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‘‘MODELADO DE UNA BATERIA DE VANADIO REDOX FLOW BASADO EN IMPEDANCIA ESPECTROSCOPICA’’

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Master Thesis

Modelling of a Vanadium Redox Flow Battery Based on Impedance Spectroscopy

Pablo Briones
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Electrochemical Energy Conversion and Storage Systems

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Abstract

All Vanadium Redox Flow Battery (VRB) attracts more and more attention since several years because some of its characteristics, such as the power is flexible that is determined by the number of cells and the size of the electrodes and the energy capacity is also flexible if different volume or concentration of vanadium electrolyte is used. With those characteristics, it can be used together with photovoltaic or wind energy resources; it can also be used to leave generated power and loads.

In this work, VRB is investigated. At first the general information about energy storage systems are introduced. Then the main structure and basic operating principle of the VRB are explained in chapter 3. The impedance spectroscopy of the VRB and the charge and discharge curves that are measured under different conditions are analyzed in chapter 4. In the following chapter the 3D model of VRB that consists of mechanical model, chemical model electrical model is set up with the program Comsol Multiphisics.

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1. Introduction

In the energy race that has been taken place for several years, not only the generation of energy is the main topic under discussion but also the storage of this energy. Currently there are not sufficient sources of energy that can fulfil the energetic needs of different persons, companies or countries. That is why a lot of investigations and developments have been made in order to generate energy for a short time and also to support the current system of energy generation, giving as result the called "Storage Systems".

Energy storage technologies have been largely recognized as a significant utility in daily requirements of energy, due to its mobile nature. Its application can be observed from a simple mobile phone to the systems which require more energy such as a vehicle. These Storage Systems are also used in together with the primary sources of energy generation in other types of applications such as load levelling and peak shaving. With these techniques the generation, transmission, and distribution of energy can be improved and it allows the companies to defer investment in additional capacity.

During the last years because of the increase in the interest of these applications a large number of investigations and developments has been made in this field, therefore this is being transforming parallel to the energy race. But some consequences have also been appeared such as the increment of the development time in order to improve the quality of the systems and increment of its associated cost. On the other hand, the interest in the Storage System has grown in consideration of the environmental concern. New laws and permits in the environmental policies have given a boost to the development of energy storage technologies.

Among all of the new technologies that have been investigated, one energy storage system that has shown some promising performance is the "Vanadium Redox Flow Battery" technology, which is also known as VRB energy storage. The first investigation in redox systems was done by the NASA and later (in 1970s) by the Electro-Technical Laboratory (ETL) in Japan. In 1984 these investigations were applied to the vanadium redox battery at

the University of New South Wales (UNSW) in Sydney, Australia. The VRB acquire the attention very quickly because it has almost unlimited capacity to use larger storage tanks. Moreover, the VRB is considered as a good solution for the application of energy support, as it can work as a secondary supply for villages and can be integrated in the grids for load levelling and peak shaving.

1.1. Goals

The main goals of the work are to improve the knowledge of a Vanadium Redox Flow Battery System (VRB) by researching and analyzing their behavior under specific parameters.

The specific goals are listed s follows:

- Measurements and analysis of charging and discharging cycles in a VRB with different currents.

- Measurements and analysis of charging and discharging cycles in a VRB with different flow rates.

- Measurements and analysis of the Electrochemical Impedance Spectroscopy for different States of Charge (SoC).

- Modelling with Comsol Multiphisics to investigate the behaviour of the VRB, where mechanical, chemical and electrical parts are all combined in only one model.

1.2. Executive Summary

In the second chapter of this document an introduction about the storage systems, observing the advantage of use this systems, also some important parameters of batteries are explained.

Then with the knowledge of batteries, the specific kind of storage system used in this work which is the Vanadium Redox Flow Battery will be observed, were its operating principle and structure are explained.

In chapter four the measurement performed with the VRB under different conditions will be observed. A range of different currents have been used and charge-discharge cycles were obtained. Also measurements with different flow rates can be observed and estimation about the optimal value is introduced. Moreover, the electrochemical impedance spectroscopy technique is applied in the battery for observing the losses and finally an equivalent electrical circuit will be obtained.

In chapter five, a model of the VRB is set up. This model was developed with Comsol Multiphisics which includes the mechanical model for the representation of the fluid flow, a chemical model for representing the reaction in the cell and an electrical model to analyse the behaviour of the cell. These three models are implemented together in the software.

2. Electric Energy Storage Systems

This chapter makes reference to the energy storage and also speaks, about the different types of electric storage systems. We'll be able to see the advantages of storing energy and also, some important applications. The diverse characteristics of several storage systems will be appointed, taking into account the advantages and disadvantages of these systems. In addition, different parameters for choosing a battery will be introduced, in order to have a better vision when looking for a storage system.

2.1. Why to Store Energy?

With the pass of the years and the increase in technologies all over the world, more and new requirements will be necessary for developing and complementing these new challenges. The storage systems are a good solution to deliver energy to many different systems.

Store the electric energy delivers a big and necessary mobility in some cases, for example in mobile applications, like mobile phones we need to include a storage system in order to make the phone work.

It is important when we talk about the starting engine in the automobile sector, have in mind a storage system supplying for a large number of consumer devices in the car. It is also important in the development of hybrid vehicles and in full vehicles, make a in the traditional supplying system of energy used in vehicles.

Together with the development of electric vehicles, we have other important reason, which is, the decrease of emissions to the environment, which has been a topic of global care.

The dependency in computers increases the dependency on reliable power supply systems and requires storage systems for giving more energy. In the case of failures in the systems it is completely necessary to have a power system supply in connection with the network. Thus, it is possible to avoid the breakdowns in the systems and loss of information in case of offices, and loss of energy generation in the case of medical applications.

Today we are in a new tendency, which is, distributed generation. Distributed generation is a new trend in the generation of heat and power. The concept of distributed energy resources allows "consumers" to generate heat or electricity for their own needs to send surplus electricity back to the power grid or share excess of heat via a distributed heating network. Distributed generation systems with cogeneration systems or combined heat and power can be very efficient, using up to 90% of the potential energy in the fuel they consume. This point is really interesting, because it affects directly the cost of the energy, decreasing the price of it for the consumer.

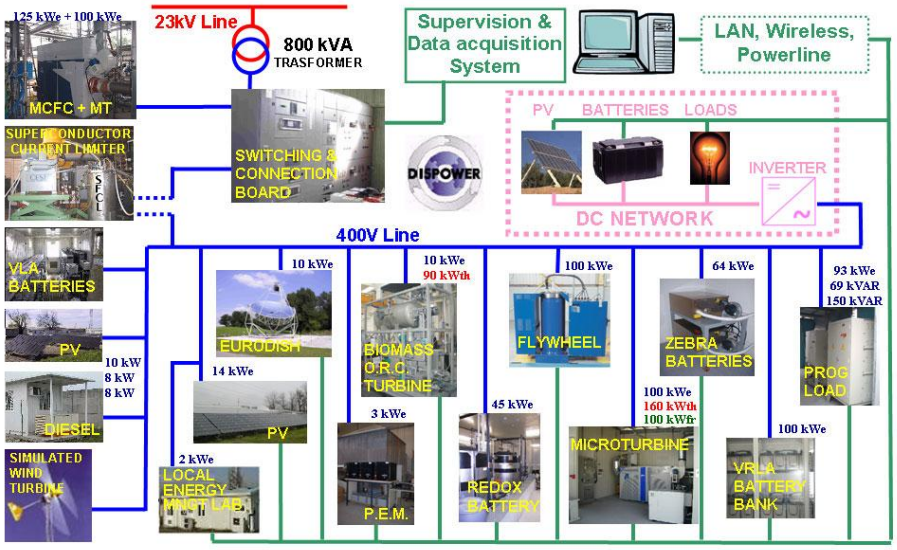


Figure 2-1: Distributed generation. The different ways to deliver energy in a grid [1]

2.1.1. Advantages of the Energy Store Systems

If we compare an electric storage system, with the conventional, existing systems like petroleum or natural gas, the electricity in the conventional systems has to be used when the energy is generated, but with an electric storage system it is possible to use the energy when it is necessary. For this reason stored energy can be more flexible and will have a wide range of applications due to its mobility.

When we are talking about the supply application, we can see the advantages when encountering problems in energy delivery over the part of the principal source. If there are

problems in a hospital, it is absolute necessary to have a power supply, like UPS, because the equipment for some patient could be disconnected. Thus, the electrical storage system in this case, plays an important role.

In this case the electric storage system must have the necessary requirements for part of the load, but we will discuss about the requirements later.

Other types of benefits exist when storing energy. For example, if we are talking about the daily consumption of energy in a house. The electricity market involves the purchase of cheaper electricity, when the consumption in the houses is lower, and the generation is bigger, and is resaled when the demand is bigger. Thus, the company increases its benefits. That happened because the market is always regulated by the supply and demand paradigm, and when the demand is lower and the supply is bigger, the prices are lower and when the demand is bigger than the supply, the prices are more expensive. Thus, is easy to see how this point works.

In relation with the last point, it is possible to use the "saved energy", accumulated when the demand is lower, in other applications. For example, in electrical vehicles: it is possible to smooth the short expiation when they brake or accelerate. An elevator is a good candidate for use this type of application. These two applications save energy and this energy can smooth the short burst of power.

In the same point it is possible for the consumer to take advantage due to the variation in prices, and accumulate energy when the price is lower, for example at night, and use the energy when the price is more expensive.

Another major advantage is using the electric storage system as other principal source of energy. When we have low demand of energy we can store the energy, and when the demand of energy is bigger than the generation, we can introduce the energy accumulated before in the system. Thus, it is not necessary to introduce other source for generate energy, thus decreasing the cost and probably gain a higher efficiency.

In the case of transmission and distribution of energy, sometimes the demand at some parts of the day can be higher than the energy supplied by the transmission line. In this case we can make use of a power supply, and accumulate energy during the period of lower demand and partly supply the extra consumption during the higher demand of energy. That is not a final installation it is only a supply of energy while another line is being build.

When we see some renewals application, like wind energy or solar energy, at some point it is not possible to generate energy due to the conditions (not wind, not radiation). In this case it is possible to accumulate energy during the periods of lower demand and deliver energy in the other case.

2.2. How to Choose a Battery?

In this section we'll discuss about some important parameters how to choose a battery. It is important to know that a perfect battery does not exist. All the batteries have different characteristics and ranges, and because of that they have its advantages and disadvantages. The most important thing when it comes to choose a battery is the following question: *"in which application will be used the battery?"*. This question will be discussed below.

2.2.1. Important Parameters for Choosing a Battery

In relation with the last question *"in which application will be used the battery?",* it is important to take some parameters into account, for example: What kind of power is needed and how many time is needed, what is the efficiency and the operation time for the battery (lifetime) and last but not least, which is the price of the battery. These parameters are explained below.

2.2.1.1. Power and Discharge time

The Power parameter is essential in the world of batteries, all the application consumed power and in relationship with time. If we looks into the world of batteries over the power parameters in a battery, it is possible to find, from a few watts (W) to a thousand Megawatts (MW), and it is also possible to find batteries working from a few seconds lasting to a years.

Due to this we can define it in two big groups, the batteries with short discharge time and with long discharge time.

In the first group it can find, the supercapacitors, flywheels and superconductive coils. These three types of storage are able to deliver high power from few milliseconds to few minutes. One application for this time of batteries is UPS (Uninterruptible Power Supply). Also these batteries are able to have a large number of maintaining cycling a high quality power.

In the second group there are pumped hydro batteries, compressed-air storage system and the flow batteries. It is possible to find an application in energy management and these batteries are able to store large quantities of energy for very long periods of time.

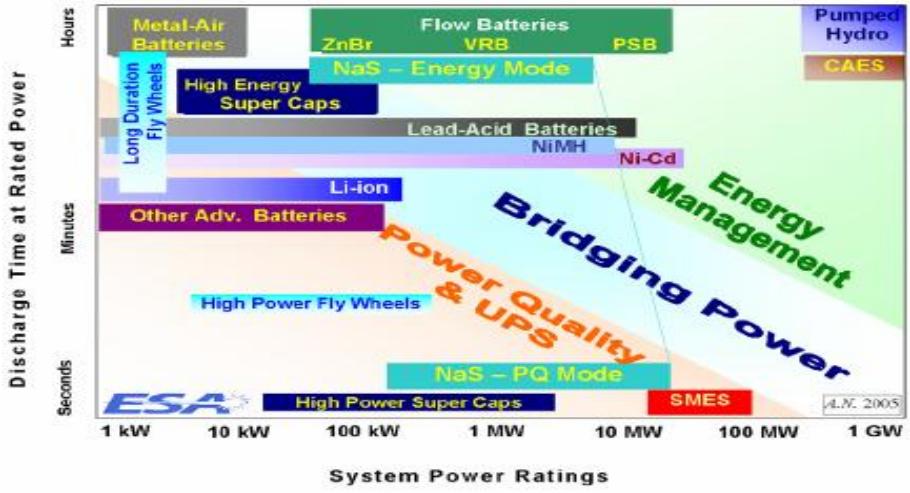


Figure 2-2: Graphic with the different type of batteries and the working areas under power and discharge time [2]

2.2.1.2. Efficiency and Lifetime

These two aspects are very important and are influenced by the operation condition of the battery. Some imply difficult conditions for the batteries and can decrease the efficiency and the lifetime of the battery. For example, the lithium-ion one has a long life time in 80% Sate of Charge (SoC), but under this condition his life time decreases drastically. The batteries are affected too due to environmental conditions.

But as seen, not all the batteries are equals, and some batteries are able to work in some conditions where others cannot. For example for high temperatures only the NaS can work and the others don't, but this battery can't work at lower temperatures.

Other batteries with high efficiency and a long lifetime cannot be used in some application, for example the supercapacitor cannot be used in applications with high energy requirement, because it is not able to store a lot of energy.

So it is possible to say, that the parameter for the efficiency is influenced too by the current density, charge and discharge characteristics and temperature. [3]

With this description it is clear that it is really necessary to know and take into account under which condition the battery will work.

2.2.1.3. Price of the Battery

Continuing with this topic it is necessary to speak about pricing. The price of the battery is another of the important parameter in the time to select a storage system. As these are different technologies, and being used in these construction processes, they all have different.

The price of the storage system depends in a big part on the power and the energy rating associated to the battery. For example the Lithium batteries are very good in this two parameters witch determine its high price.

Then it is a technical and economical analysis to determine which battery is better, taking into account the partial cost, the final cost and the delivered benefits for the storage system.

The final cost makes reference to the lifetime and the maintenance cost associated with the storage system. This parameter increases the initial cost of the battery and changes with different types of storage system.

3. Redox Flow Battery Systems

This section it will be introduced about the type of storage systems, how to use in present work and it also explains the details of the most important parameters of this storage system. A view about the different redox systems will be observed and also we will look in detail the type of redox flow battery used in this work, "Vanadium Redox Flow Battery", naming the principals aspects of this battery and considerations and changes made in the practical model.

3.1. Types of Redox Flow Cells

In this section it is possible to find the different types of redox flow systems that have been development and investigated with the past of the years. Redox flow batteries Systems are categorized by the chemistry of the electrolytes and they are:

- Bromine/polysulphide Flow Battery
- Vanadium Redox Flow Battery
- Vanadium-bromine Redox System
- Iron-chromium Redox System
- Zinc/bromine Redox Flow cells
- Zinc/cerium Redox Flow cells
- Soluble Lead-Acid Battery (undivided)
- Uranium Redox Flow Battery [4]
- Neptunium Redox Flow Battery [4]

The characteristics of these types of batteries can be observed in the [5]. In the present work it has worked with a Vanadium Redox Flow Battery (VRB), and is explaining in the next section.

3.2. Vanadium Redox Flow Battery (VRB)

In the lasts sections has been seen the characteristics of the main types of batteries explained their basic operation principle and also some important parameters. After this, has been seen too about the Redox Flow Systems and how it works, taking into account the mains characteristics, the advantages and disadvantages, some important considerations and the application of this type of batteries, observing that the RFB take advantages in large stationary storage applications.

This part of the work shows in details the specific type of redox flow battery used the Vanadium Redox Flow Battery. The Vanadium Redox Flow Batteries (VRB) was development by Maria Skyllas-Kazacos and co-workers [6, 7]. They have used vanadium in the both half cells, thus was possible to eliminate the problem of the cross contamination by diffusion of ions across the membrane. All of this is possible due the propriety of the vanadium for work in four different oxidation states, so with this propriety it is possible to use only one electroactive element instead of two.

One question can be *"Why Vanadium redox flow system and not other?"*. There are two main characteristics or answer to this question. The first is because is more easily produce the electrolyte with only one electroactive element (Vanadium), will it see how is possible to obtain the vanadium for the two half cells in this part of the work. The second answer is that other types of redox flow batteries have toxic materials and it is necessary, and required other specials conditions for this, like a recirculation pump to homogenize the electrolyte or even deposit materials on the electrode. With this the energy efficiency decrease, because it need to use more energy for make work the system.

In this work the VRB used contain only one cell, this cell is divided in two half cells separated by a permeable membrane. The electrochemical reaction take place in the on inert carbon felt which the current is collected. There are too in the systems, pipes and pumps for the flow of the electrolyte form the tanks to the both half cells.

The electrolyte is a mixed solution between vanadium and sulphuric acid. The sulphuric acid integrates the hydrogen necessary to maintain the electric balance in the system, which are past across the membrane by osmosis.

The name of a redox battery is given due the electrochemical systems where the Oxidation and Reduction reaction are involved. These terms are explained below:

- **Oxidation:** is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.
- **Reduction:** is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.

Reduction

$Oxidant + e^- \rightarrow Product$

(Gain of Electrons) (Oxidation Number Decreases)

Oxidation

$Reductant \rightarrow Product + e^-$

(Loss of Electrons) (Oxidation Number Increases)

Figure 3-1: The oxidation and reduction process

3.2.1. Main Structure of a VRB

The main structure of a VRB can be observed in the figure 3-2 where it is possible to find the different elements.

There are two tanks that contain the electrolyte, in this case vanadium *V* (VO_2^+) and vanadium *IV* (VO^{2+}) in the positive tank, and vanadium *II* (V^{2+}) and vanadium *III* (V^{3+}) in the negative tank. In the beginning when the battery is discharge from 100% SoC, the vanadium presented in the positive tank is VO^{2+} and the vanadium presented in the negative tank is V^{3+}. When the battery is charge from zero SoC and due the redox process, the vanadium presented in the positive tank is VO_2^+ and in the negative tank is V^{2+}. How that happened is explain as following:

The electrolyte present in a VRB is a solution of vanadium mixed with a diluted sulphuric acid, and the electrolyte of a VRB has an indefinite life span and is reusable, due to the flow of the electrolyte in the redox flow system.

The electrodes are current collectors and must to have a high electrical conductivity and a long cyclic life working in sulphuric acid concentration. Some investigation about the

material of the electrode was development and element like glassy carbon, carbon clava, carbon cloth and carbon felt was investigated. An electrode with carbon felt is using in this work due to its good proprieties, high specific surface area and good stability.

Other elements present in the figure 3-2 are the pump. The work of the pump is pumping the electrolyte from the tanks to the both half cells. With these elements it is possible to change the flow velocity of the electrolyte.

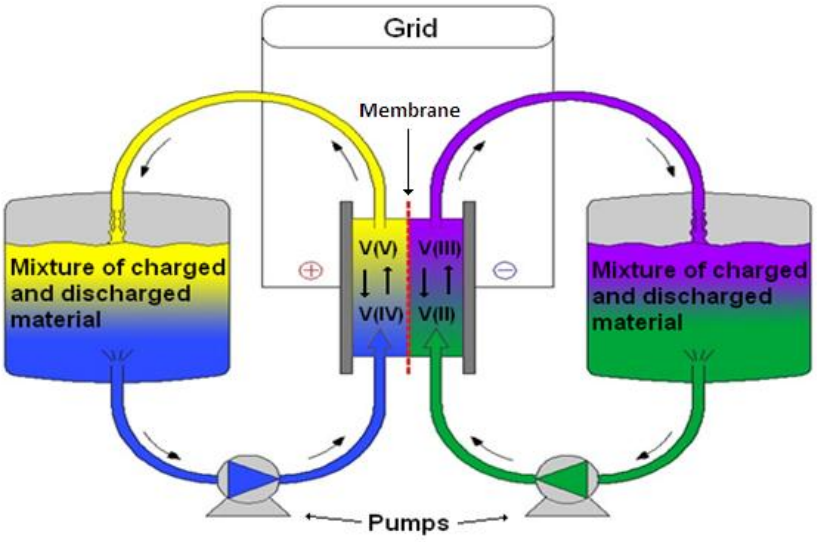


Figure 3-2: The main structure of a Vanadium Redox Flow Battery (VRB)

3.2.2. Electrolyte

The electrolyte in a vanadium redox flow battery corresponding only a one electroactive material, the vanadium. The vanadium has the characteristics to stay in four different state of oxidation. That is the reason because it is used. It is possible find the vanadium in the state of oxidation *II*, *III*, *IV* and *V*.

The electrolyte in the case of the vanadium batteries is a mixture between vanadium and sulphuric acid. The reason for use sulphuric acid is due his a good oxidant agent and deliver the necessary hydrogen for maintain the stability of the system. Below are explaining this to materials and their principal characteristics.

It is necessary known about two important proprieties of the electrolyte; the density and the viscosity. These both parameters are important in the fluid mechanics of the system. All the densities and viscosities of the vanadium *II*, *III*, *IV* and *V* are different and are influenced by the temperature and the Sulphuric Acid concentration. [8]

3.2.2.1. Vanadium

Vanadium is a chemical element with atomic number 23 located in Group 5 of the periodic table of elements. Its symbol is *V*. It is a ductile metal, soft and not abundant.

It is found in various minerals and used mainly in some steal alloys. This transition metal has a high resistance to bases, sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). It is obtained from various minerals and petroleum.

Compounds present in various oxidation states, the most common being +2, +3, +4 and +5. This characteristic can be easily observed due an interesting propriety of the vanadium; its color changes with its charge level, which in the figure 3-3. When fully charged, the catholyte is yellow and the anolyte is violet; when the VRB is discharged, the catholyte turns gradually blue and the anolyte turns green. This propriety can be estimate due the state of charge and thus the concentrations.



Figure 3-3: The different colour at different state of oxidation of the vanadium

These different type of vanadium can be obtains due an electrolysis of a Vanadyl sulphate $VOSO_4$. With the dissolution of the $VOSO_4$ it is possible to obtain Vanadium *IV* (VO^{2+}). The electrolyte is after obtains of electrolytic oxidation and reduction. [9]

3.2.2.2. Acid Sulphuric

It is a very corrosive chemical compound with the formula H_2SO_4. It is the chemical most widely produced in the world. H_2SO_4 is used as one of the many meters of industrial capacities of the countries. Also used in the production of fertilizers. It is also used for the synthesis of other acids and sulphates and petrochemicals industries.

The concept of an acid or a base has been established from various points of view. In the simplest form, an acid is defined as a compound able to donate protons ($+H$) to the water and a base as a substance that gives OH-ions into the water.

For an acid acting as such, has to do with a compound serving as the base. This is the case of water, which have double characteristic (acid or base), give the protons of sulphuric acid from the reactions.

3.2.3. Electrochemical Process

In the case of the Vanadium redox flow battery the reaction is separated in two simultaneous steps, which occurs in the each both half cell. The process that appears in this type of batteries is the reduction-oxidation (redox) that in the vanadium for each both half cells.

For understand better what happened in the cell it is possible to explain in general due to the next equations:

$$V^{3+} \leftrightarrow V^{2+} - e^{-} \quad (3.1)$$

$$V^{5+} + e^{-} \leftrightarrow V^{4+} \quad (3.2)$$

The equation (3.1) and (3.2) are general equation for charge and discharge process. During the discharge, electrons are removed from the anolyte and transferred for an external circuit or grid (like in the figure 3-2) to the catholyte. The oxidant vanadium *V* (V^{5+}) takes an electron from the reductant vanadium *II* (V^{2+}). So V^{5+} is reduced and V^{2+} is oxidized.

