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Research and characterization of battery typologies for railway applications



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Abstract

The present work of thesis was developed thanks to the initiative of Blue Engineering & Design, a design company headquartered in Rivoli (TO) with long term experience in automotive, railway and aerospace fields, and to the availability of the relator prof. Massimo Santarelli and the coordinator Ing. Arpit Maheshwari.

The project consists of teamwork to study the utilization of batteries for railway applications. This work will focus especially on the research and the characterization of battery types for railway application, on the identification of specific parameters and on the comparison between different suitable types of batteries.

The study of the topic is integrated with the theses of the other team members, Fabio Nasca and Laura Scandura, about the thermal analysis of the battery and the optimization of the thermal management system of the battery pack.

Chapter 1 shows the energetic panorama and why the energy transition towards more clean and renewable energies is needed. Then, the main Energy Storage Systems (ESS) and their applications in each field of transportation sector are described.

Chapter 2 provides a global vision of the battery market and a short summary about the commercialization and the progression of the batteries during the years. Additionally, various battery types are described briefly.

Chapter 3 lists the aspects which make battery more attractive than other EESs.

Chapter 4 explains the structure and the theoretical functioning of a battery.

Chapter 5 helps to understand the main parameters characterizing a battery.

Chapter 6 focuses the attention in Li-ion batteries, explaining why it is more used than other ones and describes the main chemistries composing electrodes and electrolyte.

Chapter 7 introduces a presentation of the functioning of the main application of the thesis: electric and hybrid vehicles with a deepened overlook on diesel-electric hybrid railway system.

Chapter 8 studies the feasibility of different batteries typologies for a Diesel Multiple Unit (DMU) developed by Blue Group firm. By means of substitution of the battery pack in place of one of the four diesel-generators, the vehicle can operate in a wider range of tracks such as underground sections and non-electrified urban stations, obtaining a strong reduction of particulate and pollutant emissions in that critical areas. The design study compares the data of different battery typologies with the energy requested by the DMU in order to find the main parameters of the batteries that support the application.

Chapter 9 explains the difficulties in using batteries as the degradation and the capacity loss and illustrates the future battery technologies under development.

In conclusion, installation of the on-board energy storage system in the existing vehicle allows to operate in catenary-free operation mode, to reduce visual pollution and to reduce energy consumption (up to 30% energy saving).

1. Introduction

Energy is the most common consumer good and comes in various form, although it can be broadly classified into two: primary and secondary.

Primary energy is defined as fuels and flows harvested directly from natural resources by extraction or capture. They include all energy forms which have not been converted in heat or mechanical work. Typical instances are oil, coal, biomass, geothermal, natural gas, etc.

Secondary energy derives from the transformation of primary energy sources. They are also known as Energy Carriers (EC). Examples are petrol, electricity, hydrogen, gasoline, diesel, etc. [1]

Industrial sector (agriculture, mines, manufactures, construction) consumes 37% of total 15 TW per year, estimated as energy consumed in 2004. Public and private transport sector consumes more or less the 20%; residential sector (space heating, lighting and appliances) use 11%; commercial sector uses only 5% of the total. [2] This is shown in *Fig. 1.1*.



Fig. 1.1 - World energy consumptions for sector - Source: [28]

It is undeniable that human activities are abusing these resources, impacting Earth's health. In fact, CO_2 levels have overstepped 400 ppm and, considering other significant greenhouse gases (GHGs) like CH₄, N₂O and fluorinated gases, the total CO₂ equivalent (CO_{2, eq}) concentration is higher than 480 ppm. [3]

Fig. 1.2 shows the increasing trend of the CO_2 concentration during the last millennium. The proof of the "human guilt" could be seen by the constant level until 1769, year in which the steam locomotive was invented and the Industrial Revolution occurred.



Fig. 1.2 - Exponential increase of CO₂ concentration in atmosphere - Source: [4]

This phenomenon is causing worrisome effects, firstly the increase of the global mean temperature, as illustrated in *Fig. 1.3*.



Fig. 1.3 - Observed change in surface temperature [1901-2012] - Source: [55]

According to scientists' estimation, human beings need to get off fossil fuel habit quickly in order to avoid a risk of giving the Earth a 2°C temperature rise. [4] A domino effect is arising

from it, the temperature rise causing ice dissolution, ice dissolution leading to sea level rise, etc. These reasons and others like population growth, negative environmental effects (global warming, ozone layer depletion, pollution, etc.) and rapid depletion of fossil fuels have resulted into the need for a more efficient and clean transportation system.

1.1 Energy Storage Systems

Most systems suffer energy losses in form of heat, usually to the environment and these wastes could be stored and recycled as resources for other processes. As a result of this, the use of energy storage systems (ESSs) helps to plug the leakages and improve the efficiency of the system, becoming an important technique towards the renewable energy transition. There are many types of ESS: *Fig. 1.4* shows the complete technologies classification.



Fig. 1.4 - Energy storage technologies classification - Source: [1]

The choice of the ESS for an application will depend on the application power and energy ratings, response time, weight, volume and operating temperature. This thesis is going to consider only electrochemical energy storage and only mention some other types. *Tab. 1* summarizes the characteristic parameters of the most used energy storage technologies.

	Flywheel	Supercapacitors	Fuel Cell	Batteries
Specific Energy	5-30 Wh/kg	2.5-15 Wh/kg	250-800 Wh/kg	20-240 Wh/kg
Power density	400-1500 W/kg	500-5000 W/kg	400+ W/kg	140-9000 W/kg
Efficiency	85-95%	90-95%	20-35%	70-90%
Cycle life	20000+	50000+	5000+	200-20000
Lifetime	~15 y	40 y	5-15 y	5-20 y
Capital cost	1000-5000 \$/kWh	300-2000 \$/kWh	15 \$/kWh	50-3000 \$/kWh

Tab. 1 - Characteristic parameters of different ESSs

In transport and grid application the main devices to store energy are:

- Batteries
- Electrostatic Double Layer Capacitors (EDLCs)
- Regenerative Fuel Cells (FC)
- Compressed Air Energy System (CAES)
- Flywheels
- Superconducting Magnetic Energy Storage (SMES)
- Thermal Energy Storage System (TESS)

1.1.1 Batteries

Batteries are closed electrochemical devices able to deliver energy, in the form of electrical energy, using the chemical energy generated by electrochemical reactions. They don't exchange mass with external environment, in fact reagents to the electrochemical reactions are the same materials that constitute the electrodes.

They are widespread EESs for power system applications. Apart from the electric grid, their energy storage application covers sectors such as hybrid electric vehicles (HEVs), marine and submarine missions, aerospace operation, portable electronic systems and wireless network systems.

1.1.2 Supercapacitors

Supercapacitors, also known Electrostatic Double Layer Capacitors (EDLCs), are electrochemical devices able to store energy in the electrochemical capacitor by simple separation charge. The two electrodes are separated by a porous membrane and immersed in an electrolyte such as propylene carbonate, so that the device could behave as an electrochemical battery too. The most important properties of EDLCs are long life cycles and high efficiencies, in contrast high cost and daily self-discharge rate don't allow to use them in large-scale and long-term applications. The supercapacitor voltage must change between 50% and 100% of its rated voltage through a dc/dc converter between the traction dc bus and the supercapacitor. In hybrid systems, supercapacitors are used together with other electric storage devices (e.g. Li-Ion) to provide with high specific power and high specific energy.



Fig. 1.5 - Supercapacitor - Source: [42]

1.1.3 Regenerative FCs

Unlike batteries, Fuel Cells are open electrochemical cells working in galvanic regime (Gibbs free energy $\Delta G < 0$).

FCs are Hydrogen Energy Storage Systems able to consume the chemical energy of the reactants (hydrogen and oxygen) in order to produce water and electricity.

They are classified depending on the material composing the electrolyte, which in turn determine the temperature range of operation:

$$\begin{array}{c} \mbox{UTFC} = \mbox{Low Temperature Fuel} \\ \mbox{Cell} \\ \mbox{HTFC} = \mbox{High Temperature Fuel} \\ \mbox{Cell} \\ \mbox{Too-800°C} \rightarrow \mbox{SOFC (Solid Oxide Fuel Cell)} \\ \mbox{600-650°C} \rightarrow \mbox{MSFC (Molten Salt Fuel Cell)} \\ \mbox{600-650°C} \rightarrow \mbox{MSFC (Molten Salt Fuel Cell)} \\ \mbox{300°C} \\ \mbox{250°C} \rightarrow \mbox{PAFC (Phosforic Acid Fuel Cell)} \\ \mbox{50-80°C} \rightarrow \mbox{PEMFC (Proton Exchange Membrane Fuel Cell)} \\ \mbox{50-80°C} \rightarrow \mbox{DMFC (Direct Methanol Fuel Cell)} \\ \mbox{Methanol Fuel Cell} \\ \mbox{Meth$$

Nowadays, SOFC are to be preferred because liquid electrolyte involves larger complexities, no corrosion occurs, efficiency is higher. Nevertheless, PEMFC dominate the market in term of stability and cost.

1.1.4 Flywheels

Flywheels are mechanical energy systems that stores electrical energy in a rotating mass coupled with motor/generator and brackets in the form of rotational kinetic energy. The electricity is used to accelerate or decelerate the flywheel that is, in discharge mode, the flywheel transfers the energy to the motor, while in charge mode, the energy returns to the flywheel. The amount of energy stored is proportional to the square of its rotational speed, that varies applying a torque aligned with its axis of symmetry. To eliminate the energy losses due to air friction, the rotor is contained in the vacuum vessel, to reduce friction losses flywheel uses magnetic and/ or hydrodynamic bearings. Flywheels are largely employed in traction

applications, especially electric rail, and as backup power/UPS.



Fig. 1.6 - Flywheel - Source: [1]

1.1.5 CAES

Although Compressed Air Energy Storages (CAES) are more known for large scale application in which the storage vessels are underground caverns, since 19th century air engines have been used to power mine locomotives.

Compression of air creates heat; the air is warmer after compression. Expansion removes heat. If no extra heat is added, the air will be much colder after expansion. If the heat generated during compression can be stored and used during expansion, the efficiency of the storage improves considerably.

Compression can be done with electrically powered turbo-compressors and expansion with turbo expanders or air engines driving electrical generators to produce electricity.

The storage system of a CAES (Compressed Air Energy Storage) is one of the most interesting characteristics of this technology, and it is strictly related to its economic feasibility, energy density and flexibility. There are a few categories of air storage vessels, based on the thermodynamic conditions of the storage, and on the technology chosen:

- Constant Volume Storage (Solution mined caverns, aboveground vessels, aquifers, automotive applications, etc.)
- Constant Pressure Storage (Underwater pressure vessels, Hybrid Pumped Hydro -Compressed Air Storage)

Recently, this alternative is propagating in cars, ships and hybrid vehicles.

1.2 ESS Applications

1.2.1 Automotive

The public transportation aims to provide the best possible service whilst minimizing the environmental impact.

Buses storing electricity are majorly battery based. Shenzhen, China, is the first city to complete the bus conversion to all electric. More than 200 of the buses of the city, named BYD K9s, are manufactured by the BYD Auto, that developed a LFP battery (540V, 600 Ah), characterized by 324 kWh of capacity and 3,2 V of cell voltage. [5]

However other storage modes exist, such as the gyrobus. An example is given by buses used by Oxford Bus Company. Their hybrid buses exploit an innovative system based on KERS (Kinetic Energy Recover System) until now only used in Formula 1. It recovers the heat lost from the braking and sends it to a flywheel, which runs at up 36.000 rpm. [6]



Fig. 1.7 - Electric Buses: BYD K9 (left), Oxford Hybrid Bus (right)

The car market distinguishes two different types of electric system:

• HYBRID

A hybrid electric vehicle (HEV) is a type of hybrid vehicle that combines a conventional internal combustion engine (ICE) system with an electric propulsion system.

Modern HEVs make use of efficiency-improving technologies such as regenerative brakes which convert the vehicle's kinetic energy to electric energy, which is stored in a battery or supercapacitor.

The hybrid market is dominated by Toyota, followed by Honda. The best-selling hybrid car is the Toyota Prius, fed with 1310 kWh NiMH batteries, composed by 28 modules and produced by Panasonic. Each battery module is made of 6 individual 1.2 V 6.5 Ah

prismatic cells in series forming a 7.2 V 6.5 Ah module with 46 Wh/kg energy density and 1.3 kW/kg output power density. [7]

Recently, Toyota is going to retire their old NiMH batteries to use Li-ion ones. In addition, Toyota is developing solid state batteries because they guarantee a higher energy density and an autonomy 50% higher than now.

