

Review of Supercapacitor Equivalent Circuit Models

Karlo Kobeščak, Tomislav Baškarad

Summary — Supercapacitors are a promising technology for addressing the challenges faced by power systems with an increasing share of inverter-based resources. Due to their unique characteristics, supercapacitors can provide ancillary services to the grid. Understanding the behavior of supercapacitors under various conditions is crucial. Therefore, modeling and analysis are of significant interest in the research of supercapacitors for a wide range of applications. This article provides a brief overview of supercapacitor technology and presents a systematic review of five equivalent circuit models of supercapacitors.

Keywords — energy storage systems, supercapacitor, equivalent circuit models, application.

I. INTRODUCTION

THE power system (PS) with a high share of variable and unpredictable renewable energy sources (RES), which are connected to the grid through power electronics devices, and a reduced share of dispatchable fossil fuel power plants due to decarbonization goals, presents a challenge in maintaining both system stability and power quality. To ensure system stability, it is essential to have dispatchable units capable of damping disturbances caused by imbalances between electricity production and consumption due to the intermittency of RES. In the future power systems, energy storage systems and converters will play a key role in maintaining system stability. Since inverters electrically separate the RES generating unit from the grid, any kind of energy source or storage can be used to contribute to the moment of inertia of the system, for example flywheels, batteries, super-capacitors, etc [1].

According to [2], the application of energy storage can be divided into two areas, as shown in Figure 1. Energy storage systems can participate in energy management or provide ancillary services. Depending on the characteristics of the storage systems, different energy storage technologies can meet the requirements to provide various services to the power system. Several different energy storage technologies have been developed and tested to date, including pumped hydro storage, batteries, supercapacitors (SC), hydrogen, compressed air, and flywheels. A comparison of these technologies is provided in Table I, while Table II presents the required characteristics of energy storage for specific applications. From the comparison, it can be concluded that the supercapacitor technology is the most suitable for providing primary frequency control and voltage control.

(Corresponding author: Karlo Kobeščak)

Karlo Kobeščak and Tomislav Baškarad are with the University of Zagreb Faculty of Electrical Engineering and Computing, Zagreb, Croatia (e-mails: karlo.kobescak@fer.unizg.hr, tomislav.baskarad@fer.unizg.hr)

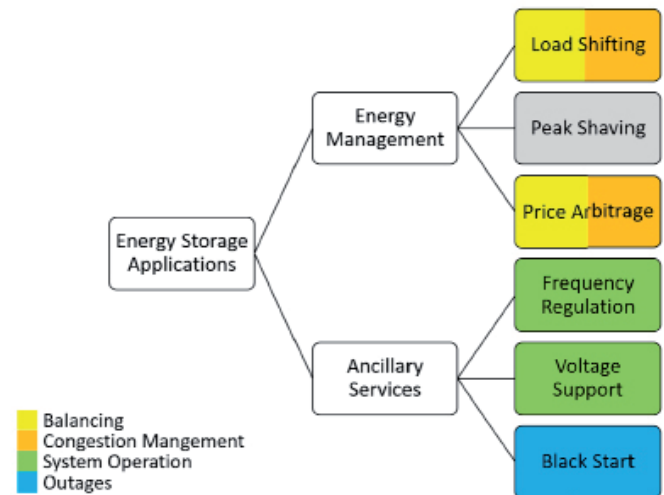


Fig. 1. Classification of energy storage application [2].

II. TYPES AND DESIGN OF SUPERCAPACITORS

Although Helmholtz described the electric double-layer capacitor as early as the mid-19th century, the technology of supercapacitors has developed more significantly since the mid-20th century, when the use of porous carbon materials led to the creation of the first electric double-layer capacitors. The structure of a supercapacitor is essentially the same as that of a conventional capacitor. A supercapacitor consists of two electrodes separated by a separator and impregnated with an electrolyte. The material of electrodes depends on the supercapacitor type. Separators are usually thin polymers, while electrolytes can be liquid, solid-state, or redox-active. Among liquid electrolytes, acetonitrile and propylene carbonate, or aqueous and are commonly used. Solid-state electrolytes include polymers or hydrogels. Compared to conventional capacitors, the high capacitance of SCs originates from the high specific area of the electrodes, which is largely determined by the used materials and their physical properties [3]. Voltage of the supercapacitor cell depends on the electrolyte technology. Based on the internal structure and energy storage mechanism, supercapacitors are today commonly classified into electric double-layer capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors. Characteristic comparison of supercapacitor types can be seen in Figure 2.

