

## 1. Introduction:

The charge of vehicles into battery electric vehicles (BEV) has been by and by for well longer than 10 years as an endeavor to move away from non-renewable energy sources). Notwithstanding, the high introductory expense of the batteries, for example, the most basic form of electric vehicle batteries, i.e Lithium ion and NiMH that are required for propulsion of electric vehicles, are followed by various shortcomings like limited range, heavy weight to gas-powered engines, and moderate regeneration of energy along with limited occupant and cargo space due to battery pack, these are the basic ingredients that have limited the electric vehicles from being at the top. Among these are the redox flow batteries that are the strongest competition to lithium ion and NiMH battery vehicles. The redox flow batteries take an edge over the conventional battery packs due to reduced time of charging and longer life of the battery pack that will be covered in this article.[1]

The VRB has comparable difficulties and advantages as the greater part of the other major RFBs. The VRB battery, nonetheless, has the huge advantage of not experiencing electrolyte cross tainting, and it can work at up to 90% effectiveness (the proficiency is regularly in the 80-90% territory). Extra advantages of VRBs over RFBs incorporate electrolyte recyclability, and lower part erosion. A significant advantage of utilizing VRBs, beside the possible money saving advantages, is the similarly (to more harmful batteries, for example, lead-corrosive batteries) little natural effect (in spite of the fact that there are poisonous components in the VRB). Also, the VRB electrolytes in every half cell don't cause tainting, e.g., because of electrolyte spillage through the PEM, when the VRFB is in the uncharged state[2].

In a Vanadium Redox Flow Battery, the vanadium exists in four different redox states; V<sup>2+</sup>/V<sup>3+</sup> and V<sup>4+</sup>/V<sup>5+</sup>. The model ideal match of electrolyte for VRB is sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) on the base that it gives adequate solvency to each of Vanadium oxidation states mentioned before. The advantage of adding the sulfuric acid is also that it builds up the ionic conductivity of the catholyte or the positive electrolyte. In addition, it gives hydrogen particle at the positive terminal.

During the release, the V<sup>2+</sup> gets oxidized to V<sup>3+</sup> in the negative electrolyte, while V<sup>5+</sup> gets reduced to V<sup>4+</sup> in the positive electrolyte, thus charging of a Vanadium Redox Flow battery is the converse of this same interaction of redox states. Also, using vanadium in both half cells makes it a dependable storage system also minding the fact that the cell limit won't crumble with the way that similar metal particles are being used in both electrolytic arrangements.

In case of cross contamination, there is no energy loss for that specific cycle. By adding a siphon to each electrolyte tank will consider the course of both the electrolyte tanks, in such arrangement, the dissemination is allowed to move through an electrochemical cell stack comprising of various cells connected in one or the other arrangement or equal.[3]

## 2. Availability of Vanadium (India Perspective):

All India total resources of vanadium as on 1-4-2005(provisional) are 24.85 million tonnes with 65390 tonnes of metal. Out of these 24.43% of ore is under reserve category and the balance in remaining resource category. The freehold resources are 18.52 million tonnes with 54620 tonnes of metal and 6.31 million tonnes with 10770 tonnes of metal in leasehold, all under the public sector. Out of the public leasehold 90.52% are in captive and 9.48% in non-captive sector.[4]

As per the NMI database, India has only the estimated resource of Vanadium ore of about 24.63 million tonnes but there is no proved/probable reserve of Vanadium established in India.

