

Chapter 5

Small-Size Vanadium Redox Flow Batteries: An Environmental Sustainability Analysis via LCA



Pasqua L'Abbate, Michele Dassisti and Abdul G. Olabi

Abstract Electrical energy production from renewable sources has dramatically grown in the recent years in the developed countries, putting the hard problem to be solved of supply discontinuity. How to reach high efficiency and reliability of electrical energy storage system is thus now one of the most challenging goals to be reached: among all, one of the most simple and widespread to use is the electrochemical storage systems. This paper analyzes the sustainability of a small vanadium redox flow battery performed by an LCA approach. This electrical energy storage system was selected for its significant advantages in use, such as the almost infinite lifetime of the vanadium electrolytes, which represent a potentially significant advantage in terms of a sustainable future made of less fossil fuels and more renewable energy. In fact, the LCA analysis performed shows that the production of the battery has a moderate impact, including the effect toxicity while at the end of life, the material and the electrolyte are completely reusable with a small fraction that goes to landfill disposal.

Keywords Vanadium redox flow battery · LCA · Electrical energy storage
Renewable energy sources · Sustainability

P. L'Abbate (✉)

Department of Civil, Environmental, Building Engineering and Chemistry,
Polytechnic of Bari, Bari, Italy
e-mail: pasqua.labbate@poliba.it

M. Dassisti

Department of Mechanics, Management and Mathematics, Polytechnic University of Bari, Bari,
Italy
e-mail: michele.dassisti@poliba.it

A. G. Olabi

Sustainable and Renewable Energy Engineering, University of Sharjah, 27272, Sharjah, UAE
e-mail: abdul.Olabi@uws.ac.uk

A. G. Olabi

Mechanical Engineering and Design, School of Engineering and Applied Science, Aston
University, Aston Triangle, B4 7ET Birmingham, UK

© Springer Nature Switzerland AG 2019

R. Basosi et al. (eds.), *Life Cycle Assessment of Energy Systems
and Sustainable Energy Technologies*, Green Energy and Technology,
https://doi.org/10.1007/978-3-319-93740-3_5

5.1 Introduction

Fossil fuels have dominated over two centuries, because of their large availability, their reduced storage volume, their high electrical energy concentration, and finally their electrical energy transferability (Dassisti et al. 2016). Electricity is a commodity representing about 12% of the total electrical energy transformed all over the world today. This percentage is keen to increase in the future, up to 34% in 2025, due to the present demand trends of global electrical energy consumption and also to the decline in the fossil fuels stock and the increased use of renewable energies in response to the global warming challenges (IEC 2012; Ibrahim et al. 2008). The contribution of electricity generated by renewable sources (wind, tide, sun, etc.) is destined to grow, according to the present trend of reduction of the greenhouse gas emission. Renewable sources are variable in time and space per sé, and this does not couple with the stability required for power supply. The most used means to face this problem is to adopt efficient and reliable electrical energy storage systems (EESS).

There are several electrical energy storage systems used so far, each based on different principles of transformation. Electricity can, in fact, be converted and stored as power potential (hydroelectric pumped, compressed air), kinetic energy, thermal energy, or chemical energy (generally hydrogen, methanol, synthetic natural gas, or electrochemical species) (Dell and Rand 2001). The most convenient means of storing electricity so far for today's applications, and for the new "green" future applications, is the use of electrochemical storage systems because of their limited dimensions and high specific electrical energy storage capacity with respect to other types of storages. There are different types of electrical energy storage systems on the market: this paper focuses on the vanadium redox flow batteries, originally developed by NASA in the early 1970s for long-term space missions (Giner 1976). These batteries are now driving attention for electrical energy storage because of their independence in electrical energy and power rating, fast response, room temperature operation, extremely long life, and potentially low environmental impact.

In particular, we focus on a specific case study of a small-scale vanadium redox flow battery (VRFB) prototype to give the flavor of the environmental sustainability through a life cycle assessment (LCA) analysis. The battery prototype was developed within an industry-funded research project aimed at optimizing VRFB for easy-to-mount civil applications. Environmental sustainability was evaluated to highlight the critical points of the design phase and potential improvements before the market entry. The LCA included also the preparation of the vanadium electrolyte, the core component of the battery. Three different processes were benchmarked: the mixing of suitable vanadium precursors (Electrolyte A), the chemical reduction of V_2O_5 by oxalic acid (Electrolyte B), and the electrochemical reduction of V_2O_5 using a homemade "H-shaped" electrolysis cell (Electrolyte C). The results of this analysis provide a benchmark reference for assessing environmental sustainability of existing storage systems in different applications.

5.1.1 Electrical Energy Storage Systems

Renewable energy sources are discontinuous per sé as affected by different meteorological or environmental conditions. This may represent a strong limitation in use due to the kind of electrical energy quality supply required so far. To partially cope with these limits, it may potentially be possible to balance the electrical energy supply network by increasing the amount of renewable generation plants installed, as well as to spread the installations of renewable generators on a larger area, or even to exploit the complementarity of several renewable sources (IEC 2012). These solutions, however, are possible upon large investments (say the number of plants and/or the improvement of the transmission networks) as well as the existence of international agreements between producers. Considering the cost of extra-renewable generation and the difficulty of building new production/transmission plants, the electrical energy storage systems (EESSs) are a promising alternative solution to this electricity storage problem. Electrical energy storage systems are, in general, devices that can store electrical energy over time before turning it into work. In case of electricity, EESSs are interposed between the place/time where electricity is generated and the place/time where it is consumed: their use is to supply the correct amount of electricity upon variable demand. They serve to recover imbalance between supply and demand, as well as to guarantee the stability and the quality of the power supply itself (voltage and frequency). EESS may also be used to reduce the cost of electricity by storing peak electricity when the price is lower, for use at peak prices at higher prices (Chen et al. 2009). EESSs furthermore support users when power failures occur and can be used in mobile applications within off-grid areas. Finally, for some applications in the transport sector, EESSs contribute to the creation of an ecological transport system by limiting the use of conventional combustion engines and increasing the use of electric vehicles with batteries.