The flow of electrons changes when the battery is charging, in this parte the reduction process taking place in the anolyte and the oxidation in the catholyte.

But in reality the reactions in the vanadium redox battery are not too simple like the present in the equation (3.1) and (3.2) due to two reasons. The first is that the vanadium V^{5+} and vanadium V^{4+} are in fact vanadium oxides, respectively VO_2^+ and VO^{2+}. And the second thing is for maintain the charge balance, it is necessary to introduce water molecules and H^+ in the reaction of the cathode. How it has already seen this water molecules are introduces in the form of solution of sulphuric acid into the system.

So the new equation taking into account these new references are development in the next equations, where the first describe the VRB reaction at the positive electrode or cathode, where the vanadium oxides VO_2^+ and VO^{2+} are presents:

$$VO_2^+ + 2H^+ + e^- \quad \leftrightarrow \quad VO^{2+} + H_2O \tag{3.3}$$

Now if it goes to the negative electrode or anode, the water molecules and the protons that are part in the positive electrode do not take part in the electrochemical reaction of the negative electrode, thus the anodic reaction stay like the equation (3.1):

$$V^{3+} \quad \leftrightarrow \quad V^{2+} - e^- \tag{3.4}$$

Finally it have that the negative part (anolyte) contain V^{3+} and the positive parte (catholyte) contain VO^{2+}, when the battery is totally discharged. After when it start with the charge of the battery reactions begin and the concentration of V^{2+} ions increases the negative part and in the same time the concentration of V^{3+} ions decrease. In the positive part is the same, the concentration of VO_2^+ ions increase and the concentration of VO^{2+} ions decrease.

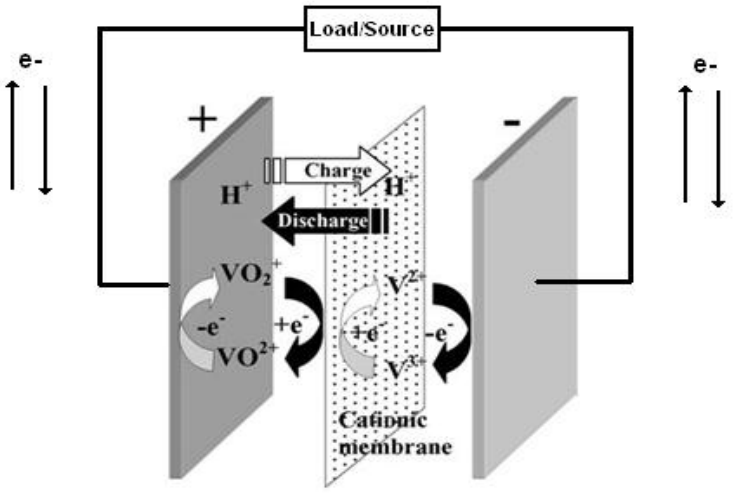


Figure 3-4: A schematic of the electrochemical reaction in a VRB [5]

3.2.4. Membrane

This section presents one of the primordial elements in the VRB, the membrane. Ion exchange membrane divides the two electrolytes of a VRB and usually used to provide proton (Hydrogen) conduction to maintain the electrical balance and effective separation of the anode and cathode electrolytes. The ideal membrane for VRB should possess low vanadium ion crossover, high ionic conductivity, and good chemical stability. The membrane physically separates the two vanadium-based electrolyte solutions, preventing self discharge while allowing for the flow of ions to complete the circuit.

Nafion is the material for the most commonly membrane used for the proton exchange in VRB system due to its high proton conductivity and good chemical stability in strong acid and oxidation condition.

Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer discovered in the late 1960 by Walther Grot of DuPont It is the first of a class of synthetic polymers with ionic properties which are called ionomers. Nafion is unique ionic properties are a result of incorporating perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene (Teflon) backbone. Nafion has received a considerable amount of attention as a proton conductor for proton exchange membrane fuel cells because of its excellent thermal and mechanical stability.

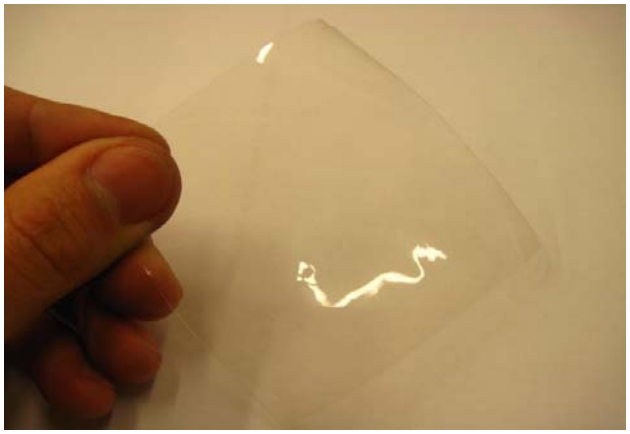


Figure 3-5: The physical structure of a nafion membrane

However, there exist problems when the nafion membrane works in the VRB, they can not 100% prevent the vanadium ions crossover, and lead to the decrease of coulomb efficiency, voltage efficiency and energy efficiency of VRB system. In order to reduce the permeation of the vanadium ions and improve the performance of VRB, various methods of modification of nafion membrane have been proposed and a series of satisfactory results had been obtained.

There are extensive research activities in the modification of nafion to reduce the methanol permeability, for example, recasting with inorganic nanoparticles, surface modification with metal thin film, surface modification with layer-by-layer self-assembly polyelectrolyte, hot-pressing with other proton conducting membrane, and in situ sol-gel reaction to incorporate inorganic oxide nanoparticles within the pores of nafion. All of above modification methods may also be used to decrease the crossover of vanadium ions through nafion membrane and, in general, improves the performance of VRB. [10]

In the VRB used in this work the modification of the membrane was due to the introduction of silicate (SiO_2) hybrids nanoparticles in the nafion membrane.

The principal characteristics of the Nafion/SiO2 hybrid membrane as separator for VRB are; reduce the permeability of vanadium ions and improve the cell performance. Nafion/SiO2 hybrid membrane was prepared by in situ sol–gel method and showed a lot of advantages in comparison with the original nafion membrane. For example, it has nearly

the same ion exchange capacity and proton conductivity as that of nafion and shows much lower vanadium ions permeability compared with the nafion membrane. The VRB single cell with Nafion/SiO_2 hybrid membrane shows a higher coulomb, energy efficiencies and a lower self-discharge rate than that of nafion system. Those studies show that the performance of VRB can be remarkably improved by filling nafion cluster with certain nanoparticles.

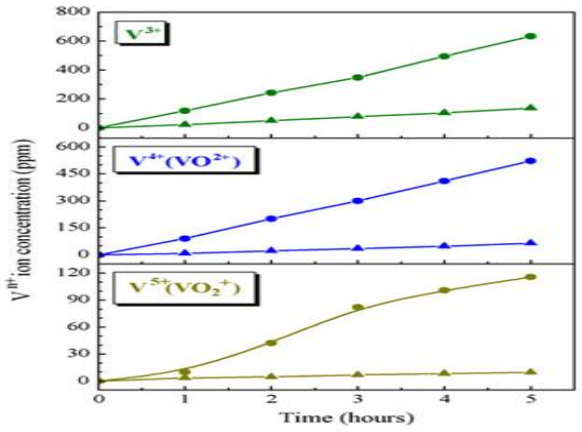


Figure 3-6: Vanadium ion concentration in the right reservoir of the cell with Nafion (●) and Nafion/SiO_2 (▲) membranes [10]

3.2.5. Electrode

The electrodes used in vanadium redox batteries are composed of high-surface area carbon materials. These materials operate across a wide range of voltage potentials with minimal hydrogen and oxygen evolution, are chemically stable with respect to the acidic electrolytes at both the anode and cathode of a cell, and are available at reasonable costs. Carbon materials have a very wide range of characteristics depending on the methods of manufacturing and preparation.

Also have been used metal electrodes such as gold and platinum but are not practical because they have a high cost. It has been found that graphite gives a good reversibility to electrode reactions, one of the requirements of the electrode in the VRB.

The electrode material used must also possess good stability during charging, good electrocatalytic properties for the vanadium reactions and poor kinetics for hydrogen and oxygen evolution so as to minimize gassing during charge. The relatively fast kinetics of the vanadium redox couples allow high coulomb and voltage efficiencies to be achieved without the use of expensive catalysts.

The carbon presents some electric properties as electrical conductivity and dielectric constant. Electrical conductivity is the ability to conduct electrical current through it. It is defined in terms of specific resistance, which is the resistance of a carbon block 1 cm in length and 1 cm^2 section. The unit is the Ω m. This property depends on the pressure, temperature and water content of coal. Dielectric constant is taken into account that the electrical conductivity. It is a measure of the electrostatic polarizability of carbon dielectric. This is related to the polarization of electrons that exist in the rings of the structure of coal. This property is closely related to the water content of coal varies with the rank of coal. But due by some research to improve the electrical characteristics of the electrode, porous graphite felt was introduced with the carbon electrode. This carbon felt is employed as the flow-through electrode, allows excellent mass-transfer and permits greater surface area for the oxidation and reduction reactions.



Figure 3-7: The physical structure of a carbon felt used in a VRB

3.2.6. Structure of a Cell

Now all the components for a VRB are known, then it is possible to do a schematic of the cell of VRB used in this work, showing all of the material presents in the cell. In the figure 3-8 it is possible to observe the main split structure of the cell of VRB used. Also is presented in the figure 3-9 the final VRB used in this work.

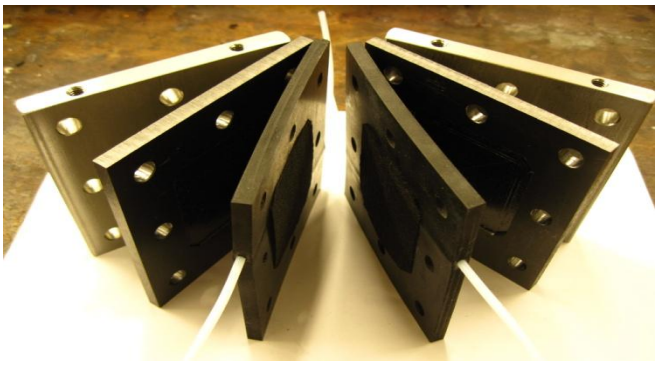


Figure 3-8: Open structure cell of the VRB

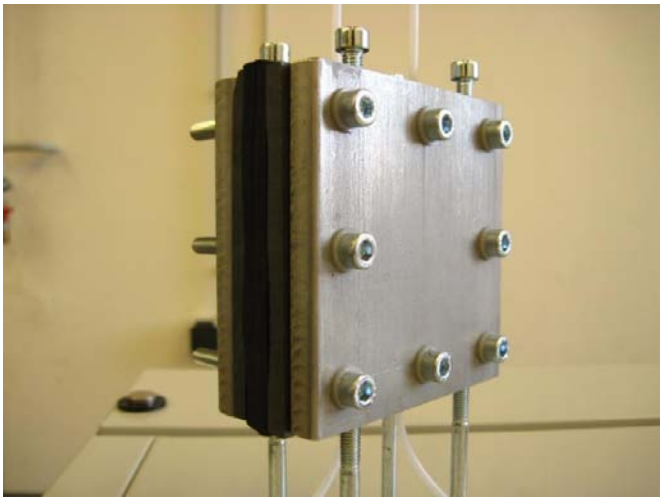


Figure 3-9: A picture of the real cell used in the work

3.2.7. Important Parameters

In this section it will be discuss about the three important parameters in relation with the Vanadium Redox Flow Battery (VRB), energy density, power density and efficiency. The firsts two parameters can be described as the amount of energy or power stored in a given system or region of space per unit volume. The difference between this to parameters is that the energy is the amount of power consumed over time, and power is how much power can be quickly deliver for the system.

The efficiency is also important and can be define in the economics as the relationship between the results (profits, goals accomplished, products, etc.) And the resources used (man-hours, investment, commodities, etc.). In storage system is the same but the results and the used resources have relation with the parameters of the system.

3.2.7.1. Energy Density

How is know, the energy density in decided by the active materials, for example in the lead acid battery, the active material are in the electrodes. In case of a Vanadium Redox Flow Battery (VRB) it is possible to find the active material dissolved in the electrolyte.

The capacity is due to the number of electrochemical reaction that is defined in Amperes-Hours (Ah). So in VRB it depends on the number of the ions and the number of ions that depends on the vanadium concentration, the volume of the tank, the Avogadro number and the elementary charge of the electron.

Thus the equation is:

$$Q_c = C_{vanadium} * V_{tank} * N_A * e \quad (\mathrm{C\ or\ A} * \mathrm{s}) \tag{3.5}$$

Now it is necessary to calculate the energy storage in the electrolyte $E_{electrolyte}$ according to the cell capacity and the voltage produce by the cell U_{cell} (in theoretic the voltage of the cell

is approximate 1.3 V, 1.0 V are produced in the cathode and -0.3 V are produced in the anode). So the equation is:

$$E_{electrolyte} = \frac{1}{2} * \frac{Q_c * U_{cell}}{3600} \quad (Wh) \tag{3.6}$$

It is possible to see that in the equation the energy in the electrolyte is divided by factor two, because the redox reaction occurs in the both half cells. Also it is necessary divided by 3600 seconds for obtain the energy storage per hour. Thus it is only necessary divided the energy storage in the electrolyte $E_{electrolyte}$ by the volume of the tank V_{tank}, so the equation of the energy density $U_{electrolyte}$ is:

$$U_{electrolyte} = \frac{E_{electrolyte}}{V_{tank}} \quad (Wh/l) \tag{3.7}$$

With this formula it is possible to know how much energy is stored in the VRB. With the $U_{electrolyte}$ it is feasible to define, due to the energy consume.

Some investigations have been done to know how work a battery in some consumption conditions, and in the figure 3-10 it is possible to see the discharge and charge curve of a VRB of 10 KW.

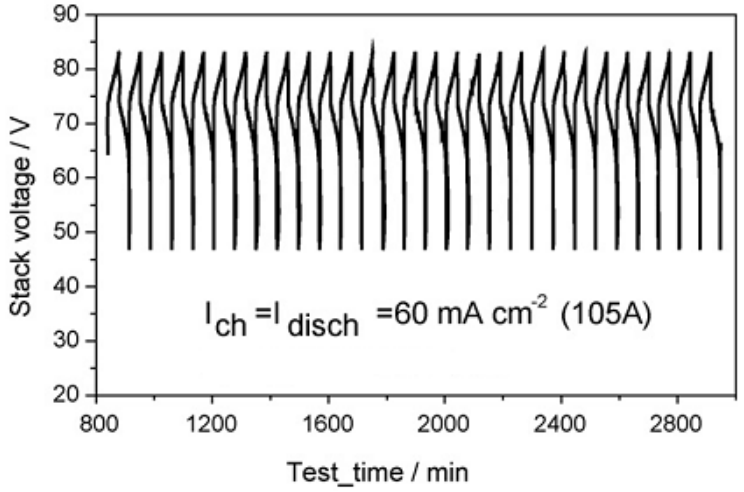


Figure 3-10: The voltage over the time for charge and discharge process with a constant current of 105A [11]

3.2.7.2. Efficiency

The efficiency η is an important parameter for the profitability of the system. With this parameter it is possible to see, if a system is profitability or not. There are 3 forms in the case of batteries for know which is the efficiency of the system; energy efficiency, voltage efficiency and coulomb efficiency. These equations are presented below.

Energy Efficiency

Is easily defined as the integral of the energy consumes by the discharge and the energy used in the charge. The equation becomes:

$$\eta_{efficiency} = \int \frac{P_{discharge}(t)dt}{P_{charge}(t)dt} \tag{3.8}$$

Where:

$P_{discharge}$: Power consumed during the discharge

P_{charge}: Power used during the charge

Voltage Efficiency

In this type of efficiency, the current in the system is constant, so the efficiency is due by the integral of the voltage during the discharge and the voltage during in the charge. The equation becomes:

$$\eta_{efficiency} = \int \frac{U_{discharge}(t)dt}{U_{charge}(t)dt} \tag{3.9}$$

Where:

$U_{discharge}$: Voltage used during the discharge

U_{charge}: Voltage used during the charge

Coulomb Efficiency

This efficiency is due by the charge withdraw during the discharge and the charge supplied during the charge. The equation becomes:

$$\eta_{efficiency} = \frac{Q_{discharge}}{Q_{charge}} = \frac{\int i_{discharge}(t)dt}{\int i_{charge}(t)dt} \quad (3.10)$$

Where:

$Q_{discharge}$: Charge withdraws during the discharge

Q_{charge}: Charge supplied during the charge

3.2.8. Advantages and Disadvantages of VRB

The main advantages of the vanadium redox flow batteries are explained here. In comparation with other redox flow systems there are some differences with which the VRB take advantages in comparison with the other types of redox flow batteries.

- A characteristic of a VRB is the low ecologic impact. In comparison with other redox flow batteries, the VRB don't have toxic material as the bromide for example. The same happened if it compare with other conventional materials like lead, zinc or cadmium. The use of aggressive chemical solutions is one of the disadvantages of redox flow batteries, but the VRB electrolyte is a solution of vanadium and sulphuric acid. The sulphuric acid is widely known in the industries.

- Other advantage in comparison with other redox flow systems and conventional batteries is how the electrolyte in the VRB is not degrade, is more easily can recycled and reuse in a new VRB.

- The electrode in the VRB is not degrading because the electrolyte the reaction doesn't take part in the electrode, only occur in the electrolyte. Also the electrolyte solution is not aggressive and electrode is not affected by the electrolyte.

- The main disadvantage of a VRB is the lower energy density, that is lower in comparison with others electrochemical systems. The lower energy density is because the active material that takes part in the reduction oxidation process (redox) is limited by the solubility of these.

3.2.9. Applications

Flow batteries were development for giving the energy to a village and using in the distributed generation but with the pass of the time emerging new applications. Flow batteries are normally considered for relatively large from 1 kW to MW stationary applications. These are load levelling, where the battery is used to store cheap night - time electricity and deliver electricity when it is more costly.

In relation with the last point the RFB are used for "Peak Shaving", where over demand are met by the battery. Also is used as UPS where the battery is used if the main power fails to provide an uninterrupted supply. However, because of flow batteries can be rapidly "recharged" by replacing the electrolyte, they have been proposed for electric vehicles.

A further potential application for redox flow batteries lies in the fact that all cells share the same electrolytes. Therefore, the electrolytes may be charged using a given number of cells and discharged with a different number. Because the voltage of the battery is proportional to the number of cells used the battery can therefore act as a very powerful dc-dc converter. In addition, if the number of cells is continuously changed (on the input and/ or output side) power conversion can also be ac-dc, ac-ac or dc-ac, with the frequency limited by that of the switching gear.

4. Measurement and Analysis of the results

The previous chapter treats of the generalities about the most common batteries and as well about the specific kind of battery used in this work Vanadium Redox Flow Battery. The most important characteristics of the battery and the principal parameters have been mentioned, and the chemical reaction and the components of the battery.

In the present work one of the main reasons is to gain a wider knowledge about this kind of battery. This is why it is necessary to use some special techniques for making measurements with the battery. One of these techniques is Electrochemical Impedance Spectroscopy (EIS).

The EIS is a derivation on the Impedance Spectroscopy (IS) and is a technique that consists in applying an ac current to a material by observing its response. The EIS is used in application when the ionic conduction is strongly predominant.

This technique is for example used in order to measure the corrosion in some material and in batteries in order to measure fuel cells and reachable batteries, with which it is possible to do an analysis of the battery and after making different theoretical models with these results, such as the electrical model of the battery.

In this chapter it will be possible to see the measurement of charge and discharge with different currents, in the range of 160mA to 1A. Therefore it is possible to observe the operating performance of the battery regarding the different consumptions. We are also able to appreciate the change of the response of the battery according to different values of flow rate, and to observe how the battery works under this variation.

4.1. Dimensions of the Battery

This short section presents the dimensions of the real battery. The battery was developed by the mechanical labour in the ISEA, and was designed due to some investigations and previous tests of other models. In this case the battery that was used is the last design for this type of battery due to the ISEA. In this case software is used for the representation of

the battery. In the Figure 4-1 the Full Split Model of the VRB can be seen and after this in the table 4-1, the dimension of each component can be found.

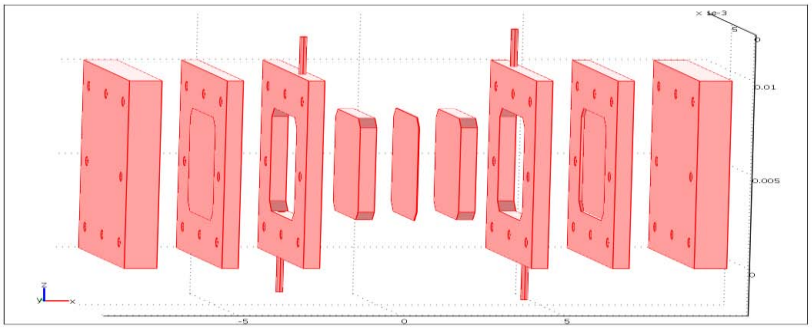


Figure 4-1: Full Split Model of the VRB

When observing the Figure 4-1 from left to right it can be found; ***Positive End plate, Positive Electrode, Insulation and pipes, Positive Carbon Felt, Membrane, Negative Carbon Felt ,Insulation and pipes, Negative Electrode, Negative End Plate.***

The negative half cell and the positive half cell have the same dimension, and it is not necessary to name this dimensions separately.

Table 4-1: The dimension of each element present in the cell

Material	**Length (mm)**	**High (mm)**	**Thickness (mm)**
End Plate	100	100	10
Electrode	100	100	5
Carbon felt	50	50	5
Membrane	55	55	0.18
Insulation	10	10	5

Now it is possible to observe that in the figure 4-1 some elements have different cuts. The carbon felt has cuts in the every corner of 5mm length and 5mm high. Also the both insulations have a hole in the middle with the same size of the carbon felt with the cuts included. The both electrodes have a cut of the same size of the carbon felt, for 1 mm of profundity in the middle.

On the other hand, 9 holes are also made to collect the cell with screws. This hole is symmetric in all of the sizes and the distance with the boundary in the corner is 12,5mm long and 12,5mm high. Also in the middle of these two holes there is another one with a distance to the boundary of 12,5mm.

The inside diameter of the pipes is 2mm and in together with the walls, it is 3mm. The pipes are in the middle of the superior and inferior boundary from 35mm of the corner.

4.2. Measurements and Analysis of the VRB Based in Impedance Spectroscopy

The use of AC impedance was known and applied in the area electrical engineering. The EIS was used for the study and characterization of materials, until the 1970's, and had a great acceptance by their characteristic signals in the frequency function, which allows analysing a system and its components.

The cause of no usage of this technique was the difficulty of collecting and processing information, as it was manually traced on polar paper charts. The problem was fixed with the advance of computer systems that facilitate the capture and organization of data.

The experimental procedure most commonly used, applies a small signal potential to an electrode and its response is measured in current at different frequencies. However, in certain circumstances, it is possible to apply a small signal current and measure the potential response of the system. Thus, the electronic equipment used processes for the measurements of potential - and current time - time, resulting in a series of impedance values for each frequency studied. This relationship of impedance values is often called "impedance spectrum."

The Alternating Current (AC) is an advantage to be a function of time and frequency; when it is applied to the order of kHz frequency, the waves are so fast that they circulate through the materials as a short circuit. That is represented due to electrical components like resistors, capacitances and inductances.

4.2.1. Basic Concepts

In this section, the basic concepts of the EIS will be introduced. Impedance is a term that describes the electrical resistance used in circuit alternating current (AC).
In a circuit of direct current (DC) the relationship between current and potential is given by Ohm's law.

$$U = I * R \tag{4.1}$$

But it is necessary to introduce the analysis in Alternating Current (AC). Therefore, is the analogy of the ohm's law is used. The resistance *R* is replaced by the impedance *Z*, in ohms. Besides the equation for AC is:

$$U(w) = I(w) * Z \tag{4.2}$$

The parameters *U(w)* and *I(w)* are working in the AC too. So it is possible to define this parameter in the function of the frequency due to angular frequency *(w)*:

$$w = 2 * \pi * f \tag{4.3}$$

Thus, when is applied a sinusoidal voltage signal it obtains a respond in current due to the equation (4.2) and the next two equations:

$$U(w) = U_{max} * sen(wt) \tag{4.4}$$

$$I(w) = I_{max} * sen(wt + \theta) \tag{4.5}$$

Where the current *I* has is the same sinusoidal signal that the *U*, but with a different amplitude and phase that the *U*. That can be observed in the next figure 4-2 a) and b).

