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Nonlinear dynamic per-unit models for electrochemical energy systems. Application to a hardware-in-the-loop hybrid simulation

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NONLINEAR DYNAMIC PER-UNIT MODELS FOR ELECTROCHEMICAL ENERGY SYSTEMS. APPLICATION TO A HARDWARE-IN-THE-LOOP HYBRID SIMULATION

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I

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Resumen

La situación energética actual está dominada por los combustibles fósiles, especialmente por el petróleo. Esta dependencia se está conviertiendo en arriesgada debido a las decrecientes reservas, a la incertidumbre de los recursos de petróleo y a las consecuencias económicas y políticas de una concentración de reservas en países de Oriente Medio. El sector transportes tiene una particular dependencia del petróleo como combustible y es una fuente de contaminación debido a su combustión.

De cara a reducir esta dependencia se están introduciendo energías renovables como fuentes alternativas de energia. Las más comunes son la eólica y la fotovoltaica, aunque existen otros tipos, como las energías mareomotriz, de gradiente térmico, biomasa o undomotriz. El principal inconveniente de estas energías es su carácter no programable, que fomenta el uso de sistemas de almacenamiento de energía.

Las energías renovables mencionadas no son aplicables a vehículos, por lo que para el sector transportes es más interesantes el uso de vectores energéticos tales como el hidrógeno. El hidrógeno puede ser un sustituto del petróleo para aplicaciones vehiculares, pero primero se han de resolver ciertos problemas, como son el elevado coste, la seguridad y el establecimiento de una infraestructura de distribución de hidrógeno. Como en el caso de los sistemas estacionarios renovables, las pilas de combustible de aplicación vehicular necesitan sistemas de almacenamiento de energía que sean capaces de suministrar picos de potencia durante la aceleración o subiendo una pendiente.

Esta situación energética ha provocado un incremento del desarrollo e investigación de sistemas electroquímicos, tales como las pilas de combustible, las baterías y los supercondensadores. Sobretodo, se está realizando un esfuerzo en el diseño, modelado, control y fabricación de estos sistemas, que permita su implantación tanto en aplicaciones estacionarias como vehiculares o portátiles.

Esta Tesis presenta el modelado dinámico no lineal de sistemas electroquímicos tales como las pilas de combustible, las baterías y los supercondesadores a través de ensayos en el dominio de la frecuencia, además de su validación con resultados experimentales. Se propone un sistemas por unidad para aquellos sistemas electroquímicos activos (pila de combustible y

batería). Estos sistemas son una herramienta útil para el diseño y comparación, debido a la gran variedad de tensiones y capacidades que pueden encontrarse, por ejemplo, en las baterías. Además, se ha propuesto un método de ensayo de espectroscopía de la impedancia para supercondensadores durante elevadas corrientes. Los resultados obtenidos y la comparación con resultados experimentales son muy positivos.

Por último, se ha realizado una simulación hardware-in-the-loop de sistemas híbridos de energía. La simulación realizada presenta un coste y complejidad menor que otros tipos de simulaciones. Esto es debido a que los elementos más caros, como es la pila de combustible, son sustituidos por una fuente de potencia programable capaz de reproducir la dinámica de tensión y corriente de la pila de combustible. Además, se propone un simulador de vehículo, capaz de reproducir, tanto la potencia demandada por el vehículo como el frenado regenerativo. La pila de combustible simulada y una batería real alimentan en paralelo al vehículo simulado, permitiendo llevar a cabo una simulación por unidad del conjunto y la prueba de diferentes estrategias de control para un determinado ciclo de conducción.

Abstract

The current energy situation is dominated by fossil fuel, especially oil. This dependency is turning critical due to the reducing reserves, uncertain oil resources, and political and economical ramifications of a concentration of fossil fuel reserves on the Middle East countries. The transportation sector is especially dependant on oil, and the combustion of oil produces environmentally harmful emissions.

Renewable energies are being introduced to reduce this fossil fuel dependency and emissions. The most extended are wind and solar photovoltaic, but other types such as tidal, thermal gradient, biomass or wave energy are also under research. The principal disadvantage of these renewable energies is its non-dispatchable nature, which forces the use of energy storage systems.

The renewable energies mentioned are not viable for the transportation sector, which considers more interesting other energetic vectors such as hydrogen. Hydrogen could substitute oil, but must first overcome cost, safety and hydrogen filling stations infrastructure problems. Just as in the case of stationary systems, fuel cells need energy storage systems, in this case to supply high power peaks during acceleration.

This energetic situation has caused an increase of the research and development of electrochemical systems, such as fuel cells, batteries and ultracapacitors. Intense research is being carried out in modeling, control and manufacture in order to apply them to both vehicular and stationary applications.

This Thesis presents the nonlinear dynamic modeling of electrochemical systems, such as fuel cell, batteries and ultracapacitors, through frequency domain tests and its validation with experimental tests. A per-unit system has been proposed for the active electrochemical systems: fuel cell and battery. This per-unit approach has revealed as a useful tool for comparison and design, due to the great disparity of voltages and capacities, e.g. in batteries, which can be found. Moreover, an experimental setup has been proposed in order to allow the electrochemical impedance spectroscopy tests of ultracapacitors during high current loads. Tests were carried out satisfactorily and a precise model was obtained.

Finally, a hardware-in-the-loop simulation for hybrid energy sources is presented. The simulation carried out has a lower cost and complexity compared to the real system. This is due to the fact that the higher cost system, the fuel cell and hydrogen installation, was substituted by a controlled dc power source able to reproduce its current and voltage evolution. Moreover, a vehicle simulator, able to reproduce the vehicle power demand and regenerative breaking is proposed. The simulated fuel cell and a real battery are connected to the simulated vehicle, allowing to carry out a per-unit simulation of different control strategies for a particular driving cycle.

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A   Vehicle frontal surface

C   Capacitance
C_d Drag coefficient
C_{dl} Double layer capacitor
C_n Battery rated capacity

DoD   Depth of discharge

E   Fuel cell internal voltage
E_0 Reversible cell potential
EL   Electronic losses
ESR   Equivalent series resistance

f   Frequency
f_0 Static friction coefficient
f_b Base frequency
f_c Cut-off frequency
f_r Resonance frequency
f_v Dynamic friction coefficient
F   Faraday constant
F_i Forces present in the vehicle while driving

g   Gravitational acceleration

I   Current
I_{ac} Current alternating component
I_b Base current
I_c Leakage current
I_{dc} Current direct component
I_{sc} Shortcircuit current

j   Imaginary unit

k_i Winding losses

L   Inductance

m   Weight

n_i Mols of gas i

OCV   Open circuit voltage

p   Constant phase element exponent
pc   Peukert coefficient
p_{H2} Hydrogen partial pressure at the anode
p_{O2} Oxygen partial pressure at the cathode
p_{H2O} Water partial pressure at the cathode
P   Power
P_b Base power

q_i^{in} Flow of i species which enter the stack
q_i^{out} Flow of i species which leave the stack
q_i^r Flow of i species which react in the stack

