Batteries for marine applications

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by

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Abstract

The significant reduction in environmental emissions stated by the new IMO legislation, which specifies an amount of sulphur in fuels below 5% for 2020 and a NOx limit with an 80% reduction respect to the actual IMO limit within SECAS’s for 2016, aim the use of batteries as a propulsion source in hybrid marine power plants.

Offshore vessels fit perfectly in the application of hybrid propulsion systems due to the large variations of energy requirements during their operation. Besides the reduction of emissions, the optimal combination between engines and batteries can be used for fast transients, smoothing the load of the engine and hence reducing the fuel consumption.

The reasons behind the selection of the Lithium Ion battery as an ideal candidate for marine applications are stated in this thesis, through the comparison between the characteristics of different battery types.

Simulation models of a Lithium Ion cell and a Lithium Ion battery pack at three complexity levels are developed in this thesis (simple, isothermal and thermal). Bond Graph approach is used for the model generation and 20Sim is used to perform the simulations.

A safe operation window is stated for all levels since the performance of Lithium Ion cells is dependent on both, the temperature and the operating voltage. Therefore, both values must be kept within determined limits in order to avoid permanent damage in the cell.

In case of the isothermal and thermal approaches, the electrochemical behaviour in the cell is considered and the main phenomena involved is represented, including: activation, conduction and diffusion, as well as, the dynamic effect of the electrochemical reactions and the heat release due to Joule heating.
Acknowledgements

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I would also like to thank my friends, especially Samita Wilson and Ulrike Neckmann, for making my life in a new country easier and happier.

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Trondheim, June 2013
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Chapter 1  Introduction

1.1 Background

The use of batteries as propulsion source in hybrid marine power plants is aimed by the significant reduction in environmental emissions stated by the new IMO legislation, what specifies that for 2020 the amount of sulphur in fuels should be less than 0.5%; while within SECA’s, for 2016 the limit for NOx should be minus 80% with respect to the actual IMO limit (Stapersma, 2010).

The large variations of energy requirements in some types of ships make the application of batteries in marine power plants very suitable, where depending on the operation carried on the batteries can be either charged or used.

As it is shown in figure 1, offshore vessels fit perfectly within this kind of operation.

![Mission profile offshore vessel](image)

**Figure 1 - Mission profile offshore vessel (Sortland, 2008)**

The optimal combination between engines and batteries must be considered. An option could be charge the batteries during the longest operation time mode, while the ship can operate only with batteries during less operation time actions; having as well the option to run with a combination of batteries and engines in some cases. This combination can also be used for fast transients in order to smooth the load of the engine and therefore, reduce the peaks of fuel consumption.
Introduction

The energy requirements of other kind of ships as bulk carriers or container ships are very different in comparison with the requirements of offshore vessels. Therefore, in these cases the optimization between engines and batteries would not be very efficient.

Currently there is a project known as FellowSHIP, which was initiated in 2003. It is a joint industry R&D project experimenting with hybrid energy systems, involving fuel cells, gas engines and batteries on board vessels and offshore platforms for sustainable energy generation. These innovations lead to a cleaner and greener future for shipping with a significant potential to reduce CO2 emissions (up to 50%) and improve energy efficiency (up to 30%) when compared to conventional power generators. Emissions of harmful substances like NOx, SOx and particles will be completely eradicated. (FellowSHIP, 2012)
Introduction

The ship chosen to test the FellowSHIP project is the Viking Lady, which is a ship operating as a supply vessel in the North Sea, designed and built in Norway.

1.2 Thesis

This thesis is the continuation of the specialization project developed during the fall semester of 2012 in order to comply with the requirements to complete the master degree in Marine Technology at the Norwegian University of Science and Technology (NTNU).

The object of this thesis is to develop and simulate the bond graph models of lithium ion batteries at three complexity levels, involving both isothermal and thermal approaches and using the software 20Sim.

1.2.1 Thesis structure

The thesis consists of five chapters including the introduction. In Chapter 2, a general approach to batteries and to the technology behind a Lithium ion battery are stated, as well as the reasons regarding its selection to be used in marine applications. In Chapter 3, bond graph models in three different complexity levels are developed for a single li-ion battery cell. In Chapter 4, three bond graph models of a complete li-ion battery pack are developed using the models obtained in the previous chapter. In Chapter 5 guidance for future work is addressed.
Chapter 2   Lithium ion batteries

2.1 Batteries Basic Theory

A battery consists of a number of cells assembled in a common container and connected together to function as a source of electrical power. (Bhatia, 2012)

An electrochemical cell is the fundamental unit of the battery that transforms chemical energy into electrical energy; this process is called electrochemical action. Therefore, the voltage of an individual cell is determined by its chemistry. (Bhatia, 2012)

The voltage across the electrodes depends upon the materials from which the electrodes are made and the composition of the electrolyte. The current that a cell delivers depends upon the resistance of the entire circuit, including that of the cell itself. The internal resistance of the cell depends upon the size of the electrodes, the distance between them in the electrolyte, and the resistance of the electrolyte. The larger the electrodes and the closer together they are in the electrolyte (without touching), the lower the internal resistance of the cell and the more current the cell is capable of supplying to the load. A simple cell consists of two electrodes placed in a container that holds the electrolyte. (Bhatia, 2012)

The electrodes are the conductors by which the current leaves or returns to the electrolyte. If a load is connected to the electrodes, electrons will flow under the influence of a difference in potential across the electrodes from the cathode (negative electrode) through the external conductor to the anode (positive electrode). (Bhatia, 2012)

The electrolyte is the solution that acts upon the electrodes. The electrolyte, which provides a path for electron flow, may be a salt, an acid, or an alkaline solution. In the simple galvanic cell, the electrolyte is in a liquid form. In the dry cell, the electrolyte is a paste. (Bhatia, 2012)
2.2 Types of Batteries

The simplest cell is known as a galvanic or voltaic cell. It consists of a piece of carbon (C) and a piece of zinc (Zn) suspended in a jar that contains a solution of water (H₂O) and sulfuric acid (H₂SO₄) called electrolyte. (Bhatia, 2012)

A primary cell is one in which the chemical action eats away one of the electrodes, usually the negative electrode. When this happens, the electrode must be replaced or the cell must be thrown away. An example of this type of cell is the galvanic cell (Zn-C). (Bhatia, 2012)

A secondary cell is one in which the electrodes and the electrolyte are altered by the chemical action that takes place when the cell delivers current. This type of cells can be recharged and the electrodes are made of different materials. The oldest form of a secondary cell is the lead-acid cell. (Bhatia, 2012)

The development of new and different types of cells in the past decade has been fast. Although the modern version is still widely in use today, it was overtaken in performance terms 50 years ago by the nickel-cadmium (NiCad) battery, which was outdated by nickel-metal hydride (NiMH) system.

The latest and highest performance secondary system is lithium-ion (Li-ion) which was developed in the late 1970’s and is now the fastest growing battery system in the world.

