VFB Maintenance Methods: Technical and Economic Issues

Nicola Poli, Giacomo Marini, Andrea Trovò[*]

Department of Industrial Engineering, University of Padua, Padova, Italy
Interdepartmental Centre Giorgio Levi Cases for Energy Economics and Technology, University of Padua, Padova, Italy

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ABSTRACT

The VFB system has been extensively studied for almost 30 years. Several plants are installed around the world, with power and energy exceeding some MW and some MWh respectively and new companies are entering the growing market. However, a real widespread application of this technology is hindered by its high capital cost. One method to make these batteries more competitive on the market is to increase their cyclability by means of appropriate maintenance procedures. Some procedures are focused on physical treatments such as the remixing of the positive electrolyte with the negative one, which causes heat generation. Other methods are focused on chemical and electrochemical regeneration procedures which make use of chemical reducing agents, catalysts or electrochemical processes. The latter requires the use of an electrolysis system in order to restore the vanadium oxidation state to the correct ratio in the positive and negative electrolyte. In the first part of this work, an extensive description of VFB technology is presented while in the second part a description of the most important and realizable maintenance procedures with their impact on the system cost is shown, considering both operative and economical points of view.

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*Corresponding Author
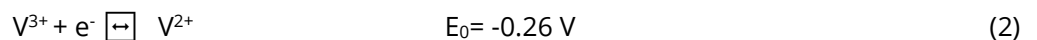Email: andrea.trovo@unipd.it
Tel: +393471621558

1. Introduction

Covering the entire global energy needs of renewable sources alone is not a simple challenge: in addition to plants that can exceed the demand for energy, it is necessary to have an electricity transmission and distribution network that is flexible and efficient. Unlike traditional power plants, energy sources such as wind, sun and other renewable sources are intermittent because they generate energy electricity according to the weather and climatic availability [1]. The variability of energy passes from the hourly time scale linked to the daily sunlight during the year, typical of photovoltaic systems, up to the minimum time scale, which is characteristic of wind generators, susceptible to rapid climatic changes. For this reason, it is essential to pay close attention to the design of electric grids, which become unstable if the power of these sources exceeds 30% of the whole generated without adequate compensatory measures, i.e. without adequate energy storage [2]. With regard to the various technologies that can be used for the storage of electrical energy, recently, Flow Batteries (FBs) have proved to be a competitive solution. These particular types of batteries use a liquid electrolyte to store electrical energy in the form of chemical energy. This conversion occurs due to redox reactions that take place inside the battery. Among the FBs, the All-Vanadium one (VFBs), presented in 1985 by the University of New South Wales (UNSW) by Skyllas-Kazacos and collaborators [3, 4], are the most promising. By using the same electrolyte for the positive and the negative side, VFBs do not present problems of cross-contamination which instead have been detected in batteries with redox pairs formed by different elements, such as: vanadium-bromine, zinc-bromine and hydrogen-bromine. The electrochemical reactions which take place inside the battery are the following [1]:

At the positive electrode:

$$VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^- \qquad E_0 = 1.00 \text{ V} \qquad\qquad (1)$$
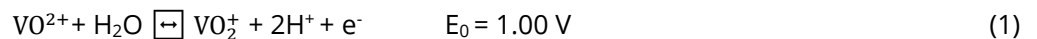
At the negative electrode:

$$V^{3+} + e^- \leftrightarrow V^{2+} \qquad\qquad E_0 = -0.26 \text{ V} \qquad\qquad (2)$$

The charge level of the battery is therefore directly connected to the percentages of V^{5+} and V^2 stored in the tanks. However, the fact that the fluid is not constantly contained in the cells, where the power is produced, ensures that the power and capacity are separated, with the consequence that virtually unlimited capacity can be obtained simply by varying the size of storage tanks. However, particular attention must be paid to the atmosphere inside the pipes and tanks: in this particular battery configuration, it is preferable that the negative and positive compartments are airtight and the electrolytes with no air inside. When this is not possible it is necessary to pump nitrogen into the negative cell, thus obtaining the removal of dissolved oxygen and blocking the diffusion of air in the compartments, preventing the oxidation of V^{2+}. The rest of the structure is composed of the central body of the battery, called the stack, formed by a series of cells. Each of them contains two electrodes and one membrane, which allow the diffusion of ions to balance the charge between the two halves cell (Figure **1**).

