Διπλωματική Εργασία

Πειραματική διερεύνηση και μοντελοποίηση της επίδοσης μπαταριάς ροής με ηλεκτρολύτες βασισμένους σε ιόντα Νατρίου

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Experimental investigation and modeling of sodium-based flow battery performance

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Abstract

In the present diploma thesis, the performance of a sodium–based flow battery cell is investigated experimentally. The sodium–based electrolytes were self–made in the lab and a full charge–discharge cycle was performed and measured. The flow battery cell was modeled with two different methods.

The flow battery cell is made of two plexiglass plates that hold the electrodes and two fittings each that facilitate the flow of electrolytes through the cell. A rubber gasket with a hydrophilic membrane divides the anode form the cathode side. The active material is Na$_2$Ti$_3$O$_7$ and the electrode silver for the anode while for the cathode it is Na$_{0.44}$MnO$_2$ and the electrode is copper. These were mixed with carbon black and subsequently suspended in a deionized water – Na$_2$SO$_4$ mix to make the electrolytes that can be pumped through the cell. The discharge experiment revealed promising results for this experimental flow battery cell.

The discharge data for voltage and current were used for the parameterization and modeling of the flow battery cell with a couple of methods. The data were first modified with some assumptions to help in the process. An equivalent circuit model of the cell with three Resistor–Capacitor branches was created with the use of Matlab and Simulink software. Another equivalent circuit model making use of the Recursive Extended Least Squares algorithm for online parameterization was also developed. They both revealed accurate results, with the RELS model almost overlaying with experimental data for large part of the SoC range.
Περίληψη

Στην παρούσα διπλωματική εργασία, διερευνήθηκε πειραματικά η επίδοση μιας μπαταρίας ροής με ηλεκτρολύτες βασισμένους σε ιόντα Νατρίου. Οι βασισμένοι στο Νάτριο ηλεκτρολύτες φτιάχτηκαν στο εργαστήριο και ένας πλήρης κύκλος φόρτισης – εκφόρτισης της μπαταρίας διενεργήθηκε και μετρήθηκε. Το κελί μπαταρίας ροής μοντελοποιήθηκε με δύο διαφορετικές μεθόδους.

Το κελί της μπαταρίας ροής αποτελείται από δύο πλάκες πλέξιγκλα πάνω στις οποίες βρίσκονται τα ηλεκτρόδια και δύο «οπές» στην καθεμία, ώστε να υπάρχει ροή των ηλεκτρολυτών μέσω του κελιού. Μια λαστιχένια φλάντζα με μια υδροφιλική μεμβράνη χωρίζει την πλευρά της ανόδου από την πλευρά της κάθοδου. Το ενεργό υλικό για την ανόδο είναι Na2Ti3O7 και το ηλεκτρόδιο ασημένιο, ενώ για την κάθοδο είναι Na0.44MnO2 και το ηλεκτρόδιο χάλκινο. Αυτά αναμίξθηκαν με μαύρο άνθρακα και στη συνέχεια χρησιμοποιήθηκαν για τη δημιουργία αιωρήματος σε απιονισμένο νερό αναμεμιγμένο με Na2SO4, ώστε να δημιουργηθούν ηλεκτρολύτες που δύναται να αντληθούν μέσω του κελιού.

Τα δεδομένα από την εκφόρτιση της μπαταρίας για την τάση και το ρεύμα χρησιμοποιήθηκαν για την παραμετροποίηση και την μοντελοποίηση του κελιού μπαταρίας ροής με δύο μεθόδους. Τα δεδομένα πρώτα τροποποιήθηκαν με μερικές υποθέσεις για να διευκολύνουν αυτή τη διαδικασία. Ένα μοντέλο ισοδύναμου κυκλώματος με τρεις κλάδους αντίστασης – πυκνωτή δημιουργήθηκε με τη χρήση των λογισμικών Matlab και Simulink. Επίσης δημιουργήθηκε ένα άλλο μοντέλο ισοδύναμου κυκλώματος με χρήση επαναληπτικού αλγορίθμου ελαχίστων τετραγώνων για παραμετροποίηση της μπαταρίας σε πραγματικό χρόνο. Και τα δύο οδήγησαν σε ακριβείς προσομοιώσεις, με το δεύτερο να πετυχαίνει σχεδόν επικάλυψη με πειραματικά δεδομένα για μεγάλο μέρος του εύρους επιπέδου φόρτισης.
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1 Introduction

The modern society uses massive amounts of energy annually, about 160,000 TWh, a number that is constantly growing. About 80% of this energy is covered by the use of fossil fuels as their specific energy makes them very appropriate for meeting this energy demand. However they come with two major problems attached. The diminishing stored amounts of fossil fuel and the severe impact their use has on the environment. Thus there is an imperative to limit their usage that is becoming evident in recent years, with measures being taken to raise the number of hybrid and electric vehicles, raise the production of renewable energy, research on more electric and all electric aircraft among others. It is no wonder that battery technology is one of the hottest research topics of our era. In this thesis the topic of flow batteries is investigated, and more specifically sodium – based. Sodium batteries can be a future alternative to lithium – ion, as they could eliminate some challenges lithium – ion batteries face. With the rapidly expanding need for large electrical energy storage in connection with renewable energy sources flow batteries can become a real solution.
2 Battery basics

2.1 Cell, module and pack

A single cell is a complete battery with two current leads and separate compartments holding electrodes (the anode or negative electrode which gives up electrons to the external circuit and the cathode or positive electrode that accepts electrons from the external circuit), separator, and electrolyte (which provides the medium for transfer of charge, as ions inside the cell between the anode and cathode, and is usually a liquid with dissolved acids, salts or alkalis). A module is composed of a few cells either by physical attachment or by welding in between cells and a pack of batteries is composed of modules and placed in a single containing for thermal management. The performance of the cells in a multicell battery will usually be different than the performance of the individual cells, as the cells cannot be manufactured completely identical, and although they are chosen to be “balanced” each cell encounters a somewhat different environment in the battery pack. The specific design of the multicell battery and the hardware used, like packaging techniques, spacing between cells, container material, insulation, fuses and other electronic controls will influence the performance as they affect the environment and temperature of the individual cells.

![Electrochemical operation of a cell during discharge](image.png)

Figure 1. Electrochemical operation of a cell during discharge
2.2 Battery capacity

Battery capacity is the measure of a battery’s ability to store or deliver electrical energy and is commonly expressed in units of Ampere – hours. The rated Ah capacity is the nominal capacity of a fully charged new battery under conditions predefined by its manufacturer. There are many design aspects that determine the capacity of a battery cell like quantity of active materials, the number, design and physical dimensions of the electrode plates and the electrolyte specific gravity. According to Peukert’s law:

\[ C_p = I^k t \]

Where \( C_p \) is the capacity with one ampere discharge rate, \( I \) the discharge current, \( K \) the Peukert’s constant and \( t \) the time of discharge. It is usually the case that the capacity of a battery will be reduced if a large current is drawn from it and raised if it is discharged with a low rate. This change in capacity occurs due to unwanted side reactions in the cell and is most noticeable in the lead – acid battery but occurs in all types, and can be seen in the figure below for a large (traction) lead – acid battery.

![Figure 2. Change in capacity with discharge rate for a nominally 42 Ah traction lead acid battery by Hawker Energy Products Inc.](image)
2.3 Rate of charge/discharge

The term used is the C-rate and is used to represent a charge or discharge rate equal to the capacity of a battery in one hour. For example for a battery with a nominal capacity of 2 Ah, 1 C is equal to a charge or discharge with a current of 2 A.

2.4 Cut-off voltage

The cut-off voltage is the lowest voltage that a battery is allowed to reach during its operation and is defined by its manufacturer.

2.5 Specific energy/power

The specific energy, also called gravimetric energy density is used to define how much energy a battery can store per unit mass. It is expressed in Wh/kg

\[
\text{Specific Energy} = \frac{\text{Rated Wh Capacity}}{\text{Battery Mass}}
\]

The specific power is the amount of power obtained per kilogram of battery and although batteries do have a maximum power, it is neither efficient nor good for their longevity for them to be used at this power for more than a few seconds. It should be noted that the power a battery outputs is more dependent on the load connected to it than the battery itself, and that high specific power normally results in lower specific energy for any particular type of battery. This difference in change of specific power with specific energy is important and it is helpful in making comparisons between different types of batteries. An example of this relation and comparison between lead – acid and nickel – cadmium batteries can be seen in the figure below.
2.6 Electromotive force

The total amount of energy per Coulomb of charge supplied by the battery is referred to as the electromotive force. It is calculated by the electric potential difference between the two electrodes of a battery cell. This is numerically equal to the battery open circuit voltage.

2.7 State of charge

The state of charge (SoC) is used to describe the remaining capacity percentage of a battery and is affected by the operating parameters such as current load and temperature. It is a critical condition parameter for battery management and thus safe operation of batteries and its accurate gauging is rather challenging. The existing methods from the literature for SoC estimation will be reviewed in a subsequent chapter. If the Ah capacity is used, the change of SoC can be expressed as:

$$\Delta SoC = SoC(t) - SoC(t_0) = \frac{1}{Ah\,Capacity} \int_{t_0}^{t} i(\tau) d\tau$$
2.8 Ampere – hour (or charge) efficiency

If everything was ideal, during the discharge the battery would return the entire charge that was put into it. However that is never the case thus the charging efficiency is less than 100%. The charging efficiency will vary for different types of batteries, temperature, rate of charge and SoC. When charged from about 20-80% SoC the efficiency is usually close to 100% but for the last 20% of the charge the efficiency is reduced significantly.

2.9 Self – discharge rate

Most batteries discharge when left unused. This is important as it means that some batteries cannot be left for long periods of time without recharging. The rate varies with battery type and other factors like temperature, higher temperatures greatly increase self – discharge. There are specially designed batteries (reserve batteries) to reduce this effect for some applications (e.g. military use) and also the technique of constantly charging batteries with a very small current (trickle charge) to keep them fully charged for longer periods of times. Flow batteries that will be studied in this thesis have a great advantage in this respect, as the tanks holding the active electrolytes can be stored separately essentially eliminating self – discharge.

2.10 State of Health

The State of Health (SoH) is used to describe the aging of the battery, as the capability of a certain battery cell to have a capacity level and provide certain amounts of power is diminished over the battery lifetime. Usual indicators are the capacity, resistance and impedance of the battery. The SoH is considered to be 100% when the battery is new and 0% when its capability to store energy or provide power has decreased below a certain threshold.
3 Types of batteries

The main categories in which batteries are characterized are primary and secondary batteries, with their main difference being that secondary batteries are rechargeable. The primary batteries are a convenient and usually inexpensive and lightweight source of power for portable electronic and electric devices. The applications of secondary batteries fall mainly into two categories. The first is applications in which the secondary battery is used as an energy – storage device, generally being connected to and charged by a prime energy source and delivering its energy to the load on demand. Examples are automotive and aircraft systems, UPS power sources, hybrid electric vehicles and stationary energy storage for electric utility load leveling. The second is applications where the secondary battery is used or discharged essentially as a primary battery, but is recharged after use rather than being discarded. Secondary batteries are used in this manner for example in portable consumer electronics. Secondary batteries are characterized by high power density, high discharge rate, flat discharge curves and good low temperature performance. Their energy densities are generally lower than those of primary batteries and their charge retention is also lower than most primary batteries. There are also special and reserve batteries focusing on high – discharge short time applications (for example in missiles and other weapon systems). These batteries have a key component, usually the electrolyte, isolated from the rest of the battery prior to activation. Therefore chemical deterioration or self – discharge is essentially eliminated and the battery is capable of meeting extremely long or environmentally severe storage requirements. Finally there are solid electrolyte batteries which are low rate (μA) and have extremely long lifetimes for applications like pacemakers or memory circuits.

The main primary battery category includes the zinc – carbon batteries which were used a lot but are now outdated, zinc – alkaline/manganese oxide which show good performance under high current drains and low temperatures, batteries with mercury oxide which are now obsolete due to environmental reasons, batteries with silver oxide which have higher cost compared to similar systems, zinc – air batteries that have high energy density for low power applications but are sensitive to extreme temperatures and humidity, magnesium – manganese oxide batteries which can produce H₂ during operation but have long shelf – life, aluminum batteries which also have high
energy density but pose some practical problems and lithium batteries which come in three subcategories according to the cathode used, are gaining in usage, have the highest energy density and can operate over a wide range of temperature, though they are relatively expensive and pose some safety considerations.

In the category of secondary batteries, the main market segment belongs to the lead – acid batteries which are used in automotive applications for starting, lighting and ignition, in industrial vehicles providing deep 6-9 hours discharge as the tractive power, in stationary applications as emergency power and in portable applications for tools and small devices. The alkaline secondary batteries subcategory contains the industrial and portable nickel-cadmium batteries which have excellent cycle life and flat voltage curves and are used in aircrafts, industrial and emergency power applications as well as electronics and tools. Nickel – iron, nickel –zinc and silver-zinc batteries offer solutions for various special applications. Silver-cadmium and nickel-hydrogen (with a fuel cell type anode) offer solutions for aerospace applications, primarily satellites. Nickel – Metal Hydride batteries offer advantages in some conditions and have been used from consumer electronic devices to industrial and propulsion applications. Lithium ion batteries have captured a large portion of the consumer market with their high specific energy and energy density as well as their long cycle life. Main applications include consumer electronic equipment, but also electric vehicles and space applications. These batteries require battery management systems to prevent over-charge/discharge, which will be discussed further in following chapters.