TABLE I:
APPLICATIONS OF ENERGY STORAGE SYSTEMS [2]

Application	Response Time	Power Rating (MW)	Discharge Duration	Cycles per Year
Load Shifting	10 – 30 min	1 – 2,000	Minutes - hours	> 3,000
Peak Shaving	10 – 30 min	0.1 – 10	30 – 240 min	250 – 500
Price Arbitrage	Minutes - hours	50 – 2,000	Hours	300 – 400
Primary Frequency Control	< 10 s	1 – 2,000	< 15 min	> 10,000
Secondary Frequency Control	10 – 30 s	1 – 2,000	< 120 min	< Primary Frequency Control
Tertiary Frequency Control	10 – 30 min	1 – 2,000	Hours	< Secondary Frequency Control
Voltage Support	Milliseconds	0.5 – 50 (MVar)	Seconds - minutes	> 15,000
Black Start	< 10 s	0.1 – 400	Minutes - hours	< 1

TABLE II:
CHARACTERISTICS OF SELECTED ENERGY STORAGE SYSTEMS [2]

Technology	Power Rating	Response Time	Discharge Duration	Cycles	Lifetime
Pumped Hydro	100 – 5,000 MW	Seconds	Hours - Days	> 100,000	30 – 60 years
Compressed Air	3 – 400MW	Minutes	Hours - Days	8,000 – 12,000	> 20 – 40 years
Flywheels	0.1 – 20MW	< 1 s	Seconds - Minutes	20,000 – 175,000	> 15 years
Supercapacitors	0.001 – 0.3MW	Milliseconds	Seconds - Minutes	10,000	30 years
Lithium-Ion Batteries	0 – 300MW	Milliseconds - Minutes	Minutes - Hours	1,000 – 3,000	5 – 15 years
Fuel Cells	Variable	< Seconds (LT)	Flexible	-	50,000 hours (LT)

A. ELECTRIC DOUBLE-LAYER CAPACITORS

EDLC is most matured and commercially used technology. Electrode materials in most EDLCs are typically composed of carbon-based materials, such as graphene, graphite, carbon nanotubes or mesoporous carbon [4]. When connected to an electric source, the charges on the electrodes attract oppositely charged ions from the electrolyte, forming layers of ions parallel to the electrodes [5]. The large specific surface area of electrode materials, resulting from their porosity, enables the absorption of a greater number of ions on the electrode surface, which leads to a higher capacitance. This type of charge storing mechanism is called non-Faradic. Electrode structure does not change during this process and as a result EDLC have higher cycle life and faster time of charge and discharge than pseudocapacitors and hybrid supercapacitors.

B. PSEUDOCAPACITORS

Pseudocapacitors have metal-oxide or conducting polymer electrodes with high electrochemical pseudocapacitance material [6]. and are some of electrode materials of interest for pseudocapacitors. Pseudocapacitors have Faradic storing mechanism - reversible redox reactions happen when potential is applied, and charges are electrochemically adsorbed on the electrode surface [4]. Redox reactions typically lead to the consumption of both electrodes and electrolytes, resulting in a faster degradation of capacitance compared to EDLCs. However, they offer the advantage of a higher capacitance and energy density [7].

C. HYBRID SUPERCAPACITORS

Hybrid supercapacitors combine two types of electrodes. One electrode is of electrostatic, often referred to as capacitive type, while other is electrochemical or battery type. These supercapacitors can be categorized into three types based on elec-

trode configuration: asymmetric hybrids, battery-type hybrids, and composite hybrids [4]. Asymmetric type pseudocapacitors' electrode as a positive, and EDLC electrode as a negative electrode. Battery type combines battery electrode and SC electrode, while composite type uses electrodes that incorporates carbon-based materials with metal oxides in a single electrode [6]. Charges are stored in both Faradic and non-Faradic processes. Hybrid supercapacitors have the highest energy density and capacitance, but also the longest charging time and non-linear relationship between open-circuit voltage (OCV) and stored charge [7].

