Review on Types of Redox Flow Batteries for Energy Storage

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Abstract - In recent times with the depletion of fossil fuels renewable energy market has seen a tremendous growth. But the problem of energy storage has remained challenging. Lithium ion batteries which have been researched since many centuries have reduced the cost of the lithium ion batteries. But the problem with lithium ion batteries has been not solved. The explosion of battery, degradation of the battery, low life cycles etc. On the other hand Flow batteries have a high potential. The problems of lithium ion battery have been solved by flow batteries such as flow batteries have low probability of explosion, high life cycles etc. This paper gives a review on the types of flow batteries, there advantages and the challenges.

Key Words: Renewable energy storage, Redox Flow batteries, Lithium ion batteries.

1. INTRODUCTION

The usage of the fossils fuels has been a main factor leading rise to the global warming effect. On the other hand potential in renewable energy has led many countries to shift towards the green energy. Many countries such as India, USA, Denmark etc. has implemented many renewable energy projects. But with there are many challenges in implementing the green energy. Energy storage is one of the major problems and has challenged researchers to think.

Today there are many different types of batteries such as lead acid, lithium ion, redox flow batteries etc. Among which lithium ion batteries are widely used. Lithium ion batteries have high energy storage, it's a mature technology, and it has fast response time and also has minimum impact of surrounding placement geology. But lithium ion batteries also have some disadvantages such as highly flammable electrolyte, harmful if fully discharged, lithium is very toxic and it not recyclable, lithium is abundant in nature etc.

Recently flow batteries have challenged the lithium ion batteries. Flow batteries have many advantages such as moderate efficiency, lower levels of gas evolution, Potential for electrolyte recycling between applications [1]. During the selection of the energy storage one must go through the following characteristics

1. Efficiency – It is the ratio of the rated output power to the rated input power. High efficiency should be chosen for the energy storage.
2. Storage capacity – It is the ability to store the energy. High storage capacity batteries are highly recommended.
3. Fast response time - To effectively execute power quality duties, fast response times are essential to mitigate voltage drops that occur during power generation.
4. Long life - Long operational life of battery is recommended. Depending upon the manufacturer and type of the battery the cost may increase on the basis of the long life.
5. Low environmental impact – Batteries is made of many compounds and uses many chemicals. One must choose the battery which has low environment impact.

1.1 Literature survey

Redox flow batteries are classified into 3 types

1. Liquid phase.
2. Solid phase.
3. Hybrid flow batteries.

1.2 Liquid phase

In these batteries chemical energy is stored in electrolyte. Batteries coming under liquid phase and workings are given below.

1.2.1 Iron Chromium Redox Flow Battery

Iron chromium battery was studied at NASA Lewis research center in the year 1970. Iron chromium battery is acidified with hydrochloric acid having redox couple as Fe^{3+}/Fe^{2+} and Cr^{3+}/Cr^{2+}.

At negative electrode - $Cr^{3+} + e^- \leftrightarrow Cr^{2+}$

At positive electrode - $Fe^{2+} - e^- \leftrightarrow Fe^{3+}$

The Ion exchange membrane in the Iron chromium RFB separates the two flowing reactant solution that prevents cross mixing of reactive cat ion. The standard cell voltage is 1.18v. The kinetic rate of Cr^{3+} to Cr^{2+} is slow because of presence of Cr^{3+} complexes such as $Cr(H2O)_6^{3+}$ and $Cr(H2O)_5^{2+}$,hence the catalyst is required such as Gold, Bismuth. As shown in Fig 1. No catalyst is required for Iron electrode required for Iron electrode. [2]

