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Second life of electric vehicle batteries: relation between materials degradation and environmental impact

1. Introduction:

Air pollution, dependency on fuels of finite supply, climate change and the increase of energy cost are some important challenges of the present world. These concerns are aggravated by transportation and power generation sectors since they are the main consumers of fossil fuels and responsible of most of the greenhouse gases (GHG) emitted in the atmosphere. The transportation sector has found in the technology of electric vehicle (EV) an emerging solution for these problems that have gained importance during the last decade. This transition to electrified transportation is being facilitated by the European Union directives restricting the emissions coming from transportation as well as the recent advances in Li-ion battery technology.

The main difference between a vehicle using electric power and a common internal combustion engine is the energy source. While one uses crude oil derivatives stored in a tank, the other one converts the stored electrochemical energy into electrical energy. This change forces car manufacturers to adapt all the traction, control, security and refrigerating systems (Hawkins et al 2012). This results in a lighter traction system, because of a smaller electric motor and no gearbox, but an overall weight increase of around 25% due to the battery system and all the electric and electronic additional components.

Although EV has no tailpipe emissions, its well-to-tank energy efficiency, coming from the electricity generation and distribution to charge the EV battery, is less performing than the one of internal combustion engine vehicles (Bradley and Frank 2009). Therefore, most of the life cycle assessments (LCA) point out the relevance of the electricity generation Mix to identify the environmental impact of the EVs during the use phase (Helms et al 2010) (Campanari et al 2009). Additionally, an environmental impact increase of around 50% during the EV production phase has also been identified, being the battery manufacture responsible for more than 40% of this impact (Patterson et al 2011). Aware of this setback, some car manufacturers have started to conceive the EV production as a whole environmentally friendly industry. For example, some companies are promoting the use of natural lighting and ventilation, solar panels and rain water harvesting in their production plants (Maini et al 2013).

On the economical side, the battery is the principal hurdle for EV competitiveness as its fabrication cost represents around 30 to 40% of the final EV price. This causes an important cost increase for the consumer. In order to solve this drawback, car manufacturers use different strategies to stimulate EV purchases. For example, Renault and Nissan offer a battery renting alternative, reducing the selling price, while other companies, like the joint venture 4R-energy (4R-energy 2013), are focused on battery second life strategies to recover some incomes by the battery re-selling or by the profit obtained from this life enlargement. This latter option is the one studied in this paper assuming that batteries are not considered appropriate for traction purposes once they reach a State of Health (SOH) of 80% (Wood et al 2011).

The study of the second life of an EV battery cannot be dissociated from the battery performance during its use in an EV (latter mentioned as "first life" in the text), the safety of the battery at the end-of-life and an accurate understanding of the loss of capacity. Therefore, in this study, we analyze the environmental impact of the second life of an EV battery in eight stationary scenarios. These obtained results have been added to the Global Warming Potential (GWP) from the first life. An overview of the different battery chemistries used for EV applications as well as their main degradation mechanisms is also presented. A correlation between the materials degradation and the second life applications is proposed.

2. Methodology:

There are many environmental impacts studied in the LCA of EV, such as climate change, resource depletion, human toxicity and eutrophication among others. However, the GWP, expressed in kg of carbon dioxide equivalent (kg CO_2 e.), is the most common environmental indicator used for the LCA of EVs for its simplicity and overall impact comprehension (Hawkins et al 2012). The scarcity or critical reserves of determined materials, such as lithium, will have no impact on our analysis because only reused EV batteries are considered in this study. Additionally and considering that there are many possible second life applications, the use of the carbon footprint or the GWP as environmental indicator is thought to be the most indicated parameter in order to achieve comparable results. Therefore, the life cycle based on the CO_2 emissions ($LCCO_2$) methodology will be followed.

The $LCCO_2$ results strongly depend on the methodology and the defined system boundaries. In this paper, the boundaries include the first and second life of EV batteries. The assessment of the second life will be evaluated considering different case studies of battery re-use. Additionally, to procure a wider comprehension of the environmental impact reduction caused by the battery re-use, a survey of the different electrode materials forming the batteries will be done incorporating the study of their potential for second life use.

Even though most of the electrified vehicles are hybrid cars using NiMH batteries, their power and energy characteristics are too low for most of the stationary applications (Andrew 2009). At the end of the hybrid vehicle life, the SOH of these batteries is very variable and well beyond the 80% defined for pure EV batteries before recycling (Leijen 2014). For these reasons, in this paper only the Li-ion batteries that have been used in an EV are considered while NiMH batteries are not included.

Figure 1 describes the complete $LCCO_2$ boundaries of an energy storage stationary application using a second life EV battery. It is the result of the combination of two existing approaches: $LCCO_2$ of an EV and $LCCO_2$ of a battery in a stationary application.

- *$LCCO_2$ of an EV:* This approach defines the system boundaries of an EV that has a battery used only in the EV. The boundaries of this assessment involve the battery and car production phases (including the GWP impacts of the materials acquisition all around the globe and the transportation between phases), the EV use and dismantling and the battery recycling phases (Fig. 1 until the end of 1st life). From different

European funded projects (UMBRELA FSEM and THEMLA) (Held and Baumann 2011), (Helms et al 2010), (Eiber and Grassmann 2012), and articles (N.Genikomakis et al 2013) it has been stated that the GHG emissions of an EV using the average European Union (EU) electricity Mix (421 g/kWh) is around 35.000 kg CO_2 e., being the EV production responsible of 11.000 kg CO_2 e. Although these results might substantially change according to the electricity Mix used, the average EU mix is used to facilitate the comparison.

