BRNO UNIVERSITY OF TECHNOLOGY
VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

FACULTY OF ELECTRICAL ENGINEERING AND COMMUNICATION
FAKULTA ELEKTROTECHNIKY
A KOMUNIKÁČNÍCH TECHNOLOGIÍ

DEPARTMENT OF PHYSICS
ÚSTAV FYZIKY

CHARGE TRANSPORT AND STORAGE IN A SUPERCAPACITOR STRUCTURE
TRANSPORT A UKLÁDÁNÍ NÁBOJE VE STRUKTUŘE SUPERKONDENZÁTORU

DOCTORAL THESIS
DIZERTAČNÍ PRÁCE

AUTHOR
AUTOR PRÁCE
Ing. Tomáš Kuparowitz

SUPERVISOR
ŠKOLITEL
doc. Ing. Petr Sedláčk, Ph.D.

BRNO 2017
Abstract

Supercapacitor (SC), or electric double-layer capacitor, represents electrical energy device, which offers high power density, short charging time, high number of charging cycles, and long-life duration. This device is of particular interest in fast energy-storage applications, where highly dynamic charging and discharging profiles are required.

Detailed study and modeling of the electrical charge transport and its storage is the output of this thesis. Processes, which occur during charging and discharging, are studied and their correlation to fading of SC's parameters is assessed. The noticeable differences between measured results and the simple SC model are: 1) the nonlinear rise and fall of SC’s voltage, and 2) the change in voltage after the charging and discharging stops. Charge redistribution during SC charging and relaxation are important.

New model of SC is proposed. Electric charge stored in SC appears to be divided into two sections. One could be attributed to the Helmholtz capacitance and the other to the diffuse capacitance. The equivalent circuit model contains time dependent resistance $R_D(t)$ between Helmholtz and diffuse capacitances.

While the SC ages, all parameters of equivalent circuit model change. The change of Helmholtz capacitance may be described most accurately by a pure exponential function. Total capacitance in relation to the number of energy cycling aging cycles $n$ or the time of cycling $t$ follows an exponential stretched law. From experiments it follows, that the greatest influence on SC’s degradation has the amount of transferred energy. The degradation due to induced Joule’s heat only has impact after 2000 hours of continuous energy cycling.

The time constant $\tau_D$ of the diffusion process is responsible for the speed of diffusion capacitance filling. The decrease of diffusion process time constant is faster for 75% discontinuous energy cycling than it is for 75% continuous energy cycling method.

The dependence of aging on SC’s equivalent series resistance parameter remains the same for both continuous and discontinuous energy cycling. It obeys the quadratic relation. The difference is that the quadratic component is of the order of magnitude smaller for 75% discontinuous energy cycling than it is for 75% continuous energy cycling.

The dependence of equivalent circuit model parameters on ambient temperature before and after aging by discontinuous energy cycling is explored. The value of total capacitance $C_T$ increases linearly with temperature. This is also true for aged samples. The slope for new samples is about 3 times higher than for aged one.

Helmholtz capacitance of SC CapXX 2.75V/2.4F is constant in temperature range 22 °C to 65 °C, with the value of Helmholtz capacitance $C_H = 2.78$ F for new samples and 2.07 F for aged ones. At temperature range below 22 °C Helmholtz capacitance decreases about 0.5 F due to the aging.

The calendar life tests are devised to simulate SC under light work load at differing ambient temperatures. Temperatures used are from -35 °C up to 65 °C. This experiment is devised to prove, that the increased temperature accelerates the electrochemical reactions, which are responsible for SC’s total capacitance degradation.
Keywords

Supercapacitor, ultracapacitor, double-layer capacitor, supercapacitor equivalent circuit model, electrical charge redistribution in supercapacitor, supercapacitor parameters degradation.

Klíčová slova

Superkondenzátor, náhradní elektrický obvod superkondenzátoru, přerozdělení elektrického náboje v superkondenzátoru, degradace parametrů superkondenzátoru.

Bibliographic citation

Declaration

I declare that I have written my doctoral thesis on the theme of “Charge transport and storage in a supercapacitor structure.” independently, under the guidance of the doctoral thesis supervisor and using the technical literature and other sources of information which are all quoted in the thesis and detailed in the list of literature at the end of the thesis. As the author of the doctoral thesis I furthermore declare that, as regards the creation of this doctoral thesis, I have not infringed any copyright. In particular, I have not unlawfully encroached on anyone’s personal and/or ownership rights and I am fully aware of the consequences in the case of breaking Regulation § 11 and the following of the Copyright Act No 121/2000 Sb., and of the rights related to intellectual property right and changes in some Acts (Intellectual Property Act) and formulated in later regulations, inclusive of the possible consequences resulting from the provisions of Criminal Act No 40/2009 Sb., Section 2, Head VI, Pt. 4.

Brno, 24th August 2017

……………………

Author’s signature
Tato práce vznikla v rámci projektu CEITEC - Středoevropského technologického institutu s pomocí výzkumné infrastruktury financované projektem CZ.1.05/1.1.00/02.0068 z Evropského fondu regionálního rozvoje.
Acknowledgement

I would like to thank to supervisor of my doctoral thesis Doc. Ing. Petr Sedlak, PhD. for methodical leading of my dissertation. Further my gratitude also goes to Prof. RNDr Josef Sikula, DrSc and Ing. Jiri Majzner, PhD for valuable advice and for contribution to experimental part of my work.

Research described in this thesis was conducted in the frame of basic research for the European Space Agencies.
Content

1 INTRODUCTION.........................................................................................................................1

2 STATE OF THE ART...................................................................................................................2
   2.1 COMPOSITION AND BASIC STRUCTURE OF SUPERCAPACITOR ........................................2
   2.2 SUPERCAPACITOR RELAXATION, RESTORATION, AND STEADY STATE VOLTAGE ..........4
   2.3 SUPERCAPACITOR’S PARAMETERS DEGRADATION..........................................................6
   2.4 HELMHOLTZ AND DIFFUSE CAPACITANCE.......................................................................6
      2.4.1 Helmholtz capacitance ..................................................................................................6
      2.4.2 Diffuse capacitance .......................................................................................................7
   2.5 MODELS OF SUPERCAPACITOR .......................................................................................7

3 AIM OF DISSERTATION THESIS............................................................................................10

4 EXPERIMENTAL SETUPS.........................................................................................................11
   4.1 HS3 STREAMER ..................................................................................................................11
   4.2 GPIB CONTROL .................................................................................................................12
   4.3 HS3 CONTROL ..................................................................................................................13
      4.3.1 Hardware layout ...........................................................................................................14
      4.3.2 Example measurement ...............................................................................................15

5 EVALUATED SC SAMPLES.......................................................................................................17
   5.1 SUPERCAPACITOR MAXWELL 2.7V/10F ........................................................................17
      5.1.1 Electrical specifications ................................................................................................18
      5.1.2 Physical characteristics ...............................................................................................18
   5.2 SUPERCAPACITOR CAPXX 2.75V/2.4F .......................................................................18
      5.2.1 Electrical specifications ................................................................................................19
      5.2.2 Physical characteristics ...............................................................................................19
   5.3 SUPERCAPACITOR NESSCAP 2.7V/10F ......................................................................19
      5.3.1 Electrical specifications ................................................................................................20
      5.3.2 Physical characteristics ...............................................................................................20

6 SUPERCAPACITOR’S ELECTRIC CHARGE AND ENERGY.......................................................21
   6.1 CHARGE DRIFT AND DIFFUSION IN SUPERCAPACITOR .................................................21
   6.2 VOLTAGE RELAXATION AND RESTORATION.................................................................22
      6.2.1 Relaxation and restoration experiment .......................................................................22
      6.2.2 Relaxation and restoration discussion .........................................................................24
   6.3 SUPERCAPACITOR RELAXATION DOMINANT CURRENT COMPONENT .........................26
      6.3.1 Supercapacitor relaxation dominant current component experiment .......................26
      6.3.2 Supercapacitor relaxation dominant current component discussion .........................26
   6.4 VOLTAGE DEPENDENT CAPACITANCE ......................................................................29
      6.4.1 Differential capacitance experiment ...........................................................................30
      6.4.2 Differential capacitance discussion .............................................................................30
   6.5 RECIPROCAL CAPACITANCE AND EFFECTIVE DEPLETION REGION THICKNESS ...........32
      6.5.1 Reciprocal capacitance and effective depletion region thickness experiment ..........32
      6.5.2 Reciprocal capacitance and effective depletion region thickness discussion .............34

7 PROPOSED SC EQUIVALENT CIRCUIT MODEL...................................................................38
   7.1 SUPERCAPACITOR’S EQUIVALENT CIRCUIT MODEL ....................................................38
      7.1.1 Helmholtz capacitance .................................................................................................39
      7.1.2 Diffuse capacitance .......................................................................................................39
      7.1.3 Resistance between the Helmholtz and the diffuse capacitance ..................................40
      7.1.4 Equivalent series resistance .......................................................................................41
      7.1.5 Leakage resistance ......................................................................................................41
   7.2 MODEL PARAMETER ESTIMATION ...............................................................................42
      7.2.1 Helmholtz capacitance .................................................................................................42
      7.2.2 Diffuse capacitance .......................................................................................................43
      7.2.3 Resistance between the Helmholtz and the diffuse capacitance ..................................44
      7.2.4 Equivalent series resistance .......................................................................................47
Charge transport and storage in a supercapacitor structure

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.5</td>
<td>Leakage resistance</td>
<td>49</td>
</tr>
<tr>
<td>7.3</td>
<td>Model reliability</td>
<td>49</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Mathematical model</td>
<td>49</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Evaluated samples</td>
<td>50</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Simulation</td>
<td>51</td>
</tr>
<tr>
<td>7.3.4</td>
<td>Reliability assessment</td>
<td>53</td>
</tr>
</tbody>
</table>

8 ACCELERATED AGING AND ITS INFLUENCE ON THE EQUIVALENT-CIRCUIT MODEL

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Energy cycling tests</td>
<td>55</td>
</tr>
<tr>
<td>8.1.1</td>
<td>Continuous energy cycling</td>
<td>56</td>
</tr>
<tr>
<td>8.1.2</td>
<td>Discontinuous energy cycling</td>
<td>67</td>
</tr>
<tr>
<td>8.2</td>
<td>Temperature dependence of equivalent circuit model parameters</td>
<td>72</td>
</tr>
<tr>
<td>8.3</td>
<td>Calendar life tests</td>
<td>77</td>
</tr>
<tr>
<td>8.3.1</td>
<td>Calendar tests of CapXX 2.75V/2.4F</td>
<td>77</td>
</tr>
<tr>
<td>8.3.2</td>
<td>Calendar tests of Nesscap 2.7V/10F</td>
<td>79</td>
</tr>
<tr>
<td>8.4</td>
<td>Effect of temperature and variable electric field on degradation of capacitance</td>
<td>80</td>
</tr>
<tr>
<td>8.5</td>
<td>Aging summary</td>
<td>81</td>
</tr>
<tr>
<td>8.5.1</td>
<td>Influence of sustained electric field</td>
<td>81</td>
</tr>
<tr>
<td>8.5.2</td>
<td>Influence of temperature</td>
<td>82</td>
</tr>
</tbody>
</table>

9 CONCLUSION | 83   |

10 REFERENCES | 86   |

11 LIST OF APPLICANT’S PUBLICATIONS | 89   |

12 LIST OF FIGURES AND TABLES | 91   |

13 LIST OF SYMBOLS AND ABBREVIATIONS | 95   |

14 LIST OF USED EQUATIONS | 98   |
1 Introduction

Supercapacitor (SC), a.k.a. ultracapacitor or electric double-layer capacitor, represents an electrical energy device, which offers high power density, short charging time, high number of charging cycles, and long-life duration. This device is of particular interest in fast energy-storage applications, where highly dynamic charging and discharging profiles with high current rates are required.

The gravimetric energy density of SC is gradually increasing with research and new technologies in this field. The energy density of lithium batteries has been surpassed by that of SC in this decade. Further, it is projected to grow in conjunction with SC's reliability and market demand. These assumptions make SC industry very commercially appealing with projected growth of roughly nine fold in this decade.

SCs found an application in automotive industry (namely for inducing brief current surges during the engine start), in storing of harvested energy for autonomous sensor nodes, or in consumer electronics such as laptops or hand-held devices. SCs are used in combination with rechargeable batteries as power buffers and inside uninterruptible power supplies, where they replace stocks of electrolytic capacitors, reducing the size of the device, and increasing its cost effectiveness. Other use of SCs is in a photo-voltaic and wind power systems, as power grid storage devices and voltage stabilizers. Knowledge, gained from learning SC's principles, finds its place in a new generation of rechargeable battery designs.

The concept of double-layer capacitance was firstly described in 1853. Despite that, the lack of understanding of their operation prevents to take a full advantage of these devices. Several phenomena (e.g. voltage dependent capacitance, charge redistribution, voltage relaxation and restoration, performance fading, and the problem of creating physically appropriate model of SC) remain the subject of wide research.

The intention of this dissertation is to analyze the aforementioned phenomena occurring in SCs. Detailed analysis and modeling of the electrical charge transport and its storage is the output of this work. New equivalent electrical circuit model of SC is also proposed. Processes, which occur during charging and discharging, are studied and their correlation to fading of SC's parameters is assessed.

This thesis is divided as follows. The state of the art understanding of SC is presented in next chapter. In chapter 3 the intentions and purpose of this work are described and goals are set. Chapters 4 & 5 deal with some utilized experimental setups and types of assessed SC samples. Chapter 6 then attempts to shed some light onto few of misunderstood SC's phenomena. And to explain the underlying physical principles, that govern some aspects of SC’s behavior. New equivalent electrical circuit model of SC is proposed in chapter 7. Performance of this model is assessed and cross-examined against other state of the art solution. The subject of accelerated aging (and its impact on SC’s parameters and on parameters of the equivalent circuit model) is assessed in following chapter 8. And finally, the thesis is concluded.
2 State of the Art

A model, describing the behavior of SC’s (a.k.a. electrochemical double layer capacitor’s) terminal voltage dependence on applied electric charge, is required for power electronics applications [1]. The first method, using a simple resistive-capacitive model (series RC circuit), showed that this approach is insufficient.

The noticeable differences between measured results and the simple model are the nonlinear rise and fall of voltage, and the change in voltage after the charging and discharging stops. This latter change cannot be simply explained out by an internal discharge, as its rate levels off after a while (see chapter 2.2). The only explanation is an internal charge redistribution between different equivalent internal capacitances.

Zubieta and Bonert [1] propose an equivalent circuit to describe the measured terminal behavior of SC. This model is able to follow measured SC characteristics more precisely. The reason why the traditional models, used to describe capacitor behavior during charging/discharging, are inadequate for electrochemical double layer capacitors are discussed by many authors f.e. F. Rafik, et al. [2], or P. Sharma and T. S. Bhatti [3].

As it is known, SC can hold large amount of charge. It can be charged very quickly to high levels. But after that the susceptibility to being charged decreases rapidly and it is very hard to push any more additional charge into SC, even though its full capacitance has not been filled yet. In order to charge SC fully, time of the order of days [4]–[6] is needed. The same thing in reverse applies for the discharging. Thus, a considerable amount of charge always remains stored inside the SC during its normal use, even after fast discharge [5]. Charge redistribution (or the redistribution of so-called “residual charge”) during SC charging and relaxation plays a key role in a general SC’s behavior [4]. This charge redistribution is reportedly caused by limited mobility of ions moving in the vicinity of carbon electrodes [6].

In the remainder of this chapter, the approximate composition and basic operation of SCs is discussed first. Then the processes of SC relaxation and SC restoration are introduced, and the topic of SC’s degradation is briefly touched. The electric charge stored in SC appears to be divided into two sections. One could be attributed to the Helmholtz capacitance and the other to the diffuse capacitance. Both are outlined in chapter 2.4. Consequently, current state of the art models of SC are presented.

2.1 Composition and basic structure of supercapacitor

Kitahara and Watanabe [7] discuss the physical construction of the double-layer capacitor. The SC consists of an activated carbon particles, that act as polarizable electrodes. These particles strongly packed are immersed in an electrolytic solution, forming a double-layer charge distribution along the contact surface between carbon and electrolyte. Both electrodes are separated by a cellulose film to prohibit galvanic connection.

Carbon is used for SC electrodes due to different allotropes (graphite, diamond, fullerenes/nanotubes), various microtextures (more or less ordered) owing to the degree of graphitization, a variety of dimensionality from 0 to 3D, and an ability for existence under different forms (from powders to fibres, foams, fabrics and composites). This makes carbon to be a very attractive material for electrochemical applications, especially for the performance in a wide range of temperatures [8].
Charge transport and storage in a supercapacitor structure

Carbon electrode is well polarizable, however, its electrical conductivity strongly depends on its thermal treatment, microtexture, hybridization and a content of heteroatoms. Additionally, the amphoteric character of carbon allows for use of rich electrochemical properties of this element from donor to receptor state. The SC electrodes are made of porous activated carbon and have a very large effective area, which is about 3-5 orders of magnitude higher than its geometric area.

![Fig. 2.1: Internal structure of SC](image)

Yoshida, et al. [9] give a description of SC’s construction. They identify the separate parts of SC (see Fig. 2.1) and give a detailed guide for SC manufacture (see Fig. 2.2). They also describe different kinds of SC electrolytes.

![Fig. 2.2: Construction of SC [9]](image)

The non-aqueous electrolyte of SC contains a solution of conductive salt. Mixtures of alkyl carbonates (ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, propylene carbonate, etc.) and tetraalkylammonium salts are commonly used. The conductivity of non-aqueous electrolytes can be enhanced by using ligands, which coordinate the anions. This reduces ion-pairing and thereby increases both ion conductivity and ion transference. The pure ionic nature of molten salts contributes to an array of unique and interesting characteristics, such as resistance to oxidation and reduction, low vapor pressure, and high ionic conductivity. Unfortunately, the strength of ionic bonds present in salts generally contributes to high melting points, making their unique liquid properties useless for room temperature applications. Ionic liquids, however, are a class of salts that have significantly depressed melting points and are therefore often used for SC’s electrolyte. [10]

Note, that the actual composition of commercially available SCs is usually a highly proprietary information. But in order to form a depletion region within the electrolyte, its work function (chemical potential) must be at least by 2 eV higher, than that of carbon electrode.

The other components, that are common to all types of SCs, remain to be the electrolyte with high ion concentration and the activated carbon electrodes.
2.2 **Supercapacitor relaxation, restoration, and steady state voltage**

The SC relaxation is a process, during which the terminal voltage of SC drops in time immediately after its charging stops. A simple example is ought to be given.

Assume an experiment, where there is a SC and a conventional capacitor of the same capacitance charged by constant voltage source. Both samples are completely discharged prior to the experiment. The charging is halted immediately, after the operating/rated voltage ($V_{op}$) is reached. Immediately after the charging ends, both capacitors are left in an open circuit condition, and their terminal voltage is observed, as shown in Fig. 2.3. Here the voltage evolution of the charging dependence is red.

![Fig. 2.3: Diagram of SC relaxation process (blue), leakage of conventional capacitor (green), after the charging by constant voltage source (red)](image)

The open circuit voltage dependence of conventional capacitor is depicted green in Fig. 2.3. It would slowly decline in time due to leakage current. This decline would ultimately stop, once the capacitor gets completely discharged.

SC also sustains a voltage change after the charging (blue line in Fig. 2.3). The leakage current of SC is very low. It is of the order of several μA, as described in [11]. This voltage drop is therefore not produced by SC’s self-discharge. Note, that the rate of its decline gradually levels, and will stop eventually at nonzero voltage value. The voltage, at which this dependence settles, is called the **steady state voltage**. Once the SC gets into steady state, its terminal voltage does not change any more (except for the actual leakage, which is not noticeable for even modestly charged SC).

The open circuit voltage dependence of recently charged SC is called the SC relaxation. SC relaxes, until it reaches steady state, at which it exhibits the steady state voltage. Note, that the steady state voltage value differs, based on the previous charging profile. Even though the process of SC relaxation is sometimes thought to be a self-discharge, different process is actually at play. In fact, the SC does not discharge, it only redistributes its charge.

El Brouji et al. [12] describe the voltage decay $V(t)$, after SC’s charging is turned off. Their electrical impedance model cannot be directly exploited in time-domain. For this they introduces a simplified model and focused on low frequency range in order to transpose the model into this domain. Their main goal is to confirm the correlation between the evolution of the impedance real part and the voltage decay phenomenon. After which a second identification procedure, (based on time-domain results) is introduced. This allows to identify parameters of the SC’s simplified impedance model for time-domain simulations. See the blue curve in Fig. 2.4 for an actual simulation of SC relaxation, and the terminal voltage (red) within 6 hours after the SC gets charged to $V_{op}$. Note, that this is SC’s open circuit voltage, and that its rate of decline levels out eventually.
Charge transport and storage in a supercapacitor structure

Fig. 2.4: Measured data of SC’s "self-discharge" or relaxation (red) and its simulation (blue) by El Brouji, et al. [12]

For such simulation the authors of [12] use the analytical equation:

\[ V(t) = V_1 + I \frac{t^{1-\gamma}}{C(2-\gamma)!}, \]  

where \( V_1 \) is SC’s voltage immediately after the charging current \( I \) gets turned off, \( \gamma \) is a parameter representing the contribution of slow phenomena, and \( C \) is capacitance.

This equation presumes, that the voltage decay only depends on the parameter \( \gamma \). Their simulation shows, that the increase of \( \gamma \) results in an increase of the voltage decay rate. From the other side, the slope of the voltage curve in log axes can be used to estimate the \( \gamma \) value from experimental results. This allows for the use of their model for SC’s terminal voltage prediction.

The main problem of this model lays in its physical interpretation of voltage decay after the charging is turned off. Authors of [12], already stipulate, that some sort of charge redistribution in electrolyte by ionic diffusion takes place, but they describe the process as a self discharge and leakage over the potential barrier.

Fig. 2.5: SC’s restoration by Bertrand, et al. [13]

Similar, but quite the opposite process is the SC restoration. Here the terminal voltage (of previously charged SC) slowly increases after its abrupt discharge, until it reaches a steady state. This SC phenomenon is not well understood nor openly discussed in contemporary science, but its existence is well acknowledged. An example
of such SC voltage restoration is shown in Fig. 2.5. Here Bertrand, et al. [13] use the discharge curve of SC to analyze model parameters. Their model is similar to that of El Brouji, et al. The SC is previously charged to the value $V_0'$. Its discharge starts at time $t_0$ and ends at $t_n$, when the SC restoration process commences. The voltage then rises slowly in time, to level off at some voltage value.

### 2.3 Super capacitor's parameters degradation

SC cells have porous activated carbon electrodes with high surface area. This and their inherent electrochemical inertness should in theory assure high power density (in comparison to batteries), high energy density (in comparison to capacitors), and an unlimited cycle life [14], [15]. The charge-storage and charge/discharge mechanisms of SC should therefore be highly reversible. But in practice the degradation of SC’s performance is observed in a time frame of several months. This fading exhibits itself mainly in the form of decreasing capacitance [10].

Electrolyte’s chemical properties are deemed to play an important role in SC’s degradation. It has been hypothesized, that impurities introduced to the electrode surface during manufacturing process are responsible for SC’s parameter fading. Reason being, that they block the active area of the electrode. Or, in the case of water, they stump the electrolyte. [16]–[18]

Various chemical processes in electrolyte itself could be responsible for parameter fading. Study of electrolyte decomposition reveals unwanted chemical reactions, that lead to hydrogen and carbon dioxide release [19], [20]. Destructive analysis of faded SC cells shows asymmetric changes in atomic composition of positive and negative electrodes [17]. In positive electrode the density of ions increases.

SC’s parameter degradation also depends on the power level of operation and on the thermal environment of the device [11], [21], [22]. Regarding the voltage, manufacturers contend that a permanent over voltage of 0.1 V acts as a temperature increase of 10 °C. As [21] shows, both temperature and voltage should be taken into consideration while determining the degradation acceleration factor.

