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Review

Aging Mechanism and Models of Supercapacitors: A Review

Ning Ma [1], Dongfang Yang [2], Saleem Riaz [3], Licheng Wang [4] and Kai Wang [1,*]

[1] School of Electrical Engineering, Weihai Innovation Research Institute, Qingdao University, Qingdao 266000, China
[2] Xi'an Traffic Engineering Institute, Xi'an 710300, China
[3] School of Automation, Northwestern Polytechnical University, Xi'an 710072, China
[4] School of Information Engineering, Zhejiang University of Technology, Hangzhou 310014, China
* Correspondence: wkwj888@163.com

Abstract: Electrochemical supercapacitors are a promising type of energy storage device with broad application prospects. Developing an accurate model to reflect their actual working characteristics is of great research significance for rational utilization, performance optimization, and system simulation of supercapacitors. This paper presents the fundamental working principle and applications of supercapacitors, analyzes their aging mechanism, summarizes existing supercapacitor models, and evaluates the characteristics and application scope of each model. By examining the current state and limitations of supercapacitor modeling research, this paper identifies future development trends and research focuses in this area.

Keywords: supercapacitors; models; aging mechanism; applications

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1. Introduction

As a new type of energy storage element, a supercapacitor has great potential in the energy field due to its high power density [1,2]. It has the advantages of high discharge power, long cycle life, wide operating temperature range, and environmental protection. It is the core device in the energy storage system [3,4]. Due to the pure electrostatic energy storage mechanism, compared with other energy storage systems based on electrochemical conversion (such as batteries), supercapacitors also have the characteristics of low internal series resistance, low-cost consumption, and fast charging and discharging speed.

A supercapacitor is a special capacitor between a traditional capacitor and rechargeable battery, which combines the high-current fast charging and discharging characteristics of an ordinary capacitor and the energy storage characteristics of a battery, filling the gap between an ordinary capacitor and battery [5,6]. According to different working principles, supercapacitors are mainly divided into two categories: electric double-layer supercapacitors and pseudo capacitance supercapacitors. The supercapacitor that has been described and mentioned in this paper is a double-layer capacitor.

The aging of supercapacitors can be divided into calendar aging and cycle aging [7]. The phenomenon of continuous aging of supercapacitors under actual working conditions is called calendar aging. The aging phenomenon of a supercapacitor in charge–discharge cycles is called cycle aging. The aging factors of a supercapacitor include external stress, self-acceleration, and manufacturer's production factors. The external stress includes voltage, temperature, charging and discharging power, etc.

The model of a supercapacitor has important theoretical value for analyzing its electrode structure and energy storage mechanism. Developing a model that accurately represents the operational characteristics of supercapacitors is essential for analyzing their electrochemical behavior. This is crucial for simulating and modeling supercapacitors, which can enable state monitoring and life prediction, leading to stable and efficient operation of energy storage systems. Such modeling can provide valuable insights into the internal mechanisms and phenomena of supercapacitors, enabling optimization of their design and performance. Accurate modeling can also help to identify and address potential failure modes and improve the safety and reliability of the supercapacitor system. Therefore, accurate modeling and simulation are of great significance in the development and application of supercapacitors. This paper introduces the working principle and applications of supercapacitors, analyzes the aging mechanism, summarizes various supercapacitor models, points out the characteristics of existing models, and looks forward to the development trend of supercapacitor modeling research.

The major key contributions of our study are summarized as follows:

- We have analyzed the aging mechanism and influence factors of supercapacitors in detail and have debated regarding recent studies.
- The various models of supercapacitors have been schematically summarized and their working principles are also debated.
- We have elaborated the advantages and disadvantages in detail for each category, as well as summarized the application of these models.

The rest of the paper has been divided into the following major sections. The basics and existing literature are explained in Section 1 (Introduction). The working principle of various types of electrochemical supercapacitors is given in Section 2. The aging mechanism and its key factors are discussed in Section 3. The various models according to their characteristics are briefly explained in Section 4. Finally, Section 5 includes the concluding remarks and future work recommendations of the study.

2. Working Principle and Applications

2.1. Working Principle

The principle of electric double-layer capacitance is electrostatic energy storage. The energy storage process is a physical process, without chemical reaction, and the process is completely reversible, which is different from the electrochemical energy storage of batteries. Since positive and negative ions are adsorbed on the surface between the solid electrode and the electrolyte, respectively, the potential difference between the two solid electrodes is caused, thereby realizing energy storage. During charging, under the action of the charge attraction on the solid electrode, the positive and negative ions in the electrolyte collect on the surfaces of the two solid electrodes, respectively. Meanwhile, during discharge, the cation and anion leave the surface of the solid electrode and return to the electrolyte body. Simultaneously, the stored charge is released through the external circuit to supply power to the load [8]. This process is shown in Figure 1.

