# DETERMINING THE PROPERTIES OF DEME-TFSI FOR GATING PURPOSES

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# Bachelor Assignment

## Determining the properties of DEME-TFSI for gating purposes

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# 1 Summary

In this bachelor assignment, the characteristics of the ionic liquid DEME-TFSI are studied for gating purposes. This bachelor thesis was initiated in the hope ionic liquid gating might be able to up the charge carrier concentration in a thin layer of a adjacent material more than any conventional methods using dielectric layers will. This might in some materials create a transition from an isolating state to another state. In the experiments conducted to characterize the ionic liquid, it was found the breakdown voltage is somewhere between 4 and 6 volts, matching literature values. Also, it was determined that the ionic liquid does solidify at around 182 K, but one needs to take care during experiments with the probe station to assure the ionic liquid does actually cool down to the temperature of the cold finger. The measurements performed at low temperatures are likely to have taken place at a higher temperature because of these conduction problems. Possible solutions to these conduction problems have been found but could not be applied in time.

Despite no accurate measurements have been done in the case of low temperature, there have been measurements at lower-than-room temperature that still showed strong indications of a lower current at lower temperatures. Qualitatively, vacuum does not seem to influence the condition of the ionic liquid (the ionic liquid still solidifies at low temperatures) but quantitatively, the measurements are strongly influenced by the pressure. It has to be found out if this change is caused by change in geometry (droplet becoming flatter because of bubbling in the ionic liquid) or whether the ionic liquid itself changes, as the bubbling at low pressure seems to suggest. The question if the bubbling is caused by evaporating water (which might reduce the mobility of the ions) or if it is caused by another effect, one that perhaps is internally damaging to the ionic liquid, is still unanswered. The assumed inverse proportional relation between current and distance between the electrodes has not been found; it is not clear if this is caused by the limited amount of measurements or if a fundamental theoretical mistake is the cause of this error. In general, the more quantitative treatment of this assignment has suffered under the limited number of measurements performed, caused by the long time required for each measurement. It is however hoped that the qualitative treatment is still able to help research in the area of ionic liquids, and helps to prevent the pitfalls that might occur during research with ionic liquids.

# 2 Acknowledgements

In finishing this bachelor assignment I hope I can finish my bachelor Applied Physics. The project proved to be tougher than I expected at first; what was supposed to have been only a part of the project swiftly turned to dominate the project and even then achieving all set goals proved to be impossible. The freedom I got in my research proved to be an educational experience. The atmosphere in the Interfaces and Correlated Electron systems group (ICE) was very good and I would like to thank all members of that group. I would like to thank everyone who has helped me during my project. First of all Francesco Coneri and Renshaw, for their coaching during the assignment and assistance in performing the experiments. I would further like to thank Dick Veldhuis, Frank Roesthuis and Cor Molenaar for the assistance they provided me in the lab, and Martin Stehno and Prosper Ngabonziza for their assistance in solving the thermal conduction problem. Furthermore, I would like to thank the master students Roel Smits and Sam Sloetjes and especially Chiel and Thijs Scholten for their advice and assistance, which they gave when it mattered. I would also like to thank my fellow bachelor students Jeroen van Dam and Tom van Dalfsen, for their enjoyable company. Finally, I would like to thank the Examination Committee of professor Hans Hilgenkamp and doctor Stefan Kooij for their exceptional patience and understanding towards me.

# Contents

# 3 Introduction

In this bachelor assignment, the characteristics of the ionic liquid DEME-TFSI are studied for gating purposes. This bachelor thesis was initiated because of an interest in discovering different methods for the gating of materials. These different methods (in this case gating using ionic liquid) might achieve results ordinary methods might not. In this case, the hope is ionic liquid gating might be able to up the charge carrier concentration in a thin layer of a adjacent material more than any conventional methods using dielectric layers will.

Over the course of the assignment however, the assignment became better defined and the weight of the assignment shifted more towards solving the problems faced and became more focused on gathering general information about DEME-TFSI. The following subjects are investigated:

1. **Do the results in this experiment match known results for DEME-TFSI?** The results of our experiments should match literature values. Experimental indications of the breakdown voltage and response to temperature shall compared to known values;
2. **Are the electrochemical properties of DEME-TFSI influenced by exposure to air?** Ionic liquids are in general hygroscopic, and DEME-TFSI is no exception. Therefore, knowing if exposure to air (and the water it contains) will dramatically influence the properties of DEME-TFSI is important;
3. **Are the electrochemical properties of DEME-TFSI influenced by exposure to vacuum?** Because the characterization of DEME-TFSI at cryogenic temperatures is performed at vacuum, it is necessary to first determine the effects the vacuum has on the ionic liquid. The hypothesis is that vacuum does not have any influence on the properties of DEME-TFSI;
4. **What is the relation between the leakage current and the distance between the electrodes?** The leakage current is another factor of interest. The hypothesis is that this is proportional to the electric field, which is inversely proportional to the distance between points (for equal voltage);
5. **How does lowering the temperature influence the electrochemical properties?** This is one of the main questions in this bachelor assignment. It is known from literature that the ionic liquid undergoes a glass transition at 182 K [5]. Below this temperature the liquid should be solid, turning it into an isolator. Above, the ions should be able to move around, where they become more mobile and conduct more when the temperature increases;
6. **Further observations of note shall also be discussed.**

These questions shall be answered using the results of the measurement, but first some background information is given.

# 4 Theory

In this section the theoretical background of this assignment shall be discussed. First the gating of materials is discussed, and then general information about ionic liquids and how this can be used for electric field doping is given.

## 4.1 Gating

The process of increasing the amount of charge carriers in a material is called doping. In general there are two methods one can use to increase the number of charge carriers in a material. The first is to introduce impurities, adding or substituting atoms with a different valence to introduce additional charge carriers. Another way to induce more charge carriers is by using an electric field to draw in more charge carriers. The electric field will move the charge carriers closer to one side of the material, locally increasing the number of charge carriers. This is called electric field doping, or gating. Normally, this is done by placing a third electrode at one side of the material, called the gate electrode, with between the electrode and the material a dielectric. A voltage is applied between this electrode and one of the other electrodes, creating an electric field that draws in the charge carriers. Unfortunately, the strength of the electric field is seriously limited by the breakdown voltage of the dielectric. Gating using an ionic liquid might provide the solution to this problem.

## 4.2 Ionic Liquids

The core of this bachelor report involves the usage of ionic liquids. An ionic liquid (IL) is a salt with a melting point low enough to make it liquid at room temperature or having it liquefy at such a temperature; usually a salt with a melting point below 373 K is considered to be an ionic liquid. An ionic liquid differs from normal liquids by virtue of it being a liquid consisting out of ions instead of electrically neutral particles. Most well-known salts have a very high melting point; sodium chloride, for example, has a melting point of 1074 K [7]. The reason for this high melting point has to do with the strength of an ionic bond: a lot of energy is normally required to break this bod. Salts with a low enough melting point to be considered ionic liquids are usually relatively complex compounds, consisting for example out of long ethyl chains. A disadvantage is that a lot of known ionic liquids are therefore difficult to handle: some are toxic, and all ionic liquids known to the author are hygroscopic, usually requiring an inert atmosphere (nitrogen in the case of the experiments done by the author) to prevent the liquid from reacting with water.