R   Universal gas constant
R_i Resistance
R_a Charge transfer resistance

SoC   State of charge
SoH   State of health
SR   Stoichiometric relationship

t   Time
t_b Base time
T   Temperature (Torque for chapter 7)
T_{cpe} Constant phase element parameter

U   Voltage
U_{bat} Battery voltage
U_{fc} Fuel cell voltage
U_{uc} Ultracapacitor voltage
$U_{C_i,L}$ Voltage drop at i capacitor or inductance
U_b Base voltage

V_{an} Volume of gas at the anode

X_i Reactance

Y   Admitance

Z	Impedance
Z_b	Base impedance
Z_w	Warburg impedance
Z'	Real part of the complex impedance
Z''	Imaginary part of the complex impedance

Greek symbols

η	Efficiency
Θ	Slope angle
ρ_{air}	Air density
τ	Time constant
ω	pulsation

Acronyms

ac	Alternating current
AGM	Absorbed glass matt
ADVISOR	Advanced vehicle simulator
CPE	Constant phase element
dc	Direct current
DMFC	Direct methanol fuel cell
EDLC	Electric double layer capacitor
EIS	Electrochemical impedance spectroscopy
FCHEV	Fuel cell hybrid electric vehicle
HEV	Hybrid electric vehicle
HIL	Hardware-in-the-loop
ICE	Internal combustion engine
MEA	Membrane electrode assembly
p.u.	Per-unit
PEMFC	Proton exchange membrane fuel cell
SOFC	Solid oxide fuel cell
VRLA	Valve regulated lead acid batteries
YARC	Arc in the Y plane
ZARC	Arc in the Z plane

Greek based acronyms

ε ARC	Arc in the complex plane

CHAPTER 1

Objectives

The general objective of this Thesis is to open a new research line about hydrogen and electrochemical systems in the Electrical Engineering Department at the Carlos III University. This first approach is more focused on the electrochemical systems itself and vehicular applications, leaving the stationary applications to the near future.

Electrochemical systems are now on the focus of researchers, due to the opportunities they offer. They specially received attention from, obviously, electrochemical engineers who develop them, and from power electronic engineers who design the power converters which interface the electrochemical system and the load.

In this Thesis electrochemical systems are studied from an electric point of view, with which dynamic nonlinear models for fuel cell, batteries and ultracapacitors will be developed. This electrical focus includes the proposal of a per-unit system for electrochemical systems, in order to facilitate the integration of the models developed with conventional power systems. The particular objectives can be described as:

- Acquire a thorough knowledge of the electrochemical systems operation and state-of-the-art of the modeling techniques.

- Select the most appropriate modeling technique and apply it to fuel cells, batteries and ultracapacitors.

- Definition of the nonlinear models for each of the electrochemical systems: circuit topology and parameters.

- Develop an experimental setup which allows the test of ultracapacitors under high current loads for electrochemical impedance tests.

- Experimental validation of the dynamic nonlinear models obtained for the fuel cell, battery and ultracapacitor.

- Development of a per-unit system and definition of base values which are able to define the particularities of each electrochemical system.

- Design a hardware-in-the-loop (HIL) simulation which allows testing hybrid energy systems in a flexible, low cost and safe way.

The Thesis contents are distributed through eight different chapters. Chapter 1 starts with an introduction to the current energetic situation and principle of operation and parts of the different electrochemical systems. The state-of-the-art for the electrochemical modeling and HIL simulation is studied during Chapter 3, whilst Chapters 4, 5 and 6 present the fuel cell, battery and ultracapacitor modeling. The HIL simulation is included in Chapter 7, as well its application to a vehicular case. Chapter 8 closes the Thesis document with the conclusions, contribution, future work and publications.

CHAPTER 2

Introduction

Electrochemical systems are capable of generating and/or storing electric energy, and have an undeniable power electric use. However, they are not classic power electric elements, such as transformer, electric machines, or even more recent solar photovoltaic panels. Therefore, this chapter presents the future energy situation, and its possible effects on the energy scene, as well as an introduction to the different types of renewable energy sources and especially electrochemical systems.

2.1. Current and future energy situation

Nowadays the energy scene is dominated by fossil fuels, such as oil, gas and coal. This strong dependency on oil causes worldwide concern due to its mutual effects on the geopolitical, economic and environmental situation.

Even though these fossil fuels are naturally produced, the rate at which they are consumed is faster than the rate at which they are produced, and causes a dependency on the available reserves. It is not straightforward to calculate the amount of oil reserves, due to the location and deepness at which they can be found. It is an extended idea that the amount of these reserves is reducing dramatically, and as a consequence the oil extraction will also be reduced. This idea is supported by the Association for the Study of
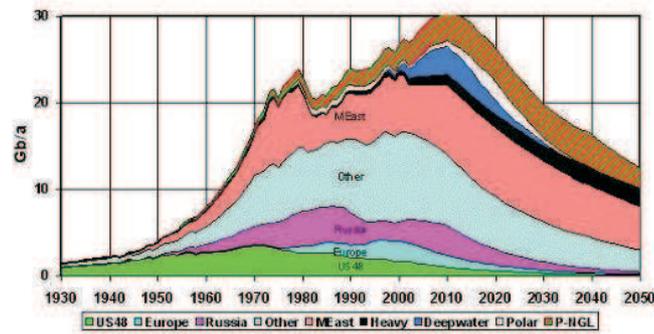
Fig. 2.1: Hubbert chart for oil peak production [1]

Peak Oil and Gas (ASPO), who predicts that the maximum oil extraction peak will be reached before 2020. This can be observed in Fig. 2.1.

Analyzing Fig. 2.1 and Fig. 2.2, it cannot be neglected that most reserves from which oil will be extracted after the peak is reached proceed from the Middle East. This fact increases concern due to their unstable political situation and future oil prices, undoubtedly high due to monopoly and reserve shortage.

However, there are dissenting voices to this, like the U.S. Geological Survey USGS (belongs to the U.S. Department of Interior). They presented the World Petroleum Assessment in 2000, in which they studied the oil reserves and resources, understanding reserves as known-but-not-exploited oil deposits, and resources as unknown oil deposits. Fig. 2.2 presents the corrected data for the USGS focus. It should be observed the difference in the location of reserves. Even though the Middle East countries keep a high percentage of reserves, North, Center and South America, as well as Europe see their resources increased.

These current decreasing reserves and uncertain resources collides with the increasing energy consumption. OECD countries continue to be the prime sink of energy, however, non-OECD countries, specially China and India will show a remarkable increase in their consumption. This is backed up by the International Energy Outlook 2009 report (published by the Energy Information Administration EIA, USA), which released the data shown in Fig. 2.3.