- *LCCO$_2$ of a battery in a stationary application*: This approach defines some possible stationary applications where EV batteries can be used according to their physical and functional specifications (from 8 to 25 kWh and 80 kW max. Power). Therefore, only small stationary applications will be studied (Andrew 2009). Some of these applications, such as solar powered island systems, are nowadays using new Lead-acid batteries. In these cases, the study will compare the impact reduction of substituting these batteries by re-used Li-ion batteries as it is shown in Figure 1. Using the LCA2GO software, and comparing with the literature (Matheys et al 2007), it is assumed that the GHG emitted by the fabrication of a Lead-acid battery are 60% of those emitted by the fabrication of a Li-ion battery with an equivalent capacity. However, their lifetime is reduced by 2.5 times (Teodorescu et al 2013). In order to do a proper LCCO$_2$ analysis, the efficiencies of the different elements involved in the study should be considered. For the calculations, the inverters are assumed to have an efficiency of 90% (Vroey et al 2013) and the lithium batteries have around 90-95% of charge-discharge efficiency (Wang et al 2012). On the other hand, Lead-acid batteries have an efficiency around 80% (Dunn et al 2011), (Van den Bossche et al 2006). Consequently, the overall charge-discharge cycle efficiency is considered to be 0.7 when using Li-ion batteries and 0.6 when using Lead-acid batteries.

- *LCCO$_2$ of a stationary application using an EV second life battery:* Combining the two previous approaches, the complete system boundaries for the 1st and 2nd life of an EV battery are obtained. These system boundaries are presented in *Fig.1* the addition, before the recycling phase, of the second life phases in the common LCCO$_2$ of an EV (represented by a dashed square). These phases are the battery re-manufacture and second life application. In this work we will maintain the same EU Mix for the energy exchanged with the grid during the second life. This final approach is the one used for the calculations all along the study.

Our new approach, involves two additional transportation steps that need to be taken into consideration; these steps include the battery transportation from the EV dismantling place to the battery remanufacturing plant and from the remanufacturing plant to the second life application destination. In both cases, the generated emissions derived are calculated similarly.

The transportation of the battery will be done by truck and only one battery will be transported at a time. This assumption is most likely not going to evolve much in the near future as the EV market is below the 1% in most of European countries. Hence, the average trip distance for the battery acquisition is assumed to be 1.000 km. The derived GHG emissions from this trip are 317 kg CO_2 e. As the studied second life applications are expected to work with one battery only, all these assumptions can also be used for the

battery delivery to the final destination. This value represents less than 1% of the total emissions of an EV during its first life. Hence, despite logistic optimizations, not much improvement on the environmental impact will be obtained

There are different ways to address the battery re-manufacture processes: the direct re-use of the battery; the dismantle of the battery into modules to re-build it as a new battery pack adapted to the second life application; and, finally, the dismantling of the battery at cell level to re-build it depending on their State of Health (SOH). As it has been shown in previous works, the best possibility to reach a positive economic balance is the direct re-use of the batteries without module manipulation (Canals Casals et al 2014). Consequently, this option will be the one used in this study. The process of remanufacture entails a visual check, a Capacity and Pulse test to determine the SOH and the few necessary adjustments to adapt the battery to the new application. The energy consumption in the remanufacture phase is calculated to be 27 kWh per battery check, which corresponds to 11,5 kg CO_2 e. that need to be added to the previous values.

In order to obtain comparable results, it is important to define the functional unit (FU) that will be used. In the LCA of an EV, the FU normally considered is the kg CO_2 e. emitted per range or per km. However, in stationary applications, the FU generally used is kg CO_2 e. emitted per battery weight (kg), per battery capacity (Ah) or per energy (kWh) exchanged with the grid (Matheys et al 2007). In this study, kg CO_2 e. emitted per functional kWh will be used given that it has no sense to use km, battery weight or battery capacity for second life applications. A functional kWh is defined as the energy (kWh) received by the consumer directly from the battery (not to confuse with the energy received from the grid or power source).

In the case of second life applications, the factors that have a major environmental impact contribution are the battery lifetime, the energy source and the system efficiency:

- *Lifetime*: The battery lifetime depends on the materials present in the battery and on the requirements of the application. The shorter the battery lifetime, the higher its environmental impact.
- *Energy source and system efficiency*: The pollution coming from the energy sources is essential for the sustainability; i.e. it is obviously cleaner to use solar panels than to burn coal. The efficiency deals with a similar issue; if a system is more efficient than another, the energy losses will be lower and, consequently, the environmental impact will be lower.

The battery lifetime factor depends on: the temperature (T), the charge and discharge requirements (C-rate), the average State of Charge (SOC), the number of cycles and the Depth of Discharge (DOD) per cycle. These identified aspects can be linked to the capacity fade as presented in *Eq.1*. From literature, (Schmalstieg et al 2014), (Teodorescu et al 2013), (Delaille et al 2013), (Ecker et al 2012) the Li-ion battery lifetime equations are obtained *(Eq.2)*, and considering the experimental data of these studies on specific Li-ion battery systems, which is the most common in EV batteries (Canals Casals and Amante García 2014), the parameters are determined *(Eq.3)*. Hence, the battery lifetime can be predicted.

$$Cfade = 1 - (\text{C-rate factor}) - (\text{SOC and Temperature factor}) - (\text{cycling factor}) \qquad \text{Eq. 1}$$

$$\mathbf{C_{fade} = 1 - (r(i, T) \cdot I) - \left((a \cdot V - b)10^6 \cdot e^{\frac{c}{T}}\right)t^{0.5} - \left(\frac{d}{\left(C_{ini}\left(e - f \cdot Log_{10}\left(\frac{DOD}{2}\right)\right)\right)}\right)A_{ccum}} \qquad \text{Eq. 2}$$

$$\mathbf{C_{fade} =}$$
$$\mathbf{1 - (r(i, T) \times I) - \left((7.543V - 21.75)10^6 \times e^{\frac{6975}{T}}\right)t^{0.5} - \left(\frac{0.15}{\left(C_{ini}\left(6000 - 3000 \times Log_{10}\left(\frac{DOD}{2}\right)\right)\right)}\right)A_{ccum}} \text{ Eq. 3}$$

Where C_{fade} is the capacity loss, $r_{(i,T)}$ is the internal resistance, I is the current intensity, V is the battery voltage, T is temperature, C_{ini} is the initial capacity of the battery, t is the time elapse and A_{ccum} is the accumulated current discharged by the battery.

