





# "Conductivity measurements of electrode materials for sodium-ion batteries with aqueous electrolyte"

Master of Science Thesis in "Energy and Environment"

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## Abstract

For the industrial production of innovative energy storage systems such as the sodium-ion battery, high efficiency, high safety, long-term cycling performance and suitable cost production solutions are needed.

The aim of this work is to evaluate the specific electrical conductivity of several electrode printing pastes in different combinations in order to find the most acceptable one. Moreover, a measurement method that can simulate - on a smaller scale - the working conditions of the customized battery design created by Fraunhofer ISE needs to be chosen or developed.

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## 1 Introduction

## 1.1 Motivation

Due to different reasons, new policies are introducing a big amount of renewable energy generated by the wind and the sun, two unpredictable resources. Up to now the share of wind power plants in Germany is around 14% and the share of photovoltaics is around 6%. Moreover, the goal for the year 2050 is to increase the share of renewable energy to 80%<sup>1</sup>. In this new context, the fluctuation of the energy supply needs to find a solution.

It is noteworthy that each potential solution must be aligned with the principles and values of the energy transition. For example, the solution aims to be safe and reliable to safeguard the future of the humankind. It is our moral obligation to leave our planet habitable and bountiful for incoming generations.

Historically, pumped storage power stations were used to balance the energy supply and demand but they cannot be installed and operated everywhere because of its huge and complex structures and costs. Therefore, a new energy storage device needs to be developed to challenge the conventional energy market as a part of the energy transition.<sup>2</sup>

One emerging technology that can act as a solution to balance the fluctuating generation and the volatile consumption to ensure power stability in an environmental friendly way is the "Sodium-Ion Battery".

Before start the industrial production of "Sodium-Ion Batteries" for large-scale electrical energy storage, several materials and components for its development are needed to be studied. This materials and components need to be highly abundant, low cost and environmental friendly.

For the development of batteries, the essential properties that indicate its performance are: *energy density* [Wh/kg], *power density* [W/kg], *lifespan* and *cycle stability*. Furthermore, the *level of stability* can be influenced by parameters such as: homogeneous particle size distribution of the active material, non-degradation of the electrolyte and electrode materials, quantity of dissolved gases in electrolytes that impact on the selfdischarging, degradation of the active materials and type of chemical reaction.

## 1.2 Goal

The focus of this master thesis is to evaluate the specific electrical conductivity of various electrode compositions in order to find a workable sodium-ion battery with aqueous electrolyte that can replace the commercialized lithium-ion batteries. The expected output

<sup>&</sup>lt;sup>1</sup> Goals of the energy transition: https://energytransition.org/

<sup>&</sup>lt;sup>2</sup> (Morris & Pehnt, 2012 - 2017)

of this work should help to find the optimal electrode composition for the industrial production of "Aqueous room-temperature Sodium Ion batteries" (ARSIBs).

It is crucial to maximize the electrical conductivity of the electrode compositions in order to avoid energy loses during the charge and discharge process of the battery, and therefore, improve the behavior of the battery.

In order to reach this goal, an appropriate experimental method has to be chosen to measure the values of the specific electrical conductivity in the Laboratory. The chosen device has to be able to simulate the working conditions in a customized battery design created by Fraunhofer ISE.

## 2 Theoretical background of batteries

#### 2.1 Important definitions<sup>3</sup>:

<u>Oxidation:</u>  $A \rightarrow A^+ + e^-$ 

<u>Reduction</u>:  $B^- + e^- \rightarrow B$ 

<u>Electrochemistry</u>: It is the study of electron transfer caused by redox reactions at the interface of an electron conductor, such as metal or semiconductor, and an ionic conductor, such as an electrolyte.

<u>Electrochemical cell</u>: It is the smallest unit of a device that converts chemical energy to electrical energy, or vice versa, using redox reactions.

<u>Battery:</u> A battery can be defined as a system that uses electrochemical reactions to directly convert the chemical energy of an electrode material into electrical energy.

<u>Classification of batteries</u>: Batteries can be classified into primary batteries, which are used once and disposed, and secondary or rechargeable batteries, which can be recharged and used multiple times.

## 2.2 Galvanic cell

A Galvanic cell is an electrochemical device that derives electrical energy from spontaneous redox reactions taking place within the cell.

It basically consists of a pair of electrodes (named "anode" and "cathode") immersed in the electrolyte connected by a salt bridge, or immersed in individual half-cells separated by an ion-permeable membrane (separator). The function of the separator is to isolate the electrodes from each other. Also, the two electrodes are connected by an external wire where the electrons flow and close the circuit.

The electrodes are made of different parts: The active material incorporates the electrochemical potential, furthermore binders, solvents and conductive additives are added to complete the electrode<sup>4</sup>. The electrolyte belongs to the family of ionic conductors and electron insulators.<sup>5</sup> Electrolytes can be distinguished into polymers, solids, solutions, gels and salts. Salt-, base-, and acid-solutions are the most familiar electrolytes which are roughly divided into two groups: organic and inorganic solutions while the later are distinguished into aqueous and non-aqueous solutions.

<sup>&</sup>lt;sup>3</sup> (Park, 2012)

<sup>&</sup>lt;sup>4</sup> (Oldham KB, 2011)

<sup>&</sup>lt;sup>5</sup> (Menictas C, 2015)

The separator materialized as a porous barrier forms part of the non-active components of a battery. Its function is to avoid the direct contact of electrodes and the electrolyte within the cell.

The external wire called current collector is a highly electronic conductive material that transports electrons through the external device.

The structure and mode of operation of both electrochemical devices (with salt bridge or with separator) are shown in the following figures:



Figure 2-1: Schematic design of a Galvanic Cell with "salt bridge" during discharge.<sup>6</sup>



Figure 2-2: Schematic design of a Galvanic Cell with "salt bridge" during charge.<sup>6</sup>

<sup>&</sup>lt;sup>6</sup> Own illustrations according to (Dell R, 2001)



Figure 2-3: Schematic design of a Galvanic Cell with "separator" during discharge.<sup>7</sup>



Figure 2-4: Schematic design of a Galvanic Cell with "separator" during charge.<sup>7</sup>

During the discharging process, oxidation takes place on the active material of the negative electrode (anode) with release of electrons. On the positive electrode (cathode), the same number of electrons is absorbed by reduction. The electrons flow over the external circuit and the load. At the same time, the ions move freely within the electrolyte and balance the charge of the system.

## 2.3 Battery Cell

A battery cell is an energy storage device usually composed of several galvanic cells connected parallel and/or serially in order to generate electrical energy by means of electrochemical reactions<sup>8</sup>. This is due to the oxidation and reduction reactions on the active materials.

The term "battery" is often used in both primary and secondary cell-based storage. However, a non-rechargeable system is a "**battery**" and a rechargeable system is an "**accumulator**". A rechargeable system is a system that can be charged and discharged

<sup>&</sup>lt;sup>7</sup> Own illustrations according to (Dell R, 2001)

<sup>&</sup>lt;sup>8</sup> (Kiehne, 2003)

several times. Both are also distinguished as **primary** and **secondary** batteries. While primary batteries are characterized by irreversible processes and thus only can be discharged once, secondary batteries have the quality to reverse chemical processes resulting in the possibility to recharge the battery.<sup>9</sup>

Primary batteries can be categorized by the type of electrolyte: aqueous or non-aqueous. Other categorization can be made.