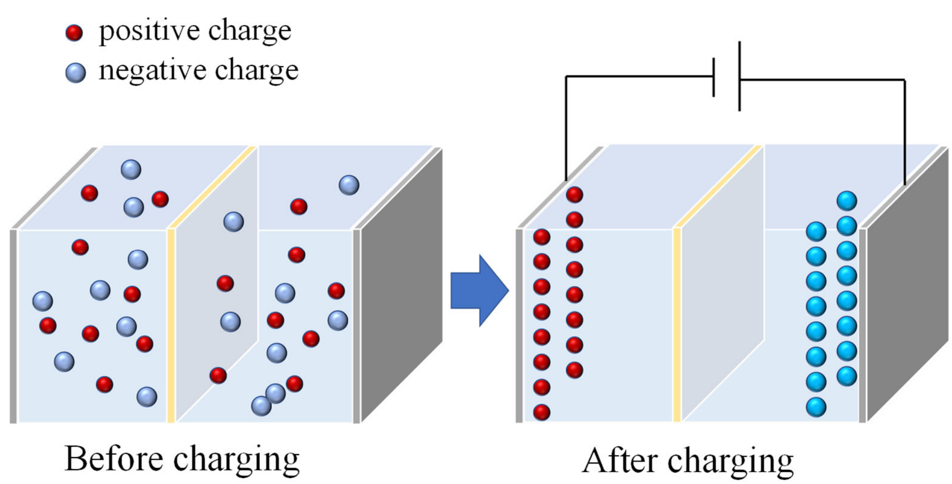

Figure 1. Operating principle of supercapacitors. Positive and negative charges are stored on the positive and negative plates, respectively, when the electrodes are connected to the external circuit.

2.2. Applications

In today's society, there is a growing demand for superior standards of energy and power supply in terms of quality, safety, and reliability. In response to this need, a novel power grid known as microgrid has emerged, which seamlessly integrates distributed power generation. In this context, supercapacitors have emerged as a new and innovative energy storage technology, capable of providing short-term power supply and energy buffering functions, ultimately enhancing the overall power quality of microgrids. As a result, supercapacitors have become one of the preferred energy storage devices for microgrids [9,10]. Supercapacitors are used as power sources in electric vehicles or hybrid electric vehicles to improve the service life of batteries. In addition to that, these are often used in wind power generation systems, photovoltaic power generation systems, distributed power generation systems, and large-scale power storage systems [11–14]. The application fields of supercapacitors are shown in Figure 2.

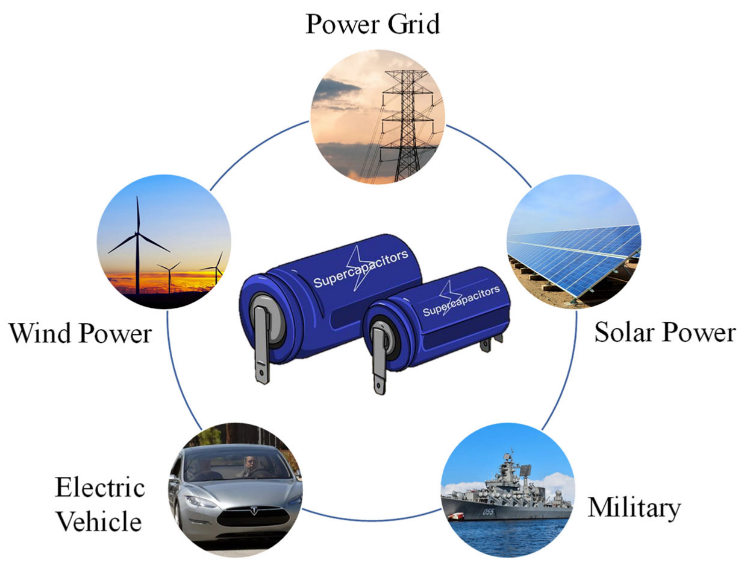

Figure 2. Application domain of supercapacitors.

3. Aging Mechanism

3.1. Overview

Activated carbon is the electrode material of supercapacitors widely used in industry at present, which mainly uses biomass resources to obtain porous activated carbon materials through physical activation or chemical activation treatment with an activator [15]. Because of its simple preparation process and low price, it is widely used in industrial manufacturing of supercapacitors. In the process of chemical activation treatment, corrosive activated materials will be used to make the porous electrode materials. After the activation treatment is completed, the electrode material will be cleaned to remove the activated substances remaining on the surface of the material. While cleaning, some residues will still be adsorbed on the electrode surface. The impurities left in the electrode during electrode manufacturing are the main source of aging and failure.

During the normal use of the supercapacitor, the residues on the electrode surface will react reversibly with the electrolyte to form solid and gaseous products [16], as shown in Figure 3. The gradual deposition of solid products on the electrode surface (as illustrated in area 1) can obstruct the porous structure and lead to a reduction in the contact area between the electrode and electrolyte. This phenomenon is commonly referred to as electrode fouling. Gaseous products may diffuse to multiple areas inside the supercapacitor. For example, when the gaseous products reach the free zone (shown in area 2), the air pressure inside the capacitor will rise; when gaseous products are adsorbed on the electrode surface (as shown in area 3), the contact area between the electrode and electrolyte will be reduced. Gaseous products may also be adsorbed on the membrane, thus blocking the path of ionic charge (shown in area 4). These products lead to an increase in the internal air pressure of the supercapacitor, which may cause electrode cracking (as shown in area 5) or shell deformation to damage the collector (as shown in area 6). The above series of reactions will lead to aging of the supercapacitor.