The lifetime of the battery can be estimated from these equations by identifying the variable parameters from the second life's requirements. To facilitate the calculations, all these parameters were considered constant for monthly periods. For example, an application that has a daily DOD of 100% will have an average voltage corresponding to 50% SOC, and the A_{ccum} would be equal to the battery capacity multiplied by the number of days per month; i.e. 37 Ah (battery capacity) · 31 days = 1147Ah.

The stationary applications can be classified according to the beneficiaries, which are basically: the electric companies and the end-users. The electric companies are paying special attention to the developments on storage systems providing energy services, such as "area regulation", "transmission and distribution deferral" and "power quality" among others (D. Rastler 2010), (Cready et al 2003), (Ciccioni et al 2012). However, these applications require high power and energy systems that imply the incorporation of hundreds of EV batteries (Heymans et al 2014) that are still not yet available. Therefore, they won't be assessed in this study.

This study is focused on single battery second life systems which are the most suitable for end-users applications. Considering the capacity and power specifications of the EV battery, three stationary applications have been determined. Each application has its particular battery cycling conditions:

- *Energy arbitrage*: In this application, the energy is bought at low fare rates (e.g. during the night) to recharge the battery and the accumulated energy is consumed during the periods when the electricity is more expensive (e.g. during the day) (Heymans et al 2014). For the calculations, the European electricity Mix is used. In this situation the battery will be fully charged and discharged (close to 100% DOD).
- *Island installations:* In this application, the system will be connected to renewable energy sources (RES) charging the batteries when the energy production excesses the demand, restituting it to the house when there is not enough energy production (Wang et al 2012). This represents an alternative to the actual systems using Lead-acid batteries or fuel generators to power up the installations. In this situation, the DOD of the battery will be around the 50%.

- *Autonomous use:* In this application, the batteries are charged by the RES but the whole system is connected to the grid, providing an energy support in case of a lack of generation from the RES (Guo et al 2014). In this case, the DOD of the battery will also be around 50%.

Based on these three stationary applications using second life batteries, the results were compared with different alternatives to power up each application, that go from using Lead-acid batteries to an electricity diesel generator, obtaining the 8 analyzed scenarios described in table 1.

The battery lifetime is obtained from Eq.3 considering the first and second life. This way, after using the battery during 10 years in an EV, we obtain a SOH of 78% at the end of the 1st life. Then the battery will continue working in the second life application until it achieves a final SOH of 60%. In the studied cases this limit corresponds to 8 or 20 years of additional use depending on the second life application. This difference in lifetime is explained by the different requirements between the island and autonomous applications corresponding to a DOD of 50% and 100%, respectively, and consequently, on C-rate.

Finally, in order to properly identify the environmental impact of the battery re-use, a comparison of the impact loads of the production, uses and end-of-life phases on a battery lifetime (considering 1st and 2nd life) will be presented.

To present growing opportunities, future expectations and research recommendations, an analysis of the materials used in the actual EV battery cells and their properties will be offered.

3. Materials

Li-ion battery technology can be divided in different chemistries presenting their own characteristics and advantages (Armand and Tarascon 2008). Over the last decades, tremendous progress has been done in developing cathode, anode and electrolyte materials, which represent the most important components of Li-ion batteries and at the same time will determine the battery performances. In this work the study is mainly focused on the cathode and the anode materials as they are the source of many degradation processes. The electrolyte is also a key component as it has many limitations such as the temperature and voltage window. However, organic electrolytes incorporate many additives which play a crucial role in improving the battery performances. These additives are usually not made public in order to preserve the competitiveness of the battery manufacturers. Therefore electrolytes will not be considered in the study. In this section an overview of the most common cathode an anode materials will be done, describing the most remarkable advantages and their main drawbacks.

Among the cathode materials, spinel oxides, olivine phosphates and layered oxides have attracted a significant interest for applications in EV (Yan et al 2014). Table 2 gathers the most commonly used

cathode materials and their main characteristics (T and Makimura 2001), (Padhi et al 1997), (David et al 1983).

Currently one of the most popular cathode compounds is the spinel $LiMn_2O_4$ (LMO) as it presents many advantages such as low cost, non-toxicity, abundant manganese resources, simple production and excellent safety (Thackeray 1995), (Xia 1996). Manganese appears as Mn (III) and Mn (IV) active species, which offers the possibility of redox reaction by insertion and extraction of Li^+ ions through the tridimensional channels of the framework. Although LMO and its variants have many advantages, they still suffer from capacity fading during cycling (Xia 1997). The spinel LMO suffers from manganese dissolution in the liquid electrolyte. The surface of the LMO particles is especially vulnerable to chemical reactions. This issue is aggravated by the Jahn-Teller distortion of Mn (III) ions and the change in crystal lattice arrangement during cycling. This effect has been highlighted when cycling the battery at 60ºC and promotes an early loss of capacity of the battery..

On the other hand, since 1997 $LiFePO_4$ (LFP) olivine has become a promising material for cathodes due to its good electrochemical properties with a very flat potential profile at 3.45 V vs. Li/Li^+ (Goodenough and Kim 2010). The lithium ions move through tunnels that are formed in the structure. Additionally, LFP presents low cost, non-toxicity, thermal stability and environmentally friendliness compared to other compounds. However, this material has low energy density due to a limited operating voltage, it has a poor rate capability, which is limited by the one dimension ionic conductivity and poor intrinsic electronic conductivity.