Table 1: Vanadium Composition and Extraction

Parameters	Composition		
Minerals [5]	Patronite	Carnotite	Vanadinite
Deposits [6]	Titaniferous magnetite	Phosphate rock	Uraniferous sandstone
Extraction Process	Acid leaching	Solvent extraction	Stripping step

Table 2: Vanadium thermophysical properties

Properties	Value
Atomic Number	23
Atomic Mass, g.mol <sup>-1</sup>	50.9414
Density, g.cm <sup>-3</sup> at 20°C	6.1
Electrical Conductivity, S/m	5×10 <sup>6</sup>
Resistivity, m Ω	2×10 <sup>-7</sup>
Thermal Conductivity, W/(m K)	31
Thermal Expansion, K <sup>-1</sup>	8.4×10 <sup>-6</sup>
Melting Point, °C	1910
Boiling Point, °C	3407
Isotopes	5
Electronic Shell	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>
Crystal structure	BCC (Body-centered cubic)

Table 3: Vanadium based electrolyte batteries properties [7]

Parameters	VFB	Li-Ion	Zinc-Air	Lead-Acid
Response Time	20 kW/s	200khz	N/A	10kW/s
Storage Capacity	120kWh	55kWh	160kWh	25kWh
Cost	\$66/kWh	\$100/kWh	\$45/kWh	\$41/kWh
Efficiency -	75-80%	99%	<60%	85%
Energy Density (Weight)	20-35Wh/L	75-200Wh/L	20-35Wh/L	60-80Wh/L
Volumetric Density (SIZE)	580Wh/L	732Wh/L	1353Wh/L	N/A
Nominal Voltage	1.15-1.55V	3.60V	1.45V	2.1V

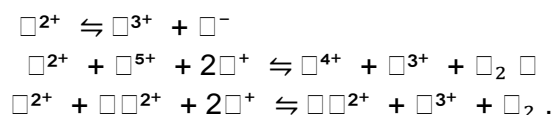
Life	20yrs	2-3yrs	3yrs	5yrs
Electrolyte	Sulphuric acid	ethylene, carbonate	KOH, NaOH	Sulphuric acid
Membrane	Carbon nanotube & nafion	PVDF-HFP gel polymer	Organic polymer porous membrane	UHMW-PE
Electrode	Carbon felt, Graphite felt	Metallic lithium, graphitic carbon	Air, Zinc	Lead/Antimony

### 3. Working and mechanism:

The general arrangement of all vanadium storage system consists of two terminals; anode and cathode, along with a membrane layer separator that takes into account the movement of hydrogen particles across this membrane film while avoiding the cross dissemination of the electrolyte arrangement of the two half cell tanks.

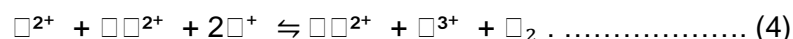
At any point when an external source is connected with the anode, electron moves through the circuit from the negative terminal/anode to the positive terminal/cathode. This happens on the principle that joining the two terminals of the battery makes the potential energy in the negative cathode increase which makes the electrons flow from the negative to the positive anode by means of oxidation of the redox states of vanadium(V<sup>2+</sup> to V<sup>3+</sup>) along with power output. Simultaneously, the connection of terminals makes the potential energy in the positive anode decrease which is caused by reduction of the vanadium redox states(V<sup>5+</sup> to V<sup>4+</sup>). While all this happens, there is movement of hydrogen particles across the membrane meant for isolating the two half cells, and this happens in order to keep up with the charge balance and also to finish the circuit. When the balance is successful in both the half cell/tanks, the reaction stops and consequently no power can be extracted from the Vanadium Redox Flow Battery.

For charging of the VFRB, the conditions are needed to turn around the interaction of the electrolyte and terminals connected to an external power source. With this, the positive cathode gathers a potential, following which oxidation happens in the positive electrolyte and with this the electrons are emitted, converting the V<sup>4+</sup> redox state to V<sup>5+</sup>. Simultaneously, negative terminal has a negative potential which is acknowledge by electrons from the positive side, and this converts the V<sup>3+</sup> redox state to V<sup>2+</sup>. The same condition of the energy storage system is reflected in reactions below. The first two conditions, going from left to right subject the reduction happening at the cathode and oxidation taking place at the anode separately[6].



Here H<sub>2</sub>O and H<sup>+</sup> protons are essential for the cathodic response and to keep up with the charge equilibrium and stoichiometry in the VFRB. The Vanadium ions; V<sup>4+</sup> and V<sup>5+</sup> are actually the vanadium oxide particles VO<sub>2</sub><sup>+</sup> and VO<sub>2</sub><sup>+</sup> respectively.