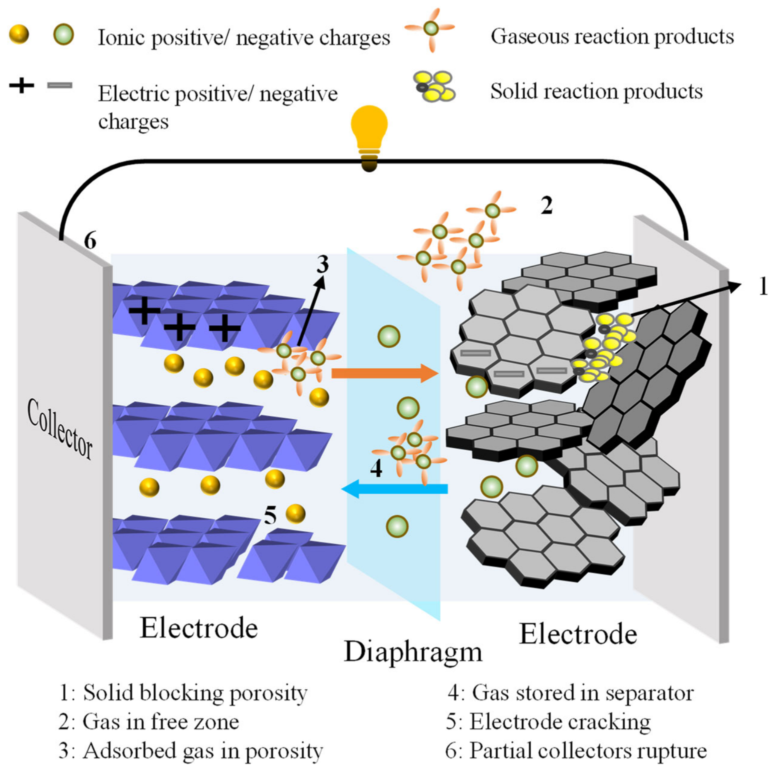

Figure 3. Supercapacitor aging principle [17]. Copyright 2022 Elsevier B.V.

Electrolyte decomposition, electrode deterioration, and shell damage are aging characteristics of supercapacitors. Capacitance loss, equivalent series internal resistance (ESR) increase, and deformation are typical effects of supercapacitor aging. Root causes, failure mechanisms, failure modes, and failure effects of EDLCs are shown in Figure 4.

Therefore, the electrolyte of supercapacitors should meet these requirements: the conductivity should be high to minimize the internal resistance of the supercapacitor; the electrolyte should have higher electrochemical and chemical stability; the operating temperature range should be wide to meet the working environment of the supercapacitor; and the size of the ions in the electrolyte should match the aperture of the electrode material.

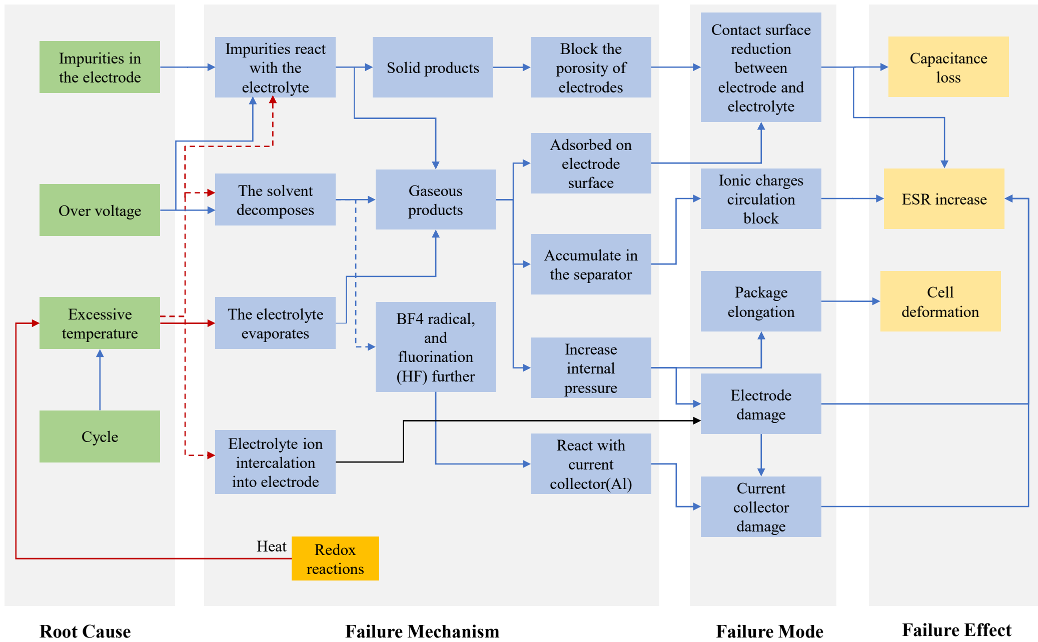

Figure 4. Root causes, failure mechanisms, failure modes, and failure effects of supercapacitors [18].

3.2. Aging Factor

3.2.1. External Stress

Taking the influence of temperature as an example, in reference [19], the supercapacitors were cyclically tested in 40–50 °C, 40–60 °C, and 50–60 °C, and the results showed that the degradation rate of the supercapacitor was significantly accelerated with the increase in temperature. The high temperature stimulates the chemical activity of each component of the supercapacitor and accelerates the aging speed. In addition, the high temperature accelerates the decomposition of electrolyte, which leads to the decrease in ion concentration. Simultaneously, the impurities generated from its decomposition block the pores of the diaphragm and electrode materials, reducing the ion mobility, reducing the accessibility of the ion to the porous structure on the electrode surface, thus causing the decrease in capacitance and the increase in ESR.