Regarding to layered structures, $LiMO_2$ materials (where M is one or more transition metal) are considered as a good choice for cathode materials because the MO_2 slabs in the structure enabling good lithium ion insertion/extraction. Although the conventional layered oxide $LiCoO_2$ has been commercialized as Li-ion battery cathode for twenty years, it can only deliver about 140 mAh/g capacity which is half of its theoretical capacity (Whittingham et al 2004). Consequently, partially substituted compounds were developed to increase the stability and the capacity values of this material. Nowadays, Ni and Mn transition metals are used for EV application. Thus NMC ($LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$) materials are a better choice to use as cathode for high performance Li-ion batteries (Thackeray et al 2005). The Li-Ni disorder in the lattice is a major factor affecting the material rate capability. In this sense, the presence of Co can help to reduce the Li^+/Ni^{2+} exchange. Moreover, NMC materials have a moderate thermal stability and tolerate fast charging rates. Other layered compounds have gained interest for EV applications; it is the case of Ni rich layered oxide (Shizuka et al 2005), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), which has a high usable discharge capacity of 200 mAh/g (Chen et al 2004). However, it has been reported that capacity fade of this material may be severe at elevated temperature (40-70ºC) due to SEI growth and micro-crack formation at the grain boundaries, which can lead in some cases to the explosion of the battery (Bloom et al 2003).

Given to the merits of high power density, safety, long cycle life and good rate capability, another candidate for cathode materials used in EVs is the monoclinic phosphate $Li_3V_2(PO_4)_3$ (LVP) (Yan et al 2012). The three dimensional structure of this phosphate allows the extraction of all three lithium ions from the lattice with a theoretical capacity of 197 mAh/g in the voltage range of 3.0 V to 4.8 V. However, the intrinsic electronic conductivity of this material is low (Hu et al 2013). In this sense and in order to improve its conductivity, substitution of vanadium by other metal cations has been proposed as it also improves its structural stability (Mateyshina and Uvarov 2011).

With respect to anode materials, graphite is the most generally used active material even though some car manufacturers have preferred the use of the lithium and titanium based spinel anode. The main characteristics of these materials are shown in Table 3 (Han et al 2014).

As it has been mentioned before, graphitic carbon has been predominantly employed as the anode material of choice due to a number of desirable characteristics, which include low cost, easy processing and chemical stability. In addition, it has a desirable electrochemical profile (Thackeray et al 2005). However the Li-ion insertion/extraction during the charge cycle induces a significant volumetric gain (around 9–10%) which places stress on the electrodes and could be determinant for cycling stability. Furthermore, with a low operating voltage of around 100 mV (vs. Li+/Li), the graphite anode may react with the electrolyte, resulting in lithium metallic deposition. This not only reduces the battery performances but poses serious concerns in terms of safety such as thermal runaway which could be aggravated at low temperature.

To overcome these issues, the spinel $Li_4Ti_5O_{12}$ material has become a promising alternative anode (Scrosati and Garche 2010). This compound shows excellent structural stability of almost zero-strain during lithium ion insertion/extraction, leading to high rate capability and reversibility during discharge-charge cycling. It also provides a stable voltage of 1.55 V against a lithium electrode with a theoretical capacity of 175 mAh/g and an actual discharge capacity of over 160 mAh/g . Furthermore, $Li_4Ti_5O_{12}$ is cheap, non-toxic, and it is easier to produce than other alloy-based anodes. On the other hand, regarding to the reaction mechanism of this spinel, it has been reported that lithium reacts according to the kinetic reaction:

$$Li_4Ti_5O_{12} + 3Li^+ + 3e \rightarrow Li_7Ti_5O_{12}, \qquad \text{(Ohzuku et al 1995), (Zaghib et al 1999).}$$

The rate capability of $Li_4Ti_5O_{12}$ is relatively low, as the poor electrical conductivity and slow lithium-ion diffusion lead to large polarization at high charge–discharge rates.

All the exposed electrode materials are the main ones used nowadays by car manufacturers and are detailed in ref 7 (Lu et al 2013). The dominant cathode material used for EV battery is LMO as it is used by Nissan, Chevrolet and Renault, associated with graphite anode. Tesla and Subaru used the same anode associated with NCA or LVP, respectively. Honda has developed a vehicle using the spinel LTO chemistry as anode, associated with the layered oxide NMC spinel.

There are many choices of battery materials for EV applications and each battery manufacturer will select the compounds that are most appropriate for their vehicle requirements. The fast improvements on the Li-ion battery topic, force the car manufacturers to be flexible and open to any new technology.

4. Results & discussion:

In this section the GWP analysis will be performed for the 8 different scenarios presented in Table 1. The evolution of GHG emissions for the first and second life of the batteries is presented in Figure 2. The 35.000 kg CO_2 e. emitted during the first life in an EV is considered the same in all the case studies, this impact corresponds to the sum of the black and dark grey parts in Figure 2. On the other hand, the GHG emissions of the battery at the second life diverge depending on the energy source and application. To analyze these results, it is important to take into consideration the lifetime of the battery. As it has been mentioned in the methodology section, all batteries do not have the same lifetime during their second life. Based in the second life endurance of Li-ion batteries (deduced from Eq.3), the battery durability on autonomous and on energy arbitrage stationary applications is 8 years, while on the rest of cases it can last up to 20 years. This could be partly attributed to the harder cycling conditions described in the methodology. Therefore, the total lifetime will be 18 years for the batteries that are used in autonomous or energy arbitrage applications and 30 years for the other cases. The accumulated GHG emissions during these periods are identified with different shades of gray in Figure 2.

Additionally, from Figure 2, it can be observed that during the first 18 years, the highest impact is found in the island fuel generator case with 60.341 kg CO_2 e. emissions. The use of batteries for energy arbitrage releases more than 52.000 kg CO_2 e., proving that the pursuit of economical profit does not necessarily brings any environmental benefit. The increase of GHG emissions for these cases is higher than that of the base case due to the efficiency and energy losses of energy storage systems.

It is visible how the GWP increases if the employed energy source has a pollutant character. In order to enable a comparison between the GWP and the durability of the battery for each application, the evolution of emissions as a function of time is presented in Figure 3. The continuous, dotted and dashed lines represent the cases without battery, with Lead-acid batteries and with 2nd life Li-ion battery respectively.

