

Environmental and preliminary cost assessments of redox flow batteries for renewable energy storage

Fernandez-Marchante C.M., Millán M., Medina-Santos J.I., Lobato J*.

Department of Chemical Engineering. Faculty of Chemical Sciences & Technologies.
Universidad de Castilla La Mancha. Campus Universitario s/n 13071 Ciudad Real.
Spain.

Abstract

The sustainable use of energy is one of the main current challenges. The increase in the use of renewable energies must also be accompanied by storage systems that respect the environment or are as less harmful as possible. In this work, Life-Cycle Assessment (LCA) “from cradle to gate” and a preliminary cost assessment of two types of redox flow batteries based on Vanadium (VRFBs) and Zinc/Cerium (ZCBs) have been studied. Ecoinvent 3.3 data base, AWARE and CML Baseline v3.04 methodologies were used to quantify the environmental burden into 12 midpoint impact categories (Water Footprint, Global warming 100a, Abiotic depletion, Abiotic depletion (fossil fuel), Ozone Layer depletion, Human toxicity, Fresh water ecotoxicity, Terrestrial ecotoxicity, Marine ecotoxicity, Photochemical oxidation, Acidification and Eutrophication). All impacts categories were higher in ZCBs than in VRFBs except water footprint and acidification. These midpoints impacts were also compared with conventional batteries (Lithium) and non-conventional ones (NaNiCl). VRFBs have the lowest environmental impact and a longer life considering the reuse of vanadium electrolytes. Regarding the cost analysis, the electrolyte is the most expensive part of both batteries.

Keywords: Vanadium redox flow battery, Zn/Ce redox flow battery, preliminary cost, LCA, renewable energy storage, carbon footprint.

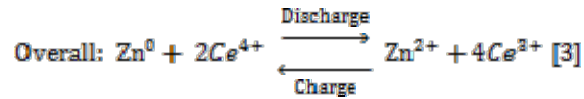
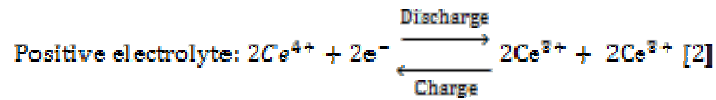
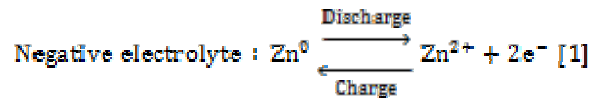
*corresponding author. Justo Lobato (justo.lobato@uclm.es)

1. Introduction

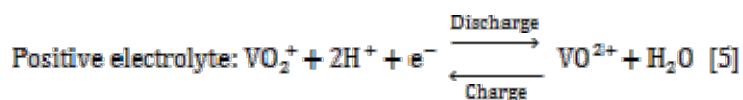
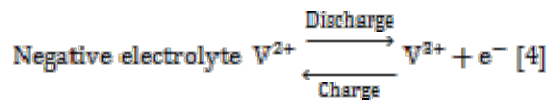
The fast development of industrial societies has relied on the exploitation of huge reserves of low-cost fossil energy resources such as coal, natural gas and oil. The future demand for energy, particularly from large newly industrialized countries, and the increasing attention to environmental and health problems lead for their gradual replacement with renewable sources. In this way, the use of renewable energies such as solar, wind, hydropower and biomass are increasing noticeably in the last decades. However, these energy sources are intermittent and unpredictable because they generate electricity according to the time and climatic availability of the resources. Therefore, the integration of renewable energy sources with different features requires more attention in the design, control and management ^[1,2]. Taking into account the above, energy storage devices are required to store the excess power in over production periods and supply it in periods of null electrical power production. Moreover, the energy storage system has been considered as a key enabler of the smart grid or future grid, which is expected to integrate a significant amount of renewable energy resources and a valuable approach for improving the reliability of the entire power system ^[3].

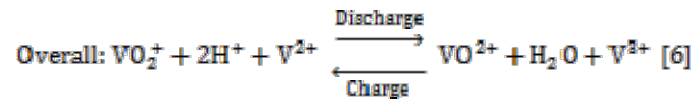
A redox flow battery (RFB) is an electrochemical device, which is able to store chemical energy and produce electricity by oxidation and reduction reactions of redox couples ^[4, 5]. They are, due to their huge amount of advantages, one of the best

alternative for the renewable energy storage. The energy storage capacity of these type of batteries can be increased with a high solution concentration and/or volume of storage tanks. Besides, the system power can be increased with a large active area or increasing the number of cells [6, 7]. There are different types of RFBs according to the different electrolytes that can be used [8]. Among the huge amount of RFBs, the present work is focused on the vanadium redox flow batteries (VRFBs) and the Zinc/Cerium batteries (ZCBs). The last ones use salts of zinc and cerium in an organic solution as negative and positive electrolytes, respectively. The charge-discharge and the overall reactions are shown in equations 1 to 3[9].



On the other hand, the all vanadium batteries use the same metal ions in both electrolytes, overcoming in this way the cross contamination and increasing the capacity and the lifespan of the cell. The charge-discharge reactions for vanadium redox couples in sulfuric acid solutions are shown in equations 4 to 6[10,11].





The Open-Circuit Potentials (OCPs) of ZCBs and VRFBs are 2.4 and 1.3 V, respectively⁶. Even though the ZCBs have a higher OCP and consequently, higher capacities can be achieved, the use of platinum in its positive electrode increases the price of this technology. However, the VRFBs use carbon felt as cathode and anode electrodes, which have a good stability and a high reversibility. Both electrochemical storage devices use Nafion® as much common membrane to separate the anode from the cathode compartment.

On the other hand, any company before starting a business activity must have a business plan, an integrated environmental analysis study and the necessary licenses to develop its activity. Life Cycle Assessment (LCA) is a technique to analyze and evaluate resources and environmental impacts associated with all the stages of a product's life including raw material, production process, packaging, energy and some other human activity, including the collection of raw material, production, transportation, consumption, final disposal¹¹. The carbon, hydric and energy footprints are one of the most important data that can be obtained from the LCA. Nowadays, an important role, to consider, is the environmental impact of these batteries. The LCA of common battery storage systems has been widely studied^[13-18]. However, there are few data related to redox flow battery systems^[13] and no LCA studies of ZCBs have been found until now.