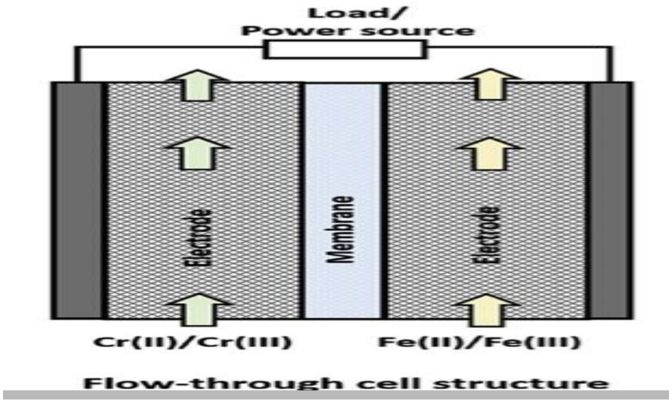

Fig-1 Schematic diagram of Iron chromium redox flow battery

Challenges-

- Iron chromium redox flow battery has low energy density that is less than 10 Whkg-1.
- Since noble catalyst should be used for the kinetic rate, the result of this will be the increase of the system cost.

1.2.2 Vanadium Redox Flow Battery

The negative half-cell consist of V^{2+} /V^{3+} and the positive half-cell consist of V^{4+}/V^{5+} as the Redox couple having the electrolyte sulfuric acid.

At negative electrode, $V^{3+} + e^- \leftrightarrow V^{2+}$

At Positive electrode, $VO^{2+} + H_2O \leftrightarrow VO^{2+} + 2H^+ + e^-$

VRFB eliminates the problem of cross contamination by diffusion of different redox ions across the membrane since the Nafion cation exchange and New Selemion anion exchange membrane were found chemically stable. As shown in Fig 2.

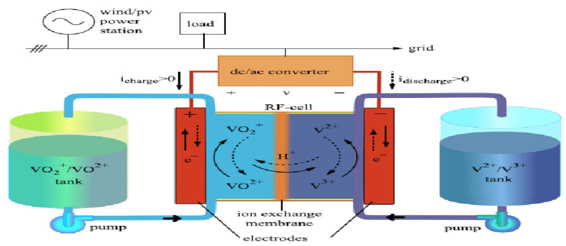

Fig-2 Schematic diagram Vanadium redox flow battery

VRFB shows the fast kinetics of vanadium couple which results in high charge and voltage also the efficiency increases from 71 up to 90 % reported with 1KW VRFB stack. Hence no catalyst is required for the VRFB. In VRFB there is no problem with overcharging and deeply discharge. The electrolyte is reusable therefore VRFB battery has long life and low cost [3].

Challenges:

- Vanadium redox flow battery has low specific energy (25-30Whkg-).
- If the concentration over 2M is increased them the precipitation occurs in the V^{5+}electrolyte at temp above 400°c and solid vanadium oxides v^{2+} or v^{3+} at temp below 100°c. Hence a low energy density is a big challenge.
- Highly oxidizing nature of V^{3+} causes the degradation of the ion exchange membrane and the positive electrode material.
- VRFB flow battery limits the selection of positive electrode such as carbon, this increase the cost of VRFB system.
- Expensive vanadium electrolyte and cell components including Nafion based membranes and electrode materials results into high cost.

1.2.3 Bromine Polysulphide Redox flow battery

The Bromine Polysulphide RFB consists of NaBr electrolyte in the positive half-cell and $Na_2 S_4$ electrolyte in the negative half-cell. It is separated by a cat ion exchange membrane to prevent sulfur anions directly with bromine.

At negative electrode, $S_4^{2-} + 2e- \leftrightarrow 2 S_2^{2-}$

At positive electrode, $3Br^- -2e^- \leftrightarrow Br_3^-$

Bromine Polysulphide has graphite as the positive electrode and porous nickel sulphide as the negative electrode. Electrical balance is obtained by the transport of Na^+across the membrane. As shown in Fig 3. The operating voltage is 1.7v at fully charged state [4].

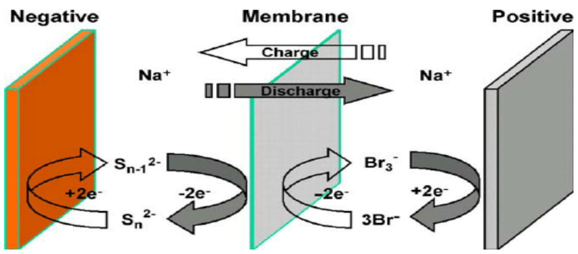

Fig-3 Principle of bromine polysulphide redox flow battery

Challenges -

- Because of crossover of ionic species through membrane there is risk of cross contamination of electrolytes.
- On electrodes or membranes buildup of sulfur species such as S^{2-} takes place which results in loss of sulfur from system
- Since mixing of electrolyte takes place in this battery they can generate heat and toxic gases such as Br_2 and H_2S.

