

Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems

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Abstract

The all-vanadium redox-flow battery is a promising candidate for load leveling and seasonal energy storage in small grids and stand-alone photovoltaic systems. The reversible cell voltage of 1.3 to 1.4 V in the charged state allows the use of inexpensive active and structural materials. In this work, studies on the performance of inexpensive active materials for use in vanadium redox-flow batteries are reported. Additionally, a cost analysis for a load leveling and a seasonal energy storage system is given based on a flow battery technology well established in Zn-flow batteries.

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1. Introduction

The availability of a reliable storage medium is of critical importance for a fail-safe electricity supply to the end customer. In large grids, the storage function is taken care of by the grid itself. However, in the case of small grids or even stand-alone electricity generation, particularly when relying to a significant degree on a stochastic supply of renewable energy such as solar or wind, reliable and inexpensive electricity storage is of crucial importance.

The technical boundary conditions to electricity storage are resulting from two distinctly different requirements depending on the service conditions of the battery. Two genuinely different fields of application can be defined, i.e. load levelling/peak shaving and seasonal energy storage.

In the case of load levelling/peak shaving, storage media showing high energy efficiency are required. Furthermore, high power density as well as the capability to withstand a large number of deep discharge cycles would be required. However, the storage device could be of moderate capacity, even moderate self discharge could be acceptable.

For applications in seasonal storage, large capacities are required. Furthermore, low rates of self-discharge would be desirable. However, moderate energy efficiency and power

density could be acceptable. The storage device would typically be operated on a great number of shallow cycles and a low count of deep cycles.

Fig. 1 shows the battery current during a typical summer month in a stand-alone PV/wind installation in Portugal. The battery (48 V) consisted of 24 lead-acid cells having a capacity of 750 Ah. PV and wind generator had a peak power of 1.4 kW each. The load was limited by the inverter to 5 kW. It is evident that this installation has a base load of approximately 3 A even during night time. During day time charging currents up to 20 A are observed. Discharge current peaks are reaching up to 55 A in single cases. The seasonal variation of charge to or from the battery of this system is shown in Fig. 3. It is obvious that the battery underwent one deep cycle during this period staying at shallow state-of-charge over an extended period of time.

During bright and sunny days as shown for example in Fig. 2 however, it is obvious that not all the energy which possibly could be harvested can be stored in the batteries. In fact, the battery reached its nominal end of charge voltage (56.4 V) quite early during the day. The battery controller then allowed for equilibrium charge at 63.4 V for several hours before setting back to normal.

As can be seen in Fig. 3, there has been an energy surplus equivalent to approximately 600 Ah accumulated over the year when adding up all current to and from the battery which could not be stored in the batteries available.

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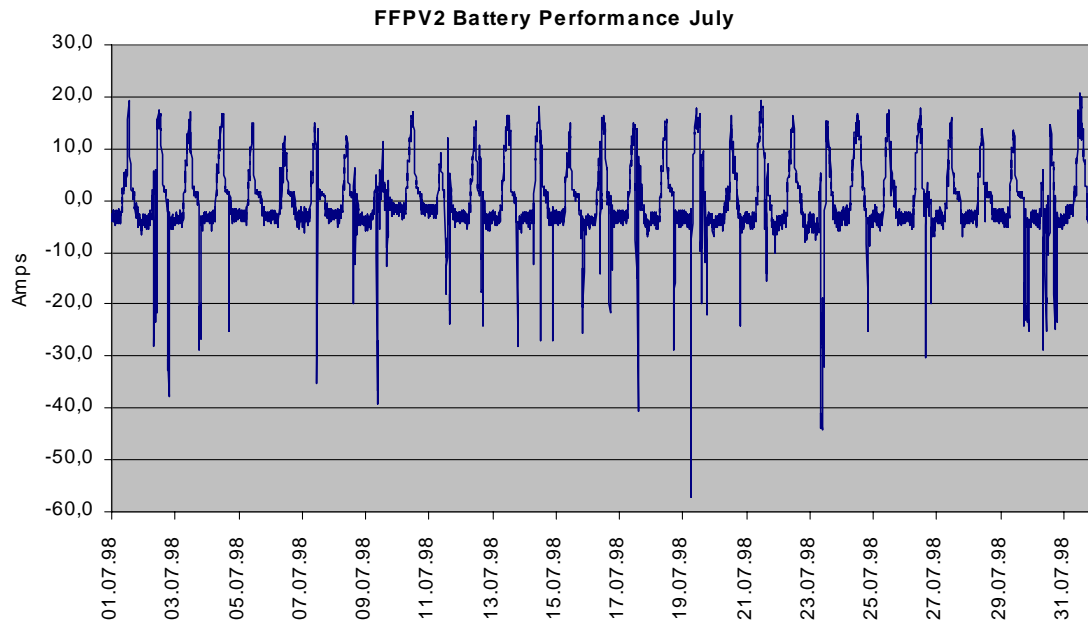


