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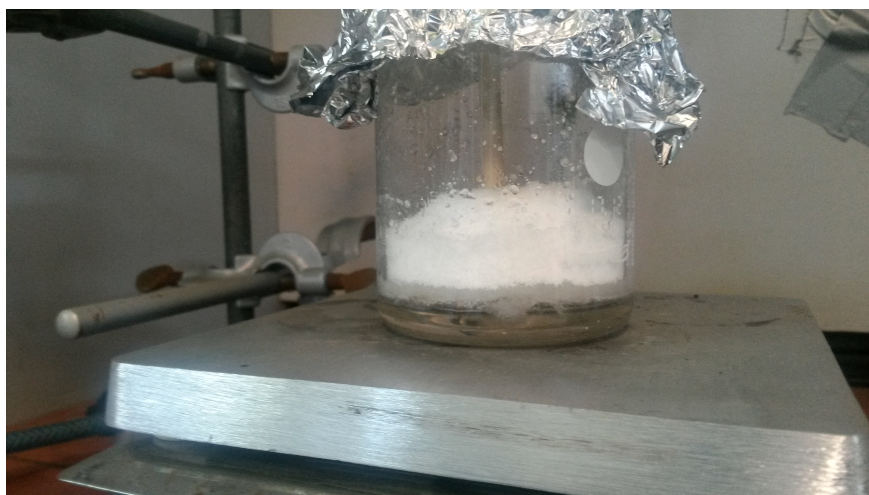# Electrochemical Removal of Impurities in Molten ZnCl$_2$-KCl-NaCl

Helene Flakke
Environmental Physics and Renewable Energy

Electrochemical Removal of Impurities in Molten $ZnCl_2$-NaCl-KCl

Helene Flakke

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Preface

Covering 30 points of what can only be described as electrochemical processing gone hay-wire it has been an interesting peek into the chemical sciences my physics classes has merely hinted at. As part of the ABC salt project Horizon2020 (grant agreement number 764089), this thesis will be the finalization of my masters in Environmental Physics at Norwegian University of Life Sciences. The field of renewable biofuels is dear to me, and it was great getting the opportunity to work as a part of this project, seeing all the various parts of a lab scale research while its happening.

My work has taught me much and more about projects, research, the industry and myself all at once. A thank you is in order to my ever-patient advisor, Heidi S. Nygård whose guidance and teaching was always where it needed to be. A similar thank you is in order for my co-advisors, Espen Olsen and Sepideh Niazi, for your troubleshooting and help at the lab.

Last but far from least a thank you must go out to Meyneth and the cat, for keeping me company, giving encouragement and advice, and forcing me to both take breaks and stay on track as needed.

_____

Helene Flakke, 15. mars 2021

Abstract

As part of the ongoing development to create renewable fuel sources the ABC salt project (Horizon2020 (grant agreement number 764089)) is creating a lab scale catalytic conversion of biomass into biofuel. The process of converting the biomass utilises a salt bed for catalysis and heat transfer as part of its process. The salt used for this will be mixed with the biomass as the biomass undergoes pyrolysis, and it is of interest to see how this salt may be reused.

Electrochemical removal of biomass remains has been proposed as a possible recycle tool, and this thesis explores this tool. The salt of interest is $ZnCl_2 - KCl - NaCl$, with 44.3-41.9-13.8 mol% composition. Electrochemically little is known about this, but the electrochemical range under standard conditions is believed to be limited to [-0.76, 1.36] V because of the zink cloride.

The biomass used will have an effect on which elements may be left in the salt. Finding ways to remove these are of importance as they might change properties of the salt such as its melting point, making reuse of the salt impossible. The biomass might leave traces of among others silicon, potassium, clorine, magnesium and calsium if its straw or pine wood, while lignin as a feedstock will leave a significant amount of sulphur from its production.

The salt is inspected electrochemically with an AUTOLAB and NOVA (2.1.4) software. The breakdown voltage is attempted confirmed and for the salt composition used can be said to be somewhere between 1.7 and 2.12 V. The electrochemical methods used are however not sufficient to tell if these or any elements are possible to remove.

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Samandrag

Som ein del av pågåande utvikling av fornybare brennstoff jobber ABC-salt-prosjektet med ein nyvinnande katalytisk omgjering av biomasse til biodrivstoff i lab-skala. Prossessen med omgjeringa av biomassen nyttar eit saltbad som varmeoverføringsmedia og katalysator. Saltet vert blanda med biomassen før biomassen går gjennom ein pyrolytisk prosess, og det er av høg interesse å attvinne saltet.

Det er føreslege å nytte elektrokjemiske metodar for å fjerne rester frå biomasse, og denne masteroppgåva ser på desse metodane. Saltet det er snakk om er $ZnCl_2-KCl-NaCl$ med ei mol%-samansetjing på 44,3-41,9-13,8. Reint elektrokjemisk er dette saltet lite kjent, men dei elektrokjemiske grensene er rekna å vera mellom [-0,76 - 1,36] V på grunn av sinkkloridet i saltet.

Typen biomasse nytta vil ha innverknad på kva grunnstoff som kan bli verande att i saltet etter mekanisk rensing. Å finne ein metode for å fjerne desse er viktig då grunnstoffa kan ha innverknad på eigenskapane til saltet som til dømes smeltepunkt, som kan gjere gjenbruk av saltet umogleg. Dersom biomassen er strå eller lignin kan det vere mellom anna silikon, kalium, kalsium, klor og magnesium. Dersom lignin vert nytta kan det føre til store mengder sulfater frå produksjonen av dette.

Saltet vert utforska med ein AUTOLAB og NOVA (2.1.4) programvare. Potensialdifferansen der saltet vert øydelagd er forsøkt stadfesta, for salt-samansetjinga nytta i oppgåva er ho funne til å vera ein stad mellom 1,7 og 2,12 V. Dei elektrokjemiske metodane som er nytta er ikkje gode nok til å seia om nokon grunnstoff frå biomassen kan fjernast.

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1 Introduction

1.1 Motivation

I love the smell of the emissions

Sarah Palin
Rolling Thunder, 2011

Sustainable biofuels is part of the emerging field of renewable energy. While traditionally bioenergy has always been in use for various purposes, e.g. cooking and heat, the prospects are copious. The International Energy Agency estimates bioenergy to account for a tenth of the energy supply today, and its contributions to modern bioenergy is five times larger than wind and solar photovoltaic[7]. While biofuels cannot and should not be used for every purpose, the existing technology and machinery to consume such fuels are widespread, and having them transition to renewable sources will be important to combat global warming. At the same time, it is important to note that the burning of renewable fuels will also have emissions of CO_2 into the atmosphere when used, similar to fossil fuels. Measures to counter the life-cycle greenhouse gas emissions should be involved when possible.

1.2 Aim

This Master thesis is written in connection to the Horizon2020 (grant agreement number 764089) ABC-salt-project: Advanced Biomass Catalytic Conversion to Middle Distillates in Molten Salts [1]. The aim of ABC-salt is to do a lab scale catalytic conversion of lignocellulose into biofuels, taking the technology readiness level (TRL) from 2 to 4. Using molten salts to aid both as a catalyst and as a first heating point for the biomass, liquefying the biomass with as little early conversion and by-products such as char and permanent gases as possible is a goal.

Figure 1 is a flowchart over the process. The feedstock goes into liquefaction, be it straw, lignin, various leftovers from the wood industries, or other related streams of biomass that otherwise would go to waste. The use of molten salt is intended to both have a catalytic effect on the pyrolysis and as a heat transfer medium, putting serious constraints on what salt to use and how to apply the process. The liquefaction process and hydro-pyrolysis stage will both have the salt mixed into the process, and
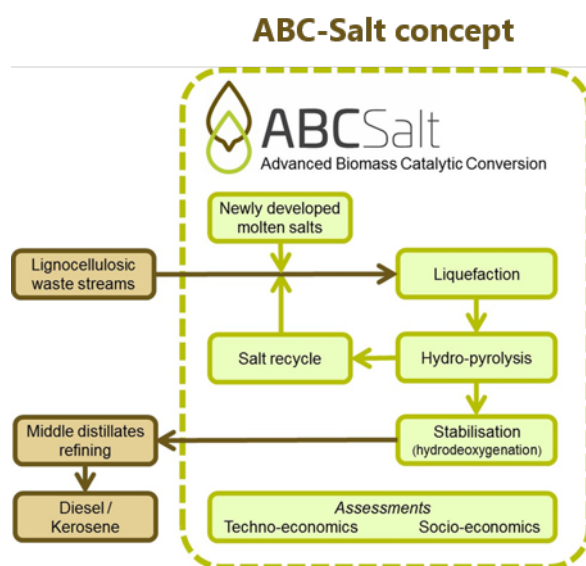
Figure 1: The ABC-salt concept flow diagram of the various stages of the process from biomass to fuel[1]

separated after pyrolysis. The yields from the pyrolysis goes on into distillation ending up as kerosene, while the salt goes to recycling.

This thesis will focus on salt recycling, specifically electrochemical removal of impurities from the spent molten salts. As the biomass goes through the hydro-pyrolysis not everything will get converted; there might be char and the salt will get pieces of DNA from the biomass mixed in. Filtering out these components will be crucial for reuse of the salt. This is done to promote reuse, and reduce cost of new salts and disposal of spent salts. The aim will be to identify which elements theoretically can be removed via electrochemical means, and later attempt to do so in a lab setting using artificial spent salt from the ABC-process. Molten salt has often been researched with various thermal storage solutions in mind, and there is little research done into electrochemical removal of impurities. The disposal of spent salt can be both expensive and harmful for the environment, and as such having proper methods for recycling will be beneficial. While the salts used in this thesis are at worst moderately harmful, the less waste generated the better. The salt that has been chosen for this purpose is known as salt #4 from earlier experiments by ABC salt. Salt #4 is $ZnCl_2-KCl-NaCl$, with a composition 44.3-41.9-13.8 mol% [8].

2 Theory/literature search

2.1 Purpose

This section is meant to give a theoretical overview of electrolysis as a basis for electrochemical removal, establish some base fact about the salts used and give an overview over which elements may be found as impurities in the salt. It will then go into some electrochemical methods that will be used on the salt.

2.2 Electrolysis

Electrolysis is a technique for separation of different elements with the help of direct current (DC). This process is by nature non-spontaneous, giving it a $\Delta G° \leq 0$. Figure 2 shows a basic electrolytic cell, where the cathode and anode are electrodes being subjected to a DC power source. For this cell to work there needs to be a medium between these conducting the current throughout. In this thesis that medium will for the most part be molten salt. The concept is to apply a voltage between the electrodes that is low enough to not break the medium, while potentially still detect and remove other elements. The Standard Electrode Potential E°[V](SHE), the standard hydrogen electrode at 1 atm, 25°C, holds the key to which elements theoretically can be removed from the salt melt electrolytically. The following table shows the electrode potentials for the constituents of the salt, measured against SHE:

Reaction			$E_e°$[V]
$Cl_2 + 2\,e^-$	$\rightleftharpoons$	$2\,Cl^-$	+1.36
$Zn_2{}^+ + 2\,e^-$	$\rightleftharpoons$	Zn	-0.76
$Na^+ + e^-$	$\rightleftharpoons$	Na	-2.71
$K^+ + e^-$	$\rightleftharpoons$	K	-2.92

Table 1: Electrode potentials of standard conditions in the salt [4]

Electrode reactions are reactions of charge transfer. At an anode, the oxidation happens, and at the cathode, the reduction happens. As charge transfer usually is done with electrons, this means the removal of electrons from the electrolytes at the anode and delivery of electrons at the cathode[9].