Another energy storage system is adopted in Toyota Yaris Hybrid-R. It uses a combination of supercapacitor and motor-generator, in place of the battery pack, in order to avoid bursts of power. [8]



Fig. 1.8 - Toyota Prius

• PLUG-IN HYBRID

Differently from normal hybrid, this technology is composed by a battery rechargeable by plugging it into an external source of electric power, as well by its on-board engine and generator.

Obviously, the cost is higher than hybrid vehicles because of a larger battery pack system.

Nissan Leaf, Tesla Model S and Chevrolet Volt are the world's top selling plug-in electric cars. They are all fed with lithium-ion batteries characterized by different electrical ranges: respectively 24 kWh, 75 or 100 kWh and 18,6 kWh.



Fig. 1.9 - Plug-in Hybrid Vehicles: Tesla Model S (up), Nissan Leaf (left), Chevrolet Volt (right)

1.2.2 Railway

ESSs are largely diffused in recovering braking energy in railway transport, playing a key role in the combination of electric energy with diesel-driven vehicles to obtain hybrid system architectures. [9]

A railway electrification system supplies electric power to railway trains and trams without an on-board prime mover or local fuel supply.

Application-wise, the battery used in railway industry can be divided into two categories: onboard (OESS) and stationary (SESS) energy storage systems.

OESSs are those installed inside the train, while SESSs are installed along the track. As OESSs are used to store the recovered energy of only one train, the power and energy capacity required is lower than SESSs. Still, they should be able to satisfy the peak power generated during braking and the energy demand of the train itself (peak power of a train can be up to 24 MW). A typical EMU (Electric Multiple Unit) of 4 wagons and 200 tons can demand up to more than 1 MW. Other critical factors when selecting an on-board battery include the sizing of the device (especially when it comes to EMUs) and safety issues (especially on passenger trains).



Fig. 1.10 - ESSs Railway operating principle - Source: [11]

Batteries can be used on-board railway cars for three main purposes: energy consumption reduction, peak power reduction and catenary-free operation. Catenary-free operation is a type of operation in which a train with electric traction motor runs on a non-electrified line using the energy from an energy storage device. On-board energy storage devices are not always an economically nor technically a feasible option, especially when it comes to heavy haul trains. In such cases, SESSs can offer a better alternative. On one hand, a SESS, compared to an on-board one, should have a higher energy capacity; on the other hand, there's more freedom regarding the sizing of the system. A stationary storage system should have both high power and energy capacity together with a long charge/discharge life cycle. [10]

VYCON's REGEN is a SESS kinetic energy recycling system based on flywheel technology. It has been integrated in the Los Angeles Metro and it is characterized by an output power of 125 kW nominal, 10000 rpm to 25000 rpm of rotational speed and 15 seconds of recharge time. [11]

Kinetic Traction Systems (KTSi) GTR flywheels use a fully integrated, permanent magnet, DC motor/generator capturing, storing and regenerating energy. The KTSi proprietary flywheel design has already been used to provide clean traction power to subway trains in several of the world's leading metropolitan transit authorities, including NYC Transit, London Underground and Lyon Metro, France. The normal operating speed range of a unit is from 430 Hz to 630 Hz (25,800 to 37,800 RPM). Each system is capable of delivering 333 kW and more than 1000 charge-discharge cycles per day for 20 years with minimal maintenance. [12]



Fig. 1.11 - Railway flywheels: VYCON REGEN (left), KTSi GTR (right)

Other railway energy storage options are batteries and supercapacitors. Kawasaki Gigacell is a particular version of NiMH cell with the following specifications:

Nominal voltage (V)	36	
Rated Capacity (Ah) (*1)	150	
Energy capacity (kWh)	5.4	
Maximum output (kW)	0.1 sec	161
(*2)	10 sec	96
Outline dimensions (mm) L x W x H (*3)	1375×223×345	
Volume (L)	106	
Weight (kg)	240	
Energy density per unit volum	51	
Energy density per unit weigh	23	

Gigacell 204 kWh high capacity has been installed in Japan (Osaka Subway, Tokyo Monorail and Sapporo Subway) and verification tests have been performed in New York Subway and Washington D.C. Subway. [13]

Two big supercapacitors energy storage systems with a rating of 2.56 MW and 25 MJ were installed at Seibu Railway Co., Ltd., in Japan in 2007. [9]

The new BOMBARDIER EnerGstor wayside energy storage system is based on supercapacitor technology, which captures and stores the otherwise unusable regenerated braking energy and recycles it back into the system. The system design is scalable, with an energy capacity ranging from 0,25 to 5 kWh or more and network energy consumption is reduced by up to 20%. [14]



Fig. 1.12 - Kawasaki Gigacell battery (left), Bombardier EnerGstor supercapacitors (right) - Source: [13], [14]

1.2.3 Marine

Batteries are the main technologies used in marine applications. A 70 meters long massive cargo ship in China has been officially launched with a battery powertrain, equipped with two 160 kW electric propellers and a mix of supercapacitors and lithium batteries for a total energy capacity of 2.4 MWh: for comparison, it is equivalent to 24 battery packs in the Tesla Model S. [15]

The first 100% electric ferry-boat, named Ampère, has been developed by Siemens and it has two onboard 450 kW electric motors, powered by Li-ion batteries with an overall output of 1 MWh. The lithium-ion batteries are recharged during the 10min loading and unloading time of each trip from the charging stations located at each shore and directly from the local hydroelectric-powered grid at night. A 260-kWh battery is also located at each shore to supply power to the vessel while it recharges. [16]



Fig. 1.13 - Ampère electric ferry boat

Different types of lead-based technologies are applied for the manufacturing of submarine batteries in order to meet the various demands and sophisticated requirements in terms of energy, performance and reliability. Sunlight is ranked among the top global players in the design and production of batteries for all types of conventional submarines. More specifically, the following technologies are available:

- Long plate positive tubular plate / Negative plate lead
- Long plate positive tubular plate / Negative plate copper stretch metal (CSM)
- Double decker positive tubular plate / Negative plate lead
- Double decker positive tubular plate / Negative plate copper stretch metal (CSM)
- VRLA long plate (CSM) / Gel electrolyte Tailor-made cells: all the above-mentioned



Fig. 1.14 - Sunlight Submarine battery - Source: [17]

technologies can be adapted to meet the tactical demands of the submarines and meet specific requirements. [17]

1.2.4 Aviation

Electrification in aviation field is still not mature, but many projects are launched. Batteries are the most common energy carrier component of electric aircraft, although their weight still limits the range achievable. Global aircraft manufacturers plan to develop hybrid system and fully electric system by 2020 and 2050 respectively.

The size of an electric motor and battery system is getting smaller and lighter and there has been an international effort towards developing a hybrid system that requires only half of the current fuel consumption. An electric aircraft produces minimal noise and vibration. It has also lighter and simpler design compared to an internal combustion engine and allows convenient access for maintenance. [18]

Airbus, Rolls-Royce, and Siemens have formed a partnership which aims at developing a near-term flight demonstrator which will be a significant step forward in hybrid-electric propulsion for commercial aircraft. [19] The E-Fan X hybrid-electric technology demonstrator is anticipated to fly in 2020 and will be powered by two 2MW electric motors integrated with batteries.

Kokam Co. designed its Li-polymer batteries for the Solar Impulse project, that is the first solar panel powered aircraft to be flown at night with a man on board and travel 40'000 km without fuel around the world. The energy collected by the solar cells is stored in batteries, whose energy density is optimized to 260 Wh/kg.



Fig. 1.15 - Airbus E-Fan X - Source: [19]



Fig. 1.16 - Solar Impulse 2

1.2.5 Agriculture

In the last years, agricultural manufacturers are developing solutions for the efficient use of electric engine types in vehicles.

The GE Elec-Trak was the first commercially produced all-electric garden tractor, powered by an onboard bank of lead acid batteries and made mostly between 1969 and 1975.

Fendt e100 Vario is a tractor fed with a Li-ion battery (LFP type) of 650 V and 100 kWh of capacity, such as the Kremer Energy T4E offers the same functionalities. [20]

Not only tractors, but also... Alkè ATX electric vehicles are multi-task pick up with lead acid, gel or Li-ion (LFP) batteries from 8.7 kWh to 20 kWh of capacity. [21]



Fig. 1.17 - Agricultural Electric Vehicles: GE Elec-Track (up), Alkè ATX (left), Fendt e100 Vario (right)

2. Global Battery Markets

As stated previously, this work focuses the attention only on electrochemical batteries, and more specifically, of the application of these storage systems in the hybrid railway transportation. In fact, as shown in *Fig. 2.1*, the battery energy storage technology has the most number of operational projects compared to other ones.



Fig. 2.1 - Number of Operational Projects of different Energy Storage Technologies - Source: [1]

Electrical traction systems are the most energy efficient systems in the railway sector, especially thanks to the availability of regenerative braking systems.

This process is feasible thanks to the application of a secondary (or rechargeable) battery. Since 1860 lead acid batteries have been used as energy sources commercially for starters for ICE vehicle or emergency power supply. It had been the first rechargeable battery and it is surprisingly still used in traction field but, because of low energy density, low rate of charging and environmental pollution, they can't meet requirements of long-term energy storage system. [22]

Since then, in order to fix this shortage, other chemistries emerged in the market. In 1899 the nickel-cadmium (Ni-Cd) battery diffused in the market but higher material costs compared to lead limited its use. Two years later, Thomas Edison replaced cadmium with iron, Ni-Fe, not achieving resounding success.

Later, the improvements of Ni-Cd made it the most widespread battery until in 1990s, environmentalists in Europe became concerned about the harm incurred when Ni-Cd is carelessly disposed. The alternative developed is nickel-metal-hydride (NiMH), a more environmentally friendly battery that is similar to Ni-Cd. [23]

Sodium-metal halide battery technologies have successfully powered electric vehicles (EVs) since 1990s because of their higher cell voltage than Na-S batteries. This type of battery is well known as Zero Emission Battery Research Activity (ZEBRA). [24] Its main characteristics are low cost, long life cycle and semisolid cathode that makes it very interesting in the EVs field. Moreover, it operates at a wide temperature range of 250-350 °C. Unfortunately, it is losing appeal because of its drawbacks like low specific power (150 W/kg), self-discharge and thermal management need.

The Li-ion battery has emerged as the dominant chemistry for EVs due to its high cell voltage, high energy density, light weight and small size. In addition, no environmental pollution and manufacturing process improvements and economies of scales are helping to reducing costs significantly.

To summarize, the different battery types in the market are listed below:

- Lead-acid (PbO₂)
- Nickel-based (NiCd, NiMH, NiFe, NiZn, NiH₂)
- Zinc-halogen-based (ZnCl₂, ZnBr₂)
- Metal-air-based (Fe-Air, Al-Air, Zn-Air)
- Sodium-beta (NaS, NaNiCl₂)
- High temperature lithium (Li-AlFeS, Li-AlFeS₂)
- Ambient temperature lithium (Li-polymer, Li-ion)

As shown in *Fig. 2.2*, the most common form of operational battery energy storage technology is Li-ion battery. In addition, as shown in *Fig. 2.3*, Li-ion batteries can surpass all other batteries in specific energy (and energy density) as well as specific power.



Fig. 2.2 - Number of Operational Projects of different battery technologies - Source: [1]



Fig. 2.3 - General comparison of main rechargeable systems used in industrial batteries - Source: Genport.it

Also, according to a group of experts of the sector [25], the technology time path about batteries for EVs will evolve as in *Fig. 2.4*:



Fig. 2.4 - Batteries time path for Electric Vehicles - Source: [25]

1) LEAD ACID

Lead-acid battery consists of a positive electrode made of leaddioxide and a negative electrode made of metallic lead immersed in diluted sulphuric acid electrolyte. Although lead acid battery is still prevalent in cost-sensitive applications including automotive starting, lighting and ignition (SLI)



Fig. 2.5 - Lead Acid battery

because of its low cost, reliability, maturity level in technology, extended life span and fast response, its use for commercial applications is limited due to the development of other high efficient and high energy density batteries. The starter battery is designed to crank an engine with a momentary high-power load lasting a second or so. The deep-cycle battery is built to provide continuous power for wheelchairs, golf cars, forklifts and more. This battery is built for maximum capacity and a reasonably high cycle count. This is achieved by making the lead plates thick. [26, 23]

2) <u>LI-ION</u>

Li-ion battery is the most promising and fastest growing battery technology for HEVs and EVs. Lithium is the lightest of all metals, has the greatest electrochemical potential and provides the largest specific energy per weight. The cathode is metal oxide and the anode consists of porous carbon. During discharge, the ions flow from the anode to the cathode through the electrolyte and separator; during charge, the direction is reversed and the ions flow from the cathode to the anode.