Table 1 provides a quick comparison of the main types of batteries. The red, amber and green shading aims to provide an overall impression of the features of each battery type. In general, battery types with mostly green shading are those with the highest performance, lowest weight, best safety record and have the least environmental impact. Those with mostly red shading offer lower performance, are heavier and have a greater impact on the environment. Amber shading is used to indicate a rating between the two.
Lithium Ion Batteries

Table 1 - Battery Comparison Guide

<table>
<thead>
<tr>
<th></th>
<th>Lead Acid (SLA)</th>
<th>Silicon</th>
<th>Ni-Cad</th>
<th>NiMH</th>
<th>Lithium-ion</th>
<th>Lithium-Polymer</th>
<th>Lithium-Phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial purchase cost</td>
<td>Low</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Medium/High</td>
</tr>
<tr>
<td>Lifetime cost</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>Very Low</td>
<td>Lowest</td>
</tr>
<tr>
<td>Safety</td>
<td>Good</td>
<td>Very good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Very good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Environmental impact</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Medium / High</td>
<td>Medium / Low</td>
<td>Low</td>
<td>Very Low</td>
</tr>
<tr>
<td>Cycle life</td>
<td>200</td>
<td>400</td>
<td>250</td>
<td>400-500</td>
<td>400-600</td>
<td>&gt;1000</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>Nominal voltage</td>
<td>2</td>
<td>2</td>
<td>1.2</td>
<td>1.2</td>
<td>3.4</td>
<td>3.6</td>
<td>3.7</td>
</tr>
<tr>
<td>WH/Kg Energy density</td>
<td>35</td>
<td>50</td>
<td>41</td>
<td>80</td>
<td>120</td>
<td>160 - 180</td>
<td>120</td>
</tr>
<tr>
<td>Volumetric energy density</td>
<td>80</td>
<td>130</td>
<td>120</td>
<td>200</td>
<td>280</td>
<td>&gt;320</td>
<td>270</td>
</tr>
<tr>
<td>Self discharge (%) per month</td>
<td>&lt;0</td>
<td>&lt;0</td>
<td>&lt;10</td>
<td>&lt;20</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Memory effect</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Rarely</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Operating temperature (C)</td>
<td>-15° to +50°</td>
<td>-50° to +70°</td>
<td>-20° to +50°</td>
<td>-20° to +60°</td>
<td>-20° to +60°</td>
<td>-20° to +60°</td>
<td>-45° to +70°</td>
</tr>
<tr>
<td>Flexible form factor</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Weight</td>
<td>Heavy</td>
<td>Heavy</td>
<td>Light</td>
<td>Light</td>
<td>Lightest</td>
<td>Lightest</td>
<td>Very Light</td>
</tr>
<tr>
<td>Charge time</td>
<td>Long</td>
<td>Fast</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Fast</td>
<td>Fast</td>
<td>Fastest</td>
</tr>
<tr>
<td>Range</td>
<td>Very Good</td>
<td>Very Good</td>
<td>Good</td>
<td>Good</td>
<td>Very Good</td>
<td>Excellent</td>
<td>Outstanding</td>
</tr>
</tbody>
</table>

(PowaRider, 2012)
Lithium Ion Batteries

Table 2 - Description of the main characteristics of a battery

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial purchase cost:</strong></td>
<td>Initial purchase cost is obviously a factor but the most useful cost is the lifetime cost.</td>
</tr>
<tr>
<td><strong>Lifetime cost:</strong></td>
<td>The relative lifetime cost is based on range and cycle life to give a meaningful comparison between different battery types.</td>
</tr>
<tr>
<td><strong>Safety:</strong></td>
<td>This alludes to the safety record to date for batteries of a given type (for charging, discharging and storage) so is a reasonably general view.</td>
</tr>
<tr>
<td><strong>Environmental impact:</strong></td>
<td>The relative impact from production and disposal of each battery type. All EV batteries are recyclable.</td>
</tr>
<tr>
<td><strong>Cycle life:</strong></td>
<td>This describes the life span of the battery and is related to the number of complete charge/discharge cycles that a battery can perform before it degrades to about two thirds of its capacity. Sometimes manufacturers multiply this by the range to provide an overall guide to the life of the battery in miles or kilometres – treat this as a very approximate guide.</td>
</tr>
<tr>
<td><strong>Nominal Voltage:</strong></td>
<td>The typical voltage per cell is fairly constant for each type of battery. Cells are combined in series to provide the useful voltage required by the motor – so gives an indication of how many cells are needed. Fewer cells provide fewer points of failure and generally less heat.</td>
</tr>
<tr>
<td><strong>Energy density:</strong></td>
<td>Energy density is the amount of energy that can be stored in a battery per unit of mass (gravimetric) or per unit of volume. Think of it as the power to weight ratio. It is a useful guide between battery types.</td>
</tr>
<tr>
<td><strong>Self discharge:</strong></td>
<td>Self-discharge is the reduction in the stored charge of the battery when not in use, it decreases the self-life of batteries and tends to occur more quickly at higher temperatures.</td>
</tr>
<tr>
<td><strong>Memory effect:</strong></td>
<td>‘Memory effect’ or ‘floating voltage’ are the common terms for voltage depression which is usually associated with Nickel Cadmium (Ni-Cad) and some Nickel Metal Hydride (NiMH) rechargeable batteries. The effect is that the battery fails to deliver its original full capacity, seemingly to have ‘remembered’ previous partial charge levels. This can be cured by fully discharging individually affected cells but not the whole battery – a tricky process so prevention is better than cure.</td>
</tr>
<tr>
<td><strong>Operating temperature:</strong></td>
<td>Batteries function best at room temperature but each type has discharge temperature limits outside which performance will degrade or cease altogether.</td>
</tr>
<tr>
<td><strong>Flexible form factor:</strong></td>
<td>Battery types with thin cells can be created in any form, shape and size.</td>
</tr>
<tr>
<td><strong>Weight:</strong></td>
<td>Performance is directly affected by weight which varies considerably between battery types. Weight figures for batteries and overall electric bike weight are usually supplied for easy comparison.</td>
</tr>
<tr>
<td><strong>Charge time:</strong></td>
<td>The time taken to reach a full charge from fully discharged. Figures for partial charging are also useful.</td>
</tr>
<tr>
<td><strong>Range:</strong></td>
<td>Not really influenced by battery type but included here for completeness – peak power output is a more useful guide to range. Manufacturers will provide figures for the maximum range on a single charge. These will have been measured under ideal conditions. They are useful for comparison purposes across model ranges from the same manufacturer but less so between manufacturers. Note that you're unlikely to see results that match the stated figures due varying environmental factors.</td>
</tr>
</tbody>
</table>

(PowaRider, 2012)
Lithium Ion Batteries

As a conclusion to the features outlined in Table 1, the following facts can be indicated (Buchmann, 2001):

- Lead Acid batteries are the most economical for larger power applications where weight is of little concern.

- Nickel Cadmium (NiCd) batteries are mature and well understood but relatively low in energy density. They are used where long life, high discharge rate and economical price are important. The NiCd batteries contain toxic metals and are environmentally unfriendly.

- Nickel-Metal Hydride (NiMH) batteries have a higher energy density compared to the NiCd at the expense of reduced cycle life. However, this type of batteries does not contain any toxic metals.