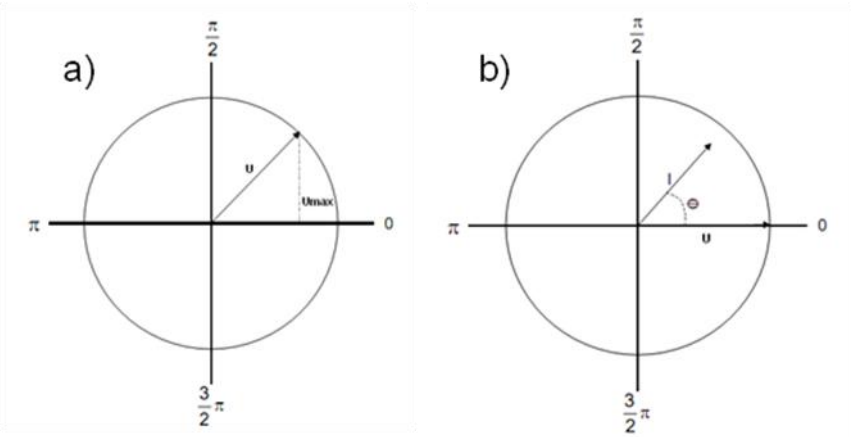


Figure 4-2: a) Phasor diagram of the AC voltage in the equation (4.4). b) The current and the voltage separate by the phase $\boldsymbol{\theta}$

There are three possibilities of changing the angle of the phase θ. The first one is when the phase angle takes values close to zero, so that indicates that Z (impedance) measured corresponds to a resistance. When the phase angle takes values less than cero, it is indicated that Z measured corresponds to a capacitor. And when the phase angle takes values more than cero, it can be seen that Z measured corresponds to an inductor.

This two new elements need to be represented by equations in order to understand their responses. Then the reactance of the capacitor and the inductor can be observed below:

$$X_C = \frac{1}{jwC} \tag{4.6}$$

$$X_L = jwL \tag{4.7}$$

Due to this representation it is possible to include the reactance of a capacitor or an inductor into the equations. The impedance Z can be defined as:

$$Z = (R + jX) \tag{4.8}$$

Therefore, for example it is possible to include in the equation (4.2), where the impedance *Z* has a real part and an imaginary part. If it included, as example, the capacitor as imaginary part, the equation (4.2) and the phasor diagram can be observed below:

$$U = U_R + U_C = I * (R - jX_C) \tag{4.9}$$

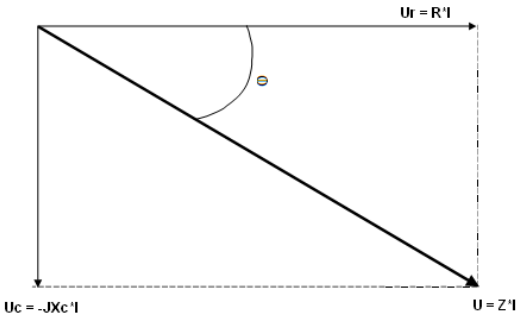


Figure 4-3: Resistance with a Capacitor in series, where the sum of these two elements is *U*

For a better compression of which parameter is measured, in the next figures can be observed two signals, the current *I* and the voltage *U*. The figure 4-4 a) is a representation of one pure resistive system, where the angle of phase for the current is identical to the angle of phase for the voltage.

The figure 4-4 b) is a representation of one system with a capacitance, so it is possible to observe the phase angle of 90º produced by the capacitance.

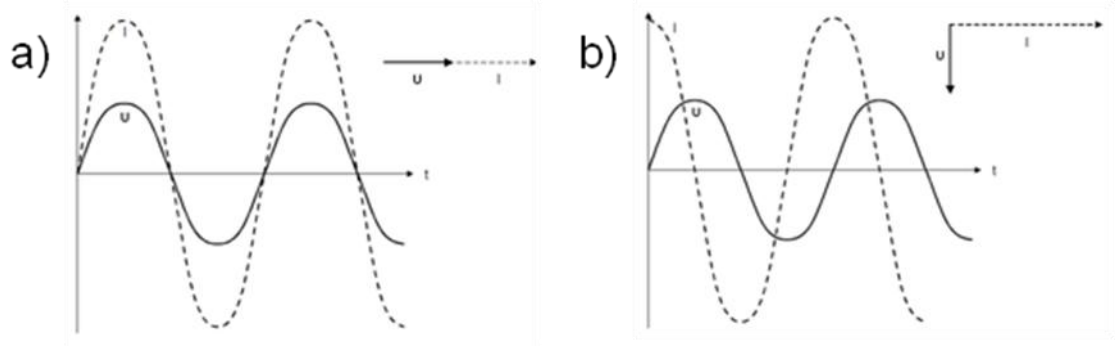


Figure 4-4: a) Show the current signal against the voltage signal in a pure resistive system. b) Show the current signal against the voltage signal in system with a capacitance

So the electrochemical impedance spectroscopy looks for the response of the input (voltage) signal due to the change of the phase and the amplitude of the output signal (current). With this parameter it is possible to do an electrical representation of the measured material, in this case a cell battery by using resistors, capacitances and inductances. As it has been seen, all the electrical components have different responses by frequency changes. That happened in the cell, the different materials which can be found in the cell, have different impedance response when the frequency is changed, and thus it is possible to define it as an electrical element.
The response of the different elements, like capacity, inductance, resistor and a mixture of this, will be analysed in the next section.

4.2.2. Visualization of the Signal

After the mathematical analysis of the output signal, it is necessary to do a graphic representation of the signal. That is the reason why it is much better to analyse the results because with the graphic representation it is possible to assimilate with some electric component in order to do, for example, the electrical modelling of the battery.
So as to do this graphic, two kinds of them will be presented, the Nyquist graphic and bode graphic.

Nyquist Graph

The Nyquist graph is a representation of a frequency response function of a signal by drawing the real part of the signal against the imaginary part. In other words, the Nyquist graph describes the response of the system over a range of angular frequencies. The Nyquist diagram is a trace polar frequency response of the system.
The advantage of the Nyquist graph is that in a single graph the frequency response of a system in the whole frequency range can be seen.
The disadvantage is that the graph does not indicate directly the contribution of all the individual factors of the transfer function.

An example of the Nyquist graph can be observed in the figure 4-5 where it is explained what has been mentioned above.

The Nyquist graph is the kind of graphic that is used in this work. But some systems use Bode diagram due to some different characteristics that the Nyquist graph does not have.

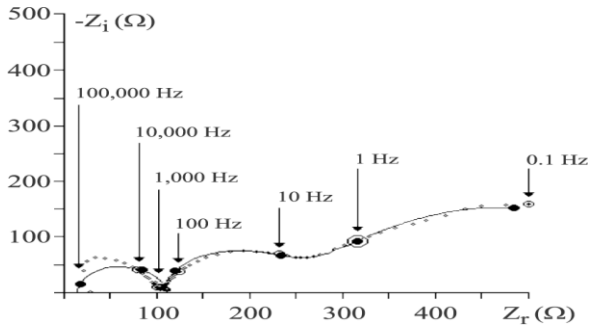


Figure 4-5: Nyquist Graph where the Z_r is the real part and $-Z_i$ the imaginary part. The frequencies are included in the graph for some point [12]

Bode Graph

The Bode graphs are representations of different impedance parameters versus frequency, and different variants. There are two kinds of representations of the bode graph:

a) Logarithm base 10 of the module of impedance against the logarithm base 10 frequency.

b) Phase Angle against logarithm base 10 of frequency. Unlike the Nyquist plots, the Bode representations contain all information from an EIS test, since the frequencies are clearly identified, but two different graphs are required. A graphic example of Bode graph can be observed in the figure 4-6 below:

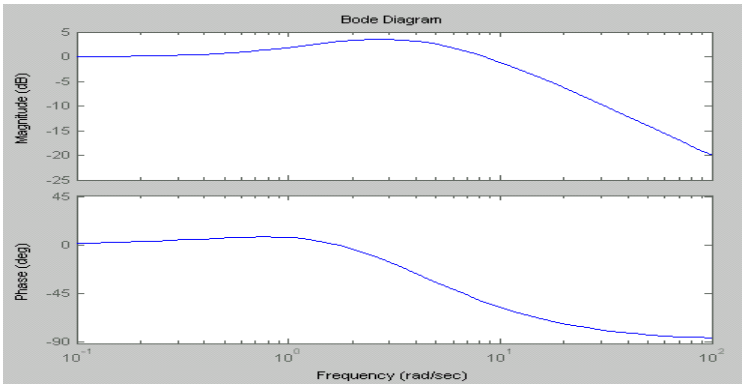


Figure 4-6: Bode diagram where the magnitude and phase are represented in two different graphs

4.2.3. Impedance Spectroscopy of Basic Elements

In this work, the Nyquist plot has been used for the representation of the impedance of the battery. For a better understanding of the impedance response of the battery, in this section the electric representation of the different kinds of impedance spectroscopy are presented by using basic elements. This representation has been shown in the lecture for battery storage system. [13]. The electric representation of the different kinds of impedances curves can be observed in the next figures, where the basic electric elements as resistance, capacitance and impedance are shown under mathematical equations and equivalent circuit representation.

a) The first representation in the figure 4-7, is about a single resistance or only real part, where the equations are:

$$\mathrm{Re}\{\underline{Z}(\omega)\} = R_i$$
$$\mathrm{Im}\{\underline{Z}(\omega)\} = 0$$

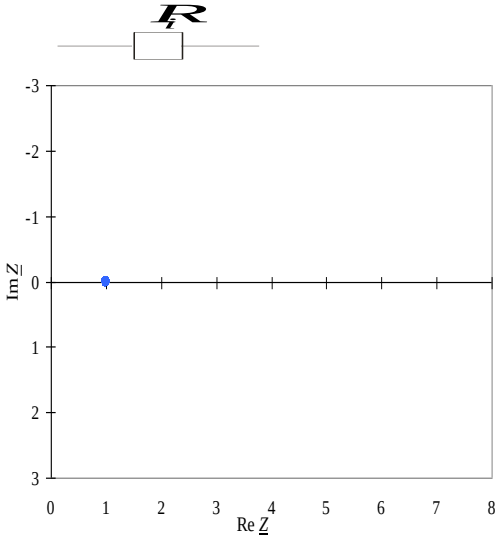


Figure 4-7: Resistance representation Nyquist plot.

b) This figure 4-8 represent the inductive part or a imaginary positive part, where the equations are:

$$\mathrm{Re}\{\underline{Z}(\omega)\} = 0$$
$$\mathrm{Im}\{\underline{Z}(\omega)\} = \omega \cdot L$$

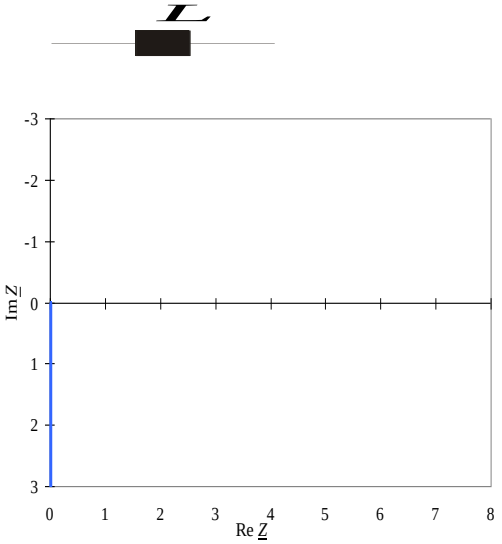


Figure 4-8: Inductive representation Nyquist Plot

c) In the figure 4-9 is possible to observe how is the respond of a series circuit with a inductance and a resistance, where the equations are:

$$\mathrm{Re}\{\underline{Z}(\omega)\} = R_i$$
$$\mathrm{Im}\{\underline{Z}(\omega)\} = \omega \cdot L$$

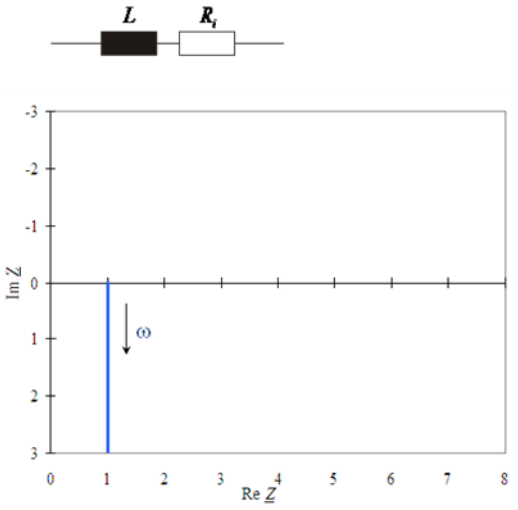


Figure 4-9: Resistance and inductive representation

d) The figure 4-10 shows the representation of a capacitor that is also a imaginary part, but negative, where the equations are:

$$\mathrm{Re}\{\underline{Z}(\omega)\} = 0$$
$$\mathrm{Im}\{\underline{Z}(\omega)\} = -1/(\omega \cdot L)$$

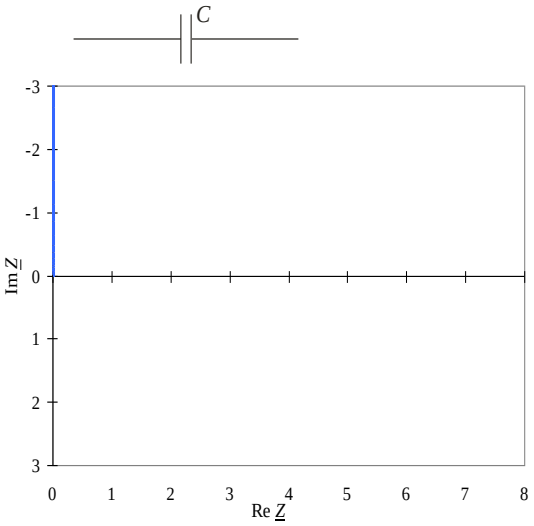


Figure 4-10: Capacitive representation

e) In the figure 4-11 it has the parallel between a capacitor and a resistance, where the result is a semicircle and the equations are:

$$\mathrm{Re}\{\underline{Z}(\omega)\} = \frac{R}{1+(\omega \cdot RC)^2}$$
$$\mathrm{Im}\{\underline{Z}(\omega)\} = \frac{-\omega \cdot R^2 C}{1+(\omega \cdot RC)^2}$$

$$\mathrm{Im}(\mathrm{Re}) = -\sqrt{\left(\frac{R}{2}\right)^2 - \left(\mathrm{Re} - \frac{R}{2}\right)^2}$$

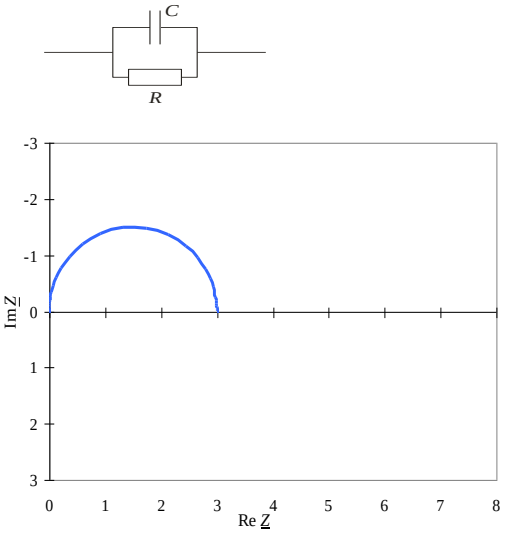


Figure 4-11: Parallel res. and cap. Representation

f) In the figure 4-12 it has two times a parallel between capacitance and resistance, with the same equations before showed.

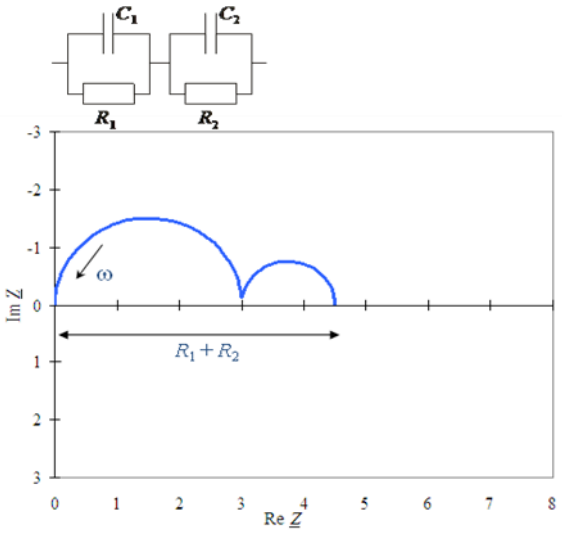


Figure 4-12: Two series-parallel cap. and res.

g) In the last figure is a mix between inductance, capacitances and resistances, for this type of curve.

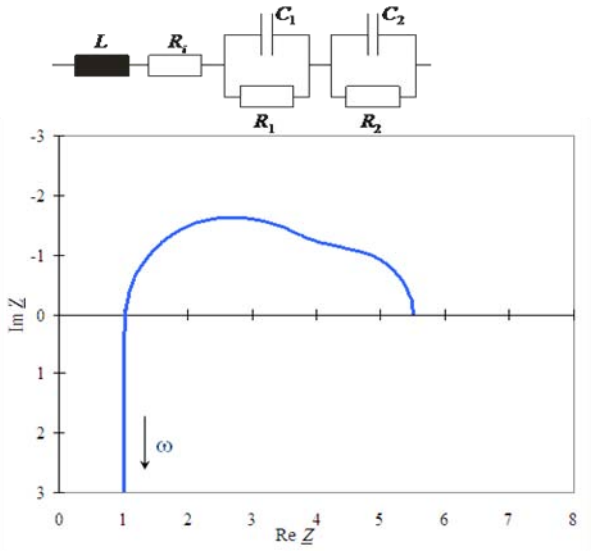


Figure 4-13: Mix of the electrical elements

4.2.4. Parameters of the Measurements

We will start with this section, talk about the equipment that is used to measure the impedance of the VRB. The equipment was the Zahner Zennium that is developed by ZAHNER-Elektrik GmbH & Co.KG, in Germany. The Zahner has a wide range of

frequency between few milli Hz and 4MHz. The interface of the Zahner is very friendly and easy to understand. It is possible to select the number of measurements pro decade and also the number of measurements pro each current, thus, it is possible to increase the accuracy of the measurements.

For the EIS measurements it has been considerd 3 point of the SoC of the VRB. The first point is 75%, the second 50% and the third 25%. All of these points were measured with a range of frequency between 23 mHz and 10kHz. Also, all of these points were measured with a constant current of 20mA, 200mA and without DC current. In this case a voltage of 10mV was applied to do these measurements.

4.2.5. Results and Analysis of the Measurements

As it was explained before, the measurements were done for three different SoC and also each SoC for three different current, 20mA, 200mA and no current. In figure 4-14 is the results that show the impedances of VRB with different SoCs and without current.

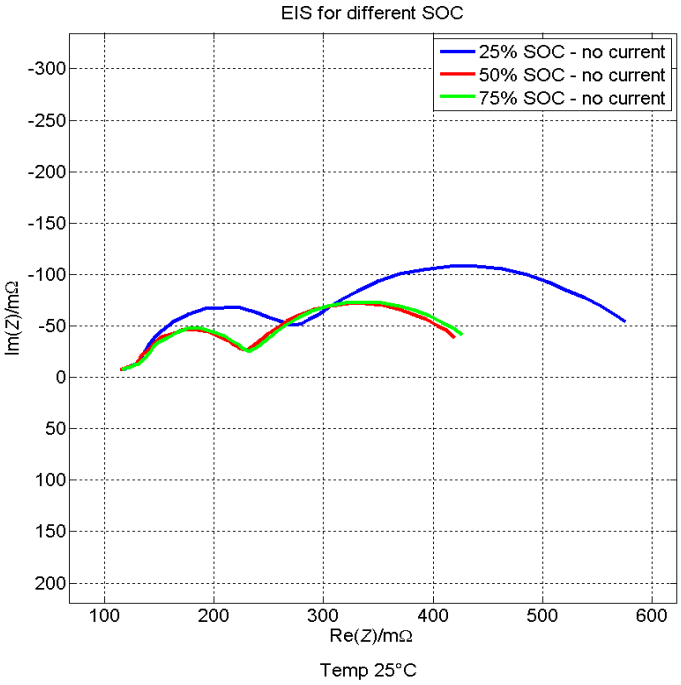


Figure 4-14: Impedance Spectroscopy for different SoCs and no charge current

All the measurements have been done by a constant room temperature 25ºC. As it is possible to see in the picture, the SoC has a direct incidence in the impedance of the battery. The battery has almost the same impedance with 50% and 75% SoCs. On the other hand, relative higher impedance can be observed with a lower SoC 25%, with increased imaginary part and real part. The conclusion can ben made that the battery is relative difficult to charge and discharge with smaller SoC because of the higher impedance.
In figure 4-15 it can be observed that the same structure of measurement but by applying 20 mA DC current.

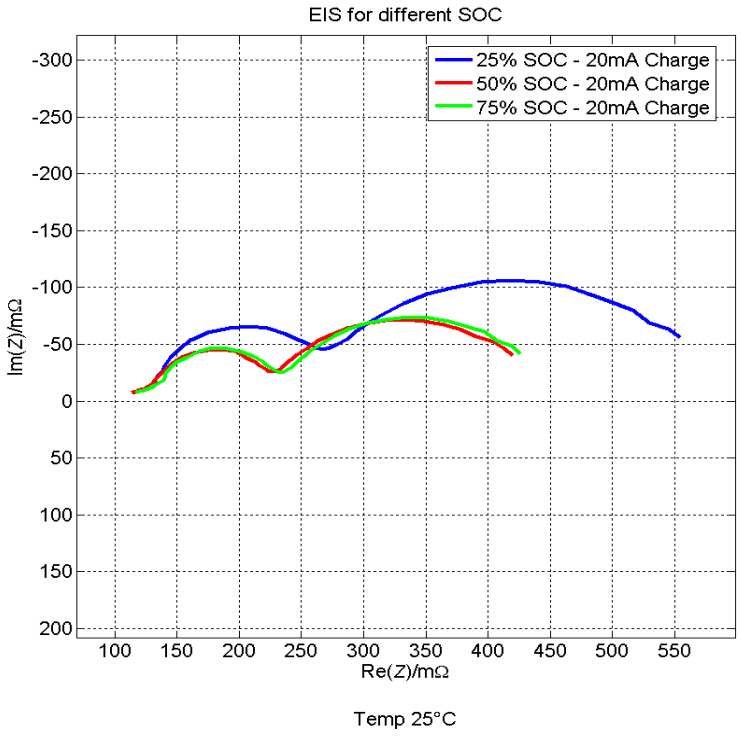


Figure 4-15: Impedance Spectroscopy for different SoCs and with 20mA charge current

The impedance behaviour of the battery is similar with the test results in figure 4-14. That is because of the small DC current. Thus, the change in the SoC of the battery is not so higher. As conclusion of this affirmation it can be stated that the battery has a higher decrement of the impedance with low SoC.

In the figure 4-16 it can be observed the same type of measurement, but now for a charge current of 200mA. The three impedances with different SoCs are similar, the impedance with SoC 25% has not too much difference with the impedances with 50% and 75% SoCs, it is because of the high DC current 200 mA. That means with higher current, the impedance can be reduced. We can see this effect in figure 4-17.

