Electrochemical Behavior of Vanadium Electrolyte for Vanadium Redox Battery — A New Technology for Large Scale Energy Storage Systems

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1. Introduction:
Demand for new energy storage systems is increasing for applications such as remote area power supply systems (like offshore platforms, telecommunication installations), stressed electricity supply systems, emergency back-up applications, as well as mobile applications. The supply of electric power to remote areas is becoming more attractive due to advancements in the photovoltaic (PV) technologies and wind power generation systems along with the development of advanced storage batteries. Energy storage systems can be used to balance fluctuations in the supply and demand of electricity. Throughout the world therefore, enormous effort and funding is diverted for the development of suitable energy storage battery systems for these applications.

Over the past twenty years, there have been a number of energy storage projects within electricity supply systems. However, the costs for engineering, on-site installation, and maintenance all proved to be more expensive than expected, so energy storage suppliers moved to a system approach, sometimes called distributed energy storage, to help solve electricity supply problems. It is distributed energy storage technologies, with next-generation storage devices, that appear most likely to fill the role for energy storage in solving the current problems of stressed electricity supply systems. These various distributed energy storage systems provide the possibility of a very wide range of storage times, from a few seconds and up ten hours.

For a battery system to be economically viable for large-scale energy storage, it must compete favorably with pumped water storage. Of all the new battery technologies currently under development around the world, the redox flow cell appears to offer the greatest promise as a low-cost, high efficiency system for large-scale energy storage. Preliminary work on redox cells was conducted initially by Kangro and Pieper [1] and Boeke [2].

After screening many possible redox couples, Thaller [3] of NASA proposed a practical redox flow battery based on the redox couples $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Cr}^{2+}/\text{Cr}^{3+}$. A prototype 10kW/80 kWh Fe/Cr redox flow battery system was constructed and tested successfully by Hamamoto et al. [4]. Unfortunately, the Fe/Cr flow cell had problems such as cross contamination of the electrolyte and poor reversibility of the chromium half-cell. To overcome the problems associated with Fe/Cr redox flow battery, Skyllas-Kazacos and co-workers [5, 6, 7] suggested Vanadium Redox Battery (VRB) employing $\text{V}^{2+}/\text{V}^{3+}$ and $\text{V}^{4+}/\text{V}^{5+}$ redox couples in the negative and positive half-cell electrolytes respectively. By using the same metal ion in different oxidation states on either side of the membrane, problems related to cross contamination are thus eliminated.

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The Vanadium Redox Battery (VRB) energy storage system is a new technological breakthrough that has the potential to deliver enormous commercial, operational and environmental benefits for the world’s electricity industry. This technology is pioneered and developed at the University of New South Wales, Australia. It has already been demonstrated as an efficient new energy storage system for a wide range of large-scale energy storage applications such as remote area power supply system, emergency back-up applications, load leveling in power plants and mobile applications [8]. A number of commercial systems up to 2 MWh have already been successfully implemented in various energy storage applications in Japan, USA, Italy and Australia. These systems all use vanadium electrolyte concentrations of 2 M or lower to avoid precipitation in the negative half-cell [V(II)/V(III)] at low temperatures, or in the positive half-cell [V(IV)/V(V)] at elevated temperatures. In order to increase the energy density of the VRB system therefore, solution-stabilizing agents have been investigated.

2. Main Features of the Vanadium Redox Battery

The main features of VRB technology are shown in Figure 1. The major components of the vanadium battery are (i) the electrodes made up of carbon felt, (ii) the electrolyte (vanadium solution in sulfuric acid), and (iii) the selective ion-exchange membrane. The cell consists of two compartments (positive half cell and negative half cell) separated by a membrane, which prevents cross mixing of the electrolytes. Each side of the cell contains an inert electrode made of highly porous carbon felt. The electrolytes, the anolyte and catholyte, are stored in two large external reservoirs. The electrolyte of the battery is prepared by dissolving vanadium oxide or sulfate in sulfuric acid solutions. The rechargeable electrolyte is pumped through the inert electrode where the electrochemical reactions occur. During charging, electrochemical reactions within the battery stack change the valence of the vanadium, the negative reaction changes V(III) to V(II) and the positive reaction changes V(IV) to V(V). This process is reversed during the discharge cycle. The redox reactions, which occur in the vanadium redox flow cell system, are as follows:

