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RFB-HY: Redox flow battery pilot installation for hydrogen generation and energy storage

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Contents

Summary

The project aimed at the demonstration of a concept developed in the Laboratory of Physical and Analytical Electrochemistry (LEPA) in EPFL, called a dual-circuit redox flow battery. In brief, it is based on a redox flow battery (RFB), which can be discharged chemically to produce hydrogen or electrochemically to generate electricity. In the former case, the discharge occurs in a separate secondary circuit, in specific reactors. In RFBs, energy is typically stored in the electroactive species dissolved in the liquid electrolytes and the capacity of the battery is therefore determined by the volume of the electrolytes, the concentration of the active species in these electrolytes and the cell potential of the battery during the discharge. In the present system, the capacity of the RFB can be increased on demand when surplus (renewable) energy is available. This gain of capacity arises from the possibility to produce hydrogen, which, in the compressed form, presents a higher energy density than a RFB.

As the bench-top prototype was successful, it became necessary to demonstrate its feasibility and its performances at a larger scale, and in real conditions of energy production and use. The results associated to the installation of a 10 kW/40kWh all-vanadium RFB, the design of the appended secondary circuit and the characterisation of the overall dual-circuit RFB system are discussed in the present report. In particular, a characterisation of the commercial RFB was conducted. Moreover, the design of a catalyst and a catalytic bed reactor for the generation of hydrogen were essential in this project to generate hydrogen by chemically discharging the negative electrolyte of the RFB. Finally, various possibilities for the chemical discharge of the positive electrolyte were also investigated.

All in all, this project was successful and brought a strong knowledge related to commercially available RFBs, to the practical aspects related to the production and storage of hydrogen, and to the needs of electricity storage technologies. Moreover, the production of hydrogen directly from the RFB in a specifically built catalytic bed reactor could be repeatedly demonstrated. Therefore, further research on this system or similar systems is continuing at the laboratory-scale and at the demonstrator-scale in order to eventually bring this system to a commercial state.

1. Project description and objectives

1.1. Project environment

The project was led by the research group of Prof. Hubert Girault (Laboratoire d'Electrochimie Physique et Analytique, LEPA) from the Ecole Polytechnique Fédérale de Lausanne (EPFL). It was conducted in partnership with Sinergy –the utilities company of Martigny, the Center of Research for Energy and Municipalities (CREM) and with a contribution of the district of Martigny and EOS Holding.

This project began in December 2013 and ended in April 2016. It was conducted in Martigny (VS), Rue des Chantons 51, on the site of the wastewater treatment plant, where a large unused building was available. Initial refurbishment works were required to adapt this building to the purposes of the project in terms of safety, access to utilities, internal appearance and practicability.

Besides the contribution of OFEN, the financing of the project involved all the partners, mainly LEPA, but also the EPFL department of infrastructure for the renovation works.

1.2. Project scientific background

This demonstration project originated from a successful research project conducted in the LEPA group with the funding of EOS Holding. It consisted of using a redox flow battery (RFB) for generating hydrogen in an additional (or secondary) plug-in circuit [1]. At the laboratory scale a vanadium-cerium RFB was developed on the basis of the following half-reactions for the charge and discharge, at the positive and negative electrodes respectively:

$$- \quad V^{3+} + 1e^{-} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} V^{2+}$$

$$+ \quad Ce^{3+} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} Ce^{4+} + 1e^{-}$$

In the dual-circuit RFB configuration (see Figure 1), once the battery is charged, it can be discharged chemically by two catalysed reactions taking place in the catalytic beds of the secondary circuit [1,2]. The charged negative electrolyte (V^{2+}) can be discharged by reacting with protons of the solution (there is originally acid in the electrolytes of the all-V RFB) to generate hydrogen (H_2) and regenerate the V^{3+} species, which is redirected in the storage tank of the battery to be charged again. This reaction is extremely slow kinetically and therefore necessitates a catalyst. The catalyst employed can be for instance a molybdenum-based material, such as molybdenum carbide (Mo_2C), as this class of compounds showed a good catalytic activity for the hydrogen evolution reaction. The overall reaction of chemical discharge of the negative electrolyte is eventually the following one:

$$2V^{2+} + 2H^{+} \xrightarrow{Mo_2C} 2V^{3+} + H_2$$

Similarly, the charged positive electrolyte (Ce^{4+}) is chemically discharged by the generation of oxygen in the catalytic bed, leading to the regeneration of the Ce^{3+} species, which is returned to the battery. Typical catalysts for this reaction in acidic conditions are iridium dioxide or ruthenium dioxide. The overall reaction is:

$$4\mathrm{Ce}^{4+} + 2\mathrm{H_2O} \xrightarrow{\mathrm{IrO_2/RuO_2}} 4\mathrm{Ce}^{3+} + 4\mathrm{H}^{+} + \mathrm{O_2}$$

On top of this chemical discharge alternative allowing the production of hydrogen, the battery retains its ability to be electrochemically discharged to generate electricity when required.

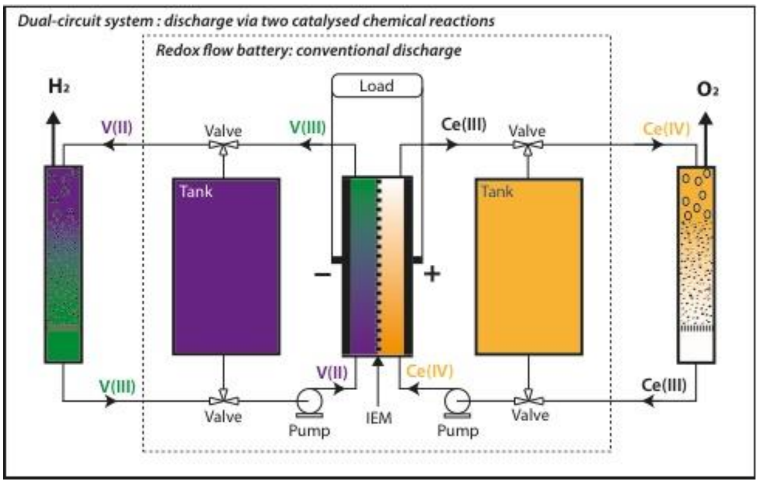

Figure 1: *Scheme of a dual-circuit cerium-vanadium redox flow battery for the production of hydrogen on demand.*

The advantage of this system compared to a conventional RFB is that the capacity of the battery is greatly increased without involving high costs and consequently its energy density is increased as hydrogen can be compressed and presents a much higher volumetric energy density (5.6 MJ/L of H_2 at 700 bar compared to 50 MJ/m^3 – or 50 kJ/L– for typical RFBs' electrolytes). It also enlarges the functionality of classical RFBs as it enables the production of hydrogen and of electricity from one single system on demand. It should be noted that this system is also very flexible as the discharge mean can be changed at any time and moreover, the battery can be charged simultaneously to the chemical discharge so as to keep a steady state of charge or to discharge the battery continuously at a slow rate in the production of hydrogen. The chemical discharge can indeed be designed in a way that allows either a slower, a similar or faster discharge rate than the electrochemical discharge. This facilitates the use of RFB in the storage of unpredictable and variable renewable energies for instance.

1.3. Project objectives

The main, general, objective of the present project was to perform the scale-up of a dual-circuit RFB system. It can however be described in more details by the following points:

1. Evaluating the feasibility of the dual-circuit RFB at a demonstrator scale
2. Performing a scale-up of the catalytic reactor for hydrogen evolution
3. Discharge the positive electrolyte to generate protons
4. Apply to this system typical profiles of energy production by wind turbines or photovoltaic installations
5. Evaluate the performances of the dual-circuit RFB
6. Raise awareness amongst people and the concerned communities and the public about energy storage, and solutions such as redox flow battery and hydrogen, through results dissemination strategies.

