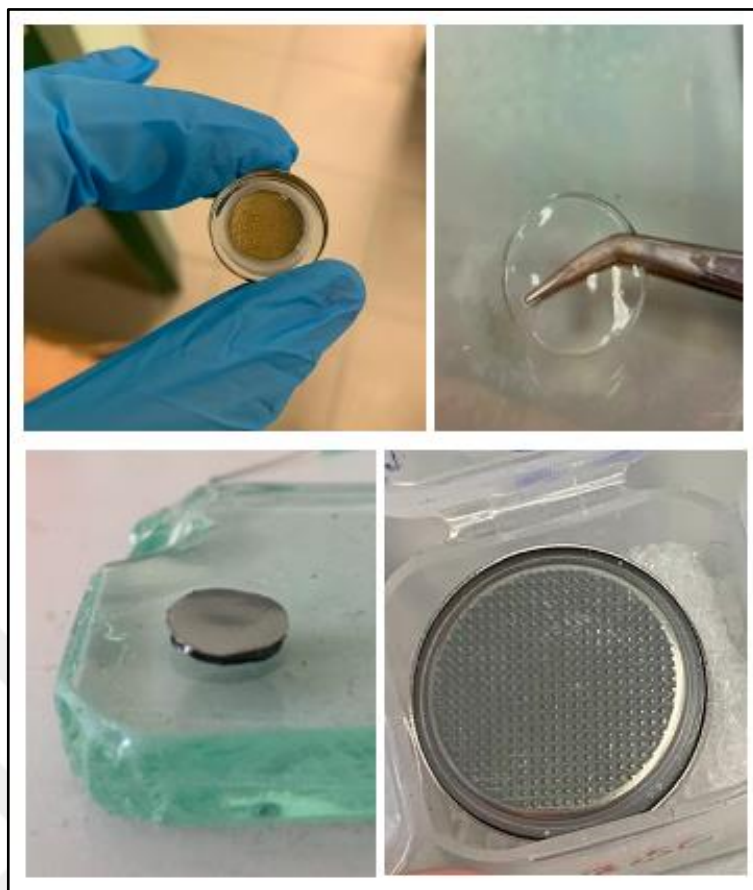


Figure 4.1: P_4^{-4} and $TAAB^{+1}$ Doped PVA Based Electrolytes of Binary SC.

The single gel electrolytes, ge@P and ge@T, are put together to prepare binary gel electrolyte, ge@bin, and the mixture of ge@P and ge@T is used to prepare mixture gel electrolyte, ge@mix. A reference gel electrolyte with KOH solution was prepared with the same configuration as single gel electrolytes. The ge@bin and ge@mix configurations were given in Figure 4.2.

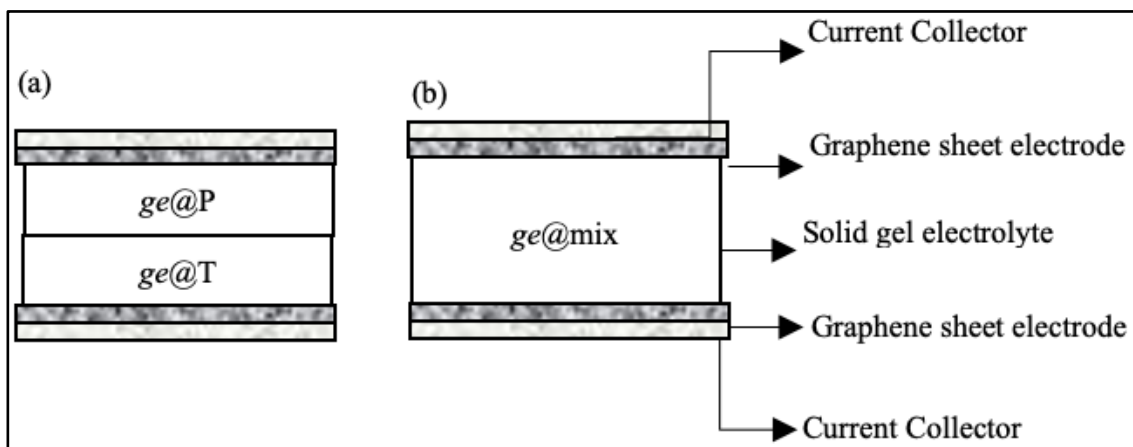


Figure 4.2: a) Binary Gel Configuration as $ge@bin$, b) Mixture Gel Configuration as $ge@mix$.

CV, GCD and EIS analysis were used for characterization of the SCs by using Gamry 1010 Potentiostat, as shown in Figure 4.3. For CV, the measurements were taken at 5 mV/s, 10 mV/s, 20 mV/s and 50 mV/s sweep rates and in the range of 0-0.8 V. The GCD analysis were taken at 3.90, 7.81 and 15.62 $mA g^{-1}$ current densities.



Figure 4.3: Gamry Potentiostat.

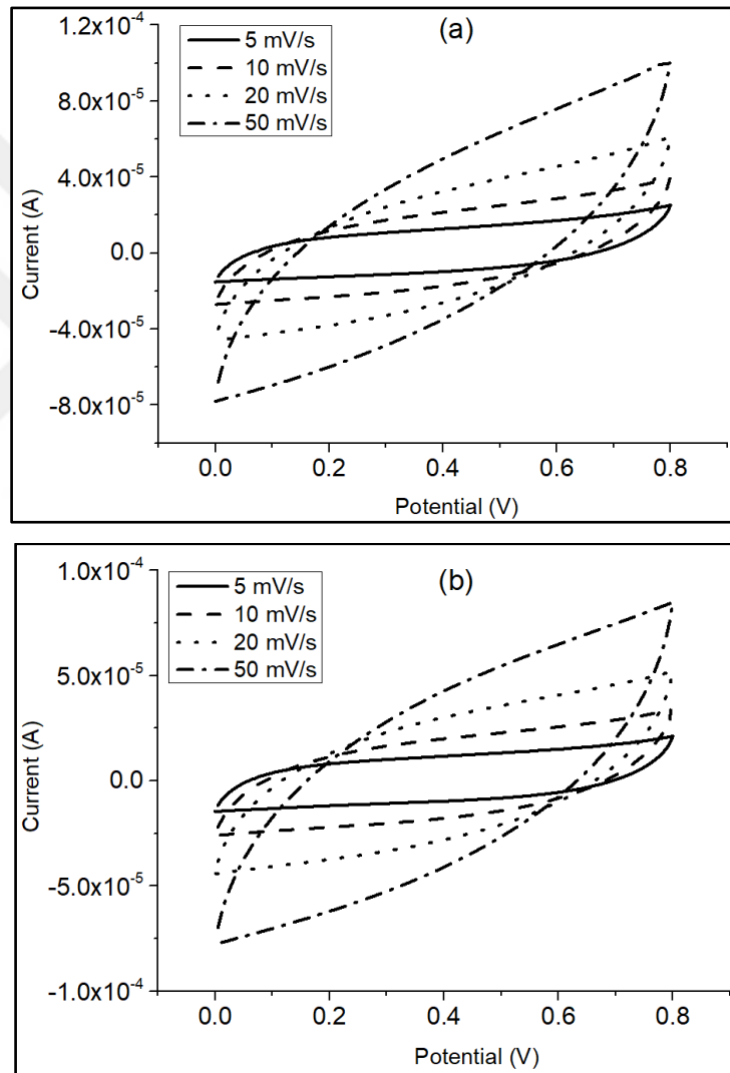
4.3. Results and Discussions

The reference gel electrolyte was chosen as KOH solution, as an extensively chosen electrolyte in literature in this study to compare the massive ionic properties of the gel electrolytes. The single electrolytes $ge@P$, $ge@T$ and $ge@KOH$ were analyzed

by CV technique as given in Figure 4.4. The ratio of P_4 to TAAB was adjusted into $\frac{1}{4}$ ratio where P_4 has 4 and TAAB has 1 counter ion for balancing the concentrations.

The CV curves of $ge@P$ and $ge@T$ shows EDLC character to resemble the properties of graphene. The single gel included SCs, $ge@P$ and $ge@T$ have higher CV areas compared to $ge@KOH$ at low sweep rates.

The reference SC, $ge@KOH$ has high mobility due to $K^+ + OH^-$ ions than $P_4^{-4} + Na^+$ and $TAAB^{+1} + Br^-$, due to their massive properties. The current-voltage behavior can be recognized more in detail at low sweep rates, with enough time.



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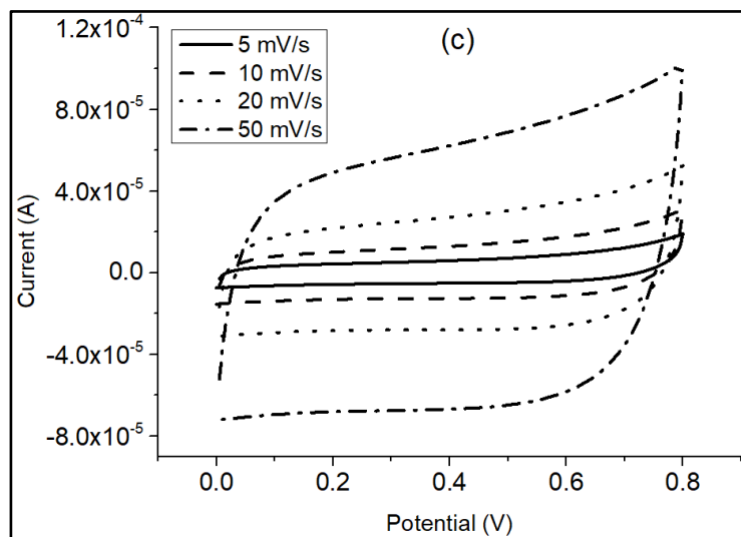
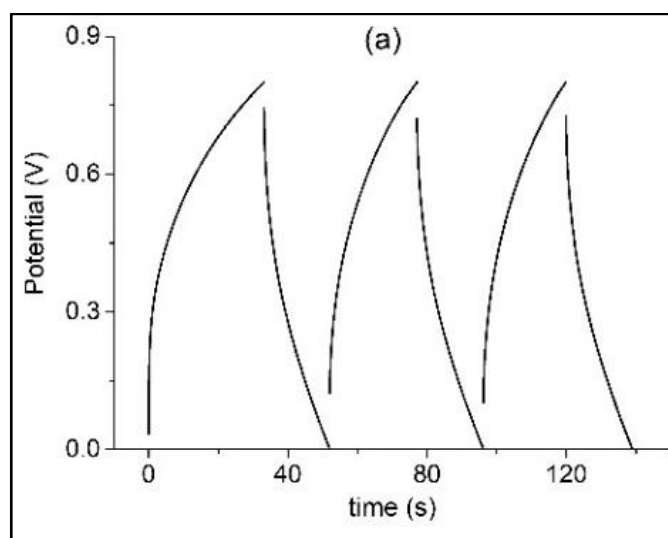


Figure 4.4: CV Curves of a) ge@P, b) ge@T, c) ge@KOH.