The ionic liquid that was chosen for this experiment was *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium iodide, usually referred to by the (easier to remember) name of DEME-TFSI. The reason this liquid was chosen was the ease of use: the Material Safety Data Sheet states that little is known about the liquid, but it certainly does not give any strict guidelines in the handling of the liquid, suggesting little risk is involved in the usage of this liquid [8].

The fact an IL consists out of ions instead of neutral particles means that under influence of an electric field the positive and negative ions will move around in the liquid, with positive particles being shifted in the direction of the electric field and the negative particles in opposite direction, just like one would expect of charged particles. This concentration of positively and negatively charged particles on each side creates its own electric field.

### 4.2.1 Electric double layer

This creation of an electric field can be used for gating. When the dielectric in the earlier example is replaced by an ionic liquid, a potential difference will split up the negative and the positive ions, with one type of ions covering the surface of the material. This is called the electric double layer, or EDL. These ions covering the surface create their own electric field, which will result in a field which increases the charge carrier density dramatically at limited depth. A surface charge carrier density of $10^{14}$ cm$^{-2}$ with an EDL-gated accumulation layer of 10 nm have been found [9]. Such a strong doping allows for a transition between isolating and superconducting or isolating and metallic phases [2] [9][10].

# 5 Practical Aspects

In this section, some of the practical aspects of the experiment will be explained. Because part of the experiment uses a vacuum, some basic information about vacuum and pumping is given. Because sputtering is used, this is also explained.

## 5.1 Vacuum

An important part of this bachelor project involved cooling down to low temperatures. To successfully cool down to these low temperatures the sample is put in a vacuum, limiting heat leakage by convection. To create this vacuum, two different vacuum pumps are used in sequence to achieve the required pressure.

### 5.1.1 Rotary Mechanical Pump

In the first phase, a relatively ordinary rotary pump (figure 1) is used to reach pressures at which the turbomolecular pump can start functioning. In this first stage, a pressure of a couple of millibar can be reached. To go to an even higher vacuum level the second stage is required.

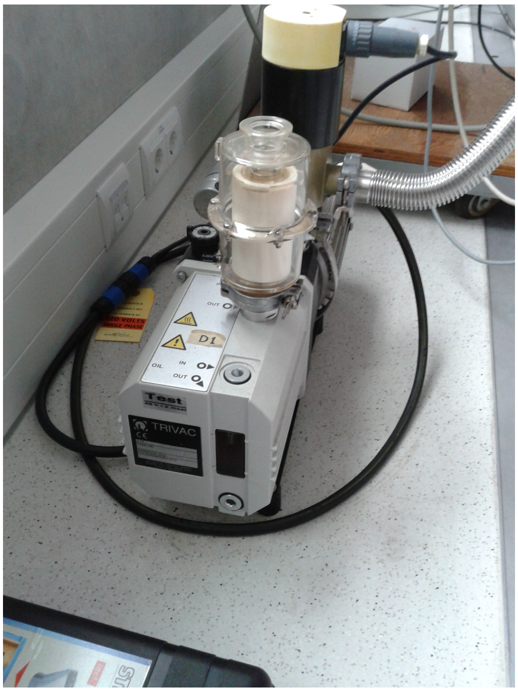

Figure 1: The rotary mechanical pump, as used in the experiment.

### 5.1.2 Turbomolecular pump

To reach an even higher vacuum level than an ordinary mechanical pump allows, a turbomolecular pump (figure 2) is added as a second stage pump. A turbomolecular pump is a compressor consisting out of multiple rotors and stators. The rotors spin at rates of 20,000 to 30,000 revolutions per minute; molecules that collide with the rotor are imparted a momentum forcing them through the pump, continually compressing the gas until, when it reaches the end of the pump, the pressure is as high as the pressure of the previous stage. During the bachelor assignment, pressures of $10^{-2}$ to $10^{-3}$ millibar have been achieved using this pump.

Figure 2: The turbomolecular pump, as used in the experiment.

### 5.1.3 Cryopump

Another method one can use to decrease the gas pressure is through cooling. It is well-known through the ideal gas law that a temperature drop will, all other conditions remaining equal, result in a pressure drop. Furthermore, once the temperature drops below the boiling point of different gases, these gases will liquefy, resulting in a pressure drop. For example, the main constituent parts of air, nitrogen and oxygen, have boiling points of 77 K and 90 K respectively. Whereas the previous two pumping methods are methods actively used in this bachelor assignment to lower the pressure (to allow the sample to be cooled without too much of a heat leak), the pressure drop caused by cooling down is more of an unintentional side effect. There is a risk that the vacuum level will through cryopumping become so high that the attached pumps will actually leak gas into the vacuum chamber. To prevent this, one needs decouple the pumping system from the cooled vacuum chamber by closing a valve.

## 5.2 Sputtering

Research in solid state physics regularly requires the creation of small scale structures. There are different methods one can use for the creation of such structures. One of these methods, sputtering, has been used during this bachelor project and therefore will now be discussed. Sputtering is a method where a material, the target, is bombarded by ions, resulting in the ejection of surface atoms. These surface atoms will thereafter land on the substrate, slowly growing a film consisting of the target material. In this way, layers of atoms of the target material are deposited on top of the substrate. For sputtering, usually a potential difference is applied between two metal plates in a neutrally charged atmosphere. When this voltage is high enough, a portion of the atoms are ionized, creating a plasma. The electrons are accelerated by the electric field and bombard neutral gas atoms, causing the reaction:

$$e^- + A \rightarrow 2e^- + A^+ \tag{1}$$

Now there are two electrons, which will both accelerate and collide again with neutral gas particles, ionizing them. Meanwhile, the ions will move in the opposite direction, colliding with the cathode and releasing even more electrons to be involved in the process. The ions will, in their bombardment of cathode, eject surface atoms. These are the basics of DC sputtering. There are also alternate forms of sputtering, like AC sputtering. If one tries to use DC sputtering to grow a layer of dielectric material, one faces the problem that the bad conductivity of the material will require the potential difference to be of several orders of magnitude larger than realistically possible. The impedance of a dielectric material decreases when the frequency increases: this means that if one uses a high enough frequency (usually around 1 MHz or higher), one can use AC currents to sputter using an acceptably low voltage. Because of the negative self-bias of the target, the target material is sputtered instead of both the cathode and anode being sputtered in equal measure. Another variant of sputtering is reactive sputtering. Reactive sputtering is sputtering done in a reactive atmosphere. Whereas normally sputtering uses an inert working gas, in reactive sputtering this working gas is mixed with a reactive gas. This reactive gas will, like the name suggests, react during the sputtering process, allowing the growth of a compound.

# 6 Measurement

## 6.1 The set-up

The measurements were performed using a probe station. The probe station (figure 3) consists out of a chamber which can contain a vacuum, with four probes which can be operated from the outside and a cold finger, a metal part on which the sample can be placed and which can be cooled using liquid helium. There are two temperature sensors inside the cold finger and a resistance used for heating, which means the temperature can be automatically regulated. The probes are used to contact the electrodes and can have tips made out of different materials. In these experiments tips of beryllium-copper and gold were used. Because the tips were not in contact with the ionic liquid (except for one measurement which did not give any good data) and the total resistance between the tips and the electrodes was in the order of single ohms, distinction between measurements performed with different tips is not made.