- Lithium Ion (Li-ion) batteries are the fastest growing battery system. Li-ion are used where high-energy density and lightweight is of prime importance. This type of batteries do not require maintenance. Nevertheless, the technology is fragile and a protection circuit is required to assure safety.

- Lithium Ion Polymer (Li-ion polymer) batteries offer the attributes of the Li-ion in ultra-slim geometry and simplified packaging.

- Lithium Iron Phosphate (Lithium-Phosphate) batteries have lower energy density than common lithium-ion batteries, but offer longer lifetimes, better power density and are naturally safer.

All characteristics stated above makes Li-ion battery an ideal candidate for marine applications.
2.3 Lithium-ion battery

As it was specified before, an electrochemical cell comprises two electrodes, an electrolyte, and constructional components such as a container, terminals etc. A variety of materials can be used as electrodes; these processed materials have higher energy than in their natural state (ABSL and AGM, 2009).

As lithium is the lightest of all metals, is an ideal material for use in cells; because besides its light weight, it has high voltage and high energy content (ABSL and AGM, 2009).

Rechargeable cells using lithium metal as an anode are not practical because of limited cycle life, but in the early 1980’s Professor John Goodenough patented the use of lithiated metal oxide as a cathode with graphite as an anode to overcome this problem. This system became known as the Lithium-ion cell (ABSL and AGM, 2009).

The lithiated metal oxide used in Li-ion cells is a highly refined, ultra-pure powder which, along with high purity graphite (ABSL and AGM, 2009).

In case of cells with lead-acid, NiCad or NiMH chemistry have electrolytes based on water. However, the electrolyte through which the lithium travels in the Li-ion cell is based on organic solvents with very low-freezing points. This means that the Li-ion cell can be effective at temperatures as low as -40°C (ABSL and AGM, 2009).

Cell design can be optimized for long discharge life, or long cycle life, or high power or wide temperature range. However, no one cell type can provide top performance in all these categories (ABSL and AGM, 2009).
2.3.1 Basic principle

When the battery is discharged, the lithium ions in the carbon material that form the anode migrate via a separator to the cathode material (lithium compound). At the same time, electric current flows through the external circuit (Varta, 2012).

When the battery is charged, electric current is forced in the opposite direction and the lithium ions in the cathode material (lithium compound) migrate via a separator to between the layers of carbon material that form the anode (Varta, 2012).

As it was discussed previously, the discovery that lithium forms intercalation compounds with certain types of graphite was decisive for the development of rechargeable batteries with lithium electrodes. The lithium-ions are stored in a layered grid of carbon or graphite, while electrons are being absorbed or released at the same time. The ion is formally discharged, but no defined chemical combining occurs (Varta, 2012).
Lithium Ion Batteries

The chemistry of a lithium-ion cell can be represented as follows:

- Overall reaction on a Li-ion cell: \( C_6 + LiCoO_2 \leftrightarrow LiC_6 + Li_{0.5}CoO_2 \)  (1)

- At the cathode: \( LiCoO_2 - Li^+ - e^- \leftrightarrow Li_{0.5}CoO_2 \Rightarrow 143 \text{ mAh/g} \)  (2)

- At the anode: \( 6C + Li^+ + e^- \leftrightarrow LiC_6 \Rightarrow 372 \text{ mAh/g} \)  (3)  
  (Nexeon, 2012)

The overall reaction has its limits (Buchmann, 2012):

- Overdischarge: supersaturates lithium cobalt oxide, leading to the production of lithium oxide possibly by the following irreversible reaction:

\[
LiCoO_2 + Li^+ + e^- \rightarrow Li_2O + CoO
\]  (4)

Figure 5 - Discharge mechanism of a lithium-ion cell (ABSL and AGM, 2009)
**Lithium Ion Batteries**

- Overcharge up to 5.2 Volts: the battery becomes unstable. Prolonged charging above 4.30V forms plating of metallic lithium on the anode, while the cathode material becomes an oxidizing agent, losses stability and produces carbon dioxide. The cell pressure rises, and if charging is allowed to continue the current interrupt device (CID) responsible for cell safety disconnects. The thermal runaway moves lower when the battery is fully charged; for Li-cobalt this threshold is between 130–150°C (266–302°F), nickel-manganese-cobalt (NMC) is 170–180°C (338–356°F), and manganese is 250°C (482°F). Overcharge leads in the composition stated above to the synthesis of cobalt oxide, as evidenced by x-ray diffraction.

\[
\text{LiCoO}_2 \rightarrow \text{Li}^+ + \text{CoO}_2 + e^- \quad (5)
\]

Most cells charge up to 4.20V/cell with a tolerance of +/-50mV/cell.
Chapter 3  
Bond Graph Modelling of a Li-ion cell

3.1 Bond graph general approach

The bond graph method has many advantages. For instance, bond graph language allows the construction of models from different energy domains based on power flow, which is represented on a bond.

Other of these advantages is the possibility of perform simulations once the model is developed. 20-Sim is the software selected to perform those simulations.

The terms used in the bond graph technique are:

- **State Variables**: these variables can be either power variables or energy variables. The power variables are effort (e) and flow (f). The product of those variables is the power transmitted by the bond. The energy variables are obtained by the integration of the power variables and are called momentum (p) and displacement (q).

- **Power ports**: A port is the point on the element or junction where the energy flows in or out. The connection between ports is made by the power bonds. Each element or junction can have one or more ports.

- **Elements**: The elements represent a physical element or transformation of energy domain. In the basic bond graph, C-, R- and I-element are used as a capacitor, resistor and inertia respectively. These basic elements have 1-port.

  For transformation of energy domain, TF- and GY-element are used as a transformer and a gyrator respectively. These elements can be used as MTF and MGY when the module involved in the transformation is a function of other variable.
Bond Graph Modelling of a Li-ion Cell

- **Junction:** The junction represents the balance of energy, mass or speed. These are multiport elements. 1-junction is used where the flow is equal and the sum of the efforts is zero. 0-junction is used where the effort is equal and the sum of the flows is zero.

- **Causality:** It determines the input and the output for the constitutive laws for the element.

The main elements used in the following models are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Representation</th>
<th>Constitutive law</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>C</td>
<td>( e = \Phi (q) )</td>
</tr>
<tr>
<td>I</td>
<td>I</td>
<td>( f = \Phi (p) )</td>
</tr>
<tr>
<td>R</td>
<td>R</td>
<td>( e = \Phi (f) )</td>
</tr>
<tr>
<td>Se</td>
<td>Se</td>
<td>( e = c (t) )</td>
</tr>
<tr>
<td>TF</td>
<td>TF</td>
<td>( e_1 = m.e_2 ) [ m.f_1 = f_2 ]</td>
</tr>
</tbody>
</table>

As an electrochemical device, a Li-ion battery is a multi-disciplinary system (Ménard et al, 2010), where the following domains are involved: electrical, chemical and thermal.
### Table 4 - Power variables from different domains (Pedersen and Engja, 2010)

<table>
<thead>
<tr>
<th>Energy domain</th>
<th>Effort (e)</th>
<th>Flow (f)</th>
<th>Momentum (p)</th>
<th>Displacement (q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical</td>
<td>Voltage [V]</td>
<td>Current [A]</td>
<td>Flux linkage [Vs]</td>
<td>Charge [As] or [C]</td>
</tr>
<tr>
<td>Chemical</td>
<td>Chem.potential [J/mol]</td>
<td>Rate of reaction [mol/s]</td>
<td>-</td>
<td>Advancement of reaction [mol]</td>
</tr>
</tbody>
</table>

Considering different factors and levels of complexity, different models can be established.

