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ABSTRACT

The vanadium flow battery has emerged as one of the most favourable types of flow batteries for a number of reasons, including the lack of cross-contamination that troubled many earlier systems such as the Fe/Cr flow battery. Because the vanadium flow battery employs the same metal ion in both electrolytes, albeit in different oxidation states, there is no cumulative loss in performance, just an effective reversible self-discharge current.

The self discharge that occurs in the vanadium flow batteries is limited to the electrolyte volume in the cells. However it can become substantial under low load conditions. The pumps also use power from the battery and may be considered as another source of self discharge. Taking these and maintenance considerations into account the layout of a 10 kW, 100 kWh, 48 V vanadium flow battery was designed as a "Multi-Stage-Operation" system to provide maximum performance at all levels of load, ease of use and optimum maintenance conditions.

Experimental: A complete energy storage system with 10 kW in power and 100 kWh in energy was designed. It consists of a vanadium flow battery with smart controller and configurable power electronics housed in a weatherproof housing. The battery can be charged and discharged at up to 10 kW and provides up to 100 kWh of energy. The smart controller ensures that the battery operates at maximum efficiency at all times and allows remote observation of various battery parameters, including a reliable state of charge (SOC) measurement. The option of different arrangements of power electronics gives almost complete freedom in specification of electrical output (dc, single or three-phase ac). The battery can also be connected to photovoltaic, wind turbine, diesel/petrol/gas/biogas generators, fuel cells and water turbines to form discrete autonomous power supplies or to be part of a micro-, mini- or smartgrid. The FB10/100 battery for "Multi-Stage-Operation" is comprised of 5 strings of 36-40 cells each in 3 separate fluid circuits. The first fluid circuit, containing a single string, is always actively pumped with electrolyte and electrically connected to the charger and load. The second and third fluid circuits contain 2 strings each and are only actively pumped and electrically connected when the voltage reaches preset limits. When the circuits are in "standby", i.e. not actively pumped and electrically connected, the self discharge is limited to the small volume of electrolyte in the cells. There is also a significant saving of pumping energy, because 3 pairs of small pumps are used in place of 1 pair of more powerful pumps. Results: In "Multi-Stage-Operation" mode, the overall battery performance is improved significantly. This is very important in off-grid installations, where loads are typically small compared to the power levels necessary for charging; i.e. a solar powered telemetric station may use 500W continuous power but

requires fast charging due to the narrow time window when solar energy is available. In example, at a 1 kW load the battery provides 25% more energy when operated in "Multi-Stage-Operation" mode compared to all stacks in operation.

Since 2008, several power station have been equipped with FB10/100 storage units and put into operation. Within the presentation a report on the latest results including technical performance and cost issues will be given.

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1. Introduction

Batteries with flowing electrolyte have been around since the 19th century [1], although this was mainly to dislodge gas from the electrodes. There were also early hybrid systems, such as the Zn–Cl₂ battery [2] and redox fuel cell [3], which were typically primary cells.

The first reference to a "modern" redox flow battery with pumps, tanks, reactors, is from Kangro [4,5]. This included a range of systems and also applications, for example with wind turbines, and photovoltaics as UPS systems.

Although a few other systems were proposed and the first serious development work was conducted by NASA [6–9] in the 70s to 80s, this was mostly on the Fe–Cr system. Pelligri also suggested vanadium couples in 1978 [10], although he was preceded by the NASA work and vanadium couples had been proposed for hybrid systems [3,11]. Skyllas-Kazacos proposed and developed the standard vanadium redox flow battery with sulphuric acid electrolyte [12–18]. Sumitomo Electric Industries had originally been developing the Fe–Cr system [19–24], following the NASA work, but changed to the vanadium system [25–27] with the Australian developments. Other Japanese companies had also taken part in the Moonlight project to look at a range of batteries, including redox flow, such as Tohoku Electric Power Co., Furukawa Electric Power Co. and the Kansai Electric Power Co. [28,29].

The vanadium flow battery has emerged as one of the most favourable types of flow batteries for a number of reasons, including the lack of cross-contamination that troubled many earlier systems such as the Fe/Cr flow battery. Because the vanadium flow battery employs the same metal ion in both electrolytes, albeit in different oxidation states, there is no cumulative loss in performance, just an effective reversible self-discharge current.