The GCD curves of the single SCs were given in Figure 4.5 at 3.90 mA g^{-1} current density with an approximate triangular shape, as a typical EDLC nature. As seen in the figure that the ge@T charges and discharges faster than other SCs and the ge@KOH is the slowest one, due to the agglomerated TAAB molecules in ge@T. In the discharge period, Br^- ions can return back to their host molecules easily. The mobility and the discharge time of the host molecules is maximum for KOH as given in Figure 4.5.



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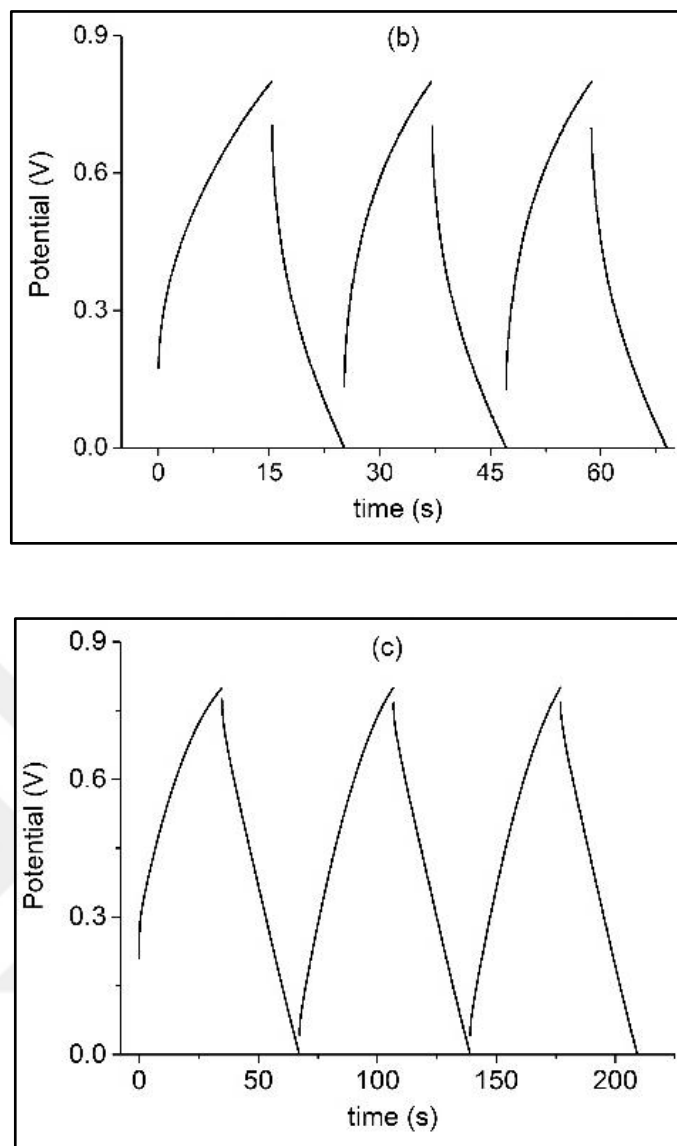


Figure 4.5: GCD Graphs of a) ge@P, b) ge@T, and c) ge@KOH.

The thickness effect of gel electrolytes through the capacitive properties, the CV measurements were performed at 1, 2, 3 and 4 mm as given in Figure 4.6 at 5 mV/s scan rate. In ge@P, through the increasing thickness, the capacitance had higher values due to the amount of ions. In the ge@T, the capacitance decreased through the increasing thickness, except of the highest thickness, then the capacitance increased and had the maximum value for 4 mm of thickness. Although the concentration of counter ions was the same, the capacitance value was bigger at 1 mm thickness of ge@T, due to the difference in internal structure of electrolytes.

In the measurements, it was obtained that due to the looser structure of ge@T, ge@P has an efficient transport for the counter ions. Also, with the increasing

thickness of ge@T, the capacitance decreases even though, the amount of charge increases in the system, due to the agglomeration of the TAAB molecules.

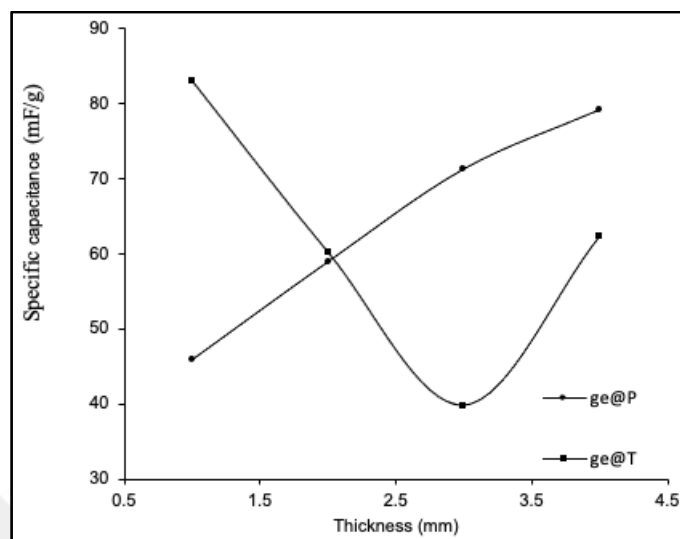
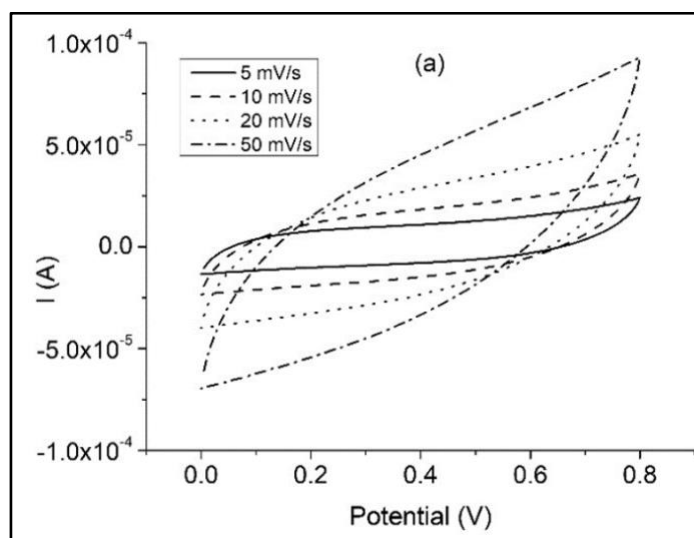


Figure 4.6: Specific Capacitance Comparison of ge@P and ge@T at Different Thicknesses.

The CV curves of ge@bin and ge@mix, were given in Figure 4.7, which have similar behavior with ge@P and ge@T. Through the small fluctuations in ge@mix CV curves at high scan sweep rates were given in Figure 4.7(b), due to the interaction of, P_4^{-4} and $TAAB^{+1}$ host molecules.



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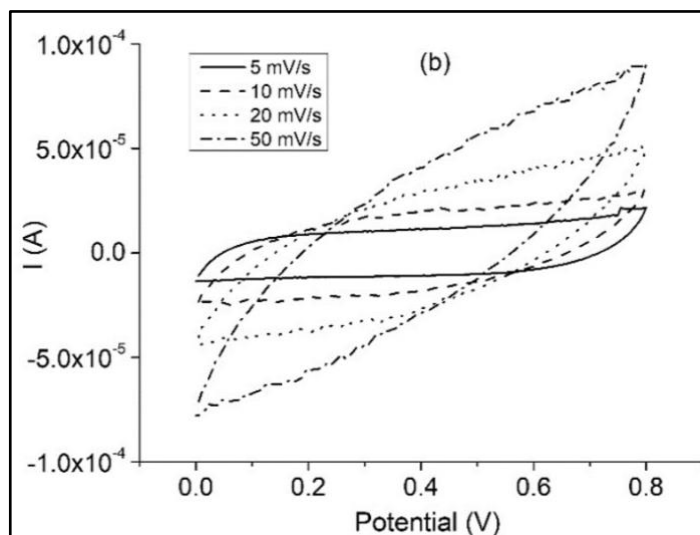


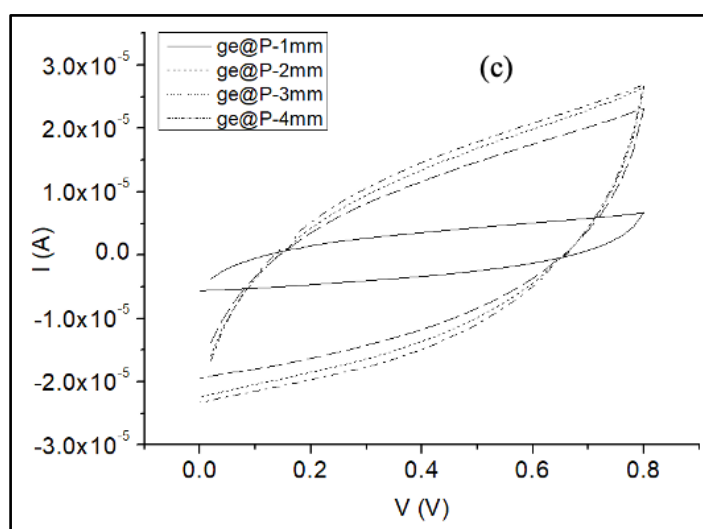
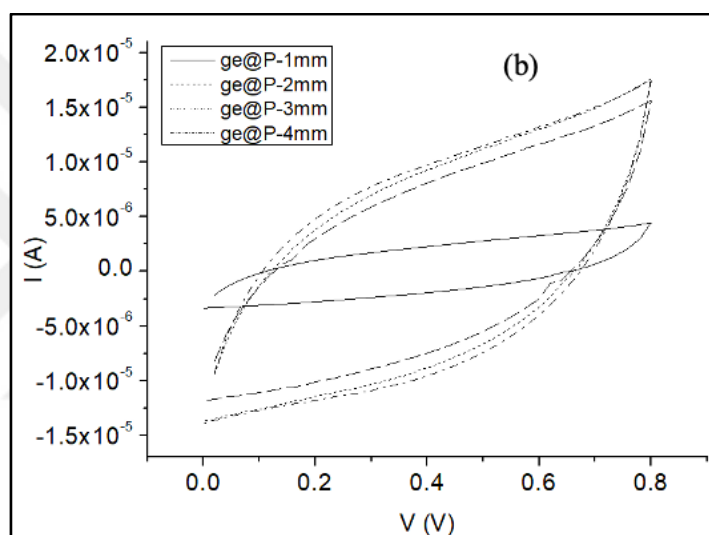
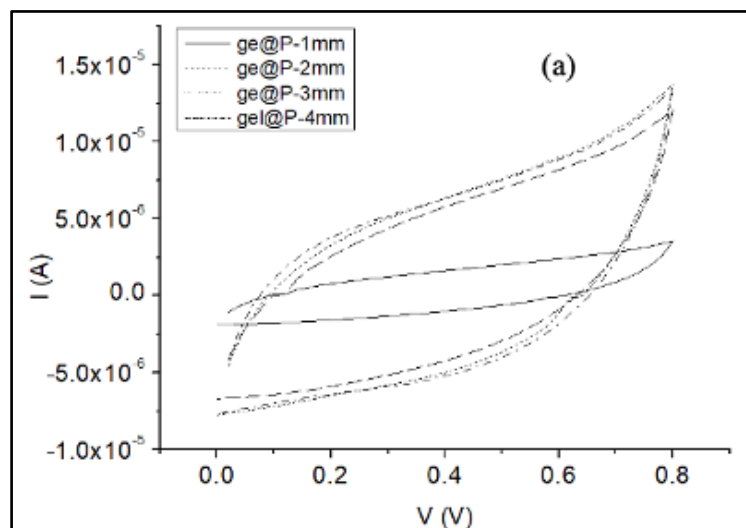
Figure 4.7: CV Curves of a) ge@bin, and b) ge@mix.