The basic equation for calculating the cell potential will be

$$E^o cell = E^o cathode - E^o anode \tag{1}$$
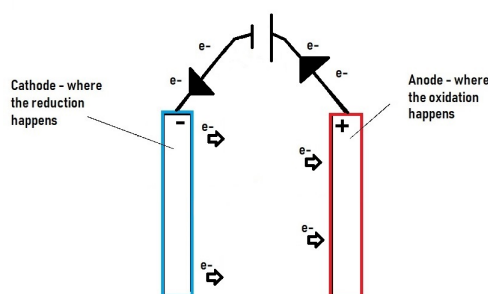
Figure 2: A basic electrolytic cell, inspired in part by [2].

where $E^o cell$ is the formal or standard electrode potential. If this sum is positive the creation of the salts is a spontaneous process, and work would need to be done to break the salts apart again. E°for the components of salt 4 should theoretically be as in table 2.

Salt	Reaction	E°cell [V]
E_{ZnCl2}	= +1.36 V - -0.76 V	= 2.39 V
E_{NaCl}	= +1.36 V - -2.71 V	= 4.07 V
E_{KCl}	= +1.36 V - -2.92 V	= 4.28 V

Table 2: E°for components of salt # 4, from table 1.

The lowest E°of these, the $ZnCl_2$ will be the limiting factor for any electrolysis done on the molten salt and might also determine which other elements may be removed electrochemically, as any higher voltage than that of $ZnCl_2$ between the electrodes will break apart the salt itself. Any element whose standard potential is found inside the range of [-0.76, 1.36] will be hypothesized to be removable electrolytically - at least theoretically. The electrode potentials will not be the same values in a system of molten salts, and should be seen as approximations or guidelines for real life molten systems. The practical reality of this will be explored experimentally in the thesis.

2.3 Early findings in literature

In an article from Nitta et al. the voltage at which the $ZnCl_2$ KCl NaCl breaks down is estimated."The electrochemical window of the melt was determined to be 1.7 V at 250 °C with the cathode limit being zinc metal

deposition and the anode limit being chlorine gas evolution." [10]. This is done at molar composition 60-20-20, and it will be necessary to do measurements on salt #4 (see table 3) to confirm the breakdown voltage at correct molar composition, ideally at a range of temperatures from melting up to any in use in the ABC-salt-project.

2.4 Salt - and molten salt

Salts are chemical compounds typically seen as small crystallines, composed of a cation and anion mixing. ABC-salt project was looking at several kinds, before landing on the salt composition used in this thesis. The salts decided on are part of the subgroup of halides. Halides have previously been used for pyrolysis of wood and lignin, and especially $ZnCl_2$ has shown promise for depolymerisation of (bio)polymers or larger molecules [11].

2.4.1 ZnCl$_2$

$ZnCl_2$ by itself has a melting point at 290 °C. It is a white crystalline in solid form, and should be noted to be hygroscopic. It is both mildly corrosive and irritating for the skin, and is a environmental hazard. The molecular weight is 136.3 g/mol [12].

2.4.2 KCl

KCl is white or colourless crystalline, and has a melting point 770 °C on its own. It is also hygroscopic, but to a lesser degree than $ZnCl_2$. The molecular 2eight is 74.55 g/mol [13].

2.4.3 NaCl

NaCl is also known as ordinary table salt. On its own it has a melting point of 800.7 °C. It is not notably hygroscopic but can be an irritant if handled incorrectly. The molecular weight is 58.44 g/mol[14].
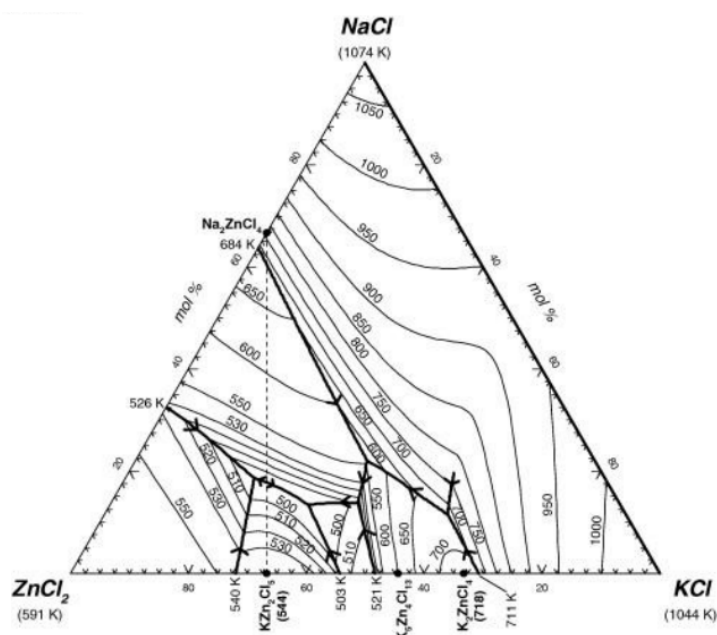
Figure 3: Modelled phase diagram of eutectic points in ZnCl2-KCl-NaCl [3].

2.4.4 NaCl-KCl-ZnCl$_2$

# salt	ZnCl$_2$–KCl–NaCl mol%	Measured melting point at NMBU [°C]
# 1	60-20-20	204.6 $\pm$ 0.41
# 2	59.5-21.9-18.6	201.8 $\pm$ 2.36
# 3	52.9-33.7-13.4	212.2 $\pm$ 0.11
# 4	44.3-41.9-13.8	205.3 $\pm$ 0.7

Table 3: Eutectic salt compositions studied by project partners, with compositions and melting points[3]

The salt mixture have several eutectic points, see figure 3, the one chosen for further study being salt #4. With a theoretical melting point at 229 °C [15] and an experimental one at 199.4 °C tested at NMBU, it fulfils the requirements of the project for a low melting point ideally below 200 °C. The salt composition used in this thesis will be that of salt #4; 44.3-41.9-13.8 mol%, unless otherwise specified. Theoretical electrochemical window is believed to be between [-0.76, 1.36], and table values will be compared to this, the real life molten one will have a different, more narrow range. The table 3 shows the four salts that was considered for the ABC salt project.

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2.5 Potential components in the spent salt

After the hydro-pyrolysis, the salt will be separated from the rest of the components and attempted recycled back for use with fresh feedstock. As the salt comes through the various filtration processes there might be remaining basic elements to remove. It is believed some of these may be removed electrolytically. The electrochemical breaking point of the salt will need to be considered here, if the work or potential applied to the salt exceeds the enthalpy of formation of the salt itself the salt may be damaged. Instead of getting into enthalpies the thesis will focus on voltages or potentials as that is more readily available with the equipment used.

Early guesses from project partners are that the salt will have traces of phosphorus P_{15} and sulphur S_{16}, both of which lie inside the range of [-0.76, 1.36] as determined by $ZnCl_2$. For phosphorus, it appears to not favour the creation of $PH_3(g)$ and free OH^- ions, even if there should be some available water in the salt mixture, making the bottom line of table 4 less likely to occur - but if it does it will likely not be removable electrochemically. The exact composition of the phosphorus is not currently known, or if it will be present at all, it is present in all DNA and some is expected to come out into the salt. Water bound in the salt can additionally create a multitude of challenges that will not be listed here.

Reaction			$E_e°[V]$
$P(white) + 3 H^+ + 3 e$	$\rightleftharpoons$	$PH_3(g)$	-0.063
$P(red) + 3 H^+ + 3 e$	$\rightleftharpoons$	$PH_3(g)$	-0.111
$S + 2 e^-$	$\rightleftharpoons$	S_2^-	-0.47627
$P + 3 H_2O + 3 e$	$\rightleftharpoons$	$PH_3(g) + 3 OH^-$	-0.87

Table 4: Electrode potentials of potassium and sulphur [5].

From table 1 the zink-part of the salt has a E°negative value of -0,76 and compared to the values of potential impurities in table 4 it seems reasonable to assume phosphorus and sulphur can be removed from the salt electrochemically without damaging the salt. Further potential components left over in the salt after current filtration will vary on the feedstock.

2.5.1 Straw

If straw is used as the feedstock one can expect to find several trace minerals, see table 5 for a list of elements found in the straw from wheat production/animal feed. The most prominent elements/minerals potassium and chlorine are already present in the salt, and it is likely some adjustments

of the salt will have to take place to bring the salt back to its original molar composition, or find another way to balance this out. Further down the list is calcium and magnesium, both outside the electrochemical window of the salt; Ca at –3.80 with a single electron or $Ca_2^+ + 2\,e \rightleftharpoons Ca$ at –2.868, and $Mg^+ + e \rightleftharpoons Mg$ –2.70

Mineral	grams/kilo dry straw
Potassium	12 g
Chlorine	6 g
Calcium	4 g
Magnesium	1.1 g
Sulphur	1,1 g
Phosphorus	0.7 g
Sodium	0.17 g
Iron	0.167 g

Table 5: Trace minerals found in wheat straw (Triticum spp.), grams per kilo dry mass [6], sorted in amounts found

The values for sulphur and phosphorus are found in table 4, and attempting to remove them without destroying the spent salts will be a major component of the thesis. Next on the list is sodium, which is a another component found in the salt already. Finally the list contains iron, albeit in very small amount. Depending on the ionic form the iron is found in, the standard potential can vary, e.g. in table 6.

Reaction			$E_e°[V]$
$Fe_2^+ + 2\,e$	$\rightleftharpoons$	Fe	-0.447
$Fe_3^+ + 3\,e$	$\rightleftharpoons$	Fe	-0.037
$Fe_3^+ + e$	$\rightleftharpoons$	Fe_2^+	0.771

Table 6: Various ionic forms iron can be found and their standard potential[5].

All of these would theoretically be possible to remove. Source material of the straw content will have further listings with smaller prevalence[6].
Second, project partners report the straw samples contains "Most abundant elements (as per our experimental characterisation): Si (0.95 wt.%), K (0.91 wt.%), Cl (0.51 wt.%) and Ca (0.27 wt.%)"[16]. Additional elements are listed in table 7. The new element here, Silicon, is expected to be on the form of quartz,SiO_2[16], and appears to be a candidate for electrolytic removal.

$SiO_2 + 4H^+ + 4e \rightleftharpoons Si + 2H_2O = 0.857$ would be the reaction in an aqueous, alkaline solution, where salt #4 is not aqueous. Nevertheless an experiment will be run to see if it is soluble and if so, electrochemically removable. Free Si should be removable, but if it is bound it will depend on the pairing and circumstances.

2.5.2 Wood - pine wood

Project partners similarly reports Cl (0.14 wt.%), Ca (0.11 wt.%), K (0.03 wt.%), Si (0.0266 wt.%) and Mg (0.023 wt.%) proposed as the expected constituents of pine wood. There has also been mentions of CaCl2 and CaCO3 as potential leftovers in the salt after initial filtering[16]. Table 7 has a list over elements found in wood ashes used in the project, with % per weight in the ash.

Element	Wheat Straw Ash(%)	Wood Ash(%)
Al	0.68	0.37
Ca	24.26	5.67
Cl	0.10	4.00
Fe	4.08	0.33
K	5.46	18.37
Mg	5.42	0.86
Mn	2.75	0.046
Na	0.96	0.45
P	0.83	0.42
S	2.06	1.37
Si	0.95	9.81
Ti	0.28	0.014

Table 7: Straw and wood ashes minerals [3]

2.5.3 Lignin and Lignoboost

Lignin sourced from paper and pulp making has been considered as a feedstock for the pyrolysis. Lignin is likely to contain sulphur as it is the type commercialized as of yet (ligno-sulphonates and Kraft lignin) where sulphur is used to remove the lignin from the rest of the pulp. Project analysis shows the average content of the LignoBoost lignin is 1.5-3.5 wt% dry biomass. The sulphur content has a 29% inorganic, 1 % elemental relative distribution with the remaining being organically bound. Furthermore it is specified that the inorganic is mostly present as SO_4. It is also expected

that most of this can be washed out, while the organically bound S poses a bigger problem[17]. As a study it would be of interest to see if this organic bound S can be electrochemically removed, if salt containing this can be obtained. As a more treated product there may be fewer impurities in the lignin, but what these are is not known.