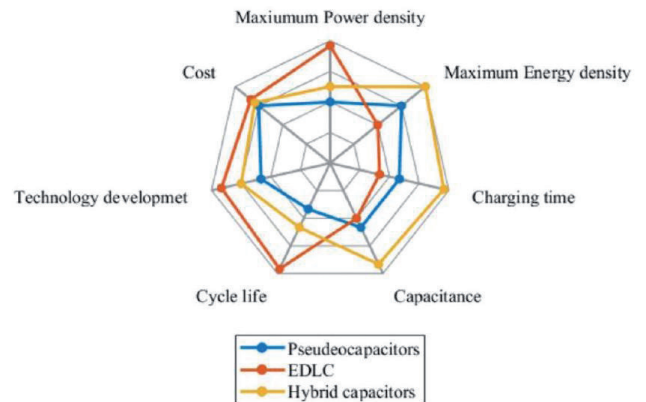


Fig. 2. Characteristics comparison of supercapacitor types [7].

III. SUPERCAPACITORS' CHARACTERISTICS

Supercapacitor characteristics vary depending on the SC type. This article focuses on EDLCs. In the literature ([2], [7]-[10]), the characteristic values of SCs differ. IEC 62391-1 classifies SCs in 5 classes depending on SCs' capacitance and internal resistance [11]. However, despite these variations, the literature agrees on the

overall advantages and disadvantages of SCs. The main upsides of SCs include high power density (10,000-60,000 W/kg), high Coulombic efficiency (85-98%), fast response times (measured in milliseconds), fast charging/discharging times (0.3-30 seconds), a high number of cycles (up to 1,000,000), and a wide operating temperature range (-40-75 °C). On the other hand, the main drawbacks of SC technology are lower specific energy (1-30 Wh/kg) and higher self-discharge rates (up to 60% per month).

In addition to their role in providing primary frequency regulation and voltage regulation services, SCs (either standalone or as part of hybrid energy storage systems) can also be used for regenerative power harvesting (e.g., in hybrid electric vehicles), power quality enhancement, microgrid stability, UPS, and as power supplies in medicine and smart devices. Due to the low voltage per SC cell (1-3 V) and low energy density, SC cells are connected in series (to achieve higher voltage) and in parallel (to increase energy capacity) for power system applications. These interconnected cells are referred to as SC modules (or banks). It is of great importance to establish metrics and characterization techniques in order to compare different SC cells. In [12], authors presented different performance evaluations and test procedures for SCs. Commonly used metrics are cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and constant current charge/discharge.

A. CYCLIC VOLTAMMETRY

Cyclic voltammetry is a method used in electrochemistry to understand the behavior and analysis of voltage windows, specific capacitance, and cycle life [7]. The CV measurement is typically conducted in a three-electrode configuration, where the working electrode is the electrode being tested, the reference electrode has a constant electrochemical potential, and the counter electrode is an inert electrode in the tested cell that completes the circuit. During CV measurement, the potential of the working or target electrode in the system is measured against the reference electrode via linear scanning back and forth between the specified upper and lower potential limits. The current passing between the working electrode and the counter electrode can be recorded and then plotted as a function of electrode potential to yield a CV plot [13]. Comparison of SC and battery CV plot is given in Figure 3.

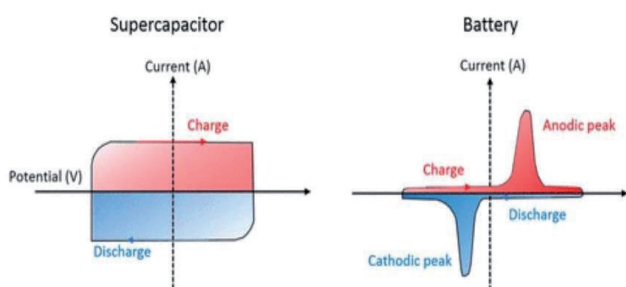


Fig. 3. Cyclic voltammetry plots of SC and battery [14]

B. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

EIS is a method for measuring supercapacitors' Equivalent Series Resistance (ESR). A sinusoidal AC excitation signal with variable frequency is superimposed on a DC potential and applied to SC and the AC response is measured. EIS is a method for frequency domain analysis of device impedance. Nyquist or Bode plots are used to illustrate the frequency dependencies of capacitance and resistance. More about EIS of EDLC can be found in [15] and physical interpretations of Nyquist plot can be seen in Figure 4.