The capacitive properties were performed at four different gel thicknesses, as electrochemical performances are given below. Our results demonstrated the comparison of the conventional serial conducted single gel formed SCs, and the binary gel electrolyte included SCs. Thickness experiments were inspected for the 2.5 M PVA - 20 mM of P₄ and 2.5 M PVA - 80 mM of TAAB electrolyte included SCs, ge@P and ge@T for 1 mm, 2 mm, 3 mm and 4 mm. The experiments given below for ge@P and ge@T were referred to CV areas with 5 mV/s scan rates to calculate the capacitances in Table 4.1.

Table 4.1: Specific Capacitance (C_s) Values of the SCs of the Different Thicknesses.

	Specific Capacitance Values of the SCs (F/g) $\times 10^{-3}$	
	ge@P	ge@T
1 mm	45.85	82.90
2 mm	58.86	60.10
3 mm	71.19	39.74
4 mm	79.06	62.17

The CV curves for ge@P and ge@T for four different thicknesses such 1, 2, 3 and 4 mm for 5-10-20 and 50 mV/s sweep rated were presented in Figures 4.8 and 4.9.



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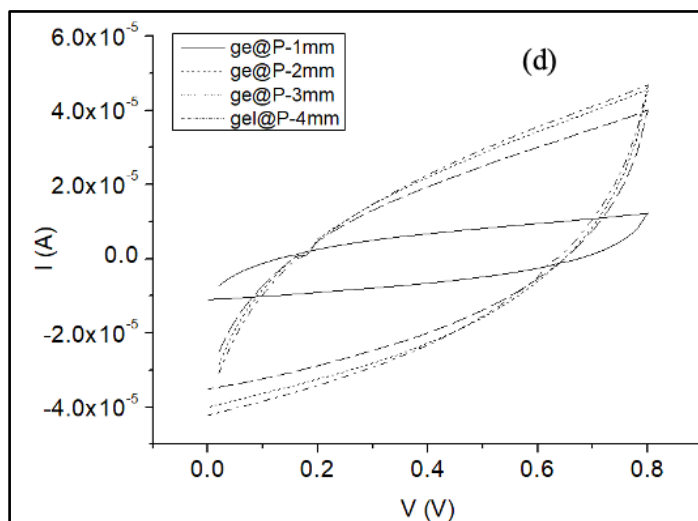
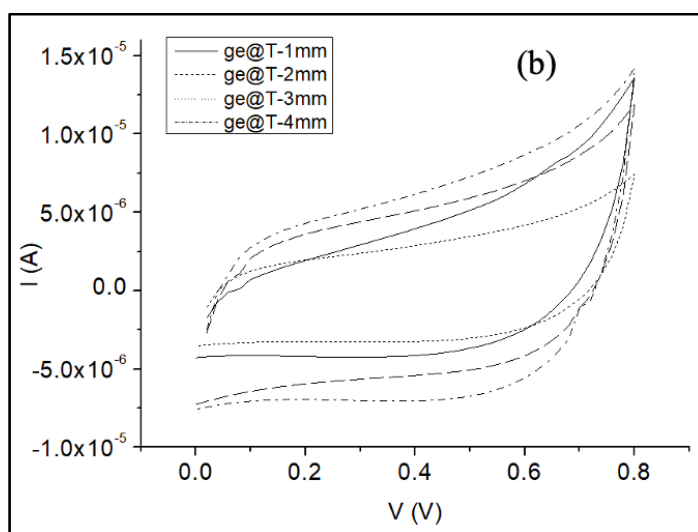
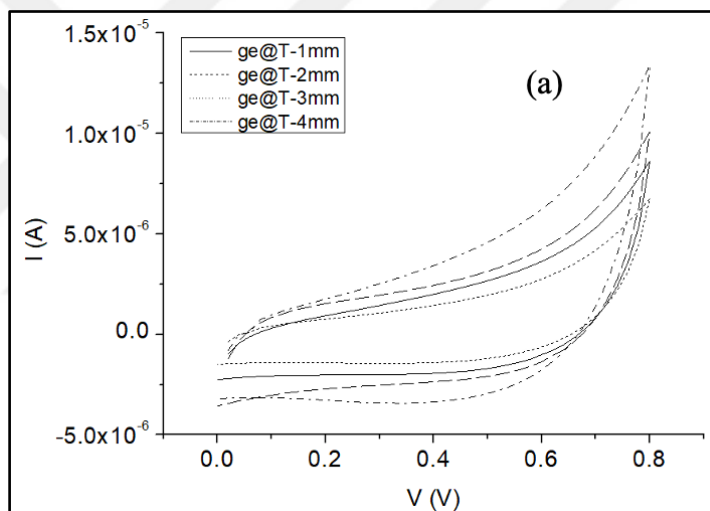


Figure 4.8: CV Curves of Solid Gel Electrolytes at a) 5, b) 10, c) 20 and d) 50 mV/s Voltage Sweep Rate ge@P of Four Different Thicknesses.



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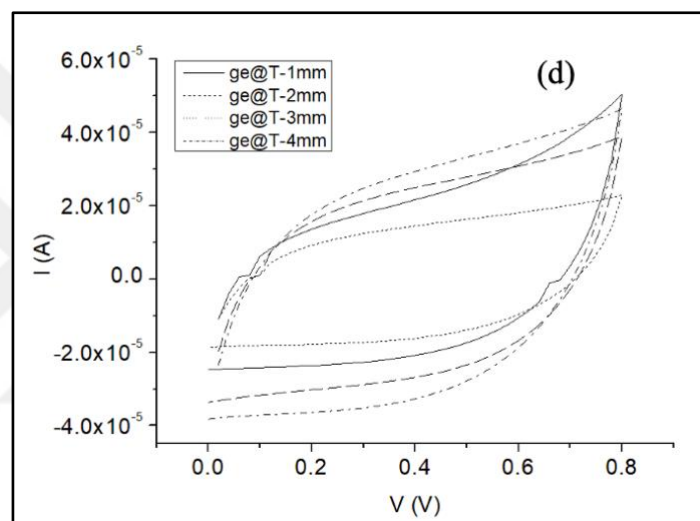
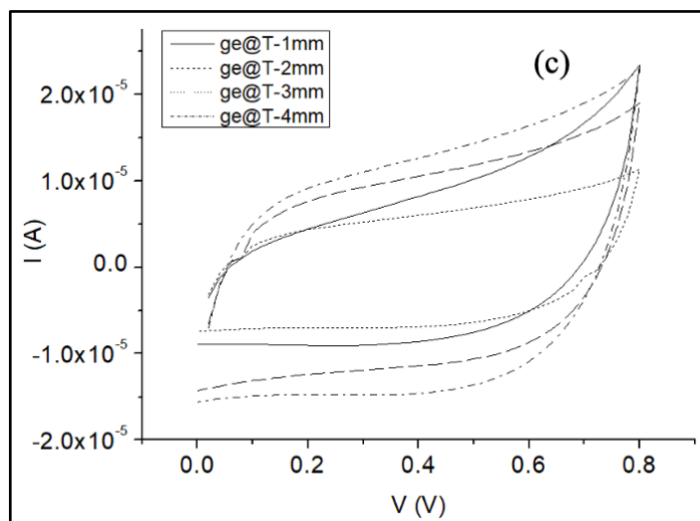


Figure 4.9: CV Curves of a) 5, b) 10, c) 20 and d) 50 mV/s Rated ge@T.

The charge-discharge times of ge@P were nearly equal to ge@bin and ge@mix at 3.90 mA g^{-1} current density as given in GCD graphs, in Figure 4.10. This is obviously seen that P₄ groups are more dominant than TAAB groups.

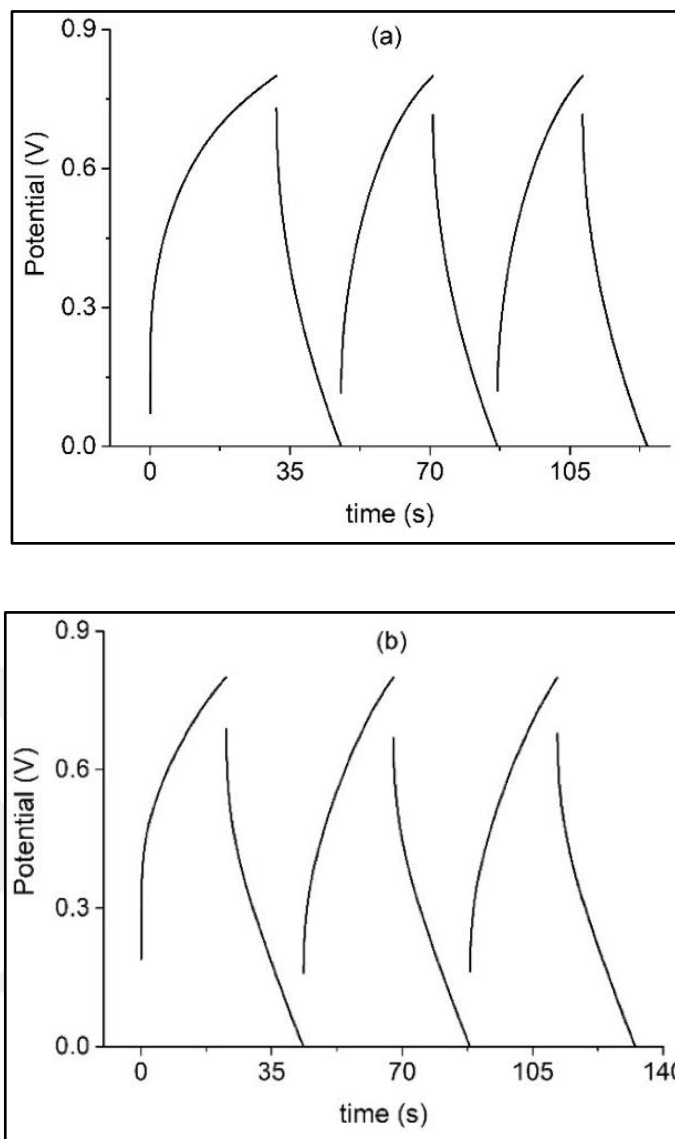


Figure 4.10: GCD Curves of Binary and Mixture SCs a) ge@bin, b) ge@mix.

