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The Prospects for Vanadium Redox Flow Battery Technologies in Electrical Power Systems

Robert H. B. Exell^{*1} and Placido M. Spaziante⁺

Abstract- A vanadium redox flow battery consists of acid vanadium sulfate electrolytes with vanadium ions in different oxidation states flowing past each side of an ion exchange membrane. The storage capacity (kWh) and the power rating (kW) are independent design parameters. They can be realized over wide ranges of scale from watts to megawatts. The laboratory prototype batteries described in this paper have a unique architecture with electronic power switching circuits that enable the battery to be charged with variable DC and AC inputs, and to deliver stable DC and AC outputs, without the use of conventional inductive inverters. Applications may include: renewable sources of electrical energy (solar, wind, etc.), load leveling in factories, buildings and the power grid, and power quality control for sensitive electronics. A new method of charging the battery by reduction of the negative electrolyte with biomass crops of sugar or starch, and oxidation of the positive electrolyte with oxygen or air, is also described.

Keywords - Electricity storage, load leveling, power quality control, solar power, sugar fuel cell, vanadium redox flow battery, wind power.

1. BACKGROUND

The need for storage is felt in many electrical systems ranging from the largest to the smallest. By leveling the production and transmission of power, energy storage could improve the economics of the national power grid and the consumption of electricity in factories and buildings. The future development of renewable sources of energy (solar photovoltaics and wind turbines) will also require high capacity energy storage systems because the time when this energy can be collected is unpredictable and different from the time when the electricity is used. Although other technologies exist, many applications will use rechargeable electrochemical batteries to provide the necessary energy storage.

A major problem for electrical power generating utilities is to meet a demand that varies rapidly throughout the day. In order to avoid brownouts and power cuts when there are peaks in the demand the utility needs the capacity to generate twice the average power demand at short notice. This requires a huge capital investment in heavy generating machinery that must be started up and closed down quickly, and which stands idle during off peak time.

The question of whether electrical utilities can use electrochemical batteries for large-scale energy storage is now being studied. The most familiar type of battery is the lead-acid battery. This has lead plates immersed in sulfuric acid with a coating of lead oxide on the positive plates. When electricity is drawn from the battery, lead sulfate accumulates on both plates. When the battery is recharged, the lead sulfate is dissolved. Repeated discharging and recharging causes the lead sulfate coatings to expand and contract, and to deteriorate, especially when the charge-discharge cycles are rapid.

Lead-acid systems are not suitable for large-scale applications.

2. FLOW BATTERIES

The large-scale storage of electricity in batteries has recently been made possible by the development of flow batteries, which have positive and negative liquid electrolytes pumped through the battery cells. Each cell has two compartments separated by an ion exchange membrane. The positive electrolyte flows through one compartment and the negative electrolyte flows through the other compartment. The electrodes of the battery are chemically inert, thus avoiding the problems of lead-acid batteries. The electrolytes are stored in separate tanks outside the stack of battery cells.

Wide variations in the design and sizing of flow batteries are possible. The current rating is determined by the effective area of the membranes in the cells; the voltage is determined by the number of cells in the stack; and the storage capacity is determined by the quantity of liquid electrolytes in the tanks. The power rating can thus be varied over wide ranges from watts to megawatts, independently of the storage capacity. This gives flow batteries an advantage over batteries in which energy storage is in the chemicals on the plates, as in lead-acid batteries.

Flow batteries can be started up and closed down quickly, and can be switched between the charge and discharge modes of operation almost instantaneously. They are not damaged by rapid charge-discharge cycles. The storage of the electrolytes in separate tanks prevents self-discharging, so the electricity can be stored for any length of time. However, protection of the electrolytes from oxidation by air is necessary.

The vanadium flow battery uses acid vanadium sulfate on both sides of the membrane in the electrochemical cells, both electrolytes being manufactured from sulfuric acid and naturally occurring vanadium pentoxide. The idea of using vanadium was first proposed in a British patent in the 1970's [1], and was developed independently in Australia a decade later.

^{*} Joint Graduate School of Energy and Environment, King Mongkut's University of Technology, Thonburi, Thailand.

⁺ Cellenium (Thailand) Company Limited, Bangkok.