2.6 Voltammetry

2.6.1 Cyclic voltammetry

Cyclic voltammetry (CV) is used to investigate the behaviour of the salt electrochemically. The reference electrode will stay at a set 0 potential while the working electrode will gradually increase to a set potential above, cycle down again to 0 and possibly below, and go back to 0. This can be repeated several times as desired. The potential sweep for salt #4 will be mostly limited between 0 and the breakdown voltage, which will be defined as the voltage where the constituents of the salt break apart and we get deposit of zink on the zink electrode or chlorine gas evolution, both of these individually indicating the salt is no longer molten salt, but ionic soup. The equation

$$E = E_0 + \nu t \tag{2}$$

shows the relation between the potential E, the scan rate ν and the time t. The scan rate will play a part at determining how and what is discovered. The sensitivity of the current changes vs potential goes up as the scan rate goes up, as the higher potentials will make the target oxidize/reduce more noticeably. The salt will be unstirred, so only diffusive mass transport will be at play besides the migration from the potential difference directly. Fick's law relates the distance x from the electrode, the concentration c, time t, and diffusion coefficient D, the diffusion and concentration also have a physical diameter D subscript:

$$\left[\frac{\partial c_A}{\partial t}\right] = D_A * \left[\frac{\partial^2 c_A}{\partial x^2}\right] \tag{3}$$

The sensitivity is thus reliant on there being a sufficient amount of available target near the electrodes. The Nernst equation relates the reduction potential to the activity (available reductive/oxidative agents), the standard electrode potential and temperature so:

$$E = E_o + \frac{RT}{nF} ln \frac{a_{(Ox)}}{a_{(Red)}} \tag{4}$$

with R being the gas constant[J/K mol], T being the temperature [K], n the amount of electrons transferred and F Faraday constant [C/mol]. The activity will often be approximated by concentration. Cyclic voltammetry is normally employed to research an analyte in a solution or some molecules present on the electrodes, in this thesis it is however going to be used to try and find electrochemical traces or marks from impurities in the molten salt.

Figure 4 (b) shows the very basic shape of a CV diagram, and the numbers are meant as indicators referencing the same points in time as the diagram in (a). As the potential increases the current begins ramping up as the oxidation takes place, this continues past the peak current 2 into the "tip" of the voltammogram, where the voltage is still increasing and the oxidation is still ongoing until the 3, where the voltage is lowered, reversing the scan and making the reduction start.

(a) Potential E versus time E

(b) i vs E, showing the characteristic duck shape
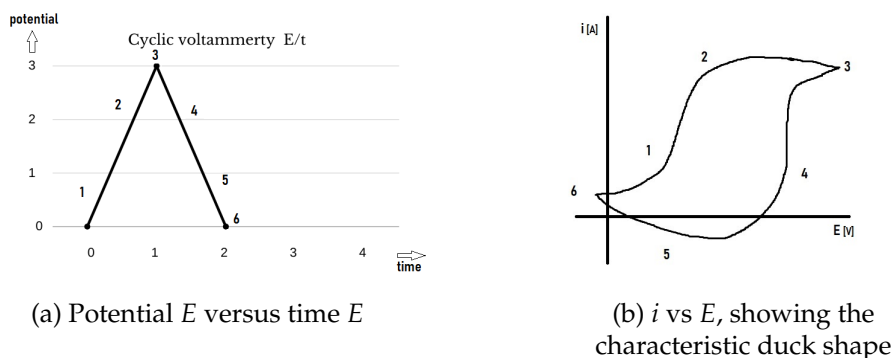
Figure 4: Time scale noted in on a plot of i vs V in a cyclic voltammogram. Time scale with matching points of an i vs E diagram

2.6.2 Staircase cyclic voltammetry

For a proper staircase voltammetry the sweep rate is determined by the ratio of step amplitude and period,

$$\frac{dE}{dT} = v = \frac{\Delta E}{\tau} \tag{5}$$

CV and Staircase CV should for the same sweep rates create very similar results. Measuring the current at the end of each potential change reduces the capacitive charging current. There will be no high sweep rates used in this thesis. In a staircase voltammetry the potential between two electrodes will be increased gradually in a "staircase" fashion. The reference electrode will be kept constant, while the working electrode will have its potential raised in increments, a certain volts per second increase, and after a time for stabilising be raised again. A third electrode (the reference) is kept near - but not in contact with - the counter electrode. These two keep the balance between the charges in and out of the salt against the working electrode in order.

2.6.3 Linear sweep voltammetry

The linear sweep voltammetry (LSV) available in the NOVA software uses a staircase approximation for the sweeping increase of the potential difference between the electrodes. It will be used as a method for identifying unknown (or known) elements in the salt melt. The eventual oxidation or reduction of any species will be shown as peaks or troughs in the graph at the relevant potential range. This will not itself be enough to identify what is actually found, but will indicate that something is found. Figure 5 shows what this might look like.
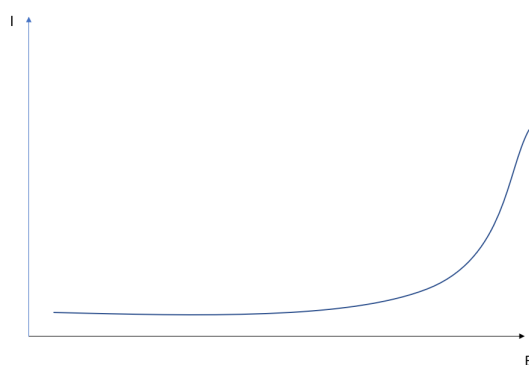
(a) LSV of clean salt
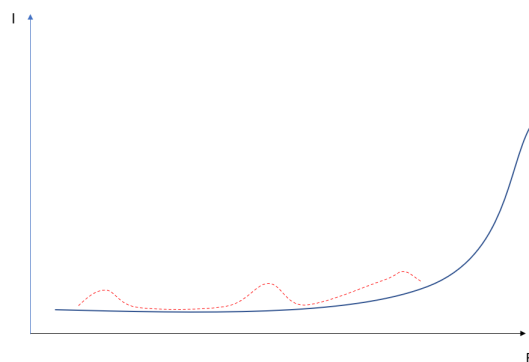
(b) LSV of salt with impurities might move the
scan into areas along the red dotted line

Figure 5: The ideal scenario during a linear sweep voltammetry, with impurities found like marked in red-dotted line. Drawn with inspiration from a miniature-lecture by Espen Olsen, NMBU

3 Method

3.1 Purpose

The purpose of the experiments in this section is at first to establish electrochemical limits of the salt, e.g. the breakdown point needs to be established before further experiments are carried out. A description of the experimental setup is covered, this will describe the conditions for the electrochemical parts. SiO_2 is attempted dissolved and potentially removed from the salt. Furthermore an attempt is made to remove straw ashes from the salt, and the same attempt is made with lignin ashes in the salt.

3.2 Experimental setup

3.2.1 The salt

The salt is kept in crystalline form in a heating cabinet at close to 200 °C for at least 24h before use. This is done to keep moisture out of the salts. The salts are then taken out of the cabinet one by one and added to a beaker, in the order of NaCl, then KCl, then $ZnCl_2$. The beaker is placed on a scale in open air, and while the salt is transferred as soon as possible it is likely some moisture will get absorbed due to the hygroscopic nature of KCl and especially $ZnCl_2$. $ZnCl_2$ is prone to form lumps and having a mortar to crush these are recommended. The salts are then stirred with a metal spoon before being transferred to the graphite crucible and placed into the furnace. The salts are measured out by weight and as such a conversion from mol % to weight % has been done for all the salts and salt combinations used in the thesis.

3.2.2 The furnace

The salt is melted and kept at desired temperature in the steel furnace shown in figure 6. The furnace itself is moved into a fume cupboard. It has a cylinder shape, heated from the sides. Inside the furnace there is a tube with sand in the bottom to absorb any stray salt without damaging the furnace itself. Inside the tube there is an additional piece of insulation to raise the crucible up by 5 cm so that its bottom will intercept the warmest area of the furnace for most effective heating and additionally giving easier access for electrodes and thermocouples as needed. The inside of the furnace with electrodes can be viewed in figure 9. Figure 7

Figure 6: The furnace used for heating the salt, one can see the K-thermocouple in green to the bottom right, as well as the red S-thermocouple more in the back
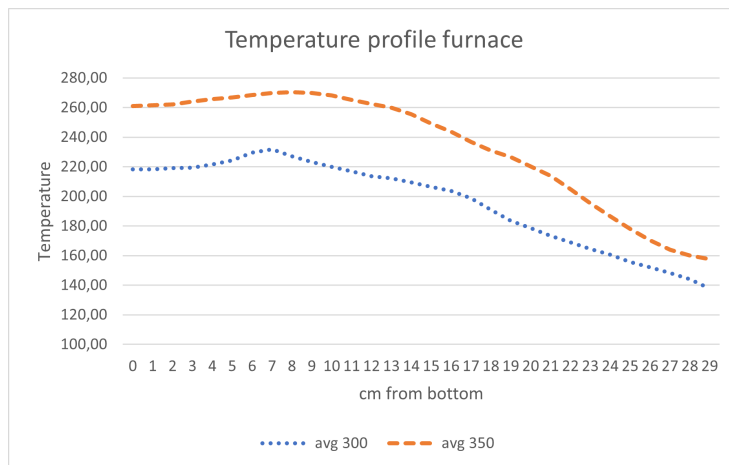

Figure 7: The temperature profile for the furnace at different temperatures used in the experiments

shows the temperature profile for the furnace as measured manually in the lab. The tube will have a source of Argon expelling other gasses from entering, keeping moisture and oxygen away from the salt. The furnace is fitted with a S-type thermocouple to measure temperature inside the salt as needed. The crucible is placed inside the tube once the salt had been added to it and then the heat is turned on. It melts in about an hour with the furnace set to 350 °C, the inner temperature of the salt going up to approximately 270 °C. While the salt is melting, the inner thermocouple and electrodes will be added.

3.2.3 Electrode setup

A zink rod is placed in the middle of the salt and the 0 V counter electrode(CE) is applied, the zink serving as the cathode. In the salt a K-thermocouple is added for the first experiments, section 3.4, logging the temperature data. The graphite crucible has an iron rod attached that will connect the other electrode, the working electrode (WE) to the graphite, which acts as the anode. An extra electrode (also zink) will be added in close proximity to the main zink rod to act as a reference electrode (RE) for the experiments covering removal of ashes. The electrodes are an extension of the AUTOLAB equipment, a PGSTAT302N. Figure 8 shows the the equipment. The electrode setup is shown in figure 9. Not pictured is the green ground electrode, which is placed on a nearby metal pole.

3.2.4 Chemicals used

Table 8 gives a list over chemicals used in the thesis.

