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Reverse Engineering Supercapacitors

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Abstract

Along with the rapid development of renewable energy, the energy storage technologies have drawn great attention by the researchers and public, since such technologies could play an important role in regulate and control the renewable energy especially for the one connected to the grid network. At present, one of the most popular energy storage technologies is the lithium battery which have been widely used around world, where the Tesla house battery is a typical application project. On the other hand, a supercapacitor (SC) is like the battery but with a higher charge and discharge rate. There are some categories of SC available in the market. Hence, it is interesting to explore the operational principles of such SC and explore the possible of such SC to replace the traditional lithium battery for renewable energy storage. In this project, different category of SCs are systematically studied in terms of their materials, structures and electrical performance through the related experiments and simulation. Moreover, financial analysis between these SC and traditional battery was carried out to further study the tech-eco feasibility of these SC for renewable energy storage system. Based on the results, it is concluded that it is difficult for SC to completely replace the traditional battery for renewable energy mainly because the energy density of supercapacitors is too small to store much energy per unit volume. A hybrid system including the SCs and batteries with both of their advantages is expected to be one of the promising technologies for the renewable energy storage in the future.

Keywords: Supercapacitor, graphene electrode, renewable energy storage system, lithium battery, Tesla battery station.

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Chapter 1 Introduction

Nowadays, human society is developing rapidly especially after the industrial revolution since 18th century. The discovery and utilization of fossil fuels like coal, oil and natural gas make the power generation involve into the people's daily life normally through the form of electricity. However, such resources have several obvious drawbacks like non-renewable and pollution generation. The concept of renewable energy technologies including wind energy, solar energy and ocean energy were hence proposed and have been developing for several decades to solve such problems. The renewable energies also have their own intrinsic restrictions like uncontrollable (e.g. PV farm power output strongly depends on the actual solar irradiation), unpredictable and limited operation time (e.g. PV farm can't work at night, wind farm can't work at too low or high wind speed or air density). The energy storage technology could store the excess generated energy and power the load when insufficient power appears for renewable energy power system, which is an important method to overcome the above restrictions. The lithium batteries are one of the dominated energy storage technologies around the world at present, where a certain amount of lithium battery stations have been established to adjust the local grid with proportional of renewable power generation. However, the lithium battery still has some limitations or drawbacks like high expense, safety is poor and there is a danger of explosion and high production requirements. The newly developed supercapacitors (SCs), also known as ultracapacitors (UCs) or electric double-layer capacitors (EDLCs), are expected to partially replace the role of traditional lithium batteries in energy storage since the SCs have unique advantages in contrast to the lithium batteries. For example, the SCs are able to store a large electrical capacitance in a limited volume with a long operational cycle lifetime. They can be repeatedly charged and discharged hundreds of thousands of times with a short charge and discharge time (or high charge and discharge rate) Moreover, the SCs have good ultra-low temperature characteristics and high current discharge capability. Therefore, it is important and essential to explore the electrical performance of SCs with different manufacturers under a various of operation conditions like temperatures and humidity.

At the stages of energy generation, transmission and utilization, it often exists a trade-off between power supply and demand in terms of energy quantity or amount, form and time offset. Such differences will significantly affect the utilization efficiency of the power. In order to compensate these differences, the effective utilization of energy often requires an artificial control process to intentionally store and release energy via a series of technologies like energy storage techniques. In general, the energy storage technologies can be classified into three major categories including mechanical energy storage, electro-chemical energy storage and electromagnetic energy storage [1]. The battery energy storage technology belongs to a kind of chemical energy storage, with characteristic of ease for storage and transportation, which has been widely used around world.

At present, the most common used batteries are lithium batteries, which are widely used in, wind, solar and other renewable energy power systems. Such batteries are also widely used as the power tools, electric transportation, military equipment, aerospace, electric vehicles and many other fields. However, the safety of lithium galvanic batteries is relatively poor, resulting in a risk of explosion and other safety hazard. The lithium-ion battery of lithium cobalt acid cannot discharge at a large current with high expense and relatively poor safety. For such batteries, the cables must be well protected to avoid external short circuit potential and prevent over charge/discharge rate. Normally an outstanding performance of lithium battery means a relatively high expense with limited use condition (i.e. limited operational temperature). The purpose of this thesis is to investigate whether SCs is an appropriate candidate as new type of energy storage device, or even as an alternative to renewable energy savings and whether it is possible to create a better and cheaper alternative to a Tesla house battery if we put a certain amount of (e.g. 200 pieces) SCs together. It is also interesting to explore the working principles of SCs under different operation conditions.

1.1 Motivation

The lithium battery is the basic unit for most of house batteries nowadays. But the high internal resistance and low power density of such battery makes it less effective in electrical performance and overall cost performance. On the other hand, lithium is a hazardous and toxic metal material, making the disposal of them maybe more expensive and dangerous than the other batteries. All above prompt people to seek a substitution product of traditional lithium battery.

The supercapacitor is thus expected to play an important role in renewable energy storage due to its unique advantages including ultrahigh power density, long cyclic lives, high cost performance and high reliability and safety. The supercapacitor is an energy storage device with features both of capacitor and battery. It has the characteristics of the capacitor which can be charged and discharged quickly and also could store the energy like battery. From the perspective of environmental protection, the fabrication materials of supercapacitor are environmentally friendly, non-toxic and low hazard. Therefore, it is essential and interesting to explore the feasibility and benefits of the substitution of supercapacitor for the traditional lithium battery. If this substitution is feasible, then the related environmental pollution, disposal cost and other financial cost will be reduced to a certain extent.

1.2 Aims of Thesis

This project aims to investigate the characteristic of various types of SCs under different operational conditions and explore whether a cluster of the tested resulting best capacitor can be used as an alternative to a Tesla house battery using lithium batteries typically. The details of methodology, results and discussion will be presented herein.

1.3 General Background

The Tesla house battery is a lithium battery typically which is most commonly used as a household battery these days. Indeed, it provides a good quality power supply but lithium is a hazardous and non-biodegradable chemical substance that have fewer charging and discharging cycles, and a short lifespan [2]. Due to rising concerns towards the environment, as human demand gradually increases, a more environmentally friendly, cost-effective and better performance substitution should be discovered. The SCs seems to be able to satisfy this point as it is a non-hazardous recyclable power storage device, which has abundant desired characteristics. The advantages of such SCs involve high power density, short charging time, higher depth of discharge performance and long lifespan.

The SCs, also known as electrochemical capacitors, become increasingly popular energy storage systems in recent years. It can be thought as a hybrid system consisting of a regular capacitor and a battery, which have completely different functions from each other. The SCs have positive and negative electrodes impregnated to the electrolyte separated by a membrane separator, where the membrane separator only permits the ion mobility but prevents electric contact. Therefore, the structure of SCs is very similar to that of a battery. For example, the batteries and SCs both have positive and negative electrodes separated by an electrolyte. However, the SCs will store energy in the form of electricity rather than chemistry, which is usually used in the batteries. Moreover, the supercapacitor has the unique and obvious advantages of lithium battery, such as high specific energy or capacity density, long cycle life (i.e., can be repeated charge and discharge hundreds of thousands of times), short charging and discharging time, good ultra-low temperature characteristics, high current discharge capacity and so on forth. In contrast to the battery, the supercapacitor has a higher power density and less pollution to the environment during its disposal stage.

In this thesis, the SCs with different manufacturers are selected for study and comparison with lithium battery in many terms of electrical properties, because it is a promising direct electronic storage device. The comparison of properties of lithium battery and supercapacitor are summarised in **Table 1** below.

Table 1: Comparison table [3, 4]

Properties	Lithium Battery	Supercapacitor
Electronic Storage	Involve chemical phase/composition change	Direct
Energy Density	High	Low
Internal Resistance	High	Low
Operating Temperature Window	Narrow	Wide
Lifespan	Short	Long
Power Density	Low	High
Disposability	Low	High
Recyclability	No	High
Cost	High	Low

The supercapacitor has a double-layer capacitor structure formation that can mainly store electrical energy at the electrodes and electrolyte interface. This storing mechanism only relies on the fast and reversible Faradic reaction found on the electrode surface, which improves the total capacitance instead of modifying the composition or chemical phase. Even though lithium batteries are found to have higher energy storage capacity as a result of their high energy density. The SCs have more magnificent characteristics that compensate for this disadvantage. Moreover, the SCs have relatively low internal resistance, wide operating temperature window and high peak current which allow them to deliver high-level current and power of about one million charge-discharge cycles. On the other hand, the charging and discharging rates are also faster due to their high-power density. Typically, these SCs are made of non-hazardous materials which allows them to be disposed and recycle. These characteristics make the SCs become more cost-effective than a lithium house battery.

1.4 Thesis Structure

As mentioned in previous part, we aim to investigate the characteristic of various types of SCs to determine if a cluster of the tested resulting best capacitor can be used as a Tesla house battery substitution in this thesis. In order to achieve the aim of this project, the objectives are theory and methodology of the performance of SCs to estimate theoretical characteristics for future comparison with the experimental results. In Chapter One, a general background about this thesis and supercapacitor was introduced along with the objective and structure of this thesis. In Chapter Two, a systematically related literature review according to the categories of fabrication materials, simulation models and experimental setup of the studied SCs were carried out to confirm the content of later chapters of the thesis. In Chapter Three, it will introduce research methods and experimental planning, which are mainly divided into modeling and methods for testing characteristics, data test simulation of SCs of different materials, and observation of the structure of the internal structure. In Chapter Four, the experimental results will be presented and discussed based on their electrical performance, where conclusion will be given at each individual experimental result and discussion. Eventually, the final design analysis is to see if the tested resulting best capacitor can be used as an alternative to a Tesla house battery. In the last chapter (Chapter Five), the conclusion about the feasibility of the substitution of lithium batteries by supercapacitor will be given.

The previous study further detailed the findings on lithium battery and supercapacitor performance, and on various supercapacitor modelling methods. With the knowledge studied, the theory and equations that are useful for the test and analysis were laid out. The experiments are categorised into the electrical test that investigates the electrical characteristics, and physical structure that analyses the internal structure of the supercapacitor. Then by following the test methodology, the experiment can be carried out successfully by knowing which measurement to be recorded and the subsequent supercapacitor performance output such as the I-V characteristic, output impedance, etc which are listed in the objective, can be found by utilising the equation listed in the methodology. Lastly, the results and analysis, and final design analysis are to be completed.

Chapter 2 Literature review

In this chapter, a series previous research about the experimental and simulation work of the supercapacitors are systematically reviewed, providing a certain of important information and guideline for our experimental design and measurement along with the associated results analysis and discussion. In order to present a clear and logical literature review, the component materials of SCs are reviewed at first and then the simulation model review is carried out. Finally, the experimental RC circuit is reviewed for the guideline of experiment.

2.1 Materials for SCs electrochemical performance

Along with the development of supercapacitor technologies, a number of different materials have been used for the fabrication of SCs components (i.e. electrode, electrolyte and membrane separator) such as polymers, chemically deposited metal oxide thin films and also ruthenium oxide, manganese oxide, cobalt oxide, nickel oxide, iron oxide, iridium oxide, perovskite, ferrites and lead dioxide[5-8]. These materials are weight, cheap, suitable morphology, fast doping-undoping process, and can be comparatively simply manufactured into electrochemical capacitors (ECs). Nevertheless, long-term stability during charge-discharge cycling may be a serious problem for the ECs using polymers. Since the shrinking and swelling of such electroactive polymers are clearly identified and result in degradation during cycling. Moreover, the charge-storage mechanism in polymer electrodes is still not well understood so far [9-11]. Therefore, the porous activated carbons (ACs), hydrous transition metal oxides and conducting polymers are the dominant materials for the electrode of supercapacitors.

Moreover, the nanostructure such as graphene and carbon nanotube were also used for the electrode of SCs. These oxide thin films are used for faradic reactions which could enhance the electrical performance including the capacitance and discharge rate of supercapacitor significantly. Moreover, the electrolyte is another important component affecting SC performance. The general requirements for the electrolyte involve large voltage window, high ionic concentration, high electrochemical stability, low resistivity, low viscosity, low volatility and low cost [7]. In compared among these components, the electrode may play more important role than the others in enhancing the overall performance of the SC. Therefore, it is essential to review the available research work on the electrode of SCs based on the category of fabrication materials and structure.

2.1.1 Activated carbon for the electrode of SCs

The activated carbons (ACs) are basic materials for EDLCs electrode due to their highly porous structure, large surface area, good adsorption property, outstanding long-term electrochemical stability and high electrical conductivity[5]. The electric double layer (EDL) phenomenon was first observed and described by Helmholtz in 1853 and later patented by Becker in 1957, who used porous carbon material with high specific area as electrodes for double layer structure formation [12]. The first SC product for commercial application was introduced by Nippon Electric Company as a memory backup device in 1971[6]. In an advanced hybrid electrochemical capacitor (HECs), the potential range at the cathode is extended to the whole potential window of AC (i.e. from 1.5 to 4.5V), which is wider potential range than the conventional electrochemical capacitors (i.e. from 0.8 to 2.7V). Since the energy density of an electrochemical capacitor can be estimated based on the equation of $E= CV^2/2$, where C is capacitance and V is the working voltage wind. The energy density of SCs using ACs as electrode could therefore be greatly increased for EDLCs. Moreover, the electrochemical performances of EDLCs are also related to the pore structure, surface area and surface chemistry of the ACs. The surface oxygen groups may develop the wettability between the carbon surface and the electrolyte solution, where the more surface oxygen groups content, the easier the interaction between interface and water molecules[13]. The surface oxygen groups may occur faradic reactions that can enhance the capacitance and self-discharge. Based on above, the ACs currently remain the most extensively used carbon material for SCs due to their low costs, accessibility and multiplicity of precursor materials[14].

2.1.2 Graphene and graphene oxide nanosphere for the electrode of SCs

The graphene is a novel EDLCs based carbon material with one-atom thick layer (i.e. 2D nanosheet of graphite), which have been widely used for SCs with advantages of ultrahigh power density and long life cycles [15]. However, since the unavoidable aggregation of hydrophobic graphene nanosheets, the surface area of graphene is always much lower than the theoretical data. Additionally, the pure graphene is difficult to be dissolved or dispersed even after the long-time ultrasonic sonication, resulting in relatively low capacitance performance [16]. The capacitance of SC using graphene electrode is generally in the rang from 100 to 200 F/g [17-20]. Moreover, the graphene nanosheets stacked loosely in porous electrodes may cause an obvious electrical contact resistance due to the discrete nature of graphitic nanoflakes, resulting in decrease on the energy and power efficiencies of SCs [21].