It can be observed that the emission's slope changes after the 1st life of the battery in the vehicle (year 10 in Figure 3) proving how it strongly depends on the second life application. Using this type of representation, the variation among the different battery technologies is more visible. The first difference is related to the steps found in the dotted curves using Lead-acid battery systems. These steps are caused by the battery replacement due to its shorter life-length. The second major difference is the softer impact slope of Li-ion battery systems, which could be ascribed to their higher efficiency.

Another way to identify the environment impact of the 8 different cases studied is to calculate the total kg CO_2 e. emitted per functional kWh (*Fig.4*). This representation shows the net GWP per kWh at the battery end-of-life, providing a clear understanding of the overall impact behavior. The line between columns is the impact balance, which represents the variations of the GWP per functional kWh taking the base case as reference. Consequently, if the emissions per functional kWh are lower (i.e. RES), the balance will be negative. On the other hand, a positive balance means that the environmental impact is higher than without battery re-use. It can be observed that the use of batteries (no matter the technology) for energy arbitrage has more than a 30% GWP increase. Moreover, in the case of Lead-acid batteries the impact balance is even higher than the direct fuel combustion, while the re-use of EV batteries in island installations (Island 2nd life) have a reduction of a 32%. Therefore, it is not environmentally desirable to use batteries for energy storage if no renewable energy sources are used.

In this diagram it can be observed that the cases leading to the worst environmental impact are the island fuel generation and energy arbitrage. In addition the use of Li-ion batteries also provides better results than the ones using Lead-acid batteries. Surprisingly the results after 30 years of the base case with the European energy Mix and no battery re-use has a ratio of 0,694 kg CO_2 e./kWh which is similar to the 0,689 ratio found for the re-use of EV batteries in autonomous installations using RES. This situation is the result of different battery lifetimes and it is explained by the evolution of the kg CO_2 e./kWh ratio along time *(Fig.5)*.

Before the battery starts to be used in an EV, it has already emitted more than 4.000 kg CO_2 e. due to its fabrication and installation processes. From this point of view, as the battery provides a higher amount of kWh, the ratio of emission per functional kWh will be lower. Figure.5 shows that steeper slopes do not directly correspond to a lower final ratio at the end-of-life. In fact, the slopes of the energy arbitrage cases are steeper than the island fuel generation. However, as the energy arbitrage cases last 12 years less than the island fuel combustion with a diesel generator they have a similar value at the end-of-life. This same situation is found in the RES system in autonomous applications.

Note that all the cases start at the beginning of the second life with a 1.6 kg/kWh. This value has been obtained dividing the emitted 35.000 kg CO_2 e. by the 22.500 kWh used during the vehicle 1st life.

As a general observation, the longer the battery endures the lower its impact per functional kWh will be. In this sense, it is important to note that the capability of a battery to be used in a second life application strongly depends on the degradation of the battery at the end of the EV life (i.e. for a capacity below 80%). It is therefore a priority to understand the degradation mechanisms of the battery components in order to determine its potential for re-use. The main degradation mechanisms of the electrode compounds presented previously are described in the following section.

During the second life, the EV batteries will be cycled under different conditions according to the selected application. It has been previously calculated how these cycling conditions affect the battery lifetime. Indeed when the battery is used for energy arbitrage or in autonomous application, it suffers a nominal

capacity drop from 80 to 60% within only 8 years. On the contrary, the lifetime of a battery connected to an island 2nd life system reaches 20 years due to more favorable condition of use. This difference is mainly due to the cycling conditions and more particularly the DOD of the charge/discharge cycles. An adequate choice of the battery chemistry in relation with the working condition is necessary to improve the battery lifetime, minimize the risks for the end-users and therefore reduce the environmental cost.

For the energy arbitrage application, the battery will be fully charged during the night and fully or partially discharged during the day. In this case, full charges and discharges of the battery should be considered, equivalent to 100% DOD: the entire electrochemical profile. For this type of application, it is important to choose an electrode chemistry able to withstand large voltage amplitude. It is well established that graphite electrodes may easily form lithium dendrites at high C-rates or when reaching low voltage of discharge (Agubra and Fergus 2013), (Sarasketa-Zabala et al 2015). The use of graphite electrodes for this energy arbitrage application will further promote the formation of dendrites and lead to a faster capacity decay of the battery. Therefore it is not advisable to use graphite as anode but another material presenting a higher voltage, such as LTO. Indeed this spinel material shows better stability during the discharge as its electrochemistry restricts the voltage to 1.55 V, which is sufficiently high to prevent lithium platting. However the use of LTO as anode will decrease the energy density of the battery and will definitely have cost consequences for the consumer. These observations will also be valid when using RES in autonomous applications as similar deep charge / discharge cycling profiles will be executed.

On the cathode side, any chemistry can be considered as each of them present pros and cons. An established choice cannot be defined as easily as for the anodes. In terms of safety, it would be preferable to use LMO or LFP cathodes as they present a better stability than NMC (Whittingham 2004), however the faster capacity fade of LMO will most probably be an important drawback for the second life use. The use of NMC cathode could also compensate the loss of energy density due to the high voltage plateau of LTO as NMC presents an energy density above 1000 Wh/kg.

The island applications present another type of cycling profile. It is expected that the battery will rarely be fully charged or discharged. The battery will accumulate the energy depending on the availability of the renewable energy and will also use it directly for the house. In this sense it is important to focus the chemistry of the battery towards materials enabling good cycling capability but discarding the properties at the end of charge and discharge. According to these constraints, both LTO and graphite can be present in the anode. The lower cost of graphite will clearly be an advantage of choice and as the full discharge of the battery is not expected regularly, the degradation of the electrode due to the lithium platting will be limited. On the cathode side, the high voltage of LMO or LVP will be an advantage as it will reduce the DOD and the absence of nickel reduces the cost of the battery. All these observations are summarized in Table 4.

4. Conclusions:

In this study, the LCCO$_2$ of an EV has been performed for different scenarios. These scenarios, mainly focused on the battery point of view, depend on the second life of the battery in stationary application. Besides, an overview of the most relevant battery chemistries used for EV applications as well as their degradation mechanisms has been presented. The study reveals that the environmental impact per functional kWh decreases with the use of the battery.