Voltage can also accelerate the attenuation rate of a supercapacitor. The authors of [20] draw a conclusion through experiments that 10 K temperature rise and a voltage increase of 100 mV have virtually the same effect on the aging behavior of a supercapacitor. The maximum working voltage of a supercapacitor is subject to the decomposition voltage of electrolyte solution; in contrast, the working voltage affects parameters such as current density and temperature, which are closely related to the stability of electrolyte.

In technical terms, the cycle life of a supercapacitor is impacted by its charge and discharge power. Higher charge and discharge power levels result in a more rapid decay of the supercapacitor's lifespan. This is due to the fact that increased power levels generate more Joule heat, which, in turn, accelerates the degradation of the supercapacitor's internal materials, increases its internal resistance, and accelerates the aging process [21].

3.2.2. Self-Acceleration of Aging

The aging process of supercapacitors is accompanied by self-acceleration, which is specifically shown as follows: (1) when supercapacitors are used in modules, due to the complexity and diversity of the application environment and uneven temperature distribution, individuals close to the heat source have a higher initial temperature, which will accelerate their aging speed and cause the ESR to rise faster, and the rise of ESR, in turn, will cause their own temperature to rise faster, thus forming a positive feedback effect [22];

(2) due to the difference in individual parameters of supercapacitors, there is a voltage imbalance between each individual in the module during charging. Specifically, the single supercapacitor with the smallest capacity has the highest charging voltage, which is most prone to overvoltage and has the most serious aging occurring during use. The more serious the aging is, the further the capacity is reduced and the charging voltage is further increased, which also forms a positive feedback effect.

3.2.3. Manufacturing Factors

Different materials and manufacturing processes also affect the service life of supercapacitors. On the one hand, the polymer that plays a bonding role in the electrode preparation process contains a large number of functional groups. During the preparation of the porous electrode, physical or chemical activation is carried out and water residues are inevitably introduced. During the normal use of the supercapacitor, the surface functional groups are decomposed by redox reaction; on the other hand, the impurity atoms on the surface of the carbon electrode that cause electrochemical phenomena also appear during the preparation of the electrode. In addition, different capacitor packaging methods will lead to significantly different life.

4. Models

4.1. Equivalent Circuit Models

Among the many models of supercapacitors, the most widely used is the equivalent circuit model. The equivalent circuit model, according to the electrical characteristics of the supercapacitor in the working process, uses various components in the circuit to characterize its internal deterioration mechanism. According to the circuit configuration and the number of components, different circuit models have different accuracy. Increasing the complexity of the circuit is helpful to improve the accuracy of the model.

4.1.1. Simple Series RC Models

The simplest equivalent circuit model is shown in Figure 5a [23]. RC series circuit only reflects the instantaneous dynamic response and can reflect the external electrical characteristics of the supercapacitor surface. Its advantages are simple parameter fitting process and high accuracy in charge and discharge calculation [24]. In order to significantly improve the accuracy of the simple RC circuit model, some online fitting methods have been proposed in the literature [25]. However, the equivalent circuit model is too simple, which also brings some disadvantages. In fact, supercapacitors are affected by various factors, resulting in performance degradation. However, this model does not consider the changes in the performance of supercapacitors in the working state and cannot deeply simulate the working principle of supercapacitors. Therefore, it is limited in complex energy storage systems. Therefore, it is very important to study an accurate degradation performance model.

Spyker and Nelms add a parallel resistance to account for the leakage current effect [26,27]. Compared with the simple RC series circuit, the model refines the resistance R. As shown in Figure 5b, the improved series RC model is composed of equivalent capacitance C, equivalent series internal resistance ESR, and equivalent parallel internal resistance EPR. Where, C is approximately equal to the nominal value of the capacitance, reflecting the aging speed of the supercapacitor, the magnitude of ESR is related to the energy loss of R during the aging process of supercapacitors, the capacitance tends to decrease, and the ESR increases; EPR represents the leakage current effect of the supercapacitor. However, the model can only fully represent the supercapacitor dynamics in a few seconds, which greatly limits its practical applicability.

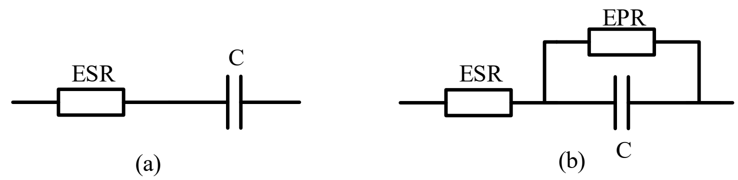

Figure 5. Simple series RC model: (**a**) simple series RC model; (**b**) the simple model of series-parallel connection.

4.1.2. Transmission Line Models

Pean, C. et al. introduced the transmission line model to simulate the distributed capacitance and electrolyte resistance determined by the porous electrode, as shown in Figure 6 [28,29]. The distributed parameter characteristics of supercapacitors are simulated by RC network and the model parameters are determined by impedance spectrum analysis. The model can have high fitting accuracy in a relatively wide frequency range. Its essence is to carry out high-order fitting of the charging and discharging curves of supercapacitors. The order of fitting can be determined according to the accuracy requirements of the model. Some of the literature has proposed the transmission lines with a variable number of branches and these range from 5 [30] to 15 branches [31]. The higher the order, the higher the accuracy of the model but the more the corresponding model parameters and the parameter identification will be very complex. In addition, the model cannot fully reflect the influence of leakage current of supercapacitors.