Life cycle analysis together with a good business plan are increasingly necessary tools for a sustainable development of society. In Europe, more and more objectives are being set in this direction, like those of Horizon Europe. New industrial terms are being developed, such as the concept of Circular Economy. The research must go hand in hand with the interests of society and help to adopt innovative ideas to companies

without endangering the environment, considering that there must be a balance between technical, environmental and economic viability. Therefore, it is interesting to perform these studies to the ZCBs and VRFBs.

In this work, an LCA and a preliminary cost analysis of Vanadium and Zinc/Cerium redox flow batteries for the renewable energy storage have been carried out and compared for the first time. AWARE and CML Baseline v3.04 methodologies were used to quantify the environmental burden into 12 midpoint impact categories in the qualitative analysis of ZCBs and VRFBs. These 12 midpoint impacts were Water footprint, GWP 100a, Abiotic depletion, Abiotic depletion (fossil fuel), Ozone Layer depletion, Human toxicity, Fresh water ecotoxicity, Terrestrial ecotoxicity, Marine ecotoxicity, Photochemical oxidation, Acidification, Eutrophication. In addition, we also provide a preliminary economic assessment of ZCBs and VRFBs systems. Moreover, a comparative environmental study of conventional, non-conventional and redox flow batteries was performed. Finally, a preliminary cost analysis of the two studied redox flow batteries was evaluated.

2. Methods and data

2.1 *FU definition*

LCA has been used to compare both redox flow batteries. The stage of life cycle analysed was “from cradle to gate” [15-19] using the SimaPro 8.4 software. This stage evaluates the impacts produced in the extraction and processing of raw materials, transport and assembly of a product. Furthermore, a functional unit (FU) was selected to compare the batteries at the same conditions. The FU was defined as 1 kWh of energy storage. This FU value (1kWh) can be applied in electrochemical processes for wastewater treatment powered with renewable energy and batteries at pilot plant scale which is one of the research line of our group^[4,9]. Moreover it is interested to point out

that VRFBs have a life span of 20 years however ZCBs are still at an experimental stage, and only 57 operating cycles of charge/discharge [10] have been demonstrated.

System boundaries of both redox batteries are shown in Figure 1 [20-21].

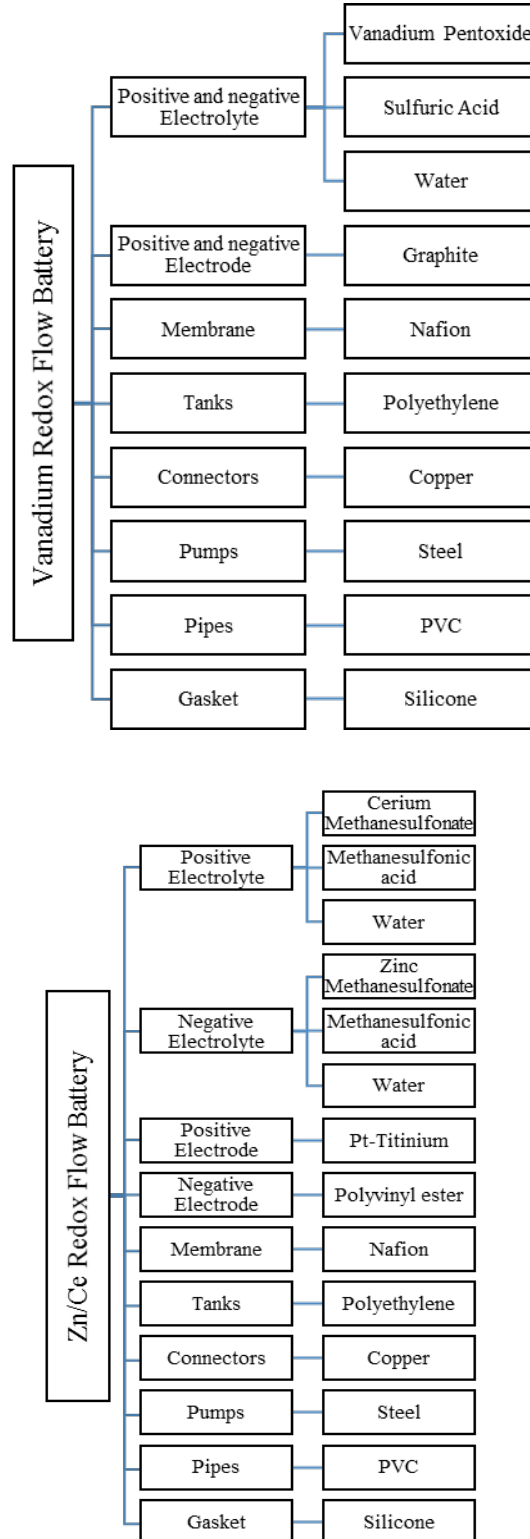


Figure 1. System boundaries of Vanadium and Zn/Ce redox flow batteries

2.2. Inventory

The impact assessments or potential effects of human health, ecosystems and natural resources are evaluated depending on the materials used in the process or the manufacturing of a product. At this stage, the different materials that make up both batteries were quantified for the defined FU. The foreground input inventories of VRFBs and ZCBs were obtained from literature ^[10, 12], experience of our research group ^[1, 2] and characteristics of our laboratory equipment. Specifications of the model systems were obtained taking into account that Vanadium electrolyte was a 2 M Vanadium concentration in 5 M H₂SO₄, Zn/Ce electrolyte was 2M Zinc and Cerium methanesulfonate, the Open-Circuit Potentials of VRFBs and ZCBs are 1.3 V and 2.4 V, respectively and Energy efficiency of VRFBs and ZCBs are considered as 80 % and 62 %, respectively. The life cycle modelling and assessment were also carried out using Ecoinvent 3.3 as the background life cycle inventory database. The transport and manufacturing processes of the battery components were also taken into account. The manufacturing processes were injection moulding, bow moulding, extrusion and metal working. Energy and auxiliary inputs were including in these manufacturing processes. The region code used was Europe (RER) for these processes. Table 1 shows specifications of the model systems for energy storage with VRFBs and ZCBs. The Lithium and NaNiCl batteries were obtained directly from the Ecoinvent 3.3 database.