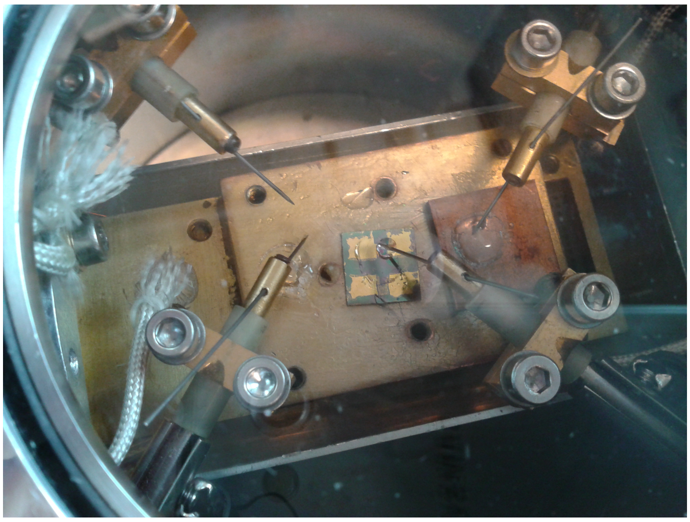

Figure 3: A close-up of the set-up, showing the four probes in the vacuum chamber. Photo taken during a test to determine the thermal conductivity of the plate with the sputtered gold electrodes.

## 6.2 The samples

Measurements have been performed with three types of electrodes: a copper PC board, a gold PC board, and a Si/SiO2 plate with gold electrodes sputtered on top. In the first instance, the copper PC board was used, but Redox reactions would already happen at limited voltages. For this reason a gold PC board was used. During low temperature measurements this PC board however proved to be too thermally isolating to allow the droplet to solidify (more about this in 7.1.2), requiring another set of electrodes which was thermally conducting. The solution was taking a plate of Si/SiO2 and sputtering gold electrodes on these.

### 6.2.1 Gold PC board

The gold PC board (figure 4) was used for the large majority of the measurements. It was used by placing a droplet on the inner electrodes and putting the probes on the outer electrodes connected to these inner electrodes. A droplet was placed, covering the entire length of the gap between the inner electrodes. For measurements over larger distances, it was assumed the current would pass through the gold electrode instead of through the ionic liquid, meaning that measuring the voltage over and current through two non-neighboring electrodes separated by one electrode is essentially the same as measuring this for an opening between two neighboring electrodes with a double the gap size between them. The inner electrodes are 1.05 ± 0.05 mm with a gap between them of 0.20 ± 0.05 mm.

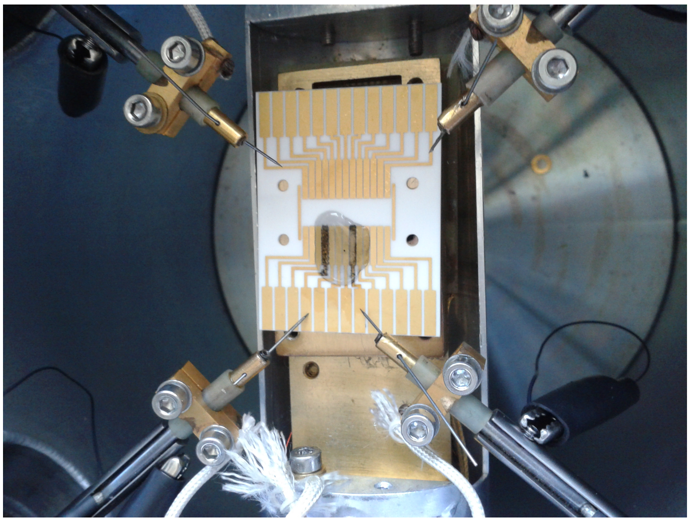

Figure 4: The gold PC board while being tested. This picture has been taken after breakdown, as shown by the blackened inner electrodes. The picture shows the general set-up of a measurement.

### 6.2.2 Sputtered gold electrodes

To be able to measure at low temperatures, a solution had to be found. A possible solution was to find something that is better thermally conducting or thinner while still being electrically isolating. Eventually, a plate of silicon with a silicon oxide top layer was used and four gold electrodes were sputtered on it. First of all, the edges and a cross op top of the sample was covered in photoresist. After this had dried, a thin layer of gold was sputtered onto the sample, by first etching the sample, then sputtering a very thin layer of titanium to provide better contact for the gold, and finally sputtering the gold (see figure 5). The photoresist was then removed by cleaning the plates with aceton and then ethanol, giving a plate with four gold electrodes isolated from each other. The gap between one of the electrodes and its closest neighbors is 1.60 ± 0.60 mm.

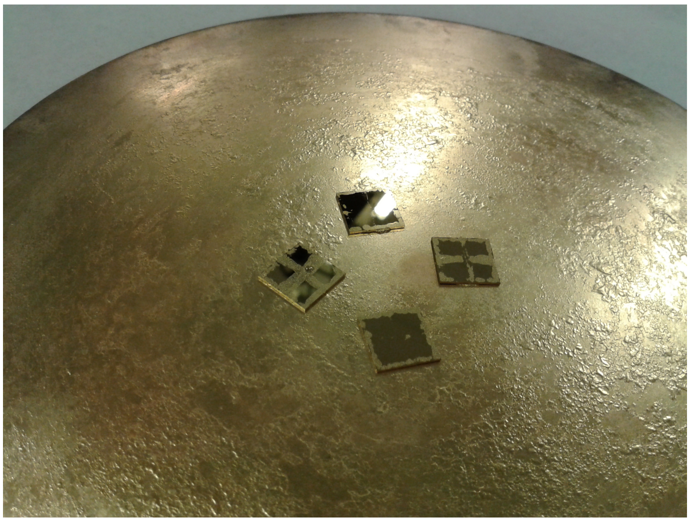

Figure 5: The Si/SiO2 plates directly after sputtering. After this step, the photoresist still has to be removed.

## 6.3 Measurement and analysis

The probes are connected to a Keithley 2401 source meter, which can be controlled by a computer. A new LabVIEW program has been written to perform this measurement. The program worked by setting the voltage at a certain level and sampling the current every period of time $dt$, for a certain time. Once this time has passed, the voltage will be set a step higher and the sampling will begin anew. For a positive sweep, this process will be performed from zero to a certain maximum value and back to zero with a certain step size. For a full sweep, the voltage will move from zero to positive to zero to negative to zero. The result is a file for every voltage with the current measured against the time.