Instead, it is impermeable to electrons which are thus forced to flow in an external circuit supplying electric current. The voltage of the system and the relative power derive from the number of cells and their connections. Finally, there is a whole system of pipes that make the fluid flow, making it pass through the stack to load/unload it, managed by pumps and valves that regulate its flow rate [1].

1.1. Advantages and Disadvantages

VFBs present several advantages with respect to other electrochemical energy storage technologies which make them now very competitive on the market. By using the same electrolyte in both cells, the migration of ions through the membrane does not cause cross-contamination of the electrolyte. Only charge imbalances take place, but the electrolyte can be regenerated by a low-cost regeneration process. Moreover, since the kinetics of the electrochemical reactions are fast, the use of catalysts is not necessary and the reactions take place at room temperature. The system works at low pressure (under one bar) and no evolution of gas is produced when the system is not overcharged. This redox flow battery can be deeply discharged without causing damage to the components, contrary to the Lithium-ion. They have a long calendar life, which depends only on the deterioration
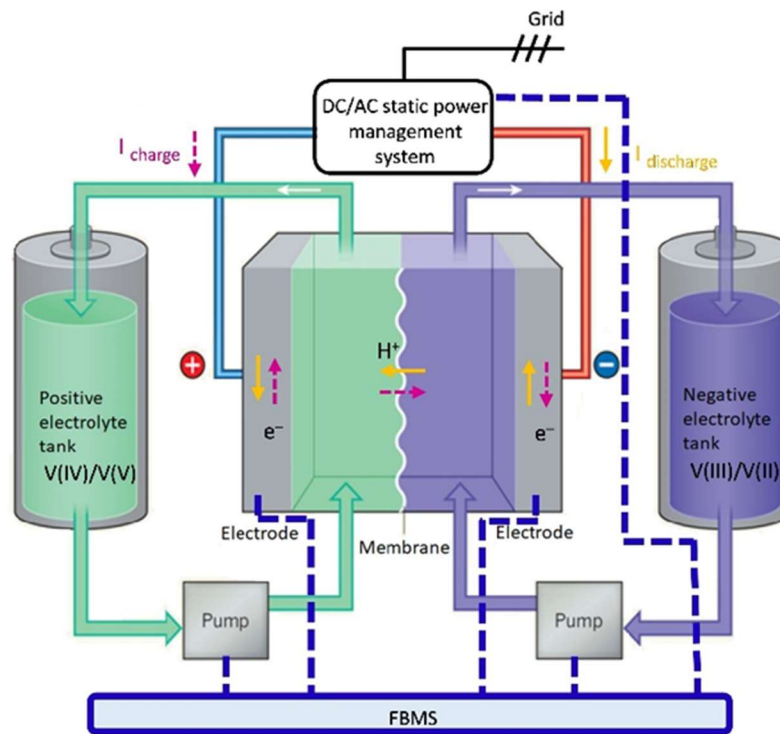
Figure 1: Schematic of the electrolyte and electron path [1].

of the membrane and the eventual replacement of this. The possibility of storing the fluid in separate tanks eliminates the problem of self-discharge. Room temperature and low pressure make VFBs a technology with high safety measures. In fact, the electrolyte, although acid, only needs a circuit consisting of pumps, plastic pipes and cheap canisters to be able to circulate [5]. As result, some interesting features of this technology that make it particularly promising are the following: scalability and flexibility, high cycle efficiency, the possibility of mechanical and electrical refills in a short time, long life, rapid response and reduction of environmental impact [6]. These elements make them ideal in applications with renewable sources. In fact, a great deal of research has been carried out for the application of VFB in these fields and there are many plants that have already been built especially in support of "wind farms". VFBs also have some disadvantages, including, as mentioned above, the low energy density which makes them not applicable in electric vehicles. Another defect to which a lot of attention must be paid, especially in the design phase, is the development of electric currents (called "shunt currents") along the flow distribution channels, which produce additional losses and affect the electrical efficiency of the system. Shunt currents can be minimized by means of a careful analysis of the design of the stack. In these fields, several efforts by many researchers have been done and are still carried out to make these batteries more competitive: increasing the energy density and efficiency of the entire system and reducing its cost are examples of these efforts [7].