At the positive electrode:

\[ \text{discharge} \]
\[ \text{VO}_2^+ + 2H^+ + e^- \rightarrow \text{VO}^{2+} + H_2O \quad E^\circ = 1.0 V \]
\[ \text{charge} \]

At the negative electrode:

\[ \text{charge} \]
\[ V^{3+} + e^- \rightarrow V^{2+} \quad E^\circ = -.26 \]
\[ \text{discharge} \]

The standard cell potential is thus \( E^\circ(\text{cell}) = 1.26 \) V at concentrations of 1 M and 25 °C. A stack of these energy producing cells can be connected in series in a bipolar manner. The physical size of the battery stack determines the power available from the battery and the volume of the electrolyte in the reservoirs; determine the kWh energy storage of the battery.

3. Advantages of VRB

The VRB system offers many advantages over conventional lead-acid batteries. It has very high efficiency, a reasonable energy density, high charge/discharge rates, a long lifespan independent of state-of-charge and load profiles, and low maintenance.

Additionally, it is possible to simultaneously charge the battery at one voltage while discharging it at another voltage. This unique feature can be utilized to make a minimum cost, high efficiency, and maximum power point tracker or allows the battery to operate as a DC transformer, electro-chemically transforming a current and a voltage into a different current and voltage. Instant recharge is possible by replacing discharged electrolyte with fresh charged solution.
The solution can be electrically recharged at high rates about 8-10 times faster than lead-acid batteries. The capacity of the battery can be simply increased by adding extra electrolyte to the reservoirs. The solution life is indefinite and can be recycled continuously, so that replacement costs are low and there are no waste disposal problems. The vanadium battery system is considered to be environmentally friendly.

4. Electrochemical Behavior of Vanadium Electrolyte:
The electrochemical behavior of supersaturated vanadium(V) solutions was studied using cyclic voltammetry as this is an effective electro-analytical technique for determining the variations in the positions of the V(V)/V(IV) redox couple peaks at different V(V) concentrations in various total sulfate/bisulfate levels. Information about reversibility of the V(V)/V(IV) system was obtained. The effect of various parameters such as V(V) concentration, total sulfate/bisulfate concentration, and elapsed time on the electrochemical activity of V(V) solutions was investigated.

Effect of V(V) Concentration
This subsection deals with the study of the effect of increasing V(V) concentration on the electrochemical behavior of the V(V)/V(IV) redox couple. The CV of 2, 3, 3.5, 4, and 5 M V(V) solution in 6 M total sulfate/bisulfate obtained using a glassy carbon electrode at a scan rate of 0.02 V/s is shown in Figure 2.

To discuss the effect of V(V) concentration, the anodic and cathodic peak currents for the V(V)/V(IV) couple obtained from Figure 2 were plotted as a function of V(V) concentration in Figure 3. The magnitude of peak current increases linearly as V(V) concentration was increased from 2 M to 3.5 M, however, a further increase in V(V) concentration above 3.5 M decreases the peak heights.

The decrease in peak currents with increasing V(V) concentration above 3.5 M may be due to the sharp increase in viscosity of the V(V) solution[9]. This sharp increase in viscosity results in a decrease in diffusion coefficient of the vanadium ions, which in turn leads to a decrease in peak currents. Furthermore, changes in the interfacial tension properties of the more concentrated solution may reduce the wettability of the glassy carbon electrode in the solution, thereby reducing the effective surface area and decreasing peak currents [10].