5.1.2 Electrochemical Storage Systems

There are several electrical energy storage systems that convert and store electricity as power potential, kinetic energy, thermal energy, or chemical energy. The most common means of converting and storing electricity is the adoption of electrochemical storage systems. These systems, which are typically named batteries, have been diffused since 1890 with the lead–acid battery (used in mobile and stationary applications) having a life expectancy of 6–15 years, cycle efficiency of 80–90%, and easy recyclability and recharge. This type of batteries is cost-effective, but has low electrical energy density and, due to its hazard risk, its use is forbidden or restricted in different jurisdictions.

In 1915, nickel cadmium and nickel hydride (NiCd, NiMH) batteries were invented, with a higher power density than lead–acid batteries (Liyu et al. 2011), higher number of cycles, and able to operate at low temperatures (–20 °C up to

–40 °C). Due to the toxicity of cadmium, later the NiMHs were built, currently replaced in portable and mobile applications by lithium–ion batteries. Another type is the sodium–sulfur battery, which reaches life cycles of about 4500 cycles and has a discharge time of 6.0–7.2 h: to maintain operating temperatures, a heat source is needed, which uses the accumulated electrical energy, thus partly reducing battery performance. Nickel sodium chloride (NaNiCl) battery, better known as ZEBRA (Zero Emission Battery Research), is a high-temperature battery and has been marketed since 1995, successfully implemented in several electrical vehicle designs (Think City, Smart EV).

Lithium–ion batteries have then become the most important storage technology for portable and mobile applications since the beginning of 2000. Generally speaking, this kind of battery has a very high efficiency, typically in the range of 95–98%, is very flexible and has 5000–6000 duty cycles of lifetime. The main obstacle is the high cost (more than 500 €/kWh): they can only compete with lead–acid batteries for those applications which require short discharge times. Safety is a serious issue in lithium–ion battery technology. Most of the metal oxide electrodes are thermally unstable, and can decompose at elevated temperatures, releasing oxygen which can lead to a thermal runaway (IEC 2012).

Flow batteries are now receiving attention for their electrical energy conservation lasting hours or days with a power up to several MWs (Alotto et al. 2014; Dassisti et al. 2015). Flow batteries are classified as redox batteries and hybrid batteries. In a hybrid fluorescence battery (HFB), one of the active masses is stored internally within the electrochemical cell, while the other remains in the liquid electrolyte and is stored externally in a tank. Hybrid cells thus combine the features of conventional secondary batteries and redox flow batteries. The operating range of these batteries is between 5 and 40 °C; this is due to the solubility limit of V^{3+} in sulfuric acid below 5 °C and to the V^{5+} instability above 40 °C. Recently, researchers at the Department of Energy's Pacific Northwest National Laboratory (USA) found that the addition of hydrochloric acid to sulfuric acid, particularly 2.5 parts of sulfuric acid and 6 parts of acid hydrogen, increases the storage of batteries by increasing their electrical energy capacity by 70% and expanding the operating temperature range, i.e., between –5 and 50 °C (Li et al. 2011).

5.2 VRFB and Their Applications

A redox flow battery (RFB) refers to an electrochemical system that generates a so-called redox system on the surface of the inert electrodes, responsible for the conversion of electrochemical energy (Chuna et al. 2015). Several redox pairs have been studied and tested in RFBs, such as a FeTi system, a Fe–Cr system, and a polyS–Br system.

The first-generation vanadium redox battery (VRB) used sulfuric acid and vanadium species in both semiconductors as electrolytic solution. Vanadium in solution comes from the vanadium pentoxide compound (V_2O_5), which is found in minerals

Table 5.1 Existing types of batteries with vanadium electrolyte

Characteristic	V/V	V/Br	V/Air
Solution	Sulphuric acid	Bromidic acid	Sulphuric acid
Reaction	$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}$ $\text{V}^{2+} \rightleftharpoons \text{V}^{3+} + \text{e}^-$	$2\text{VBr}_2 + 2\text{Br}^- \rightleftharpoons 2\text{VBr}_3 + 2\text{e}^-$ $\text{ClBr}_2^- + 2\text{e}^- \rightleftharpoons 2\text{Br}^- + \text{Cl}^-$	$4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$ $4\text{V}^{2+} \rightleftharpoons 4\text{V}^{3+} + 4\text{e}^-$
Electrical energy density (Wh/kg)	25	50	41
Standard potential (V)	1.23	1.3	1.49

such as vanadinite and carnotite, present in countries such as Russia, South Africa, and China.

With the vanadium ions, also the bromium can be used, obtaining the pair (Br³⁻–/3Br⁻). Another type is the vanadium/air battery, which is still in the experimental phase and uses the pair V²⁺/V³⁺ in a semicircle and the other pair O₂/H₂O. In Table 5.1, the three typologies are given with reactions occurring within the cell and their respective energy density and standard potential (Tang et al. 2012).

The most widespread form of rechargeable vanadium battery uses vanadium redox pairs in both semiconductors. The electrolyte solution is stored in two separate tanks, and simultaneously pumped into the cells where the oxidation reaction occurs, which can lead to battery charge or discharge. The power of the battery depends on the size and number of electrochemical cells, while the capacity of the battery depends on the amount of electrolyte stored in the tanks. Oxidation reactions occurring within the cell are visible in Table 5.1. During the discharge process, a reduction of V⁵⁺ in V⁴⁺ occurs, with consequent acquisition of electrons and oxidation of V²⁺ in V³⁺ and the release of electrons. In the charging process, V⁴⁺ oxidation in V⁵⁺ occurs with consequent release of electrons and the V³⁺ reduction in V²⁺ with electron capture (Weber et al. 2011). Figure 5.1 shows a schematic diagram of a redox flow battery with electron transport in the circuit, ion transport in the electrolyte and across the membrane, active species crossover, and mass transport in the electrolyte.

Cell stacks and electrolyte tanks can be placed in distinct locations: consequently, storage media can be placed in places where storage containers do not affect the production space (e.g., under a floor or in parking facilities). Vanadium as an electrolyte, compared with other types of electrolytes, based on different redox pairs (iron/chromium, bromine/polysulphide, vanadium/bromine, zinc/bromine) (Bartolozzi 1989), has the unique feature of having the same metal ions in both positive and negative electrodes. In case of mixing of positive and negative electrolytes, the battery capacity does not diminish and does not suffer permanent capacity losses. Vanadium redox batteries can be upgraded at a relatively low incremental cost by increasing the volume of the electrolytes (using large tanks) to have more electrical energy stored. Adding new cell batteries allows to increase power (thus allowing quick supply through the exchange of solutions).