1.4. Project tasks

In order to evaluate the dual-circuit system at a larger scale, the present demonstration project was set-up. Instead of a cerium-vanadium redox flow battery, an all-vanadium redox flow battery was implemented as it was not possible to obtain a commercially available cerium-vanadium RFBs on the market. Operationally, the project was initially planned to be divided in the following tasks:

1. Buy and install an all-vanadium RFB to understand in depth its functioning and evaluate thoroughly its performances as a conventional RFB.
2. Perform the scale-up of the catalytic reactor for the discharge of the negative electrolyte leading to the production of hydrogen.
3. Connect this reactor to the RFB and generate hydrogen by chemical discharge of the RFB.
4. Evaluate the performances of the catalytic reactor for hydrogen evolution.
5. In parallel to tasks 2 to 4, investigate at the laboratory scale the discharge reactions for the positive electrolyte (V(V)), in order to be able to discharge it chemically and to keep the protons balance in the system.
6. Implement the positive electrolyte chemical discharge reactor in the dual-circuit RFB.
7. Evaluate the performances of the overall system.
8. Apply to this electrochemical system typical electricity production profiles by wind turbines and typical consumption profiles.
9. Organise visits for the demonstration to professionals and open days for the public.
10. Prepare publications, presentations and report writing for results reporting in suitable international and national research communities.

2. Outcomes of the project

2.1. Installation and characterisation of the all-vanadium RFB

The first part of the demonstration project concerned the RFB, which is the central part of the dual-circuit system. In the frame of the present project, the focus was not on the construction, the improvement or the optimisation of a RFB, but more on its modification for being chemically discharged in a secondary circuit for the generation of hydrogen. Bearing this in mind, it was decided to buy a commercially available RFB instead of building one. As only all-vanadium and Zn-Br RFBs were found to be commercially available at the time of the beginning of the project, we selected an all-vanadium RFB, since it was the closest to a Ce-V RFB in terms of the nature of the electroactive species of the electrolytes. It was supplied by Gildemeister Energy Solutions (http://energy.gildemeister.com/de/speichern). This 10 kW/40 kWh RFB (Figure 2) was installed on the demonstration site in Martigny in May 2014.

As the battery was installed indoor, the requirements for its installation were a solid enough and flat floor (as the level of the liquid electrolytes are constantly measured), a smooth floor surface (for the installation process), an internet connection (for the remote control and monitoring by the supplier services) and the installation of a suitable extraction system for the venting of the limited amount of hydrogen possibly produced at the negative electrolyte in specific conditions. The battery was delivered all-built by a truck and transported up to the doorway by a crane, deposited on small wheels and pushed inside the building at its final position. The electrolytes were then pumped in the battery storage tanks onsite, and after its connection to the grid, the battery could be started. The initial charge required to prepare the electrolytes was performed by the installation team and the battery could be almost immediately operated. However, for its control, it necessitated the design of a Labview-based interface interacting with the battery via a Modbus protocol.

The dimensions of the battery are: 4.7m x 2.2m x 2.5m (LxWxH) for a full weight of 7’000 kg. It is worth noting that this model was the smallest of the production range of this supplier. As a consequence, some of its components appeared to be oversized as they were also designed for higher capacities and power outputs. This is the case mainly of the size of the electrolyte tanks, the capacity of the pumps and the ventilation system. However, this system presents the advantage to be modular. In other terms, we could still add readily and handily supplementary stacks or increase the electrolytes volume if it was desired to increase the power (up to maximum 30 kW) or the capacity (up to maximum 130 kWh) of the RFB, respectively. During the length of the project, the all-vanadium RFB contained 1 m^3 of each electrolyte and 6 stacks of 20 cells electrically connected in series. These stacks were connected in series in pairs, which were branched in three parallel strings on the central DC line.

Figure 2: *The all-vanadium RFB installed as the heart of the demonstration system in Martigny.*

Once the RFB was fully operational, its performances “as received” were evaluated by measuring charge-discharge cycles at various AC power values (with the RFB control system, the battery could only be charged or discharged at chosen AC power set points). It could be noted that even if the nominal AC power output of the battery was 10 kW, it was possible to obtain power output up to 15 kW. This was related to the presence of three 5 kW inverters. In more details, for the discharge, DC currents between 25 and 300 A could be obtained with DC voltages remaining between 41 and 63 V, depending on the state-of-charge (SOC) of the battery and the AC power set point.

Series of charging and discharging curves are shown in Figure 3 (the AC power shown here included the secondary consumer’s consumption). It can be observed that the set AC power output/input can be kept constant until one of the voltage limits is reached, towards the end of the charge/discharge. This is explained by the fact that, at that point, the control changes to a constant voltage control mode and the value of the AC power decreases as the current decreases. The presence of voltage limits can be explained by the fact that excessively high voltages will induce degradation of the electrodes in the stack and a lower efficiency due to side reactions. The presence of a lower voltage limitation is certainly inherent of the electrical components of the inverters (those being in charge of the algorithms of charge and discharge for a certain applied AC power set point). This has to be taken into account while evaluating the integration the battery in a network and implementing it for a specific energy storage service.

From this dataset (and others) it was possible to first calculate the AC energy efficiency of the system, which was determined to be between 50 and 60 %, for 15 and 4 kW respectively. The corresponding DC/DC efficiencies were 60% and 69 %. The consumption associated to the so-called “secondary consumers” of the battery, *i.e.* pumps, inverters (when considered), cooling fans, control system and sensors, *etc.* is included in these values. They represent therefore the efficiencies for the fully integrated system. As mentioned earlier, some parts of the battery are over-dimensioned (*e.g.* pumps), partially explaining this rather low energy efficiency.

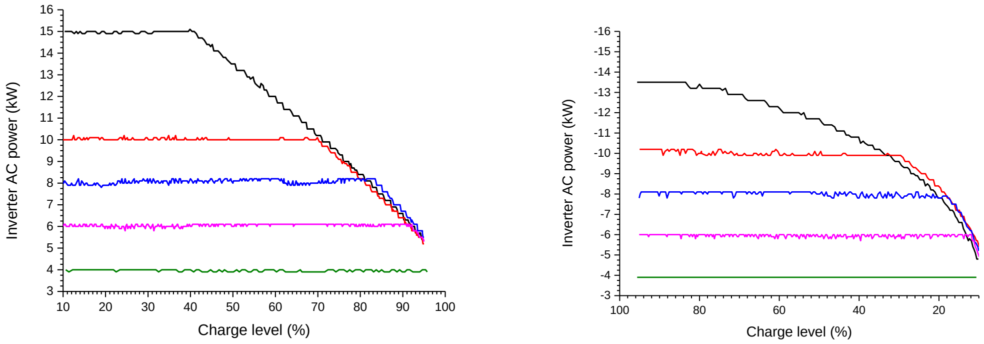

Figure 3: *AC power of the charge (left) and discharge (right) for set points of 4, 6, 8, 10 and 15 kW.*

In order to obtain performances which are more representative of those of a higher scale RFB (thus less affected by its self-consumption rate), the electronic equipment, pumps and ventilation systems have been connected to an external power supply, avoiding then the consumption of the battery energy by these elements. As such, the performances exhibited by the battery were directly related to its electrochemical component. As indicated by the RFB supplier, in these conditions, **an energy DC-DC efficiency of 80% could be reached**, corresponding to an energy efficiency of about 70% in AC-AC mode. These energy efficiencies were however only obtained for charging and discharging power of 4 to 6 kW and efficiency decreases slightly for higher power values. The AC/DC and DC/AC efficiencies were also determined to be about 88% and 93% respectively (over the whole power range).

A self-discharge rate of the battery of about 10% per day was observed in the standby mode. This is due to the intermittent pumping of fresh electrolyte in the stacks of the RFB, inherent to its control system. As, in the standby mode of the RFB, the electrolytes located in the stacks are discharged due to cross-mixing of vanadium ions through the membrane, the discharge electrolytes are pumped out and replaced by fresh (*i.e.* more charged) electrolytes in order for the stack to be at any point able to provide the energy for the external grid or for pumping. In this way, the battery discharges in about 10 days, but, again, this self-discharge rate can also be corroborated to the oversized design of the present RFB and could be improved by changing the control system or fully stopping the battery.