#### 2.3.1 Principle of Operation: Different electrode potentials

Depending on the type of active material which is used, electrodes have a certain normal potential  $E^0$  relative to another electrode because it is not possible to measure the absolute potential of a single electrode.<sup>10</sup> This electrode is the Standard Hydrogen Electrode (SHE) and serves as a zero point and reference within the electrochemical series of voltages. Sodium, for example, has a negative standard potential of  $E^0 = -2.71$  V and represents a strong reducing agent while fluorine has a positive potential of  $E^0 = +2.87$  V and has a strongly oxidizing effect. On the basis of these potential differences, the designations of positive or negative electrode within the battery system are explained. By means of the normal potentials, sequences of redox reactions can be described. The more positive the corresponding normal potential is, the more oxidizing the material is. In this case, the oxidizing agent absorbs electrons and is thereby itself reduced. In the case of the reducing agent it is exactly the opposite, electrons are released and oxidized. The more negative the normal potential of the substance, the more it reduces. In order to determine whether a redox reaction takes place between prescribed substances, the electromotive force of the system, abbreviated EMF formula:

$$EMF = \Delta E^0 = E^0(Cathode) - E^0(Anode)$$
 (Equation 1)

A prerequisite for the expiration of a redox reaction is that the electromotive force of the overall reaction is positive, that is:

$$\Delta E^0 > 0 \forall \qquad (Equation 2)$$

The potentials of negative and positive electrode constitute the precondition to release and to consume electrons and thus starting a chemical reaction.<sup>11</sup> Secondary batteries are either in the state of charging/discharging or in equilibrium. As soon as the battery is forced away from equilibrium by current flow, reactions start to take place and result in the conversion of energy. A reaction within a battery can only occur due to different electrode potentials.

For example, the electrode materials for the negative electrode can be:

<sup>9 (</sup>Sterner M, 2014)

<sup>&</sup>lt;sup>10</sup> (Root, 2011)

<sup>&</sup>lt;sup>11</sup> (Schmidt, 2003)

Metal	Half cell	Electrochemical reaction	Electrode potential [V*]	Abundance on earth [%]
Li	Li / Li+	Li⁺ + e⁻ ≓ Li	-3,045	0,006
Ca	Ca / Ca <sup>2+</sup>	Ca <sup>2+</sup> + 2e <sup>-</sup> ⇔ Ca	-2,760	3,39
Na	Na / Na⁺	Na⁺ + e⁻ <b>⇒</b> Na	-2,711	2,64
Mg	Mg / Mg+	Mg⁺ + e⁻ ≓ Mg	-2,375	1,94
Al	AI / AI <sup>3+</sup>	$AI^{3+} + 3e^{-} \rightleftharpoons AI$	-1,761	7,57
Zn	Zn / Zn <sup>2+</sup>	$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$	-0,76	0,012
Fe	Fe / Fe <sup>2+</sup>	$Fe^{2+} + 2e^{-} \rightleftharpoons Fe$	-0,409	4,7
Cd	Cd / Cd <sup>2+</sup>	$Cd^{2+} + 2e^{-} \rightleftharpoons Cd$	-0,403	0,00003
Pb	Pb / Pb <sup>2+</sup>	$Pb^{2+} + 2e^{-} \rightleftharpoons Pb$	-0,126	0,0018

Table 1: Comparison (vs. Normal hydrogen electrode) of metals investigated as negative electrode materials in batteries.<sup>12</sup>

Table 1 reveals that the Sodium (Na) appears to be an attractive alternative to the Lithium (Li) because of its similar electrochemical properties: one ion with a very close electrode potential to the Lithium, and its widespread availability. In this way, sodium-ion batteries with aqueous electrolyte may represent a promising approach for large-scale storage of electrical energy.<sup>13</sup>

Different expressions such as the open-circuit voltage (OCV) or the Electromotive force (EMF) are used to describe the voltage across terminals<sup>14</sup>. The OCV is a parameter measuring the magnitude or likelihood of a spontaneous reaction and dimensions of the reaction<sup>15</sup>.

The overall battery voltage under load is given by the standard electrochemical potential, reduced by the polarization effects.

## 2.3.2 Charging process<sup>16</sup>

As soon as the current begins to flow from the cathode to the anode, the inverse chemical reactions occur and the battery is being charged. However, a good charging process is usually divided in two stages: first the rising of the voltage at a constant current and then, when the peak voltage is reached the current start to decrease keeping the voltage in the

<sup>&</sup>lt;sup>12</sup> Course "Electrochemistry for energy storage", KIT, 2016.

<sup>&</sup>lt;sup>13</sup> (Li, Yung, Y.Jiang, Zhang, Huang, & Wang, 2016)

<sup>14 (</sup>Dell R, 2001)

<sup>&</sup>lt;sup>15</sup> (Root, 2011)

<sup>&</sup>lt;sup>16</sup> (Park, 2012)



same saturation point. When the current blow to zero, the chemicals reactions are completed, and the battery becomes fully charged and ready to be used.

Figure 2-5: Charge basic stages of a battery.

The charge controller is responsible for charging the battery and contains a three-level protection system. If this three-level protection system does not function properly, the battery may exceed its normal charging range and becomes overcharged.

When the battery is overcharged the temperature rises and could lead to a collapse or even an explosion.

In the formation process of batteries, the batteries are fully charged with a low current to remove impurities and to provide the electrodes the final chemical structure. In order to determine the capacity, the batteries are completely discharged.

## 2.4 Performance of Batteries

## 2.4.1 Capacity<sup>17</sup>

The capacity of a battery is the product of its current and time, and is measured in <u>mAh</u>. The current is determined as the total amount of charge when the battery is completely discharged. The theoretical capacity  $C_T$  is determined by the amount of active materials and is calculated as follows:

<sup>&</sup>lt;sup>17</sup> (Park, 2012)

$$C_T = xF$$
 (Equation 3)

F is the Faraday constant and x is the number of moles of electrons produced from the discharging process.

Another term is the practical capacity  $C_P$  which is smaller than the theoretical capacity because reactants are not 100% utilized in discharge.

#### 2.4.2 Coulombic efficiency

The Coulombic efficiency describes the efficiency with which charge (electrons) is transferred into a system facilitating an electrochemical reaction.<sup>18</sup> The word "Coulomb" refers to the unit for charge. In order to charge the battery, certain reactions need to happen and therefore a fixed amount of electrons are needed. An ideal battery has a coulombic efficiency of 100%. However, in practice the chemical reactions are not 100% reversible and this leads to a decrease of the efficiency.

#### 2.4.3 Energy efficiency

Energy efficiency is the ratio between the used energy during the discharging process and the consumed energy required to charge the battery prior the consumption. It informs how good the performance after each cycle is.

$$Energy \ efficiency = \frac{used \ energy}{consumed \ energy}$$
(Equation 4)

The energy efficiency can also be written as the input energy less the losses divided by the input energy.

$$Energy \ efficiency = \frac{energy \ input-losses}{enrgy \ input}$$
(Equation 5)

The losses come from polarization and coulombic inefficiency such as corrosion.<sup>19</sup>

#### 2.4.4 Self-discharge

Self-discharge describes the loss in usable capacity over time when no current flow is established and is typically provided as a loss of capacity in percentage points per month or year<sup>20</sup>. The rates are dependent on temperature as well as the Depth of Discharge (DoD) and may be higher at first with a small DoD, and become slower over time. The self-discharge rates are mainly determined at room temperature<sup>21</sup>. The self-discharge decreases the energy efficiency<sup>22</sup>.