¹ Corresponding Author:

FAX: 66-2-872-6978, E-mail: exell@jgsee.kmutt.ac.th

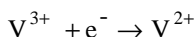
The Australian technology [2] was licensed to various companies for commercialization, including Mitsubishi and Sumitomo in Japan, Pinnacle (Australia), and Vantack VRB (Canada). Work has also been done in Germany by Zentrum für Sonnenenergie und Wasserstoff-Forschung Baden-Württemberg.

A life cycle environmental comparison of vanadium flow batteries and lead-acid batteries [3] has found that the environmental impact of vanadium batteries is of the order one quarter of that of lead-acid batteries, and the net energy storage efficiency is of the order 5% greater in a vanadium battery system, taking into consideration primary energy needs during the life cycle. The long cycle life and recycling ability of vanadium batteries justify their development and commercialization.

The purpose of this paper is to describe research on vanadium batteries and associated technologies by Cellennium (Thailand) Company Limited over the last few years, licensed by the holder of the patents Squirrel Holdings Limited. The work has focused on safety issues, improvements in the total system efficiency, designing cell stacks that can be manufactured at low cost, and developing a method for the easy preparation of the electrolyte. Associated technologies include a method using electronic power switching to charge the battery with variable DC and AC inputs, and deliver stable DC and AC outputs, without using conventional inductive inverters. A new method of charging the battery by reducing the negative electrolyte with sugar or starch, and oxidizing the positive electrolyte with oxygen or air, is also described.

3. VANADIUM FLOW BATTERIES

A vanadium flow battery has acid vanadium sulfate on each side of an ion-exchange membrane. The oxidation states of the vanadium in the discharged state are V^{3+} on the negative side and V^{4+} on the positive side. The half reactions during charging are



on the negative side, and



on the positive side.

This gives oxidation states V^{2+} on the negative side, and V^{5+} on the positive side, in the fully charged battery. The reactions are reversed during discharging. The open circuit voltages are 1.1V in the discharged state and 1.6V in the fully charged state.

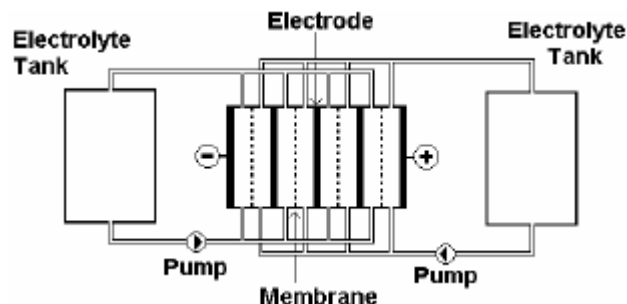


Fig. 1. A conventional flow battery stack.

Conventional flow batteries have horizontal stacks of vertical cells (Fig. 1). The cells are connected electrically

in series, and the electrolytes are fed to the cells in parallel. Parallel flow entails certain problems. Electrical shunt currents in the channels feeding the electrolytes to the cells bypass the intended electrical path through the cells. These shunt currents cause corrosion, loss of energy efficiency, and nonuniform distribution of current to the cells. Moreover, to ensure uniform electrolyte distribution to the cells and prevent blockages, flow rates are higher than needed for the electrochemical reactions. In the new flow architecture in the Squirrel batteries [4] the cells are horizontal in a vertical pile with the electrolytes fed upwards through the cells in series (Fig. 2). This almost eliminates bypass currents. It increases safety because a blockage can be detected at once and the dangerous electrolysis of water can be prevented. It is also efficient because the electrolyte flow rates (and pumping power) needed are lower than with parallel feed.

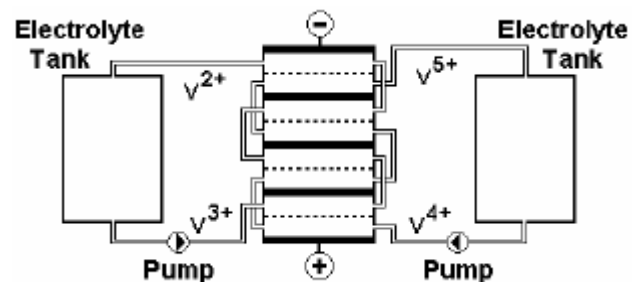


Fig. 2. A Squirrel flow battery stack.