In an overall view, the RFB was judged to be well designed and constructed, in the sense that good quality materials and equipment were used and everything was integrated to make a product ready-to-use and exhibiting potentially a long lifetime. It is intended to last for 10-20 years, including some maintenance checks and changes (pumps and possibly stacks). Its response time is directly dictated by the one of the inverters and showed to be a few seconds (approximately 2-5 s). Moreover, little maintenance, through handy and inexpensive actions such as stack exchange, pump exchange or electrolytes regeneration lead to a greatly extended lifetime of the battery. Finally, in terms of safety, the battery follows the European standards and is expected to be safe compare to Li-ion battery for instance. Besides electrical circuits issues, no major dangers can occur, especially due to the double walled retention trays installed for protection against electrolyte leakage and the corresponding sensors. Moreover, it can be noted that no accidents or incidents occurred at all during the two years of the project, showing that this battery seems reliable.

2.2. Design of a catalyst and of a catalytic bed for the reaction of hydrogen evolution

The second part of the demonstration project consisted of the design and assembling of a reactor where the reaction between V^{2+} with the H^+, both present in the negative electrolyte, to generate hydrogen and regenerate the discharged V^{3+} electrolyte can take place. First, we focused on the design and preparation of the catalyst. Indeed, even if it is thermodynamically feasible, this reaction requires a catalyst to increase its rate. The focus is here on molybdenum carbide (Mo_2C) as it is inexpensive, it was shown to be active for the considered reaction and it is stable in the acidic and reaction conditions.

Previously, we studied Mo_2C in the form of a powder for this reaction. The diameter of the particles was ranging from 1 to 5 µm diameter. Therefore, building a fixed catalytic bed able to convert a flow rate of about 1 L/min would require a high amount of this powder, which would lead to several issues, such as a high resistance of the catalytic bed to the electrolyte flow (requiring high pumping energies), preferential flow paths (non-optimal use of the catalyst), accumulation of bubbles inside the bed (decreasing the active surface of the catalyst), and difficulty to filtrate thoroughly the electrolyte. In order to circumvent these limitations related to the powder state of the catalyst the most common solution is to deposit the catalyst, for instance in a nanoparticulate form or in the form of a micro- or a nano-film, on a (inactive) catalyst support. This support can present different shapes and may be characterized by various degree of porosity. The higher the porosity, the higher the amount of catalyst that can be deposited per volume of support (as the ratio surface/volume increases). The shape of the support particles is important for the mass transfer of the reactants and products and when attrition is an issue. Here, solid beads particle will be employed.

With such considerations in mind, we started to synthesize nanoparticles of Mo_2C on 3 mm alumina beads, depositing either 5 wt% Mo_2C or 10 wt% Mo_2C on the solid support beads. As seen on Figure 4 (left), microscopy imaging (High-resolution scanning electron microscopy, HRSEM) allowed characterizing the size and the distribution of the catalyst nanoparticles. The particle size was approximately about 40 nm in diameter, and they were particularly homogeneously distributed on the surface of the support. The rate of the reaction at the surface of this catalyst was fast, as it was measured with a pressure sensor in an airtight 10 mL reactor. However, it was observed that when the catalyst was repeatedly employed, the size of the catalyst sphere decreased and tiny black particles were observed in the final solution. This led us to the conclusion that the catalyst was slowly disaggregating during the reaction and it was explained by the formation of hydrogen bubbles in the pores of the support. Indeed, this support was actually formed of sintered small particles with a high porosity and it could be mechanically torn apart by the growing pressure of hydrogen in the pores situated between the sintered alumina particles. As a consequence, a non-porous, solid, ceramic 3 mm beads support was used instead for the Mo_2C nanoparticles. The deposition of Mo_2C led to different shape of particles, as can be seen on the HRSEM micrograph shown on Figure 4 (right). This catalyst also exhibited a sufficiently fast reaction rate for the considered reaction and showed to be stable over time. This catalyst was used in the reactor described below.

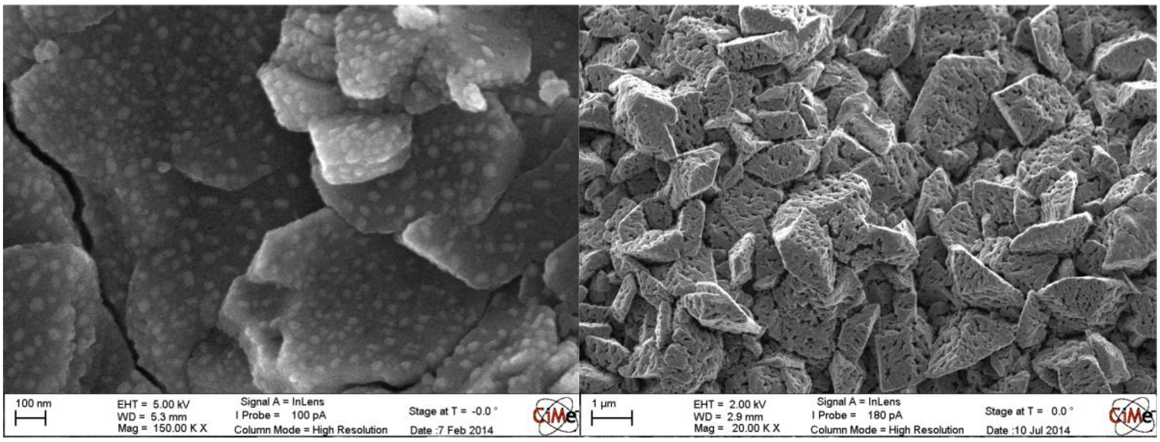

Figure 4: *HRSEM images of Mo_2C nanoparticles deposited on the alumina bead support (left) and on the ceramic beads support (right).*

In parallel to the design of the catalyst, the reactor for the reaction of hydrogen production was considered. Based on preliminary experiments conducted in the laboratory, it was first decided to build a horizontal fixed bed reactor for the following reasons: this configuration avoids the preferential electrolyte paths in the catalytic bed, it avoids an inhomogeneous hydrogen flow due to the accumulation of bubbles followed by their sudden release and it promotes the release of hydrogen bubbles from the bed, helping to keep a high active surface area of the catalyst in the bed. Moreover, this kind of catalytic bed favours a high exchange surface between the liquid and gas phases, facilitating therefore the transfer of hydrogen from the aqueous solution to the gas phase, increasing the amount of hydrogen collected in the reactor. A horizontal configuration presents also a thinner layer of catalyst (less bubbles accumulated) and the flow of electrolyte is horizontal, allowing a more efficient use of the catalyst. The later point however, was not true when the catalytic bed was long, because the flow of electrolyte had the tendency to follow the path of least resistance, leading to a flow occurring at the surface of the catalytic bed only and a stagnation of discharge electrolyte at the basis and in the catalytic bed. In order to avoid this effect, the reactor was divided into smaller segments placed in series.

In practice, the inner diameter of the transparent polycarbonate tube was 8 cm, it was filled with catalytic beads (prepared as detailed above) up to the 2/3 of the height and it was, in total, 1 m long (Figure 5, left), but composed of 5 stages of equivalent length. The weight of the catalyst was approximately 3 kg (catalyst + support), which corresponded to about 15 g of Mo_2C. The negative electrolyte flow rate for this reactor electrolyte was about 200 mL/min and the maximum allowed pressure was 3 bar. When tested in the large-scale system, an unforeseen issue appeared, which was not observed in the laboratory-scale experiments: it was the extensive formation of foam in the catalytic bed and in the headspace of the reactor, caused by the formation of large amount of tiny hydrogen bubbles and the high viscosity of the solution (high vanadium concentrations). As a result, the flow of electrolyte was slowed down and at the end, practically stopped. At least, the presence of foam everywhere in the catalytic bed showed that the design was suitable in terms of contact between the catalytic particles and the charged solution.