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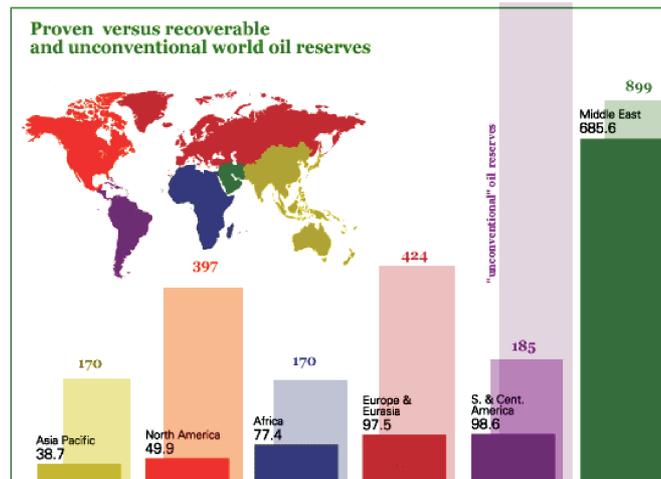
Fig. 2.2: Proven (darker) vs. recoverable (shaded) oil reserves [2]

Fig. 2.3: Historic world energy consumption [3]

The increased 44 % of energy consumption from 2006 to 2030 will genera-te an increment in the carbon dioxide production, which will mostly proceed from non-OECD countries. The International Energy Outlook report expects non-OECD countries to generate a 77 % more carbon dioxide than OECD countries, due to their increasing economic and energy consumption growth. OECD countries are expected to maintain or slightly increase its emissions, as shown in Fig. 2.4.

With this general scene in mind, other energy sources, such as renewable ones are being explored in order to reduce environmental impact and oil de-pendency. Renewable energies have been historically used, principally water
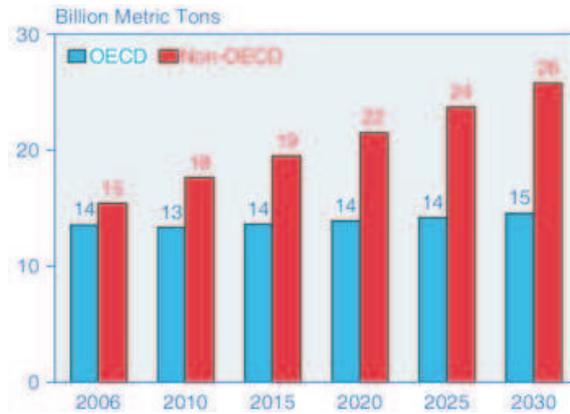
Fig. 2.4: Historic world carbon dioxide production [3]

for water mills and wind for boat propulsion. As shown in Fig. 2.5 water is still the most popular renewable energy source, followed by wind. However, there are other types of renewable energies. A non-exhaustive list of other renewable energies is [5]:

- Tidal energy: It is reliable and predictable, but difficult to actually setup.

- Solar photovoltaic: The sun path is also predictable, but weather introduces unpredictable energy output.

- Wave energy: Highly dependant on wind.

- Thermal gradient energy: It is specially interesting in tropical seas.

- Geothermal energy: Produces non-negligible emissions and is related to seismic activity.

- Biomass energy: It can be programmable.

One of the most important disadvantages of these renewable energies, apart from their higher cost, is its intermittent nature. Currently, fossil power plants do not present this problem due to its dispatchable nature, but a power system with a heavy renewable penetration needs some sort of energy storage in order to store the unused energy, instead of spilling it.

Energy storage is still a challenge and is receiving special attention due to its highly attractive hybridization with renewable energies. There is a wide range of technologies at different maturity levels, such as [30]:
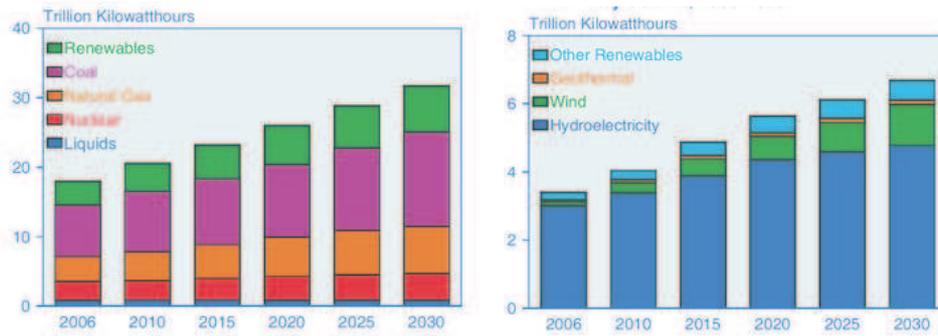
Fig. 2.5: Electricity generation by fuel (left) and renewable source (right) [3]

- Electrochemical storage: ultracapacitors.

- Kinetic energy storage: Uses the energy due to movement, as applied by flywheels.

- Potential energy storage: it can be elastic (spring application) or gravitational.

- Chemical energy storage: batteries are the most common example.

- Thermal and chemical energy storage: transforms the solar energy to chemical energy.

- Magnetic energy storage: stores energy in a magnetic field created by the flow of direct current through a superconductive coil.

These storage technologies can be used for stationary, transport and portable applications, but the renewable energies mentioned before are more focused for stationary applications [31] (even if, e.g., photovoltaic energy can be used for both transportation and portable systems) due to the fact few of these storage systems are applicable to transport, and those which apply (electrochemical, chemical and kinetic) present low energy densities. Therefore, transport systems need other propulsion systems with higher energy densities, which, in most cases, require some type of fuel. Oil replacement in the transportation sector is essential to reduce the harmful emissions and reduce the oil dependency. According to the 2007 Eurostat Energy, Transportation and Environment Indicators report, transportation (specially road transport) consumes a significant percentage of the total energy consumed, as seen in Fig. 2.6.
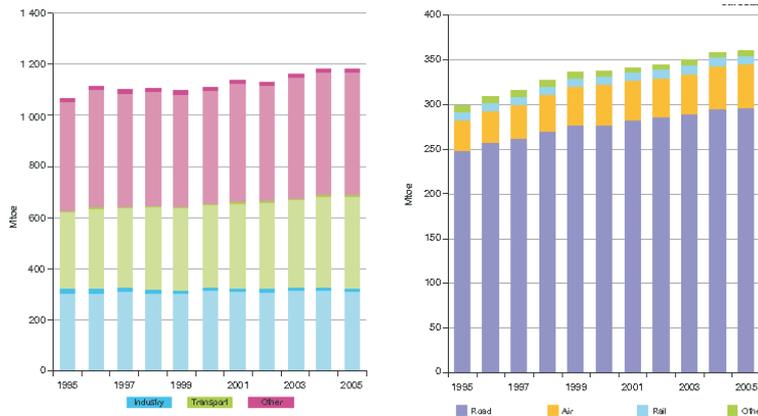
Fig. 2.6: European energy consumption by sectors (left) and transportation modes (right) [4]

A variety of fuels are being tested as a substitute of oil, some of which, as classified by the U.S. Department of Energy, present the characteristics presented in Fig. 2.7. Some of these fuels are already being used, especially biodiesel, natural gas, ethanol, methanol and propane. Hydrogen is also being used in order to study its viability as energy vector. However, it is not used in a large scale. This is due to the fact that there are still some challenges to be overcome. These challenges include onboard storage, transport, cost and safety.