On the other hand, the graphene oxide which is an intermediate during the synthesis of graphene by the method of oxidation-exfoliation-reduction of graphite powder presents a higher capacitance as an electrode material for SCs. However, due to the less stacking stability and poor conductivity, such graphene oxide can not be directly used as the electrode material for SCs according to some of previous research [22]. The nanocomposites of graphene oxide with conducting polymer or metal oxides also present high capacitances and good cycling performances. It is believed that the capacitive performance of porous carbon could be determined by the surface area, pore geometry, electrical conductivity and chemicals including oxygen, nitrogen or phosphorus, where the enhancement of total capacitance by adding such chemicals through additional faradaic reactions is called the pseudo-capacitance effect. The graphene oxides have advantages of both a high surface area and enriched oxygen-containing functional groups, and hence are expected to be good choice as the electrode materials for SCs. In the research work of Xu et al.[16], the electrochemical performance of graphene oxide and graphene were compared as electrode materials for SCs. The graphene oxides with much less BET surface area give a higher capacitance than graphene, since the abundant oxygen-containing functional groups of graphene oxides provide additional pseudo-capacitance effect. Furthermore, the graphene oxides with lower cost and shorter processing time also present striking rate performance and outstanding cycle durability compared to those of graphene. Thus, the graphene oxide may be a better candidate of electrode materials for SCs rather than the graphene itself.

2.1.3 Layered MoS_2-graphene composites for the electrode of SCs

According to the research work of Ke-jing Huang et al. [23], it is believed that promotion of efficient charge transport and diffusion of electrolyte as well as prevent of volume expansion and aggregation of electroactive materials could make contribution to the enhancement in specific capacitance and cycling stability due to 3D MoS_2 graphene interconnected conductive network. MoS_2 graphene composite is a promising material for high-performance SCs, which is a novel EDLCs based carbon material that is one atom thick. Because of its high specific surface area, excellent stability and good electrical conductivity, it is used as electrode material for SCs. Moreover, the MoS_2 provides a good surface modification of graphene to improve its dispersion and processability and good functionality for a high-performance capacitor. The MoS_2 has an analogous structure to the graphite composing of three atom layers (i.e. one Mo layer sandwiched by two layers of S, which are stacked by weak van der Waals interaction [24].). The higher intrinsic fast ionic conductivity[25] (than oxides) and theoretical capacity [26](than graphite) of MoS_2 have drawn greater attention of capacitor researchers. Soon and Lohz found that the performance of SCs using MoS_2 electrode is comparable to that that of SCs using nanotube electrode, giving rise to faradaic capacitance and thus enhancing charge storage capabilities [27]. However, the electronic conductivity of MoS_2 is still lower compared to graphite and its specific capacitance is still limited for energy storage application. To overcome such drawbacks of MoS_2, the combination of graphene and MoS_2 for the electrode of SCs may give one possible solution.

2.2 Simulation models of SCs

The SCs modelling is the most fundamental analysis of the supercapacitor system for circuit design, performance prediction, condition monitor, and control synthesis. There are a various of SC models established for different purposes, such as aging simulation, detecting thermal and electrical behaviour and so on forth. Model construction according to the system's specific purpose is expected to be one of the best substitutions system with the lowest financial cost in the future, where the accuracy depends on the assumptions and requirements of the application. According to the previous research work [3, 4, 28-30], the equivalent circuit models, electrochemical models, intelligent models, and the fractional orders model were found to be the most used models to estimate the electrical behaviours. These categories of models will be reviewed in this part.

2.2.1 Equivalent circuit models

This model type implements the parameterized capacitor-resistor (RC) networks to simulate the electrical behaviour of SCs. They are simple and easy to be employed because the models formula are derived using ordinary differential equations (ODEs) with the experimental results and data are assumed to be collected under certain conditions [28]. However, this makes them inadequate in modelling the dynamic of UCs operating under a wide range of conditions which poses a discrepancy with the real circuit. Moreover, the internal information is vague because this model has no physical representation for their parameters and states. But the simplicity of the structure and high modelling accuracy compensate their disadvantages, making them suitable in real time energy management synthesis. The accuracy of different models varies according to the structure of the electric circuit configuration and element number. The model accuracy can be elevated by employing more complicated electrical circuit configuration.

The most common equivalent circuit models of SCs from the literature are illustrated in **Figure 1** below. The simplest equivalent circuit model proposed by Kim et al. is an equivalent resistor [4] connected with a capacitor in series [31]. However, the self-discharge of SCs is not involved in this model. Hence, Spyker and Nelms added the other resistor (R_P) in parallel with the capacitor to simulate the self-discharge, forming the classical equivalent circuit model (see **Figure 1a)**) [32]. **Figure 1b)** illustrates a variable resistor to further characterize the self-discharge in the three-branch model proposed by Zhang and Yang [33]. **Figure 1c)** displays a dynamic model using electrochemical impedance spectroscopy established by Buller et al.[34], which is consists of a series resistor, a bulk capacitor, and two parallel RC networks. In **Figure 1d)**, the transmission line models involving the transient and long-term behaviour were introduced for simulation of the distributed capacitance and electrolyte resistance depending on the porous electrodes.

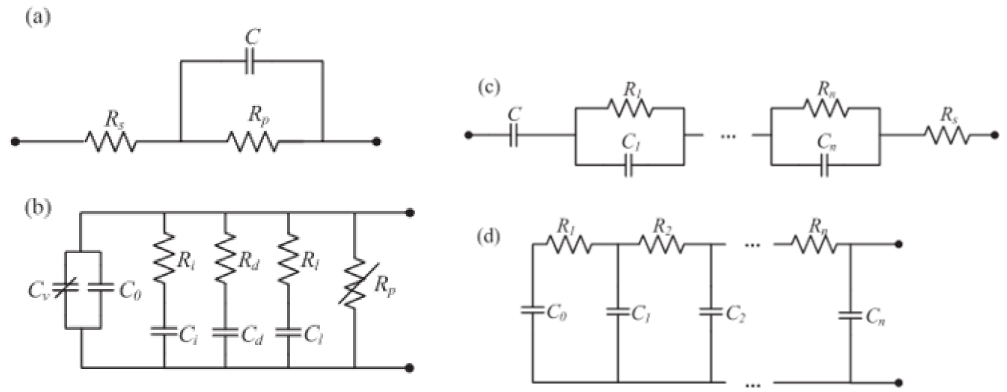

Figure 1: Equivalent circuit models for SC are demonstrated, where Rs and Rp stand for the resistors in series and parallel.

2.2.2 Electrochemical models

The electrochemical model was first established by Helmholtz who first discovered the EDL phenomenon. In the Helmholtz's model, all the charges were presumed to be absorbed at the surface of electrodes. This model was later improved by other researchers [35], where ion mobility in the electrolyte solutions due to diffusion and electrostatic forces was taken into consideration (i.e. Gouy-Chapman model). Then Stern integrated both of the Helmholtz model and Gouy-Chapman model, where the EDL was divided into two individual layers (i.e. Stern layer and diffuse layer) [36]. Then the total capacitance of EDL could be thought to be the sum of above two layers connected in series. In 2013, Wang and Pilon developed a 3D model for SCs concerning 3D electrode morphology, finite ion size and field dependent electrolyte dialectic permittivity [37]. In general, the electrochemical models aim to capture the real inner UCs reaction process by engaging coupled partial differential equations (PDEs) which results in a high accuracy modelling. However, the calculation efficiency of this model is relatively low, and it restricts their implementations on the embedded system for real time management and control of the energy [3].

2.2.3 Intelligent models

The intelligent models can be used to predict the performance of the energy storage system such as batteries and SCs. Most of the intelligent modelling techniques usually have the ability to describe the complicated non-linear relationship between performance and its influencing factors without well understanding on the underlying mechanism in detail. It is known that the accuracy and generality of models are strongly determined by the great amount of high-quality training data, resulting in a widespread application of intelligent methods for the design and performance prediction of SCs. **Figure 2** below shows an example of the process of neuron body with multiple inputs and single output or result, where the high-quality training data collecting size must be decent to ensure the accuracy and versatility of the model.

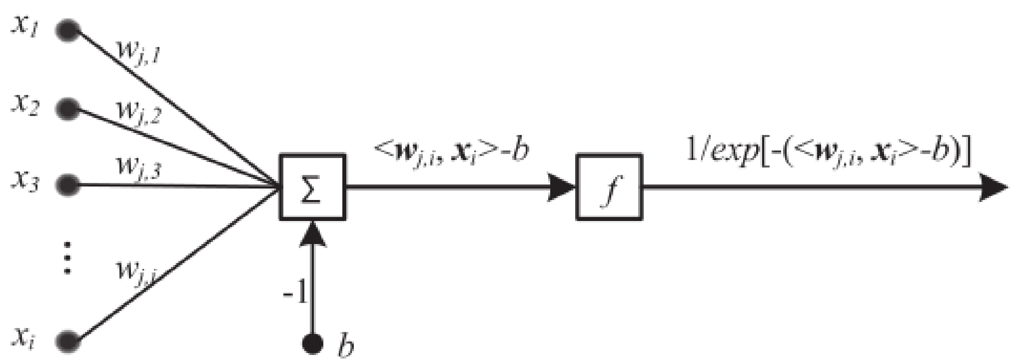

Figure 2: Example neuron body with multiple inputs (from left) and single output (on the right).

In the artificial neural network (ANN) model constructed by Farsi and Gobal, the influences of several intrinsic characteristic on the performance of SC are verified [38]. In this model, the parameters which are key for SC prototype design including crystal size, surface lattice length, exchange current density of the active material and cell current are set to as the input. Moreover, a model for SC behaviour simulation was established by Wu et al.[39], where the input (i.e. terminal voltage and temperature) and output (i.e. two influencing factors put into the model parameter calculation) parameters were predicted through an established ANN model. Eddahech et al. also established a one-layer feed-forward ANN to express the performance of SC as a complex function of current rate, temperature, chemistry and history, which is valid through power cycling with the resulting model used for voltage control purpose [40]. The ANN models have been used for battery-SC hybrid energy storage device to estimate the State-of-Charge (SOC)[41] or track the output voltage subject to current, temperature and voltage variations[42]. Therefore, the intelligent models using ANN network have been manifested to provide useful information on the transient behaviour of an SC, involving many factors into the simulation modes.

2.2.4 Fractional-order models

The Fractional-order calculus has been introduced to improve the accuracy of the SC modelling applications [29, 30]. The resulting Fractional-order model consider of non-integer order differential equations. Such model is constructed based on the non-integer order differential equations, which have a better ability to capture the dynamics of SC performance especially in comparing with the integer-order equivalent circuit models. An example of the fractional-order model is shown in **Figure 3**, where the model consists of a series resistor, a parallel resistor, a constant-phase element and a Walburg-like element.

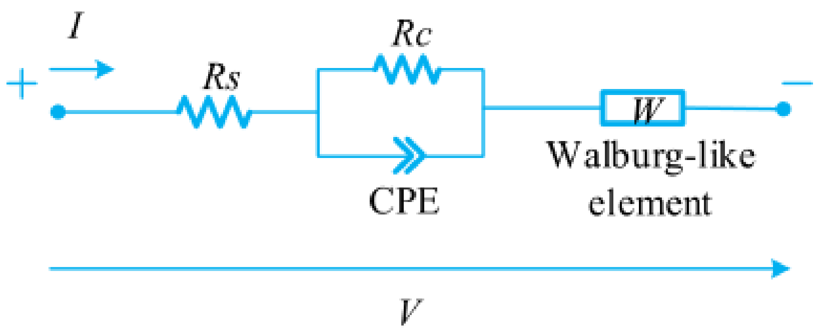

Figure 3: Example of SC fractional-order model.[3]

The first explore by introducing a half-order calculus into SC capable of representing the SC behaviour with high credibility and reducing computational burden was done by Riu et al in 2004[43]. Nevertheless, the potential of improving modelling accuracy is unavoidably limited since the factional differentiation order was fixed in the model parameterization process. Later, Martynyuk and Oritgueira also proposed a factional-order model for SCs, where the impedance data identified the input parameters [44]. Moreover, the non-linear fractional order model by frequency analysis was derived by Bertrand et al.[45], and further an excellent fitting to the whole frequency range was achieved by a Havriliak-Negami based function model presented by Martin et al[46]. However, the accuracy of the parameterized model is highly dependent on the accuracy and availability of the impedance spectra of SCs. On the other hand, the time-domain data [47] and step voltage response collected from the constant current charge test[48] could be used as the parameters for fractional-order model.

The four categories of models used to simulate the electrical behaviour of SCs for reference and evaluation are briefly summarizes and compares as shown in **Table 2**. Based on the findings, it is known that in this project, the electrical behaviour of the supercapacitor can be mimic easily by parameterized the RC networks, in other words, by using equivalent circuit models. This model formulations employ a simple and easy implementation by using the ordinary differential equations. And by increasing sophistication, the model accuracy can be elevated. We know that by using equivalent circuit model, we can model the manipulation of the reactive load from simple and cheap capacitor first, to test the electrical system connections, then eventually the much expensive and complicated supercapacitor.[3]

Table 2: Summary of model types for SC electrical behaviour simulation. [2]

Category	Subclass	Upside	Downside
Electrical behavior	1). Electrochemical models	Description of inside physical-chemical reactions; High possible accuracy	Heavy computation; Immeasurability of some parameters
	2). Equivalent circuit models	Moderate accuracy; Relatively easy implementation and model identification	Absence of physical meanings; susceptible to aging process
	3). Intelligent models	Good modeling capability; disclosure of the influencing factors to desirable model output	Sensitive to training data quality and quantity; poor robustness
	4). Fractional-order models	Better capability to fitting experimental data; few model parameters	Heavy computation;

2.3 Experimental characterizations of SC based on R-C model

The standard R-C model is a circuit consisting of a resistor R and a capacitor C connected in series, which is commonly used for global management of embedded energy [49, 50]. **Figure 4** shows that the model reflects the energy characteristics of SCs, especially in terms of storage capacity, where a constant current I_C is supplied to the R-C circuit for charge process. The measurement associated with the R-C model test is carried out by the most of SC manufacturers and suppliers for the redaction of the database.