1.2. Applications

Given their low energy density (compared to conventional static batteries as Li-ion), VFBs are particularly suitable for large-scale stationary energy storage, in situations where volume and weight are not limiting factors. This includes useful applications, such as: peak shaving, frequency regulation, load levelling, black start, grid support, uninterruptible power supply (UPS) and seasonal storage. For example, one of the uses as a peak shaving tool is in the context of rapid charging of electric vehicles: although the low energy density makes it impossible to install this type of battery inside cars, it could be exploited for vehicle charging at moments of maximum energy demand [8].

For load levelling and UPS, various companies exploit them in systems of multiple powers: they are essential especially in high-cost power plants where the use of large-scale energy storage systems allow to avoid annoying

problems. By switching them on and off in fact, the VFBs can be used as a buffer battery to protect the electrical grid against faults on the transmission and distribution systems, to supply electricity for the orderly shutdown of the IT systems or to switch on the backup generator, thanks to their fast response (less than a second) [9].

Ultimately, since the failure of an electrical power system during the energy production can often lead to the collapse of the grid system, a clearly costly and devastating phenomenon, the application of a VFB system that guarantees rapid stabilization and a maximum short duration overload output of several times that of the rated capacity, is able to effectively prevent serious damage to the system.

These characteristics make the VFBs attractive even for both voltage and frequency control of networks [10]. Recently the market for these batteries has been expanding considerably and there are various companies that use them for the aforementioned applications: some examples are VFB Power System, Sumitomo Electric Industries, Mitsubishi Chemicals, Premium Power, Prudent Energy, Ashlawn Energy and V-fuel. Thanks to the large capacity and long discharge time, these batteries are particularly promising in coupling with renewable energy systems [11]. The generation of energy often does not correspond to the demand for power, so it is essential to have an element that stores excess energy to release it later during periods of greatest demand. This is particularly useful in the case of wind turbines, which typically peak at night when energy demand is low. While many hydroelectric plants are able to reverse their operation and store energy through pumping, wind turbines are often found in remote locations, requiring local storage to optimize their efficiency. Energy storage is also important for buildings without an electrical grid connection, outside inhabited areas, which can use a photovoltaic, micro-hydraulic or wind system to produce electricity and store it in a battery for later consumption [12].