An overview of types of hydrogen storage can be consulted in [32]. Basically there are two states in which hydrogen can be stored: gas or liquid. Gas state storage includes high pressure tanks, underground storage, storage with metal hydrides, which allow a lower storage pressure and storage in microspheres or nanotubes. Liquid storage is specially useful when high density is needed, as in aeronautical applications, but presents the inconvenience of cryogenic temperatures and the presence of the corresponding insulator. These storage challenges also influence the transport and distribution of hydrogen [33].

One of the principal drawbacks for a safe use of hydrogen is its small molecular size, which allows it to leak through pores or joints. Therefore, the storage tanks, joints and pipes used for the hydrogen flow must observe strict security measures. Due to its low atomic weight, if hydrogen leaks outdoors it quickly disperses in the surrounding atmosphere, and the risk of explosion

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	Main source	Energy content (lower heating value)	Energy content (higher heating value)	Energy comparison (% of gasoline energy)	Physical state	Price ($/l)
Gasoline	Crude oil	8,974 kWh/m3	9,611 kWh/m3	100%	Liquid	0,644
Diesel	Crude oil	9,929 kWh/m3	106,19 kWh/m3	111%	Liquid	0,67
Biodiesel	Fats and oil from soy bean, waste, cooking oil, etc.	9,241 kWh/m3 for B100	9,891 kWh/m3 for B100	103% for B100 and 109% for B20	Liquid	0,812
Compressed Natural Gas(CNG)	Underground reserves	1,309e-5 kWh/g	1,45e-5 kWh/g	119,68 g has 17.3% of the energy in 1 l of gasoline	Compressed gas	0,45
Electricity	Coal, nuclear, natural gas, hydroelectric, wind and solar	N/A	N/A	0,264 kWh electricity contains 3% of the energy in 1 l	Electricity	N/A
Ethanol	Corn, grain and cellulose	5,9 kWh/m3 for E100	6,534 kWh/m3	E100 contains 66%	Liquid	0,562
Hydrogen	Natural gas, methanol and water electrolysis	3,33e-5 kWh/g	3,941 e-5 kWh/g	119,6 g has 44.4% of the energy in 1 l of gasoline	Compressed gas or liquid	4-8 $/kg 2005 2-3$/kg expected 2015
Liquified Natural Gas (LNG)	Underground reserves	5,776 kWh/m3	6,556 kWh/m3	64%	Cryogenic liquid	3 $ per 293 kWh [EIA]
Methanol	Natural gas, coal or woody biomass	44,254 kWh/m3	5,04 kWh/m3	49%	Liquid	0,22 $/l [Methanex]
Propane	By-product of petroleum refining or natural gas processing	6,566 kWh/m3	7,06 kWh/m3	73%	Pressurized liquid	25,06 c$/l

Fig. 2.7: Characteristics comparison for different fuels [5]

is very small if hydrogen does not reach the stoichiometric proportion needed to explode (4000 ppm). If the leak occurs indoors, the risk is remarkably higher, therefore, hydrogen and oxygen sensors should be always used. If finally the hydrogen leaked explodes, it will only happen when the hydrogen is present in high concentrations and a spark ignites it. The flame produced by hydrogen is hardly visible and emits less radiation than the generated by gasoline [34].

But the hydrogen has also got positive safety characteristics. Hydrogen is not toxic, as gasoline or derivates and the explosion energy by unit of stored energy is the smallest compared to the rest of fuels. These characteristics, summed up with the high efficiency of the fuel cells which generate electric power with hydrogen as fuel makes hydrogen an interesting possibility as a future energy vector.

2.2. Electrochemical systems

As mentioned earlier, this Thesis will focus on hybrid electric systems in which all the power sources have an electrochemical basis, and no conventional energy sources such as internal combustion engines are included.

2.2.1. Fuel cells

Even though fuel cells are nowadays on the focus of researchers, governments and private companies as a possible substitute of conventional energy systems, this technology is known since the 19th century. It was Sir William Grove who in 1839 first presented a fuel cell formed by two platinum electrodes submerged in an acid solution and discovered that an electric current flowed between the electrodes [35]. However, it was not until the 20th century that Nernst presented the thermodynamic laws which defined its operational principle and setup the first operative fuel cell, based on solid oxides and ceramic.

There are different technologies for fuel cells: polimeric, ceramic, molten
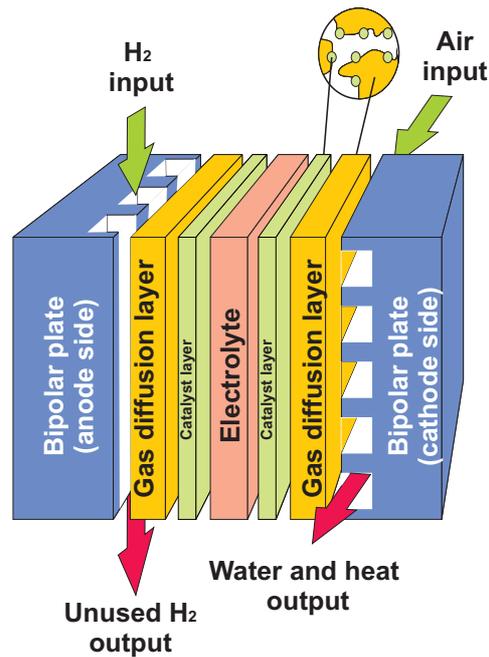
Fig. 2.8: Components of an individual fuel cell

carbonates, phosphoric, etc. Each of these technologies is especially appropriate for a particular application. For example, polimeric based fuel cells are convenient for transportation due to the fast start-up, ceramic fuel cells are useful in high power stationary applications whilst direct methanol are used in small portable systems [36]. This Thesis is more focused on the transportation application, therefore, emphasis is done in polimeric based fuel cells. An overview of other fuel cell technologies can be consulted in [35].

2.2.1.1. The stack and operational principle

The heart of fuel cells is the fuel cell stack, which is the element which converts the chemical energy to electricity. The stack is a series combination of individual cells in which the reaction takes place. The components of each cell: electrolyte, electrodes (anode and cathode), catalyst layer and gas diffusion layer are pointed out in Fig. 2.8.