In case of the simple battery model, it is just an electrical model where only the internal resistance of the battery is considered.

However, in case of intermediate and complex models, the bond graph structure represents the behaviour of the electrochemical cells in charging and discharging conditions, where electrochemical principles are considered in order to reflect the main phenomena that appear in the battery.

In the intermediate model, the battery is considered isothermal. While in the complex model, the thermal behaviour is also included.
3.2 Lithium-ion cells

3.2.1 Simple model

The basic model is represented by a simple voltage source which only includes the internal resistance of the battery.

The load voltage can be defined as:

\[ e_L = e_S - R \cdot i \]  \hspace{1cm} (6)

In order to develop a more accurate model some modifications were performed (Fig.7)

Where, from left to right:
- Current square-wave generator represents the AC waveform.
- \( Se \) represents voltage source.
- \( R \) represents the internal resistance.
- \( C \) represents the battery itself.
- \( R \) represents the wiring that connects the battery to the load.
- \( I \) represents the load of a rotating machine.

![Bond graph model of a simple battery](source)

Figure 6 - Bond graph model of a simple battery (Pedersen and Engja, 2010)

![Bond graph model of a simple battery cell](source)

Figure 7 - Bond graph model of a simple battery cell
Manufacturers rate a battery by assigning a nominal voltage which follow an agreed convention. In the case of, Li-ion batteries the nominal voltage is 3.6V/cell. But some manufacturers rate their Li-ion cells as 3.7V or higher.

The fact is that there is a maximum upper range of 4.2V and a minimum lower range of 2.5V. The reason behind this range is that if the cell is discharged below the 2.5V level, the cycle life could be reduced; and if the cell is discharged below 1V, the cell would not be recoverable and should be discarded. (Corvus, 2012) At the same time, as it was stated before, if the cell is overcharged up to 5.2V, cobalt oxide will be formed.

Therefore, to minimize all these risks the voltage should be kept in a range of 2.5 - 4.2 V/cell.

3.2.1.1 Implementation of the simple model

As a consequence of the stated above, the following data is used to run the simulation:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se (V)</td>
<td>4.75</td>
</tr>
<tr>
<td>R (Ω)</td>
<td>0.00711</td>
</tr>
<tr>
<td>C (F)</td>
<td>9000</td>
</tr>
<tr>
<td>R (Ω)</td>
<td>0.0552</td>
</tr>
<tr>
<td>I (µH)</td>
<td>9100</td>
</tr>
</tbody>
</table>

- Se value is stated in order to get the maximum voltage within the established range.
Bond Graph Modelling of a Li-ion Cell

- R value is calculated from the data sheet from (Corvus Energy, 2012) as follow: \( E = V \times C = 44.4 \times 150 = 6.66 \text{kWh} \)
  
  The difference between this value and the one given in the data sheet (6.5 kWh) is 0.16 kWh (160 Wh). Applying Ohm law, \( V = I \times R \), the resistance can be calculated: \( E = C^2 \times R \), where 160 = 150^2 \times R; therefore, \( R = 7.11 \times 10^{-3} \Omega \).

- C value is stated after performing several trials, being this value the one that gives the best result.

- R value is given by Fig. 12 in (Ménard et al, 2010).

- I value is stated after performing several trials using standard inductor values and being the chosen value the biggest one among those standard values.

3.2.1.1.1 Results

In this case, the voltage is the maximum established by the range, 4.2 V. While the capacity is higher than in the other two cases due to the lack of losses introduced by the complexity of a chemical reaction.

The current square-wave source gives automatically charging and discharging outputs.

![Figure 8 - Simple battery cell voltage response [V]](image-url)
3.2.2 Isothermal model

In order to develop the model of a battery some phenomenon must be considered. Typically in an electrochemical device the following phenomena are exhibited: activation, conduction and diffusion. Moreover, the dynamic effect of the electrochemical double layer and the particular behavior in a battery related to internal chemical energy storage have to be considered. This model is fully developed in (Ménard et al, 2010).

The assumptions made for this model are the following:

1. Every phenomenon is represented by its energy effect at a macroscopic level.
2. The proposed model is described by a single equivalent undissociated electrode; indeed only the contribution of both electrodes can be measured, the contribution of each electrode cannot be separately evaluated.
3. Potential parasitic reactions are not considered.
4. The proposed model is a constant temperature one.
5. Battery ageing is not mentioned in the modeling.

3.2.2.1 Theoretical approach of the isothermal model

3.2.2.1.1 Electrochemical conversion and energy storage

*Electrochemical conversion*

The OCV between two electrodes of a battery is also called electromotive force. The OCV depends on the state of charge (the energy stored in the battery). This dependence relation is expressed by the electrochemical field and using thermodynamical laws.

Considering the second law of thermodynamics:

\[ \Delta G = \Delta H - T \cdot \Delta S \] (7)

Where, \( \Delta H \) is the global chemical energy released during the reaction and could be entirely recovered, but only in heat form. \( T \cdot \Delta S \) is the heat produced during the reaction. Therefore, only the so-called free enthalpy \( \Delta G \) can be converted into work, in this case, in electrical energy. This free enthalpy variation is also a chemical potential. \( \Delta H \) and \( \Delta S \) are considered independent of the temperature.

Hence, the ideal instantaneous power conversion from electrochemical to electrical power can be modelled by the expression of both energies.

\[ E = - \frac{\Delta G}{nF} \] (8)

\[ I = nFJ \] (9)

where \( E \) is the battery OCV, \( n \) is the number of electron moles exchange per mole of lithium ions, \( F \) is the Faraday constant, \( I \) is the current of the battery and \( J \) is the molar flow of lithium ions.
Observing the equations (8) and (9), it is clear that the conversion can be made by a transformer element.

\[ -\Delta G |_{J} \stackrel{nF}{\Rightarrow} \Delta G |_{I} \]

Figure 6 - Conversion between chemical and electrical domains

This relation clearly shows that the chemical potential, \( \Delta G \), is directly converted into electrical potential, \( E \), using a transformer ratio equal to \( nF \).

**Energy storage**

In a battery, the chemical potential, \( \Delta G \), also depends on the energy stored in the battery. Therefore, \( \Delta G \) can be expressed as the sum of two terms, a reference enthalpy variation and an available amount of chemical stored free energy.

\[ \Delta G = \Delta G^0 + \Delta G_{\text{storage}} \quad (10) \]

Where the reference enthalpy at \( T = 298 \, \text{K} \) is expressed as:

\[ \Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (11) \]

And \( \Delta G_{\text{storage}} \) is the chemical potential available, which is related to the amount of lithium ions stored in the electrodes. To express this relation, Nernst equation is used.

\[ \Delta G_{\text{storage}} = -RT \cdot \ln \left( \frac{(n_{\text{tot}}-n)^a}{(n+n_{\text{el}})^b} \right) \quad (12) \]

where, \( R \) is the molar ideal gas constant, \( n_{\text{tot}} \) is the total quantity of lithium in the battery, \( n \) is the consumed quantity of lithium ions, \( n_{\text{el}} \) is the initial quantity of lithium in the electrolyte and \( a \) and \( b \) are empirical coefficients to consider the activity contribution of the different species involved in the reaction.