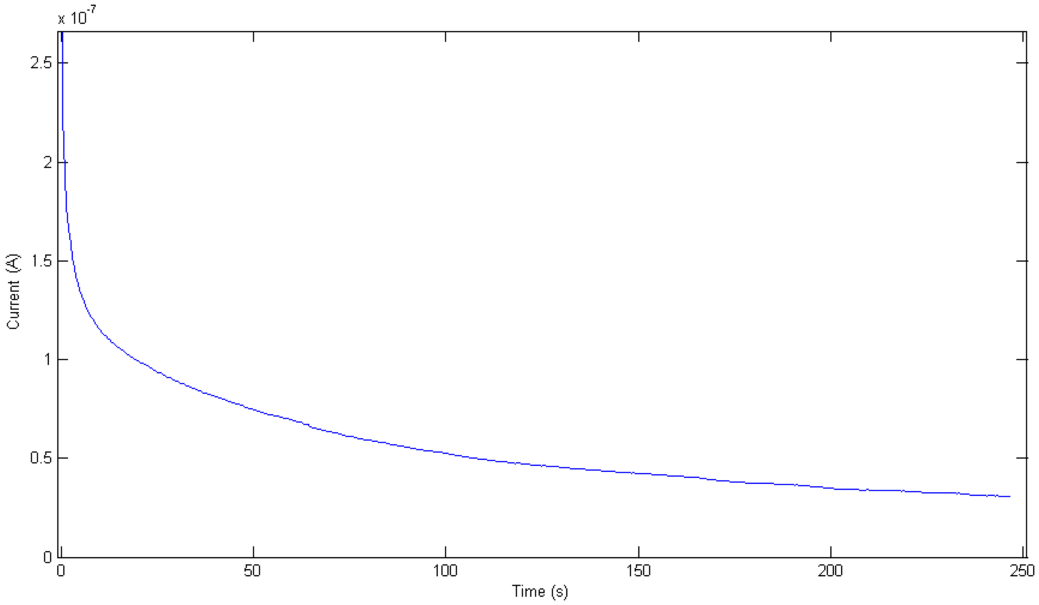

Figure 6: Measurement 4: current against time after the jump from 1.5 V to 2 V

As can be seen from figure 6, after every step in the voltage, there is a spike in the current followed by an exponential decay of the current to a certain value, the leak current. All these files are analyzed by a MATLAB program, giving a leakage current and a characteristic time $\tau_{long}$. These leak currents can be plotted against the voltages giving V,I curves like figure 7. All this data has been compiled in a table, table 1 in the appendix. The characteristic time has been analyzed, but no serious relation could be determined in this time for the different measurements because the large variance in some of the interesting measurements. The MATLAB program already filtered out the two most extreme values and impossible values (negative characteristic times), but still the results were not suitable for the determination of any further relation. Therefore this shall not be treated in the next chapter.

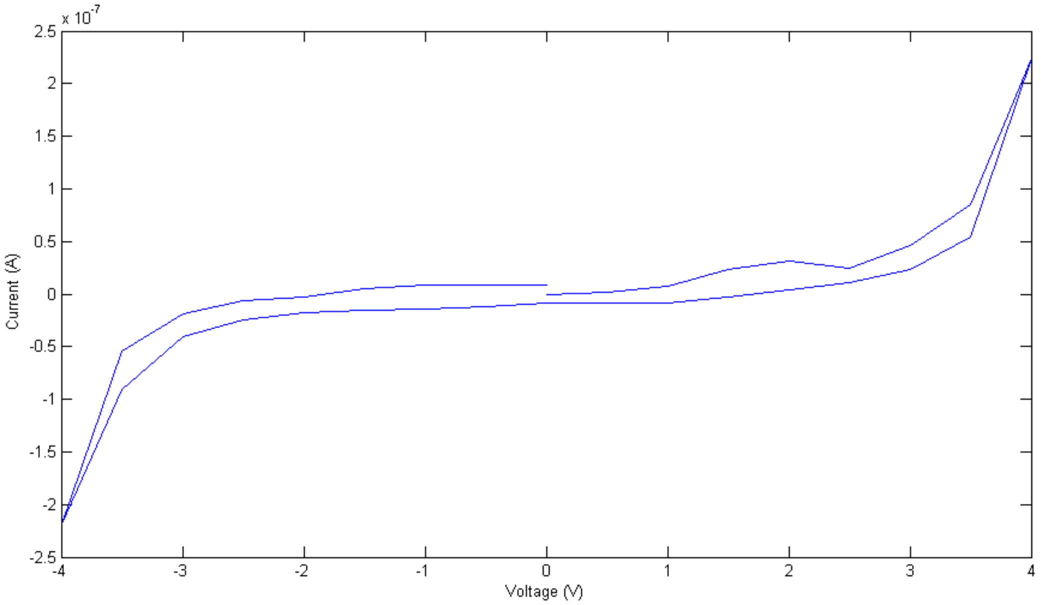

Figure 7: Measurement 4

# 7 Results and Discussion

## 7.1 Do the results in this experiment match known results for DEME-TFSI?

To make sure the results found in the measurements are reliable, the results are first checked against known results for DEME-TFSI. The two properties that are going to be compared are the breakdown voltage and the behavior at low temperatures, especially whether the glass transition can be recognized.

### 7.1.1 Breakdown voltage

The breakdown voltage of DEME-TFSI is known to be somewhere between 4.5 and 5.5 V [5]. In measurements 10 and 11 the breakdown voltage should be reached. One can see in figure 8 the breakdown voltage (the voltage at which the current dramatically increases) is somewhere between 4 and 6 volts, matching the known information.

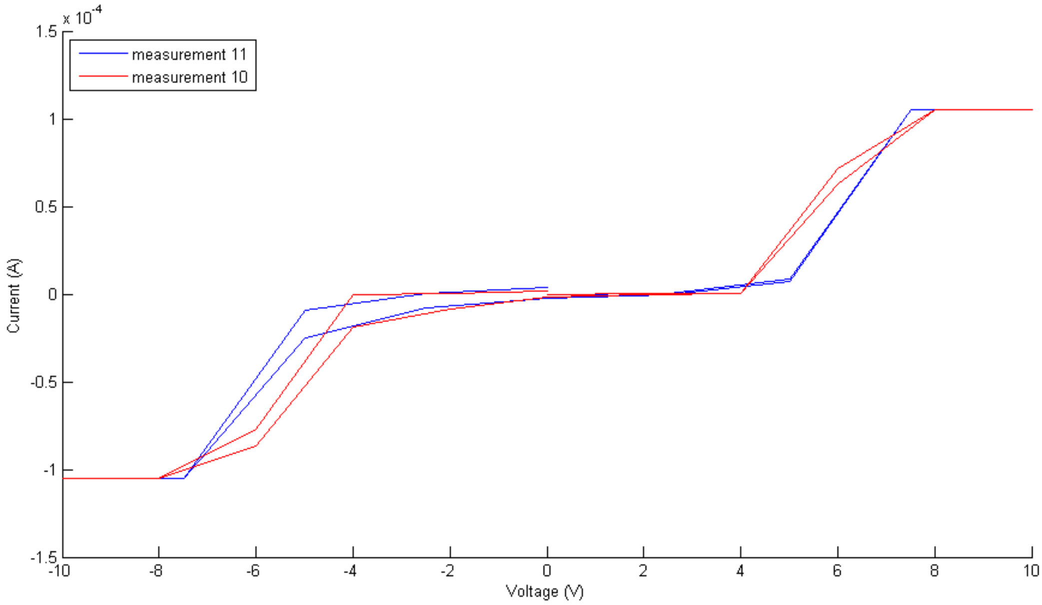

Figure 8: A comparion of measurement 10 and 11. One can see the breakdown voltage is for both measurements somewhere between 4 and 6 volts.

### 7.1.2 Temperature

It is known that DEME-TFSI has no melting point, but becomes more viscous when the temperature drops and has a glass transition at 182 K [5]. During the measurement series, however, it became quickly apparent that the ionic liquid did not appear to solidify at that temperature or at any temperature that could be reached by the set-up. This led to different possible hypotheses:

1. The droplet is not at the measured temperature; it actually is still above the glass transition temperature. The temperature is measured at the cold finger. The bad thermal conductance of the PC board used, combined with heat radiated in and the thermal conductivity of the probes means the temperature of the droplet is above 182 K;

2. The low temperature measurements performed in this assignment were done under high vacuum, while the measurements performed for the literature values were done under atmospheric pressure in a nitrogen atmosphere. The low pressure might influence the phase of the ionic liquid;

3. The used ionic liquid came from a bottle which had been opened and closed repeatedly, deteriorating the quality of the liquid because it is repeatedly in contact with open air;
4. The ionic liquid actually did undergo a phase transition, but the phase transition does not result in any apparent change to the exterior of the droplet.

