Performance of a Vanadium Redox flow battery for the storage of electricity produced in photovoltaic solar panels

*Rubén López-Vizcaíno^a, Esperanza Mena^a, María Millán^b, Manuel A. Rodrigo^b, and
Justo Lobato^{*,b}.*

^aDepartment of Chemical Engineering, Institute of Chemical & Environmental
Technologies, University of Castilla-La Mancha, Campus Universitario s/n, 13071
Ciudad Real, Spain

^bDepartment of Chemical Engineering, Faculty of Chemical Sciences & Technologies,
University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

***Corresponding Author**

Dr. Justo Lobato. Phone +34 902 204 100 Ext 3411; Fax: +34 902 204 130; e-mail:
justo.lobato@uclm.es

ABSTRACT

An assessment of a bench-scale vanadium redox flow battery (VRFB) undergoing an
accelerated ageing has been carried out under two operation modes: a galvanostatic-
charging mode, where a constant current density was always applied, and solar-panel
charging mode, where different current densities were applied according to the solar
radiation profiles obtained during three consecutive days in Winter, in Ciudad Real, a
town in the center of Spain. The accumulated and delivered charge capacities and the

different efficiencies were analyzed. The concentrations of different vanadium ions were also measured. Both modes allow reaching similar efficiencies and charge/discharge capacities but they do not affect in the same way to the accelerated degradation of the performance of the electrochemical cell. Moreover, the ratio power density/energy density was very comparable for the two operation modes tested in this work. These results indicate that VRFBs are suitable devices for the storage of the electricity produced in photovoltaic solar panels.

KEYWORDS

Accelerated degradation; Energy storage; Photovoltaic solar panels; Redox Flow Battery; Vanadium

1. INTRODUCTION

Nowadays, there is a huge demand of energy and, simultaneously, a very important necessity to minimize the use of fossil fuels. Over the last two centuries, population of Earth and industrial activities have grown exponentially both strongly related to each other. The electric energy demand surpass 20×10^3 TWh/year and is growing at a rate of about 3 % per year [1]. In this period, the main energy source has been fossil fuels, achieving the 66% of the total electric production [1-4]. This fact has unleashed a strong energy dependence of the society to this type of fuels and it has caused important environmental pollution problems. To overcome these problems, great efforts are being made nowadays, in order to develop clean energy not dependent of oil, gas and coal. Solar and wind energy are the most promising alternatives with a great deal of applications based on the use of photovoltaic panels and wind turbines. However, direct application

of electric energy generated in both devices is limited because of the important changes in the solar irradiation and wind speed, which are difficult to be coupled with a varying demand. Moreover, the intermittent and sometimes unpredictable production of these types of green energies limit their use in application which need a continuous electric energy supply. This issue could be solved with energy storage devices which are able to storage the electric surplus production of renewable energy [5-7].

Regarding this, numerous researchers have focused their works in the development and study of the different energy storage systems such as: Pumped hydroelectricity energy storage, compressed air energy storage, thermal energy storage, flywheel energy storage, superconducting magnetic energy storage, super-capacitors, and electrochemical energy storage [1, 6].

One of the most promising electrochemical energy storage systems are the Redox Flow Batteries (RFBs) [3, 8-11]. RFBs are composed of an electrochemical cell and two electrolyte tanks, used for anolyte and catholyte storage. Electrochemical cell allows changing chemical energy into electric energy and vice versa by the oxidation/reduction reactions of electroactive species employed. These species are the authentic energy storage systems. Currently, different kinds of RFBs exist, depending on the composition of electrolyte: iron/chromium [12-14], iron/cadmium [15], quinone/bromide [16], vanadium/bromine [17] and all vanadium [18, 19], among others. The All Vanadium Batteries (VRFBs) have taken great interest because of advantages related to use the same active electrochemical metal in both electrolytes, mainly, reduction of efficient losses due to contamination of membrane, electrodes and electrolytes, which are produced by crossover of species between electrolyte compartments of electrochemical cell. The electrolytes employed in this battery are V^{2+}/V^{3+} into negative electrolyte compartment and V^{4+}/V^{5+} (VO^{2+}/VO_2^{+}) in the positive one. The electrochemical half-cell reactions

involved in the charge battery are the following equation 1 and 2 (discharge process presents the reverse reactions):

The standard OCV at 25°C is $E^0=1.26\text{V}$, but in real cells could achieve 1.5 V totally charged because the operation conditions are different to standard ones and it is in agreement with the values achieved by other authors [20]. The most relevant results obtained in the development of VRFB were achieved by Skyllas-Kazacos's group [19, 21], obtaining patent in 1986 (AU Patent 575247—1986). In addition, many researches have been focused on optimization of all components that composed of VRFB (membrane [22-25], electrodes [26-28], bipolar plates [29-32] electrolyte supply [33, 34], among others), however few works have been carried out according to the direct coupled between photovoltaic panel and VRFBs [35-37].