Item	CAS	Lot #	Quality	Supplier
	EC	Prod #	% purity	
Ar(g)	231-147-0	100324	99.99	AGA AS
$ZnCl_2$(s)	7646-85-7		puriss,	Sigma
			98.5-100.5	Aldrich
KCl(s)	7447-40-7		puriss,	Sigma
			99.5-100.5	Aldrich
NaCl(s)	7647-14-5		puriss, ACS	Sigma
			$\geq$99.0	Aldrich
SiO_2(s)	14808-60-7	20D034111		VWR
	238-878-4	27461.298	99 %	

Table 8: Chemicals used in the experimental work
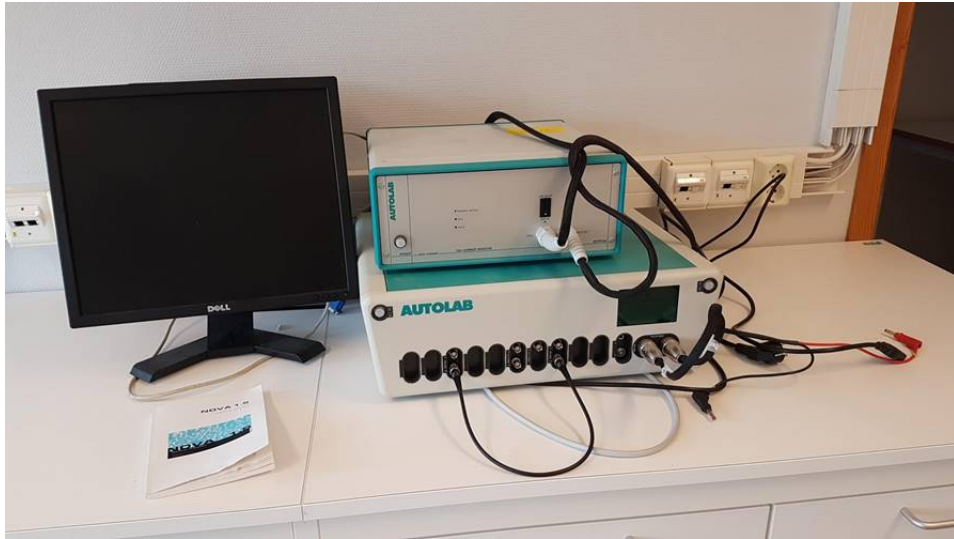
(a) Autolab with extra unused module on top
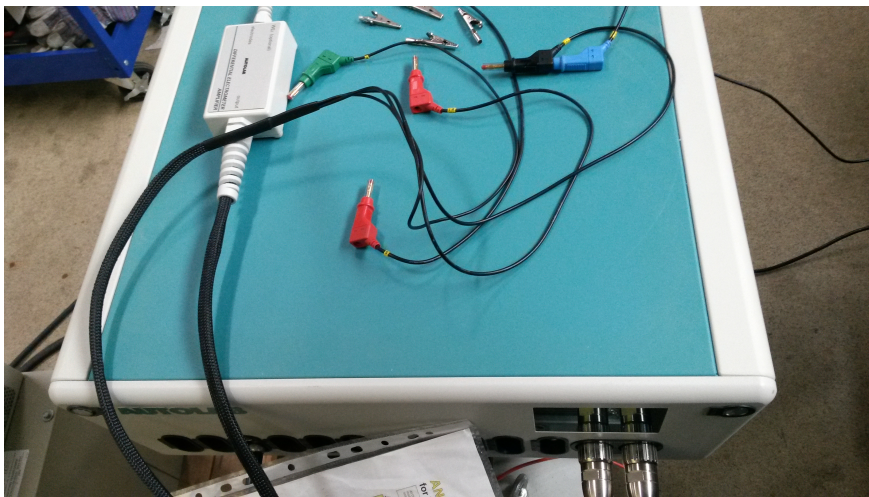
(b) Electrodes on the autolab

Figure 8: The autolab used in the experiment and its electrodes

Figure 9: The blue is reference-electrode (RE), black is counter-electrode (CE), and the red is working electrode (WE) coupled with sensing (S or WS)

3.3 NOVA

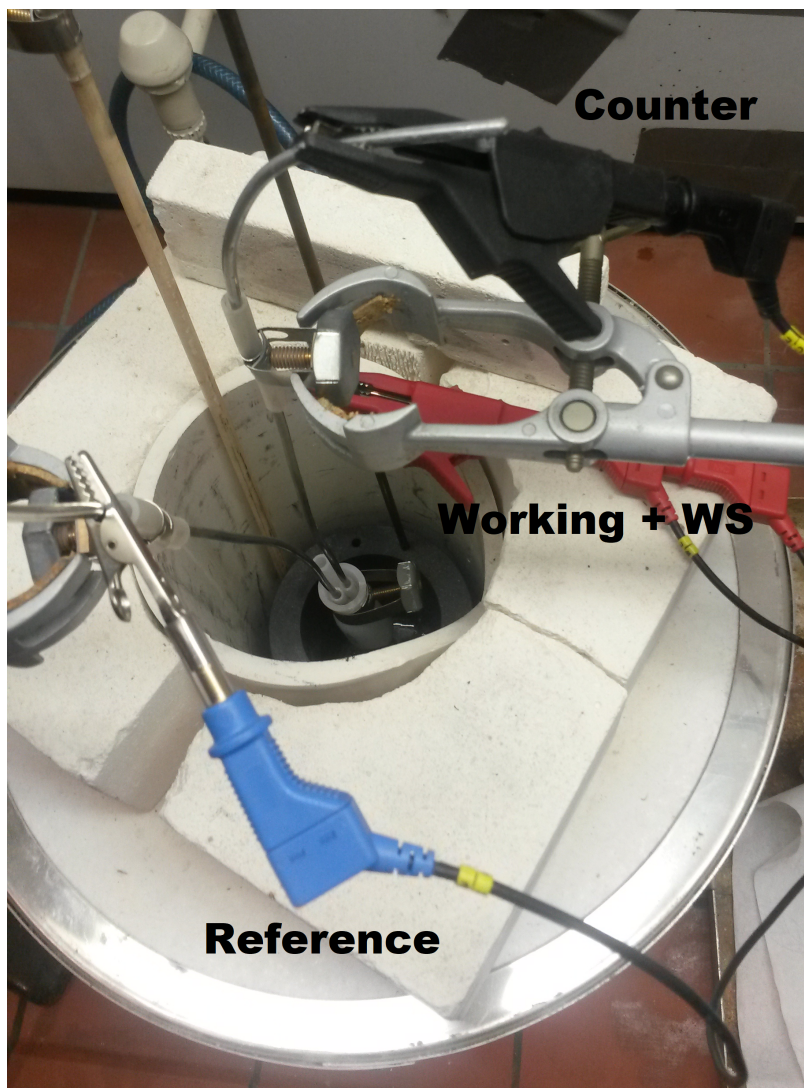By the use of an AUTOLAB instrument (PGSTAT302N) and NOVA 2.1.4 software the current or voltage between the electrodes can be measured and specific voltages or currents applied, while scans are performed. For this thesis the AUTOLAB will be set to potentiostatic mode, with a few different scan setups running. One can use the scan setups from the default library and just change the parameters in the Properties tab to suit ones preference like in figures 10, 11. There is a further option of building the
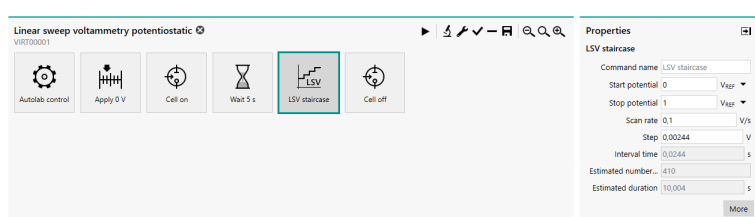
Figure 10: Default library - Linear sweep voltammetry (LSV)
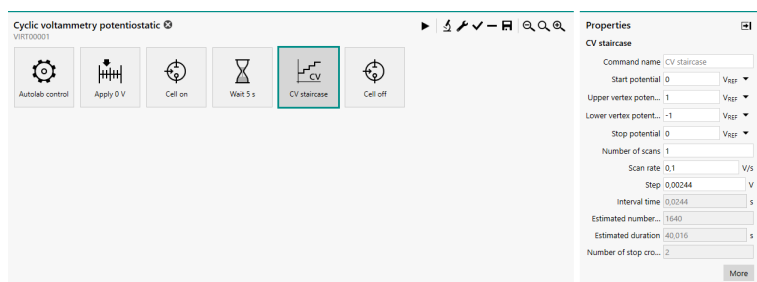
Figure 11: Default library - Cyclic voltammetry (CV)

desired procedures as seen in figure 12, where a Linear Sweep Voltammetry staircase (LSV) is followed by a Cyclic Voltammetry staircase (CV). Additionally each measurement can have data processing applied to be done ahead of time via the microscope symbol near the "run" button. Processing can also be done after the fact, the Data page showing after experiments are done allows various data handling. Figure 13 shows an example of an LSV data page after the experiment has been ran. The derivative was already coded in to be done ahead of time, while others are added later. The NOVA software is able to run Cyclic Voltammetry linear scan instead of the staircase version, however that would have required an additional module on the AUTOLAB instrument and has therefore not been done.

Figure 12: Building a procedure to cover whichever measurements and data handling are desired

Figure 13: Example of a procedure ran in NOVA with data and data analysis graphs at the bottom

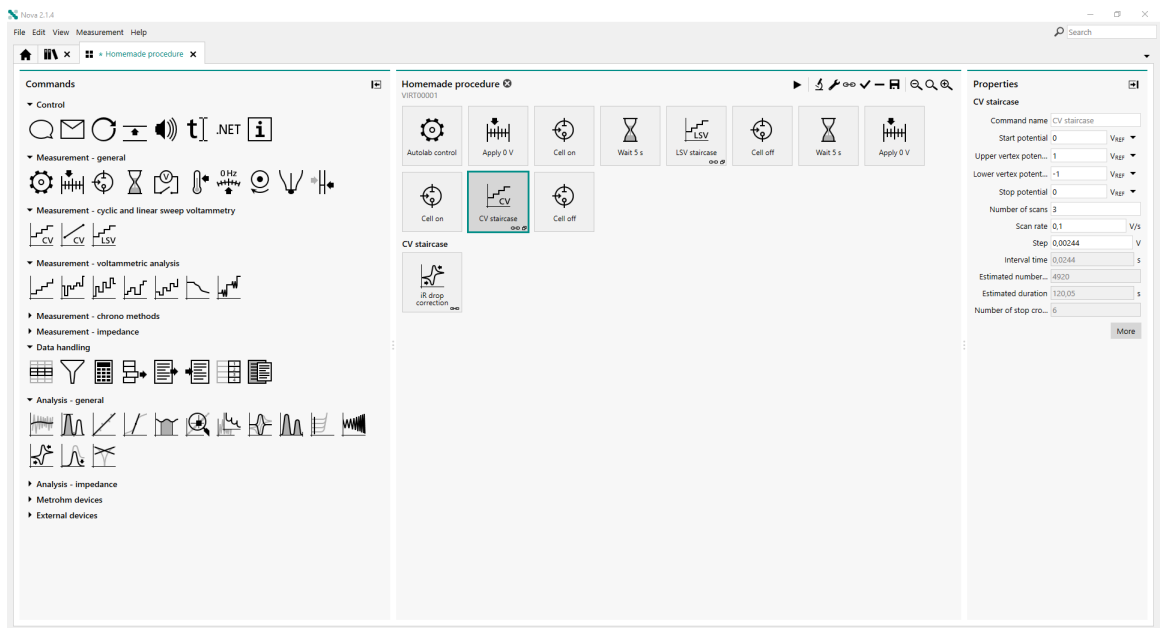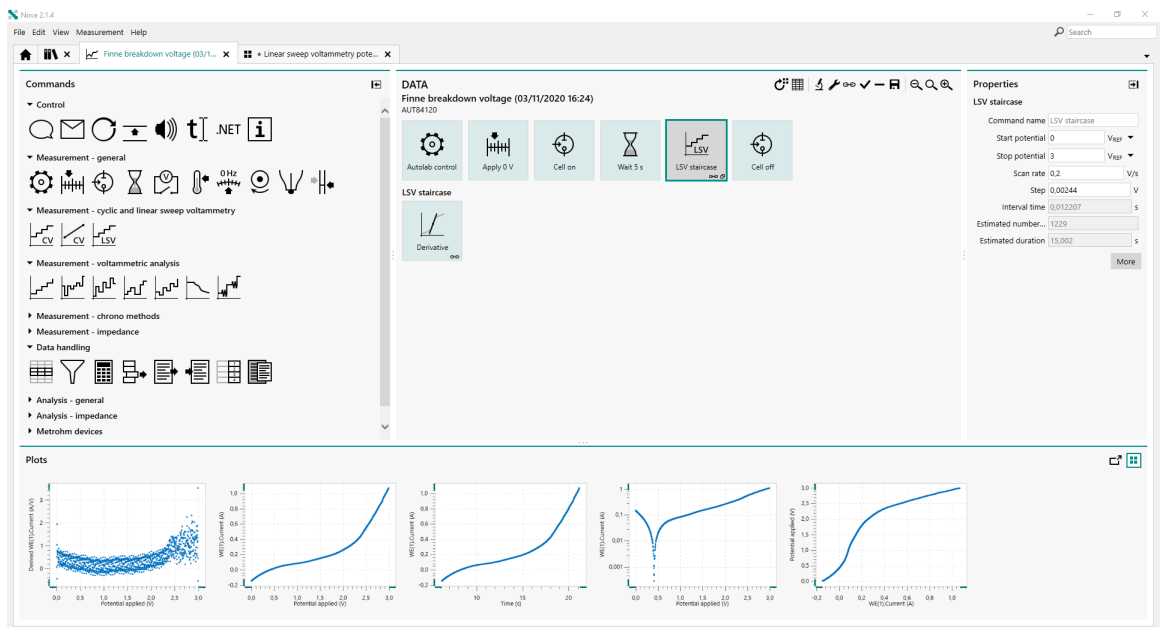## 3.4 Confirming electrochemical limits