There are different types of Li-ion battery:

- LiCoO₂ (LCO)
- $LiMn_2O_4$ (LMO)
- LiNiMnCoO₂ (NMC)
- LiFePO₄ (LFP)
- LiNiCoAlO₂ (NCA)
- $Li_4Ti_5O_{12}(LTO)$

Their drawback is the cost, which is still too high, but the diffusion in the market is helping to reduce the price of a Li-ion battery.



Fig. 2.6 - Li-ion battery

3) <u>NI-BASED</u>

Nickel-Cadmium (NiCd) and Nickel-Metal-Hydride (NiMH) batteries are the most important in this category.

NiCd battery was the dominant rechargeable battery in the '90s. The advantages in its use are fast recharge, long cycle life, deep discharge rates with no damage or loss of capacity but it has some problems too: cadmium and nickel are toxic heavy metal, the battery suffers from the memory effect. At present, this type of battery is no longer marketed for public use in the European Union, following the prohibition of the use of cadmium in portable batteries (Directive 2006/66/EC).

Instead, NiMH is more environmental friendly and has higher specific energy and energy density, such that it is adopted for portable products, HEVs & EVs, and other potential industrial standby applications.

4) <u>NA-S</u>

Sodium-Sulphur battery, also known as molten salt or thermal battery, is made of liquid sulphur at the cathode and liquid sodium at the anode separated with solid beta alumina tube

and NaSICON (Na Super Ionic Conductor). The reactions require a temperature of 300-350°C to guarantee the liquid state of the electrodes, so it needs to be heated for an optimal operation. High cost and short service life made it not so attractive, until ZEBRA (Zeolite Battery Research Africa Project) or NaNiCl₂ battery had been invented. Similarly to Na-S battery, it operates at high temperatures. Typical applications are forklifts, railways, ships, submarines and electric cars (Ford Ecostar 1991).



Fig. 2.7 - NaS battery - Source: [1]

5) FLOW BATTERIES

A flow battery stores the energy in the electrolyte contained in tanks and then pumped in the electrode to generate electricity; the charging mode follows the opposite path. The amount of energy that can be stored in the battery depends on the size of the tanks, so the parameters of the battery can be easily chosen.

The most important technologies are reported in the following table:

Technology	Potential	Efficiency
Zinc Bromide (ZnBr), [17]	1.8	70 %
Vanadium Redox (VRB), [18], [19]	1.2 – 1.6	80 %
Polysulphide Bromide (PSB), [20], [21]	1.5	
Zinc-Air, [22]	1.6	50 %

Tab.	2 -	Flow	batteries	technol	logies
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Vanadium flow batteries are the more present typologies in pre-commercialization.

3. Advantages in using batteries

Nowadays, main railway traction system is thermal, especially fed by diesel. But, electrical traction system using batteries gives advantages over other power sources for many aspects, even if none of the improvements fully satisfies today's energy needs.

ENERGY STORAGE

Batteries are an excellent fit for many applications that require long-term energy storage. Rechargeable batteries hold less energy than non-rechargeable ones because of higher self-discharge. For example, a Ni-based battery lose 10-15% of capacity in the first 24 hours after charge, then 10-15% per month, while lead-acid and Li-based systems have a lower self-discharge. [27]

Fig. 3.1 shows this typical characteristic.



Fig. 3.1 - Self-discharge on time of a Ni-based battery

• <u>SPECIFIC ENERGY (or CAPACITY)</u>

This parameter is much higher for fossil fuels (the energy by mass of gasoline is over 12'000 Wh/kg), but, as showed previously in *Fig. 2.3*, specific energy of Li-ion batteries ("only" 180 Wh/kg) is the higher compared to the other energy storage systems.

• <u>EFFICIENCY</u>

The battery has the advantage of delivering energy more effectively than a thermal engine. The efficiency of Li-ion batteries is 90%, much higher than 25/30% or 20 to 60% of ICE and fuel cells efficiency respectively.

This is due to the fact that the conversion from chemical to electrical energy is not subject to restrictions of Carnot cycle. *Fig. 3.2* shows the maximum value reached in the energy conversion efficiencies.



Fig. 3.2 – Energy Conversion process maximum efficiencies

• <u>READINESS</u>

Battery is a power source that provides energy instantaneously without wait, unlike other power components that need to warm up before to start the production. For example, the ICE or the fuel cell requires a few minutes to gain power while battery power flows within a fraction of a second.

• <u>POWER BANDWITH</u>

Rechargeable batteries have a wide power bandwidth, or rather they can handle small and large loads without complications. This feature is shared with the diesel engine, while the fuel cell works best within a specific load, so as the jet engine operates most efficiently at a defined RPM. [27]

ENVIRONMENT AND INSTALLATION

Electrification plays a significant role in decarbonization of the transportation sector since over 10% of GHG emissions are resulted from road transport. [28]

Batteries are cleaner systems than ICEs, they don't emit any harmful substance for the environment and their cooling system are not composed by noisy vents.

In addition, batteries offer good shock and vibration tolerance and can be installed in any position, differently from ICEs.

OPERATING COST

Li-ion and Ni-based batteries are convenient for portable devices, while lead-acid are economical for wheeled mobility and stationary applications. Price and weight grow for the electric powertrain in larger vehicles. [27]

Compared with non-rechargeable batteries, electric energy from rechargeable ones is more economical, even if the analysis must be completed with the total cost of ownership, including cost per cycle, longevity, eventual replacement and disposal.

The same is done comparing the cost to generate 1 kW of power that includes initial investment, fuel consumption, maintenance and eventual replacement. [29] *Tab.3* shows costs for different power sources generating 1 kW of energy. The low cost of fuel per kWh of Li-ion battery mitigates the current high cost of the equipment, but the experts predict a price reduction with the increasing diffusion of the technology in the next years.

Fuel type	Equipment to generate 1kW	Life span	Cost of fuel per kWh	Total cost per kWh
Li-ion Powertrain	\$500/kW (20kW battery costing \$10,000)	2,500h (repl. cost \$0.40/kW)	\$0.20	\$0.60 (\$0.40 + \$0.20)
ICE in vehicle	\$30/kW (\$3,000/100kW)	4,000h (repl. cost \$0.01/kW)	\$0.33	\$0.34 (\$0.33 + \$0.01)
Fuel cell - portable - mobile - stationary	\$3,000–7,500	2,000h 4,000h 40,000h	\$0.35 -> -> ->	\$1.85 – 4.10 \$1.10 – 2.25 \$0.45 – 0.55
Solar cell	\$12,000, 5kW system	25 years	\$0	~\$0.10*
Electricity electric grid	All inclusive	All inclusive	\$0.20 (average)	\$0.20

Tab. 3 - Costs for different power sources generating 1 kW of energy

4. Battery structure and functioning

Chemical energy can be defined as the property of a stream of mass characterized by high value of the Gibbs free energy. The classical way to take advantage of chemical energy in order to produce electrical power is:

- produce heat at high temperature T (thermochemical transformation)
- produce mechanical power at the shaft in a thermodynamic cycle fed by heat at high T (thermomechanical transformation)
- produce electrical power in an alternator (electromechanical transformation)

But the simpler and more efficient way to exploit chemical energy is using electrochemical transformations.

Battery is a closed electrochemical cell able to convert directly chemical energy into electrical one, ensuring low value of irreversibility and high efficiencies. In addition, they can work both in direct and inverse operation:

- chemical to electrical energy transformation ($\Delta G < 0$, negative Gibbs free energy): spontaneous reaction for power production.
- electrical to chemical energy transformation ($\Delta G > 0$, positive Gibbs free energy): nonspontaneous reaction for chemical species production.

A very simple scheme of an electrochemical cell is shown in the following Fig. 4.1.



Fig. 4.1 – Electrochemical cell scheme

The central layer is named *electrolyte*. It physically separates the electrodes and it is characterized by:

- very low molecular diffusivity
- very low electronic conductivity
- very high ionic conductivity

The layer on the left is the *anode*. It is the electrode where the reaction of oxidation occurs, in which the equilibrium is established with a delivery of free electrons:

$$R_1 \rightarrow ION + e^-$$

The layer on the right is the *cathode*. It is the electrode where the reaction of reduction occurs, in which the equilibrium is established with a gain of free electrons:

$$R_2 + ION + e^- \rightarrow P$$

At the end, the global phenomenon is a redox reaction:

$$R_1 + R_2 \rightarrow P$$

where R_1 and R_2 are the reactants and P the final product.

Even if the presence of the electrolyte doesn't allow the contact between the two reactants, the reaction however occurs because ions, that are oxidized from of reactant R_1 , can travel across the electrolyte and the electrons e⁻ can travel in an external circuit.

The charge separation, maintained through the interposition of the electrolyte, gives rise to generation of electrical fields on both electrodes, among which a potential difference ΔV is created. By closing the external circuit, the equilibriums at electrodes are broken and a current I is generated by electrons flow.

The electronic current obtained in the process is the useful effect of the direct transformation from chemical energy of reactants to electric power, defined through the Ohm's law as:

$$W_{el} = \Delta V \cdot I$$

Differently from open electrochemical cells like fuel cells or electrolyzers, batteries don't exchange mass with external environment. Materials participating in the electrochemical reactions are the same materials that constitute the electrodes and, in some case, also the electrolyte layer. Reactants are taken and products are accumulated inside the electrodes, therefore they modify their composition during the process.

Usually, a battery can produce power (direct functioning) or restore the chemical potential of reactants (inverse functioning), working in reversible operation both phase $\Delta G < 0$ and phase $\Delta G > 0$.



Fig. 4.2 – Charge/Discharge configuration of a battery

Fig. 4.2 shows modes of operation of a battery. In addition, it is noticeable that anode is always the electrode from which the flow of electrons exits, so as cathode is always the electrode from which the flow of electrons enters. Therefore, anode and cathode change their names during charge and discharge phases. For example, during the discharge process, cathode is the positive pole and anode is the negative pole, while during the charge process, the opposite is true such that the anode is the positive pole and the cathode is the negative pole.

As said in the previous chapters, many typologies of battery and many chemistries are available in the market, but in this context, the explanation of the functioning is referred to a Li-ion battery, more precisely to a LCO battery; the functioning of other Li-ion batteries is similar.



*Electron and Li-ion move reversely at charging



In discharging mode, positive and negative electrodes are composed of $LiCoO_2$ and graphite carbon respectively, while the electrolyte consists of liquid lithium salts like $LiPF_6$ or $LiBF_4$ or of a solid polymer like polyethylene oxide plus salt ($LiClO_4$, $LiCF_3SO_3$, etc.).

The total reaction occurring in a LCO battery in discharge configuration is:

$$C_6Li_x + Li_{1-x}CoO_2 \rightarrow 6C + LiCoO_2$$

where:

• Co (cobalt) is the metal that affects the thermodynamic behaviour of the battery, thus affecting the achievable ΔG . It can be substituted with the specific metal of the other Li-ion battery types.

• x is the number of sites in which Li^+ ions can be intercalated in anode structure.

The total reaction is the final effect of the reaction of oxidation at the anode side:

$$C_6Li_x \rightarrow 6C + xLi^+ + xe^-$$

and of the reaction of reduction at the cathode side:

$$Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow LiCoO_2$$

Therefore, during the process, Li⁺ ions are transported to and from negative or positive



Fig. 4.4 - LCO battery mode of operation

electrodes by oxidizing metal Co during charge and by reducing metal Co during discharge. Rechargeable Li-ion battery are based on a process called *intercalation*, that consists of the reversible penetration of Li⁺ ion inside the crystalline structure Co of the electrode. More precisely, if the structure is shaped in "tunnel mode" the process is called *insertion*. However, generally, these terms are used as synonyms.

In a completely charged battery in open circuit conditions, the lithium atoms intercalated in the anode are in equilibrium with the Li^+ ions in the electrolyte layer.

As the circuit is closed, the equilibrium is broken and Li^+ ions start travelling from anode to cathode, producing the discharge process. First, the lithium atoms inside the anode neighbouring the electrolyte layer are extracted; as the discharge goes on, all the atoms are extracted until even those furthest away undergo de-intercalation.