For polimeric based fuel cells, really called proton exchange fuel cells (PEMFC), the fuel which must be supplied is hydrogen and oxygen (or air). The hydrogen is in gaseous state and enters the fuel cell through the canals of the bipolar plates (anode side), which allows the gas to distribute evenly
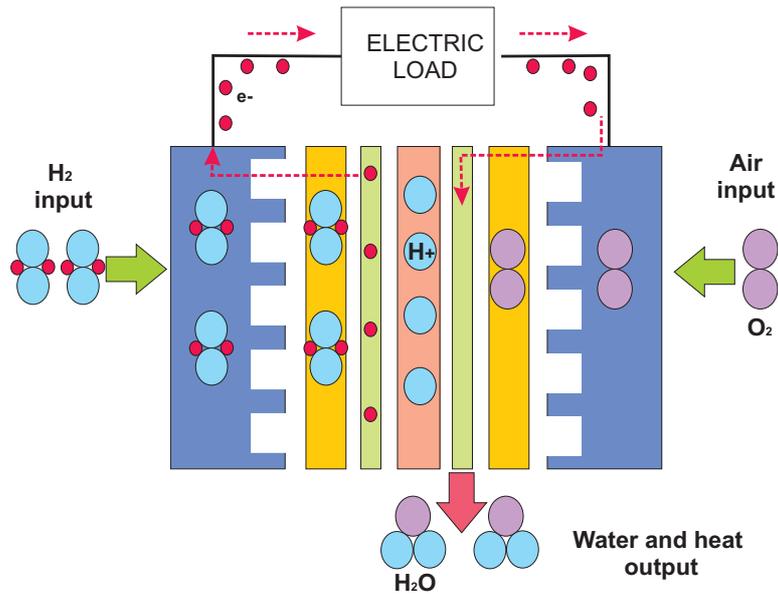
Fig. 2.9: PEMFC operation principle

through all the surface of the gas diffusion layer. On the other side, the oxygen or air does exactly the same thing on the cathode side. Once both gases have gone through the gas diffusion layer, they reach the catalyst layer, which is platinum based for PEMFCs. The catalyst of the anode side dissociates the hydrogen molecule in protons and electrons (see Fig. 2.9). The electrons flow through the electric load to which the fuel cell is connected whilst the protons go through the polymeric electrolyte until they reach the cathode side. Once on the catalyst layer of cathode side, the hydrogen protons react with the oxygen present in the air and the electrons which leave the electric load, generating water and heat.

$$
\begin{aligned}
2 \cdot H_2 &\rightarrow 4 \cdot H^+ + 4 \cdot e^- \\
O_2 + 4 \cdot e^- + 4 \cdot H^+ &\rightarrow 2 \cdot H_2O
\end{aligned}
\tag{2.1}
$$
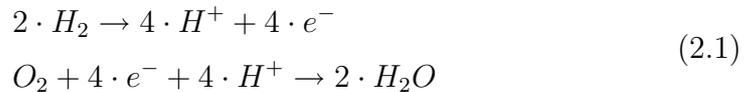
In order to ensure a correct reaction and operation, the bipolar plates should be light, resistant, conductor of electricity and impermeable to gases, in order to ensure a correct distribution of gases through the gas diffusion layer. The most common materials are graphite or metal [37].

The gas diffusion layers help to diffuse the gas to the catalyst layer, conducts electrons from the anode and to the cathode and extracts the water produced in the cathode. To facilitate the water and gas flow, the gas diffu-

sion layer can be made impermeable by adding Teflon.

The catalyst layer is not, as the bipolar plates or the gas diffusion layer, a "solid" structure, but a deposit of catalyst particles on the gas diffusion layer. The reason for this is that the catalyst width is not relevant for the reaction which takes place. Only the surface which the catalyst layer exposes to the gas diffusion layer can alter the reaction (a larger surface is always preferable). The most common material is platinum, but other transition metals such as palladium and titanium could be applied. The use of a precious metal such as platinum increases the manufacture cost, and is therefore, another reason to keep low the amount of platinum used.

One of the distinctive elements in a fuel cell is its electrolyte. As we are focusing on the PEMFC, the electrolyte is a polymeric membrane which is normally made out of Nafion (really it is a derivate of Teflon and Nafion is the commercial name given by its manufacturer). This polymeric membrane should be chemically and thermally stable, in order to endure the action of oxidative agents, as well as relatively high temperatures. The membrane should also be proton conductive, to carry the hydrogen protons from the anode to the cathode. To achieve this the membrane must be humid, something which is possible due to the water generation on the cathode side. However, humid does not mean flooded. A flooded membrane could lead to a short-circuited fuel cell, so the water management is an important issue in fuel cells. Even if the membrane should be only proton conductive, there is a small amount of electrons and hydrogen molecules which directly crosses the membrane to reach the cathode, but no reaction occurs, so the output voltage of the cell will be lower than expected.

In the fuel cell argot, instead of talking about electrolyte, catalyst, etc. it is very common to call the assembly electrolyte+both catalyst layers Membrane Electrode Assembly 3 (MEA 3). If the both gas diffusion layers are included to the previous assembly, it is called Membrane Electrode Assembly 5 (MEA 5).
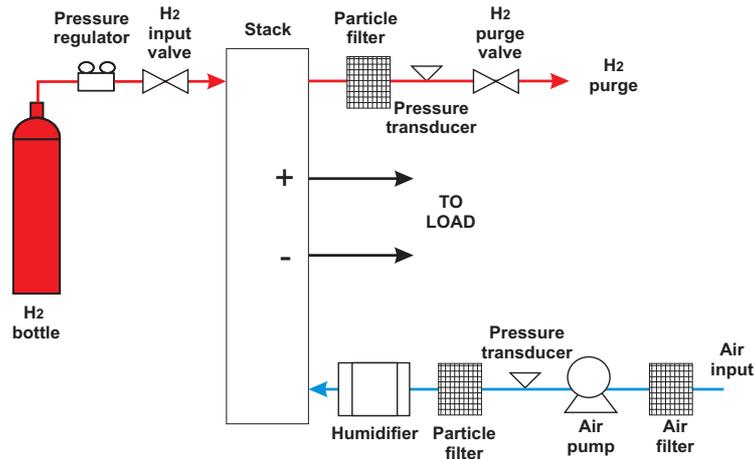
Fig. 2.10: PEMFC auxiliary systems

2.2.1.2. Auxiliary systems

At the beginning of this section we said the stack was the central element of the fuel cell. However, to ensure its correct operation other systems need to be included, as explained in [37]. These systems supply the gases, cool the stack, etc. Fig. 2.10 presents these auxiliary systems for a simple PEMFC.

The hydrogen gas is stored in a compressed bottle at high pressure (up to 200 bar), but lowers it pressure to about 10 bar through the pressure regulator. The hydrogen input valve is controlled by the fuel cell control system and the user interface software. 10 bar is still not low enough, so the fuel cell may have its own pressure regulator to reduce it further. Not all the hydrogen supplied to stack reacts, so the fuel cell control system purges periodically the unused hydrogen. This unused hydrogen can either be expelled to the atmosphere or be reused at the hydrogen input.