3.1 Discharge characteristics for secondary batteries

At this point we will focus on the Nickel – Metal Hydride batteries to study some of the discharge and charge characteristics of secondary batteries. These batteries have many applications, having being used not only for consumer electronics but for example as the tractive power in the successful experiment of the GM EV1, a production electric vehicle, and every other first generation hybrid – electric vehicle. The Nickel – Metal Hydride batteries traits make them suitable for special applications. For example in the paper by Mansour et al. (Mansour, Rebholtz, Kalfas, Abhari, 2015) an in-house developed wireless data acquisition board which has a fast and high resolution analog-to-digital recorder and logger is described for measurements in the rotating frame of reference for study of inter – blade row interactions on the
aerodynamic blade excitation. NiMH batteries can be used to provide the power on such on-board measurement systems in challenging conditions.

NiMH batteries are similar to nickel-cadmium ones, with the exception that they utilize hydrogen absorbed in a metal alloy for the active negative material. This metal hydride electrode has a high energy density that allows for a larger volume for the positive electrode and thus a battery of larger capacity or longer service life when compared to nickel-cadmium batteries. They can be constructed in a sealed form leading to a battery requiring no maintenance, while the absence of cadmium leads to minimal environmental problems, as they are made from environmentally friendly and recyclable materials. The active metal of the positive electrode in the charged state is nickel oxyhydroxide. The negative active material is hydrogen in the form of a metal hydride which is capable of undergoing a reversible hydrogen absorbing reaction as the battery is charged. An aqueous solution of potassium hydroxide is the major component of the electrolyte. In sealed batteries a minimum amount is used with most of the liquid absorbed by the separator and the electrodes. This facilitates the diffusion of oxygen to the negative electrode at the end of the charge for the oxygen recombination reaction. This is essentially a dry cell construction and the cell is capable of operating in any position. During discharge the nickel oxyhydroxide is reduced to nickel hydroxide

\[ \text{NiOOH} + \text{H}_2\text{O} + e \rightarrow \text{Ni(OH)}_2 + \text{OH}^- , \quad E = 0.52 \, \text{V} \]

and the metal hydride is oxidized to the metal alloy

\[ \text{MH} + \text{OH}^- \rightarrow \text{M} + \text{H}_2\text{O} + e , \quad E = 0.83 \, \text{V} \]

Thus the overall reaction on discharge is

\[ \text{MH} + \text{NiOOH} \rightarrow \text{M} + \text{Ni(OH)}_2 , \quad E = 1.35 \, \text{V} \]

The sealed metal hydride cell uses an oxygen recombination mechanism to prevent buildup of pressure due to the generation of gases at the end of charge or overcharge. The negative electrode employed has a higher effective capacity than the positive, so when the positive reaches full charge earlier it begins to evolve oxygen. The oxygen gas diffuses through the separator to the negative electrode, where it oxidizes or recharges the hydrogen electrode to produce water and prevent pressure buildup. The charge current needs to be
regulated during the end of charge or overcharge to limit the generation of oxygen below the rate of recombination to prevent the buildup of gases and pressure. The nickel-metal hydride cell is also designed with a discharge reserve in the negative electrode to minimize gases and degradation in the event of over – discharge, therefore the useful capacity of the cell is determined by the positive electrode. The alloy storing the hydrogen is formulated to be stable over a large number of charge-discharge cycles, to have good hydrogen storage capability to increase energy density and capacity, to have thermodynamic properties suitable for absorption/desorption, low hydrogen equilibrium pressure, high electrochemical reactivity and high oxidation resistance. Two types of alloys are generally used, rare-earth alloys based on lanthanum nickel (LaNi₅ known as the AB₅ class) or alloys consisting of titanium and zirconium (known as the AB₂ class). The latter one can have higher capacity per weight and volume, but over a very broad and demanding operating range of temperature and discharge rate the first ones are favored, thus AB₅ alloys dominate the portable sealed NiMH market.

These batteries get a relatively flat discharge voltage profile and as expected the voltage is lower for higher currents and lower temperatures, as the I-R drop is higher. However due to the low resistance of the nickel metal-hydride battery this voltage drop is less pronounced compared to other primary or secondary batteries. The ampere-hour capacity is also dependent on the discharge current and temperature. The delivered capacity can be increased with continuing the discharge to lower cutoff voltages, but too low end voltage can result in cell damage. Typically the best performance is obtained between 0° and 40° C. The performance of the battery is affected by a small degree for higher temperatures but more severely for lower discharge temperatures due to the increase in the internal resistance. The internal resistance is low due to the use of thin plates with large area and an electrolyte with high conductivity. There can be an observable drop in capacity for low discharge rates and high temperatures due to the effect of self – discharge. If these batteries are discharged in a multicell series-connected configuration, the lowest capacity battery will be discharged first, and if the discharge continues this cell will be driven to an over – discharged condition of reversed polarity. Prolonged periods of operation under this state will lead to the production of gases, higher cell pressure and thus
deterioration of the cell. Therefore if three or more cells are connected in series their capacities should be within ±5%.

The discharge characteristics for the voltage of typical cylindrical 1.2 V nominal cells in various C rates and for 20\(^{\circ}\)C and 45\(^{\circ}\)C can be observed in the figure below. The voltage of the cell is reduced in a more rapid fashion for the higher temperature.

![Figure 4. Discharge performance a-0.2 C, b-1 C, c-2 C, d-3 C rate (Handbook of Batteries)](image)

For the same nominal cell the capacity versus ambient temperature for various discharge rates:
The low and high rate discharge performance of a nominal 7.2 V battery shows similar characteristics. The service life of this battery is 500 IEC standard cycles, but can reach up to 1000 cycles for charge and discharge rates of 0.1 and 0.2 C respectively.
The type of discharge also has a significant impact on the performance of the nickel metal-hydride battery, and every secondary battery type. When discharged under constant resistance, the hours of service are less than when discharged under constant current, which in turn are significantly less than those of a discharge under constant power. In every case the total power output is the same for all three modes. The difference on the voltage, current and power curves can be seen in the figures below for a nominal 1000 mAh battery.

Figure 7. Voltage, current and power profiles for constant resistance, power and current discharge, sealed cylindrical NiMH 1000 mAh battery (Handbook of Batteries)
3.2 Self–discharge

A reversible drop in voltage and loss of capacity can occur when the battery is discharged and recharged repetitively without performing a full discharge. The discharge profile shows two steps and the cell does not deliver the full capacity up to the original cutoff voltage. This is referred to as memory effect and the battery can be restored to original capacity with a few full discharge-charge cycles. This voltage depression and capacity loss can be minimized or avoided altogether by discharging to an appropriate end voltage. The effect is more pronounced for higher discharge rates as in this case the depth of discharge is lower and less of the active material is cycled.

The state of charge and capacity of nickel metal-hydride batteries deteriorates in storage due to self-discharge. This is caused by secondary reactions within the cells, in the case of NiMH batteries that is the reaction of residual hydrogen in the cell. The higher the temperature storage is, the faster the self-discharge. This is also dependent on cell size and design as well as charge-discharge conditions. The charge retention characteristics of a typical NiMH cylindrical cell are in the following figure.

![Figure 8. self-discharge effect on sealed cylindrical NiMH battery for various temperatures (Sanyo Electrical Co. Ltd.)](image)

3.3 Charge characteristics for secondary batteries

The performance of the battery and its overall life are affected by the charging process. It is thus important to have effective charging, which is achieved by
charging the battery to its full capacity, limiting the extent of overcharge and avoiding high temperatures or fluctuations in temperature. The majority of the charging happens with a constant – current method. The charging reaction is exothermic and thus the battery temperature rises during charging. The rise is steeper towards the end due to the additional heat released from the oxygen recombination reaction. After peaking there is a voltage drop, which can be used for controlling the end of charge along with the steeper temperature rise. The control of this last charging phase is very important for the life of the battery as stated before. The battery can also be charged with a fast charged procedure, in which case the rate of temperature increase is used for charge control with a thermal cutoff backup.

The charge characteristics of a typical NiMH cell with the voltage and temperature rise towards the end as has already been discussed for various charge rates:

![Figure 9. Voltage and temperature during charge of cylindrical NiMH battery (Handbook of Batteries)](image-url)
There are a few methods for charge control. The monitoring of the voltage and termination of the charge when the voltage starts to decrease is common with NiMH batteries. The monitoring of the battery temperature and charge termination at a level that indicates the beginning of overcharge is also widely used. The rate of temperature increase can also be used for charge control to minimize the influence of ambient temperature. The comparison of cutoff voltage for these charging techniques:

![Comparison of charge termination methods](image)

**Figure 10. Comparison of charge termination methods (Handbook of Batteries)**

A common method used for a safe fast charge of NiMH batteries is starting with a high rate (1 C), terminating this after reaching a specific voltage or by a temperature rise rate, and continuing the same way with ever decreasing charge rates. A trickle charge of 0.033 to 0.05 C can be maintained indefinitely. This is quite similar to the method for charging of Lithium–ion batteries where after the constant current charge a constant voltage charge is used for the final capacity topping and a periodic topping is used to keep the battery charged. Deep discharged batteries need to first be charged with a trickle charge and after some voltage is recovered they can be charged with a higher rate or else there can be permanent capacity loss.
4 Flow Batteries

4.1 Flow batteries introduction

While conventional batteries store energy in solid or aqueous electrolytes that are stored permanently in the encasing of the battery, flow batteries use liquid electrolytes that are stored in external tanks and circulated through the battery with pumps. Inside the cell the liquid electrolytes are separated by a membrane which only permits certain ions to go through, much like Lithium – ion batteries. The electrolytes can either work by means of redox (reduction – oxidation) reactions in which case we have a redox flow battery (RFB), or with intercalation reactions like Lithium – ion batteries. A typical RFB cell can be seen in the diagram below.

![Diagram of RFB cell](image)

**Figure 11.** RFB cell (Mohamed, Sharkh, Walsh, 2009)

The main parts of which the flow battery is consisted are the tanks that hold the electrolytes, the pump that forces the electrolytes to flow through the cell, the two electrodes and the membrane that separates the anode and...
cathode electrolytes. There are three main types of flow batteries that have been developed, which are the zinc – bromine batteries, redox batteries (mainly the Vanadium Redox Battery or VRB) and the polysulfide – bromine or Regenesys system that is much like a redox system but both electrode reactions involve neutral species. In general RFBs are more like fuel cells except that in fuel cells the electrolyte remains within the cell. In either case of redox or intercalation reactions, ions flow through the membrane while electrons flow around the external circuit to produce electricity. The advantage of flow batteries is that they could be rapidly recharged by draining the used electrolytes and replacing them with already charged ones, much like refueling in a petrol station. Another very important advantage especially as it pertains to energy storage issues, is that charged electrolytes can be stored and utilized at will avoiding the self – discharge process that happens in conventional batteries (3-5% capacity per 30 days of storage for Lithium – ion batteries). Furthermore, since flow batteries add a convection term to the diffusion at the electrode surface they are limited only by the reaction rate thus it is easier to charge or discharge them with higher current rates. Finally the maximum power available is related with the size of the cells stack while the energy capacity is related to the available liquid electrolyte, so that the battery can be dimensioned for the maximum power demand and subsequently the energy capacity can be increased just by increasing electrolyte volume while the actual battery pack remains the same. (Campillo, Ghaviha, Zimmerman, Dahlquist, 2015)

4.2 Influence of architecture and material properties on VRB

A recent study has been performed (Houser, Clement, Pezeshki, Mench, 2016) to compare the serpentine and interdigitated flow channel designs using experimental cell performance data and numerical simulations. The two flow field designs can be seen in the figure below.
The experiments for these flow channels were conducted with a 1.7 M vanadium sulfate solution in 3.3 M sulfuric acid, with 50 mL of electrolyte on each tank, while carbon paper was used for the electrodes. Experiments were conducted at 250 mA/cm$^2$ and 500 mA/cm$^2$ current densities full discharges up to a cutoff voltage of 0.2 V for 20 mL/min and 90 mL/min flow rates. Also tests were performed using one, three and five layers of carbon paper electrodes to investigate the impact of electrode thickness on mass transport. For the lower flow rate the discharge curves can be seen in the figure below. The results show that the interdigitated design has superior performance in this case and better mass transport. This design was able to utilize 15% more of the theoretical capacity for 250 mA/cm$^2$ and 33% more capacity for the higher current discharge.
Current distributions were recorded near the cutoff voltage and a 6 seconds average is shown in the figure below. Higher current corresponds to increased reaction thus better local mass transport. For the serpentine design the edges are relatively high current zones while the center of the active area is a low current zone. That is due to high pressure drop in the serpentine channels leading to the mass transport being focused near the inlet area. The interdigitated design shows an opposite trend as all of the electrolyte passes through the electrode in a linear flow circuit and the mass transport is focused in the center where the path through the porous media is shorter.

Experimental and simulation results for the pressure drop show that it is greater for the serpentine design with the difference growing as the flow rate is increased.
Figure 15. Experimental and simulated pressure drop data (Houser et al. 2016)

However the discharge curves for the higher flow rate (90 mL/min) show that the mass transport difference mostly vanishes, with the curves for both current densities being very close, and the serpentine design even slightly outperforming the interdigitated for the lower current density. The two architectures also respond differently to the change of electrode thickness. As the thickness is increased the difference in the discharge curves is diminished, from a 13% and 29% depth of discharge difference for the two current densities to almost the same depth of discharge for five electrode layers.
This study shows that convective mass transport in the electrodes of Vanadium Redox Flow Batteries is critical to overall cell performance and operation. However, no optimal architecture can be defined regardless of the conditions, as electrode properties, current density and electrolyte properties have a varying impact on the performance of each architecture.