The peak potential separation (\(\Delta E_p\)) with increasing V(V) concentration is shown in Figure 4. The value of \(\Delta E_p\) increases with increasing V(V) concentration indicating increasing irreversibility of the system. The peak currents of 2-5 M V(V) solutions in 5, 6 and 7 M total sulfate/bisulfate is shown in Figure 5 which has reproduced similar behavior as that of V(V) solutions in 6 M total sulfate/bisulfate. The optimum V(V) concentration to obtain highest peak current with a peak potential separation of about 0.15 V is therefore, about 3 - 3.5 M and the system may be considered as quasi-reversible.
Figure 2. Cyclic voltammogram in 6M total sulfate/bisulfate

Figure 3. Effect of V(V) concentration on peak currents in 6M total sulfate/bisulfate

Figure 4. Effect of V(V) concentration on peak potential separation in 6M total sulfate/bisulfate

Figure 5. Effect of V(V) concentration on peak currents in 5, 6 and 7M total sulfate/bisulfate

Effect of Total Sulfates/Bisulfate Concentration
The effect of total sulfate/bisulfate concentration was investigated by taking the CV of V(V) solutions at constant V(V) concentration and varying total sulfate/bisulfate concentration.

A typical CV obtained for 4M V(V) solution in 5, 6 and 7M total sulfates using a glassy carbon electrode at a scan rate of 0.02 V/s is shown in Figure 6. Similar CV’s were obtained for 2, 3, and 5 M V(V) in 5, 6 and 7M total sulfates. Increasing the concentration of total sulfate/bisulfate decreases the magnitude of peak current as illustrated in Figure 7. Increasing the total sulfate/bisulfate concentration is believed to increase the formation of electrochemically inactive vanadium-sulfate complexes and polyvanadic species and in turn increases viscosity. The combined effect of formation of electrochemically inactive species and increase in viscosity, therefore, is to decrease the peak current heights for the V(V) solutions. It can also be observed that the effect is more pronounced at 5M V(V) concentration in 7M total sulfate/bisulfate.
From the analysis of the effect of both V(V) concentration and total sulfate/bisulfate concentration, it can be suggested that the highest concentrations of vanadium(V) and total sulfate/bisulfate may be 3M and 6M respectively to be able to achieve maximum electrochemical activity, in the vanadium redox battery.

Effect of Elapsed Time
The electrochemical behavior of vanadium(V) solutions with elapsed time was studied using cyclic voltammetry. The cyclic voltammogram (CV) of all V(V) solutions in different concentrations of total sulfate/bisulfate was obtained to investigate the effect of elapsed time on peak current and peak potential separation. It was found that at 20 °C, the 3M V(V) solution in 5M total sulfate/bisulfate is stable over a period of 1000 hours without changing its electrochemical behavior significantly.

Effect of Additives
One of the main objectives of this study was to stabilize supersaturated V(V) solutions so as to increase the energy density of the vanadium redox battery. Efforts were made to increase the existing concentration of 2 M V(V) solution to higher levels. Therefore, precipitation rates in vanadium solutions with concentrations above 3M V(V) were studied and found to be significantly fast at temperatures of above 30 °C. Stabilizing V(V) solutions at concentrations above 3M would be of interest for mobile applications. A detailed investigation was thus undertaken to stabilize V(V) solutions of 3M and above at 40 °C by using various chemical scale inhibitors. The study focused on increasing the induction times of V(V) solution in different total sulfate/bisulfate concentrations at various temperatures using antiscalants. It was found that 3.0 - 3.5M V(V) solution in 5 – 6 M total sulfate / bisulfate is a suitable composition for a high energy density battery operating at temperatures between 20 and 40 °C.

The electrochemical behavior of V(V) solution after adding a novel chemical formulation KS11 was studied using 4 M V(V) solution containing 5 M total sulfate/bisulfate at 40 °C. The cyclic voltammogram obtained before and after addition of KS11 to V(V) solution at a scan rate of 0.02 V/s at a glassy carbon electrode were very similar indicating that the addition of KS11 did not affected the electrochemical behavior of V(V) solution.

For regions like Arabian Gulf where atmospheric temperatures are above 40 °C precipitation of V(V) species may occur, and hence the vanadium electrolyte needs to be optimized further. This is possible by changing the composition (vanadium and sulfate/bisulfate concentrations) of the electrolyte and
determining the optimum composition for operating the battery at temperatures of about 50 °C. The concentration of 3.0 – 3.5 M vanadium can be maintained if suitable additives are developed to stabilize the electrolyte. Thus, the vanadium electrolyte will be more stable so that the operating temperature range of the batteries can be from 10 °C to 50 °C.