For the air flow system, the air is taken from the surrounding atmosphere; therefore, it needs to be filtered in order to avoid particles entering the fuel cell stack. To keep the fuel cell stack adequately supplied with oxygen, the air pressure is increased with an air pump. The pressure is measured through a pressure transducer and the air is humidified before entering the fuel cell cathode.

It is not included in Fig. 2.10, but fuel cell systems can also present a

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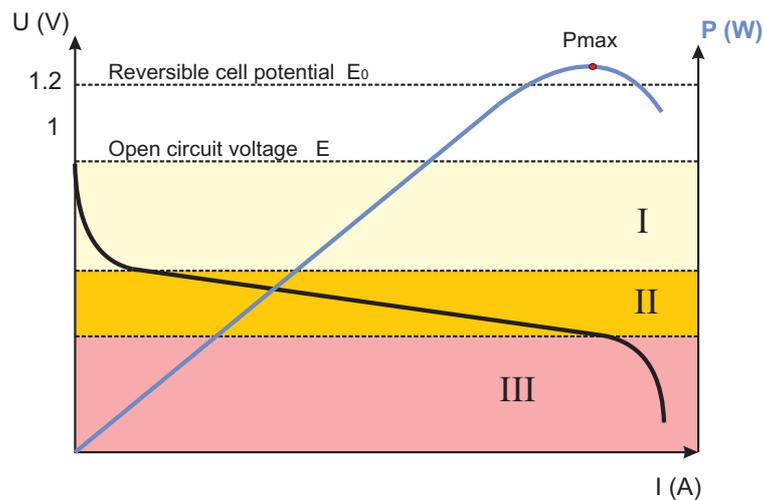Fig. 2.11: PEMFC characteristic curve

blower or fan. With this element the fuel cell stack is cooled, in order to keep the fuel cell stack in its operating temperature range. The fan duty cycle is controlled by the fuel cell control system, which increases the fan duty cycle when the temperature reaches a certain threshold.

Apart from these auxiliary systems used to keep the fuel cell in correct and secure operating conditions, the electric connection of the fuel cell to the load can be done directly. However, the fuel cell output is an unregulated voltage, so a power converter is normally connected in between. The power converter nature (DC/DC or DC/AC) as well as its topology will depend on the final application. Also, the fuel cell is a power source which generates power, but does not sink it. Hence, a power diode can be connected at the fuel cell terminals to reject any power reflux.

2.2.1.3. Characteristic curve

The ideal voltage of an individual cell is 1.2 V, however, if the voltage is measured when the cell is at open circuit, the voltage will not surpass 1 V. This difference is due to the fact that ideally no reaction occurs when the fuel cell is at open circuit, but really there is a small consumption of reactants which cause this voltage drop.

The fuel cell voltage decreases for increasing load current, but it is not

a completely linear dependency. For low currents the voltage is a nonlinear curve (area I in Fig. 2.11) which is due to the activation polarization. This activation polarization is the overpotential which must be overcome before the reaction occurs. This phenomenon takes place both at the anode and cathode, but is dominant at the cathode side.

At medium currents, the voltage follows a linear evolution (area II in Fig. 2.11). This voltage drop is due to the ohmic polarization. Due to the linear nature this phenomenon can be represented by a resistance, which includes the resistance to the electrons flow from the catalyst layer to the electric load and to the protons flow from the anode to the cathode through the membrane.

Area III in Fig. 2.11 is due to the concentration polarization, present at high load currents. It is caused by the impossibility to increase the reactants concentration in order to increase the fuel cell output current.

Taking into account all these voltage drops, the final fuel cell voltage is:

$$U_{FC} = E - \Delta U_{act} - \Delta U_{ohm} - \Delta U_{conc} \tag{2.2}$$

2.2.2. Batteries

The principle in which the batteries are based was discovered by Luigi Galvani in 1780. He demonstrated with two different metals acting as electrodes and a frog as electrolyte that current could flow through the frog. But the battery as we know it was setup by Alessandro Volta in 1800. He developed the idea presented by Galvani by connecting the cells in series, so as to obtain a higher voltage. The batteries began to be used industrially with the Daniell battery in 1836, as well as an energy source for the telegraph.

Depending on the material from which the electrodes are manufactured and the electrolyte used, batteries present different characteristics. The most traditional battery is the lead-acid battery, followed by the nickel-cadmium, nickel-metal hydrides and lithium based batteries (lithium-ion or lithium-polymer). These are the basic and most commonly used batteries, but there is a wide spectrum of batteries which present more unusual materials, such as vanadium, silver, zinc, etc. In this Thesis we are going to work with an
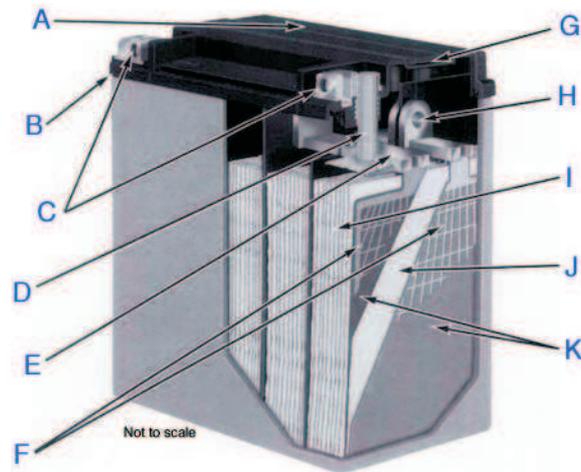
Fig. 2.12: Parts of a commercial battery [6]

Exide-Tudor lead-acid battery especially manufactured for traction purposes.

2.2.2.1.   Parts and operational principle

Some parts of the battery resemble to those of the fuel cell, which is inevitable due to the fact that both are electrochemical systems. However, there is an outstanding difference between fuel cells and batteries. The difference lies in the supply of reactants, which can be done externally (fuel cells or flow batteries) or can be found inside the system casing (battery case). For the fuel cell case, it will generate electric energy indefinable whilst hydrogen is supplied to the anode and oxygen to the cathode. However, a battery has a finite time during which it can supply energy due to the fact that the reagent depletes when the discharge time is due.

Fig. 2.12 shows the elemental parts of a battery.

- A: Valve to allow the exit of gasses which can be produced during overcharging.

- B: Battery case.

- C: Positive and negative terminals.

- D: Connector between plates to terminal.

- E: Positive top plate.

- F: Positive and negative plates.

- G: Top sealing.

- H: Negative top plate.

- I: Plate separating material.

- J: Plate separator (separates the positive and negative plates.)

- K: Positive and negative plates.

The battery positive and negative plates can be mounted on a same plate, called bipolar plate. The positive plate is made out of lead dioxide, whilst the negative plate is a sponge texture lead. In between the positive and negative plates we can find the electrolyte. Even if in the batteries commonly used in vehicles for auxiliary load supply, the electrolyte is liquid (dilute sulphuric acid), batteries for traction purposes normally use non-liquid electrolytes [38]. This non-liquid electrolyte commonly has a gel or AGM (Absorbed Glass Matt) structure, which avoids the loss of electrolyte, which would negatively affect the battery operation.