ESR is very important parameter of SC, because it restricts the rates at which the capacitance can be charged or discharged upon application of a given current or voltage [13].

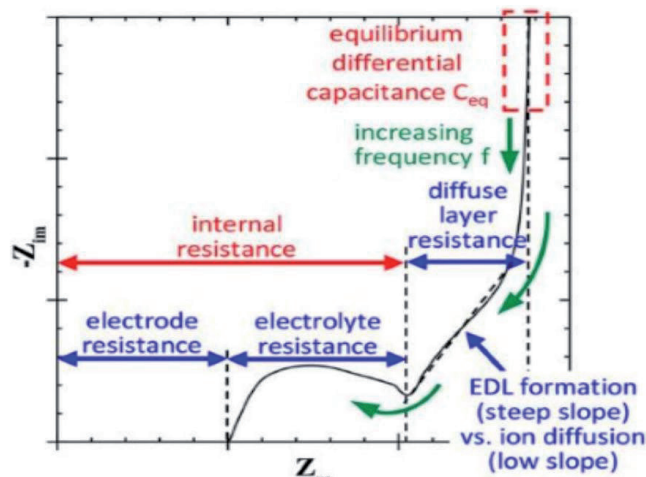


Fig. 4. Physical interpretations of EDLC Nyquist plot [15]

C. CONSTANT CURRENT CHARGE/DISCHARGE

Galvanostatic charge-discharge test is reliable and widely used method to determine capacitance energy density, power density, ESR and cycle life of SC. Constant cell current is applied, and cell voltage is measured as a function of charging or discharging time. Voltage – time characteristics between capacitor terminals in capacitance and internal resistance measurement described by IEC 62391-1 can be seen in Figure 5.

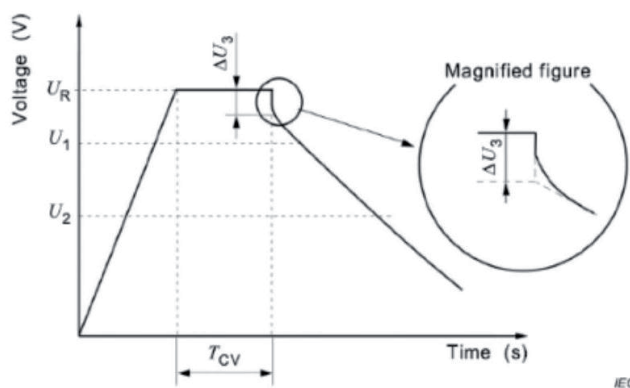


Fig. 5. Voltage - time characteristics [11]

IV. SC MODELING

To analyze a system incorporating a SC, it is crucial to establish an accurate SC model. There are several SC models presented in literature. Models differ on complexity, purpose and accuracy.

A. OVERALL LITERATURE REVIEW

Authors in [3] provide a review of different types of EDLC models. They present electrochemical models, equivalent circuit models (ECM), and fractional-order models as suitable for modeling the electrical behavior of supercapacitors. Electrochemical models exhibit high accuracy but low computational efficiency, making them suitable for embedded systems in realtime energy

management and control. Fractional-order models improve modeling accuracy by incorporating fractional-order calculus. Additionally, they discuss intelligent models, such as artificial neural networks (ANN) and fuzzy logic, which can capture complex non-linear relationships between inputs and outputs but require large amounts of training data. Equivalent circuit models, due to their structural simplicity and decent modeling accuracy, are widely accepted for real-time energy management synthesis.

The same authors, in [16], compare the complexity, accuracy, and robustness of three ECM types for SCs: the classic model, multi-stage ladder model, and dynamic model. They conducted Dynamic Stress Tests and a self-designed pulse test to collect data for model characterization and used a genetic algorithm to identify optimal model parameters. Their findings show that the most complex ladder model has the lowest accuracy and robustness, the classic model has the second-best performance, and the dynamic model provides the best compromise between model precision, robustness, and complexity. It is worth noting that none of the three models account for voltage-dependent capacitance.