2. Economical Aspects

In order to make the VFBs a competitive alternative for energy storage, it is necessary to reduce the overall cost of the plant, going, as far as possible, to lower the costs of the individual components. Surely a wider market and a regularized production plan would help a lot: large-scale production of each element of the VFBs would considerably reduce the manufacturing cost, significantly affecting the final price [13]. In fact, the values that can be obtained by considering the current state of the markets and technologies applied to flow batteries are very different from those obtainable by assuming a future circumstance in which the electrochemical energy storage devices are subject to production in large quantities. Strong market competition and engineering advances generate more offers and prices fall. Unfortunately, these conditions do not exist for flow batteries nowadays and only in some countries are starting to take shape. Various studies have been carried out to try to understand what the cost-sharing was within a storage system with vanadium flow batteries. Many factors influence this kind of analysis: one of the most important are membranes, one of the key components of the stack. There are many different types with considerable price variations. To give an example, two types, currently in use in VFBs, such as the Nafion N-117 and a SPEEK membrane with the same thickness of 100 μm, have a cost of 400 € per square meter and 60 € per square meter respectively [14]. Such a price difference also brings very different prosperities. To calculate the electrolyte costs, the normal prices of sulfuric acid (0.05 € kg^{-1}) and water (1.70 € m^{-3}) are assumed, while the price of vanadium is assumed equal to 20 € kg^{-1} according to a price projection of vanadium pentoxide (V_2O_5), which is the basic substance for the production of the electrolyte. The price of V_2O_5 has been highly volatile since the 2000s, oscillating between values of 2 € kg^{-1} up to 45 € kg^{-1} [15]. It is clear that vanadium represents the most expensive item of the electrolyte [16]. Obviously, further components are necessary to connect the battery to the grid: converters sized with adequate powers, copper cables with a diameter suitable for high currents, pumps whose sizing is linearly linked to the flow rate to which the electrolyte must flow, and an entire system of pipes, which due to the acidity of the chemical elements can be made of steel, coated with PTFE, or directly in plastic material. Other aspects that should be evaluated as the costs of these batteries are the maintenance process. Maintenance processes are necessary to increase the lifetime of the battery. For VFB systems there are physical, chemical and electrochemical maintenance processes [18]. Physical processes do not require any additional devices; an example of this type is the mixing process, where the positive and the negative electrolyte are mixed together in order to counteract the effect of crossover.
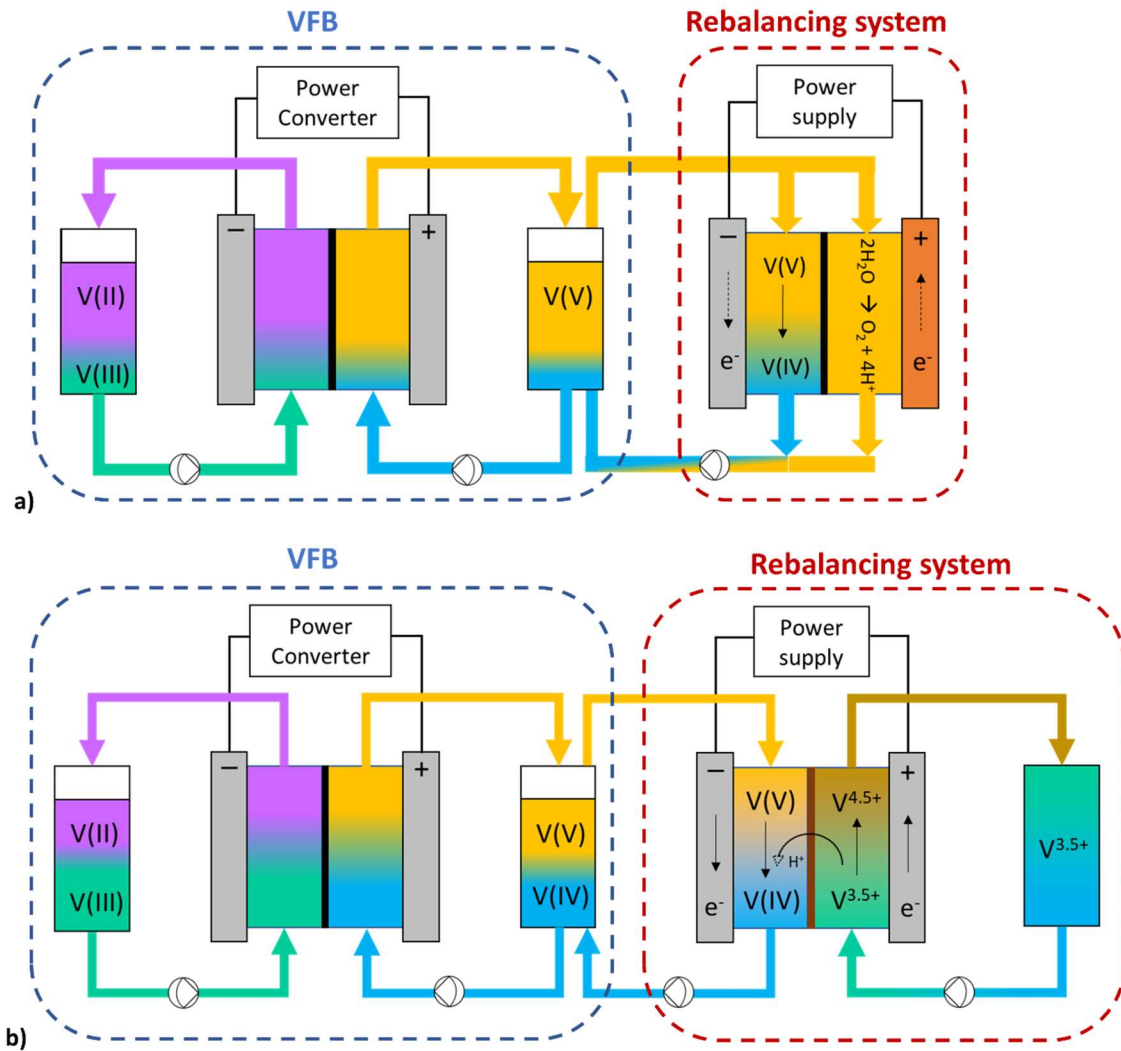
Figure 2: Electrochemical regeneration processes: a) scheme of the VFB with the Electrolysis Regeneration System (ESR); b) scheme of the VFB with the Vanadium Regeneration System cell (VSR).