<sup>&</sup>lt;sup>18</sup> (Bard & Faulkner, 2000)

<sup>&</sup>lt;sup>19</sup> (Dell R, 2001)

<sup>&</sup>lt;sup>20</sup> (Garche, 2009)

<sup>&</sup>lt;sup>21</sup> (Root, 2011)

<sup>&</sup>lt;sup>22</sup> (Garche, 2009)

The DoD represents the fraction of capacity or energy removed from a fully charged battery<sup>23</sup>. A DoD rate of 100 % is defined at a specified cut-off voltage by the manufacturer which represents the end point of discharge. The cut-off voltage is defined by the manufacturer and is fairly arbitrary<sup>24</sup>. The cut-off voltage is greatly dependent on the performance of a battery when a current flow is established and its resulting current-voltage diagram. The DoD is required for the practical operation of a battery.

The State of Charge (SoC) determines the fraction of the full capacity or energy that is still available for further discharge<sup>25</sup>, already considering the DoD.

SoC = 100% - DoD (Equation 6)

## 2.4.5 Cycle life (N charge)

Cycle life is the term used to illustrate the maximum number of charge-discharge cycles before the battery becomes degraded. The challenge is to determine the threshold representing the end of battery life. Very often an arbitrarily limit is set at 80% of its rated capacity symbolizing a degradation that has been progressed too far to further use the battery for its initial purpose<sup>26</sup>. The cycle life is influenced by various factors such as the exposure to deep discharge cycles or overcharging.

## 2.4.6 Energy and Power Density<sup>27</sup>

#### 2.4.6.1 Energy Density

Energy density is the amount of charge stored per unit mass or volume. The units are Wh/kg or Wh/l.

For power storage, the applications have no volumetric constraints, thus the energy density per unit of mass is not appropriate. This is because power storage batteries occupy fixed positions and are used in a wide area.

#### 2.4.6.2 Power Density

Power density is the amount of electrical energy released per unit of time, and per unit of mass or volume. If the mass is chosen, the power density takes the name "gravimetric power density" and it is generally measured by W/kg, or W/g for the studies into the laboratory. In the other case, when volume is chosen, the power density is called: "volumetric power density" and its units are W/m<sup>3</sup> or W/l. W – watt – is one Joule per second.

<sup>&</sup>lt;sup>23</sup> (Root, 2011)

<sup>&</sup>lt;sup>24</sup> (Kiehne, 2003)

<sup>&</sup>lt;sup>25</sup> (Dell R, 2001)

<sup>&</sup>lt;sup>26</sup> (Vincent CA, 1997)

<sup>&</sup>lt;sup>27</sup> (Park, 2012)

The factors that affect the gravimetric power density are shown in the following formula:

$$P_{\text{as gravimetric density}} = \frac{I * V}{m}$$
 (Equation 7)

And for the gravimetric power density, the factors are the following formula:

$$P_{\text{as volumetric density}} = \frac{I * V}{m}$$
 (Equation 8)

Therefore, to get a high power density, a high current and a high voltage is needed in the lower amount of mass or in the smallest volume.

Also, the power can be written as:

$$P = \frac{V^2}{R} \qquad (\text{Equation 9})$$

In consequence, a high voltage is needed and the inner electrical resistance should be minimized to increase the power output per unit of mass or volume. The selection of the materials plays an important role to reach this goal.

## 2.5 Aqueous room-temperature Sodium Ion Battery

Despite the great achievement of lithium-ion batteries, the insufficient and unevenly distributed lithium resources as well as the increasing cost and its toxic qualities might restrict their application in large-scale electrical energy storage systems.<sup>28</sup> Consequently, to overcome this situation, new efforts are being dedicated to the investigation of Sodium-ion batteries with aqueous electrolytes that share similar scientific and technological principles to the well-known lithium-ion batteries.

Shi Qu introduced the basic concept of an aqueous sodium ion supercapacitor. The cell type described in his scientific paper represents a type of hybrid system combining both typical characteristics of accumulators and electric double-layer capacitors (EDLC). This is reflected above all in the different storage mechanisms during the charging and discharging phase of the respective active material. For the positive electrode, crystalline NaMnO<sub>2</sub> is used, while a highly porous activated carbon is used on the anode side. The electrolyte is a 0.5 molar solution of Na<sub>2</sub>SO<sub>4</sub> in water. Two processes within the cell are of particular interest for the function of the hybrid system. On the one hand, the so-called intercalation, which allows an ion transition on the NaMnO2, and on the other electrostatic field effects, which is developed on the activated carbon electrode surface.

Recently, for the development of Sodium-Ion batteries with aqueous electrolytes a wide choice of electrode materials is arising. Apart of the particular requirements for this work – which include safety and environmental concerns - one of the most important properties and requirements for the materials to be used for the printing pastes is its inner resistance. A low resistance leads to a better performance and usability of the battery.

<sup>&</sup>lt;sup>28</sup> (Han, Gonzalo, Singh, & Rojo, 2015)

## 3 Physical background

## 3.1 Electrical resistance (R)

The electrical resistance  $\mathbf{R}$  is the property of a body that opposes or limits the flow of a electric current through it. A low resistance indicates a material that readily allows the flow of electric current, for example, a metal.

The most common way to measure the resistance is by the Ohm's empirical law. The Ohm's empirical law defines the resistance as the ratio of the voltage **U** applied between two electrodes (measured in volts, V) to the current between them (I, measured in amperes, A). The unit of the resistance is ohm ( $\Omega = V A^{-1}$ ):

R = U/I (Equation 10)

## **3.1.1** Contact Resistance (*R*<sub>contact</sub>)

When the resistance of a material is measured, the obtained value consists of several resistances. One of them is the  $R_{contact}$  and is attributed to the resistance emerged by contacting interfaces. It is also known as "Interface resistance".

 $R_{total} = R_{contact} + R_{others}$  (Equation 11)

A method for measuring the contact resistance is to construct several copies of the resistor with different lengths. Apart of the length, all the other parameters must be kept constant.

Then, the contact resistance can be found by extrapolating the value of the contact resistance to the limit of a zero-length resistor. This value would be divided by two to get the contact resistance for each connection.

The following plot illustrates an example:



Figure 3-1: Plot of the contact resistance estimation.

The idea of this study is to find the contact resistance exposed in the device that is going to be used to measure the electrical conductivity afterwards.