To circumvent this foaming process, a second reactor configuration was designed. It consisted of a vertical reactor composed of 8 stages in cascade, each of the stages retaining part of the horizontal reactor characteristics described above (Figure 5, right). Indeed, each of the stage contains a fixed catalytic bed in which the electrolyte was fed at the basis of the bed and exited at the top of the bed to be drained out to the next stage. A large headspace was designed in order to avoid the displacement of foam in the hydrogen collecting tubing nearby the top of each stage. A reactor was built again in 8 cm (internal diameter) transparent polycarbonate tube, in order to allow a visual inspection and observation of the reaction (Figure 5, right). Each of the stage contained 800 g of the Mo_2C/ceramic catalytic beads (in total 32 g of Mo_2C catalyst for the whole reactor). The amount of catalyst required in this catalytic bed was estimated from the kinetic parameters of Mo_2C determined at the laboratory scale and for a negative electrolyte flow rate of 1L/min and considering a full conversion of the fully charged negative electrolyte to its discharge state.

In order to be functional, it was necessary to integrate other components to the hydrogen reactor demonstration system. First of all, compressed air-driven membrane pumps were used to drive the negative electrolyte from the RFB pipe to the reactor (here we used two intermediate tanks, one situated before and one placed after the reactor) and back to the battery negative storage tank. An automatically-controlled proportional valve was used to set the flow rate of electrolyte in the reactor. At the electrolyte outlet of the reactor, two consecutive filters were added in order to retain any particles of catalyst of more than 1 µm and 0.25

µm diameter. This is essential to avoid any catalytically active particles entering in the RFB because it would generate hydrogen in the battery itself, and prevent its charge (or at least decreases the efficiency and increasing the self-discharge). The produced hydrogen exits from the headspace of every stage, and the operating pressure of the reactor is between 1.3 and 1.5 bar. A compressed air-driven compressor was activated when the threshold pressure of 1.5 bar was reached in the reactor, pumping hydrogen into the storage tank until the pressure of the reactor dropped under 1.3 bar.

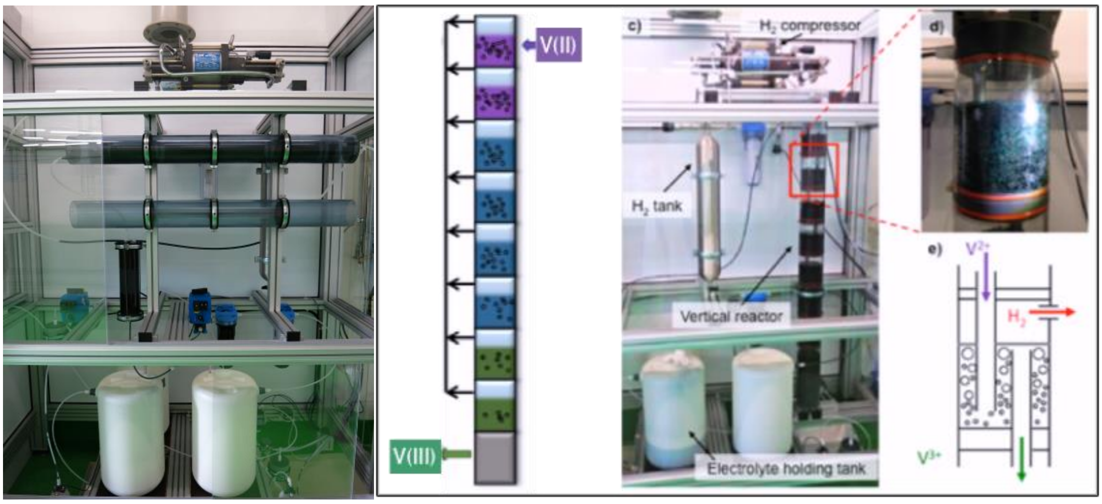

Figure 5: *Picture of the horizontal (left) and vertical (right) catalytic bed reactors, which were implemented in the dual-circuit demonstration system for hydrogen production from the negative electrolyte.*

In order to characterise the final (vertical) reactor for the chemical discharge of the battery, series of experiments aiming at determining the effects of the flow rate of the electrolyte passing through the bed and of the state of charge (SOC) of the negative electrolyte of the battery on the hydrogen production rate were conducted. The main goal of these experiments was to evaluate the optimal conditions of flow rates for different SOCs of the battery in order to obtain a full conversion of the V^{2+} to V^{3+}. In Figure 6, the evolution of the rate of hydrogen evolution as a function of the flow rate (right) and as a function of the SOC of the negative electrolyte (left) is depicted. It can be observed that the rate of hydrogen production is linearly dependent on the SOC and on the flow rate of the electrolyte in the tested ranges. This experiment was required in order to assess that the conversion of the V(II) to V(III) was completed and that the maximum of hydrogen could be produced through a single passage of the electrolyte through the bed. According to this experiment, for discharging the fully charged negative electrolyte a flow rate up to 500 mL/min is feasible. In this range, the full conversion of the electrolyte was confirmed visually as only a very small amount of hydrogen bubbles were appearing in the last stage of the reactor and the color of the electrolyte was clearly corresponding to that of the V(III) discharged state of the negative electrolyte of the RFB. In the range between 500 mL/min and 1L/min, the conversion appeared to be full, but the rate was increasing much less, most probably due to a decrease of the available surface area of the catalyst. Finally, it can be noted that at flow rates higher than 1 L/min, it was clearly observed that the electrolyte was not fully converted, first as many bubbles were formed in the last stage and even in the tubing before the filter and in the filter, and from the color of the discharge solution. However, as a proof of the good functioning of the filter, no hydrogen evolution was observed downstream to the filters. In order to be sure of having a full conversion, the experiments were usually performed at a flow rate of 300 to 500 mL/min.

In terms of stability of the catalyst, it can be noted that the second catalytic bed has currently been used for approximately 1 year and still is active almost like originally. It was not used continuously, but in series of experiments conducted periodically. Between the experiments, it was kept in the discharged V(III) electrolyte. Even if no detailed study of the catalyst stability in these conditions has been conducted in the frame of this project, this indicates that **Mo_2C is a robust and stable catalyst** and that the nanoparticles are well attached to the ceramic support. Indeed, the formed bubbles are clearly appearing around the particles and not in the whole solution.

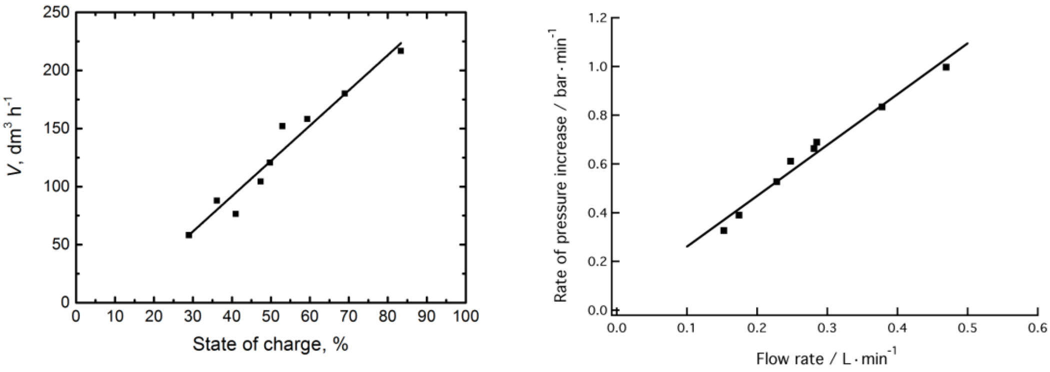

Figure 6: *Linear dependence of the rate of hydrogen production as a function of the SOC of the negative electrolyte of RFB (left) at a flow rate of 300 mL/min and its flow rate in the reactor (right) at a SOC of 83%.*

Overall, the reactor for hydrogen production is fully satisfactory, since it could be build using low-cost materials, it could produce relatively large amount of hydrogen from the negative electrolyte of the battery and the catalyst remained stable. Another advantage of this design is the possibility to easily scale-up the circuit by adding parallel hydrogen generation reactors to accelerate the discharge of the negative electrolyte.