Chemical and electrochemical processes are used to regenerate the electrolyte. Indeed, due to side reactions (such as hydrogen evolution or V(II) oxidation) the electrolyte result in an unbalanced state. Usually, the positive electrolyte has a state of charge higher than the negative one. For this reason, both the chemical and the electrochemical regeneration process reduce the positive electrolyte in order to re-balance the two reservoirs. To do that, they require specific materials or devices. In particular chemical processes make use of reducing agents, such as oxalic acid (OA) or ethanol (EtOH), while electrochemical processes make use of electrolysis cells [18]. In particular, in this work, two similar electrochemical regeneration systems are considered: one is called *Electrolysis Regeneration System (ERS)* (Figure **2a**) and *VFB Regeneration System (VRS)* (Figure **2b**) respectively. Both use an electrolysis cell where the electrolyte undergoes an electrochemical-reduction process, but the way in which this reduction occurs is different. The ERS process, developed at the Fraunhofer Institute of Chemical Technologies (Germany), uses an electrolysis cell similar to a VFB one: there is the same membrane and the same negative electrode, where the reduction of V(V) ions takes place. The positive electrode instead is made of titanium and iridium oxide in order to catalyze the water oxidation and close the circuit [19]. The VRS process was tested by Rudolph *et al.* [20] and later by Z. Li *et al.* [21].

The electrolysis module comprises an electrolysis cell and a third reservoir where a standard $V^{3.5+}$ electrolyte is stored. In this case, the electrolysis cell is exactly a VFB cell, where, in order to minimize the crossover from the positive half-cell to the negative one, an anion exchange membrane must be used. In order to make an economical comparison between these different regeneration processes, an important index has been used: the

Levelized Cost of Storage (LCOS) [18]. Results of the Levelized cost of storage (LCOS) for different energy to power ratios are illustrated in Figure (**3**). As it is possible observing, the LCOS decreases as the power of the system rises as well as the E/P ratio increases. Indeed, for E/P = 4h the LCOS is between 0.66 and 0.05 € kWh^{-1}, and for E/P = 10h the LCOS is between 0.33 and 0.26 kWh^{-1}. The difference between the maintenance procedures in each of the four cases is less than 0.01 € kWh^{-1}, underling a similar behaviour from an economical point of view. In Fig. 4, instead, there is a comparison of the cost structures between a residential system (Fig. 4a) with a power and energy to power ratio of P = 10 kW and E/P = 4h respectively, and an industrial system (Figure **4b**) with P = 1 MW and E/P = 10h respectively. The bar diagram above shows the most important cost voices for the VFB: capital costs (CAPEX) and operative costs (OPEX).
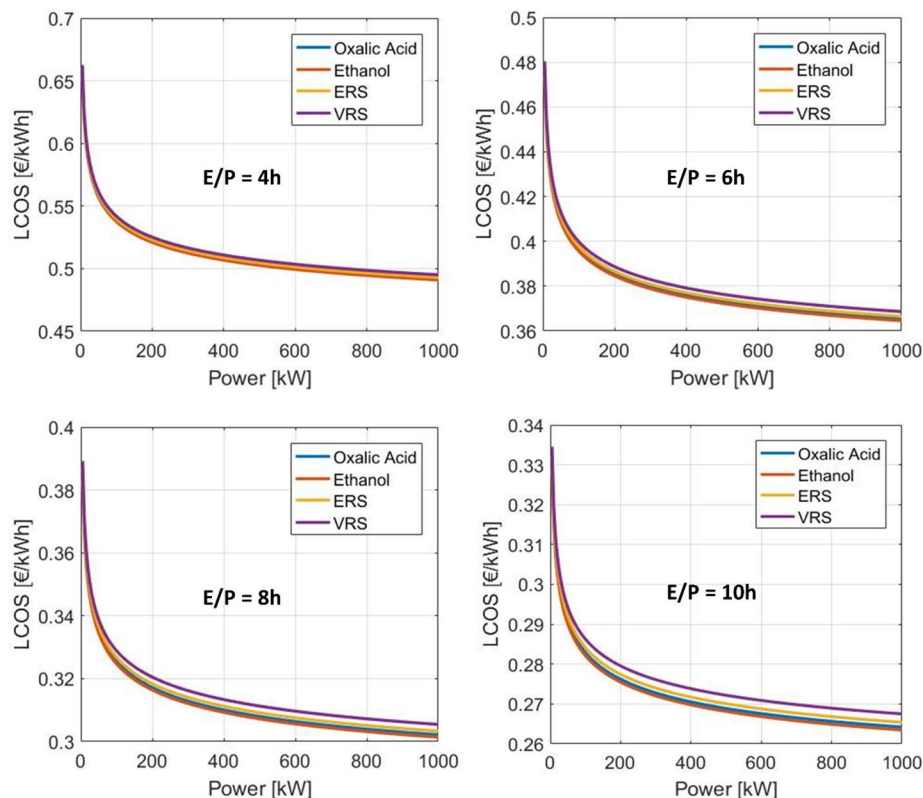