1.3 Solid Phase

In these batteries chemical energy is stored in active metal on the electrode plates. Batteries coming under solid phase and workings are given below.

1.3.1 Soluble lead acid Redox Flow Battery

Pb(II) and Pb(IV). The electrolytes are formulated from lead oxide, lead carbonate or aqueous lead methanesulfonate , $Pb(CH_3SO_3H)^2$, and methanesulfonic acid (MSA), CH_3SO_3H. During charging the oxidation reaction occurs at Pb^{2+} which leads to deposition of lead oxide on positive electrode [5]. During discharging electrodeposits dissolve back into electrolyte. As shown in Fig 4. Soluble lead redox flow batteries have low cost as there is absence of membrane and can be easily scalable.
Following are the reactions taking place at electrodes

Negative: $Pb^{2}+ 2e^{-} \rightarrow Pb$

Positive: $Pb^{2+} + 2H_2O - 2e^{-} \rightarrow PbO^2 + 4H$

Overall: $2Pb^{2+} + 2H_2O \rightarrow Pb + PbO^2 + 4H^+$

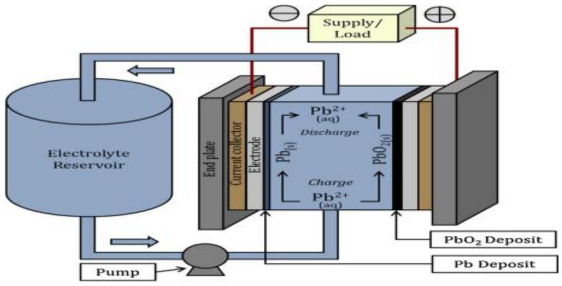

Fig – 4 Soluble Redox Flow batteries

Challenges -

1. Growth of Pb dendrite at the negative electrode.
2. Poor reversibility PbO_2 at the positive electrode.

1.3.2 Zinc Nickel Redox Flow Battery

These types of batteries consists cell stack, electrolyte reservoir, pump and flow plate. As shown in Fig 5. Zinc nickel redox flow battery uses an inert metal collector as negative electrode, highly concentrated zinc acid alkaline solution as electrolyte and nickel oxide as positive electrode. In the battery two simultaneous reactions occur. During discharging with the help of the pump, electrolyte flows into the cell stack and NiOOH is converted to Ni $(OH)^2$ in solid phase. On the negative electrode zinc is oxidized to zincate. The reverse process occurs during charging.

Following are the reaction that takes place in the battery. Zinc nickel redox flow battery is low cost, environmentally acceptable and has high standard potential with high energy densities. [6]

$$2NiOOH + 2H_2O + 2e^{-} \rightarrow Ni(OH)^2 + OH^{-}$$

$$Zn + 4OH^{-} \rightarrow Zn(OH)_4^{2-} + 2e^{-}$$

$$Zn + 2NiOOH + 2H_20 + 2OH^{-} \rightarrow 2Ni(OH)^2 + Zn(OH)_4$$

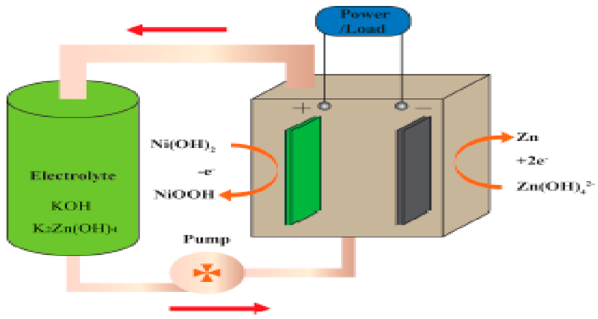

Fig-5 Zinc Nickel Redox Flow Battery

Challenges –

1. Formation zinc dendrites.
2. Decrease in cycle life of ZNBs.

1.4 Hybrid Redox Flow Battery

In these batteries redox couples dissolve in liquid electrolyte. Batteries coming under liquid phase and workings are given below.