### 4.3 Pressure losses and flow rate optimization in VRB

A study (Tang, Bao, Skyllas-Kazacos, 2013) on the influence of the flow rate to concentration overpotential and pressure losses has been performed to develop a variable flow strategy that can raise system efficiency. Overpotential is the difference between thermodynamically determined reduction potential and actual measured electrode potential. Three processes mainly lead to overpotential, which are activation, ohmic drop and concentration overpotential. Activation overpotential is associated with the activation energy for initiating electron transfer at the electrode surface. Ohmic drop is associated with the resistances electrical current encounters
through the cell. In a flow battery these are mainly electrode, electrolyte and membrane resistances. Concentration overpotential exists due to mass transfer limitations created by the concentration gradient between the electrolyte solution and electrode surface for large currents. It is particularly pronounced at the end of charge or discharge in a flow battery when the concentrations of the active species are low. The flow rate of the electrolytes can impact significantly the concentration overpotential and result in premature voltage cutoff that will limit the usable capacity of the battery. This effect can be seen in the figure below for a fully charged cell discharged under a constant flow rate.

![Figure 17. Cell voltage and concentration overpotential (Tang, Bao, Skyllas-Kazacos, 2013)](image)

One way to overcome this issue is with a higher constant flow rate during cell operation that will reduce concentration overpotential as can be seen in the figure below. However the pump losses will significantly increase for the higher flow rate reducing system efficiency which must be considered in flow battery design.
The researchers employed a flow factor to manipulate the magnitude of the flow rate which is incorporated into the theoretical flow rate, to study its effect on the battery efficiency:

\[
Q = \text{Factor} \frac{I}{nF_{\text{reactant}}}
\]

with \(n\) being the electrons involved in the redox reaction. A 5 kW and 15kWh system consisted of 40 individual cells with 200 L of 2 M vanadium electrolyte solution on each side is used to evaluate the effect of flow rate. Simulations were performed with 5% SoC as initial condition and voltage cutoff limits of 36-72 V. The flow rate profiles and the simulated efficiencies under 60A charging and 80 A discharging currents can be seen in the following figures.
The coulombic, voltage and energy efficiencies all show an increasing trend with increasing flow factor for both constant and variable flow rates. A peak in energy efficiency can be obtained at a certain flow factor that optimally trades off the effects from concentration overpotential and pump losses. Employing variable flow rates leads to greater efficiencies with a maximum of 73% system efficiency for a flow factor of 7. Variable flow rates are also shown to deliver better discharge capacity, and despite under constant flow rate the larger rates deliver more capacity, the efficiency is reduced due to large pump losses. The variable flow rates can achieve significantly lower pump energy consumption as can be seen in the figure below.
Finally more combinations of charge and discharge currents were simulated to estimate the optimal flow rate factor. By modeling the concentration overpotential and analyzing pressure losses in all the components an optimized flow rate factor of 7.5 was determined for the 40-cell stack VRB system.
5 Intercalation Reactions

The battery researched experimentally is based on sodium intercalation reactions, that is the transfer of \( \text{Na}^+ \) ions to produce electricity, so this type of reaction will be discussed here briefly. During the charge and discharge processes, sodium ions are inserted or extracted from interstitial space between atomic layers within the active materials of the battery. This is the same principle of operation with Lithium – ion batteries, which are often referred to as rocking-chair batteries because of the moving of ions from one side to another. A representation of the operation of Lithium – ion batteries can be seen on the figure below.

![Lithium battery operation](image)

*Figure 22. Lithium battery operation (Scrosati et al. 2010)*

These electrolyte materials need to have two key properties. One is the open crystal structure, which can facilitate the insertion or extraction of ions, and the other is the ability to accept compensating electrons at the same time.
6 Battery modeling

Batteries, and especially high performing ones, are complex electrochemical devices with a distinct nonlinear behavior depending on various internal and external conditions, thus the monitoring of battery state during operation is a necessary and challenging task. This task becomes more challenging by considerable changes in battery characteristics over its lifetime due to aging. Therefore special algorithms for battery monitoring are required. An important requirement of a battery monitoring algorithm is the determination of battery characteristics, which depend significantly on battery internal and external conditions (e.g. SoC, current, temperature). Another consideration is the influence of the battery load profiles, as usually measured signals like current, voltage and temperature can be very different depending on the battery load. A high load for example can cause fast temperature changes that can lead to inhomogeneous temperature distribution within battery cells. That brings us to a third requirement when designing battery monitoring systems, which is the limitation that the safe operating area of the battery imposes. Limits such as maximum charge and discharge current and maximum/minimum voltages and temperatures affect the calculation of available energy and power. Furthermore the characteristics of the hardware that will be employed for measuring and controlling the system, like its cost and accuracy, pose limitations on the algorithms that can be utilized for battery monitoring. There are various categories of battery models including empirical or mathematical models, electrochemical models, molecular models, electrical and multi – physics models.

6.1 Methods for SOC estimation

6.1.1 Coulomb counting

With battery capacity known and battery current measured, the coulomb counting method permits accurate calculation of changes in the SoC, essentially by integrating the current. However the initial SoC must be known beforehand for estimation of SoC and when the method is performed for extended periods of time accumulated measurement errors might cause significant inaccuracy. Therefore this method is usually used in combination
with other techniques. The main advantage is low cost of implementation and computing power.

### 6.1.2 OCV-based estimation

In this method the relationship between Open Circuit Voltage (OCV) and SoC is used to estimate the SoC. When a load stops being connected to the battery the OCV gradually increases to reach the Electromotive Force (EMF) at the end of the relaxation period. This equilibrium voltage takes a considerable amount of time to be achieved, so these models are based on methods that estimate the EMF by considering the relaxation only over a limited amount of time. Simple functions such as two asymptotes (Aylor, Thieme, Johnson, 1992) or exponential functions (Yang, Liu, Tsai, Chin, 2008) or more complex empirical models have been used to describe the OCV relaxation curve, as well as models based on theoretical consideration of the battery diffusion (Waag, Sauer, 2013).

### 6.1.3 Electrical models

Electrical models are the most popular form for model-based SoC estimation. These can be Equivalent Circuit Models (ECM) or pure mathematical models, with the model described by one or more equations that employ electrical quantities in either case. The SoC can be incorporated in the model or the Open Circuit Voltage can be estimated in the model and the OCV-SoC relationship utilized to estimate the SoC. Most of these models are semi-empirical and can be calculated in two steps. The first step is the characterization of the battery cell where the initial characteristics and conditions of the cell are measured (e.g. capacity, voltage response, OCV) and the second is the parameterization where the parameters of the model are calculated. A common disadvantage for electrical models is that the model parameters can be calculated accurately only for new batteries in the laboratory. Adaption of the models to account for battery aging can be done with complex algorithms and is practical for only quite simple models. The common advantage is that these models can be deployed for estimations at any battery condition during charging and discharging as long as the model is able to reproduce the battery cell behavior at this condition. The simulation time and computing power required to run these models even for simulating transient conditions is lower than that of electrochemical models. Electrical models can operate in an open-loop approach where SoC is calculated directly from transformation of the model equations and in a closed-loop
approach with adaptive techniques. The disadvantage of the open-loop method is its lower accuracy as the model is expected to exactly reproduce the behavior of the battery with no possibility to consider the inaccuracies inherent in the model, however it requires less computing power which could be an important consideration depending on the application.

6.1.3.1 $R_{\text{int}}$ model

![Diagram of $R_{\text{int}}$ ECM schematic]

\[ U_L = U_{\text{oc}} - I_L R_0 \]

*Figure 23. $R_{\text{int}}$ ECM schematic*

This is the most basic and simple model of zero order that is comprised of two elements only, an ideal voltage source $U_{\text{oc}}$ to define the open circuit voltage and a resistance $R_{\text{int}}$ to define the internal resistance, both of which can be functions of SoC, SoH (State of Health) and temperature.
6.1.3.2 Thevenin model (first order RC)

![Thevenin ECM schematic](image)

\[
\begin{align*}
\dot{U}_{Th} &= -\frac{U_{Th}}{R_{Th}C_{Th}} + \frac{I_L}{C_{Th}} \\
U_L &= U_{\infty} - U_{Th} - I_L R_o
\end{align*}
\]

Figure 24. Thevenin ECM schematic

The Thevenin or first order RC model is comprised of a resistance in series and an RC branch, as well as an ideal voltage source, which are used to estimate battery cell response in transient loads for a particular SoC. The internal resistances include the ohmic resistance $R_0$ and the polarization resistance $R_{Th}$. The open circuit voltage and the rest of the parameters are a function of SoC.

6.1.3.3 PNGV model

![PNGV ECM schematic](image)

The PNGV model can be obtained by adding a capacitor in series based on the Thevenin model to describe the changing of open circuit voltage generated in the time accumulation of load current. (Hongwen, Rui, Jinxin, 2011)
6.1.3.4 Dual polarization model (second order RC)

This model is a modification of the Thevenin model where a second RC branch has been added in series with the first one. This is done to better encapsulate in the model the obvious polarization that is observed in many battery tests and is not simulated very accurately with the Thevenin model especially at the end of charge or discharge, due to the difference between concentration and electrochemical polarization. In this model other than the Open Circuit Voltage there is the internal ohmic resistance $R_0$ and the effective resistances $R_{pa}$ and $R_{pc}$ characterizing electrochemical and concentration polarization respectively. Lastly the effective capacitances are used to simulate the transient response for either charge or discharge and describe the electrochemical and concentration polarization separately. These models can be developed with even more parameters (i.e. adding RC branches) resulting in more accurate estimation at the cost of added complexity or by adding a hysteresis branch to estimate the voltage difference between charge and discharge for the same operating conditions.

6.1.3.5 Impedance based model

Figure 26. Dual polarization ECM schematic

Figure 27. Impedance-based ECM schematic
These models are based on complex resistances. The method of Electrochemical Impedance Spectroscopy (EIS) is used to calculate a complicated model of AC-equivalent resistances in the frequency domain which are then turned into an equivalent circuit \((Z_{ac})\) that correlates the impedance characteristics to the electrical components of the battery. However this process is rather complicated and the models can be used only for constant SoC and temperature making them unable to estimate battery cell response in real – time. Also especially for lithium – ion batteries the dependence of the battery impedance parameters to SoC changes significantly over the battery lifetime so these parameters alone cannot be good estimators of the SoC as the battery ages for this type of battery. One interesting application of this method can be found in the paper “Adaptive estimation of the electromotive force of the lithium-ion battery after current interruption for an accurate state-of-charge and capacity determination” (Waag, Sauer, 2013), where an OCV-estimation method as discussed above is proposed that also utilizes impedance parameters to create a real – time capable algorithm that was implemented on a low – cost microcontroller. In this paper five Equivalent Circuit Models which can be seen in the figure below were compared, and the algorithm was developed with the \(Z_{ARC}\) one as it was found to produce the minimum error.

![Figure 28. Five ECMs to represent the OCV relaxation process (Waag, Sauer, 2013)](image-url)
The algorithm is based on the simplex minimization of the cost function of the difference between measured and predicted OCV. The results showed (figure below) that the predicted EMF from the model, although not completely accurate especially for discharge under transient conditions prior to relaxation, reduces the inaccuracy of SoC estimation compared to using the measured OCV. The SoC and capacity could be estimated accurately even a few minutes after current interruption.

Figure 29. Comparison of the OCV relaxation models (Waag, Sauer, 2013)

Figure 30. Results of EMF estimation for Li-ion cell with NMC cathode material after dynamic load (Waag, Sauer, 2013)
6.1.3.6 **Runtime – based model**

This type of model is comprised of three different parts (Sun K., Shu Q., 2011). The first one contains the resistance $R_{\text{transient}}$ and capacitance $C_{\text{transient}}$ and estimates the transient performance of the battery cell. The second part contains the resistance $R_{\text{self-discharge}}$, capacitance $C_{\text{capacity}}$ and voltage source $V_{\text{lost}}$ which estimate the resistance for self-discharge of the battery, the battery’s total capacity and the voltage drop due to internal losses respectively. The third part estimates the battery cell’s voltage and SoC and contains the resistance $R_{\text{series}}$ which models the battery cell’s internal resistance and the voltage source $V_{\text{OC}}(\text{SOC})$ which models the cell’s SoC. So this model utilizes a complex circuit network that can simulate the battery cell’s run – time and DC-voltage response for constant current discharge. However the estimation inaccuracy rises for transient loads.

6.1.3.7 **Model for predicting battery run – time and I-V characteristics**

This is a combination of the Thevenin, impedance – based and runtime – based equivalent circuit models. The capacitance $C_{\text{BATT}}$ and the current controlled current – source are used to model the battery cell’s capacitance, SoC and run – time. The RC circuit ($R_{\text{transient}}$ and $C_{\text{transient}}$) is used to estimate cell response under transient loads. A voltage – controlled voltage source is used to bridge the SoC with the Open Circuit Voltage. This model can estimate
battery run – time, steady – state and transient response as well as other dynamic electrical characteristics like usable capacity and OCV.