From section 2.2 the electrochemical range was theorised to be [-0.76, 1.36], a span of 2.12 V. The article by Nitta et.al. meanwhile establishes a range of 1.7 V from experimental data on molten salts. These can be therefore assumed to be the starting limits of exploration - starting below 1.7 and ramping up, while watching to see what happens to the salt electrochemically. The NOVA procedure "Linear sweep voltammetry - staircase" was used for all experiments in this section, the example in figure 13 being one of the procedures made and used for electrochemical limits. The salt is melted and handled according to the setup described in section 3.2.2.

3.4.1 Salt #1

To establish the electrochemical limits of the salt the experiment will initially be carried out on salt with the more known Salt # 1 composition, 60-20-20 mol% $ZnCl_2 - KCl - NaCl$. 100 g of Salt # 1 is measured out, and the parameters set in NOVA was a scan rate of 0.2 V/s, and a start potential at 0, an end potential of 3 V, in the LSV preset program.

3.4.2 Salt #4

The LSV procedure was carried out on 100 g of salt # 4 using two different set of scan rates, 0.05 V/s and 0.2 V/s, and the end potential ended up being set at 2.5 V. Salt # 4 was ABC salt project current chosen salt, and it has a composition of 44.3-41.9-13.8 mol%, it is not known if or how this affects the breakdown limit.

3.5 Creation of straw and lignin ashes

Samples of the straw and lignin used in the project was obtained. The numerical composition of the lignin is not exactly the same as the reference material, the amounts of each component might vary. To create ashes without open flames a procedure intended to measure ash content was used[18]. The muffle furnace used has a ramping programs and the steps used were taken, with modification, from section 10.4.2 in the procedure:

- Measure out sample amounts in porcelain beakers

- Put beakers in muffle furnace

- Ramp from room temperature to 105°C. Hold at 105°C for 15 minutes

- Ramp to 250°C over 15 minutes. Hold at 250 °C for 30 minutes

- Ramp to 575°C over 17 minutes. Hold at 575°C for 180 minutes

- Allow temperature to drop to 105°C and hold as long as necessary.

- Take ashes out and let cool

- Transfer content to storage in plastic vials, measuring the weight of content

3.6 Removal of SiO$_2$

As an attempt to remove SiO$_2$ it is first interesting to see if this dissolves in the setup the salt and biomass will be in at all. 50 g of salt #4 was put to melt in a glass beaker. There was no argon or electrodes supplied for the first part, the glass beaker was placed on a Stuart Heat-Stir device in a fume cupboard. Aluminium foil was wrapped around the glass beaker in an attempt to conserve heat, the temperature was not measured but is assumed to be between melting point and 300 °C, due to the heating devices limitations and heat loss to the surroundings. Once the salt is

Figure 14: A picture of the SiO$_2$ before being added to the salt

molten, a magnetic stirrer is added and a picture is taken. 5.00 g of SiO$_2$ is added to the liquid salt and the stirrer is turned on. The salt is kept heated and insulated during this and the stirring is turned on. The attempt to see if this dissolves or not in the salt at all - if there are bubbles or the sand goes invisible further experiments will be carried out electrochemically, if the sand stays intact it is assumed the salt is too acidic to dissolve the SiO$_2$, or the temperature is too low. According to the packaging of the SiO$_2$ only about 1 % should dissolve in an acidic solution. The SiO$_2$ was purchased at 99 % purity. The salt was checked on again after 15 minutes of stirring and constant heat, and a picture is taken.

3.7 Removal of straw ashes

The intent is to recreate the salt as closely as possible to the salt that will actually be used by ABC-salts process. This was done by burning straw into ashes via the procedure in section 3.5 and add the ashes to the salt for electrochemical testing. Samples of the straw used in the project was obtained from project partners and as such should match the elemental content as described in table 7. For 50 g of salt 0.08 g of straw ashes were added, figure 15 shows the ashes added to the salt. This is rapidly mixed

Figure 15: Picture of the straw in the salt

together and added to the crucible, before the salt is heated up. The procedure setup in 3.2.2 is followed. In addition to the one zink electrode, the counter electrode (CE), another zink electrode is added in close proximity, as a reference electrode. The reference electrode (RE) does not have any voltages applies, it merely acts as a neutral reference point. In NOVA two different voltammetric measurement procedures are used, namely the Cyclic Voltammetry staircase(CV) and the Linear Sweep Voltammetry staircase(LSV). For both the CV and LSV scans, the scan rate *nu* were set to between 0.02 - 0.3 V/s. For the CV, the potential was set between 0 and 2 V. The LSV had a few different end potentials set, from 0 to 2 or 2.4 V.

3.8   Removal of lignin ashes

In an attempt to recreate the salt with lignin used as the biomass, ashes of lignin was created and added to the salt. The ashes were made according to the procedure in section 3.5, and the second round of ashes were used, from table 9. The lignin ash added up to 0.13 g of lignin ashes, this was added to 50 g of salt #4.

Figure 16: Picture of the lignin alongside the salt

The lignin is stirred into the salt and all is transferred to the graphite crucible and heated up. The setup is the same as described in section 3.5. Additionally the third reference electrode (RE) is added. In NOVA, both the Cyclic Voltammetry and the Linear Sweep Voltammetry was set around 0.2-0.4 V/s and a potential cap of 2.4 V. All scans are done in a staircase fashion and the idea is to look for spikes or troughs in the data material that can indicate a current flow caused by the ionization of trace elements in the salt.

4 Results/discussion

4.1 Establishing electrochemical limits

The electrochemical limits were studied using NOVAs Linear Sweep Voltammogram - procedure, which gives a staircase profile ramping up from start to finish. Furthermore the graphs were derived to try to pinpoint the area where change happen.

4.1.1 Salt # 1

To establish an electrochemical baseline for the salt and get an idea of what the salt will look like in pure form the experiment of breaking down salt # 1 was carried out. Figure 17 shows what the salt looks like with a gradual ramping up of potential difference between the electrodes, with a scan rate of 0.2 V/s. The graph shows a slow increase in current as the volt-
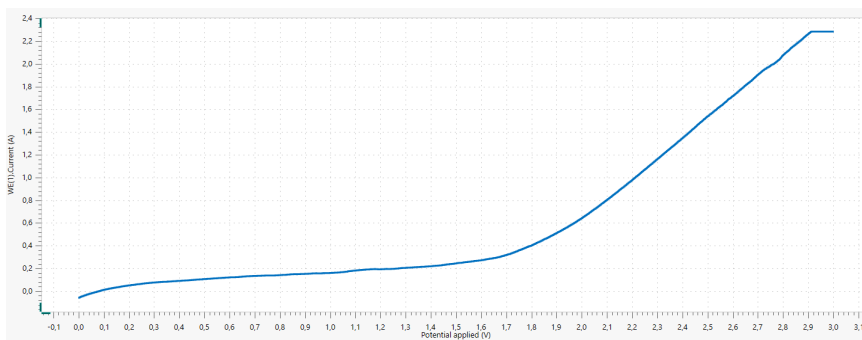
Figure 17: Salt # 1 run through the LSV staircase, ν at 0.2 V/s

age is ramped up, with a clear change of increase by 1.6-1.8 V. The figure was derived using built in derivative function in the software. Figure 18 shows the derived graph of figure 17, with the salt both having a change in the 1.6-1.7 area and also has a more pronounced scatter effect from 2.4 V onward.

The marked increase in current has been interpreted as the point where the salt starts breaking down, as the available ions would conduct more current. The scan shown here was not the first scan done on the salt and it was the first experiment conducted. A lot of equipment testing and scans were run on a separate instance of the salt before this scan was done on nearly fresh salt. Figure 18 does show some spikes and changes in the salt early on before the 1.7 mark, this might be due to external impurities in the salt or ions available from previous scans might have left some free ions in
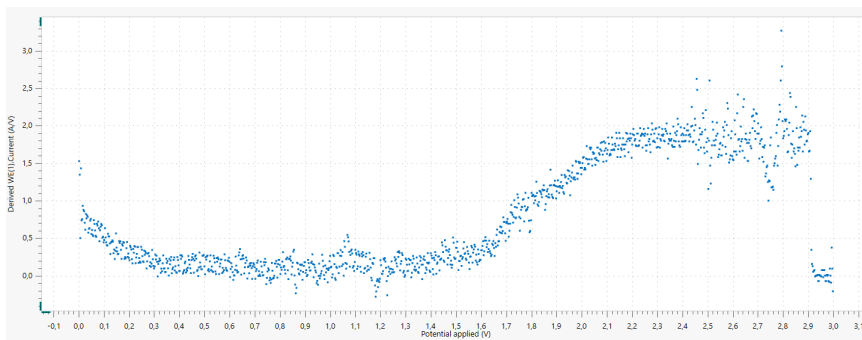
Figure 18: Salt # 1, derived graph from figure 17

the salt. The current range of 2.4 A should also be noted, this is a very large current and most other graphs shown later will have a more narrow range. Furthermore, it should be noted that nowhere else was there this amount of deviation/scattering and large currents, and its unclear just how reliable this is. There might be some start-up errors as its the first experiment done, especially concerning the voltage limits being set too high by accident or starting the programs wrong. There might also be issues related to the graphite crucibles as they were completely new here. Furthermore human error in preparing the salt or other equipment might be at play.