### 2.4 Helmholtz and diffuse capacitance

It has been long established, that the voltage relaxation and restoration of SC are the products of diffusion like processes. These are well described by the Helmholtz theory. This theory (improved on by Gouy, Chapman, and Stern) permits to explain the different physical phenomena that occur on the interface between an ionic electrolyte and an electronic electrode. The interface is modeled by two superficial distributions of charges, the first one as electronic for the electrode, and the second one as ionic of opposed sign for the electrolyte. Even though it is demonstrable, that these processes occur within SC, their concrete parameters, impact, and modeling are interpreted inconsistently among authors. Mainly the impact of SC aging has large influence on its change. The basic equations and description of Helmholtz processes are described below. [2], [3], [23], [24]

#### 2.4.1 Helmholtz capacitance

Helmholtz capacitance [4], [5], [23] is composed of thin layer on electrode/electrolyte interface. Electric charge stored in Helmholtz capacitance reacts immediately to the voltage change on electrodes. During charging by constant current, the voltage of SC’s electrodes does not increase linearly with time, as would be expected for regular parallel plate capacitor.
2.4.2 **Diffuse capacitance**

The voltage change on electrodes reacts with some time delay to change of electric charge distribution in depletion region, due to the motion of electric charge by diffusion. The region near the electrode has lower charge density due to the drift, which creates a charge gradient. This layer with lower charge density then fills slowly by charge from the bulk electrolyte. [23], [24]

![Diagram of charge carriers during SC charging process](image)

The combination of both aforementioned principles has an influence on the distribution of charge in time during the charging process. Visualization of this effect is presented in Fig. 2.6. Capacitance of SC is driven by the Helmholtz layer, consisting of charge stored on electrode/electrolyte interface, at first. The charge in electrolyte is assumed to be drifted by an electric field closer to the electrode/electrolyte interface. A concentration gradient forms. It is produced by electric charge, with respect to both electrode/electrolyte interface vicinity and the electrolyte volume. The force acting on the charge in the vicinity of the electrode/electrolyte interface, due to the charge concentration gradient, is compensated by the electrostatic force acting on the charge, because of the internal electric field. The dependence of internal electric field on the distance from the electrode/electrolyte interface is maximal on the interface, while the value decreases with the distance to the electrolyte volume. Since the drift of additional charge from electrolyte volume decreases, a depletion region is assumed to be formed. Additional charge diffuses from the electrolyte volume into the depletion region due to the concentration gradient of electric charge.

The diffusion process lasts until the electric field, produced by charge in the depletion region, reaches an equilibrium with electric field, produced by charge in electrolyte volume. The decrease of distance between electric charge on the electrode, and electric charge in electrolyte causes the increase of SC’s capacitance. The diffuse current decreases in time as the charge concentration gradient decreases.

2.5 **Models of supercapacitor**

SC's model represents an important tool for evaluation and prediction using analytical methods or simulation e.g. [25] before practical deployments; as well as to overcome some major obstacles for SC application, namely charge redistribution mechanisms [4]–[6], [26]. Various models of different kinds were proposed to predict or describe SC’s behavior under numerous conditions in power storage applications. These types can be summarized into groups according to the way of identifications [4] (time-domain leading to RC-equivalent circuit model [1], [4], [6], [24], [27]–[32], frequency-domain by impedance spectroscopy model [2], [33]–[35], [13], [36], and thermal electrochemical [26], [37], [38]), according to the degree of complexity (simple
The simplest and most common model represents an equivalent electrical circuit which consists of an ideal capacitor (representing the SC’s capacitance), an equivalent series resistor (representing the losses on leads, carbon electrodes, and electrolyte), and an equivalent parallel resistor (representing the SC’s self-discharge process) [3]. This model gives results for quick estimation, not for characterization of the real SC, since it ignores important physical phenomena, such as charge redistribution or voltage dependence of SC’s capacitance.

An evolutionary step of equivalent electrical circuit model represents an introduction of voltage-dependent capacitance described in [29]. Nevertheless, it is still insufficient for characterization of long-term behavior [23].

To model a 30-minute behavior, Zubieta and Bonert [1] proposed an equivalent circuit of three parallel branches (immediate, delayed, and long-term), shown in Fig. 2.7. Each branch of the equivalent circuit is formed by the series connection of a capacitor and a resistor, and has a different time constant to fit accurately experimentally observed behavior. The immediate branch contains a voltage-dependent capacitor. A parallel resistor connected to these branches represents current leakage. Although the three-branch model accurately predicts the performance of SC in mentioned time frame, it fails in a description of self-discharging. Ladder model [30], transmission line model [24] or the four-branch model can overcome this issue for longer times.

The purpose of the equivalent circuit is to provide a model of the terminal behavior of the SC in power electronics circuits. Therefore, the following requirements have been set before formulating the equivalent circuit structure [1]:

1. The model structure should be related to the physics of the device, but it should be as simple as possible to be a practical tool for design engineers.
2. The model should describe the terminal behavior of the SC over the range of 30 minutes with sufficient accuracy.
3. It should be possible to determine the electrical parameters of the proposed model using measurements at SC’s terminals.

Based on the physical aspects mentioned above and the desire for a practical engineering model, the following choices for the equivalent circuit were formulated:

1. Represent the SC with RC circuits but keep the number of RC elements as low as possible for practical reasons.
2. Include the non linear capacitance effect only in one RC element.
3. Include a parallel leakage resistor.

Modeling a two-terminal device with more than two internal elements [1] is always somewhat arbitrary, and additional assumptions (as above) have to be made to define a useful circuit. The decision about the number of RC circuits of the equivalent circuit model depends on the time span of the transient response to be covered, and on the feasibility to identify in a repeatable and consistent way the equivalent circuit parameters.

![Fig. 2.8: Faranda's model [31]](image)

Faranda, et al. [31] proposed the simplified two-branch model, which describes the short-term behavior of the device by the first RC branch, and the delay-term and long-term behavior using the second branch (see Fig. 2.8). The model is popular among engineers, since it is sufficient for prediction of SC's behavior in minutes. For longer times, Diab et al. [40] introduced a third RC branch, that models the nonlinear SC's self-discharge.

![Fig. 2.9: Zhang's model [27]](image)

Zhang, et al. [27] proposed to substitute a constant equivalent parallel resistance in Faranda model for a variable leakage resistance, which takes into account the effects of various self-discharge mechanisms.

![Fig. 2.10: Torregrossa's model [4]](image)

Torregrossa, et al. [4] accurately model the diffusion phenomenon of the residual charge through two current sources added to Zubieta’s equivalent electrical circuit (see Fig. 2.10). Their model gives more accurate results in comparison to Zhang’s model even for longer times.

Several more models are mentioned in the introductory paragraph of this section. These are not described in depth. Because they are generally either based on pure heuristics, or they are the outcome of adding some more branches to an already described model. Nevertheless, these models are very difficult to implement due to high number of components and hard (or even impossible) to identify variables.
3 Aim of Dissertation Thesis

The aim of this dissertation is to analyze phenomena associated with supercapacitor’s (SC) electric charge transport and storage. This namely includes the research of process of SC’s charge redistribution. For this the understanding of the underlying physical basis for such redistribution needs to be obtained and analytically described.

Experimental setup for SC’s accelerated aging is developed. This might be used for long term parallel measurement of several samples. Three kinds of accelerated aging methods will be explored:

1. The continuous energy cycling at room temperature.
2. The discontinuous energy cycling at room temperature.
3. And the calendar life tests at varying potentials and ambient temperatures.

Such tests are devised to run for hundreds to thousands of hours. Influence of continuous and discontinuous cycling at different energy levels is evaluated. And the impact of aging modes on SC’s performance is assessed. The aim is to determine, whether the induced self-heating and increased charge transfer could lead to a different degradation process than that of a calendar life test.

Mutual correlation of SC’s parameters at the beginning, during and at the end of aging is assessed. Changes of SC’s parameters (capacitance, impedance, etc.) is linked to physical changes (electrode area, electrolyte’s conductivity, electrolyte’s permittivity, etc.) and electrochemical changes (electrolyte degradation) of SCs during the aging test.

Off-the-shelf SCs is analyzed, evaluated, and scrutinized upon their merit.

The construction of simplified equivalent circuit model is attempted. Such model must suffice two prerequisites:

1. The model is not based on heuristics, meaning that its components has to be linked to actual physical principles. It is not enough to simply simulate SC. The internal behavior of the model must have its basis in reality.
2. It should build upon the state of the art (ladder) models, simplifying them while increasing their accuracy.
4 Experimental setups

This chapter describes some of the actual experimental setups, that were utilized to perform SC measurements in our laboratory. It is to be noted, that most of the dedicated long term aging measurements (see chapter 8) were performed in confines of EGGO Space s.r.o. company laboratories.

The development of mentioned experimental setups was financially supported by the Internal Grant Agency of Brno University of Technology, grant No. FEKT-S-17-4626. The followup research activity was in turn conducted under the ARTES 5.1 program element funded by the European Space Agency (4000105661/12/NL/NR).

Some of the selected measurement software is attached to this thesis in an appendix. It is given to the public domain, under the restriction of GNU GPL v. 2 license.

4.1 HS3 Streamer

Throughout most of the measurements, TiePie engineering HS3 handyscope device (see Fig. 4.1) is used for data acquisition and more. This device has two channel voltage acquisition capability and arbitrary function generator output. It is connected to Microsoft Windows enabled computer through an USB cable.

![HS3 Streamer](image)

*Fig. 4.1: TiePie engineering HS3 handyscope [50]*

First step in SC measurement setup is pure real-time voltage acquisition of terminal characteristics at up to 10 kHz sampling frequency (USB 2.0 limitation). This is what the HS3Streamer is for. It is a console application, that allows to utilize the streaming measurement of HS3 device quickly.

In this kind of measurement, only the voltage gets recorded to a coma-separated-value file. The operation of other hardware within the measurement setup is done either by hand or by other means.

The use of the HS3Streamer software is great for setting up quick “one-off” measurements. The description of this program, including its source files, is included in appendix to this thesis, because of the lack of such a free tool to operate the TiePie handyscope devices online. Note, that other TiePie engineering handyscopes may also be operated by the program, given that correct drivers are installed and linked.

![SC measurement layout](image)

*Fig. 4.2: HS3 Streamer example usage measurement layout*
HS3Streamer is a very simple tool for performing very simple measurements. One such kind of measurement is the monitoring of terminal voltage and transferred charge of SC. For this the experiment is set up as shown in Fig. 4.2. The SC is connected to a constant voltage power source for charging. The SC is charged through a low resistance $R$ for current measurement. The HS3 ground is connected between SC and $R$. The resistor serves as a shunt, its voltage is recorded on the first HS3 channel (anchored at point $V_1$). Second HS3 channel is connected to SC’s negative terminal, measuring the inverse voltage of $V_2$. The power source is connected to $+SRC$ at point $V_1$ and $-SRC$ at point $V_2$.

This way the SC gets charged through the shunt resistor. Both the voltage of the shunt resistor and of the SC gets recorded. The HS3Streamer may also be setup to measure two parallel samples, e.g., during charging and discharging. This tool is used to acquire characteristics for [41]–[43] and data presented in chapter 6.3.

### 4.2 GPIB Control

Next logical step is a slightly more advanced setup of single solution, that both performs the measurement and controls the utilized power source. Here the aim is to produce constant current power source, for constant current charging and discharging measurements. Using constant current gives much better control over the transferred charge, and allows for fast charging of SC. Example of this might be the measurement published in [44]. Note, that the term power source might be slightly misleading here. In fact a constant current regulator might be a better description, since it does not convert mains.

The measurement station (see Fig. 4.3) consists of a programmable constant-current power regulator, 12 V rechargeable battery for supplying the constant current, two multimeters Agilent 34410A (one employed to measure the SC voltage and the other to measure the charging current, utilizing current shunt Agilent 34330A), and the control computer (PC). Both multi-meters are connected to PC via IEEE-488 (GPIB) parallel bus. The current regulator itself is controlled by PC over the RS232C serial bus.

The schematic of the precision current regulator is shown in Fig. 4.4. The regulator allows for changing the direction of the current, using an H-bridge configuration. The bridge is made of four Insulated-Gate Bipolar Transistors (IGBTs) denoted T1-4. These IGBTs are switched by a means of four optocouplers, controlled by PIC 18F microprocessor, made by Microchip company. The microprocessor is connected to the PC via RS232C serial bus.

The value of current is adjusted by MOSFET transistor (denoted T5 in Fig. 4.4), connected in feedback loop via electromagnetic current transducer. This setup has a very low load branch however, which produces slight transients, when the charging is
switched on. An external digital-analog converter is used to set the desired value of current. This converter is controlled by the microprocessor as well.

As a source of energy for the charging system a 12 V rechargeable sealed lead-acid battery is used. The battery is capable of supplying 10 A at over 10 V, which is necessary due to high power loss of IGBTs. The battery is used to eliminate transition effects, produced by standard laboratory power supplies. And to improve the stability of the control feedback loop.

In addition, a short-circuit relay is installed in parallel to the measured sample. This relay allows for the complete disconnecting of the SC from the charging circuit. Or the short-circuiting of the sample.

The apparatus allows for the measurement of charging and discharging characteristics in the range of ±10 A (sourced current). The sampling frequency is roughly 2 Hz, the bottleneck being the GPIB bandwidth. The measurement software is implemented in MathWorks’ MATLAB environment. The picture, showing the entire measurement setup at work, is shown in Fig. 4.5.

### 4.3 HS3 Control

The final evolutionary step of utilized experimental setups is the precision current regulator, controlled solely by HS3 device. It is created to mitigate several inherent shortcomings of previous solution, namely:

1. **Low sampling frequency**, influenced by GPIB bus bandwidth.
2. **Complex communication layout**, using RS232 in addition to GPIB.

3. **High power consumption**, requiring unnecessarily large heat sinking.
   - This is mainly the result of the use of IGBTs, which have by default circa 4 V collector-emitter saturation voltage in any charging configuration of the H-bridge.
   - And the use of battery for power source, which does not have output voltage trimming capability and must be recharged ever so often.

4. **Large physical size**, making it difficult to produce and utilize several parallel measurements at a time (f.e. if they all need to fit around an oven).

5. **Feedback loop precision**, which already is of the high order, but may be improved by replacement of the transducer with a shunt resistor.

6. **SW implementation**, requiring both the MATLAB environment and VISA drivers installed.

In order to address these shortcomings, the following new precision constant current regulator (CS1) is developed. The hardware layout of this regulator is explained in the following section. And an example measurement is presented later. Note, that the control software for CS1 device is attached in appendix to the thesis.

### 4.3.1 Hardware layout

As hinted above, the aim is to produce a single printed circuit board design, that would be small enough to fit several parallel measurements next to each other. This board is only to perform the constant current regulation. It has to be in turn powered via separate laboratory power supply for bias and sourced DC current to be regulated. The reason for using this extra step during measurement is CS1’s ability to acquire voltage and current characteristics at high frequencies, to be controlled by a computer, and to handle negative currents at high precision. The board layout of CS1 device is presented in Fig. 4.6. Its full schematic is in an appendix to the thesis.

![Fig. 4.6: Precision constant current source – printed circuit board layout](image)

CS1 is capable of supplying precision current of ±5 A. This range is deemed sufficient, since the full current capabilities of previously mentioned regulator (chapter 4.2) were rarely completely utilized. The value of 5 A is not an arbitrary number, but is derived from the capabilities of Agilent E3631A laboratory supply, which is used to power the measurement instead of a battery. To achieve negative currents, again an H-bridge configuration is used. Every IGBT is replaced by MOSFET and high power diode in series, neither of which requires a heat sink.
The input current of CS1 is preconditioned, using a regulator integrated circuit. Then a MOSFET is used for the regulation itself. The current regulator and the MOSFET are the only things that require cooling, hence a very small heat sink may be utilized. The current value and direction through the sample are measured using the shunt resistor. This has the advantage of faster voltage to current conversion then a transducer can achieve.

The dynamic transition period of CS1 is below 10 ms, even for full current swing. The current set error is around 0.3%. And its load regulation is below 1 μA.

See Fig. 4.7 for a snapshot of the CS1 board during an actual measurement. In the picture the blue rectangle shows where does the connection to HS3 device occur. Red circle highlights measured sample SC. Four devices are present in the back of the scene. Top left is the auxiliary power supply (cca 1 A at 10 V). Bottom left is the bias supply, powering the on board electronics and cooling. In the right there are two Agilent multimeters. The top one shows reference sample voltage. The bottom Agilent device measures the current flowing from the auxiliary power supply to CS1.

Fig. 4.7: HS3 Control measurement setup during an actual SC characterization experiment

HS3 handyscope device is utilized to master the measurement (see chapter 4.1). Its advantage over previous measurement is that it reduces all the communication with measurement PC to a single bus. The two input channels are used to acquire the voltage of both the sample and of the shunt resistor at up to 10 kHz sampling frequency. The arbitrary function generator output of HS3 is used for setting of the current of CS1. The overall diagram of HS3 Control measurement setup is in Fig. 4.8.

Fig. 4.8: Experimental setup for HS3 Control measurement

4.3.2 Example measurement

As an example of usage of this measurement setup, a snippet of a long term 100% energy cycling aging measurement is presented. The purpose and meaning of this measurement is explained in chapter 8.1.1. In essence, it perpetually charges and...
Charge transport and storage in a supercapacitor structure

discharges the sample SC by a constant current pulses. The voltage of SC’s terminals oscillate from 0 V to 2.7 V.

The measurement snippet is in Fig. 4.9. The blue curve shows the evolution of sample voltage during the 2.7 A cycle test. The red points represent the relative current flowing through the sample. Note, that the red line shows the voltage of the shunt resistor.

![Graph of voltage and current vs time](image)

*Fig. 4.9: Closeup of 100% energy cycling measurement of SC Nesscap 10F/2.7V*

The CS1 is also used for SC’s equivalent circuit model parameters estimation (characterization of SC), as explained in chapter 7. This source is f.e. used in experiments from [43], [45] and to obtain data presented in chapters 6.4 and 6.5.
5 Evaluated SC samples

Three types of off-the-shelf SCs are analyzed in this thesis. All are relatively small issue and small capacitance SCs, designed to be used on printed circuit boards. This chapter summarizes their features. Parameters marked with an asterisk are not official manufacturers data, but only estimations.

It is assumed, that the underlying physical principles are common to all kinds of SCs (even though precise parameter values and influence may differ). Samples with relatively low capacitance are therefore utilized for practical reasons, because the aging experiments may be performed faster. E.g. charging of 10 F capacitor takes of the order of magnitude less time than charging of 100 F one.

Outline of all following sections is the same. First, each sample is introduced. Then the electrical and temperature characteristics are presented. And finally sample’s physical specifications are given.

5.1 Supercapacitor Maxwell 2.7V/10F

Samples manufactured by Maxwell Technologies, Inc. Their true designation is: Maxwell Technologies BCAP0010 P270 T01 10F 2.7V, but for simplicity will be referred to simply as samples of SC Maxwell (2.7V/10F). Following figure Fig. 5.1 shows an example of such SC, that has already underwent measurement process.

![Real-life sample of SC Maxwell 2.7V/10F](image)

Fig. 5.1: Real-life sample of SC Maxwell 2.7V/10F
5.1.1 *Electrical specifications*

Rated capacitance ............................... 10 F  
Capacitance tolerance* ......................... ± 20 %  
Maximum ESR initial ............................ 75 mΩ  
Rated voltage 65 °C / 85 °C ...................... 2.7 V / 2.3 V  
Absolute maximum voltage ....................... 2.85 V  
Absolute maximum current ...................... 7.2 A  
Maximum 1 second peak current .............. 8 A  
Maximum leakage current ....................... 30 μA  
Operating temperature max / min ............. -40 °C / 85 °C  
Specific power .................................. 3.3 kW/kg  
Specific energy ................................. 2.9 Wh/kg

5.1.2 *Physical characteristics*

Length .......................................... 30 mm  
Diameter .......................................... 10 mm  
Typical mass .................................... 3.5 g  
Mounting method ................................ through-hole

![Fig. 5.2: SC Maxwell 2.7V/10F schematics [46]](image)

5.2 *Supercapacitor CapXX 2.75V/2.4F*

Samples CapXX HS130 P2C361 2.40F 26mΩ 2.75V, produced by CAP-XX Ltd., are referred to as SC CapXX (2.75V/2.4F) in this thesis. The information, given in the datasheet, is very sparse. These samples are of comparatively lower quality than the other two assessed, but are utilized nevertheless, to get an idea of low capacitance and low price solution. Fig. 5.3 shows a battery of these SCs, prepared for measurement.

![Fig. 5.3: Real-life SC CapXX 2.75V/2.4F samples](image)
Following information is mainly retrieved from sample’s datasheet [47].

5.2.1 Electrical specifications

Rated capacitance ........................................ 2.4 F
Capacitance tolerance* .................................. ± 20 %
Maximum ESR initial ..................................... 72 mΩ
Rated voltage ................................................. 2.75 V
Absolute maximum voltage ......................... 2.9 V
Absolute maximum current .......................... 3 A
Maximum 1 second peak current ................. 30 A
Maximum leakage current ............................. 2 μA
Operating temperature max / min ........ -40 °C / +85 °C
Specific power ........................................... W/kg
Specific energy ......................................... Wh/kg

5.2.2 Physical characteristics

Length ...................................................... 40 mm
Width ........................................................ 17 mm
Thickness .................................................. 1.7 mm
Mounting method ......................................... surface-mount

5.3 Supercapacitor Nesscap 2.7V/10F

SC Nesscaps are manufactured by Nesscap Ltd. company, under the name: Ultracapacitor 2.7V / 10F ESHSR-0010C0-002R7. For simplicity these capacitors are going to be referred to as SC Nesscap (2.7V/10F). Photo of an actual sample, that already underwent an evaluation process, is depicted in Fig. 5.4.

![SC Nesscap 2.7V/10F](image1.png)

Fig. 5.4: Real-life sample of SC Nesscap 2.7V/10F

Electrical characteristics of brand new samples are similar to those of SC Maxwell 2.7V/10F. This type of SC stands out among its competitors however in short-
term use, and is therefore one of the most studied types. It is utilized for most of the measurements and examples given in this thesis.

Following information is mainly retrieved from sample’s datasheet [48].

5.3.1 Electrical specifications

Rated capacitance ........................... 10 F
Capacitance tolerance ......................... -10 % / +20 %
Maximum ESR initial .......................... 30 mΩ
Rated voltage 65 °C / 85 °C .................... 2.7 V / 2.3 V
Absolute maximum voltage ..................... 2.85 V
Absolute maximum current .................... 5.6 A
Maximum 1 second peak current .............. 10.3 A
Maximum leakage current ...................... 23 μA
Operating temperature max / min ............. -45 °C / 85 °C
Electrolyte permittivity* ....................... 10^{10} F/m
Electrolyte work function* ..................... 7 eV
Electrode effective area* ....................... 200 m²
Specific power ................................. 19 kW/kg
Specific energy ............................... 3.2 Wh/kg

5.3.2 Physical characteristics

Length ............................................... 30 mm
Diameter ........................................... 10 mm
Typical mass .............................. 3.2 g
Mounting method .......................... through-hole

Fig. 5.5: SC Nesscap 2.7V/10F schematics [48]
6 Supercapacitor’s electric charge and energy

This chapter deals with the description of inherent SC properties. It identifies and explains SC behavior and tries to tackle several SC phenomena. The following chapter 7 derives from these findings to produce authentic equivalent model, that captures the physical essence of the SC structure.

Two fundamental equations hold true for regular parallel plate capacitor. Relation between the change of stored charge, capacitance and change of terminal voltage for conventional capacitor is given by:

\[ dQ = C \, dV \]

(2)

from which the relation for the steady state voltage may be extrapolated:

\[ V = \frac{Q}{C} . \]

(3)

6.1 Charge drift and diffusion in supercapacitor

By the application of electric field to electrodes, Helmholtz double layer is formed immediately, as explained in chapter 2.4. By another words, the electric field in close proximity to the electrode then causes the drift of charged particles towards it.