6.1.4 Adaptive filters and observers

Adaptive techniques from control theory can be utilized to improve accuracy of model – based SoC estimation and enable estimation by more complex models. These techniques estimate SoC with closed-loop methods, thus the deviation between measured and modeled battery voltages is used for the correction of the estimated states, effectively reducing the influence of model and measurement inaccuracies. The most widely used adaptive filter technique is the Kalman filter, and can be encountered in many forms with various battery models, the more complex and nonlinear models employing more modern extensions of the Kalman filter. The extended Kalman filter though has the disadvantage of linearizing battery nonlinearities. Other forms of the filter that could achieve better results include the sigma – point Kalman filter, the unscented Kalman filter, the central – difference Kalman filter and the fractional – order Kalman filter. The Gauss – Hermite Quadrature filter that is in general similar to the sigma – point Kalman Filter can also be used. All Kalman filter variants require the knowledge of model and measurement noise covariance, otherwise the model can have poor performance or very slow adaptation. The adaptive Kalman filter, adaptive extended Kalman filter and adaptive sigma – point Kalman filter can be used to additionally estimate noise covariances at the expense of computing power. Another solution that can be applied is the H – infinity filter (Yang, Yu, Kim, 2013)

An example of adaptive Kalman filtering use can be found in the papers “State and Parameter Estimation of a HEV Li-ion Battery Pack Using Adaptive Kalman Filter with a New SOC-OCV Concept” (Dai Haifeng, Wei Xuezhe, Sun Zechang, 2009) and “Research on SOC Estimation Based on Second-order RC Model” (Tiezhou Wu, Lunan Liu, Qing Xiao, Quan Cao, Xieryang Wang, 2012). In these papers an estimator for the battery State of charge (SoC) and parameters is researched by means of adaptive Kalman filtering and second order RC battery models. In the first paper an augmented form of the Kalman filter is used for battery parameter identification. Equivalent electrical models with Kalman filters are researched as a more accurate way of SoC estimation compared to the more usual coulomb counting method where current integration can lead to significant error. The first paper also proposes a
modified SoC calculation method where the actual capacity instead of the nominal is utilized, resulting in a single Open Circuit Voltage – SoC curve for different conditions. However this also requires beforehand knowledge of actual capacity in addition to the SoC. The equivalent electrical model used for the battery representation in both papers is the second order RC:

![Battery Model Diagram](image)

The discrete state – space system for this model is as follows, with the states being SoC, $U_{RC1}$ and $U_{RC2}$, the input of the model the current $I(t)$ and the output the terminal voltage $U(t)$, $k$ the sample point, $C$ the cell actual capacity and $\tau_1=R_1C_1$, $\tau_2=R_2C_2$ the time constants for the RC circuits:

$$
\begin{bmatrix}
    \text{SOC}_{k+1} \\
    U_{RC1}^{k+1} \\
    U_{RC2}^{k+1}
\end{bmatrix} =
\begin{bmatrix}
    1 & 0 & 0 \\
    0 & e^{-\frac{\Delta t}{\tau_1}} & 0 \\
    0 & 0 & e^{-\frac{\Delta t}{\tau_2}}
\end{bmatrix}
\begin{bmatrix}
    \text{SOC}_k \\
    U_{RC1}^k \\
    U_{RC2}^k
\end{bmatrix} +
\begin{bmatrix}
    \frac{\eta \Delta t}{C} \\
    R_1(1-e^{-\frac{\Delta t}{\tau_1}}) \\
    R_2(1-e^{-\frac{\Delta t}{\tau_2}})
\end{bmatrix} I_k
$$

$$
U_k = U_{OCT}(\text{SOC}_k) - i_k R_0 - U_{RC1}^k - U_{RC2}^k
$$

The general framework for the discrete system is

$$
\begin{cases}
    x_{k+1} = f(x_k, u_k) + w_k \\
    y_k = g(x_k, u_k) + v_k
\end{cases}
$$

where the process noise and the sensor noise are $w_k$ and $v_k$ respectively, which bear the characteristics $E[w_k]=q_k$, $E[w_k w_j^T]=Q_{kj}$, $E[v_k]=r_k$, $E[v_k v_j^T]=R_{kj}$, $E[w_k v_j^T]=0$. Then the adaptive Kalman filter process operates much like the traditional one, while it corrects the process noise and the measurement noise of the system as measured data are filtered to estimate the states, effectively deducing the effect caused by the change of noise and enhance the reliability and accuracy of state estimation. It can be summarized with the following equations:
\[
A_k = \left. \frac{\partial f(x_k, u_k)}{\partial x_k} \right|_{x_k=x_{k-1}} \\
C_k = \left. \frac{\partial g(x_k, u_k)}{\partial x_k} \right|_{x_k=x_{k-1}} \\
x_{k/k-1} = f(x_{k-1/k-1}, u_k) + q_k \\
P_{k/k-1} = A_k P_{k-1/k-1} A_k^T + Q_k \\
K_k = P_{k-1/k-1} C_k^T / (C_k P_{k-1/k-1} C_k^T + R_k) \\
P_{k/k} = (I - K_k C_k) P_{k/k-1} \\
\hat{y}_k = y_k - g(x_k, u_k) - r_k \\
x_{k/k} = x_{k/k-1} + K_k \hat{y}_k \\
r_{k+1} = (1 - d_k) r_k + d_k [y_k - g(x_k, u_k)] \\
R_{k+1} = (1 - d_k) R_k + d_k (\hat{y}_{k+1}^T \hat{y}_{k+1} - C_{k+1} P_{k+1/k} C_{k+1}^T) \\
q_{k+1} = (1 - d_k) q_k + d_k (x_{k+1/k+1} - A_{k+1} x_{k+1/k} - B_{k+1} u_k) \\
Q_{k+1} = (1 - d_k) Q_k + d_k (K_{k+1} \hat{y}_{k+1}^T \hat{y}_{k+1} K_{k+1}^T + P_{k+1/k+1} - A_{k+1} P_{k+1/k} A_{k+1}^T)
\]

Where \( d_k = (1-b)/(1-b^{k+1}) \) and \( b \) a factor that was set to 0.92 for the first and 0.96 for the second paper. The augmented state system used in the second paper is:

\[
\begin{pmatrix}
SOC_{k+1} \\
U_k^{R C_1} \\
U_k^{R C_2} \\
C_{k+1} \\
R_{k+1}
\end{pmatrix} = f(x_k, u_k) = \begin{pmatrix}
1 & 0 & 0 \\
0 & e^{-\eta \Delta t} & 0 \\
0 & 0 & e^{-\eta \Delta t/2} \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix} \begin{pmatrix}
SOC_k \\
U_k^{R C_1} \\
U_k^{R C_2} \\
C_k \\
R_{k}
\end{pmatrix}
\]

\[
\begin{pmatrix}
\frac{\eta \Delta t}{C_k} \\
R_k (1 - e^{-\eta \Delta t}) \\
R_k (1 - e^{-\eta \Delta t/2}) \\
0 \\
0
\end{pmatrix} \times i_k
\]

\[
U_k = g(x_k, u_k) = U_{OCV}(SOC_k) - i_k R_{0,k} - U_k^{R C_1} - U_k^{R C_2}
\]
where the model state vector has been augmented with the C and $R_0$ model parameters.

In both papers there was accurate estimation of SOC. For the first paper we can see the estimation of SoC in the picture below from the adaptive filter (SOC1) and from accurate current integration considering Coulombic efficiency (SOC2) for a simple pulse current profile. The SoC estimation error is less than 3% while in a sequence of random cycles representing the load a battery pack in a Hybrid Electric Vehicle might experience the error was calculated at less than 1.5%.

![Figure 33. SOC variance (Haifeng, Xuezhe, Zechang, 2009)](image)

with the second paper’s estimation also reaching a maximum error of similar magnitude. Other notable results included the reduction of inner resistance as cell temperature increased.

![Figure 34. Error percentage for regular Kalman (left) and adaptive Kalman (right) (Tiezhou, Lunan, Qing, Quan, Xieyang, 2012)](image)
The Kalman filtering with its predictor-corrector mechanism significantly raises the accuracy for the simple equivalent electrical model utilized.

A problem associated with the Kalman filter variants is that the model and measurement noises are considered to be Gaussian, which is not always the case for real applications. When the noises are not exactly Gaussian the system can be stable, but inaccuracy will be higher. The use of Particle filters and Unscented Particle filters has been proposed to avoid this, but they require significantly higher computing power (He, Liu, Zhang, Chen, 2013). Another complication when using Kalman filters is that the system may not be observable under all conditions, for example when the current is constant, however solutions can be found for this. The main advantage of KF – based SoC estimation is that it can be performed accurately and continuously during battery operation given that the battery model is comprehensive and well – parameterized. This poses a problem as the battery ages and to address this dual or joint Kalman Filters can be utilized.

6.1.5 Observers and controllers

Various approaches employing observers and controllers for closed – loop model – based SoC estimation have been proposed in the literature. These methods combine ampere – hour counting with a computationally simple observer or controller. Their main advantage is their simplicity and sufficient accuracy however they also require additional algorithms to adapt the parameters for battery aging. An example of such a method can be found in the paper “On battery State of Charge estimation: a new mixed algorithm” (Codeca, Savaresi, Rizzoni, 2008). Briefly, in this paper the model – based method is used to dynamically correct the estimation performed by the Coulomb – counting, as Coulomb – counting uses only one signal and measurement inaccuracies will result in increasing drift of the estimation result with time. Testing the performance of either method it becomes evident that if a positive offset is present on the current measurement the Coulomb – Counting estimation will decrease faster while the Model – Based estimation will decrease slower, so an algorithm that combines both could try to take advantage of this behavior, because each of the estimations compensates the other. The algorithm used to combine the two estimations is:

- the current and voltage of the battery cell are measured (with some measurement noise, introduced by the sensors)
• the current is integrated, and a Coulomb-Counting estimation (SoC\textsubscript{i}) of the SoC is obtained

• the direct model of the cell is fed with the SoC estimation and the measured (noisy) current, the model output is the estimated cell voltage

• a close-loop controller is designed around the cell model, the direct cell model represents the plant of the control system, the SoC is the input variable, whereas the voltage is the controlled output; the reference output is the measured cell voltage; the measured current is a disturbance; a simple integral controller is used

• the SoC input of the cell model is obtained as sum of SoC\textsubscript{i} and the output of the feedback integral controller

• the estimated SoC is the input of the cell model, in the closed-loop configuration.
As it is evident from the figure above, the combination of the two methods yields better simulation results for the Li–Ion cell for which it was tested.

6.1.6 Least – Squares – based filters

Recursive Least – Squares (RLS) filters have also been proposed for SoC estimation. Kalman and other filters that have been mentioned previously consider the input signals as stochastic while RLS filters consider them as deterministic. This is advantageous for battery monitoring applications as the
main challenge for an adaptive filter becomes not to deal with stochastic measurement noises but with the inaccuracy of the deterministic battery model. An advantage for RLS algorithm estimation is that it does not require complex matrix operations such as inversion and can therefore be implemented on low-cost microcontrollers. Furthermore, it permits simultaneous estimation of the model parameters to consider their change over the battery lifetime. The disadvantage is that the algorithm may suffer from significant divergence problems when the battery model inaccurately reproduces battery behavior or when strongly nonlinear battery models are used. The use of such an algorithm will be discussed further in the experiment section of this thesis as one was utilized to estimate parameters for a model of the experimental battery.

6.1.7 Electrochemical models

Electrochemical models can also be used for model-based SoC estimation, their advantage being that they inherently include the dependence of the battery response on the SoC and temperature, while electrical models must store their parameters as look-up tables for various SoC and temperature combinations. However, these models tend to be more complex thus not permitting the use of low-cost microcontrollers and limiting the options of model parameters that can be adapted on-line to account for the aging of the battery cell. Electrochemical models are based on equations that describe phenomena of electrochemical kinetics and ion transfer, the power generation mechanisms, battery cell voltage and current, radicals concentration, reaction rates and others as a function of time and space. An example of an electrochemical model can be found in the paper “State of Charge Estimator for NiMH Batteries” (Barabrisi, Canaletti, Glielmo, Gosso, 2002), where the kinetic of reactions and diffusion phenomena are used in a state-space dynamic model. NiMH batteries consist of a hydride negative electrode and a nickel oxide positive electrode which for this model are described by the porous electrode theory, per which they are treated as a superposition of two continua, one representing the electrolyte solution and the other the matrix (solid phase) (Paxton, Newman, 1997). These two phases are in contact in an equivalent surface for the positive electrode $S_{pos}$ and thickness $l_{pos}$. The four reactions occurring in a NiMH cell are:

- **Nickel electrode (positive)**

  \[
  \text{NiOOH} + H_2O \leftrightarrow \text{Ni(OH)}_2 + OH^-
  \]
\[
\begin{align*}
2OH^- & \leftrightarrow 1 \frac{2O_2}{20} + H_2O + 2e^- \\
\text{Metal hydride electrode (negative)} & \\
\frac{1}{p}MH_p + OH^- & \leftrightarrow H_2O + \frac{1}{p}M + e^- \\
\frac{1}{2}O_2 + H_2O + 2e^- & \leftrightarrow 2OH^-
\end{align*}
\]

where \( p \) varies with different types of metal hydride active materials. Based on these the current densities \( j_i \) can be calculated by the Butler – Volmer equations for the first three and a limiting – current equation for the fourth due to the large electrochemical force for the oxygen reduction. From these equations for the equilibrium potentials can also be found. The states used in the model are oxygen pressure, concentration of nickel active material and concentration of metal hydride active material. The mass balance of the nickel material on the first electrode:

\[
\frac{d(Fn_{Ni(OH)_2})}{dt} = -S_{pos}j_1 \Rightarrow \frac{dC_{Ni(OH)_2}}{dt} = -\frac{j_1}{I_{y,pos}F}
\]

which is the first equation for the model. The second is the mass balance of the nickel material on the positive electrode:

\[
\frac{dC_{MH}}{dt} = -\frac{j_3}{I_{y,neg}F}
\]

And the third model equation, the mass balance on the oxygen:

\[
\frac{dp_{O_2}}{dt} = \frac{RT}{V_{gas}}S_{pos}j_2 + S_{neg}j_4
\]

These equations compose the model without diffusion. Once an electrochemical reaction is initiated, the concentration of reactants will not be uniformly distributed in the active material. Assuming that the protons in the hydroxide film will move by diffusion and that this is not a function of the SoC, the concentration of \( \text{Ni(OH)}_2 \) can be described by Fick’s law:

\[
\frac{dC_{Ni(OH)_2}}{dt} = D_{pos} \frac{d^2C_{Ni(OH)_2}}{dx^2}
\]
which will replace the first equation of the model. This equation is discretized for N slices of the active material film with a second order polynomial function to give the set of ordinary differential equations:

\[
\frac{dC_k}{dt} = D_{pos} \left( -\frac{2}{\Delta x^2} C_k + \frac{1}{\Delta x^2} (C_{k-1} + C_{k+1}) \right) \\
C_0 = C_1 \\
C_N = C_{N-1} - \Delta x \frac{j_1}{FD_{pos}}
\]

The SoC estimator is obtained by averaging the concentration of Ni(OH)\textsubscript{2} on the thickness of the active material:

\[
SOC = 1 - \frac{1}{N-1} \sum_{k=1}^{N-1} \frac{C_k}{C_{Ni(OH)_{2,max}}}
\]

The estimator was tested on two different charge/discharge profiles and performed well as can be seen in the figure below.