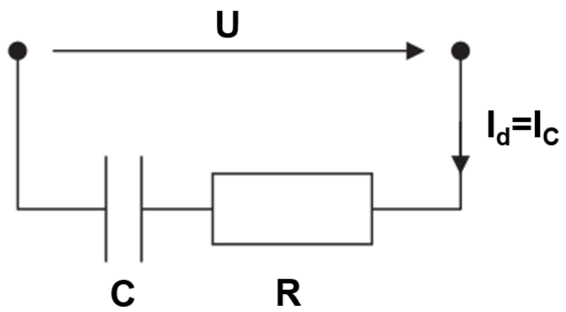

Figure 4: Equivalent electrical circuit for R-C model

2.3.1 Experiment for single R-C model characterizations

The method according to the reference [4] shows that, during initial discharge, a supercapacitor is charged by applying a constant current (I_C) until the voltage reaches its rated value (U_R). Then the supercapacitor voltage is adjusted to U_R within 30 min, and constant current (I_d) is applied to discharge the supercapacitor. The discharge current I_d in the unit of mA equals the four times the product of capacitance and rated value voltage and also equals to the charge current (i.e. $I_C=I_d=4 \cdot C \cdot U_R$).

The stand test temperature should be between 15 and 35℃ according to the available standard. For most of the suppliers, the characteristic test is carried out at 25℃ normally. The impact of ambient temperature effect on the performance of SCs are also implemented by test the SC at other different temperatures including -20, -5, +10+40 and +55℃, where equations (1) and (2) are used to measure capacitance C and resistance R, respectively.

$$C = I_d \cdot (t_2 - t_1)/(U_1 - U_2) \quad \textbf{(1)}$$

In the above equation (1), C is the capacitance (F), I_d is the discharge current (in A), U and t are the measured voltage (V) and time (s)[4].

On the other hand, the internal resistance of SC could be calculated from the voltage drop which could be observed at the application of the charge or discharge current. The resistance is obtained according to equation (2) below

$$ESR = \Delta U_3/I_d \quad \textbf{(2)}$$

where *ESR* stands for the Equivalent Serial Resistance (in Ω), I_d is the discharge current (in A) and ΔU3 is the voltage drop (V). The voltage drop ΔU3 is obtained by the difference between U_R and the value determined on the voltage tangent at the beginning of the discharge[4].

By testing different SCs, the results are given in order to compare them with data table values, especially to show the effect of temperature on storage capacity, and to verify the model simulation by comparing with experiments. The experimental values are consistent with those given by the supplier. The comparison between the simulation and experiment of the R-C model shows that the gap exists at low voltage because the capacitor is independent of voltage. This is a disadvantage of the R-C model. Finally, they proved that the constant current characteristic is an easy power test to determine the R-C model.

2.3.2 Experiment for multiple R-C branch model characterizations

The multiple R-C branch model composed several R-C branches with higher accuracy than the single branch one to take into consideration of the internal physical phenomena of SC, which is constructed by Zubieta and Bonert [51]. **Figure 5** presents the equivalent circuit of such model, where the time constants of each R-C branch are different from each other. The first or main branch represents the regular charge or discharge process, which is consisted of an internal resistance Ri in series with two capacitors in parallel (i.e. voltage independent Ci0 and voltage dependent Ci1) with time constant of around 1s. The second branch represents the charge redistribution phenomenon, which can be observed after charge or discharge when current equals to zero. This branch is composed of a resistance Rd in series with a capacitor Cd., where its corresponding time constant is about few minutes. The third branch represents the phenomenon of auto-discharge, which is composed of a resistance R1 in serial with a capacitor C1. The time constant of the long-term branch is about several minutes. In contrast with the single R-C model, this multiple R-C model takes into consideration of the influence of the voltage on the capacitance, charge redistribution and auto-discharge.

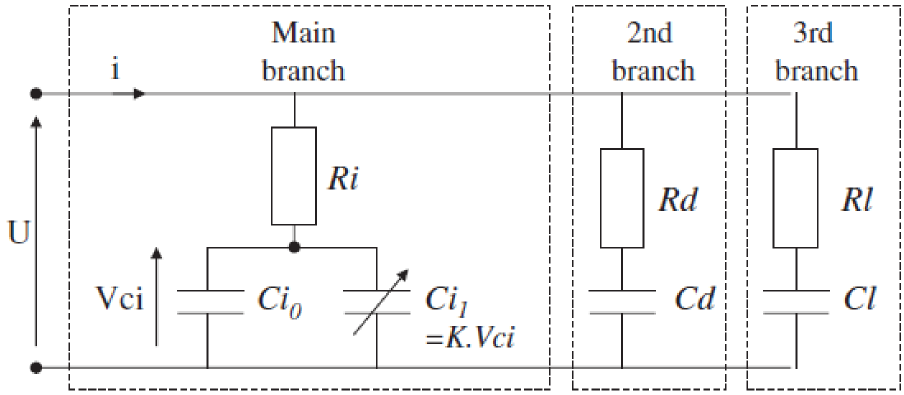

Figure 5: The three R-C branch model takes into consideration of the influence of the voltage on the capacitance, charge redistribution and auto-discharge.

Chapter 3 Methodologies

The experiment was carried out to study the supercapacitor internal structure with the best performance for the modelling of the final house battery substitution design. The number of capacitors needed to achieve the same or better performance than a Tesla house battery can be estimated with the selected supercapacitor, and hence the volume and weight of the final design can be predicted. This chapter outlined the methodology of acquiring the measurements and observation required to find the performance characteristics of supercapacitor with respect to their internal material structure. The method of processing the resulting data from the experiment is outlined in the following parts as well. In general, the experiments are mainly divided into two parts, which are 1) the electrical measurements that study the electronic properties of the selected SCs and 2) the physical characterizations used to explore the microscopic material structure of the SCs.

3.1 Electrical Measurements

3.1.1 Fast Charge and Fast Discharge test

The electrical measurements were carried out by utilizing the related experimental equipment from the Electronic Projects Lab in the School of Electrical and Electronic Engineering at the University of Adelaide. In order to ensure the safety of all the experiment, the safety risk assessment was completed before start at first. The method of isolation to isolate the reactive load and the signal generator is carefully selected to minimize the effect of the explosive risk of the reactive load as much as possible. In order to explore the performance of charging and discharging of selected SCs, a double- bladed knife switch is selected to control the charge/discharge process. **Figure 6** demonstrated the designed experimental circuit, where a DC power source is connected in series with the SC (i.e. switch on for charging) or disconnected from the circuit (i.e. switch off for discharging) via the double-bladed knife switch. Two multimeters or oscilloscopes are connected in parallel and series with the SC to monitor its voltage and current flow through it.

By using the selected isolation and power supply method, the internal resistance or *ESR* of SC can be calculated by using the method mentioned in the chapter of literature review (see equation 2).

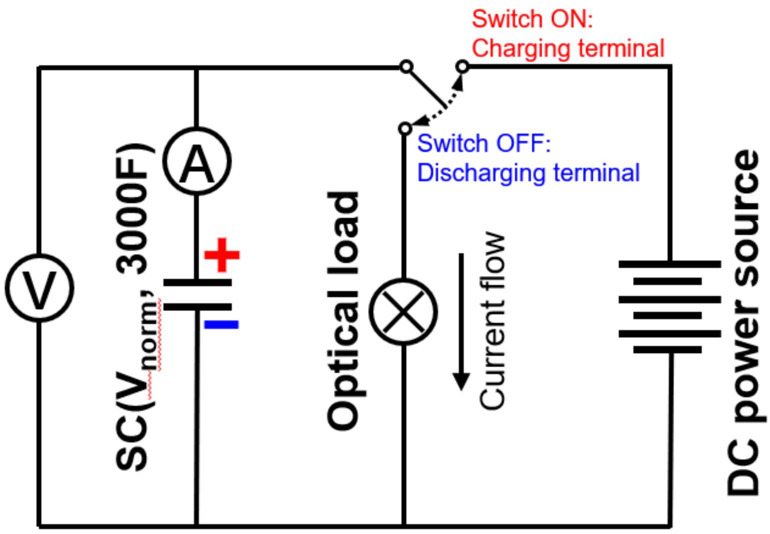

Figure 6: Fast charge and Fast discharge test.

On the other hand, we use three different brands of supercapacitors for test simulation, data from the manufacturer's datasheet.the resistance of connected optical load (R_L) can be calculated based on the available data, where R_L = 100m Ω. By using a multimeter, record the resulting potential difference of the optical load (V_L) which is 2.7V. Therefore, the current flow through the load can be calculated based on the Ohm's Law (i.e. $I = -V_L/R_L$). By measuring R_n with different frequency, where n at high frequency is *s* and *p* at low frequency. This is because R_p take longer time to discharge, so it cannot be measured with high frequency. The nominal voltage of the supercapacitor can be measure by using oscilloscope and tabulated as shown in **Table 3**. Then, the corresponding capacitance, ESR and hence output impedance can be calculated.

Table 3: Electrical test data record and process.

SCs	Frequency, f (kHZ)	R_n(m Ω)	V_D (V)	ω (rad/s)	Capacitance, C (F)	Output Impedance, 1 / ESR (/Ω)
GDCPH	5	0.28	25.124m	31400	3000F	100
	20	0.28	25.289m	125600		
Batscap	5	0.25	26.258m	31400	3000F	102.8
	20	0.25	24.315m	125600		
Maxwell	5	0.29	26.258m	31400	3000F	100
	20	0.29	24.315m	125600		

3.1.2 Integrate and Fit method for capacitor model

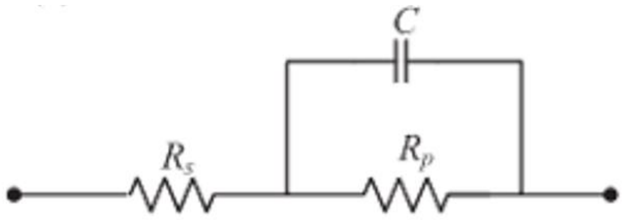

Figure 7: model of capacitor model

The voltage of capacitor could be extract from the difference between the DC power resource and resistance connected in series with the capacitor.

$$V_c(t) = V_d(t) - R_s \cdot I_d(t) \quad (3)$$

The current(I_p) flows through the other resistance in parallel with the capacitor(R_p) could be calculated by the ratio between voltage of capacitor and R_p.

$$I_p = \frac{V_c(t)}{R_p} = \frac{1}{R_p} \cdot V_d(t) - \frac{R_s}{R_p} \cdot I_d(t) \quad \textbf{(4)}$$

Similarly, the current flows through the capacitor could be calculated based on the product of capacitance and change rate of voltage between the capacitor.

$$I_c = C \cdot \frac{\partial V_d}{\partial t}\left(V_c(t)\right) = C \cdot \frac{\partial V_d(t)}{\partial t} - R_s \cdot C \cdot \frac{\partial I_d(t)}{\partial t} \quad \textbf{(5)}$$

According to the KCL, the total current through the main strand is the sum of the currents flowing through the capacitor and parallel, which are ic and ip respectively. Hence, the derivation formulas are shown as below.

$$I_d(t) = I_p(t) + I_c(t) = \frac{1}{R_p} \cdot V_d(t) - \frac{R_s}{R_p} \cdot I_d(t) + C \cdot \frac{\partial V_d(t)}{\partial t} - R_s \cdot C \cdot \frac{\partial I_d(t)}{\partial t} \quad \textbf{(6)}$$

$$\boldsymbol{V_d(t) = -R_p \cdot C \cdot \frac{\partial V_d}{\partial t} + \left(R_p + R_s\right) \cdot I_d(t) + R_s \cdot R_p \cdot C \cdot I_d(t) + k1} \quad \textbf{(7)}$$

$$\varphi_d(t) = -R_p \cdot C \cdot V_d(t) + (R_p + R_s) \cdot q_d(t) + R_s \cdot R_p \cdot C \cdot i_d(t) + k_1 \quad \textbf{(8)}$$

$$R_p \cdot C \cdot V_d(t) = -\varphi_d(t) + (R_p + R_s) \cdot q_d(t) + R_s \cdot R_p \cdot C \cdot i_d(t) + k_1 \quad \textbf{(9)}$$

$$V_d(t) = -\frac{1}{R_p \cdot C}\varphi_d(t) + \frac{1}{C}(1 + \frac{R_s}{R_p}) \cdot q_d(t) + R_s \cdot i_d(t) + k_2 \quad \textbf{(10)}$$

Sample and write as a linear model, $V_d(t,k) = V_{d,k}, \varphi_d(t,k) = \varphi_{d,k}, q_d(t,k) = q_{d,k}, I_d(t,k) = I_{d,k}$.

$$\begin{bmatrix} v_{d,k} \\ \vdots \\ \\ \end{bmatrix} = \begin{bmatrix} \varphi_{d,k} & q_{d,k} & i_{d,k} \\ \vdots & \vdots & \vdots \\ & & \end{bmatrix} \begin{bmatrix} -\frac{1}{R_p \cdot C} \\ \frac{1}{C}(1 + \frac{R_s}{R_p}) \\ R_s \\ k_2 \end{bmatrix} \quad \textbf{(11)}$$

$$\begin{bmatrix} \theta_1 \\ \theta_2 \\ \theta_3 \\ \theta_4 \end{bmatrix} = \begin{bmatrix} -1/(R_p \cdot \mathrm{C}) \\ (1 + (R_s / R_p)) / \mathrm{C} \\ R_s \\ k_2 \end{bmatrix} \quad \textbf{(12)}$$

$$\boldsymbol{\theta_1 = -\frac{1}{R_p \cdot C}} \quad \textbf{(13)}$$

$$\theta_2 = 1/\mathrm{C} - \theta_3 \cdot \theta_1 \rightarrow C = \frac{1}{\theta_2 - \theta_1 \cdot \theta_3}, Rp = \frac{-1}{\theta_1 \cdot C} \quad \textbf{(14)}$$

$$\boldsymbol{\theta_3 = R_s} \quad \textbf{(15)}$$

$$\boldsymbol{\theta_4 = K_2} \quad \textbf{(16)}$$

3.1.3 Slow internal discharge test

Figure 8 shows the circuit diagram of the slow internal discharge test.

This test is to estimate the discharge rate of the SC disconnected with the load or the slow self-discharge rate. This experiment is to explore the time period of the stand-by condition of the SC.