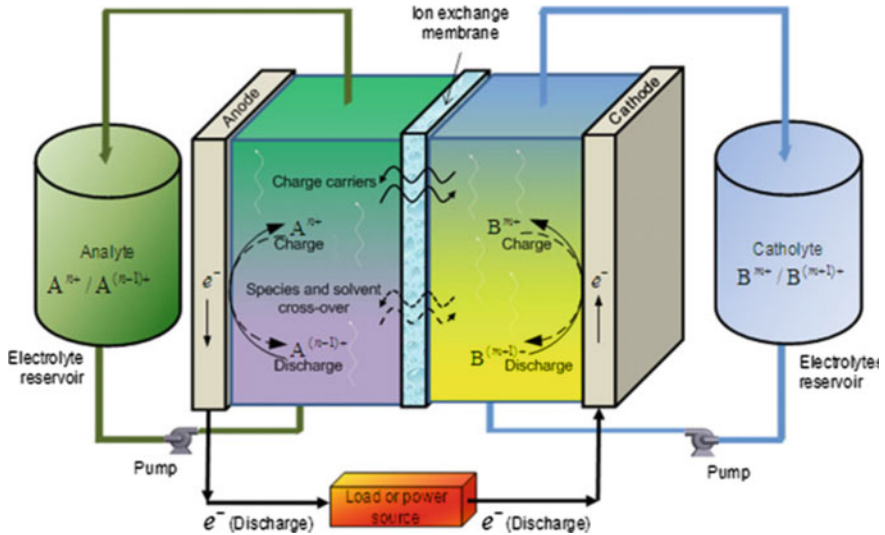


Fig. 5.1 A schematic diagram of a redox flow battery. *Source* Weber et al. (2011)

VRFB technology is most frequently used for renewable energy sources (Nehrir et al. 2011; Beaudin et al. 2010; Kear et al. 2012) as well as for large fixed electrical storage systems, where batteries need to be stored for long periods, with little maintenance while maintaining an almost ready state (Poullikkas 2013). VRFB is also suitable for a wide range of electrical energy storage applications in industry (Chen et al. 2009; Skyllas-Kazacos et al. 2010): say, in the telecommunications industry, as a backup unit in UPS systems, for increased security of supply and stabilization of renewable (Beaudin et al. 2010; Chen et al. 2009; Nehrir et al. 2011), etc. In Japan, for instance, several multi-MWh systems have been installed; one of these systems stores up to 500 kW for 10 h (5 MWh) (Beaudin et al. 2010).

One of the largest VRFB installations has been applied to stabilize a 32 MW wind farm to provide a maximum power of 4 MW/6 MW units in Tomamae Wind Villa in Japan (Chen et al. 2009). The Japan Institute of Energy (2001) and the Rice Research Institute in Denmark (2006) installed a battery to understand the potential of the VRB for everyday wind management. Vantek (250 kW, 2 h) has also installed the first major commercial VRFB outside Japan to Eskom in South Africa (Nehrir et al. 2011).

5.3 LCA of a VRFB Small-Scale Prototype

This paragraph presents the LCA study for a real small-scale redox flow battery (VRFB) prototype following the ISO 14040 and ISO 14044 standards (ISO 2006a,

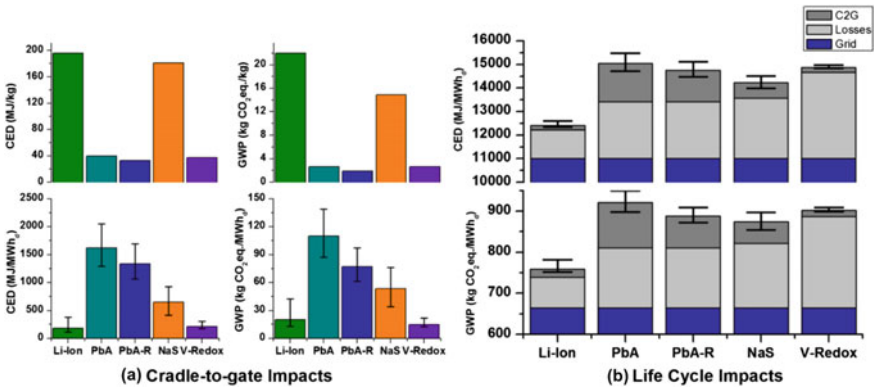


Fig. 5.2 Life cycle battery impacts showing the cradle-to-gate and life cycle stages impacts of batteries. *Source* Hiremath et al. (2015)

b). This battery prototype was developed within an industry-funded research project to optimize small-size VRFBs for several civil applications. Environmental sustainability has been addressed during design and experimentation, to evaluate critical points and support eco-design before entering the market. In Rydh (1999), comparisons are made up of the large vanadium redox (VRFB) stream battery for lead–acid batteries (PbA) for a Swedish scenario. A broader perspective is discussed in Rydh and Sandén (2005) where all the components of a battery photovoltaic system are faced. It is clearly stated that, when it comes to relatively new technologies, there are strong uncertainties about productive efficiency. This in turn can lead to inconsistent system boundaries. This question is clearly discussed in Pehnt (2006) which proposes a dynamic approach to LCA against the LCA state-quo; authors in Hiremath et al. (2015) present a comparative life cycle assessment of cumulative electrical energy demand (CED) and global warming potential (GWP) of four stationary battery technologies: lithium–ion, lead–acid, sodium–sulfur, and vanadium redox flow (see Fig. 5.2). In Arbabzadeh et al. (2015), a life cycle assessment (LCA) model is developed to determine the system configuration needed to achieve a variety of CO₂-eq emission targets and prove that adding VRFB as energy storage could be economically preferable in off-grid configuration only when wind curtailment exceeds 66% for the examined system. In Unterreiner et al. (2016), the ecological impact of recycling and reuse of materials of VRFB were compared with lead–acid, lithium–ion batteries proving that the Li–ion battery has the lowest ecological impact among the three battery technologies provided that for VRF batteries there is still no established recycling process up to date.