Figure 3: Levelised cost of storage for four different energy to power ratio (E/P), parametric with the regeneration system used.

The capital cost of a residential VFB system is between 1500 – 1600 € kWh^{-1}; for an industrial system is around 650 – 770 € kWh^{-1}, a bit less than half of the residential one. In the residential case, the power and plant costs are the largest expenditure item (~ 600 € kWh^{-1} and 450 € kWh^{-1} respectively); in the industrial case are the energy and power costs (~ 230 € kWh^{-1} each.). In both cases, the capital investment for the regeneration costs is very low for the chemical reducing agents (< 3 € kWh^{-1}), and more expensive for the electrochemical systems (~ 200 € kWh^{-1}). Regarding the operative costs, pumping is the largest expenditure item: around 30 € kWh^{-1} year^{-1} and 8 € kWh^{-1} year^{-1} for residential and industrial systems respectively. The difference is due to the pump efficiency (η_{pm}), which is usually higher in larger pumps. Mixing costs, which do not depend on the regeneration system used and are linearly dependent on the capacity energy, are a bit less than 2 € kWh^{-1} year^{-1}. Also, the regeneration costs are equally distributed between the two configurations, but chemical regeneration is more expensive (~ 6 € kWh^{-1} year^{-1}) than the electrochemical ones. The yearly operative cost for ERS is around 0.5 € kWh^{-1} year^{-1} and for VRS is around 2 € kWh^{-1} year^{-1}. The former is lower because the oxygen evolution reaction, which takes place in the anodic side of each ERS cell, requires a lower cell potential (= 0.23 V) than the VRS cell (1.25 V) [21]. In the pie diagrams, the cost structures for