As shown in Figure 2, it is necessary to understand the redox flow batteries as the assembly of a set of elements such as: electrolytes, electrodes, membrane, housing etc. to carry out an LCA.

Table 1. Specifications of the model systems for storage of energy with VRFB and ZCB

Material (VRFB)	Component	Mass (kg/kWh)	Material (ZCB)	Component	Mass (kg/kWh)
Vanadium pentoxide	Electrolyte	10.44	Cerium methanesulfonate	Electrolyte	7.17
Sulfuric acid	Electrolyte	14.07	Zinc methanesulfonate	Electrolyte	1.98
Graphite	Electrode	0.73	Methanesulfonic acid	Electrolyte	7.97
			Titanium	Electrode	0.61
			Platinum	Electrode	0.24
			Polyvinyl ester	Electrode	0.18
Water	Electrolyte	19.87	Water	Electrolyte	12.41
Nafion	Membrane	0.01	Nafion	Membrane	0.005
Polyethylene	Tanks	0.54	Polyethylene	Tanks	0.53
Copper	Connectors	0.60	Copper	Connectors	0.30
PVC	Pipes	0.25	PVC	Pipes	0.12
Steel	Pumps	0.33	Steel	Pumps	0.34
Silicone	Gasket	0.92	Silicone	Gasket	0.46
	Total	47.74		Total	32.33
Transport	Component	Freight (kgkm)	Transport	Component	Freight (kgkm)
aircraft intercontinental lorry 3.5-7.5 metric ton	Electrolyte (V)	7.20E+04	aircraft intercontinental light commercial vehicle	Electrolyte (Ce)	9.90E+04
	Electrolyte (V)	5.90E+03	light commercial vehicle aircraft intercontinental light commercial vehicle	Electrolyte (Ce)	2.67E+03
			light commercial vehicle aircraft intercontinental light commercial vehicle	Electrolyte (Zn)	377
			aircraft intercontinental light commercial vehicle	Electrode (Titanium)	6.69E+03
light commercial vehicle	other components	1.02E+03	light commercial vehicle	other components	1.30E+03
Processing		unit	Processing		unit
Electricity (medium voltage)	2.37	kWh	Electricity (medium voltage)	1.69	kWh
Natural gas	4.06	MJ	Natural gas	2.13	MJ

2.3 Methods

CML Baseline is a LCA methodology developed in Europe in Centre of Environmental Science. The advantage of the CML Baseline method is its scientific soundness. It has reference values for the standardization of indicators worldwide, European level and Dutch level. CML baseline indicators are category indicators at mid-point level and shown a problem-oriented approach [22].

AWARE has emerged as an internationally recommended method for applying the ISO 14046 standard and conducting water scarcity footprint analyses. The AWARE method is considered as one of the most suitable for the assessment of sustainable water resource management from the point of view of water availability [23].

These methodologies were used to quantify the environmental burden into 12 midpoint impact categories in the qualitative analysis of ZCBs and VRFBs [24-26]. Finally, comparative environmental study of conventional, non-conventional and redox flow batteries was made using CML baseline methodology.

2.3.1 Water footprint

AWARE^[27, 28] method was used to calculate the water footprint. The water footprint was considered to recognize the quantity of water consumed in the manufacturing process of both batteries.

2.3.2 Depletion of abiotic resources

This impact category is concerned with protection of human welfare, human health and ecosystem health. This impact category indicator is related to extraction of minerals and fossil fuels due to inputs in the system. The Abiotic Depletion Factor (ADF) is determined for each extraction of minerals and fossil fuels (kg antimony equivalents/kg extraction) based on concentration reserves and rate of de-accumulation [26].

2.3.3 Climate change

Climate change can result in adverse effects upon ecosystem health, human health and material welfare. Climate change is related to emissions of greenhouse gases to air. The model used to characterize global warming was developed by Intergovernmental Panel on Climate Change (IPCC). The global warming was used to measure the potential global warming for a 100-year time horizon expressed in kg carbon dioxide/kg emission [28].

2.3.4 Stratospheric Ozone depletion

The model employed in Ozone depletion was developed by the World Meteorological Organization and defines the potential for the disappearance of the ozone layer as the kilograms of equivalent CFC-11 per kilogram of emission ^[29].

2.3.5 Human toxicity

This category concerns effects of toxic substances on the human environment. Health risks of exposure in the working environment are not included. Characterization factors, Human Toxicity Potentials (HTP), are calculated with USES-LCA, describing fate, exposure and effects of toxic substances for an infinite time horizon. For each toxic substance HTP's are expressed as 1,4-dichlorobenzene equivalents/ kg emission. The geographic scope of this indicator determines on the fate of a substance and can vary between local and global scale ^[26, 30-33]

2.3.6 Ecotoxicity (Freshwater aquatic ecotoxicity, Marine ecotoxicity and Terrestrial ecotoxicity)

This category indicator refers to the impact on freshwater ecosystems, as a result of emissions of toxic substances to air, water and soil. Ecotoxicity Potential (FAETP) are calculated with USES-LCA, describing fate, exposure and effects of toxic substances. The time horizon is infinite. Characterization factors are expressed as 1,4-dichlorobenzene equivalents/kg emission. The indicator applies at global/continental/regional and local scale ^[26, 30].

Marine ecotoxicity and Terrestrial ecotoxicity, refer to impacts of toxic substances on marine ecosystems and terrestrial ecosystems and are calculated in a similar way.

2.3.7 Photooxidant formation

Photochemical Ozone Creation Potential (POCP) for emission of substances to air is calculated with the UNECE Trajectory model (including fate) and is expressed in kg ethylene equivalents/kg emission [26, 30].

2.3.8 Acidification

Acidification Potential (AP) for emissions to air is calculated with the adapted RAINS 10 model, describing the fate and deposition of acidifying substances. AP is expressed as kg SO₂ equivalents/ kg emission [26, 30].