As stated in equation 5, the chemical potential is the sum of the two terms specified above. Since, \( \Delta G_{\text{storage}} \) represents a lithium storage, it is considered a C-element; while, the reference enthalpy can be considered as a constant. Therefore, the bond graph model including energy storage is as follow:
3.2.2.1.2 Activation and electrochemical double-layer phenomena

Activation phenomenon takes place at the electrode-electrolyte interface and is related to the electrochemical reaction (Fig. 13). These phenomena can be described by the Butler-Volmer law (8), which links the voltage drop $\eta$ with the electron transfer current $I_t$.

$$X \xrightarrow{\text{oxidation}} X^+ + e^- \quad \xleftarrow{\text{reduction}}$$

![Chemical reaction taking place at the interface electrode-electrolyte](image)

Where $I_t = I_0^0 \left[ \frac{[X]}{[X]_0} \right] e^{-\left( \frac{\alpha F}{RT} \right)} - I_0^0 \left[ \frac{[X^+]}{[X^+]_0} \right] e^{-\left( \frac{(1-\alpha) F}{RT} \right)}$ (13)

The reducing and oxidizing species concentrations at the beginning of the diffusion layer can also be considered, $[X]_{SOC}$ and $[X^+]_{SOC}$ (14).

$$I_t = I_0^0 \left[ \frac{[X]}{[X]_{SOC}} \right] e^{-\left( \frac{\alpha F}{RT} \right)} - I_0^0 \left[ \frac{[X^+]}{[X^+]_{SOC}} \right] e^{-\left( \frac{(1-\alpha) F}{RT} \right)}$$

Where $I_0^0 \left[ \frac{[X]}{[X]_{SOC}} \right]$ and $I_0^0 \left[ \frac{[X^+]}{[X^+]_{SOC}} \right]$ are associated to the activation phenomenon, while $\left[ \frac{[X]_{SOC}}{[X]_0} \right]$ and $\left[ \frac{[X^+]_{SOC}}{[X^+]_0} \right]$ are associated to diffusion phenomenon.
Bond Graph Modelling of a Li-ion Cell

But in the case of a Li-ion battery, electron transfer phenomenon is kinetically reversible as the ion diffusion speed is much lower than the ion consumption speed.

This is the reason why Tafel law is used instead of Butler-Volmer law. Additionally, assuming that the model is described by a single undissociated electrode as the oxidizing and the reducing reactions are symmetrical, the Tafel law is stated as follows:

\[ \eta = \frac{RT}{\alpha F} \ln \frac{l_1}{l_0} - \frac{RT}{\alpha F} \ln \frac{[X]_{SOC}}{[X]_0} \]  

(15)

Where \( l_0 \) is defined as:

\[ l_0 = l_0^b \left( \frac{n_{tot} - n}{n_{tot}} \right) \]

(16)

Where \( n_{tot} \) is the total quantity of ions in the battery and \( n \) is the consumed quantity of lithium ions at any moment.

Two voltage drop are considered, a voltage drop due to activation phenomenon and a voltage drop due to diffusion phenomenon.

\[ \eta = \eta_{act} + \eta_{diff} \]

(17)

With \( \eta_{act} = \frac{RT}{\alpha F} \ln \frac{l_1}{l_0} \) and \( \eta_{diff} = \frac{RT}{\alpha F} \ln \frac{[X]_{SOC}}{[X]_0} \)

Furthermore, experimental results show that activation phenomenon is linear as function of the current. Therefore, it can be modeled as a dissipative element, \( R_{act} \).

\[ R_{act} = \frac{\eta_{act}}{l_1} = \frac{RT}{\alpha F l_0} \]

(18)

The electrochemical double layer phenomenon is a dynamic phenomenon combined with the activation phenomenon.

During the operation of the battery, electrons pile up on the electrode side and lithium ions pile up on the electrolyte side. Two different conductive areas are in contact, which creates a Helmholtz layer, equivalent to an electrical capacitor; therefore, it is called electrochemical double-layer capacitor, \( C_{dl} \).
As this double-layer capacitor stores energy, it is responsible for fast dynamics in the battery and the dynamic output voltage $E - \eta_{\text{act}}$ is imposed by the instantaneous state of charge of this double-layer capacitor.

3.2.2.1.3 Ohmic phenomena

Ohmic losses are related to electric conduction phenomenon, which take place in all conductors and interfacial contacts of the battery. They are typically represented as resistances.

The resistance of the electrolyte seems higher than the other ones. In fact, the ions that flow through the electrolyte have less mobility than the electrons of the external electric
Bond Graph Modelling of a Li-ion Cell

circuit. This phenomenon causes a voltage drop $\eta_{\text{elec}}$ in the case of a battery discharge, proportionate to the current. Therefore, it can be modeled as a dissipative element, $R_{\text{elec}}$.

![Bond graph model including ohmic phenomena modeling](image)

Figure 11 - Bond graph model including ohmic phenomena modeling

3.2.2.1.4 Diffusion phenomena

Insertion materials used in Li-ion batteries are porous electrodes into which lithium ions diffuse causing energy dissipation. In case of lithium ions, this diffusion is not uniform.

![Lithium distribution in the electrodes during a discharge](image)

Figure 12 - Lithium distribution in the electrodes during a discharge

As seen in (16), diffusion phenomenon generate a voltage drop $\eta_{\text{diff}}$ towards the OCV. This voltage drop evolves over time with very slow dynamics. This phenomenon is generally called relaxation phenomenon in the case of an open-circuit battery.

The diffusion term can be expressed by the Fick diffusion law in the diffusion layer.

$$\frac{[X]_{\text{SOC}}}{[X]_0} = 1 - \frac{I}{I_{\text{lim}}}$$  \hspace{1cm} (18)

Where $I_{\text{lim}}$ is the diffusion current limit, which can be linked to the consumed quantities of lithium, $I_{\text{lim}} = k(n_{\text{tot}} - n)$.  

25
Assuming in (11) that $I_{\text{lim}}$ is much greater than $I_t$, the resistance $R_{\text{diff}}$ can link the voltage drop $\eta_{\text{diff}}$ to the current $I_t$.

\[
R_{\text{diff}} = \frac{\eta_{\text{diff}}}{I_t} = \frac{R T}{\alpha F I_{\text{lim}}}
\]

(19)

Slow diffusion dynamics are modeled by a C element called $C_{\text{diff}}$, while the losses are modeled by a dissipative element R called $R_{\text{diff}}$. As these diffusion phenomena are related to a matter storage behavior, they are located in the chemical field of the model.

