Research progress of vanadium redox flow battery for energy storage in China

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Abstract

Principle and characteristics of vanadium redox flow battery (VRB), a novel energy storage system, was introduced. A research and development unified laboratory of VRB was founded in Central South University in 2002 with the financial support of Panzhihua Steel Corporation. The laboratory focused their research mainly on the selection and preparation of electrode materials, membrane material and modification, stable concentrated electrolyte producing approach, test cell configuration design and optimization. Some relevant foundation problems, such as state of vanadium in sulfurous acid with various additives, the difference of electrochemical reaction rate in anode and in cathode, the crossover of vanadium ions and so on, have been emphasized. The details of these studies have been given and discussed. A 5kW VRB stack was fabricated in the laboratory and its performances, especially electrochemical performance such as voltage efficiencies, energy efficiencies, and durability, were fully tested. The results will be shown in the talk.

The key technologies of developing VRB, such as to improve the activity of its electrode materials, the stability of electrolyte and selectivity of separator, were also discussed. In addition, the research progresses in other laboratories in China were briefly introduced.

Keywords: Vanadium redox flow battery; Energy storage system; Vanadium

1. Introduction

In recent years, the volume of oil import and coal production increase rapidly by year with the economic growth, but a great deal of fossil energy consumption caused serious environmental pollution. As in the case of a series of problems such as environmental endurance and energy stabilization, people in China thus turn to develop and utilize the renewable energy from wind and solar than excessively depend upon fossil energy source. At such a time, countermeasures are needed to assure system stability by preventing power output fluctuations, e.g., when there is no wind or sunshine at night. It is therefore important to use batteries in combination with solar and wind power generation.

At the same time, China is abundant in vanadium resource, which accounts for about 11.6% of the world reserves [1]. There is huge amount of waste slag which contains a lot of vanadium at Panzhihua Steel Corporation in south west of China. Only about 10,000 tons of vanadium is reused in petrochemical catalysis or/and steels additive every year [1].

Since 1995, a lot of universities and institutes in China have engaged in the development of vanadium redox flow battery (VRB), which is a new type of secondary battery for electric power storage first successfully demonstrated and commercially developed by Skyllas-Kazacos and co-workers in the University of New South Wales, Australia in 1984 [2–4].

Compared with other redox batteries such as zinc bromine battery, sodium sulfur battery and lead acid battery (the data were listed in Table 1), the VRB performs higher energy efficiency, longer operation life as well as lower cost, which made it the most practical candidates for energy storage purposes. Meanwhile, the VRB system

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showed prospect in peak shaving, uninterruptible power supply, voltage and frequency control, stabilization of wind turbine output, hybrid with photovoltaic cells and some other energy backup systems.

2. Operating principles and features of VRB

The configuration of a redox flow battery was shown in Fig. 1. The VRB system consisted of two electrolyte tanks filled with the electrolytes of V(II)/V(III) and V(IV)/V(V) in sulfuric acid solution, respectively, two electric pumps, and a battery stack. The electrolytes were pumped into the stack where electrochemical reaction occurred. An ionic membrane in the stack separated the cell as well as electrolytes into cathodic and anodic. The electron exchange took place at the electrodes in the aqueous phase according to the following reactions (discharge in the right direction):

**Positive electrode:**

$$\text{VO}_2^+ + \text{H}_2\text{O} \xrightleftharpoons{\text{charge}} \text{VO}_2^{2+} + 2\text{H}^+ + e^{-}.$$  

**Negative electrode:**

$$\text{V}^{3+} + e^{-} \xrightleftharpoons{\text{charge}} \text{V}^{2+}.$$  

The VRB system is the only redox flow battery using ions of the same metal in both the half-cells, which eliminated electrolyte cross-contamination as experienced by the Fe/Cr redox battery. The state of charge (SOC) can be measured continuously; therefore, the capacity remaining in the battery can be read instantly. By the use of tapping cells in the battery, it can be charged at one voltage and discharged at another while also supporting an external load if needed.

3. Research and development progress in China

VRB systems have been investigated by a number of world government and independent research organizations since 1984, especially in Australia, Japan, Canada, etc. It has been widely tested in many field including wind generation and photovoltaic system, golf cart power, peak shaving, load leveling, as well as UPS.

In China, about seven groups subordinated various universities or institutes, such as Central South University, China Academy of Engineering Physics, Beijing University, Tsinghua University, Northeastern University, Institute of Metal Research Chinese Academy of Science and Dalian Institute of Chemical Physics, engaged in the research of VRB system and relative materials. Meng et al. [5,6] in China Academy of Engineering Physics concentrated their attentions on the behavior of carbonaceous materials in a mixture of pentavalent and tetravalent vanadium sulfuric acid solution. Sui and his co-workers [7,8] from Northeastern University investigated effects of additives such as alkali metal sulfate, alkali metal oxalate, urea and glycerin in the vanadium sulfuric acid solution on its electrochemical performance and conductivity.