## 3.2 Electrical conductivity (σ)

The electrical conductivity measures how good the material is to allow the flow of electrons through it. It is regularly represented by the Greek letter  $\sigma$  (sigma) and its units are Siemens per meter (S/m). For its calculation, it is necessary to know the dimensions of the material: length **I** and cross sectional area **A**, and the electrical resistance **R**; or, it can be calculated as the reciprocal of the electrical resistivity  $\rho$ .<sup>29</sup>



Figure 3-2: Material with length "I" and cross sectional area "A", with electrical contacts on both ends.<sup>30</sup>

<sup>&</sup>lt;sup>29</sup> (Kumar, 2003)

<sup>&</sup>lt;sup>30</sup> Source: https://en.wikipedia.org/wiki/Electrical\_resistivity\_and\_conductivity

$$\sigma = 1/\rho$$
 (Equation 12)

$$\rho = R \frac{A}{l}$$
 (Equation 13)

Where  $\rho$  is the electrical resistivity of the selected material, **R** is the electrical resistance of a uniform specimen of the material, **A** is the cross-sectional area of the specimen, and **l** is the length of the piece of material

Every material has its own characteristic electrical conductivity. For example, rubber is a material with large  $\rho$  and small  $\sigma$  - because even a very large electric field in rubber results in almost no current flow through it. On the other hand, copper is a material with small  $\rho$  and large  $\sigma$  - because even a small electric field leads to a high current.

The electrical conductivity depends on:

- the type of material and how pure is the material,
- the temperature,
- the force applied between connections,
- oxidation of the surface,
- the measurement procedure,
- and the circulating current.

Since the materials Aluminum and Copper are being used in this study, the registration of electrical conductivity is required:

 $\sigma_{Al} = 3.50 \times 10^7$  S/m at 20°C <sup>31</sup>  $\sigma_{Cu} = 5.96 \times 10^7$  S/m at 20°C <sup>32</sup>

#### 3.2.1 Percolation effect in electrical conductivity

The percolation effect in electrical conductivity consists in a theory that can explain the dramatic increase of the conductivity due to the mechanical compression of an isolated volume composed of highly conductive particles.

Initially the highly conductive particles are randomly distributed and separated. No current or a very less current flow through the volume.

<sup>&</sup>lt;sup>31</sup> (Serway, 1998)

<sup>&</sup>lt;sup>32</sup> (Phillips, 2009)



Figure 3-3: Schematic representation of the layout of an insulated system

After compressing the volume, the high conductive particles get in contact an electrical conductive path appears. This phenome is shown as follows:



Figure 3-4: Schematic representation of the generated conduction after applying mechanical compression.

## 4 Development of measurement methods for the Electrical Conductivity and the Contact Resistance

## 4.1 Testing mode

## 4.1.1 2-wire

In this mode, no external voltage source is needed to create contact closure to the ground. The current flows from the high terminal to the low terminal, and the resistance is calculated. It is a good method to measure high resistances, for example resistances higher than  $10\Omega$ .

## 4.1.2 4-wire

In 4-wire mode, the test current is sourced to the test resistance through one pair of test leads, and the test voltage across the resistance under test is measured from another set of test leads. As a result, the 4-wire mode is more accurate for low resistance measurements.

As this mode introduces a current, the current should be as low as possible in order to avoid the heating up of the materials. The temperature has an effect in the properties and the fixed temperature for this study is a room temperature of 25°C or so.

## 4.2 Testing device

## 4.2.1 Digital Multimeter Keithley 2100 6 1/2<sup>33</sup>

The Keithley Instruments Model 2100 is the selected measurement instrument to test the electrode components. It basically consists in a multimeter with a digital resolution of 6  $\frac{1}{2}$  digits.

The measurements functions include the 2-wire and 4-wire measurement of the resistance, which are schematized in Figure 4-2 and Figure 4-3.

The accuracy of the measurements at two or 4-wire resistance can go from  $100\Omega$  to  $100M\Omega$ . For battery applications, the lowest resistance mode is selected:  $100 \Omega$ . In this case, the obtained value has 6 digits, for example:  $154,835 \Omega$ 

In order to improve the accuracy, the measurements should be taken in stable conditions without perturbations such as magnetic waves.

<sup>&</sup>lt;sup>33</sup> (Keithley Model 2100 6 1/2-Digit Resolution)



Figure 4-1: Model 2100 2-wire resistance



Figure 4-2: Model 2100 4-wire resistance

## 4.3 Testing components

## 4.3.1 ECC-Std measurement device made by EL-CELL<sup>34</sup>

The ECC-Std is an electrochemical test cell designed for testing laboratory batteries. It is very simple to assemble and provides an accurate level of the measurements between  $\pm$  0.2  $\Omega$ .

It is not necessary to build a two-electrode configuration in the cell; this product can be applied to measure the electrical conductivity of only one electrode material as it is required for this study.

The cell parts that get in contact with the electrode materials are made of stainless steel 1.4404 and PEEK, and can thus withstand all the electrode materials used in sodium-ion batteries with aqueous electrolyte. Therefore, this device is reusable.<sup>35</sup>

The technical dimensions are shown in the following illustration (Figure 4-3):

<sup>&</sup>lt;sup>34</sup> Product description: https://el-cell.com/products/test-cells/standard-test-cells/ecc-std

<sup>&</sup>lt;sup>35</sup> Features: https://el-cell.com/products/test-cells/standard-test-cells/ecc-std



Figure 4-3: Dimensions in mm of the ECC-Std by EL-CELL.<sup>36</sup>

As a normalized testing device, the inner diameter of the cell is 18 mm with <0.1 mm electrode concentricity. It offers a fast assembly and dismantling and easy cleaning of cell components. The minimum volume of the electrode material required is 0.05 cm<sup>2</sup>.

The mechanical pressure on electrode is adjustable, reproducible and homogeneous. This pressure comes from the spring and depends on the thickness of the electrode stack: the higher the thickness, the higher the pressure. The Figure 4-4 illustrates the behavior.



Figure 4-4: Spring load on stack vs. stack thickness for different springs. Standard is FED9015.<sup>37</sup>

<sup>&</sup>lt;sup>36</sup> Specifications: https://el-cell.com/products/test-cells/standard-test-cells/ecc-std

In order to get comparable results, the thickness of the electrode material in the cell stack should be exactly the same among all the experiments, thus the applied compressing force will be exactly the same. It is noteworthy that the compressing force has a strong impact in the contact resistance.

An image of the device is shown in Figure 4-5:



Figure 4-5 EL-CELL measurement device empty.

## 4.3.2 Two Cu Coins measurement device

Due to the thicknesses limitation of the ECC-Std measurement device and its difficulty to measure wet materials, another device was made to satisfy these requirements.

It consists in two Copper coins with a diameter of 18 mm each connected with the testing device (Figure 4-5). This method offer more levels of freedom to simulate the working conditions of the future battery.

<sup>&</sup>lt;sup>37</sup> User manual ECC-Std, page 5.



Figure 4-6 Two Cu Coins measurement device

## 4.3.3 Aluminum cylinders for the validation procedure

For the examination of physical and electrochemical properties of batteries, standardized design is adopted for practical aspects. The selected diameter for the cylinders is 18 mm.

The thicknesses of the aluminum cylinders go from 5 mm to 20 mm (Figure 4-7). The physical arrangement has to fit with the adopted standardizations.



Figure 4-7: Aluminum cylinders

The mask device consists in three plates with different thickness – 2mm, 4 mm and 6 mm-(Figure 4-8). In the center, a circular hole with a diameter of 18 mm is made. The holes act as the external shape where the paste is fulfilled. Then to take out the shaped paste disk from the mask, an external circular aluminum disk (Figure 4-9) on the bottom helps the pushing action. Furthermore, the external circular aluminum disk acts as the basement of the shaped paste disks and helps its shipment.