Saha P. and Dey S. et al. [32] used a combination system consisting of frequency and time techniques to describe the transmission line, taking the leakage effect into account.

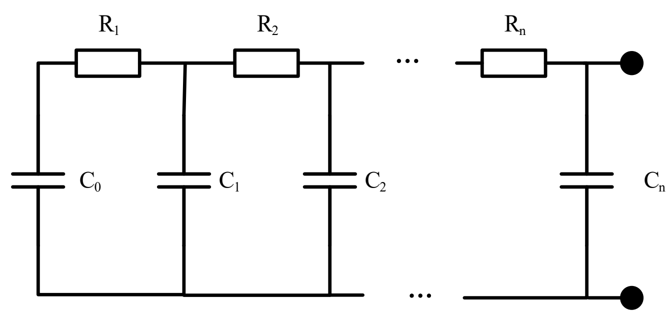

Figure 6. Transmission line model.

4.1.3. Multi-Branch RC Network Models

The form of the multi-branch RC model is similar to that of the transmission line model. What is different from the transmission line model is that each branch of the model has a different time constant, and each branch acts independently in different time periods of the charging and discharging process. A ladder circuit composed of multiple RC branches with different time constants can be used to capture the distribution characteristics of capacitance and resistance of supercapacitors.

Most of the authors have used the three-branch model, which is proposed by Zubieta and Boner [33], as shown in Figure 7. It has included three RC branches: immediate branch, delay branch, and long-term branch, for which each branch has captured the characteristics of supercapacitors on different time scales. The immediate branch reflects the performance of the supercapacitor in the transient charging and discharging process, which is usually limited to a few seconds. The delay branch reflects the performance of the supercapacitor during charging and discharging in a few minutes. The long-term branch reflects the performance of the supercapacitor in the charging and discharging process within tens of minutes. In addition, the resistance R_L reflects the leakage current effect of the supercapacitor and the influence of a long time on the energy storage process. The nonlinear capacitor is connected in parallel with the constant capacitor as a voltage-dependent capacitor and is incorporated into the direct branch. Then, the parameters of the three branches are extracted by observing the terminal voltage evolution in the constant current charging process. For this model, Rajani et al. [34] presented a novel average point method to extract the model parameters. Analogous model representations were devised by other researchers with different characterization methods [31,35–37].

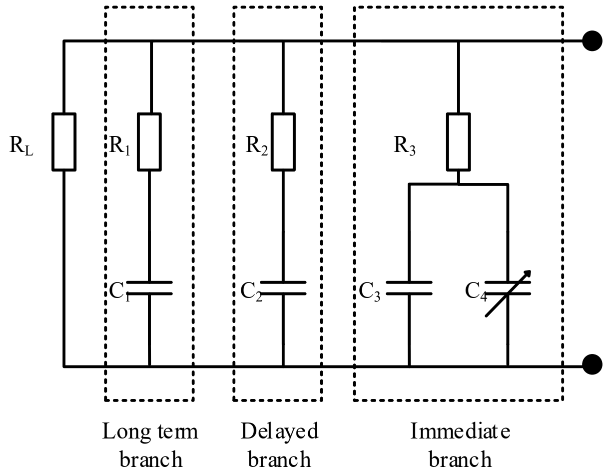

Figure 7. Third-order RC model.

4.2. Electrochemical Models

Helmholtz [38] first discovered the capacitive characteristics at the interface between solid conductor and liquid ionic conductor in 1853 and proposed the double-layer model in 1874. Helmholtz thought that the charge is evenly distributed at both ends of the electrode and electrolyte interface; he modeled this phenomenon as a conventional capacitor with distance for charge separation H, as shown in Figure 8a, where ψs is the local electric potential . Because the conductivity of the electrolyte is poor, the charge on the electrolyte side cannot be evenly distributed. The capacitance calculated according to the model is too large. However, this model shows the energy storage principle of supercapacitor in an intuitive and simple way and is a classic physical model of a supercapacitor. Gouy [39] put forward the model of side charge dispersion distribution in solution in 1910, and Chapman [40] made a detailed mathematical analysis of the model in 1913, as shown in Figure 8b. This model takes into account the spatial distribution of the charge on the electrolyte side, which is also called the diffusion layer. The calculated capacitance value based on the model is still larger than the actual value, because the model assumes that the ions are point charges, that is, they can be infinitely close to the electrode electrolyte interface. Stern proposed an improved model based on Gouy and Chapman's double-layer model. Stern believed that the double electric layer at the interface between the electrode and solution is composed of a compact layer and a diffusion layer. Under the action of electrostatic and thermal movement of particles, part of the ionic charges in the solution is adsorbed on the electrode surface to form a compact double electric layer, that is, the double electric layer capacitance can be seen as a series connection of the compact layer capacitance and the diffusion layer capacitance [41], as shown in Figure 8c. Later, Graham further established the metal solution interface model. He subdivided the compact layer into two layers: the inner Helmholtz layer and the outer Helmholtz layer. Generally, electrochemical models have high accuracy but low calculation efficiency.