Contemporarily, Li⁺ ions travel across the electrolyte layer and start being intercalated in the cathode structure. First, the occupied sites are those neighbouring the electrolyte layer, then the intercalation process goes on until even the furthest sites are occupied.
In charging mode, electrodes trade places, while electrolyte remains the same. The total reaction occurring in a LCO battery in recharge configuration is:

$$LiCoO_2 + 6C \rightarrow C_6Li_x + Li_{1-x}CoO_2$$

that is the final effect of the reaction of oxidation at the anode side:

$$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe$$

and of the reaction of reduction at the cathode side:

$$6C + xLi^+ + xe^- \rightarrow C_6Li_x$$

Here the functioning is an inversion of the discharge configuration.

To follow, total reactions of other battery typologies are shown:

• Lead Acid

 $Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$

• Ni-Cd

 $Cd + 2NiO(OH) + 2H_2O \leftrightarrow Cd(OH)_2 + 2Ni(OH)_2$

• Ni-MH

$$MH + NiO(OH) \leftrightarrow M + Ni(OH)_2$$

• Na-S

$$2Na + xS \leftrightarrow Na_2S_x$$

The following table shows how Li-ion battery globally has better characteristics in terms of energy. This features make Li-ion batteries attractive in market among commercial devices with higher energy density.

	Lead Acid	Ni-Cd	Ni-MH	Na-S	Li-ion
Specific Energy	20-35 Wh/kg	40-50 Wh/kg	70-95 Wh/kg	150-240 Wh/kg	75-200 Wh/kg
Energy Density	54-95 Wh/L	70-90 Wh/L	pprox 150 Wh/L	150-250 Wh/L	200-500 Wh/L
Specific Power	≈ 250 W/kg before efficiency falls	$pprox 220 \ { m W/kg}$	200-300 W/kg	150-200 W/kg	500+ W/kg
Nominal Cell Voltage	2 V	1,2 V	1,2 V	2 V	3,3 - 4.2 V
Life Cycle	≤ 800 before decrease to 80% capacity	1200 before decrease to 80% capacity	1000 before decrease to 80% capacity	1200 before decrease to 80% capacity	≈ 1200 before decrease to 80% capacity
Energy Efficiency	85-90%	60-90%	50-80%	70%	80-90%

Tab. 4 - Characteristic parameters of different battery types

5. Main parameters

In order to understand the background process of the battery, this section is going to introduce and clarify the parameters that characterize a battery.

• <u>CHEMISTRY</u>

This argument has already been discussed in the previous chapters. The most common battery chemistries are lead, nickel and lithium, and each system needs a designated charger. Charging a battery on a charger designed for a different chemistry may appear to work at first but might fail to terminate the charge correctly.

ENERGY DENSITY, SPECIFIC ENERGY and SPECIFIC POWER

These parameters reflect the measurements of the performance of any power source like engines or batteries. The higher the energy density or specific energy of the fuel, the more energy may be stored or transported for the same amount of volume or mass. Specific energy defines battery capacity in weight (Wh/kg); energy density, or volumetric energy density, reflects volume in liters (Wh/l). Products requiring long runtimes at moderate load are optimized for high specific energy; the ability to deliver high current loads can be ignored.

Specific power, or gravimetric power density, indicates loading capability. Batteries for power tools are made for high specific power and come with reduced specific energy (capacity).

A battery can have high specific energy but poor specific power as is the case with the alkaline battery, or low specific energy but high specific power as with the supercapacitor.

Ragone diagrams are plots used in the field of onboard applications to compare technologies and illustrate their energy/power compromise (see *Fig. 2.3*).

<u>STATE OF CHARGE and DEPTH OF DISCHARGE</u>

State of charge (SoC) reflects the battery charge level and it is the equivalent of a fuel gauge for the battery pack in EVs/HEVs. In other words, it is the amount of capacity that remains after the discharge from the fully charged condition. The units of SoC are percentage points (0% empty; 100% full). Direct determination of SoC is not usually possible. However, it can be theoretically calculated using battery voltage and current. SoC is sometimes divided into:

- Absolute state-of-charge (ASoC), the ability to take the specified charge when the battery is new.
- Relative state-of-health (RSoC), available charge level taking capacity fade into account.

In addition, could be defined the State of Health (SoH) as the measure of the general condition of the battery and its ability to deliver the specified performance compared with a fresh battery. It takes into account such factors as charge acceptance, internal resistance, voltage and self-discharge. *Fig. 5.1* summarizes battery state-of-health and state-of-charge graphically.



Fig. 5.1 - Relationship of battery state-of-health and state of charge - Source: BatteryUniversity.com

The complementary quantity is the depth of discharge (DoD). Deep discharging beyond the cut-off voltage must be avoided, especially under heavy loads, to prevent serious damage to the batteries. The withdrawal of at least 80% of battery (rated) capacity is referred to as deep discharge.

• <u>CAPACITY</u>

This property establishes how much electric charge the battery can store. Capacity is the leading health indicator of a battery, but estimating it on the fly is complex.

It is linked to the availability of sites in the electrode hosting the ions. In turn, this depends on the electrode surface and on the type of nanostructure of electrode material. Capacity is also a function of other battery parameters such as the magnitude of the current, the allowable terminal voltage of the battery, the temperature and other factors.

The measurement unit of a battery's capacity is Ah (1 Ah = 3600 C). Ah is the discharge current a battery can deliver over time. In many applications, it is preferable to measure energy stored E in the battery as watt-hour (Wh). The energy capacity of a battery measured in Wh can be converted to Ah using Ohm's law and depends on the capacity C, on the number of cells in the stack n and on the DoD:

$$E = C \cdot V_{stack} = C \cdot V_{cell} \cdot n$$

where V is the voltage.

• <u>VOLTAGE</u>

A very important characteristic of a battery is the Open Circuit Voltage (OCV), that is the voltage between the battery terminals when it is not connected to an external load or no electric current flows between the terminals. It is function of other parameters such as State of Charge (SoC), temperature and past discharge/charge history.

The voltage between the terminals when the battery is connected to a load is called Terminal Voltage. The measurement unit of the voltage is volt (V).

OCV is potential drop in case of ideal conditions, which corresponds to condition with no current. When the circuit is closed, a current $I \neq 0$ starts flowing in the external circuit, breaking the chemical equilibriums which were taking place to the electrode. The system is no more in ideal conditions, but it is operating in real conditions and the potential drop across the cell will be always lower or higher than OCV.

The relationship between the potential drop across the cell and the intensity of the current flowing in an electrochemical cell varies from cell to cell and it is called *polarization curve* ($V_c = V_c(I)$), showed in *Fig. 5.2*:



Fig. 5.2 - Polarization curve of an electrochemical cell - Source: [57]

Voltage decreases when the current grows because of the irreversibilities associated to the transport phenomena.

Because of the electrolyte cell dimensions, the x-axis of the polarization curve represents the current density, that is the current intensity referred to the surface it is conduced across:

$$i = \frac{I}{S} \qquad \left[\frac{A}{m^2}\right]$$

The curve can be divided in three regions. Each of the different trends are associated to a different charge/mass transport phenomena:

- Region of Activation Polarization: at low current the activation overvoltage, generated by the *charge transfer* related to kinetic behaviour of electrochemical reaction both at the anode and at the cathode, prevails.
- Region of Ohmic Polarization: in the central quite linear part of the graph the ohmic overvoltage, generated by the *charge conduction* related to ion conduction in the electrolyte and electrons conduction in electrodes and external circuit, prevails.
- Region of Concentration Polarization: at high current the diffusion overvoltage, generated by the mass transport related to molecular diffusion through the pores of the electrodes, prevails.

But polarization of a closed cell is not function only of current like in open cells, but of SoC too ($V_c = V_c(I, SoC)$). It is illustrated in *Fig. 5.3*:



Fig. 5.3 - Polarization curve of a battery - Source: [56]

Batteries usually are marked with nominal voltage, but the value of a cell changes during the functioning time. Therefore, the convention is to refer the voltage in the full charge condition, that is the OCV in SoC = 100%.

Connecting n_c cells in series, the stack voltage will be:

$$V_{stack} = n_c \cdot V_c$$

• <u>C-RATE</u>

C-rate of a battery is the current to which a system must be discharged (charged) so that it becomes from an SoC (DoD) equal to 100% to a DoD (SoC) equal to 100% in one hour. A discharge of 1C draws a current equal to the rated capacity. For instance, a battery rated at 100 Ah provides 100 A for one hour if discharged at a rate of 1C. The same battery discharged at 0.5C provides 50 A for 2 h. At 2C, the same battery delivers 200 A for 30 min. 1C is often referred to as a 1 h discharge; 0.5C would be a 2 h discharge, and 0.1C is a 10 h discharge. *Tab. 5* illustrates typical times at various C-rates.



Tab. 5 - C-rate and service times when charging and discharging batteries of 1Ah

While lead- and nickel-based batteries can be discharged at a high rate, the protection circuit prevents the Li-ion Energy Cell from discharging above 1C. The Power Cell with nickel, manganese and/or phosphate active material can tolerate discharge rates of up to 10C and the current threshold is set higher accordingly. [30]

The maximum current at which the battery can be continuously discharged is called the *maximum continuous discharge current*, which is usually defined by the battery manufacturer in order to prevent excessive discharge rates that would damage the battery or reduce its capacity. [31]

<u>LIFETIME</u>

In addition to its composition and structure, lifetime of a battery depends on the utilization mode and on the operation conditions. For instance, batteries work better in specific temperature ranges, and the submission to inappropriate conditions increases very much the rate of aging, regardless they are discharged or not. Usually, the aging of the battery performance has two origins: the *cycle fade* and the *calendar fade* that is the elapsed time before the battery is not usable at all. An increase in the temperature whether the battery is in active use or not and an increase of the SoC severely affect the degree of degradation. *Fig. 5.4* illustrates the capacity fade of a prismatic LCO cell stored at different temperatures in the range 15-60 °C at float potential of 3,8 V.



Fig. 5.4 - Time evolution of the capacity fade for a LCO cell - Source: [32]

The *cycle life* corresponds to the number of charge–discharge processes a battery can fulfill before its nominal capacity falls below 80%. The relationship between cycle life and depth-of-discharge (DoD) appears to be logarithmic. The *shelf life* is the time spent before a battery is out of use during storage.

The *coulombic efficiency*, CE in %, is the ratio between the discharge capacity and the charge capacity for each cycle:

$$CE(\%) = \frac{Q_{disch}}{Q_{ch}}$$

thus, the rate of capacity loss is inverse proportional to the duration of the test, t_{ts} , given by:

$$\psi = \frac{1 - CE}{t_{ts}}$$

The rate of capacity loss is representative of numerous effects such as the growth of the solid electrolyte interphase (SEI) layer, the aging of the crystallographic structure of electrode materials, impurities dissolved in the electrolyte, unwanted chemical reactions, side effects, and generation of other compounds.

SEI is a passivation layer laid down at the surface of the lithium anode, 1-3 nm thick, which is instantly formed by the reaction of the metal with the electrolyte (this is called

"formation cycle"). This film, which acts as an interphase between the metal and the solution, has the properties of a solid electrolyte. It is a poor ionic conductor in nature, has a corrosive effect and grows with the cycling life of the battery. *Fig. 5.5* sketches the process of the formation of dendrites and deposition of lithium grains at the surface of the electrode (a) for the first discharge process with formation of the SEI and (b) upon cycling.



Fig. 5.5 - Scheme of the formation of dendrites and SEI - Source: [32]

After the departure from the anode surface during discharge, the Li particles migrate to the cathode; the phenomenon is reverse for the charge. The deposition of Li^+ ions coming from the cathode participates to the nucleation of dendrites, because particles do not have memory to seat back on the same site as before. Finally, the continuous dissolution and dendrite formation occur at the expense of the mechanical stability of the anode, which damages the whole battery operation. [32]

6. Li-ion batteries

Lithium-ion batteries are well known as most widespread power components of portable electronic devices such as smart phones, tablets and laptops, but, beyond this application, batteries have huge potential for the implementation of EVs due to a healthy small carbon footprint. [33]

Good performance of lithium can be understood from the periodic table of elements: lithium is the most lightweight alkaline metal and the least electronegative element in nature. For this, lithium is a good electron donor, that means a high reduction potential (E $^{0} = -3.045$ V) [34].

The combination of lithium with a very electronegative material is able to cause





a high electric potential difference; in addition, the light molecular weight make its density relatively low.