Figure 4-8 Mask device



Figure 4-9: Aluminum disks

## **4.3.5** Plastic Rings with two different thicknesses

The plastics rings (Figure 4-10) are presented as a solution for the measurements in wet conditions. They are able to enclose the paste in different thicknesses and allow its measurements.

The mode of operation is to put the paste inside the hole and apply a fixed pressure between both extremes.



Figure 4-10 Plastic Rings with two different thicknesses

## 4.4 Testing materials

## 4.4.1 Carbon Black

Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar, and a small amount from vegetable oil. Carbon black is a form of paracrystalline carbon that has a high surface-area-to-volume ratio, albeit lower than that of activated carbon. It is dissimilar to soot in its much higher surface-area-to-volume ratio and significantly lower (negligible and non-bioavailable) PAH (polycyclic aromatic hydrocarbon) content. However, carbon black is widely used as a model compound for diesel soot for diesel oxidation experiments.<sup>38</sup>

The presence of carbon black in the mixed material of the anode and cathode of batteries is to improve the electrical conductivity of the electrolyte.

## 4.4.2 Activated Carbon

Activated carbons are manufactured carbonaceous non-hazardous products having a porous structure and a large internal surface area. The chemical structure of activated

<sup>&</sup>lt;sup>38</sup> (Ceresana, 2013)

carbon can be defined as a crude form of graphite with a random or amorphous structure, which is highly porous over a broad range of pore sizes, from visible cracks and crevices to cracks and crevices of molecular dimensions.

Activated carbon has a very high internal surface area (up to 1500m2/g) and is thus an ideal material for adsorption.<sup>39</sup> The phenomenon of adsorption occurs when molecules of a liquid or gas are trapped by either an external or internal surface of a solid.

## 4.4.3 NASICON-structured materials as promising electrode materials

"The NASICON-structured materials with the formula unit of  $A_x B_y (XO_4)_3$  where A, M and X are alkali metal, transition metal and nonmetal atoms, respectively, can be described as three-dimentional polyanionic frameworks of corner sharing MA<sub>6</sub> octahedral and XO<sub>4</sub> tetrahedral with interconnected channels for the diffusion of alkali ions."<sup>40</sup>

"The redox potentials of NASICON-Structured materials can be turned by changing the elemental composition and/or the valence states of the transition metal ions."<sup>41</sup>

#### 4.4.3.1 Na<sub>3</sub>MnTi(PO<sub>4</sub>)<sub>3</sub>

The average voltage of Na<sub>3</sub>MnTi(PO<sub>4</sub>)<sub>3</sub> for the electrode is 1,4 V with an energy density of 40 Wh/kg<sup>42</sup>

"The NASICON-type Na<sub>3</sub>MnTi(PO<sub>4</sub>)<sub>3</sub> forms a three-dimentional framework based on  $MnO_6$  or TiO<sub>6</sub> octahedral sharing all of its corners with PO<sub>4</sub> tetrahedral."<sup>43</sup>

## 4.4.3.2 NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>

The average voltage of  $NaTi_2(PO_4)_3$  for the anode electrode is between  $1,1V^{44}$  and  $1,4V^{45}$  depending on the cathode electrode connected. Furthermore, the energy density goes from 30 Wh/kg<sup>46</sup> to 48 Wh/kg<sup>47</sup>

"The NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> has a sodium-ion insertion potential well-above the evolution of  $H_2$  in an aqueous NaSO<sub>4</sub> electrolyte."<sup>48</sup>

<sup>&</sup>lt;sup>39</sup> https://www.desotec.com/en/carbonology/carbonology-academy/activated-carbon

<sup>&</sup>lt;sup>40</sup> (Goodenough, Hong, & Kafalas, 1976) (Manthiram & Goodennough, 1989)

<sup>&</sup>lt;sup>41</sup> (Padhi, Nanjundaswamy, Masquelier, Goodenough, & Electrochem, 1997)

<sup>&</sup>lt;sup>42</sup> (Gao & Goodenough, 2016)

<sup>&</sup>lt;sup>43</sup> (Gao & Goodenough, 2016)

<sup>&</sup>lt;sup>44</sup> (Thackeray, C.Wolverton, & Isaacs, 2014)

<sup>&</sup>lt;sup>45</sup> (Hou, Li, Liang, Zhu, Qian, & Mater, 2015)

<sup>&</sup>lt;sup>46</sup> (Thackeray, C.Wolverton, & Isaacs, 2014)

<sup>&</sup>lt;sup>47</sup> (Hou, Li, Liang, Zhu, Qian, & Mater, 2015)

<sup>&</sup>lt;sup>48</sup> (Park, Gocheva, Okada, Yamaki, & Electrochem, 2011)

## 4.5 Measuring methods

## 4.5.1 Standard method

## 4.5.1.1 ASTM D25749

The fixed designation ASTM D257 is a standard method for DC resistance or conductance of insulating materials. This method covers direct-current procedures for the measurement of dc insulation resistance, volume resistance, and surface resistance. From such measurements and the geometric dimensions of specimen and electrodes, both volume and surface resistivity of electrical insulating materials can be calculated, as well as the corresponding conductivities.

The resistance or conductance of a material specimen or of a capacitor is determined from a measurement of current or of voltage drop under specified conditions. By using the appropriate electrode systems, surface and volume resistance or conductance may be measured separately. The resistivity or conductivity can then be calculated when the required specimen and electrode dimensions are known.

According to this method a pressure of 50 N/cm<sup>2</sup> is applied on the specimen. This pressure would represent a compressing force of 1240 kg between the plates of the NAWIN battery (Figure 4-11).



Figure 4-11: Illustration of dimensions for the separator of the NAWIN battery

It is assumed that the compressing force applied to the NAWIN battery would be around 100 kg, and therefore, a self-made method needs to be developed to respect this requirement.

<sup>&</sup>lt;sup>49</sup> (ASTM, 2007)

## 4.5.2 Self-made methods

The self-made measurement device should be able to simulate the working conditions in a smaller scale. It should provide the same operation conditions in order to get a better understanding of its components by the comparison of the measurements.

Among the working condition, it is worth to mention:

- The room temperature: 20 25° C
- Pressure between the materials should be around 4 N/cm<sup>2</sup>. This value comes from the assumption of a compressing force between the plates of the battery of 100kg.
- The state of the materials should be the same as in the battery. If they are wet, the measurements should be taken in wet conditions as well.

#### 4.5.2.1 Measurements with the ECC-Std measurement device

For the measurement of the anode materials with the ECC-Std measurement device, a mask device was developed to shape the anode material coins. A set of paste coins with different characteristics was made.

Since, it was difficult to determine the pressure in the chamber of the ECC-Std measurement device and it was hard to shape the exactly same form for each paste coin.

A decision to move on to do the measurements without taking out the paste coins from one cylindrical mask was taken so it is easier to fix compressing force of 4 N/cm<sup>2</sup>

#### 4.5.2.2 Measurements with plastic rings

The procedure to measure the characteristics of the anode paste is much easier and accurate when the paste stays in a cylindrical form. Furthermore, the procedure turns to be more applicable and reliable.