2.3. Design of a reaction for the chemical discharge of the positive side of the redox flow battery

In parallel to the chemical discharge of the negative electrolyte to produce hydrogen, it was necessary to discharge the positive electrolyte to the same extent in order to avoid an imbalance between both electrolytes (*i.e.* both electrolytes do not have the same SOC). Besides the selection of a suitable discharge reaction, it was also required to design the corresponding secondary circuit connected to the RFB. Regarding the choice of the discharge reaction, it depended first on the electroactive species to be chemically discharged. In the abovementioned research, the charged positive electrolyte species was Ce^{4+}, however in the all-vanadium RFB, it was the V(V) species (more precisely, VO_2^+) which needed to be discharged. In the original proposal, it was mentioned that we could replace the whole vanadium positive electrolyte by a new cerium positive electrolyte. However, this appeared to be difficult for several reasons.

First of all, cerium salts are relatively expensive, especially in a sufficiently pure state, even in such a large quantity. For instance, 1 kg of cerium carbonate 99.9% costs about 500 CHF (Feb. 2015) if supplied by Treibacher Industrie AG (Germany) – this company being known to provide suitable purity cerium salts. And the approximate mass of cerium carbonate required to balance the charge of the negative electrolyte is 730 kg. The budget of the project was not allowing such an expense for cerium salt. Furthermore, several technical challenges were also encountered with cerium. In particular, as Ce(IV) is a strong oxidant it provokes corrosion of most of the materials which are commonly used in the RFB industry. This also means that it will corrode the carbon-based electrodes present in the stack, where the electron exchange has to occur. Moreover, in the current state of research cerium does not allow to be dissolved at as high concentrations as vanadium for instance, which may involve a decrease of the energy density of a RFB (slightly compensated by the increase of the cell voltage, though). However, even if several challenges were associated to the use of cerium in redox flow batteries, it is studied all around the world for various RFB chemistries, such as zinc-cerium and cerium-hydrogen.

At the laboratory scale, it was originally chosen for its ability to generate oxygen due to its high oxidant power. Indeed, V(V) is not able to oxidize water to produce oxygen. The reaction of water oxidation was preferred as it provided the protons (one proton per cerium which reacts), which were consumed in the negative side and in the overall system, the only reactant that needed to be added was water. For this reason, cerium was still studied at the laboratory-scale in the frame of this project, especially with the objective of optimizing the electrolyte composition to improve the solubility of the cerium salt but also of improving the rate of the reaction of electron transfer at the surface of carbon electrodes, in order that it does not require high voltages and limits the electrode corrosion. In this purpose, various inorganic and organic acids were evaluated as well as mixtures of acids with various proportions. The solubility of Ce^{3+} and Ce^{4+} in these various solutions was measured and cyclic voltammetry measurements were conducted in order to determine their electron transfer kinetic parameters. However, no significant enough improvements were achieved that would allow for the use of cerium at a larger scale.

Another alternative that was studied was the use of a mixed electrolyte including both cerium and vanadium salts as positive electrolyte, in order to discharge the battery chemically by only discharging the cerium cations, and electrochemically by discharging mostly the vanadium cations (and the cerium if it has not been discharged chemically). Especially, it was observed that the solubility of Ce^{4+} was higher in the presence of vanadium ions dissolved in the solution. Various mixed systems were tested in a bench-scale RFB, however, no significant results were obtained, due to a lower kinetics of the vanadium electron exchange reaction in the acid allowing the highest solubilities of cerium. This approach shall however be investigated further.

As discussed above, for being able to discharge chemically the positive electrolyte of the 10 kW/40 kWh all-vanadium RFB, it was required to develop other reactions. The requirements for these reactions were the following ones: it needs to be thermodynamically feasible, and to consume one proton per V(V) discharged, and ideally the reaction product should be handily separated from the electrolyte (ideally being a solid, a gas or a non-miscible liquid). Three reactions were studied: the oxidation of hydrazine, of sulfur dioxide and of hydrogen sulfide. The equations for these three reactions are:

hydrazine, N_2H_4 $$4VO_2^+ + 4H^+ + N_2H_4 \longrightarrow 4VO^{2+} + 4H_2O + N_2$$

sulfur dioxide, SO_2 $$2VO_2^+ + SO_2 + 2H^+ \longrightarrow 2VO^{2+} + H_2SO_4$$

hydrogen sulfide, H_2S $$2VO_2^+ + H_2S + 2H^+ \longrightarrow 2VO^{2+} + S + 2H_2O$$

None of these reactions requires a catalyst, which facilitates greatly the design of the secondary circuit. In the case of hydrazine or hydrogen sulfide oxidation reactions, the only product is respectively nitrogen gas or solid sulfur, which are easy to separate from the electrolyte. These alternatives are therefore relatively straightforward to be implemented, even at a larger scale.

However, for sulfur dioxide, sulfuric acid is produced, which is dissolved in the solution and would then be accumulated in the electrolyte if not removed. An anionic membrane could be used to extract the sulfate ions specifically from the solution, but this process can be associated with leakage of a small amount of vanadium ions and water, which would affect the composition of the electrolyte. Another alternative which was studied in the frame of this project was the use of a fuel cell performing the discharge of V(V) electrolyte at the cathode and the simultaneous oxidation of SO_2 at the anode (Figure 7). This allows the production of a sulfuric acid-containing solution already separated from the electrolyte. It would be particularly helpful for the desulfurization of gas streams which are produced in the refinery industry, for instance. This chemical discharge option was studied at the laboratory-scale, where a fuel cell system was build and tested (see [3]), however it requires more research before being possibly implemented at a demonstrator scale, especially for the development of suitable electrocatalysts and to find or develop an optimal membrane material.

The reaction of hydrazine oxidation was implemented in the demonstration system. It involved a batch reactor where both the charged V(V) electrolyte and the hydrazine were mixed. The reaction is fast and generates heat, the rate of hydrazine addition in the reactor should therefore be well controlled and slow. In our conditions, no cooling system needed to be installed. Moreover, it is also necessary to dilute the hydrazine (at least by a factor of 2) in order to avoid the formation of a hydrazine sulfate complex when hydrazine enters in contact with sulfuric acid, as it precipitates. This way, the positive electrolyte could be discharged in parallel to the negative electrolyte discharge for the production of hydrogen. It should be noted that this option was selected only because of its simplicity of implementation. Indeed, it presents no advantage to oxidize hydrazine, which is a fuel, and this is not a sustainable reaction as hydrazine needs to be produced by reduction before. However, as the objective of the project focused more on the production of hydrogen, it was required to develop an easy-to-implement chemical discharge of the positive electrolyte.

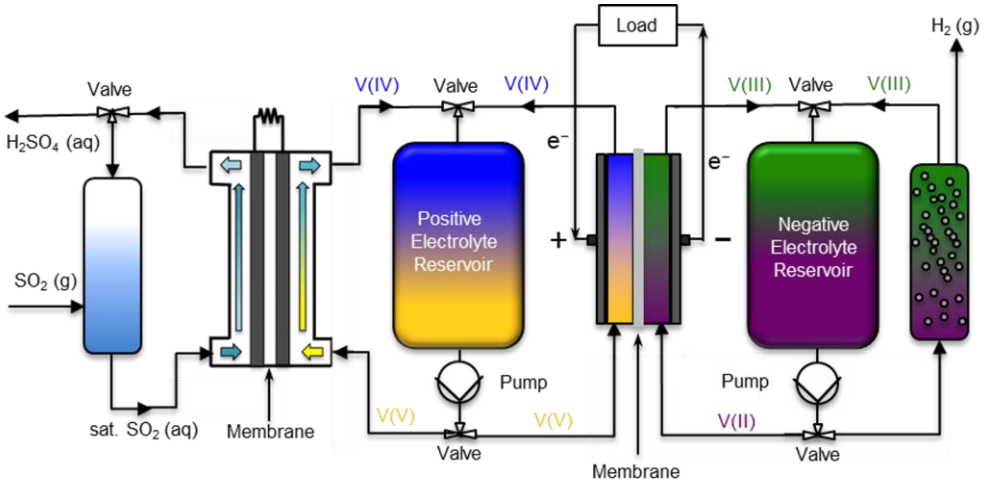

Figure 7: *Dual-circuit associated to a fuel cell for the chemical discharge of the V(V) electrolyte. Beside the production of H_2, it generates sulfuric acid as side product, which can be purified and then considered as a useful product [3].*

As a conclusion of this section, it can be noted that even if several solutions were studied and developed for the chemical discharge of the positive electrolyte, and even if the chemical discharge of the positive electrolyte was possible in the demonstrator system, no fully satisfactory reactions were developed, in terms of sustainability or technical feasibility. This remains the weakest point of the present project and more research is required to face this issue. In particular, alternative positive electrolyte species –which would be associated with alternative chemical discharge reactions, other designs of the coupling between RFB and hydrogen production, and fuel cell systems such as the one developed for SO_2 could be further investigated.