![Figure 13 - Isothermal bond graph model of a lithium-ion battery](image)

### 3.2.2.2 Implementation of the isothermal model

In order to adapt the model developed by (Ménard et al, 2010) some modifications were performed. With the purpose of identify each energy domain, the chemical domain is in black color, while the electrical is in red.
Bond Graph Modelling of a Li-ion Cell

Figure 14 - Bond graph model of an isothermal battery cell
### Table 6 - Isothermal Li-ion battery cell bond graph model parameters

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Parameter (Unit)</th>
<th>Represents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy storage</strong> (3.3.1.1)</td>
<td>ΔH(^0) (J/mol)</td>
<td>Reference enthalpy variation</td>
</tr>
<tr>
<td></td>
<td>ΔS(^0) (J/K.mol)</td>
<td>Reference entropy variation</td>
</tr>
<tr>
<td></td>
<td>n(_{el}) (mol)</td>
<td>Initial quantity of li-ions in the electrolyte</td>
</tr>
<tr>
<td></td>
<td>n(_{tot}) (mol)</td>
<td>Total quantity of li-ions in the battery</td>
</tr>
<tr>
<td></td>
<td>R (J/K.mol)</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td></td>
<td>T (K)</td>
<td>Reference temperature</td>
</tr>
<tr>
<td><strong>Electrochemical conversion</strong> (3.3.1.1)</td>
<td>n (mol)</td>
<td>Number of electron moles exchanged for one mole of lithium ions</td>
</tr>
<tr>
<td></td>
<td>F (As/mol)</td>
<td>Faraday constant</td>
</tr>
<tr>
<td><strong>Activation and double layer</strong> (3.3.1.2)</td>
<td>(I_0^{act}) (A)</td>
<td>Activation current for fully charged battery</td>
</tr>
<tr>
<td></td>
<td>(\alpha)</td>
<td>Transfer coefficient</td>
</tr>
<tr>
<td></td>
<td>C(_{dl}) (F)</td>
<td>Double - layer capacity</td>
</tr>
<tr>
<td><strong>Ohmic</strong> (3.3.1.3)</td>
<td>R(_{elec}) (Ω)</td>
<td>Electrolyte resistance</td>
</tr>
<tr>
<td><strong>Diffusion</strong> (3.3.1.4)</td>
<td>k (A/mol)</td>
<td>Empirical coeff linked to the diff current limit</td>
</tr>
<tr>
<td></td>
<td>C(_{diff}) (F)</td>
<td>Capacitor modeling diffusion phenomena</td>
</tr>
</tbody>
</table>
# Bond Graph Modelling of a Li-ion Cell

## Table 7 - Implementation data for isothermal battery cell model

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy storage</strong></td>
<td>( \Delta H^0 ) (J/mol)</td>
<td>-278000</td>
</tr>
<tr>
<td></td>
<td>( \Delta S^0 ) (J/K.mol)</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>( n_{el} ) (mol)</td>
<td>0.08644</td>
</tr>
<tr>
<td></td>
<td>( n_{tot} ) (mol)</td>
<td>0.86443</td>
</tr>
<tr>
<td></td>
<td>( R ) (J/K.mol)</td>
<td>8.3144</td>
</tr>
<tr>
<td></td>
<td>( T ) (K)</td>
<td>298</td>
</tr>
<tr>
<td><strong>Electrochemical conversion</strong></td>
<td>( n ) (mol)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>( F ) (As/mol)</td>
<td>96485.34</td>
</tr>
<tr>
<td><strong>Activation and double layer</strong></td>
<td>( i_{0\text{act}} ) (A)</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>( C_{\text{dl}} ) (F)</td>
<td>9000</td>
</tr>
<tr>
<td><strong>Ohmic</strong></td>
<td>( R_{\text{elec}} ) ((\Omega))</td>
<td>0.0552</td>
</tr>
<tr>
<td><strong>Diffusion</strong></td>
<td>( k ) (A/mol)</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>( C_{\text{diff}} ) (F)</td>
<td>9000</td>
</tr>
</tbody>
</table>

The reasons behind the chosen data stated above are:

- **Energy storage phenomena**
  - \( \Delta H^0 \) and \( \Delta S^0 \): reference values for lithium
  - \( n_{el} \): 10% of the total quantity of lithium ions
Bond Graph Modelling of a Li-ion Cell

- \( n_{\text{tot}} \): according to the International regulations regarding transportation of dangerous goods, an Equivalent Lithium Content (ELC) can be calculated by the rated capacity (Ah) x 0.3, obtaining the mass of lithium in grams. Therefore, the typical rated capacity of a cell is 20 Ah (Muratori, 2009) gives 6 gr; applying this value to the equation below, the number of moles can be easily determined:

\[
 n = \frac{m}{M_w} \quad (20)
\]

where, \( m = 6 \ \text{gr} \)

\[
 M_w_{\text{Lithium}} = 6.941 \text{gr/mol}
\]

- Electrochemical conversion phenomena
  - \( n \): as it is stated in (2.3.1) equations (2) and (3), the number of electron moles exchanged for one mole of lithium ions is 1.

- Activation and double layer phenomena
  - \( I_{\text{act}} \): value used in the simple model given by (Corvus Precautions and Safety, 2012).
  - \( C_{\text{dl}} \): value used in the simple model and stated after performing several trials.

- Ohmnic phenomena
  - \( R_{\text{elec}} \): value given by (Ménard et al, 2010 – Fig.12).

- Diffusion phenomena
  - \( k \): value stated after performing several trials. This value gives the best results, which means higher voltage output and more stable response.
  - \( C_{\text{diff}} \): value used in the simple model and stated after performing several trials.

- Global data
  - \( R \): ideal gas constant.
  - \( T \): reference temperature given by (Ménard et al, 2010).
  - \( F \): Faraday constant.
  - \( \alpha \): value given by (Ménard et al, 2010)
Bond Graph Modelling of a Li-ion Cell

- \( I \): value used in the simple model and stated after performing several trials using standard inductor values.

### 3.2.2.2.1 Results

In this case the voltage and the capacity are lower than in the simple model due to the losses related to the chemical phenomena.

![Figure 15 - Isothermal battery cell voltage response [V]](image)

![Figure 16 - Isothermal battery cell charge response [As]](image)
3.2.3 Thermal model

The greater specific power and energy content of Li-ion batteries allow overcoming limitations in meeting the power demands typical of Ni-MH batteries. Moreover they are able to withstand a wider range of temperatures. (Muratori, 2009)

Since the performance, life and reliability of Li-Ion batteries are quite dependent on the operating temperature, great interest has been devoted to study cooling solutions and control algorithms for thermal management. (Muratori, 2009).

Detailed studies of the temperature distribution within Li-Ion battery cells have been proposed by several authors, which are extremely useful to gain understanding on how the temperature distribution affects the performance of a battery cell. (Muratori, 2009)

In order to develop the thermal model of a battery cell some specific phenomenon must be considered. The model developed in this thesis uses the isothermal model developed in (Ménard et al, 2010) as a basis, where RS dissipative elements are added and directly coupled replacing the R elements. Besides, other heat transfer processes are considered such as convection and thermal storage, represented as R and C elements respectively.