The arrangement corresponds of two Copper coins connected with cables to the 4-wire testing device and in between the plastic ring fulfilled with the paste in study (Figure 4-12). A compressing force of 4,1 N/cm<sup>2</sup> is applied. The fixed diameter is 18 mm, so the compressing force needs to be 1,0635 kg or 10,4332 N.



Figure 4-12: Schematic arrangement of the measurement system with plastic rings

In order to achieve a compressing force of  $4,1 \text{ N/cm}^2$  between the two copper coins a manufactured plate of 1,08 kg is placed on the top of the upper copper coin.

## 4.6 Machines for the paste preparation

In the following, the most important tools for the paste preparation are presented.

## 4.6.1 Precision balance

For the weighting of the components, a high precision balance is needed. The laboratory of Fraunhofer ISE is equipped with a Sartorius balance LE244S (Figure 4-13) with a readability of 0,1mg and a weighing capacity of 240g. <sup>50</sup>

<sup>&</sup>lt;sup>50</sup> Specifications of the Sartorius LE244S



Figure 4-13: Sartorius balance LE244S

## 4.6.2 Three-roll mill

The manufacturing of the paste needs a homogeneous integration of all of its components. The selected device to achieve this requirement is the EXAKT three roll mills (Figure 4-14) which can integrate all the particles with a very good quality.



Figure 4-14: EXAKT three roll mills electronic version, the full device on the left side, and the three rolls in operation conditions on the right side.

## 5 Experiments

As explained at the beginning, the aim of this work is to quantify the electrical conductivity of electrode materials with the highest accuracy as possible and at the most realistic conditions as possible (pressure and mixing portions of the electrode paste) prevailing in the battery pack.

For this propose, a sequence of actions need to be applied to find the most suitable device and electrode paste. All the experiments are carried out in the laboratories of Fraunhofer ISE and thus all the actions should be adapted to its facilities.

## 5.1 Design of the experiment

The planning actions are the following:

- 1. Construction of the measurement device.
- 2. Validation of the measurement device.
- 3. Selection of the measurement device.
- 4. Development of the measurements.
- 5. Analysis of the results.

## 5.2 Construction of the measurement device

The set-up of the devices involves:

- 1. The connection of the cables with the copper coins: To do so, two holes of 1cm length and 1.5 mm diameter were made in the copper coins.
- 2. The correct assembly of the testing device.
- 3. The application of the same compressing force, same voltage, same current (1mA) without heating up the device.

## 5.3 Validation of the device

Despite of the rejection of the EL-CELL measurement device in last chapter due to its limited degrees of freedom to adapt to the working conditions of the NAWIN battery, the validation of the device is considering both devices again to have a deeper look at the behavior of the contact resistance of each one.

The measurement of the contact resistance is used to evaluate the performance of measuring device. A good performance of the measuring device is the one with the most accuracy match between the known contact resistance and the experimental value of the

contact resistance for the same material. Furthermore, the point distribution of the measurements should be taken into account.

In this section, the different thicknesses method to find the contact resistance is implemented. All the measurements are carried by the **4-wire** testing method. The selected material to evaluate the contact resistance is Aluminum.

The standard values of resistance of the Aluminum are calculated with the formula:

$$R = \rho \frac{l}{A}$$
Where  $\rho = 2.82 * 10^{-8} \Omega \text{m}$ , <sup>51</sup>
And  $A = \frac{\pi * d^2}{4} = 0,000254469 \, m^2$ .

The results are shown in Table 2:

Table 2: Standard	resistance	of different	thickness	of Aluminum
	resistance	or unicicilit	UNCKINCSS	or / dummun

Aluminum:	50 mm	100 mm	150 mm	200 mm
R <sub>Al-Standard</sub>	5,54095 μ <b>Ω</b>	11,0819 μ <b>Ω</b>	16,6228 μ <b>Ω</b>	22,1638 μ <b>Ω</b>

#### 5.3.1 Chart analysis

As an example, two extreme charts are shown: the one on the left side is showing a perfect match between the known contact resistance and the linear trend line with an Ohmic behavior of the measured resistance, and the one on the right side is showing an erratic behavior of the measurements of the resistance with the un-match between the known contact resistance and the linear trend line (Figure 5-1).

The closer the behavior to the first chart, the better the measurement device.

<sup>&</sup>lt;sup>51</sup> https://en.wikipedia.org/wiki/Electrical\_resistivity\_and\_conductivity



Figure 5-1: On the left side, an example of a perfect match between the known contact resistance and the linear trend line. On the right side, an example of the un-match between the known contact resistance and the linear trend line (right one).

#### 5.3.2 Cu Coins measurement device

The validations of the copper coins measurement device is made by measuring the contact resistance of the Aluminum through the measurement of different thickness of cylinders made of Aluminum.



Figure 5-2: Schematic arrangement of the different thicknesses method



Figure 5-3: Visual view of the different thicknesses method for the cupper coins device (without any weight on top)

The equivalent circuit for this case is:



Figure 5-4: Equivalent circuit

This leads to the following formula:

$$(2 * R_{Cu} + R_{Mat} + 2 * R_{Cont}) * I = U$$
 (Equation 14)

$$2 * R_{Cu} = \rho \frac{l}{A} = 1,68 * 10^{-8} \Omega m \frac{0,007 m}{0,000254469 m^2} = 0,4621388 \mu \Omega$$

#### 5.3.2.1 Results without additional weight on top

additional weight on top.					
Device	Nr.	50 mm	100 mm	150 mm	200 mm
Cu Coins	1	0,011 Ω	0,213 Ω	0,093 Ω	0,106 Ω
Cu Coins	2	0,226 Ω	0,096 Ω	0,199 Ω	0,28 Ω
Cu Coins	3	0,111 Ω	0,354 Ω	0,350 Ω	0,308 Ω
Avera	age	0,116 Ω	0,221 Ω	0,214 Ω	0,231 <b>Ω</b>
Standard c	leviation	0,088 Ω	0,110 Ω	0,110 Ω	0,089 Ω
Standard	d error	0,062 Ω	0,075 Ω	0,075 Ω	0,063 Ω
Confidence interval		0,267 Ω	0,321 <b>Ω</b>	0,321 Ω	0,272 Ω

Table 3: Results of the contact resistance measurement of the copper coins device withoutadditional weight on top.



Figure 5-5: Plot of the resistance with bars of standard error of the copper coins device under atmospheric pressure. In blue the dots of the experimental values and in green the linear regression that predicts the contact resistance with its predicted standard error.

## $R_{Contact\,Al-Cu} = 0,0554\,\Omega \pm 0,1106\,\Omega$

#### 5.3.2.2 Results under a compressing force of 10,5 N.

Table 4: Results of the contact resistance measurement of the copper coins device under a compressing force of 10,5 N.

Device	Nr.	50 mm	100 mm	150 mm	200 mm
Cu Coins	6	0,001 Ω	0,002 Ω	0,003 Ω	0,004 Ω
Cu Coins	7	0,002 Ω	0,003 Ω	0,004 Ω	0,005 Ω
Avera	ige	0,0015 Ω	0,0025 Ω	0,0035 Ω	0,0045 Ω
Standard d	leviation	$0,0005~\Omega$	0,0005 Ω	0,0005 Ω	0,0005 Ω
Standard	l error	0,0005 Ω	$0,0005~\Omega$	0,0005 Ω	0,0005 Ω
Confidence	e interval	0,0064 Ω	0,0064 Ω	0,0064 Ω	0,0064 Ω



Figure 5-6: Plot of the resistance with bars of standard error of the Copper coins device under a compressing force of 10,5 N. In blue the dots of the experimental values and in green the linear regression that predicts the contact resistance with its predicted standard error.