2.4. Performances of the dual-circuit all-vanadium RFB system

As a first result, it can be observed that a demonstrator dual-circuit RFB could be built, characterised and utilised. It was based on a commercial all-vanadium RFB coupled with a secondary circuit for the production of hydrogen on demand and for the chemical discharge of the V(V) electrolyte by hydrazine. The operation of the battery and of the secondary circuit was controlled by a LabView-based software, which was also able to monitor the battery charging and discharging and to switch between the electrochemical and chemical discharge.

In terms of the productivity of hydrogen in the current system design, using the above-described vertical reactor and a flow rate of 1 L/min, it was possible to discharge the full 40 kWh battery in 17h, which is equivalent of 2.4 kW electrochemical discharge. It is worth to note that the total amount of catalyst was 6.4 kg, but corresponded to only 32g of Mo_2C, showing that this catalyst was efficient for the considered reaction. If one wants to be able to chemically discharge the battery at a higher rate, hydrogen generation reactors could be added in parallel to the existing ones. For instance, for a discharge power equivalent to the nominal charge power of the battery (10 kW), it is required to add between 4 and 5 such reactors in parallel. This system would allow to chemically discharge the battery simultaneously to the charging process, leading a stable battery SOC.

Using the full capacity of the battery in chemical discharge leads to approximately 1.3 kg of hydrogen, an amount sufficient to drive a classical fuel cell car for about 100 km. This is a reminder of the low energy density of RFBs and shows how the production of hydrogen can greatly increase their energy density. Indeed, 1.3 kg of hydrogen can be stored in a volume of less than 23 L (at 700 bar), whereas, it would involve 2 m^3 of electrolytes. If we also consider the increase of volume generated by the secondary circuit itself, the energy density is probably very similar. However, this comparison becomes definitely more favorable when larger capacities are involved.

In terms of efficiency of the conversion of electricity to hydrogen, it is not straightforward to calculate it as it is required to take into account the reaction of the chemical discharge of the positive electrolyte and depends on the definition of the boundaries of the system considered. The energy efficiency of a system being the ratio between the energy input in this system and the energy output of this system, it can be written in the present case as:

$$\eta = \frac{W_{\mathrm{H_2}} + W_{\mathrm{Ep}}}{W_{\mathrm{Ec}} + W_{\mathrm{r}}}$$

Where η is the energy efficiency, W_{H2} is the energy contained in hydrogen (based on the so-called higher heating or lower heating values – HHV or LHV– of hydrogen), W_{Ep} is the AC electricity produced (by the fuel cell in the case of the SO_2 oxidation in a fuel cell for the discharge of the V(V) electrolyte), W_{Ec} is the AC electricity consumed (for the charge of the battery) and W_r is the energy contained in the reactant used for the positive electrolyte discharge (in terms of HHV or LHV of the reactant). With this calculation procedure, the dual-circuit RFB system allows an AC energy efficiency based on the HHV (LHV) of 48.4% (44.7%) in case of the use of N_2H_4, of 52.5% (49%) when H_2S is used, of 56% (49%) when SO_2 is employed, and of 67.3% (60.8%) when the SO_2-fuel cell system is implemented. The efficiency of the system when the fuel cell involving the oxidation of SO_2 for the discharge of V(V) is comparable to typically claimed water electrolysis efficiencies for fully integrated electrolysers.

The dual-circuit RFB concept was mainly investigated in the perspective of storing renewable energies, especially surpluses of renewable energy. Indeed, the secondary circuit was intended to be employed when the battery is already full and there is still energy available to be stored. This energy is considered to be extremely inexpensive and sometimes even free. Alternatively, the secondary circuit could be designed to discharge the battery faster than it can be electrochemically discharged. This is possible only because inexpensive materials are used and as the reactor configuration allows a modular design of the secondary circuits power. Reactors for hydrogen production can therefore be enlarged and/or cumulated to accelerate the chemical discharge rate. Finally, in terms of applications, this system is particularly suitable as a plateform between grid and electrical mobility as it is able to supply either electricity to a (fast) charger for electric cars and hydrogen to fuel cell cars.

A modeling and optimization work based on the demonstrator system was performed in collaboration with the group of Prof. Dominique Bonvin at EPFL in the frame of a master thesis. It consisted first of building a model for the all-vanadium RFB able to reconstitute its behavior when typical profiles of energy production or energy consumption (practically the sum of both was considered) were applied. The obtained model was simpler than most of the models available in literature, however it was shown to be accurate enough to seize the behavior of the battery during charge and discharge. In the second step, the reactor for hydrogen production was integrated in the model in the form of a means of hydrogen production fed from the discharge of the battery. The final step was devoted to determining the gain of installing a dual-circuit RFB system in a small network including a photovoltaic or a wind turbine energy source (scaled down to the capacity of the battery) and a few households as energy consumption means and which was connected to the grid for releasing the surplus of energy or consuming electricity when needed. The optimization work focused on the objectives of minimizing the flow of electricity from the grid and maximizing the profit. As a result, it was observed that the addition of a dual-circuit RFB was beneficial for the micro-grid in terms of profit. This study will also be continued in a more in-depth analysis of the integration of such a system in the current energy landscape.

All in all, the dual-circuit RFB concept is only viable if the cost of appending a secondary circuit for a certain capacity of hydrogen production is lower than the cost associated to an increase of the same capacity of the battery by increasing the volume of the electrolytes. The overall cost associated to a system allowing the production and storage at 200 bar of 13 kg of hydrogen can be estimated to be around 25’000 CHF, based on the cost of the material bought for the demonstrator system. This amount of H_2 can be produced in 10 days in our current system, but it could be generated in 2 days in presence of 5 parallel hydrogen reactors. However, the safety aspects related to the presence of hydrogen also have to be considered and safety measures may also increase slightly the cost. Moreover, the cost of the compounds required for the equivalent discharge of the positive electrolyte needs to be as well added. However, even in these conditions, if a comparison is made with the cost of increasing 10 times the capacity of the battery by increasing the volume of electrolytes, passing from 2 m^3 to 20 m^3 of electrolytes in the battery, would certainly cost more, as the cost of electrolytes is often considered in the RFB community to constitute half of the price of the battery. A full detailed economic analysis should be performed in order to be able to evaluate the economic advantage of this system.

3. Dissemination of the results

Various ways of dissemination of the presence of the demonstration project and of the obtained results were pursued. Most importantly, as it was defined to be a demonstrator project, a large number of visits were organised. Altogether, amongst others, we obtained the visibility of the project by:

- Scientists from all over the world, mostly during the visit associated to the conference of the International Society of Electrochemistry in Lausanne, chaired by Prof. Hubert Girault, in August 2014.
- Scientists from Switzerland, especially at the inauguration and in the frame of communications in the Heat and Electricity Storage (HaE) SCCER (to which we participate), and in the HaE and the Mobility SCCERs annual meetings and in one of the OFEN hydrogen meetings.
- Swissgrid, as three collaborators came to visit our site to discuss our strategy and our technology in spring 2016.
- EOS Holding, who is also supporting the project.
- Energy distribution companies in Valais, but also in Vaud, Fribourg, Jura and Geneva, especially through visits at our site, but also through several invited presentations.

- Politicians, in particular in Valais, around Martigny and Sion, through visits of the demonstration system and through diverse presentations.