To figure out which of these hypotheses was correct, a number of small experiments were performed. First, a droplet of DEME-TFSI was placed on a metal object, which was lowered into a piece of Styrofoam holding liquid nitrogen. The droplet itself remained above the liquid nitrogen surface. In a matter of seconds, the droplet appeared to freeze, showing a clear phase change. Performing this experiment repeatedly for both the old and the new ionic liquid and tapping and manipulating the droplet showed this was the actual droplet undergoing a phase change, not a layer of ice covering the outside of an otherwise unchanged droplet. This means hypothesis 4 could be rejected.

To test both the second and third hypothesis droplets of both the old and the new ionic liquid were put on the cold finger in the probe station, after which the chamber was pumped to vacuum level and the system was cooled down. Care was taken to make sure the new liquid was not spoiled. Both the old and the new liquid appeared to solidify (see figure 9), essentially rejecting hypotheses 2 and 3.

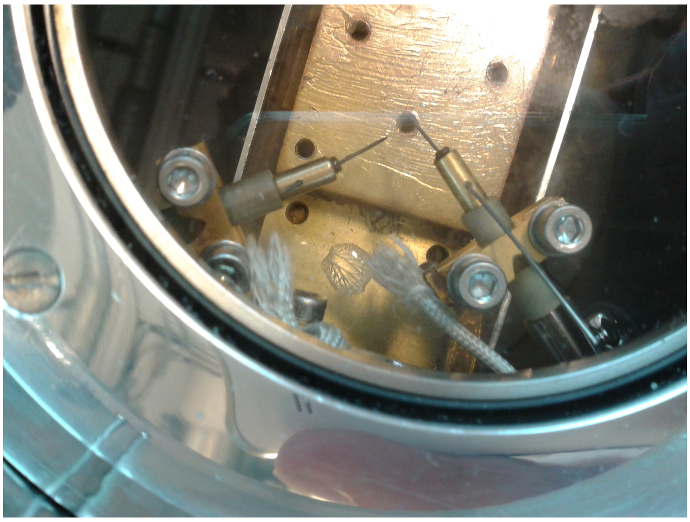

Figure 9: A droplet of ionic liquid placed on the cold finger in the probe station. One can see the formation of crystals, creating a clear distinction between the two states of the liquid.

This means the fact the droplet is not solidifying is a heat conduction problem. Unfortunately, to solve this problem, the plate on which the droplet is plate needs to be thermally conduction as well as electrically insulating. This is a combination that is contradictory in itself. In the end, this problem was solved by taking a thin plate of silicon topped with silicon dioxide and sputtering gold electrodes on top of this plate. The SiO2 was electrically isolating enough to isolate the electrons from each other, but thin and thermally conducting enough to allow the droplet to solidify at low temperatures.

Another problem is the fact the probes are connected to the outside world and therefore are hotter than their surroundings. This heat flow is large enough to, in the case of direct contact between the probes and the droplet, once again turn the droplet liquid. Letting the probes cool down by making them touch the cold finger during a period of time does not prevent this problem, indicating the heat conductance of the needles is to high. A possible way to reduce this influence is to reduce the heat conductance, by lengthening the electrode or finding a thermally less conducting material.

## 7.2 Are the electrochemical properties of DEME-TFSI influenced by exposure to air?

It is known that DEME-TFSI is hygroscopic, like many other ionic liquids [5]. This begs the question if exposure to air will result in a change of electrochemical behavior. Figure 10 shows a striking similarity between measurement 4, performed with the old ionic liquid, and measurement 23, performed with the new ionic liquid. It appears exposure to air does not seriously influence the behavior of the liquid.

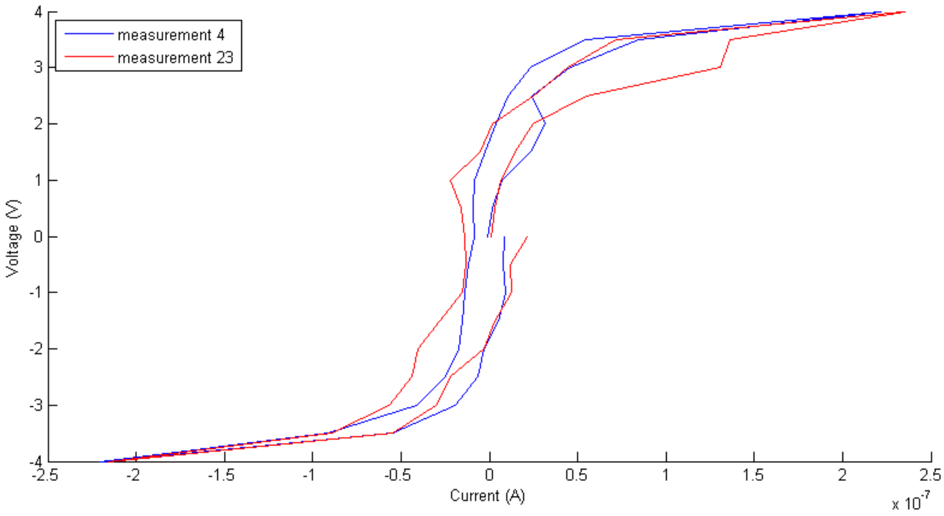

Figure 10: A comparion of measurement 4 and 23. It can be seen that the characteristic of measurement 4 (performed with the old ionic liquid) matches in a general sense the characteristic of measurement 23, performed with the new liquid.

## 7.3 Are the electrochemical properties of DEME-TFSI influenced by exposure to vacuum?

Because the characterization of DEME-TFSI at cryogenic temperatures is performed at vacuum, it is necessary to first determine the effects the vacuum has on the ionic liquid. There are qualitative indications that the ionic liquid changes when the pressure drops: both the old and the new ionic liquid show bubbling when the pressure is lowered, akin to the boiling of water. After a while the bubbling stops. It is not clear what exactly causes the bubbling. It seems likely the bubbling is caused by the boiling of a part of the ionic liquid, where the boiling stops once the liquid has been vaporized. This liquid might very well be water, which might mean the new ionic liquid is contaminated as well. An effect of the bubbling is that the droplet becomes flatter and more spread out. This change in geometry might influence the results of the measurement.

In figure 11 it is shown there is a significant difference between the measurement in a nitrogen atmosphere (measurement 29) and at vacuum (measurement 30), where operating in vacuum seems to reduce the current. Whether this has something to do with the changed geometry or with changed properties of the ionic liquid (vaporizing of water or damaging of the liquid due to the vacuum) is unclear.