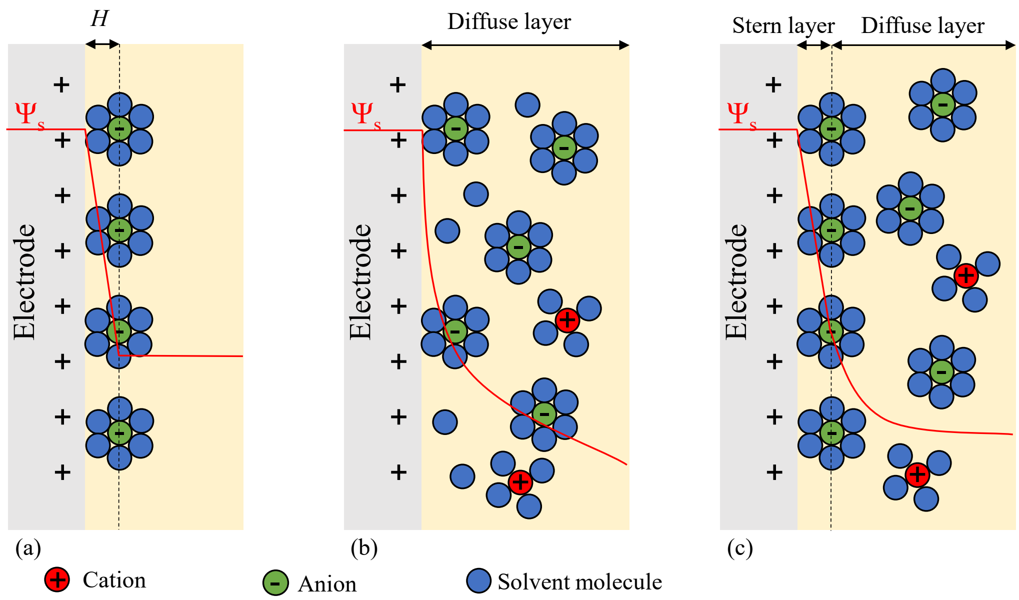

Figure 8. Schematics of the electric double−layer structure showing the arrangement of solvated anions and cations near the electrode/electrolyte interface in the Stern layer and the diffuse layer. Schematic of three basic electrochemical models of the supercapacitor: (**a**) Helmholtz model, (**b**) Chapman model, (**c**) combined mode. Reprinted with permission from Ref. [26].

4.3. Intelligent Models

This kind of model can be regarded as a black box. Without considering the internal mechanism of the supercapacitor, the relationship between input and output can be obtained by training a large amount of charging and discharging historical data. Sadiq Eziani et al. [42] took the voltage and current of supercapacitor as the input of ANN to estimate the SOC of the supercapacitor used for braking energy recovery of a railway system and achieved good results. Liu et al. [43] presented a stacked bidirectional long short-term memory recurrent neural network; the simulation results show that, when the number of hidden layers is two, the network has excellent performance and the predicted RMSE and MAE are 0.0275 and 0.0241, respectively.

The utilization of this model provides an advantageous capability to approximate the nonlinear properties of a given system, with infinite precision in theory. However, it is subject to the lack of a well-defined physical interpretation, and the parameters involved in its expression are highly intricate. Additionally, the model necessitates an extensive amount of training data, requiring a considerable amount of training time. It is noteworthy that the neural network learning algorithm, in its current state, has not fully addressed the issues of underfitting and overfitting, leading to suboptimal performance. Consequently, the applicability of this model may be limited. The neural network model is shown in Figure 9.

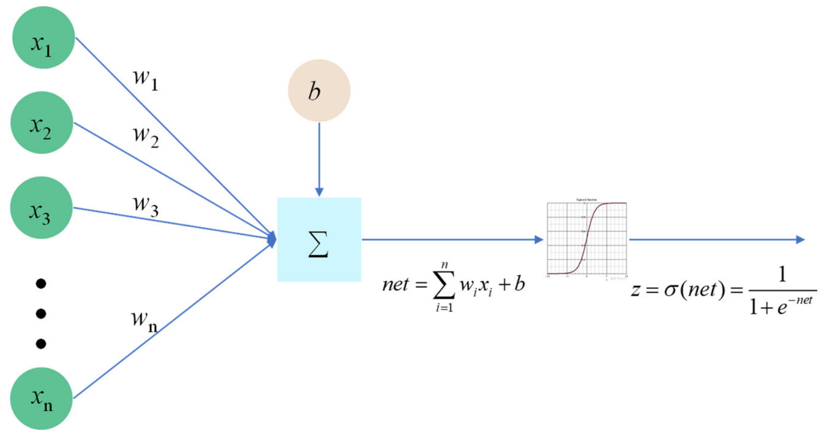

Figure 9. Neural network model. In the figure, x_1~x_n are input signals, w_1~w_n is the weight, *b* is the offset, and *z* is the activation function.

4.4. Fractional-Order Models

The resistance and capacitance parameters of supercapacitors are not constant and are affected by factors such as frequency. It is found that the fractional equivalent circuit model can more accurately describe the nonlinear characteristics of supercapacitors. It is found that the current and voltage of supercapacitors are fractional calculus [44], so the equivalent circuit model of a supercapacitor using fractional order components is proposed [45]. The typical fractional order model of a supercapacitor is shown in Figure 10, which consists of a series and a parallel resistor, a constant phase element (CPE), and Walburg-type elements [46]. Riu D and Retiere N et al. proposed a half-order FOM. Freeborn [47] established a simple FOM based on the series connection of a resistor and a CPE.

The fractional order model of supercapacitor uses fractional order components to describe the dynamic behavior of a supercapacitor. Compared with the integer order model, fractional order components can bring additional degrees of freedom to the model in order, which can not only improve the accuracy of the model, but also reduce the complexity of the model [48,49].