On the other hand, the loss of efficiency of RFB during their lifetime is one of the major handicaps for the full-scale application of this technology and this makes necessary to conduct accelerated ageing tests, because it is not practical to spend several months in trying to determine whether or not a RFB material will fail similarly as compared with another. In trying to obtain an accelerated ageing procedure, different strategies can be applied trying to degenerate rapidly electrodes, membranes or current collectors. Typically, there is not only one factor in the degeneration of the RFB but the confluence of several, as it is pointed out in the literature [38], in which it is stated that overlaid changes in the cathode's TPB (triple phase boundary) and in the special conditions between the two electrodes and membranes are the key responsible of the ageing. As the

ageing in real conditions would take several months of operation and we only aimed to observe how the green energy powering can affect the performance of RFB, in the design of the tests we decided to use a membrane with a low performance in order to simulate this ageing, whose choice was based on previous studies carried out in our laboratories. Significance of the membrane degradation in the performance of RFB has been pointed out in recent works [39] in which over the life-tests no chemical changes in the membrane were observed but mechanical and thermal aging of the membrane which lead to the formation of a film at the membrane-solution interface, explaining a high influence on the ageing.

For this reason, the authors of this work intend to increase the knowledge about this topic. In this context, the objective of the present work is to compare the performance of a VRFB undergoing an accelerated degradation, during several charge/discharge cycles in which the charging process was made according to a current pattern produced by photovoltaic solar panels, with the performance of the same VRFB, in tests where it was followed a more conventional galvanostatic-charging procedure. The accelerated ageing was obtained by using a membrane that underwent a rapid degradation under the operation conditions reached.

2. MATERIALS AND METHODS

In this section, analytical techniques, experimental setup and experimental procedure carried out in this work are described.

2.1 Experimental Setup

A scheme of experimental setup is shown in Figure 1.

Figure 1. Pictures of the experimental setup.

Electricity produced by two photovoltaic panels connected in series (each panel with a power of 150 W, each one with an area of 1.313 m², they were supplied by ATERSA S.A.) was monitored with an in-house made computer software made with Labview (National Instruments). More information about this device can be found elsewhere [40, 41].

The bench-scale RFB device used in this work has been supplied by Baltic Fuel Cells and it is composed of two differentiated modules: a quick connect fixture (qCf-RFB) that is a system especially designed for testing of RFB and a commercial cell (cF40-RFB).

qCf-RFB is a device that allows the compression of the internal components of the cF40-RFB using a centric clamping vise. The fore of the vise is directly applied to the active area, enabling fully reproducible test conditions. In addition, qCf-RFB provides a temperature regulation by pumping of a thermal fluid (Huber P20.275.50) located in external thermostatic bath (Huber). Cell cF40-RFB is a commercial single electrochemical cell with an active area of 40 cm^2 ($w = 52 \text{ mm}$, $h = 77 \text{ mm}$). Only graphite and plastic materials are exposed to the electrolyte. Moreover, the electrodes were compressed to 50 % from its initial thickness (12 mm initial thickness each electrode) and graphite plates were not mechanized.

A commercial vanadium electrolyte was used in this work (Golden Energy Fuel Cell., Ltd, China). It had a 2 M vanadium concentration (VO^{2+} in the positive electrolyte and V^{3+} in the negative electrolyte) in 3 M H_2SO_4 . A peristaltic pump (maximum flow rate 50 ml/min, Heidolph Pumpdrive 5001) was used to deliver the electrolyte to the RFB cell at a constant flow rate (20 ml/min). The negative electrode tank reservoir (containing V^{2+} , which is an instable specie, and V^{3+}) was purged with a nitrogen stream to avoid the oxidation of the V^{2+} due to presence of oxygen during the charge and discharge experiments.

Carbon soft felt electrodes were used as cathode and anode, provided by SGL Group, and a cationic exchange membrane (STERION L-180) was used to separate the compartments. This membrane is a Nafion-like membrane, with a thickness of $175 \text{ }\mu\text{m}$ and a weight per unit of area of 360 g m^{-2} . Previously to be used in the cell, the electrodes

were washed with boiling NaOH 1 M and, after that, with Milli-Q water until neutral pH in order to increase the hydrophilicity of the material [42]. As it is going to be explained in the text, this membrane undergoes a rapid degradation during the tests, reflected on an increase in the vanadium species permeability. This allows us to evaluate with a short test, the effects of a rapid ageing of the system, because the influence of the harsh conditions reached in the VRFB on the cell materials are known to be the main weakness of the technology.

2.2 Chemical and Electrochemical Characterization Techniques

Total vanadium concentration was measured off-line using an inductively coupled plasma spectrometer, Liberty Sequential from Varian. In order to evaluate the total metal concentration, samples were diluted to 50:50, v/v using 4 N HNO₃ so as to ensure the total solubility of the metal. Vanadium ion concentrations used as reactive in charge VRFB process (VO²⁺, positive electrode and V³⁺, negative electrode) were measured employing an UV-visible spectrometer, Cary 300 from Agilent. The characteristic absorbance peaks analyzed were at 767 nm for VO²⁺ (blue) and at 406 nm for V³⁺ (green).

Electrochemical parameters were controlled and monitored using an Autolab PGSTAT302N (Metrohm) potentiostat controlled by the NOVA 1.11 program. Charge and discharge procedures were programmed using the chrono potentiometry method. Patterns obtained from the solar radiation variation were used to calculate a proportional current profile that was applied for the charge of the VRFB using the potentiostat. In this way, the temporal variation in the OCV and voltage values were monitored during the application of the corresponding value of current density.

3. RESULTS AND DISCUSSION

As stated before, this work aims at studying the differences found in the performance of a VRFB charged under galvanostatic conditions and with solar panels, during accelerated ageing tests, attained with the use of highly degradable membranes in the VRFB device.