The environmental performance of the VRFB batteries was made not only on “cradle-to-gate analyses” but considering also their use stage impact. The proportion of cradle-to-gate impacts in the life cycle impacts of the batteries varies from around 2% (for Li–Ion and V-Redox) to 12% (for PbA) (Hiremath et al. 2015). In Fig. 5.2, it is clear how the manufacturing phase has only a minor impact on the life cycle

impacts of the battery compared to its use phase. In the case of Li-Ion and V-Redox batteries, despite both of these are sustainable at the cradle-to-gate stage, the former performs better than the latter when use stage impacts are taken into account. The increasing competitiveness of Li-Ion battery, due to the increasing GHG emissions in the power-grid mix, is mainly due to the effect of its round-trip efficiency. That is, the higher the round-trip efficiency, the better the relative performance of that battery technology at higher environmental loads and vice versa.

5.4 LCA of Small-Scale Vanadium Redox Flow Battery Prototype

Provided there is no source of literature that addresses a small-scale VRFB battery, the aim of the present chapter is to give figures of the environmental sustainability of a small vanadium redox flow (VRFB) battery, to provide a reference benchmark of small VRFB not yet on the market, with a nominal power of 0.15 kW.

As concerns the LCI assumptions, reaction and mixing energy has been considered, expressed in terms of power and storage energy capacity to enable evaluation independently from sizing. In addition, all the raw material extraction and their production were taken into account. As concerns energy, input energy to the hydraulic system and the charge energy per cycle were assumed. For transportation and packaging, all transportations for raw materials were considered. Packaging was not considered, provided its impact was not significant on the overall life cycle. A fixed number of use and disposal were considered too. The hypothesis of a continuous running for 24 h/day over the period of 20 years was made, with an average energy delivery of 1.2 kWh/day for 20 years. Vanadium electrolyte is assumed to have a very long lasting life and its only treatments are filtering before reuse, provided it is self-recovery. The electrolyte with active material is thus assumed to last indefinitely. A deionized water refill was assumed of 100 ml in 20 years. The only consumables are the SPEEK ionic membranes, which were assumed to be replaced every 5 years. As concerns the hydraulic system, a 5-year maintenance is assumed with replacement of seals. At the end-of-life membranes are brought to landfill as well as the pumps. All the other materials have been considered as fully reusable.

System boundaries are given in Fig. 5.3. The functional unit is described in Table 5.2 since the same prototype is taken as reference. The unit processes considered are production of all raw materials of the parts to be assembled (electrodes and cells, membranes, laboratory-prepared vanadium electrolyte, battery cases, hydraulic system), assembly, use, and disposal. The VRFB was assembled and tested in Apulia (Southern Italy). All VRFB components came from southern Italy, except for electrolyte synthesis reagents from northern Italy and Vanadium pentoxide from South Africa. Most of the primary data were obtained by direct measurements in the laboratory where the battery was built and tested for operation and integrated with the literature. Secondary data were obtained with the Ecoinvent v 2.1 database

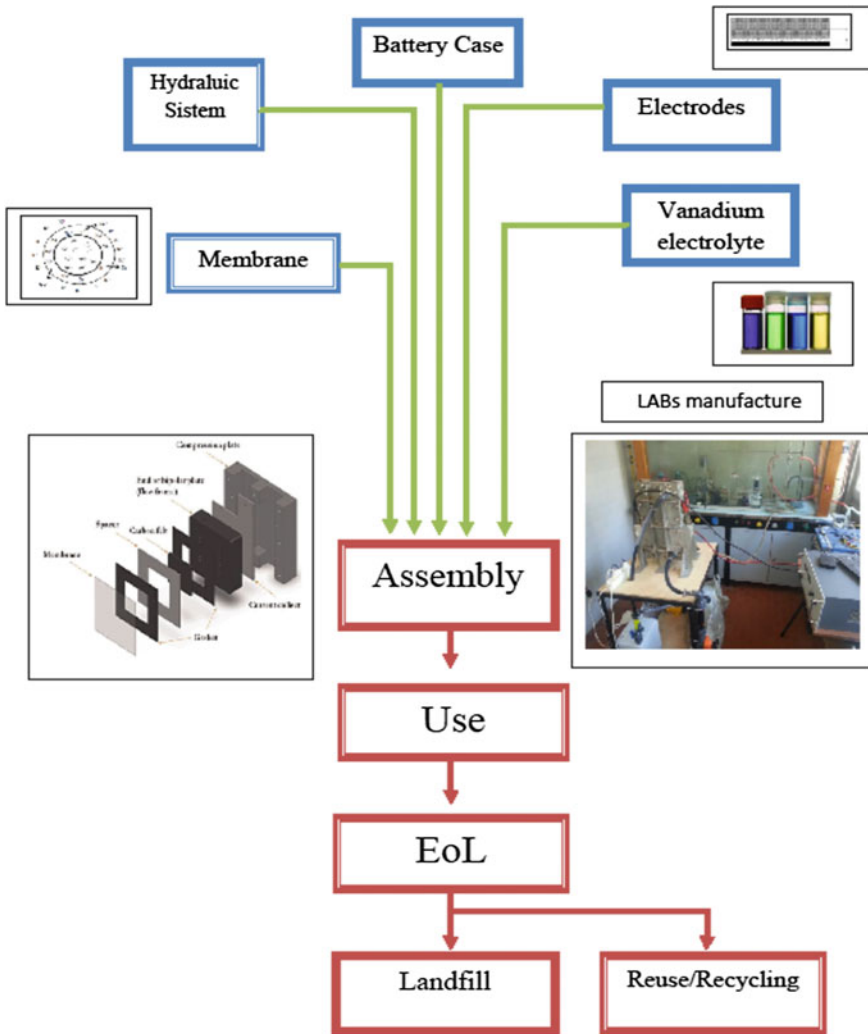


Fig. 5.3 VRFB prototype system boundaries

(Frischknecht et al. 2007; Jungbluth et al. 2008). The software adopted to perform the analysis was CMLCA developed by the Center of Environmental Science at Leiden University (Netherlands). The methods used for impact assessment are USE-tox™ (Rosenbaum et al. 2008), IMPACT2002+ (Jolliet et al. 2003) and ReCiPe 2008 (Goedkoop et al. 2009) for the benchmarking purposes above referred to as the environmental sustainability of EESSs.