2.3.9 Eutrophication

Eutrophication (also known as nutrification) includes all impacts due to excessive levels of macro-nutrients in the environment caused by emissions of nutrients to air, water and soil. Nutrification potential (NP) is based on the stoichiometric procedure of Heijungs et al., (1992) [30] and expressed as kg PO₄ equivalents per kg emission.

3. Results and discussion

3.1 Influence of the components redox flow battery in the environmental analysis

3.1.1. Carbon footprint and Ozone depletion

Figure 2 shows the contribution of the different parts of the evaluated RFBs to two environmental impact categories, global warming and ozone layer depletion. It can be observed that the cerium electrolyte and the titanium electrode are the materials that make up the carbon footprint (global warming) representing 92% of the ZCBs. The Vanadium electrolyte is responsible for 89% of the total emissions of VRFBs [34]. Cerium's electrolyte has the greatest influence. This is because the Cerium is a rare earth that is found in nature in very low concentration, so a large quantity of soil must be processed for extraction, so this indicator increases due to the extraction method and transport, fundamentally.

Regarding the other environmental impact indicator it can be observed that the contribution of ZCBs in the ozone depletion as the kilograms of equivalent CFC-11 per kilogram of emission is higher than the VRFB's one. Moreover, 87% of CFC-11 emissions coming from ZCBs are due to obtaining the cerium electrolyte as it has been mentioned in the previous section. On the other hand, the main emissions source in VRFBs are owing to the vanadium electrolyte.

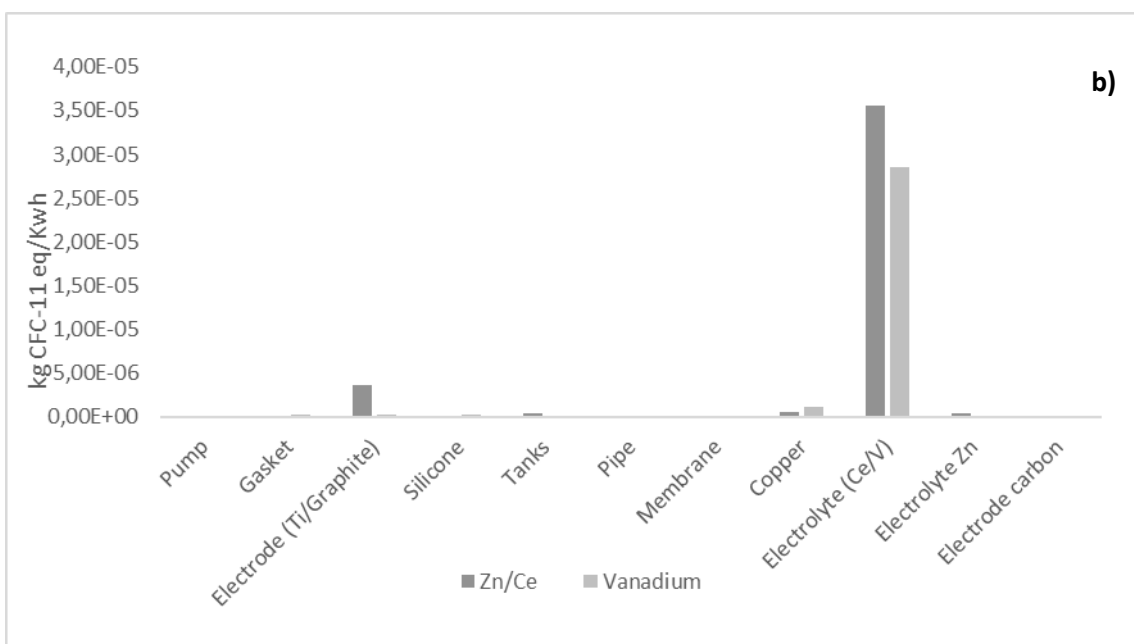
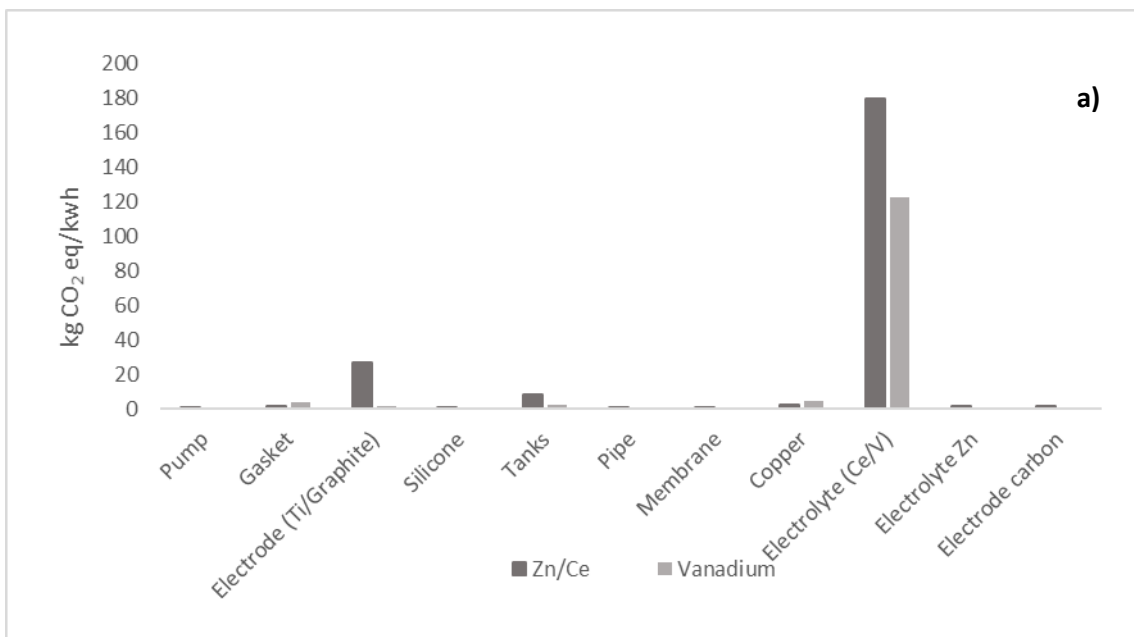


Figure 2 Environmental impact of the different components of the two studied redox flow batteries a). Global warming potential as kg CO₂ eq. per kWh; b). Ozone depletion as the kilograms of equivalent CFC-11 per kWh

The obtained results from different LCAs cannot be compared from different publications because they do not have the same location and materials. However, LCAs of VRFB can be a reference to analyse the environmental of other RFBs as Zn/Ce. No LCA studies of ZCBs have been found in literature.