In this way equation (1) can be changed into condition (2).



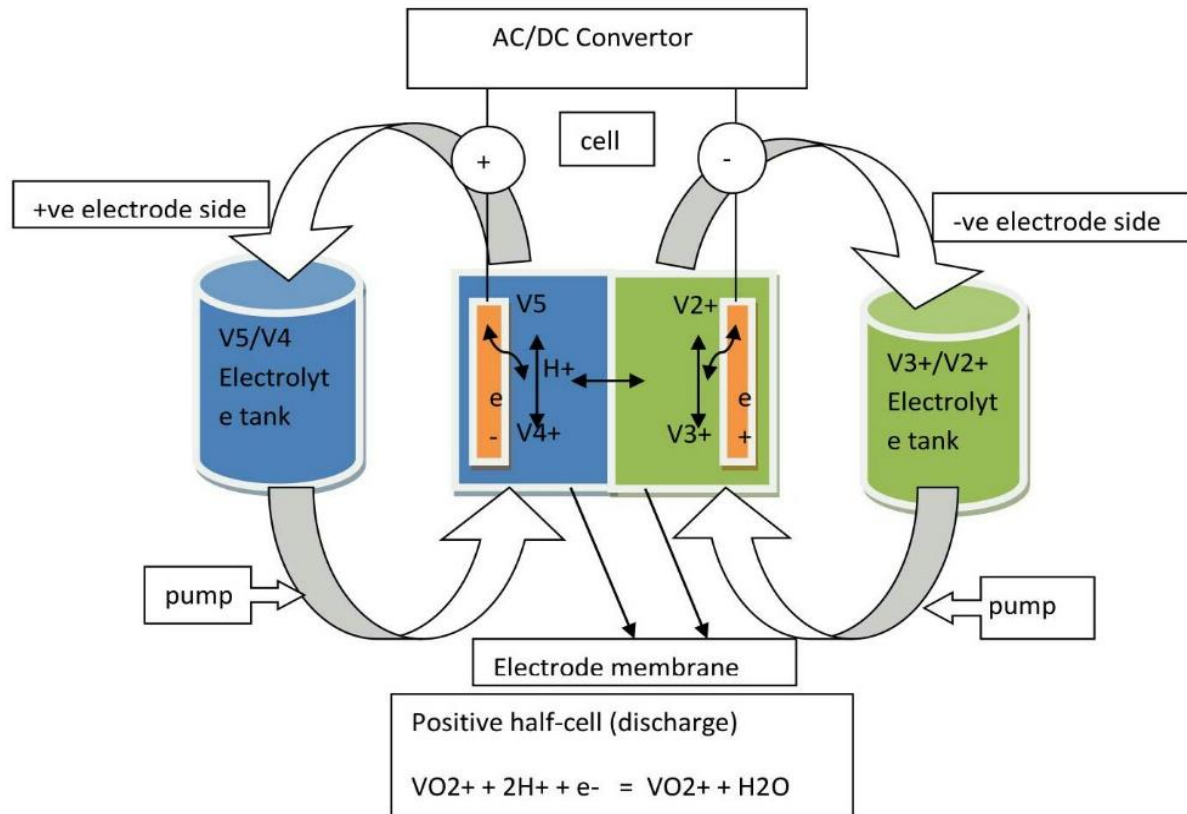
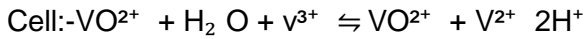
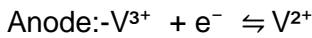
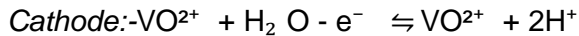
**Reactions Involved: Vanadium Redox Flow Battery (VRFB)**

Fig. 1: Working of a Vanadium Redox Flow battery

**Nomenclature:**

$\text{VO}_2$ : Vanadium Oxide

$\text{H}_2\text{O}$ : Water (l)