The first two were selected considering the toxicity of the vanadium element, to investigate the toxicity of the organism and of humans, the latter being screened

Table 5.2 VRFB prototype analyzed

Characteristics	Value
Number of stack	1
Nominal power	150 W
# Cells/stack	5
Average voltage at end discharge (SoC = 0.2)	6 V
Energy density of electrolyte	36.18 Wh/l
Electrolyte volume	6 l
Overall efficiency	0.85
Average current	25 A
Charge energy	176.47 Wh
Discharge energy	127.5 Wh
Cycle time (charge and discharge)	~3 h

with particular attention to the noncarcinogenic and carcinogenic fraction. With the ReCiPe method, a combined use approach of midpoint impacts and environmental damage assessment (endpoint) is proposed. Subsequently, an LCA comparison was performed considering three different processes of vanadium electrolyte preparation in the laboratory.

The battery prototype considered was made up of polypropylene loaded with graphite, stainless steel plates, steel screws, and brass current collectors. Carbon felt GFD 4.6 EA was used for VRFB electrodes, coated with niobium to avoid hydrogen evolution. The most important property of the electrodes is that they have a large surface area in order to provide high current densities. The membrane adopted was an ion-exchange membrane (commercial sulfonate PEEK), separating the positive and the negative electrolyte solutions. Ion-exchange membrane must allow the ion transfer within the electrolyte while preventing electrons to pass through. Cells were made of high-density PP. Bipolar plates were made of SIGRACET—BPP. Electrolyte is stored in external tanks outside the cell stack. Tanks were made of plastic materials (PE) to resist the low pH environment. Pumps, valves, and piping components were also in plastic (PVC) resistant at low pH environments.

The electrolyte was obtained in the laboratory by a mixing process (method A). Required quantity of precursors V^{2+}/V^{3+} is dissolved in a solution of $1M H_2SO_4 + 2M HCl$ and mixed with magnetic stirrer for 3 h. Energy inputs include the energy used for the hydraulic system, the magnetic stirrer, the charge energy per cycle, the energy used for the processes of extraction, and production of reagents and materials. All transports of raw materials were considered, while the packaging was not considered as their impact was not significant for the life cycle calculation (0.05% contribution). For the use phase, it was assumed a continuous operation for 24 h/day over a period of 20 years, with an average energy delivery of 1.2 kWh/day. It is assumed that vanadium electrolyte is completely reused, by performing only a mechanical filtration process and adding deionized water (about 100 ml over 20 years). The only consumables

are the SPEEK ionic membranes, which are supposed to be replaced every 5 years. Regarding the hydraulic system, it takes 5 years of maintenance to replace the gaskets. In the EoL phase, the membranes and gaskets are brought to the dump, while battery cases, electrodes, and electrolyte solution are reused/recycled.

Impact categories analyzed were (Goedkoop et al. 2009) agricultural land occupation [ALOP ($\text{m}^2 \times \text{year}$)], natural land transformation [NLTP (m^2)], marine eutrophication [MEP (kg)], freshwater eutrophication [FEP (kg)], particulate matter formation [PMFP (kg)], marine ecotoxicity [METP100 (kg)], terrestrial acidification [TAP20 (kg)], terrestrial ecotoxicity [TETP100 (kg)], water depletion [WDP(m^3)], metal depletion [MDP (kg)], fossil depletion [FDP (kg)], photochemical oxidant formation [POFP (kg)], climate change [GWP20 (kg)], ionizing radiation [IRP_I (kg)], freshwater ecotoxicity [FETP100 (kg)], urban land occupation [ULOP ($\text{m}^2 \times \text{year}$)], human toxicity [HTP100 (kg)], and ozone depletion [ODP inf, x (kg of ODS x and kg CFC-11 equivalents/kg)].

5.5 LCA Results for the VRFB Prototype

The results obtained are grouped into five graphs. The first graph (Fig. 5.4) shows categories of toxicity obtained using the method impact 2002+ and reporting impact categories: Human Health Photochemical Oxidation, Human Health Ionizing Radiation, Human Respiratory Health Effects, and Human Health Human Toxicity (see results in Table 5.3). From Table 5.3 and the graph in Fig. 5.4, it is clear that the total damage on human health is due to the category of human respiratory health effects. The main contribution is given by the use phase. The high values of the use phase originate by the use of fossil fuels for electricity employed at the start of the battery at each cycle. As for the assembly process, the widest contribution is given by the electrolyte production (75%). With the USEtox™ method, it is possible to distinguish between carcinogenic and noncarcinogenic human toxicity. The results in Table 5.4 and the graph in Fig. 5.5 confirm the most impactful from the point of view of toxicity due to the use phase. As concerns, the human toxicity balance is of 50.3% for noncarcinogenic and 49.7% for carcinogenic.

According to the method ReCiPe, Midpoint (I) was used to benchmark the impacts of the three processes abovementioned considering assembly, use, and disposal. The impact categories are reported with the results in Table 5.5 according to the impact categories mentioned above and the related measurement units.

Figure 5.6 shows the results of this analysis. The use phase has the stronger contribution to each category of environmental impact investigated. On the other hand, Fig. 5.7 shows how the production processes of the various components used to assemble the battery have a significant environmental burden. It is clear that the element having the greater effect on the environmental impact of the battery assembly phase is the electrolyte production.

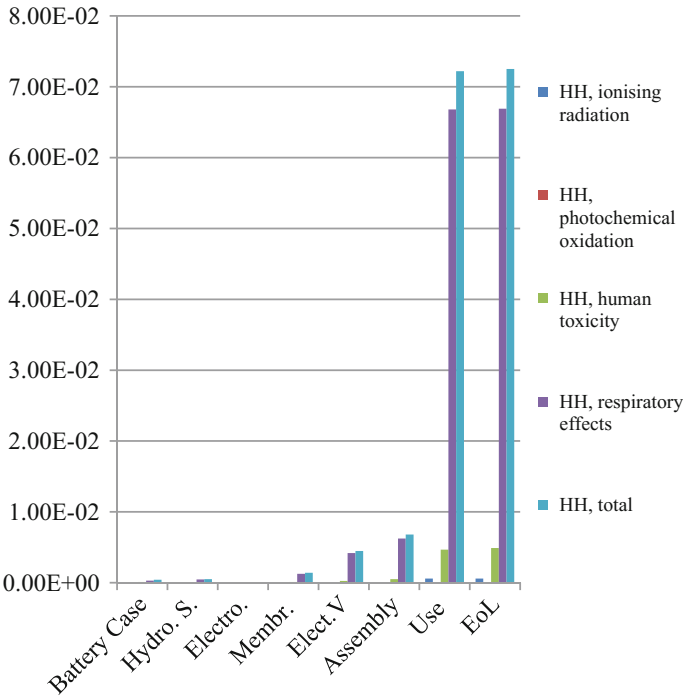


Fig. 5.4 Environmental impact assessment of the VRFB prototype using the impact 2002+, toxicity category in (DALY/kg emission) Jolliet et al. (2003)