The change of the number of charge carriers at the electrode/electrolyte interface may be quantified by linear differential equation, as it moves by constant drift velocity. The elementary charge change on Helmholtz double layer \( dQ_H \) is proportional to the charge on this double layer and the change of time \( dt \):

\[ dQ_H = Q_H \frac{dt}{\tau_H} , \]

(4)

where \( Q_H \) is the charge on Helmholtz double layer and \( \tau_H \) is its time constant of this change.

For diffusion process, the movement of charge carriers does not follow linear pattern, but its speed is proportional to square root of time and the diffusion constant. For this the following differential equation may be stipulated. The time dependence of elementary charge change \( dQ_D \) due to diffusion is:

\[ dQ_D = \frac{Q_D \, dt}{2 \sqrt{t \cdot \tau_D}} , \]

(5)

where \( Q_D \) is charge stored in diffusion layer and \( \tau_D \) is the time constant for electric charge diffusion.

El Brouji et al. tried to model these processes using (1) in [12]. The use of power of time in nominator and factorial in denominator allows to approximate the diffusion process, but such solution is not sufficient. Equation 5 describes the charge carrier’s
Charge transport and storage in a supercapacitor structure

displacement due to diffusion properly. Also this solution gives better results, as there is
only single constant to be obtained from fitting by simpler equation.

Dynamic of such drift depends on many factors, such as the charge carrier’s
mobility, mass, cross-section, etc. These factors should not change in time, hence the
time constant should remain the same for any given electrolyte. In reality though, the
influencing factors change with SC aging, and so do time constants \( \tau_H \) and \( \tau_D \). The
magnitude of such change is discussed in chapter 8.

6.2 Voltage relaxation and restoration

It is assumed that both: the process of SC relaxation, and the process of SC
restoration (as described in chapter 2.2) are driven by the same underlying physical
principle. This principle has its basis in relations, described in previous chapter. Electric
charge in SC is stored on electrodes as well as inside its electrolyte.

When a completely discharged SC gets charged, Helmholtz double layer is
formed at its electrode/electrolyte interface by the drift of free charge carriers towards
the charged electrode of opposite polarity. Throughout this thesis it is said, that the
Helmholtz double layer is being charged, even though solely the charge within the
electrolyte is redistributed. This occurs immediately with a time constant of seconds.

The resulting gradient of charge density allows for additional charge to diffuse
toward the electrode from the electrolyte bulk. Throughout this thesis it is said, that the
diffusion capacitance gets charged, while obviously only charge redistribution within
the electrolyte occurs, such redistribution has the effect of decrease of SC’s terminal
voltage. This forms the diffusion capacitance with time constant of the order of hours.

When a charged SC is briefly short-circuited, the Helmholtz double layer
disintegrates. Charge on electrode is discharged entirely, however the state of charge in
electrolyte remains mostly unchanged. The free charge carriers, stored near the opposite
polarity electrodes (what used to be the Helmholtz layer), are then redistributed by
diffusion back to the electrolyte. As the opposite polarity charge carriers slowly diffuse
away from the electrode, SC’s terminal voltage increases.

6.2.1 Relaxation and restoration experiment

To test the hypothesis above, simple experiment is conducted.

Fig. 6.1: Charging of SC Nesscap 10F/2.7V by constant
voltage source, entire charging duration [41]
Charge transport and storage in a supercapacitor structure

SC in series with load resistance is connected to DC power source for time interval of 600 seconds. Voltage on SC’s terminals (blue) and charging current (red) are recorded. Acquired characteristics are shown in Fig. 6.1. [41]

Operating voltage $V_{op} = 2.695$ V is reached within the time interval of 50 seconds. This is precisely the moment, when the process of SC relaxation commences. After that the voltage is kept at constant value for additional 550 seconds (see Fig. 6.2). The charge delivered to SC is estimated by integration of the charging current in both intervals: 0 to 50 s, and 0 to 600 s. The charge delivered to SC is $Q_{50s} = 27.5$ C and $Q_T = 32.08$ C, respectively. [41]

![Fig. 6.2: Charging of SC Nesscap 10F/2.7V by constant voltage source, first 80 seconds closeup](image)

Immediately after the charging, the SC is discharged through a shunt resistor $R = 0.25$ Ω. Time dependence of discharge current and voltage on SC terminals is shown in Fig. 6.3. The voltage on SC’s terminals reaches zero value within 12.5 s. The charge taken out from SC by discharge is $Q_d = 27.4$ C. [41]

![Fig. 6.3: Time dependence of discharge current (red) and voltage (blue) of SC Nesscap 10F/2.7V, closeup of discharging](image)

The overall voltage characteristic of the experiment is shown in Fig. 6.4. It is to be acknowledged, that the leakage current of SC Nesscap is negligible [11]. It is of the order of 1 to 10 μA, so the charge loss is less than 50 mC during the entire experiment.
6.2.2 Relaxation and restoration discussion

From the comparison of $Q_{50s}$ and $Q_d$ it follows, that during the initial 50 seconds of charging, the charge is stored mostly on SC’s electrode/electrolyte interface. Then during additional 550 seconds of charging, the charge gets stored mainly by diffusion. The time dependence of charging current in time interval 50 to 600 seconds can be approximated by analytical function based on (5). Here the charging current exponentially decreases with square root of time, which corresponds to charge redistribution by diffusion. For the diffusion layer charging current it holds:

$$I_D = I_2 + I_1 e^{-\sqrt{t}/\tau},$$

where $I_2 = 7.2$ mA is expected limiting current, $I_1 = 30.9$ mA, and $\tau$ is its time constant influenced by $R$. This charging current fit can be seen in figure 6.5. [41]

Here $I_1 + I_2 = 38.1$ mA is the value of diffusion layer charging current in the beginning of its charging in time 50 seconds. $I_2$ represents the value of the current at
Charge transport and storage in a supercapacitor structure

infinity, but is not equal to SC’s leakage current. Measured value of \( I_2 \) is about 3 orders of magnitude higher than the one expected for leakage. This shows both that the charge diffusion is still in progress, meaning that more charge could be stored in electrolyte, and that the analytical function does not take leakage current into account. [41]

Discharging took very short time. It is therefore safe to assume, that only the charge stored on electrodes was channeled out during discharge. This allows for the approximation of the amount of charge stored in electrolyte \( Q_D = Q_T - Q_d = 4.68 \) C. Helmholtz capacitance \( C_H = Q_d / V_{op} = 27.4 / 2.695 = 10.17 \) F and the total capacitance after charging \( C_T = Q_T / V_{op} = 32.08 / 2.695 = 11.90 \) F may also be inferred using (3).

Once the SC terminals are shorted, all charge from its electrodes is discharged. Charge \( Q_D \) is then redistributed back to electrodes (SC restoration) and the voltage on SC’s terminals increases. This is presented in Fig. 6.6, where the time scale was shifted by 614.25 s, so that the restoration originates in time 0 s. The time dependence of restoring voltage can be modeled by exponential stretched law, which shows (same as (6)) that the charge redistribution is driven by diffusion process. The analytical function for restoring voltage is:

\[
V = V_4 \left( 1 - e^{-\frac{t}{\tau_D}} \right),
\]

where \( V_4 = 0.461 \) V is the restored SC’s voltage at infinity, and \( \tau_D = 104 \) s is its time constant, as SC Nesscap 10F/2.7V has dominant diffuse current component (explained in next chapter). [41]

\[
V = V_4 \left( 1 - e^{-\frac{t}{\tau_D}} \right),
\]

Fig. 6.6: Time dependence of voltage on SC’s terminals (black) and its fit (blue) during the SC restoration after the SC short-circuit, time \( t = 0 \) s corresponds to time 614.25 s of the measurement.

The experiment conclusively shows, that the electric charge of SC with carbon electrodes is stored not only in Helmholtz double layer (at the interface between the surface of a conductive electrode and an electrolyte), but also in the electrolyte itself (by the means of charge distribution by diffusion). The charge on electrodes creates Helmholtz double layer, which is formed immediately with time constant on the order of seconds. The charge storage in electrolyte (diffuse capacitance) is going on with time constant of the order of hundreds of seconds. The charge redistribution in SC structure is described by diffusion process. The capacitance of SC’s Helmholtz double layer is close to SC’s rated value. The overall capacitance of SC may however be larger thanks to its diffusion layer, this phenomenon is explained in the following chapter 6.4.
6.3 *Supercapacitor relaxation dominant current component*

Helmholtz’s theory states, that charge moves both by drift and by diffusion during the charging process (see chapter 2.4). Once the charging stops, so does the electric field applied to SC’s terminals. The result of which is subsequent SC relaxation, as briefly described in chapter 2.2. The relaxation is (same as SC restoration evaluated in previous chapter) driven mainly by charge diffusion. It may be safely modeled in that way for longer time intervals. Immediately after the charging ends however, the relaxation model must encompass both the diffusion current and the reversed drift current components.

The ratio of diffusion current component and drift current component differs for different SCs. Its mainly influenced by the electrolyte composition, which is different for each manufacturer. Simple experiment, exploring such a ratio, is described in this chapter.

**6.3.1 Supercapacitor relaxation dominant current component experiment**

Experiment, exploring the dominant relaxation current component, is described in this section. As stated in chapter 5, three different SC models are evaluated in this thesis. In this experiment, only data for SC Maxwell 2.7V/10F and SC Nesscap 2.7V/10F are presented, for clarity. It is to be noted, that SC CapXX 2.75V/2.4F has similar characteristics to SC Nesscap.

![Graph showing SC Maxwell 2.7V/10F and SC Nesscap 2.7V/10F charging and portion of subsequent relaxation](image)

*Fig. 6.7: SC Maxwell 2.7V/10F (green) and SC Nesscap 2.7V/10F (blue) charging and portion of subsequent relaxation*

First the SC is charged by constant current pulse $I_c = 2$ A for 10 s interval. Charge transferred to SC is from $Q_T = I_c \cdot t = 20$ C. Then the open circuit voltage of SC is monitored for time interval of 2000 s. First 100 s of the entire experiment are depicted in Fig. 6.7 for both presented SCs.

**6.3.2 Supercapacitor relaxation dominant current component discussion**

As described above, the total duration of SC relaxation may be very reliably fitted by analytical function, which considers the relaxation to be a diffusion driven process. This holds true for every studied type of SC, because in time horizon of 2000 s the diffusion component of relaxation becomes dominant. Example of such fit for SC Maxwell 2.7V/10F is shown in Fig. 6.8.
The diffusion driven process of SC relaxation is linked to exponential stretched law. It may be fitted by function derived from (5) and (6):

\[ V = V_{2\infty} + \Delta V e^{-\sqrt{t} / \tau_D} , \]  

where \( V_{2\infty} \) is voltage at the end of the relaxation process, \( \Delta V \) is voltage drop due to the relaxation, and \( \tau_D \) is relaxation time constant.

In Fig. 6.8 a closeup of the first 20 s of the relation from Fig. 6.8 is shown. It is noticeable, that the data fit (red) does not properly cover the beginning of relaxation. This is due to the fact, that SC Maxwell 2.7V/10F has a high drift current component, which is dominant at the beginning of relaxation.

If the drift current component, described by time constant \( \tau_{dr} \) was solely responsible for SC relaxation, its analytical function would be from (4):

\[ V = V_{2\infty} + \Delta V e^{t / \tau_{dr}} . \]  

\[ V_{2\infty} \] is voltage at the end of the relaxation process, \( \Delta V \) is voltage drop due to the relaxation, and \( \tau_D \) is relaxation time constant.
The process of relaxation beginning may therefore be approximated by combination of drift and diffusion processes:

\[ V = V_2 + A e^{t/\tau_{dr}} + B e^{t/\tau_{df}}. \]  

(10)

where \( \tau_{df} \) is time constant characterizing the diffusion process in the beginning of relaxation, \( \tau_{dr} \) (from (9)) is time constant of drift process within the same interval, \( A \) and \( B \) are components that together produce the voltage drop \( \Delta V \) at the end of drift current influence during the beginning of relaxation, and \( V_2 \) is SC’s voltage at end of this time interval. (see Fig. 6.9.)

It is assumed, that \( \tau_{df} = \tau_D \) of the entire 2000 s stretch of the relaxation process.

\[ V_1 = 2.30 \text{ V} \]
\[ \Delta V = V_1 - V_2 = 2.30 - 1.68 = 0.62 \text{ V} \]

**Fig. 6.10:** SC Maxwell 2.7V/10F contribution of drift current component (red) and diffusion current component (blue) to the voltage change at the beginning of relaxation process

Figure 6.10 shows the ratio of drift and diffusion current processes of SC Maxwell 2.7V/10F. It is obvious, that the drift current has 10 times higher effect during beginning of SC relaxation. Its influence quickly diminishes however, with time constant \( \tau_{dr} = 7.73 \) s. The diffusion current has in this time interval much lesser impact, but remains acting much longer, as its time constant is \( \tau_{df} = 311 \) s.

\[ V_1 = 2.30 \text{ V} \]
\[ \Delta V = V_1 - V_2 = 2.30 - 1.68 = 0.62 \text{ V} \]

**Fig. 6.11:** SC Nesscap 2.7V/10F entire relaxation period (blue) and its fit by analytical function (red)
For SC Nesscap 2.7V/10F similar relation may be inferred. The data fit of the entire SC relaxation period gives diffusion time constant $\tau_D = \tau_{df} = 240$ s, shown in Fig. 6.11. From this the ratio of drift and diffusion current components may be obtained, as depicted in Fig. 6.12. Here the diffusion current component has of the order of magnitude larger impact, and therefore the drift current component may be neglected. This is true for all samples of SC Nesscap 2.7V/10F and SC CapXX 2.75V/2.4F.

![Fig. 6.12: SC Nesscap 2.7V/10F contribution of drift current component (red) and diffusion current component (blue) to the voltage change at the beginning of relaxation process](image)

The drift current component must be accounted for while working with SCs, that have such component dominant, in order to model the beginning of relaxation properly. Of the studied samples, this is true for SC Maxwell 2.7V/10F. SC Nesscap 2.7V/10F and SC CapXX 2.75V/2.4F have dominant diffusion current component. For this the drift current may be omitted during calculations. It is obvious, that the overall diffusion process is applied during the entire relaxation duration. The drift component is simply added to it during the beginning of relaxation process, as electric field applied to Helmholtz layer disintegrates. For this, two different time constants need to be applied. Note, that the same principle also applies for SC restoration, if the SC is discharged by applied electric field.

### 6.4 Voltage dependent capacitance

As mentioned above, the physics of SC predicts a voltage dependent value of capacitance. This in practice means, that the value of its capacitance changes as does change its steady terminal voltage. Steady voltage is one, that does not change anymore (due to SC relaxation or restoration), but only due to the effect of SC's leakage alone.

The charge on SC with carbon electrodes is stored not only in Helmholtz double layer (at the interface between a conductive electrode and an electrolyte), but also in the electrolyte itself (by the means of charge redistribution by diffusion within the electrolyte). Helmholtz capacitance is charged immediately with time constant of the order of seconds, while the charge stored in diffusion capacitance is redistributed by diffusion process, which leads to increase of total capacitance of the sample. This diffuse capacitance is charged with time constant on the order of hundreds of seconds. The increase of capacitance (due to the charging of diffuse capacitance) leads to decrease in potential on SC’s terminals. Simple experiment that demonstrates this effect and an analytical method of such dependence estimation are presented. [41], [49]
6.4.1 Differential capacitance experiment

Experiment, showing the existence of SC’s voltage dependence, is described above in chapter 6.2.1. In this section a faster and more straightforward solution is presented. The method proposed allows for the precise evaluation of SC’s differential capacitance $C_δ$. [41]

![Fig. 6.13: Voltage vs. time for charging of SC Nesscap 10F/2.7V by constant current 0.25 A (light blue squares), 0.5 A (dark blue circles) and its approximations (black)](image)

This experiment is again illustrated on SC Nesscap 10F/2.7V. Firstly, the SC is completely discharged by leaving it short circuited for several days to weeks. The same condition of samples also generally holds for a brand new sample. The sample SC is charged by a constant current pulse $I_c$ up to its rated voltage. This voltage dependence is recorded and is used for the evaluation. The aim is to use magnitude of current somewhere in the middle range of SC’s comfortable zone, so that the sample does not overheat. Two different measurements of the same sample are presented for currents $I_c = 0.5$ A and $I_c = 0.25$ A in Fig. 6.13.

6.4.2 Differential capacitance discussion

Voltage dependence vs time of SC’s charging by constant current is presented in Fig. 6.13. Here black lines show an approximation of charging voltage, as would be witnessed by conventional capacitor. It server to highlight the characteristic bend in charging curves. Blue lines represent the actual measured voltage dependencies for both utilized charging currents. These voltage curves are shifted to initiate at graph’s origin. The charge transferred to the sample can be extrapolated in relation to its voltage on terminals. This relation is presented in the following figure. Note, that the x-axis and the y-axis are swapped.

Electric charge in relation to potential could be approximated by $2^{nd}$ order polynomial function:

$$Q = C_H V + \frac{1}{2} C_{Hδ} V^2,$$  \hspace{1cm} (11)

where $C_H$ is Helmholtz capacitance and $C_{Hδ}$ is constant, which characterize voltage dependence of SC’s capacitance. [41]
Charge transport and storage in a supercapacitor structure

Fig. 6.14: Stored electric charge vs. voltage for charging of Nesscap 10F/2.7V by constant current 0.25 A (light blue squares), 0.5 A (dark blue circles) and its polynomial approximation

Capacitance is, given by the first derivative of stored charge in relation to applied voltage (2). Hence it follows, that differential capacitance:

\[ C_\delta = C_H + C_{H\delta} V. \]  \hspace{1cm} (12)

Using (12), the actual dependence of \( C_\delta \) may be plotted (see Fig. 6.15). Here the value for \( V = 0 \) V corresponds to Helmholtz capacitance.

The physical reason, why SC’s capacitance depends on voltage and time, follows from the electric charge distribution in SC’s active region. In parallel plate capacitor, the distance between positive and negative electric charge is constant, while in SC this distance is dependent on the electric field value and time. This happens due to that the charge moves between diffusion and Helmhotz layers. Distance between the positive and the negative charge decreases with increasing electric field and therefore SC’s capacitance is a function of applied voltage and time. Note, that the experiment could
also be reversed, measuring the discharge characteristic of previously completely charged SC. [41]

Mathematical method for obtaining capacitance estimation in relation to steady state voltage is described by (12). It is shown how to extrapolate this information from charging or discharging characteristic of SC. Way to estimate the value of SC’s Helmholtz capacitance \( C_H \) is presented. The constant, which characterize SC’s differential capacitance in relation to voltage of its terminals, is also described. The voltage dependence of measured SC’s differential capacitance is shown in Fig. 6.15 and it is linked to its effective electrode thickness. This property of SC is thoroughly described in the following chapter.

### 6.5 Reciprocal capacitance and effective depletion region thickness

The topic of SC’s charging duration dependence on its effective electrode thickness is briefly touched in previous chapter. This section explains the physical basis for such occurrence. Also the reciprocal capacitance concept is explained in this chapter. An experiment, describing this phenomenon, is presented. This experiment is conducted on SC Nesscap 10F/2.7V samples.

![Diagram of single electrode of SC Nesscap 2.7 V / 10 F at steady state](image)

SC structure consists of two porous carbon based electrodes. The effective electrode area of evaluated samples is roughly \( A = 200 \, \text{m}^2 \). The space between electrodes is filled with an anion-rich electrolyte, and cellulose separator. The permittivity of the electrolyte turns out to be roughly \( \varepsilon = 10^{10} \, \text{F/m} \), and its work function is roughly 7 eV. The diagram of single SC electrode is presented in Fig. 6.16. Note, that circa 2 eV energy gap exists in the depletion region (between 5 eV carbon electrode work function and 7 eV of the electrolyte), which is responsible for gradual change in ionic charge density in close proximity to the electrode. Potential energy is depicted by red curve. An effective capacitance is created on such interface. This capacitance turns out to be roughly 20 F for SC Nesscap 2.7V/10F, as there are two such capacitances in series, one at each electrode. [45]

#### 6.5.1 Reciprocal capacitance and effective depletion region thickness experiment

SC must be discharged first. Then it is charged up to its \( V_{op} \) by a constant current pulse. Several different charging currents are employed, ranging from 0.5 A to 1 A.

As stated before, SC Nesscap 2.7V/10F was evaluated. The charging dependencies of this sample are presented in Fig. 6.17. The duration of charging \( \Delta t \) varies from 4.6 s to 50.8 s, honoring equation 2 for regular parallel plate capacitor.
Fig. 6.17: Charging of Nesscap 2.7V/10F using varying currents in time

Again, the non-linear behavior of SC’s charging may be approximated by 2nd order polynomial function (12). Parameters of mentioned fit and different charging times are presented in the following table.

Table 1: Charging characteristic quadratic fit for varying currents of SC Nesscap 2.7V/10F

<table>
<thead>
<tr>
<th>$I_c$ [A]</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{ch}$ [F]</td>
<td>7.35</td>
<td>7.13</td>
<td>7.01</td>
<td>6.87</td>
</tr>
<tr>
<td>$C_{chδ}$ [F/V]</td>
<td>3.48</td>
<td>3.30</td>
<td>3.10</td>
<td>3.04</td>
</tr>
<tr>
<td>$Δt_c$ [s]</td>
<td>50.76</td>
<td>27.78</td>
<td>11.89</td>
<td>4.60</td>
</tr>
</tbody>
</table>

Above charging characteristics are very consistent among all 10 F SCs. It only changes with the SC aging, as described later in chapter 8.

Fig. 6.18: Reciprocal capacitance of Nesscap 2.7V/10F for varying currents in time
6.5.2 Reciprocal capacitance and effective depletion region thickness discussion

Given the charging fit parameters, SC reciprocal capacitance may be calculated. Using (3) it follows, that the reciprocal capacitance is \( C^{-1} = \frac{V}{Q} \).

Using the same approach as in chapter 6.4.2, the time dependence in Fig. 6.18 can be converted to dependence of stored charge, as shown in following Fig. 6.19.

\[
\frac{d}{m} = 2 \varepsilon A C^{-1},
\]

where \( \varepsilon \) is electrolyte permittivity, \( d \) is distance between electrodes or thickness of depletion region, and \( A \) is the effective area of its electrode.

Relation of such effective depletion layer thickness is plotted in Fig. 6.20. From this figure it becomes obvious, that SC’s effective depletion layer thickness is inversely...
Charge transport and storage in a supercapacitor structure

proportional to both the amount of stored charge, and the charging duration. Note, that the effective depletion layer thickness is increased for higher charging currents (shorter charging duration).

It has been established, that the effective depletion layer thickness of SC changes. It happens both due to the amount of charge transferred into it, and due to the time it takes. The effect of varying depletion layer thickness can be quantified using Gauss’ law, as the integration of electric field over the electrode area:

$$\frac{Q}{\varepsilon} = \oint \vec{E} \cdot d\vec{A} ,$$

where \( \vec{E} \) is vector of electric field and \( d\vec{A} \) is vector of increment of area, representing elementary area of the electrode surface. Using the divergence theorem, equation 14 can be transformed into the following form:

$$\nabla \cdot \vec{E} = \frac{\rho}{\varepsilon} ,$$

where \( \rho \) is the electric charge density. For electric field intensity, immediately at single electrode boundary, it therefore holds:

$$E_0 = \frac{\rho d}{\varepsilon} = \frac{enA d}{\varepsilon A} = \frac{I \cdot t}{\varepsilon A} = \frac{enA}{C} ,$$

where \( e \) is elementary charge and \( n \) is negative charge count. It must hold, that \( E_0 \) is countered by positive charge buildup on carbon electrode.