In [17], the authors review ECMs and propose a new identification procedure for estimating state-space model parameters for series, parallel, and basic configurations.

A comprehensive review of SC modeling techniques is provided in [18], where the authors classify, explain, and compare these techniques, along with descriptions of the experimental methods used to measure the modeled properties. The simple RC circuit, multi-branch model, and dynamic model are briefly discussed.

Description and characterization methods for the RC model, two-branch Zubieta-Bonert model, and the dynamic SC model are presented in [19]. Some ECMs are summarized in [20], while [21] provides a literature review and simulates the two branch SC model in Simulink, which is also experimentally validated.

The comparison of EMCs is given in [22] together with a method of translating the parameters from one model to another so that the user can choose the model that best suits their particular need. The drawback of this work is that none of the compared models includes voltage dependent capacitance.

The authors of [23] address different aspects of SC models and propose small- and large-signal models for simulation and control, based on a first-order RC model. The same model is used in [24] to discuss SC module selection and design.

Krpan et al., in [25], compare the stored energy and discharge profiles of ideal and realistic SC models. In [26], a detailed RC circuit model proposed by Tironi and Musolino is simplified and used to model SC banks for power system dynamics studies.

A comparison of RC, two-branch, Zubieta, and series models is provided in [27]. In this work, the Maxwell BCAP3000 SC is tested, and measurements are used to estimate model parameters using MATLAB/Simulink's parameter estimation tool. The SC models are then compared based on their accuracy and execution time requirements for real-time simulations.

Other works discussing various SC models and parameter identification procedures include [28]-[37].

V. SUPERCAPACITOR EQUIVALENT CIRCUIT MODELS

ECMs represent a tool for estimating the electrical performance of SC. SC usually operate in two modes of charge: constant voltage (CV) and constant current (CC), and three discharge modes: constant resistance (CR), constant power (CP), and constant current. Specific energy and power densities are of interest when modeling SCs for power system applications because the mass

of the storage device affects the design of the system. Compared to lithium-ion batteries, SCs have a significantly higher specific power density but a lower energy density. This section provides an overview of commonly used and proven applicable equivalent circuit models of SCs, arranged from simpler to more complex ones. ECM models can be seen in Figure 6. Models are: a) RC model, b) "classic" model, c) simplified theoretical, d) ZubietaBonert and e) Tironi-Musolino.

A. RC MODEL

Simplest model of SC accounts only for ideal capacitance and ESR connected in series. This model is used by manufacturers in datasheets. The model parameters are obtained by the constant current charge-discharge method described in IEC 62391-1 [11]. Since parameters are available in manufacturers datasheet, it is not necessary to perform any tests on cells in order to use a model in simulations. Charging and discharging times depend on time constant. In CP discharging mode, time of discharge is described with:

$$t = (V_0 - V) \frac{C}{I_c} \quad (1)$$

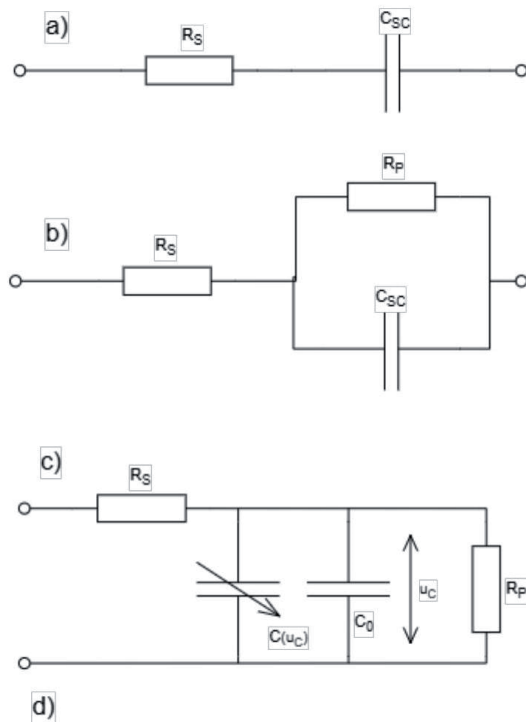
where

$$V = V_0 - \frac{I_c}{C} t \quad (2)$$

V_0 is initial voltage and I_c is constant current of discharge. Specific energy density in Wh/kg and specific power density in W/kg are given in Eqs. 3 and 4, where m is SC cell mass.