The discharge curves at 91 mV, 94 mV, 98 mV and 115 mV are used to calculate the δV values as given in Figures 4.3 and 4.8, for ge@P, ge@T, ge@bin, and ge@mix, respectively. The corresponding R_{ESR} were calculated by using Equation 1.4 as 193.6 Ω , 200.0 Ω , 208.5 Ω and 244.7 Ω , respectively. The internal resistances of ge@T were higher than ge@P, ge@bin, and ge@mix, due to the internal structure of loose TAAB molecules, compared to ge@P. The counter ions of TAAB molecules trapped in the denser regions agglomerate due to the hydration.

The specific capacitance, energy and power densities were given in Table 4.2. Specific capacitance, power and energy density were higher at lower current densities, then decreases with the increasing current density. The specific capacitances of ge@T

and ge@bin have lower values comparing to the other SCs. In ge@T, due to the agglomeration, the capacitance decreases at the constant voltage through the limited charge stored. In ge@bin, TAAB gel included layer prevents transport to the efficiently through the electrode. In ge@mix, P₄ molecules prohibits agglomeration and TAAB disperses in the system, then the electrolyte matrix transform into a more open system and the ions can transport easily through the electrodes. This increases the capacitance to the maximum values.

Table 4.2: Specific Capacitance, Power and Energy Values of P₄ and TAAB Based Electrolytes.

	Specific Capacitance (F/g) x 10 ⁻³				Specific Power (W/kg)				Specific Energy (Wh/kg) x 10 ⁻³			
	ge@P	ge@T	ge@bin	ge@mix	ge@P	ge@T	ge@bin	ge@mix	ge@P	ge@T	ge@bin	ge@mix
Current Density (mA g ⁻¹)												
3.90	95.8	6.2	87.0	97.9	1.6	1.4	1.7	1.5	8.5	4.1	7.7	8.7
7.81	54.4	34.4	49.0	63.0	4.0	5.2	4.0	3.9	4.8	3.1	4.3	5.6
15.62	26.7	13.5	19.0	19.0	11.0	11.3	8.3	10.5	2.4	1.2	1.6	1.6

Due to the aggregation of TAAB, the specific energy values of ge@T and ge@bin are lower than ge@P and ge@mix which is the result of trapping ions in the denser regions. However, in the regions where the TAAB molecules near the electrodes, the specific power values are slightly higher. According to the CV and GCD results, the schematic representation of the process is given in Figure 4.11. These conclusions can be summarized as follow.

i. The highly massive host molecules have lower mobility when compared with their counter ions. In addition, the counter ions of the host molecules have a distribution where reach the electrode easily. However, the host molecules can shield some part of the counter ions due to the distribution, especially at high sweep rates as observed in the CV curves.

ii. TAAB molecules agglomerate through different situations in the charge transport process as given in Figure 4.11(b). In the first situation, in the dense regions the counter ions can be trapped and it prohibits their motion under the applied field. This increases the internal resistance of SCs including TAAB molecules. In the second

situation, their effective masses increase significantly, then TAAB molecules move very slowly when compared with their counter ions.

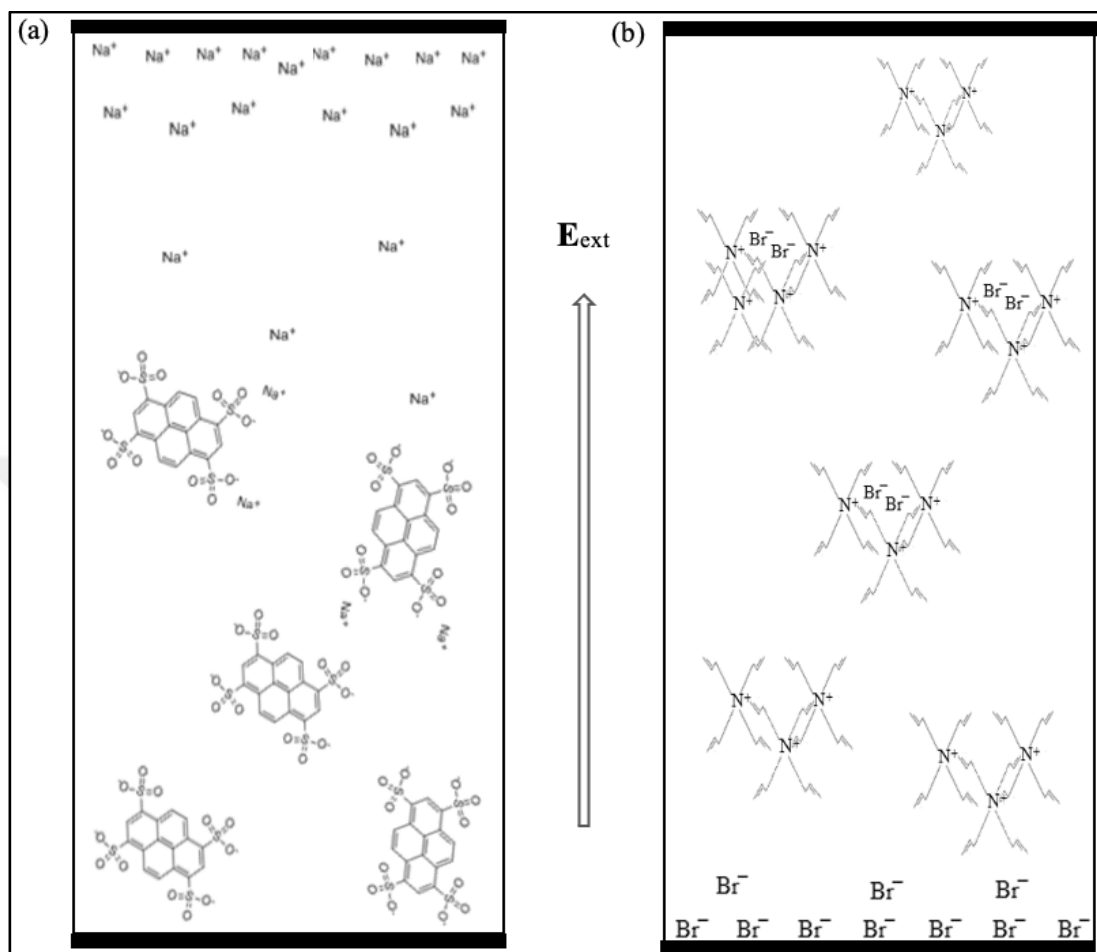


Figure 4.11: The Representation of the Transport in a) $ge@P$ and b) $ge@T$.

The situation in the $ge@bin$ and $ge@mix$ electrolytes can be defined schematically as seen in Figure 4.12. The transport property mostly resembles the property of the $ge@P$ electrolyte with 4 counter ions and hence, P_4 molecules prohibit the agglomeration by struggling the TAAB molecules as shown in Figure 4.12(a). In the binary structure given in Figure 4.12(b) the TAAB molecules again agglomerate in the gel electrolyte. At the interface of $ge@P$ and $ge@T$, some of the ions of P_4^{-4} and $TAAB^{+1}$, can pass through the interface to the opposite sides which results in an induced electric field, E_{INT} , at the interface. As given in this scheme, an opposite and additional charged capacitance is occurred at the interface.

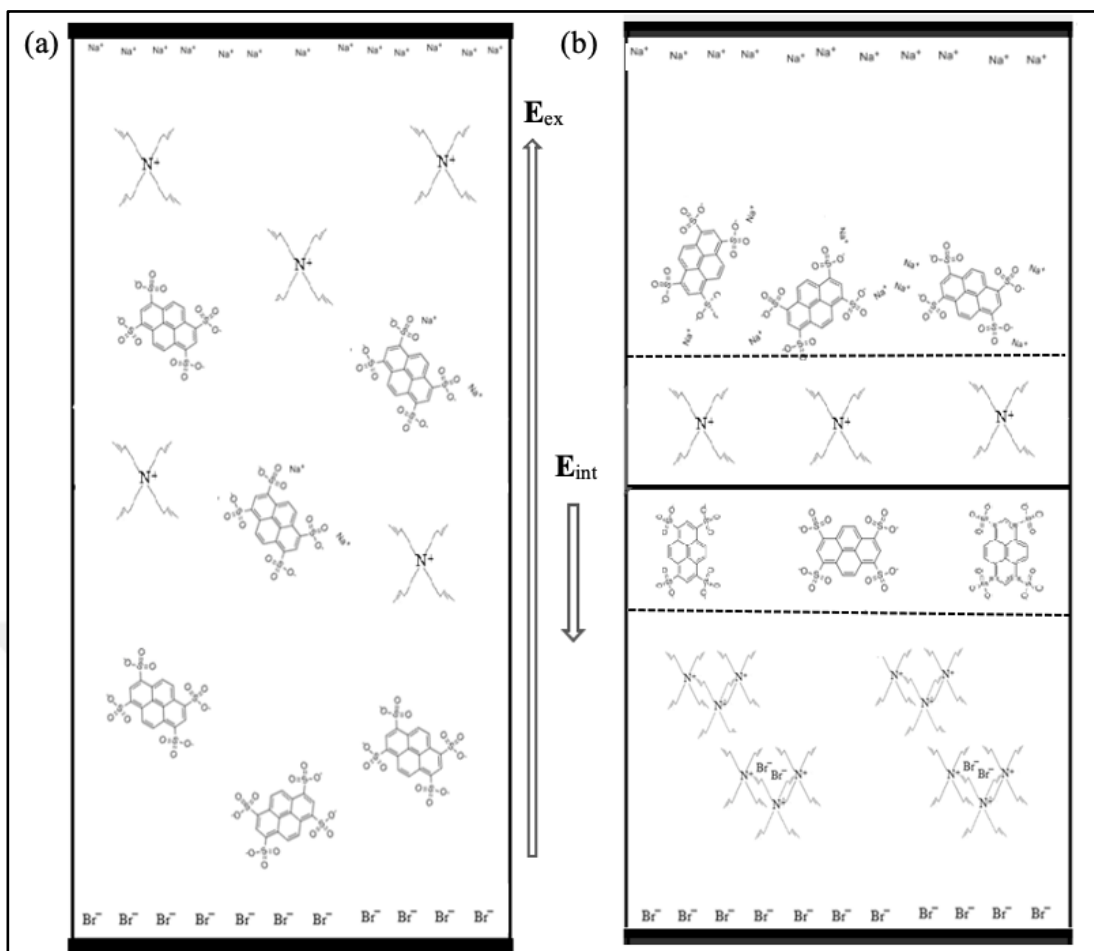


Figure 4.12: The Schematic Representation of the Ionic Transport in a) ge@mix and b) ge@bin Electrolytes.