AC/DC: Alternating current/Direct Current

V5/V4/V3/V2: Redox states of vanadium in electrolyte

In the vanadium setup, there is no strong reason to keep up the equilibrium between the positive and negative sides of the system. In the positive half cell, the Vanadium is arranged as oxy-cations, which are down against the irreversible precipitation as  $\text{V}_2\text{O}_5$  if the electrolyte's temperatures exceeds  $-50$  to  $-60$  deg C. When this precipitation takes place, it happens as a regular considerate mixture not  $\text{V}_2\text{O}_5$ .

The optimal working temperature of the VRFB is recognized between  $10$  to  $40$  deg C. Hence dynamics cooling of the system is used if the surrounding temperatures exceed the  $40$  to  $45$  deg C mark. With this, the available option to cool the system effectively benefits the system for longer working and staying miles away from any damage. Besides, if the system overheats anyhow, its best to cut off the power or usage of the cell until it cools off to optimum temperatures.

As it is know that the cell voltage is  $1.4$  to  $1.6\text{V}$ , and the cell power density range in hundreds  $\text{mW}/\text{cm}^2$ . The DC-DC production of such type of batteries is predicted to the scope of  $60$ - $80\%$ . As per EPRI, the VFRB is a reasonable alternative of energy storage system with range of  $100\text{kW}$  to  $100\text{MW}$  along with capacity to run in the range of  $2.8$  hours[9]. Re-stimulating the battery moves electrons through the bipolar plate from the

positive side to the negative side and causes hydrogen ( $H^+$ ) particles to diffuse across the layer to the negative side. A comparable reaction happens in reverse during discharge. Early executions of VRFB had energy efficiencies around 70% and later headways incited efficiencies of more than 80%.[8]

#### 4. Manufacturing Processes:

- The Vanadium as known to the mankind exists as a soft grey ductile element in its purest form and is derived from mineral iron ore, carbonaceous shale or phyllites and even steel slag. Vanadium is the chemical compound of the periodic table which is depicted by the symbol 'V' and also the atomic number of 23. In other forms, it can also exist as a hard, silvery-grey malleable (can be extended by hammer or pressure) transition metal. In this form of the Vanadium, which is quite rare, it is required to be artificially isolated to proceed with the formation of an oxide layer that stabilizes the free metal (Vanadium) from further oxidation.
- On the planet earth, the Vanadium can be found in four principle forms that is; vanadiferous titanomagnetite deposits; sandstone hosted vanadium deposits; shale-hosted deposits; vanadate deposit. Among these existing forms, the most important source of raw vanadium is the vanadiferous titanomagnetite deposit that is commonly found around the globe.
- Other basic sources of the Vanadium includes metal raw material, concentrates, metallurgical slags, and oil stores, in which the concentration of Vanadium is obviously low compared to the deposits aforementioned. About a great deal of Vanadium is reused and amongst recycling, the most essential kinds of discretionary flow of this recycled metal are steel scrap, which reuses vanadium content and spent catalysts. Other process of reusing and producing refined vanadium includes calcium chloride, cooking besides, depleting, dissolvable extraction, and molecule exchange.
- The last proportions of vanadium to be discussed are vanadium metal ferrovanadium (iron-vanadium blend), vanadium pentoxide which are unique vanadium compounds found but are dependent on the ideal application of this metal.
- Discussing the chief raw Vanadium source for reuse of metallic vanadium will always land us on titaniferous magnetites. It is observed that Vanadium and Vanadium mixtures are been recovered through various mechanical methods. Such methods are also known for recovery of aluminium and magnesium metals from smelters and treatment offices along with production of uranium.
- For the final part of Vanadium sources and production, we head to vanadium left in the raffinate after the dissolvable extraction of uranium from mineral leachate is reduced to a characteristic stage that results in a dissolvable extraction process, back-isolated with sodium carbonate and hastened with ammonium sulfate as ammonium metavanadate in the end of the process. Following this, the compound is calcined to leave Vanadium pentoxide.
- The most common treatment of basic vanadium bearing metals includes beating and cooking with sodium chloride or sodium carbonate at around 850 deg C. This constructs water dissolvable sodium metavanadate. In the next process, it is depleted with water, a polyvanadate (red cake) which is supported with sulfuric catalytic at pH 2-3. Now, it is warmed at 700 deg C to form dim, vanadium pentoxide and this reduction secures the vanadium metal.
- Pure metal can be overcome with reduction of vanadium pentachloride with hydrogen or magnesium, reducing vanadium pentoxide with aluminium or calcium, and electrolysis of basic refined vanadium in consolidated dissolvable base metal halides.
- Another method of refining vanadium aluminium mixes utilizes refinement using fluid salt electrolysis principle method. Here Carbon is not the first pick for reduction to keep up with essential separation from the expansion of vanadium carbides.