![Figure 36. SoC estimation (Barabrisi, Canaletti, Glielmo, Gosso, 2002)](image)

6.1.8 Estimation using fuzzy logic and methods of machine learning

Fuzzy logic can be used as an extension of other SoC estimation techniques, for example to connect the battery SoC with impedance parameters to have an estimation based on impedance as discussed previously. Fuzzy logic can
also be used to link battery SoC with the measured battery voltage, current and temperature, so the estimation is basically based on static battery characteristics. In any case the results will have the disadvantages of the underlying methods. Artificial Neural Networks can also be used, with three groups of methods: direct SoC estimation with Artificial Neural Networks, Artificial Neural Network based voltage estimation combined with a controller or Kalman Filter and Artificial Neural Network based correction of a coulomb counter. Direct SoC estimation with ANNs is generally similar to that of the model – based methods described previously, the difference being that the SoC is modeled by an ANN rather than a deterministic electrical model. The advantage is that no exact knowledge about the behavior of the battery is required, however a large amount of data is needed to train the ANN and the ANN trained for a new battery cannot be accurate for a more aged battery. Also due to the open – loop approach online training of the ANN and therefore adaption to the aging state is not possible. Closed – loop estimation using ANNs can be performed, with the estimated SoC used as an input in the ANN, while the output is the battery voltage which is compared to the measured battery voltage and the difference is used to correct the SoC estimation. The advantage of the closed – loop approach is that it permits training of the ANN online during battery operation, however this process requires high computational power and can encounter problems like over – fitting. This method is particularly useful for batteries whose behavior cannot be accurately modeled by simple electrical models as is the case for lead – acid or NiMH batteries. ANN – based correction of the Coulomb counting method can be employed to improve the accuracy of the counter, by using the ANN to model the dependence of the battery capacity and/or charge/discharge efficiency on the temperature and short – time load history. Furthermore fuzzy – based neural networks of two types (adaptive neuro – fuzzy inference system (W.X. Shen, C.C. Chan, E.W.C. Lo, K.T. Chau, 2002) and local linear model tree (A.R.P. Robat, F.R. Salmasi, 2007)) have been used in the literature for SoC estimation. This method has a similar open – loop approach to the direct SoC estimation with ANNs and therefore has the same disadvantages. Also similar to the direct SoC estimation using ANNs and fuzzy – based neural networks the Support Vector Machines method can be utilized, and similar to the neural networks requires extensive training thus carrying the same disadvantages.
6.1.9 Empirical or mathematical models

These models employ empirical equations or mathematical methods for estimation of battery behavior, like operation time, efficiency and capacity of the battery. The basis for the equations is a large quantity of experimental data for voltage – depth of discharge, internal resistance – time etc. in various conditions so that they can model the battery behavior. The computational simplicity of these models turns into light simulations but their accuracy can be limited, though there have been proposed many modifications of some classic models to address some of the accuracy issues, like flaws during the relaxation time due to hysteresis effects (Meng, Luo, Ricco, Swierczynski, Stroe, Teodorescu, 2018). Some typical empirical models are the Shepherd model, the Unnewehr Universal Model, the Nernst Model, the Peukert Model and the Kinetic Battery model (KiBaM).

<table>
<thead>
<tr>
<th>Model Type</th>
<th>Model Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shepherd model</td>
<td>( y_k = E_0 - R_i_k - \frac{K_1}{z_k} )</td>
</tr>
<tr>
<td>Unnewehr universal model</td>
<td>( y_k = E_0 - R_i_k - K_1 z_k )</td>
</tr>
<tr>
<td>Nernst model</td>
<td>( y_k = E_0 - R_i_k - K_2 \ln(z_k) + K_3 \ln(1-z_k) )</td>
</tr>
</tbody>
</table>

6.2 Methods for SoH estimation

As it has already been stated the capability of a certain battery cell to have a capacity level and provide certain amounts of power is diminished over the battery lifetime due to aging. The battery State of Health (SoH) is used to quantify this aging, with usual indicators being the capacity, resistance and impedance of the battery. The SoH is considered to be 100% when the battery is new and 0% when its capability to store energy or provide power has decreased below a certain threshold. This threshold is often defined at 80% of the nominal capacity for hybrid electric vehicle applications, or when battery resistance is double the original value. The SoH of 0% does not indicate that the battery cannot be used further, but merely that it has reached some predefined criteria for replacement. As stated earlier, the determination of the SoH basically lies in determining the battery capacity and resistance, so typical methods for estimating these parameters are the methods used for SoH estimation.
There are five main approaches to estimate battery capacity. The first group consists of methods considering the change in the measured battery OCV before and after charging or discharging, whose only parameter is the SoC – OCV relationship (Kessels, Rosca, Bergveld, Bosch, 2011). The second group of methods estimates the OCV change from the battery voltage measured under load, for which accurate battery models are required with parameters adaptable to the aging state of the battery (Roscher, Assfalg, Bohlen, 2011). The third group of methods augments electrical models of the battery to include information about the capacity in the form of a parameter, performing joint estimation of the battery SoC and capacity (Bhangu, Bentley, Stone, Bingham, 2005). The adaptive filters mentioned above for SoC estimation can also be used in this case with their respective advantages and disadvantages. Similar to the other methods, a significant change in the battery SoC is required to accurately estimate the capacity. The fourth group of methods is a dual estimation of the battery SoC and capacity again model based, similar to the joint estimation with the difference of employing two adaptive filters instead of only one (Hu, Youn, Chung, 2012). The advantage is that lower computing power is required, even though there are two adaptive filters, as the dimensions of the respective model matrices are lower. The final method for estimating capacity is significantly different from the other described above, being based on the incremental capacity analysis (ICA) and differential voltage analysis (DVA) techniques (Bloom, Jansen, Abraham, Knuth, Jones, Battaglia, Henriksen, 2005). These are quantitative approaches to investigate inner chemical reaction and capacity fade. The different plateaus and voltage gradients of the charge – voltage (Q-V) curves are used to calculate the DVA spectrum.

As for the estimation of battery impedance, there are three groups of methods utilized. The first is methods that estimate battery impedance at various frequencies and employ impedance spectroscopy and other related methods (Mingant, Bernard, Sauvant-Moynot, 2012). The second is methods that represent the battery with an electrical model and estimate its parameters in the time domain. Many of the models described earlier and the various adaptive filters can be thus utilized for the estimation of battery impedance also. The third group of methods represents the battery with an electrochemical model, which again can be combined with other adaptive estimators.
There have also been proposed some other methods for estimation of battery SoH that don’t require explicit estimation of the battery capacity or particular impedance parameters. There are methods based on the measurement of the absolute voltage or voltage drop when a certain load is applied, which are very similar to methods based on battery resistance estimation (Zhang, Grube, Shin, Salman, Conell, 2011). There are methods that employ fuzzy logic, using as inputs battery impedance and other battery parameters or calculated battery characteristics (Zenati, Desprez, Razik, Rael, 2010). Finally there is a different approach, in which instead of measuring battery characteristics in a present battery state and using them for the SoH estimation, the battery conditions (temperature, number of load cycles, accumulated ampere – hours etc.) are observed over the battery lifetime and used in a lifetime model which can employ methods like neural networks and SVM to estimate the battery SoH (Nuhic, Terzimehic, Soczka-Guth, Buchholz, Dietmayer, 2013).

6.2.1 Methods for Remaining Useful Life estimation

With the help of the SoH estimation, the battery’s Remaining Useful Life (RUL) can also be estimated. The RUL is the remaining time or number of load cycles until the battery reaches a SoH of 0%. There are two concepts for estimating the RUL, which are summed up in the figure below.
The first concept makes use of the lifetime model, as it has been described in the previous section, which can be utilized to predict the battery RUL when the future battery conditions and loads are taken as inputs. To estimate the future conditions, the observation of the battery usage in the last predefined time period or a predefined reference load profile is used (Nuhic et al. 2013). The disadvantage of this method is that it relies solely on the accuracy of the lifetime model and no recalibration mechanism exists. The other concept for RUL estimation requires two parts. The first is the estimation of the present battery characteristic that is selected for defining the battery lifetime, which can be battery capacity, impedance, their combination or the SoH based on measurements as described in the previous section. The second part is the prediction model that uses those characteristics as an input, analyzes its change in the past and predicts its change in the future. The RUL is the predicted time period until the characteristic reaches the threshold value defined as the end of life of the battery (Micea, Ungurean, Andrstoiu, Groza, 2011).
7 Experiment with sodium – based flow battery cell

7.1 Preparation of electrolytes

For the battery that was experimentally researched in the lab, two sodium based active materials were used. For the anode the material is Na$_2$Ti$_3$O$_7$ and the electrode used is silver, while the active material utilized for the cathode is Na$_{0.44}$MnO$_2$ and the electrode is copper. The preparation procedure of these active materials for the electrolytes was as follows: Na$_2$CO$_3$ was mixed and ground with TiO$_2$ and MnO$_2$ respectively for a sufficient amount of time to ensure their proper mixing. These mixtures were subsequently heated in ovens, beginning from 200° C for about 2 hours, moving on to 500° C for five hours and then to 700° C and finally to 900° C for 12 hours.

![Figure 38. Electrolyte material heated in furnace](image)

During this process the solids were taken out about every hour to be checked and ground again. All this was done to ensure that the final product was not one big piece of sintered material, but retained its original dust form that can be turned to a suspension with the ability to be pumped, as past experience has shown that if the materials were put quickly in high temperatures for long periods they would sinter in large pieces. After the heating process, both solids were mixed with carbon black 20% w/w concentration, which is used to increase the conductivity of the electrolytes and the stability of the final suspension. The disadvantage to carbon black use is the increase in the
viscosity of the electrolytes which will negatively impact the energy consumption for the flow battery pumps. This process took 30 minutes for each electrolyte, to ensure proper mixing of the active materials with the carbon black. The next step was the creation of the solution in which the solids will be suspended. For this deionized water was mixed with Na$_2$SO$_4$ in concentration of 1M (140 g/L) and to this 1% w/v starch was added to help homogenize the final mix. 50 grams of each of the solids were suspended in increasing quantities of the H$_2$O- Na$_2$SO$_4$ solution until the mixture was judged to be eligible for pumping. The final ratio was 660 ml of solution for 50 grams of solids.

![Figure 39. Electrolyte suspension stirred and heated](image)

The suspension was heated to 100°C while being stirred for about one hour to ensure proper mixing while a few grams of flour were added as it is a big molecule that could help bind the final suspension better.

### 7.2 Experiment rig

The cell used in the experiment is made of two plexiglass plates, which have a thickness of 10 mm and length and width of 200 mm. A square space with side of 100 mm and a depth of 2.5 mm has been milled out in each to make space for the electrodes. The electrodes are plates of wavy form to increase the total surface with dimension 90x100 mm. Each plexiglass plate has two holes with fittings to facilitate the flow of electrolytes through the cell. The two sides of the battery cell are divided by a rubber gasket on which the membrane is secured. The membrane is hydrophilic with a pore size of 0.1
μm, and dimension of 11x11 mm. Before assembly the membrane was left overnight in an aqueous solution of 70% ethanol. The membrane is attached watertight on the rubber gasket with silicone and the two plexiglass plates are also attached watertight to the gasket with silicone.

![Battery membrane and fitting on rubber gasket](image)

Figure 40. Battery membrane and fitting on rubber gasket

Two slang pumps are used to produce flow for each electrolyte from its container while a small tube returns the electrolyte from the cell to the container. The cathode electrolyte with Na$_{0.44}$MnO$_2$ as active material is circulated in the side with the copper electrode while the anode electrolyte with Na$_2$Ti$_3$O$_7$ is circulated in the side with the silver electrode.

### 7.2.1 Chronicle of the experiment

Together with the electrolyte preparation, the battery cell was taken apart and cleaned, as dried up electrolyte material from previous experiments was still in the cell. This involved thorough cleaning and sanding of the electrodes to clean their surface and ensure no surface is lost and replacing of the hydrophilic membrane.
Once this was completed the cell was assembled however some of the silicone used run in one of the fittings and dried blocking it, so the cell had to be disassembled again. After assembling it a second time everything was operational and a full charge was performed, however after the relaxation period allowed after the charge the channels became clogged and the flow could not be restored to perform a discharge. At this time it was also observed that a significant amount of salts started emerging from the cathode electrolyte container and also from the anode. This could also be the reason for the channel clogging. The large amount of salt can be explained by the leftover $-\text{CO}_3$ root from the original solids mix. The battery was taken apart and reassembled, but again one of the channels was blocked during the process and required for it to be disassembled again. During the next assembly the membrane became too damaged from all the previous work and so the cell was disassembled one last time to replace the membrane. After that the battery was ready and a full charge and discharge cycle was performed without any problems in the flow of either channels.