The assumptions made for this model are the following:

1. The heat transfer coefficient (h) and other thermal coefficients are assumed to be constant.
2. The heat generated is assumed to be homogeneously distributed within the cell.
3. The temperature is calculated within the cell, with no heat transfer through the cell walls.
4. A reference temperature of 20ºC (293 K) is considered.
5. No cooling systems are considered.
3.2.3.1 Temperature Effects

Heat is a major battery killer, either excess of it or lack of it, and Lithium secondary cells need careful temperature control. (MPowerUK, 2005)

1. Low temperature operation

Chemical reaction rates decrease in line with temperature. (Arrhenius Law) The effect of reducing the operating temperature is to reduce rate at which the active chemicals in the cell are transformed. This translates to a reduction in the current carrying capacity of the cell both for charging and discharging. In other words its power handling capacity is reduced. (MPowerUK, 2005)

2. High temperature operation

Operating at high temperatures brings on a different set of problems which can result in the destruction of the cell. In this case, the Arrhenius effect helps to get higher power out of the cell by increasing the reaction rate, but higher currents give rise to higher $I^2R$ heat dissipation and thus even higher temperatures. This can be the start of positive temperature feedback and unless heat is removed faster than it is generated the result will be thermal runaway. (MPowerUK, 2005)

- Thermal runaway

Several stages are involved in the build up to thermal runaway and each one results in progressively more permanent damage to the cell. (MPowerUK, 2005)

- The first stage is the breakdown of the thin passivation SEI (Solid Electrolyte Interface) layer on the anode, due to overheating or physical penetration. The initial overheating may be caused by excessive currents, overcharging or high external ambient temperature. The breakdown of the SEI layer starts at the relatively low temperature of $80^\circ\text{C}$ and once this layer is breached the electrolyte reacts with the carbon anode just as it did during the formation process but at a higher, uncontrolled, temperature. This is an exothermal reaction which drives the temperature up still further.
As the temperature builds up, heat from anode reaction causes the breakdown of the organic solvents used in the electrolyte releasing flammable hydrocarbon gases (Ethane, Methane and others) but no Oxygen. This typically starts at 110 ºC but with some electrolytes it can be as low as 70ºC. The gas generation due to the breakdown of the electrolyte causes pressure to build up inside the cell. Although the temperature increases to beyond the flashpoint of the gases released by the electrolyte the gases do not burn because there is no free Oxygen in the cell to sustain a fire. The cells are normally fitted with a safety vent which allows the controlled release of the gases to relieve the internal pressure in the cell avoiding the possibility of an uncontrolled rupture of the cell - otherwise known as an explosion or more euphemistically "rapid disassembly" of the cell. Once the hot gases are released to the atmosphere they can of course burn in the air.

At around 135 ºC the polymer separator melts, allowing the short circuits between the electrodes.

Eventually heat from the electrolyte breakdown causes breakdown of the metal oxide cathode material releasing Oxygen which enables burning of both the electrolyte and the gases inside the cell. The breakdown of the cathode is also highly exothermic sending the temperature and pressure even higher. The cathode breakdown starts at around 200 ºC for Lithium Cobalt Oxide cells but at higher temperatures for other cathode chemistries.
The performance of Lithium Ion cells is dependent on both the temperature and the operating voltage. The diagram below shows that, at all times, the cell operating voltage and temperature must be kept within the limits indicated. Once outside those limits permanent damage to the cell will be initiated.

![Li-ion cell Operating Window](image)

Figure 17 - Li-ion cell Operating Window (MPowerUK, 2005)

3.2.3.2 Implementation of the thermal model

Some modifications, respect to the previous model, were executed in order to be able to calculate the temperature of the cell during the cell performance. As it was done before, with the purpose of identify each energy domain, the chemical domain is in black color, while the electrical is in red and thermal in yellow.
Bond Graph Modelling of a Li-ion Cell

Figure 18 - Bond graph model of an thermal battery cell
The parameters used in this model are the same as the ones used in the isothermal model plus the ones related to the thermal domain, which are included in the tables below.

Table 8 - Thermal Li-ion battery cell bond graph model parameters

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Parameter (Unit)</th>
<th>Represents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissipation (RS)</td>
<td>R (ºK/W)</td>
<td>Thermal resistance</td>
</tr>
<tr>
<td>Convection (R)</td>
<td>h (W/m²K)</td>
<td>Heat transfer coefficient</td>
</tr>
<tr>
<td></td>
<td>A (m²)</td>
<td>Surface area</td>
</tr>
<tr>
<td>Thermal storage element (C)</td>
<td>m (g)</td>
<td>Mass</td>
</tr>
<tr>
<td></td>
<td>c₉ (J/gK)</td>
<td>Specific heat at constant volume</td>
</tr>
</tbody>
</table>

Table 9 - Implementation data for thermal battery cell model

<table>
<thead>
<tr>
<th>Phenomenon</th>
<th>Parameter (Unit)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissipation (RS)</td>
<td>R (ºK/W)</td>
<td>0.0552</td>
</tr>
<tr>
<td></td>
<td>h (W/m²K)</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>A (m²)</td>
<td>0.02785</td>
</tr>
<tr>
<td>Convection (R)</td>
<td>m (g)</td>
<td>425</td>
</tr>
<tr>
<td>Thermal storage element (C)</td>
<td>c₉ (J/gK)</td>
<td>795</td>
</tr>
</tbody>
</table>
The data chosen for the thermal domain implementation belong to (Muratori, 2009), where the surface area is calculated from the width and height (129 x 216 mm) of the chosen cell as an example, while weight and heat transfer coefficient are directly given.

In case of the specific heat ($c_v$), the value is given by several papers related to thermal characterization of Li-ion batteries (Muratori, 2009; Pesaran and Keyserm 2001; Maleki et al, 1999).

3.2.3.2.1 Results

During the operation of the cell, heat is generated due to the $I^2R$ losses through the internal resistance (Joule heating). Besides, the chemical reactions are dependent on the temperature; therefore, the maximum value for voltage and capacity are the same as in the isothermal model but are achieved slower due to heat dissipation.

Figure 19 - Thermal battery cell voltage response [V]
The effects of voltage and temperature on cell failures tend to be immediately apparent, but their effect on cycle life is less obvious. We have seen before (3.2.3.1) that operations outside of the recommended operating window can cause irreversible capacity loss in the cells. (MPowerUK, 2005)
The graph above shows that, starting at about 15 °C, cycle life will be progressively reduced by working at lower temperatures. Operating slightly above 50 °C, also reduces cycle life; but by 70 °C, the threat is thermal runaway. The battery thermal management system must be designed to keep the cell operating within this range. (MPowerUK, 2005)

According to the information stated in Fig.22, the operation temperature obtained in the simulation (40°C + 20°C (reference) = 60°C) is within the cell operating range. Therefore, there is no threat for the cell cycle life.

Figure 22 – Cycle Life vs Temperature in a Li-ion Cell (MPowerUK, 2005)
Chapter 4  Bond Graph Modelling of a Li-ion battery

The goal of this chapter is to develop a Li-ion battery pack connecting the Li-ion cell models developed in the previous chapter in series and parallel. As it was performed before, three complexity levels are set up: simple, isothermal and thermal.