The use of lithium has some disadvantages such as its high reactivity with nitrogen, oxygen and water; reason why Li-ion batteries must work in specific environment ($H_2O < 100$ ppm), which is one factor that provokes degradation of the batteries and can reduce the security of the devices.

Based on application, the lithium ion battery market is categorized into energy, automotive, consumer, military, industrial, and medical. Industrial sector includes mining, cranes, smart grid, and valves; automotive sector includes buses, trains, trucks, cars, airplanes, e-bikes, and e-scooters; and consumer sector includes smartphones, uninterruptible power supply (UPS), mobile phones, and tablet PCs. The automotive application category is expected to witness the fastest growth in the market during the forecast period, owing to the increasing penetration of electric vehicles in various countries, including Norway, Germany, and China. [35]

The commercialization of Li-ion battery began in 1991, although the first one was built in 1970s by Michael Stanley Wittingham, who used lithium metal and titanium sulphide as electrodes. In 2006, first worldwide factory for high power Li-ion cells, for the automotive industry was established in Nersac (France). [36] Since then intensive developments and technological diversification have taken place and this with an expanding range of applications. [33]

As said, there are many types of Li-ion batteries. Their names depend on the chemistry which the cathode is made of. A summary of the main chemistries is given below:

• Lithium Cobalt Oxide (LCO): The cell is composed by cobalt oxide (LiCoO₂) cathode and graphite carbon as the anode. Its high specific energy makes Li-cobalt the popular choice for mobile phones, laptops and digital cameras. However, due to safety concerns with using this chemistry for transport applications, several alternatives are being developed or researched. In fact, the cell has a poor thermal stability and rates of charging above 1C cause the cell to overheat. A thermal runaway, due to the exothermic release of oxygen when a lithium metal oxide cathode is heated above a certain point, is the cause of a possible fire of the cell.

Other limitations are high cost, short cycle life of 500 to 700 deep cycles and a limited calendar life.

- Lithium Manganese Oxide (LMO): The cathode consists in lithium insertion in manganese "spinel" structures. It has been commercialized by Moli Energy since 1996 because Mn is much cheaper and less toxic. LiMn₂O₄ is still in development and holds potential for higher power and energy density and, in addition, a further advantage of manganese spinel is higher stability. In contrast, the cycling performance of LMO is still not satisfactory because the layered structure has a tendency to change into spinel structure during Li ion extraction and because Mn leaches out of LMO during cycling. However, the problem with the use of LiMn₂O₄ is not the cycling life (number of cycles before aging), but the calendar life, which is very limited by the dissolution of manganese in the electrolyte. In addition, as any chemical process, the kinetics of this dissolution process increases with temperature. An illustration of this effect was given by the failure of LiMn₂O₄-based batteries that equipped electric cars in the US after a hot summer in 2013, which forced the car-maker to recall these cars to change the batteries. [32]
- Lithium Nickel Cobalt Aluminium Oxide (NCA): LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ is the result of the attempt to improve the thermal stability and the electrochemical performance of LCO adding a small amount of aluminium. The NCA cell delivers high specific energy and specific power, and has a long life. NCA has slightly lower voltage and hence better safety characteristics, compared to LCO-based cells with a lower cost. Despite the

improvement, the Battery Management System (BMS) must manage the instability of these batteries in order to avoid fires. NCA is largely used in Panasonic battery by Boeing and Tesla and is currently being tested by JCS, GAIA, Matsuhita and Toyota.

- Lithium Nickel Manganese Cobalt Oxide (NMC): One of the most successful Li-ion systems is a cathode combination of nickel, manganese and cobalt. Nickel is known for its high specific energy but low stability; manganese has the benefit of forming a spinel structure which gives low internal resistance but offers a low specific energy. Combining the metals enhances each other strengths. Cobalt needs to enhance the structure stability further. This chemistry has similar or higher achievable specific capacity and operating voltage while having lower cost since the Co content is reduced. LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂ is the common form of NMC and is widely used in the battery market. [37] High specific power NMC is usually chosen for power tools and for vehicle power-trains.
- Lithium Iron Phosphate (LFP): This type of battery is different from the previous because often don't use graphite carbon as the anode. In fact, generally the cathode, composed by LiFePO₄ is coupled with Li₄Ti₅O₁₂ (LTO). LFP technologies are thought to perform similar to NCA batteries, but with a higher degree of safety due to a more stable electrode material with less susceptibility to thermal runaway and other threats and potential for lower costs. [38] The major weaknesses of the LiFePO_4 cathode include its relatively low average potential, low electrical and ionic conductivity, reduced performance in cold temperature and higher aging at elevated temperatures. Substitution of graphite with LTO considerably reduces the volume changes at the anode due to insertion of lithium. For this reasons, this technology gives good performances in laboratory. Intensive research over the last decade resulted in significant improvements in both performance and mechanistic understanding of LFP. Reduction in particle size in combination with carbon coating and cationic doping were found to be effective in increasing the rate performance. [37] These characteristics makes them the best candidates in the future markets of transport and energy storage from photovoltaic and wind farm.

• Lithium Titanate (Li₄Ti₅O₁₂): Besides the technology already described in LFP, LTO as anode can be coupled with LMO, LCO or NMC as cathode in order to potentially provide very safe and stable cells. This battery is capable of charging/discharging at higher C-rates (4-C or greater). Other advantages are zero-strain property, no SEI film formation and no lithium plating when fast charging and discharging at low temperature. The main drawback is the cost of the battery due to less applications and to the high titanium price. Typical uses are electric powertrains, UPS and solar-powered street lighting. [39]

The following figure *Fig. 6.2* compares the properties of the six battery typologies described previously, while *Tab. 6* below summarizes the values of the general performance characteristics of some of the most common lithium-ion chemistries that are in use today [40]. LTO has very good characteristics but it is much expensive because of the titanium presence, while NMC seems to be the chemistry with the best possible compromise considering all the properties.



Fig. 6.2 - Graphs of the properties of battery types - Source: [39]

	Lithium Iron Phosphate	Lithium Manganese Oxide	Lithium Titanate	Lithium Cobalt Oxide	Lithium Nickel Cobalt Aluminum	Lithium Nickel Manganese Cobalt
Cathode chemistry descriptor	LFP	LMO	LTO	LCO	NCA	NMC
Specific energy (Wh/kg)	80-130	105-120	70	120-150	80-220	140-180
Energy density (Wh/L)	220-250	250-265	130	250-450	210-600	325
Specific power (W/kg)	1400-2400	1000	750	600	1500-1900	500-3000
Power density (W/L)	4500	2000	1400	1200-3000	4000-5000	6500
Volts (per cell) (V)	3.2-3.3	3.8	2.2-2.3	3.6-3.8	3.6	3.6-3.7
Cycle life	1000-2000	>500	>4000	>700	>1000	1000-4000
Self-discharge (% per month)	<1%	5%	2-10%	1–5%	2-10%	1%
Cost (per kWh)	\$400- \$1200	\$400-\$900	\$600-\$2000	\$250-\$450	\$600-\$1000	\$500-\$900
Operating temperature range (°C)	-20 to +60	-20 to +60	-40 to +55	-20 to +60	-20 to +60	-20 to +55

Tab. 6 - Li-ion chemistries properties comparison - Source: [40]

7. Electric and hybrid vehicles

At the end of the 19th Century, electrical energy was used in railway and road transport; the experimental electric vehicle "La Jamais Contente" (The Never Satisfied) exceeded 100 km/h in 1899. However, the difficulty of storing electrical energy in sufficient quantities, within reasonable volume and weight limits, represented one of the major obstacles in the development of autonomous electric vehicles that are able to travel medium- to long distances.

At present, the development of renewable energy sources and the demand for low-carbon modes of transport are generating renewed interest in the storage of electrical energy, which becomes a key element for sustainable development. From this moment on, modern storage technologies make it possible to envisage the development of electric vehicles with acceptable performance levels, more efficient electrification of aircraft, the development of hybrid autonomous vehicles and locomotives, but also using storage to improve energy efficiency and to secure the supply of electrical transport systems. [41] Many guided vehicles, trams, trains, underground trains capture electrical energy from a grid or a third rail during the movement. This system is adopted by buses too, like the trolleybus, which require double of electrical energy from an overhead line when there is no possible current by the rails.

The most energy efficient vehicle available today is the electric vehicle. However, commercialization of full electric vehicles is still hampered by high purchase prices, short driving ranges and long recharging times. These facts have led to the construction of hybrid vehicles. Therefore, HVs may be regarded as transitional technologies towards fully EVs, in order to avoid fossil resources or pollution during use, but now hybridization of vehicles is increasingly the solution to give up the fossil fuel consumption, one of the main reasons of global CO_2 emission, to reduce the noise pollution in urban areas, to optimize the energy consumption of trains that complete journeys using electrified and non-electrified lines.

By definition, a hybrid vehicle is a vehicle which employs two sources of energy. A HEV is, therefore, a type of vehicle which can be powered with electrical energy derived from a source, an energy storage element or an energy converter.

Hybrids achieve improved efficiencies by employing several techniques. An important technique is regenerative braking. During braking the kinetic energy of the vehicle is normally dissipated as heat, but in HV generators convert the kinetic energy into electricity. This could be immediately used or stored in an EES for a following use. Therefore, hybrid electric vehicles are most feasible for use in urban traffic, where there is a frequent need for braking.

Batteries are the most used storage technologies because of their power capacities and the much

higher specific energy, as shown in Ragone diagram in *Fig. 2.3*, but sometimes they are integrated with at least another EES, creating a hybrid electrical energy storage. Advantages of each EES technology can be utilized to achieve specific performance, meet harsh working environments, optimize the whole system performance or improve the cycle efficiency. One project in the theme of a hybrid supercapacitor-battery system, funded by E.ON, was completed in UK offering large storage capacity and very fast charge/discharge rates. Another project funded by UK EPRSC, named "Ultra battery feasibility – investigation into the combined battery – supercapacitor for hybrid electric vehicle application", was completed in 2012. [42]

7.1 Configurations and operating principles for hybrid

There are four different levels of hybridization available in vehicles:

- *Micro hybrid* is fed by a combustion engine which includes a certain number of basic functions provided by a battery. Therefore, it doesn't use electric motors to propel the vehicle, but it provides an integrated alternator/starter that uses start/stop system, which switches the engine off during idling. The electrical power is approximately 2 kW. Typical fuel efficiency increase is around 10% compared to a non-hybrid.
- *Mild hybrid* is a configuration in which the combustion engine runs at all times. It is assisted by electric motors to provide a power boost to help acceleration, but they can't drive solely electrically. Mild hybrids also employ regenerative breaking and the start-stop system. Compared to a micro HEV, the electric motor, alternator, and battery pack are larger and play a greater role in the operation of the vehicle. This level of hybridization corresponds to power levels ranging from 8 to 20 kW. Typical fuel efficiency increase is around 20-25% compared to a non-hybrid.
- *Full hybrid* is similar to mild hybrid because it utilizes the same electric components such as an electric motor, alternator, and battery pack, but they're much larger in size. The vehicle can be actuated separately by each engine, can be propelled fully electric at low speeds and use the internal combustion engine at higher speeds or when the electric energy stored in the car battery is low. Actually, this configuration is the most widespread in the market. This requires that the levels of electrical power be higher than 20 kW. Typical fuel efficiency increase is around 40-45% compared to a non-hybrid.
- *Plug-in hybrid* is an HEV charged by the electric power grid, which makes it possible to operate it in all-electric mode for short journeys. While the engine operates, fuel efficiency is similar to a full HEV. PHEVs are ideal in urban commuting where trips are short, but are also equipped for long trips. The combustion engine is actuated when

the batteries are exhausted or above a certain speed. The electrical power is 30 kW or more.

The effect of the regenerative breaking and the use of electric motors of a hybrid car on CO_2 emissions is shown in *Fig. 7.1*. According to this graph, hybrid vehicles have substantial tailpipe CO_2 emission reductions only at relatively low speeds. The graph assumes that at speeds below 50 km/h, the vehicle is operated in an urban area with the corresponding traffic dynamics. [43]



Fig. 7.1 - Direct CO₂ emission of various technologies - Source: [43]

When compared to the vehicles using combustion engines, the standard CO₂ emissions are reduced by 8% when using the micro hybrid, 30% using the mild hybrid and 45% using the full and rechargeable hybrids. [44]

In order to assess the potential of the battery, a number of hybrid architecture configurations have been designed. A battery system is typically composed of the following subsystem and components: a stackable Battery Box (size adjusted according to the application need), a BTMS (Battery Thermal Management System) for thermal regulation when needed according to the severity of the mission profile, and some interconnections (electrical, mechanical and hydraulic between subsystems and between battery system and the application).