power and plant are shown, which are the costs with more components. Power costs are equally divided in both the system: flow-frames and membranes are the most expensive components in the stack. Regarding the plant cost, the battery management system and AC/DC converter are the largest investment to be taken into account.
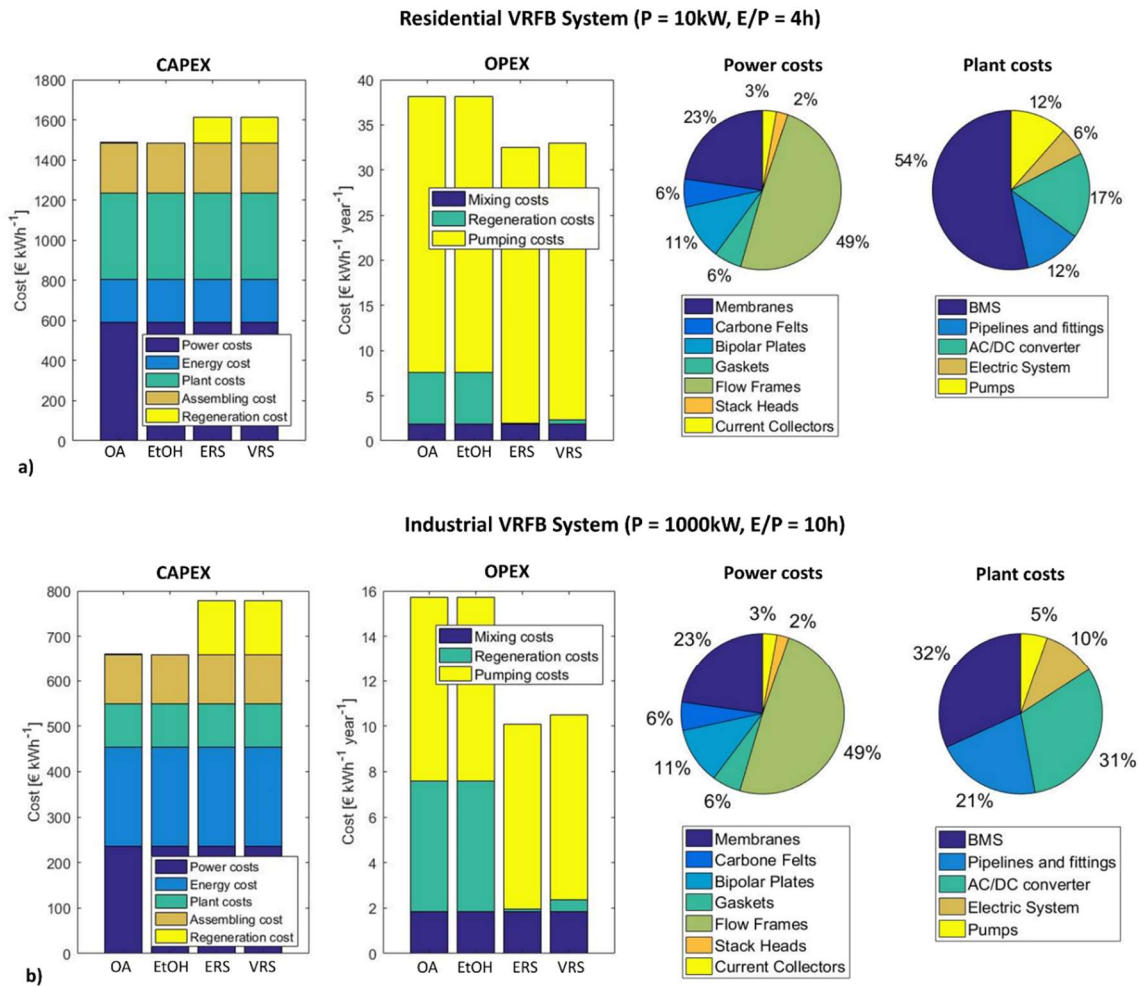
Figure 4: Comparison of cost structures regarding the capital costs (CAPEX), the operative costs (OPEX), the power and plant costs, between a residential system (a) and an industrial system (b).

3. Conclusion

In this work, a description of the VFB features including the most important and realizable maintenance procedures and their impact on the system cost is presented, considering both operative and economical points of view. In order to evaluate how the maintenance costs impact the VFB economy, specific cost indicators have been used, in particular the Levelized cost of storage (LCOS) and the net present value (NPV). This analysis shows how the LCOS of a vanadium redox flow battery decreases as the energy stored and E/P ratio increases, in the case of 20-year daily operations. For E/P = 4h the LCOS is between 0.65 and 0.5 € kWh^{-1}, and for E/P = 10h the LCOS is between 0.33 and 0.27 € kWh^{-1}, depending on the maintenance procedure adopted. Moreover, the study suggests that an industrial system is more profitable than the residential one. Indeed, a VFB system with a power P = 1MW and E/P = 10h (industrial size) has a capital investment of about 680 € kWh^{-1}, while a residential system has a capital investment of about 1500 € kWh^{-1}.

Acknowledgements

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