$$E_d = \frac{1}{2} \frac{CV^2}{m} \quad (3)$$

$$P_d = \frac{1}{4} \frac{V^2}{mR_{ESR}} \quad (4)$$



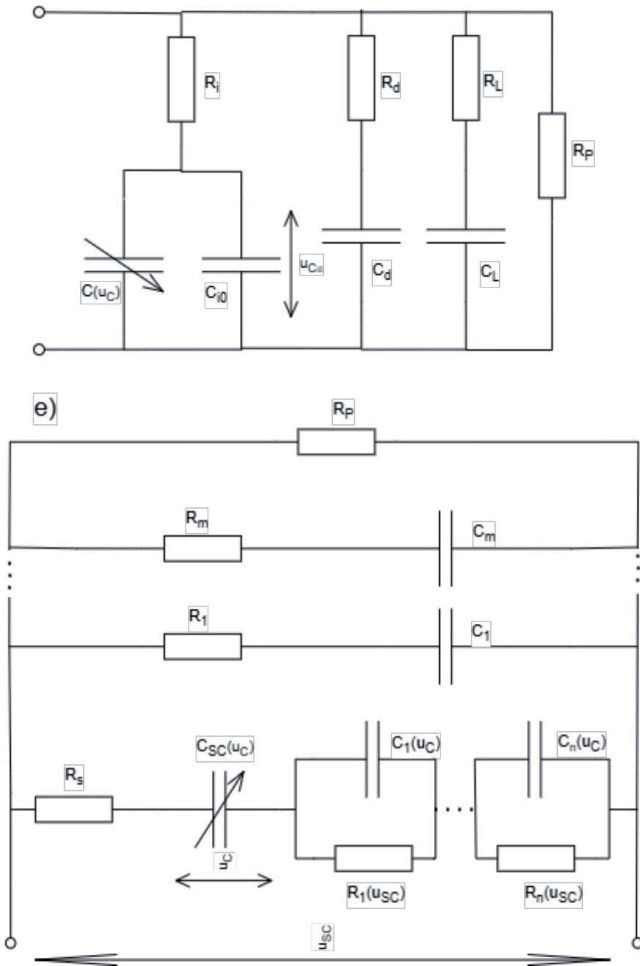


Fig. 6. SC models: a) RC model b) classical c) simplified theoretical model d) Zubieta-Bonert e) Tironi-Musulino

B. CLASSIC MODEL

Since RC model does not model self-discharge phenomena of SC, an additional resistance R_p was connected in parallel with capacitance to take self-discharge in account. is sometimes also referred as - Equivalent parallel resistance and can be either found in manufacturer datasheet, determined through EIS or by constant current charge/discharge and calculation described in [32]. R_p value is usually much greater than R_{ESR} and can be omitted if charging and discharging is done at a fast rate. When SC cell is discharged in CC mode, voltage cell can be expressed by Eq. 5.

$$V = -I_C R_{ESR} + V_0 - (V_0 + I_C R_p) \left[1 - \exp\left(-\frac{t}{R_p C_{SC}}\right) \right] \quad (5)$$

Time required for SC to be fully discharged is then:

$$t = C_{SC} \frac{(V_0 - I_C R_{ESR})}{I_C} \quad (6)$$

The equation for specific energy density is same as for RC model (Eq. 3) and change in models is included in Eq. 5. It is worth noting that quadratic drop in potential means that of stored energy is depleted before voltage reaches the usable range of .

Power density can be expressed as Eq. 7:

$$P_d = \frac{I_C}{m} [-I_C R_{ESR} + V_0 - (V_0 + I_C R_p) \left[1 - \exp\left(-\frac{t}{R_p C_{SC}}\right) \right]] \quad (7)$$

By increasing the time of discharge, the power density of the supercapacitor will gradually decrease. Maximum power density is obtained by deriving Eq. 7 and at $t = 0$ it is the same as Eq. 4. It is clear that R_{ESR} has a much stronger effect on power density than R_p .