The fitting model of EIS spectrum was given in Figure 4.13. Two different RC networks with two different time constants at high frequency region was given in Figure 4.15. where the first capacitor represents the charging at the electrodes and the second one, charging at the interface.

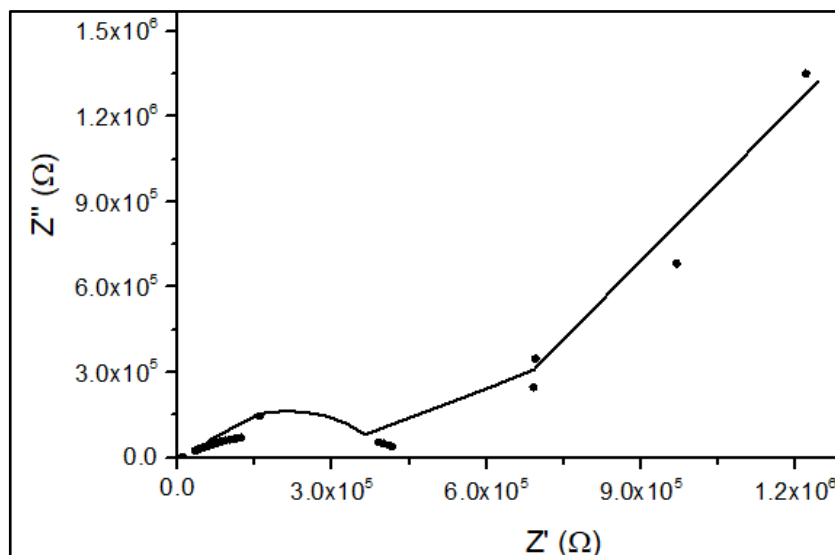
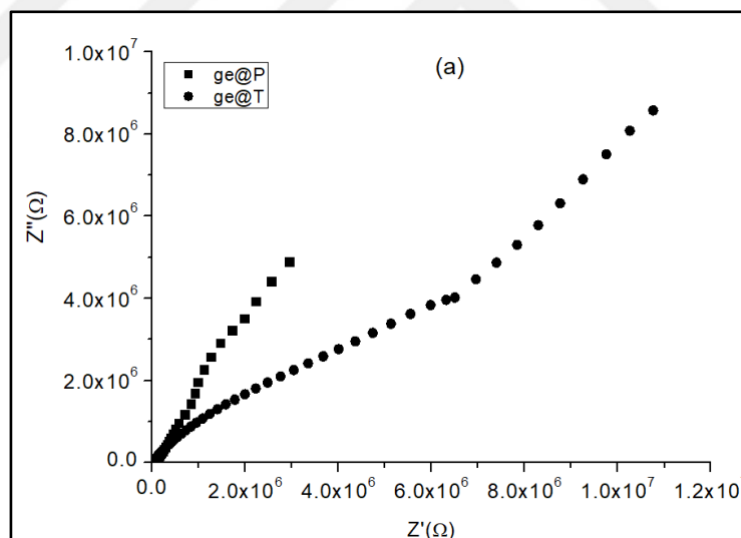


Figure 4.13: EIS Spectrum of ge@bin and Fitting Line of 0.01-100 kHz.

The EIS spectra for ge@P, ge@T and ge@mix in 0.01 Hz to 100 kHz frequency range was given below in Figure 4.14.



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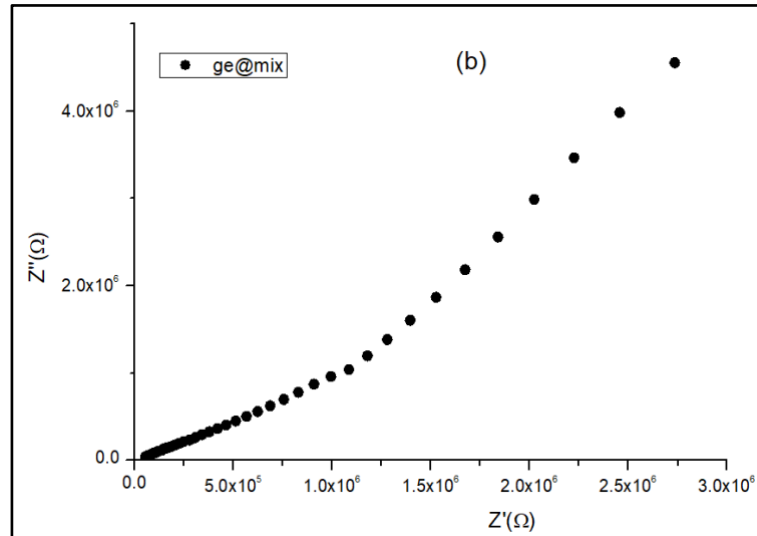


Figure 4.14: EIS Spectrum of a) ge@P and ge@T and b) ge@mix in 0.01-100 kHz Frequency Range.

The components of the Randle circuit were R_{ESR} , R_{INT} as parallel interface resistance, R_{DL} as double layer resistance, W , as warburg element, C_{INT} as interface capacitance and C_{DL} as double layer capacitance, as given below in Table 4.3.

Table 4.3: The Randle Circuit Elements for ge@bin.

The components of the Randle circuit	The values of the components
R_{ESR}	50797
R_{DL}	4.5066 E-11
R_{INT}	3.1513 E05
W	63396
C_{INT}	2.8669 E-11
C_{DL}	3.9328 E-08

The modelling of Randle circuit for ge@bin was given in Figure 4.15. where C_{INT} , C_{DL} , R_{ESR} , R_{INT} , R_{DL} and W were interface capacitance, double layer capacitance, ESR, interface resistance, double layer resistance and warburg element, respectively [97-98].

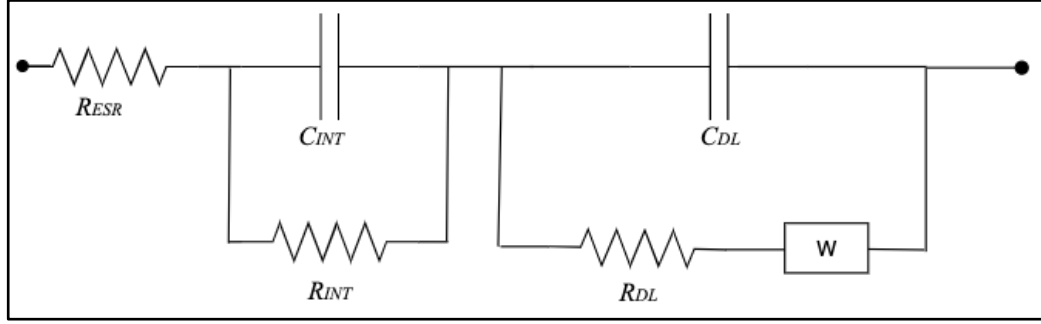


Figure 4.15: The Electrical Model of ge@bin.

The classical Randle circuit was applied to the binary SC system, where C_{DL} is the series equivalent capacitance of ge@P and ge@T electrolytes, respectively. $C_{ge@bin}$ was calculated by using $C_{ge@P}$ and $C_{ge@T}$ as an assumption as given in Table 4.2, it was considered that there was difference between the calculated and the measured capacitances as seen in Table 4.4.

Table 4.4: Specific Capacitance (C_s) Values of the SCs.

Current Density (mA g ⁻¹)	$C_{ge@bin}$ (F/g) × 10 ⁻³		C_{INT} (F/g) × 10 ⁻³
	Calculated	Measured	
3.90	31.2	87.0	48.6
7.81	21.1	49.0	37.0
15.62	9.0	19.0	17.0

The expected capacitance of ge@bin and the measured capacitance are not the same. The reason for not getting the expected capacitance for ge@bin is in consequence of additional capacitance of the interface of ge@P and ge@T electrolytes. In addition, due to the double layer capacitors and the interface capacitor which is charged oppositely, the equivalent capacitance of ge@bin can be calculated by Equation 4.1.

$$\frac{1}{C_{ge@bin}} = \frac{1}{C_{DL}} - \frac{1}{C_{INT}} \quad (4.1)$$

where $C_{\text{ge@bin}}$, C_{DL} and C_{INT} are the capacitances of ge@bin electrolyte, double layer at the interface, and the interface of binary gels, respectively. The capacitance of the single electrolytes; ge@P, and ge@T can be used to calculate C_{DL} .

C_{INT} values were calculated and tabulated in Table 4.4. at different current densities by using single gel electrolytes from Table 4.2. The interface capacitance values of ge@P are bigger than those of devices and nearly equal to ge@T electrolyte. In addition, the calculated capacitance values are higher than $C_{\text{ge@bin}}$ values, where single gel electrolytes, connected in series. As a conclusion; one of the efficient way to obtain higher performance and capacitance values at SCs is using binary gel electrolytes.

The capacitive retention of the SCs was represented in Figure 4.16. As given in the capacitive retention graph, ge@P and ge@bin are more stable than ge@T and ge@mix, due to the looser structure of ge@T, when compared with the ge@P. In addition, the aggregated regions of ge@T and ge@mix may also affect the charging properties of the system, where more ions may be trapped in these aggregated regions as a result of continuous charge-discharge processes.

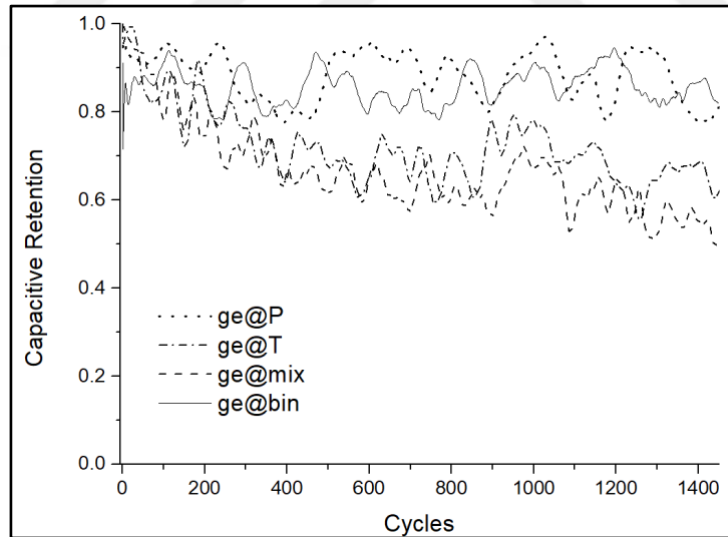


Figure 4.16: Capacitive Retention of SCs upto 1500 Cycles.

As a conclusion; P_4^{-4} and TAAB^{+1} as highly massive host molecules and Na^+ , Br^- as their counter ions were compared to obtain the ionic transportation in the PVA gel electrolyte.

Due to the low mobility, highly massive host molecules decrease the charge stored at the electrodes and cover their counter ions.

In addition, TAAB causes trapping of counter ions in dense regions due to the aggregation and loose structure, without a significant position change during the charge-discharge process. As a conclusion, using binary electrolytes increases the performance of SCs by changing the ion concentration.