4. PREPARATION OF THE ELECTROLYTE

Vanadium pentoxide V_2O_5 is only slightly soluble in sulfuric acid. Existing chemical methods of electrolyte preparation are costly. The new method devised by Squirrel [5] is simple and inexpensive (Fig. 3). Vanadium pentoxide powder, sulfuric acid and water are fed continuously into vanadium electrolyte solution circulating through a cascade of electrolytic cells. The cells in the cascade have an asymmetric form so that the reduction of vanadium occurs on the large area of the negative electrodes, but the area of the positive electrodes is too small for oxidation to occur. The product of the process is a mixture containing 50% V^{3+} ions and 50% VO^{2+} ions.

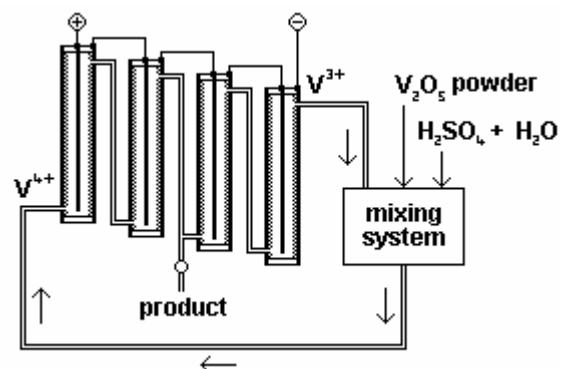


Fig. 3. Apparatus for preparing the electrolyte.

In the practical operation of vanadium batteries there are mechanisms by which one electrolyte becomes fully charged (or discharged) before the other. These mechanisms include imperfect reversibility of the passage of ions through the membrane, or oxidation of vanadium ions when air tightness of the system is imperfect. At

present, vanadium batteries are stopped from time to time for rebalancing the electrolytes. It is now possible, however, to divert some of the electrolyte through one or more asymmetric cells described above for rebalancing without stopping the battery.

5. REGENESYS

Regenesis is a regenerative fuel cell system (a flow battery) developed in the United Kingdom [6]. The uncharged electrolytes are sodium bromide and sodium polysulfide. They are separated by a membrane that allows sodium ions through while preventing the sulfur from reacting directly with the bromine. On charging, the bromide is converted to tribromide and the polysulfide is converted to sulfide.

A bromide-sulfide plant of size 15MW/120MWh has been constructed. Innogy Holdings, which owned the Regenesis technology, was acquired by the German multi-utility group RWE AG at a price that indicated a confidence in the future of regenerative fuel cells for the large scale storage of electricity. Plants of size 25MW/250MWh were planned, but RWE decided to halt work in 2003 for business reasons.

These developments, although not followed through to completion, show that large utility-scale flow battery systems are technically feasible. Comparing vanadium flow batteries with Regenesis, one can say that vanadium batteries could have higher efficiencies, are safer because there would be no dangerous results from accidental mixing of the electrolytes, and costs are expected to be less than the costs of Regenesis. For safety reasons Regenesis cannot be scaled down to compete with vanadium batteries in medium and small-scale applications.

6. VARIABLE INPUTS AND OUTPUTS

In conventional DC-DC converters for stepping up the voltage of a direct current supply, and in DC-AC inverters for producing an alternating current, the DC is first converted to AC by means of inductive generators. The AC is then stepped up (or down) to the desired voltage by means of an inductive transformer. If needed, the alternating current can be rectified and smoothed to produce a DC output at the new voltage. These systems have an efficiency 60-80%, and the AC outputs can have harmonics that are problematic if the AC power is to be fed into an AC power grid.

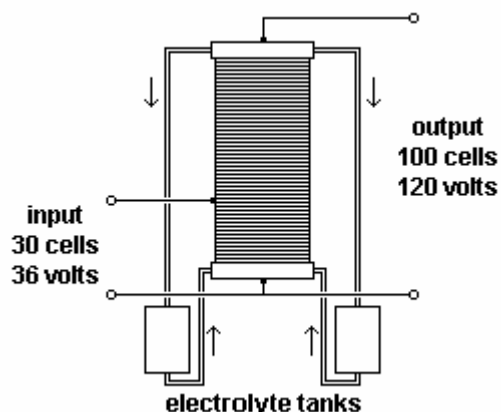


Fig. 4. A DC transformer.