Fig. 1. Current going to and from a battery of a stand-alone combined photovoltaic and wind energy system during a typical summer month in an installation in Portugal. The generators had a peak power of 1.4 kW each. Load was limited to 5 kW by the inverter. The battery consisted of a 48 V (24 cells) 750 Ah lead–acid battery.

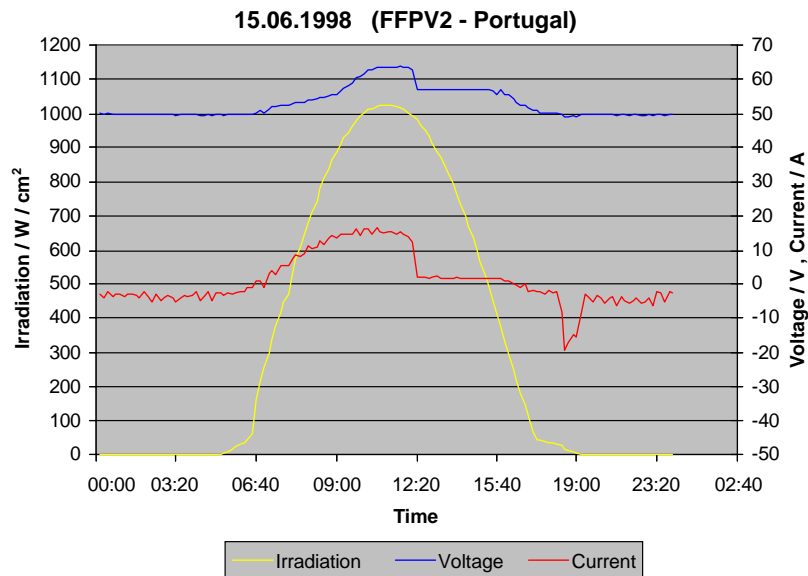


Fig. 2. Balance of irradiation, voltage and battery current during a bright summer day at the PV/wind system described in Fig. 1.

As can be seen from the data shown in Figs. 1–3, an ideal storage device for small grids or stand-alone power supplies must be able to carry out load leveling on a day to day basis, additionally, it should be able to provide seasonal buffer.

2. Properties of electrochemical power sources

Normally, secondary batteries such as the well known and reliable, lead–acid battery are used to act as a buffer in small electric grids or stand-alone PV/wind applications. Never-

theless, seasonal storage and buffering of high loads are difficult to achieve since capacity and power of the system are closely related to the cell construction. Furthermore, in applications involving seasonal energy storage, the lead–acid battery will be operated at low states of charge for extended periods.

Fuel cells are converting chemical energy available from the oxidation of fuel (e.g. hydrogen or methanol) by an oxidant (e.g. oxygen from air) directly into electricity. Their operating behavior is similar to a primary battery having an infinite capacity. Fuel production (e.g. by water electrolysis

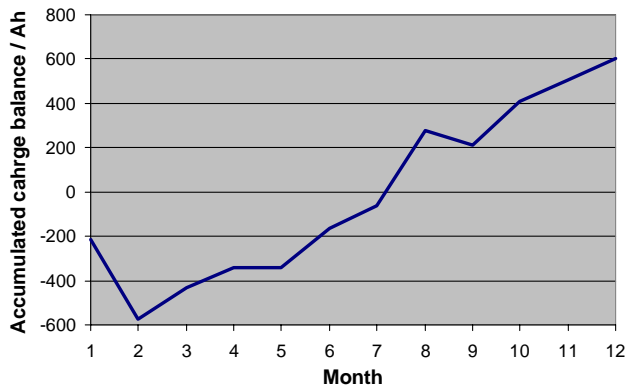


Fig. 3. Accumulated charge balance over 1 year of a 750 Ah 48 V battery used in a stand-alone PV/wind system as described in Fig. 1.

or steam reforming) is normally carried out in a separated reactor. In fuel cells, capacity and power of the system are completely separated.