There are three configurations of power trains:

Series hybrid is the simplest hybrid configuration. In a series hybrid, the electric motor is the only means of providing power to the wheels. The motor receives electric power from either the battery pack or from a generator run by a gasoline engine. Both the engine/generator and the use of regenerative braking recharge the battery pack. Series hybrids perform at their best during stop-and-go traffic, where gasoline and diesel engines are inefficient. The vehicle's computer can opt to power the motor with the battery pack only, saving the engine for situations where it's more efficient. The lack of mechanical coupling between the combustion engine and the wheels makes it possible to actuate the combustion engine to its best performance without any constraints on the vehicle speed. The engine is typically smaller in a series drivetrain because it only has to meet certain power demands; the battery pack is generally more powerful than the one in parallel hybrids in order to provide the remaining power needs. This larger battery and motor, along with the generator, add to the vehicle's cost, making series hybrids more expensive than parallel hybrids. [45]



Fig. 7.2 - *Series hybrid configuration - Source:* [44]

Parallel hybrid is the most common hybrid system as of 2016. In vehicles with parallel hybrid drivetrains, the engine and electric motor work in tandem to generate the power that drives the wheels. Parallel hybrids tend to use a smaller battery pack than series drivetrains, relying on regenerative braking to keep it recharged. When power demands are low, parallel hybrids also utilize the motor as a generator for supplemental recharging, much like an alternator in conventional cars. This configuration enables a direct coupling between the combustion engine and the wheels, thus avoiding the losses. This reduces, but does not eliminate, the efficiency benefits of having an electric motor and battery in stop-and-go traffic. For this configuration, two types of transmission components can be implemented in practice: a five-speed manual gearbox (DSR – discrete speed ratio), identical to that of a conventional vehicle and a continuous speed variation system (CSR – continuous speed ratio).



Fig. 7.3 – Parallel hybrid configuration - Source: [44]

Series-parallel hybrid merges the advantages and complications of the parallel and series drivetrains. This type of complex hybridization combines the two solutions presented above, the engine can both drive the wheels directly (as in the parallel hybrid) and be effectively disconnected, with only the electric motor providing power (as in the series hybrid). With gas-only and electric-only options, the engine operates at near optimum efficiency more often. At lower speeds, it operates more as a series vehicle, while at high speeds, where the series drivetrain is less efficient, the engine takes over and energy loss is minimized. This system incurs higher costs than a pure parallel hybrid since it requires a generator, a larger battery pack, and more computing power to control the dual system. Yet its efficiencies mean that the series/parallel hybrid can perform better - and use less fuel - than either the series or parallel systems alone. [45]



Fig. 7.4 – Series-parallel hybrid configuration - Source: [44]

7.2 Diesel-electric hybrid railway system

For each application, railway technology varies greatly in its energy consumption due to the differences in the intended applications of the trains. The operation of a railway line is, therefore, characterized by two important criteria:

- the frequency of stops. Several stops within a few kilometers are imposed on locomotive used for urban lines. In contrast, a TGV traveling on a high-speed line or a national train can cover between 100 and 200 km before coming to a halt in a station. Regional lines, meanwhile, stop every 30 km.
- the second criterion is the commercial speed of the line. This corresponds to the nominal speed of trains along the line. The diversity of transport alternatives: urban, regional, national or international and high-speed, will determine the operating speed of the line (from 30 km/h of average speed for urban lines to 360 km/h for high-speed trains).

The railway traction is characterized by a range extending from 50 kW to 20 MW. To achieve such levels of power, two kinds of railway traction are operated: electric and diesel. [44] Together they compose the hybrid railway system.

A hybrid train is a locomotive, railcar or train that uses an onboard rechargeable energy storage system, placed between the power source (often a diesel engine prime mover) and the traction transmission system connected to the wheels.

Surplus energy from the power source, or energy derived from regenerative braking, charges the storage system. During acceleration, stored energy is directed to the transmission system, boosting that available from the main power source. In existing designs, the storage system can be electric traction batteries, or a flywheel. The energy source is diesel, liquefied petroleum gas, or hydrogen (for fuel cells) and transmission is direct mechanical, electric or hydrostatic.

Although the most commonly used battery for road vehicles was the nickel metal hydride battery because of its cost, high performance such as the power density of a lithium-ion battery is still highly attractive.

A capacitor with larger capacity can realize high energy efficiency since it will allow averaging of engine power generation, expansion of idling stops of the engine, and reduction of charge/discharge loss of a capacitor.

The following items have to be discussed when determining a specific capacity [46]:

> Capacity for storing regenerative braking energy.

Average braking energy used for making a single stop: approximately 1 kWh.

> Electric energy necessary to run a railcar along a flat area.

Electric energy necessary to run a railcar for 5 km between stations: approximately 3 kWh.

The basic principle of this system is to control power generation of the engine in such a manner that "the sum of energy generated by the car motion (which changes with car speed) and stored energy (stored in the battery) is kept constant regardless of speed". When the car speed is increased, energy generated by the car motion, or the potential regenerative energy of the car, is also increased. Therefore, the battery should be charged less while the car is in motion than the time when the car is not in motion, or the regenerative energy cannot be collected when the brake is used. In other words, the appropriate state of battery charge changes with car speed, and the system should be controlled so that the battery can be charged to that appropriate level until the engine power generator starts to operate.



Fig. 7.5 - Basic principle of regenerative energy management - Source: [46]

The system reacts in different way for every status in which the railcar is involved. Major car statuses are as follows:

- Departure from a station: The car is set into motion on battery power. The power generating engine starts operating when the car accelerates.
- During cruise: The power generating engine operates at its highest efficiency, and the secondary battery discharges/charges depending on running loads.
- While running up a slope: The power generating engine operates at its maximum output level.

- While running down a slope: The battery is charged by the regenerative brake. Car speed is controlled by the engine exhaust brake.
- When braking: The power generating engine stops. The battery is charged by the regenerative brake.
- When making a stop at a station: The power generating engine stops. Service energy is supplied from the battery.



Fig. 7.6 - Major car control modes - Source: [46]

According to Hitachi, tests in Japan have shown that the hybrid system can cut harmful emissions by up to 50% and fuel bills by a fifth. Emission levels and fuel costs are increasingly important factors in the rail industry.

8. Battery design for DMU railway vehicle

This part of the work is focused on identification of the best sizing, design and modeling of onboard battery energy storage for an existent Diesel Multiple Unit (DMU) train model developed by *Blue-Group Engineering and design*, firm who supported me on the development of this master thesis.

A diesel multiple unit or DMU is a multiple-unit train powered by on-board diesel engines (in non-electrified area) and, according to transmission design criteria, by an additional power supply system such as pantograph or third rail (in urban or underground area). Diesel-powered single-unit railcars are also generally classed as DMUs. A DMU requires no separate locomotive, as the engines are incorporated into one or more of the carriages.

8.1 Vehicle layout and specification

The Blue-Group firm developed a DMU railway vehicle that comprises four wagons distinguished into two types called *car 2* and *car 4*, head and body of the trainset respectively, and for each car uses diesel engine coupled with alternator, providing power to auxiliary equipment and to electric motors responsible for providing tractive effort. Because of safety issues, the vehicle has been developed such that it is capable to complete its mission even in case of failure of two of the four diesel engines. *Tab. 7* and *Fig. 8.1* synthesize technical details of both car types and the overall vehicle arrangement.

	Car 2	Car 4	
Length/Height/Width	27.18 / 4.28 / 2.82	25.72 / 4.28 / 2.82	[m]
Wheel diameter	915		[mm]
Track gauge	1435		[mm]
Boogie wheelbase	2500		[mm]
Nominal Boogie centre	19		[m]
spacing			
Axle load [tons/axle]	18		[tons/axle]
Number of axles	4	4	[-]
Primary power source: diesel	560	560	[kW]
engine			
Transmission system: electric	180 x 2 units	180 x 2 units	[kW]
motor			
Maximum speed	120	[km/h]	
Wheel arrangement	(2B)(22) (22)([-]	
Layout	Driver's Cabin and passenger	Passenger	
	compartment	compartment	
Capacity	228 201		[persons]

Tab. 7 - Car 2 and Car 4 technical details



Fig. 8.1 - Layout of the train arrangement

Electric motors are constituted by two units rated 180 kW each with regenerative braking. A 4 wagons train weights around 200 tons without including passengers. This train has capability to have 858 passengers, if assume each passenger as average has 75 kilograms, then total weight of passengers is about 64.4 tons. In order to design energy storage for DMU, the mass of passengers also must be considered, therefore in the study with passengers it is proximately 264.4 tons.

Both car types have frame based on H-shape where the trailer and motor bogies are fitted, on the front and rear part of the frame respectively, as it is shown in *Fig. 8.2*. HVAC units, brake resistor bank and the diesel generator, installed with a control and monitoring system, a fire fighting system and a cooling system inside a power pack, are roof-mounted. The power pack weighs about 8 tons and provides power to traction converter, auxiliary converter (medium voltage MV loads) and to a battery charger (low voltage LV loads). More in detail, diesel generator supplies power to the rectifier that converts alternating current (AC) to direct current (DC); then power flows to traction and auxiliary converters and the battery charger. The traction converter again converts DC to AC, supplying power to two traction motors connected to two different shafts of the same motor bogie. Essentially, the heating/cooling system of car 2 differs from car 4 because of the HVAC unit of the driver's cabin.

Regenerative braking has been individuated as the most promising energy recovery strategy by [47], therefore both car types are equipped with electro-dynamic (ED) and pneumatic braking systems: the former operates in normal braking operation, whereas pneumatic braking sisted at very low speed, in emergency operations or in case of failure of ED braking system. Indeed, when the vehicle has to decelerate, the control unit sends a braking signal to the traction converter that enables the motor to act as a generator, applying a resistant torque to the wheel-axle of the motor bogie. The existing vehicle has been developed such that, during the braking phase, part of the ED braking power feeds auxiliary equipment, while the exceeding part is wasted through the brake resistor bank. Once vehicle reached very low speed (i.e. in the proximity of the station), the control unit activates pneumatic braking system ensuring short braking distance despite its high operational costs.



Fig. 8.2 - Car 2 equipment



Fig. 8.3 - Car 4 equipment

	Car 2	Car 4
Electric motors	2 x 180 kW	2 x 180 kW
Compressors	7.5 kW	7.5 kW
Compartment HVAC units	24 kW x 2 units	24 kW x 2 units
Driver HVAC unit	5.8 kW	None
220V sockets	2 kW	2 kW
Power pack cooling system	18 kW	18 kW
Total	435.5 kW	441.3 kW

Tab. 8 - Car 2 and Car 4 loads

8.2 Design Structure

The principal idea is to find the best size and model battery pack that satisfies vehicle's power demand during the entire urban track described next. This energy storage is a roof-mounted system that replaces one of the three diesel generators as shown in *Fig. 8.4* in order to obtain a hybrid vehicle able to recover ED braking energy, to reduce pollutant emissions, to reach non-electrified urban stations and to operate in underground tracks where diesel generator use is forbidden.



Fig. 8.4 – DMU hybridization process

The breaking energy recover is stored inside the battery which will use that in case of necessity as non-electrified area, so that reduce diesel generators use to the minimum required.

The size of the battery depends on the itinerary, more specifically on its characteristics as track slope, speed profile and acceleration. In this case, DMU travels for 19.46 km from Rebaudengo Station to the central station of Porta Nuova passing from the station of Porta Susa, then coming back to Rebaudengo with the same inverse path.

Using the modified Davis formula, tractive and braking efforts have been calculated and used for the calculation of the vehicle power demand. *Tab. 9* shows input data of the current study.

INPUT DATA					
Total energy demand [kWh]	196	Including auxiliary equipment			
Maximum Tractive Power [kW]	1614	Electrical Power			
Maximum ED Braking Power [kW]	1584	Electrical Power			
Maximum Braking Power [kW]	4088	Pneumatic and Electric braking			
Desired Voltage [V]	950	Based on electrical requirements			
Minimum Voltage [V]	850	Based on electrical requirements			
Power Pack mass [46]	800				
Diesel Generator Power [kW]	560	One diesel-generator each car			

Tab. 9 - Input data for battery pack sizing

This DMU is supplied at 950 V and the ranges of voltage for battery cells are usually between 1 to 4 V. Furthermore, in order to achieve 950 V by the series connection of the cells, many of them are required.