3.1.2 Human Toxicity

Figure 3 shows the amount kg 1,4-DB eq/kWh which is related with the human toxicity indicator for each component in both batteries. Results show that the components of ZCB that contribute to increase the human toxicity are the Ce electrolyte (66%) and the copper collectors (25%). As VRFBs have a greater number of cells because its cell voltage is lower than the one of ZCBs, the contribution of copper in these batteries (VRFB) reaches 66% of the toxicity of the batteries and the vanadium electrolyte accounts for 31% of the total. If both batteries are compared, the ZCBs are more toxic than the VRFBs in this environmental impact category.

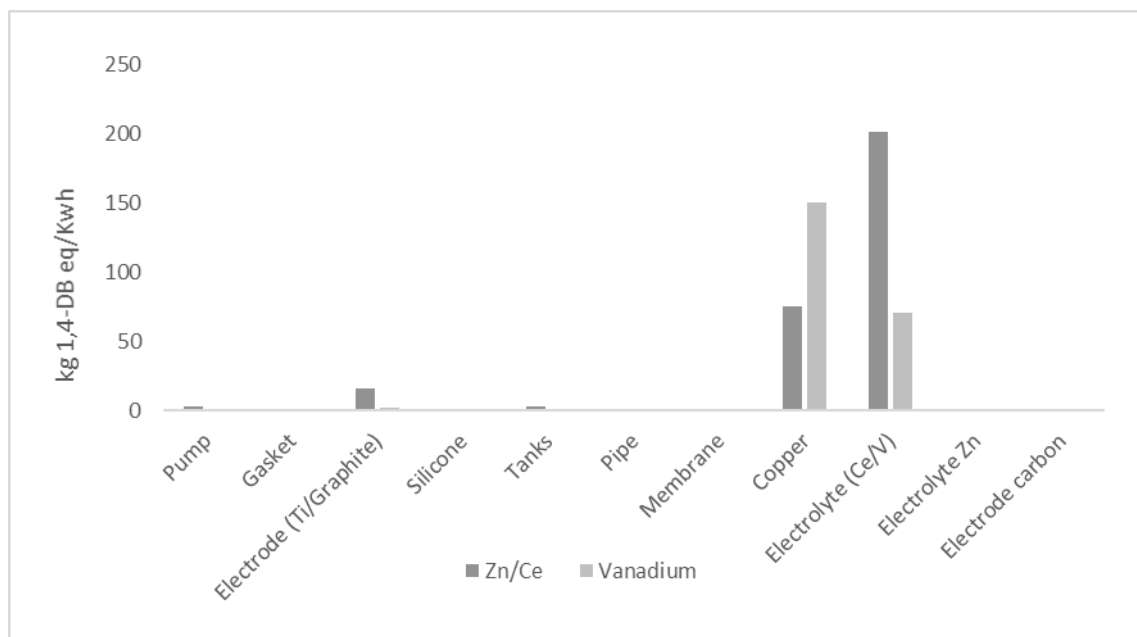


Figure 3. Human toxicity as kilograms of 1,4 dichlorobenzene per kilogram of emissions

3.1.3 Water footprint

Nowadays, the supply of water with good properties is an important issue for society. So, it is important evaluate what is the water consumption in different industrial activities. Thus, the water foot print was calculated using the AWARE method, as it has been previously explained, for the two redox flow batteries. Figure 4 shows the amount of water consumed expressed in m³ for each component of both batteries. The electrolytes are again the ones that have the greatest impact, reaching the electrolytes of cerium and zinc 75% and 10%, respectively, of the total contribution of this type of battery. Likewise, 94% of the water consumption in the manufacture of the VRFB is due to its electrolyte. Moreover, if both batteries are compared, it can be clearly observed that the manufacturing of VRFB requires four times more of water than the ZCB.