## $R_{Contact\,Al-Cu} = 0,00025\,\Omega \pm 0,00058\,\Omega$

#### 5.3.3 EL-CELL measurement System

The next device to evaluate is EL-CELL measurement System. Without a compressing force, the measurements look like the following:



Figure 5-7: Visual view of the different thicknesses method for the EL-CELL device (without any weight on top)

#### 5.3.3.1 Results without additional weight on top

Device	Nr.	50 mm	100 mm	150 mm	200 mm
EL CELL	4	0,635 Ω	0,767 Ω	1,122 Ω	1,746 Ω
EL CELL	5	0,283 Ω	0,470 Ω	0,714 Ω	1,518 Ω
Avera	age	0,46 Ω	0,62 Ω	0,92 Ω	1,63 <b>Ω</b>
Standard o	deviation	0,18 Ω	0,15 Ω	0,20 Ω	0,11 Ω
Standard	d error	0,18 Ω	0,15 Ω	0,20 Ω	0,11 Ω
Confidence	e interval	2,24 Ω	1,89 Ω	2,59 Ω	1,45 Ω

 Table 5: Results of the contact resistance measurement of the ELL CELL device without additional weight on top.





## $R_{Contact Al - Stainless steel} = -0,0239 \,\Omega \pm 0,2505 \,\Omega$

The above prediction of the contact resistance between the aluminum and the stainless steel is a negative number which is unrealistic. However, if the range of uncertainty is considered, the value of the contact resistance can become positive. The range of uncertainty is more than ten times the estimator of the media and this informs that informs a low quality of the measurements.

#### 5.3.3.2 Results under a compressing force of 10,5 N.

Table 6: Results of the contact resistance measurement of the ELL CELL device under a compressing force of 10,5 N.

Device	Nr.	50 mm	100 mm	150 mm	200 mm
EL CELL	8	0,00904 Ω	0,00989 Ω	0,00961 Ω	0,01145 Ω
EL CELL	9	0,00788 Ω	0,00889 Ω	0,0105 Ω	0,01087 Ω
Aver	age	0,0085 Ω	0,0094 Ω	0,0101 Ω	0,0112 Ω
Standard	deviation	0,0006 Ω	0,0005 Ω	0,0004 Ω	0,0003 Ω
Standar	d error	0,0006 Ω	0,0005 Ω	0,0004 Ω	0,0003 Ω
Confidenc	e interval	0,0074 Ω	0,0064 Ω	0,0057 Ω	0,0037 Ω



Figure 5-9: Plot of the contact resistance with bars of standard error of the ELL-CELL device under a compressing force of 10,5 N. In blue the dots of the experimental values and in green the linear regression that predicts the contact resistance with its predicted standard error.

 $R_{Contact Al - Stainless steel} = 0,0038 \,\Omega \pm 0,000548 \,\Omega$ 

#### 5.3.4 Analysis and selection of the measurement device

The first measurements without additional weight on top are not reliable due to the dispersion of the experimental values. This is shown by the R-squared criteria. The R-squared is a number between cero and one, and shows the linear relationship between two variables. The closer the R-squared is to one, the higher the linear correlation. For both set of samples without additional weight on top, the R-square value was under 0,8 where the expected R-square was one since the evaluated material was Aluminum, a linear behavior is expected for metals. Therefore, the measurements without additional weight should be neglected.

In this context, the selection of the most convenient device comes from the comparison of the performance from each device under a pressure of 10,5 N.

The R-squared of the cooper coin device under a pressure of 10,5 N was 0,8333 and for the EL-CELL device under the same conditions was 0,8100 which means a slightly better correlation for the cooper coins device. Moreover, the experimental contact resistance found between the Aluminum and the cooper coins was  $0,00025\Omega \pm 0,00058\Omega$  and the experimental contact resistance found between Aluminum and Stain steel was  $0,0038\Omega \pm$  $0,00548\Omega$ . A small contact resistance is considered better because the measured system receives fewer perturbations. Last but not least, the cooper coins device offers more degrees of freedom to adapt the measurements to the working conditions of the battery and a small level of complexity which occasionally can increase the errors. Due to the mentioned arguments, the most convenient measurement device for this study is the two copper coins.

In other hand, it is not possible to take into account the experimental values of the measured Aluminum resistant as one of the driver to select the most appropriate device since both results are two orders of magnitude bigger than the standard values of Aluminum (see Table 7). This difference is because of the propagation of errors and the luck of accuracy of the measurement devices. In the case of the EL-CELL, the level of accuracy is  $\pm 0.2\Omega^{52}$ . As consequence, that precision of both devices cannot be in  $\mu\Omega$ .

	50 mm	100 mm	150 mm	200 mm
<b>R<sub>Al, Standard</sub></b>	5,541 μ <b>Ω</b>	11,082 μ <b>Ω</b>	16,623 μ <b>Ω</b>	22,164 μ <b>Ω</b>
<b>R</b> <sub>Al,</sub> Cu Device	994,5 μ <b>Ω</b>	1994,5 μ <b>Ω</b>	2994,5 μ <b>Ω</b>	3994,5 μ <b>Ω</b>
<b>R</b> <sub>Al, EL CELL</sub>	883,4 μ <b>Ω</b>	1783,4 μ <b>Ω</b>	2483,4 μ <b>Ω</b>	3583,4 μ <b>Ω</b>

Table 7: Comparison of the Std. values of Aluminum and the experimental values of each device.

\*For the repeatability and reproducibility of the obtained results, the statistical variability and errors should be considered.

<sup>&</sup>lt;sup>52</sup> Informed value by the company EL-CELL GmbH

## 5.4 Development of the measurements

For the study of the electrode material, three levels of carbon black are being compered: 10%, 20% and 30% of carbon black. The percentage of blinder is always 10% and the percentage of active materials is calculated to complete 100% of the mix.



Figure 5-10: Illustration of the mixtures of Active Material - NaTi2(PO4)3 -, Binder SBR and Carbon Black with an emphasis in 3 levels: 10%, 20% and 30%.

The mask device is implemented for the production of the paste coins that can be placed in the standardized test device (El-Cell) or between the two Coper coins.



Figure 5-11: Images taken during the production of the paste coins with the mask device.



Figure 5-12: Material for study

Difficulties identified in this process:

- It is difficult to separate the paste from the mask in some cases.
- Part of the paste sticks on the mask (mass lose).
- Part of the paste sticks on the Aluminum coin after drying it (mass lose).
- The drying of the paste before the incorporation in the cell leads to the reduction of its area (Figure 5-13) as the cohesive forces within the paste exceed the adhesive forces between the paste and the charge collector.



Figure 5-13: Reduction of the area after dried the paste, higher cohesive forces.

• The drying of the paste before the incorporation in the cell leads to dry fractures (Figure 5-14) as the adhesive forces between the paste and the charge collector exceed the cohesive forces within the paste, causing cracks. Maybe the binder (SBR) is the cause.