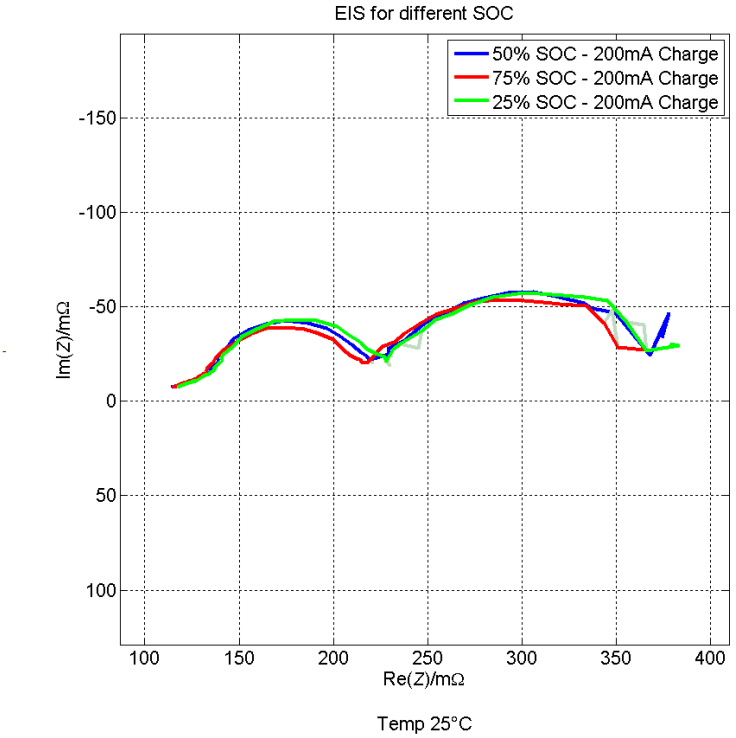


Figure 4-16: Impedance Spectroscopy for different SoCs and 200mA for charge

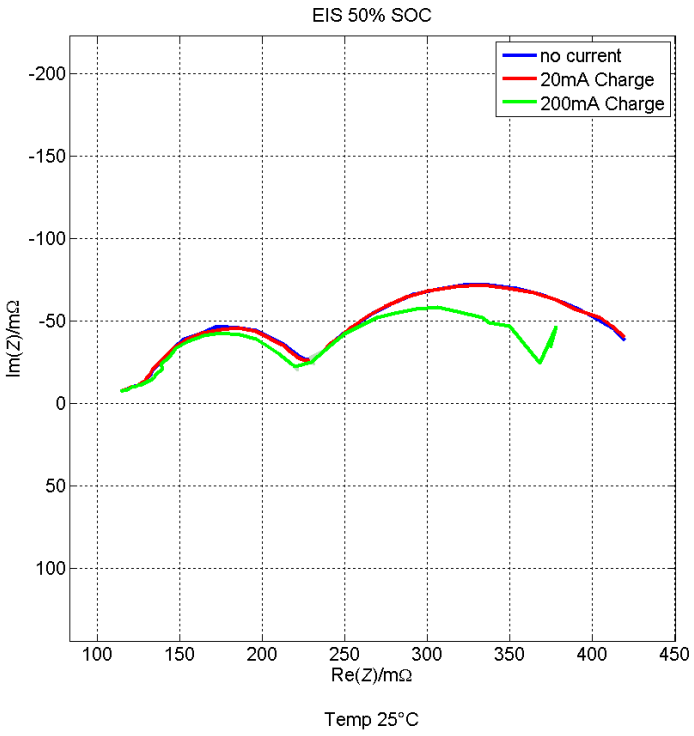


Figure 4-17: Impedance Spectroscopy for 50% SoC and different currents

In the figure 4-17 the variation of the impedance for one SoC i.e. 50% can be observed. As we can see, the variation is only significant when a higher charge current is applied, with a difference near to 100mΩ. For the other 2 cases not higher changes are observed, because the current of 20mA has not a big impact on the battery.

These are the impedance measurements that were done for the VRB. For this result it is possible to get some ideas of why this impedance has this curve. Some effects must be clear to make an interpretation of these curves.

In the EIS measurements a typical shape of curve was observed, two semicircles. The first semicircle have been analysed for other kind of batteries and has a representation of a Double-Layer effect. A charge zone is formed on the layer between the electrode and the electrolyte, caused by the short distance and the large surface in porous electrodes, the amount of charge cannot be neglected. The amount of charge that is stored in this layer depends on the electrode voltage. As the behaviour resembles to a capacitor, this effect is called electrochemical double layer or, more practical, double-layer capacitance. Different

models that describe the electrochemical double layer have been introduced. One of these models is the Helmholtz model, as it is described in the figure 4-18.

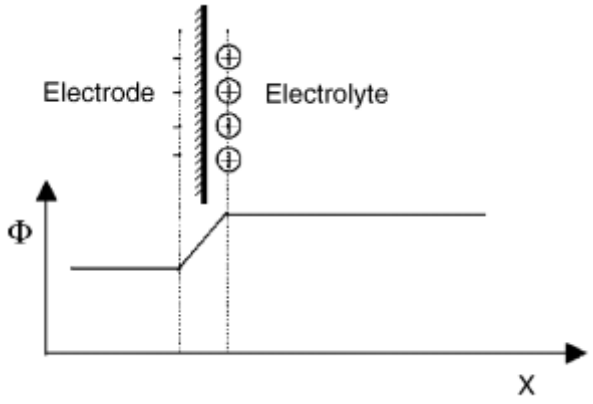


Figure 4-18: Helmholtz model to describe double-layer capacitance [14]

As the double-layer capacitor is on the electrode surface, it occurs in parallel to the electrochemical charge transfer reaction. The electrochemical charge transfer reaction is typically described by the electrochemical potential and charge transfer over-potential as given by the Butler-Volmer equation. The charge transfer over-potential is described by the charge transfer resistor R_{CT} and the double-layer capacitor by the capacitor C_{DL}, as seen in the figure 4-11. The serial ohmic resistor describes the ohmic resistance of the electrolyte, the current collector and the active mass. It is important to know that C_{DL} and R_{CT} are not constant elements. They are impacted by the state of charge, the temperature, the age of battery and the current.

The first semicircle can be described with this explanation, because this phenomens are presented also in the VRB.

But this first semicircle doesn't have the same characteristics of a complete semicircle. From the measurements, it is possible to see that the semicircle is flat and is due to a ZARC element, as it is possible to observe in the figure 4-19. This ZARC element is present when it has an electrode with a higher porosity. This is easy to understand by the porosity of the carbon felt coupling with the graphite electrode.

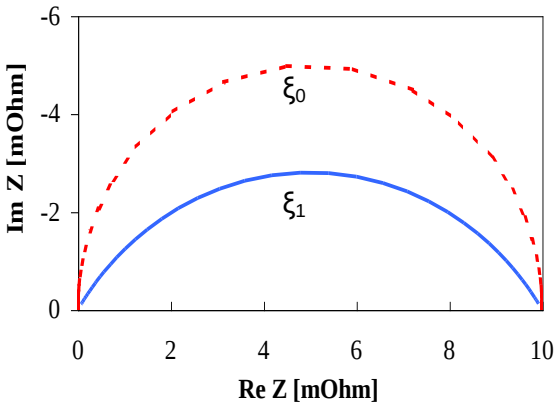


Figure 4-19: Representation of a ZARC element

As it is possible to see in the figure 4-19, when a ZARC element is present in the battery, the semicircle is more flat and depends on the value ξ. This value is changing between 0 and 1 which can be represented by the next equation where the values of resistance and capacitance are represented as ZARC elements.

$$Z = \frac{R_1}{1+R_1*C_1*(jw)^{\xi}} \tag{4.10}$$

The diffusion could be a parameter to observe other effects in other batteries. Within batteries, the transportation of ions is done by diffusion, migration and convection. Diffusion is caused by the gradient in concentration, whereas migration is caused by forces of the electric field and convection is from temperature or density differences or the external force. Those forces may have different directions. Migration is often hindered by solvated molecules that cover the ion. In most cases, the diffusion is mostly responsible for the mass transportation. Diffusion can be found at different locations inside the cell:

- In the free electrolyte: as the ions are produced one electrode and are consumed on the other electrode, the ions have to move between the electrodes.

- Within the porous electrode the electrochemical reaction can take place anywhere (inner or outer part of the porous electrode) on the active mass surface: as the diffusion within the porous electrode is limited by geometry, it plays an important role in the dynamic behavior of batteries.

The limitations for the diffusion of the ions result in locally changed ion concentrations. From the electrical perspective, the diffusion results in an over-potential because of the reduced or increased ion concentration at the location of charge transfer. As a reservoir for ions exists in the free electrolyte and in the porous structure of the electrodes, that's why the diffusion shows a dynamic characteristic.
Different types of diffusion in the batteries have been observed with EIS which is shown in the figure below.

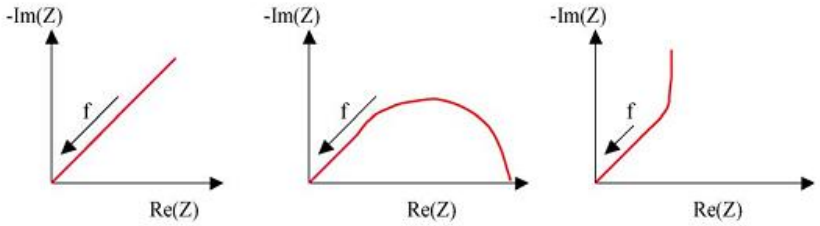


Figure 4-20: Different kinds of diffusion [14]

In our case a little amount of diffusion in the VRB is considered and sometimes it is almost neglected, because the diffusion is limited by the pumping of the electrolyte into the cell and also because the sulfuric acid doesn't take part in the reaction. The curve in the middle of the figure 4-20 represents a limited diffusion in the system, which means that this diffusion could be considered as the second semicircle in the EIS measurements. The diffusion in a battery is represented as a Warburg element and is called Warburg impedance Z_w. This diffusion is represented by the next equation where the diffusion elements are represented as "d" elements.

$$Z_W = \sqrt{\frac{R_d}{jw * C_d}} * \tanh\left(\sqrt{R_d * jw * C_d}\right) \tag{4.11}$$

With these effects explained above it is possible to derive an equivalent circuit of the battery which will be presented in the next section.

4.2.6. Equivalent Circuit

With the results of the impedance test it is possible to obtain an equivalent circuit for VRB. In this case, software developed in the ISEA it used to estimate the electrical representation of the VRB. This software is programmed in MatLab and called Impedanzfit, and has the ability to calculate the parameters by using the measurement results.

The Impedanzfit requires equations for estimating the electrical parameters. These equations came from the basic representation of element as described in the section 4.2.4 and from the Warburg impedance as explained in the section 4.2.5. In this case two models were obtained with the software; the first was considered as one ZARC element and a lower diffusion. The results were in relation with the original parameters. These results and the equation used are shown below where R_0 is the pure resistive part of the VRB.

$$R_0 + \frac{R_1}{1+R_1*C_1*(jw)^{\xi}} + \sqrt{\frac{R_d}{jw*C_d}} * \tanh\left(\sqrt{R_d * jw * C_d}\right) \qquad (4.12)$$

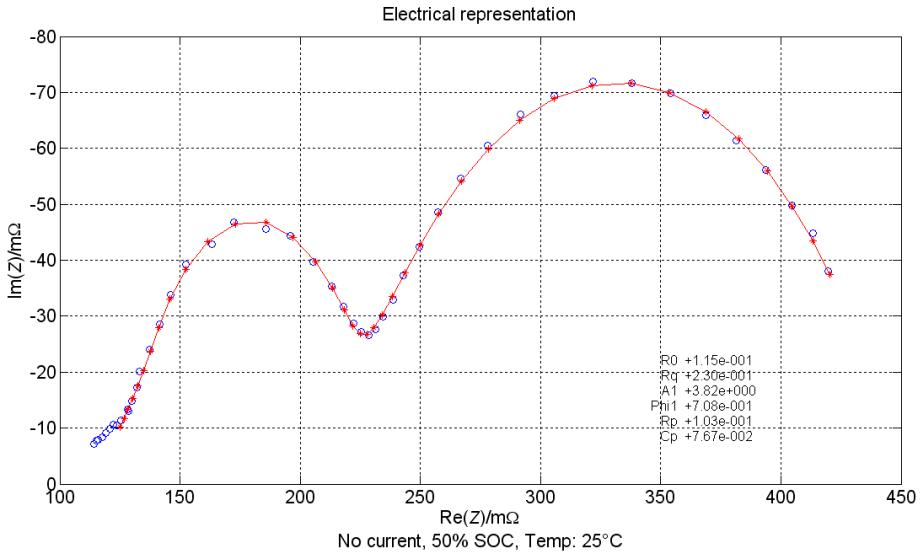


Figure 4-21: Representation for one ZARC element and lower diffusion

On other hand, estimation for two ZARC elements was done with good results. The results and the equation used in this part are shown below, where the two ZARC elements are represented by different number.

$$R_0 + \frac{R_1}{1+R_1*C_1*(jw)^{\xi}} + \frac{R_2}{1+R_2*C_2*(jw)^{\xi}} \tag{4.13}$$

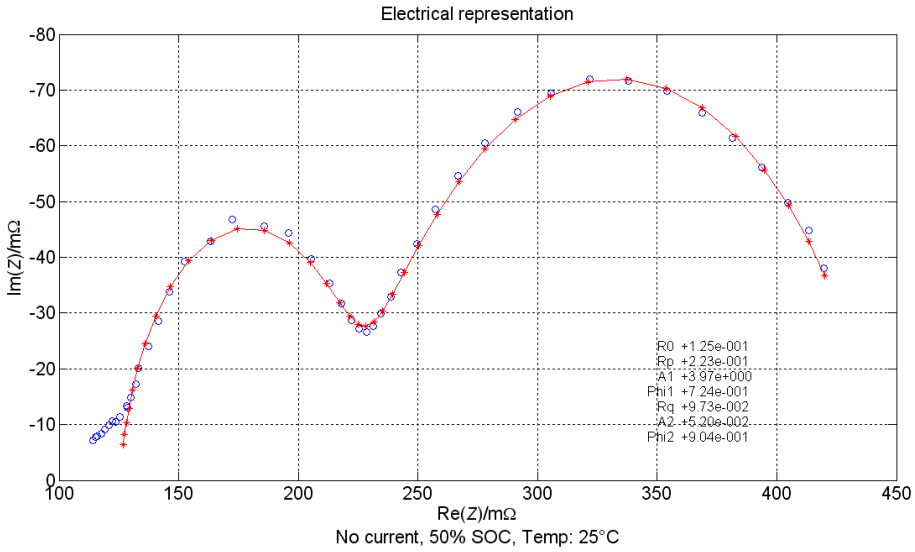


Figure 4-22: Electrical representation of two ZARC elements

In this case the representation is also similar with the original values. If two ZARC elements are used then the second semicircle have similar characteristics as of the first, but not so much information about the impedance in VRB exists and it is not possible to say why the second semicircle have this shape of curve.

4.3. Measurements and Analysis of the VRB with Different Values of Currents

In this section of the chapter we will see the different result that has been obtained from the measurements of the VRB with different values of constant currents.

In this case the measurements were carried out by software for the control of the constant current and also for defining the upper and lower limit of the voltage in the battery. In this

case the upper voltage of the battery was defined as 1.8V and the lower voltage as 0.8V. Thus, for the analysis of the state of charge (SoC) of the battery, we will consider that the SoC is 0% when the battery voltage is at 0.8V and is 100% when the battery voltage is at 1.8V. These parameters are controlled with software developed in the ISEA. With this software it is possible to control the charge or discharge of the VRB with different constant currents and for the number of cycles we want.

This software can control the programmable power supply, which is developed by HAMEG, and has the model number HM8143. In this case the power supply controls the current and the voltage independently. In [15] the data of this equipment is presented.

Also it should work with the flow rate of the electrolyte inside the tanks. This work has been done by a Multi Chanel Pump Tower, developed by CAT. With this pump it is possible to control the flow rate of the electrolyte. In [16] the data of this equipment is presented.

4.3.1. Parameters of the Measurements

In this section all of the parameters used for the measurements in the VRB are shown and also it is explained why they are chosen. These parameters make the limitation of the operational work of the battery, so it is needed to know which parameters are used and why they are used.

4.3.1.1. Determination of SoC

The measurements were developed always with a constant maximum voltage and a constant minimum voltage. In this case the maximum voltage was 1.8V, considerer as the 100% of the SoC in the VRB, and the minimum voltage was 0.8V, considerer as the 0% of the SoC.

Table 4-2: Show the voltage relation with the SoC for the VRB

Voltage (V)	***SoC (%)***
1.8	100
0.8	0

These parameters were defined by the criteria of the other works developed in the institute. It is considered that when a value of 1.8V for maximum charge of the battery, there is no more reaction in the cell, or the reactions are less, thus it is possible to consider that for this maximum value the state of charge (SoC) is 100%. It's the same with the minimum value.
Also it is possible to observe when the battery is at 100% or at 0%, due to the particular property of the vanadium that has been explained before. The colour of the vanadium changes when it is fully charged or fully discharged. It has V^5 and V^2 when it is fully charged the colour for V^5 is yellow or orange and for V^2 is lilac. And when the battery is fully discharged the colour of the V^4 and V^3 are blue and green. That was observed on all the measurements.
The parameter of maximum voltage of 1.8V was chosen, because with a higher voltage we will have gas bubbles inside the battery and they could make defect in the battery or even destroy the battery. Thus this parameter will be more secure for the battery.

4.3.1.2. Volume, Concentration and Flow Rate of the Electrolyte

The volume of the electrolyte is 200ml in each tank. This volume was chosen because of the capacity of the battery. The energy of the VRB is due to the volume of the electrolyte and the concentration of the electrolyte, in this case it is 0.8mol/L, and if we have a higher volume or higher concentration, the battery can work for longer time.

In this case the Vanadium is solved in a 38% sulphuric acid solution. The value was selected by personal option, because other experiments in the institute were developed with 0.5mol/l, and we want to know that how the battery will react with this value.

In the case of the flow rate, the selection was similar to the volume, and also depends on the capacity of the equipment. In this case the flow rate was 50mL/min and then it was changed to other value, to know how the battery reacts. This change could be observed in the section 4.4 of this chapter.

Table 4-3: Show the volume per tank, flow rate and concentration of the VRB system

Volume per tank (mL)	***Flow Rate (mL/min)***	***Concentration (mol/L)***
200	50	0.8

4.3.1.3. Currents for Charge and Discharge

Different constant currents for charging and discharging of the battery were selected. With some measurement it was possible to see the real time it takes and then a range of currents was defined. In this case the range of measurement was between 160mA and 1A. In the table 4-4 the values of all of the current used in this work can be seen.

Table 4-4: Show the range of current in this experiment

Number	***Current (mA)***
1	160
2	320
3	480
4	640
5	1000

With this current it is possible to show and make an analysis of the behaviour of the VRB under the conditions mentioned before. In the next section the results of the measurements and their analysis are given.

4.3.2. Results of the Measurements

In this section we will see the graphics that correspond to the response of the VRB for 5 different constant currents based on the parameters mentioned before. Figure 4-23 shows the curve of discharge of the battery with these 5 different currents.

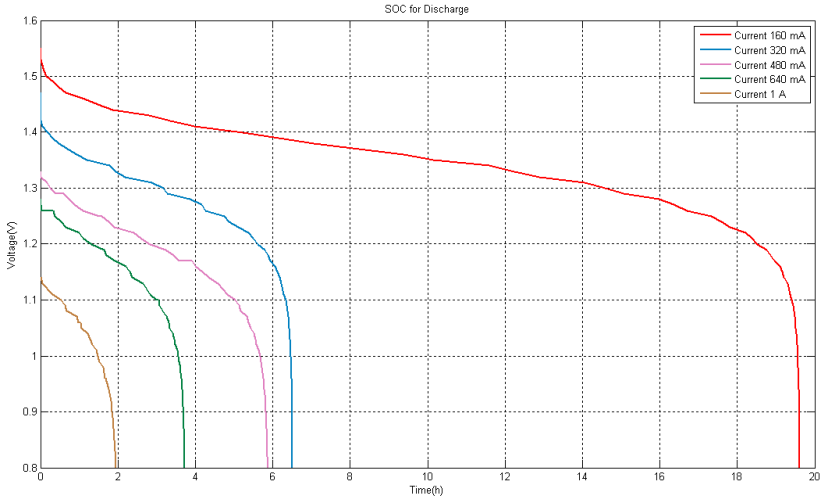


Figure 4-23: Discharge curves with different constant currents

In the Figure 4-24 we can see the same kind of curve for the charging process using the same values of currents.

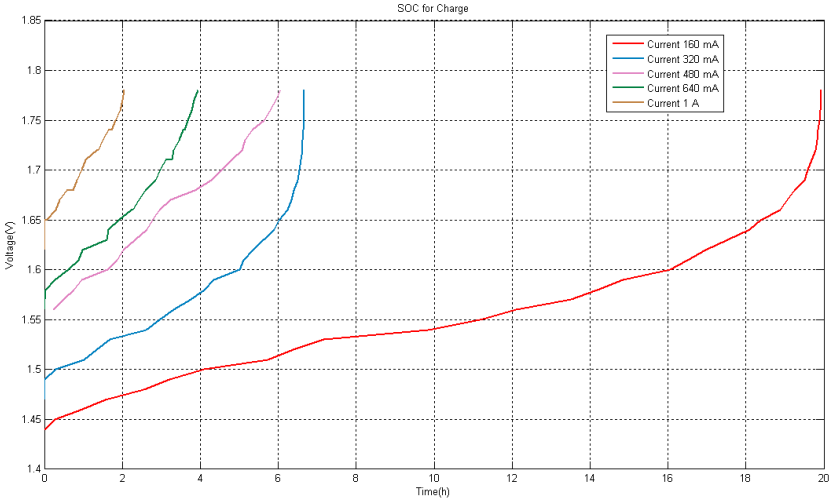


Figure 4-24: Charge curves with different constant currents

Finally, in the Figure 4-25, we can see the SoC of the VRB in charging and discharging process, thus it will be easier to compare the results obtained for the charging and discharging process.

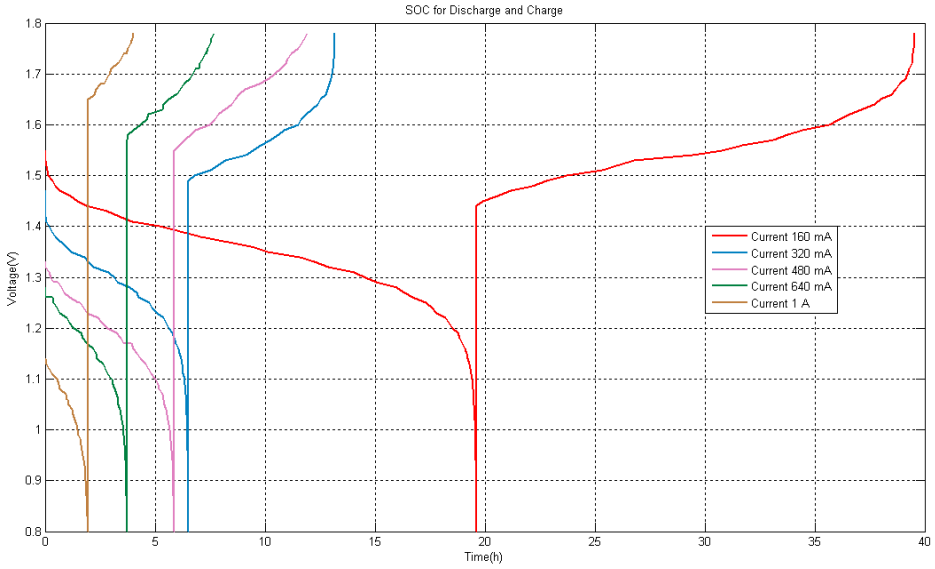


Figure 4-25: Charge and discharge curves with different constant currents

4.3.3. Analysis of the Results

After observing the results under the parameter previously given, we are able to make an analysis of the measurements. In the analysis it will be possible to understand why the battery has this kind of curve and what it means by this curve.