Table 4:

Component	Procedure
<b>Nafion Membrane</b> [12]	Polymerization reaction of tetrafluoroethylene (TFE) and a co-monomer
<b>sPEEK(Sulfonated polyetheretherketone) Membrane</b> [12]	PEEK is formed from the polycondensation of hydroquinone with DFB in a basic solution, in addition to which sulfonation is carried out in concentrated sulfuric acid
<b>Electrode</b> [12]	Assembled
<b>Stack Frame</b> [12]	Steel structure consisting of two double T-profiles
<b>Electrolyte</b> [12]	Assembled
<b>Electrolyte tank</b> [12]	Glass fiber reinforced plastic production
<b>Current Collector</b> [12]	Assembled
<b>Cell frame</b> [12]	Extrusion
<b>Gaskets</b> [12]	Materials- FKM, EPDM, Silicon
<b>Inverter</b> [12]	Assembled
<b>Copper Cables</b> [12]	Cable production
<b>Pumps</b> [12]	Pump Production
<b>Pipes</b> [12]	Steel pipes with Teflon lining
<b>Heat Exchanger</b> [12]	Assembled
<b>Process Control system</b> [12]	Assembled

## 5. Recycling

- The recycling part of the Vanadium Redox flow batteries involves a recycling efficiency of 95% for the metal parts that can be readily dismantled. The energy input needed for dismantling is equivalently low since the battery parts can be destroyed on a large-scale level as homogenous portions and approximated with the ecoinvent cycle 'iron piece arranging and squeezing'. The electrolyte doesn't corrupt essentially however most likely requires some re-handling and cleansing. For this reason, the power input needed for re-adjusting the electrolyte is represented, assessed dependent on electrochemical counts (measure of power needed for bringing the electrolyte portions from a homogeneous blend to the necessary oxidation states).
- Contrasted with the lithium-particle battery reusing module should be near maintainability. Reusing of Li-Ion and particularly of VRFB is as yet in a beginning stage, and without a doubt, exceptionally restricted information can be found. A few cycles exist for the reusing of LIB, yet explicit cycles for recuperating the materials contained in LFP-LTO batteries are not accessible. Existing conventional reusing measures

recuperate copper and steel from the cell lodging, in addition to cobalt (pyrometallurgical course) or cobalt, manganese, and  $\text{LiCO}_3$  (hydrometallurgical course). Recuperation of phosphate or titanium may be in fact conceivable, however current modern reusing measures don't target recuperating these metals, why it isn't viewed as further. Because of the exceptionally restricted information accessibility, an improved-on approach is utilized for the finish-of-life model of the LFP-LTO battery. The battery establishment is destroyed precisely and the racks and plate lodgings are isolated from the battery cells. The energy inputs needed for destroying and compaction are approximated dependent onecoinvent interaction 'scrap arranging and squeezing'. Steel parts, links, squander electronic segments, and waste plastic are shipped off isolated explicit recyclers, utilizing ecoinvent information for reusing these segments. The energy and material information sources needed for the cell reusing are demonstrated dependent on ecoinvent (half aqueous and half pyrometallurgical reusing). An overall reusing effectiveness of 90% is expected for the essential metals steel and copper and for lithium in the hydrometallurgical course, while the leftover portion is shipped off squander treatment by cremation. For all metal parts that can be promptly destroyed (mechanical partition on a large scale), a reusing proficiency of 95% is expected.[12]

- Still the different individual methods of vanadium involve roasting and leaching of vanadium from the secondary resources, recovery of vanadium using solvent extraction, recovery of vanadium using ion exchange and pyrometallurgical processing of vanadium containing sources.