The membrane in vanadium redox flow battery served not only as a separator of catholyte and anolyte but also as a proton conductor. It was one of the determinants to the input/output efficiency of the battery and attracted numerous research attention. Qiu et al. [9] in Tsinghua University prepared a poly (vinylidene fluoride)-graft-poly (styrene sulfuric acid) (PVDF-g-PSSA) membrane using solution-grafting method. These membranes exhibited high conductivity with a value of $3.22 \times 10^{-2} \text{S cm}^{-1}$ at $30^\circ\text{C}$. ICP studies revealed that the PVDF-g-PSSA membrane showed dramatically lower vanadium ion permeability compared to Nafion 117. Trivalent vanadium ions had the highest permeability through all these membranes in contrast to pentavalent vanadium ions with the lowest.

The VRB with the low-cost PVDF-g-PSSA membrane exhibited a higher performance than that with Nafion 117 under the same operating conditions, and its energy efficiency reached 75.8% at 30 mA cm$^{-2}$. The performance

<table>
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<th>Table 1: Comparison of competing storage technologies</th>
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<td>Technology</td>
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<td>VRB</td>
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<td>Lead acid</td>
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of VRB with the PVDF-g-PSSA membrane can be maintained after more than 200 cycles at a current density of 60 mA cm\(^{-2}\). The results from cycling experiments revealed that the PVDF-g-PSSA membrane has good chemical stability in vanadium solutions. Furthermore, the solution-grafting method of preparing a PVDF-g-PSSA membrane is very simple, which could lead to a significant cost reduction in the production of a commercial redox flow battery.

Yan et al. [8,10] in the Institute of Metal Research Chinese Academy of Science impregnated a microporous separator (Daramic) in a 5 wt% Nafion solution to obtain a proton-conducting composite membrane with modified properties for VRB. Nafion uptake by Daramic with thickness 0.25 mm is 6.5 wt%. The new Daramic/Nafion composite membranes give acceptable low electrical resistance of 2.4 \(\Omega\) cm\(^{-2}\), although the measured area resistances are higher for the composite membranes with different thickness than that for the untreated membranes. A reduction in water uptake of the membranes is observed after impregnation. Open circuit voltage measurement with time of the proton-conducting composite membrane showed promising results compared with that of the untreated Daramic membrane when used in the VRB. They also evaluated several commercial ion exchange membranes for application in VRB [11]. The results showed that, except for JAM anionic exchange membranes, other membranes, including DF120 cationic and anionic exchange membranes, JCM cationic exchange membrane, were unsuitable due to their high permeation of vanadium ions and poor chemical stability in the V (V) solutions. A novel cationic exchange membrane was prepared by incorporation of poly (sodium 4-styrenesulfonate) into the JAM anionic exchange membrane by in situ polymerization. Some significant cationic exchange capability was imparted to the composite membrane. The composite membrane prepared by this method also showed lower permeability to vanadium ions and higher average current and energy efficiencies for the VRB in comparison with the untreated membrane. The vanadium redox cell with the JAM composite membrane has a better performance than that with Nafion 117.

In addition, Zhang and his co-workers, a research group in China Academy of Dalian Institute of Chemical Physics, who had been devoted in the research of sodium multi-sulfide/Br\(_2\) redox flow battery, transferred their attentions to the fabrication of VRB system last year. They reported recently that a 10 kW VRB system was successfully set up in Dalian [12].

3.1. VRB progress in CSU

China is abundant in vanadium resource, which accounts for about 11.6% of the world reserves and Panzhihua collected more than 87% of vanadium resource in China. The vanadium mineral form in Panzhihua is vanadium titanium iron intergrowth magnetite. Since 2002, with the financial support from Panzhihua Steel Corporation, Huang and his group in Central South University devoted their interests in the research of VRB related key materials covered electrolytes [13], cathode and anode materials [14–16], collector [17] and membrane modification [18], as well as the system optimization.

3.1.1. Preparation of electrolyte

A novel procedure for preparing VOSO\(_4\) from vanadium-bearing slag produced by Panzhihua Steel Corporation was proposed [13]. Concentrated electrolyte which showed excellent chemical and electrochemical stability in the range of 5–50 °C as well active reactivity was yielded from a mixture of VOSO\(_4\), V\(_2\)O\(_3\), V\(_2\)O\(_5\) and other additives.