5. EFFECT OF CONDUCTIVE LAYER AND ION CONCENTRATION ON THE PERFORMANCE OF PVA BASED GEL ELECTROLYTE FOR SUPERCAPACITORS

5.1. Introduction

Improving the performance of EDLCs by using conductive layer in gel electrolyte is a new approach except long cycle life and high-power and in terms of increasing the conductivity via ionic transport [101].

In this thesis, the effect of conductive layer between binary electrolytes is investigated within a charging mechanism and an electrical circuit model as SCs in series with an external capacitance effect. The binary electrolyte as a solid-state gel polymer electrolyte and the electrode component as graphene and PEDOT:PSS coated nickel was chosen. Polyvinyl alcohol (PVA) based crosslinked binary gel configurations with the doping agents including K^+ and OH^- ions were synthesized in different molarities and put on the two porous nickel bands as electrodes which have been located between the electrolytes to construct the SCs, respectively.

The binary SCs which have not a conductive layer between electrolytes have higher molarities, owing to interface layer with an increasing extra capacitance effect to the whole system, in compliance with the conventional serial connected two capacitor system, as a second serial connected capacitor effect. As given in reference [102], the interaction of metal ions inside the electrolyte increases the electrochemical performance of the SC device, due to its quick electron relay. In the thesis, a conductive nickel plate layer was used to compare the capacitive behaviors, increasing of the energy densities and the electrical circular models with SCs not including a conductive layer between electrolytes. The conductive layer provides an external polarization between two electrolytes in the diffusion plane, in addition to the interface of electrode and electrolyte, which increases the amount of the charge stored due to the external double layer. The ions which are located in the middle of the electrolyte gain mobility and reaches to the edges of the electrolyte [103-105].

Barzegar, Farshad, et al. studied with the binary electrolytes with conductive additives to exhibit a high energy density. In the reference, the mixture of PVA and KOH based electrolytes; carbon black added PVA and KOH based electrolyte and PVA-KOH polyaniline were prepared and with dropping hydrogel electrolytes with AC electrodes and a separator [106].

The results of the proposed binary SCs with and without a conductive layer were compared with each other and single SCs, in higher and lower molarities, respectively.

5.2. Materials and Methods

PVA polymer matrix was crosslinked with glutaraldehyde and HCl as an initiator, and KOH was used as the ionic group to construct the solid-state electrolytes, which were supplied by Merck. PEDOT:PSS and graphene powder was used as the active component to construct the electrode material on porous nickel, which were supplied from nanografi nano teknoloji.

The electrode layer was constructed into two electrode system with the mass of 0.093 g of 0.5 ml PEDOT:PSS and 50 mg graphene powder. The active material was streamed with drop cast method on nickel plates of disc shape of 3.14 cm² surface area and 35 µm thickness. The whole system was annealed at 80 °C for 5 minutes.

The PVA based gel polymer electrolytes were synthesized with 1 g of PVA and 10 ml distill water, then stirred for 4 h and at 60 °C. 900 µl of glutaraldehyde was used to crosslink PVA solution, then stirred for 1 h, at 30 °C. Then 900 µl of HCl was added and stirred for a while. The pre-gel solution was waited for 2 days to obtain crosslinked PVA solutions, then waited in aqueous solutions of KOH at many concentrations, 0.5, 1, 1.5 and 2 M for 2 days to obtain saturated electrolytes as shown in Figure 5.1. The electrolytes of 10 mm, and 1mm of thickness of circular design into 4 pieces for single gels and 16 pieces for binary gels were prepared.



Figure 5.1: PVA-KOH Based Electrolytes, Electrodes and Binary SC.

Single electrolyte including SCs were assembled by putting the electrolyte between electrodes in sandwich form and represented as S1, S2, S3, and S4 where 1 to 4 shows 0.5, 1, 1.5 and 2 M of KOH solutions for single electrolytes. Two different sets of binary SCs were constructed with and without a conductive Ni layer. The binary SCs with a conductive Ni layer between their electrolytes are represented as BC11, BC12, BC13 and BC14. The binary SCs without a conductive Ni layer are represented as B11, B12, B13 and B14. The numbers of 1, 2, 3, and 4 corresponds to 0.5, 1, 1.5 and 2 M aqueous solution of KOH. The PVA based SCs including binary gel electrolytes with a conductive layer were assembled in sandwich form as seen in Figure 5.2.

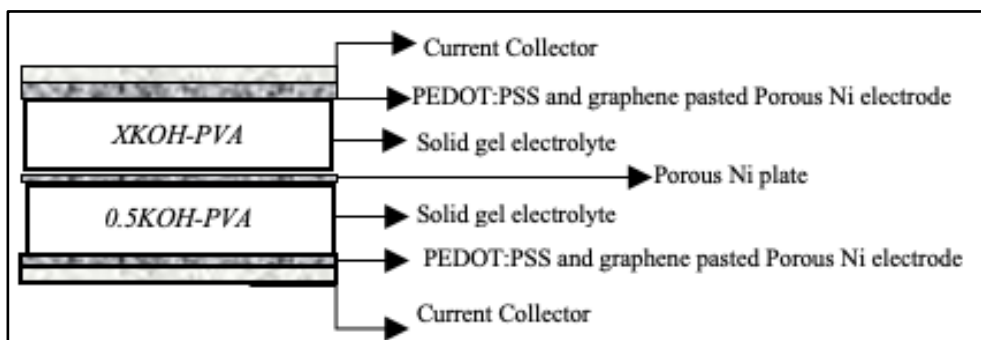


Figure 5.2: The Binary SC with Conductive Layer, where X Shows the Concentration, KOH in the Gel Electrolyte as 0.5, 1, 1.5 and 2 M.

The characterization of SCs were executed with CV, GCD, and EIS techniques by using PS trace potentiostat at room temperature, as seen in Figure 5.3. The electrochemical performance of the system was measured with sweep rates of 100, 50, 10 and 5 mV/s, and in the range of 0-1 V for CV analysis. Then, the GCD experiments were analyzed at 2.15 mA g^{-1} current density for time scale in second units. For EIS, with a 0.01V amplitude of 10^{-2} to 10^5 Hz frequency range was applied to the SCs. SEM analysis were taken by using Quanta FEG 250 Field Emission.



Figure 5.3: PS Trace Potentiostat.

5.3. Results and Discussions

SEM analysis of the electrode which was prepared with PEDOT:PSS and graphene powder on nickel plates. In the SEM analysis, the dark areas correspond PEDOT:PSS and the light areas represents graphene parts, as shown in Figure 5.4.

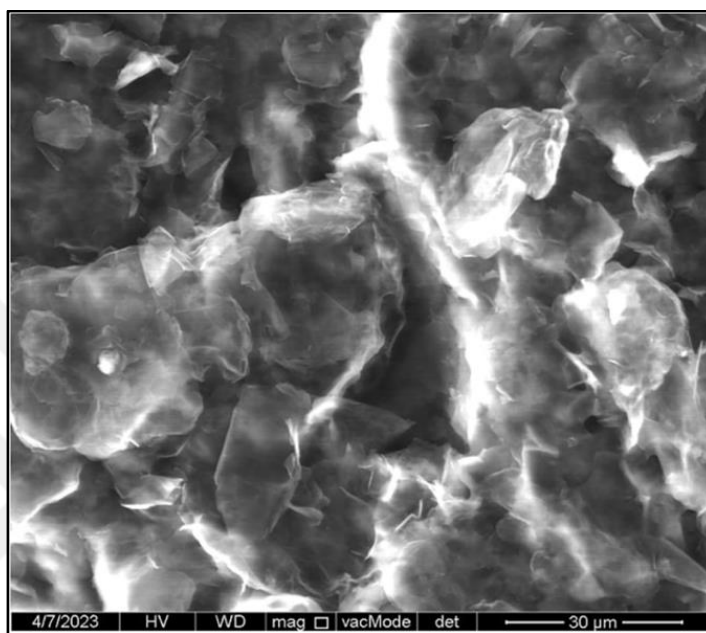


Figure 5.4: SEM Image of the Electrode Used in the SC Assembly.

The CV curves of SCs, which are including single electrolytes, S1 to S4 were presented in Figure 5.5. which show similar behaviors, resembled mainly the properties of EDLC character [107]. The CV area and the current values gradually increase, due to the more ions contributing to the charging process, with the increasing concentration of the KOH solutions.

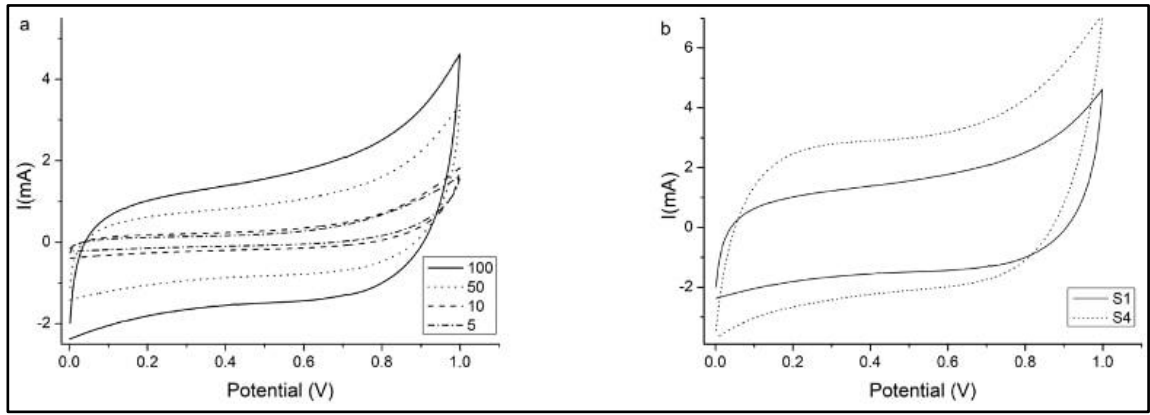


Figure 5.5: CV Curves of Single SCs a) S1 for 100, 50, 10 and 5 mV/s Voltage Sweep Rates, b) S1 and S4 for 100 mV/s Voltage Sweep Rate.

The CV curves of binary solid gel electrolytes without a conductive layer included SCs, B11 to B14 were shown in Figure 5.6.