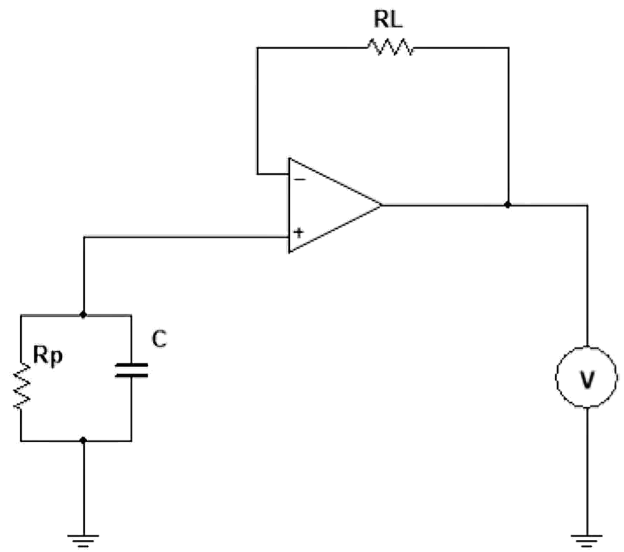

Figure 8: Slow internal discharge test.

3.2 Material and Structure Characterizations of SCs

After all the data being recorded and analysed, the SCs will be cut apart and their inner materials and structure will be observed in the Adelaide Microscopy Center. The structural difference with respect to their subsequent performance will be analysed and supercapacitor with the optimum structure to be used in the final house battery design analysis will be identified. According to the microscopy results (e.g. optical microscopy images), it is believed that the electrode materials used for supercapacitors are mainly activated carbon materials for most of the commercialized SCs. Because the cost of such carbon is relatively low with a high specific surface area, which is a must for the electrode material of supercapacitors. However, the conductivity of activated carbon is generally medium. The microstructure is mainly in the form of micropores, so the resistance of the electrolyte is relatively large, resulting in a slow penetration process of electrolyte into the electrodes and a slower storage and transmission of charge. Although the overall electrical performance of such commercialized SCs is limited due to above factor, the cost of manufacturing such SC is reasonably low which can basically meet the requirements of the market.

The details of the characterization experimental procedures are described as below. First, we prepared the goggles, cutter, small light bulb, wrench, vise, protective gloves, before disassembling, first discharge treatment, we connected the two screws of capacitor with small light bulb, until the small light bulb went out, now we are sure that everything is safe. There are two big screws for the wiring device on the top of 2.8V 3000F, and there is a thermal grease on the other side. After removing the plastic shell, there is a cube made of silver aluminium inside. Then, we unscrewed the screw with a wrench, cut it slowly along the edge of the top with a vise, and then cut the top with a cutter. The top is a piece of aluminium plate about 4mm thick. Through observation, we found that there are two exhaust holes, which are used to discharge excess pressure when charging. Then, when we looked inside the supercapacitor, we found that there were a lot of liquid electrolytes that looked like oil and smelled like chemicals. And a positive electrode and a negative electrode, consisting of a number of layers of electrodes folded, each layer of electrodes between a large bundle of wire to the terminal.

Then, we pour out the electrolyte, there are a lot of small vertical bar separation, and a large separation horizontal to distinguish the positive and negative poles, each small separation with some insulating paper, insulating paper is black carbon powder in the middle, the outermost layer of insulating paper. Take out the paper inside, you can find that it is folded, unfolded to find that it is black and white connected rectangular paper.

The structure of supercapacitor (**Figure 9**) is mainly composed of four parts: Polarizing electrodes, electrolyte, collector and electrolyte diaphragm (separator) [52]. Every part of a supercapacitor has a role to play in operation.

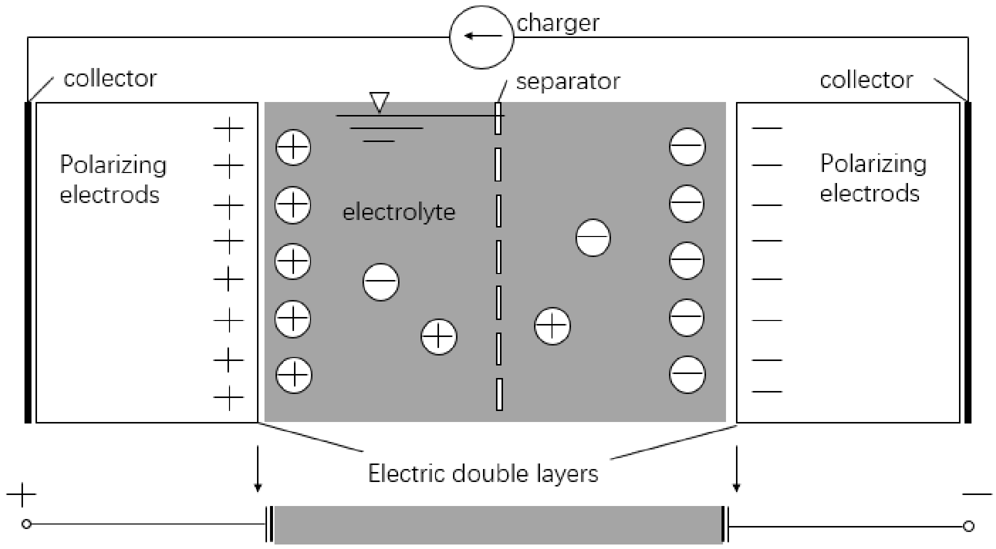

Figure 9: The internal structure of a supercapacitor

Due to the Covid-19, we can not further investigated the internal structure of the SC. But we could get to know the electrode materials of these three SCs are graphene, activated carbon and Carbon aerogel according to the information provided by the suppliers.

Chapter 4 Results and Discussions

This chapter mainly describes the characterizations results of SC electrical properties following by the SC internal material characterization and results analysis, engineering cost and performance analysis. The possibility of the SC replacing the existing lithium battery energy storage is also analysed and discussed.

4.1 Characterization and analysis of SC electrical properties

Figure 10 shows the simulation of discharge process for three different brands (i.e. GDCPH, Batscap and Maxwell) of supercapacitors using the available nominal data provided by the manufacturers. The initial voltage of these SCs are staying at around 2.7V for ~20s since the initiation of the discharge process. Then the voltage of all SCs starts to linearly decrease along with the time with similar decay rates, where the Maxwell one presents the slowest decreasing trend. After around 120s, the voltage of all SCs reaches their nominal lowest value which is the end of the discharge process. It shows the lowest voltages of discharge of these SCs are all above 0.5V, where the highest one is still the Maxwell SC (i.e. 0.7V) with the longest discharge time (i.e. 130s).

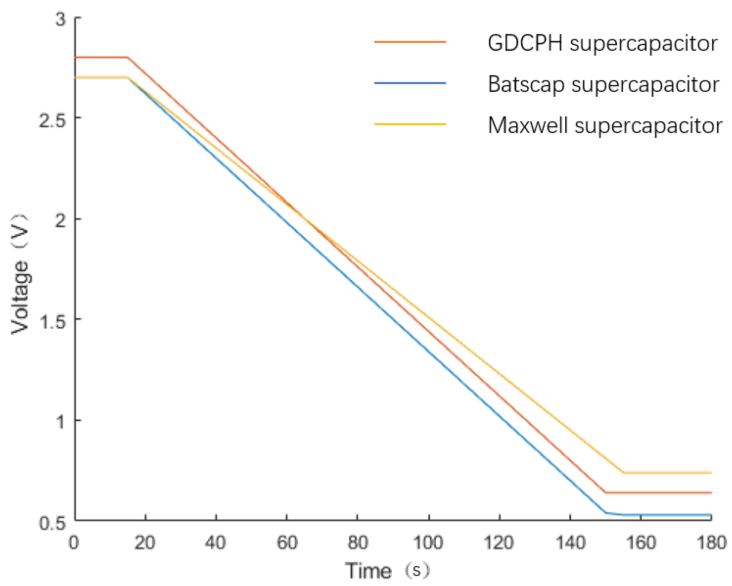

Figure 10: Simulation for 3000F supercapacitor discharge at constant current by the simulation software of Multisim.

The key performance indicators of supercapacitors include the specific capacitance, energy density and power density, internal resistance and cycle stability. For a supercapacitor, each pair of electrodes consist a capacitor. Therefore, for a supercapacitor, the total capacitance is obtained by connecting the two capacitors in series. If the positive capacitor is represented by C_p and the negative capacitor by C_n, the total capacitance is:

$$\frac{1}{C_T} = \frac{1}{C_p} + \frac{1}{C_n} \quad \textbf{(17)}$$

In the experiments, researchers are more concerned about the specific capacitance of supercapacitors, which can be divided into two types: mass specific capacitance, (i.e. the capacitance value per unit mass), and volume specific capacitance which is the capacitance per unit volume[53].

Energy density and power density are the main indicators to characterize the performance of supercapacitors. The higher the energy density is, the more electric energy the supercapacitor can store. The higher the power density is, the more energy the supercapacitor can release per unit time. Generally speaking, the theoretical maximum energy density E and power density P of an ideal supercapacitor can be calculated by the following two formulas:

$$E = \frac{1}{2}CV^2 = \frac{QV}{2} \quad (18)$$

$$P = \frac{1}{4R_s}V^2 \quad (19)$$

In the formula, C is specific capacitance; V is the potential window, that is, the difference between the positive oxygen evolution potential and the negative hydrogen evolution potential of the electrolyte; R_s is equivalent series resistance of capacitor; Q is the total charge stored in the capacitor. It can be seen from Equation (5) that the energy density of supercapacitor is proportional to the square of specific capacitance and potential window, the size of specific capacitance is related to electrode material, and potential window is related to electrolyte. The energy density and power density of the supercapacitor are proportional to the square of the potential window, so it is more effective to expand the potential window to improve the performance of the supercapacitor than to increase the specific capacitance value[51].

The internal resistance of a supercapacitor refers to the series resistance between the positive capacitor and the negative capacitor, which has a lot to do with the electrode material, electrolyte, diaphragm and assembly method. Generally speaking, small internal resistance is beneficial to the performance improvement of supercapacitors. The greater the electrode thickness, the higher the internal resistance, generally the best electrode thickness is less than 150μm. And the aperture of the material should not be too small, generally more than 1.5nm, in order to facilitate the ions in the electrolyte into and fully infiltrate, form a double electric layer, avoid internal resistance[4, 6].

The resistance of the electrolyte is also the main factor affecting the internal resistance of the supercapacitor. For the water electrolyte, the diameter of the ions is small, the mobility is high, and they can easily pass through the diaphragm and enter the pores of the electrode, so the internal resistance is very small. For organic electrolyte, solute is generally an organic polymer, the diameter is large, the migration process is much more likely to be blocked, and it is difficult to enter the pores of the electrode, the internal resistance is relatively large[51].

Cyclic stability refers to the ability of a supercapacitor to maintain its electrical performance after multiple charges and discharges, mainly reflected in whether the attenuation degree of capacitance value is too large after multiple charges and discharges. Circulation charge and discharge cycle stability with super capacitor capacitance attenuation degree calibration after thousands of times, in the first cycle measured capacitance values as initial value, after thousands of times of charge and discharge cycle device capacitance values as the ultimate value of the initial value and final value between every record hundreds of times a capacitance can draw the super capacitor capacitance change with charge and discharge frequency curve[7]. The capacitance retention of the supercapacitor can be obtained by comparing the initial value with the final value. Due to the erosion of electrode materials by electrolyte, especially Faraday pseudocapacitor, the capacitance value of supercapacitor has a certain attenuation[36]. However, the cycle life of supercapacitors is still far ahead of batteries, which is a big advantage of supercapacitors.

4.1.1 Results analysis of SC charging at different conditions

Figure 11 and **Figure 12** below shows the time dependent voltage change trend (V(d)-t) and time dependent current change trend (I-t) during the SC **charging**. The red curve of V(d)-t was collected by using a 2.7V/2.8V supercapacitor with 0.0993Ω resistance and a DC power resource(blue curve). And the green curve of I-t is the change of current in the circuit. It shows the charging rate **increases** rapidly at the first **800s** and the voltage gradually reaches a constant at around **2.2V**. The constant DC power resource provides a 2.4V voltage for SC charging. Since the connected resistance is **relatively small**, most of the voltage from power resource is allocated for charging the SC.