In order to do this, solar radiation was monitored for three consecutive days (25th to 27th January of 2016) in Winter in Ciudad Real, Spain (38.59 N 3.55 O). The time-course of the solar radiation measured over this period is shown in Figure 2. The first and second days correspond to very sunny winter days, for which the maximum solar radiation achieved was 560 W m⁻². The third day was a typical foggy day with a much lower irradiation of only 295 W m⁻². Variability of weather conditions is very high but this profile can be considered as representative of typical conditions in south Spain, so it was used in this work as a typical cycle pattern of solar irradiation to evaluate the charge of the VRFB.

Figure 2. Solar radiation profile in Ciudad Real, Spain during three different days (25th to 27th January).

To compare the response of the VRFB under the intermittent energy supply of the solar panels, two different charge modes were compared. The first one is a conventional galvanostatic charging procedure, and consisted of the application of a constant current density (6.25 mA cm^{-2} corresponding to 0.25 A). The second procedure aims to simulate a direct charge from photovoltaic energy (solar panels-charging procedure). That means that the application of current was not constant and varied according to the profiles of the renewable energy source shown in Figure 2. Thus, the solar radiation profiles, shown in Figure 2, were beard in mind, and the maximum values were applied during the noon, and the minimum ones correspond with the night hours. The total charge ($Q_{\text{charge}} = 11.64 \text{ Ah}$) supplied to the system was in both cases (using a constant current and using the solar radiation profile) the same, in order to attain comparable both operating modes. Hence, differences are expected to depend only the on charging mode. Taking all this into

account, Figure 3 shows the applied current profiles versus time in the charge/discharge cycles, during the three days of the experiment carried out for each operating mode. That is, using a constant current (in the galvanostatic mode) and using a variable current density according to the solar profile of Figure 2 and supplied by the potentiostat in order to reach the same total charge that in the galvanostatic mode. The current applied to the RFB (Figure 2) was smaller than the current obtained from the solar panel due to the mechanical cell limitations. If the voltage exceed 2 V the graphite bipolar plates could be damaged and the electrodes could corrode. Then, taking into account the cell resistance the current had to be adjusted to keep the materials in safe conditions.

With the aim of getting comparable and reproducible cycles, the charge step was finished when an abrupt increase in the value of cell voltage was reached, corresponding with OCV around 1.57-1.59 V. On the other hand, the discharge step was finished when the OCV decreased down to 1.36-1.38 V. These OCV criteria are typically processed in the literature to obtain a first estimation of state of charge (SOC) in vanadium redox flow batteries [43, 44]. However, the relation between SOC and OCV is not constant and depends on the type of the battery [45, 46]. For this reason, is necessary determine the real SOC to improve the knowledge of the behavior of these setups (see Table 2).

Figure 3. Electric current profiles during the three charge/discharge cycles. Solid line: Solar radiation charging mode; Dashed line: galvanostatic charging mode. $Q_{\text{charge}} = 11.64$ Ah.

The effect of the type of energy supply used for the charging step, was assessed on a bench-scale VRFB, in which 200 mL of 2 M V^{3+}/V^{4+} in 3 M sulfuric acid was used at constant volumetric flow rate of 20 mL/min and constant temperature 30 °C. Figure 4 shows the variation in the cell voltage and OCV during the three cycles of charge/discharge in the three days of the experiment for both operation modes. As it can be observed, in the charge stage, as the SOC of the battery increases, OCV and voltage of the cell also increase. In a similar way, during the discharge stage, a decrease in the values of these parameters is observed as the SOC of the battery decreases.

As expected, by applying the galvanostatic charging mode (this means applying a constant current), the typical charge-discharge curves are obtained. Meanwhile, in the case of the solar panels-charging mode (applying the current pattern obtained from the solar panels) the charge curves are quite different and different cell voltage peaks can be observed. These changes were expected, because the applied current was not constant and changed according the solar irradiation profiles. On the contrary, in the case of the discharge curves, both tests showed the same trends because the same constant current density was applied (-6.25 mA cm^{-2}) in this step.

On the other hand, as 2 mol dm^{-3} need to be transferred across the cell in order to complete the formation of V^{4+} in the positive reservoir and the volume of electrolyte is 0.2 dm^{-3} in our system, the total number of mol transferred in our system is 4 mol of electrons ($0.2 \text{ dm}^3 \times 2 \text{ mol dm}^{-3}$). Since 1 mol of electrons is equivalent to 26.8 Ah, hence 10.72 Ah ($26.8 \text{ Ah mol}^{-1} \times 0.4 \text{ mol} = 10.72 \text{ Ah}$) are expected to be required. Assuming that the cell is charged at a constant current of 0.25 A, the formation charge is expected to be completed in approximately 43 h ($10.72 \text{ Ah} \div 0.25 \text{ A} = 43 \text{ h}$). If we observed the experimental values for both modes, it can be seen that for the galvanostic-charging mode, the charge time required was 47 h, which represents a difference of only 9.3 % with respect to the expected value. In the case of the solar panel-charging mode (where non-constant current was applied), the charge time was 48 h, which is only 11.6 % above the theoretical value. In comparing these results with other found in the literature, these difference can be considered as low. For example, Mohamed et al [47] reached values of 4.5 % when a direct constant current of 80 mA cm^{-2} was applied while they reached 23.7 % at 20 mA cm^{-2} .

Figure 4. Charge/discharge response of VRFB. (A) Galvanostatic-charging procedure ($I = 0.25 \text{ A}$) and (B) Simulating solar panel-charging procedure (see current profile of Figure 3). Solid line: Cell voltage; Dashed line: OCV. $Q_{\text{charge}} = 11.64 \text{ Ah}$. $T = 30 \text{ }^{\circ}\text{C}$.