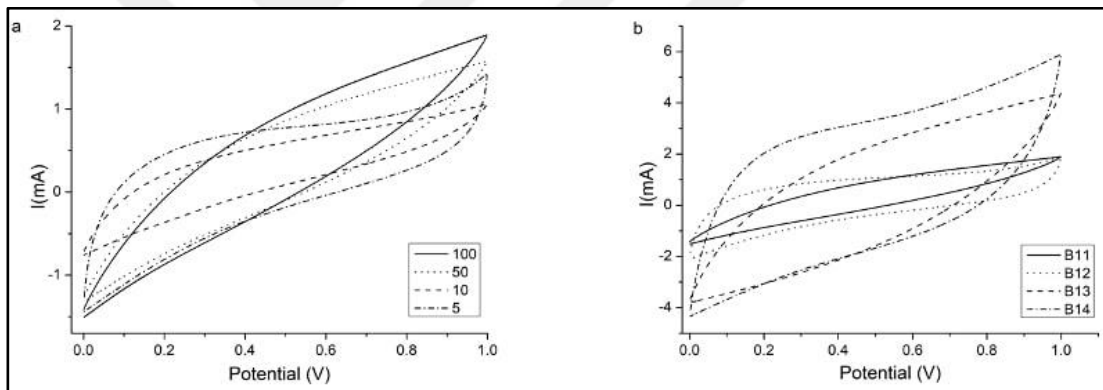


Figure 5.6: CV Curves of Binary SCs Including a Conductive Layer for Different Configurations a) B11 for 100, 50, 10 and 5 mV/s Voltage Sweep Rates, b) B11 - B14 for 100 mV/s Voltage Sweep Rate.

The CV curves of the binary SCs with a conductive layer between electrolytes BC11 to BC14 were given in Figure 5.7. The CV curves of the binary SCs all have EDLC properties similarly with the other configurations, and with the increasing KOH concentrations their CV areas gradually increases.

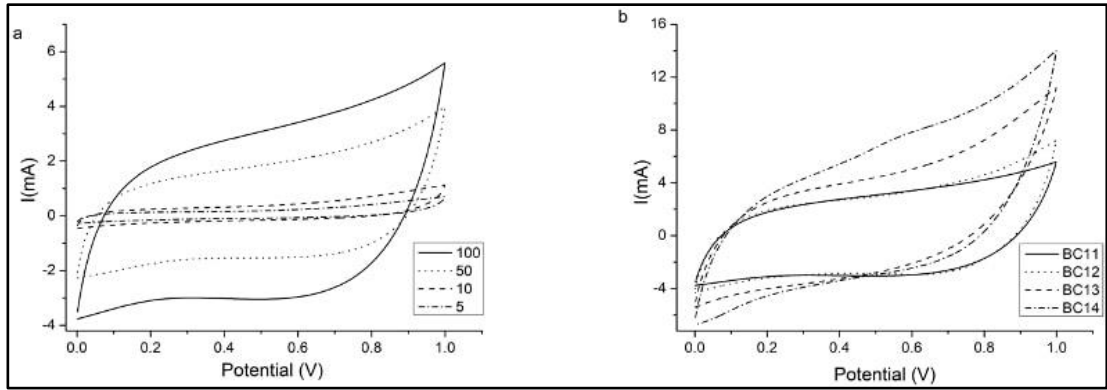


Figure 5.7: CV Curves of Binary SCs which have a Conductive Layer. (a) BC11 for 100, 50, 10 and 5 mV/s Voltage Sweep Rates, (b) BC11- BC14 for 100 mV/s Voltage Sweep Rate.

The comparison between the CV curves of the highest concentration included SCs, S4, B14, and BC14 was shown in Figure 5.8. The current levels decreased for the highest molarities of binary SC which is not including a conductive layer, B14 when compared with the highest molarities of single SC, S4. This is mainly concerned by an additional electrolyte between electrodes, due to the increasing internal resistance. This is also verified by the capacitance values presented in Table 3.2 where the capacitance values of binary SC, B14 are lower than single SC, S4 and binary SC with a conductive layer, BC14. Additionally, it is obvious that the CV areas and the current values are the highest for the highest concentration of binary SC with a conductive layer, BC14, comparing to S4 and B14. This is possible due to the additional charging at the gel-conductive layer interface of the binary gel electrolytes as presented in Table 3.2.

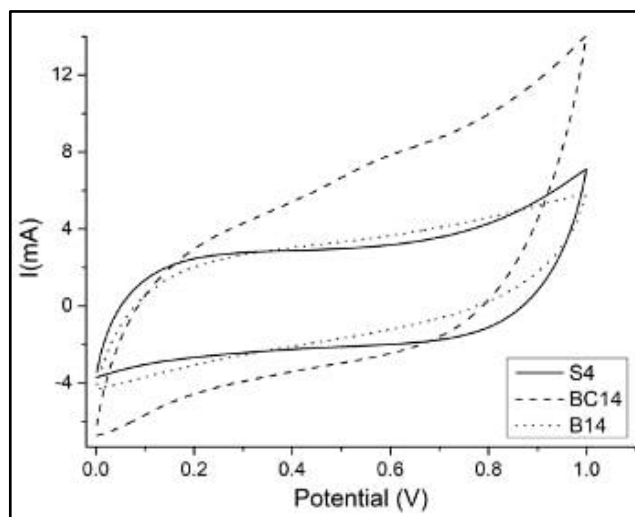


Figure 5.8: CV Curves of SCs with the Highest Molarities of Solid Gel Electrolyte Including S4, BC14 and B14 at 100 mV/s Voltage Sweep Rate.

The transport of the ions with an additional charging can be seen as sketched in Figure 5.9. Here, the system constructs an additional double layer due to the accumulation and the electrostatic interactions of the ions on the both sides of the conductive layer. This additional conductive layer contributes to the equivalent capacitance of the capacitor by total charging in the process [108-110].

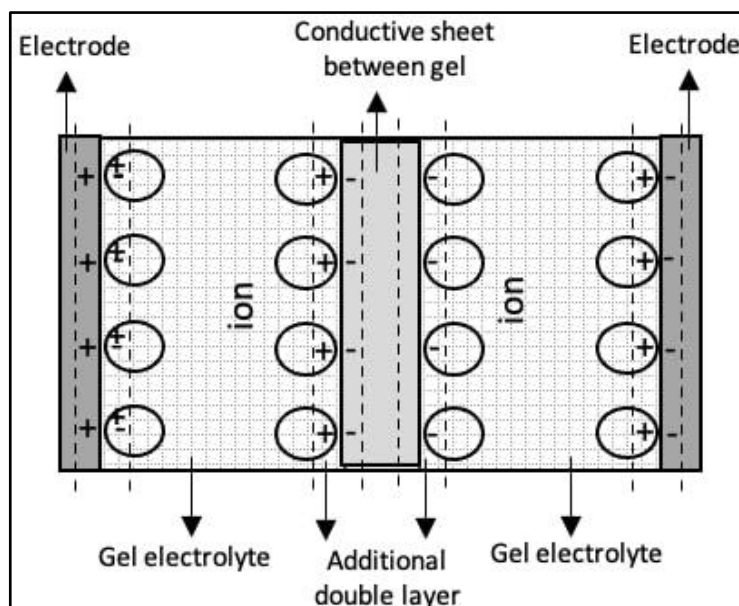


Figure 5.9: The Transport of the Ions with an Additional Double Layer.

The GCD curves for 2.15 mA g^{-1} current density of the single and binary SCs with and without conductive layer between the electrolytes were shown in Figure 5.10. The GCD curves have a triangular shape, resemble mainly the properties of EDLC character. The charge-discharge time of both types of SCs increases with the increasing concentration of the ions as seen in the graphs. Here, the results clearly show that, more time is required for the interaction of more ions with the electrode, as expected [111]. Additionally, due to the thickness of the binary electrolyte form, BC1Xs have higher IR drops when compared with SXs.

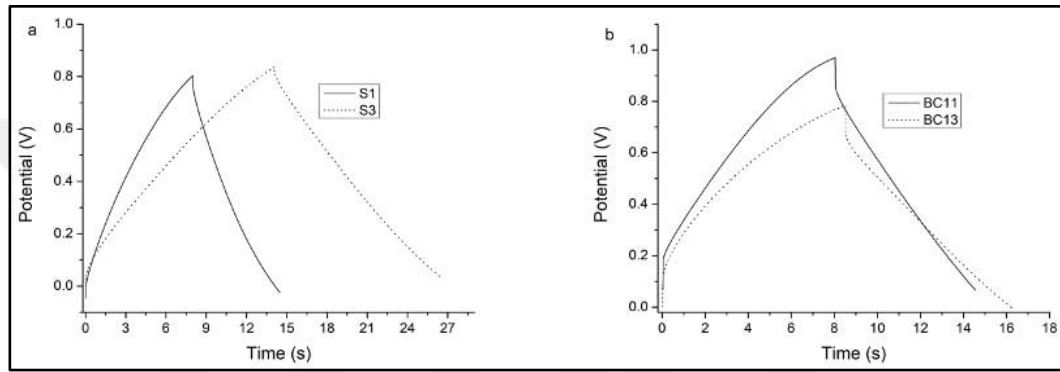


Figure 5.10: GCD Curves of a) S1 and S3, b) BC11 and BC13.

EIS analysis of single SCs; S1, S3 and binary SCs with a conductive layer; BC11, BC13 were taken between 10^{-2} to 10^5 Hz. The EIS graphs were given in Figure 5.11. Semicircle contours of single and binary SCs are both visible that indicate a RC network in the system. Additionally, the contour shapes of BC11 and BC13 diverge in little scales from semicircular, due to an additional RC network of the conductive layer between the electrolytes. After adding a second RC network, the best fit was obtained as given in the fitting of the EIS data in Figure 5.11(b). The changes in R_{ESR} , and, R_{CT} as charge transfer resistance depend on the increasing ionic concentration as clearly shown in the spectra, while the decreasing R_{ESR} and increasing R_{CT} are observed, as expected. By the increasing concentration of the ions, the ionic conductivity enhances and due to the higher ion population on the electrode-electrolyte, [112] transfer the charges need much more energy which is resulted in increasing of R_{CT} .

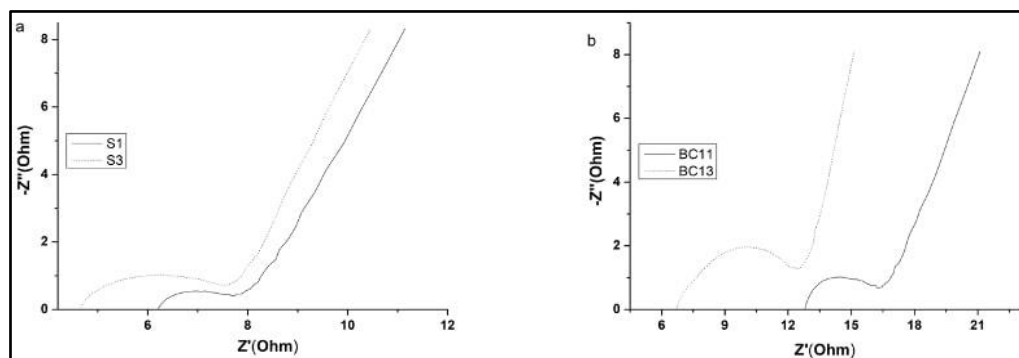


Figure 5.11: EIS Curves of Single SCs, a) S1 and S3 b) BC11 and BC13.

The randle circuits used for modelling SCs are given in Figure 5.12. Here, R_{ESR} , R_{DL} , R_{INT} , W , C_{DL} , and C_{INT} , are ESR and parallel, interface, double layer resistance and capacitance, and warburg term.