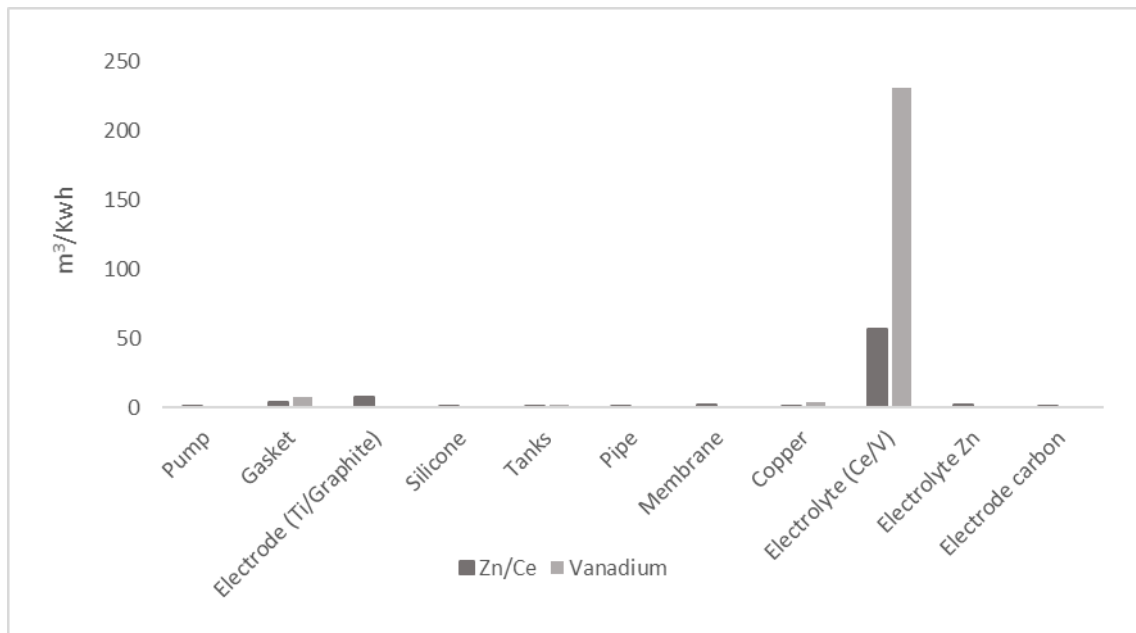


Figure 4. Water footprint as m³ used

3.2 Analysis of the midpoint results

The CML Baseline midpoint results of ZCBs and VRFBs and their uncertainty analysis in terms of confidence interval are shown in Table 2. All the impact values of the different studied impact categories obtained for the ZCBs are higher than the ones obtained for the VRFBs except acidification.

For example, as shown in Table 2, for the carbon footprint of VRFBs, the environmental impact is 136.5 kg CO₂ eq and the potential impact value is 117.9-159 kg CO₂ eq, for the carbon footprint of ZCBs the impact is 224.4 kg CO₂ eq (64 % higher) and the potential impact value is 191.4-264.9 kg CO₂ eq. So, this means that from the environmental point of view, the all vanadium redox flow batteries are more recommended than the Cerium based batteries in spite of the latter ones have a higher standard voltage than the former ones.

Table 2. Uncertainty analysis of the midpoint results. Values are presented per (1kWh) functional unit

Vanadium Redox Flow Battery					
Impact category	Unit	Impact value	Standard Deviation	Potential impact value	
Global warming (GWP100a)	kg CO ₂ eq	136.5	10.5	117.9	159.0
Abiotic depletion	kg Sb eq	1.41E-03	2.71E-04	9.94E-04	2.05E-03
Abiotic depletion (fossil fuels)	MJ	2.05E+03	3.98E+02	1.61E+03	3.08E+03
Ozone layer depletion	kg CFC-11 eq	3.05E-05	9.98E-06	2.11E-05	6.11E-05
Human toxicity	kg 1,4-DB eq	225	66	133	400
Fresh water aquatic ecotox.	kg 1,4-DB eq	59.1	27.1	28.7	113
Terrestrial ecotoxicity	kg 1,4-DB eq	0.782	0.131	0.643	1.14
Marine aquatic ecotoxicity	kg 1,4-DB eq	1.86E+05	8.23E+04	9.24E+04	3.83E+05
Photochemical oxidation	kg C ₂ H ₄ eq	6.87E-02	1.41E-02	4.91E-02	1.03E-01
Acidification	kg SO ₂ eq	1.67	0.351	1.19	2.57
Eutrophication	kg PO ₄ eq	0.286	0.114	0.179	0.580
Zn/Ce Redox Flow Battery					
Impact category	Unit	Impact value	Standard Deviation	Potential impact value	
Global warming (GWP100a)	kg CO ₂ eq	224.4	18.8	191.4	264.9
Abiotic depletion	kg Sb eq	1.67E-03	4.29E-04	1.11E-03	2.69E-03

Abiotic depletion (fossil fuels)	MJ	3.68E+03	6.07E+02	2.66E+03	5.03E+03
Ozone layer depletion	kg CFC-11 eq	4.08E-05	1.69E-05	2.03E-05	7.79E-05
Human toxicity	kg 1,4-DB eq	301.6	60.5	209	446
Fresh water aquatic ecotox.	kg 1,4-DB eq	69.8	21.9	41.3	126
Terrestrial ecotoxicity	kg 1,4-DB eq	1.51	0.481	0.868	2.79
Marine aquatic ecotoxicity	kg 1,4-DB eq	1.11E+06	3.29E+05	5.93E+05	1.91E+06
Photochemical oxidation	kg C ₂ H ₄ eq	8.06E-02	1.04E-02	6.27E-02	1.02E-01
Acidification	kg SO ₂ eq	1.55	0.211	1.19	1.97
Eutrophication	kg PO ₄ eq	0.372	0.117	0.250	0.681

3.3 Sensitivity analysis

To carry out a sensitivity analysis the effect of the electrolyte transportation issue in two parameters of the LCA was considered. Figure 5 shows the contributions of electrolyte transport of ZCBs and VRFBs in global warming and human toxicity. It can be clearly observed that the electrolyte transport factor increases substantially these impacts in both types of batteries. Thus, in the case of the CO₂ foot print (Global warming), when not transportation is assumed, the CO₂ foot print decreased around 60 % for the case of the VRFB and 50 % approx. for the case of the ZCB. In the case of the human toxicity, if not transport of electrolyte is considered in the study, a reduction of the impact around 27 % is reached in both types of batteries.

These results highlight that the transport of electrolyte has a great influence on the environmental analysis. Thus, the use of the electrolytes in places closer to their manufacturing facilities could decrease the environmental impact of the batteries. In the case of the VRFBs as vanadium (a widely used material) it could be interesting to carry out future studies using vanadium recovered from other uses or activities, such as the vanadium-depleted catalysts from the sulfuric acid production industry. Nevertheless, this assessment is out of the scope of this paper.