More in details, here are some links and references were communications related to the present project were published or discussed:

On the internet:

1) First Youtube video: https://www.youtube.com/watch?v=SdgkqdrADjY (last accessed: 31/07/2016).
2) Second Youtube video: https://www.youtube.com/watch?v=E8X5S_fZXjA (last accessed: 31/07/2016).
3) Third Youtube video: https://www.youtube.com/watch?v=faEC2IyQBCg (last accessed: 31/07/2016).
4) The website of the demonstration project: http://lepa.epfl.ch/RFBdemo (last accessed: 31/07/2016).
5) On the EPFL News website: http://actu.epfl.ch/news/au-cur-des-stations-services-de-demain/#.VGTbu9BXXxk.twitter (last accessed: 02/08/2016).
6) Annual report SCCER 2015, p. 36: http://www.sccer-hae.ch/resources/AnnualReport2015/Annual_Report_SCCER-Storage_2015_web.pdf (last accessed: 31/07/2016).
7) Article from Mr. Benedikt Vogel on the OFEN website: De l'Hydrogène à partir d'une batterie: http://www.bfe.admin.ch/php/modules/publikationen/stream.php?extlang=fr&name=fr_339392107.pdf. (last accessed: 02/08/2016).
8) Article Cleantech Alps: http://www.cleantech-alps.com/fr/actualites/news/details/de-l-hydrogene-a-partir-d-une-batterie-0-1165 (last accessed: 02/08/2016).
9) Article on the ee-news platform, 18th of April 2016, by Mr. Benedikt Vogel: http://www.ee-news.ch/de/article/33383 (last accessed: 02/08/2016).
10) On the LEPA twitter and Facebook accounts.

In the scientific (peer-reviewed) literature:

1) Amstutz et al., Renewable hydrogen generation from a dual-circuit redox flow battery, *Energy and Environmental Science* **7**: 2350-2358 (2014).
2) Dennison C.R. et al., Redox flow batteries, hydrogen and distributed storage, *CHIMIA International Journal for Chemistry* **69**(12): 753-758 (2015).
3) Peljo P. et al., All-vanadium dual circuit redox flow battery for renewable hydrogen generation and desulfurisation, *Green Chemistry* **18**: 1785-1797 (2016).

Presentations and posters at conferences:

- "Developments in the design, fabrication and implementation of a dual-circuit redox flow battery", Kathryn E. Toghill *et al.*, International Flow Batteries Forum 2014 (IFBF 2014) in Hamburg (Germany), 3 July 2014 (Presentation).
- "Adaptation of a redox flow battery to generate hydrogen from surplus renewable energy: principle and pilot project", Véronique Amstutz *et al.*, 65th annual meeting of the International Society of Electrochemistry conference – Ubiquitous Electrochemistry, Lausanne (Switzerland), 5 Sept 2014 (Presentation).
- "A dual-circuit redox flow battery for hydrogen production", Pekka Peljo *et al.*, Multiscale renewable energy storage 2014 (MRES 2014) in Boston (United States of America), 20 August 2014 (Presentation).
- "Adaptation of a redox flow battery to generate hydrogen from surplus renewable energy", Véronique Amstutz *et al.*, 10th European Symposium on Electrochemical Engineering, in Chia (Italy), 2 Oct 2014 (Presentation).
- "Conversion of electricity into hydrogen using a dual-circuit redox flow battery", Véronique Amstutz *et al.*, SCCER Annual Conference, Villigen (Switzerland), 4 Nov 2014 (Poster).
- "Hydrogen production by redox flow batteries", Hubert Girault *et al.*, UNSW Materials and Electrochemistry Symposium, University of South Wales, School of Materials Science and Engineering (Australia), 5 Dec 2014 (Presentation).
- "A demonstrator for the conversion of surplus renewable energy to hydrogen", Véronique Amstutz *et al.*, 5th Euro-Mediterranean Hydrogen Technologies Conference (EmHyTeC 2014), in Taormina (Italy), 11 Dec 2014 (Presentation).
- "Redox Flow batteries for on demand hydrogen production", Hubert H. Girault *et al.*, 9th International Symposium on hydrogen and energy, 25–30 Jan 2015, Emmetten, Switzerland (Presentation).
- "Production d'hydrogène pour complémenter le stockage électrochimique de l'énergie", Hubert H. Girault *et al.*, Séminaire des Gaziers Romands, 11–12 Feb 2015, Glion, Switzerland (Presentation).
- "Two levels energy storage: redox flow battery and hydrogen", Véronique Amstutz *et al.*, Conference to Association pour l'innovation et la recherche énergétique (RIE), 30 April 2015, Martigny, Switzerland (Presentation).
- "Hydrogen production with a redox flow battery. Water splitting with junk electricity", Pekka Peljo *et al.*, 3rd International Symposium on Green Chemistry, 3–7 May, 2015, La Rochelle, France (Presentation).
- "Megabatteries and hydrogen generation to fuel cars", Hubert H. Girault *et al.*, 5th May 2015, Académie des Sciences, Institut de France, Paris, France (Presentation).

- “Nouvelle technologie de batterie et influence sur la distribution électrique”, Véronique Amstutz *et al.*, Conference at ESR (Energie Sion Région), 12 June 2015, Sion, Switzerland (Presentation).
- “Advancements in the demonstrator of the dual-circuit all-vanadium redox flow battery for hydrogen generation”, Véronique Amstutz *et al.*, International Flow Battery Forum 2015, 16 – 18 June 2015, Glasgow, UK (Poster).
- “New Chemistries for electricity storage in fluid phases”, Hubert H. Girault *et al.*, 15–18 June 2015, 11th ECHEMS, Bad Zwischenahn, Germany (Plenary Lecture).
- “Redox Flow Batteries and Hydrogen Production: Two Complementary Storage Systems”, Christopher R. Dennison *et al.*, Batteries redox flow pour le stockage des énergies renouvelables, 26 June 2015, Nancy, FR (Invited lecture).
- “Ongoing Work in Redox Flow Batteries”, Christopher R. Dennison *et al.*, Abengoa Research Inauguration, 8 July 2015, Sion, CH (Presentation).
- “Fast e-Fuelling Stations”, C. R. Dennison, Alberto Battistel *et al.*, SCCER Mobility Annual Conference 2015, 26 – 27 August 2015, Zürich, CH (Poster).
- “Redox Flow Batteries, hydrogen production and photo-ionic cells”, Hubert H. Girault *et al.*, ISACS17 Challenges in Chemical Renewable Energy, 8–11 Sep 2015, Rio de Janeiro, Brazil (Presentation).
- “Redox Flow Batteries and Hydrogen Production for e-mobility”, Hubert H. Girault *et al.*, Seminar at Fudan University, 27 Sep 2015, Shanghai, China (Presentation).
- “Redox Flow Batteries for E-Mobility”, Hubert H. Girault *et al.*, ISE Satellite Meeting, 1–3 Oct 2015, Hong Kong, China (Plenary Lecture).
- “Strategies for enhancing the energy density of redox flow batteries”, Véronique Amstutz *et al.*, ISE Satellite Meeting, 1–3 Oct 2015, Hong Kong, China (Presentation).
- “Fast e-Fuelling Stations”, C. R. Dennison, Alberto Battistel *et al.*, The SCCER Heat and Electricity Storage 3rd Symposium, 26 October 2015, Villigen, CH (Poster).
- “Modeling and Optimal Control of a Redox Flow Battery”, Timm Faulwasser *et al.*, 13th Symposium on modeling and experimental validation of fuel cells, batteries and electrolysers, 22 March 2016, Lausanne, Switzerland (Presentation).
- “Demonstration of the synergies between hydrogen generation and a flow battery”, Véronique Amstutz *et al.*, International Flow Battery Forum, 8 June 2016, Karlsruhe, Germany (Presentation).

In popular science journals:

1) Girault H.H., Clean Hydrogen on demand, *Pan European Network Government* **15**: 168-169 (Aug. 2015), web link: http://www.paneuropeannetworkspublications.com/GOV15/files/assets/basic-html/page-1.html# (last accessed: 02/08/2016).
2) Vogel B., Wasserstoff aus der Batterie, Swiss Engineering STZ 113, pp.12-15 (May

2016), http://www.paperlit.com/webreader/read/swissengineeringkiosk/2016-05-01#/swissengineeringkiosk/2016-05-01?page=1 (last accessed: 02/08/2016).