If we observe the figure 4-23, it is possible to find some difference between the curves for different values of currents. These differences are:

- The time of charge and discharge of the battery

- Voltage difference between charge and discharge

- The increasing and decreasing voltage

4.3.3.1. The Time of Charge and Discharge of the battery

The reaction time of the VRB means the time that the battery takes during a full charging or discharging process. In other words, it is the time that the battery needs for a complete reduction or oxidation process.

If we think which parameters have to be considered to estimate the full reaction time in a VRB, the first parameter that it is necessary to consider is the current. The current represent the consumption in the battery and it is known that with more consumption, the power demand must be higher. In the case of a battery, the power demand has a limit and depends on the storage system. With this it is possible to understand that with more current the time of reaction must be lower.

In the case of the VRB another important parameter that has to be considered is the volume of the electrolyte. For the VRB, with more volume of the electrolyte time of reactions inside the battery is higher because we have more reactants to react. That means that with more volume of electrolyte the capacity of the battery must be higher.

In together with the volume of the tanks, we also need to consider the concentration of the reactant in the electrolyte. In this case the reactant is the vanadium and the concentration of the vanadium in the electrolyte solution must be considered to make an estimation of the reaction time. With more concentration of reactants, the time of reaction and also the power must be higher.

Other important parameter is the number of electrons involved in simple reaction. If we have more electrons involved in a simple reaction, the current generated for a simple reaction must be higher and also the time of reaction, capacity and the power of the battery must be increased.

With this parameter and in according with the first Faraday Law, that mean that “the mass of a substance produce at an electrode during electrolysis is proportional to the number of moles of electrodes transferred at that electrode”. In the case of the VRB, the number of vanadium ions involved in a redox reaction is directly proportional to the electric current.

With all of these considerations we are able to express the reaction time in the equation below:

$$t = \frac{C_v * V * n * F}{I} \quad (s) \tag{4.14}$$

Where:

C_v: Concentration of vanadium

V: Volume of the tank

n: Number of electrons involved in a simple reaction

F: Faraday constant

I: Current

In the case of the VRB the number of electrons n involved in a simple reaction is equal to 1. Now we are able to calculate the full reaction time. Resolving the equation (4.15) we have:

$$t = \frac{0{,}8\left(\frac{mol}{l}\right) * 0{,}2\,(l) * 1 * 96485\,(A*s/mol)}{1(A)} \quad (s) \tag{4.15}$$

$$t = 4{,}2\ h \tag{4.16}$$

In this case we know that the reaction time for a full process is 4.2 hours with a constant current of 1A. If we compare this theoretical time with the real time, we can see that they are different. It is possible to say that the differences between the real and the theoretical time is because we are calculating the full charge or discharge process for all of the particles until the battery its completely charge or discharge. But in the real measurement, due to the conditions explained before, the battery will not be fully empty. Therefore, some particles don't take part in the reaction.

Also the losses in the battery decrease the energy which can be storaged in the VRB when it is charged and decrease this voltage when it is discharged, thus the battery take less time to go until the maximum limit of the voltage (for charge) or the minimum (for discharge).

The equation (4.14) has provided a very important parameter in the VRB; this parameter is the reaction rate. Physically, an electron is released by the oxidation of a vanadium ion, this electron travels through the electrodes and is captured by the reduction of another

vanadium ion in the opposite half-cell. In the case of a stack composed of N_{cell} cells, the electrons travel through the bipolar electrode to the adjacent cell are N_{cell}. Thus, for one electron flow through the external electrical circuit, N_{cell} redox reactions have occurred. Therefore, the total molar flow rate or rate of reaction of electrons for a stack is obtained by multiplying the number of cells. Thus, the reaction rate is [17]:

$$Rate = \frac{N_{cell}}{e * N_A *} * i(t) = \frac{N_{cell}}{F *} * i(t) \ (\frac{mol}{s}) \tag{4.17}$$

Where:

N_{cell}: Number of cells in the battery
N_A: Avogadro number
e: elementary charge of a electron
i: current in the cell

4.3.3.2. Voltage Difference between Charge and Discharge

In this point we will discuss the reason why there are differences in the voltage when the battery starts with the charge or with the discharge. As it is possible to see in the figure 4-25, some differences are observed in the voltage for the different currents and for different charge or discharge state of the battery.

For a better understanding of this phenomenon, it is necessary to know the Open Circuit Voltage (OCV) of the battery. According to the investigations [18] for determining the standard potential in an OCV of the battery, we are able to say that:

$$U_{VRB} = U_{Cathode} - U_{Anode} \ (V) \tag{4.18}$$

Where

$U_{Cathode} = 1 \ (V)$
$U_{Anode} = -0{,}26 \ (V)$

$$U_{standard} = 1 - (-0{,}26)\ (V) \tag{4.19}$$

$$U_{standard} = 1{,}26\ (V) \tag{4.20}$$

This voltage is the standard potential used for calculating the voltage variation in the VRB, along with the variation of the concentration of the different kind of vanadium inside the battery.

The equation that describes this phenomenon is the Nernst equation (4.21), which says that the voltage of the VRB U_{VRB} depends on the concentration of the reactants in the electrolyte [19]:

$$U_{VRB} = U_{standard} + \frac{R*T}{F} * Ln\left(\left(\frac{C_{VO_2^+} * C_{H^+}^2}{C_{VO^{2+}}}\right) * \left(\frac{C_{V^{2+}}}{C_{V^{3+}}}\right)\right)\ (V) \tag{4.21}$$

Where:

R: Universal gas constant, 8,314 J*K^{-1}/mol^{-1}

T: Temperature of the Battery

F: Faraday constant, 9648,533 ×104 C*mol^{-1}

C: Different vanadium concentrations

The above equation represents the OCV of the VRB for the different concentrations. But when the battery is connected to a load and the current starts to flow, these normal conditions are no more valid and the voltage of the battery is different to the voltage before explained.

This difference is represented as the energy that the battery needs to force a redox reaction and proceed to work at the required rate, this different is called overvoltage.

This overvoltage can be separated in four types; ***ohmic losses and ionic losses, the activation overvoltage and the concentration overvoltage***. All of these losses are increased when the current increases. In the discharge this overvoltage reduces the available voltage in the battery and in consequence the power. Below this different kind of losses will be explained.

Ohmic and Ionic Losses

These kinds of overvoltage are in relation with the internal impedance of different elements present in the cell of a VRB and they are related to the electrical resistance, which is the ability of a material to resist the flow of electrons or ions.

The ohmic overvoltage U_{ohm} is because of the resistance of electrodes $R_{electrode}$, resistance of collector $R_{collector}$ and the current. The overvoltage of the ohmic losses could be represented by the next equation:

$$U_{ohm} = (R_{electrodes} + R_{collector}) * I = R_{ohm} * I \ \ (V) \tag{4.22}$$

In this case the resistance of the materials must be considered for obtaining a better result in the time of building an electrical model.

In the case of the Ionic overvoltage, we are talking about the losses in the electrolyte and the membrane. These two elements oppose the flow of the ionic current. The resistivity of ionic liquids $R_{electrolyte}$ changes with the solution composition and its concentration. The electrolyte has a conductance G directly proportional to the surface A and inversely proportional to the distance L between the electrodes. This term of conductance determines the electrolyte's ability to conduct electricity.

$$G = \sigma * \frac{A}{L} \quad \left(\frac{1}{ohm}\right) \tag{4.23}$$

Where σ is the specific conductivity of the electrolyte.

Thus, the ionic losses R_{ionic} could be represented by:

$$U_{ionic} = (R_{electrolyte} + R_{membrane}) * I = R_{ionic} * I \ \ (V) \tag{4.24}$$

All of these losses make a difference between the voltage before represented in the Nernst Equation and the real voltage. But as we have already seen in the section of the impedance spectroscopy measurements, the ohmic losses are not only resistive but also have an

imaginary part due by capacitors and they are changing with the SoC of the battery and with the temperature. That is why the better representation of the VRB about the impedance losses is given by the electrochemical impedance spectroscopy and its equivalent circuit.

Activation Overvoltage

This kind of overvoltage is due to chemical conditions of the electrolyte. The current in a VRB is limited by the rate of the mass transfer of reactance to the electrode or by the rate of one of the two redox reactions.

When there is a current flowing in the battery and external grid. The battery is not in equilibrium state, that's why an overvoltage is necessary to overcome the activation energy of the battery.

Under equilibrium conditions the rate of oxidation and reduction reactions in the battery are the same, therefore no current is flowing and an overvoltage is not necessary for the activation of the redox process.

This type of losses U_{act} could be found in the Butler-Volmer equation, which was explained in [20].

$$I = I_0 * A * \left(e^{\frac{\alpha * n * F * U_{act}}{R * T}} - e^{\frac{-(1-\alpha) * n * F * U_{act}}{R * T}} \right) (A) \qquad (4.25)$$

Where:

I: current flow in the grid

I_0: exchange current, value of anodic current or absolute value of cathodic current under equilibrium conditions

α: Charge transfer coefficient

A: surface area of the battery

n: number of exchange electrons in a simple reaction

Concentration Overvoltage

The concentration overvoltage U_{con} is another type of chemical losses and is produced by the difference of concentration between the bulk solution and the surface of the electrode.
In order to maintain a stable current, it is necessary to refresh the electrolyte fast enough because the concentration overvoltage occurs when the reaction rate is so high that the electroactive reactants species are not able to reach the electrode or the product species aren't able to leave the electrode fast enough. In this case the current will not be stable and thus the voltage is not stable too and it will be lower. The transportation of the reactant is produced by 3 kinds of mechanisms: diffusion, migration and convection.

4.3.3.3. The Increasing and Decreasing Voltage

When we talk about the increasing and decreasing voltage, we are talking about the variation in the charge or discharge voltage after starting the charging or discharging process. As we have seen in the last section, when the current starts to flow in the battery, we have losses that are called overvoltages. After this jump of the voltage the battery starts to be charged or discharged and it can be seen in the Figure 4-26 that the charging or discharging voltage is continuously changing.

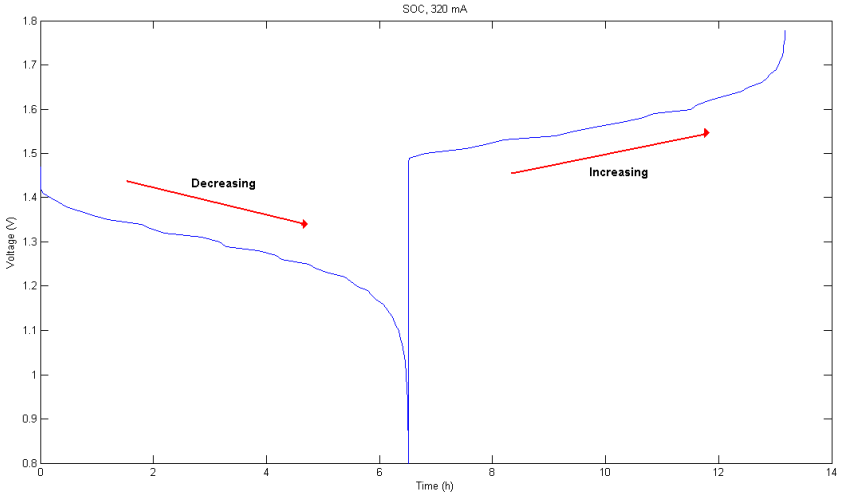


Figure 4-26: Show the increment and decrement of the voltage in the cell, for 320A

The voltage is changing during charge and discharge. This is because of a simple reason that is the mixing of the vanadium. As we know, we have two tanks where the vanadium reacts. When it is fully charged, one of these tanks has only V^5 and the other has only V^2. At this moment the battery has a stable and constant voltage. When we start with the discharging process, this voltage is no more stable and starts to change continuously until the battery is completely empty.

For example in the positive half cell, the V^5 changes in to V^4, this is because positive cell gains electrons and therefore the positive half cell is more negative than before. The redox reaction of the two half cells in the battery are given below:

$$V^{3+} \quad \leftrightarrow \quad V^{2+} - e^- \tag{4.26}$$

$$V^{5+} + e^- \quad \leftrightarrow \quad V^{4+} \tag{4.27}$$

For a better understanding let's have a look on the figure 4-26, a curve with a current of 320mA. In this case we can observe this phenomenon and the voltage makes a variation between 1.47 V and 1.78V which is equal to a total difference of 0.31V.

One possibility for obtaining a constant voltage all the time is to avoid two tanks for each half cell, one tank with a lot of vanadium in the same state of oxidation and the other empty tank where the vanadium is deposited after the reaction. But this solution could be expensive because of the higher cost for vanadium. And we must change the electrolyte flow directions for changing the charge stage to discharge.

Also it is possible to increase the flow rate to a higher value, and for a certain SoC of the VRB the change of concentration inside the cell and the variation of the voltage could be minimized.

4.3.3.4. Efficiency of the Cell

The efficiency of the cell can be calculated in different ways which can be seen in the section 3.2.7.2. In this case the coulomb efficiency is chosen which can be calculated from the results obtained in the previous section. As we know that the coulomb efficiency is given by:

$$\eta_{efficiency} = \frac{Q_{discharge}}{Q_{charge}} = \frac{\int i_{discharge}(t)dt}{\int i_{charge}(t)dt} \tag{4.28}$$

It is clear from the above equation that for calculating the efficiency we should know the charging and discharging current in a certain period of time. In this case we obtained the time and also the current from the performed experiment. The current was always the same for charging and discharging. In the table below the efficiencies of the battery with different values of current are shown, which are calculated from the results of the figure 4-25.

Table 4-5: Show the Energy, Voltage and Coulomb efficiency of the cell

Current (mA)	Energy efficiency (η)	Voltage efficiency (η)	Coulomb efficiency (η)
160	85,90%	85,90%	98,37%
320	80,40%	80,40%	97,64%
480	69,76%	69,76%	96,76%
640	66,51%	66,51%	94,57%
1000	58,29%	58,29%	95,69%

This is only the efficiency of the cell for charging and discharging cycles. We are not taking into account the mechanical losses of the pump. With this result it is possible to see that the efficiency of the cell is between 94% and 98%, which means that the battery is almost symmetric in time during charging and discharging due to the coulomb efficiency, but in the voltage efficiency it is possible to see that with more current the losses increase dramatic, also the energy efficiency is the same because we was used a constant current.

4.4. Measurements and Analysis of the VRB for Different Flow Rates

In this section we will investigate different results from the measurements of the VRB with different flow rates and rates of current used before.

The purpose of this section is to obtain estimation for the better flow rate in the battery. It is known that the VRB depends on a Pump used for the transportation of electrolyte from the tanks to the cell where the redox reaction takes place. Therefore it is necessary to make an analysis considering different parameters of the battery.

The entire explained above is directly related with some energetic considerations that are necessary to perform the special cases of the redox systems.

4.4.1. Basic Concepts

In order to determine a suitable flow rate for better operation of the battery, analysis with two extreme cases should be performed, one with the maximum flow rate and other with the minimum. These two flow rates are defined as Q_{max} and Q_{min}.

The flow rate Q depends directly upon the current I and the SoC. The SoC is related with the concentration of electrolyte in the cell, thus the flow rate depends upon the concentration of electrolyte in the cell.

In the case of VRB we have two different kinds of concentration in the cell, the Input concentration C_{in} and the output concentration C_{out}. In the Figure 4-27 it can be observed that the C_{in} is the concentration that enters into the cell and the C_{out} is the concentration that leaves the cell after the reactions inside the stack. Therefore if we talk about the discharge process in the positive half cell, the C_{in} of the V^{5} must be higher that the C_{out} of the V^{5} and the C_{in} of the V^{4} must be lower that the C_{out}.

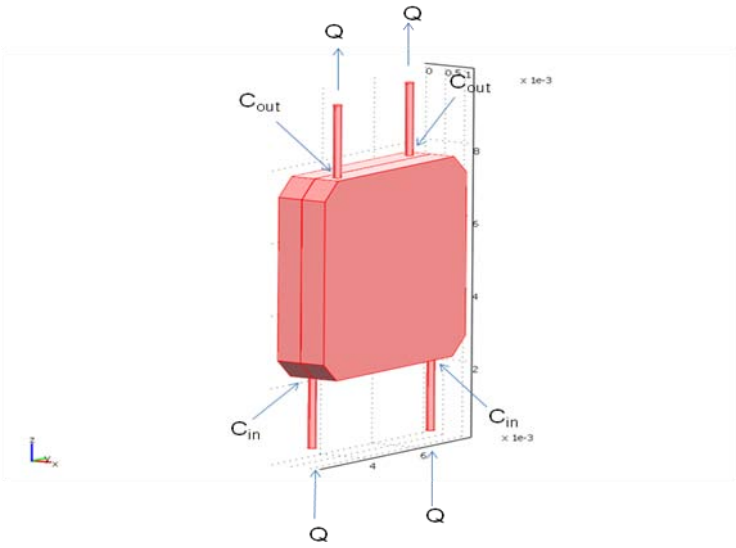


Figure 4-27: Different concentration in the stack and the flow direction

In the start up the concentration C_{in} depends upon the initial concentration in the tanks $C_{initial}$ of the vanadium, the volume of the tank V_{tank}, and of course upon the current. All of these parameters are in relation with the flow rate of the electrons which can be represented by the faraday constant.

$$C_{in} = C_{initial} + \frac{1}{V_{tank}} \int \frac{a}{F} i(t) \quad (mol/l) \tag{4.29}$$

The value of a in the above equation is equal to -1 when the battery is in charging process and 1 when it is in charging process.

In the equation (4.30), it can be observed how the flow rate is used for calculating the output concentration C_{out} in the battery, in relation with the variables defined before and also with different number of cells N_{cell}.

$$C_{out} = C_{in} + \frac{a * N_{cell}}{F} * \frac{i(t)}{Q(t)} \quad (mol/l) \tag{4.30}$$

Other parameter which it is necessary to know for the future optimization of the flow rate, is the Power of the cell P_{cell} and also the power consumed for the pump P_{pump}. With these

parameters we are able to calculate the efficiency of the VRB, a very important parameter in the world of batteries.

The P_{cell} can be easily determined by Kirchhoff law. As we know that the current I_{cell} and voltage in the cell are constant. The voltage obtain by the measurement is along with the losses, so we can say that the Voltage in the cell U_{cell} is equal to the total Voltage U_{total} minus the Voltage of the losses U_{losses}. This last Voltage is due to the sum of the ohmic losses and the ionic losses. This overvoltage is added during charging and is subtracted during discharging. Thus the P_{cell} could be determined by the equation below:

$$P_{cell} = U_{cell} * I_{cell} = (U_{total} \pm U_{losses}) * I_{cell} \quad (W) \tag{4.31}$$

Also it is necessary to know the power that the battery needs to work. This power decreases the efficiency of the battery and is represented by the Power of the Pump P_{pump}. Thus it is possible to obtain the Power of the VRB by using the equation below:

$$P_{VRB} = P_{cell} - P_{Pump} \quad (W) \tag{4.32}$$

It should be noticed that during discharging the power of the cell is positive and the power of the pump is negative, while during charging the power of the cell is negative because it is provided by an external circuit and the power of the pump must be added. This difference is shown in the equation below:

$$P_{VRB,charging} = -P_{cell} - P_{pump} \quad (W) \tag{4.32}$$

$$P_{VRB,discharging} = P_{cell} - P_{pump} \quad (W) \tag{4.33}$$

4.4.2. Optimization of the Flow Rate

Now we know the principal aspects of the flow rate Q and power of the VRB. We know that flow rate depends upon the SoC and the current. Also we know the energetic considerations in the case of the VRB.

With this knowledge, we can set the maximum and the minimum flow rates and can compare which of these two cases will be better.

4.4.2.1. Maximal Flow Rate

It is necessary to define a control strategy for the pump. If the condition for a maximum Flow rate is taken, then the pump should transfer enough electroactive species for the reactions in the battery.

The maximum flow rate of the battery could be estimated by the equation (4.34) which shows the efficiency of the VRB along with the mechanical losses of the pump. Thus depending upon the efficiency we want it is possible to determine a maximum flow rate.

$$Q_{max} \rightarrow \frac{P_{cell}}{P_{cell}+P_{pump}} \tag{4.34}$$

From the data sheet of the pump it is known that the maximum power of the pump, when the flow rate is maximal, is 160 Watt.

If we want to calculate the efficiency of the battery η_{VRB} in this case, it is necessary to define the current I_{cell} and the voltage U_{cell}. For this calculation we will use a constant current of 1A and the value of the voltage could be estimated as the voltage when the battery is in 50% of the SoC. If we look in the figure 4-23 we can say that this voltage could be 1.22 V. Thus the power of the cell can be obtained by multiplying the current and the voltage:

$$P_{cell} = 1A * 1.22V \tag{4.35}$$

$$P_{cell} = 1.22\ W \tag{4.36}$$

Thus, the efficiency must be:

$$\eta_{VRB} = \frac{1.22W}{1.22W+160W} \tag{4.37}$$

$$\eta_{VRB} = 0.7\% \tag{4.38}$$

If we observe the value of the equation (4.38) the efficiency is very low. This is happened because the VRB used in this work is only for investigation and development and the power generated by the battery is lower. Therefore if we want to obtain a high efficiency we should increase the number of cells and also the size of the cells and the tanks. Some investigations with larger battery have been developed and are working with an efficiency of about 60% [21]. Also it is clear from the equation (4.35), if we increase the current is increasing, the power will also increase and therefore the efficiency will be higher.

The VRB have two difficult points in the operation mode; one when the battery is almost fully charged and second when it is almost fully discharge. In these two situations, the battery must have enough electroactive species for delivering a constant response. If we consider this case, a higher flow rate will be necessary to deliver enough of this electroactive species. But on the other hand, this control strategy is not the best solution because it needs a higher flow rate only in these two extreme points which are only a little time of the complete operation mode of the VRB. Thus power is being lost and the efficiency of the battery decreases.

In this case, it is working under a limit in the operation mode, with a maximal voltage and a minimal voltage (table 4-2). With this type of operation the battery does not work between 0% and 100% of the real SoC, the battery is working above 0% and under 100% of the SoC. For this reason in this investigation it is not necessary to consider these two extreme points (when the battery is almost fully charged or discharged), because the battery have always enough reactants. This method decreases the operation mode of the battery and also the power delivered by the cell, thus the efficiency decreases too. But on the other hand if we use the other method and the flow rate is increased to a maximum value then the efficiency will decrease too.

4.4.2.2. Minimal Flow Rate

As we can see the method for the maximum flow rate is not efficient, because it uses more energy than the necessary for the battery. Now we will investigate the other method when the Flow rate is minimal.

In this method we will use the concentrations C_{in} and C_{out}, which are already defined in section 4.4.1. It is possible to determine the minimum flow rate Q_{min}, when the output concentration C_{out} is minimal when the battery is at discharge mode or maximum at charge mode (this value must be defined by the applicant). The input concentration C_{in} is at a minimum or maximum value depending on the discharge or charge mode (for this condition it is necessary to choose a time when the battery is almost discharged or charged). If we consider that the two operation modes are symmetric, it is possible to choose one of the modes without any problem.

In this case the discharge mode has been chosen for calculating the minimum flow rate. The Q_{min} can be found by using equation (4.39) and with these two considerations:

$$Q_{min} = \frac{a * N_{cells} * I}{F * (C_{out,min} - C_{in,min})} \ (ml/min) \tag{4.39}$$

The first condition which is necessary to give is the time when the battery is almost discharge. We have chosen this time when the battery is at 98% of the SoC. As we know from the equation (4.29) that the C_{in} depends on the time and is possible to estimate the time with the equation (4.14).