Anyhow, from an environmental point of view, the use of batteries is only advisable in association with renewable energy sources. If that is not the case, the environmental impact caused by the losses derived from the energy storage should be added to the emissions coming from the pollutant energy source acting as a multiplier factor.

Nowadays the improvements of the Li-ion battery performances for EV applications are mainly focused towards high energy and power density. However cycling and calendar behavior are necessary to improve the re-use of the battery in a second life application. As it stands graphite is commonly used as anode among car manufacturers due to its low cost and good electrochemical performance. However this material presents important degradation mechanisms such as lithium platting. Other anode such as LTO could also be a candidate to electrode material in the second life use but its high voltage prevents its development in EV batteries. On the cathode side, oxides and phosphates are widely used and reveal good stability upon cycling. LFP material presents good cycling stability whereas manganese-based electrodes suffer from a faster degradation that may be unfavorable for second-life use.

We observed that it is necessary to select the battery chemistry according to the secondary application of the EV battery. These applications are directly related to the energy source and will influence the battery charge and discharge conditions such as the working DOD: full charge-discharge cycles that consume the battery life-length rapidly and partial charge-discharge cycles extending the battery life. However, further investigation on the degradation of the electrode at the end of the second life would be necessary to identify the most suitable systems.

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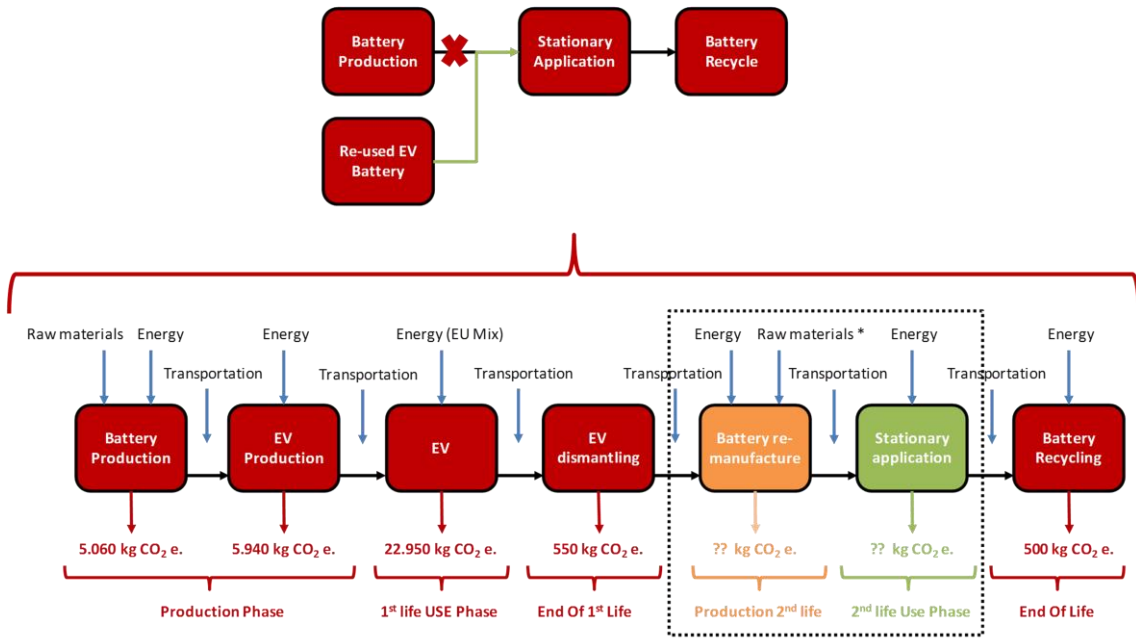4r-energy. http://www.4r-energy.com/en/company/. Accessed 13 Feb 2014

Fig. 1: *Description of the LCCO$_2$ system boundaries of a storage stationary application using an EV second life battery instead of a new one.*
* The raw materials for the battery re-manufacturing or repurpose are considered negligible because of its low impact.
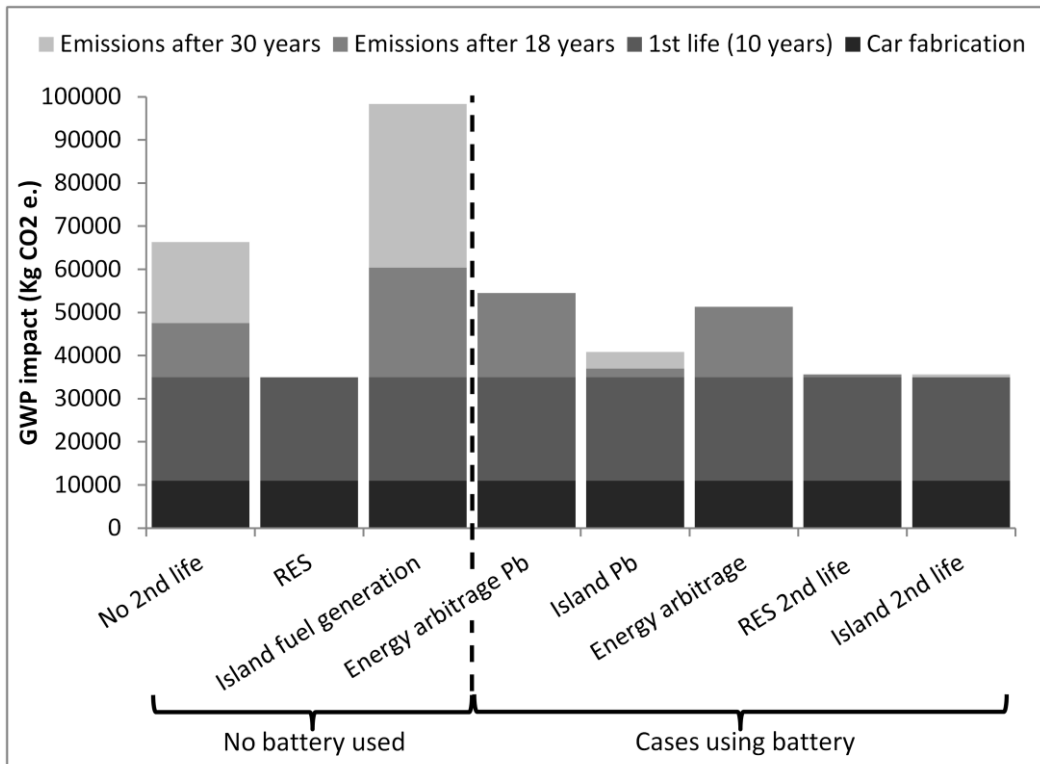