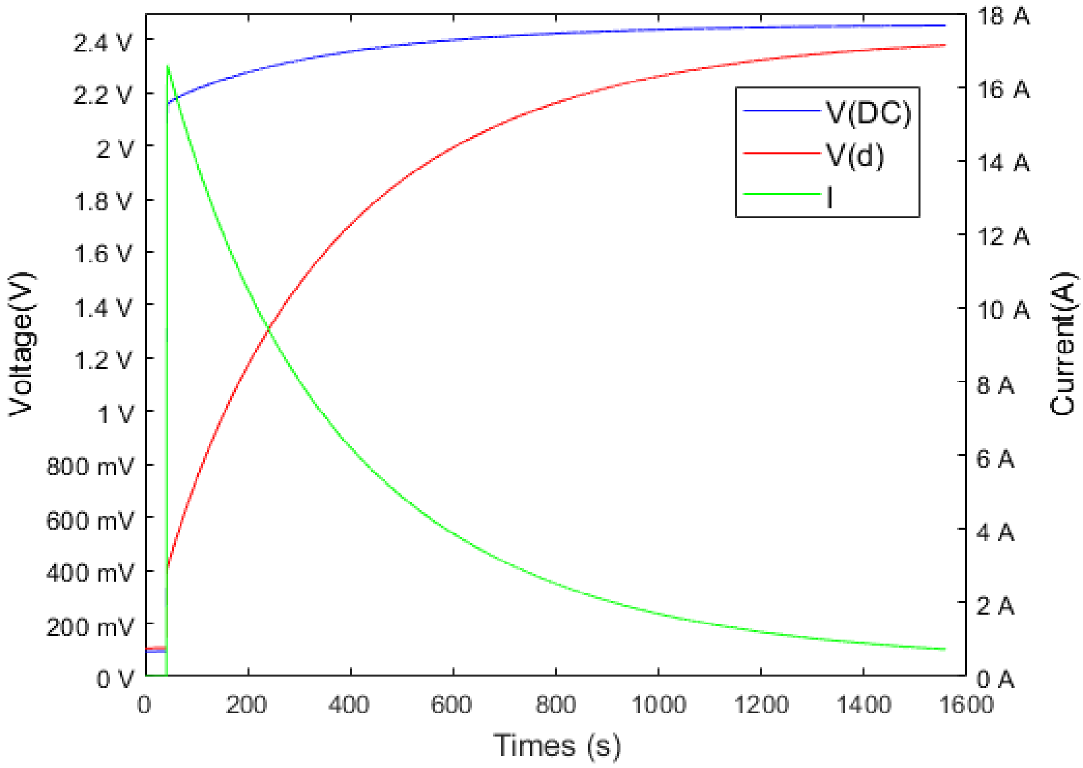

Figure 11: 2.7V 3000F GDCPH supercapacitor with 0.0993Ω resistor (charging)

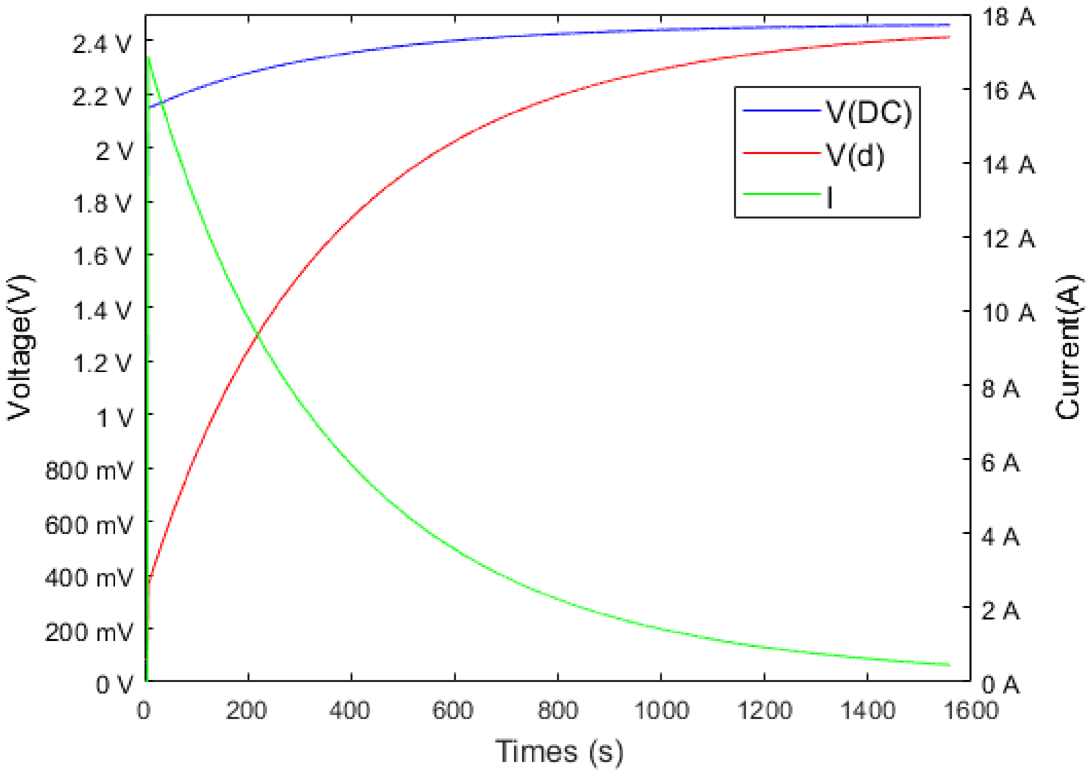

Figure 12: 2.8V 3000F GDCPH supercapacitor with 0.0993Ω resistor (charging)

4.1.2 Results analysis of SC discharging at different conditions

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Figure 14: 2.8V 3000F GDCPH supercapacitor with 0.0993 Ω resistor (discharging)

below shows the time dependent voltage change trend (V(d)-t) and time dependent current change trend (I-t) during the SC **discharging**. The red curve of V(d)-t was collected by using a 2.7V/2.8V supercapacitor with 0.0993 Ω resistance(R) and the voltage between R is represented by the blue curve. And the green curve of I-t is the change of current in the circuit. It shows the charging rate **decreases** rapidly at the first **600s** and the voltage gradually reaches a constant at around **0V**. The voltage between R decrease from around 200mV voltage for SC discharging, and then it slowly goes down to 0. It can be seen that the discharge time of SC is very close to the charging time.

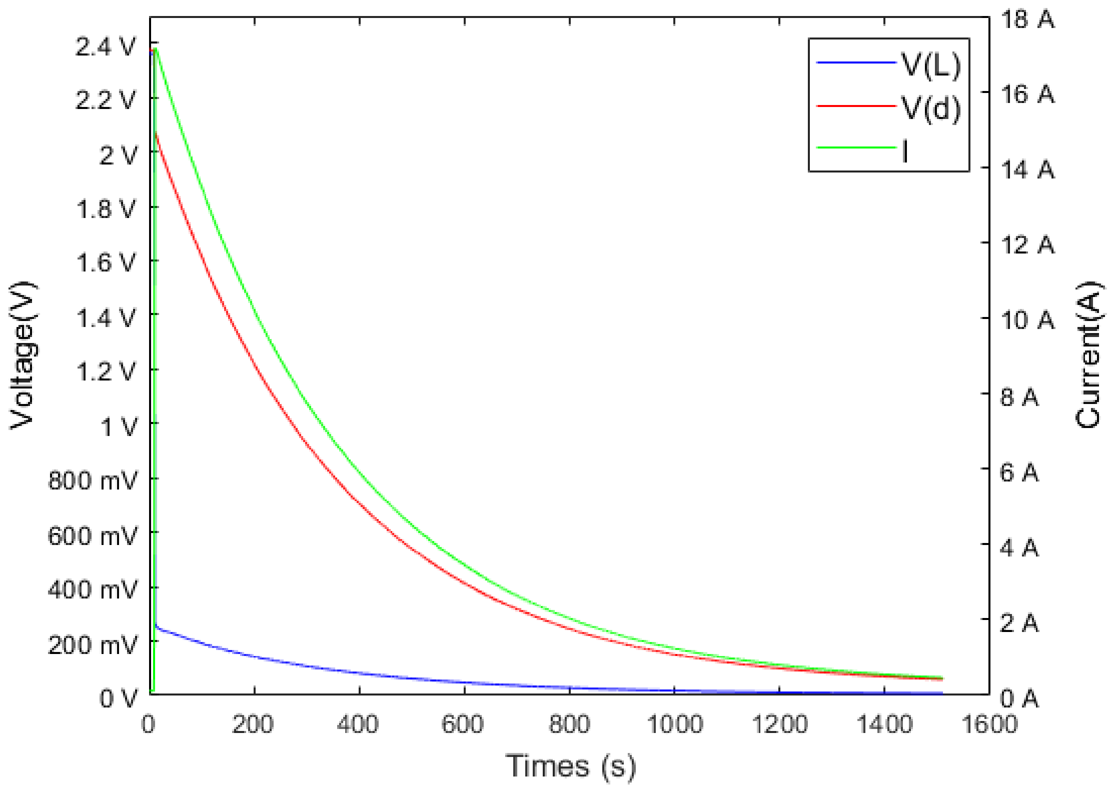

Figure 13: 2.7V 3000F GDCPH supercapacitor with 0.0993Ω resistor (discharging)

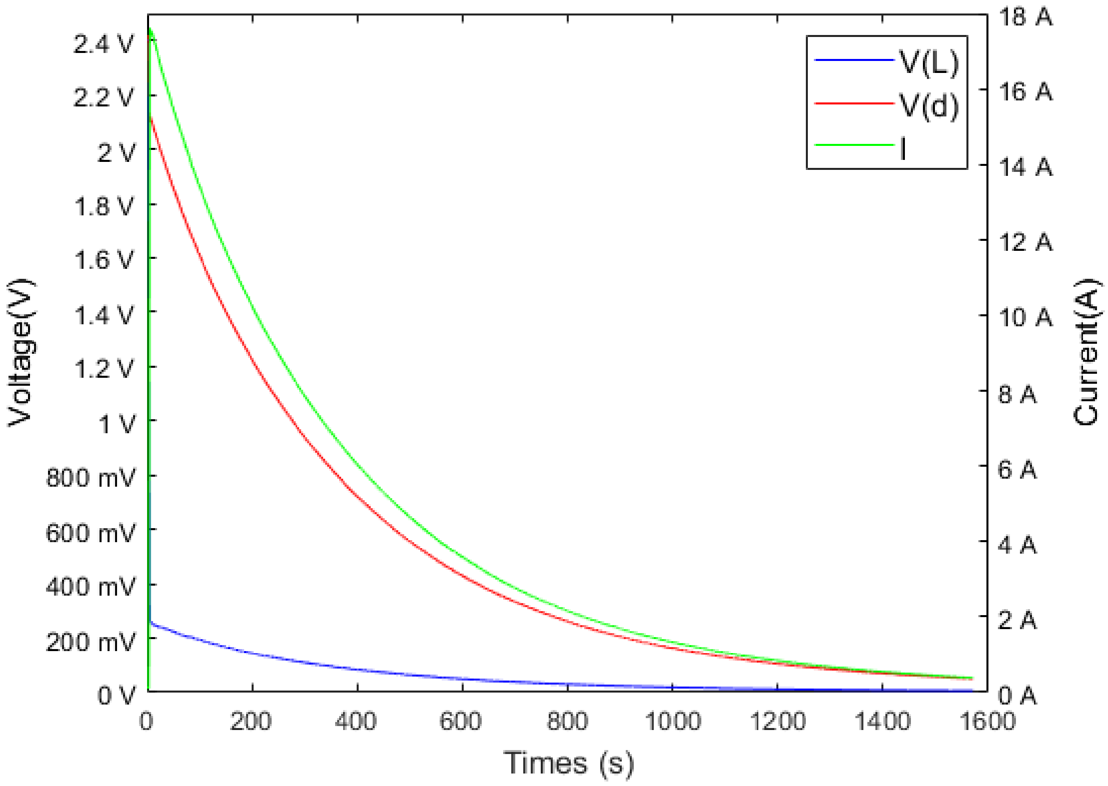

Figure 14: 2.8V 3000F GDCPH supercapacitor with 0.0993Ω resistor (discharging)

4.1.3 Results analysis of SC self-discharging

Figure 15 below shows the time dependent voltage change trend (V(d)-t) during the SC self-discharging. The red curve of V(d)-t was collected by using 2.7V supercapacitor and the blue curve was collected by using 2.8V supercapacitor. 2.8V SC was measured from 2.453V, and 2.7V SC was measured from 1.953V. At the end of the measurement, the voltage of 2.8V is 2.277V and the voltage of 2.7V is 1.717V. It can be seen that the discharging voltage of 2.8V SC is slightly smaller than that of 2.7V SC, which mean that self-discharging of 2.7V SC goes out faster.

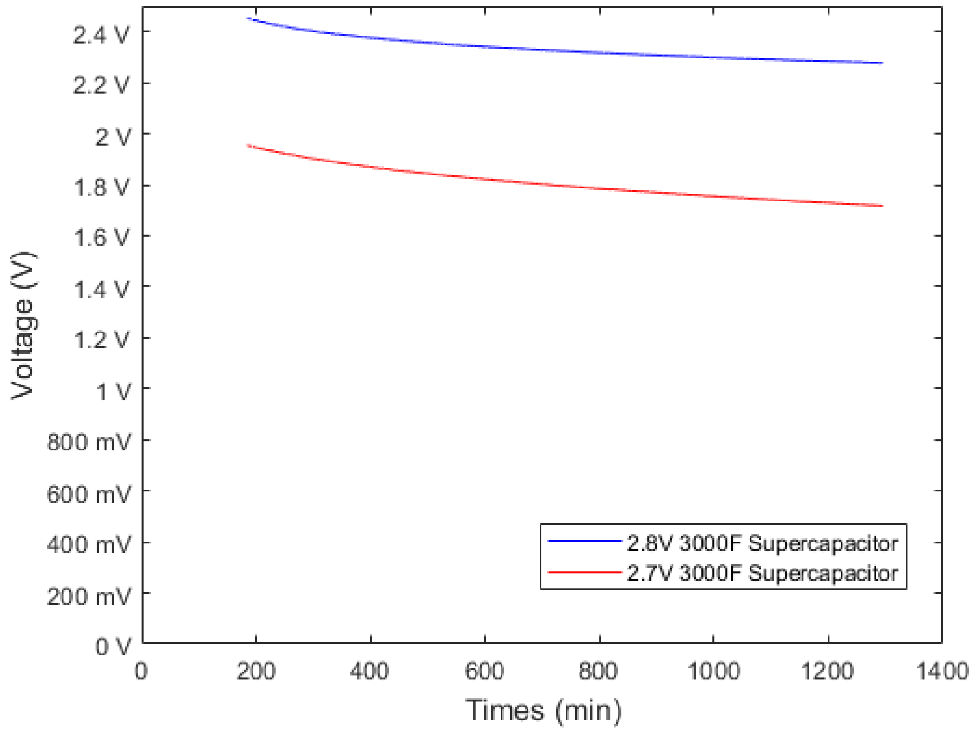

Figure 15: Self-discharging for 2.7V &2.8V 3000F GDCPH supercapacitor.

4.1.4 Results analysis of common capacitor test

Figure 16 and **Figure 17** below shows the time dependent voltage change trend (V(d)-t) during the 10000uF capacitor charging and discharging with 15.62Ω resistance. It can be seen that charging and discharging are very fast.