8.3 Batteries design for DMU traction

Selecting the right power source to satisfy the specifications of a given transport application may be a complex process.

The first step of a possible approach is the comprehensive view of the project's technical specifications and of the economical expectations of the project leader. This may sound obvious, but knowing exactly what the performance of a power source should be is not always easy. For instance, the accurate description of the operating temperature conditions of the cells or the location where the device will be used are very important information.

Then, in order to design the battery pack for this DMU, a detailed electrical analysis has to be carried out; particularly the desired voltage of the loads leads to the necessary number of cells in series (n_s) . The calculation is given by:

$$n_s = \frac{V_{requested}}{V_{cell}}$$

The configuration in series of two cells allows to obtain the double nominal voltage of a single cell in output, maintaining the same capacity. It is enough that the voltage of the battery pack is close to the requested voltage, because a power converter matches the two values.

Capacity of batteries also need to be considered and should be big enough to supply enough energy to the train. In order to increase the life cycle of batteries, it is better to choose a bigger capacity so each time when the battery intervenes, it will discharge by the smaller percentage of their total capacity. However, since usually lithium batteries suffer deep-discharge cycle, it is necessary to oversize the installed energy of the battery pack. By acting in this way, Depthof-Discharge of the battery pack will not exceed its maximum allowable value. In this analysis, a DoD equal to 80% is chosen.

$$W_{pack} = \frac{W_{requested}}{DoD}$$

where W_{pack} is the battery pack energy and $W_{requested}$ is the energy required by the DMU. Dividing by the desired voltage, the battery pack capacity is obtained:

$$C_{pack} = \frac{W_{pack}}{V_{requested}}$$

Another important parameter in this design is to find out the maximum discharge current by the batteries. The highest peak currents will allow selecting high-, low- or moderate-rate cells. It is important ensure that current never exceeds maximum allowed value during operations, this could occur in the worst condition operation that takes place when battery pack has low SoC level meanwhile vehicle requires high power (i.e. departure phase). This is taken in account in the number of branches to be assembled in parallel (n_p) in the battery pack. It is easy to calculate:

$$n_p = \frac{C_{pack}}{C_{module}}$$

where the module is the system of multiple cells connected in series.

The configuration in parallel of two cells allows to obtain the double capacity of a single cell in output, maintaining the same voltage.

The choice of a battery may simply be based on its maximum acceptable weight or size. In addition to the mass of the total number of cells inside the modules, the weight shall be increased by a factor of 20% because of auxiliary systems such as cooling system. Since onboard energy storage is used, it is important to choose a lighter weight battery for this specific design.

Life cycle of batteries also is important because if it is too short, then batteries need to be replacing more often, with significant increase of the maintenance costs.

The design of the battery pack often implies the selection of the proper material for the cell container, of a reliable connector (corrosive environments may lead to the adoption of gold-plated contacts when the batteries have to operate for many years), and protection components. The cell may be encapsulated into an epoxy resin for better protection or simply varnished.

The economic aspects of the projects will obviously have to be analyzed. Of course, the price of the cell or the battery pack will be considered, but other costs will affect the economic balance of the project, such as the battery development, the qualification tests, the tooling, and the replacement. [48]

Therefore, once explained the steps for the sizing and for the choice of the right chemistry, a first test has been conducted considering only the theoretical voltage of the main battery typologies. Since they are connected in series, voltages must be summed up to cover the desired voltage requested by the DMU. In this way, each battery has a minimum number of cells in series configuration to reach 950 V. The following *Fig. 8.5* has been obtained by a code developed in Matlab \mathbb{R} .







The figure shows that lead acid and sodium sulphur batteries require the most number of cells (more or less 800 cells) to meet the DMU voltage. On the contrary, LCO, NMC and LFP batteries need much less cells, almost one third than lead acid.

Considering one module is composed by 12 cells for every battery type, the numbers of modules connected in series meeting the DMU voltage are illustrated in *Fig. 8.5*.

The 66 modules of lead acid are too high both in economical and in spacing/dimensional terms, while Ni based batteries require almost the double of the modules than LCO and NMC.

But this test is based on theoretical nominal voltage of batteries, it could be more accurate if the test is applied with commercial battery packs already present in market.

Different battery designs which can use them as energy storage system for the described DMU are illustrated in the following lines:

Saft Ni-MH NHP 10-340: this Nickel Metal-Hydride battery is specifically designed for high power applications providing excellent energy density and maintenance-free operation. The module is available in the configuration with 12 V and 34 Ah. This battery is used for energy & power applications, hybrid vehicles, buses, trucks and boats and for hybrid railway applications. Its main advantages are high specific power and energy, high cycle life, maintenance free, excellent safety and resistance to abuse, integrated high efficiency liquid cooling and the fully recyclability. [49]



Module characteristics

High power modules	NHP 10-340
Electrical characteristics	
Nominal voltage (V)	12
Rated capacity at C/3, after charge at constant current (Ah)	34
Power density (W/I)	970
Specific power (W/kg)	520
Energy density [Wh/I]	90
Specific energy (Wh/kg)	50
Dimensions	
Height (mm)	165
Length (mm)	169
Width (mm)	173
Weight (kg)	9

Fig. 8.6 - Saft NiMH NHP 10-340 specifications - Source: [49]

RS Sealed Lead Acid AMP9069: this is a lead acid battery used for several applications: telecommunications, solar systems, wind power systems, engine starting, wheelchairs, floor cleaning machines, golf trolley and boats. These batteries can be stored for more than 6 months at 25 °C with a self-discharge ratio less than 3% per month. The inspection of the battery voltage is recommended every month, while the equalization of the charge is recommended every three months. Its bigger limitation is the weight, approximately 32,3 kg.



Specification

-			
Cells Per Unit	6 12		
Voltage Per Unit			
Capacity	100.0Ah@20hr-rate to 1.80V per cell @25°C		
Weight	Approx 32.3 kg		
Max. Discharge Current	1000 A (5 sec)		
Internal Resistance	Approx 5.5mΩ		
Operating Temp.Range	Discharge : -15∼50°C (5∼122°F) Charge : 0∼40°C (32∼104°F) Storage : -15∼40°C (5∼104°F)		
Nominal Operating Temp. Range	25±3°C (77±5°F)		
Float charging Voltage	13.5 to 13.8 VDC/unit Average at 25°C		
Recommended Maximum Charging Current Limit	25A		

Fig. 8.7 - RS Lead Acid AMP9069 specifications - Source: [58]

Toshiba SCiB Type3-23 2P12S: SCiB modules consist of multiple cells to obtain necessary capacity and voltage. In the 2P12S and 2P9S modules, multiple cells are housed in a fire-resistant plastic case and include a cell monitoring unit (CMU) for monitoring voltage and temperature, which can be transmitted through a Controller Area Network (CAN). The Type3-23 consists of 12 series connections of 2 cells connected in parallel and has a total capacity of 45 Ah (22,5 Ah for each branch). This SCiB module is suitable for applications that support social infrastructure including industrial, power grid and railway systems as well as for home applications.

BATTERY MODULE TECHNICAL DATA				
Nominal voltage	27.6	V		
Capacity (at C/5)	45	Ah		
Minimum/Maximum	18.0/32.4	V		
Voltage				
Maximum	160	A		
charge/discharge	(continuous)			
current	350 (in-rush	A		
	current)			
Operative	-30 to 45	°C		
temperature range				
Dimensions	190 x 361 x	mm		
	125			
Mass	15	kø		



Fig. 8.8 - Toshiba LTO SCiB Type3-23 2P12S specifications - Source: [47]

Samsung NMC 26FM: This 54V lithium ion battery pack has a 15S10P configuration with 26Ah capacity and 52A maximum continuous discharge rating (adjustable). 18650 lithium-ion battery packs are constructed by spot-welding 18650 cylindrical cells in serial or parallel. The resultant battery has high energy density and cycle life with low cost compared to other power options. Cylindrical cell formats also show high reliability compared to other format options. The 15S10P battery pack specifications make it suitable for electric cars, boats, and many other applications. The battery uses high-quality Samsung 26FM (ICR18650-26FM) cylindrical cells imported from Malaysia, which have a medium gravimetric energy density rating and a medium maximum continuous current discharge rating compared to other cells.



15S10P BATTERY PACK WITH	SAMSUNG 26FM CELLS SPECIFICATIONS TABLE				
	BASIC				
Manufacturer	Voltaplex Energy				
Brand	Samsung				
Series	15.00 S				
Parallel	10.00 P				
Country of Manufacture	China				
	CELL				
Cell type	18650				
Cell model	Samsung ICR18650-26FM				
Cells in total	150 x 18650 cells				
	SIZE				
Weight, max.	7.05 kg				
Volume	~3300.96 cm ³				
Length, max.	27.60 cm (approximate)				
Width, max.	18.39 cm (approximate)				
Height, max.	6.50 cm (approximate)				
	VOLTAGE				
Voltage, charge max.	63.00 V				
Voltage, nominal	54.00 V				
Voltage, discharge end	41.25 V				
CAPACITY					
Capacity, max.	26.00 Ah				
	CURRENT				
Constant charge current, max.	26.00 A				
Constant charge current, max.	26.00 A				
Charge current, standard	13.00 A				
Discharge current, standard	5.20 A				
Max. continuous discharge current	52.00 A				
Peak discharge theoretic, 4 sec	90.00 A				
C-rate (charge, max.)	1.00 C				
C-rate (discharge, max.)	2.00 C				
POWER					
Watts (charge, max.)	1442.9 W				
Watts (discharge, max.)	2885.9 W				
	ENERGY				
Energy, max.	1404.00 Wh				
Density volumetric theoretic	557.00 Wh/L				
Density gravimetric theoretic	205.00 Wh/kg				

Fig. 8.9 - Samsung NMC 26FM specifications - Source: [60]

These batteries have been compared to define the number of modules connected in series and parallel, the battery pack weights and the cost of each system that satisfies the demand required by the DMU.

Following the approach described in this chapter, *Fig. 8.10* and *Fig. 8.11* have been obtained in Matlab®.



Fig. 8.10 - Comparison between different battery models in terms of number of modules connected in series and parallel to meet DMU energy demand



Fig. 8.11 - Comparison between different battery models in terms of weight

Fig. 8.10 shows that the required number of batteries of selected NMC battery is the lowest among all the models, with 180 modules followed by LTO and lead acid systems. Instead, the comparison reveals the unsuitableness of NiMH system.

This convenience is thanks also to the number of cells composing the module. In fact, the NMC module contains 150 cylindrical cells against the 12 prismatic cells of LTO model, advantage that affects the comparison among total voltage and capacity of the two systems. In order to take in account this disparity, it's fair considering in the analysis the dimensions, the weights and the costs of each device.

As showed in *Fig. 8.11*, the weight of NMC model is very low, while lead acid model reaches prohibitive weights, more than double of LTO model.

In addition, the dimension of NMC module is similar to the other ones. Its volume is the lowest and the whole system encumbers less space than the other batteries.

BATTERY MODELS DIMENSIONS					
	Length [cm]	Width [cm]	Height [cm]	Volume [cm ³]	
RS Lead Acid	50,8	11	22,5	12573	
Saft Ni-MH	16,9	17,3	16,5	4824,105	
Toshiba LTO	12,5	36,1	19	8573,75	
Samsung NMC	6,5	27,6	18,4	3300,96	

Tab. 10 - Comparison of battery models dimensions

Regarding the cost, the market is continuously in movement. The price of lithium-ion batteries has fallen steeply as their production scale has increased and manufacturers have developed more cost-effective methods. When the first mass-market EVs were introduced in 2010, their battery packs cost an estimated \$1000 per kilowatt-hour (kWh). EVs are forecast to cost the same or less than a comparable gasoline-powered vehicle when the price of battery packs falls to between \$125 and \$150 per kWh. Analysts have forecast that this price parity can be achieved as soon as 2020, while other studies have forecast the price of a lithium-ion battery pack to drop to as little as \$73/kWh by 2030. [50]

In addition, the cost differs depending on the geometry of the battery. The cost per kWh of the pouch cell is still higher than with the cylindrical 18650 cell but this is changing. In 1995, the pouch cell surprised the battery world with a radical new design. Rather than using a metallic cylinder and glass-to-metal electrical feed-through, conductive foil-tabs were welded to the electrodes and brought to the outside in a fully sealed way. The pouch cell makes most efficient use of space and achieves 90–95 percent packaging efficiency, the highest among battery packs. Eliminating the metal enclosure reduces weight, offering a simple, flexible and lightweight solution to battery design.