Flow-type batteries can be considered an intermediate between classical secondary batteries and fuel cells. In flow-type batteries, energy is stored by driving electrochemical reactions, e.g. by electrolysis of metal salts. In this case the same reactor is used for charging and discharging of the storage system. They are consisting of storage tanks containing the active mass, typically as a solution of metal salts as well as an electrochemical reactor, typically a cell stack, capable of electrically charge and discharge the salt solutions. Self discharge can be minimized by minimizing the contact time of fuel or reactants inside the stack.

From a practical point of view, storage of the reactants is a very important issue in the system layout. Generally speaking, the storage of gaseous fuels such as hydrogen or methane requires either large high pressure tanks or cryogenic storage which itself is prone to “thermal self discharge”.

As compared to solid-state batteries, there are the following potential advantages:

- essentially, no self-discharge during the storage period;
- no solid-state phase changes during charge and discharge;
- state-of-charge can be determined easily from Nernstian equation using a single indicator cell;
- the electrolyte solutions containing the active species can be used infinitely.

Table 1
Redox couples and their electrochemical standard potentials [10]

Negative		Positive	
V^{3+}/V^{2+}	-0.255 V	$VO_2^+ + 2 H^+/VO^{2+} + H_2O$	+0.991 V
		HVO_3/VO^{2+}	+1.250 V [8]
		$VO^{2+}/H_2VO_4^-$	+1.314 V [8]
Cr^{3+}/Cr^{2+}	-0.407 V	Fe^{3+}/Fe^{2+}	+0.771 V
$ZnO_2^{2-} + 2 H_2O/Zn + 4OH^-$	-1.215 V	$O_2 + 2H_2O/4OH^-$	+0.401 V
Zn^{2+}/Zn	-0.762 V	$Br_2(aq)/Br^-$	+1.087 V
$2S/S_2^{2-}$	-0.428 V		

3. The vanadium redox-flow battery

Redox-flow batteries have been described initially in the early 1970s [1]. Some of the technically interesting redox couples are listed in Table 1. Initially, redox-flow batteries were based on the Fe^{2+}/Fe^{3+} redox couple at the positive electrode and the Cr^{2+}/Cr^{3+} redox couple at the negative electrode. Poor reversibility of the chromium half-cell, cross contamination of the half-cell solutions by diffusion as well as a considerable evolution of hydrogen as a side reaction at the negative electrode turned out to be the most serious drawbacks of the system despite the fact that systems up to the kW range have been built in the US [2] and Japan. An extensive review of redox-flow battery development up to the late 1980s has been given by Bartolozzi [3]. In the late 1980s, an all vanadium redox-flow battery has been suggested by Skyllas-Kazacos and coworkers [4–6]. The vanadium single metal system is involving the same metal in both half-cells. The negative half-cell is using the V^{2+}/V^{3+} redox couple whereas the positive half-cell is generally using the V^{4+}/V^{5+} redox couple. The positive and the negative vanadium redox couples show sufficient kinetics [7,8]. However, only V^{5+} , V^{4+} and V^{3+} are stable in air. V^{2+} is easily oxidized by atmospheric oxygen. The basic thermodynamics of the all-vanadium redox-flow battery has been described in [9].

Since pure graphite proved to be unstable in contact with the positive electrode several studies have been carried out to identify appropriate electrode materials [7,11–13]. Additionally, the properties of separator membranes used in redox-flow batteries have been studied extensively [14–17].

Since vanadium salts are considered more expensive than iron or chromium, inexpensive sources of vanadium have been investigated. An inexpensive source of vanadium can be found in the boiler soot when burning certain qualities of mineral oil [18].

Although V^{2+} , V^{3+} and V^{4+} species are easily soluble in sulfuric acid even in high concentrations, the long term stability of concentrated V^{5+} solutions is rather limited due to the formation of insoluble V_2O_5 precipitates preferably occurring at elevated electrolyte temperatures.