A stack of flow battery cells with taps along its length can be used as a DC-DC transformer for stepping a DC voltage up or down (Fig. 4). To step the voltage up the current is fed into a low voltage tap and drawn out of a high voltage tap. A similar method can step the voltage down without the losses incurred in a resistive potentiometer load. If there are taps at many voltages along the battery stack, a programmed electronic power switching circuit can create a sinusoidal output free from harmonics for feeding into an AC power grid (Fig. 5) [7].

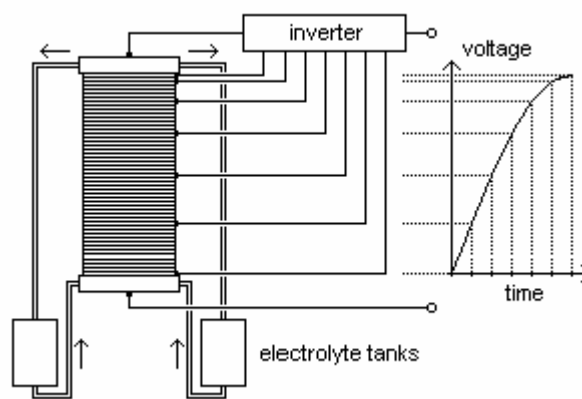


Fig. 5. Principle of the Squirrel DC-AC inverter.

With electronic switching on the input side of the battery, maximum power point tracking of inputs from solar photovoltaic arrays is possible, and inputs from wind turbines running at variable rotation frequencies depending on fluctuating wind strengths can be accepted.

7. CELLS WITH MONOPOLAR ELECTRODES

The battery stacks described above have bipolar electrodes between the individual cells, each electrode being positive on one side and negative on the other side. Stacks with bipolar electrodes are subject to certain practical limitations when used with electronic power switching for variable inputs and outputs. All the cells have the same membrane area, so a constant voltage cannot be maintained as the current load varies due to the internal resistance of each cell.

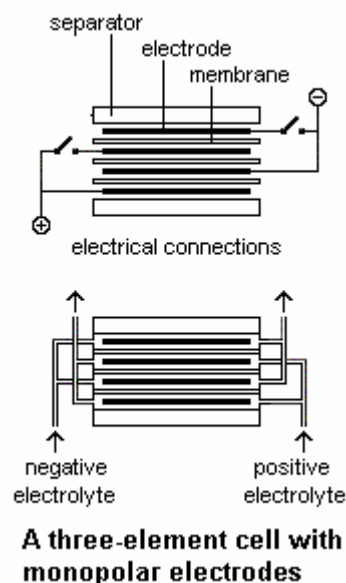


Fig. 6. Cells with monopolar electrodes.

To overcome this difficulty a new stack architecture has been devised using monopolar electrodes in which the membrane area of individual cells can be varied (Fig. 6) [8]. The cells are divided into elements, each having a separate membrane between monopolar electrodes of opposite polarity. The separators between cells are electrical insulators impervious to the electrolytes. Switches are provided so that the number of operating electrodes, and hence the number of membranes, in each cell can be varied. Moreover, different cells in a stack may have different numbers of elements; this is important when a sinusoidal output is created using the switching method outlined earlier.

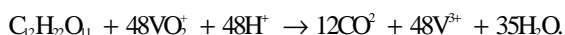
Other advantages of stacks with monopolar electrodes include the absence of any hydraulic pressure stress across the electrodes, and the possibility of using different materials for positive and negative electrodes.

8. FURTHER APPLICATIONS OF THE TECHNOLOGY

Several other potential applications of the Squirrel technologies exist besides the transfer of electricity from variable renewable energy sources to the point of use. They include the possibility of running stand-alone diesel generator sets at steady speeds adjusted to average loads instead of at variable speeds with dummy loads to guard the system against damage due to sudden drops in the demand. Another application will be to supply a high quality electrical output for use with telecommunications and other sensitive electronic equipment.