Fig. 2: *Global Warming Potential (GWP) of an EV considering its battery 1st and 2nd life. The black stripe represents the EV fabrication impact. The dark grey corresponds to the first life in EV (years 0 to 10). The medium dark grey represents the first 8 years in second use (years 10 to 18).The soft grey corresponds to the rest of second life until battery end-of-life (years 18 to 30).*
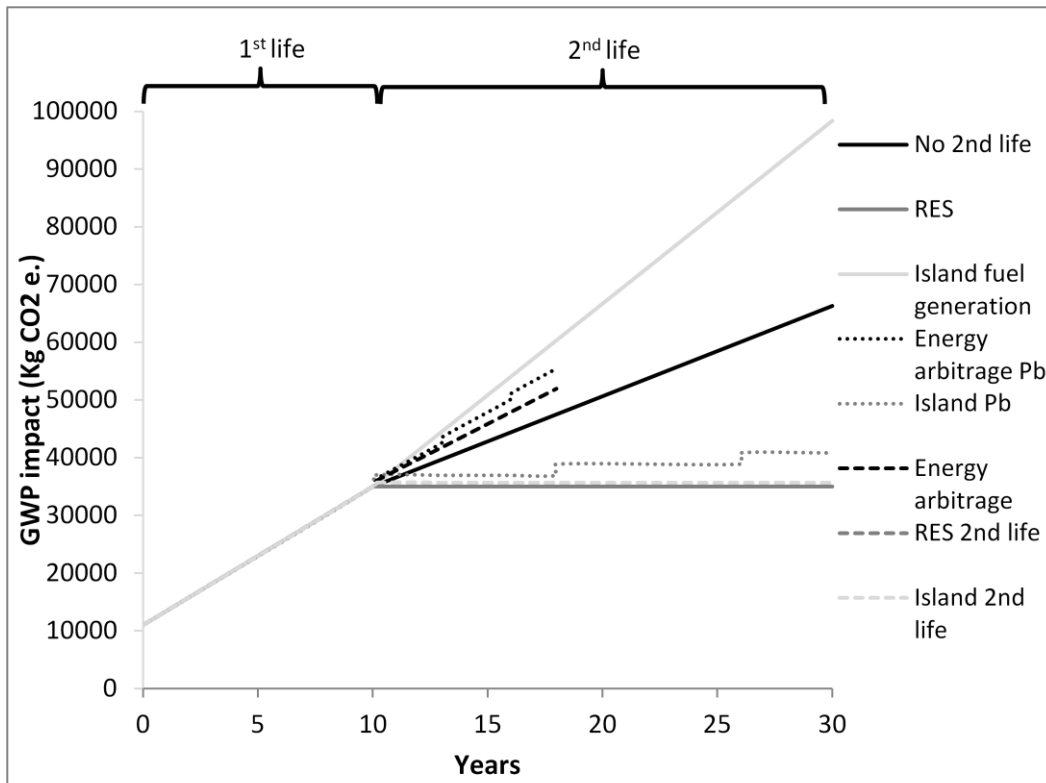
16

Fig. 3: *GWP as a function of time for the 8 scenarios studied. The continuous, dotted and dashed lines represent the cases without battery, with Lead-acid batteries and with 2nd life Li-ion battery respectively.*
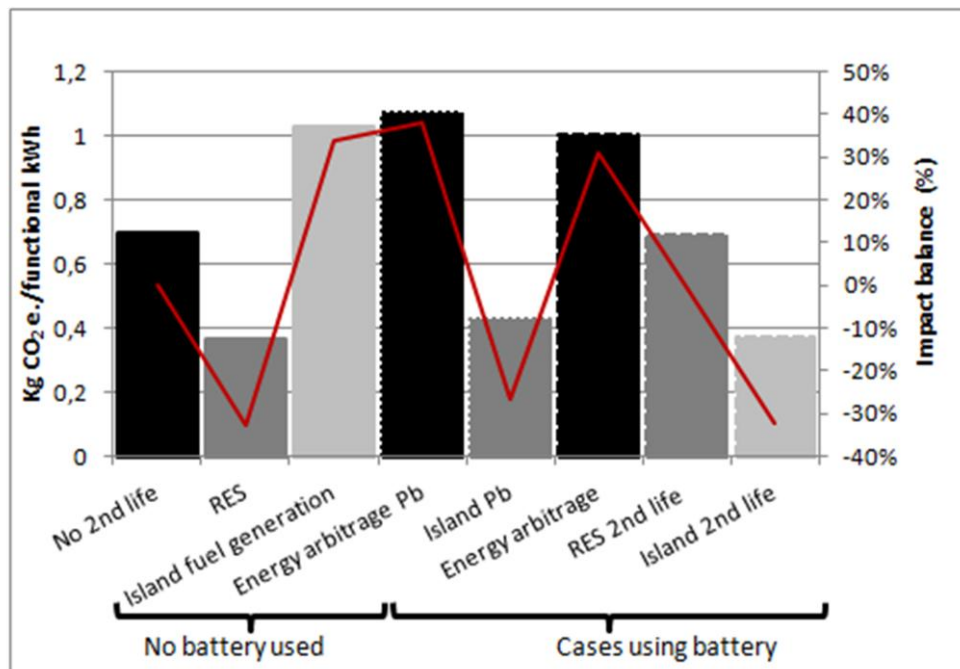