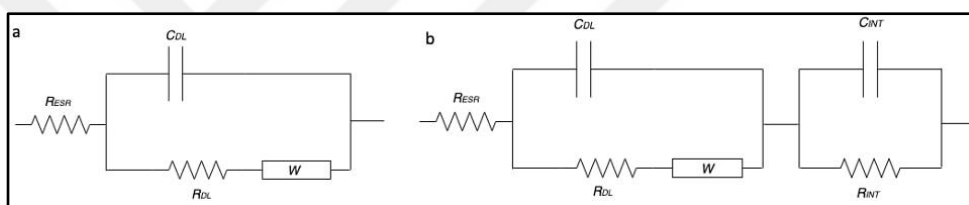


Figure 5.12: Electrical Circuit Model for the (a) SXs (b) BC1Xs.

The parameters obtained from fitting were given in Table 5.1. The internal resistances are higher for binary SCs and shows a decreasing behavior when molarity of KOH solution increases in electrolyte solutions.

Table 5.1: The Values of the Randle Circuit Components for the Single SCs, S1 to S4, the Binary SCs with a Conductive Layer, BC11 to BC14, and Binary SCs without a Conductive Layer, B11 to B14.

	$R_{ESR} (\Omega)$	$R_{DL} (\Omega)$	$R_{INT} (\Omega)$	$W (\sigma)$	$C_{DL} (\mu F)$	$C_{INT} (\mu F)$
S1	6.2	0.5	-	18.1	22.0	-
BC11	12.8	1.1	1.1	18.5	30.0	10.0
S2	4.6	1.2	-	25.5	24.0	-
BC12	11.9	1.0	2.0	27.0	40.0	10.0
S3	4.7	1.6	-	28.5	27.0	-
BC13	6.7	1.0	2.2	30.0	45.0	16.0
S4	6.3	1.9	-	55.0	30.0	-
BC14	5.3	1.5	2.5	60.0	55.0	20.0

SX and BC1X were fitted with the model as given in Figure 5.11. There is an extra charging mechanism when compared with SX, which were fitted as given in Figure 5.11 (b), therefore systems have not R_{INT} and C_{INT} elements in the RC network. The capacitance, energy and power densities were tabulated in Table 5.2. The specific capacitance values increase as the ionic concentration is increased as expected and generally BC1X series capacitors have minimum values.

Table 5.2: Specific Capacitance (C_s), Specific Power (P_s) and Specific Energy (E_s) Values of the Single SCs, S1 to S4, Binary SCs without a Conductive Layer, B11 to B14, and Binary SCs with a Conductive Layer, BC11 to BC14.

	Specific Capacitance (C_s) (F/g)		Specific energy (E_s) (Wh/kg)		Specific power (P_s) (W/kg)	
	5 (mV/s)	100 (mV/s)	5 (mV/s)	100 (mV/s)	5 (mV/s)	100 (mV/s)
S1	7.9	3.4	1.1	0.4	697.5	279.0
B11	7.9	0.8	1.0	0.1	1511.2	167.4
BC11	6.9	5.9	0.9	0.8	669.6	585.9
S2	12.3	3.9	1.7	0.5	1046.2	348.7
B12	8.8	1.5	1.1	0.2	697.5	139.5
BC12	8.4	6.1	1.1	0.8	1395.0	976.5
S3	17.5	4.9	2.4	0.6	878.8	251.1
B13	12.7	3.4	1.7	0.4	895.1	244.1
BC13	10.5	6.9	1.5	0.9	906.7	558.0
S4	19.7	5.4	2.6	0.8	962.5	292.9
B14	17.9	5.1	2.4	0.6	1104.3	313.8
BC14	12.4	9.4	1.7	1.3	1046.2	837.0

This is due to the additional capacitor at the conductive layer interface which is connected as series to the double layer capacitor. The specific energy values also change similar to the specific capacitances. On the other hand, the specific power densities of BC1Xs are higher than those of other configurations especially at high sweep rate which is due to the fast discharge.

The obtained values of the specific capacitance increase with the higher molarities of the electrolyte solution and as shown in Table 5.2. There are a few major effects on the energy density and capacitance value of SCs, which are properties of the electrode and electrolyte and the concentration. The double layer thickness which increases the capacitance of the SC depends on concentration of the electrolyte and the size of ions [113]. The conductivity of KOH solution increases with the concentration and becomes maximum in an average molarity, then decreases when it reaches to the higher molarities as reported by Gilliam et al [114]. The ionic transport can be easier

as if the electrolyte concentration is higher. The concentration of electrolyte is depended on the ionic mobility.

In EDLC based SC systems, a double layer effect occurs between the surfaces of the electrode-electrolyte layer and results in a capacitance of C_{DL} . The solid-state gels that form the electrolyte structure of our binary system and the interface gel that causes C_{INT} , which is located between the two gels. Ions into the electrolyte move through the electrical field after the charge transfer in the system. The electrical model of the binary SCs, can be constructed by adding an additional capacitance, C_{INT} and a warburg (W) -impedance- element due to the diffusion effect in the system. The capacitance, C_{INT} , was named as interface capacitance which occurs at the contact point of two different gel electrolytes with a conductive layer, which was added as series to the double layer capacitance.

Therefore, it can be clearly shown that the warburg impedance occurs in single and binary SCs by diffusion differences regarding to the mobility of molecules in the system, W impedance element is also including in the circuit.

In order to construct an experimental electrical model of the binary SCs which have a conductive layer between electrolytes, different group of molarities were synthesized and compared the specific capacitance, energy and power values of the single and binary SCs. Our results demonstrated the comparison of the conventional single gel formed SCs, and the binary SCs. According to our experimental model, the capacitance values reveal that, moreover, in compare with the conventional SC system, then the interface layer makes an increasing extra capacitance effect for the binary SCs with a conductive layer.

The effect of conductive layer between binary electrolytes is investigated within a charging mechanism and an electrical circuit model as SCs in serial with an external capacitance effect with C_{DL} and C_{INT} capacitances. Within the scope of our research, the configuration and the relation of the binary electrolyte of the system with the doping agents including K^+ and OH^- ions in different molarities are demonstrated.

The binary SCs which have not a conductive layer between electrolytes have higher molarities, owing to interface layer with an increasing extra capacitance effect to the whole system, in compliance with the conventional serial connected two capacitor system, C_{DL} and C_{INT} , as a second serial connected capacitor effect. As given in reference [115], the interaction of metal ions inside the electrolyte increases the electrochemical performance of the SC device, due to its quick electron relay. In this

thesis, a conductive Ni plate layer was used to compare the capacitive behaviors, increasing of the energy densities and the electrical circular models with SCs not including a conductive layer between electrolytes. The conductive layer provides an external polarization between two electrolytes in the diffusion plane, in addition to the interface of electrode and electrolyte, which increases the amount of the charge stored due to the external double layer. The ions which are located in the middle of the electrolyte gain mobility and reaches to the edges of the electrolyte [116-117].

In the case of adding a conductive layer between the gels, the system gains an external mobility, then the capacitance values increase. In comparison with binary structural SCs, the redox active material in the gel structure interacts with conductive layer and occurs an extra charging [118].



6. CONCLUSION

Energy storage technologies are widespread in the deployment of renewable energy sources, replacing with battery technology, that deliver a large energy in a short time [119]. SCs are a growing field in energy storage from past to future through the global economy and the urban living standards, so it will be important in the future. SCs are one of the most promising choice with high efficiency, stability, and environmentally friendly properties [120]. The SCs were supposed to give many applications to hybrid electric vehicle. As SCs market grows into effective and practical appliances, demanding high power; such; electric vehicles and robot with possibilities of bridging the power-energy gap [121-123]. SCs help improving air quality and reducing pollution. SCs are going to replace batteries by many applications such as; memory backup systems in computers, portable consumer electronics, hybrid vehicle brakes, and wind turbines [24, 124-126]. SCs have the unique ability with providing a large amount of compatibility with renewable energy sources such cyclical nature of wind, solar, and wave type systems in order to replace fossil fuels.

In this thesis, binary solid gel-based electrolytes with PVA as a polymer matrix and P_4 , TAAB and KOH as ionic solutions were synthesized to design SCs into different compositions. The counter ions and their massive host molecules P_4^{-4} and $TAAB^{+1}$ were analyzed to investigate the effect of binary electrolyte structure, ionic transport and charge storage properties.

The mobility of functional groups into the polymer matrix evaluated to pointed out the massive ions, and the thickness of electrolytes, agglomeration of the host molecules and the binary configurations. The binary electrolyte included SC was compared to single and mixture electrolyte included SCs where host molecules P_4 and TAAB are massive and edging a part of the counter ions. The agglomeration of TAAB cause different charge transport situations, such; trapping counter ions in dense regions and provides motion of the counter ions and their effective masses and the internal resistances increase considerably and move slowly compared to the counter ions [80, 87]. The reference electrolyte including $K^+ + OH^-$ ions have mobility more than $P_4^{-4} + Na^+$ and $TAAB^{+1} + Br^-$.

In addition, binary solid gel-based electrolytes with crosslinked PVA based polymer matrix and KOH as ionic solutions were synthesized to design SCs in

different molarities and structures. The effect of conductive layer between binary electrolytes with the doping agents including K^+ and OH^- ions was investigated in order to understand the charge storage properties that occurring additional charging and the ionic transport relation due to the mobility.

The binary SCs which have a conductive nickel layer between electrolytes have an increasing extra capacitance effect to the whole system. BC1Xs (SCs including binary electrolytes with a conductive layer) have the maximum capacitance comparing with the SXs (SCs including single electrolytes) and B1X (SCs including binary electrolytes without a conductive layer) systems. The interaction of metal ions inside the binary electrolyte increases the electrochemical performance due to its quick electron relay. The conductive layer in the diffusion plane provides an external polarization between binary electrolytes to gain mobility with the ions which are located in the middle of the electrolyte, in addition to the interface of electrode and electrolyte (Helmholtz plate). The conductive layer provides ionic transport easily through the electrodes which makes the structure of the electrolyte more open and causes additive capacitance leading to an effective building-up for double layer.

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AUTOBIOGRAPHY

Tuğçe Pınar Öztürk has finished her primary education and high school in Istanbul. She has graduated from Kocaeli University, department of physics for undergraduate program and Istanbul Technical University, department of physics engineering for master program. In 2015, she has started PhD at Gebze Technical University and Istanbul Technical University with her co-advisor through the thesis studies. She has been working in corporate companies on international funding projects at Turkcell and Is Bankasi and Arcelik. Concurrently, she has been studying on experimental physics, specifically on energy storage devices, supercapacitors in Istanbul Technical University physics laboratory.

APPENDICES

Appendices A: Publications within the Scope of Thesis

Öztürk, T. P., Gelir, A., Keshtiban, N. A., Yargı, Ö., Özdemir, O. B., Mucur, S. P., & Seçgin, A. (2023). Synthesis and characterization of PVA-based binary-gel electrolytes including massive ions. *Journal of Solid State Electrochemistry*, 1-10.