In the beginning of charging process, the electric field dependence in electrolyte in proximity to carbon/electrolyte interface is shown in Fig. 6.21 (brown line). Here the electric field intensity \( E_0 \) starts off immediately at the electrode and decreases with distance \( x \), until it reaches zero at the end of electrolyte effective depletion region \( d \). Electric charge density (blue line) is constant at SC steady state. The total charge within the depletion region is \( Q = e \cdot n \cdot A \cdot d \). For the evolution of electric field intensity with distance \( x \) it holds:
Charge transport and storage in a supercapacitor structure

\[ E(x) = \int \frac{\rho}{\varepsilon} \, dx = \frac{\rho}{\varepsilon}x \bigg|_0^d = \frac{\rho}{\varepsilon}(d-x) = E_0 \left(1 - \frac{x}{d}\right). \]  \hspace{1cm} (17)

Integration of (17), with respect to distance from carbon electrode to the end of constant charge region, gives the relation of potential within electrolyte:

\[ V(x) = \int_0^x E(x) \, dx = E_0 x - \frac{\varepsilon n}{2 \varepsilon} x^2. \]  \hspace{1cm} (18)

The relation of potential distribution in relation to distance from capacitor electrode is depicted in figure below. The red curve represents potential distribution of parallel plate capacitor, which is only bound by the term \( V(x) = E_0 x \) of (18). This is because the electric field intensity in parallel plate capacitor remains constant, due to the stability of atoms inside its structure. In parallel plate capacitor the electric intensity is maintained solely by charge stored on electrodes, whereas in SC the intensity is also formed by freely moving charge within the electrolyte.

![Electric potential distribution in depletion region in relation to distance from single electrode for SC (green) and regular parallel plate capacitor (red)](image)

The green curve of Fig. 6.22 represents the potential distribution inside SC with free moving charge carriers in close proximity to the electrode, as predicted by (18). Note, that the initial intensity vector slope \( E_0 \) must be same for both parallel plate capacitor and SC, as it reflects original charge buildup on Helmholtz layer.

In other words, the relation of electric intensity over area, and the potential evolution within electrolyte are thus linked to unidirectional charge distribution around the opposite polarity electrode. The charge concentration gradually changes, influenced by the electric field, which results in change of reciprocal capacitance and effective depletion region thickness.

The slow movement of charge by drift within the applied electric field results in change of charge density distribution near carbon electrode. Therefore, as shown in Fig. 6.23, the charge concentration changes in time from steady state concentration (blue) into the one designated in red. Note, that the overall number of charge carriers within distance \( d \) to the electrode surface does not change due to drift, and that a depletion
region is created in the area above the red curve and below the blue one. Thus created depletion region is then slowly filled by charge from the bulk electrolyte by diffusion. This increases the number of charge carriers within the distance $d$ from electrode, which has the effect of effective decrease of $d$. Since the diffusion is time dependent process, the effective depletion region thickness $d$ depends both on the transferred charge (drift) and the charging duration (diffusion).

![Graph showing charge concentration](image)

*Fig. 6.23: Electric charge concentration within SC at steady state (blue) and after the drift (red)*

From the above findings it concludes, that the depth of the depletion region near carbon electrode is within 3 nm thick. This is of several orders of magnitude less, than the size of cavities of activated carbon electrode. All the relevant electrolyte phenomena must occur within this distance and are therefore not dependent on the cavity size. This depletion region is therefore much thinner than previously expected in [12], where SC behavior is explained out by varying surface roughness and pore size dispersion.
7 Proposed SC Equivalent Circuit Model

As described in the State of the Art section, many equivalent circuit models of SC were proposed before. All mentioned models do however suffer from some drawbacks. Most prevalent being its inaccuracy in prediction of SC behavior, not having basis in physical reality (i.e. pure analytical models based on heuristics), having hard to establish parameter values, or being overly difficult to use for having large amount of components.

This part of this thesis proposes new 5 parameter SC equivalent electrical circuit model (ECM). This model is very simple and relatively easy to utilize for real-life SC behavior estimation. It is constructed to reflect the underlying SC’s physical properties. It reaches extremely good accuracy, with less then 5% error. This model is first issued in renown Journal of Power Sources [44]. But its use and application are also well published in other periodicals [41], [42], [45], [49].

This chapter is divided as follows. First the ECM is explained, and its characteristics are linked to above described physical principles. Then the method for determination of used parameters is described. Lastly the efficacy and accuracy of the model is discussed.

7.1 Supercapacitor’s equivalent circuit model

Model fulfilling all the aforementioned criteria is described in this section. Here the SC is modeled by circuit, consisting of two ideal capacitors, two regular resistors, and one resistor with time dependent resistance value. Capacitors mentioned represent the capacitance of Helmholtz double layer $C_H$ and the increase of capacitance due to the diffusion of charges into the electrolyte $C_D$. The two ordinary resistors are the equivalent series resistance (ESR) $R_S$ and parallel leakage resistance $R_L$. The time dependent resistance $R_D(t)$ represents the resistance between $C_H$ and $C_D$. The resistance $R_D(t)$ increases with the square root of time of charging and covers the decreasing probability for another charge carriers’ transport by diffusion. Scheme of this model is shown in Fig. 7.1. [44]

![Fig. 7.1: Proposed 5 parameter SC equivalent electrical circuit model](image)

The remainder of this chapter holds the detailed explanation of every single parameter of this model, including a method of its determination. Example of deriving values of these parameters, based on real-life measurement, is described in the following chapter 7.2. Then, in chapter 7.3, the ECM is verified and its error is assessed.
7.1.1 Helmholtz capacitance

The capacitance of Helmholtz double layer, marked \( C_H \) in Fig. 7.1. This is the SC’s immediate capacitance. Meaning, that it is responsible for holding most of the charge during fast charging, and that it is able to release all its charge immediately. The charge of Helmholtz capacitance is in real-life SC stored on the electrode/electrolyte interface.

There are three ways \( C_H \) may be charged or discharged.

1. From outside, by applying voltage to SC’s electrodes. In this way the charge goes through \( R_S \) with time constant \( \tau_H = R_S C_H \).

2. From inside, by the interaction with SC’s diffusion layer, represented by capacitance \( C_D \). In this case the charge traverses time dependent resistance \( R_D(t) \). This corresponds to transfer of charge by diffusion (diffusion current), thoroughly described in following chapter 7.1.3.

3. Or it can be discharged through leakage resistance \( R_L \). This corresponds to SC’s leakage, described in chapter 7.1.5.

The physical principle behind Helmholtz capacitance is explained in 2.4.1. Equation 4, shows how the charge inside Helmholtz layer changes in time. It is clear, that the relation is linear through its time constant \( \tau_H \). This exactly corresponds to RC circuit connected in series, as ECM predicts. Note, that charge stored in \( C_H \) causes drift of charge in electrolyte, as depicted in Fig. 7.2.

7.1.2 Diffuse capacitance

Diffuse capacitance (designated \( C_D \) in Fig. 7.1) represents the ability of electrolyte to effectively hold charge. Such charge is held in a form of ions, that diffuse into the depletion region from the electrolyte bulk, after the charge drift occurs near the
Helmholtz layer. In the model this capacitance is connected to the rest of ECM through a time dependent resistance $R_D(t)$, described in the next section. Diffuse capacitance actually contributes to the overall capacitance of SC. This total capacitance manifests itself as the sum of diffuse and Helmholtz capacitances:

$$C_T = C_D + C_H .$$

(19)

Diffuse capacitance gets charged, when the voltage $V_H$ of $C_H$ is greater than the voltage $V_D$ of $C_D$. Since both $C_D$ and $C_H$ are effectively in parallel, the charge in ECM transfers into $C_D$, until an equilibrium of potentials is reached. This is a manifestation of the SC relaxation process. During this the charge buildup on Helmholtz layer (by drift) creates a depletion region near the electrode. The drift of additional charge from electrolyte bulk decreases due to low electric field in larger distance from the electrode, as explained in chapter 6.5. This forms a depletion region characterized by lower electric charge concentration. Such depletion region has therefore a low charge density, which allows for the diffusion of charge into this region from within the electrolyte bulk (see Fig. 7.2). The incoming charge serves to counter the effect of charge stored on electrodes, reducing the overall electric field intensity, that the charge on electrode exerts. This has the effect of terminal voltage decrease.

When the voltage of $C_H$ suddenly drops below the level of $C_D$ (e.g. in the case of SC short-circuit), the diffuse capacitance slowly discharges itself through $R_D(t)$ into the Helmholtz one. This is observed as SC restoration on its terminals. It is a result of previously drifted charge not being held at Helmholtz double-layer anymore. The charge density near the electrode increases suddenly, which leads to its diffusion into the electrolyte bulk. This process is the opposite to the one described in paragraph above.

### 7.1.3 Resistance between the Helmholtz and the diffuse capacitance

Charge applied to SC is eventually redistributed by the diffusion process. It either transfers from $C_H$ to $C_D$ or vice versa. Either way it passes the time dependent diffuse resistance of ECM, designated $R_D(t)$ in Fig. 7.1. This variable resistance represents the decreasing probability of another charge carriers’ transport by diffusion.

The first charge transfer scenario (SC relaxation) is discussed in this thesis, but the same process is applicable in reverse for SC restoration, disregarding the drift component, as there is no electrical field applied. Since the total charge stored inside the system does not change, the following relation holds true:

$$Q_T = Q_H + Q_D ,$$

(20)

where $Q_T$ is total charge stored in SC, $Q_H$ is charge stored in Helmholtz double-layer and $Q_D$ is charge stored in diffusion layer.

Considering the Helmholtz capacitance to be constant, its voltage is directly proportional to its stored charge from (3). Since the voltage of Helmholtz capacitance obeys equation 8 during relaxation, following is true for charge stored at $C_H$:

$$Q_H = Q_{H∞} + Q_{D∞}e^{-\sqrt{t_D}/\tau} ,$$

(21)

where $Q_{H∞}$ is charge stored on $C_H$ at infinity, $Q_{D∞}$ is charge stored on $C_D$ at infinity, and $t_D$ is time constant of the relaxation process.
For charge stored in diffuse layer it then holds:

$$Q_D = Q_{D\infty}(1 - e^{-\sqrt{t/\tau_D}}).$$  \hfill (22)

The charge transport between $Q_H$ and $Q_D$ in time can be expressed in a form of diffuse current, flowing from one to another:

$$I_D = \frac{dQ_D}{dt},$$  \hfill (23)

where $dQ_D$ is change in diffusion layer charge.

By the first derivative of combination of (22) and (23), considering that the overall charge $Q_T$ remains constant, the following relation for the diffuse current in time is obtained:

$$I_D(t) = Q_{D\infty} \frac{e^{\frac{t}{\tau_D}}}{2\tau_D} = I_{D\infty} \frac{e^{\frac{t}{\tau_D}}}{\sqrt{t/\tau_D}},$$  \hfill (24)

where $Q_{D\infty}$ is charge stored in diffusion layer once the diffusion process has finished, $\tau_D$ is time constant of the change of its charge, and $I_{D\infty} = Q_{D\infty} / 2\tau_D$ is diffuse current constant. Note, that the diffuse current is produced by both the drift and the diffusion processes.

For the time dependent resistance between Helmholtz and diffusion layer it holds from Ohm’s law:

$$R_D(t) = \frac{V_H - V_D}{I_D(t)},$$  \hfill (25)

where $V_H$ is voltage of $C_H$ and $V_D$ is voltage of $C_D$.

### 7.1.4 Equivalent series resistance

Resistance $R_S$ represents the DC ESR of SC in ECM, as depicted in Fig. 7.1. It constitutes of leads and the carbon electrode resistance. It directly influences the Helmholtz capacitance time constant during SC charging and discharging process through the relation $\tau_H = R_S C_H$. ESR is also responsible for voltage step at SC terminals, while the magnitude of current, passing through the SC, changes. The ESR does not directly influence any other processes.

### 7.1.5 Leakage resistance

The leakage resistance $R_L$ is directly proportional to SC's leakage current and steady state voltage. This parameter is situated parallel to $C_H$ in ECM, so that its estimation is easier. It would however might be more appropriate to model the leakage resistance as parallel to $C_D$ but in practice it would make no difference, because the leakage current of SC is negligible. [11]
7.2 Model parameter estimation

Each component of ECM, as depicted in Fig. 7.1, is discussed in previous chapter. This section presents method, that might be utilized for ECM’s parameters determination for a real SC sample.

Method based on physical processes during charge/discharge of SC is used for model parameter determination. All model parameters are retrieved using analytical description from measurements of terminal characteristics of SC. Same as for experiment, explained on page 30, the SC sample should be properly discharged beforehand. Then the SC is charged by constant current pulse $I_c$, after which the SC relaxation period is observed, same as for experiment in chapter 6.3.1. Time dependence of such measurement is presented in Fig. 7.3 for SC CapXX 2.74V/2.4F, where large portion of relaxation period is cutoff for clarity.

![Figure 7.3: SC CapXX 2.75V/2.4F charging and portion of subsequent relaxation during the equivalent circuit model parameters determination](image)

The $I_c$ used should be at the upper boundary of SC’s comfortable zone. Charging current ought to be as high as possible, in order to minimize the charge loss to the diffusion layer, so that only the Helmholtz capacitance gets charged within this interval. On the other hand, the charging current must be low enough, in order not to induce any thermal effects in SC.

The duration of subsequent relaxation period monitoring is optional. It is recommended to be as long as possible, because longer measurement allows for more precise data fitting. Time period of 2000 s should be sufficient in most scenarios.

From analytical evaluation of the above measurement, each parameter of ECM may be inferred.

7.2.1 Helmholtz capacitance

In order to determine the Helmholtz capacitance value, capacitor needs to be charged by constant DC current pulse. After that the voltage of capacitor is measured. First 2000 seconds of the SC relaxation period are shown in Fig. 7.4 for SC Maxwell 2.7V/10F. Relation depicted in this figure starts immediately after the charging is cutoff.
After the charging interval, the voltage drop (during which the diffuse capacitance is being charged) across SC's terminals is monitored. This voltage characteristic could be fitted by function (8). Since the studied type of SC has drift current component dominant, its influence on beginning of relaxation must be taken into account. This is achieved by fitting the beginning of the relaxation by equation 10. From its fit, the proper value of maximum relaxation voltage $V_i = 1.93 + 0.048 + 0.417 = 2.39 \text{ V}$ may be extrapolated.

Note, that (as described in chapter 6.3) the data fit by (8) would be sufficient for samples of SC Nesscap 2.7V/10F and SC CapXX 2.7V/10F, because their diffusion current component is dominant. Even though this method may be utilized for any SC sample in order to achieve better evaluation precision.

Also note, that the actual measured value of SC terminal voltage (immediately after the charging stops) may be used for $V_i$. This method only leads to slight error, if large enough sampling frequency is utilized for the relaxation measurement and proper measurement setup is utilized.

Since the charging pulse is relatively brief, it may be assumed, that only the Helmholtz capacitance is charged in this time interval, and that the charge transferred to the diffuse capacitance is negligible. This means, that at the end of the charging, the charge stored in Helmholtz capacitance is $Q_H = Q_T = 22.81 \text{ C}$ for evaluation run depicted in Fig. 7.4. From (3) it then follows, that $C_H = Q_H / V_1 = 9.54 \text{ F}$.

As explained in chapter 6.4, the capacitance of SC is voltage dependent. This results in the above described phenomenon of bent charging characteristic. This bent is produced by slow charging of diffuse capacitance already during the initial charging pulse. This results in slight error in Helmholtz capacitance estimation, while using the method based on data fitting, described above. An alternative method for $C_H$ estimation would be the fitting of charging relation by equation 11, as explained in chapter 6.4.2. The value of $C_H$ would then be the one obtained from (12). This method produces for given sample the value of Helmholtz capacitance $C_H = 9.48 \text{ F}$.

Even though the second method is more precise, the first one shall be used from now on for following reasons:

1. Results are generally within 4% margin of error, which is negligible in the context of entire measurement.
2. The charge leaking to the diffuse capacitance may be neglected, due to the short duration of the charging pulse and mutual ratio between charge stored in Helmholtz double layer and diffuse layer.
3. Results are much easier to obtain, because the method is straight forward and does not require precise measurement setup.

### 7.2.2 Diffuse capacitance

From data fit depicted in Fig. 7.4, the diffuse capacitance may be obtained. For the observed voltage drop it holds, that $\Delta V = V_i - V_{2\infty} = 0.46 \text{ V}$. Note, that the last measured value of relaxation ($V_2$) might be used instead of $V_{2\infty}$, which would only lead to slight decrease in precision.

Taking into consideration the overall SC capacitance and the Helmholtz capacitance; the value of diffuse capacitance is from (19) and (3):

$$C_D = C_T - C_H = Q_T / V_{2\infty} - Q_H / V_i .$$

(26)
Charge transport and storage in a supercapacitor structure

The calculated value for experiment presented in Fig. 7.4 is \( C_D = 2.34 \) F. From (19) the total SC capacitance is \( C_T = 11.82 \) F. Same as for Helmholtz capacitance, the total capacitance and hence the diffuse capacitance could be evaluated more precisely using method described in chapter 6.4.

\[ Q_{1000} = \frac{0.0484 + 0.417 + 2.99}{1.93} = 2.75 \text{ V/2.4 F} \]

\[ V_{d} = 0.417 \]

\[ V_{0} = 1.93 \]

**Fig. 7.4:** SC Maxwell 2.7V/10F voltage relaxation during the equivalent circuit model parameters determination (blue), its data fit by analytical function accounting for diffusion process (red), and data fit by analytical function accounting for drift at beginning of SC relaxation

### 7.2.3 Resistance between the Helmholtz and the diffuse capacitance

In order to determine the diffuse resistance \( R_D \), the dependence of electric current \( I_D \) flowing from the Helmholtz capacitance to the diffuse capacitance must be established. The change of this current is given by (24).

Experiment presented in this section is followup on a measurement of SC CapXX 2.75V/2.4F from Fig. 7.3. The charge applied to SC during charging is \( Q_T = 7.87 \) C. Its relaxation period is depicted in Fig. 7.5. Its relaxation characteristic is fitted by function, that accounts for drift current component, even though it is not dominant in this kind of SC.

\[ V_{1} = 2.74 \text{ V} \]

\[ V_{d} = 0.417 \]

\[ V_{0} = 1.93 \]

\[ V_{c} = 2.75 \text{ V/2.4 F} \]

**Fig. 7.5:** SC CapXX 2.75V/2.4F relaxation (blue) and its data fit by analytical function (red)
The diffusion time constant is established to be $\tau_D = 310$ s. Its voltage at the beginning of relaxation is $V_I = V_H = 2.742$ V and the voltage at end of relaxation is approximated to be $V_{2\infty} = 1.54$ V. Its steady state voltage before the charging has started is $V_0 = V_D = 0$ V (see Fig. 7.3), because the SC was fully discharged before the measurement. From (3) and (26), SC’s Helmholtz and diffuse capacitances may be inferred. They are 2.88 F and 2.24 F, respectively.

Figure Fig. 7.6 shows the evolution of charge stored in Helmholtz capacitance, obtained from relaxation, using (3). It is again fitted by (10). It follows, that the charge stored in $C_H$ at the end of the diffusion capacitance charging process is $Q_{H\infty} = 4.43$ C. From (20) the charge stored in diffusion capacitance at the end of relaxation is $Q_{D\infty} = 3.44$ C.

- 45 -
In order to experimentally reaffirm the above finding, diffusion current may be calculated from measured data. First the relation of charge stored in diffuse layer is established. From Fig. 7.6 using (20) it follows, that the charge stored in diffuse capacitance is given by the following dependence. Note, that both Fig. 7.6 and Fig. 7.8 converge at the same value \( Q_{D\infty} \).

Fig. 7.7: SC CapXX 2.75V/2.4F time dependent resistance solved analytically

Fig. 7.8: SC CapXX 2.75V/2.4F dependence of charge stored in diffuse layer in time

Fig. 7.9 may be derived from Fig. 7.8, since the charging current is constant. Fig. 7.9 shows the magnitude of diffuse current, during SC relaxation. It is fitted by equation 24. The data fit shows, that both \( t_D \) and \( Q_{D\infty} \) (estimated earlier) were slightly wrong. Precisely they ought to be 316 s and 5.55 C, respectively. The impact of this alteration is minuscule however. In Fig. 7.5 only the estimated value of \( V_I \) would change to 2.748 V. This is an acceptable fault in model estimation, comparable to rounding error.
Charge transport and storage in a supercapacitor structure

\[ y = a \exp\left(\frac{-x}{b}\right) + \frac{c}{x^d} \]

\[ R_D(t) = \frac{V_H}{I_D(t)} \]

\[ T = 25 \, ^\circ C \]

\[ I_c = 0.5 \, A \]

\[ Q_T = 7.87 \, C \]

\[ C_H = 2.88 \, F \]

\[ C_D = 2.24 \, F \]

**Fig. 7.9:** SC CapXX 2.75V/2.4F diffuse current, flowing from Helmholtz to diffuse layer experimental data (red) and fit by analytical function (blue)

Experimentally obtained value of diffuse current in time allows for more precise estimation of diffuse resistance. The value of \( R_D(t) \) (obtained, using Ohm’s law) in first 80 seconds of SC relaxation is plotted in Fig. 7.10. In the beginning of relaxation period, noticeable divergence of experimental and calculated data is observed. This is most likely due to slight drift current component of SC CapXX 2.75V/2.4F, which is not accounted for in equations 24 and 27. Note, that such imprecision does have almost zero impact on actual SC modeling.

**Fig. 7.10:** SC CapXX 2.75V/2.4F time dependent resistance solved analytically (blue) and experimentally (green), first 80 seconds of relaxation

### 7.2.4 Equivalent series resistance

Value of SC’s ESR may most easily be acquired from voltage step \( \Delta V_{ESR} \), which occurs when the magnitude of DC current through the SC changes. The value is then from Ohm’s law \( R_S = \frac{\Delta V_{ESR}}{I_c} \). This is demonstrated on SC Nesscap 2.7V/10F in following Fig. 7.11.

Notice, that there are two mentioned voltage steps in Fig. 7.11. The first one occurs when the charging is switched on and SC’s terminal voltage rises from \( V_0 = 0 \, V \).
to $V_{c0} = 0.18$ V. The subsequent voltage step occurs when the charging is switched off and SC’s voltage drops from $V_{c1} = 2.75$ V to $V_i = 2.66$ V.

In theory both presented values of $\Delta V_{ESR}$ should be the same, given by relation $\Delta V_{ESR} = V_{c0} - V_0 = V_{c1} - V_i = 0.17$ V. In practice though, both values do not match by ~3 mV (rounding is employed in presented figures). This is due to the fact, that the power source used for charging (see chapter 4.2), even though very precise, suffers from transient effect, while increasing current from none to 5 A. The first value of $\Delta V_{ESR}$ should therefore not be used for precise ESR determination. The resulting $R_S = 34$ mΩ for measurement in Fig. 7.11.

One more common pitfall of ESR evaluation ought to be mentioned. It is the influence of dominant electrolyte current component on determination of $V_i$. As shown in Fig. 7.12, which probes the relaxation of SC Maxwell 2.7V/10F from Fig. 7.4, the voltage of SC’s terminals might need to be extrapolated back to the precise moment, when the charging is cutoff. This must be done always in the case the measurement sampling frequency is low. Note, that the time axis in Fig. 7.12 is shifted, so that the charging ends precisely in time 0 s. For this experiment the value is $R_S = 64$ mΩ.
7.2.5 Leakage resistance

The leakage resistance $R_L$ is directly proportional to the leakage current of measured SC employing Ohm’s law. As shown in [11] and stated in chapter 7.1.5, the value of leakage current is of the order of several $\mu$A for all evaluated SCs, which produces measurement error of less than 0.1 percent. Therefore the leakage resistance model parameter could be neglected.

In order to evaluate the leakage resistance precisely, method published in [11] may be used. Its estimation does take several weeks for every evaluated sample. Hence not deemed practical. In ECM the value $R_L$ in range from 10 kΩ to 1 MΩ could be successfully utilized.

7.3 Model reliability

Previously in this chapter, new five-parameter SC model is proposed. It is explained and linked to SC’s underlying physical behavior. And method for its parameter evaluation is presented. In this section the model is put to work for 4000 second simulation. Its mathematical model is described first. Then studied samples are presented. And finally its precision is assessed based on divergence from actual measured data and the model is compared to another state of the art solution.