In newspapers:

1) "La STEP comme un laboratoire grandeur nature!", Le Nouvelliste, 28th of May 2014, http://www.lenouvelliste.ch/articles/valais/martigny-region/la-step-comme-un-laboratoire-grandeur-nature-328550
2) Monay Patrick, "La station-service du future prend forme à Martigny", 24heures, 12th of November 2014, http://www.24heures.ch/auto-moto/La-stationservice-du-futur-prend-forme-a-Martigny/story/24501184 (last accessed: 02/08/2016).
3) Carrupt Aline, "Martigny met les gaz sur l'hydrogène", Le Nouvelliste, 12th of November 2014, http://www.lenouvelliste.ch/articles/valais/martigny-region/martigny-met-les-gaz-sur-l-hydrogene-353214 (last accessed: 02/08/2016).
4) Davaris S. "Du soleil et du vent en boîte", *Impact Journalism Day – Tribune de Genève*, 20th of June 2015, http://ijd.tdg.ch (last accessed: 02/08/2016).
5) Davaris S. "Du soleil et du vent en boîte", *Impact Journalism Day – 24heures*, 20th of June 2015, http://ijd.24heures.ch (last accessed: 02/08/2016).
6) Davaris S. "Storing wind, solar energy", *Impact Journalism Day – The Straits Times (Singapore)*, p. D5, 20th of June 2015.
7) Davaris S. "Almacenando el sol y el viento", Impact Journalism Day – *Excelsior, El Periodico de la Vida Nacional (Mexico)*, p. 6, 20th of June 2015.

At the TV or on radio:

1) On the 11th of November, at the 19H30 journal of the RTS: http://www.rts.ch/play/tv/19h30/video/la-revolution-des-vehicules-ecologiques-est-en-marche?id=6298594 (last accessed: 02/08/2016).
2) On the 12th of November, at the journal on Canal 9: http://canal9.ch/le-journal-du-12-11-2014/ (last accessed: 02/08/2016).

Some of the visits organised on the site:

1) Open day during the whole day and visit of high profile guests from EPFL in the evening of the 26th of May 2014 for presentation of the project, of the vision of the laboratory and the objectives of the project.
2) Visit associated to the 2014 International Society of Chemistry (ISE) Annual meeting taking place in Lausanne (31st of August – 5th of September 2014). A visit of the demonstrator site was organised for the interested participants. We had visits from participants interested in RFBs from the whole Europa in a rather informal way.
3) Official inauguration of the installation on the 11th of November 2014. About 60 persons were participating, including Professors from EPFL, politicians and visitors

4) Visit for the participants of the 2015 EuroTech Winter School on the 11th of February 2015: 60 students for all over Europe discovered the project. Dr. Heron Vrubel gave a presentation of the project and students could ask questions.
5) Visit from the RIE association members (Association for the Energy Research and Innovation) after a presentation made to them in Martigny on the 30th of April 2015. A visit of about 20 experts in the field of energy conversion, storage and management.
6) Numerous other visits from small group from the whole Europe, mostly scientists, but also regional politicians and experts in the field of energy storage over the 2 years.

4. National and international cooperation

At the national level, this project was in itself strongly connected with the utilities company of Martigny, Sinergy, the district of Martigny and a research centre, CREM, also situated in Martigny. These partnerships led to numerous enthusiastic discussions about the applicability of the concept and about the future of this project, of the battery technologies and of energy storage in general. The set-up of a hydrogen economy was also widely discussed in the frame of the project.

Moreover, this project was also involved in the frame of the Swiss Competence Center for Energy Research Heat and Electricity storage (SCCER HaE) for the period 2014-2016. It is included in the working package (WP) 3, which is in charge of studying and developing hydrogen production and storage means and appeared to be, so far, the only demonstration system of this WP. Through the SCCER, collaboration with scientists at the PSI was set up for a thorough life-cycle analysis of the present system. This did not result in clear results so far due to the difficulty of finding the appropriate data as this kind of battery were only sparsely studied in this perspective.

In the frame of EPFL, collaboration with the group of Prof. Dominique Bonvin was established for the modelling and the optimization of the use of the dual-circuit RFB. Moreover, with the moving of the laboratory to the new EPFL Energypolis Campus in Sion, new collaborations with professors of the HES Sion are being discussed to continue this project.

At the international level, the project has mainly evolved in a national environment. The all-vanadium RFB however has been provided by Cellstrom, an Austrian company, which is part of Gildemeister, a german company. Along this first year, the concept of dual-circuit RFB and the advancement of the demonstrator system was presented in numerous high-visibility and specific international conferences during the whole project time, mostly abroad and several posters have also been exposed to international conferences. The project attracted interest, in particular for its innovative approach to perform water electrolysis and to circumvent the low energy density of RFBs. However, some people also showed scepticism and expect more proofs of its viability, which was the main goal of this pilot scale project. Future international collaborations were envisaged, which may however only start after the end of the present project. For instance, the project was included into proposals for EU funding.

5. Evaluation of the project and outlook

In view of the results obtained in the frame of this demonstration project that are summarized in the present report, the project can be considered as successful. Indeed, the milestones have been reached. We achieved the main goal of the project, which was the scale-up of the system and we have been able to produce hydrogen from the RFB charged electrolytes. We demonstrated therefore that this concept was technically feasible and is worth to be studied and developed further. We strongly believe that with more development works, it has a good potential for a further commercialization, especially in the form of a dual-circuit system that could be appended to a classical RFB. It can also be noted that RFBs based on cerium have regained interest amongst researchers and will hopefully leads to significant advancements in these cells design. This way, the system could potentially be re-orient towards the full indirect water electrolysis in acidic conditions, as initially intended. Moreover, alternative approaches for indirect water electrolysis are currently being published in high-impact factor journals, showing a new trend and strong interest in the research field for this water electrolysis perspective.

Moreover, a large amount of new knowledge was acquired by the research team. This includes a much better understanding of the functioning of RFBs, of their technical challenges but also on their acceptance level by energy storage experts and by the public. We believed that we could raise awareness about this type of batteries, which were almost unknown in Switzerland at the beginning of the project. Moreover, the development of the dual-circuit itself brought insights on the requirements of such a process in terms of large amount of catalyst fabrication capabilities, but also on the necessity of designing a cost-effective system to justify its addition to a classical RFB. We also had to face the technically safety aspects –and the absence of clear norms in Switzerland– associated with the production of hydrogen and its storage.

In terms of outlook, the research and development of a chemical discharge of the positive electrolyte will be continued. It may focus on the use of SO_2 in the fuel cell system, as described above, but alternative methods and systems are also being currently imagined for this reaction.

Moreover, based on the aspects discussed above, we believe that the pure redox flow battery system is very promising for the storage of energy at the scale of 100 kWh-several MWh. Indeed, they are particularly well suitable for responding to fluctuations of the production of electricity by photovoltaic panels and wind turbines. We therefore plan to connect in

DC the battery bought in the frame of this project with a series of photovoltaic panels (approximately 7 kW) in order to evaluate the gain of efficiency due to the DC-DC connection, but also to test in more details the response of the battery to such a variable power input. Moreover, design and dimensioning questions, such as the relationship between the power of the photovoltaic panel installation and the capacity of a coupled RFB will be investigated. This arrangement shall require a new control system for the battery, which will be develop in the frame of our laboratory and it shall be implemented by the end of 2016 in the demonstrator site of Martigny, if the project is accepted by the local authorities.

Finally, preliminary experiments showed that it was possible to produce hydrogen under (high) pressure using the chemical discharge of the negative electrolyte by direct electrochemical compression. In this case, no (or less) compression energy from an external compressor is required, improving significantly the efficiency of the electrolysis process. Moreover, in terms of engineering it is simpler to design a high-pressure chemical reactor than a high-pressure electrochemical cell or stack. This approach is currently being investigated at the more fundamental level and may be investigated at the demonstrator level in the future.

6. References

[1] Amstutz V. *et al.*, *US Patent Application N°61/606712*, PCT 2013.

[2] Amstutz V. *et al.*, *Energy Environ. Sci.* **7**, 2350-2358 (2014).

[3] Peljo P. *et al.*, *Green Chem.* **18**, 1785-1797 (2016).