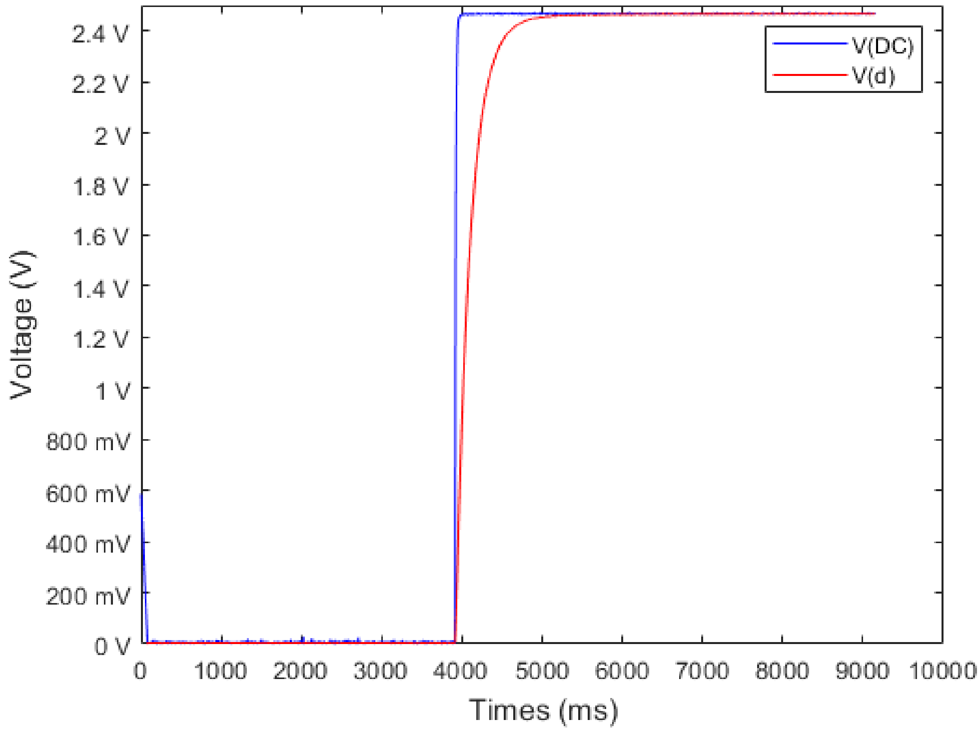

Figure 16: Charging for 10000uF capacitor.

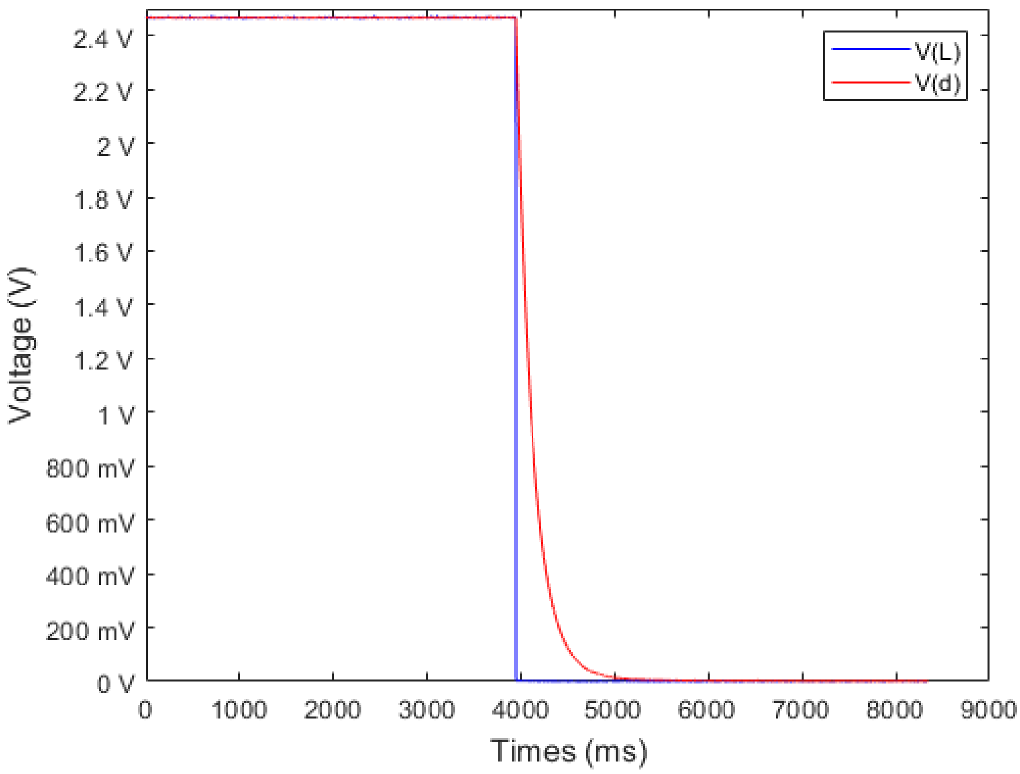

Figure 17: Discharging for 10000uF capacitor.

4.1.5 Comparison and discussion

Figure 18 and **Figure 19** showed a comparison of voltage and current changes in two supercapacitors as they were charged and discharged. Curve with similar colour was selected to represent the same measurement variable. It can see that the overall change is not very obvious, especially for the discharge, the curves are basically the same. And for charging, there are some small errors in the voltage change, 2.8V SC gets a higher voltage than 2.7V SC during the same time.

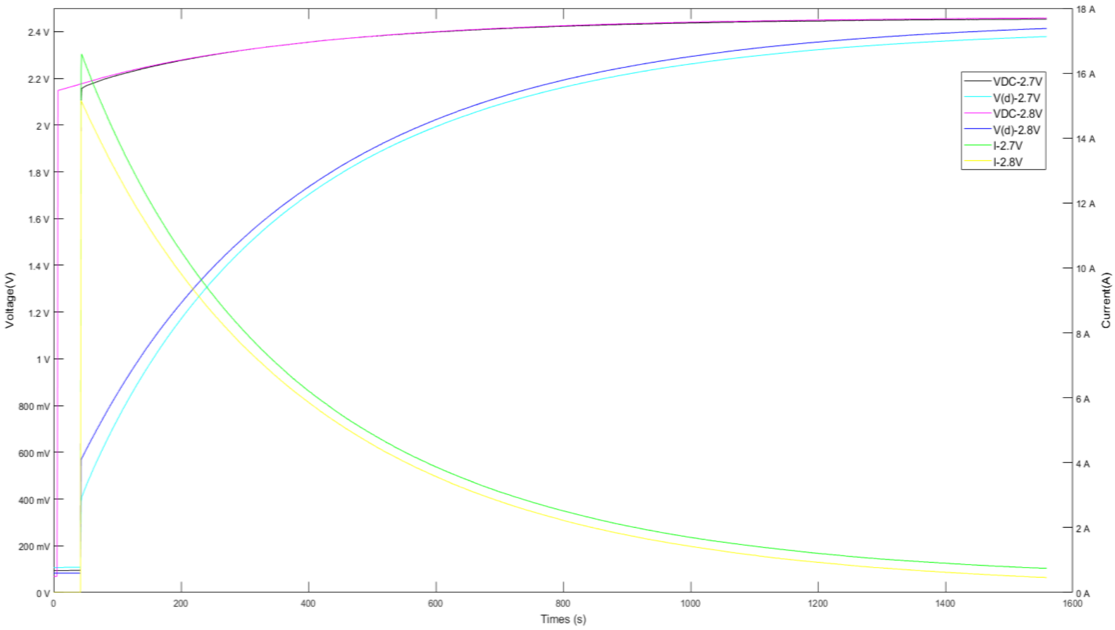

Figure 18: Compare the changes during charging of 2.7V and 2.8V supercapacitors

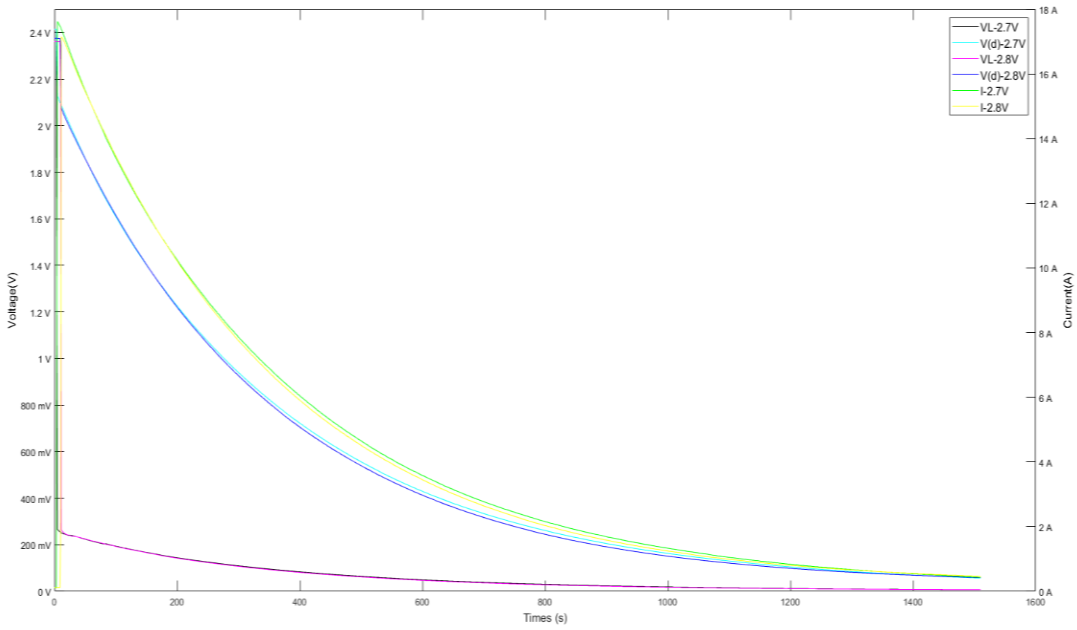

Figure 19: Compare the changes during discharging of 2.7V and 2.8V supercapacitors

By comparison, it can be seen that the charging speed of 2.8V SC is faster than 2.7V SC. Compared with ordinary capacitors, the storage capacity of supercapacitors is much larger than it.

4.1.6 Estimate and error

By comparing Estimate error of 2.7V and 2.8V SC during charging of **Figure 20** and **Figure 21**, it can be seen that the error fluctuation of 2.8V SC is less than 2.7V SC. This shows that the measurement result of 2.8V SC is more accurate.

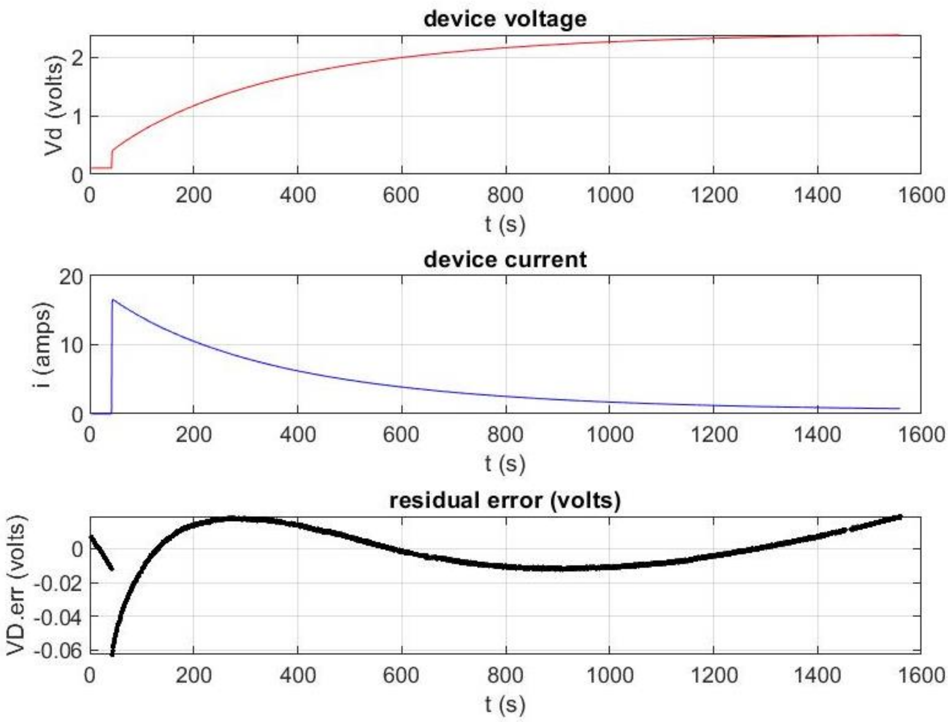

Figure 20: Estimation error for 2.7V SC Charging

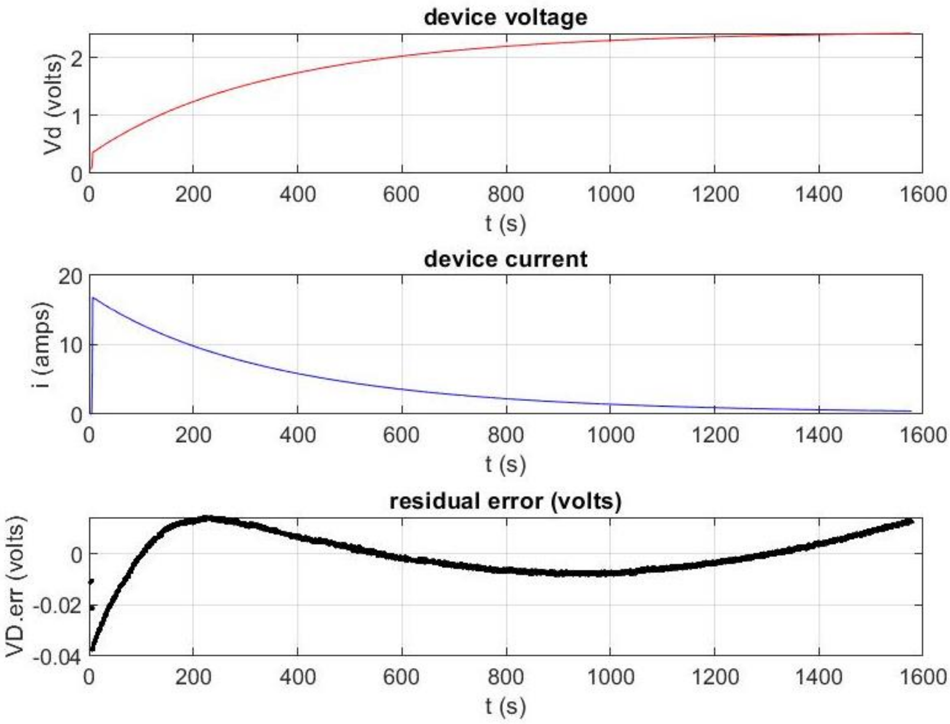

Figure 21: Estimation error for 2.8V SC Charging

By comparing Estimate error of 2.7V and 2.8V SC during discharging of **Figure 20** and **Figure 21**, it can be seen that the error fluctuation of 2.8V SC is very small, and the error fluctuation of 2.7V SC is between -0.01V to 0.01V.