Vanadium ion would be diversified when the environment such as pH value, temperature, coexisted ion in the solution varied. For example, vanadium ions in positive tanks aggregated into binuclear and subsequently more complex species depending on the vanadium ions concentration and pH value of electrolyte solution. When the pH value was in the range of 2–6, the main species was orange deca-vanadate ion, which can exist in several protonated forms.

\[
\begin{align*}
V_{10}O_{28}^{6-} + H^+ & \rightleftharpoons V_{10}O_{27}(OH)^{5-}, \\
V_{10}O_{27}(OH)^{5-} + H^+ & \rightleftharpoons V_{10}O_{26}(OH)_2^{4-}, \\
V_{10}O_{26}(OH)_2^{4-} + H^+ & \rightleftharpoons V_{10}O_{25}(OH)_3^{3-}, \\
V_{10}O_{25}(OH)_3^{3-} + H^+ & \rightleftharpoons V_{10}O_{24}(OH)_4^{2-} \overset{H^+}{\rightleftharpoons} VO_2^+.
\end{align*}
\]

The \(V_{10}O_{24}(OH)_4^{2-}\) ion was unstable. It would react with further acid to give dioxovanadium (V) ion (VO\(^{2+}\)), while in alkaline solution, breakup of the \(V_{10}O_{28}\) unit was much more difficult.

It was found experimentally that crystalloid would appear in concentrated negative electrolyte (more than 2 M vanadium ion) stored under normal temperature, especially at a lower temperature. Composition of the crystalloid was confirmed to be \(V_2(SO_4)_3\cdot H_2O\) by XRD, XPS, FT-IR and thermal analysis. The influence of a number of additives such as phosphoric acid, sodium phosphate, ammonium phosphate, EDTA, sodium sulfate, etc., on the stability, conductivity, and electrochemical properties of a negative electrolyte was investigated. It was revealed that acetylacetone was the most effective stabilizer and phosphoric acid was the secondary. Conductivities of the electrolytes with additives less than 2 wt% were almost constant. The stabilization mechanism of the additives is being studied in the laboratory. After researching the kinetics progress among various vanadium ions, solvent, electrolyte, surface active agent, as well as the effect of additive agent, acid, temperature, concentration on vanadium ion complexing...
structure. A scientific evaluation system for vanadium electrolyte was established.

3.1.2. Electrode and membrane

An ideal electrode should possess high electric conductivity and long cyclic life in sulfuric acid containing concentrated and oxidizing pentavalent vanadium ion (VO$_2^+$). Huang et al. studied the behaviors of glassy carbon, carbon clava, carbon cloth, carbon felt, Ti, Pb, Au as well as carbon black-graphite powder composite materials served as anode or cathode [14,15,17]. Carbon, especially the graphite felt (GF), due to its high specific surface area and good stability, was a competitive anode compared with metal. However, the poor electrochemical activity of commercial GF was still one of the major drawbacks that limited the power density and voltage efficiency of VRB system.

An approach combined electrochemical oxidation along with chemical modification was employed to improve the electrochemical activity of the GF electrode [19–21]. Fig. 2 presented the cyclic voltammograms of GF electrode before and after electro-oxidation in a mixture of 3.0 mol L$^{-1}$ H$_2$SO$_4$, 0.0087 mol L$^{-1}$ V(IV), and 0.0087 mol L$^{-1}$ V(V). Fig. 3 exposed the charge–discharge curves of GF oxidized at 50 mA cm$^{-2}$ for various times. From these two figures, it could be seen that the performance of electro-oxidized GF improved evidently, and the activity increases with the increase in oxidation degree. The average current efficiency reaches 94% and average voltage efficiency reaches 85% under a current density of 50 mA cm$^{-2}$. The improvement in the electrochemical activity is ascribed to the increase in the number of COOH groups and specific surface.

Fig. 4 displayed the SEM photographs of GF before and after electrochemical oxidation. It was obvious that the GF surface is eroded by electrochemical oxidation, resulting in the surface area increase.

XPS spectra (Fig. 5) indicated that the O/C ratio on the surface of GF increases with the product of electrochemical oxidation time and current density. When the product increased from 0 to 3000 C g$^{-1}$, the O/C ratio augmented from 0.085 to 0.15. Combined with the FT-IR spectra, the increase in the O/C ratio was supposed to be the increment in COOH functional groups during electrochemical oxidation treatment, and mechanism for electrochemical oxidation of GF was brought forward [19,21].

Conductive plastic, titanium foil and graphite plate were employed as bipolar electrode materials, and their electrochemical activity and durability in electrolyte were explored during the charge–discharge course. Taking their conductivity, permeation and mechanical properties all round, conductive plastic was recognized to be the most appropriate bipolar electrode materials.