In this example we will use a current for 640mA and we know the time of the total reaction for this current (as previously calculated in the section 4.3.3.1.). This time is 6.7 h for full discharge. If we assume a linear approximation for the time of discharge we can say that when the battery is at 2% of the SoC the total time must to be 98% of the time. Thus the time is:

$$t_{2\%\ SOC} = t_{total} - t_{2\%\ of\ total} \tag{4.40}$$

$$t_{2\%\ SOC} = 6{,}7h - 0{,}134h \tag{4.41}$$

$$t_{10\%SOC} = 6{,}56h \tag{4.42}$$

With this time we can define the minimal C_{in}, by using the equation (4.29).

$$C_{in,min} = C_{initial} + \frac{a*I*t_{2\%\ SOC}}{V_{tank}*F}\ (mol/l) \tag{4.43}$$

$$C_{in,min} = 0{,}8\frac{mol}{l} - \frac{1*0.640A*6{,}56h}{200ml*96485C/mol}\ (mol/l) \tag{4.44}$$

$$C_{in,min} = 0{,}01675\ (mol/l) \tag{4.45}$$

Now we have calculated the minimum value of C_{in}, we need to know the minimum value of C_{out}. This value must be defined by the user and the minimum value that C_{out} can take is 0 mol/L. Thus we can calculate the minimum value of the flow rate with the equation (4.39):

$$Q_{min} = \frac{-1*1*0.640A}{96485C/mol*(0-0{,}01675mol/l)}\ (ml/min) \tag{4.46}$$

$$Q_{min} = 23\ (ml/min) \tag{4.47}$$

Now, we have seen the two methods for determining the best operation mode of the VRB. In the first method a maximum Flow rate Q_{max} was chosen. While in the second method a minimum flow rate Q_{min} was chosen. These two methods have advantages and disadvantages in consideration with the power of the battery.

It needs to be clear in some concepts. The first is that the flow rate Q is inversely proportional to the concentration in the cell. As we can see in section 4.4.1, and we also know that the concentration has a direct relation with the voltage of the battery, according to the Nernst equation discussed in the section 4.3.3.2.

With this knowledge we can see that when the flow rate is at minimum Q_{min}, the range of variation for the vanadium concentration is maximal and also the variation in the cell voltage becomes maximal too. On the other hand when the flow rate is at maximum Q_{max},

the variation of the vanadium concentration is minimal and therefore the cell voltage is more stable.

Thus we can conclude that the power in the cell becomes maximal when the battery is in discharging mode and is minimal when the battery is in charging mode. This can be a good solution for the battery if we only consider the power of the battery, but the power of the pump is also important which determines the operational mode, because the mechanical losses of the pump are most significant that the increase of the power with the maximum flow rate.

For this reason the chosen minimum flow rate Q_{min} has always the best performance in comparison with the maximum flow rate Q_{max}.

4.4.3 Analysis of the Results

Now with all of the parameters that have been seen in the previous section, it will be show the result under these. In this case because of the time, only one current was measured for different flow rates. The magnitude of the current was 640mA and the different flow rates were 330 ml/min and 25 ml/min. The purpose of these measurements is to make a comparison between these two values. One value for the maximum flow rate Q_{max} and the other for the minimum Q_{min}, these values has been calculated with the previous optimization. In the figure 4-28 a) and b) we can observe the result of the measurement under these conditions.

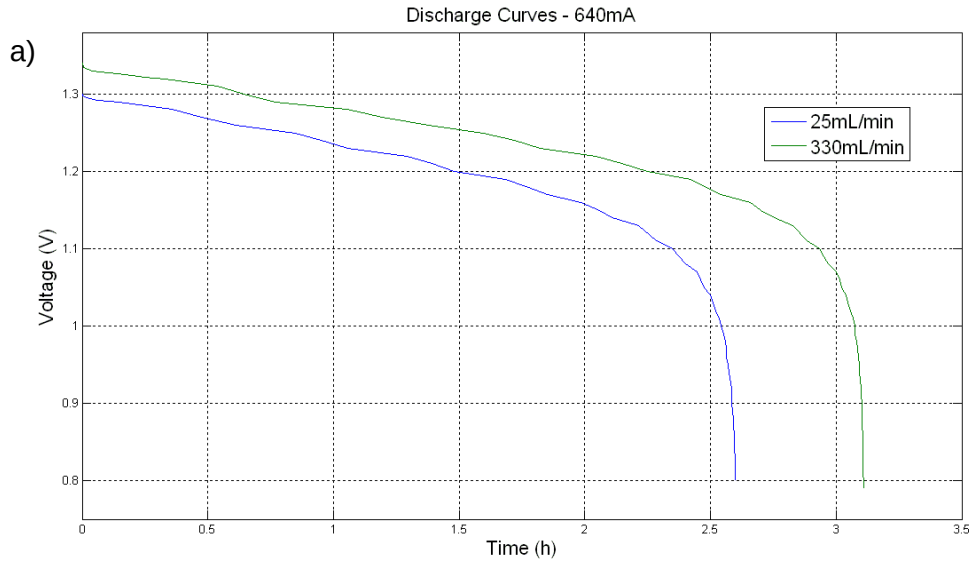


Figure 4-28: a) Discharge Curves with different flow rate

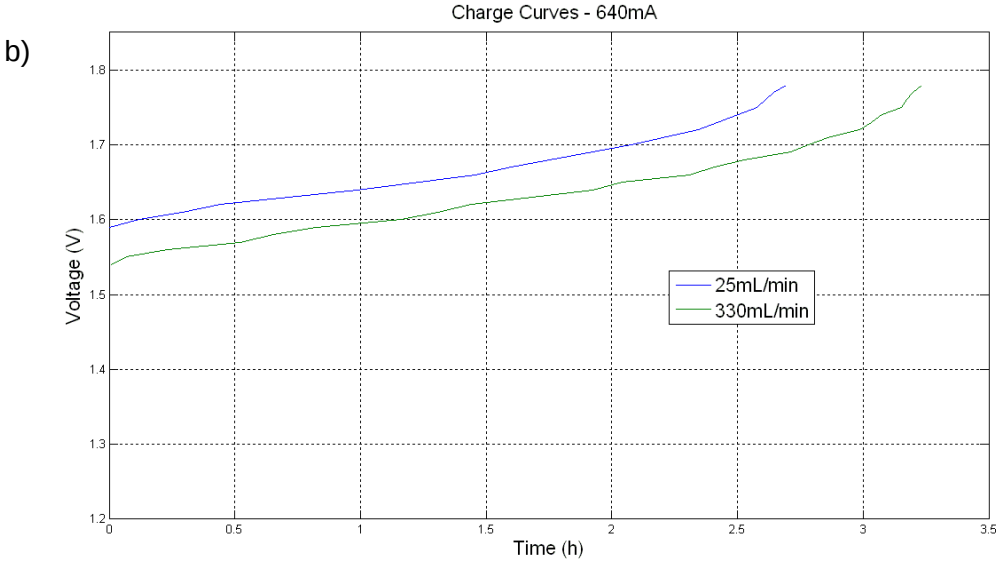


Figure 4-29: b) Charge curves with different flow rate

As we can see in the figure 4-28 a) and b), there are two differences between these two curves. The one with flow rate 330 mL/min has the reduction of the capacity of the battery. This phenomenon happens due to the increment in the losses in the VRB, which can also be

observed in the figure. For example for the curve with 330 ml/min, the initial voltage is near to 1.55V while for the curve for 25 ml/min the initial voltage is 1.6V. This increment of the voltage is due to the decrement of the impedance in the cell. First measurement was carried out for the curve of 330 mL/min and after 1 day the other experiment was carried out. Also it is necessary to considerer the conditions of work for this two measurements. The battery was working without a good insulation for the oxygen, that's why V^2 has reaction with the oxygen in air and some reactants have made a jump to V^3. Conversion of V^2 to V^3 also decreases the capacity of the battery because the V^5 will have no more reactants to react, when the battery is in charging state. For a better understanding the figure 4-29 a diagram shows this process.

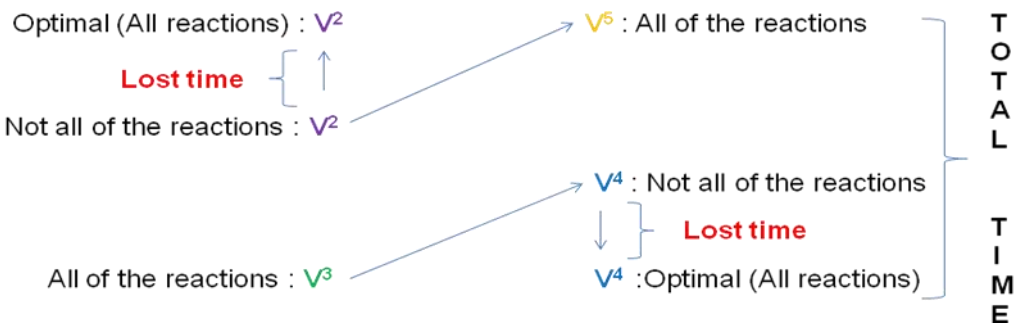


Figure 4-30: Lost of the capacity due to reaction of V^2 with oxygen in the air

The difference in the two curves is not significant if we will not consider the decrement in the capacity due to the losses and self discharge. This means that the use of a high flow rate does not produce large variation in the voltage of the battery, we have the same shape of curve for decreasing and increasing voltage. Then the voltage not stable, how was discussed in the section 4.4.2.2, and is not a greater contribution in the power of the VRB. Maybe with the higher flow rate which has been used, it will be possible to obtain a stable flow rate and thus the power of the cell will be increased. But with the pump used in this case it is not possible to work with a higher flow rate.

Now we can conclude that the minimum flow rate estimated for this case has always a better solution, because it directly decreases the mechanical losses of the pump and therefore the efficiency of the battery is improved.

4.5. Measurement Considerations

In this part we will have an insight look to know more about the behaviour of the VRB, which means that it will be possible to find some problems in the method used which have to be considered. These considerations are function of the complete system, the electrolyte, the pumps and also the cell.

Electrolyte Considerations:

- It is necessary be careful with the electrolyte in the tanks. The V^2 has a lot of problem with the self discharge because of the reaction with the oxygen in the air, which decreases the capacity of the battery. To avoid this phenomenon it is necessary to have a close system and introduce other gas for maintaining the solution inside the tanks without oxygen. In our case nitrogen was used in the process, but it is not possible to assure the presence of nitrogen all the time, therefore some problems could be produced in the system. Also it is better to keep the battery in discharge sate and pump all the electrolyte out of the cell when it is not working, thus there are less possibilities to have reaction between V^2 and oxygen.

- Also in relation with the same point it is necessary to consider the best conditions for the first measurement of the vanadium V^2 and V^5, which means which means both parts should be fully charged. Because if this is not the case the capacity of the battery is immediately affected by this effect.

- The temperature of the electrolyte is also important, because it is directly proportional to the cell voltage, according to the Nernst equation. For these reasons a good solution of this problem is to keep the tanks in water at a constant temperature and then stable results can be obtained.

Pumps Considerations:

- In the present work, one of the most common problems was because of the pump. As the battery used for investigation is small therefore the pump is also small, this is the reason why the pump doesn't have a big area which the electrolyte can pass. Because small crystals of the solution get stuck with the walls, after some time the accumulation of these crystals make a block and the pump is stopped. This phenomenon happens because when temperature in the system is higher, some water from electrolytic solution evaporates and the amount of water is not enough for remove all the small crystals of the solution. Therefore some crystal are drier and take a place in the connection between the pump and the pipe, these crystals accumulate there and therefore stop the system. To avoid this phenomenon cooling equipment was used to cool the system and this problem was removed.

Cell Considerations:

- There are also some problems exist in the cell. The first problem is to avoid the contact between the positive and the negative electrode. This happened because the union of the cell is done with the help of screws and these screws cannot take the positive and the negative at the same time, therefore it can create a short circuit. A simple solution for this problem is to insulate the screw with an insulating material. It is also possible to take some contact inside the cell and for this reason will be better make the insulation for all of the screw.

- When the battery is fully charged and the pump is stopped, it is possible to have some corrosion in the positive half cell. The V^5, which is in the positive half cell, is a very aggressive material under this condition and when the electrolyte is maintained inside the cell for a certain period of time (in my case 1 week), the positive graphite electrode is corroded by the positive solution. To avoid this phenomenon it is necessary to release the entire electrolyte of the cell and the pipe, after the measurement and when the

battery is not working, therefore it helps with the safety of the system. Also there is a contribution for the accumulation of crystals in the pump.

5. Modelling of the VRB

This is the final chapter about the VRB. Here we will talk about the modelling of the VRB under specific conditions. The purpose of the model is to obtain a physical representation of the VRB and to visualise some of the changes inside the cell.

The modelling of some systems or elements for example the VRB is a very important step in the development and investigation of new technologies. When we create a model for a system it is possible to recreate the real components of the system after performing, analysing and getting some conclusion from the simulation of the element or system. These conclusions are really important because with them we can say whether the system under investigation can be developed in future or not. Also int he case of element it is possible to simulate under some specified conditions and then observe the response. This part of the process is really important because you can possibly save money in some cases and also can get the information about the system when it is running. With a simulation or model the user is more prepared at the time of building the real system.

The model that we will see is a union among the mechanical model, the chemical model and also a part of the electrical model of the VRB. Thus we will be able to observe the fluid of the electrolyte in the cell, the changes in the concentration of the vanadium in the cell, along with the voltage and the current distribution in the cell with different concentrations of vanadium.

The program that has been used is Comsol Multiphisics, this program is a software package for analysing and performing finite element modelling for various physical and engineering applications, especially coupled phenomena and multiphysics. With the Comsol it is not only possible to visualize the results in 3D but also in 2D, thus we can see the different comportment of the elements under some conditions. In this case the model of the VRB has been built in 3D.

5.1. 3D Modelling of the VRB

In this section we will see the 3D modelling of the VRB. The parameters present in this model are; the variable concentration of the vanadium inside the cell. This variable concentration includes the mechanical fluid and also the reaction of the vanadium in the cell. Also it was possible to include an electrical response of the cell under these conditions. For obtaining this 3D model it is necessary to work with 2 different modules in the COMSOL. The first module represents the mechanical fluid in the cell, in other words it is the behaviour of the flow rate *Q* inside the cell. The second module represents the chemical reaction of the vanadium inside the cell. With this module it is possible to observe the changes of the vanadium concentration dependent on the flow rate of the first module.
For a better understanding this section will be separated and explained in 3 parts. In the first part the mechanical model of the flow rate is considered, in the second part the chemical model for the reaction of the vanadium in the cell is considered while in the third part an electrical representation is included which depends on the previous two modules.

5.1.1. Mechanical Model: Flow Rate in the Cell

In this section the mechanical model of the VRB will be explained. Here we are considering the mechanical part of the VRB, which means the flow rate.
In the Comsol it is possible to find a tool for calculating the fluid flow inside a material. This tool is basically an equation named “incompressible Navier-Stokes”.
The Navier–Stokes equations are named after Claude-Louis Navier and George Gabriel Stokes, this equation describes the motion of fluid substances. We got these equations by applying Newton's second law to fluid motion, together with the assumption that the fluid stress is the sum of a diffusing viscous term (proportional to the gradient of velocity) and a pressure term. These equations are useful because they describe the physics of many things regarding academic and economic interest. They can be used to model the weather, ocean currents, water flow in a pipe, air flow around a wing and motion of stars inside a galaxy. The Navier–Stokes equations in their full and simplified forms help in the design of aircraft

and cars, the study of blood flow, the design of power stations, the analysis of pollution and many other things.

In this case we are using the Navier-Stokes equation for calculating the flow of the electrolyte (fluid) in the cell, thus it will be possible to understand the behaviour of this material which is related directly with the reactants.

This section will be explained in two parts, the first for explains how this model was developed and the second for observing the results and their analysis.

5.1.1.1. Modelling of the Fluid Flow

In this part we will work with the Comsol for understanding how to use it and how we can include the parameters. The first step is to select the "Incompressible Navier-Stokes" equation in the principal window of the Comsol for 3D models. After this the equation is aggregated in the work space of the program.

If we want to work with this equation or with any equations, it is necessary to make the physical model of the element that has to be modelled. For making the model we can find all the documentation in the Comsol, including explanation of the tools and of all the functions of the program. The physical model of the VRB is shown in figure 5-1, where we can observe the positive and the negative half cells of the VRB. In this case only this part of the cell was simulated because the electrolyte works only in this part of the cell and therefore the fluid flow. The chemical and the electric part is also simulated with the same model because the reactions happen in this part of the cell and it is possible to calculate the voltage and the current with the parameters obtained with these models. This is one of the functionalities of the Comsol and it is possible to use directly the output parameters of one equation as the input parameters of the other.

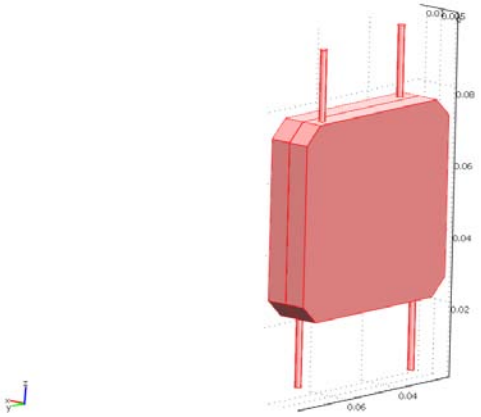


Figure 5-1: Model of the two half cell of the VRB, where is the electrolyte work

With the model in the hand, we can start to work with the equation and also with the physical model. For doing this we need to define two conditions which are the subdomains conditions and the boundary conditions. These two options are found with all kinds of equations in the Comsol. In this case they are under the "incompressible Navier-Stoker".

The first conditions that will be defined are in the subdomain part. The subdomain means every physical elements present in the model and here they are defined by the conditions and real characteristics of the material involved. For example in our case, it will be necessary to define some characteristics of the electrolyte, the fluid we are using and also the characteristics of the material where the electrolyte go through. The figure 5-2 shows the interface where the subdomain parameters are introduced.

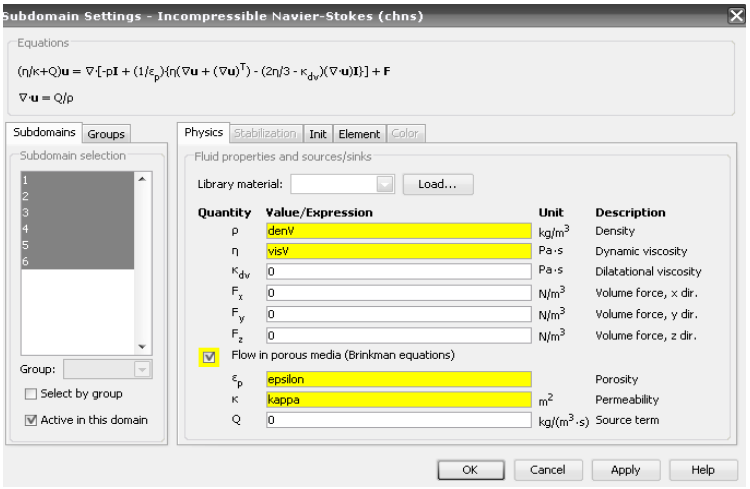


Figure 5-2: Subdomains parameters interface of Comsol

In figure 5-2 we can see some yellow bocks, these blocks are showing the parameters that were previously defined for this work. In the first part it is possible to observe the parameters for density *denV* and dynamic viscosity *visV*, both of them are for the V^5. These parameters are exclusively used for the electrolyte of fluid conditions. Also it is necessary to introduce the material from where the fluid will pass. This condition is defined by using the Brinkman equations, using the porosity and the permeability of the material, in this case of the carbon felt.

All of these conditions must be implemented for all of the elements present in the model. In this case we have 6 subdomains and they can be observed in the left part of figure 5-2. Also in the figure 5-2 only the positive part of the cell is shown, where the density and the concentration of V^5 are defined. But in the negative part it must be defined by the parameters of this side. Otherwise, in the case of this model we have only carbon felt in 2 subdomains, therefore only these subdomains must have the parameters of porosity and permeability. We can see this implementation in the figure 5-3 and 5-4.

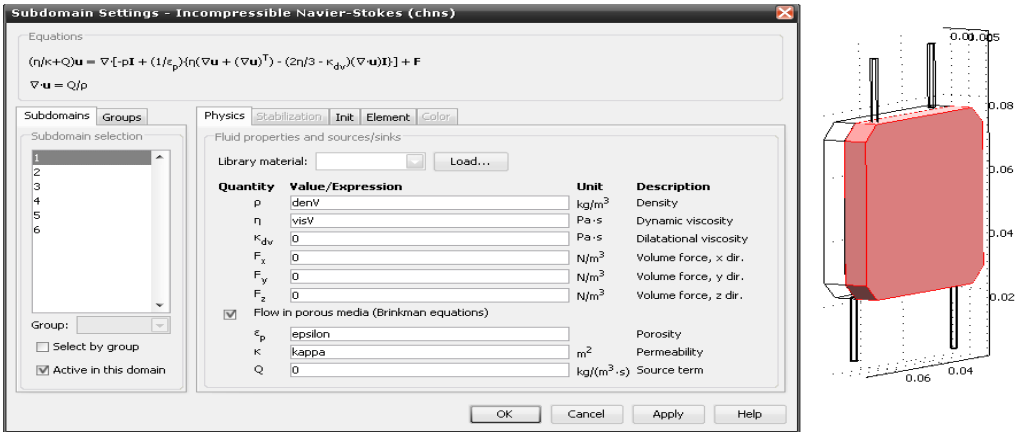


Figure 5-3: Definition parameters only for one subdomain, in this case positive half cell

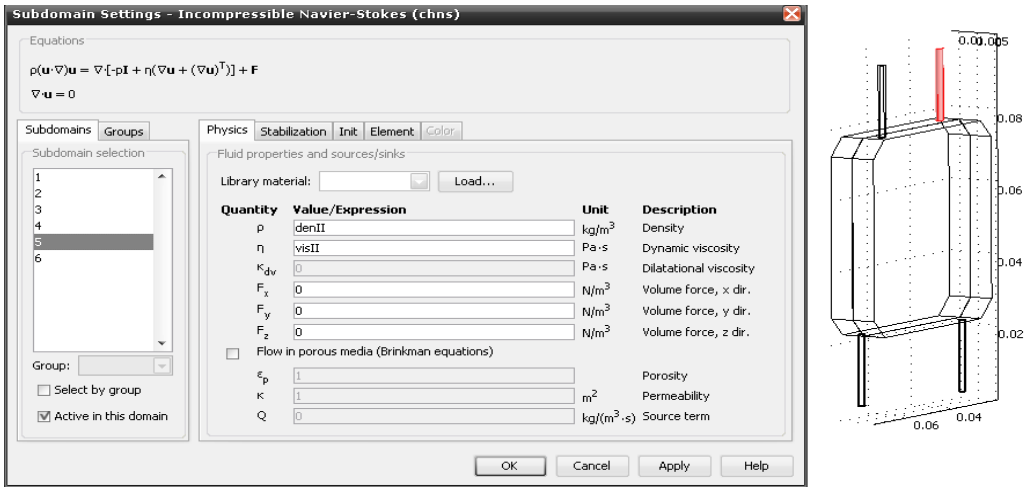


Figure 5-4: Definition parameters for the pipes in the VRB, without porous parameters

Now we know how to define the characteristics of the materials present in the model, we need to know how this parameters are used. This step is defined by the boundary conditions found under the incompressible Navier-Stokes equation in the work place of the Comsol. The boundary condition means which role is played by every face of the elements. For example, for which face the electrolyte go in and for which go out. Also it is possible to define some conditions of these boundaries, which depends on the type of boundary defined. The figure 5-5 and 5-6 show how the conditions were defined for the electrolyte in this case. For both the half cells the inlet parameter of the fluid were defined in the lower part of the cell in accordance with the real model and the outlet parameters of the fluid were defined in the upper part.