7.3.1 Mathematical model

The ECM is difficult to simulate by common tools based of SPICE (Simulation Program with Integrated Circuit Emphasis) family, such as MicroCap, OrCAD, etc. This is commonly either due to algebraic loop malfunctions, occurring while evaluating the time dependent resistance. Or due to the inability to implement such a time dependent resistance within the software altogether. Usually the proper implementation requires deep understanding of the utilized modeling software. To overcome this difficulty, the ECM is mathematically described by a system of equations, which are solved by numerical techniques. The evaluation run itself is performed in MathWorks’ MATLAB environment. [44]

![Fig. 7.13: Equivalent circuit model connected to constant current source for simulation scenario [44]](image)

Figure above shows the modeled scenario. Here the ECM is connected to an ideal current source with parallel internal resistance $R_P$.

The equations, that govern the model, are developed based on node voltage analysis. For voltage of SC’s terminals $V_1$ it holds:

$$V_1 = \frac{R_P}{R_P + R_S} V_2 + \frac{R_P R_S}{R_P + R_S} i,$$  \hspace{1cm} (29)

where $R_S$ is SC’s ESR, $V_2$ is voltage of Helmholtz capacitance, and $i$ is current flowing through the ideal current source.
Charge transport and storage in a supercapacitor structure

For the change of voltage of SC’s Helmholtz capacitance $C_H$ (designated $V_2$ in Fig. 7.13) it holds:

$$\frac{dV_2}{dt} = \frac{V_2}{R_S C_H} - \frac{V_2}{R_S C_H} - \frac{V_2 + V_3}{R_L C_H} + \frac{i R_p R_s}{C_H (R_p + R_S)}, \quad (30)$$

where $R_L$ is SC’s leakage resistance, $V_3$ is voltage of diffuse capacitance, and $R_D(t)$ is time dependent diffuse resistance, prescribed by its value $R_{D1}$ and elapsed time.

Finally for the change of voltage $V_3$ of SC’s diffuse capacitance $C_D$ it holds:

$$\frac{dV_3}{dt} = \frac{V_2 - V_3}{R_D(t) C_D} + \frac{i R_p R_s}{C_H (R_p + R_S)}, \quad (31)$$

For the time dependent resistance $R_D(t)$ the value is obtained from:

$$R_D(t) = \begin{cases} R_{D1} \sqrt{t-t_0}, & \text{for } t > t_0 \\ 0.001 \Omega, & \text{for } t \leq t_0 \end{cases}, \quad (32)$$

where $t_0$ is the moment, when the current $i$ starts to flow.

The value $0.001 \Omega$, for time dependent resistance before the charging starts, is picked arbitrarily. This value is utilized in order to reach convergence of numerical solutions within the equation system.

7.3.2 Evaluated samples

Measurement and simulation of subsequent run is presented for two SCs. These are samples of SC CapXX 2.75V/2.4F and SC Nesscap 2.7V/10F. First the model parameters are established. Then the model may be calculated and verified for different charging current on the same sample.

Fig. 7.14: ECM parameter value determination for SC Nesscap 2.7V/10F, measured data (blue) and data fit (black), charging current 5 A

Fig. 7.14 above shows a relaxation period of another sweep (at room temperature) of SC Nesscap 2.7V/10F. This SC is charged by $I_c = 5$ A. Total charge
transferred to it is 18.36 C. The sample of SC Capxx 2.75V/2.4V, discussed in previous section 7.2, is the second evaluated sample. ECM parameters of both samples are summed up in Table 2.

Table 2: Evaluated equivalent circuit model parameters for simulated SCs

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_\text{H}$ [F]</th>
<th>$C_\text{D}$ [F]</th>
<th>$R_{\text{D1}}$ [Ωs$^{0.5}$]</th>
<th>$R_\text{s}$ [mΩ]</th>
<th>$R_\text{L}$ [kΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC CapXX 2.75V/2.4F</td>
<td>2.88</td>
<td>2.24</td>
<td>13.98</td>
<td>54.69</td>
<td>38</td>
</tr>
<tr>
<td>SC Nesscap 2.7V/10F</td>
<td>8.08</td>
<td>1.63</td>
<td>13.82</td>
<td>34.48</td>
<td>100</td>
</tr>
</tbody>
</table>

### 7.3.3 Simulation

Parameters of the two studied samples are shown in table above. This section verifies the predictive capability of presented model. From these parameters another charging run, utilizing different current, is simulated. Then the actual measurement is performed and both characteristics are compared. The value $R_\text{p} = 0.1 \, \text{GΩ}$ is used for current source, utilized for the measurement.

For evaluated SC CapXX 2.75V/2.4F an alternative current $I_\text{c} = 2.5$ A is used. The charging current is applied for 2 seconds in order to transfer charge $Q_T = 5$ C. Both the result of the simulation and the data obtained from its subsequent measurement are shown in Fig. 7.15. In this figure only the charging duration closeup is presented.

![Fig. 7.15: Closeup of charging portion of simulation (red) and measured data (blue) for CapXX 2.75V/2.4F, charging current 2.5 A](image_url)

The following Fig. 7.16 shows the overall measurement and simulation of SC CapXX 2.75V/2.4F.
For evaluated SC Nesscap 2.7V/10F an alternative current $I_c = 4$ A is used. The charging current is applied for 5 seconds in order to transfer charge $Q_T = 20$ C. Both the result of the simulation and the data obtained from its subsequent measurement are shown in Fig. 7.17. Again, only the charging duration closeup is presented first.

Closeup of the overall 4000 s run of SC Nesscap 2.7V/10F is shown in Fig. 7.18. Here the model is compared to the prediction made by the state of the art model, produced by Zubieta and Bonert. [1] First of all it is to be noticed, that the ECM does not cover the immediate beginning of relaxation better then Zubieta’s model. This is a product of drift current component of SC Nesscap 2.7V/10F, which was not accounted for during the ECM parameter evaluation in chapter 7.3.2. Even with such a deficiency though, the proposed model gives excellent results within the overall run. Zubieta’s model on the other hand follows the immediate beginning of relaxation very precisely, but completely diverges within 200 s of relaxation.
7.3.4 Reliability assessment

As mentioned above, ECM omits drift processes, which causes in the worst case scenario an absolute error of 0.1 V for fully charged capacitor. The relative error is however below 5% for the entire measurement. For longer time intervals (over 500 s) the relative difference between the experiment and the simulation is below 0.5%. The accuracy of ECM is evaluated based on its empirical probability. This represents the ratio of the number of outcomes in which a specified event occurs, to the total number of trials. [44]

Fig. 7.19 shows the dependence of empirical probability in comparison to the relative error of simulation compared to the actual measurement. For ECM 70% of monitored interval is within the 1% relative error margin. For the rest of the monitored
interval the relative error always remains under 5%. In comparison with the state of the art solution, presented in Fig. 7.20, the ECM gives much better results.

Fig. 7.20: The dependence of empirical probability on relative error between simulation results of Zubieta’s model and experimental data
This chapter pursues the analysis of SC aging. As stated before, SC should in theory have infinite cycle life, due to the electrochemical inertness of its main components. In practice though, the state of health of SC, which is manifested through the degradation of its ECM parameters, is strongly dependent on the abuse SC sustains throughout its lifetime. Such an abuse is inflicted on SC by several different means, which all stem from the expected kinds of usage of said device.

Firstly, the effect of charge transport during charging/discharging must be considered. Next thing to account for is the effect of temperature, which may either be of environmental source or a Joule’s heat produced by charging/discharging currents. The last studied manner of degradation is the effect of keeping SC at constant voltage within varying ambient temperature. This includes the overcharging of SC for prolonged periods.

In order to artificially inflict the kind of damage SC sustains during its normal operation, several experimental methods are devised to test it. These methods are based on SC’s basic work profile during its actual deployment. Two general kinds of such methods are employed and presented, these are the energy cycling tests and the calendar life tests.

### 8.1 Energy cycling tests

This family of induced aging methods is based on cyclic charging and discharging of studied SC samples. Such processes alter the relative amount of energy stored within tested SC. Energy of conventional capacitor is given by the equation:

\[
E = \int V \, dQ,
\]  

(33)

where \( E \) stands for stored energy and \( V \) is potential of SC’s terminals.

Introduction of fundamental equation 2 into equation 33 allows for the extrapolation of following (34). This equation sets up a firm dependence between stored energy, conventional capacitance, and terminal voltage of conventional capacitor.

\[
E = \frac{1}{2} C V^2.
\]  

(34)

Energy cycling tests are based on periodic constant current charge pulses up to SC’s maximum operating voltage \( V_{op} \) during every cycle. It then must be discharged back to 0 V in order for 100% of the energy to shift in and out. Or (from (34)) back to \( \frac{1}{2} V_{op} \) to shift 75% of stored energy in and out of the sample.

It has been mentioned that these tests require pulses of constant current. Both the charging current \( I_c \) and the discharging current \( I_d \) have the same magnitude and are chosen to be as high as possible. The aim is for each cycle to take the least amount of time, which leads to opting for very high currents. Too high currents are not desirable, because their use may burn the sample. Therefore a compromise on the value of charging and discharging currents must be reached.
Taking into consideration all previously mentioned equations, the following holds for the relation between current, capacitance, change in time, and change in terminal voltage for energy cycling tests:

\[ I_c = I_d = C \frac{dV}{dt}. \] (35)

It is to be noted, that the currents are picked in advance (using (35) and the nominal capacitance of a brand new sample) and are not changed for the total duration of the experiment. Therefore the actual duration of every single cycle shrinks, as the aging progresses (this effect is thoroughly described later in section 8.1.1).

As already hinted, each energy cycling test starts off with fully charged SC (terminal voltage equal to \( V_{op} \)). Sample SC is charged by constant voltage source for at least 24 hour period prior to energy cycling test commencement. All energy cycling tests, presented in this section, are performed at room temperature at roughly 22°C.

The depreciation of SC’s parameters (due to energy cycling tests) is evaluated in relation to both, the total duration of these tests in hours, and the total number \( n \) of endured test cycles. Parameters are evaluated every \( 10^5 \) cycles. Following ECM parameters are analyzed: \( C_T, C_H, C_D, \tau_D, R_S, \) and \( R_{D1} \). The charging current \( I_c = 5 \) A is used for ECM evaluation. In addition, a conventional DC capacitance (\( C_{DC} \)) and DC ESR (\( R_{DC} \)), are evaluated using an RLC Meter.

Note, that this section only contains results of aging of SC Nesscap 2.7V/10F and SC Maxwell 2.7V/10F. Samples of SC CapXX 2.75V/2.4F are left out, because their parameter decline is very fast, and they generally malfunction within \( 3 \times 10^5 \) cycles of any energy cycling test. This does not give enough data to draw reliable conclusions. Two main kinds of energy cycling tests, introduced and evaluated in sections 8.1.1 and 8.1.2, are used.

### 8.1.1 Continuous energy cycling

Continuous energy cycling (CEC) comprise of discharging followed immediately by charging, which constitutes a single test cycle. Two distinct energy methods are used. Namely they are referred to as “continuous 100% energy cycling” (100% CEC) and “continuous 75% energy cycling” (75% CEC) tests, where the percentage corresponds to amount of energy transferred in and out of SC within every cycle.

![Diagram of SC’s voltage dependence for 100% energy cycling test (green) and 75% energy cycling test (blue)](image-url)

\( V_{op} \):

\( V_{t/2} \):

\( V_{t/4} \):

\( T \):

\( I_c \):

\( C_T \):

\( C_H \):

\( C_D \):

\( \tau_D \):

\( R_S \):

\( R_{D1} \):

\( C_{DC} \):

\( R_{DC} \):

Fig. 8.1: Diagram of SC's voltage dependence for 100% energy cycling test (green) and 75% energy cycling test (blue)
Diagram of an expected voltage dependence of an ideal capacitor (for both continuous energy cycling tests) is depicted in Fig. 8.1. It is customary to use the same value of current for both 75% and 100% energy tests, so that the effect of induced Joule’s heat is the same for both. The value of $I_c = I_d = 2.7$ A is selected for both CEC methods. The effect of self-heating may therefore be neglected in comparison. Note, that the sample’s temperature increases by roughly 20 °C as a results of CEC.

As shown in the figure above, single cycle of 100% CEC should last twice as long as single cycle of 75% CEC, because (while using constant current) the discharge to 0 V takes twice as long than the discharge to $\frac{1}{2} V_{op}$.

SC Nesscap and SC Maxwell are evaluated for CEC aging tests. Three samples of each form a single measurement batch. All plotted results are median values of each batch. Both kinds of studied SCs have nominal capacitance $C = 10$ F and operating voltage $V_{op} = 2.7$ V. From (35) it follows, that for both measured types should single cycle of 100% CEC and single cycle of 75% CEC last roughly 20 seconds and 10 seconds, respectively.

Table 3: Duration of 100% continuous energy cycling tests

<table>
<thead>
<tr>
<th>No. of cycles [-]</th>
<th>$1 \times 10^5$</th>
<th>$2 \times 10^5$</th>
<th>$3 \times 10^5$</th>
<th>$4 \times 10^5$</th>
<th>$5 \times 10^5$</th>
<th>$6 \times 10^5$</th>
<th>$7 \times 10^5$</th>
<th>$8 \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell 2.7V/10F [h]</td>
<td>566</td>
<td>1107</td>
<td>1587</td>
<td>2005</td>
<td>2413</td>
<td>2785</td>
<td>3073</td>
<td>-</td>
</tr>
<tr>
<td>Nesscap 2.7V/10F [h]</td>
<td>518</td>
<td>1015</td>
<td>1481</td>
<td>1913</td>
<td>2327</td>
<td>2735</td>
<td>3141</td>
<td>3551</td>
</tr>
</tbody>
</table>

The overall duration in hours of 100% CEC measurement for each batch is shown in Table 3. These times show how long did the slowest of the batch take. After each $10^5$ cycles, the CEC is halted and ECM parameters are evaluated. The batch, that finishes first, has to wait for all the other to adjourn, as each other round of measurement (set of $10^5$ cycles) is started off simultaneously for all batches. For this the SCs remain shorted for up to a week after each round, during which the ECM parameters are evaluated, all other batches finish, and SCs get charged back to $V_{op}$ for another round of CEC.

![Fig. 8.2: Charging dependence of SC Maxwell 2.7V/10F before (red) and after (blue) $4 \times 10^5$ cycles of 100% continuous energy cycling for charging current 5 A; green line shows a theoretical dependence of an ideal 10 F capacitor](image)

Note, that the overall times of cycling shrink for each measurement round. The first and the last round of 100% CEC of SC Maxwell 2.7V/10F take 566 hours and 288 hours, respectively. This is produced by both the capacitance decrease and ESR of aged...
samples increase. Fig. 8.2 shows a portion of ECM parameters evaluation of single SC Maxwell 2.7V/10F sample. The green curve shows a voltage dependence of an ideal capacitor with ESR equal to zero and rated capacitance 10 F. The time of charging would then be 5.4 seconds from (32). The red curve shows the charging and subsequent voltage drop of a brand new SC sample. The blue shows the same after the SC undergo 4x10⁵ cycles of 100% CEC.

The influence of increased ESR on cycle shortening is obvious from the dependence shown in Fig. 8.2. The voltage drop, induced by reversing the direction of current, creates a voltage offset for both the initial and the final voltage determination. The measurement software produces the current switch once the voltage 2.7 V or 0 V is reached, which is thus sooner.

The change of ESR, induced by CEC aging is mostly linear to quadratic. This applies for both series resistance \( R_s \) and DC series resistance \( R_{DC} \), which should in theory be the manifestations of each other.

While the SC ages, its total and its immediate capacitances fade. The effect of decreased Helmholtz capacitance \( C_H \) on the decrease of the cycle duration is obvious from Fig. 8.2. It occurs because the decline in amount of charge SC can immediately hold results in shorter charging time, which results in steeper charging curve. The slope of theoretical (green) charging curve is the same as for brand new sample (red). The slope of charging for aged sample (blue) is larger. As does the value of capacitance gradually decrease, so does the cycle time slowly shortens.

Times for aging rounds of 75% CEC tests are summed up in Table 4.

<table>
<thead>
<tr>
<th>No. of cycles</th>
<th>[–]</th>
<th>1x10⁵</th>
<th>2x10⁵</th>
<th>3x10⁵</th>
<th>4x10⁵</th>
<th>5x10⁵</th>
<th>6x10⁵</th>
<th>7x10⁵</th>
<th>8x10⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell 2.7V/10F [h]</td>
<td></td>
<td>336</td>
<td>621</td>
<td>870</td>
<td>1143</td>
<td>1381</td>
<td>1630</td>
<td>1877</td>
<td>2142</td>
</tr>
<tr>
<td>Nesscap 2.7V/10F [h]</td>
<td></td>
<td>336</td>
<td>621</td>
<td>872</td>
<td>1145</td>
<td>1383</td>
<td>1632</td>
<td>1879</td>
<td>2144</td>
</tr>
</tbody>
</table>

Parameters, acquired during the aging in relation to the number of endured cycles, are listed in following Tables 5-8. After that some selected dependencies are shown graphically and their relations are discussed. Four sets of CEC agings were performed. These are 100% CEC and 75% CEC for SC Maxwell and SC Nesscap, both 2.7V/10F.

The cycling is performed for eight rounds. It is only interrupted, when the first sample of the batch goes out of commision. This occurs almost always for the SC Maxwell type first, meaning that SC Nesscap has higher cycle life.

Table 5: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 100% continuous energy cycling for SC Maxwell 2.7V/10F

<table>
<thead>
<tr>
<th>Cycles</th>
<th>( \Delta_t [s] )</th>
<th>( C_H [F] )</th>
<th>( C_D [F] )</th>
<th>( C_{DC} [F] )</th>
<th>( R_s [m\Omega] )</th>
<th>( R_{D1} [\Omega s^{-5}] )</th>
<th>( R_{DC} [m\Omega] )</th>
<th>( \tau_D [s] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.73</td>
<td>9.72</td>
<td>3.07</td>
<td>9.95</td>
<td>59.2</td>
<td>13.71</td>
<td>58.8</td>
<td>258</td>
</tr>
<tr>
<td>1x10⁵</td>
<td>4.23</td>
<td>8.80</td>
<td>1.86</td>
<td>9.1</td>
<td>66.6</td>
<td>14.10</td>
<td>73.2</td>
<td>119</td>
</tr>
<tr>
<td>2x10⁵</td>
<td>3.98</td>
<td>8.54</td>
<td>1.95</td>
<td>8.7</td>
<td>80.8</td>
<td>12.28</td>
<td>79.1</td>
<td>111</td>
</tr>
<tr>
<td>3x10⁵</td>
<td>3.70</td>
<td>8.24</td>
<td>2.04</td>
<td>8.5</td>
<td>90.0</td>
<td>12.24</td>
<td>97.2</td>
<td>101</td>
</tr>
<tr>
<td>4x10⁵</td>
<td>3.48</td>
<td>8.09</td>
<td>2.04</td>
<td>8.3</td>
<td>114.2</td>
<td>12.09</td>
<td>106.2</td>
<td>97.1</td>
</tr>
<tr>
<td>5x10⁵</td>
<td>3.25</td>
<td>7.68</td>
<td>2.14</td>
<td>8.1</td>
<td>123.0</td>
<td>11.53</td>
<td>117.6</td>
<td>92.0</td>
</tr>
<tr>
<td>6x10⁵</td>
<td>2.87</td>
<td>7.17</td>
<td>2.38</td>
<td>7.8</td>
<td>147.5</td>
<td>9.89</td>
<td>128.2</td>
<td>77.9</td>
</tr>
<tr>
<td>7x10⁵</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Samples malfunction</td>
</tr>
</tbody>
</table>
## Charge transport and storage in a supercapacitor structure

Table 6: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 100% continuous energy cycling for SC Nesscap 2.7V/10F

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$\Delta t$ [s]</th>
<th>$C_H$ [F]</th>
<th>$C_D$ [F]</th>
<th>$C_{DC}$ [F]</th>
<th>$R_s$ [mΩ]</th>
<th>$R_{D1}$ [$\Omega s^{-5}$]</th>
<th>$R_{DC}$ [mΩ]</th>
<th>$\tau_D$ [s]</th>
<th>$t_0$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.69</td>
<td>9.27</td>
<td>4.28</td>
<td>8.95</td>
<td>34.6</td>
<td>11.31</td>
<td>26.9</td>
<td>274</td>
<td></td>
</tr>
<tr>
<td>1x10^5</td>
<td>4.05</td>
<td>7.88</td>
<td>1.90</td>
<td>8.13</td>
<td>32.4</td>
<td>17.63</td>
<td>28.1</td>
<td>185</td>
<td></td>
</tr>
<tr>
<td>2x10^5</td>
<td>4.00</td>
<td>7.86</td>
<td>1.81</td>
<td>7.95</td>
<td>39.8</td>
<td>18.67</td>
<td>30.9</td>
<td>198</td>
<td></td>
</tr>
<tr>
<td>3x10^5</td>
<td>4.02</td>
<td>7.99</td>
<td>1.86</td>
<td>7.9</td>
<td>46</td>
<td>19.14</td>
<td>30.2</td>
<td>208</td>
<td></td>
</tr>
<tr>
<td>4x10^5</td>
<td>3.72</td>
<td>7.66</td>
<td>1.84</td>
<td>7.84</td>
<td>40.3</td>
<td>20.03</td>
<td>29.4</td>
<td>220.5</td>
<td></td>
</tr>
<tr>
<td>5x10^5</td>
<td>3.92</td>
<td>7.71</td>
<td>2.04</td>
<td>7.73</td>
<td>35.5</td>
<td>19.99</td>
<td>31.3</td>
<td>259.5</td>
<td></td>
</tr>
<tr>
<td>6x10^5</td>
<td>3.84</td>
<td>7.64</td>
<td>2.00</td>
<td>7.6</td>
<td>43</td>
<td>20.58</td>
<td>32.2</td>
<td>266.5</td>
<td></td>
</tr>
<tr>
<td>7x10^5</td>
<td>3.69</td>
<td>7.42</td>
<td>2.07</td>
<td>7.5</td>
<td>50</td>
<td>20.51</td>
<td>36.3</td>
<td>275</td>
<td></td>
</tr>
</tbody>
</table>

- 8x10^5 Samples malfunction

Table 7: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% continuous energy cycling for SC Maxwell 2.7V/10F

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$\Delta t$ [s]</th>
<th>$C_H$ [F]</th>
<th>$C_D$ [F]</th>
<th>$C_{DC}$ [F]</th>
<th>$R_s$ [mΩ]</th>
<th>$R_{D1}$ [$\Omega s^{-5}$]</th>
<th>$R_{DC}$ [mΩ]</th>
<th>$\tau_D$ [s]</th>
<th>$t_0$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.69</td>
<td>9.71</td>
<td>3.09</td>
<td>10</td>
<td>58.0</td>
<td>13.30</td>
<td>57.1</td>
<td>267</td>
<td></td>
</tr>
<tr>
<td>1x10^5</td>
<td>4.52</td>
<td>9.41</td>
<td>2.09</td>
<td>9.48</td>
<td>62.6</td>
<td>14.60</td>
<td>62.2</td>
<td>158</td>
<td></td>
</tr>
<tr>
<td>2x10^5</td>
<td>4.39</td>
<td>9.24</td>
<td>1.94</td>
<td>9.35</td>
<td>66.4</td>
<td>15.16</td>
<td>62.9</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>3x10^5</td>
<td>4.39</td>
<td>9.09</td>
<td>2.04</td>
<td>9.31</td>
<td>62.8</td>
<td>13.94</td>
<td>63.1</td>
<td>139</td>
<td></td>
</tr>
<tr>
<td>4x10^5</td>
<td>4.34</td>
<td>9.03</td>
<td>2.01</td>
<td>9.25</td>
<td>65.4</td>
<td>13.96</td>
<td>63.2</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>5x10^5</td>
<td>4.30</td>
<td>8.99</td>
<td>2.02</td>
<td>9.18</td>
<td>65.2</td>
<td>13.73</td>
<td>64.5</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>6x10^5</td>
<td>4.28</td>
<td>8.94</td>
<td>1.91</td>
<td>9.1</td>
<td>68.4</td>
<td>13.94</td>
<td>65.1</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>7x10^5</td>
<td>4.25</td>
<td>9.00</td>
<td>1.99</td>
<td>9.05</td>
<td>70.6</td>
<td>13.55</td>
<td>66.5</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>8x10^5</td>
<td>4.20</td>
<td>8.73</td>
<td>1.97</td>
<td>8.99</td>
<td>69.8</td>
<td>12.34</td>
<td>66.1</td>
<td>99.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 8: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% continuous energy cycling for SC Nesscap 2.7V/10F