The stability of V^{5+} containing electrolytes has been investigated [19,20]. It has been found that 0.9 molar V^{5+} solutions are stable even at elevated temperatures. However, the apparent stability of solutions containing higher con-

centrations is only kinetically controlled. Furthermore, the stability of V^{5+} solutions towards precipitation can be increased by increasing the concentration of sulfuric acid. The stability of high concentrations of vanadium in sulfuric acid also increased in partly charged solution, i.e. when mixtures of V^{5+} and V^{4+} salts are present. Similar results have been found in our own laboratories [21]. This investigation also showed that the use of complexing agents does not lead to a significant improvement of the stability of technical electrolyte which is in contrast to work reported earlier [22]. Nevertheless, it has been claimed that V^{5+} precipitates could be redissolved during discharge of the battery [19].

An environmental assessment of the vanadium redox-flow battery has shown benefits as compared to conventional lead–acid batteries [23].

Based on its properties, the vanadium redox-flow battery can be considered as a suitable candidate for load leveling/peak shaving and as a seasonal energy storage device in stand-alone photovoltaic applications [8].

4. Layout of a vanadium redox-flow battery for stand-alone photovoltaic systems

A battery design for substitution of the battery described in the introduction operated under conditions shown in Fig. 1 has been developed by Powercell in order to substitute the lead–acid batteries.

In this battery, electrodes of an area of 1.100 cm^2 are completely welded in a polymer frame. The polymer frames themselves are welded to form a battery stack. When analyzing the system requirements, a maximum sustained charging current of 25 A (23 mA/cm^2) for a 36-cell battery (nominal voltage 48 V) is expected. A maximum discharge current of 60 A (55 mA/cm^2) should be sustained for several minutes by the same battery.

In principle, flow-type batteries can be designed to flow the electrolyte through a porous electrode (flow-through-design). A different basic construction principle is to pass the electrolyte in front of an activated electrode (flow-by-design). Fig. 4 shows a schematic drawing of both construction principles.

Based on a general study [24], a flow-by design has been chosen initially for this work since it was considered more advantageous for the application intended. In this case, highly active electrodes would be required in order to achieve current densities sufficient for the application intended.

Initially, the properties of active components (i.e. carbon electrode and separators) have been investigated in a laboratory-sized single cell having an active area of 10 cm^2 . The cell has been charged at a current density of 40 mA/cm^2 up to a voltage of 1.7 V followed by a constant voltage charge for 15 min. After charge, the cell has been discharged at 40 mA/cm^2 to a voltage of 0.9 V. The charging voltage has been limited to 1.7 V in order to avoid damage to the

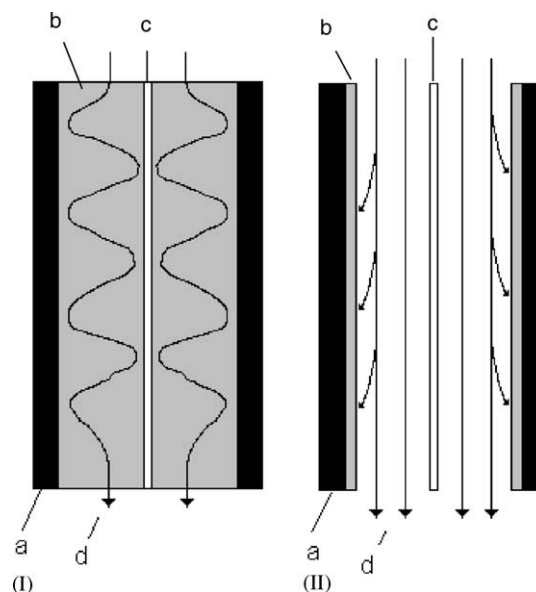


Fig. 4. Schematic picture of different flow battery design principles: (I) flow through geometry; (II) flow-by geometry. (a) electrode, (b) active layer, (c) separator, (d) electrolyte flow.

glassy carbon current collectors which has been observed to occur rapidly at voltages above 1.9 V.

In order to compare the electrode performance, the average voltage upon charge as well as the average voltage upon discharge have been calculated and compared. Furthermore, the voltage at the start of discharge and at the start of charge are compared.

In total, 30 different activation layers made from mechanically robust porous materials (e.g. cloth, felt or other non-woven structure) having a thickness up to 0.5 mm have been investigated. Fig. 5 shows a comparison of the most promising materials. It has been found that PAN-based carbon felts produced at a graphitization temperature of $1900\text{ }^\circ\text{C}$ and thermally treated at a temperature of $400\text{ }^\circ\text{C}$ in air for 30 h are showing acceptable performance in single cell experiments.