The reactions which take place in a battery are different, depending if it is a charge or discharge process. For a discharge process, Fig. 2.13, the positive terminal reacts with the sulphate ions present in the electrolyte to produce lead sulphate. The sulphate ions of the electrolyte also react with the lead dioxide of the negative electrode to also produce lead sulphate. Therefore, both plates produce lead sulphate whilst the electrolyte looses the sulphuric acid and increases its water content.

For the charge process, an external power source is connected between the terminals of the battery. The initial state is the one left when the battery is discharged, that is, both electrodes are lead sulphate. With the charge process, the sulphate present in the electrodes return to the electrolyte, which recovers its sulphuric acid nature. And the positive electrode changes from lead sulphate to lead whilst the negative electrode changes to lead dioxide. Further information can be found in [39].
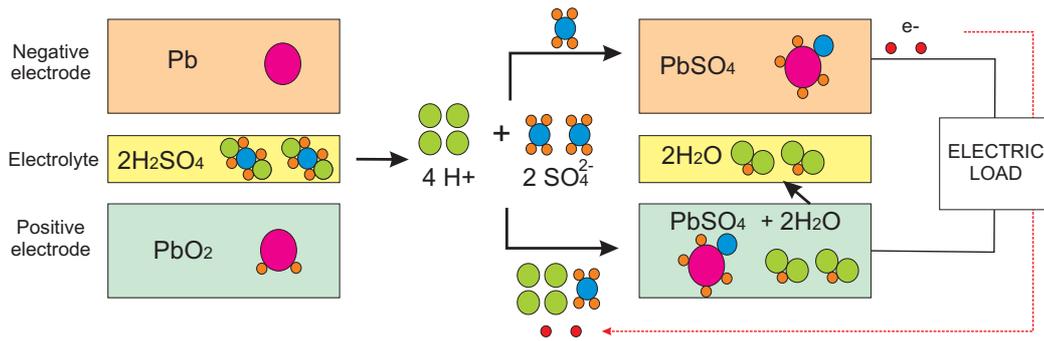
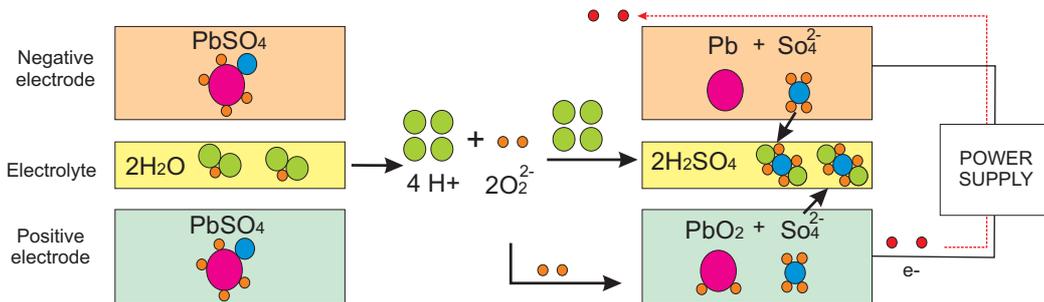Fig. 2.13: Reactions during the battery discharge process

Fig. 2.14: Reactions during the battery charge process

To avoid overcharge it is desirable to follow the recommendations made by the manufacturer. If not, gasification may take place. This gassing phenomena happens when there is no more lead sulphate on the electrodes to react, as they are already lead (positive electrode) or lead dioxide (negative electrode). So oxygen is formed at the negative electrode and hydrogen at the positive electrode. In traditional (flooded) batteries, these gasses leave the battery casing, causing the loss of electrolyte. But nowadays, traction batteries are sealed, so gasses are trapped inside the casing, to allow its recombination to water.

Other problems which may be present in a battery are sulphatation and corrosion [40]. Sulphatation takes place when a battery is kept discharged during a long period of time, causing the lead sulphate present in the electrodes to form crystals, which are difficult to reverse to lead or lead dioxide. The corrosion takes place on the electrodes, increasing the internal electric resistance of the battery. Also, large crystal will be formed, reducing the active surface and the battery capacity.
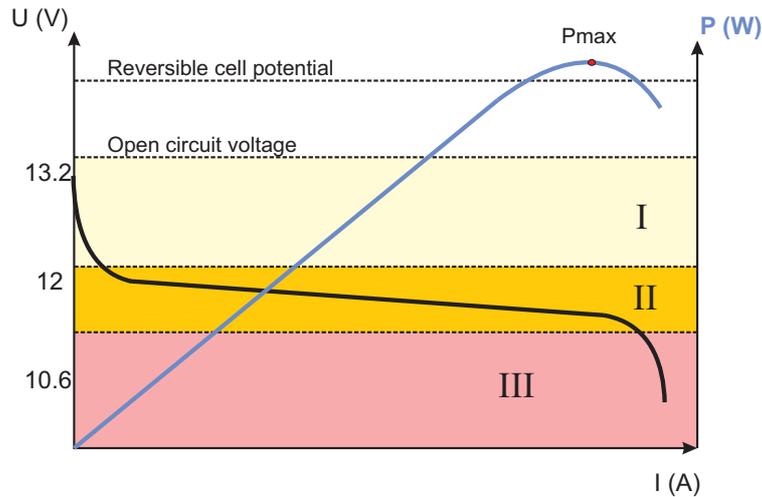
Fig. 2.15: 12 V Lead acid battery characteristic curve

2.2.2.2. Characteristic curve and principal variables

The characteristic curve of a battery is very similar to the one obtained for a fuel cell. Fig. 5.1 presents the characteristic curve for a 12 V battery module. The same three areas defined for the fuel cell: activation, ohmic and concentration polarizations can be also observed for the batteries.

But this characteristic curve does not completely define a battery. To know the rated battery discharge duration at the rated current it is necessary to define the battery capacity in A·h. For example, normally the principal characteristics are given as: 12 V, 100 A·h (20 h) lead acid battery. This means that the battery is capable of discharging during 20 h if the discharge current is $100/20 = 5$ A.

Other particular variables used for batteries are:

- Open circuit voltage (OCV): Voltage measured in open circuit at the terminals of the battery after a certain relax time has gone by.

- State of charge (SoC): Remaining battery capacity, measured as a percentage of the rated capacity.

- State of health (SoH): It reflects the general condition of the battery, as well as the ability to follow particular loads when compared to a fresh battery.

- Depth of discharge (DoD): Amount of energy extracted from the battery. It is normally expressed as a percentage of the rated capacity.