Conductive plastic were fabricated by mixing SEBS, PP, ABS, LDPE and HDPE with conductive fillers such as carbon black, graphite powder and graphite fiber in a closed plastic refining machine at 160–190 °C. To overcome the deterioration in the mechanical properties of polymer composites with high carbon loading, a range of chemically resistant rubbers was blended into the composites. The
SEBS/PP composite exhibited eximious electrical, mechanical, permeation, and electrochemical characters and was chosen as the candidate of electrode matrix material for the vanadium redox battery. Fig. 6 shows the structure of a bipolar electrode, which is composed of a layer of conductive plastic and two layers of GF.

Although the battery performance was affected by a number of factors, the fundamental knowledge of negative and positive electrode reactions was still important to optimize the battery operation and to realize high energy efficiency. Based on the studies of electrochemical behavior of V(IV)/V(V) redox couple on glassy carbon and gold electrode along with graphite electrode using cyclic voltammetry, polarization curve measurement, impedance spectroscopy and rotating disk electrode (r.d.e), the diffusion coefficient and dynamic parameter of V(IV)/V(V) redox couple on graphite electrode were obtained [15]. It was realized that the redox process of V(IV)/V(V) couple on glassy carbon electrode was not only a simple charge transfer reaction, it involved the post-chemical transforming process with the transfer of oxygen atom.

Fig. 7 shows that the positions of current peaks varied with scanning rate. Fig. 8 displays that peak current densities was not a linear function to the square root of scanning rates for V(IV) oxidation. These results suggested that the V(IV)/V(V) redox reaction on GF electrode was a quasi-reversible process. The Tafel slope value (0.124 V/decade) obtained from the polarization curve (Fig. 9) agreed well with the theoretical value (0.12 V/decade), which supposed the electron transfer step was the rate-determining step.
Impedance spectra (Fig. 10) at various potentials were studied and simulated by equivalent circuits, which revealed the impedance value of the electron transfer step modified was much higher than the others, suggesting that the electron transfer step was the rate-determining step.

The performances of several kinds of membrane (Nafion membrane, FYM, J-160, J-80 and PE-01 ion exchange membrane) in vanadium solution, including their impedance, chemical stability, diffusion and electrodialysis of vanadium ion, were investigated. Results showed that the PE-01 membrane has low permeability but high area resistance and poor chemical stability. After crosslinking with DVB, subsequently modified by Zr$_3$(PO$_4$)$_4$, the comprehensive performance of PE-01 improved. This membrane has been used in 3 M sulfuric acid containing 2 M vanadium ion for two years, the permeability of vanadium ion in this membrane is only $\frac{1}{4}$ of that in Nafion, and its conductivity is close to that of Nafion.

3.1.3. Design and optimization of configuration

Intrinsic relation between output performance and liquid transmission, temperature and liquid flow were discussed in-depth, including the heat emanation, overcharge–overdischarge ability the uniformity of each battery. Double-cycle closed circuit configuration was adapted. Valuable progress was also obtained in frame and sealed materials [22].

One kW vanadium battery stack (Fig. 11) was designed and tested for operation. The system achieved voltage efficiencies above 82.0% under 40–60 mA cm$^{-2}$, cost below ¥1950 kWh. As can be seen from Fig. 12, when the stack discharged at 80% SOC, the output current was 22–36 A, the output potential was 30–22 V, and the maximal output power climbed to 1 kW. The working state of the system performed reposefully with the close potential of different single cell under 40 mA cm$^{-2}$ at 45% SOC or 80% SOC (Fig. 13).

4. Prospect

As China is abundant in vanadium resources, to develop VRB system in China can not only improve the utilization of the resource but also contribute to the national energy conservation and emission reduction.
efficiency and the safety of energy, but also ameliorate environment and utilization of resource. Therefore, the flow battery energy storage technology has been emphasized in the National 11th Five-year Plan of China. VRB has now reached commercial state. In September 1997, Kashima-Kita built a 200 kW/4 h-rate battery interconnected to the company’s power plant grid system for load leveling [23]. And especially in 2001, a vanadium energy storage system (VESS) incorporating a 250 kW/520 kW h VRB was established in South Africa, which is significant in that it is the first large-scale commercial trial of user-based applications for the VRB [24]. However, there are still many problems that need to be solved. Electrode materials, membrane and bipolar plate are crucial to VRB.

It is expected that various joint venture arrangements will be established between VRB and interested companies. One such cooperating with us is currently being negotiated with a Chinese bus company to install vanadium redox fuel cells into electric buses along with the installation of recharging/refuelling stations for the Beijing Olympic Games in 2008. Potential market for battery electric buses and Taxis in China is vast. The Government recently appropriated funds to purchase 12,000 battery electric and rechargeable batteries for redox flow cell applications. J Power Sources 1985;15:179–90.

References