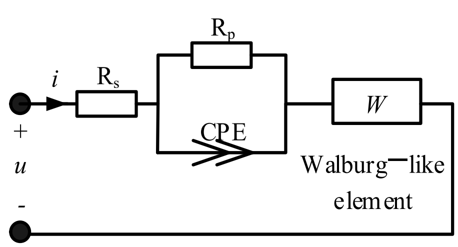

Figure 10. Fractional order model structure.

The model types for SC electrical behavior simulation are summarized in Table 1.

Table 1. Summary of model types for SC electrical behavior simulation.

Models	Advantages	Disadvantages
Equivalent circuit models	Simple and intuitive; convenient for analysis, calculation, and simulation; moderate accuracy	Susceptible to aging process
Electrochemical models	Description of inside physical–chemical reactions; high possible accuracy	Cannot reflect the dynamic process of charging and discharging; heavy computation; immeasurability of some parameters

Intelligent models	Can approximate the nonlinear characteristics of the system; good modeling capability	Absence of physical meanings; sensitive to training data quality and quantity; poor robustness
Fractional-order models	Better capability to fitting experimental data; few model parameters	Heavy computation

4.5. Self-Discharge Models

Among all kinds of electrochemical energy storage devices, supercapacitors had faced the most serious problem of self-discharge [50]. Smith and Tran et al. [50] compared the self-discharge behavior of commercial supercapacitors (2000F, Maxwell) and lithium-ion batteries (2.4 Ah, E-one moli energy corporation) in the charged state. The results show that the energy loss of the supercapacitor is as high as 22%, which is seven times more than the energy loss of the lithium-ion battery (3%) within 72 h of open-circuit storage time. The self-discharge problem can be seen. Conway and Pell et al. [51] have studied the self-discharge phenomenon of supercapacitors in the 20th century and proposed a mathematical model to describe the self-discharge process. Yang et al. [52] presented a self-discharge model in consideration of variable leakage resistance, as shown in Figure 11. The first branch contains R_1 and C_1 ($C_0 + K_V \times V$), which provides the instant behavior of the supercapacitor in response to the charging process. The second branch is the delayed branch, which represents the charge redistribution in the medium and long term, containing R_2 and C_2. The variable resistor R_3 in the third branch represents the leakage resistor corresponding to the self-discharge rate of the supercapacitor. Ricketts and Ton-That [53] pointed out that SC self-discharge is caused by two different mechanisms, i.e., ion diffusion and leakage current. Tete Tevi [53] proposed to cover the electrode with a thin insulating layer made of polyphenylene oxide (PPO) material, which can reduce the leakage current in the electric double-layer capacitor, thus slowing down the self-discharge of the supercapacitor. Increasing the thickness of the diaphragm (the thickness of the supercapacitor) can increase the diffusion distance of the reactant, thereby reducing the driving force of the concentration gradient of the self-discharge. Furthermore, it is worth noting that the pore structure of electrode materials is also an important factor [54].

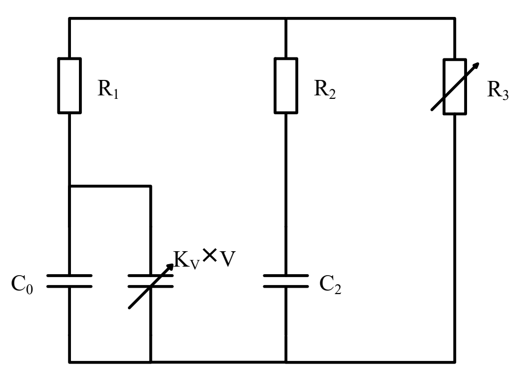

Figure 11. Self-discharge models.

4.6. Thermal Models

The previously proposed models are unable to predict the internal temperature of the supercapacitor. Thermal behavior is a very important aspect in the application of supercapacitors. Working in a bad thermal environment will reduce the performance parameters of supercapacitors, and the uneven distribution of temperature field in supercapacitors will cause the imbalance of individual performance. At present, most of the research on thermal behavior focuses on lithium-ion batteries, and the analysis of thermal behavior of electric double-layer supercapacitors is relatively lower. The development of a thermal model for a supercapacitor involves establishing a correlation between temperature variations and the corresponding changes in the supercapacitor's performance. This model is intended to serve as a theoretical framework for managing the thermal behavior of the supercapacitor.

Gualous H. [55] states that increment of the temperature increases the supercapacitor capacitance but reduces the ESR. Some studies have shown that higher temperatures will speed up the self-discharge process of the supercapacitor.

The thermal models of supercapacitors can be roughly divided into two categories:

- Heat generation: this kind of model describes the influence of its own heating on its temperature field [20,56–58]. The modeling purpose of this kind of model is to analyze the temperature change characteristics and temperature field distribution characteristics of supercapacitors when they work, which is mainly applied to the thermal management analysis of supercapacitor energy storage systems.
- Heat transmission: this kind of model describes the relationship between temperature and the change in model parameters [55,59]. Its modeling method is usually based on the equivalent circuit model to carry out a large number of experiments, determine the curve of model parameters with temperature, and then establish mathematical expressions through corresponding data processing. This kind of model is of great significance for studying the dynamic characteristics of supercapacitors under different ambient temperatures. The thermal model presented in Ref. [60] is shown in Figure 12. In the model, the heat generation is modeled as a current source, which is a function of the supercapacitor current; C_{th} represents the thermal capacity of the supercapacitor, R_{th} denotes the equivalent thermal resistance of the supercapacitor, and T_a denotes the surrounding air temperature.