C. SIMPLIFIED THEORETICAL MODEL

Capacitance of EDLC is voltage dependent. Incremental change in charge dQ at certain capacitor voltage produces an incremental change in voltage dV . This change is nonlinear, however, most authors use linear expression to fit this behavior, expressing capacitance as:

$$C_{SC}(u_c) = C_0 + k u_c \quad (8)$$

is initial linear capacitance and is a constant coefficient in [F/V]. This is supported by the experiments and results presented in [38], where the authors concluded that the relationship between Helmholtz capacitance and voltage bias is linear, while the total capacitance exhibits a sublinear dependence. The change in capacitance is typically several farads within the range from zero to the rated voltage of the supercapacitor, but this varies depending on the specific supercapacitor.

In ECM presented in [23] this is represented as constant capacitance C_0 in parallel with variable capacitance $C(u_c) = k u_c$. Voltage dependent capacitance implies that stored energy also varies with voltage.

Leakage current is modeled with a shunt resistor R_p whose resistance can be determined from the criterion that SC_p voltage decays at 4% of V_0 after 72 hours or from an electrode metric of $2 \mu A/F$ [23]. In series is connected ESR R_s .

Capacitor current is defined as:

$$\begin{aligned} i_c &= \frac{\delta Q}{\delta t} = \frac{\delta [C_{SC}(u_c) u_c]}{\delta t} \\ &= \left(C_{SC}(u_c) + u_c \frac{dC(u_c)}{du_c} \right) \frac{du_c}{dt} \\ &= (C_0 + 2k u_c) \frac{du_c}{dt} \end{aligned} \quad (9)$$

This is derived by utilizing the definition of total capacitance, which is expressed as the ratio between the total charge at a specific voltage $Q(u)$ and the voltage at that particular value, as described in Eq.10. Another possible definition of voltage dependent capacitance is the so-called “differential capacitance”, which is defined as the local derivative of $Q(u)$ with respect to u , presented in Eq. 11.

$$C_{tot}(u) = \frac{Q(u)}{u} \quad (10)$$

$$C_{diff}(u) = \frac{dQ(u)}{du} \quad (11)$$

If "differential capacitance" was used, supercapacitor current would be:

$$i_c = C_{SC}(u_c) \frac{du_c}{dt} \quad (12)$$

For linear capacitors, $C_{diff} = C_{tot}$. The difference between differential and total capacitance can be found in [39].

Energy stored in SC can be expressed as

$$\begin{aligned} E_C &= \int u_c i_c dt = \int u_c (C_0 + 2ku_c) \frac{du_c}{dt} dt \\ &= u_c^2 \left(\frac{C_0}{2} + \frac{2}{3} ku_c \right) \end{aligned} \quad (13)$$

Finally, specific energy is then:

$$\begin{aligned} E_C &= \int u_c i_c dt = \int u_c (C_0 + 2ku_c) \frac{du_c}{dt} dt \\ &= u_c^2 \left(\frac{C_0}{2} + \frac{2}{3} ku_c \right) \end{aligned} \quad (13)$$

Specific power is defined as Eq.15, its maximum is again the same as in Eq. 4.

$$E_d = \frac{u_c^2 \left(\frac{C_0}{2} + \frac{2}{3} ku_c \right)}{m} \quad (14)$$

Notice that in this model, Eq. 13 and Eq. 15 describe specific energy and power density stored, and not energy/power injected or extracted from the cell terminals. For that i_{sc} and u_{sc} should be used, where $i_{SC} = i_c + \frac{u_c}{R_p}$ and $u_{SC} = u_c + i_{SC} R_S$.

If SC is discharged by constant current I_0 then maximum discharge time is:

$$t = \frac{C_0 V_0 + k V_0^2}{I_0} \quad (16)$$

where V_0 is the voltage of the fully charged SC.