The self discharge that occurs in the vanadium flow batteries is limited to the electrolyte volume in the cells. However it can become substantial under low load conditions. The pumps also use power from the battery and may be considered as another source of self discharge. Taking these and maintenance considerations into account the layout of a 10 kW, 100 kWh, 48 V vanadium flow battery was designed as a "Multi-Stage-Operation" system to provide maximum performance at all levels of load, ease of use, and optimum maintenance conditions.

In summary, the vanadium flow battery has outstanding properties over conventional batteries due to

- the liquid energy carriers, which allow individual combinations of energy and power and state of charge reading,
- the fact that only one metal species is involved in the electrochemical redox reaction, which results in almost unlimited use of the energy carrying liquids and in turn is an important economic factor since the liquids can be reused without recycling,
- the chemical reaction upon charging is of an endothermic nature, giving opportunity to charge at same rates as discharges can be performed,
- the electrode/current collector materials are robust against deep discharges.

During product development, the unique features of the technology have been topped by a functional design. This includes:

weather-proof housing, intelligent battery control and temperature management, state of charge (SOC) control, multi stage operation, and remote control function.



Fig. 1. Cellcube FB 10/100 overall design showing fluid lines and power stacks.

2. Experimental

Flow battery design starts with the application requirements. Battery design for off-grid applications in remote areas with the input from renewable resources will have to focus on very low power consumption for pumps, controls, and communication system, and typically have power to energy ratio of 1:10 or higher, depending on the bridging time when no input generation is available. On the other hand, batteries for weak grid support require power to energy ratios of 1:1 or lower, depending on the typical out time of the grid. This paper describes a system that can meet the requirements for remote off-grid users.

A complete energy storage system with 10 kW nominal power and 100 kWh energy was designed. It consists of a vanadium flow battery with smart controller and configurable power electronics housed in a weatherproof housing. The battery can be charged and discharged at up to 10kW and provides up to 100kWh of energy. The smart controller ensures that the battery operates at maximum efficiency at all times and allows remote observation of various battery parameters, including a reliable state of charge (SOC) measurement. The option of different arrangements of power electronics gives almost complete freedom in specification of electrical output (dc, single or three-phase ac). The battery can also be connected to photovoltaic, wind turbine, diesel/petrol/gas/biogas generators, fuel cells and water turbines to form discrete autonomous power supplies or to be part of a micro-, mini- or smart-grid. In Fig. 1, a picture of the Cellcube FB10/100 is shown.

The most obvious difference to other flow battery designs is the position of the tanks, which are located in the bottom half of the container. These and other technical details are shown in the technical drawings in Fig. 2.

The Cellcube FB10/100 battery was originally designed for offgrid applications with the requirement of fast charging when sun/wind is available, and slow discharging, due to small loads. In such a case, power consumption from pumps, and self-discharge in the power stacks need to be reduced. For this application, the "Multi-Stage-Operation" was constructed. It is comprised of 5 strings of 36–40 cells each in 3 separate fluid circuits. The first fluid circuit, containing a single string, is always actively pumped with electrolyte and electrically connected to the charger and load. The second and third fluid circuits contain 2 strings each and are only actively pumped and electrically connected when the voltage reaches preset limits. When the circuits are in "standby", i.e. not actively pumped and electrically connected, the self-discharge is limited to the small volume of electrolyte in the cells. It amounts 33 W per string. There is also a significant saving of pumping energy,



Fig. 2. (a and b) Schematics of the technical layout of the Cellcube FB10/100.



Fig. 3. Schematic layout of the "Multi-Stage-Operation" mode, showing number and position of pumps, power stacks connected to strings and electrical connections. A high current switch (HCS) connects and disconnects the individual strings of the battery.

because 3 pairs of small pumps are used in place of one pair of more powerful pumps. A schematic of the electrical connections and fluid lines of the multi stage system is given in Fig. 3.