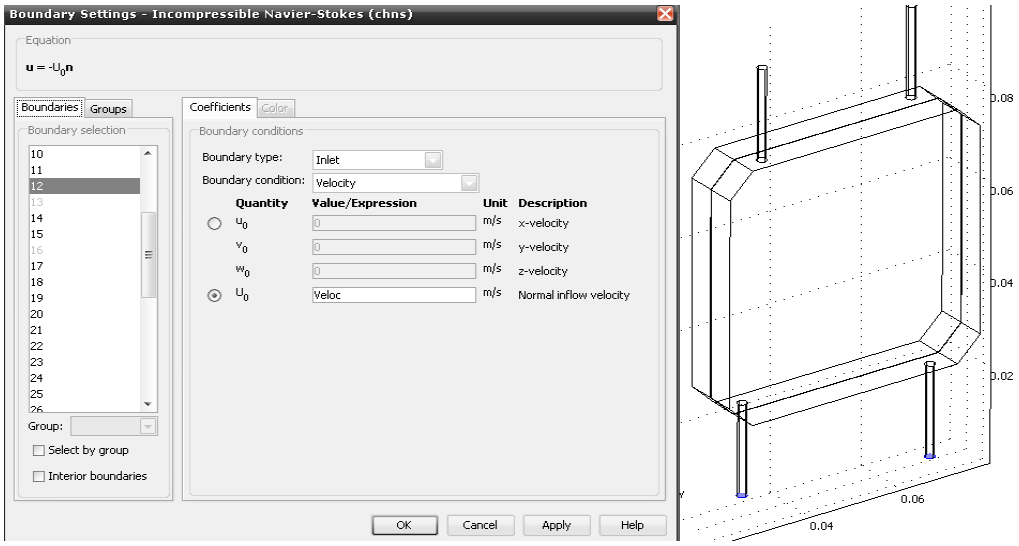


Figure 5-5: Boundary conditions of the inlet Fluid Flow in the VRB.

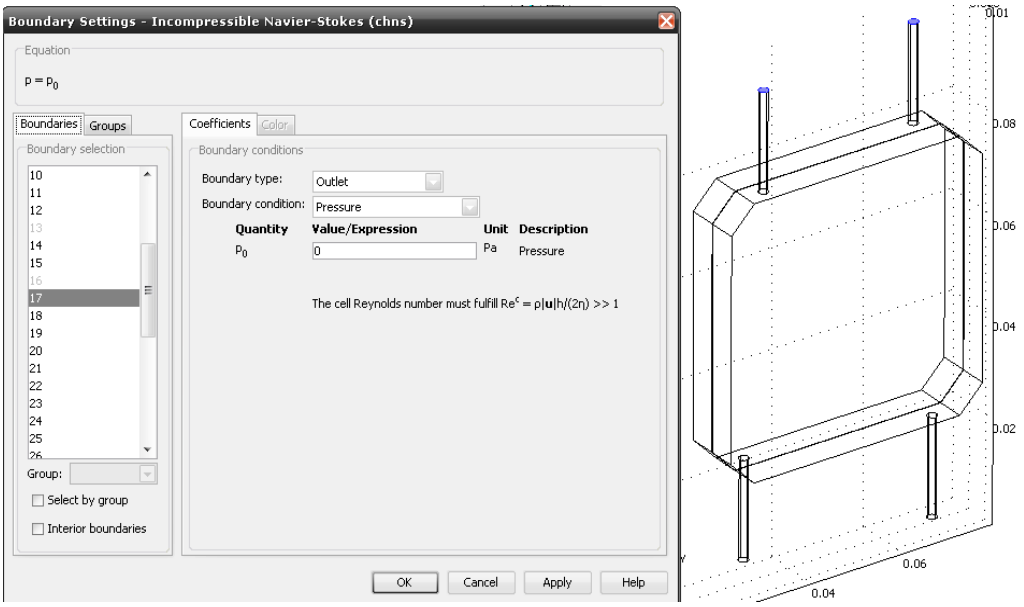


Figure 5-6: Boundary conditions of the outlet Fluid Flow in the VRB

All of the parameters that are not in the Comsol must be defined by the user. In this case all of the constant parameters and initial conditions were defined in the window named "constants". In this window you can define the parameters like density of V^5 (*denV*),

Normal inflow velocity (*Veloc*) and etc. The constants window where these parameters were defined can be seen in figure 5-7.

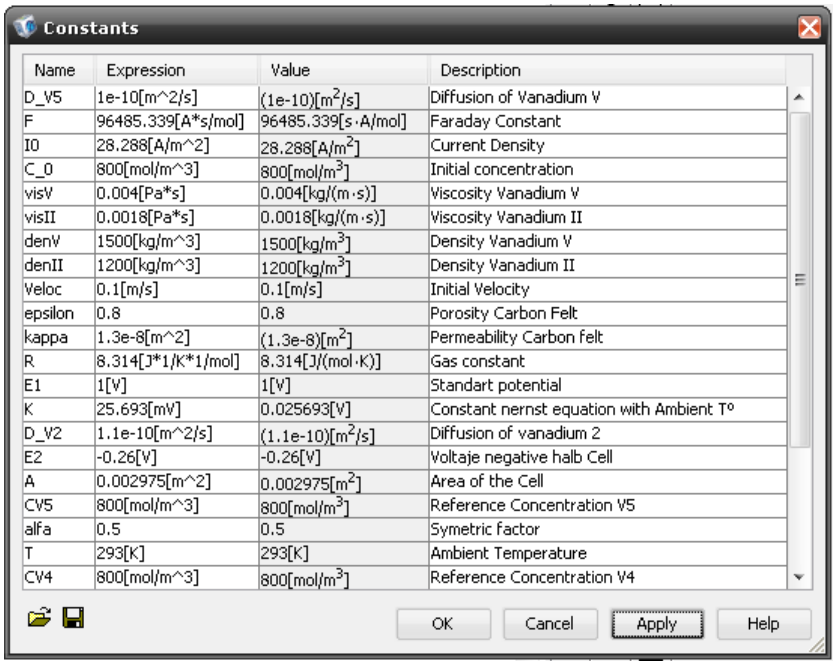


Figure 5-7: Definition of constant parameters in Comsol

In this model the values that have been used for the negative and the positive half cell are actually the values for V^2 and V^5 respectively. That is why the variation between V^2 and V^3 and between V^4 and V^5 are little and were considered equal, but it is also possible to introduce a change in dependency of other values, for example the concentration, that will be calculated in the next section. So in this model the battery is considered as symmetric on both the parts.

5.1.1.2. Results and Analysis

The results of the analysis in the mechanical model will be separate in 2 parts. The first part show how is the flow of the electrolyte in one of the half cells without the porous material (carbon felt). The second case show how is the flow of the electrolyte with porous material.

Also will be possible see the pressure in both cases. All of these parameters are giving by the incompressible Navier-Stokes equation.

As we have already seen, the carbon felt is defined by the activation of the porous option according to the Brinkman equation. In the figure 5-8 we can see the velocity flied of the electrolyte in one of the half cells and pressure of that cell. Here the parameters of the electrolyte in the positive and the negative half cell are very similar. Therefore it is not necessary to show the positive and the negative cell separately. Because the parameters of the positive and the negative cells are similar therefore we will always works with the positive cell in exception of the electrical model.

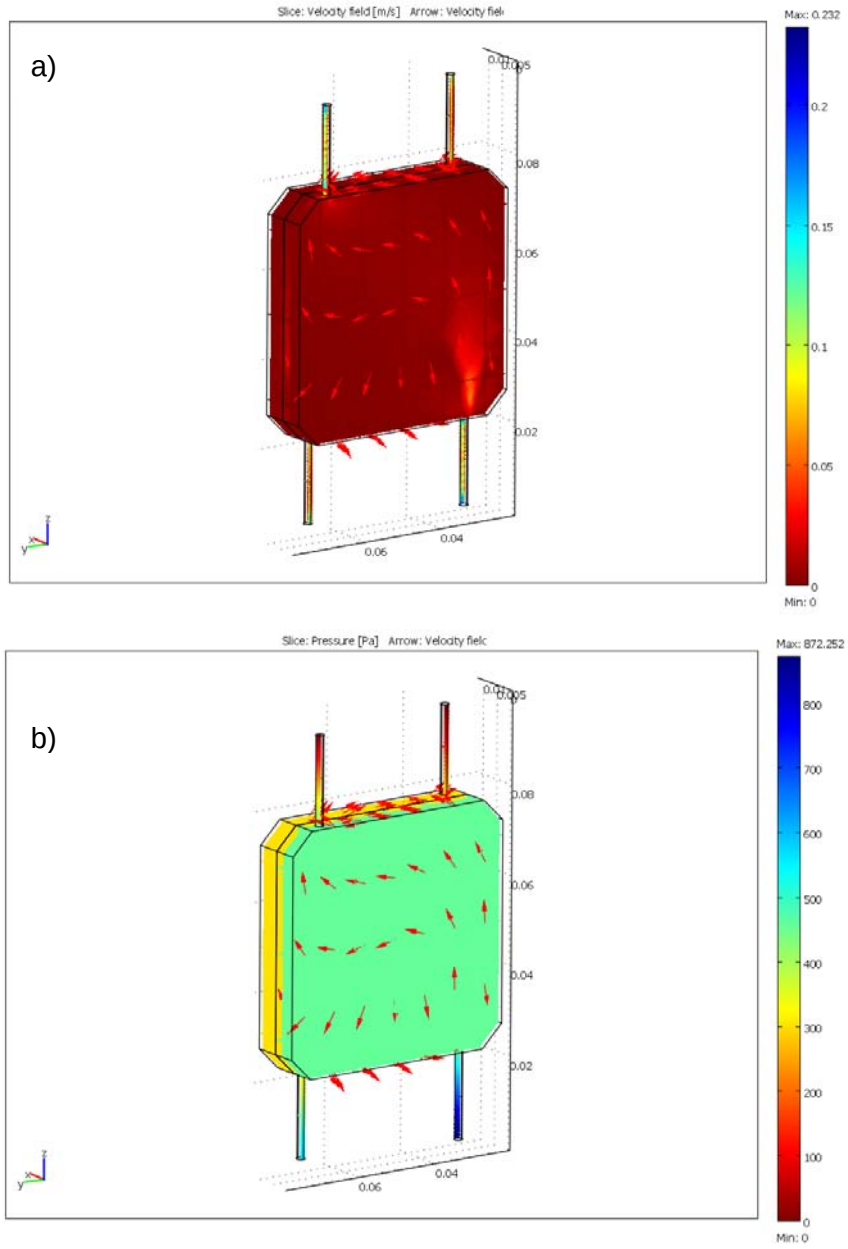


Figure 5-8 a): Fluid Flow without porous media. b) Pressure in the cell without porous media

As we can see in the figure 5-8, the fluid of the electrolyte in the battery without carbon felt is not linear and it has different directions. In this case the fluid is the minimal fluid calculated according to the conditions explained in section 4.4.2.2 (23 mL/min), and the unit which is used in the program is m/s. For this reason it is necessary to calculate the volumetric velocity and then divide it by the area of the pipe. The pressure of the system

can also be observed as shown in the figure 5-8; we can see that the pressure is higher when the electrolyte goes inside the cell and is lower when it leaves. The figure 5-9 shows the same conditions but considering the porous media or carbon felt.

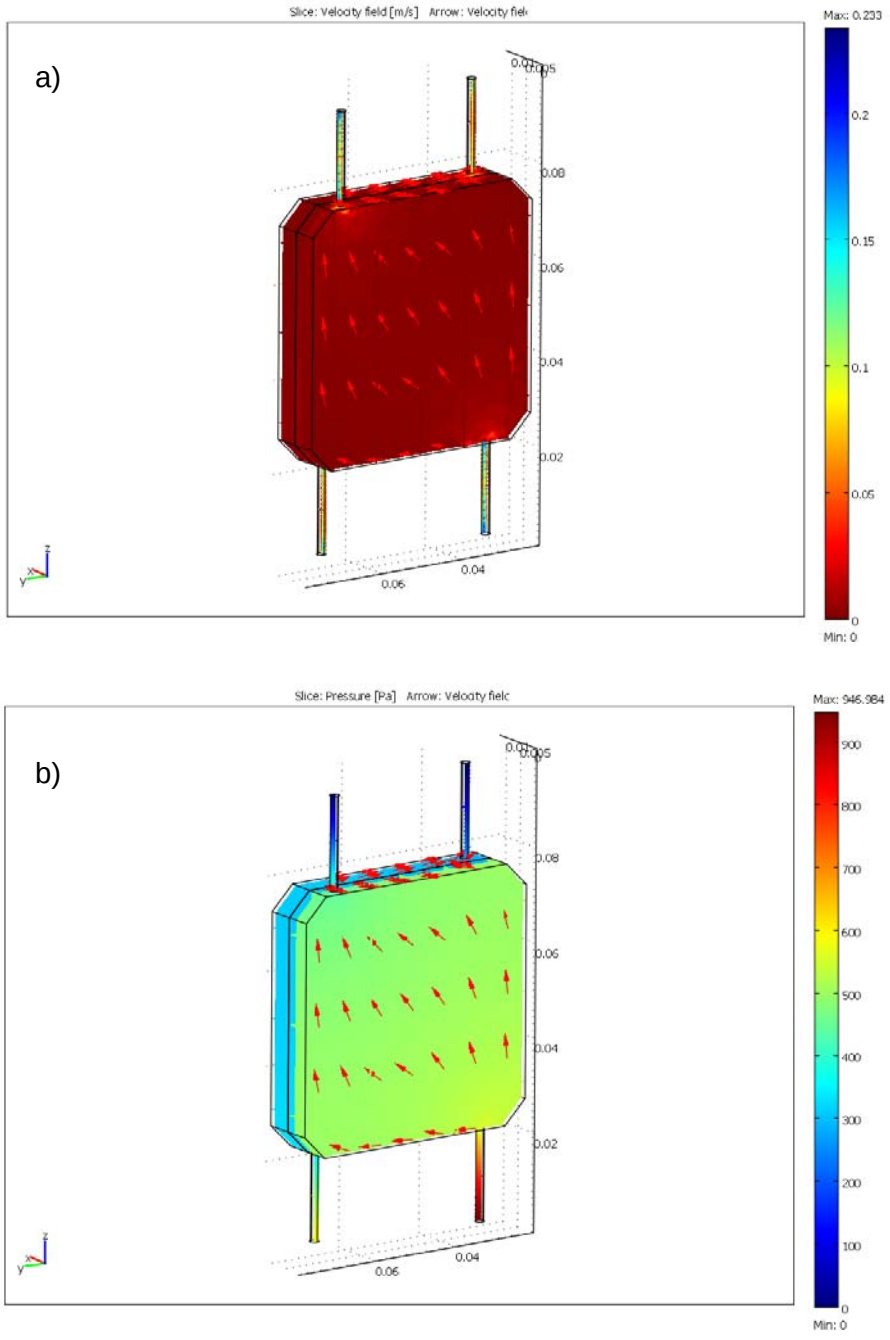


Figure 5-9: The figure a) Fluid Flow with porous media. b) Pressure in the cell with porous media

Now we have the other case that is with the porous media and the results can easily be observed. In the figure 5-9 a) the velocity field of the electrolyte with porous media is much better that the velocity field of the electrolyte without porous media. It has advantages in the distribution of the electrolyte and on its linearity; therefore we can say that is more symmetric. Also the integration of the carbon felt plays an important role in the increment of the voltage because of good conductivity of electrons and also in the distribution of the reactants because they can react in all part of the cell. On the other hand the pressure is shown in figure 5-9 b). The difference between figure 5-8 and 5-9 can easily be observed, the change of pressure inside the cell say that the porous material is working and the pressure is decreasing while the fluid flow through the cell.

5.1.2. Chemical Model: Concentration in the Cell

In this section the chemical model of the VRB will be explained. it is needed to consider the change of the concentration in the VRB, which means to work directly with the reaction rate in the cell.

Comsol has other tool for working with this type of problems and in the chemical engineering module it is possible to find the Convection and Diffusion equation.

In diffusion, Convection and Diffusion application modes for the Chemical Engineering Module, Fick's law describe the diffusive transport in the flux vector. Fick's law is adequate when the diffusing species is diluted with respect to a solvent.

In this case we are using this equation for calculating the change of concentration in the cell due to the rate of reaction and also by the distribution of the fluid inside the cell. This last part is done by using the mechanical and chemical model together. This section will be explained in two parts, the first part explains how this model was developed and the second for observing and analysing the results.

5.1.2.1. Modelling of the Concentration

Now we know better how to work with Comsol. The first step is to select the equation of the Model navigator and define two different "dependent variables". These variables are the concentrations of vanadium inside the cell, for example *c_A* is used for the concentration of V^5 and *c_B* for the concentration of V^4. This step can be observed in figure 5-10.

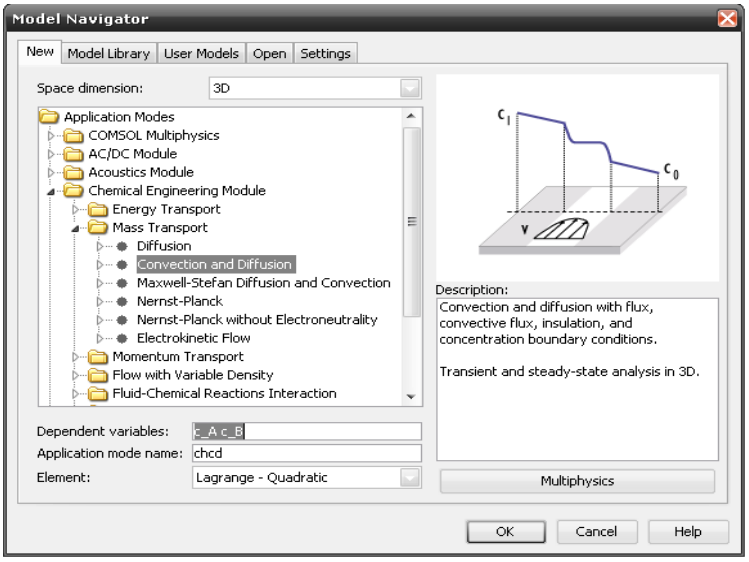


Figure 5-10: Definition of variables in Convection and diffusion equation

After performing this step we will be in the work window and similar to the previous model it is needed make a definition of the subdomains parameters and also the boundary parameters.

The subdomain parameters in this equation make reference to the diffusion of the electrolyte, the rate of reaction present in this work and also to the velocity of the fluid in the cell. This last parameter can be used from the mechanical model present in the last section. In figure 5-11 we can see the subdomain window where the parameters were defined. The diffusion parameter was obtained from the investigation of the electrolyte in the institute. The reaction rate is obtained from the coupling of electrical and chemical model. As it has been seen in section 4.3.3.1, the reaction rate depend upon the current transferred, the faraday constant and also upon the volume. This parameter will be

explained in the next section with the electrical model. The velocity parameters in 3 directions have been calculated by the mechanical model and used as input parameters in this equation.

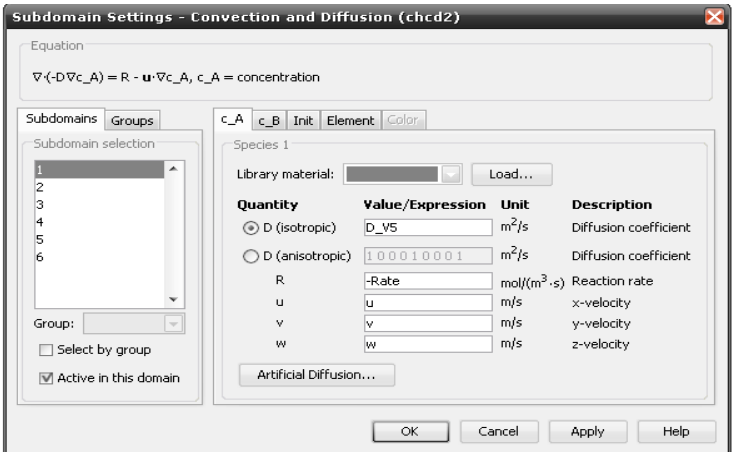


Figure 5-11: Definition of subdomain parameters for V^5

As we can see that the reaction rate is considered to be negative in this part, which means that the concentration *c_A* (in this case V^5) is decreasing with the ~~past~~ passage of time. But it is also necessary to define what happen with the concentration *c_B* (in this case V^4). We know that when one concentration decreases, in the VRB, the other increases with the same rate. Using this relation it is possible to say that the reaction rate of the V^4 is same but positive. Thus, one of the reactants decreases in concentration while the other increases. Due to this reason the battery is considered to be symmetric, which means the rate of reaction in the negative part is the same as in the positive. The subdomain parameters for the concentration *c_B* (V^4) are shown in figure 5-12.

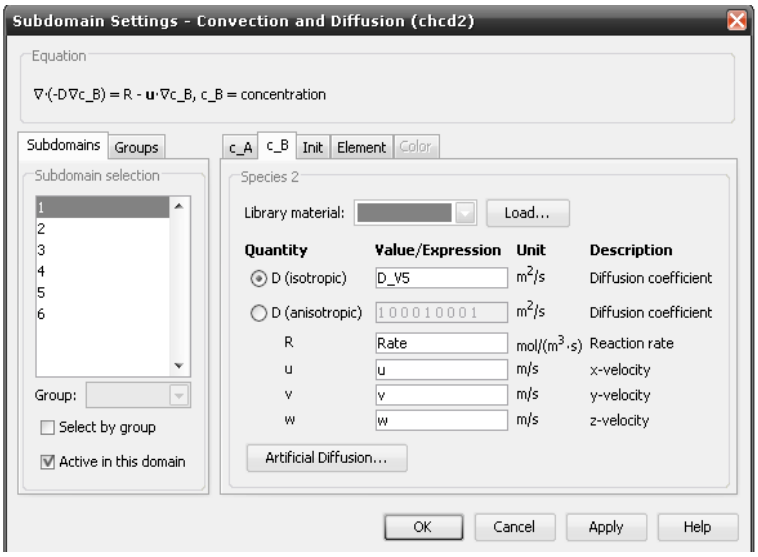


Figure 5-12: Definition of subdomain parameters for V^4

Only the diffusion parameter is different in the positive and the negative half cell because of the little differences between the solutions.

The next step is to define the boundary conditions of the model for this equation. The boundary parameters in this case are the initial parameters of the concentration. The concentration *c_A* has an initial parameter of 0.8 mol/l or 800mol/m^3. In this case the Comsol works with the last parameter. On the other hand the initial concentration of *c_B* is zero and will increase with the time, these boundary condition are defined for the inlet of the model. The outlet parameters are defined as "connective flux" which means the flow of molecules in the fluid. The figures 5-13 and 5-14 show the definition *c_A* for inlet and outlet parameters.

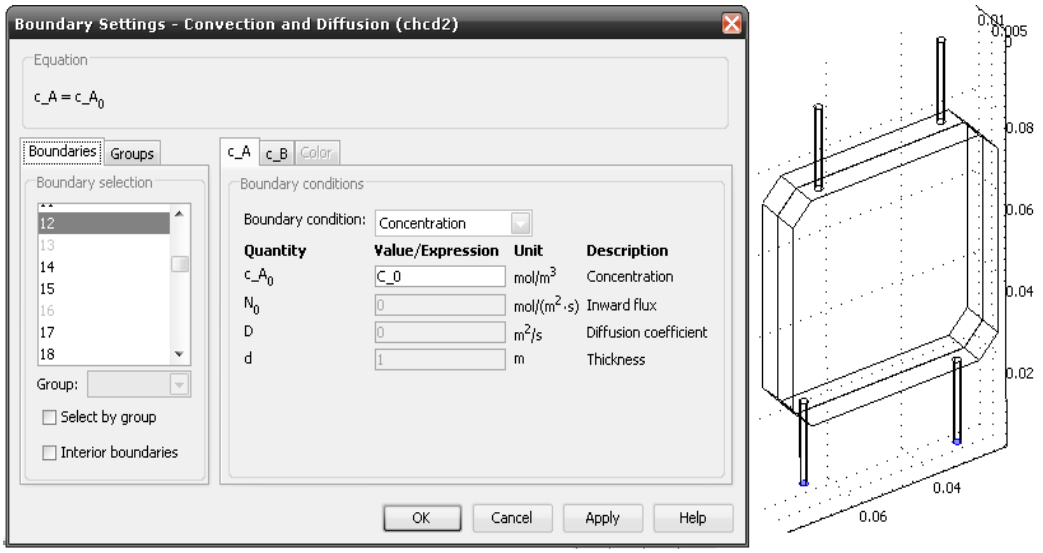


Figure 5-13: Definition of boundary inlet conditions, convection and diffusion equation

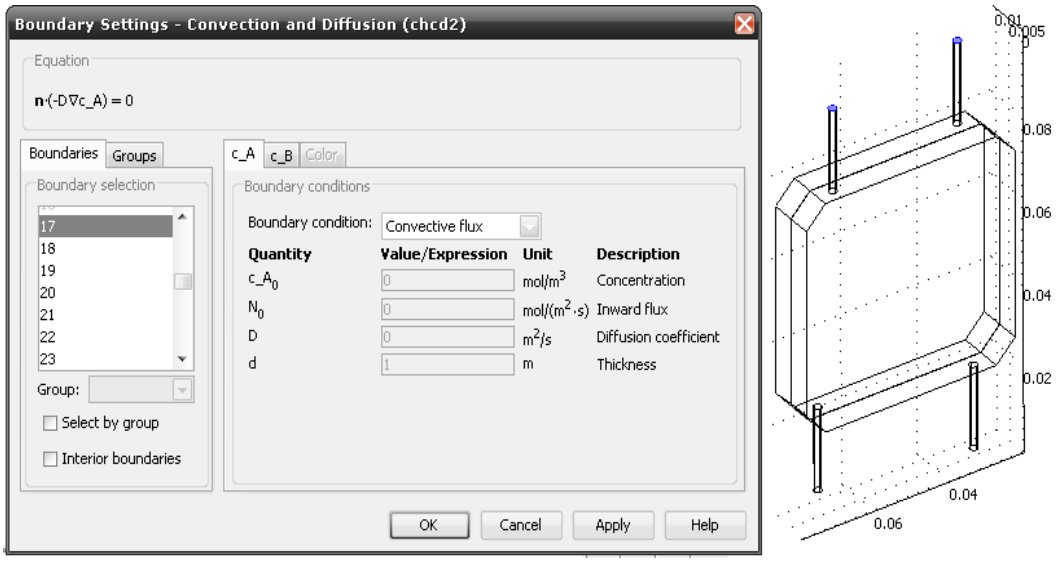


Figure 5-14: Definition of boundary outlet conditions, convection and diffusion equation

The definition of the values for the concentration *c_B* is not showed in the figures, but has only one change and it is in the inlet values where the initial concentration is cero.