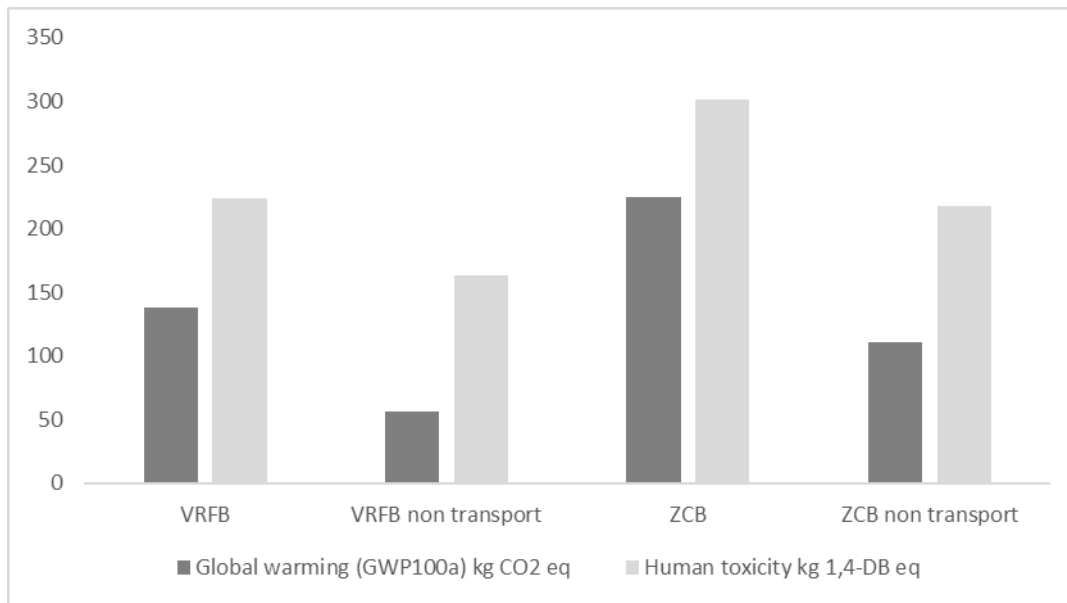


Figure 5. Effect of the electrolyte transportation in the global warming and human toxicity for the two studied batteries. Values are presented per (1kWh) functional unit

3.4 Preliminary Economic Survey

The cost of **ZCBs and VRFBs** manufacturing has been studied, based on the cost of the battery components. For its calculation, the budgets provided by different suppliers were considered, obtaining the total cost of each of the two types of redox flow batteries. Figure 6 shows the batteries cost breakdown in percentage terms. Upper panel of that figure analyses the ZCB battery and lower panel depicts the VRFB. The total cost of ZCB and VRFB batteries are 67.67 €/kWh and 142.4 €/kWh, respectively (the calculation was estimated taking into account market price in July 2017). Note that the total cost of VRFB is 100% more expensive than the ZCB counterpart. Essentially, the most important percentage cost of this type of batteries are electrolytes. Considering the case of VRFBs, their electrolyte constitutes 73.4 %. Regarding Zn/Ce batteries, the cost of both titanium electrode and Ce electrolyte is also important.

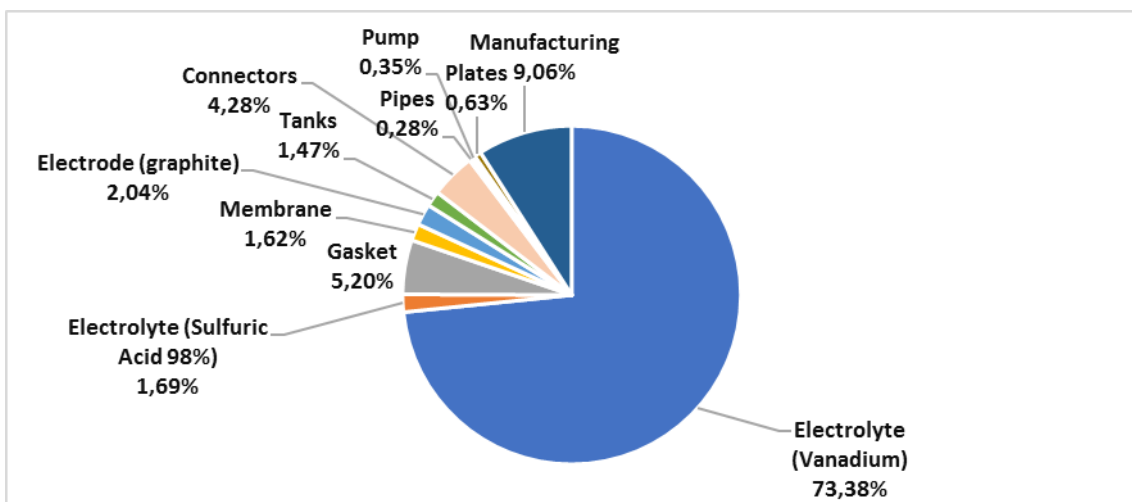
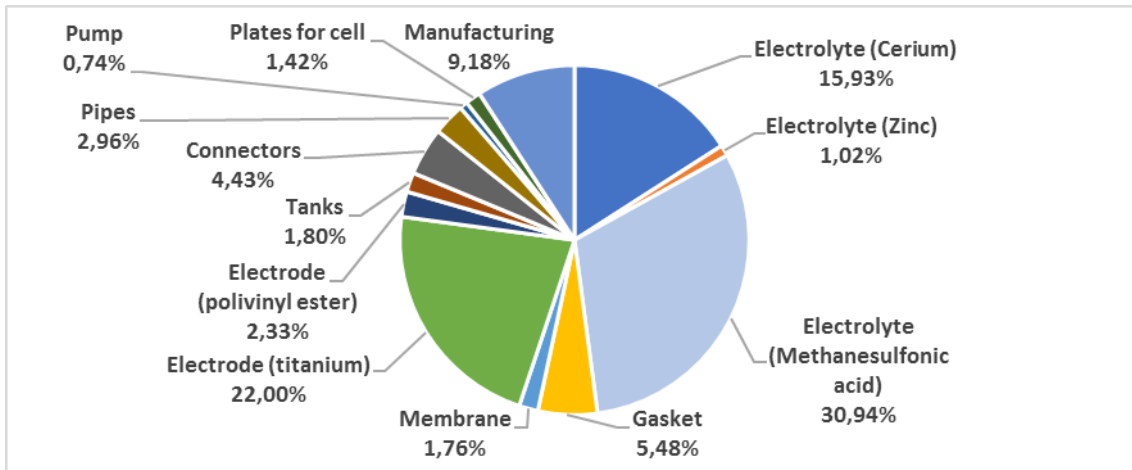


Figure 6. Cost of the redox flow batteries. Upper panel shows ZCB battery. Lower panel shows VRFB battery.