One interesting feature that can be drawn from Figure 4 is that the duration of charge-discharge cycles is shortened in both operation modes from cycle to cycle, as expected

because of the accelerated ageing caused by the membrane selected STERION L180 (values shown in Table 1). Thus, it decreased from 66 h in the first cycle (47 h charging and 19 of discharging) down to 21 h in the third cycle (15 h charging and 6 h discharging). A similar behavior was obtained in the other solar panel-charging mode, decreasing from 64 h in the first cycle (47 h charging, 17 h discharging) down to 26 h in the third cycle (14 h charging, 12 h discharging).

Table 1. Duration (h) of charge/discharge cycles under the both different operation modes

Mode	Cycle 1		Cycle 2		Cycle 3	
	Charge	Discharge	Charge	Discharge	Charge	Discharge
Galv.	47	19	27	13	15	6
I= constant						
Solar	47	17	27	14	14	12
I ≠constant						

To understand this important degradation of the performance of the VRFB, permeability of the membrane was measured before use and after their use in the three cycles. Permeability to V^{3+} in pure solutions rose from $1.77 \cdot 10^{-5}$ up to $6.27 \cdot 10^{-5} \text{ cm}^2 \text{ h}^{-1}$, while permeability to V^{4+} increased from $1.40 \cdot 10^{-4}$ up to $2.71 \cdot 10^{-4} \text{ cm}^2 \text{ h}^{-1}$. These values are high enough to explain the accelerated ageing of the membranes and supports the important effects of the electrolyte on the degradation of the membrane of the VRFB and hence in the degradation of its performance, because it favors the crossover of vanadium species to the other VRFB compartment.

Figure 5 compares the accumulated and the delivered charges during the charge-discharge cycles carried out in the two different operation modes. It can be clearly seen how the accumulated and delivered charges decrease with the number of cycles, regardless of the operation mode, consequence, as explained before, of the higher crossover of species associated to the higher permeability, in turn caused by the accelerated degradation of the membrane. In comparing the values reached with both operation modes, it can be pointed out that the VRFB operated with the solar panel-charging procedure seems to have a less important degradation.

Hence, after some time, the concentrations of the V^{5+} and V^{2+} ions are expected to decrease due to the permeation of vanadium through the membrane. The diffusion of V^{2+} and V^{3+} from the negative-half cell can lead to the self-discharge reactions shown in eqs. 3 to 5, in the positive-half cell [48].

Similarly, V^{4+} and V^{5+} ions from the positive side can react with the active species in the negative half-cell as [48] according to eqs. 6 to 8.

Figure 5. Accumulated and delivered charge capacity over the three cycles under the different operation modes. White bars: galvanostatic-charging procedure ($I = 0.25$ A); Black bars: simulating solar panel-charging procedure (see current profile of Figure 3).

In order to check this hypothesis, the variation of total vanadium concentration and the electrolyte volume in the reservoir tanks were monitored. Thus, Figure 6 shows the electrolyte volume values at different times for the both operation mode and the variation of total vanadium ions in each half cell, normalized to the initial value, at time 0 h.

It can be observed that a decrease of the electrolyte volume and vanadium ions occurs during the tests carried out under the both operation modes. This decrease is similar in both half-cell, regardless, as well, of the operation mode. A similar decrease of both volume of electrolyte and vanadium concentration has been also observed by Jiang et al [25] using different types of Nafion membranes. During the charge/discharge cycling, the transfer rate of V^{2+} and V^{3+} are higher than those of VO^{2+} and VO_2^+ , thus bring the net

transfer of vanadium ions from the negative to positive half-cell [49]. This effect is easily observed when the battery was charged using a constant current (galvanostatic mode). It seems that when a variable current is applied (solar profile charging procedure) the loss of both volume of electrolyte and vanadium concentration is lower comparing with the other operation mode tested in this work. Taking into account that the same thicker Nafion-like membrane was used in both operation modes and the imbalance of vanadium ions is caused primarily by the crossover of the vanadium species through the membrane [50] it seems that the charged of a VRFB simulating the solar profile (renewable source) leads a lower deterioration of the Nafion-like membrane. Once the essay finished (three charge/discharge cycles), the battery was disassembled and it was noticed that the carbon felt electrodes behaved like sponges and they appeared soaked of electrolyte. This fact could also explain the high loss of volume during the first cycle, because during this cycle the electrodes are dry and have the maximum absorption capacity.

Figure 6. Evolution of (A) electrolyte volume in the reservoir tanks and (B) normalized total vanadium concentration during the charge/discharge cycles of the VRFB. Filled markers: positive half-cell; Unfilled markers: negative half-cell. Solid line: galvanostatic-

charging procedure ($I = 0.25 \text{ A}$); Dashed line: simulating solar panel-charging procedure (see current profile of Figure 3).

In order to get more information about the processes that occurred in each half-cell, the main species in each compartment of the battery were analyzed by UV-visible. Figure 7 shows the evolution with time of VO^{2+} and V^{3+} ions, in the positive half-cell compartment and negative one, respectively.