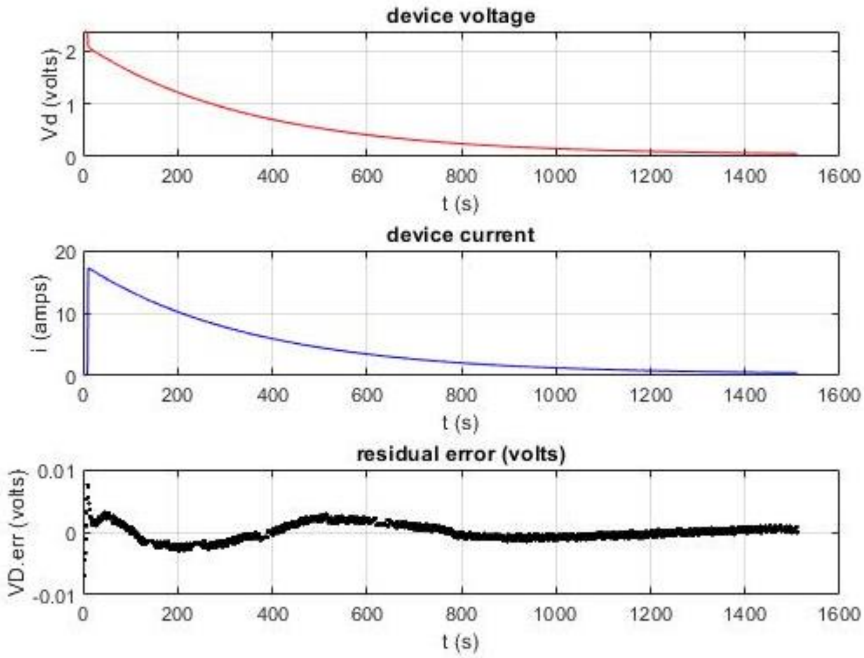

Figure 22: Estimation error for 2.7V SC Discharging

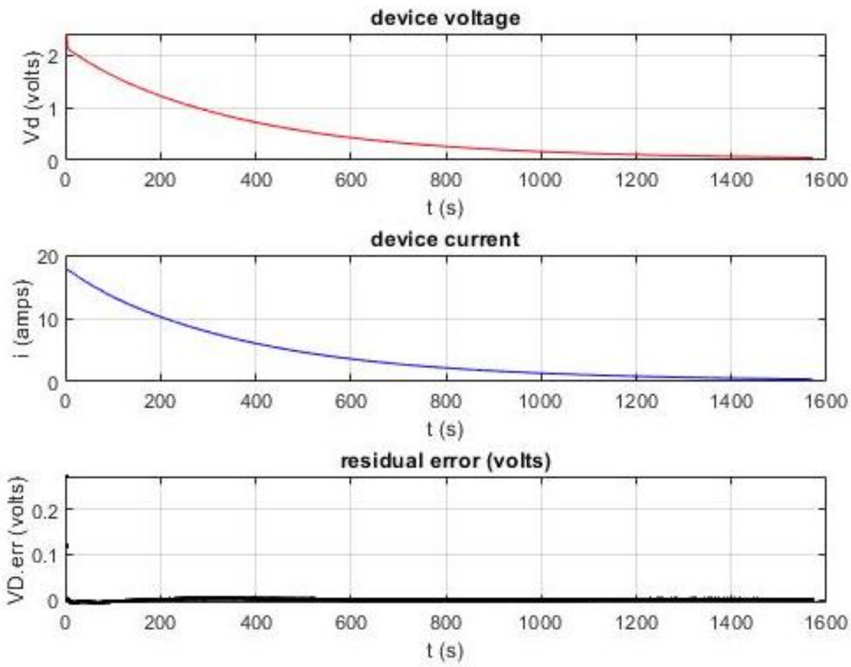

Figure 23: Estimation error for 2.8V SC discharging

In general, the error range of the Charging experiment is around 0.06, which may be caused by factors such as the impedance of the wires and the environment during the experiment. For discharge, the error is very small. It can be seen that the power supply may provide fluctuating current, resulting in significant errors.

4.2 SC internal material characterization and analysis

It has been known that the SC is consists of collectors, electrodes, electrolyte and membrane separator, where the overall performance of SC is strongly determined by the materials of these components. The electrode and electrolyte seem play more important role in the electrical properties of the SC. For the electrode, it requires a high conductivity and large specific surface area with ideally porous structure for greater capacitance which means greater energy storage capacity. **Figure 24** below systematically summarizes specific capacitance of SC using different electrode material. It shows that the SC with electrode of RuO_2 has the highest capacitance in average, where the highest capacitance of such SC is around 1200F [53] . However, such SCs is not widely used in current market due to its high cost and complicated structure.

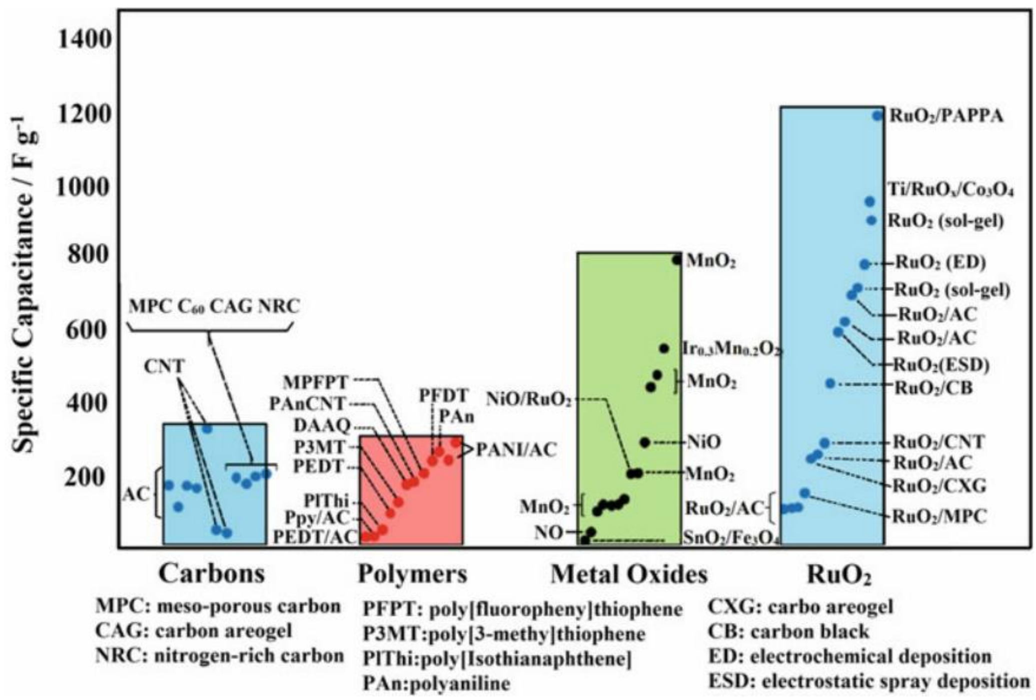

Figure 24: Specific capacitance of supercapacitor using different electrode materials. [53]

In our study, the materials of the three samples were activated carbon, carbon aerogel and graphene.

Activated carbon is a porous material composed of amorphous carbon and graphite microcrystals. It is generally called activated carbon when the specific surface area of porous carbon is greater than $500 m^2/g$. Because activated carbon has a large specific surface area due to its micropores, it is common to use an electrode material containing activated carbon as the electrode of a supercapacitor, so that the surface is in contact with the electrolyte. However, the conductivity of activated carbon is not strong, so in the use of activated carbon electrode, ordinary activated carbon can be chemically modified, so that it has good conductivity, high apparent density and high specific capacity, and add acetylene black conductive agent to enhance the conductivity of activated carbon electrode [54, 55].

Carbon aerogel is a new kind of nanoporous material first discovered by Pekala, an American. By adjusting the pore size of carbon aerogel, it has better electrical conductivity. In addition, because the carbon aerogel material obtained by sol-gelation reaction is generally massive, it is necessary to grind the massive aerogel ball into micron powder (~ 10μm), which is not only time-consuming and laborious, but also expensive. Therefore, a direct preparation method of powdered carbon aerogel appeared, which can meet the needs of diverse applications. However, at this stage of the preparation of carbon aerogels process is relatively complicated, in the preparation of carbon aerogels are often the precursor of supercritical drying technology, the method is of high cost and complex process, production cycle is long, difficult to mass production, and has a certain risk, so countries researchers are exploring the preparation of ambient pressure instead of supercritical drying process[7, 56].

Graphene material, as the electrode material of the new supercapacitor, uses its two-dimensional structure, has a large specific surface area, low specific gravity, and the thickness of single sheet layer is distributed between 0.34nm and 2nm. The existence of functional groups on the surface makes the monolayer graphite material and electrolyte fully wet. Compared with traditional super capacitor with activated carbon as electrode material, it saves energy. Compared with carbon nanotubes as the electrode material of the supercapacitor, the cost is low. The new type of supercapacitor has good performance, with high specific capacitance and high energy density (up to $50whkg^{-1}$), and its specific power up to $40kwkg^{-1}$[17, 22].

Graphene has many characteristics that other materials do not have. Its advantages mainly include good electrical conductivity, large surface area, small density, special thermal conductivity, optical properties, high mechanical properties, etc., which are ideal for the requirements of electrode materials for supercapacitors.

4.3 Project cost and performance analysis

According to the experimental data, it is found that the overall performance of SCs with graphene electrodes is the best among the selected SCs (i.e. V=2.7V, C=3000F). Assuming the discharge completion at 1V with zero current leakage, then the total quantity of electrical discharge (Q_d) will be 5100 C(As) according to the formula of $Q=C \cdot \Delta V$, which equals to a battery with capacitance of 1.42Ah. In fact, the real access capacitance will be lower than the theoretically calculated one due to the large leakage current of SC. If we set the completion of discharge at 0V, then the capacitance of such SC will be 8100C or 2.25Ah. If 200 identical such SC are combined together, then the capacitance of such SC unit will be 450Ah.

We then compared such SC with the Tesla batteries (i.e. Powerwall). The Powerwall is a kind of domestic rechargeable lithium battery, which is a kind of energy storage wall in fact. Such energy storage wall is consisted of lithium battery packs, liquid thermal control system and a software adopting the signals of invertors for a solar power system. It can not only be used as an energy storage device but also provide the energy for an ordinary household. The Powerwall (i.e. capacitance of 13.5kWh) with capacitance of can be installed on the wall of the home to store the power generated by household solar power generation. It can be used to reduce the load of family circuit, as a standby power supply in case of emergency, and can also be used for family life. As for its stored power, it is allowed to come from different channels, including solar energy, power grid and even electric vehicles like model S.

The lithium battery are certainly has its advantages, such as the short construction period, low operation cost is low, the impact on the environment and is not restricted by geographical conditions, and so on, but it doesn't change the lithium battery charge and discharge life constraints, as well as its power on the storage capacity is limited, if want to recharge electric cars, requires several Powerwall series is enough, and so, And that's where the cost goes -- considering that even the $3,000 minimum price tag could cost the average household several years of electricity, that's not a big deal by itself[29, 57].

Table 4: Comparison of double layer capacitance between lithium battery and supercapacitor[57]

Characteristic contrast	battery (lithium battery)	double layer capacitance
Energy conversion	Chemical energy -- electrical energy	electrical energy
Internal reaction	REDOX chemical reaction	Polarizes electrolyte physical reaction
Process reversibility	Charge and discharge process is reversible and energy conversion is losable.	The charge-discharge process is reversible
Using the loss	Decreased activity of a chemical medium The cathode material is passivated and the capacity decays Charge and discharge energy conversion loss anode material	Improper use of electrolyte leakage
Internal impedance	The internal resistance decreases when charging and rises when discharging	Low impedance, adjustable according to pressure requirements
Charge and discharge	speed generally charge and discharge rate is 1-5, the maximum discharge rate can be up to 10	The higher the charging current, the faster the charging speed, which can reach 95% of the rated capacity within 10 seconds
Charge and discharge time	A full charge of 5-6 hours	a few seconds
power density	Low 50-200w/kg	high, low impedance leads to high power output 1000-2000w/kg
Single nominal voltage	lithium battery 3.0-3.7v	Around 1.2-1.5v
affected by temperature	Large, significant activity plan temperature relationship range:-25℃--+45℃	Small, very small active polarization range: -40℃--+70℃
The energy density	High,20-100wh/kg	Low, 1/10 of the battery, 3-15wh/kg
Charge and discharge efficiency	>95%	>95%
Cycle life	The average is about 5000-10,000 Large charging and discharging rate has great influence on life	>100000 times

Charge holding capacity	Thick gate at low self discharge	There is almost no self-discharge
Environmental protection	Even with the use of harmless chemicals, there is still potential contamination	There is almost no chemical contamination
Engineering use	Large scale series and parallel connection of monomers	The monomer is connected in parallel on a large scale, and can be used in series after the pressure equalization measures are removed
Use the maintenance	Battery seal is maintenance-free	Completely maintenance-free
Cost per Wh	$20(typical)	$0.5-$1.00(large system)

As can be seen from the table, double-layer capacitors have great advantages in storage and service life, but also have great disadvantages in energy density, which will become the focus of research on double-layer capacitors and even supercapacitors in the future.

When using supercapacitors instead of batteries, they are an expensive substitute. Compared to batteries of the same capacity, the cost can sometimes become very high, for example 10-20 times higher.

Supercapacitors have more positive applications than batteries. But there are downsides to the battery. Therefore, the use of SCs is highly dependent on the type of application.

Chapter 5 Conclusions and Outlook

According to the content of previous chapters, two parts of conclusion and outlook could be presented in this chapter. The summary and conclusion part will briefly review the experimental and simulation results and highlight the important results and conclusion of the project. The outlook part will point out the future work of this project and guide the development direction of SC for renewable energy storage system

5.1 Summary and Conclusion

This paper mainly studies the performance of supercapacitors and uses three kinds of supercapacitors of different materials for comparison. We completed the performance test of supercapacitors in the laboratory, and obtained the VI diagram of charge and discharge.

Under the condition that the accuracy of the manufacturer's data was 100% correct, we used the R-C model for simulation and obtained the corresponding comparison diagram. Combined with different materials, we finally analyzed that the performance of the graphene material was the best. Replacing lithium batteries with supercapacitors for home use is difficult to achieve in life applications, mainly because the energy density of supercapacitors is too small to store much energy per unit volume. If this aspect is improved, it could be a good substitute.