## 7.4 What is the relation between the leakage current and the distance between the electrodes?

Another factor of interest is the leakage current. In general, it is assumed this is related to the electric field as:

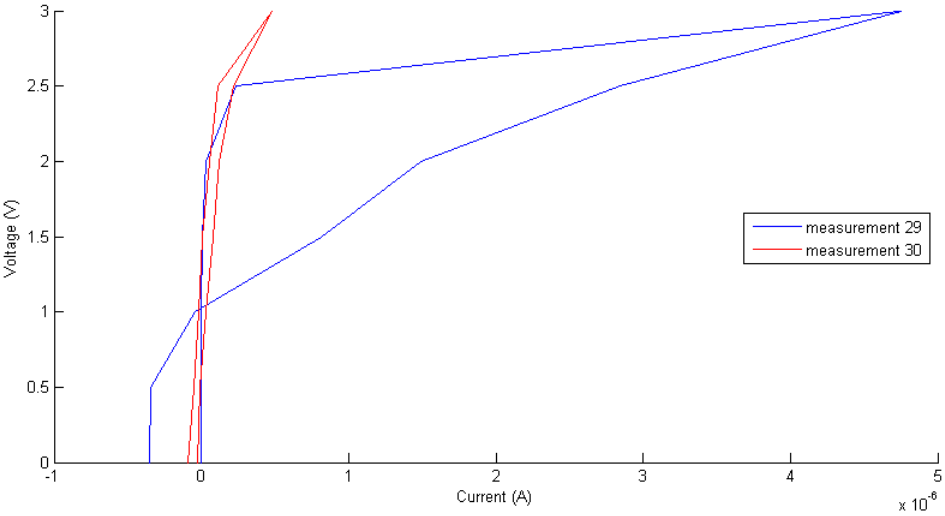

Figure 11: A comparion of measurement 29 and 30. Measurement 29, performed in a nitrogen atmosphere, differs significantly from measurement 30, performed in vacuum, indicating a significant influence on measurement results by vacuum.

$$I \sim E \sim \frac{V}{r} \tag{2}$$

This would suggest an inverse relation between the current and the distance for equal voltages. By comparing measurements 3 and 4 (figure 12) one can try and reach conclusions. The assumption would have been that measurement 4 would have a three times as large current for similar voltages. The measured difference is a factor 50. Even if we assume the gold electrodes lying between the measured points do not conduct, than we only get a factor 13 difference. Clearly it seems the hypothesis not supported the results, but more measurements need to be done the be certain of this result.

## 7.5 How does lowering the temperature influence the electrochemical properties?

It has been noted during measurements that at lower temperature the ionic liquid becomes more viscous, until it undergoes a glass transition at 182 K. This would suggest ion movement and therefore conduction will decrease when the temperature decreases, until it stops after the ions get frozen in after undergoing the glass transition. The thermal conduction problems described earlier have cast a shadow of suspicion on all measurements at lower temperature, or to be more correct: it is clear from the fact the droplet remained liquid at every measured temperature that the temperature of the cold finger is nowhere near the temperature of the droplet. Still, under the assumption that there is a positive correlation between the temperature of the cold finger and the temperature of the droplet, we can infer if conductivity decreases when the temperature is decreased. In figure 13 a measurement at room temperature (measurement 23) is compared to measurements at cryogenic temperatures. It can clearly be seen the former is far larger than the latter measurements. In the latter measurements (figure 14) it can be seen the coldest temperature still has the lowest values, but all these measurements lie close together, closer than one would assume if one knows measurement 24 is supposed to have been at 10 K. The logical explanation is that for a continually lowering temperature of the cold finger the limited conduction by the PC board results in the temperature moving asymptotically to some temperature above the the glass transition temperature.

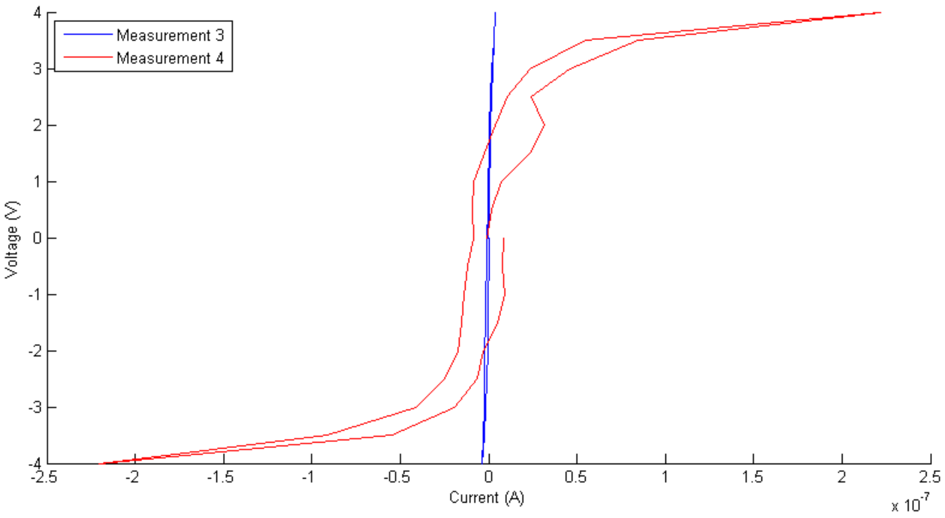

Figure 12: A comparion of measurement 3 and 4. Whereas measurement 4 is performed at three times the distance of measurement 3, there is a factor 50 difference in current strength between the measurements, indicating the relation between the distance and the current is not inversely proportional.

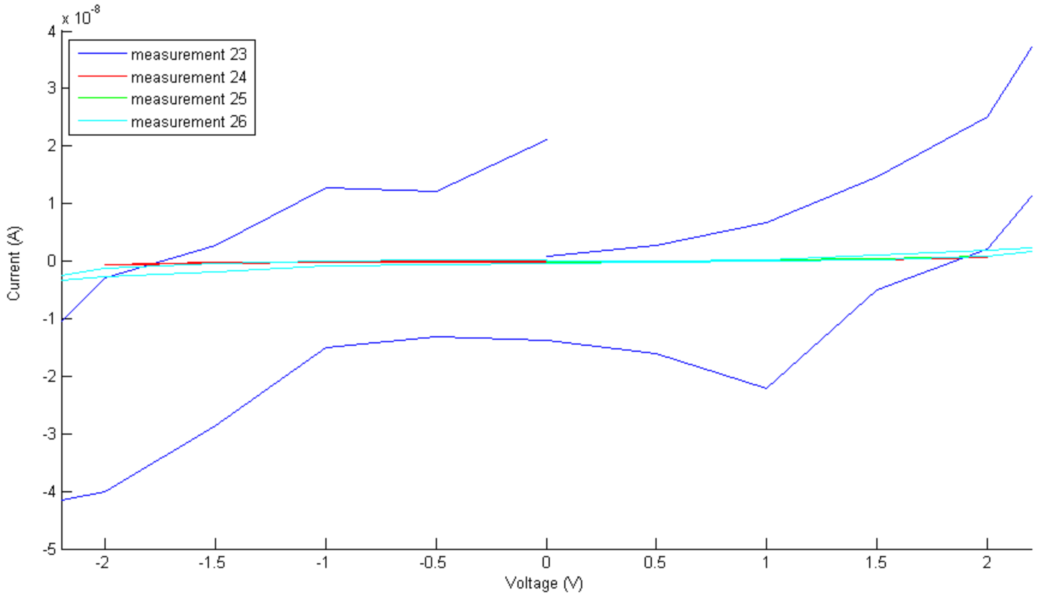

Figure 13: A comparion of measurements 23, 24, 25 and 26. One can see that the measurement at room temperature (measurement 23) shows far larger currents than the measurements performed at lower temperatures.