3. Results

3.1. Battery performance

Battery performance is given as charge and discharge behavior. In Fig. 4, state of charge (SOC) in % and DC-power are shown as a function of time. The battery charges at 12.6 kW in the low SOC regime and up to about 47%. Then, charging power decreases gradually until about 87% SOC has been reached. From then, charging is proceeding slowly due to a pre-set voltage limit to avoid hydrogen evolution from overcharging. The onset for voltage controlled charging results in a sudden drop in the charging power. From Fig. 4, it can be seen that 87% SOC are reached within 11 h in a string of 36 cells. This SOC indicates the typical level, up to which the battery



Fig. 4. Cellcube FB10/100 charging power and state of charge (SOC) as a function of time.



Fig. 5. Cellcube FB10/100 discharging behavior and state of charge (SOC) as a function of time.



Fig. 6. Cellcube FB10/100 performance at 1 kW load in "Multi-Stage-Operation" mode compared to "all strings pumping".

can be charged easily. In order to decrease the charging time, more cells will have to be added. The data shows stem from strings with 36 cells.

In Fig. 5, discharge of the battery is shown as a function of time. It can be seen, that constant power of about 12.5 kW is given off between 87% and 28% SOC. This regime demonstrates the optimum operation capacity. Although discharge can proceed to lower SOC values without damaging the battery, in practical use the battery capacity will be limited by the inverters due to pre-set voltage limits. Again, with more cells per string, more capacity could be drawn from the battery.

In "Multi-Stage-Operation" mode, the overall battery performance is improved significantly. This is very important in off-grid installations, where loads are typically small compared to the power levels necessary for charging; i.e. a solar powered telemetric station may use 500 W continuous power but requires fast charging due to the narrow time window when solar/wind energy is available. In Fig. 6, state of charge (SOC) of the battery at a 1 kW load is shown when operated in "Multi-Stage-Operation" mode compared to all stacks in operation. A total energy of about 25% is gained using multi stage operation. However, there is also a disadvantage using "Multi Stage Operation", and this is due to the response time to higher loads, which is needed to start up pumps of circuits 2 and 3. A delay time of up to 1 min is observed until full power can be delivered. With appropriate power management, this disadvantage can be easily overcome. When all 3 fluid circuits are in operation, the response time to a sudden increasing load is quite fast. In Fig. 7, the battery response in terms of power and voltage as a function of time is shown when 10 kW halogen lamps were switched on. The battery provides the required power within a few milliseconds.



Fig. 7. Cellcube FB10/100 response of voltage and current to a sudden maximum load as a function of time with "all strings pumping".

Table 1

Cellcube FB10/100 availability at different output powers and corresponding DC battery powers.

DC power [kW]	AC power [kV A]	Available discharging time [h]		
2.2	2	44		
3.75	3.6	23		
6.1	5.5	15		
8	7.2	11		
8.15	7.4	10		
9.55	8.65	9		
11.9	10.6	5		

The goal of the product design was to achieve a turn-key solution. The parameters important to the customer are therefore related to output data such as AC power or energy. To a good part, the AC output power is related to the size and quality of the inverter. In Table 1, characteristic DC battery powers, corresponding AC output powers and discharge times are given.

Another important feature of the FB10/100 design is the temperature management with in the various compartments. The two compartments of the battery are both vented diagonally with air to maintain the inside temperature at a certain level. The battery operates at its optimum between 20 and 30 °C, however, care has to be taken not to exceed temperatures where vanadium pentoxide species can precipitate. Precipitation is a function of the total vanadium concentration, SOC, and temperature. Therefore, the system is equipped with several temperature sensors and control functions. Ventilation is used to keep the temperature within the optimum operating regime.

In Fig. 8 energy output at different power levels is shown as a function of the energy consumed by ventilation, pumps and controls in relation to the energy to the inverter. At all 3 power levels shown, the energy losses are less than 10%.

3.2. System cost

The total initial cost of the storage system is comprised of: (i) cost related to power, (ii) cost related to energy, and (iii) cost related to balance of plant. In flow batteries, cost/kW and cost/kWh, can be related to the cost of power modules and the cost of electrolyte including tanks, and sensors, respectively. The remainder then refers to the balance of plant cost and will be dependent on the ratio between power and energy. By simply dividing the total cost by the number of kWs and kWhs without the information on the ratio between kW and kWh has no meaning for comparison. Since the ratio kW kWh⁻¹ will vary from different product designs, it is suggested that cost comparison among energy storage systems and grid electricity should be based on the cumulated energy delivered over the lifetime of the battery. This should be treated as a business



Fig. 8. Cellcube FB10/100 Energy output at different load levels in "Multi Stage Operation". Data were taken at different temperatures T2 > T1; this is reflected in a higher energy consumption for the ventilation.