## **5.4.1** Alternative solutions:

It is extremely important to have homogeneous measurements with exactly the same parameters per iteration to arrive in comparable results. That why the paste coins were discarded. Different shapes, different weights, fissures, and so on, are issues that need to find a solution.

The study of the best solutions starts below:

#### 5.4.1.1 Measurement of the powder

Convert the dried coins in powder with a mortar, measure the conductivity and then register the weight of it.

Powder	Thickness (mm)	Ohms	Weight
00J1	4,3	4525	1,2319
00J1 - R	4,3	4084	1,2269
00J2	4,3	1204	0,8535
00J3	4,3	404	0,8193

Table 8: Results of measuring the powder

These values are not worth for the goal of this thesis because it does not simulate the real working conditions. The operating paste is wet.

#### 5.4.1.2 Measurement in wet conditions

The wet paste requires attention in the borders. Important deformations can occur and also when the paste gets in contact with other surface, part of it will stick there, so the measurement of the weight would be no precise.



Figure 5-15: Wet paste in between two aluminum coins

As a solution for this issue, the measurements of the paste in wet condition would better take place in a ring with a known inner diameter and a known thickness.



Figure 5-16: Wet paste into the plastic ring

## 5.5 Finding of the best composition for the anode paste

For the finding of the best anode composition 3 pastes where made:

• Paste made of Activate Carbon and Carbon Black with Sodium sulfate solution 1mol/liter.

- Paste made of NaMnTi(PO4)3 and Carbon Black with Sodium sulfate solution 1mol/liter.
- Paste made of NaTi2(PO4)3 and Carbon Black with Sodium sulfate solution 1mol/liter.

After a learning period, the method selected for these measurements is the Cupper coins with plastic discs where the paste goes in. A blinder is not necessary for this case. The introduced paste should be as wet as in the working conditions.



Figure 5-17: An image of the selected measurement device



Figure 5-18: An image of the measurement procedure

# 5.5.1 Paste made of Activate Carbon and Carbon Black with Sodium sulfate solution 1mol/liter

This paste is made only for the study of the conductivity of the Carbon Black. A second material is added, Activated Carbon, within a solution of Sodium sulfate solution 1mol/liter, three levels of Carbon Black are being studied.



Figure 5-19: Illustration of the mixtures of Activated Carbon and Carbon Black with an emphasis in 3 levels: 10%, 20% and 30%.

The idea of this paste is to get to know the behavior of the Carbon Black that can further help the understanding the behavior of other pastes also composed of Carbon Black and other materials with an unknown behavior.

Table 9: Results of the measurements of the mix made of Activate Carbon and Carbon Black withinthe addition of Sodium sulfate solution 1mol/liter

Activated Carbon	Carbon Black	Thickness [m]	Diameter [m]	Weight on top [kg]	Resistance [Ω]	Specific Conductivity [S/m]
70 %	30 %	0,0104	0,013	1,0879	1,154	67,90
70 %	30 %	0,0156	0,013	1,0879	1,844	63,74
80 %	20 %	0,0104	0,013	1,0879	1,219	64,28
80 %	20 %	0,0156	0,013	1,0879	1,952	60,21
90 %	10 %	0,0104	0,013	1,0879	2,181	35,93
90 %	10 %	0,0156	0,013	1,0879	4,689	25,07

# 5.5.2 Paste made of NaMnTi(PO4)3 and Carbon Black with Sodium sulfate solution 1mol/liter

The mix of NaMnTi(PO4)3 and Carbon Black with Sodium sulfate solution 1mol/liter can be used as a anode material. The compositions to evaluate are the following:



Figure 5-20: Illustration of the mixtures of NaMnTi(PO4)3 and Carbon Black with an emphasis in 3 levels: 10%, 20% and 30%.

The measurements are informed in Table 10 where the composition with the highest specific conductivity is highlighted.

NaMnTi(PO4)3	Carbon Black	Thickness [m]	Diameter [m]	Weight on top	Resistance [Ω]	Specific Conductivity [S/m]
70%	30%	0,0104	0,013	1,0879	4,386	17,86
70%	30%	0,0156	0,013	1,0879	6,184	19,01
80%	20%	0,0104	0,013	1,0879	7,165	10,94
80%	20%	0,0156	0,013	1,0879	11,375	10,33
90%	10%	0,0104	0,013	1,0879	22,818	3,43
90%	10%	0,0156	0,013	1,0879	41,726	2,82

# 5.5.3 Paste made of NaTi2(PO4)3 and Carbon Black with Sodium sulfate solution 1mol/liter

The mix of NaTi2(PO4)3 and Carbon Black with Sodium sulfate solution 1mol/liter can be used as a anode material. The compositions to evaluate are the following:



Figure 5-21: Illustration of the mixtures of NaTi2(PO4)3 and Carbon Black with an emphasis in 3 levels: 10%, 20% and 30%.

The measurements are informed in Table 11 where the composition with the highest specific conductivity is highlighted.

NaTi2(PO4)3	Carbon Black	Thickness [m]	Diameter [m]	Weight on top [kg]	Resistance [Ω]	Specific Conductivity [S/m]
70%	30%	0,0104	0,013	1,0879	2,856	27,43
70%	30%	0,0156	0,013	1,0879	4,476	26,26
80%	20%	0,0104	0,013	1,0879	3,582	21,87
80%	20%	0,0156	0,013	1,0879	5,372	21,88
90%	10%	0,0104	0,013	1,0879	8,743	8,96
90%	10%	0,0156	0,013	1,0879	14,780	7,95

Table 11: Paste made of NaTi2(PO4)3 and Carbon Black with Sodium sulfate solution 1mol/liter

## 5.6 Analysis of the results

The reason why the experiments were carried out with the self-made method was to identify the internal specific conductivity of the components of the battery under working conditions. The self-made method could better simulate the working conditions on a smaller scale than the restricted ELL-CELL measurement device.

Due to the few amounts of measurements it is not possible to express the results with statistical parameters. However, big differences were identified to indicate that the composition with the best specific conductivity is the mix of 70%  $NaTi_2(PO4)_3$  and 30% of Carbon Black within the addition of Sodium sulfate solution 1mol/liter, with an approximate value of 27 S/m.

This result might help with the selection of the best anode paste as one of the factors to take into account. Other factor that involves this decision – apart of the cost and the availability of the materials – is the specific capacitance which is reduced with high amounts of Carbon Black.

## 6 Conclusion

In conclusion, the developed self-made method to measure the electrical conductivity performance of the electrode printing pastes results in a practical way to predict its internal specific conductivity under working conditions. However, other factors play an important role and therefore, the material with the best electrical conductivity might not be the best for the optimization of the whole battery system.

If the decision for the selection of the most acceptable anode material comes solely from the type of material with the best electrical conductivity, this study recommends the use of mix of 70% NaTi2(PO4)3 and 30% of Carbon Black within the addition of Sodium sulfate solution 1mol/liter.

## 7 Outlook

The materials and components of this study that showed a good performance can be selected for more rigorous evaluations. For example, they can be analyzed with the implementation of the follow techniques:

- laser diffraction analysis to measure the particle size distribution,
- rheology to measure the behavior of slurries during the printing process,
- viscometer to analyze the viscosity,
- the implementation of the scanning electron microscopy image (SEM).

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