## 7.6 Further observations of note

### 7.6.1 Behavior of DEME-TFSI under the influence of light

During initial measurements it became apparent the ionic liquid responded to increasing light intensity. Shining a light beam on the droplet results in an increase in the absolute value of the current; this will once again disappear when the light source is deactivated. The exact nature of this physical effect is hard to determine. It might be that the sample is heated by power radiated by

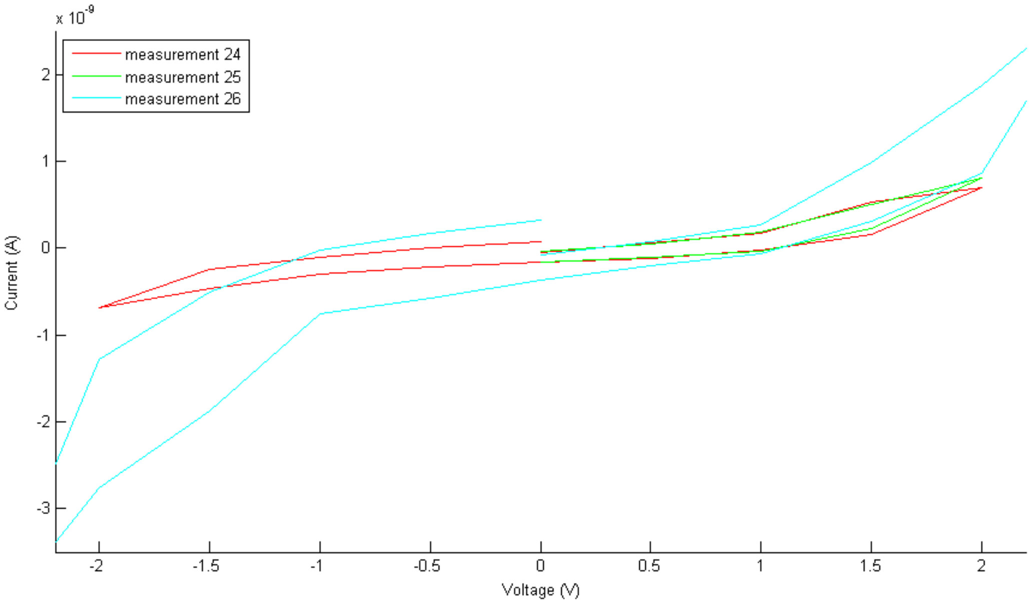

Figure 14: A comparion of measurements 24, 25 and 26. Once again one can see that, in general, the measurement at the lowest temperature (measurement 24, at 10 K) has a lower current at each voltage than measurement 25 (at 150 K), which is still lower than measurement 26 (at 170 K).

the light source, increasing conduction. The power of the light source is small however, and a lot of the light is reflected. An alternative is that the ionic liquid is photoactive, where photons striking the ionic liquid instigate a reaction that improves conductance. Whatever the nature of the effect is, it is interesting to look at the size of the effect. This is especially important because the droplet was exposed to ambient light during the measurement, as covering the set-up to prevent light falling in would prevent observing the ionic liquid during the experiment, an important element of researching this liquid qualitatively.

### 7.6.2 Effect of breakdown on ionic liquid

As discussed before, breakdown can happen when too high a voltage is applied to the ionic liquid. It is therefore interesting to see how the liquid behaves under non-breakdown conditions after breakdown has been achieved. It can be seen that measurement 16, though it would be expected due to distance between electrodes that the measurement is somewhere in between 2 and 4, actually allows for a far larger current to run than one would expect. At ±4 volt, the measured current of 16 is more than 20 times as large as the current of 4. This is a clear indication that breakdown permanently influences the ionic liquid.

## 7.7 General discussion of the performed measurements

During this bachelor assignment the boundaries of the research have shifted. At first, characterization of the ionic liquid was supposed to be merely a part of the assignment, but during the assignment this part swelled up to form the bulk of the assignment. At the same time, assumptions that appeared to be obvious are cast into doubt. A major problem during the experiment was the limited thermal conductivity between the cold finger and the ionic liquid droplet. Whereas this problem was the main problem faced during the experiment itself, the results showed several other problems. First of all, nearly all hypotheses have been rejected, meaning the (granted, sometimes relatively simple) models assumed did not hold under these circumstances. An even larger problem in the performed research is that the time it took finish measurements (regularly requiring more than an hour) combined with the large number of different measurements attempted means measurements have not been repeated. This in essence makes it difficult to conclude if the results

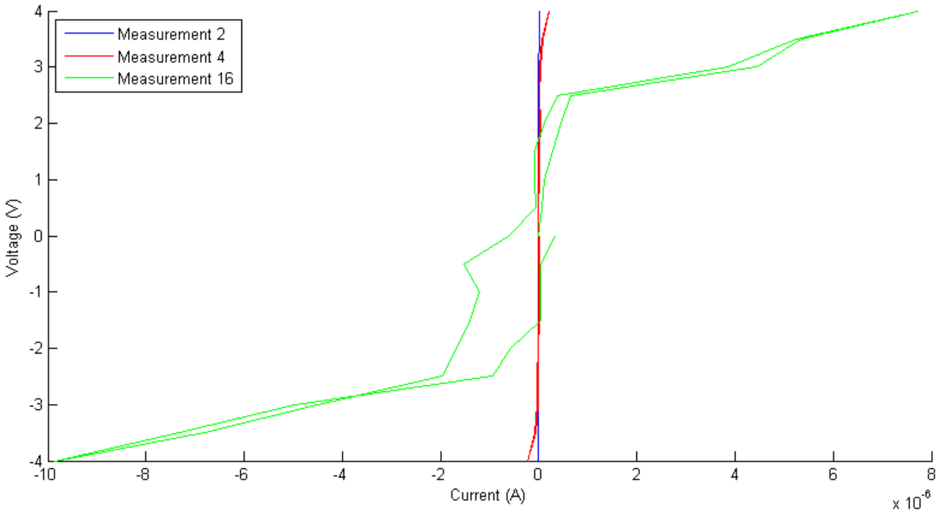

Figure 15: A comparion of the measurements 2, 4 and 16. Measurement 2 is performed with thrice the distance of measurement 4, and measurement 16 at twice the distance. Measurement 16 is however performed with ionic liquid which has suffered a breakdown, causing far higher voltages.

show a trend or if these are errors or statistical aberrations. In retrospect, the author is also at guilt for this, for he did not have the foresight to structure his measurements in such a way that these would be easily comparable.

### 7.8 Recommendations

For future research there are several recommendations that can be made First, due to limited time, no measurement using the newly sputtered electrodes could be performed at low temperatures. This means the actual measurements at low temperatures (where the droplet has roughly the same temperature as the cold finger) have not been done, preventing characterization of the liquid at that temperature. There are a number of important measurements that can be done at low (below 182 K) temperature, for example looking at the speed at which frozen in ion distribution becomes random again after the electric field disappears (if this happens at all). In this paper the methods that are required for successful cryogenic measurements have been established: it is hoped these are of use for future research in the field of ionic liquids.

# 8 Conclusion

In the experiments conducted to characterize the ionic liquid, it was found the breakdown voltage is somewhere between 4 and 6 volts, matching literature values. Also, it was determined that the ionic liquid does solidify at around 182 K, but one needs to take care during experiments with the probe station to assure the ionic liquid does actually cool down to the temperature of the cold finger. The measurements performed at low temperatures are likely to have taken place at a higher temperature because of these conduction problems. Possible solutions to these conduction problems have been found but could not be applied in time. Despite no accurate measurements have been done in the case of low temperature, the compromised measurements still showed strong indications of a lower current at lower temperatures.