488 Table 2

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Cost comparison	FB10/100	with	conventional	batteries.

Description	Unit	Battery type					
		Mass production			Series > 1000	Series < 20	Series > 100
		Pb/acid cheap quality	Pb/acid good quality	Pb/acid top quality	Li-ion	FB10/100 stacks, tanks, liquids, pumps, controller	FB10/100 stacks, tanks, liquids, pumps, controller
Sales price	\in kWh ⁻¹	150	200	300	1000		
Investment/installation	€	15,000	20,000	30,000	100,000	70,000	60,000
Nominal energy	kWh	100	100	100	100	100	100
Cycles (50% DOD)		1200	1,700	2,000			
Cycles (70% DOD)					3,000	5,000	5,000
Cumulative energy	kWh	60,000	85,000	100,000	210,000	350,000	350,000
Number installations for performance break even		5.8	4.1	3.5	1.7	1.0	1.0
Total Investment for performance breakeven	€	87,500	82,353	105,000	166,667	70,000	60,000
Price from Investment	$\in kW_{cum}^{-1}$	0.250	0.235	0.300	0.476	0.200	0.171

Calculations based on cumulative energy performance. Costs relate to battery pack only, balance of plant not included. O+M costs 30–50% higher for Pb/acid batteries.

case with initial investment, replacement and maintenance cost. The total cost over the lifetime of the energy storage system can then be expressed in \in kWh_{lifetime}⁻¹.

Following this idea, a first attempt of a cost comparison with other battery technologies was made. In Table 2, 3 qualities of Pb/acid, Li-ion and V-flow batteries are compared on the cumulative energy basis and under the assumption that operation and maintenance costs are similar for all battery types discussed. In order to compare the sales price for the V-flow battery, stacks, tanks, electrolyte, pumps and controls were quoted only. The nominal energy is given at 100 kWhs. Typical DOD and cycle numbers were taken into account and the total number of kWh over the battery life was calculated. The maximum energy may be achieved by the V-flow battery due to number of cycles and this total energy value was taken as a measure for the cumulative kWh comparison. As a result, the V-flow battery will achieve the lowest price kWh⁻¹. For the same total energy, the total investment for, i.e. a top quality Pb/acid battery will be €150,000, and in case of Li-ion €240,000. Although the initial investment is relatively high for V-flow battery, the electrolyte does not lose value and can be reused in a new installation. This will be another benefit at a later stage and was not taken into account in the discussion.



Fig. 9. Solar electric charging station at the SOLON Headquarter in Berlin.

In general, the Vanadium Flow Battery cost is mostly related to materials cost and some, but less than 10% to labor cost. Since some of the cell components are still in an industrial development stage, there is also room for cost reduction besides economy of scale.



Fig. 10. Energy storage at the edge of the grid in solar homes operated by the local grid.

3.3. Applications

The Cellcube FB10/100 unit can serve in a large variety of applications, which can be categorized in 4 market segments:

- (a) off-grid power supply in combination with renewable resources from solar or wind,
- (b) on-grid storage, where renewables enter the grid,
- (c) back-up power in weak grids with frequent (daily) power outages, and
- (d) storage to support grid management when significant amounts of renewable power feed into the grid.

Since 2008, several power stations have been equipped with Cellcube FB10/100 storage units and put into operation. Of these, the most attractive applications are related to electric mobility; fuelling electric cars with solar energy on a 24 h demand side program. An example of a solar filling station with 24 h power supply is shown in Fig. 9. Another very interesting application is the home storage at the edge of the grid, especially when intermittent power from renewable sources is generated. A schematic of such a home storage is shown in Fig. 10. Solar cells on the roof produce electric power that can be used directly in the house or in case of overproduction stored in the battery. If demand from the house is exceeding solar production, electricity will be taken from the battery or the grid, depending which is more economical. On the other hand, the battery is operated by the local grid and can be used as intermediate storage in grid management. Although the storage units are relatively small, many of them would make up for large virtual storage. For realization, public private partnership models need to be developed in terms of ownership, rights and duties. For evaluation, economic, social, and environmental issues have to be considered in a straightforward and fair manner.