The objective is to obtain similar outputs to the ones given in (Corvus Energy, 2010)

Table 10 - Corvus Energy Data Sheet AT6500 (Corvus Energy, 2010)

<table>
<thead>
<tr>
<th>Specification</th>
<th>AT5800-250-24-5M</th>
<th>AT6500-250-48*</th>
<th>AT6500-125-96*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technology</td>
<td>Lithium NMC</td>
<td>Lithium NMC</td>
<td>Lithium NMC</td>
</tr>
<tr>
<td>Maximum Voltage</td>
<td>29.4V</td>
<td>56.4V</td>
<td>100.8V</td>
</tr>
<tr>
<td>Nominal Voltage</td>
<td>35.6V</td>
<td>44.4V</td>
<td>88.8V</td>
</tr>
<tr>
<td>Minimum Voltage</td>
<td>18.6V</td>
<td>32.4V</td>
<td>64.8V</td>
</tr>
<tr>
<td>Capacity</td>
<td>225Ah</td>
<td>150Ah</td>
<td>75Ah</td>
</tr>
<tr>
<td>Continuous Current</td>
<td>250A</td>
<td>250A</td>
<td>125A</td>
</tr>
<tr>
<td>Energy</td>
<td>5.8Wh</td>
<td>6.5Wh</td>
<td>6.5Wh</td>
</tr>
</tbody>
</table>

The unit conversion of data from the Data Sheet from Corvus Energy is:

- Voltage = 44.4 V
- Capacity = 150 Ah = 540,000 As
- Power = 6.5 kWh = 2.34 \times 10^7 Ws

4.1 Simple Li-ion battery

In the case of the simple level, a connection of five (5) branches in parallel with two (2) cells in series on each branch is implemented. On the left side of the battery, the voltage source and its internal resistance is represented; while the load is represented on the right side.

As it was stated in the Simple Li-ion cell development, the internal resistance regarding the voltage source was calculated from the data sheet in (Corvus Energy, 2010) with a
value of $7.11 \cdot 10^{-3} \Omega$. While the wire resistance of the load was given by (Ménard et al, 2010) and has a value of $0.0552 \Omega$.

![Figure 23 – Simple Li-ion battery pack model](image)

In Fig. 24, both parallel and series connections (that belong to the first two rows of Fig.23) are clearly shown. The Sf element is not acting as a source itself, it is just used to set up the parameter regarding the amperage increase (that should be 75 A per cell (Corvus Energy, 2010)) and belongs to the parallel connection.

![Figure 24 – Simple Li-ion battery pack model connections](image)

4.1.1 Results

The results plotted show how the battery is charging in the beginning; and afterwards, it is kept charging with the load connected. Therefore, the maximum value is kept constantly. The AC current gives the square wave form.
Bond Graph Modelling of a Li-ion Battery

Figure 26 - Simple Li-ion battery pack capacity response [As]

Figure 25 – Simple Li-ion battery pack voltage response [V]

Figure 27 - Simple Li-ion battery pack power response [Ws]
4.2 Isothermal Li-ion battery

In case of the isothermal model, a connection of six (6) branches in parallel with two (2) cells in series on each branch is employed. As it was stated in previously, the source is on the left side of the model, being in this case a chemical potential source. While the load is kept on the right side.

![Diagram of Isothermal Li-ion battery pack model]

Figure 28 – Isothermal Li-ion battery pack model

In Fig. 29, both parallel and series connections (that belong to the first two rows of Fig.28) are shown. As in the previous model, the Sf element is not acting as a source itself, it is just used to set up the parameter required to increase the amperage.

The difference between the chemical and the electrical part it is shown by the colours of the bonds, being the chemical part represented in black and the electrical represented in red.

![Diagram of Isothermal Li-ion battery pack model connections]

Figure 29 – Isothermal Li-ion battery pack model connections

4.2.1 Results

Some problems were found in the capacity response since an output that was increasing linearly was generated. This problem may be caused by the model linearization. Therefore, a sentence setting a maximum value of 540.000 As was included.
Bond Graph Modelling of a Li-ion Battery

Figure 32 - Isothermal Li-ion battery pack capacity response [A\text{s}]

Figure 31 - Isothermal Li-ion battery pack voltage response [V]

Figure 30 - Isothermal Li-ion battery pack power response [W\text{s}]
4.3 Thermal Li-ion battery

In case of the thermal model, a connection of eleven (11) branches in parallel with two (2) cells in series on each branch is implemented.

![Figure 33 – Thermal Li-ion battery pack model](image)

As it was stated in the thermal li-ion cell, the losses due to the heat release reduce the value of the outputs; therefore, a bigger number of parallel branches than in the previous cases is required.

In Fig. 34, the connections in series and parallel are shown. In this case, each domain is also identified by different colors; being the black, the chemical domain; the red, the electrical domain; and the yellow, the thermal domain.

![Figure 34 – Thermal Li-ion battery pack model connections](image)
4.3.1 Results

Figure 35 - Thermal Li-ion battery pack voltage response [V]

Figure 36 - Thermal Li-ion battery pack capacity response [As]

Figure 37 - Thermal Li-ion battery pack power response [Ws]
In this case, the model does not present any problem and the simulation is performed perfectly.

Since the heat release is mainly produced by the losses through the thermal resistance $I^2R$ (Joule heating), the temperature is directly related to the current drawn into the system. Therefore in this model, the temperature is bigger than in the cell model and has a total value of $73.8^\circ C$ (considering the reference temperature of $20^\circ C$). It should be kept in consideration that in this model no cooling is assumed.
Chapter 5   Conclusion and Further work

Within this master thesis six models were developed. At first for a single cell, at three complexity levels, and then for complete battery packs based on each type of single cell.

A summary of the results achieved in the battery packs is shown in the table below:

Table 11 - Li-ion battery packs results

<table>
<thead>
<tr>
<th>Model</th>
<th>Voltage [V]</th>
<th>Capacity [As]</th>
<th>Power [Ws]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Sheet Corvus</td>
<td>44,4</td>
<td>540,000</td>
<td>2,34.10+7</td>
</tr>
<tr>
<td>Simple</td>
<td>41,4</td>
<td>372,500</td>
<td>1,54. 10+7</td>
</tr>
<tr>
<td>Isothermal</td>
<td>41,3</td>
<td>540,000</td>
<td>2,23. 10+7</td>
</tr>
<tr>
<td>Thermal</td>
<td>41,8</td>
<td>376,304</td>
<td>1,57. 10+7</td>
</tr>
</tbody>
</table>

The results obtained do not match perfectly due to the complexity behind the chemical reactions involved. It would have been necessary to measure the parameters required in the models in the Corvus Li-ion battery pack used as a reference, in order to obtain more accurate results.

Therefore in the future, a series of laboratory tests should be carried out in order to establish a comparison between the data obtained using the models and the data obtained from the tests, so the precision of the models can be increased.

Another series of tests using a hybrid propulsion system should be performed as well to give the possibility to study the interactions between the systems involved in a complete power plant.
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