## 6. Applications (Automotive)

Redox flow batteries prowess in rapid and safe recharge in battery electric vehicles (BEV) by electrolyte exchange. This is seen as the most efficient, practical route for bringing renewable energy (RE) to transport; 'well to wheel' efficiency is more than four times better than Hydrogen and because the 'electric fuel' is recycled continually, operating costs can equal conventional diesel fueled vehicles. 24-hour vehicle availability can overcome the energy and power limitations of flow batteries.

To compete successfully with the flexibility and low cost of established diesel and LPG vehicles, electric city vehicles – taxis, buses and delivery vans need to have a highly flexible operating capability with minimum downtime. Currently flow battery technology achieves an electrolyte energy density, around 25Wh/kg similar to industrial lead acid batteries and therefore cannot match the >100Km range between charges achieved by advanced batteries such as Lithium Ion. Flow battery technology can largely offset this disadvantage by rapid refueling and considerably lower operating costs.

### Features are:

- Vanadium Redox Flow Battery (VRFB) technology with enhanced electrolyte energy density. System will operate with any fully liquid flow battery system including air cathode types.
- Twin Catholyte and Anolyte electrolyte tanks with internal moving membrane separate charged from discharged electrolytes. Tanks are sealed to the atmosphere and always full, so that venting is eliminated and tank volume is minimized on board the vehicle and in the base station.
- A four way (two in, two out) dry-break coupling incorporates selective porting valve which ensures that appropriate tank ports are aligned before fuel pumping commences

- Safe nonflammable 'electric fuel' allows high flow rates and energy transfer at 600kW equivalent. Customers may be billed on a per kWh basis
- Electrolyte is continually re-energized in the refueling station by wind, solar or grid energy according to availability. Off peak baseload power can be utilized and undesirable grid loads during peak times can be avoided. Vehicle may also be recharged by mains power [5].

## 7. Abstract:

In an effort to reduce world emissions by electric vehicles and machines with internal combustion engines has led to the development of batteries that are more powerful and efficient than the common lead acid battery. The most popular batteries being used for such as installation of lithium ion, but due to its short lifetime, charging time, and costs has driven researcher to other technologies to replace it. Vanadium redox flow batteries have come into the light recently as a means of replacing rechargeable batteries in electric vehicles and has previously be used mainly to store energy for load leveling. It possesses many qualities that would be beneficial to electrify vehicles. The battery has the ability for power and energy to be sized independently which is not dissimilar to internal combustion vehicles. It also has the potential for a tolerance to low discharges, fast response time, and can quickly be refueled by replacing the electrolyte; just like is done when a car refuels at the gas station.

## 8. Conclusions:

From the above analysis is can be concluded that:

1. The initial and maintenance cost of the VFRB is more to the comparison of conventional batteries like Li-ion, NiMH and even Lead-Acid batteries. The high production cost will make the VFRB to grow popularity in budget-based market like India.
2. The substantially long life of VFRB can convert to better efficiency, but the production costs limit the usage of VFRB even in automotive world.
3. The composition and production is better to the conventional batteries, but once again, the limited exploitation of the Vanadium resource in India will limit the future, full-fledged usage of VFRB.
4. The recycling is equally efficient to that of the Lithium ion batteries, the overall composition and production includes less diversified components,(as the electrolyte is same in both half-cells), the redox flow batteries take an edge in longevity of materials which don't corrode away easily.

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