1.4.1 Zinc-Bromine flow batteries (ZBFB):

Zinc bromide flow batteries employ redox couple Zn^{2+}/Zn and Br^2/Br^-. It uses inexpensive and abundant zinc bromide as an electrolyte.

At negative side, $Zn \leftrightarrow Zn2^+ + 2e-$
At positive side, $Br^2 + 2e^- \leftrightarrow 2Br^-$
Because of high potential of Zn and Br it has high energy density of around 65-75Whkg-

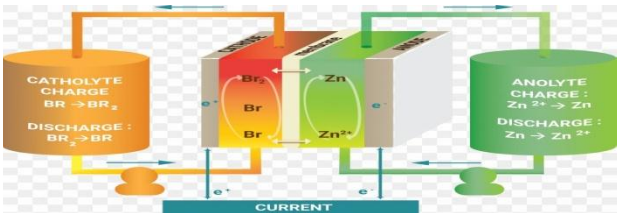

Fig-6 Principle of Zinc Bromine Flow batteries

During charge metallic plate zinc is plated onto the negative electrode from electrolyte while bromine is generated at positive electrode [7]. As in shown in Fig 6

Challenges -

- Zinc dendrite formation is one of the major challenge in ZBFB battery, it increases internal resistance
- Due to increase in internal resistance there is low power density due to low electrolyte conductivity and because of large polarization in positive electrode.
- Recently to suppress zinc dendrite formation, Methane sulfonic acid (MSA) is used to increase ionic conductivity, it reduces the battery internal resistance and also because of MSA battery efficiency increases.

1.4.2 Vanadium Air Flow Battery (VARFB):

In the vanadium air redox flow battery the positive redox couple that is (VO^{2+}/VO_2^+) is substituted by the (H_2O/O_2) couple. The energy density is increased than the Vanadium redox flow battery (VRFB). As shown in Fig 7.

At the negative electrode, $V^{2+} \leftrightarrow V^{3+} + e^-$
At the positive electrode, $O_2 + 4H^+ + 4e^- \leftrightarrow H_2O$
The O_2 for the discharging process is given by the ambient air. [8]

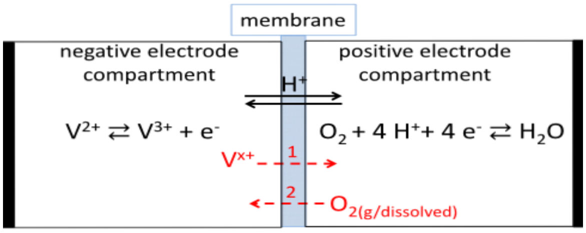

Fig-7 schematic of vanadium air redox flow battery.

The red transfer process indicates undesired transfer process.

Challenges -

- During charging, the oxygen is produced on the porous positive electrode which gets contact directly with the membrane, Therefore the produced oxygen can permeate in dissolved or gaseous or dissolved form from positive to negative electrode which can reduce the performance of a vanadium air redox flow battery.
- Another challenge is the vanadium crossover from the negative electrode to the positive electrode which can lead to reduced columbic efficiency and can lower the life cycle of the battery due to irreversible loss of capacity. Recently modification had been done on the membrane of the VARFB that is N117 membranes (PEI/Nafion) has been utilized it has enhanced the columbic efficiency.