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$\Delta t$ [s]</th>
<th>$C_H$ [F]</th>
<th>$C_D$ [F]</th>
<th>$C_{DC}$ [F]</th>
<th>$R_s$ [mΩ]</th>
<th>$R_{D1}$ [$\Omega s^{-5}$]</th>
<th>$R_{DC}$ [mΩ]</th>
<th>$\tau_D$ [s]</th>
<th>$t_0$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.688</td>
<td>9.03</td>
<td>4.74</td>
<td>8.99</td>
<td>26.0</td>
<td>10.81</td>
<td>26.3</td>
<td>261</td>
<td></td>
</tr>
<tr>
<td>1x10^5</td>
<td>4.48</td>
<td>8.70</td>
<td>3.10</td>
<td>8.44</td>
<td>32.2</td>
<td>15.32</td>
<td>26.9</td>
<td>309</td>
<td></td>
</tr>
<tr>
<td>2x10^5</td>
<td>4.300</td>
<td>8.45</td>
<td>2.14</td>
<td>8.33</td>
<td>41.6</td>
<td>17.22</td>
<td>27.3</td>
<td>227</td>
<td></td>
</tr>
<tr>
<td>3x10^5</td>
<td>4.190</td>
<td>8.32</td>
<td>2.09</td>
<td>8.24</td>
<td>41.8</td>
<td>17.02</td>
<td>29.1</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>4x10^5</td>
<td>4.188</td>
<td>8.33</td>
<td>2.25</td>
<td>8.16</td>
<td>38.2</td>
<td>18.15</td>
<td>29.9</td>
<td>234</td>
<td></td>
</tr>
<tr>
<td>5x10^5</td>
<td>4.140</td>
<td>8.13</td>
<td>2.02</td>
<td>8.1</td>
<td>36.0</td>
<td>19.72</td>
<td>28.1</td>
<td>241</td>
<td></td>
</tr>
<tr>
<td>6x10^5</td>
<td>4.14</td>
<td>8.12</td>
<td>2.13</td>
<td>8.03</td>
<td>36.4</td>
<td>18.60</td>
<td>30.7</td>
<td>246</td>
<td></td>
</tr>
<tr>
<td>7x10^5</td>
<td>4.297</td>
<td>8.13</td>
<td>2.82</td>
<td>8.03</td>
<td>36.0</td>
<td>15.89</td>
<td>30.8</td>
<td>291</td>
<td></td>
</tr>
<tr>
<td>8x10^5</td>
<td>4.141</td>
<td>8.14</td>
<td>2.41</td>
<td>8</td>
<td>45.4</td>
<td>18.38</td>
<td>32</td>
<td>280</td>
<td></td>
</tr>
</tbody>
</table>
Charge transport and storage in a supercapacitor structure

First explored SC parameter is the total capacitance. In tables above it is presented as a conventional DC capacitance \( C_{DC} \), measured by an LRC meter, and the \( C_T \), which may be obtained using (19). The change of total capacitance in relation to the number of energy cycling aging cycles \( n \) follows an exponential stretched law:

\[
C(n) = C_\infty + \Delta C e^{-n / n_{EC}},
\]

(36)

where \( C_\infty \) is expected capacitance value at infinity, \( \Delta C \) is the drop of capacitance due to aging, and \( n_{EC} \) is the constant, which characterizes the capacitance degradation in number of endured charging cycles.

The same dependence in relation to the time of cycling \( t \) is described by:

\[
C(t) = C_\infty + \Delta C e^{-t / \tau_{EC}},
\]

(37)

where \( \tau_{EC} \) is the time constant of aging process.

Equations (36) and (37) hold for the change of \( C_T \) and \( C_{DC} \) for roughly 2000 hours of CEC aging by current 2.7 A (for both SC types). After that the capacitance decrease becomes linear. This linear drop-off (see Fig. 8.3) is an indicator of looming SC failure, and it initiates after the capacitance decreases by ~20%, depending on the temperature.

The prime suspect for the 2000 hour milestone is the influence of increased temperature (induced by Joule’s heat) on the capacitance decrease, as it is also observed for many ECM parameters for both CEC methods. This explanation is taken at face value in this section. Note, that for varying cycle currents, this milestone shifts.

Fig. 8.3: Change of DC capacitance of SC Nesscap 10F/2.7V in relation to duration of 100% continuous energy cycling

Fig. 8.3 shows the decline of \( C_{DC} \). Its expected capacitance is \( C_\infty = 7.66 \text{ F} \) before the drop occurs. The \( \tau_{EC} \) of \( C_{DC} \) fading for SC Nesscap at 100% CEC is 487 hours, and for 75% CEC it is 956 hours, which is about twice as much, corresponding to the 25% difference in energy cycling. Hence this relation seems to be quadratic in comparison to the difference in amount of transferred energy.

Note, that Fig. 8.3 has an extra value (green). After the first sample of the batch malfunctions (in time 3223 hours), the average value of remaining samples is 7.5 F.
The evolution of $C_T$ is presented on SC Maxwell 2.7V/10F. Its fading again follows (37) and (36), as shown in Fig. 8.4 for 100% CEC and Fig. 8.5 for 75% CEC, respectively. Again, the drop occurs during at around 2000 hours or after $7 \times 10^5$ 75% CEC cycles. Beware that Fig. 8.4 is relation of time and Fig. 8.5 is relative to cycles.

\[ y = a + b \exp\left(-\frac{x}{c}\right), \quad r^2=0.99 \]
\[ a=10.1, \quad b=1.36, \quad c=232 \]

**Fig. 8.4**: Change of total capacitance of SC Maxwell 10F/2.7V in relation to duration of 100% continuous energy cycling

The total capacitance of SC Maxwell deprecates with time constant 232 hours for 100% CEC, and 416 hours for 75% CEC. The ratio of capacitance degradation for both energy cycling methods is again 2, as expected.

For SC Maxwell the expected total capacitance value at infinity is about 10 F to 11 F for all CEC methods. The exponential decline is however faster for 100% CEC (see Fig. 8.4), than for 75% CEC (see Fig. 8.5). This is because the SC does not get discharged entirely. The sustained electric field then prevents foreign particles to clog the electrode surface. Such particles are ions present in the electrolyte, that are held beneath the electrolyte’s depletion region by electric field. This is behavior commonly seen in electrochemical cells (batteries).

\[ y = a + b \exp\left(-\frac{x}{c}\right), \quad r^2=0.99 \]
\[ a=10.1, \quad b=1.98, \quad c=8.13E4 \]

**Fig. 8.5**: Change of total capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% continuous energy cycling

While the evolution of total capacitance depends on the square root of time, the change of Helmholtz capacitance may be described most accurately by a pure
exponential function. It is so, because the Helmholtz capacitance’s behavior is mostly influenced by the fast motion of charge on the electrode/electrolyte interface by drift, and therefore does not succumb to diffusion like behavior. The capacitance then drops exponentially, as does the effective electrode area decreases linearly by physical aggravation, induced by varying electric field.

On the contrary the total capacitance is described in relation to the square root of time, because its deprecation is influenced by the change of diffuse capacitance. Note, that $n_{EC} \sim 10^5$ for $C_t$ and $C_H$ change of SC Maxwell 2.7V/10F for 75% CEC.

\[ y = a + b \exp \left(\frac{x}{c}\right), \quad r^2 = 0.99 \]
\[ a = 8.93, \quad b = 0.780, \quad c = 1.9685 \]

Fig. 8.6: Change of Helmholtz capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% continuous energy cycling

Fig. 8.6 shows the decrease of Helmholtz capacitance due to 75% CEC aging. Again, the capacitance drops suddenly after 2000 hours due to induced Joule’s heat. This drop occurs earlier with SC Maxwell than with SC Nesscap (see Fig. 8.7). The drop of Helmholtz capacitance is faster for SC Nesscap however, as it is to reach the value $C_H = 7.27$ F at infinity, whereas the SC Maxwell would settle at $C_H = 8.93$ F.

\[ y = a + b \exp \left(\frac{-x}{c}\right), \quad r^2 = 0.98 \]
\[ a = 8.09, \quad b = 0.943, \quad c = 2.22E5 \]

Fig. 8.7: Change of Helmholtz capacitance of SC Nesscap 10F/2.7V in relation to the number of cycles for 75% continuous energy cycling

The total capacitance is linked to the Helmholtz one. In order to understand their relation, the diffuse capacitance and the diffuse resistance must be studied.
The value of diffuse capacitance $C_D$ decreases sharply due to aging at first. It follows an exponential decline, which is induced by the polarization of electrolyte within its first use. This exponential decline happens within the first or up to the second aging round though, so it is not clearly visible in presented data. It may be approximated by a line in this time horizon.

Relation for change of diffuse capacitance is quadratic. As does the ability of electrolyte to quickly react to change of charge on Helmholtz double layer decrease, so does the diffuse capacitance. Once the decrease of $C_H$ surpasses the drop of $C_D$ however,
the electrode area becomes smaller, allowing again the electrolyte to hold more charge. In other words, once the decrease of $C_H$ reaches certain point, the $C_D$ increases. Same as (11), the quadratic behavior of diffuse capacitance $C_D$ in conjunction with purely exponential Helmholtz capacitance $C_H$ have effect on total capacitance $C_T$.

Diffuse capacitance behaves the same for both studied kinds of SCs. The same however does not hold for the value of its diffusion time constant.

For SC Nesscap the time constant exponentially drops within the first measurement round, same as the diffusion capacitance does. It then increases linearly in relation to the number of measured cycles. At time 2000 hours (or $4 \times 10^5$ cycles) the value leaps sharply and continues in the linear trend. This behavior must be related to the composition of SC’s electrolyte, but is not yet understood.

For SC Maxwell the evolution of $\tau_D$ undergoes completely different process. It decreases exponentially with square root of time (same as the total capacitance) during several aging cycles. This results in faster diffusion process of aged sample. This is to
be expected, as the effective area of electrode and the amount of charge capable to participate in diffusion process decrease with aging, which makes the diffusion process faster. The diffusion time constant then drops linearly even further after the 2000 hours milestone.

The change of ECM resistance between Helmholtz and diffuse capacitances $R_D(t)$ is presented by its diffusion resistance constant $R_{D1}$. For this resistance the behavior is inverse to that of a diffusion process time constant. Neither studied SC is notably affected by the heat induced by aging.

For SC Maxwell 2.7V/10F. The value decreases super-linearly in time (see Fig. 8.12) and linearly in the number of cycles. The slope of decline is proportional to the energy cycling method used, with higher energy the slope is steeper. This behavior is not yet explained.
Charge transport and storage in a supercapacitor structure

For SC Nesscap 2.7V/10F the aging is governed by an exponential stretched law, as depicted in Fig. 8.13. The increase of resistance in relation to the number of endured aging cycles is described by:

\[ R(n) = R_0 + \Delta R \left( 1 - e^{-\frac{n}{n_{EC}}} \right), \]  

(38)

where \( R_0 \) is the original value of resistance before the aging, \( \Delta R \) is the increase of resistance due to aging, and \( n_{EC} \) is constant, which characterizes the resistance degradation in number of endured charging cycles.

The increase of \( R_{D1} \) in relation to the total elapsed aging time \( t \) is given by:

\[ R(t) = R_0 + \Delta R \left( 1 - e^{-\frac{t}{\tau_{EC}}} \right), \]  

(39)

where \( \tau_{EC} \) is the time constant of aging process.

The increase of \( R_{D1} \) shows that with aging it is increasingly harder for the diffusion layer to charge, which is also seen by the increase of \( \tau_D \) for the same SC type.

![Fig. 8.14: Change of equivalent series resistance of SC Maxwell 10F/2.7V in relation to duration of 100% continuous energy cycling](image)

Both the ECM ESR (\( R_S \)) and the DC ESR, measured using conventional LRC meter, increase quadratically in time with aging. The increase seems to be linear in the number of cycles. This perceived discrepancy results from the fact, that the duration of single cycle shrinks due to the change of capacitance and ESR, as described above. The rate of ESR change differs proportionally to percentage of CEC method implored, suggesting that the change of the value depends on electric field. This means that higher energy method used has a detrimental effect on series resistance, and that the temperature involved should not be the culprit.

The evolution of series resistance of SC Maxwell is shown in Fig. 8.14 in relation to the time of cycling. It declines generally two times faster than that of SC Nesscap, which is shown in Fig. 8.15 in relation to the time of cycling.

The value of ESR does not seem to react specifically to the 2000 hours milestone. It generally does not succumb to decline by increased temperature in a noticeable way.
Its increase solely due to temperature may therefore be neglected. It is supposed, that the increase of ESR is mainly influenced by the decrease of electrode’s effective area due to aging, and by the degradation of electrolyte’s conductivity. The first is responsible for parabolic bend of the deprecation dependence, and the later is responsible for its slope.

The value of DC ESR and the value of $R_S$ have similar trend as expected, but the value of DC ESR does not seem to give consistent results. This is most likely due to the inability of modern LRC meters to handle such a large capacitance.

Discontinuous energy cycling (DEC) is essentially the same as CEC, with the only difference being an additional time interval after each charging and discharging segments, during which the SC remains in open circuit condition. It is devised to simulate sporadic load profile of some applications. Only the “discontinuous 75% energy cycling” variant of this test is presented.
Charge transport and storage in a supercapacitor structure

Charging and discharging currents are again the same \( I_c = I_d = 1.35 \text{ A} \). This should in theory result in charging and discharging period of 10 seconds for 10 F SC from (35). Note, that within the dead time period, the diffuse capacitance of sample gets charged (SC relaxation) or discharged (SC restoration) gradually, as shown in Fig. 8.16. Such voltage shift results in shortening of the charging and discharging periods, as is obvious from the diagram. Note, that the SC in example is not completely charged prior to the cycling, but rather discharged, which manifests itself in charging period being longer than the discharging one. Note, that sample’s temperature increases by \( \sim 8 \text{ °C} \) as a result of 75% DEC test at 1.35 A.

The duration of the dead time interval is set to be equal to the theoretical charging and discharging times at the beginning of the aging. As SC parameters fade, the charging and discharging period shortens, but the dead time interval does not change. Therefore single dead time interval corresponds to roughly \( \frac{1}{4} \) of the cycle at the beginning of the aging and becomes larger in proportion to charge/discharge segments as the cycling progresses. It is important to notice, that due to differing cycle duration, single 75% DEC cycle takes roughly the same amount of time as two 75% CEC cycles.

Again the SC Nesscap and SC Maxwell are presented, same as in previous section 8.1.1. Their total time duration and measured parameters are summed in following tables 9-11.

### Table 9: Duration of 75% discontinuous energy cycling tests

<table>
<thead>
<tr>
<th>No. of cycles</th>
<th>Maxwell 2.7V/10F [h]</th>
<th>Nesscap 2.7V/10F [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x10⁵</td>
<td>1108</td>
<td>1070</td>
</tr>
<tr>
<td>2x10⁵</td>
<td>2110</td>
<td>2124</td>
</tr>
<tr>
<td>3x10⁵</td>
<td>3206</td>
<td>3180</td>
</tr>
<tr>
<td>4x10⁵</td>
<td>4286</td>
<td>4236</td>
</tr>
<tr>
<td>5x10⁵</td>
<td>5366</td>
<td>5268</td>
</tr>
</tbody>
</table>

### Table 10: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% discontinuous energy cycling for SC Maxwell 2.7V/10F

<table>
<thead>
<tr>
<th>Cycles</th>
<th>( \Delta t ) [s]</th>
<th>( C_H ) [F]</th>
<th>( C_D ) [F]</th>
<th>( C_{DC} ) [F]</th>
<th>( R_S ) [mΩ]</th>
<th>( R_{D1} ) [Ωs⁻¹]</th>
<th>( R_{DC} ) [mΩ]</th>
<th>( \tau_D ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.72</td>
<td>9.83</td>
<td>3.12</td>
<td>10</td>
<td>60.4</td>
<td>13.81</td>
<td>56</td>
<td>267</td>
</tr>
<tr>
<td>1x10⁵</td>
<td>4.59</td>
<td>9.36</td>
<td>2.16</td>
<td>9.42</td>
<td>58.6</td>
<td>13.67</td>
<td>60.8</td>
<td>149</td>
</tr>
<tr>
<td>2x10⁵</td>
<td>4.38</td>
<td>9.11</td>
<td>1.99</td>
<td>9.2</td>
<td>64.8</td>
<td>13.59</td>
<td>66.2</td>
<td>128</td>
</tr>
<tr>
<td>3x10⁵</td>
<td>4.28</td>
<td>9.05</td>
<td>1.85</td>
<td>9.1</td>
<td>67.4</td>
<td>13.50</td>
<td>67.1</td>
<td>116</td>
</tr>
<tr>
<td>4x10⁵</td>
<td>4.30</td>
<td>8.98</td>
<td>1.93</td>
<td>8.99</td>
<td>71.4</td>
<td>13.48</td>
<td>68</td>
<td>109</td>
</tr>
<tr>
<td>5x10⁵</td>
<td>4.11</td>
<td>8.92</td>
<td>1.97</td>
<td>8.91</td>
<td>71.8</td>
<td>12.98</td>
<td>71.7</td>
<td>110</td>
</tr>
</tbody>
</table>

### Table 11: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% discontinuous energy cycling for SC Nesscap 2.7V/10F

<table>
<thead>
<tr>
<th>Cycles</th>
<th>( \Delta t ) [s]</th>
<th>( C_H ) [F]</th>
<th>( C_D ) [F]</th>
<th>( C_{DC} ) [F]</th>
<th>( R_S ) [mΩ]</th>
<th>( R_{D1} ) [Ωs⁻¹]</th>
<th>( R_{DC} ) [mΩ]</th>
<th>( \tau_D ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.672</td>
<td>9.18</td>
<td>4.64</td>
<td>8.99</td>
<td>26.7</td>
<td>12.24</td>
<td>25.9</td>
<td>352</td>
</tr>
<tr>
<td>1x10⁵</td>
<td>4.48</td>
<td>8.67</td>
<td>3.50</td>
<td>8.33</td>
<td>29.8</td>
<td>15.77</td>
<td>26.5</td>
<td>390</td>
</tr>
<tr>
<td>2x10⁵</td>
<td>4.33</td>
<td>8.56</td>
<td>3.10</td>
<td>8.17</td>
<td>38.4</td>
<td>16.21</td>
<td>27.7</td>
<td>326</td>
</tr>
<tr>
<td>3x10⁵</td>
<td>4.27</td>
<td>8.44</td>
<td>2.35</td>
<td>8.02</td>
<td>41.8</td>
<td>17.99</td>
<td>28.8</td>
<td>274</td>
</tr>
<tr>
<td>4x10⁵</td>
<td>4.11</td>
<td>8.12</td>
<td>2.13</td>
<td>7.95</td>
<td>41.6</td>
<td>19.41</td>
<td>30.3</td>
<td>270</td>
</tr>
<tr>
<td>5x10⁵</td>
<td>4.11</td>
<td>8.15</td>
<td>2.41</td>
<td>7.86</td>
<td>42.0</td>
<td>18.00</td>
<td>31.5</td>
<td>284</td>
</tr>
</tbody>
</table>

Note, that all presented results are for 75% DEC aging test. This fact will not be reiterated in this section.
Charge transport and storage in a supercapacitor structure

Same as for previous section, the DC capacitance is described first. Its evolution for SC Nesscap is shown in Fig. 8.17. The time constant of SC fading is roughly two times larger than that of SC Maxwell under the same conditions, and of an order of magnitude larger than that of SC Nesscap 100% CEC from Fig. 8.3. The value of $\tau_{EC}$ is roughly four times higher than it is for 100% CEC method. This means that the depreciation occurs faster in relation to cycling time for DEC aging.

The expected value of DC capacitance at infinity is 7.24 F for SC Nesscap, which is considerably less than both that for 75% CEC and 100% CEC methods. This must be induced either by the introduction of open circuit segments, or a flaw in measurement using an LRC meter for such a big capacitance. The influence of Joule’s heat ought to be smaller for 75% DEC than it is for 75% CEC, as the sample has time to cool down, therefore it should not be the culprit. This is also the reason, why there is no linear drop-off of ECM parameters, as there is for CEC aging (it should occur before the time of 4000 hours).

**Fig. 8.17: Change of DC capacitance of SC Nesscap 10F/2.7V in relation to duration of 75% discontinuous energy cycling**

**Fig. 8.18: Change of DC capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% discontinuous energy cycling**
The study of $C_T$ might shed more light into the source of capacitance deprecation. The dependence of this parameter is presented in Fig. 8.18. The decline of total capacitance is only by 0.4 F worse, than that of 75% CEC method from Fig. 8.5 for SC Maxwell. The cycle constant is roughly the same for both 75% methods, meaning the decline has the same speed in relation to transferred energy.

Fig. 8.19: Change of Helmholtz capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% discontinuous energy cycling

The value of total capacitance is given by the sum of $C_H$ and $C_D$. The Helmholtz capacitance may be fitted by an exponential function. Such fit gives virtually the same results in relation to endured aging cycles (transferred energy) for both 75% cycling methods of SC Maxwell, as shown in Fig. 8.19 and Fig. 8.6. This proves, that the greatest influence on the degradation of electrode has the amount of transferred energy for SC Maxwell. The influence of electrode clogging is then greater for SC Nesscap. It generally occurs more for DEC due to open circuit periods without any applied electric field. The degradation due to induced Joule’s heat only has impact after 2000 hours of CEC by current 2.7 A, at which point is the SC damaged anyway. The change of diffusion capacitance must then be responsible for $C_T$ decline.

Fig. 8.20: Change of diffusion capacitance of SC Maxwell 10F/2.7V in relation to duration of 75% discontinuous energy cycling
The evolution of $C_D$ for SC Maxwell is presented in Fig. 8.20. Again, as described previously for Fig. 8.8, the depreciation is exponential at first and turns into quadratic later. Its linear component increase in comparison to the 75% CEC method from Fig. 8.8 by 100%. Note, that it is roughly four fold in relation to the number of endured cycles, which is to be expected. Such a change must be induced by changes in electrolyte. The open circuit period must in turn be responsible for the electrolyte change. This may be explained by permittivity decrease, as the electrolyte has time to diffuse back to its original state during the period without applied electric field.

The time constant of diffusion process $\tau_D$ is responsible for the speed of diffusion capacitance filling. Its value behaves as expected for SC Maxwell, presented in Fig. 8.21. Its evolution for SC Nesscap is not presented as it behaves inexplicably.

**Fig. 8.21: Change of diffusion time constant of SC Maxwell 10F/2.7V in relation to duration of 75% discontinuous energy cycling**

The decrease of diffusion process time constant is faster for 75% DEC method than it is for 75% CEC method. The value of the time constant decreases to 93.8 hours approaching infinity, in comparison to 121 hours from Fig. 8.11.
The value of diffusion resistance constant still declines quadratically for SC Maxwell (see Fig. 8.22). This behavior is not yet understood. The value of $R_{D1}$ for SC Nesscap follows (38) and (39).