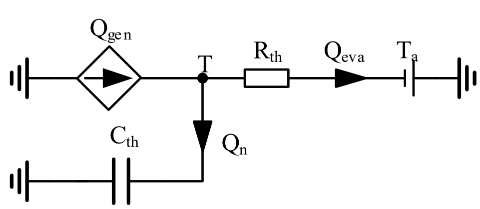

Figure 12. Supercapacitor thermal models.

4.7. Porous Electrode Models

The basic unit of the electric double-layer supercapacitor is composed of a pair of porous material electrodes, a collecting plate, an electrolyte, and an isolating film. Among them, the porosity of electrodes is the most important parameter to characterize the internal characteristics of supercapacitors, and it is also the main reason why supercapacitors differ from conventional electrolytic capacitors. The porous equivalent circuit model of an electric double-layer capacitor is an impedance ladder circuit model derived from the corresponding control equation and one-dimensional hole model [61]; its corresponding trapezoidal equivalent model is shown in Figure 13a. z_x and z_y are the impedances of unit length, and their directions are parallel to the x-axis of hole depth and perpendicular to the y-axis of hole depth, respectively.

The hole impedance model can be equivalent to the series connection of an ideal resistance and an ideal capacitor. Because the current is uniformly distributed on the corresponding resistance and capacitance, the equivalent circuit with several hole impedance models connected in series can approximate the porous characteristics. The equivalent circuit is composed of stray inductance L_s, equivalent series resistance R_s (sum of contact resistance, electrolyte solution resistance, and isolation film resistance), and porous electrode impedance Z_{pore} in series. The porous equivalent circuit model of a double-layer supercapacitor is shown in Figure 13b.

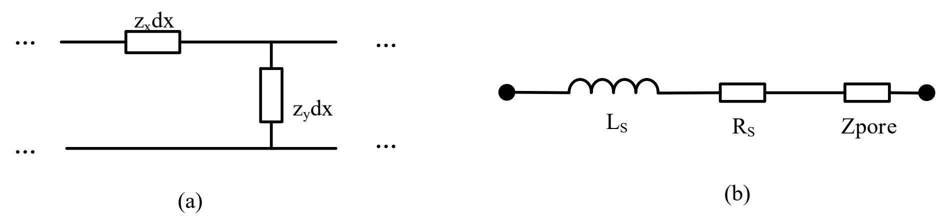

Figure 13. Porous electrode model: (**a**) trapezoidal equivalent model; (**b**) porous equivalent circuit model of double-layer supercapacitor.

4.8. Dynamic Models of Electrochemical Impedance Spectroscopy

The model consists of two RC networks in parallel and a series resistor. The dynamic model is used to replace the direct branch of the three-branch model, and a shunt leakage resistor is introduced to form a combined supercapacitor model. Among them, the series resistance and capacitance compose an equivalent circuit model with temperature-related parameters, which can estimate voltage or temperature through electrochemical impedance spectroscopy [62].This model is shown in Figure 14.

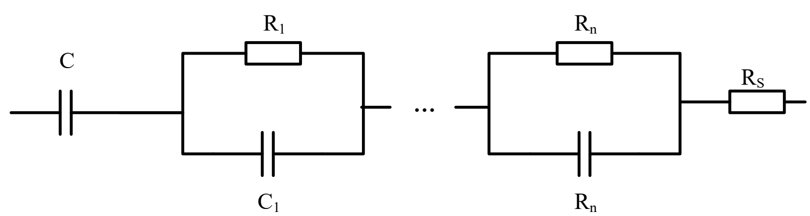

Figure 14. Dynamic model of electrochemical impedance spectroscopy.

5. Summary and Prospect

The modeling of supercapacitors is a key step to achieve different goals. This paper summarizes the aging mechanism and various models of supercapacitors. Through the above analysis of the current research status of supercapacitor modeling, it can be seen that different models can be established from different angles, and each model has its own scope of application. There is a contradiction between accuracy and complexity in the establishment of the model. Finding a compromise solution between the two is the key to the establishment of the actual system model.

The main problems of existing supercapacitor models are:

1. Some models have complex structures, such as the transmission line model, which is composed of many RC networks in series, parallel, and nested structures. The RC network parameters of each circuit are related to the internal structure and working state and are different from each other [63–65].
2. Parameter identification is difficult. At present, AC impedance analysis and circuit analysis are mainly used for supercapacitor model parameters. AC impedance analysis uses a lot of equipment, selects a lot of data when calculating parameters, and the calculation process is complex. The circuit analysis method uses the curve of voltage versus time to obtain the corresponding parameters. This method requires less equipment and is simple and convenient, but the structure of the model itself should not be too complex [66–68].

Although many achievements have been made in supercapacitor modeling, each model has its own advantages and disadvantages in limited applications. In the process of addressing the practical engineering problem, it is important to conduct an exhaustive evaluation of the benefits and drawbacks of diverse models in order to identify the most appropriate model. Given that there is no universally accepted model that can entirely and precisely capture the physical attributes of supercapacitors, the study of modeling for supercapacitors remains a critical area of interest in subsequent research [69–74].

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