Table 5.3 Results of environmental impact assessment of the VRFB prototype/method impact 2002+ (unit ecopoints)

Categories impact	Battery case	Hyd.S.	Electr.	Membrane	Electrolyte	Assemb.	USE	EoL
HH. ion. radiation	6.2E-07	3.1E-07	2.2E-08	1.7E-05	2.3E-05	4.2E-05	0.000593	0.000594
HH. pho.oxidation	2.63E-07	4.04E-06	8.56E-09	1.04E-06	6.08E-06	1.14E-05	6.94E-05	6.95E-05
HH. hum. toxicity	0.000115	3.47E-05	2.89E-07	0.000103	0.000255	0.000508	0.00467	0.0049
HH. resp. effects	0.000305	0.000464	3.70E-06	0.00127	0.00419	0.00624	0.0668	0.0669
HH. total	0.000421	0.000504	4.02E-06	0.0014	0.00448	0.0068	0.0722	0.0725

5.6 Comparison of Synthesis Processes for the Preparation of the Vanadium Electrolyte

From the results obtained, it has been found that the production of the vanadium electrolyte contributes more to the environmental impact of the components used to assemble the VRFB. With a second LCA study, three different syntheses of the

Table 5.4 Environmental impact assessment of VRFB using the USEtox™ (Rosenbaum et al. 2008)

Impact category	Elect.V	Assembly	Use	EoL	Unit
USEtox. human toxicity. carcinogenic	1.75E-06	3.92E-06	2.53E-05	2.67E-05	CTU
USEtox. human toxicity. non-carcinogenic	2.35E-06	6.89E-06	2.67E-05	2.70E-05	CTU
USEtox. human toxicity. total	4.10E-06	1.08E-05	5.40E-05	5.47E-05	CTU

Table 5.5 Results of environmental impact assessment of VRFB, using the ReCiPe midpoint (I), for the processes of assembly, USE, and EoL

IC	Assembly	USE	EoL	Unit
ALOP	0.51	5.51	0.02	m ² a
NLTP	0.02	0.195	0	m ²
MEP	87.7	1.09E+03	0	kg N-Eq
FEP	87.7	1.09E+03	0	kg P-Eq
PMFP	0.133	1.36	0.01	kg PM10-Eq
METP100	0.33	3.41	0.06	kg 1.4-DCB-Eq
TAP20	0.389	4.57	0.01	kg SO ₂ -Eq
TETP100	0.00877	0.0663	0.0003	kg 1.4-DCB-Eq
WDP	0.215	3.41	0	m ³
MDP	5.38	11.3	0.1	kg Fe-Eq
FDP	32	339	0	kg oil-Eq
POFP	0.331	2.81	0	kg NMVOC
GWP20	87.7	1.09E+03	0	kg CO ₂ -Eq
IRP_I	9.89	138	0	kg U235-Eq
FETP100	0.418	4.02	0.07	kg 1.4-DCB-Eq
ULOP	0.452	2.81	0.02	m ² a
HTP100	4.26	21.4	0.4	kg 1.4-DCB-Eq
ODPinf	8.89E-06	9.03E-05	0.00E+00	kg CFC-11-Eq

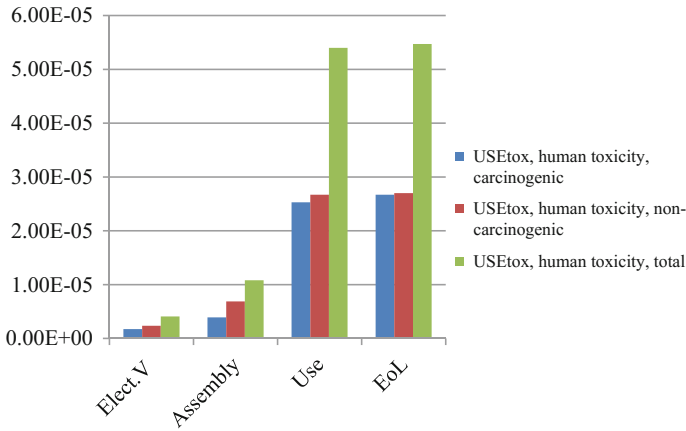


Fig. 5.5 Environmental impact assessment of the VRFB prototype using the USEtox™ Rosenbaum et al. (2008)

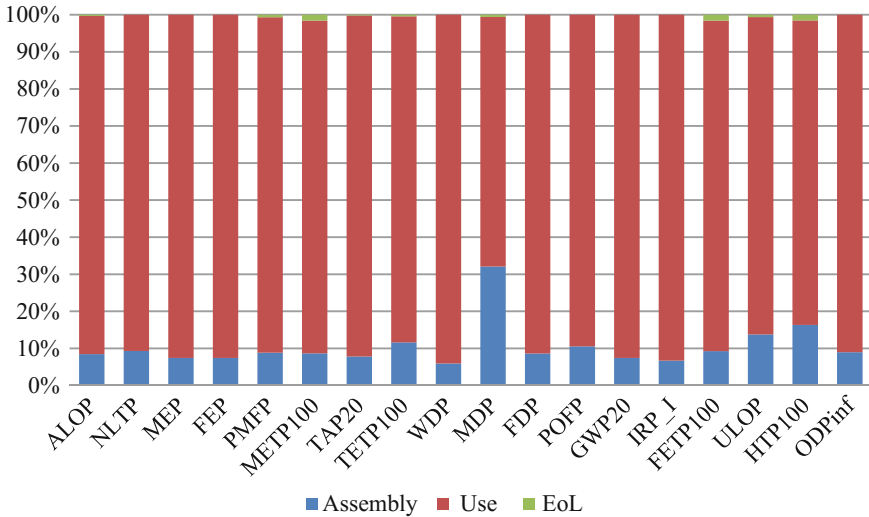


Fig. 5.6 Environmental impact assessment of VRFB, using the ReCiPe midpoint (I), for the processes of assembly, USE, and EoL

electrolyte conducted in the laboratory were compared. The selected functional unit (FU) is 6 L of electrolyte produced, and the system boundaries are from the “cradle to the door.” The raw materials considered are the reagents used for the three syntheses, while consumables, laboratory glassware, and equipment used for the three processes (except electrodes and cells) have been excluded from the analysis. The transport of reagents was calculated as the distance from the place of purchase to the electrolyte preparation site. All reagents come from northern Italy with the exception