As it was expected, there was a decrease of species during the charge stages and an increase during the discharge one, because the V^{4+} and V^{3+} ions are the reactive species during the charge and they are the product species during the discharge (see eqs. 1 and 2). This trend was observed in both operation modes. In the positive half-cell, the oxidation rate of the V^{4+} ions during the first cycle is lower when the cell is operating under a constant current density (galvanostatic-charging mode) than when it is operating under the solar radiation profile (solar panels-charging mode). However, during the discharge of this first cycle, the amount of V^{4+} ions is higher in the case of the galvanostatic-charging mode. In the following cycles, the amount of V^{4+} ions is similar for both operation modes. In the case of the negative half-cell, there are no significant differences in the values of V^{3+} ions for both operation modes.

A decrease of the amount of V^{4+} and V^{3+} in the positive and negative compartment, respectively, is achieved as the cycles going on. This behavior could explain why the time required in the charge/discharge cycles decreases with time, as it was observed in Figure 5. In turn, this decrease can be explained in terms of the higher crossover associated to the degradation of the membrane.

From the data show in Figure 7, SOC values according to the equations 9 and 10 were calculated [51].

$$\text{Negative electrolyte SOC} = \frac{cV^{2+}}{cV^{2+}+cV^{3+}} \quad (9)$$

$$\text{Positive electrolyte SOC} = \frac{cV^{5+}}{cV^{4+}+cV^{5+}} \quad (10)$$

As it can be seen, the SOC values depend on the concentration of the ions involved in the reaction of each compartment (cV^{2+} , cV^{3+} , cV^{4+} and cV^{5+} are the concentration of the different vanadium ions, V^{2+} , V^{3+} , V^{4+} and V^{5+} respectively) . Thus, a SOC value of 1 means that the battery is full charged, and values around 0 mean that is totally discharged. The obtained values are shown in Table 2.

Table 2. SOC values obtained from data of Figure 7 and equations 9 and 10.

	Positive compartment		Negative compartment	
	Galvanostatic-charging mode	Solar panel charging mode	Galvanostatic-charging mode	Solar panel charging mode
1 st Charge	0.977	0.782	1.000	1.000
1 st Discharge	0.007	0.191	0.093	0.215
2 nd Charge	0.991	0.939	0.749	0.959
2 nd Discharge	0.044	0.224	0.094	0.202
3 rd Charge	0.770	0.991	0.640	0.731
3 rd Discharge	0.441	0.323	0.308	0.183

These values (shown in Table 2) indicate that the charge was not complete in the second and third cycle. This fact could explain the lower values of Q (Ah) observed in Figure 5 during those cycles. The SOC values of the second and third cycle of the solar panel-charging mode are higher than the ones for the galvanostatic-charging mode, which would explain also the higher values of charge reached during the second and third cycles for

the VRFB when it was operating under the solar profile charging mode which simulates that the battery was coupled with the renewable energy supply (see Figure 5). Thus, it seems that the solar radiation profiles (i.e. when not a constant current is supplied) produce higher values of V^{5+} ions and lead to higher values of SOC in the positive compartment.

On the other hand, it is known that the corresponding loss in capacity with cycle number is a function of the charge and discharge current and the relative magnitude of the mass transfer coefficients of the four vanadium ions [52]. Taking into account that the same discharge current was applied to the both modes studied in this work. Since in the operating mode simulating the solar profile charge i.e the current applied was non constant, it is clear that this parameter has a great influence on the stability of the battery. It is also known that the net transfer of vanadium is caused by the concentration difference of the vanadium species between the positive and negative half cells [49] and the transfer of vanadium ions with the bound water affects the transfer of water across the two half cells [53]. Thus, as it has been observed in Figures 6 and 7, that the concentration of vanadium ions is different according to the operation mode. So, it is clear that the vanadium ion crossover will be also different and dependent on the charge procedure.

Figure 7. Evolution of total amount of (A) V^{4+} in the positive half-cell and (B) V^{3+} in the negative half-cell during the charge/discharge cycles of the VRFB. Solid line: galvanostatic-charging procedure ($I = 0.25$ A); Dashed line: simulating solar panel-charging procedure (see current profile of Figure 3).

Table 3 shows the different efficiencies (coulombic, voltage and energy efficiencies) obtained by the VRFB in the two tests carried out, calculated according to equations shown elsewhere in the literature [43]. The values are not very high, but comparable with the efficiencies obtained in other works. Thus, Leung et al.,[54] reached coulombic efficiencies of 55 % and energy efficiencies ($\eta_E = \eta_C \times \eta_V$) of 46 % using a Nafion CEM, whereas Watt-Smith et al. [43] showed voltage and energy efficiencies around 60 %. Furthermore, the efficiencies reached in the solar panel-charging mode were similar to the values obtained under the galvanostatic-charging mode, clearly pointing out that charging vanadium redox-flow batteries with photovoltaic systems does not exhibit drawbacks as compared to the typical galvanostatic charging procedure. In turn, the system charged with not constant current, that is, simulating the renewable source, seems to be even more robust, according to the results of the accelerated ageing tested in this work.

Table 3. Efficiencies obtained during the different essays, Coulombic efficiency (η_C); Voltage efficiency (η_V) and Energy efficiency (η_E).