### 7.3 Results

The charge curve of the battery was determined by the indications on the power supply unit that was used for charging the battery. The charging period of the battery was about six hours. The voltage was set constant to 1.2 Volts during the whole duration of the charge period.
The first measurement performed in the battery after charging was for determining the open circuit voltage, that is the voltage when the battery is idle for some time period and no power is drained from or being added to it.
This was measured after the battery had remained idle for about one and a half hour after charging, and its value was determined to be 1.084 Volt.

After this test the battery was discharged on a 35 Ohm resistance. As it was expected, there was a voltage drop under load compared to the open circuit voltage. The discharge lasted 1 hour and 46 minutes (6378 seconds of measurements) at which point the voltage started to drop more rapidly and the power was 12% that of the first measurement so the battery was deemed depleted.
During the discharge it became evident that the electrolytes in the tanks needed constant stirring, since when they were stirred the voltage and current would pick up a little and would also stabilize more. The discharge curves for the battery are:

**Figure 46. Voltage discharge curve**

**Figure 47. Current discharge curve**
7.4 Accuracy of measurements

The estimation and depiction of the uncertainty of a measured quantity is an important step so that the measurement can be used further, e.g. in a simulation of the measured phenomenon. The quantification of the uncertainty of the measurements made is needed so that the results can be utilized and compared with each other or other reference values. The most important step is the identification of uncertainty sources that have an impact on the measurements, which in some cases can be found in the manual of the measurement instrument manufacturer, otherwise a way to quantify them has to be explored. The process for calculating the measurement uncertainty can be found in the Guide to the expression of uncertainty in Measurements (GUM) and a case where this process is used in the paper by Behr, Kalfas & Abhari (2006) in which the uncertainty of measurements with probes in turbomachinery is calculated. Briefly, the steps to be undertaken in the process is to define the measurement problem, express the measured quantities as probability density functions in various ways depending on the information known about the measuring instrument and calculate the resulting uncertainty using the Gaussian Error Propagation formula in case the desired result is based on the measurement of multiple quantities. An
important part is defining the type of the measured variable, which can be either:

- **Type A:** Statistical information about measurement uncertainty is gathered during the measurements.
- **Type B:** Statistical information about measurement uncertainty is known before the experiment takes place (measurement instrument manufacturer manual etc.)

If we have a measurement instrument for which its manufacturer provides that the uncertainty of the measurement is ±a%, as is the case for the multi-meter used to measure the voltage and current in the flow battery experiment, that is only the full scale deflection is known and we assume that the uncertainty follows a uniform distribution. If the instrument measures a quantity Y that has a value of x then the uncertainty of the measured value will be Y = x±0.01·a·x. This however leads to the problem of determining the frequency with which the measured value will lie in the positive or negative interval. A statistical analysis should be used to quantify the uncertainty of the measured value, so the uniform distribution is used for which the variance is:

\[ V(Y) = \frac{(2 \cdot 0.01 \cdot a \cdot x)^2}{12} \]

and the standard deviation can be calculated:

\[ u(Y) = \sqrt{V(Y)} = \frac{0.02 \cdot a \cdot x}{\sqrt{3}} \]

This represents the uncertainty a measurement of Y=x will have which will be \( Y = x \pm \frac{0.02\cdot a \cdot x}{\sqrt{3}} \) with a confidence interval of 67% that follows the uniform distribution. For our measurement instrument we have from the manufacturer for the value range that is relevant for our experiment that the current accuracy is ±1.2% and the voltage accuracy ±0.5%, so based on the above we have for the range of our voltage and current measurements:
Figure 49. Uncertainty of current measurement

Figure 50. Uncertainty of voltage measurement
8 Modeling of the flow battery cell

8.1 Equivalent circuit model

The first part of the discharge curve with the response that happens when a battery is connected to load and the current is increased quickly was used to obtain the battery characteristics for a modified equivalent battery model. This part of the discharge curve is divided in time periods with the points \( T_0, T_1 \) and \( T_2 \). \( T_0 \) is the time point in which the battery is connected to the load and the voltage drops, \( T_1 \) is the time point in which the voltage has stopped dropping due to the sudden current change and picks up a little in value and \( T_2 \) is the time point where the battery is considered to have transitioned in stable operation under load.

![First part of discharge curve](image)

**Figure 51. Time points on discharge curve**

The method followed for parameter determination is the one proposed by Shugang Jiang (SAE International 2011) slightly modified as the battery was not disconnected after a short time period. The modified equivalent circuit model is:
The two time constants of the system are $\tau_1=R_1C_1$ and $\tau_2=R_2C_2$. The open circuit voltage is measured directly as detailed earlier, and the internal resistance $R_0$ is calculated easily from the voltage drop the moment the battery is connected to load:

$$R_0 = \frac{V_{t}(T_0^-) - V_{t}(T_0^+)}{I}$$

Which in our case was calculated to be $R_0=20.2$ Ohm. The data from time $T_1$ to time $T_2$ are used to identify the time constants of the system. The initial states are $V_{10}=V_1(T_1)$ and $V_{20}=V_2(T_1)$ and we have: $V_1(t - T_1) = V_{10}e^{t-T_1/\tau_1}$ and $V_2(t - T_1) = V_{20}e^{t-T_1/\tau_2}$. We define $U=V_1+V_2$ so we have

$$U(t - T_1) = V_{10}e^{t-T_1/\tau_1} + V_{20}e^{t-T_1/\tau_2}.$$ 

Also $V_{i}=V_{oc}-V_0-V_1-V_2$ thus $U(t-T_1)=V_{oc}-V_i(t-T_1)$, so that $U$ is a known variable as we have measured $V_{oc}$ and circuit voltage. To establish a regression equation that can be used for parameter identification two variables are defined and calculated from test data:

$$X(t - T_1) = \int_{T_1}^{t} U(\tau - T_1) d\tau \text{ and } Y(t - T_1) = \int_{T_1}^{t} X(\tau - T_1) d\tau$$

By using these two equations and the equation of $U(t-T_1)$ a regression equation that doesn't have the exponential terms in it can be formed:

$$Y(t - T_1) = -X(t - T_1)(\tau_1 + \tau_2) - U(t - T_1)\tau_1\tau_2 + (V_{10}\tau_1 + V_{20}\tau_2)(t - T_1) + (V_{10} + V_{20})\tau_1\tau_2$$

This can be expressed in matrix form:
Or $B=AP$, so that the least squared error solution is $P=(A^TA)^{-1}A^TB$.

The calculations and numerical integration were performed in Matlab and for our case yielded a $P$ matrix of:

$$P = 10^4[0.6357 \ 9.0112 \ 0.4056 \ 5.212]^T$$

from where the time constants and initial voltages can be calculated. Also by using $V_1(T_1) = V_{10} = IR_1(1 - e^{-\frac{T_1}{\tau_1}})$ and the respective equation for $V_2$, we can obtain $R_1$, $R_2$, $C_1$ and $C_2$. For our case it is $\tau_1=6342.8$ sec , $\tau_2=14.207$ sec, $V_{10}=0.639$ Volt, $V_{20}=-0.0606$ Volt, $R_1=10512.4$ Ohm, $R_2= 5.102$ Ohm, $C_1=0.6033$ F and $C_2=2.7846$ F.

However upon feeding the model with our current discharge curve it was not able to accurately reproduce the battery’s behavior, after the first couple of minutes a large and increasing deviation occurred. This is due to the experimental data used to calculate the parameters; it seems that current pulses are indeed needed to accurately capture the battery’s behavior. This led to the next section where an online identification of the battery parameters was investigated using a recursive least – squares algorithm, which have been discussed briefly in the theoretical background.

### 8.2 Recursive Extended Least Squares

The methodology that was followed for this can be found in the paper “Online identification of lithium-ion battery parameters based on an improved equivalent-circuit model and its implementation on battery state-of-power prediction” (Feng, Yang, Zhao, Zhang, Qiang, 2015). The model is based on the one RC equivalent circuit, to which a colored noise $w(t)$ is added to cover other battery dynamics not considered in the one RC model, like diffusion phenomena. In application $w(t)$ is updated by the recent measured data of the battery cell’s current and voltage and thus can emulate the real battery dynamics.
Figure 52. One RC ECM with colored noise $w(t)$ (Feng, Yang, Zhao, Zhang, Qiang, 2015)

The mathematical model of this Equivalent Circuit Model is:

$$V_{p}(t) = \frac{I(t)}{C_{p}} - \frac{V_{p}(t)}{R_{p}C_{p}}$$

$$V_{t}(t) = V_{oc} - V_{p}(t) - R_{in}I(t) + w(t)$$

The colored noise $w(t)$ is modeled by the moving average values of a white noise $n(t)$, with $n_c$ the order of the moving average model:

$$w(t) = \sum_{i=1}^{n_c} c_i \times n(t - i) + n(t) = \sum C(z) \times n(t)$$

where $C(z) = [1 \quad c_1 z^{-1} \quad c_2 z^{-2} \quad \ldots \quad c_{n_c} z^{-n_c}]$

Additionally to the parameters that need to be estimated for a traditional one RC circuit model, the noise model $C(z)$ needs to be identified. Assuming that $V_{oc}$ and $R_{in}$ are constant during a short sampling period, the terminal voltage can be expressed as:

$$V_{t}(t) = V_{oc} - (R_{in} + R_{p})I(t) - R_{in}R_{p}C_{p} \frac{dI(t)}{dt} - R_{p}C_{p} \frac{dV_{t}(t)}{dt} + w(t)$$

Which is rewritten in the form:

$$V_{t}(t) = \kappa^{T}(t)\theta(t) + n(t)$$

$$\kappa^{T}(t) = \begin{bmatrix} 1 & I(t) \frac{dI(t)}{dt} & \frac{dV_{t}(t)}{dt} & n(t-1) & \ldots & n(t-n_c) \end{bmatrix}$$

$$\theta(t) = [\theta_1(t) \quad \theta_2(t) \quad \theta_3(t) \quad \theta_4(t) \quad c_1(t) \quad \ldots \quad c_{n_c}(t)]^{T}$$

$$= [V_{oc} \quad -(R_{in} + R_{p}) \quad -R_{in}R_{p}C_{p} \quad -R_{p}C_{p} \quad c_1(t) \quad \ldots \quad c_{n_c}(t)]^{T}$$
The vector $\theta(t)$ is the parameter vector that needs to be identified. The input vector $\kappa(t)$ cannot be inputted directly as the regressive values of $n(t)$ are immeasurable, so the recursive extended least–squares algorithm is used to calculate $\theta(t)$:

$$
\hat{\theta}(t) = \hat{\theta}(t-1) + P(t)\hat{\kappa}(t)\left[V_t(t) - \hat{\kappa}^T(t)\hat{\theta}(t-1)\right]
$$

where $\hat{\theta}(1) = \hat{\theta}(2) = ... = \hat{\theta}(n_c) = \theta_0$

$P(t)$ is the gain factor which is updated:

$$
P(t) = \frac{1}{\lambda} \left[ P(t-1) - \frac{P(t-1)\hat{\kappa}(t)\hat{\kappa}^T(t)P(t-1)}{\lambda + \hat{\kappa}^T(t)P(t-1)\hat{\kappa}(t)} \right]
$$

where $P(1) = P(2) = ... = P(n_c) = p_0E$

with $E$ the identity matrix and $\lambda$ the forgetting factor, which is typically valued between 0.9 and 1 as a value too small can cause instability. A value equal to 1 means the forgetting factor does not work. The regressive values of the noise $n(t)$ can be approximated by the residual value of measured and estimated voltage and thereafter $\kappa(t)$ can also be estimated:

$$
\hat{n}(t-i) = V_t(t-i) - \hat{\kappa}(t-i)^T\hat{\theta}(t-i)
$$

where $i = 1, 2, ..., n_c$

$$
\hat{\kappa}^T(t) = \begin{bmatrix}
1 & I(t) & \frac{dI(t)}{dt} & \frac{dV_t(t)}{dt} & \hat{n}(t-1) & ... & \hat{n}(t-n_c)
\end{bmatrix}
$$

where $\hat{\kappa}^T(1) = \hat{\kappa}^T(2) = ... = \hat{\kappa}^T(n_c) = \kappa_0$

With the vector $\theta$ calculated, the battery parameters can be obtained:

$$
V_{oc} = \theta_1
$$

$$
R_{in} = \frac{\theta_2}{\theta_4}
$$

$$
R_p = -\theta_2 - \frac{\theta_3}{\theta_4}
$$

$$
C_p = \frac{\theta_4}{\theta_2\theta_4 + \theta_3}
$$

For our experimental data this was implemented in Matlab with the following script:

```matlab
clear
load('voltage.mat')
```
load('Voc.mat')
load('time.mat')
load('current.mat')
THhat(1,:)=[Voc 0 0 1 1 l 1 l l 1];
Khat(:,1)=[1;current(1);(current(2)-current(1))/(time(2)-time(1)); (voltage(2)-voltage(1))/(time(2)-time(1)); 0;0;0;0;0;0];
n=6;
lamda=0.998;
P{1}=1000*eye(10);
for t=2:length(time)
    for i=1:n
        if t>n
            nhat(i)=voltage(t-i)-THhat(t-i,:)*Khat(:,t-i);%nhat
        else
            nhat(i)=voltage(t-1)-THhat(t-1,:)*Khat(:,t-1);
        end
    end
    Khat(:,t)=[1; current(t); (current(t)-current(t-1))/(time(t)-time(t-1)); (voltage(t)-voltage(t-1))/(time(t)-time(t-1)); transpose(nhat(1:n))];
P{t}=(1/lamda)*(P{t-1}-(P{t-1}*Khat(:,t)*transpose(Khat(:,t))*P{t-1})/(lamda+transpose(Khat(:,t))*P{t-1}*Khat(:,t))));
    THhat(t,:)=THhat(t-1,:) + transpose(P{t}*Khat(:,t)*(voltage(t)-THhat(t-1,:)*Khat(:,t)));
end
Voc11=THhat(:,1);
Ri=THhat(:,3)./THhat(:,4);
Rp=THhat(:,2)-THhat(:,3)./THhat(:,4);
Cp=(THhat(:,4).^2)/((THhat(:,2).*THhat(:,4))+THhat(:,3));