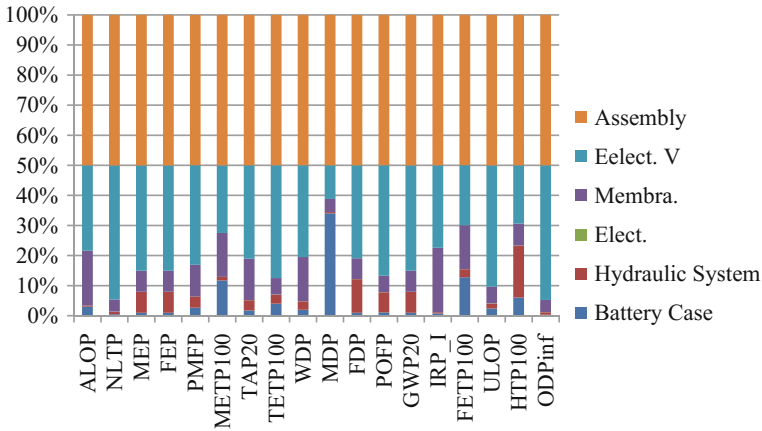


Fig. 5.7 Environmental impact assessment of VRFB using the ReCiPe midpoint (I) of production processes: electrolyte, membrane, hydraulic system, battery case, electrodes, and assembly

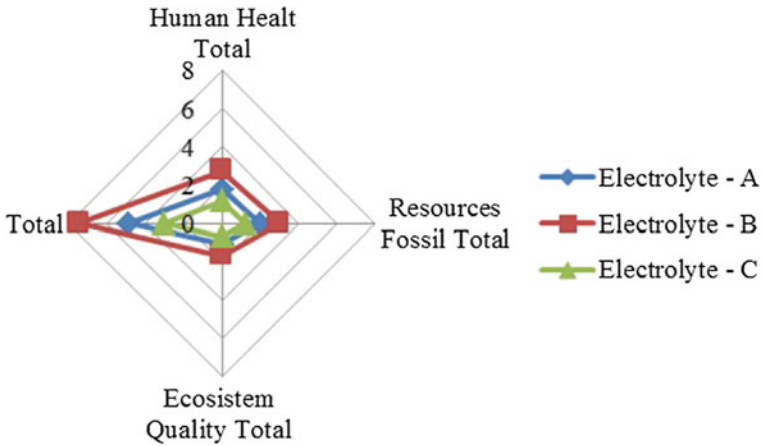


Fig. 5.8 Environmental impact assessment, using the ReCiPe endpoint (I/A), comparison of environmental damage (figures in ecopoints)

of deionized water (domestic production) and V_2O_5 (from South Africa). The energy used for the preparation of each reagent or raw material has been considered, as well as each energy input of the preprocessing phases of the electrolyte. No containers for packaging and storage of the finished product have been considered. ReCiPe 2008 (Goedkoop et al. 2009) is used as a method for measuring environmental impacts. In this case, three indicators of environmental damage were used: damage to human health, damage to ecosystems, and damage to the availability of resources.

Figure 5.8 shows that the results obtained by comparing the three different synthesis procedures of vanadium electrolyte are reported. The synthesis produced by

Electrolyte C is the lowest impact, while the Electrolyte B preparation process has the highest impact (Guinée 2002).

5.7 Conclusions

Renewable energy adoption is one of the viable strategies to respond effectively to the problem of global warming posing, on the other hand, the problem of adequate and reliable electrical energy storage systems. Among the existing ESSs, batteries have an important role: among the various types of batteries, the most interesting from a sustainability point of view are the vanadium redox flow batteries. This kind of battery still requires a large amount of space, while it is an environmentally sustainable battery, easy to regenerate, and recycle many of its components. In fact, the LCA analysis presented shows that the production of the battery has impacts that make this kind of battery viable for mass diffusion, including the effect toxicity, which is usually an important aspect for other types of existing types of batteries. At the end of life being the material and the electrolyte completely reusable, only a small fraction goes to landfill disposal. The improvement of sustainability of this kind of battery should then be concentrated on the use phase. In our case, the highest impact is due to the use of Italian power mix to operate the battery at each cycle over the 20 years lifetime considered. Surely using electrical energy from renewable sources can significantly reduce the resulting impact. The preparation of the vanadium electrolyte is a second critical point; from the comparison of the three sequences of electrolyte preparation processes (A, B, and C), we have identified the electrolyte preparation C as the best methodology in terms of environmental sustainability. Provided the electrolyte vanadium has been produced in the laboratory, in view of mass production, a significant improvement of the environmental sustainability is expected (Rydh and Sandén 2005). These results can be easily extended to other VRFB size units—provided the same technology and materials are adopted—thus allowing an easy benchmarking of the EESS applications.