Fig. 8.12 compares the price of the cylindrical, prismatic and pouch cells, also known as laminated. [51]



Fig. 8.12 – Prices in \$/Wh of Li-ion battery geometries during the years - Source: [51]

Each selected NMC module costs approximately \$750, therefore batteries for this design will cost \$135000, which is excluded the cost of DC-DC converter and electrical connection. LTO and lead acid batteries costs are not far from this one, in fact they are around \$141600 and \$144000 respectively.
9. Li-ion battery issues and future prospects

9.1 Capacity loss and degradation

Beyond the many advantages in using Li-ion battery, some issues of these devices must be discussed to complete the panorama.

As already mentioned in previous chapters, during first cycles of charge-discharge, a Li-ion battery suffers an irreversible capacity loss. The phenomenon occurs in both the electrodes (where there is the intercalation), even if for different reasons.

At the cathode, it is due to the non-elastic deformation of the structure that hosts ion. Basing on the material, the capacity loss varies from 3 mAh/g for a LCO to 30 mAh/g.

At the anode, it is due to the instantaneous reaction between electrolyte and electrode when they touch each other. The result is the formation of SEI, that sticks to the anode and makes it passive. On one hand this process protects the anode, on the other hand it consumes lithium useful for the charge transportation. The loss capacity due to this phenomenon is high, typically 20 or 30 mAh/g, and depends on shape, dimensions and quality of the crystalline structure of the electrode.

Another important aspect in the Li-ion battery design is the ratio between the capacities of the two electrodes. The experience shows that the anode must have a higher capacity than the cathode. This precaution avoids the appearance of a metal lithium film at the anode, that could create unwanted substances and resulting risks for the security of the battery.

The degradation of a Li-ion battery is caused by the aging and it is accelerated by the occurring of some phenomena.

9.1.1 Change of volume

Excepted LTO chemistry, a first effect is the consequence of the change of volume due to the insertion and extraction of lithium in the anode, particularly marked during a deep discharge. The sequence of these variations results in a fatigue that makes damages in the crystalline structure until, in extreme cases, a pulverization. More often, like in graphite, micro-cracks occur in which the electrolytic solution enters, in particular at the end of deep discharge where the variation of volume is the largest. This interaction assembles additional SEI that becomes more thick, to the detriment of the active material. The result is a lower capacity and a higher resistance at the interface.

9.1.2 Dissolution of SEI

The lower capacity of the cathode - than the anode – makes the electrode very vulnerable to the oxidation at the end of the charge process. Dissolved species of these reactions act as catalysts with anodic SEI, breaking it up, in particular at the end of the discharge where the SEI is less stable. This can get back partially the capacity lost by the cathode, with the risk that it exceeds the anodic one, and the disadvantages of this situation have been already explained.

9.1.3 Migration of cathode species

The species released by the cathodic degradation can migrate to the anode and here react and produce additional surface layer. An example is the dissolution of manganese into the electrolyte in case of LMO chemistry. As any chemical reaction, this oxidation is faster with temperature.

Sometimes, in particular for Ni-based batteries, the oxygen released by the cathode moves to the carbon anode, forming some unwanted gases like CO_2 . These phenomena cause clear worries about the safety of these devices.

9.1.4 Corrosion

Any residual presence of water will engender corrosion of the collectors. The lithium salt used in the Li-ion batteries is normally LiPF_6 , which has a very good conductivity, and presents the advantage of protecting the collector in aluminum from corrosion. However, it reacts with water to form hydrofluoric acid HF that is very corrosive and thus attacks metallic collectors according to the reaction:

$$LiPF_6 + 4H_2O \rightarrow 5HF + LiF + H_3PO_4$$

It is thus primordial to take care during the manufacturing of the battery to avoid the introduction of any trace of water. [32]

9.2 Future battery technologies

Developing Li-ion batteries for transport able to deal with society's fluctuating energy needs is a formidable challenge, especially from a materials perspective. In addition to the classical figures of merit (specific energy and power, lifetime, cost and safety), other issues are not yet fully recognized, such as the low relative abundance of materials (lithium is already viewed by some alarmists as the gold of this next century) and the large energy cost of battery manufacture and recycling.

Consequently, the only viable path towards a 'greener and more sustainable' battery is rooted in our ability to design electroactive materials that have comparable performances to today's electrodes, but cost less energy and release less CO_2 during production. There are various approaches that have been explored towards this goal:

- the development of novel eco-efficient processes and bio-inspired approaches for the synthesis of inorganic compounds obtained at a temperature nearer to environmental one. In fact, traditional processes need higher temperatures, more than 500°C, but recently, LiFeSO₄ was produced at 280°C. Beyond the energetic saving, working at lower temperature allows a better management of the chemistries' geometries. In 2012, Ghodssi's group reported the fabrication of nanostructured V₂O₅ cathodes and nanotubes of silicon for anodes using the tobacco mosaic virus (TMV) as a biotemplate. [52]
- the promotion of a new concept of renewable electrodes based on the use of organic compounds synthesized using 'green chemistry' from natural resources. Has been discovered the molecule Li₂C₆O₆ reversibly (de)inserts four Li⁺ ions at around 2.8 V, leading to an energy density of 1500 Wh/kg of electrode versus Li^o, nearly twice what can be achieved with today's NMC electrodes (880 Wh/kg). Another advantage of these technologies is the abundance of the materials.
- the development of new technologies beyond Li-ion batteries such as Li-S and Li-air (Li-O₂), Al-air, Na-ion, Mg, Ca and redox-flow systems, in combination with an increasing interest in recycling processes. Li-O₂ cells are often synonymously called Li-air cells even though they currently use pure O₂ rather than 'air'. [52]



Fig. 9.1 - Future batteries previsions - Source: [53]

9.2.1 Li-S battery

The lithium-sulphur battery uses extremely cheap materials and sulphur has a high specific capacity of 1673 mAh/g, five times more energy by weight than Li-ion. In a Li-S battery, the graphite electrode is replaced by a sliver of pure lithium metal that does double duty as both the electrode and the supplier of lithium ions: it shrinks as the battery runs, and reforms when the battery is recharged. And the metal oxide is replaced by cheaper, lighter sulphur that can really pack the lithium in: each sulphur atom bonds to two lithium atoms, whereas it takes more than one metal atom to bond to just one lithium. All of that creates a distinct weight and cost advantage for Li–S technology.

It offers high gravimetric capacities and theoretical energy density. Chemical engineer Elton Cairns predicts that a commercial-sized cell could achieve an energy density of around 500 Wh/kg. [53] Although this technology seems to be the closest to becoming a commercially viable successor to Li-ion, the rapid capacity fading due to dissolution of polysulphides poses a significant challenge for practical applications.

9.2.2 Li-O₂ battery

Another option towards more sustainable battery systems is moving to metal–air systems (Li–, Na– and Mg–air batteries) using O_2 as the positive electrode, which is similar to the concept of fuel cells. The positive electrodes in such systems are generally composed of black carbon and manganese oxide catalysts; therefore, they are much cheaper than the cobalt-based positive electrodes currently used in Li-ion batteries. [52]

Such batteries have a huge weight advantage over other types, because they do not have to carry around one of their main ingredients. A lithium-oxygen (Li-O) battery can, in theory, store energy as densely as a petrol engine, with a theoretical densities one order of magnitude higher than Li-ion battery and practical values until 1000 Wh/kg.

Researchers who have tried to make it work over the past 20 years have wrestled with unwanted side reactions: carbon in the electrolyte and electrode material react with the lithium and oxygen to form lithium carbonate, so that in every cycle, some 5–10% of the battery capacity is lost. After 50 cycles or so, the battery suffocates.

But recently, a team of American researchers has overcome this challenge coating the anode with a thin layer of lithium carbonate that allows the ions to go selectively inside the electrolyte avoiding unwanted substances in it. The reticulated and spongy structure cathode has been coated with a catalyst made by molybdenum disulphate. Finally, researchers have used a hybrid electrolyte (made by ionic liquid and dimethyl sulphoxide) to easy reactions between lithium and oxygen, mining interactions with other elements of the air. In this conditions, this battery has demonstrated to work for over 750 cycles of charge/discharge.

9.2.3 Zn-air batteries

As one of the most abundant elements in the earth's crust, zinc has been the chosen electrode material for several types of primary batteries ever since the first battery prototype developed by Volta more than 200 years ago. Among all metal–air systems, zinc–air batteries are the most practically viable choice. They possess some desirable features such as a high theoretical energy density, low cost, great safety and environmental friendliness. The theoretical energy density of zinc–air is 1086 Wh/kg, about 5 times higher than that of Li-ion; its operational cost is estimated to be less than 10 \$/kWh, only a small fraction of that Li-ion. Very recently, electrically rechargeable zinc–air batteries have emerged and undergone rapid development. Their rechargeability is realized by developing new bifunctional air cathodes and bifunctional

oxygen electrocatalysts that can facilitate both the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during charge. In addition, zinc-air

batteries can also be mechanically recharged by physically substituting the zinc electrode and electrolyte. [54]

9.2.4 Na⁺, K⁺, Mg²⁺, Ca²⁺ batteries

The foreseen demand for lithium, dictated by the expanding electric vehicle and grid applications, brings fear of lithium shortage. It also raises geopolitical issues related to uneven global distribution of lithium around the world. This uncertain situation has led researchers to look for both new chemistries dealing either with monovalent (K^+ , Na^+) or divalent (Mg^{2+} and Ca^{2+}) cations as well as means to efficiently recycle lithium. [52]

The most abundant and cheaper alternative is sodium, with a concentration of 23000 ppm. Similar to Li-ion challenges, mastering the solid electrolyte interphase through the use of new solvents, sodium-salts, additives, binders, and so on will be essential to realizing higher performances with Na-ion batteries. Interestingly, sodium salts are much less toxic than their lithium counterparts. They are also easier to obtain in their anhydrous state and easier to purify. The penalties of this choice are due to the higher density of mass (23 g/mol compared with 6,9 g/mol of lithium), considering same capacities.

Apart from Na-ion chemistry, cells based on divalent, abundant and cheap metals (magnesium and calcium) are also gaining some interest, despite lower specific capacities.

Conclusions

According to the OECD, urban air pollution is set to become the primary environmental cause of mortality worldwide by 2050 because of the high concentration of emission sources in limited spaces. Beyond the pollutant, the climate-change emissions are raising, like CO₂, a gas which doesn't have effect of the human health but contributes to the greenhouse effect and therefore, to the global warming. Debating this types of emission, the evaluation is that one fifth of them is caused by transportation sector. The result is a transition towards a more sustainable and 'green' solution, especially a hybrid or electric engine type. In this transition, the presence of energy storage systems is fundamental in order to recover energy from braking and store energy in surplus.

Batteries are very promising and efficient devices and they have been discussed in this work, explaining the functioning, the different chemistries, the advantage, the disadvantage and the main parameters, with a particular mention to Li-ion batteries, which have high energy densities, tiny memory effects and low self-discharges.

The analysis of this work examines the research of the best suitable onboard battery energy storage for an existent Diesel Multiple Unit (DMU) train model developed by *Blue-Group Engineering and design*, replacing one of the three diesel generators with a roof-mounted battery pack. A first test has been conducted considering the theoretical nominal voltage of some battery typologies connected in series in order to cover the desired voltage of the DMU. It has shown LCO, NMC and LFP are the chemistries requiring the smaller number of cells.

Then, the same DMU has been analyzed with the same approach comparing commercial battery modules. Among them, Samsung NMC 26FM pack has revealed very good properties, a suitable battery for the described DMU. In fact, the satisfying results obtained by Matlab® show its advantages both in total number of modules and weight and volume and price terms. Because of lack of information about thermal parameters, the behaviour of this commercial NMC battery has not been investigated by theses of the other team members, Laura Scandura and Fabio Nasca, about the thermal analysis of the battery and the optimization of the thermal management system of the battery pack, but they studied a battery characterized by same chemistry and similar specifications. However, the thermal analysis of the Samsung NMC battery could be an interesting investigation for the future, if in possession of enough information.

But the evolution of the battery technologies in the market are something to be reckoned with. It is unpredictable, but in the next decades, new chemistries could replace Li-ion batteries because of better properties discovered by lab tests.

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