The dependence of aging of ESR remains the same as for CEC. It obeys the quadratic relation, and is only presented for sample of SC Nesscap in Fig. 8.23. The difference is that the quadratic component is of the order of magnitude smaller for 75% DEC than it is for 75% CEC. This is partly the product of open circuit interval. After the subtraction of this open circuit interval from measurement times, the decline of ESR is of the same order for both. This is because the damage to the electrode is the same. The rest of the quadratic fit difference might be the product of smaller electrolyte conductivity decrease, as it is not allowed to polarize so fast thanks to open circuit periods.

$$y = ax^2 + bx + c$$
$$a = 7.12 \times 10^{-8}, \quad b = 7.22 \times 10^{-4}, \quad c = 25.8$$

**Fig. 8.23: Change of DC resistance of SC Nesscap 10F/2.7V in relation to duration of 75% discontinuous energy cycling**

### 8.2 Temperature dependence of equivalent circuit model parameters

The dependence of ECM parameters on ambient temperature before and after DEC aging is explored. It is interesting for applications, that don’t require full SC’s power, but might want to utilize SC at different temperatures. Example of such application are the starter SC batteries in automobile industry. The values of utilized temperature range from -35°C up to 65°C.

The values presented in Table 12 show the average ECM parameters dependence on ambient temperature for brand new samples of SC CapXX 2.75V/2.4F. Also in the table are the dependencies for the same set of samples after they undergo $10^6$ cycles of 75% DEC aging by current 1.35 A at room temperature. The SC is properly cooled/warmed to the ambient temperature, at which its ECM parameters are acquired. The charging current used for evaluation is $I_c = 0.5$ A.

In other words, three samples of SC CapXX are used for each studied temperature. Firstly they are immersed in these conditions and their ECM parameters are evaluated. These results are called “new” in Table 12. Then these samples are cycled at room temperature. And finally they are evaluated again the same way as before aging. These later results are referred to as “aged” in Table 12.

Graphs, showing the appropriate parameter change due to temperature and aging, are presented, the presumed origin of these dependencies is discussed, and the
Charge transport and storage in a supercapacitor structure

activation energy of these processes is calculated. The value of activation energy is obtained from corresponding log \( C \) vs. 1000/T curves. The study of activation energy of processes in SC’s active region is a mean of assessing the electrolyte’s quality. It shows the dependency of charge concentration vs temperature. This has an influence over SC’s ESR and capacitance. The lower the activation energy is, the lower is the change of capacitance and ESR with increased temperature.

Table 12: Average ECM parameters of new and aged samples of SC CapXX 2.75V/2.4F in relation to the ambient temperature during evaluation

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>State</th>
<th>( \Delta t ) [s]</th>
<th>( C_H ) [F]</th>
<th>( C_D ) [F]</th>
<th>( R_S ) [mΩ]</th>
<th>( R_{DI} ) [Ωs(^{-5})]</th>
<th>( \tau_D ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-35</td>
<td>new</td>
<td>12.53</td>
<td>2.27</td>
<td>0.64</td>
<td>140</td>
<td>52.6</td>
<td>168</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>8.125</td>
<td>1.58</td>
<td>0.51</td>
<td>190</td>
<td>37.6</td>
<td>58</td>
</tr>
<tr>
<td>-15</td>
<td>new</td>
<td>12.74</td>
<td>2.34</td>
<td>0.58</td>
<td>140</td>
<td>59.8</td>
<td>214</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>9.7</td>
<td>1.8</td>
<td>0.3</td>
<td>80</td>
<td>73.2</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>new</td>
<td>14.0</td>
<td>2.55</td>
<td>1.04</td>
<td>82</td>
<td>54.4</td>
<td>458</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>11.0</td>
<td>2.03</td>
<td>0.33</td>
<td>50</td>
<td>102.6</td>
<td>214</td>
</tr>
<tr>
<td>25</td>
<td>new</td>
<td>15.11</td>
<td>2.75</td>
<td>1.83</td>
<td>67.2</td>
<td>26.2</td>
<td>197</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>11.14</td>
<td>2.04</td>
<td>0.36</td>
<td>48</td>
<td>119</td>
<td>303</td>
</tr>
<tr>
<td>45</td>
<td>new</td>
<td>14.98</td>
<td>2.73</td>
<td>1.77</td>
<td>44</td>
<td>25.4</td>
<td>222</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>11.45</td>
<td>2.09</td>
<td>0.53</td>
<td>37</td>
<td>88.9</td>
<td>437</td>
</tr>
<tr>
<td>65</td>
<td>new</td>
<td>15.80</td>
<td>2.88</td>
<td>2.42</td>
<td>38</td>
<td>26.3</td>
<td>309</td>
</tr>
<tr>
<td></td>
<td>aged</td>
<td>11.42</td>
<td>2.08</td>
<td>0.76</td>
<td>35.2</td>
<td>72.2</td>
<td>410</td>
</tr>
</tbody>
</table>

Temperature dependencies of total capacitance \( C_T \) are presented in Fig. 8.24. Results obtained before aging are depicted in blue. It is apparent, that the value of capacitance increases linearly with temperature. This is also true for values after the aging (red). Note, that the slope of these two dependencies does not match. For this the influence of Helmholtz and diffuse capacitances must be assessed.

![Fig. 8.24: Dependence of total capacitance for SC CapXX 2.4F/2.7 V on ambient temperature before (blue) and after 75% discontinuous energy cycling (red) ](image-url)
Helmholtz capacitance seems to be constant in temperature range 22 to 65 °C, with the value $C_H = 2.78 \text{ F}$ for new samples (see Fig. 8.25). The same holds for aged samples, the decrease due to aging is 0.71 F.

Helmholtz capacitance at temperature range below 22 °C decreases about 0.5 F due to the aging. The dependence at this range is also linear, given by the slope $1 \times 10^{-2} \text{ F/K}$ for both new and aged samples.

The activation energy of Helmholtz capacitance may be obtained from its logarithm vs. inverse temperature relation. The activation energy characterizes the aging behavior of the capacitance. For new samples, the activation energy is 17 meV, and for aged samples, it is 36 meV.

The temperature dependencies of diffuse capacitance for new and aged samples are presented in Fig. 8.26. Note, that the diffuse capacitance increases with temperature before aging, but remains constant afterwards. This results in varying slopes of total capacitance dependence in Fig. 8.24.
ESR decreases with increasing temperature, as shown in Fig. 8.27. Its value increases slightly after the aging. The difference of ESR prior and after the aging is most noticeable at low temperatures, where it reaches 50 mΩ.

From the relation of log($R_S$) vs. reciprocal temperature, the activation energy of ESR can be obtained. The activation energy depends on aging. It is 50 meV for high temperature range, and 140 meV for temperatures below 5 °C for new samples. And 125 meV in the whole temperature range for samples after aging. This is a confirmation, that the conductivity of electrolyte decreases due to 75% DEC aging.

Temperature dependence of resistance $R_{DJ}$ is shown in Fig. 8.29. Its value is constant (26 Ω) for temperatures above 20 °C for the dependence before the aging. This is to be expected, as these are the normal operating conditions for this kind of SC. For lower temperatures the value increases, which must be due to low ion mobility at low temperatures.
After the aging the value seems to be highest (120 Ω) at around the room temperature. The increase of this parameter’s dependence for low temperatures after 75% DEC aging is probably related to low temperature ions conductivity. Activation energy of $R_D$ after the aging is about 180 meV in the temperature range -35 to 5 °C (see Fig. Fig. 8.29).

**Fig. 8.29:** Dependence of diffusion resistance constant for SC CapXX 2.4F/2.7 V on ambient temperature before (blue) and after 75% discontinuous energy cycling (red)

Time constant of diffusion process $\tau_D$ increases linearly with temperature, as shown in Fig. 8.30. This is due to the higher probability for an ion to overcome the potential barrier at higher temperatures, and it is true for both new and aged samples. The slope of the linear dependence is about 4 times higher for samples after aging, hinting that the diffusion process slows down as a result of the aging for positive temperature range. It does however speed up for negative temperature values, which is not understood.

**Fig. 8.30:** Dependence of diffusion process time constant for SC CapXX 2.4F/2.7 V on ambient temperature before (blue) and after 75% discontinuous energy cycling (red)

The value of energy for ion to overcome the potential barrier during diffusion can be estimated from the dependence of time constant $\tau_D$ vs. reciprocal temperature 1000/T.
The activation energy before and after the aging is 160 meV and 180 meV, respectively. This is roughly 8 times higher in comparison with SC Nesscap.

### 8.3 Calendar life tests

Unlike the energy cycling tests, the calendar life tests are devised to simulate SC under light work load at differing ambient temperatures. Temperatures used are again from range -35°C up to 65°C. The idea behind using an alternate temperatures is the same as in previous section 8.2. In addition this experiment is devised to prove, that the increased temperature accelerates the electrochemical reactions, which are responsible for capacitance degradation. In this test, the stored energy of the SC is sustained by maintaining the voltage at constant value for long time period (over 11 000 hours). The range of applied voltages is for different experiments from 0.6x$V_{op}$ to 1.2x$V_{op}$ (this means overcharging the SC).

Life tests are performed for all studied SC types and all different test conditions. Presented are only the results of SC CapXX and SC Nesscap, as the behavior of SC Maxwell is similar to that of SC Nesscap. The aim of these tests is to determine the influence of aging on SC DC capacitance $C_{DC}$ and DC ESR $R_{DC}$. The results of periodic characterizations are used to monitor the evolution of SC parameters. Measurements of calendar life tests are performed by the EGGO Space s.r.o. company, using standard measuring tools.

Note, that this section does not contain any accompanying tables of raw data. This is because the amount of data presented is too large to be printed. Therefore only visual representation is utilized. Also the ECM parameters are not evaluated during calendar tests, so that the samples don’t have to be discharged, and the continuation of the measurement is not interrupted for longer than few minutes. This section only server to present an experimental method of data gathering, that will be fully utilized in following chapter 8.4.

#### 8.3.1 Calendar tests of CapXX 2.75V/2.4F

First presented is the evolution of DC capacitance of SC CapXX. Deliberately selected combinations of temperature and applied voltage are shown in Fig. 8.31. Note, that the applied voltage 1.2 $V_{op}$ corresponds to 3.3 V for SC CapXX.

![Fig. 8.31: Change of capacitance for SC CapXX 2.75V/2.4F during calendar life tests for varying temperatures and voltage](image-url)
First thing to notice, is the effect of overcharging the SC. Increasing the applied field by 20% over the rated voltage at room temperature results in similar effect, as the overheating of the sample at (or slightly below) its rated voltage. Overcharging the sample at very low temperature does not yield the same results however. This must be due to the fact, that very low temperatures impede the progress of electrochemical changes of electrolyte.

\[ C_{DC} / \% \]

**Fig. 8.32:** Change of relative capacitance for SC CapXX 2.75V/2.4F during calendar life tests for varying temperatures and applied voltage

In order to get a better idea of the rate of SC’s deprecation, the DC capacitance may be expressed in terms of percentage, as shown in Fig. 8.32. Such a percentage shows how much of the capacitance, related to its initial value, still remains in the sample. This gives a better idea, of when the linear capacitance drop-off occurs, in relation to SC’s capacitance loss.

**Fig. 8.33:** Change of DC resistance for SC CapXX 2.75V/2.4F during calendar life tests for varying temperatures and applied voltage

The DC resistance of SC remains mostly constant, as presented in Fig. 8.33. The overall trend of \( R_{DC} \) seems to be slightly increasing, but the perceived increase is hidden in measurement error. As stated before, the use of an LRC meter might not give
satisfying results, because of SC’s large capacitance and the device’s short acquiring duration. The obviously deviating values are however correct. These sharply increasing trends correspond to complete SC failure, and lag behind the total drop of DC capacitance just before sample’s malfunction.

8.3.2 Calendar tests of Nesscap 2.7V/10F

Calendar life tests of SC Nesscap produce DC capacitance change presented in Fig. 8.34. Note the gray and black data fits by (37), which highlight the change and subsequent capacitance drop-off for samples at room temperature and at 45 °C, respectively. Both highlighted dependencies are for voltage level 1 $V_{op}$.

![Fig. 8.34: Change of capacitance for SC Nesscap 2.7V/10F during calendar life tests for varying temperatures and applied voltage](image)

The above Fig. 8.34 is also converted to loss in percents as shown in Fig. 8.35.

![Fig. 8.35: Change of relative capacitance for SC Nesscap 2.7V/10F during calendar life tests for varying temperatures and applied voltage](image)

The DC resistance in relation to calendar life tests for SC Nesscap is presented in Fig. 8.36. Note, that its value does not decline solely due to the temperature. It only
Charge transport and storage in a supercapacitor structure

significantly increases for samples, that are on the verge of malfunctioning, such as the overheated (blue triangle) and overcharged (red triangle) dependencies.

![Graph showing change of DC resistance for SC Nesscap 2.7V/10F during calendar life tests for varying temperatures and applied voltage](image)

8.4 Effect of temperature and variable electric field on degradation of capacitance

The effect of energy cycling and calendar life tests on capacitance degradation is assessed in this section. The aim is to figure out, if the self-heating could lead to different deprecation processes than those of varying electric field. Previous sections of this chapter show, that the change of both the stored charge and the sample’s temperature may have major impact on SC’s capacitance decline. This could for example be caused by intrinsic impurities in or the lowering of ion concentration of electrolyte.

![Graph comparing influence of different aging methods on the change of DC capacitance for SC Nesscap 2.7V/10F](image)

The temperature increase of SC due to CEC at 2.7 A is roughly 20 °C. If the only source of SC’s capacitance degradation is the increased temperature, the capacitance evolution for CEC methods should overlap with appropriate life cycling one. The 75% and 100% CEC methods should correspond to the 0.75 \( V_{op} \) and 0.5 \( V_{op} \) calendar life
tests at temperature 42 °C, respectively. The CEC dependencies should definitely be in between 22 °C and 45 °C calendar tests at \( V_{op} \). Fig. 8.37 shows comparison of precisely these relations. Here the capacitance decrease in percents is compared. It is to be noted, that the two CEC methods surpass even the extended margin of calendar tests.

Same comparison is also performed for SC Maxwell. This relation of both CEC methods, in comparison to 0.8 \( V_{op} \) at 45 °C, is presented in Fig. 8.38.

![Fig. 8.38: Comparison of influence of different aging methods on the change of DC capacitance for SC Maxwell 2.7V/10F](image)

From Fig. 8.37 and Fig. 8.38 it follows, that the total capacitance depreciation must also be dependent on transferred charge. Note, that all relations in presented plots obey the equation (37). From its data fit it is clear, that SC looses \( \sim 12\% \) of capacitance as a result of increased temperature, and additional \( \sim 5\% \) or \( \sim 10\% \) of capacitance due to energy cycling for 75% CEC or 100% CEC, respectively. Hence the impact of variable electric field must be taken into account as an additional source of capacitance degradation. This additional increase is partially responsible for linear drop-off.

### 8.5 Aging summary

Two main variables seem to affect the SC’s degradation. These are the effect of sustained electric field and the effect of temperature. Their influence on the change of SC’s parameters is described below.

#### 8.5.1 Influence of sustained electric field

The application of electric field to SC results in the polarization of its electrolyte within short time span. Once the field dissipates, the free ions are allowed to move around by diffusion like processes. This results in the clogging of electrode surface by impurities. The decrease of electrode effective area is thus linear. This results in:

1. Smaller value of Helmholtz capacitance, which decreases exponentially. This is the main reason why 75% DEC produces larger capacitance decrease than the 100% CEC aging method. This difference is most noticeable for SC Nesscap and SC CapXX, which have a high diffusion current component, meaning that the electrolyte composition is inferior to that of SC Maxwell in this aspect.

2. And larger value of series resistance, which is quadratic. This is why both 75% energy cycling tests produce the same ESR increase. The ESR increase is
generally smaller for SC Nesscap than for SC Maxwell. Note, that the higher value of ESR for SC Maxwell is also due to the difference in electrolyte composition (conductivity).

The change of applied electric field produces changes in electrolyte. These changes are most notably manifested through:

1. Electrolyte’s polarization within the applied electric field. Resulting (among others) in its conductivity increase, which is much more profound for SC Nesscap and SC CapXX. This has an influence on SC’s ESR change.

2. Permittivity decrease, once the electric field dissipates. This is produced gradually, once the polarized electrolyte recombines back to its original state. Note, that this recombination is an electrochemical reaction, and as such its reproducibility is not 100%. This results in reduction of ions, that can participate in diffusion capacitance charging.

3. Another result of electrolyte change due to sustained electric field is the impediment of diffusion process time constant ($\tau_D$) decline.

The amount of charge that shifts in and out of SC is responsible for the speed of SC’s deprecation. With increasing amount of transferred charge, the total capacitance $C_T$ or $C_{DC}$ fades faster during energy cycling. Such speed may be described by the means of $n_{EC}$ and $\tau_{EC}$ from (36) and (37), respectively. With increasing amount of transferred charge, the rate of total capacitance deprecation increases. The deprecation of the value of total capacitance itself is then mostly dependent on the value of applied electric field and sample’s temperature. After a sufficient (temperature dependent) capacitance decline, its value starts to drop-off linearly.

8.5.2 Influence of temperature

The rate of SC’s parameters decline is also dependent on its operating temperature. This can be either the ambient temperature or the one induced by Joule’s heat. The increased temperature generally promotes chemical reactions, that occur in electrolyte. After a certain (temperature dependent) time, SC’s parameters start to fail rapidly. This noticeable change signals the half of SC’s life, under sustained conditions.

For SC with electric field equal to its $V_{op}$ applied, this halftime is roughly 4000 h to 8000 h at room temperature; 2000 h to 4000 h at 45 °C; and below 2000 hours at 65 °C. As can be seen, SC generally operates better at lower temperatures. After this failure, the total capacitance, Helmholtz capacitance, and diffusion time constant of SC decline linearly until the SC malfunctions. Note, that this drop-off seems to be linear, but it is most likely the compound of electrochemical and physical processes, that occur inside the electrolyte, and are not yet analytically described. It is most likely to be driven by a complex super-linear relation.
9 Conclusion

Setup for measurement of supercapacitor’s (SC) charging and discharging dependencies is created. This setup is capable of charging by constant current ±5 A. It also can observe the open circuit voltage of SC in the mean time at high sampling rate.

Chapter 6 deals with the study of charge transport in SC’s diffuse layer. This layer is responsible for SC relaxation after charging, and SC restoration after a fast discharge. The chapter also describes the time dependence of diffuse and drift current components of electrolytes for different manufacturers. SC Maxwell has a high drift current component, while SC Nesscap and SC CapXX have high diffuse current component.

SC’s effective depletion layer thickness is assessed for varying magnitudes of charging currents. Its thickness decreases linearly with the charge transferred to SC. It changes from 2.75 nm to 2.1 nm. The thickness is of several orders of magnitude less, then the size of activated carbon cavities.

New SC’s equivalent circuit model (ECM) is constructed. It reflects the underlying physical properties of SC. ECM consists of Helmholtz capacitance ($C_H$), diffuse capacitance ($C_D$), equivalent series resistance ($R_S$; ESR), leakage resistance, and time dependent resistance $R_D(t)$. Error of the model is below 5%. The model is compared to the state of the art solution by Zubieta.

Two methods of accelerated SC aging are presented; these are the continuous (CEC) and discontinuous (DEC) energy cycling tests, and the calendar life tests.

While the SC ages, its capacitance fade. The change of total capacitance ($C_T$) in relation to the number of energy cycling aging cycles or the time of cycling follows an exponential stretched law. This equation holds for roughly 2000 hours of CEC aging by current 2.7 A for SC Maxwell and NessCap. After that the capacitance decrease becomes linear. Source of this linear drop-off is increased temperature induced by Joule’s heat on increasing series resistance.

The total capacitance of SC Maxwell deprecates with time constant 232 hours for 100% CEC, and 416 hours for 75% CEC. The ratio of capacitance degradation for both energy cycling methods is 2.

While the evolution of total capacitance depends on the square root of time, the change of Helmholtz capacitance may be described most accurately by a pure exponential function. It is so, because the Helmholtz capacitance’s behavior is mostly influenced by the fast motion of charge on the electrode/electrolyte interface by drift, and therefore does not succumb to diffusion like behavior.

The drop of Helmholtz capacitance for SC Nesscap is much faster in comparison with Helmholtz capacitance of SC Maxwell. It is to reach the value $C_H = 7.27$ F at infinity, whereas the SC Maxwell would settle at $C_H = 8.93$ F. The value of diffuse capacitance $C_D$ decreases sharply due to aging at first. It follows an exponential decline, which is induced by the polarization of electrolyte within its first use. This exponential decline happens within the first or up to the second aging round. Diffuse capacitance behaves the same for both studied kinds of SCs.

Diffusion time constant $\tau_D$ for SC Nesscap increases linearly in relation to the number of measured cycles, while for SC Maxwell it decreases exponentially with square root of time. This behavior must be related to the composition of SC’s electrolyte.
The change of ECM resistance between Helmholtz and diffuse capacitances $R_D(t)$ is presented by its diffusion resistance constant $R_D(t)$, which is dependent on the square root of diffusion process time constant $\tau_D$.

Both the ESR ($R_S$) and the DC ESR increase quadratically with aging time. The slope differs by the energy cycling method implored. It is supposed, that the increase of ESR is mainly influenced by the decrease of electrode’s effective area due to aging, and by the degradation of electrolyte’s conductivity.

Discontinuous energy cycling is essentially the same as continuous energy cycling, with the only difference being an additional time interval after each charging and discharging segments, during which the SC remains in open circuit condition. As SC’s parameters fade, the charging and discharging period shortens, but the dead time interval does not change. The expected value of DC capacitance at infinity is 7.24 F for SC NessCap, which is considerably less than both that for 75% CEC and 100% CEC methods. This is probably induced by the introduction of open circuit segments. The influence of Joule’s heat ought to be smaller for 75% DEC than it is for 75% CEC, as the sample has time to cool down. This is also the reason, why there is no linear drop-off of ECM parameters, as there is for continuous energy cycling aging.

The study of total capacitance $C_T$ might shed more light into the source of capacitance depreciation. The decline of total capacitance is only by 0.4 F worse, than that of 75% CEC method for SC Maxwell. The cycle constant is roughly the same for both 75% methods, meaning the decline has the same speed in relation to transferred energy.

The value of total capacitance is given by the sum of $C_H$ and $C_D$. The Helmholtz capacitance $C_H$ may be fitted by an exponential function. Such fit gives virtually the same results in relation to endured aging cycles (transferred energy) for both 75% cycling methods of SC Maxwell. This proves that the greatest influence on the SC degradation has the amount of transferred energy. The degradation due to induced Joule’s heat only has impact after 2000 hours of CEC.

The time constant of diffusion process $\tau_D$ is responsible for the speed of diffusion capacitance failing. Its value behaves as expected for SC Maxwell. The decrease of diffusion process time constant is faster for 75% DEC method than it is for 75% CEC method. The value of the time constant decreases to $\tau_D = 93.8$ hours approaching infinity, in comparison to $\tau_D = 121$ hours for 75% continuous energy cycling.

The value of diffusion resistance constant $R_D(t)$ still declines quadratically for SC Maxwell, while for SC Nesscap 2.7V/10F the $R_D(t)$ during aging increases and it is governed by an exponential stretched law.

The dependence of aging of ESR is the same for CEC and DEC methods. It obeys the quadratic relation. The difference is that the quadratic component is of the order of magnitude smaller for 75% DEC than it is for 75% CEC. This is partly the product of open circuit interval. After its subtraction from measurement times, the decline of ESR is of the same order for both. This is because the damage to the electrode is the same. The rest of the quadratic fit difference might be the product of smaller electrolyte conductivity decrease, as it is not allowed to polarize so fast thanks to the open circuit periods.

The dependence of equivalent circuit model (ECM) parameters on ambient temperature before and after aging by 75% DEC is explored. It is interesting for applications, that don’t require full SC’s power, but might want to utilize SC at different temperatures. The values of utilized temperature range from -35°C up to 65°C.
The values presented show the average ECM parameters dependence on ambient temperature for brand new samples of SC CapXX 2.75V/2.4F. The dependence for the same set of samples after they undergo $10^6$ cycles of 75% DEC aging by current 1.35 A at room temperature. The SC is properly cooled/warmed to the ambient temperature, at which its ECM parameters are acquired.