D. ZUBIETA-BONERT MODEL

One of the most commonly used, well-tested, and described models is one presented by Zubieta and Bonert in [30]. This model is even used in Matlab/Simscape SC model [40]. Variation of this model was presented in [34], so-called two branch model, where one RC branch is omitted. Different names are used for this model: parallel, multibranch, two branch, Zubieta, etc. This model achieved best accuracy for the energy stored in a SC and self-discharge [18]. The Zubieta-Bonert model consists of three RC branches and resistance to leakage R_p in parallel to those branches. Each branch has a distinct time constant. First branch or "immediate" branch is modeled as ESR R_S in series with linear voltage dependent capacitor $C_{SC}(u_c) = C_{i0} + C(u_c)$ where $C(u_c) = ku_c$. This branch models behavior of SC in time range of seconds in response to a charge action. Authors used "differential capacitance" to derive stored energy.

$$i = C \frac{du}{dt} \quad (17)$$

$$E = \int uidt = \int u_c (C_{i0} + ku_c) du_c \quad (18)$$

Then for a constant charging current I and at a specified voltage V , the stored energy is:

$$E = \frac{C_{i0}}{2} V^2 + \frac{k}{3} V^3 \quad (19)$$

The second or "delayed" branch dominates terminal behavior in the range of minutes, it is composed of R_d and C_d . The third branch ("long-term" branch), consisting of R_L and C_L , determines the behavior for times longer than 10 minutes.

E. TIRONI-MUSOLINO MODEL

Tironi and Musolino proposed a model aimed at power electronic applications in a frequency range of 0,01 Hz –1kHz [28]. The same authors presented an identification procedure for this model in [29].

This model is very similar to Zubieta-Bonert, difference is in first (immediate) branch, where Tironi and Musolino replaced it with series model proposed by Buller et al. in [41]. Transfer function Z_p (also called pore impedance) represents dynamic behavior of the device at high frequencies [28] is described by:

$$Z_p(j\omega, V) = \frac{\tau(V) \cdot \coth(\sqrt{j\omega\tau(V)})}{C(V) \cdot \sqrt{j\omega\tau(V)}} \quad (20)$$

Parameter $\tau(V)$ can be calculated as:

$$\tau(V) = 3 \cdot C(V) \cdot (R_{dc} - R_i) \quad (21)$$

where R_{dc} is the resistance experimentally obtained at very low frequencies (essentially DC).

This transfer function is modeled with variable capacitance C_{SC} connected in series with n RC parallels. Parameter of first branch are:

$$C_{sc}(u_c) = C_0 + k_v u_c(t) \quad (22)$$

$$C_k = \frac{1}{2} C_{sc}, k \in \{1 \dots n\} \quad (23)$$

$$R_k = \frac{2\tau(u_c)}{k^2 \pi^2 C_{sc}} \quad (24)$$

Krpan et al. showed in [26] that the significance of parallel RC groups depends on the difference between R_{dc} and R_S and that at least one parallel group should be included in the model. On the other hand, the number of RC branches (delayed and long-term) depends on the interested time scale. Cell voltage is described as:

$$u_{sc}(t) = i_{sc}(t) R_S + u_c(t) + \sum_{k=1}^n u_{c_k} \quad (25)$$

and first branch current is:

$$i_{sc} = (C_0 + ku_c) \frac{du_c}{dt} \quad (26)$$

Power density can then be obtained as in Eq. 15.

VI. CONCLUSION AND FUTURE WORK

A literature review reveals that the same models or their variations are often referred to by different names. In some studies, certain models are omitted, while others demonstrate superior suitability in terms of complexity and accuracy. Additionally, the criteria used for model comparison are frequently inconsistent and poorly defined, with model complexity often being a subjective assessment. Model parameters are typically determined based on experimental measurements, which are not always available. This lack of data makes it challenging to evaluate model accuracy in such circumstances.

In this article, five different equivalent circuit models (ECMs) for supercapacitors (SCs) are presented: the RC model, classic model, simplified theoretical model, ZubietaBonert model, and Tironi-Musolino model. Each model is accompanied by a physical explanation, and the influence of various parameters on model behavior is analyzed.

Future work should focus on experimental validation of the models, investigation of models for complete SC modules rather than individual SC cells and exploring the feasibility of incorporating SC models into control system design.

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