4.1.2 Salt #4

In trying to find the breakdown voltage of salt #4 the linear sweep voltammetry staircase (LSV) procedure was used, and the graphs produced was derived with respect to the voltage. The four graphs covers two different scan rates, nu = 0.2 V/s and nu = 0.05 V/s. The graphs are appearing to have the same shape, but the current flow through the faster scan one is twice as large. The reason for this can be a few different things, first of all the slow scan was done first and it might have left residual ions in the salt. Secondly, the rapid change in potential might have made the salt more unstable and not left enough time for the apparatus to get a proper reading of the current, but rather a snap-shotted current that kept increasing as the potential between the electrodes increased. From figures 19 and 21 there is no easily discernible point where the current changes a lot - it gradually increases. While there is a certain amount of curve bending the one in figure 17 is a lot clearer.

Looking at the two derived figures 20 and 22 there are no large deviations from the straight line before the 2.4 and 1.95 V mark respectively.
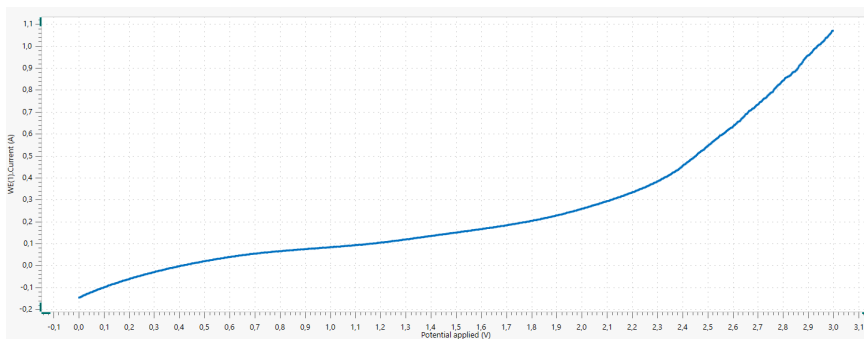
35

Figure 19: Salt # 4 run through the LSV staircase, ν at 0.2 V/s
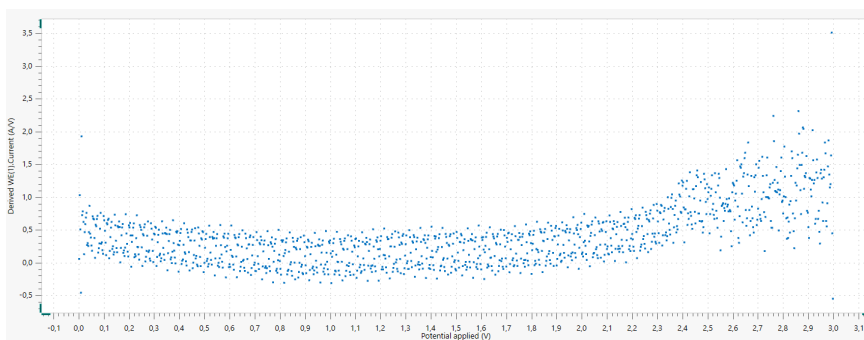

Figure 20: The derived of figure 19,ν at 0.2 V/s
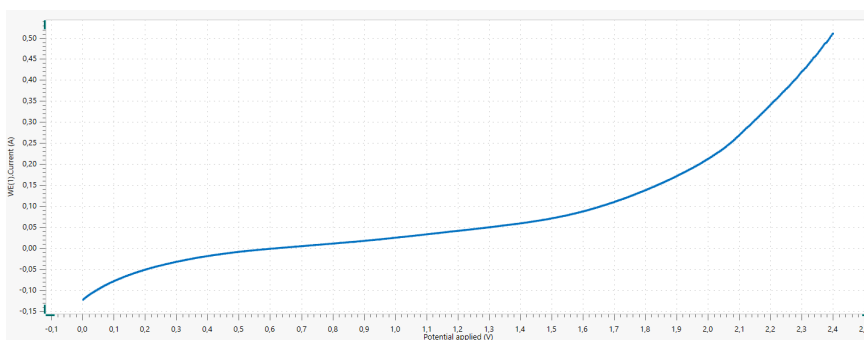

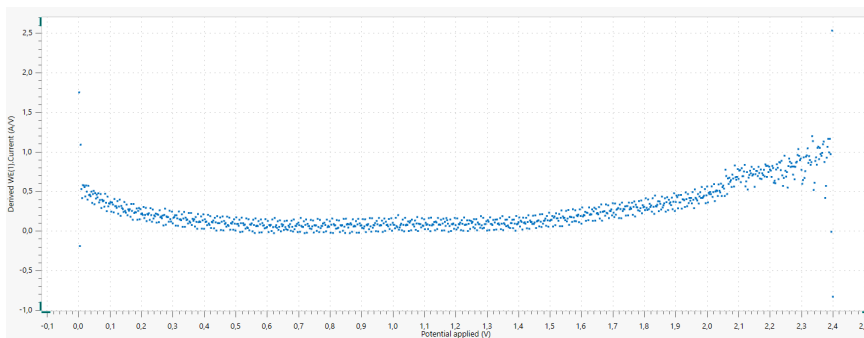Figure 21: Salt # 4 run through the LSV staircase, ν at 0.05 V/s

Figure 22: The derived of figure 22, ν at 0.05 V/s

Both of those are above the limits established for salt #1, and the presumed theoretical limit of 2.12 V is also nearby. Considering the limiting factor of the electrochemical window for either salt is the $ZnCl_2$ it is not unreasonable that the salt with less mol% of $ZnCl_2$ to have a higher tolerance of potential difference across the salt. The points on the derived figures 20 and 22 where the dots starts scatter will be seen as the point where enough of the $ZnCl_2 - KCl - NaCl$ has broken down that a large and unreliable current starts flowing. There is likely to be a point before this point where the salt has broken down, but the experiments done is not sufficient at pointing out where this is. An estimate will be set somewhere between 1.7 and 2.12 nevertheless, for further experiments. The 2.12 is the theoretical limit, and it is likely to be an overestimation. The 1.7 is sat as a conservative estimate from literature[10] and not having any counter-indications in the scans.

4.2 Removal of SiO$_2$

Salt # 4 was heated in a clear beaker and once molten the SiO$_2$ was added, and attempted stirred for 15 minutes. No changes are observed over the time period, with the colour staying the same, the magnetic stirrer kept making scraping noises and no bubbles were seen emerging from the salt. Images of the salt before and after addition of SiO$_2$ is found in Figure 23. There was no additional electrochemical attempts on the salt. Reasons for the SiO$_2$ not dissolving might be related to temperature. The temperature could not be determined more closely as the equipment was in use in another experiment and is merely estimated to be between 200-300 °C due to the salt melting and the maximum heat obtained on the heating device in an earlier experiment and carries significant uncertainty. Additionally the salt might be acidic, or any other number of reasons. However, if SiO$_2$ is present as sand, it will likely be possible to filter out mechanically and pose less of an issue for ABC-salts process. If Si$_2^-$ is indeed electrochem-

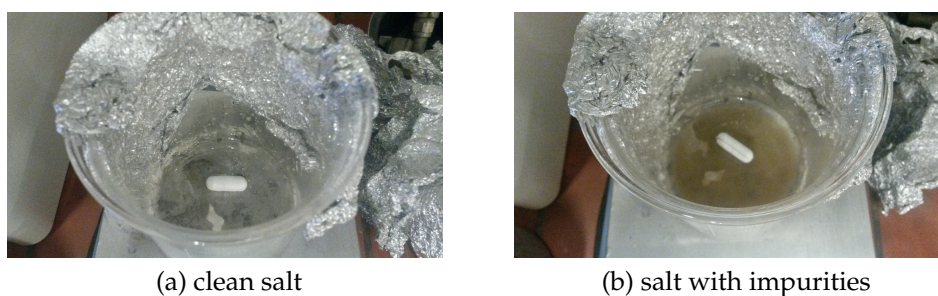|	
(a) clean salt	(b) salt with impurities

Figure 23: Salt #4 with and without SiO$_2$ added

ically removable has however not been determined and the hypothesis of it being removable stands unresolved.

4.3 Creation of straw and lignin ashes

Using the ramping muffle program detailed in subsection 3.5, the following amount of ashes were created. Table 9 will show comparison weight of before and after ash creation, and serves as a reference table for how much ashes/straw/lignin experiments are carried out on.

First round:	Weight before	Weight after
Straw	2.00 g	0.08 g
Straw	10.00 g	0.53 g
Lignin	2.00 g	<0.01 g
Lignin	10.00 g	0.06 g
Second round:		
Lignin	20.00 g	0.06 g
Lignin	20.00 g	0.07 g

Table 9: Mass of ashes created from straw and lignin

Figure 24 shows the first round of ashes made. The lignin ashes appeared as a beige powder. The straw ashes came out as back/white small strips of ashes. The initial 10 g lignin and 10 g straw appeared to form not only ashes but partially un-combusted particles, and were not used in any experiments.

Figure 24: The leftover ashes of(left to right): 2g straw, 10g straw, 2g lignin, 10 g lignin

4.4 Removal of straw ashes from salt

Straw ashes were created from the same straw as used by the ABC-project for content determination, as listed in table 7. The straw were readied and added to the salt as described in 3.7. The scans are done looking to find electrochemical signatures of the various elements. Better results might have been obtained had the salt been heated up, kept at a smaller voltage range and then the straw ashes been stirred in later, with scans redone for comparison.

4.4.1 CV

The first figure, figure 25 shows a Cyclic Voltammetry staircase (CV) plot of the salt with straw ashes in it. Initially there are a few points of interest, figure 26 shows the line part more zoomed in. The scan starts along the top line with increasing current, goes up the underside of the "seal" and goes down again on the top, with the line tracing on the way down having scatter around 0.90 - 0.75, then again at 0.30 and around the end from 0.10 down to 0. From 0 V up to the end point at 2 V the salt is having an increase in current, indicating a loss of electrons at the anode and an oxidation is taking place. The end potential of 2 V is set too high from where the salt is expected to break down(as per 4.1.2) and there is oxidation of $ZnCl_2$ taking place, ripping the salt apart and potentially also having some gas formation. This is the peak cathodic current happening on the graphite crucible. The scatter effects seen around the upper voltage end should be seen as the salt indeed breaking apart, and as the voltage goes down again the salt recombines, or is being reduced back to $ZnCl_2$. It is thought that the area with scatter again at 0.90->0.75 is the fully formed Cl_2g recombining with Zn and not some actual reaction reduction of any element from the ashes. There could also be a reaction with an element that is masked by the salt recombining, but the reaction is only seen tracing down towards the zink again.