9. A SUGAR POWERED FUEL CELL

It was discovered ten years ago [9] that a vanadium battery can be charged by reducing the negative electrolyte from oxidation state V^{4+} to state V^{3+} with sugar or starch in the presence of a platinum catalyst. The reaction is



The positive electrolyte can be oxidized from state V^{4+} to V^{5+} with oxygen or air, also in the presence of a platinum catalyst, in accordance with the reaction

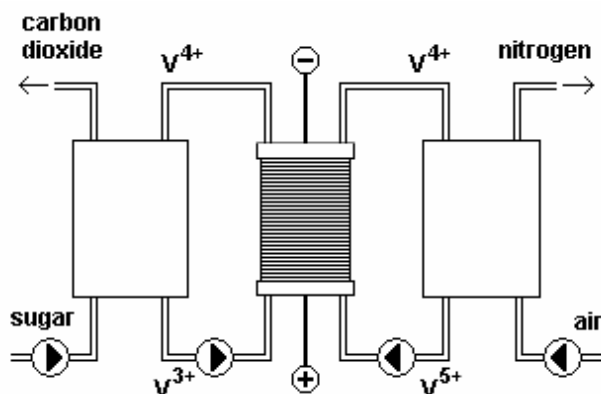
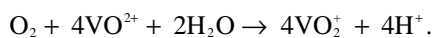


Fig. 7. A sugar powered fuel cell.

Although the reaction is not as far as can be achieved by electrical charging, one nevertheless obtains an open circuit voltage of 0.65V across the battery charged in this manner (Fig. 7) [10]. It can be shown that this way of

converting the chemical energy in sugar to electricity is more efficient than by the thermal route, through combustion and the use of a thermodynamic heat engine, since the Carnot cycle losses are avoided.

Several years of intensive research will be needed to fully understand the processes involved, and to improve reaction rates. It is hoped that eventually the system will be cost effective, especially where sugar (in sugar cane or sugar beet) or starch (in cassava or potatoes) are local agricultural products.

The carbon dioxide produced is chemically pure, so it can be sold, or used in greenhouses to enhance photosynthesis in plants. It does not contribute to global warming because it comes originally from the atmosphere through photosynthesis.

REFERENCES

- [1] Pelligri, A. & Spaziante, P. M. 1980. Process and accumulator for storing and releasing electrical energy. UK Patent GB 2 030 349 A.
- [2] University of New South Wales. 2002. The Vanadium Redox Battery. Retrieved May 2004 from <http://www.ceic.unsw.edu.au/centers/vrb/>.
- [3] Rydh, C.J. 1999. Environmental assessment of 3 vanadium redox and lead-acid batteries for stationary energy storage. *Journal of Power Sources* 80: 21-29.
- [4] Pellegrini, A. & Broman, B. M. 1999. Redox flow battery system and cell stack. World Intellectual Property Organization, WO 99/39397.
- [5] Pellegrini, A. & Broman, B. M. 2002 Vanadium Electrolyte Preparation Using Asymmetric Vanadium Reduction Cells and Use of an Asymmetric Vanadium Reduction Cell for Rebalancing the State of Charge of the Electrolytes of an Operating Vanadium Redox Battery. World Intellectual Property Organization, WO 02/15317 A1.
- [6] Davidson, B.; Calver, T.; Price, A.; and Simchock, D. 2000. Large-scale storage solution? The Regenesys™ regenerative fuel cell. *Renewable Energy World* 3(1): 84-91.
- [7] Spaziante P.M.; Kampanatsanyakorn K.; and Zocchi A. 2003. Transformerless Static Voltage Inverter for Battery Systems, World Intellectual Property Organization, WO 03/007464 A2.
- [8] Exell, R. H. B. and Spaziante, P. M. 2004. Potential contributions of regenerative fuel cells to photovoltaic systems. *Technical Digest of the International PVSEC-14*, (14th International Photovoltaic Science and Engineering Conference, Bangkok, 26-30 January 2004): P-213, pp. 939-940.
- [9] Larsson, R. & Folkesson, B. 1995. Method for producing electric energy in a biofuel-powered fuel cell. World Intellectual Property Organization, WO 95/17773.
- [10] Larsson, R.; Folkesson, B.; Spaziante, P.M.; Veerasai, W.; and Exell, R.H.B. 2006. A high-power carbohydrate fuel cell. *Renewable Energy* 31 (4): 549-552.