Again feeding this model with our experimental data as we can see in the figure below the estimation of the Open Circuit Voltage is not accurate as there is a large under-estimation.
Once more it seems that our experimental data used for parameter identification are not as suitable for this, as it is basically a constant resistance discharge. A typical experiment for parameterization of a battery cell will have multiple steps and various measurements. First a full charge–discharge cycle is performed and the open circuit voltage is measured for 100% and 0% SoC after a rest period. Then multiple experiments of charge and discharge with pulse current at various C-rates, temperatures and SoC are performed. A typical flow chart for such an experiment can be seen below.
At this point some assumptions were made to modify the experimental measurements so that they can be used to characterize our experimental flow battery more accurately using the RELS algorithm above, as well as using some MathWorks® tools that will be explained in following chapters. These assumptions regard the relaxation curve of the experimental flow battery after current interruption, and are that 40% of the voltage difference from the OCV will be recovered 10 seconds after current interruption, another 30% after 30 seconds and 95% will be recovered 320 seconds after current interruption. Also the ratio of OCV to voltage under load was measured precisely for the fully charged battery and was considered to be the same throughout the SoC range. With our experimental data now as they are in Figure 55. Voltage,Current and SoC for flow battery experiment after data modification below the RELS algorithm described previously was used once more.
They now include 34 current pulses and the results for the OCV estimation that can be seen in Figure 56. OCV estimation with RELS algorithm for modified data show remarkable difference. The estimation (blue line) is accurate for a large range of the SoC, showing some over-estimation for SoC near 100% and little over-estimation for SoC near 0%. These are however the most difficult areas to model accurately and considering all the assumptions made the result is actually very accurate.

Figure 55. Voltage, Current and SoC for flow battery experiment after data modification (current in mA)
8.3 Multiple RC model

The experimental data enhanced with the assumptions as explained above were created in order to be used for a Simulink model of the flow battery. Using MathWorks® tools, estimation techniques, and measured battery data the parameters for the Equivalent Circuit Battery block can be generated. The Equivalent Circuit Battery block implements a resistor-capacitor (RC) circuit battery with open circuit voltage, series resistance, and 1 through N RC pairs. In the process of calculating the parameters for the model which will be described in the following the choices of 1-5 RC pairs are compared through their time constants. In our case three RC pairs were used for the results that will follow. The model contains blocks from the Library Powertrain Blockset/Energy Storage and Auxiliary Drive/Network Battery and can be seen in the Simulink UI below:
8.3.1 Equivalent circuit battery block

For the estimation of the battery cell’s SoC and terminal voltage the block utilizes the current load flowing from the battery and the battery temperature. The battery cell’s voltage is estimated with the use of parameters in Look – Up Tables which are functions of the SoC and battery temperature and for their creation another block of the same Simulink library can be utilized, the Estimation Equivalent Circuit Battery block. Specifically, the Equivalent Circuit Battery block implements these parameters as lookup tables that are functions of the SOC and battery temperature:

- Series resistance $R_0=f(\text{SoC}, T)$
- Battery open circuit voltage $E_m=f(\text{SoC}, T)$
- Battery capacity $C_{\text{batt}}=f(T)$
- Network resistance $R_n=f(\text{SoC}, T)$
- Network capacitance $C_n=f(\text{SoC}, T)$

To calculate the terminal voltage of the battery cell, the block uses these equations:

$$V_T = E_m - I_{\text{batt}}R_0 - \sum_{1}^{n} V_n$$
\[ V_n = \int_0^t \left( \frac{I_{\text{batt}}}{C_n} - \frac{V_n}{R_n C_n} \right) dt \]

\[ \text{SoC} = -\frac{1}{C_{\text{batt}}} \int_0^t I_{\text{batt}} dt \]

\[ I_{\text{batt}} = \frac{I_{\text{in}}}{N_p} \]

\[ V_{\text{out}} = N_s V_T \]

\[ P_{\text{batt}} = V_{\text{batt}} I_{\text{batt}} \]

\[ P_{\text{BattLoss}} = I_{\text{batt}}^2 R_0 + \sum_{n=1}^{n} \frac{V_n^2}{R_n} \]

These equations use the variables:

Table 2. Variables used in Equivalent Circuit Battery block

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SoC</td>
<td>State – of – charge</td>
</tr>
<tr>
<td>(E_m)</td>
<td>Battery open – circuit voltage</td>
</tr>
<tr>
<td>(I_{\text{batt}})</td>
<td>Per module battery current</td>
</tr>
<tr>
<td>(I_{\text{in}})</td>
<td>Combined current flowing from the battery network</td>
</tr>
<tr>
<td>(R_0)</td>
<td>Series resistance</td>
</tr>
<tr>
<td>(N_p)</td>
<td>Number parallel branches</td>
</tr>
<tr>
<td>(N_s)</td>
<td>Number of RC pairs in series</td>
</tr>
<tr>
<td>(V_{\text{out}}, V_T)</td>
<td>Combined voltage of the battery network</td>
</tr>
<tr>
<td>(V_n)</td>
<td>Voltage for n-th RC pair</td>
</tr>
<tr>
<td>(R_n)</td>
<td>Resistance for n-th RC pair</td>
</tr>
<tr>
<td>(C_n)</td>
<td>Capacitance for n-th RC pair</td>
</tr>
<tr>
<td>(C_{\text{batt}})</td>
<td>Battery capacity</td>
</tr>
<tr>
<td>(P_{\text{batt}})</td>
<td>Battery power</td>
</tr>
<tr>
<td>(P_{\text{BattLoss}})</td>
<td>Battery power loss</td>
</tr>
<tr>
<td>(T)</td>
<td>Battery temperature</td>
</tr>
</tbody>
</table>
The equivalent circuit battery block with its inputs and outputs (there are more possible outputs like battery power loss not shown in this particular photo) can be seen in Figure 58. The outputs were monitored with scope blocks in our case and these were also used to export the results in the Matlab workspace in an array format. The inputs of the equivalent circuit battery block are battery current as a time series and battery temperature. In our case there are experimental data available for one ambient temperature only so the model is parameterized for this temperature.
In the mask of the block the rest of the information is given, namely the look–up tables with parameters like open–circuit voltage, series resistance and battery capacity as well as the SoC breakpoints for which the parameters are given. Also the number of RC pairs of the model is defined here, in our case three RC pairs are used as it will be discussed in the following sections. In further tabs in the mask the look–up tables for resistances and capacitances of the RC pairs are defined as well as the upper and lower voltage limits for the battery cell if the user wants to define them.
8.3.2 Estimation equivalent Circuit Battery block

The Estimation Equivalent Circuit Battery block implements a resistor-capacitor (RC) circuit battery model that can be utilized to create lookup tables for the Equivalent Circuit Battery block. The lookup tables are functions of the SoC. The Estimation Equivalent Circuit Battery block calculates the combined voltage of the network battery using parameter lookup tables which are tables of the SoC. To acquire the SOC, the block integrates the charge and discharge currents, in effect using the Coulomb – counting method. Specifically, the block implements these parameters as lookup tables that are functions of the SOC:

- Series resistance \( R_0 = f(SoC, T) \)
- Battery open circuit voltage \( E_m = f(SoC, T) \)
- Network resistance \( R_n = f(SoC, T) \)
- Network capacitance \( C_n = f(SoC, T) \)

The equations used by the Estimation Equivalent Circuit Battery block with the same variables as before:
\[ V_T = E_m - I_{bat}R_0 - \sum_{1}^{n} V_n \]

\[ V_n = \int_{0}^{t} \left( \frac{I_{batt}}{C_n} - \frac{V_n}{R_n C_n} \right) dt \]

\[ SoC = -\frac{1}{C_{batt}} \int_{0}^{t} I_{batt} dt \]

\[ I_{batt} = I_{in} \]

\[ V_{out} = V_T \]

In Figure 61 the Estimation Equivalent Circuit Battery block is given with its inputs and some of its outputs. The current flowing through the battery (BattAmp) is the single input here, while other outputs can be chosen from the info port like the voltage of the n-th RC pair if so desired.

![Figure 61. Estimation Equivalent Circuit Battery block](image)

The mask for the Estimation Equivalent Circuit Battery block is very similar to the Equivalent Circuit Battery block’s with the same three tabs to define look-up tables and cell limits.
Furthermore the Estimation Equivalent Circuit Battery block contains two more layers where the equivalent circuit is created and the calculations described above are performed, transferring the results to the outer block.
8.3.3 Algorithm for battery cell parameterization

To complete the model the parameters of the equivalent circuit need to be estimated and entered in the look–up tables in the masks of the above blocks. This is achieved by using MathWorks® tools, estimation techniques, numerical optimization methods and measured battery data in a Matlab script, which helps define the number of RC pairs and provides initial estimates for the parameters for the equivalent circuit, which are then optimized to better fit the experimental dataset. The results are used to define the blocks of the Simulink model. The steps in this process are:

8.3.3.1 Step 1: Load and Preprocess data

For the script to operate correctly, the experimental data should be a pulse discharge sequence that ranges from 100% to 0% of the SoC, while the change in SoC for each pulse should not be greater than 5%. The variables that are needed are voltage and current of the battery cell as time series with the temperature being constant for each dataset. The sample rate should be a minimum of 1 Hz and ideally 10 Hz. Finally the relaxation time allowed between pulses should be sufficient to ensure that the battery cell approaches steady–state voltage. The accuracy limits for the measurements are as follows:

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Accuracy</th>
<th>Ideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>±5 mV</td>
<td>±1 mV</td>
</tr>
<tr>
<td>Current</td>
<td>±100 mA</td>
<td>±10 mA</td>
</tr>
<tr>
<td>Temperature</td>
<td>±1 °C</td>
<td>±1 °C</td>
</tr>
</tbody>
</table>

In the first step, after the experimental data are loaded the beginning and end of each pulse and relaxation period is identified. Also it can be defined whether different time constants for the RC pairs will be used for the load and relaxation part of each pulse. For our flow battery the data used are the ones after the assumptions described previously and shown in Figure 64, and the time constants were chosen to be the same for pulse and relaxation periods. In Figure 65 the identification of different current pulses and relaxation periods is shown.
Figure 64. Input data for parameter identification (current in mA)
The relaxation and current pulse periods are defined on the part of exponential increase and decrease of the voltage curve for each pulse and are used to estimate the time constants of the RC pairs \((\tau=RC)\) and their resistance, while the curve parts with almost vertical rapid change in the voltage are used to estimate the open circuit voltage and the series resistance.
8.3.3.2 Step 2: Determine the number of RC pairs
In the second step after the pulse and relaxation periods have been defined a comparison of the performance of the time constant for one through five RC pairs is performed, with the help of Matlab’s Curve Fitting Toolbox. In essence in this part of the script a first estimation on how the estimated from the model battery voltage will be with each of the five choices on RC pair number, for the relaxation part of three different pulses across the SoC range. This can be seen in the figures below. One pulse is near the beginning of the dataset, the second near the middle and the third near the end of the dataset. The choice of RC pair number is sort of a balancing act; too many RC pairs will raise significantly the model complexity and may not add as much in accuracy as it might over – fit the model, while too few will increase the error of fitting to the real curves. Any decision to change the number of RC pairs at this point will make necessary a rerun of the first step of the script.

![Figure 66. Pulse near the beginning of the dataset, curve fitting comparison for different numbers of RC pairs](image)

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Figure 67. Pulse near the middle of the dataset, curve fitting comparison for different numbers of RC pairs

Figure 68. Pulse near the end of the dataset, curve fitting comparison for different numbers of RC pairs

From the above figures it can be concluded that the choice of model with one RC pair results in large error (residual). The model with two through five RC pairs results in more satisfactory results, with a maximum error at 10 mV for
the middle pulse, with very minute difference between them. With three RC pairs there is a little less residual voltage especially for the middle pulse, so for our case with the flow battery this initial choice was kept and the Simulink model was developed with three RC pairs. The almost nonexistent difference in accuracy with four and five RC pairs does not justify the raise in model complexity that these choices would introduce.

8.3.3.3 Step 3: Estimate Parameters
In this step the final model parameters are estimated after a number of curve fitting and optimization processes. For this step the MathWorks® tools utilized to solve the parameterization problem are the Curve Fitting Toolbox, Optimization Toolbox, Simulink Design Optimization and the Parallel Computing Toolbox. First the initial values for the open – circuit voltage and series resistance are estimated. This part inspects the voltage immediately before and after the current is applied and removed at the start and end of each pulse. It uses these data for a raw calculation estimating what the open-circuit voltage and the series resistance should be. This first estimation for our flow battery can be seen in the figures below, with the time constants and resistances for the RC pairs being zero as no estimation has yet been performed for these parameters.
Figure 69. First estimation for OCV and series resistance for our flow battery
In the next part an initial estimation of the time constant for each RC pair is calculated. It is important that for initialization the time constants have different value from one another, otherwise the optimization process may not be able to discern between them later. The time constants are calculated with an exponential fit to each pulse curve, which can be seen in the figure below for the 33rd pulse, as well as how the time constants vary for each pulse after this part in the next figures. The resistances for the three RC pairs have not been estimated at this point so they all have zero value again.
Figure 71. Exponential fit for initial time constant calculation, pulse 33

Figure 72. Time constants after first estimation ($E_m$ and $R_0$ from previous part)
With the first estimation of the time constants calculated, we can observe how the model performs simulating the battery cell voltage in the figure below. There is a large overshoot in the very beginning of the simulation but after this the simulation result is close to the data, at least up to the lower SoC region when the deviation becomes a little larger, even though at this point no optimization has been performed on the parameters ($R_{1,2}$ & $R_3$ have not yet been estimated at all).
Next a first estimation of the resistances of the RC pairs is performed for each of the current pulses. This part takes the data for each pulse and treats it as a linear system. It attempts to fit the resistance values for each RC branch with a linear curve fit. Optionally, as was done for our application, there can be further adjustment of the open circuit voltage and series resistance values, and if these are adjusted there is also the option of whether to retain the optimized values of these or to discard them. The curve fit for one pulse can be seen in the figure below. The yellow curve is based on the previous results.
with only the time constants estimated, the red curve on the newly estimated parameters and the blue curve on the actual data. The improvement is obvious. In following figures the newly estimated parameters are presented and the simulation of the current pulses with these parameters, which still suffers from a large overshoot in the very beginning but overall has improved.