Another aspect that should be considered is the volatility price of metals and rare earths, as Vanadium, Zinc and Cerio ^[35]. In other words, significant prices variations can have a strong effect of the final price of the batteries making them unfeasible from an economic point of view. Therefore, risk management strategies should also be analysed for coping with pricing risk.

3.5 Comparative environmental study of conventional, non-conventional and redox flow batteries

The indicators selected for the comparative evaluation of the impact **have been**: Global warming, Abiotic depletion, Abiotic depletion (fossil fuel), Ozone Layer depletion,

Human toxicity, Fresh water ecotoxicity, Terrestrial ecotoxicity, Photochemical oxidation, Acidification, Eutrophication. These indicators have been evaluated by the point of view of the battery pack and the components that form it. The representation and analysis of the results are the aims of this stage.

Table 3 shows the CO₂ footprint values per kg of battery and per kWh of 6 types of batteries, one based on lead, two based on Li ion, other based on Na, and the two novel redox flow batteries (Vanadium, Zn/Ce) studied in this work.

Table 3. CO₂ footprint of different batteries

Author (year)	electrolyte	GWP 100a kg CO ₂ eq/kg	Energy density Wh/kg	GWP 100a kg CO ₂ eq /kWh
Baumann et al., 2017	valve regular lead acid	2.33	45	51.6
Baumann et al., 2017	NaNiCl	13.01	112	116
Baumann et al., 2017	LiFePO ₄	13.98	83	168.5
Baumann et al., 2017	Li-Ion	14.19	52	270.9
this work, 2019	Zn/cerium	6.94	31	224.4
Rydh et al., 1999	Vanadium	3.20	17	183
this work, 2019	Vanadium	2.86	21	136.5

It must be highlighted that there are factors that significantly affect the CO₂ footprint generated. These variables are the type of material extraction, transport or distance from the mine to the place where the batteries are assembled as it was pointed out in our sensitivity analysis and batteries production. Thus, it is not easy to make a fair comparison among the different batteries. Nevertheless, it can be observed that VRFBs have a lower CO₂ footprint value than conventional lithium batteries and ZCBs but higher than lead acid and NaNiCl batteries. The carbon footprint value of VRFBs (per kg of battery) obtained in this work is quite similar to other CO₂ footprint values of VRFBs found in bibliography using the same FU (kg of battery). Thus, the GWP impacts presented by Rydh et al., 1999^[17], Hiremath et al., 2015^[13], Weber et al., 2018

^[36] and this work are 3.2, 2.0, 5.6 and 2.86 kgCO₂ eq/kg, respectively. Comparing the lead batteries (the most used in the market) and the novel VRFB it can be observed that the GWP impact is similar in both batteries when it is expressed in terms of kg but when it is normalised per kWh, the CO₂ foot print value of the RFBs is more than twice the value of the lead battery because of the lower energy density reached by the RFB.

Table 4 shows the environmental impact of for batteries, NaNiCl, lithium and redox flow batteries (Vanadium, Zn/Ce). In this study, the contribution of electrolyte transport has not been considered. The obtained results are of the order of those showed in the literature ^[13,17,36-38]. The environmental impact of vanadium redox flow batteries is lower than the one of the conventional lithium batteries and NaNiCl batteries. The differences of these impacts depend on the type of metal that the electrolyte contains (Li, V, Zn, Ce, Cl, Ni, Na). Previous studies show that vanadium electrolyte is less aggressive ^[17, 34, 37] and has a lower environmental impact than other liquid electrolytes used in other redox flow batteries. On the other hand, ZCBs have the highest Terrestrial ecotoxicity impact reaching the double value with respect to its “sister” battery, VRFB. It can be also observed that Lithium batteries show the highest values for the following impact categories, Abiotic depletion Ozone layer depletion, Human toxicity, Fresh water ecotoxicity and Eutrophication which make them not very eco-friendly.

Table 4. Environmental impact of different batteries production (non electrolyte transport)

Impact category	Unit	NaNiCl	Lithium	Zn/Cerium	Vanadium
Abiotic depletion	kg S eq/kWh	0.0033	0.0081	0.0016	0.0014
Abiotic depletion (fossil fuel)	MJ/ kWh	628.7	1766.5	1942.1	827.1
Ozone Layer depletion	kg CFC/ kWh	9.38E-06	3.38E-05	2.22E-05	2.31E-05
Human toxicity	1-4 DB eq/ kWh	279.3	688.8	216.4	168.1
Fresh water ecotoxicity	1-4 DB eq/ kWh	159.6	336.2	65.7	58.1
Terrestrial ecotoxicity	1-4 DB eq/ kWh	0.621	1.015	1.447	0.762
Photochemical oxidation	Kg C ₂ H ₄ /kWh	0.212	0.101	0.119	0.086

Acidification	Kg SO₂/ kWh	5.196	2.212	0.943	1.190
Eutrophication	PO₄ eq/ kWh	0.403	1.248	0.286	0.233

4. Conclusions

LCA and a preliminary cost analysis have been performed to two redox flow batteries ZCB and VRFB based batteries for renewable energy storage using the SIMAPRO v8.4 software. From this assessment it can be concluded that:

- Regarding the components of each battery, the electrolyte is the component with the most environmental impact, independently of the type of RFB.
- The consideration of the electrolyte transport in the LCA of the two novel batteries for renewable energy storage has a great impact on the results. Above all, in the case of the CO₂ foot print.
- All the impact values of the different studied impact categories obtained for the ZCBs are higher than the ones obtained for the VRFBs except acidification and water foot print.
- In both batteries, the electrolyte (ion plus solvent) is the most expensive part of the battery but in the case of the vanadium battery, the vanadium ions are the most expensive while in the case of the ZCBs, the solvent of the electrolyte is the one that has the mayor contribution to the cost. So, the use of another solvent to reduce the cost of this battery would be advisable.
- When the foot print values of different batteries are compared it must be paid attention to the parameter of normalization. Different results are obtained for the case of kgCO₂eq/kg or kgCO₂eq/kWh. Nevertheless, our results regarding the VRFB are similar to others found in literature which means that our study has obtained consistent and reliable results.

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