5. Economics of Vanadium Redox Battery
A Life-Cycle Cost Study performed by Chalmers University [11] showed that the VRB has the lowest life-cycle cost of all batteries studied, is comparable to lead-acid batteries, has very long life and lowest of ecological impact over the production and life-cycle of all batteries studied. Cost estimates of VRB by the UNSW group and independent consulting groups place mass production costs between $100 and $300 per kW for the cell stack and $30 to $50 per kWh for the electrolyte [12]. It should be noted that apart from cost, the VRB has some additional advantages discussed above.

6. Applications of VRB in Power Sector
It has been proved that the VRB system has several advantages such as overload capacity, long life, quick time-response, easy increase of capacity, normal temperature operation, and environmentally friendly. Therefore, it can be used for a variety of applications such as load leveling, power quality control, emergency power, back-up power, stabilization of renewable energy. As VRB can supply high power output for longer period of time, it can provide load leveling capabilities when and were desired. In case of securing a place for a particular application with long time capacity, electrolyte tanks can be installed separately from VRB cell stacks [13].

VRB can support power quality issues such as voltage dip because of the fast time response less than 1msec and the maximum short-time overload output of several times that of normal output. Because of the features such as quick response and over load capacity, VRB can also be used as uninterruptible power supply (UPS) system for protection against faults on the power utility transmission and distribution systems that may result in plant shutdown and resulting loss of production at factories [14].

Since the charged electrolyte of VRB system is stored in separate positive and negative tanks, no self-discharge will occur during stand-by mode. Consequently, VRB system can restart even after a long-term halt simply by starting the pump to flow electrolyte to the cell stacks within 1min. These features of VRB system are suitable for emergency power applications. Furthermore, VRB can be used for back-up power of long time capacity when the electrolyte tanks are just up to the designed volume as battery cells and electrolyte tanks can be installed separately. VRB can also operate as UPS and emergency units reliably as the VRB system runs consistently to level up the loads. Some of the practical application of VRB system is given in Table 1 [15].

<table>
<thead>
<tr>
<th>Installation Date</th>
<th>Application</th>
<th>VRB Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec. 1996</td>
<td>Field Test (Load-Leveling)</td>
<td>450kW/2h</td>
</tr>
<tr>
<td>Feb. 2000</td>
<td>Load-Leveling (Office Building)</td>
<td>100kW/8h</td>
</tr>
<tr>
<td>Sep. 2000</td>
<td>Field Test (Load-Leveling)</td>
<td>200kW/8h</td>
</tr>
<tr>
<td>Mar. 2001</td>
<td>Wind Turbine Generation</td>
<td>170kW/6h</td>
</tr>
<tr>
<td>Mar. 2001</td>
<td>Voltage Dip Protection</td>
<td>3MW/1.5s</td>
</tr>
<tr>
<td>Mar. 2001</td>
<td>Load-Leveling</td>
<td>1.5MW/lh</td>
</tr>
<tr>
<td>Mar. 2001</td>
<td>Photo-Voltaic Generation</td>
<td>30kW/8h</td>
</tr>
</tbody>
</table>
7. Conclusions and Recommendations

Several demonstration projects at both UNSW and in Japan have shown the technical viability of the vanadium battery for a wide range of stationary and mobile applications. Besides lower estimated manufacturing costs, the attractive features offered by VRB are: rapid charging and discharging rates, indefinite electrolyte life, higher energy efficiencies, longer life and low maintenance.

Also, increasing the vanadium concentration to 3 M will allow a 50% increase in the energy density compared with the 2 M solutions used to date. This has been achieved with the use of additives to inhibit the precipitation of the supersaturated vanadium solutions so that an energy density of around 40 Wh/kg is now possible. Further work is currently underway at UNSW to double this to 80 Wh/kg by in-situ regeneration of V(V) using air oxidation of the discharged V(IV) solution, thus allowing twice the driving range to be achieved in electric vehicle applications.

However, research and development work is needed to widen the operating temperature range up to 50°C by optimizing the electrolyte composition to be able to utilize this new technology in regions (like Arabian Gulf) where higher atmospheric temperatures are encountered. Optimization of vanadium electrolyte is possible and additive development work can be undertaken to further stabilize the electrolyte at higher operating temperatures.

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9. References