Qualitatively, vacuum does not seem to influence the condition of the ionic liquid (it still solidifies at low temperatures) but quantitatively, the measurements are strongly influenced by the pressure. It has to be found out if this change is caused by change in geometry (droplet becoming flatter because of bubbling in the ionic liquid) or whether the ionic liquid itself changes, as the bubbling at low pressure seems to suggest. The question if the bubbling is caused by evaporating water (which might reduce the mobility of the ions) or if it is caused by another effect, one that perhaps is internally damaging to the ionic liquid, is still unanswered. The assumed inverse proportional relation between current and distance between the electrodes has not been found; it is not clear if this is caused by the limited amount of measurements or if a fundamental theoretical mistake is the cause of this error. In general, the more quantitative treatment of this assignment has suffered under the limited number of measurements performed, caused by the long time required for each measurement. It is however hoped that the qualitative treatment is still able to help research in the area of ionic liquids.

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# 9 Appendix

## 9.1 Measurement table

For an overview of all measurements done, this table has been added. $\tau_{long}$ and $\sigma_{long}$ are the characteristic decay time and the standard deviation of this time.

Table 1: All measurement series

| Date | nr | Material | T (K) | switch time | dt | Vmin | Vmax | Vstep | distance (mm) | $\tau_{long}$ | $\sigma_{long}$ | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 24-7-2013 | 1 | Gold PC | 295.0 | 500.0 | 1000.0 | -2.5000 | 2.5000 | 0.5000 | 0.60 ±0.15 | 130.1023 | 21.3979 | |
| 25-7-2013 | 2 | Gold PC | 295.0 | 200.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.60 ±0.15 | 48.9052 | 13.8819 | |
| 25-7-2013 | 3 | Gold PC | 295.0 | 200.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.60 ±0.15 | 47.8722 | 14.1523 | |
| 26-7-2013 | 4 | Gold PC | 295.0 | 250.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | 48.8072 | 5.5218 | |
| 29-7-2013 | 5 | Gold PC | 100.0 | 250.0 | 500.0 | 0.0000 | 3.0000 | 1.0000 | 1.00 ±0.25 | 53.1168 | 2.6307 | 1 |
| 29-7-2013 | 6 | Gold PC | 50.0 | 250.0 | 500.0 | -3.0000 | 3.0000 | 1.0000 | 1.00 ±0.25 | 76.6868 | 10.6061 | 1 |
| 29-7-2013 | 7 | Gold PC | 20.0 | 250.0 | 500.0 | -3.0000 | 3.0000 | 1.0000 | 1.00 ±0.25 | 90.4165 | 33.2414 | 1 |
| 30-7-2013 | 8 | Gold PC | 75.0 | 250.0 | 500.0 | -3.0000 | 3.0000 | 1.0000 | 0.60 ±0.15 | 220.4147 | 45.1705 | 1 |
| 30-7-2013 | 9 | Gold PC | 10.0 | 250.0 | 500.0 | -3.0000 | 3.0000 | 1.0000 | 0.60 ±0.15 | 65.4717 | 12.7691 | 1 |
| 31-7-2013 | 10 | Gold PC | 295.0 | 250.0 | 500.0 | -10.0000 | 10.0000 | 2.0000 | 1.40 ±0.35 | 31.2862 | 2.2658 | 2 |
| 31-7-2013 | 11 | Gold PC | 295.0 | 250.0 | 500.0 | -10.0000 | 10.0000 | 2.5000 | 0.60 ±0.15 | 28.5062 | 3.4623 | 2 |
| 31-7-2013 | 12 | Gold PC | 295.0 | 250.0 | 500.0 | 0.0000 | 10.0000 | 2.0000 | 0.20 ±0.05 | 30.0621 | 3.9088 | 2 |
| 31-7-2013 | 13 | Gold PC | 295.0 | 250.0 | 500.0 | -3.0000 | 3.0000 | 1.0000 | 0.20 ±0.05 | 25.7313 | 1.2907 | 3 |
| 1-8-2013 | 14 | Gold PC | 295.0 | 150.0 | 200.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | 26.3366 | 1.8996 | 4 |
| 1-8-2013 | 15 | Gold PC | 295.0 | 150.0 | 200.0 | -8.0000 | 8.0000 | 0.4000 | 0.80±0.20 | 638.1084 | 1445.0000 | 2 |
| 1-8-2013 | 16 | Gold PC | 295.0 | 150.0 | 200.0 | -4.0000 | 4.0000 | 0.5000 | 0.40±0.10 | 27.9280 | 4.1602 | 3 |
| 1-8-2013 | 17 | Gold PC | 295.0 | 150.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | 28.3933 | 5.3821 | |
| 1-8-2013 | 18 | Gold PC | 295.0 | 75.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | 14.7708 | 2.0467 | |
| 1-8-2013 | 19 | Gold PC | 295.0 | 25.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | - | - | |
| 1-8-2013 | 20 | Gold PC | 295.0 | 5.0 | 100.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | 4.8015 | 0.0000 | |
| 2-8-2013 | 21 | Gold PC | 200.0 | 150.0 | 500.0 | 0.0000 | 3.0000 | 0.5000 | 0.20 ±0.05 | 23.5125 | 3.9776 | 5 |
| 2-8-2013 | 22 | Gold PC | 150.0 | 150.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | 28.7468 | 3.7847 | 5 |
| 5-8-2013 | 23 | Gold PC | 295.0 | 250.0 | 500.0 | -4.0000 | 4.0000 | 0.5000 | 0.20 ±0.05 | 52.8152 | 18.4589 | 6 |
| 6-8-2013 | 24 | Gold PC | 10.0 | 200.0 | 500.0 | -2.0000 | 2.0000 | 0.5000 | 0.20 ±0.05 | 56.5809 | 10.2729 | 5,6 |
| 6-8-2013 | 25 | Gold PC | 150.0 | 200.0 | 500.0 | 0.0000 | 2.0000 | 0.5000 | 0.20 ±0.05 | 65.0094 | 10.4202 | 5,6 |
| 6-8-2013 | 26 | Gold PC | 170.0 | 200.0 | 500.0 | -2.5000 | 2.5000 | 0.5000 | 0.20 ±0.05 | 37.9927 | 8.3078 | 5,6 |
| 6-8-2013 | 27 | Gold PC | 190.0 | 200.0 | 500.0 | -3.0000 | 3.0000 | 1.0000 | 0.20 ±0.05 | 31.6127 | 3.5241 | 5,6 |
| 8-8-2013 | 28 | BeCu Probe | 100.0 | 200.0 | 500.0 | -1.5000 | 1.5000 | 0.5000 | 2.00±1.00 | 328.0574 | 214.0161 | 6,7 |
| 20-9-2013 | 29 | Sputtered | 295.0 | 200.0 | 500.0 | 0.0000 | 3.0000 | 0.5000 | 1.60 ± 0.60 | 56.8646 | 22.1067 | |
| 20-9-2013 | 30 | Sputtered | 295.0 | 200.0 | 500.0 | 0.0000 | 3.0000 | 0.5000 | 1.60 ± 0.60 | 36.3516 | 2.1587 | |

In the column *Remarks* there are different numbers. This is the meaning of these numbers.

1. The measurement is not actually at this temperature: lack of thermal conduction results in a temperature difference between the cold finger and the droplet;
2. A Redox reaction is taking place;
3. Measurement is being performed with a droplet which has broken down before;
4. Same droplet as yesterday;
5. Not actually at this temperature (same as 1);
6. New ionic liquid has been used for this measurement;
7. This measurement has been done by direct contact with the probe.