   The small dip at 0.30-0.25 might be the result of something in the ashes reacting to the potential applied. Bringing back the "range of [-0.76, 1.36] V" from section 2.2 the zink-anode being 0.3 V away would correspond to around -0.4 V $\pm$ 0.2 V, making sulphate or iron both potential elements, in addition to elements not considered here at all. There is uncertainty if this method for estimating range can even be applied directly. This is highly speculative however, it might be nothing, or it might be the final chlorine recombining. This method of electrochemistry tells not what is found and further work would be of interest. The reaction does only happen on the
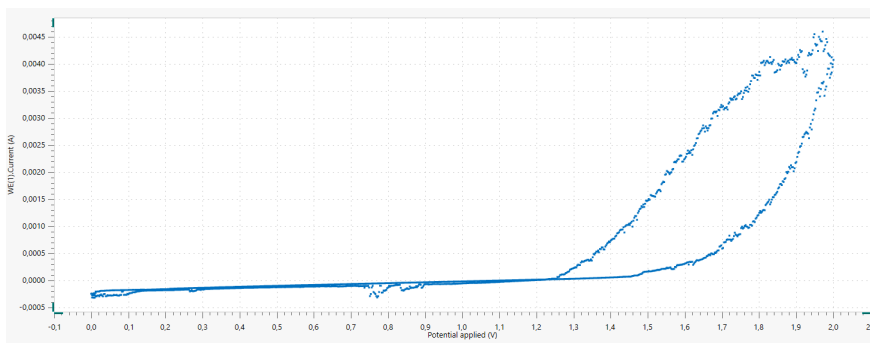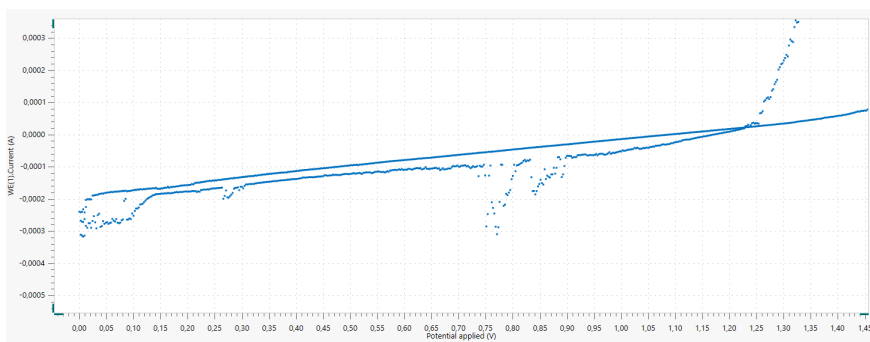
Figure 25: CV at a 0.05 V/s scan rate

Figure 26: A zoom-in of the beginning and end of the scan depicted in figure 25

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way back from peak voltage and not too much emphasis should be placed on this dip.

The rounded tip towards 0 V would be the anodic peak current, and some sort of reaction is happening at the zink anode at the time. It is again a little unclear just what, it might be chloride reacting to the zink or an element with a negative reduction potential near that of zink. The figures in this part is shown for the 0.05 V/s scan rate, other figured at faster scan rates had similar shapes and as such only this is shown as an example.

4.4.2 LSV

The figures here will show Linear Sweep Voltammetry staircase (LSV) scans of the salt with straw ashes added. Figures 27 and 29 shows the graph at different scan rates. The intent was to look for any deviations from the smooth current goes up as potential difference goes up. None is seen directly. The graphs are derived with the NOVA derivative function, mapping the current/potential against potential. No peaks are seen in any of these figures apart from the end point, which do vary so that the slower the scan rate the lower the potential is before the scatter effect starts. The figures in question are 28 and 30.
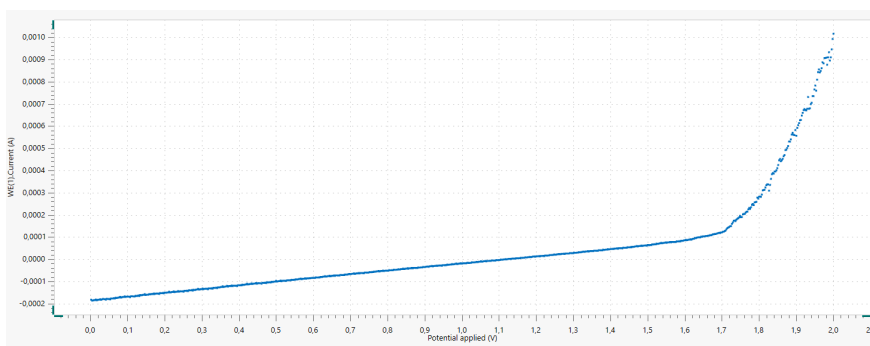

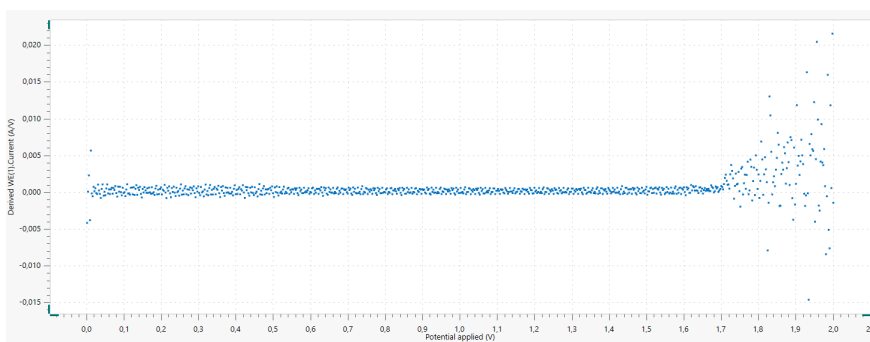Figure 27: LSV at a scan rate of 0.3 V/s

Figure 28: The derived function of figure 27

The few points at the start of each graph is being overlooked as calibration errors. The reasoning behind the earlier scatter on the slower scan rates are somewhat consistent with what is found in 4.1.2 where the slower scan rate allows the diffusion and migration of the ions to take place before the measurement is taken at the end of each step. As a staircase approximation the slower scan might be more true to how the true linear scan
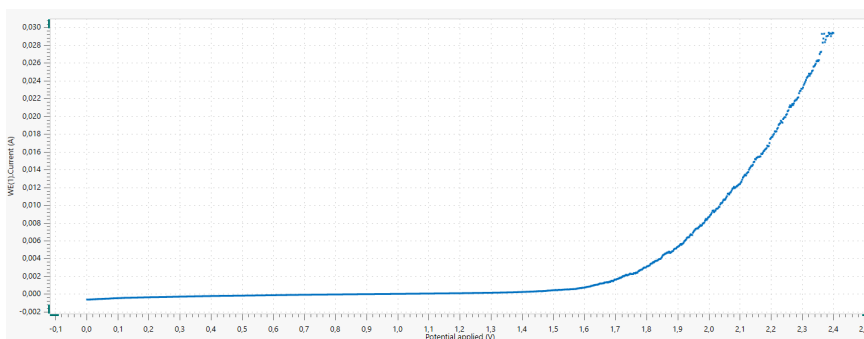
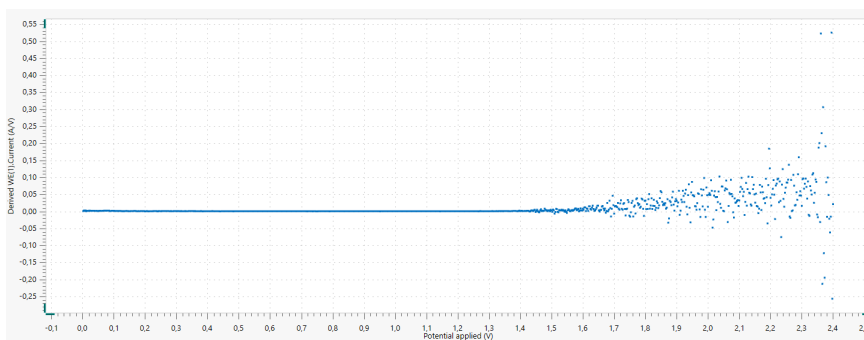Figure 29: LSV at a scan rate of 0.02 V/s

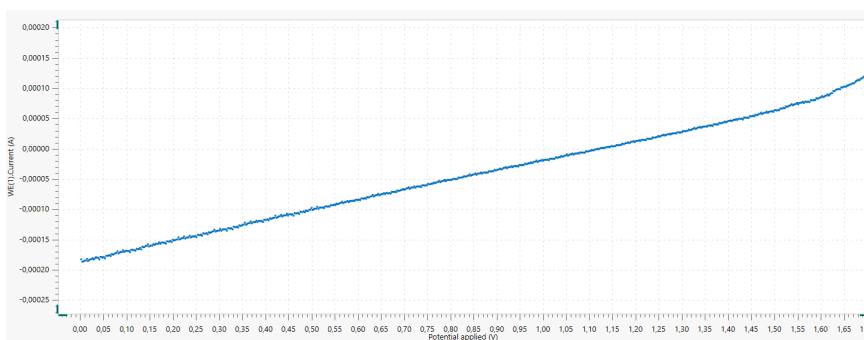Figure 30: The derived function of figure 29

Figure 31: zoom-in from the first half of figure 27

would be, but there is no way to verify this. Furthermore the scans are done at too high a voltage and the salt might be breaking further and further apart for each scan done - the breakdown voltage was believed to be higher at the time of the experiments. Figure 31 shows a zoom in on the low voltage end of figure 27. The 0.3 scan rate was one of the earlier scans done on the salt and the curve is following a simple linear form with no discernible deviations that might indicate any impurities. Only 0.08 g of ashes were mixed into the salt, and with 50 g of salt there is a risk that the ashes are simply too diluted to be of any use at all. For further tests making a lot more ashes, or at a later stage doing tests on salt from the ABC process that has accumulated the relevant elements would be desirable.

4.5 Removal of lignin ashes from salt

Lignin ashes were created from the same lignin as used by the ABC-project for content determination, but any amounts listed might not be the exact same. The ashes were readied and added to the salt as described in 3.8. The scans are done looking to find electrochemical signatures of the various elements, first and foremost sulphur for lignin. Better results might have been obtained had the salt been heated up, kept at a smaller voltage range and then the lignin ashes been stirred in later, with scans redone for comparison. A total of 0.13 g of lignin ashes were added to 50 g salt.

4.5.1 CV

A scan with Cyclic Voltammetry staircase (CV) was done on several different scan rates. Figures 32, 33, and 34 shows these cyclic scans, done for one round each only. The top line on each of them is the initial positive scan rate nu with voltage increasing. They all end at different points and with some differences in the currents measured, but keep a similar shape for each. Looking more closely at the 34 one there is a small peak on the top line in the 0.6-0.7 V range. This same peak can be found looking closely at all of the figures in this subsection. Sulphur has an expected point near -0.4 (see 4), and in a context where -0.7 = 0 this should gives sulphur a match near 0.3-0.4 V range and not as far up as this peak is seen. It is not immediately clear that this is sulphur, and as the entire lignin has been ashed it might be a lot of different impurities that is being picked up here. The next subsection 4.5.2 will look more into this.
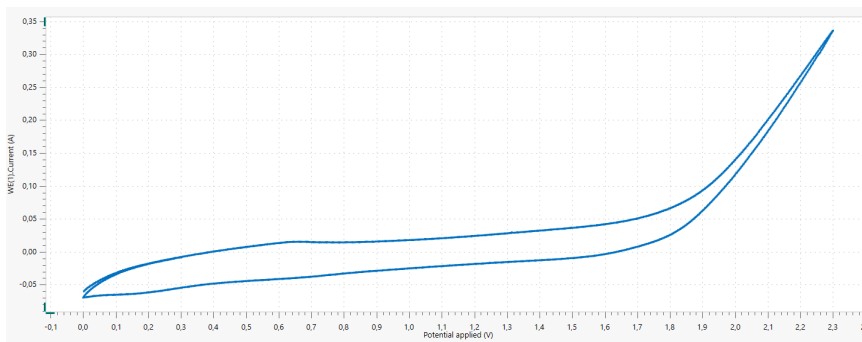