Figure 76. Linear curve fit for $R_n$ estimation and adjustment of OCV and $R_0$. 
Figure 77. Model parameters after $R_n$ estimation
Figure 78. Model parameters after $R_n$ estimation

Figure 79. Simulation of battery cell voltage and residual voltage after $R_n$ estimation
Finally all the parameters ($E_m$, $R_0$, $R_n$, and $\tau_n$) are adjusted once more, this time using Simulink Design Optimization with a non–linear least–squares data–fitting solver being utilized. A comparison of the model performance before and after this final optimization of the model parameters can be seen in the figure below for the 33rd current pulse. The reduction of mean residual voltage achieved is significant, about 87% for this current pulse. The main areas that induce most of the error are at the beginning of the steep increase and decrease parts of the voltage curve.

Figure 80. Final parameter optimization for 33rd current pulse

In the following figures are the final values of the equivalent circuit model parameters after the optimization and the result of the simulation of the modified current pulse data with these parameters. The error for the high SoC range still remains large but the simulation has successfully captured the dynamics of the actual data. The simulation for smaller SoC and up to about 25% SoC is more accurate for the voltage magnitude with error varying from close to 0% up to about 25%. While that is not optimal, there were a lot of assumptions made to be able to use this dataset for the model parameterization, therefore the simulation can be considered successful. Also these assumptions could be changed and perhaps lead to an even better result with more trials and errors.
Figure 81. Final parameter values across SoC range
Figure 82. Final parameter values across SoC range
8.3.3.4 **Step 4: Set Equivalent Circuit Battery Block Parameters**

In the last part of the algorithm the look–up tables with the above calculated parameters are defined so that they can be imported to the equivalent circuit battery block in the Simulink model. Also in this part the different temperatures for which the parameters were estimated are defined. In the case that there are measurements available for one temperature only, the estimated parameters are duplicated a second time in the look–up tables so that the temperature-wise regression yields the same result for any input temperature.

8.3.4 **Discharge at constant resistance load simulation**

Going back to the original measured data of discharge on a constant resistance load, the measured current will be the input for the Simulink model whose development was described on the previous sections, so that the terminal voltage from the simulation can be compared to the measured. Also the SoC and power estimations are presented in the following figures.
Figure 84. Voltage simulation for constant resistance load with Simulink model

Figure 85. State of charge estimation for constant resistance load with Simulink model
Unlike when the dataset is presented as current pulses, the model slightly underestimated the voltage for this load at every SoC. Again considering all the assumptions made in order to develop the model the simulation is considered successful. Especially between the SoC of about 90-25% the simulation is close to the measured data with error of about 15%. For the lower SoC region, which generally is considered the most difficult region to simulate as the battery runs out of charge, there is larger deviation in the voltage simulation. This happens because the model predicts that the battery has reached the SoC level of 0% before the end of our dataset, which is not that inaccurate, as by this time the power and voltage has already been reduced significantly compared to the initial measurement. Observing the estimated open circuit voltage plotted against SoC in the figure below, we can see the spike in OCV in the lower SoC region that is unexpected, but other than this the simulated data can successfully depict the battery cell behavior.
Figure 87. OCV-SoC from the Simulink model
9 Conclusions

- A simple method for producing liquid form sodium – based electrolytes was established
- Measurements of a charge – discharge cycle were performed
- The characteristics of the battery were extracted and utilized for modeling
- Stable voltage within a 4% of initial open circuit voltage margin for a 55% SoC interval
- 16.44 mAh capacity
- 13 mWatt maximum power
- 90% larger open circuit voltage than static experiment (no electrolyte flow)
- 28% larger mean power than static experiment (no electrolyte flow)
- The simple discharge experiment with the measurements that were taken were utilized with the aid of some assumptions for modeling of the flow battery, without requiring further more complicated experiments and measurements
- RELS algorithm model almost overlaying with experimental data curve for large part of the SoC range
- Third order RC model has an error of about 15% for large part of the SoC range
- Modeling results were very accurate especially considering the assumptions made to obtain them
Συμπεράσματα

- Εφαρμόστηκε μια απλή μέθοδος για την παραγωγή ρευστών ηλεκτρολυτών βασισμένων σε ιόντα νατρίου
- Έγιναν μετρήσεις σε έναν πλήρη κύκλο φόρτισης – εκφόρτισης της μπαταρίας
- Τα χαρακτηριστικά της μπαταρίας εκτιμήθηκαν και χρησιμοποιήθηκαν για τη μοντελοποίησή της
- Σταθερή τάση μέσα σε ένα περιθώριο 4% της αρχικής τάσης ανοιχτού κυκλώματος για 55% του εύρους του επιπέδου φόρτισης (SoC)
- 16.44 mAh χωρητικότητα
- 13 mWatt μέγιστη ισχύς
- 90% αύξηση στην τάση ανοιχτού κυκλώματος συγκριτικά με προηγούμενο στατικό πείραμα (χωρίς ροή των ηλεκτρολυτών μέσα από το κελί)
- 28% αύξηση στην μέση ισχύ συγκριτικά με προηγούμενο στατικό πείραμα (χωρίς ροή των ηλεκτρολυτών μέσα από το κελί)
- Το απλό πείραμα της εκφόρτισης σε σταθερή αντίσταση χρησιμοποιήθηκε επιτυχώς για τη μοντελοποίηση του κελιού με τη βοήθεια μερικών υποθέσεων, χωρίς την διενέργεια περαιτέρω πολύπλοκων θετικών πειραμάτων και παραπάνω μετρήσεων
- Το μοντέλο του κελιού με τη βοήθεια RELS αλγόριθμου σχεδόν ταυτίζεται με τα πειραματικά δεδομένα για μεγάλο μέρος του εύρους του επιπέδου φόρτισης
- Το μοντέλο τρίτης τάξης RC είχε σφάλμα περίπου 15% για μεγάλο μέρος του εύρους του επιπέδου φόρτισης
- Τα αποτελέσματα των μοντέλων του κελιού ήταν εξαιρετικά ακριβή, ειδικά αναλογιζόμενοι της υποθέσεως που έγιναν κατά τη δημιουργία τους
10. Bibliography

1. Linden D., Reddy T., Handbook of Batteries, McGraw Hill
2. Larminie J., Lowry J. ELECTRIC VEHICLE TECHNOLOGY EXPLAINED, Wiley
3. Kwo Young et al., Electric Vehicle Battery Technologies, Springer
6. Στεφόπουλος Γ., (2014) ΡΕΥΣΤΟΜΗΧΑΝΙΚΗ ΜΕΛΕΤΗ, ΠΕΙΡΑΜΑΤΙΚΗ ΔΙΑΚΡΙΒΩΣΗ ΚΑΙ ΣΤΑΤΙΣΤΙΚΗ ΑΝΑΛΥΣΗ ΚΑΙΝΟΤΟΜΟΥ ΠΡΟΑΝΑΜΕΙΚΤΗ ΑΕΡΑ-ΚΑΥΣΙΜΟΥ, ΑΡΙΣΤΟΤΕΛΕΙΟ ΠΑΝΕΠΙΣΤΗΜΙΟ ΘΕΣΣΑΛΟΝΙΚΗΣ
7. Bajracharya Q., DYNAMIC MODELING, MONITORING AND CONTROL OF ENERGY STORAGE SYSTEM, Karlstad University
11. Andreas Poullikkas, A comparative overview of large-scale battery systems for electricity storage, Renewable and Sustainable Energy Reviews 27 (2013) 778-788
12. Meng, Guo, Niu, Zhao, Xu, Li, Mai, Advances in Structure and Property Optimizations of Battery Electrode Materials, Joule 1, 522–547, November 15, 2017
26. Tiezhou Wu, Lunan Liu, Qing Xiao, Quan Cao, Xieyang Wang, Research on SOC Estimation Based on Second-order RC Model, TELKOMNIKA, Vol.10, No.7, November 2012, pp. 1667~1672
29. Ahmad RAHMOUN, Helmuth BIECHL, Modelling of Li-ion batteries using equivalent circuit diagrams, PRZEGŁAD ELEKTROTECHNICZNY (Electrical Review), ISSN 0033-2097, R. 88 NR 7b/2012
34. Tianheng Feng, Lin Yang, Xiaowei Zhao, Huidong Zhang, Jiaxi Qiang, Online identification of lithium-ion battery parameters based on an improved equivalent-circuit model and its implementation on battery state-of-power prediction, Journal of Power Sources 281 (2015) 192-203
37. Hongwen He, Rui Xiong and Jinxin Fan, Evaluation of Lithium-Ion Battery Equivalent Circuit Models for State of Charge Estimation by an Experimental Approach, Energies 2011, 4, 582-598
38. Baccouche et al., Improved OCV Model of a Li-Ion NMC Battery for Online SOC Estimation Using the Extended Kalman Filter, Energies 2017, 10, 764
40. Hongwen He, Xiaowei Zhang, Rui Xiong, Yongli Xu, Hongqiang Guo, Online model-based estimation of state-of-charge and open-circuit
voltage of lithium-ion batteries in electric vehicles, Energy 39 (2012) 310-318
41. Yinjiao Xing, Wei He, Michael Pecht, Kwok Leung Tsui, State of charge estimation of lithium-ion batteries using the open-circuit voltage at various ambient temperatures, Applied Energy 113 (2014) 106–115
42. Kharbachi e al., Reversibility of metal-hydride anodes in all-solid-state lithium secondary battery operating at room temperature, Solid State Ionics 317 (2018) 263–267
49. Tarun Huria, Massimo Ceraolo, Javier Gazzarri, Robyn Jackey, High Fidelity Electrical Model with Thermal Dependence for Characterization and Simulation of High Power Lithium Battery Cells, 2012 IEEE


56. Li Ran, Wu Junfeng, Wang haiying, Li Gechen, Prediction of State of Charge of Lithium-ion Rechargeable Battery with Electrochemical Impedance Spectroscopy Theory, 2010 IEEE


59. H. Rahimi-Eicher, F. Baronti and M.-Y. Chow, Modeling and Online Parameter Identification of Li-Polymer Battery Cells for SOC estimation, 2012 IEEE


63. H. Rahimi-Eicher, F. Baronti and M.-Y. Chow, Online Adaptive Parameter Identification and State-of-Charge Coestimation for Lithium-Polymer Battery Cells, IEEE TRANSACTIONS ON INDUSTRIAL ELECTRONICS, VOL. 61, NO. 4, APRIL 2014


65. M.R. Jongerden and B.R. Haverkort, Battery Modeling
66. Michael A. Roscher, Dirk Uwe Sauer, Dynamic electric behavior and open-circuit-voltage modeling of LiFePO4-based lithium ion secondary batteries, Journal of Power Sources 196 (2011) 331–336
67. Carmelo Speltino, Domenico Di Domenico, Giovanni Fiengo and Anna Stefanopoulou, Experimental Validation of a Lithium-Ion Battery State of Charge Estimation with an Extended Kalman Filter
70. Tremblay, Dessaint, Experimental Validation of a Battery Dynamic Model for EV Applications, World Electric Vehicle Journal Vol. 3 - ISSN 2032-6653 - © 2009 AVERE
71. Benger et al., Electrochemical and thermal modeling of lithium-ion cells for use in HEV or EV application, World Electric Vehicle Journal Vol. 3 - ISSN 2032-6653 - © 2009 AVERE
74. Min Chen, Rincón-Mora, Accurate Electrical Battery Model Capable of Predicting Runtime and I–V Performance, IEEE TRANSACTIONS ON ENERGY CONVERSION, VOL. 21, NO. 2, JUNE 2006
75. A. Zenati, P. Desprez, H. Razik, S. Rael, Impedance measurements combined with the fuzzy logic methodology to assess the SOC and SOH of lithium-ion cells, Proceedings of IEEE Vehicle Power and Propulsion Conference (VPPC), 2010, pp. 1-6
78. Shugang Jiang, A Parameter Identification Method for a Battery Equivalent Circuit Model, 2011 SAE International
79. Schweighofer et al., Modeling of High Power Automotive Batteries by the Use of an Automated Test System, IEEE TRANSACTIONS ON INSTRUMENTATION AND MEASUREMENT, VOL. 52, NO. 4, AUGUST 2003
80. Liang Chen, Qingwen Gu, Xufeng Zhou, Saixi Lee, Yonggao Xia & Zhaoping Liu, New-concept Batteries Based on Aqueous Li1/Na1 Mixed-ion Electrolytes, DOI: 10.1038/srep01946
82. Ørjan Gjengedal, Preben Joakim Svela Viey, Marta Molinas, Battery Modeling and Kalman Filter-based State-of-Charge Estimation for a Race Car Application, 2017 IEEE