Temperature dependencies of total capacitance $C_T$ increases linearly with temperature. This is also true for values after the aging. The slope for new samples is about 3 times higher than for aged one.

Helmholtz capacitance of CapXX 2.75V/2.4F is constant in temperature range 22 °C to 65 °C, with the value $C_H = 2.78$ F for new samples and $2.07$ F for aged one. At temperature range bellow 22 °C Helmholtz capacitance decreases by about 0.5 F due to the aging. The dependence at this range is also linear, given by the slope $1 \times 10^{-2}$ F/K for both new and aged samples. The diffuse capacitance increases linearly with temperature before aging, but remains constant afterwards.

ESR decreases with increasing temperature, as the electrolyte conductivity also increases. Its value increases slightly after the aging. The difference of ESR prior and after the aging is most noticeable at low temperatures, where it reaches 50 mΩ.

The diffusion resistance constant $R_{D1} = 26$ Ω for temperatures above 20 °C before the aging. This is to be expected, as these are the normal operating conditions for this kind of SC. For lower temperatures the value increases, which must be due to low ion mobility at low temperatures. After the aging the value seems to be highest (120 Ω) at around the room temperature. For higher than room temperatures the value of $R_{D1}$ decreases. The increase of this parameter’s dependence for low temperatures after 75% DEC aging is probably related to low temperature ions conductivity.
10 References


Charge transport and storage in a supercapacitor structure


Charge transport and storage in a supercapacitor structure


11 List of applicant’s publications

Papers in Journals


Papers in Conference Proceedings


Charge transport and storage in a supercapacitor structure


Research Reports


List of figures and tables

Fig. 2.1: Internal structure of SC ................................................................. 3
Fig. 2.2: Construction of SC [9] ................................................................. 3
Fig. 2.3: Diagram of SC relaxation process (blue), leakage of conventional capacitor (green), after the charging by constant voltage source (red) ................................................................. 4
Fig. 2.4: Measured data of SC's "self-discharge" or relaxation (red) and its simulation (blue) by El Brouji, et al. [12] ................................................................. 5
Fig. 2.5: SC's restoration by Bertrand, et al. [13] ........................................ 5
Fig. 2.6: Illustration of the Stern’s model of charge carriers during SC charging process [24] ............... 7
Fig. 2.7: Zubieta’s model [1] ...................................................................... 8
Fig. 2.8: Faranda's model [31] ................................................................... 9
Fig. 2.9: Zhang's model [27] .................................................................... 9
Fig. 2.10: Torregrossa's model [4] .............................................................. 9
Fig. 4.1: TiePie engineering HS3 handyscope [50] ........................................ 11
Fig. 4.2: HS3 Streamer example usage measurement layout ....................... 11
Fig. 4.3: Experimental setup for GPIB Control measurement [44] .................. 12
Fig. 4.4: GPIB Control precision current regulator schematic [44] ............... 13
Fig. 4.5: GPIB Control measurement setup during an actual SC characterization experiment ................................................................. 13
Fig. 4.6: Precision constant current source – printed circuit board layout ................................................................. 14
Fig. 4.7: HS3 Control measurement setup during an actual SC characterization experiment ................................................................. 15
Fig. 4.8: Experimental setup for HS3 Control measurement ......................... 15
Fig. 4.9: Closeup of 100% energy cycling measurement of SC Nesscap 10F/2.7V ................................................................. 16
Fig. 5.1: Real-life sample of SC Maxwell 2.7V/10F ..................................... 17
Fig. 5.2: SC Maxwell 2.7V/10F schematics [46] ........................................... 18
Fig. 5.3: Real-life SC CapXX 2.75V/2.4F samples ....................................... 18
Fig. 5.4: Real-life sample of SC Nesscap 2.7V/10F ..................................... 19
Fig. 5.5: SC Nesscap 2.7V/10F schematics [48] ........................................... 20
Fig. 6.1: Charging of SC Nesscap 10F/2.7V by constant voltage source, entire charging duration [41] 22
Fig. 6.2: Charging of SC Nesscap 10F/2.7V by constant voltage source, first 80 seconds closeup [41] 23
Fig. 6.3: Time dependence of discharge current (red) and voltage (blue) of SC Nesscap 10F/2.7V, closeup of discharging ................................................................. 23
Fig. 6.4: Overview of the entire charge/discharge experiment on SC Nesscap 10F/2.7V ................................................................. 24
Fig. 6.5: Time dependence of diffusion layer charging current (black) in time interval 50 to 600 seconds and its data fit by analytical function (red) ................................................................. 24
Fig. 6.6: Time dependence of voltage on SC’s terminals (black) and its fit (blue) during the SC restoration after the SC short-circuit, time t = 0 s corresponds to time 614.25 s of the measurement ................................................................. 25
Fig. 6.7: SC Maxwell 2.7V/10F (green) and SC Nesscap 2.7V/10F (blue) charging and portion of subsequent relaxation ................................................................. 26
Fig. 6.8: SC Maxwell 2.7V/10F entire relaxation period (green) and its fit by analytical function (red) ................................................................. 27
Fig. 6.9: SC Maxwell 2.7V/10F entire relaxation period (green) and its fit by analytical function based on diffusion (red) and accounting for drift (black) ................................................................. 27
Fig. 6.10: SC Maxwell 2.7V/10F contribution of drift current component (red) and diffusion current component (blue) to the voltage change at the beginning of relaxation process ................................................................. 28
Fig. 6.11: SC Nesscap 2.7V/10F entire relaxation period (blue) and its fit by analytical function (red) ................................................................. 28
Charge transport and storage in a supercapacitor structure

Fig. 6.12: SC Nesscap 2.7V/10F contribution of drift current component (red) and diffusion current component (blue) to the voltage change at the beginning of relaxation process ...........................................29

Fig. 6.13: Voltage vs. time for charging of SC Nesscap 10F/2.7V by constant current 0.25 A (light blue squares), 0.5 A (dark blue circles) and its approximations (black) .........................................................30

Fig. 6.14: Stored electric charge vs. voltage for charging of Nesscap 10F/2.7V by constant current 0.25 A (light blue squares), 0.5 A (dark blue circles) and its polynomial approximation ..................................31

Fig. 6.15: Differential capacitance of SC Nesscap 10F/2.7V for charging current 0.25 A (light blue squares) and 0.5 A (dark blue circles) ........................................................................................................31

Fig. 6.16: Diagram of single electrode of SC Nesscap 2.7 V / 10 F at steady state [45] .............................................32

Fig. 6.17: Charging of Nesscap 2.7V/10F using varying currents in time .................................................................33

Fig. 6.18: Reciprocal capacitance of Nesscap 2.7V/10F for varying currents in time ...............................................33

Fig. 6.19: Reciprocal capacitance of Nesscap 2.7V/10F for varying currents in relation to transferred charge ............................................................34

Fig. 6.20: Effective depletion layer thickness of Nesscap 2.7V/10F for varying currents in relation to transferred charge ..................................................................................................................34

Fig. 6.21: Electric field dependence in electrolyte near carbon electrode for constant electric charge density ................................................................................................................................................35

Fig. 6.22: Electric potential distribution in depletion region in relation to distance from single electrode for SC (green) and regular parallel plate capacitor (red) ..........................................................................................36

Fig. 6.23: Electric charge concentration within SC at steady state (blue) and after the drift (red) .........................37

Fig. 7.1: Proposed 5 parameter SC equivalent electrical circuit model .................................................................38

Fig. 7.2: Diagram of charge transfer in between Helmholtz and diffusion layers of SC [44] .................................39

Fig. 7.3: SC CapXX 2.75V/2.4F charging and portion of subsequent relaxation during the equivalent circuit model parameters determination .................................................................42

Fig. 7.4: SC Maxwell 2.7V/10F voltage relaxation during the equivalent circuit model parameters determination (blue), its data fit by analytical function accounting for diffusion process (red), and data fit by analytical function accounting for drift at beginning of SC relaxation ............................................44

Fig. 7.5: SC CapXX 2.75V/2.4F relaxation (blue) and its data fit by analytical function (red) ............................44

Fig. 7.6: SC CapXX 2.75V/2.4F charge stored in Helmholtz layer (red) and its data fit (black) ......................45

Fig. 7.7: SC CapXX 2.75V/2.4F time dependent resistance solved analytically ......................................................46

Fig. 7.8: SC CapXX 2.75V/2.4F dependence of charge stored in diffuse layer in time ........................................46

Fig. 7.9: SC CapXX 2.75V/2.4F diffuse current, flowing from Helmholtz to diffuse layer experimental data (red) and fit by analytical function (blue) ...........................................................................47

Fig. 7.10: SC CapXX 2.75V/2.4F time dependent resistance solved analytically (blue) and experimentally (green), first 80 seconds of relaxation .................................................................................47

Fig. 7.11: ESR determination for SC Nesscap 2.7V/10F, charging current 5 A .......................................................48

Fig. 7.12: ESR determination for SC Maxwell 2.7V/10F, measured data (blue) and data fit (green), charging current 5 A .........................................................................................................................................48

Fig. 7.13: Equivalent circuit model connected to constant current source for simulation scenario [44] 49

Fig. 7.14: ECM parameter value determination for SC Nesscap 2.7V/10F, measured data (blue) and data fit (black), charging current 5 A ........................................................................................................50

Fig. 7.15: Closeup of charging portion of simulation (red) and measured data (blue) for CapXX 2.75V/2.4F, charging current 2.5 A .........................................................................................................51

Fig. 7.16: Simulation (red) and measured data (blue) for SC CapXX 2.75V/2.4F, charging current 2.5 A ..........52

Fig. 7.17: Closeup of charging portion of simulation (red) and measured data (blue) for SC Nesscap 2.7V/10F, charging current 4 A ........................................................................................................52

Fig. 7.18: Closeup of charging portion of simulation (red), measured data (blue), and Zubieta’s model prediction (black) for SC Nesscap 2.7V/10F, charging current 4 A ....................................................53

Fig. 7.19: The dependence of empirical probability on relative error between simulation results of equivalent circuit model and experimental data [44] ................................................................53
Fig. 7.20: The dependence of empirical probability on relative error between simulation results of Zubieta’s model and experimental data ..........................................................54

Fig. 8.1: Diagram of SC’s voltage dependence for 100% energy cycling test (green) and 75% energy cycling test (blue) ........................................................................................................56

Fig. 8.2: Charging dependence of SC Maxwell 2.7V/10F before (red) and after (blue) 4x10^5 cycles of 100% continuous energy cycling for charging current 5 A; green line shows a theoretical dependence of an ideal 10 F capacitor ..................................................57

Fig. 8.3: Change of DC capacitance of SC Nesscap 10F/2.7V in relation to duration of 100% continuous energy cycling ..........................................................60

Fig. 8.4: Change of total capacitance of SC Maxwell 10F/2.7V in relation to duration of 100% continuous energy cycling ..........................................................61

Fig. 8.5: Change of total capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% continuous energy cycling ..........................................................61

Fig. 8.6: Change of Helmholtz capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% continuous energy cycling ..........................................................62

Fig. 8.7: Change of Helmholtz capacitance of SC Nesscap 10F/2.7V in relation to the number of cycles for 75% continuous energy cycling ..........................................................62

Fig. 8.8: Change of diffuse capacitance of SC Maxwell 10F/2.7V in relation to duration of 75% continuous energy cycling ..........................................................63

Fig. 8.9: Change of diffuse capacitance of SC Nesscap 10F/2.7V in relation to duration of 100% continuous energy cycling ..........................................................63

Fig. 8.10: Change of diffusion time constant of SC Nesscap 10F/2.7V in relation to the number of cycles for 100% continuous energy cycling ..........................................................64

Fig. 8.11: Change of diffusion time constant of SC Maxwell 10F/2.7V in relation to duration of 75% continuous energy cycling ..........................................................64

Fig. 8.12: Change of diffusion resistance constant of SC Maxwell 10F/2.7V in relation to duration of 100% continuous energy cycling ..........................................................65

Fig. 8.13: Change of diffusion resistance constant of SC Nesscap 10F/2.7V in relation to the number of cycles for 100% continuous energy cycling ..........................................................65

Fig. 8.14: Change of equivalent series resistance of SC Maxwell 10F/2.7V in relation to duration of 100% continuous energy cycling ..........................................................66

Fig. 8.15: Change of DC resistance of SC Nesscap 10F/2.7V in relation to duration of 100% continuous energy cycling ..........................................................67

Fig. 8.16: Diagram of SC’s voltage dependence for single cycle of 75% discontinuous energy cycling test for 10 F SC and charging current 1.35 A; theoretical dependence (green) and actual dependence affected by SC charge redistribution (blue) ..........................................................67

Fig. 8.17: Change of DC capacitance of SC Nesscap 10F/2.7V in relation to duration of 75% discontinuous energy cycling ..........................................................69

Fig. 8.18: Change of DC capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% discontinuous energy cycling ..........................................................69

Fig. 8.19: Change of Helmholtz capacitance of SC Maxwell 10F/2.7V in relation to the number of cycles for 75% discontinuous energy cycling ..........................................................70

Fig. 8.20: Change of diffusion capacitance of SC Maxwell 10F/2.7V in relation to duration of 75% discontinuous energy cycling ..........................................................70

Fig. 8.21: Change of diffusion time constant of SC Maxwell 10F/2.7V in relation to duration of 75% discontinuous energy cycling ..........................................................71

Fig. 8.22: Change of diffusion resistance constant of SC Maxwell 10F/2.7V in relation to duration of 75% discontinuous energy cycling ..........................................................71

Fig. 8.23: Change of DC resistance of SC Nesscap 10F/2.7V in relation to duration of 75% discontinuous energy cycling ..........................................................72

Fig. 8.24: Dependence of total capacitance for SC CapXX 2.4F/2.7 V on ambient temperature before (blue) and after 75% discontinuous energy cycling (red) ..........................................................73
Charging characteristic quadratic fit for varying currents of SC Nesscap 2.7V/10F

Table 1: Charging characteristic quadratic fit for varying currents of SC Nesscap 2.7V/10F

Table 2: Evaluated equivalent circuit model parameters for simulated SCs

Table 3: Duration of 100% continuous energy cycling tests

Table 4: Duration of 75% continuous energy cycling tests

Table 5: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 100% continuous energy cycling for SC Maxwell 2.7V/10F

Table 6: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 100% continuous energy cycling for SC Nesscap 2.7V/10F

Table 7: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% continuous energy cycling for SC Maxwell 2.7V/10F

Table 8: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% continuous energy cycling for SC Nesscap 2.7V/10F

Table 9: Duration of 75% discontinuous energy cycling tests

Table 10: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% discontinuous energy cycling for SC Maxwell 2.7V/10F

Table 11: DC ESR, DC capacitance, and ECM parameters in relation to the number of cycles of 75% discontinuous energy cycling for SC Nesscap 2.7V/10F

Table 12: Average ECM parameters of new and aged samples of SC CapXX 2.75V/2.4F in relation to the ambient temperature during evaluation
List of symbols and abbreviations

Abbreviations

AC – Alternating current
CEC – Continuous Energy Cycling test
CS1 – Precision constant Current Source/regulator, developed for the SC measurement
DC – Direct current
DEC – Discontinuous Energy Cycling test
ECM – Equivalent five parameter electrical Circuit Model of SC
ESR – Equivalent Series Resistance
GPIB – General Purpose Interface Bus, IEEE-488 standard
IGBT – Insulated-Gate Bipolar Transistor
SC – Supercapacitor
SOH – State Of Health

Symbols

A – Effective area of electrode

C – Capacitance
C\(^{-1}\) – Reciprocal capacitance
C\((n)\) – Capacitance dependence on the number of endured energy cycling life tests
C\((t)\) – Capacitance dependence on the total time of aging
C\(_d\) – Differential capacitance
C\(_D\) – Diffuse capacitance in ECM
C\(_{DC}\) – Conventional DC capacitance
C\(_H\) – Helmholtz capacitance in ECM
C\(_{HS}\) – Voltage dependence of C\(_H\)
C\(_T\) – Total capacitance
C\(_∞\) – Expected value of capacitance tending to infinity during aging tests
ΔC – Capacitance drop due to aging

d – Distance between electrodes; or Thickness of depletion region

e – Elementary charge
E – Energy; or Electric field
E\(_0\) – Electric field intensity at electrode’s surface
ε – Permittivity

I – Electric current
I\(_1\) – Diffusion layer charging current during relaxation
I\(_2\) – Diffusion layer charging current after the relaxation is over
I\(_c\) – Charging current
I\(_d\) – Discharging current
I\(_D(t)\) – Current flowing in/out of C\(_D\)
I\(_D∞\) – Diffuse current constant, equal to Q\(_D∞\) / 2τ\(_D\)
Charge transport and storage in a supercapacitor structure

\( l \) – Variable distance

\( n \) – Number of elementary charges; or Number of endured charging cycles

\( n_{EC} \) – Constant characterizing parameter depreciation in relation to the number of endured energy cycling tests

\( Q \) – Electric charge

\( Q_c \) – Charge of charging process

\( Q_d \) – Discharged charge

\( Q_D \) – Electric charge stored on diffuse layer

\( Q_{Dw} \) – Electric charge stored on diffuse layer at the end of the diffusion process

\( Q_H \) – Electric charge stored on Helmholtz double layer

\( Q_{Hw} \) – Electric charge stored on Helmholtz double layer at the end of the diffusion process

\( Q_T \) – Total charged transferred to SC during charging

\( R \) – Resistance

\( R(n) \) – Resistance dependence on the number of endured energy cycling life tests

\( R(t) \) – Resistance dependence on the total time of aging

\( R_0 \) – Initial value of resistance during aging

\( R_d(t) \) – Time dependent resistance between \( C_H \) and \( C_D \) in ECM

\( R_{diff} \) – Diffuse resistance parameter constant

\( R_{DC} \) – Conventional DC ESR

\( R_p \) – Parallel resistance in ECM, responsible for leakage or self-discharge of SC

\( R_s \) – Internal resistance of utilized current source, used during modeling

\( R_s \) – Series resistance in ECM, responsible for SC’s ESR

\( \Delta R \) – Resistance increase due to aging

\( \rho \) – Electric charge density

\( t \) – Time

\( T \) – Temperature

\( \tau \) – Time constant

\( \tau_{df} \) – Time constant of diffuse current component in the beginning of relaxation

\( \tau_{dr} \) – Time constant of drift current component in the beginning of relaxation

\( \tau_{EC} \) – Time constant of parameter depreciation during energy cycling test

\( \tau_{H} \) – Time constant of change of \( Q_H \)

\( \tau_0 \) – Time constant of change of \( Q_D \)

\( \Delta t \) – Duration of charging

\( V \) – Voltage

\( V_0 \) – SC’s voltage prior to the charging

\( V_1 \) – SC’s voltage immediately after the charging has finished, before the SC relaxation begins; or Voltage of SC’s terminals during ECM simulation; or Oscilloscope’s first input channel

\( V_2 \) – SC’s voltage after the relaxation is finished and steady state occurs; or Voltage of \( C_H \) during ECM simulation; or Oscilloscope’s second input channel

\( V_{2w} \) – Expected voltage of SC at infinity after complete SC relaxation (also referred to as \( V_2 \))

\( V_3 \) – SC’s voltage immediately after the discharging has finished, before the SC restoration begins; or Voltage of \( C_D \) during ECM simulation
Symbols related to charging, SC relaxation, discharging, and SC restoration are highlighted in the following diagram.
14 List of used equations

(1) \[ V(t) = V_1 + I_1 \frac{t^{1-\gamma}}{C(2-\gamma)t} \] , [12]  
(2) \[ dQ = C \, dV \]  
(3) \[ V = \frac{Q}{C} \]  
(4) \[ dQ_H = Q_H \, \frac{dt}{\tau_H} \]  
(5) \[ dQ_D = \frac{Q_D \, dt}{2 \sqrt{t} \cdot \tau_D} \]  
(6) \[ I_D = I_2 + I_1 \, e^{-\sqrt{\tau_D}t} \]  
(7) \[ V = V_4(1 - e^{-\sqrt{\tau_D}t}) \]  
(8) \[ V = V_{2\infty} + \Delta V \, e^{-\sqrt{\tau_D}t} \]  
(9) \[ V = V_{2\infty} + A e^{\sqrt{\tau_D}t} + B e^{-\sqrt{\tau_D}t} \]  
(10) \[ V = V_{2\infty} + A e^{\sqrt{\tau_D}t} + B e^{-\sqrt{\tau_D}t} \]  
(11) \[ Q = C_H \, V + \frac{1}{2} C_{H\delta} \, V^2 \]  
(12) \[ C_\delta = C_H + C_{H\delta} \, V \]  
(13) \[ d = 2 \, \varepsilon \, A \, C^{-1} \]  
(14) \[ \frac{Q}{\varepsilon} = \oint E \cdot d\vec{A} \]
\[ \nabla \vec{E} = \frac{\rho}{\varepsilon} \]

\[ E_0 = \frac{\rho d}{\varepsilon} = \frac{enA d}{\varepsilon A} = \frac{I \cdot t}{\varepsilon A} = \frac{enA}{C} \]

\[ E(x) = \int_0^d \frac{\rho}{\varepsilon} dx = \frac{\rho}{\varepsilon} d - x = E_0 \left( 1 - \frac{x}{d} \right) \]

\[ V(x) = \int_0^x E(x) dx = E_0 x - \frac{en}{2\varepsilon} x^2 \]

\[ C_T = C_D + C_H \]

\[ Q_T = Q_H + Q_D \]

\[ Q_H = Q_{H\infty} + Q_D e^{-\sqrt{t}/\tau_D} \]

\[ Q_D = Q_{D\infty}(1 - e^{-\sqrt{t}/\tau_D}) \]

\[ I_D = \frac{dQ_D}{dt} \]

\[ I_D(t) = Q_{D\infty} e^{-\sqrt{t}/\tau_D} = I_{D\infty} e^{-\sqrt{t}/\tau_D} \]

\[ R_D(t) = \frac{V_H - V_D}{I_D(t)} \]

\[ C_D = C_T - C_H = Q_T/V_{2\infty} - Q_H/V_1 \]

\[ R_D(t) = \frac{V_H}{I_{D\infty} \sqrt{t/\tau_D}} = \frac{2\tau_D V_H}{Q_{D\infty} \sqrt{t/\tau_D}} = 2 \frac{V_H \sqrt{t/\tau_D}}{C_D V_{2\infty} \sqrt{t}} = R_{D1} \sqrt{t} \]
Charge transport and storage in a supercapacitor structure

\( R_{D1} = \frac{2 V_H \sqrt{I_D}}{C_D V_{2\infty}} \)

\( V_1 = \frac{R_p}{R_p + R_S} V_2 + \frac{R_p R_S}{R_p + R_S} i \)

\[
\frac{dV_2}{dt} = \frac{V_2}{R_p C_H} - \frac{V_2}{R_p C_H} - \frac{V_2 + V_3}{R_D(t) C_H} + \frac{i R_p R_S}{C_H (R_p + R_S)}
\]

\[
\frac{dV_3}{dt} = \frac{V_2 - V_3}{R_D(t) C_D} + \frac{i R_p R_S}{C_H (R_p + R_S)}
\]

\( R_D(t) = \begin{cases} R_{D1} \sqrt{t-t_0}, & \text{for } t > t_0 \\ 0.001 \Omega, & \text{for } t \leq t_0 \end{cases} \)

\( E = \int V \, dQ \)

\( E = \frac{1}{2} C V^2 \)

\( I_c = I_d = C \frac{dV}{dt} \)

\( C(n) = C_\infty + \Delta C \sqrt{n} \)

\( C(t) = C_\infty + \Delta C \sqrt{t} \)

\( R(n) = R_0 + \Delta R \left( 1 - e^{-\sqrt{n} / n_{\infty}} \right) \)

\( R(t) = R_0 + \Delta R \left( 1 - e^{-\sqrt{t} / t_{\infty}} \right) \)