Fig. 4: *In columns: GWP per functional kWh for the different cases at the end of the battery lifetime. The red line corresponds to the impact balance compared to the base case.*
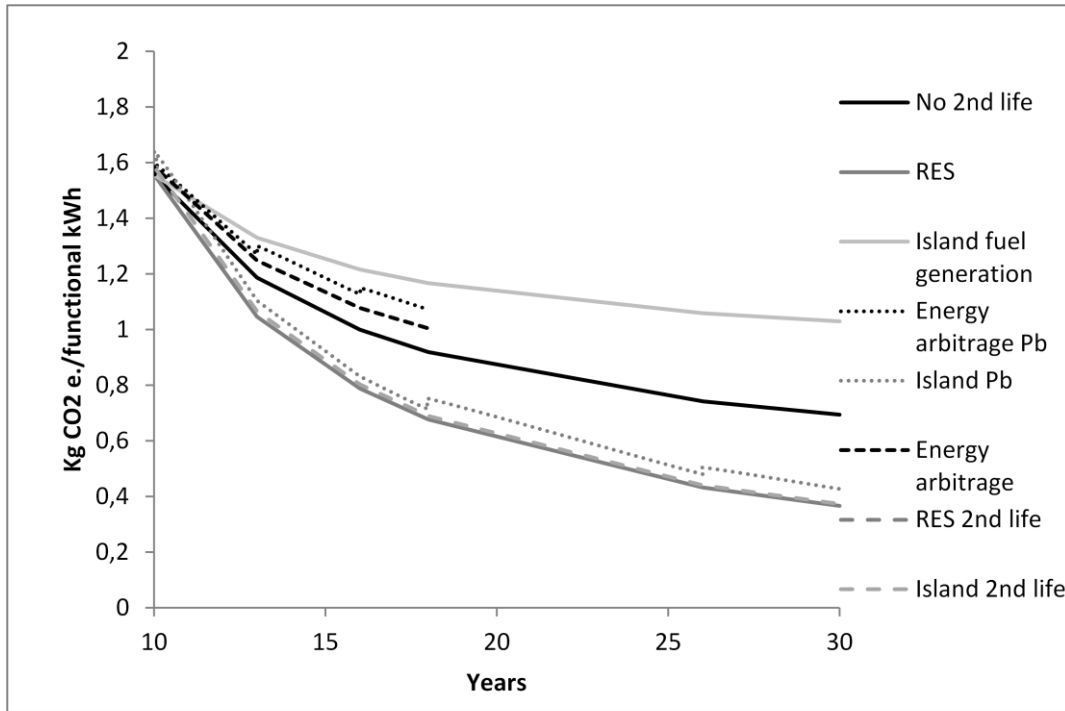
Fig. 5: *Evolution of the average kg CO2 e. emitted per functional kWh during the second life in the different scenarios.*

Table 1: *Study cases and scenarios analyzed.*

Scenario	Stationary application	Description	Battery	Lifetime (Years)
Base case (No 2nd life)	None	No battery is used in this option. The EV is directly dismantled after 10 years and, during the following 20 years, the average energy used in a house is taken from the grid.	No	10+20
RES	Autonomous use	No battery is used in this option. The EV is directly dismantled after 10 years and, during the following 20 years, the average energy used in a house is taken from renewable energy systems.	No	10+20
Island fuel generator	Island installation	No battery is used in this option. The EV is directly dismantled after 10 years and, during the following 20 years, the energy is obtained from a common diesel generator.	No	10+20
Energy arbitrage Pb	Energy Arbitrage	The EV is directly dismantled after 10 years and, during the following 8 years, the energy arbitrage is done with new Lead-acid batteries (three battery packs are needed to cover the 8 years expected for the equivalent EV Li-ion re-used battery).	Lead-acid battery	10+8
Island Pb	Island installation	The EV is directly dismantled after 10 years and, during the following 20 years, the energy is obtained from RES and it is connected to new Lead acid batteries (3 batteries are needed to cover the 20 year life-length expected for the equivalent EV Li-ion re-used battery).	Lead-acid battery	10+20
Energy arbitrage	Energy Arbitrage	After the 10 year use in the EV, the battery is re-used for energy arbitrage in a house during 8 more years. The energy is taken from the electricity grid.	Re-used Li-ion battery	10+8
RES 2nd life	Autonomous use	After the 10 year use in the EV, the battery is re-used during 8 years more for RES storage in a house connected to the grid for sporadic energy support.	Re-used Li-ion battery	10+8
Island 2nd life	Island installation	After the 10 year use in the EV, the battery is re-used for over 20 years more in island conditions connected to a RES.	Re-used Li-ion battery	10+20

Table 2: Main characteristics of the most common materials used as cathode for EV applications.

Type of Material	Composition	Operating Voltage vs Li/Li$^+$ (V)	Capacity (mAh/g)	Energy density (Wh/kg)	Safety	Cycle life
Spinel	$LiMn_2O_4$	4.0-4.2	148	592-620	Good	Average
Olivine	$LiFePO_4$	3.45	170	585	Good	Average
Layered	$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	3.85	276	1062	Poor	Good
Phosphate	$Li_3V_2(PO_4)_3$	3.8	197	749	Good	Good

Table 3: Main characteristics of the common materials used as anode for EV applications

Type of Material	Composition	Operating Voltage vs Li/Li$^+$ (V)	Capacity (mAh/g)	Energy density (Wh/kg)	Safety	Cycle life
Graphite	C	0.1	280–330	28-33	Poor	Average
Spinel	$Li_4Ti_5O_{12}$	1.55	160	248	Good	Good

Table 4: Summary of the compatibility between the battery chemistry and potential stationary applications for second life EV batteries.

	Cathodes				Anodes	
	LMO	LFP	NMC	LVP	Graphite	LTO
Energy arbitrage	+++	+++	++	+	-	+++
RES 2nd life	+++	+++	++	+	-	+++
Island 2nd life	+++	++	+	+++	+++	+