5.1.2.2. Results and Analysis

Some problems in the program are discovered in this part of the model. The first problem was the divergence of the chemical model with the mechanical model for real values. For example, in the mechanical model uses an initial velocity of 0.25 m/s which is approximately equal to the value of the minimal flow rate Q_{min}. But if we combine the mechanical and chemical models the flow rate is limited. With velocity of 0.25 m/s the Comsol can not converged So it is necessary to use other value of initial velocity if the two models are combined, the velocity is 2.5e-5 m/s, 10000 smaller that the real value.
In this case the reaction rate is obtained from the standard rate constant for an equilibrium system [20]. This value must be changed in according with the Butler-Volmer equation but due to the time it was not possible to calculate the reaction rate with Comsol and therefore the rate is used as constant.

With all of these considerations the program was running and was possible to observe the results which describe the performance of the cell but not in accordance with the real values. The concentration changes during discharge still can be observed. The figure 5-15 shows the change in the concentration *c_A* and *c_B* (for V^5 and V^4 respectively). The concentrations of V^2 and V^3 in negative cell show similar behaviours to V^5 and V^4 accordingly. And for this reason they are not shown in the figure. These results depend on the electrical part of this work.

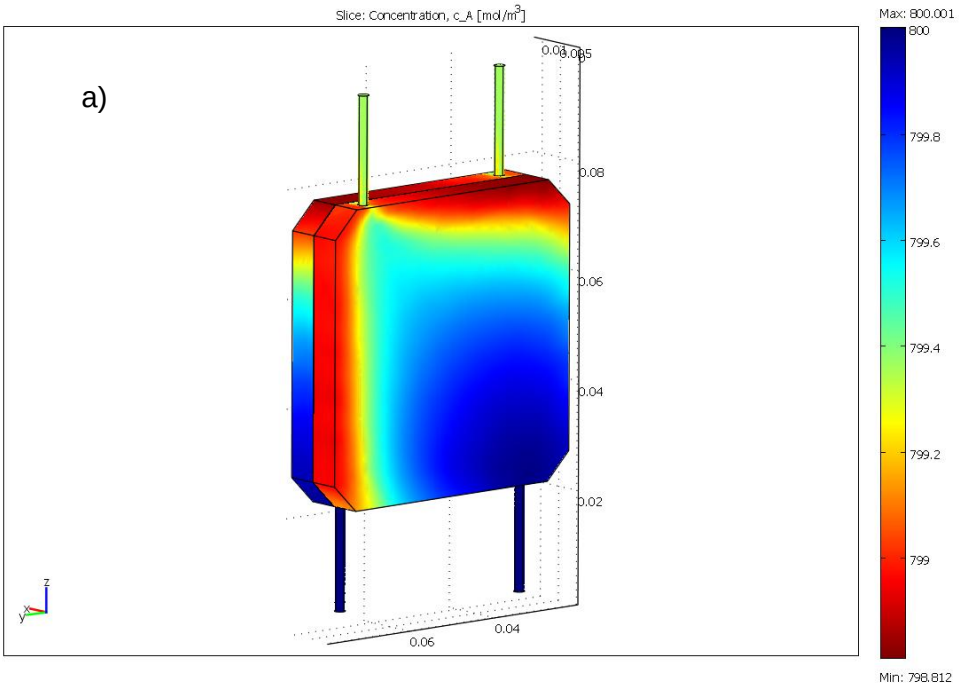


Figure 5-15: a) Change of concentration of V^5

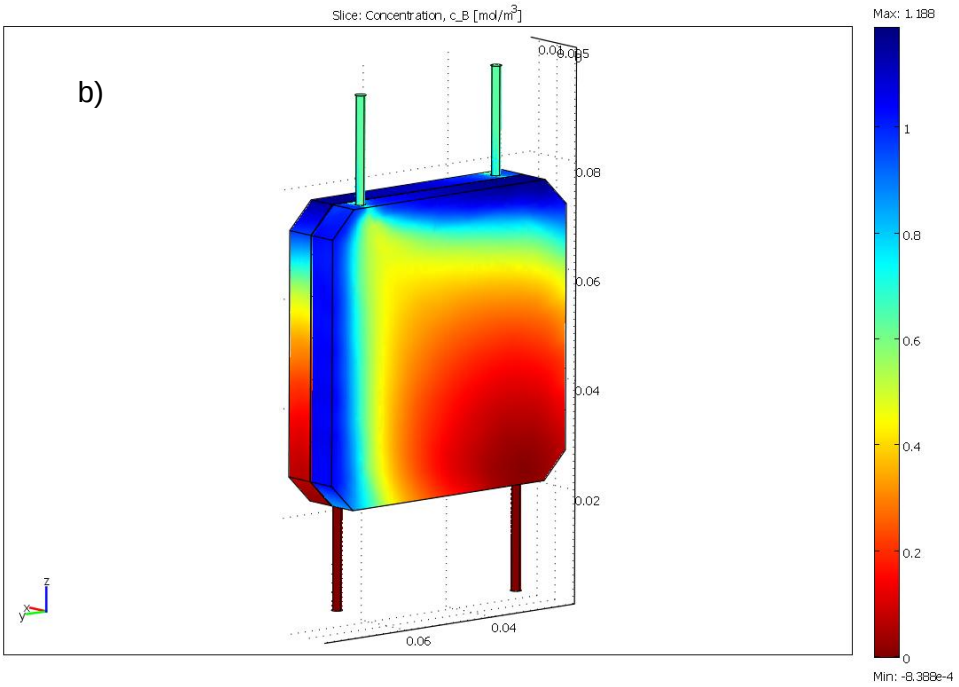


Figure 5-16: b) Change of concentration of V^4

As has been explained before this values are not the real values, but it is possible observe the change of concentration when the fluid goes through the cell and at the same time reactions happen.

5.1.3. Electrical Model: Voltage of the Cell

The electrical model presented in this model describes how the battery works depending on some theoretical equations. These equations were explained in this work, these equations include: The Nernst equation for calculating the cell potential and the Butler-Volmer equation for calculating the current of the cell (this equation was not implemented in the model because of the time constraint). These two equations are related with the two models presented before, thus it is possible to use the concentration (that depends on the fluid flow) for calculating the variation of voltage and current in these parts of the cell.

As it has been done before it is necessary to make the definition of the parameters. In this case this definition is different because the equations are not present in the program and it is necessary to insert these equations manually. For this insertion of equations for the different subdomains will be defined. In this case one subdomain (number 1) represents the positive part while the other (number 4) represents the negative. The definition of these equations was made in "subdomain expressions" in the main window. Here it is possible to define equation for each subdomain which can be observed in the figure 5-16 and 5-17.

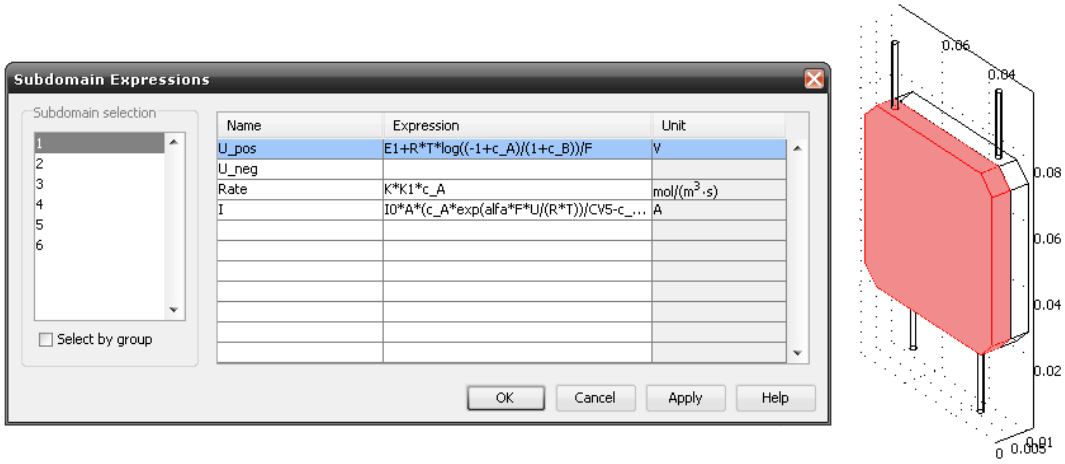


Figure 5-17: Definition of equations for the positive subdomain

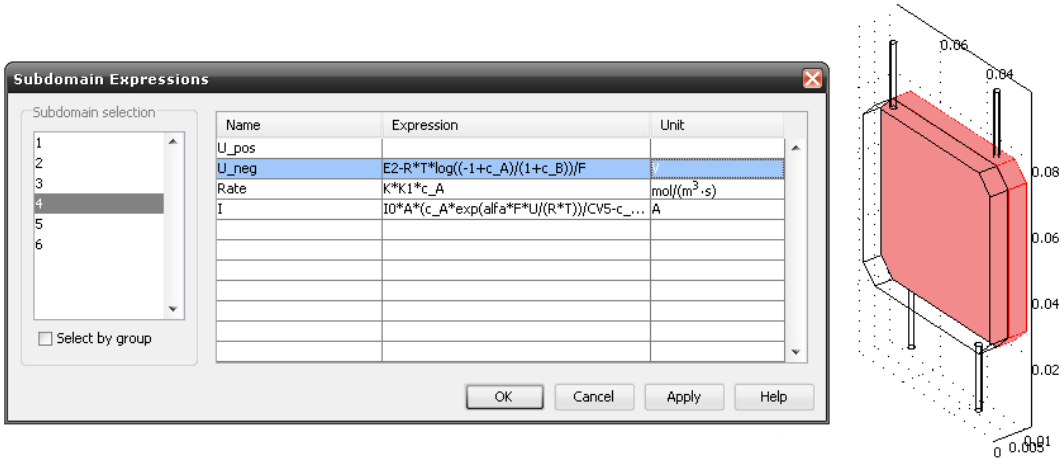


Figure 5-18: Definition of equations for the positive subdomain

In the figure it is possible to see that these three equations are defined by constants. These constants are shown in the figure 5-18. The Nernst equation is divided into two parts, one for the positive half cell and the other for the negative. Thus we are able to calculate the voltage in the two half cell depending on the concentration.

Also it is possible to observe the rate of reaction necessary to calculate the change of concentration, this reaction rate must be in relation with the current described by the Butler-Volmer equation, but in this case it was considered to be constant because it was not possible to set the value of the Butler-Volmer current.

The Nernst equation is defined as *U_pos* and *U_neg* for each half cell and the reaction rate was defined as *Rate*.

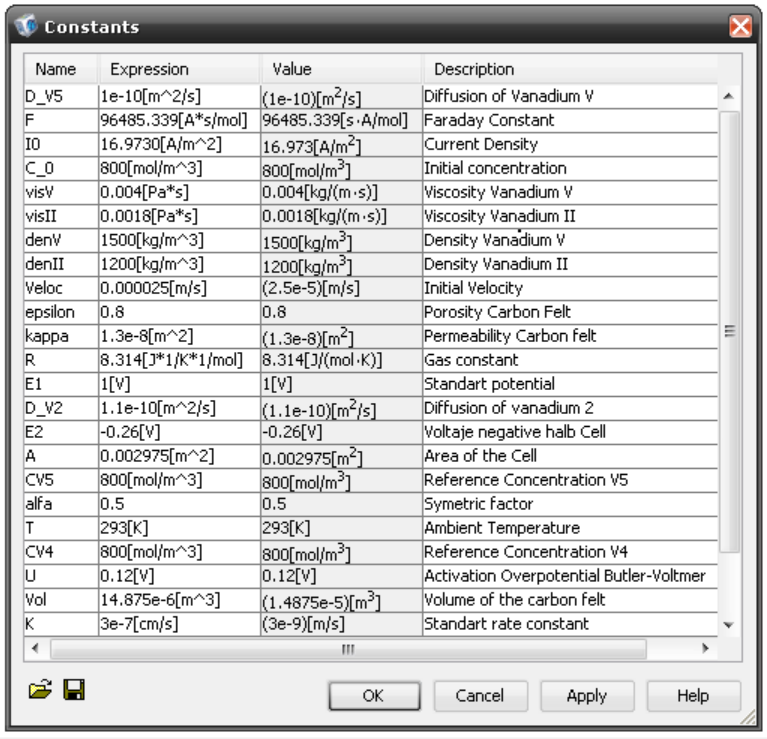


Figure 5-19: Definition of all the constant parameters for the model.

Some parameters of the last three figures have to be explained. For example the values of *E1* and *E2* in the figure 5-18 are defined as the standard potential for each half cells. In this case the Nernst equation for the full cell was separated in two parts and the hydrogen is neglected.

$$U_{pos} = E1 + \frac{R*T}{F} * \log\left(\frac{c_{V5}}{c_{V4}}\right) \tag{5.1}$$

$$U_{neg} = E2 + \frac{R*T}{F} * \log\left(\frac{c_{V2}}{c_{V3}}\right) \tag{5.2}$$

The concentration of the two half cells are considered symmetrical thus only the concentration of V^5 (*c_A*) is used in the equation of the Comsol for the both half cells.

It was not possible to set the correct parameter for calculating the Butler-Volmer equation, it is not possible to calculate the Butler-Volmer equation only by using Comsol because

some conditions to execute iteration loops are required for estimating the Butler-Volmer voltage U_{act}. In this case the use of Matlab could be the solution for integrating this parameter in Comsol, because Comsol can export the model in a Matlab file.

But the other values involved in the Butler-Volmer equation were calculated manually. The value of I_0 is the exchange current density in the cell and could be calculated with the Butler-Volmer equation with two possibilities. The first is when the current is small enough and the second possibility is that the overpotential is large enough or use high flow rate. In this case we have used the first method. The measurement was done with a current of 2mA, in operational mode for obtaining U_{op}, and in open circuit for obtaining U_{ocv}. For this current difference between U_{op} and U_{ocv} was 0.001. For this case the Butler-Volmer equation is explained below where A is the area of the graphite felt.

$$\left(U_{op} - U_{occ}\right) = \frac{R*T}{F} * \frac{I}{A*Io} \tag{5.3}$$

$$(0.001V) = \frac{8{,}314\,(J*1/K*1/mol)*293\,(K)}{96485.339[A*s/mol]} * \frac{2mA}{2.975e^{-8}(m^2)*Io} \tag{5.4}$$

$$Io = \ 16{,}973\ (\mathrm{A/m^2}) \tag{5.5}$$

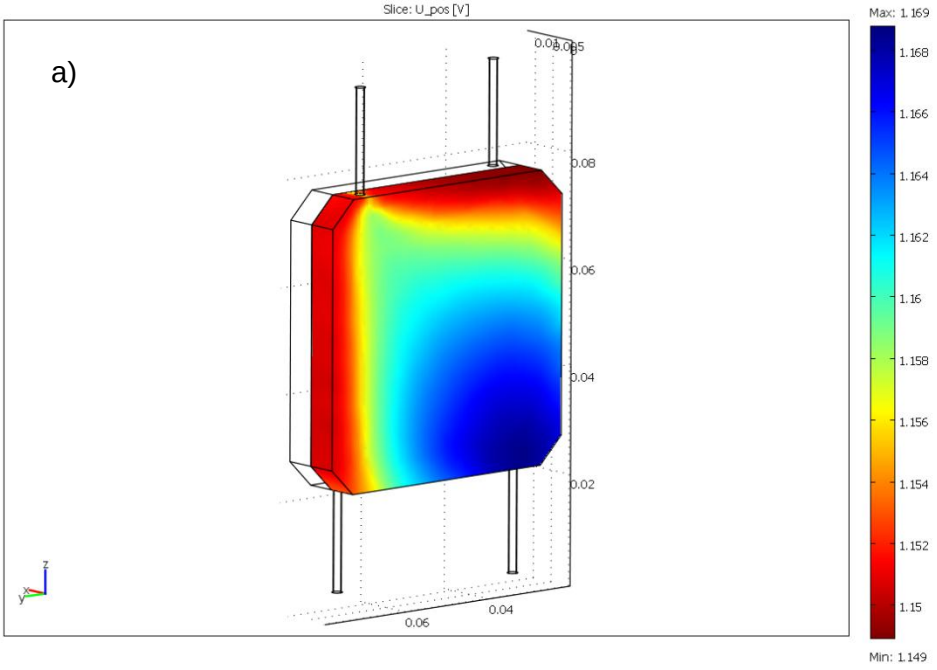
It is known that the values of the result in the Nernst equation depend upon the concentration. But also it is possible to define the Butler-Volmer equation in dependency of the concentration and the standard concentration $C_V^{\cdot}$ (which is defined in the Comsol as *CV5* and *CV4* respectively and in our case this is 0.8ml/l).

$$I = I_0 * A * \left(\frac{C_{V5}}{C_{V5}^{\cdot}} exp^{\frac{\alpha*n*F*U_{act}}{R*T}} - \frac{C_{V4}}{C_{V4}^{\cdot}} exp^{\frac{-(1-\alpha)*n*F*U_{act}}{R*T}}\right)(A) \tag{5.6}$$

The parameter of *alfa* or α is the symmetric factor in the Butler-Volmer equation and describe the symmetric behaviour of the charge and discharge curves, 0.5 is used in this work.

5.1.3.1. Results and Analysis

In the final section of this chapter the electrical result will be presented based on the equations explained before. Figure 5-20 shows the voltage of the positive cell *U_pos* and negative cell *U_neg* for the variation of concentration between 0.8mol/L (SoC 100%) and 0.798mol/L approx. These both parameters were calculated with the standard rate constant [20].



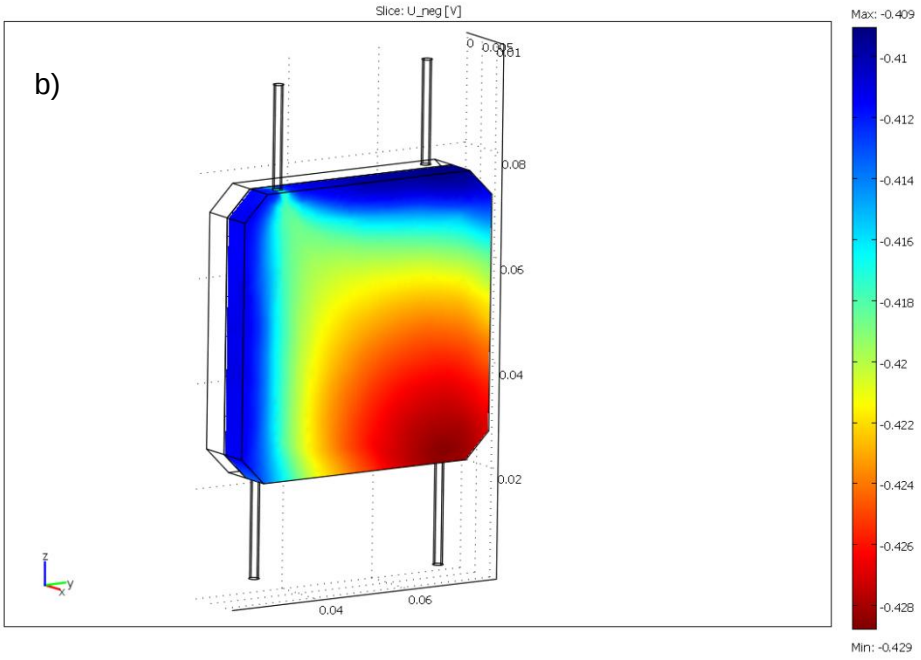


Figure 5-20: a) Voltage in the positive half cell. b) Voltage in the negative half cell

In the figure 5-20 it is possible to observe the changes on the voltage in the cell because of the concentration. In this case the variation of the concentration is not so large and therefore the variation in the voltage is also small. If we make the sum between the maximal value of the positive half cell and the minimum values of the negative half cell it possible to obtain the maximal value of the full Nernst equation, this value is close to 1.6V. Also these values are found in the inlet of the cell, when the battery is fully charged. After the passage of electrolyte through the cell the voltage is decreased because of the reaction and concentration changes in the cell.

6. Conclusions

- VRB is in theory a relative simple system. But for the real, some considerations should not be ignored. These considerations can be separated in three types: Electrolyte considerations, pumps considerations and cell considerations. The oxidation of the V^2 with oxygen in air in negative half cell should be avoided that results in a decrement of the capacity. Also the pumps should always keep clean to provide a smooth electrolyte flow. To avoid the corrosion in the positive half cell the electrolyte should be pumped out of the cell when the battery is not being used. At the same time, it can also avoid the crossover through the membrane of the electrolyte.

- With the charge and discharge curves with different currents of the VRB it is possible to observe in the thesis that all of the measurements done for the battery have very high coulomb efficiency between 98% and 94%. Because the coulomb efficiency has a direct relation with the capacity of the battery. So it also shows the high capacity of the VRB.

- To use a minimal flow rates is always the best way to get maximal efficiency with VRB. In this case was not possible calculate the power of the pump for a minimal flow rate but it suppose lower. The comparison between flow rate 25 mL/min and flow rate 330 mL/min doesn't show much change in the shapes of discharging curve and charging curve. In this work the flow rate of the pump is limited up to 330 mL/min.

- In Electrochemical Impedance Spectroscopy (EIS) measurements we can see that the impedance increases faster when the SoC is lower near to 25%. The impedances for 50% SoC and 75% SoC are similar. On the other hand, the impedance decreases dramatically if a 200 mA DC current is implied to VRB.

- EIS measurement can also help to understand the behaviour of the VRB. The first semicircle of the EIS measurements is because of the double-layer capacitance and charge transfer between the electrode and electrolyte that still includes a ZARC element due to the porosity of the carbon felt. The second semicircle of the impedance

spectroscopy is probably because of the diffusion process in the cell. But it is necessary to investigate more about this phenomenon for VRB in the future.

- With the Comsol it is possible to combine the different models using the output of one model as input parameters for the other model, the mechanical, the chemical and the electrical model for VRB. But Comsol is not perfect for flow batteries. It is impossible to simulate the real flow rate with combination of all models.

- Because of the time limitation, it is impossible to implement the complete electrical model for VRB. The Butler-Volmer equation must be calculated with other program such as MatLab that can be implemented in Comsol. It could be a challenge for our successors.

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