Cycle	Operation Mode					
	Galvanostatic-charging mode			Solar panel-charging mode		
	η_C	η_V	η_E	η_C	η_V	η_E
1 st	40.7	94.8	38.6	34.9	90.8	31.7
2 nd	48.8	85.8	41.9	42.5	73.0	31.0
3 rd	38.9	81.0	31.5	49.6	82.2	40.8

Figure 8 shows the Ragone plots obtained for the battery for both operation modes. These data are obtained taking into account the average voltage and the charge delivered in the discharge stages and the mass of active specie (vanadium) contained in the electrolyte. It must be highlighted that the operation mode does not influence on the power/energy ratio because similar values were reached in both modes. Moreover, the obtained values were close to the typical and expected values for the flow battery. In this work, power density values around 1 W kg^{-1} were reached which are comparable with the reported by Nguyen and Savinell (2010) for these systems (power density ranges from 5 to 30 W kg^{-1} [55] specific energy density values around 20 W h kg^{-1} were obtained in our study which are in agreement with the range published for this kind of system ($15\text{-}25 \text{ Wh kg}^{-1}$ for $1.5\text{-}2 \text{ M}$ vanadium/sulphate in both half cells [21]).

Figure 8. Ragone plots. (■) Direct photovoltaic solar panel-charging procedure; (▲) Galvanostatic-charging procedure.

Although results presented in this work are preliminary, vanadium redox flow batteries have several advantages comparing with the well-known and commercialized Li-ion systems. In this way, the efficiency of the demo developed VRFB is lower than the Li-ion batteries (65-70% and 90-94%, respectively), but the demonstrated reliability of the

technologies is considerably higher in the case of the vanadium redox systems (>10000 again 4500 cycles). In the same way, higher capacities derived from higher discharge times have been obtained for the VRFB (4-40 MW h) comparing with the Li-ion batteries (4-24 MW h) [56]. To be closer to a real application of this technology, a battery system management and a scale up of the battery (stack of cells) would be required in order to manage in a better way the solar energy storage and to be able to connect it to an application device.

4. CONCLUSION

An assessment of a VRFB undergoing an accelerated ageing has been carried out under two operation modes and results obtained allows to concluded that there are some relevant differences between charging the VRFB in galvanostatic mode (j is constant) or with variable current powered according to a typical solar irradiation profile (j is not constant).

The values of SOC (calculated from the vanadium ion concentration measurements) indicate that the stability of the battery charged with non-constant current (i.e. simulation solar-panel charging mode) was higher than the one charged in galvanostatic mode (j is constant). Thus, the charge/discharge capacities were higher in the case of the application of a non-constant current during the charge of the battery. Furthermore, the operation of the RFB simulating solar panel charging procedure leads to a lower vanadium species crossover effect which means a lower deterioration of the membrane and could explain its higher stability.

On the other hand, the energy efficiency (η_E) of the battery when it was working under non-constant current was lower than when it was working under constant current, at the end of the third cycle, the (η_E) was close to 41 % when the solar profile was simulated

(non constant current) and only 31.5 % when the battery was working under galvanostatic mode.

Thus, the obtained results support the claim that the vanadium redox flow batteries are suitable as energy storage systems for solar renewable energy. Further work is required to translate the promising results achieved in the laboratory to a full-size battery such as long term tests (more days and more charge/discharge cycles) and check the influence of other solar energy profiles.

Acknowledgments

The authors acknowledge funding support from the Spanish Government through the MINECO Projects CTM2013-45612-R and CTM2016-76197-R (AEI/FEDER, UE) and CYTEMA E2TP Program of the University of Castilla- La Mancha.

REFERENCES

- [1] P. Alotto, M. Guarnieri, F. Moro, Redox flow batteries for the storage of renewable energy: A review, *Renewable Sustainable Energy Rev* 29 (2014) 325-335.
- [2] Z. Yang, J. Zhang, M.C.W. Kintner-Meyer, X. Lu, D. Choi, J.P. Lemmon, J. Liu, Electrochemical energy storage for green grid, *Chem. Rev.* 111(5) (2011) 3577-3613.
- [3] A.Z. Weber, M.M. Mench, J.P. Meyers, P.N. Ross, J.T. Gostick, Q. Liu, Redox flow batteries: A review, *J Appl Electrochem* 41(10) (2011) 1137-1164.
- [4] C.A. Powell, B.D. Morreale, Materials challenges in advanced coal conversion technologies, *MRS Bulletin* 33(4) (2008) 309-315.
- [5] B.S. Lee, D.E. Gushee, Electricity storage: The Achilles' heel of renewable energy, *Chemical Engineering Progress* 104(3) (2008) S29-S32.
- [6] H. Chen, T.N. Cong, W. Yang, C. Tan, Y. Li, Y. Ding, Progress in electrical energy storage system: A critical review, *Progress in Natural Science* 19(3) (2009) 291-312.
- [7] G.L. Soloveichik, Battery technologies for large-scale stationary energy storage, *Annu. Rev. Chem. Biomol. Eng.* 2 (2011) 503-527.
- [8] C. Ponce de León, A. Frías-Ferrer, J. González-García, D.A. Szánto, F.C. Walsh, Redox flow cells for energy conversion, *J Power Sources* 160(1) (2006) 716-732.