A total of 12 different separator materials have been investigated. As expected, anion exchange membranes showed the highest Ah and voltaic efficiencies. However, it has been found that inexpensive oil filled microporous separators typically used in lead–acid batteries show similar performance as expensive cation exchange membranes such as Nafion 112. Furthermore, microporous separators coated with a thin layer of a cation exchange resin (Nafion 112) are showing acceptable reversibility and stability in the electrolyte thus confirming previous results of Chieng et al. [15]. However, imbalances with respect to water transport have been observed.

In general, the following conditions have to be met for the operation of vanadium redox-flow cells.

- Electrodes require high electric conductivity and good wettability.

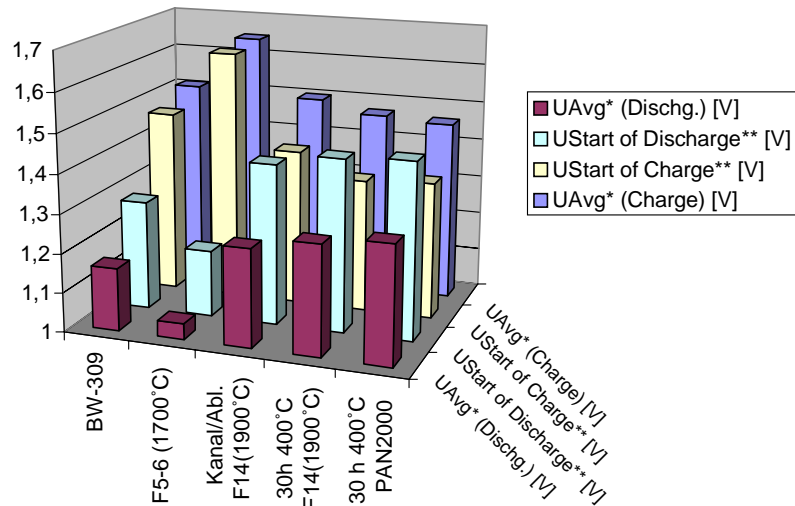


Fig. 5. Comparison of characteristic data of activation layers at a current density of 40 mA/cm^2 at room temperature. Negative electrolyte: 1 mole/l $\text{V}_2(\text{SO}_4)_3$ in 2.5 mole/l H_2SO_4 . Positive electrolyte: 1 mole/l VOSO_4 in 2.5 mole/l H_2SO_4 . Constant current charge at 40 mA/cm^2 up to 1.7 V afterwards constant voltage charge for 15 min. Constant voltage discharge at 40 mA/cm^2 .

- Charging voltage has to be limited to a maximum of 1.7 V in order to avoid damage to the carbon current collectors.
- Good electrical contact to the bipolar plates/current collectors is essential, this is best achieved when the activation layers are thermally bonded to the current collector.
- Access of oxygen to the negative electrolyte compartment has to be avoided.

When operating the cell, full reversal of the cell polarity has been possible without damaging the cell. An additional important parameter influencing the Ah efficiency is the flow velocity of the electrolyte. High Ah efficiency is observed at high flow velocities. Furthermore, higher current densities can be achieved when operating the cell at high electrolyte flow velocity.

In order to optimize the contact area between electrolyte and the electrodes, structured activation layers have been used. The flow channel structures have been embossed to the raw PAN felt before carbonization.

5. Cost analysis

Based on laboratory cell experiments carried out in this project, the amount of $6 \text{ kg V}_2\text{O}_5/\text{kWh}$ of battery capacity could be confirmed. Furthermore, a 2 kW system could be realized using a 32-cell stack of 1100 cm^2 active area operating at an average discharge voltage of 1.1 V at a current density of 52 mA/cm^2 .

Based on the current raw material situation and after a critical assessment of materials cost and the production technology available at Powercell and potential suppliers of vanadium electrolyte, the following cost estimation can be given for the battery developed within this project (Table 2). Costs for stack production are taken for a lot of 1700 units. Since the electrolyte is the most expensive part, costs for electrolyte preparation are taken on a single order basis.

With regard to the data given by Skyllas-Kazacos et al. [25], higher costs are assumed for V_2O_5 and electrolyte preparation which are due to the current market situation.