1.4.3 All Vanadium aqueous Lithium Ion battery (VALB):

All vanadium aqueous lithium ion battery is constructed using $LiVOPO_4$ cathode,VO_2 anode and 20M LiTFSI aqueous electrolyte. As shown in Fig 8

At cathode, $LiVOPO4 - e^- \leftrightarrow VOPO_4 + Li^+$

At Anode, $VO_2 + Li^x + xe^- \leftrightarrow LixVO_2$

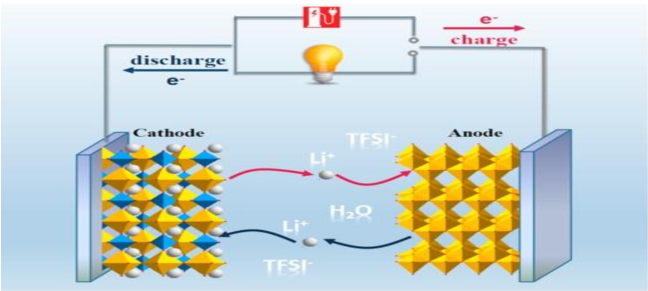

Fig-8 Schematic diagram of all vanadium aqueous Lithium ion battery (VALB)

VALB gives excellent electrochemical performance with an average operating voltage of 1.4V .It has very high density of 84Whkg-.The battery has excellent cycling stability with 84 capacity retention of current density of 100 mAg- over 1000 cycles hence the battery has long lifetime. All Vanadium aqueous lithium ion battery can operate at wider temperature range of 20-800°c [9].

2. CONCLUSION

Redox flow batteries are found to be most suitable batteries for the energy storage. The three types of redox flow batteries are (1) all liquid phase battery. (2) All solid phase battery and (3) Hybrid redox flow battery. Comparing all three types of battery all types of batteries has some challenges among them Hybrid redox flow batteries has found out be most comprising and reliable battery for the energy storage. Recently developed battery all vanadium aqueous Lithium ion battery (VALB) has very high density of 84 WhKg- with long lifespan. To improve the performance of the RFB, Electrodes, ion-exchange membranes, cells, and electrolytes are the keys for the development of the Redox flow batteries.

REFERENCES

[1] Kyle Lourenssen, James Williams, Faraz Ahmadpour, Ryan Clemmer, Syeda Tasnim, "Vanadium redox flow batteries: A comprehensive review", Journal of Energy Storage, 25(2019)10084.

[2] Y.K. Zeng, X.L. Zhou, L. An, L. Wei, T.S. Zhao, "A high-performance flow-field structured iron-chromium redox flow battery", Journal of Power Sources, 324(2016)738-744.

[3] Yu Shia , Chika Ezea, Binyu Xiongb, Weidong Hec, Han Zhangd, T.M. Lime A, Ukilf, Jiyun Zhaoa, "Recent development of membrane for vanadium redox flow batter applications: A review", Applied Energy,238(2019),202-234.

[4] Lina Wang, Xiaofei Wang, Jingyuan Liu, Hao Yang, Cuimei Fu, Yongyao, Xia, Tianxi Liu, " A rechargeable Metal free full – liquid sulphur-bromine battery for sustainable energy storage".Journal of Material Chemistry, " 2018, 6, 20737–20745.

[5] Shivangi Kosta, R Sneha, Kuldeep Rana, Design, Fabrication and Electrochemical performance of Soluble Lead Redox-Flow Battery for Energy Storage, National Power System Conference.

[6] Shouguang Yao , Peng Liao , Min Xiao , Jie Cheng, Wenwen Cai, Study on Electrode Potential of Zinc Nickel Single-Flow Battery during Charge, Energies,2017.

[7] M.C. Wu, T.S. Zhao, L. Wei, H.R. Jiang, R.H. Zhang, "Improved electrolyte for zinc-bromine flow batteries", Journal of Power Sources,384(2018),232-239.

[8] Jan grosse Austing, Carolina Nunes Kirchner, Lidiya Komsiyska, Gunther Wittstock b, "Layer-by-layer modification of Nafion membranes for increased life time and efficiency of vanadium/air redox flow batteries", Journal of Membrane Science, 510(2016),259-269.

[9] Miaomiao Shao, Jintao Deng, Faping Zhong, Yuliang Cao, Xinping Ai,Jiangfeng Qian, Hanxi Yang, An all-vanadium aqueous lithium ion battery with high energy density and long lifespan,Energy Storage Materials,volume-18,March 2019,92-99.