Figure 32: CV scan with lignin ashes at a $v = 0.3$
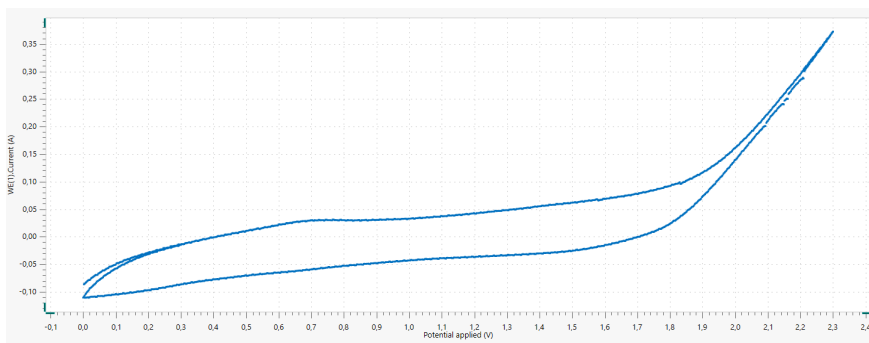
46

Figure 33: CV scan with lignin ashes at a ν = 0.3, a second scan done with same settings
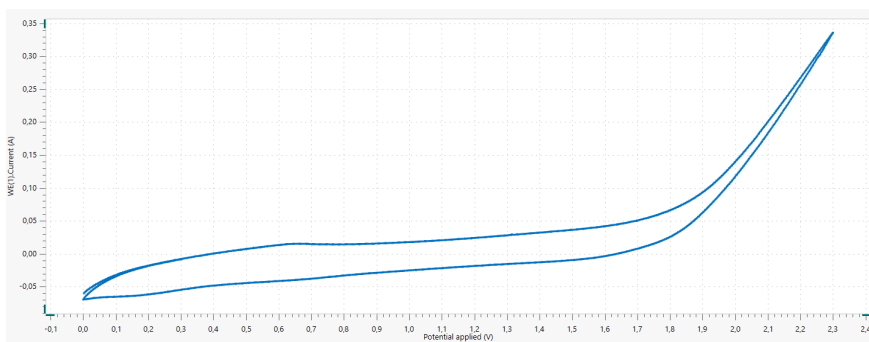

Figure 34: CV scan with lignin ashes at a ν = 0.05

4.5.2 LSV

The figures found in this section are from Linear Sweep Voltammetry staircase (LSV) procedure on lignin-ashed salt. First, figures 35 and 36 shows a similar small peak near the 0.7 V point for both scans at different scan rates ν. This is theorised to be an electrochemical trace of some element in the ash, but no definite proof of one. The figure 37 is a zoomed in image of part of figure 36, to get a better look at the peak in question. Comparing it to the quick theoretical imagery in figure 5 the peak is very small, but it is there and notable. While it is not outside the realm of possibilities
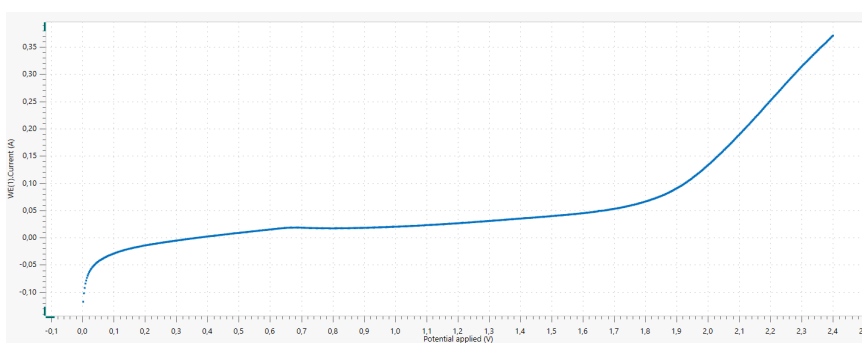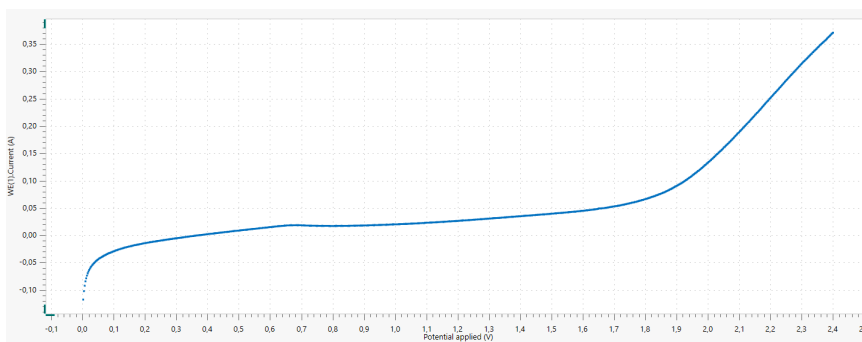

Figure 35: LSV scan at $\nu = 0.3$ V/s

Figure 36: LSV scan at $\nu = 0.05$ V/s

that this is a trace of sulphur from the lignin it cannot be said for sure, and to avoid speculative hypothesis about what this might be it will simply be noted that there appears to be something around this point, and that more research is needed. If a direct comparison of voltage points is made it points away from it being sulphur, at least in pure form. The thesis lack information about the lignin content to make any further guesses at the reason for the current spike - it might even be some external impurity not

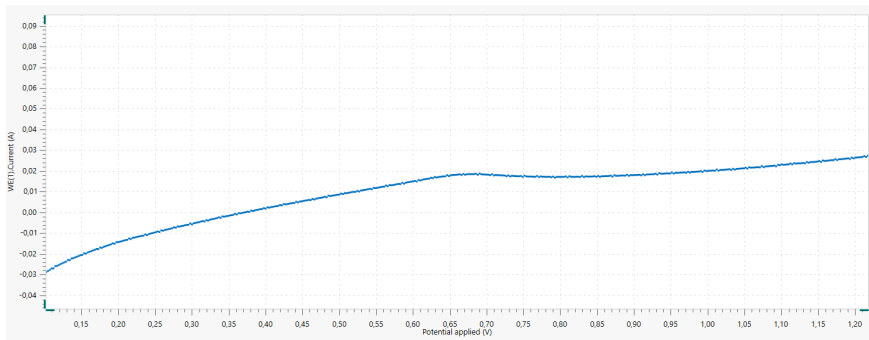Figure 37: Zoomed in image of part of figure 36

related to the salt or lignin at all. More ashes in the salt, a proper linear sweep program and other methods to determine the actual content of the ash is in place. The lignin ash removal section also has the issues of the salt being subjected to too high potential difference during the experiment as does every other electrochemical experiment done.

5 Conclusions

5.1 Main conclusion

There is little work done on electrochemical methods in molten salts. For $ZnCl_2$ – KCl – NaCl the molar composition of the salt do seem to matter, such that the less $ZnCl_2$ there is the more robust the salt will be when subject to potential differences. The salt does seem somewhat stable below the breakdown voltage, here set to somewhere between 1.7 and 2.12 V, however more research should be done with more suitable equipment to get a more accurate image of the electrochemical properties as a whole.

The electrochemical methods used in the thesis did not bring about great results in terms of solidly establish that any element can in fact be easily removed with electrodes. Some few pointers were seen toward the lignin in particular, but this is at best tentative. Additionally the concentration of impurities may have been too low to give visible currents as available ions would be too few. The lack of positive results should however not be seen as an indication that there is nothing to find, but rather that the equipment and methods used might not be suitable.

5.2 Further work

Obtaining a potentiometer with true linear sweep options would be recommended. Furthermore getting a more detailed overview over the content of the biomass, not for the element amounts but rather its reduction potentials and forms. Having the salt go along the pyrolysis several times with the biomass and getting some salt with accumulated impurities and analysing this might yield better results and identification. Identification with other methods like chromatography would also be helpful. The salt chosen by ABC-salt-project has a low melting point, but this does come at the expense of a narrow electrochemical window and finding other methods of cleaning out impurities might be necessary.

References

[1] A. B. C. salt, "Abc salt home page." https://www.abc-salt.eu/, August 2020. Accessed August 2020.

[2] "Online science." https://www.online-sciences.com/tag/electrolytic-cell-vs-galvanic-cell/, 2019. Accessed on 12-08-2020.

[3] A. B. C. salt, "Deliverable d3.4 study of hydrolysis reactions of selected molten salts." Internal project documents, 2019. Email from Heidi Nygård.

[4] D. Pletcher, *A first course in electrode processes*, p. 9. The electrochemical consultency, 1991.

[5] D. R. Lide, "Crc handbook of chemistry and physics." https://web.archive.org/web/20150924015049/http://www.fptl.ru/biblioteka/spravo4niki/handbook-of-Chemistry-and-Physics.pdf, Oct 2003. Downloaded 2020-09-09.

[6] I. C. A. A. A. Nutrition, "Wheat straw dry mass residuals." https://www.feedtables.com/content/wheat-straw, Dec 2020. Accessed 30-11-2020,These tables are the result of a collaboration between INRA (now INRAE), CIRAD and AFZ - Ajinomoto Animal Nutrition.

[7] "Iea fuels and technology." https://www.iea.org/fuels-and-technologies/bioenergy, Aug 2020. Accessed on 2020/10/07.

[8] S. Niazi, E. Olsen, and H. S. Nygård, "Hydrolysis of eutectic compositions in the $ZnCl_2$ KCl NaCl ternary system and effect of adding zno," *Journal of Molecular Liquids*, vol. 317, p. 114069, 2020.

[9] R. Chang and J. Overby, *General Chemistry - The Essential Concepts*, pp. 661–694. McGraw hill, 2011.

[10] K. Nitta, T. Nohira, R. Hagiwara, M. Majima, and S. Inazawa, "Physicochemical properties of $ZnCl_2$ KCl NaCl eutectic melt," *Electrochimica Acta*, vol. 54, no. 21, pp. 4898 – 4902, 2009.

[11] E. Sada, H. Kumazawa, and M. Kudsy, "Pyrolysis of lignins in molten salt media," *Industrial & Engineering Chemistry Research*, vol. 31, no. 2, pp. 612–616, 1992.

[12] N. C. for Biotechnology Information (2020), "Pubchem compound summary for cid 5727." https://pubchem.ncbi.nlm.nih.gov/compound/ZINC-chloride, Oct 2020. Accessed on 2012-11-11, National Center for Biotechnology Information (2020).

[13] N. C. for Biotechnology Information (2020), "Pubchem compound summary for cid 4873." https://pubchem.ncbi.nlm.nih.gov/compound/4873#section=Computed-Properties, Oct 2020. Accessed 25-10-2020, National Center for Biotechnology Information (2020).

[14] N. C. for Biotechnology Information (2020), "Pubchem compound summary for cid 5234." https://pubchem.ncbi.nlm.nih.gov/compound/5234#section=Boiling-Point, Oct 2020. Accessed on 2012-11-11, National Center for Biotechnology Information (2020).

[15] C. Robelin and P. Chartrand, "Thermodynamic evaluation and optimization of the $NaCl + KCl + MgCl_2 + CaCl_2 + ZnCl_2$ system," *The Journal of Chemical Thermodynamics*, pp. 377–391, 2011.

[16] D. J. Nowakowski. Private email correspondence, OCT 2020. Dr, MSc, Eng.; AMIChemE, MRSC. Aston University, Energy and Bioproducts Research Institute. About experimental data about the straw and wood samples used, about biomass, salt and interractions + some modelling.

[17] J. wallinder. Private email correspondence, JAN 2021. MSc Research Engineer, RISE Research Institutes of Sweden. About the sulphur content in lignin, the amount bound and molecular structure of the lignin, and some notes about modeling.

[18] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, and D. Templeton, "Determination of ash in biomass - laboratory analytical procedure (lap)." https://www.nrel.gov/docs/gen/fy08/42622.pdf, July 2005. Technical Report NREL/TP-510-42622.