Table 2
Cost estimation for a 2 kW, 30 kWh system based on an annual production of 1700 units

	Amount required	Cost per unit	Total cost (2 kW, 30 kWh)
Current density	52 mA/cm^2		
Electrode area	$1.75 \text{ m}^2/\text{kW}$		
V_2O_5 energy density	6.0 kg/kWh		
Activation felt	$3.5 \text{ m}^2/\text{kW}$	$\text{€} 50 \text{ m}^{-2}$	$\text{€} 350$
Bipolar plates		$\text{€} 65 \text{ kW}^{-1}$	$\text{€} 130$
Flow frames, etc.		$\text{€} 435 \text{ kW}^{-1}$	$\text{€} 870$
Separator	$2.1 \text{ m}^2/\text{kW}$	$\text{€} 25 \text{ m}^{-2}$	$\text{€} 105$
V_2O_5	180 kg	$\text{€} 13.6 \text{ kg}^{-1}$	$\text{€} 2448$
Electrolyte preparation	For 180 kg V_2O_5	$\text{€} 3 \text{ kg}^{-1}$	$\text{€} 540$
Tanks	2 at 55001	185 ECU	$\text{€} 370$
Pumps	2	$\text{€} 160$	$\text{€} 320$
Battery management system	1	$\text{€} 500$	$\text{€} 500$
Total			$\text{€} 5673$

Table 3

Cost estimation for a 2 kW, 300 kWh system to be developed within this project based on an annual production of 1700 units

	Amount required	Cost per unit	Total cost (2 kW, 30 kWh)
Current density	52 mA/cm ²		
Electrode area	1.75 m ² /kW		
V ₂ O ₅ energy density	6.0 kg/kWh		
Activation felt	3.5 m ² /kW	€ 50 m ⁻²	€ 350
Bipolar plates		€ 65 kW ⁻¹	€ 130
Flow frames, etc.		€ 435 kW ⁻¹	€ 870
Separator	2.1 m ² /kW	€ 25 m ⁻²	€ 105
V ₂ O ₅	1800 kg	€ 13.6 kg ⁻¹	€ 2448
Electrolyte preparation	For 1800 kg V ₂ O ₅	€ 1.5 kg ⁻¹	€ 2700
Tanks	2 at 55001	€ 420	€ 840
Pumps	2	€ 160	€ 320
Battery management system	1	€ 500	€ 500
Total			€ 29975

Furthermore, higher production costs for the components (bipolar plates, flow frames) of the completely sealed stack have to be taken into account. However, significant savings with respect to data given in [25] have been possible due to the use of less expensive separators which are commercially available in large quantities and activation layers which can be produced easily in large volumes.

The stack costs quoted in Table 2 are slightly higher than stack costs using standard materials used in the fabrication of Powercell Zn-flow batteries since this cost estimation allows for more expensive raw materials (separators, carbon activation layer). These costs become almost identical with the costs quoted in [25] however, a different distribution becomes evident.

Based on the assumptions shown in Table 2, production costs of less than € 6000/2 kW, 30 kWh module can be expected. Such a system would allow a 10 days autonomy in central Europe.

Table 3 shows the cost analysis for a larger storage capacity (300 kWh). Stack, pump and battery management system costs are identical to the values assumed in Table 2 since no technological changes are necessary in these components. Costs for electrolyte production are assumed to be down to € 1.51⁻¹ since larger quantities of electrolyte can be produced more economically. The value has been confirmed by vanadium suppliers. It can be seen from Table 3 that system costs for a 300 kW system are slightly below € 30000. However, the costs of vanadium redox-flow batteries are very sensitive to the market price for V₂O₅. If, vanadium can be produced as a by-product from boiler soot, still lower cost could eventually be achieved.

6. Summary

Vanadium redox-flow batteries could be a reasonable alternative for load leveling and seasonal energy storage in small grids and stand-alone photovoltaic systems.

It could be shown in laboratory experiments that cells could be operated using inexpensive components such as

structured carbon felt electrodes and coated microporous separators.

Limitations were encountered concerning the stability of the positive electrolyte towards irreversible precipitation of V₂O₅, eventually clogging the electrode. This has been particularly severe when the cell was operated at operation at elevated temperatures.

A cost analysis shows that vanadium redox-flow batteries could compete with current high capacity lead–acid batteries used in stationary applications.

Further work is required to translate the results achieved in the laboratory to a full-size battery.

Acknowledgements

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