2.2.3. Ultracapacitors

Ultracapacitors are energy storage systems which belong to the family of capacitors. Conventional capacitors store energy by collecting positive charges on one electrode and negative charges on the other electrode, with an electrolyte in between. This charge separation is responsible for the potential created between both electrodes. However, ultracapacitors do not use the electrolyte in the same way, they use another technology, electric double layer, which allows them a massive charge separation.

The use of energy storage through electric double layer was first reported in 1957 by H. Becker, who worked at General Electric. The device as we know it nowadays was presented by Robert Rightmire, a chemist at Standard Oil Company of Ohio (SOHIO) at 1962. Another SOHIO researcher, Donald Boos continued in 1970 the research initiated by Rightmire.

2.2.3.1. Parts and operational principle

Ultracapacitors are formed by two metal electrodes (foils, which are not bulky) coated with activated carbon, immersed in an electrolyte and separated by a paper separator, as seen in Fig. 2.16 [7]. Electrons accumulate in one of the electrodes (the one connected to the negative terminal) and attract positive ions of the electrolyte [41]. On the other electrode, positive charges accumulate, attracting the negative electrolyte ions, while current flows through the external load. The separator avoids current from flowing directly between both electrodes and causes the effect of having two charge layers, which is why ultracapacitors are also called electric double layer capacitors (EDLC). Due to the fact that the electrodes are made out of a high porous material which present small diameter pores (order of nm) the charge can be stored in the mircopores at the interface between the electrode and the electrolyte. Moreover, the electrode surface is much larger than, for example, batteries, and can reach $2000 m^2$/g [42]. This combination of large surface and small separation between charges allows to reach capacitances of farads
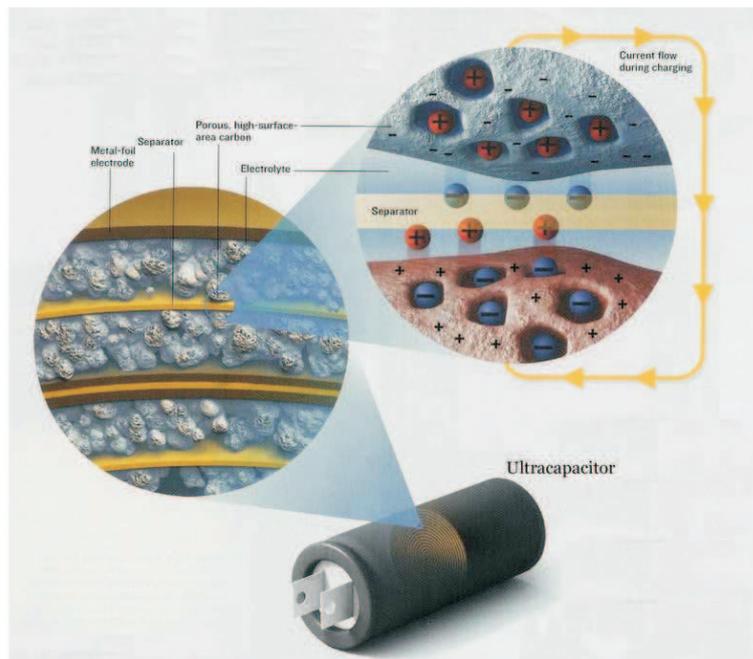
Fig. 2.16: Components and operation of ultracapacitors [7]

and thousands of farads. One of the drawbacks of the small separation is the maximum voltage, which depends on the dielectric breakdown characteristics, and causes ultracapacitors to be low voltage systems (3.5 V maximum).

These operation characteristics define ultracapacitors as high power sources, which are able to supply very high power peaks during very short periods of time. The differences between power and energy densities for different energy storage systems can be consulted in Fig. 2.17.

In addition to high power density, ultracapacitors present a long cycle life and endure deep cycles at high rates for 1.000.000 cycles without severely affecting its characteristics. Moreover, ultracapacitors can be stored during long periods of time and remain near to its original conditions.

Another particular characteristic of ultracapacitors is its small internal resistance, called electric series resistance (ESR). This makes the packaging of ultracapacitors in modules a difficult issue, as the contact and current collector resistances should be kept low enough to allow the ultracapacitor act during high power loads.
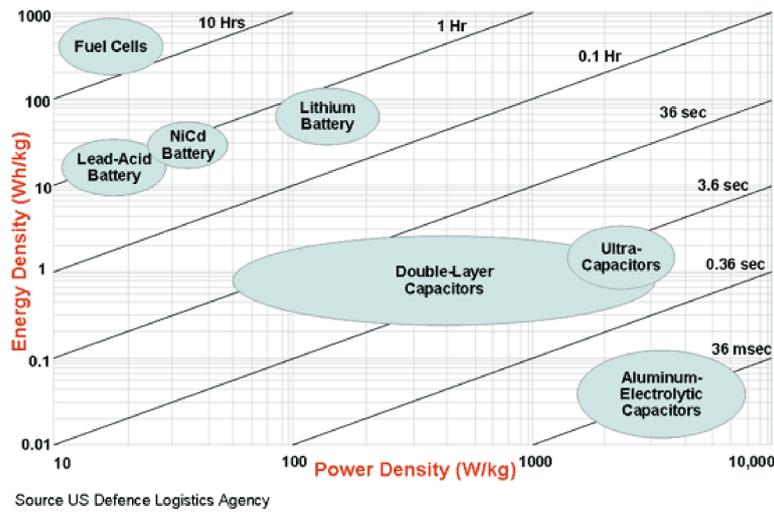
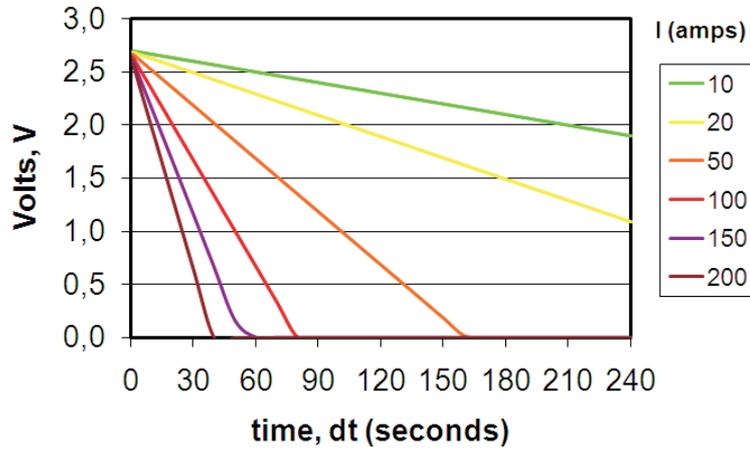Fig. 2.17: Ragone chart for different energy storage systems

Fig. 2.18: 3000 F Maxwell ultracapacitor

2.2.3.2. Characteristic curve

There is not a unanimity in which is the characteristic curve for an ultra-capacitor. However, manufacturers used discharge profiles, as the one shown in Fig. 2.18, which is the discharge profile given by Maxwell Technologies for the 3000 F 2.7 V ultracapacitor.