5.2 Outlook

Batteries and supercapacitors have their own advantages and disadvantages, and both have advantages and disadvantages in their applications. At present, large power battery, the lithium battery is trained in welcome, is also the hotspot of lithium battery research and development, and in the bus, tram, and other areas of the low power requirements into application stage, the future lithium batteries will mainly from the anode materials and electrolyte, the diaphragm, the internal structure was improved, enhance its high-power application, and security. The low energy density of supercapacitors limits their application in vehicles. In the future, improvements will be made towards high energy density, mainly from materials, to improve the manufacturing level of diaphragm and electrode surface area, so as to achieve the energy of lead-acid batteries.

From the perspective of technology development, the combination of supercapacitor and battery can combine the advantages of both, which will be the direction of new technology development. The hybrid supercapacitor, also known as superbattery, is composed of two different electrodes of supercapacitor and battery in its internal structure. Super battery realizes the performance complementation of the two energy storage methods, with low-cost, high-energy density, high energy storage, long cycle life and strong adaptability to the environment. The development and application of the superbattery will bring a revolutionary breakthrough.

References

[1] T. M. I. Mahlia, T. J. Saktisahdan, A. Jannifar, M. H. Hasan, and H. S. C. Matseelar, "A review of available methods and development on energy storage; technology update," *Renewable and Sustainable Energy Reviews,* vol. 33, pp. 532-545, 2014/05/01/ 2014.

[2] B. E. Conway, *Electrochemical supercapacitors : scientific fundamentals and technological applications*. New York: Plenum Press, 1999, pp. xxviii, 698 p.

[3] L. Zhang, X. Hu, Z. Wang, F. Sun, and D. G. Dorrell, "A review of supercapacitor modeling, estimation, and applications: A control/management perspective," *Renewable and Sustainable Energy Reviews,* vol. 81, pp. 1868-1878, 2018.

[4] N. Devillers, S. Jemei, M.-C. Péra, D. Bienaimé, and F. Gustin, "Review of characterization methods for supercapacitor modelling," *Journal of Power Sources,* vol. 246, pp. 596-608, 2014.

[5] Y. Zhang, H. Feng, X. Wu, L. Wang, and L. L. Zhang, "Progress of Electrochemical Capacitor Electrode Materials: A Review," *International Journal of Hydrogen Energy,* vol. 34, no. 11, pp. 4889-4899, 2009.

[6] P. Sharma and T. S. Bhatti, "A review on electrochemical double-layer capacitors," *Energy Conversion and Management,* vol. 51, no. 12, pp. 2901-2912, 2010/12/01/ 2010.

[7] G. Wang, L. Zhang, and J. Zhang, "A review of electrode materials for electrochemical supercapacitors," *Chemical Society Reviews,* 10.1039/C1CS15060J vol. 41, no. 2, pp. 797-828, 2012.

[8] S. Faraji and F. N. Ani, "The development supercapacitor from activated carbon by electroless plating—A review," *Renewable and Sustainable Energy Reviews,* vol. 42, pp. 823-834, 2015/02/01/ 2015.

[9] C. Yuan, X. Zhang, Q. Wu, and B. Gao, "Effect of temperature on the hybrid supercapacitor based on NiO and activated carbon with alkaline polymer gel electrolyte," *Solid State Ionics,* vol. 177, no. 13, pp. 1237-1242, 2006/05/01/ 2006.

[10] T. S. Sonia *et al.*, "Composite supercapacitor electrodes made of activated carbon/PEDOT:PSS and activated carbon/doped PEDOT," *Bulletin of Materials Science,* vol. 36, no. 4, pp. 547-551, 2013/08/01 2013.

[11] A. Lewandowski, M. Zajder, E. Frąckowiak, and F. Béguin, "Supercapacitor based on activated carbon and polyethylene oxide–KOH–H2O polymer electrolyte," *Electrochimica Acta,* vol. 46, no. 18, pp. 2777-2780, 2001/05/31/ 2001.

[12] B. H, "Low voltage electrolytic capacitor," US, 1957.

[13] M. Selvakumar and D. K. Bhat, "Microwave synthesized nanostructured TiO2-activated carbon composite electrodes for supercapacitor," *Applied Surface Science,* vol. 263, pp. 236-241, 2012/12/15/ 2012.

[14] M. Inagaki, H. Konno, and O. Tanaike, "Carbon materials for electrochemical capacitors," *Journal of Power Sources,* vol. 195, no. 24, pp. 7880-7903, 2010/12/15/ 2010.

[15] C. Liu, Z. Yu, D. Neff, A. Zhamu, and B. Z. Jang, "Graphene-Based Supercapacitor with an Ultrahigh Energy Density," *Nano Letters,* vol. 10, no. 12, pp. 4863-4868, 2010/12/08 2010.

[16] B. Xu, S. Yue, Z. Sui, X. Zhang, and S. Hou, "What is the choice for supercapacitors: graphene or graphene oxide?," *Energy & Environmental Science,* vol. 4, no. 8, pp. 2826-2830, 2011.

[17] L. L. Zhang, R. Zhou, and X. S. Zhao, "Graphene-based materials as supercapacitor electrodes," *Journal of Materials Chemistry,* 10.1039/C000417K vol. 20, no. 29, pp. 5983-5992, 2010.

[18] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, "Graphene-Based Ultracapacitors," *Nano Letters,* vol. 8, no. 10, pp. 3498-3502, 2008/10/08 2008.

[19] M. Pumera, "Graphene-based nanomaterials for energy storage," *Energy & Environmental Science,* 10.1039/C0EE00295J vol. 4, no. 3, pp. 668-674, 2011.

[20] D. Yu and L. Dai, "Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors," *The Journal of Physical Chemistry Letters,* vol. 1, no. 2, pp. 467-470, 2010/01/21 2010.

[21] X.-F. Wu, Z. Zhou, and W.-M. Zhou, "Electrical contact resistance in filaments," *Applied Physics Letters,* vol. 100, no. 19, p. 193115, 2012.

[22] Y. Wang *et al.*, "Supercapacitor Devices Based on Graphene Materials," *The Journal of Physical Chemistry C,* vol. 113, no. 30, pp. 13103-13107, 2009/07/30 2009.

[23] K.-J. Huang *et al.*, "Layered MoS2–graphene composites for supercapacitor applications with enhanced capacitive performance," *International Journal of Hydrogen Energy,* vol. 38, no. 32, pp. 14027-14034, 2013.

[24] H. S. S. RamakrishnaMatte *et al.*, "MoS2 and WS2 Analogues of Graphene," *Angewandte Chemie International Edition,* vol. 49, no. 24, pp. 4059-4062, 2010.

[25] N. Zheng, X. Bu, and P. Feng, "Synthetic design of crystalline inorganic chalcogenides exhibiting fast-ion conductivity," *Nature,* vol. 426, no. 6965, pp. 428-432, 2003/11/01 2003.

[26] J. Xiao, D. Choi, L. Cosimbescu, P. K. Koech, J. Liu, and J. P. Lemmon, "Exfoliated MoS2 Nanocomposite as an Anode Material for Lithium Ion Batteries," *Chemistry of Materials,* vol. 22, pp. 4522-4524, 2010.

[27] J. M. Soon and K. P. Loh, "Electrochemical Double-Layer Capacitance of MoS[sub 2] Nanowall Films," *Electrochemical and Solid-State Letters,* vol. 10, no. 11, p. A250, 2007.

[28] X. Hu, S. Li, and H. Peng, "A comparative study of equivalent circuit models for Li-ion batteries," *Journal of Power Sources,* vol. 198, pp. 359-367, 2012.

[29] J. Xu, C. C. Mi, B. Cao, and J. Cao, "A new method to estimate the state of charge of lithium-ion batteries based on the battery impedance model," *Journal of Power Sources,* vol. 233, pp. 277-284, 2013.

[30] B. Wang, S. E. Li, H. Peng, and Z. Liu, "Fractional-order modeling and parameter identification for lithium-ion batteries," *Journal of Power Sources,* vol. 293, pp. 151-161, 2015.

[31] S. Kim, W. Choi, K. Lee, and S. Choi, "Advanced Dynamic Simulation of Supercapacitors Considering Parameter Variation and Self-Discharge," *IEEE Transactions on Power Electronics,* vol. 26, no. 11, pp. 3377-3385, 2011.

[32] R. L. Spyker and R. M. Nelms, "Classical equivalent circuit parameters for a double-layer capacitor," *IEEE Transactions on Aerospace and Electronic Systems,* vol. 36, no. 3, pp. 829-836, 2000.

[33] Y. Zhang and H. Yang, "Modeling and characterization of supercapacitors for wireless sensor network applications," *Journal of Power Sources,* vol. 196, no. 8, pp. 4128-4135, 2011/04/15/ 2011.

[34] S. Buller, E. Karden, D. Kok, and R. W. De Doncker, "Modeling the dynamic behavior of supercapacitors using impedance spectroscopy," *IEEE Transactions on Industry Applications,* Article vol. 38, no. 6, pp. 1622-1626, 2002.

[35] D. L. Chapman, "A contribution to the theory of electrocapillarity," *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science,* vol. 25, no. 148, pp. 475-481, 1913/04/01 1913.

[36] O. Stern, "The theory of the electrolytic double shift," *Z. Elektrochem. Angew. Phys. Chem.,* vol. 30, pp. 508-516, 1924.

[37] H. Wang and L. Pilon, "Mesoscale modeling of electric double layer capacitors with three-dimensional ordered structures," *Journal of Power Sources,* vol. 221, pp. 252-260, 2013/01/01/ 2013.

[38] H. Farsi and F. Gobal, "Artificial neural network simulator for supercapacitor performance prediction," *Computational Materials Science,* vol. 39, no. 3, pp. 678-683, 2007/05/01/ 2007.

[39] C. H. Wu, Y. H. Hung, and C. W. Hong, "On-line supercapacitor dynamic models for energy conversion and management," *Energy Conversion and Management,* vol. 53, no. 1, pp. 337-345, 2012/01/01/ 2012.

[40] A. Eddahech, O. Briat, M. Ayadi, and J.-M. Vinassa, "Modeling and adaptive control for supercapacitor in automotive applications based on artificial neural networks," *Electric Power Systems Research,* vol. 106, pp. 134-141, 2014/01/01/ 2014.

[41] T. Weigert, Q. Tian, and K. Lian, "State-of-charge prediction of batteries and battery–supercapacitor hybrids using artificial neural networks," *Journal of Power Sources,* vol. 196, no. 8, pp. 4061-4066, 2011/04/15/ 2011.

[42] J.-N. Marie-Francoise, H. Gualous, and A. Berthon, "Supercapacitor thermal- and electrical-behaviour modelling using ANN," *IEE Proceedings - Electric Power Applications*, vol. 153, no. 2, pp. 255-262[Online]. Available: https://digital-library.theiet.org/content/journals/10.1049/ip-epa_20050096

[43] D. Riu, N. Retiere, and D. Linzen, "Half-order modelling of supercapacitors," in *Conference Record of the 2004 IEEE Industry Applications Conference, 2004. 39th IAS Annual Meeting.*, 2004, vol. 4, pp. 2550-2554 vol.4.

[44] V. Martynyuk and M. Ortigueira, "Fractional model of an electrochemical capacitor," *Signal Processing,* vol. 107, pp. 355-360, 2015/02/01/ 2015.

[45] N. Bertrand, J. Sabatier, O. Briat, and J.-M. Vinassa, "Fractional non-linear modelling of ultracapacitors," *Communications in Nonlinear Science and*

Numerical Simulation, vol. 15, no. 5, pp. 1327-1337, 2010/05/01/ 2010.

[46] R. Martín, J. J. Quintana, A. Ramos, and I. de la Nuez, "Modeling of Electrochemical Double Layer Capacitors by Means of Fractional Impedance," *Journal of Computational and Nonlinear Dynamics,* vol. 3, no. 2, 2008.

[47] A. Dzieliński, G. Sarwas, and D. Sierociuk, "Time domain validation of ultracapacitor fractional order model," in *49th IEEE Conference on Decision and Control (CDC)*, 2010, pp. 3730-3735.

[48] T. J. Freeborn, B. Maundy, and A. S. Elwakil, "Measurement of Supercapacitor Fractional-Order Model Parameters From Voltage-Excited Step Response," *IEEE Journal on Emerging and Selected Topics in Circuits and Systems,* vol. 3, no. 3, pp. 367-376, 2013.

[49] P. Thounthong, S. Rael, and B. Davat, "Control Strategy of Fuel Cell and Supercapacitors Association for a Distributed Generation System," *IEEE Transactions on Industrial Electronics,* vol. 54, no. 6, pp. 3225-3233, 2007.

[50] G. F. N. Rizoug, B. Barbedette, "Hybrid Supply For Automotive Application Using Supercapacitors," *2010 IEEE Vehicle Power and Propulsion Conference,* pp. 1-7, 1-3 Sept. 2010.

[51] L. Zubieta and R. Bonert, "Characterization of double-layer capacitors for power electronics applications," *IEEE Transactions on Industry Applications,* vol. 36, no. 1, pp. 199-205, 2000.

[52] J. K. P. Kamal K. Kar, Sravendra Rana, *Handbook of Polymer Nanocomposites. Processing, Performance and Application*. 2015, pp. XIII, 601.

[53] F. Rafik, H. Gualous, R. Gallay, A. Crausaz, and A. Berthon, "Frequency, thermal and voltage supercapacitor characterization and modeling," *Journal of Power Sources,* vol. 165, no. 2, pp. 928-934, 2007.

[54] K. K. Kar, *Handbook of Nanocomposite Supercapacitor Materials I* (Springer Series in Materials Science). Springer, Cham, 2020, pp. XXI, 364.

[55] M. Mastragostino, C. Arbizzani, L. Meneghello, and R. Paraventi, "Electronically conducting polymers and activated carbon: Electrode materials in supercapacitor technology," *Advanced Materials,* vol. 8, no. 4, pp. 331-334, 1996.

[56] Y. Zhang, H. Feng, X. Wu, L. Wang, and L. L. J. I. J. o. H. E. Zhang, "Progress of Electrochemical Capacitor Electrode Materials: A Review," *International Journal of Hydrogen Energy,* vol. 34, no. 11, pp. 4889-4899, 2009.

[57] S. M. Lambert, V. Pickert, J. Holden, X. He, and W. Li, "Comparison of supercapacitor and lithium-ion capacitor technologies for power electronics applications," *5th IET International Conference on Power Electronics, Machines and Drives (PEMD 2010),* pp. 1-5, 2010.