Acknowledgments The authors acknowledge Duferco Project from Inreslab s.c.a.r.l. Monopoli for partially supporting the present analysis. This work has been published under the moral patronage of the SOSTENERE group of the AITEM (www.aitem.org)

References

- Alotto P, Guarnieri M, Moro F (2014) Redox flow batteries for the storage of renewable energy: a review. *Renew Sustain Energy Rev* 29:325–335. <https://doi.org/10.1016/j.rser.2013.08.001>
- Arbabszadeh M et al (2015) Vanadium redox flow batteries to reach greenhouse gas emissions targets in an off-grid configuration. *Appl Energy* 146:397–408
- Bartolozzi M (1989) Development of redox flow batteries. A historical bibliography. *J Power Sources* 27:219–234

- Beaudin M, Zareipour H, Schellenberglabe A, Rosehart W (2010) Energy storage for mitigating the variability of renewable electricity sources: an updated review. *Energy Sustain Dev* 14:302–314
- Chen H, Cong TN, Yang W et al (2009) Progress in electrical energy storage system: a critical review. *Prog Nat Sci* 19:291–312. <https://doi.org/10.1016/j.pnsc.2008.07.014>
- Cunha A, Martins J, Rodrigues N, Brito FP (2015) Vanadium redox flow batteries: a technology review. *Int J Energy Res* 39:889e918. <http://dx.doi.org/10.1002/er.3260>
- Dassisti M, Mastorilli P, Rizzuti A, L'Abbate P, Cozzolino G, Chimienti M (2015) LCA of in-house produced SMALL-SIZED vanadium redox-flow battery. *State Art Energy Dev* 11:232
- Dassisti M, Mastorilli P, Rizzuti A, Cozzolino G, Chimienti M, Olabi AG, Matera F, Carbone A (2016) Vanadium: a transition metal for sustainable energy storing in redox flow batteries. In: Saleem H (editor-in-chief) Reference module in materials science and materials engineering. Elsevier, Oxford, pp 1–24. ISBN 978-0-12-803581-8
- Dell RM, Rand DA (2001) Energy storage—a key technology for global energy sustainability. *J Power Sources* 100:2–17
- Frischknecht R, Jungbluth N, Althaus HJ, Doka G, Heck T, Hellweg S et al (2007) Ecoinvent v2.0: overview and methodology. Dübendorf, Switzerland: swiss Centre for Life Cycle Inventories. Technical Report No. 1 Ecoinvent
- Giner J, Swette L, Cahill K (1976) Screening of redox couples and electrode materials
- Goedkoop M, Heijungs R, Huijbregts M, Schryver AD, Struijs J, Zelm RV (2009) “ReCiPe 2008.” A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level, 1, Netherlands, 2009, 1–126
- Guinee JB (2002) Handbook on life cycle assessment operational guide to the ISO standards. *Int J Life Cycle Assess* 7:311e3
- Hiremath M, Derendorf K, Vogt T (2015) Comparative life cycle assessment of battery storage systems for stationary applications. *Environ Sci Technol* 49:4825–4833
- Ibrahim H, Ilinca A, Perron J (2008) Energy storage systems—characteristics and comparisons. *Renew Sustain Energy Rev* 12(5):1221–1250
- International Electrotechnical Commission (2012) White paper electrical energy storage. <https://www.iec.ch/whitepaper/energystorage/?ref=gs promo>
- ISO (International Organization for Standardization) 14040 standard (2006a) Environmental management—life cycle assessment—principles and framework
- ISO (International Organization for Standardization) 14044 standard (2006b) Environmental management—life cycle assessment—requirements and guidelines
- Jolliet O et al (2003) IMPACT 2002+: a new life cycle impact assessment methodology. *Int J Life Cycle Assess* 8(6):324
- Jungbluth N, Tuchschnid M, de Wild-Scholten M (2008) Life Cycle Assessment of Photovoltaics: update of ecoinvent data V2. 0. ESU-services Ltd
- Kear G, Shah AA, Walsh FC (2012) Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects. *Int J Energy Res* 36:1105–1120. <https://doi.org/10.1002/er1863>
- Li X, Zhang H, Mai Z, Zhang H, Vankelecom I (2011) Ion exchange membranes for vanadium redox flow battery (VRB) applications. *Energy Environ Sci* 4(4):1147–1160
- Liyu L, Kim S, Wang W, Vijayakumar M, Nie Z, Chen B et al (2011) A stable vanadium redox-flow battery with high energy density for large-scale energy storage. *Adv Energy Mater* 1:394e400. <http://dx.doi.org/10.1002/aenm.201100008>
- Nehrir MH, Wang C, Strunz K, Aki H, Ramakumar R, Bing J, Nehrir Z (2011) A review of hybrid renewable/alternative energy systems for electric power generation: configurations, control, and applications. *IEEE Trans Sustain Energy* 2(4):392–403
- Pehnt M (2006) Dynamic life cycle assessment (LCA) of renewable energy technologies. *Renew Energy* 31(1):55–71
- Poullikkas A (2013) A comparative overview of large-scale battery systems for electricity storage. *Renew Sustain Energy Rev* 27:778–788

- Rosenbaum RK et al (2008) USEtox—the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *Int J Life Cycle Assess* 13(7):532
- Rydh CJ (1999) Environmental assessment of vanadium redox and lead-acid batteries for stationary energy storage. *J Power Sources* 80(1–2):21–29
- Rydh CJ, Sandén BA (2005) Energy analysis of batteries in photovoltaic systems. Part I: performance and energy requirements. *Energy Convers Manage* 46(11–12):1957–1979
- Skyllas-Kazacos M, Kazacos G, Poon G, Verseema H (2010) Recent advances with UNSW vanadium-based redox flow batteries. *Int J Energy Res* 34(2):182–189
- Tang Ao et al (2012) Thermal modelling and simulation of the all-vanadium redox flow battery. *J Power Sources* 203:165–176
- Unterreiner L, Jülch V, Reith S (2016) Recycling of battery technologies—ecological impact analysis using Life Cycle Assessment (LCA). *Energy Proced* 99:229–234
- Weber AZ, Mench MM, Meyers JP, Ross PN, Gostick JT, Liu Q (2011) Redox flow batteries: a review. *J Appl Electrochem* 41(10):1137
- Jungbluth, Niels, Matthias Tuchschild, and Mariska de Wild-Scholten. "Life Cycle Assessment of Photovoltaics: update of ecoinvent data V2. 0." ESU-services Ltd (2008).
- Goedkoop, M.; Heijungs, R.; Huijbregts, M.; Schryver, A. D.; Struijs, J.; Zelm, R. V. *ReCiPe* 2008; Netherlands, 2009, 1–126
- Frischknecht R, Jungbluth N, Althaus HJ, Doka G, Heck T, Hellweg S et al. (2007) *Ecoinvent v2.0: Overview and methodology*. Dübendorf, Switzerland: Swiss Centre for Life Cycle Inventories. Technical Report Ecoinvent No. 1