4. Conclusions

The strategy employed by the vanadium redox flow battery, Cellcube FB10/100, in "Multi-Stage-Operation" is shown to give more efficient use of the stored energy than the standard single stage operation. The first systems have been installed with renewable power supplies to provide 24 h off-grid electricity for mobility applications. In comparison with other battery technologies, vanadium flow batteries require less investment per delivered kWh over the battery life. Large scale applications will depend on local regulations rather than cost issues.

References

- [1] E.A. Jahncke, GB Patent 18977958 (1897).
- [2] A.R. Upward, C.W. Ridham, US Patent 357646 (1884).
- [3] P.A. Pissoort, FR Patent 754065 (1933).
- [4] W. Kangro, DE Patent 914264 (1949).
- [5] W. Kangro, DE Patent 1006479 (1954).
 [6] L.H. Thaller, US Patent 3996064 (1975).
- [7] J. Giner, L. Swette, K. Cahill, Screening of redox couples and electrode materials, Contract report for NASA, Lewis Research Centre NASA-19760 (1976).
- [8] M. Warshay, L.O. Wright, J. Electrochem. Soc. 124 (1977) 173-177.
- [9] N. Hagedorn, M.A. Hoberecht, L.H. Thaller, NASA redox cell stack shunt current, pumping power, and cell performance tradeoffs, Technical Report DOE/NASA/12726-11 NASA TM-82686 (1982).
- [10] A. Pelligri, P.M. Spaziante, GB Patent 2030349 (1978).
- [11] H.F. Schaeffer, K.V. Kordesch, US Patent 3279949 (1961).
- [12] E. Sum, M. Rychcik, M. Skyllas-Kazacos, J. Power Sources 16 (1985) 85–95.
- [13] E. Sum, M. Skyllas-Kazacos, J. Power Sources 15 (1985) 179–190.
- M. Skyllas-Kazacos, M. Rychcik, R. Robins, AU Patent 575247 (1986).
 M. Skyllas-Kazacos, M. Rychcik, R.G. Robins, A.G. Fane, J. Electrochem. Soc. 133
- (1986) 1057–1058.
- [16] M. Rychcik, M. Skyllas-Kazacos, J. Power Sources 19 (1987) 45-54.
- [17] M. Skyllas-Kazacos, WO Patent 8905526 (1987).
- [18] M. Skyllas-Kazacos, D. Kasherman, D.R. Hong, M. Kazacos, J. Power Sources 35 (1991) 399-404.
- [19] M. Fukaya, T. Shigematsu, M. Kondou, JP Patent 60101881 (1983).
- [20] M. Kondou, T. Shigematsu, JP Patent 60258866 (1984).
- [21] H. Matsubara, M. Kondou, T. Shigematsu, JP Patent 60257076 (1984).
- [22] T. Shigematsu, M. Kondou, JP Patent 61022574 (1984).
- [23] M. Hirose, JP Patent 63016574 (1986).
- [24] N. Mori, M. Hirose, JP Patent 62176065 (1986).
- [25] T. Kumamoto, T. Shigematsu, T. Itou, T. Ito, N. Tokuda, JP Patent 08138716 (1994).
- [26] T. Shigematsu, T. Kumamoto, JP Patent 07211347 (1994).
- [27] T. Itou, T. Shigematsu, T. Ito, N. Tokuda, JP Patent 3574514 (1995).
- [28] K. Ashizawa, S. Shimizu, Y. Higuchi, M. Ohtomo, in: A.R. Landgrebe, Z.-I. Takehara (Eds.), Symposium on Batteries and Fuel Cells for Stationary and Electric Vehicle Applications, Electrochemical Society, Honolulu, Hawaii, 1993, pp. 143–157.
- [29] P.C. Butler, S.E. Klassen, Materials for Advanced Rechargeable Batteries, Report SAND93-2023 (1993).