- [9] Z. Huamin, Z. Yu, L. Zonghao, W. Xiaoli, Redox flow battery technology, *Progr. Chem.* 21(11) (2009) 2333-2340.
- [10] T. Shigematsu, Redox flow battery for energy storage, *SEI Tech Rev* (73) (2011) 4-13.
- [11] S. Bebelis, K. Bouzek, A. Cornell, M.G.S. Ferreira, G.H. Kelsall, F. Lapicque, C.P. de Leon, M.A. Rodrigo, F.C. Walsh, Highlights during the development of electrochemical engineering, *Chemical Engineering Research & Design* 91(10) (2013) 1998-2020.
- [12] G. Codina, A. Aldaz, Scale-up studies of an Fe/Cr redox flow battery based on shunt current analysis, *J Appl Electrochem* 22(7) (1992) 668-674.
- [13] G. Codina, J.R. Perez, M. Lopez-Atalaya, J.L. Vasquez, A. Aldaz, Development of a 0.1 kW power accumulation pilot plant based on an Fe/Cr redox flow battery Part I. Considerations on flow-distribution design, *J Power Sources* 48(3) (1994) 293-302.
- [14] M. Lopez-Atalaya, G. Codina, J.R. Perez, J.L. Vasquez, A. Aldaz, Optimization studies on a Fe/Cr redox flow battery, *J Power Sources* 39(2) (1992) 147-154.
- [15] J. Cheng, H.M. Zhang, Y.H. Wen, G.P. Cao, Y.S. Yang, Study on a Cd-Fe redox flow battery in a sulphuric acid electrolyte, 2011 International Conference on Chemical, Material and Metallurgical Engineering, ICCMME 2011, Beihai, 2012, pp. 1519-1523.
- [16] Q. Chen, L. Eisenach, M.J. Aziz, Cycling analysis of a quinone-bromide redox flow battery, *J Electrochem Soc* 163(1) (2016) A5057-A5063.
- [17] H. Vafiadis, M. Skyllas-Kazacos, Evaluation of membranes for the novel vanadium bromine redox flow cell, *Journal of Membrane Science* 279(1-2) (2006) 394-402.
- [18] Annual Review Journal of the Institute of Materials Engineering Australia LTD, *Mater Forum* 32 (2007).
- [19] M. Skyllas-Kazacos, Vanadium redox flow batteries, *Encyclopedia of Electrochemical Power Sources* (2009) 444-453.
- [20] M.H. Chakrabarti, S.A. Hajimolana, F.S. Mjalli, M. Saleem, I. Mustafa, Redox Flow Battery for Energy Storage, *Arabian Journal for Science and Engineering* 38(4) (2013) 723-739.
- [21] M. Skyllas-Kazacos, G. Kazacos, G. Poon, H. Verseema, Recent advances with UNSW vanadium-based redox flow batteries, *Int. J. Energy Res.* 34(2) (2010) 182-189.
- [22] E. Agar, K.W. Knehr, D. Chen, M.A. Hickner, E.C. Kumbur, Species transport mechanisms governing capacity loss in vanadium flow batteries: Comparing Nafion® and sulfonated Radel membranes, *Electrochim Acta* 98 (2013) 66-74.
- [23] Y. Baek, N.S. Kwak, T.S. Hwang, Synthesis and characterization of vinylbenzyl chloride-co-styrene-co- hydroxyethyl acrylate (VBC-co-St-co-HEA) Anion-exchange membrane for all-vanadium redox flow battery, *Polymer Korea* 35(6) (2011) 586-592.
- [24] L. Cao, L. Kong, L. Kong, X. Zhang, H. Shi, Novel sulfonated polyimide/zwitterionic polymer-functionalized graphene oxide hybrid membranes for vanadium redox flow battery, *J Power Sources* 299 (2015) 255-264.
- [25] B. Jiang, L. Wu, L. Yu, X. Qiu, J. Xi, A comparative study of Nafion series membranes for vanadium redox flow batteries, *Journal of Membrane Science* 510 (2016) 18-26.
- [26] J.Z. Chen, W.Y. Liao, W.Y. Hsieh, C.C. Hsu, Y.S. Chen, All-vanadium redox flow batteries with graphite felt electrodes treated by atmospheric pressure plasma jets, *J Power Sources* 274 (2015) 894-898.
- [27] A. Di Blasi, N. Briguglio, O. Di Blasi, V. Antonucci, Charge-discharge performance of carbon fiber-based electrodes in single cell and short stack for vanadium redox flow battery, *Appl. Energy* 125 (2014) 114-122.
- [28] A. Di Blasi, O. Di Blasi, N. Briguglio, A.S. Aricò, D. Sebastián, M.J. Lázaro, G. Monforte, V. Antonucci, Investigation of several graphite-based electrodes for vanadium redox flow cell, *J Power Sources* 227 (2013) 15-23.
- [29] B. Caglar, P. Fischer, P. Kauranen, M. Karttunen, P. Elsner, Development of carbon nanotube and graphite filled polyphenylene sulfide based bipolar plates for all-vanadium redox flow batteries, *J Power Sources* 256 (2014) 88-95.

- [30] B. Caglar, J. Richards, P. Fischer, J. Tuebke, Conductive polymer composites and coated metals as alternative bipolar plate materials for all-vanadium redox-flow batteries, *Adv. Mater. Lett.* 5(6) (2014) 299-308.
- [31] J. Choe, K.H. Kim, D.G. Lee, Corrugated carbon/epoxy composite bipolar plate for vanadium redox flow batteries, *Compos. Struct.* 119 (2015) 534-542.
- [32] G.J. Hwang, Y.H. Oh, C.H. Ryu, H.S. Choi, Electrochemical properties of current collector in the all-vanadium redox flow battery, *Korean Chem. Eng. Res.* 52(2) (2014) 182-186.
- [33] H. Al-Fetlawi, The electrolyte monitoring of a vanadium redox flow battery, *ECS Transactions*, Electrochemical Society Inc., 2013, pp. 33-48.
- [34] R. Badrinarayanan, J. Zhao, K.J. Tseng, M. Skyllas-Kazacos, Extended dynamic model for ion diffusion in all-vanadium redox flow battery including the effects of temperature and bulk electrolyte transfer, *J Power Sources* 270 (2014) 576-586.
- [35] C. Fabjan, J. Garche, B. Harrer, L. Jörissen, C. Kolbeck, F. Philippi, G. Tomazic, F. Wagner, The vanadium redox-battery: An efficient storage unit for photovoltaic systems, *Electrochim Acta* 47(5) (2001) 825-831.
- [36] C.J. Rydh, B.A. Sandén, Energy analysis of batteries in photovoltaic systems. Part I: Performance and energy requirements, *Energy Convers. Manage.* 46(11-12) (2005) 1957-1979.
- [37] C.J. Rydh, B.A. Sandén, Energy analysis of batteries in photovoltaic systems. Part II: Energy return factors and overall battery efficiencies, *Energy Convers. Manage.* 46(11-12) (2005) 1980-2000.
- [38] J. Noack, G. Cognard, M. Oral, M. Küttinger, N. Roznyatovskaya, K. Pinkwart, J. Tübke, Study of the long-term operation of a vanadium/oxygen fuel cell, *J Power Sources* 326 (2016) 137-145.
- [39] H.D.P.I. Leo J. Small, Cy H. Fujimoto and Travis M. Anderson, Diels Alder Polyphenylene Anion Exchange Membrane for Nonaqueous Redox Flow Batteries, *J Electrochem Soc* 163(1) (2016) A5106-A5111.
- [40] F.L. Souza, C. Saez, J. Llanos, M.R.V. Lanza, P. Canizares, M.A. Rodrigo, Solar-powered CDEO for the treatment of wastewater polluted with the herbicide 2,4-D, *Chemical Engineering Journal* 277 (2015) 64-69.
- [41] F.L. Souza, C. Saez, J. Llanos, M.R.V. Lanza, P. Canizares, M.A. Rodrigo, Solar-powered electrokinetic remediation for the treatment of soil polluted with the herbicide 2,4-D, *Electrochim Acta* 190 (2016) 371-377.
- [42] H. Zhou, H. Zhang, P. Zhao, B. Yi, A comparative study of carbon felt and activated carbon based electrodes for sodium polysulfide/bromine redox flow battery, *Electrochim Acta* 51(28) (2006) 6304-6312.
- [43] M.J. Watt-Smith, P. Ridley, R.G.A. Wills, A.A. Shah, F.C. Walsh, The importance of key operational variables and electrolyte monitoring to the performance of an all vanadium redox flow battery, *J. Chem. Technol. Biotechnol.* 88(1) (2013) 126-138.
- [44] C.Y. Ling, H. Cao, M.L. Chng, M. Han, E. Birgersson, Pulsating electrolyte flow in a full vanadium redox battery, *J Power Sources* 294 (2015) 305-311.
- [45] S. Lee, J. Kim, J. Lee, B.H. Cho, State-of-charge and capacity estimation of lithium-ion battery using a new open-circuit voltage versus state-of-charge, *J Power Sources* 185(2) (2008) 1367-1373.
- [46] W.-Y. Chang, The State of Charge Estimating Methods for Battery: A Review, *ISRN Applied Mathematics* 2013 (2013) 7.
- [47] M.R. Mohamed, P.K. Leung, M.H. Sulaiman, Performance characterization of a vanadium redox flow battery at different operating parameters under a standardized test-bed system, *Appl. Energy* 137 (2015) 402-412.
- [48] A. Tang, J. Bao, M. Skyllas-Kazacos, Dynamic modelling of the effects of ion diffusion and side reactions on the capacity loss for vanadium redox flow battery, *J Power Sources* 196(24) (2011) 10737-10747.

- [49] Q. Luo, L. Li, Z. Nie, W. Wang, X. Wei, B. Li, B. Chen, Z. Yang, In-situ investigation of vanadium ion transport in redox flow battery, *J Power Sources* 218 (2012) 15-20.
- [50] Q. Luo, L. Li, W. Wang, Z. Nie, X. Wei, B. Li, B. Chen, Z. Yang, V. Sprenkle, Capacity Decay and Remediation of Nafion-based All-Vanadium Redox Flow Batteries, *ChemSusChem* 6(2) (2013) 268-274.
- [51] X.L. Zhou, T.S. Zhao, L. An, Y.K. Zeng, X.H. Yan, A vanadium redox flow battery model incorporating the effect of ion concentrations on ion mobility, *Appl. Energy* 158 (2015) 157-166.
- [52] H. Prifti, A. Parasuraman, S. Winardi, T.M. Lim, M. Skyllas-Kazacos, Membranes for Redox Flow Battery Applications, *Membranes* 2(2) (2012) 275.
- [53] C. Sun, J. Chen, H. Zhang, X. Han, Q. Luo, Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery, *J Power Sources* 195(3) (2010) 890-897.
- [54] P.K. Leung, Q. Xu, T.S. Zhao, L. Zeng, C. Zhang, Preparation of silica nanocomposite anion-exchange membranes with low vanadium-ion crossover for vanadium redox flow batteries, *Electrochim Acta* 105 (2013) 584-592.
- [55] T.N.a.R.F. Savinell, Flow Batteries, *The Electrochemical Society Interface* 19(3) (2010) 54-56.
- [56] B. Dunn, H. Kamath, J.M. Tarascon, Electrical energy storage for the grid: A battery of choices, *Science* 334(6058) (2011) 928-935.

614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634