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# Developments in Redox Flow Battery Containing Organic Compounds

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***Abstract:-*** The demand for versatile energy storage is continuously increasing day by day as we are moving towards modernity. Electrical energy produced from renewable &non-renewableresources. Nonrenewable resources are used for producing electricity since last 300 years but because of pollution problems we are moving towards more clean sources of energy production. This demand of clean electrical energy lights up the use of Redox flow batteries to store energy & supply when there is a use. Redox flow battery uses inorganic materials but because of expensive metal used in electrolytes it causes a concern & generates the need of low cost material.

The solution to this problem is given by organic compounds that have high voltage, high charge capacity. Hence this review focuses on preparation of Organic based redox flow batteries.It discusses fundamental developments related to Redox flow organic batteries.

***Keywords:*** *Redox Reaction, Fuel Cell, Quinoxaline, Benzoquinone, Redox Flow Batteries.*

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**Introduction:**

Redox flow energy batteries provide solution to energy storage at large scale. As energy demand is increasing from alternate renewable resources these energy storage devices are also needed to meet demands of electricity. In recent years' various developments have been made to produce electricity from non-conventional sources & this energy needs to be stored to make its supply continuous. Robust energy storage devices are required to deliver stable & flexible electricity that follow standard for voltage & frequency for grid connected or off grid [1, 2]. In last 30 years, many energy storage techniques have been developed. Electrochemical method is one the most attractive methods to store energy. This method involves 2 categories: (A) Fuel Cell (B) Rechargeable Batteries.

Electrochemical method involves Redox reaction at respective electrodes present in the system. Rechargeable batteries are based on principle of electrochemical process. It involves metal & metal ion which undergo chemical reaction and store energy in form of electromotive force. Redox flow battery is recognized as one of the most attractive methods amongst electrochemical technologies for energy storage in range of up to tens of MW/MWH [3]. RFBs store all charge in electrolytes recirculated through the cell whereas in rechargeable batteries, charge is stored entirely within the cell. This method of charge storage enables RFBs to be more safe & economical than conventional batteries.

RFB is economic & efficient way because of its very high potential, high efficiency & extremely long charge/discharge cycle life. Other important features of this technology are scalability, flexibility & long durability, fast responsiveness & reduced environmental impact.

RFB is based on oxidation-reduction reaction which occurs in two liquid electrolytes. These electrolytes can be inorganic, organic & hybrid.

RFB can be more easily scaled than rechargeable batteries without incurring loss in power density only by increasing the electrode active surface area & storage capacity can be increased by increasing volume of the electrolytes & concentration. Various metal based RFBs have been developed. Vanadium RFB is example of most developed system & it is a good one because of its high reversibility & large output but its high cost prevents it from market penetration. So need of economical RFB led to development of organic based RFBS. Organic molecule may yield high cell voltage with simple change in their chemical structure & with introduction of some polar groups, solubility can be increased.

Organic (Hydrocarbon) compounds can provide the possibility of a high solubility in both aqueous & non aqueous electrolytes. For example

1) Quinoxaline is soluble up to 4.0 mol/dm$^3$ in potassium hydroxide solution. Its solubility can be reduced by addition of salts & solvents.

2)Methyl p-benzoquinone has a solubility upto 6.0 mol/dm$^3$in acetonitrile [4].

In aqueous system, it's a very difficult task to obtain high solubility & high voltage simultaneously. In contrast non aqueous system suffers from high electrolyte resistance, chemical instability, low utilization & crossover of materials. Some restrictions are there for both the systems that they should use low molar mass molecule to obtain higher specific capacity. Despite these limitations, the energy density of organic – inorganic system in aqueous (16 Whdm$^{-3}$) and non-aqueous (200 Whdm$^{-3}$) [5] is nearly comparable to commercial RFBs in aqueous (35 Whdm$^{-3}$) and non-aqueous (240 Whdm$^{-3}$) batteries. Recently, Dmelloetal have assessed the design parameters of RFBs in both aqueous & non-aqueous electrolytes [6]. He recommended that the most effective approach to reduce overall cost of non-aqueous battery is to increase cell voltage and simultaneously decrease the cost contribution of both specific resistance of the battery and other are use of low molar mass active material and using low salt ratio.

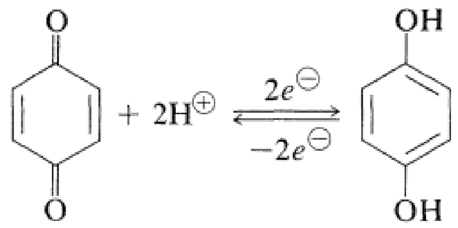
Organic based Redox flow batteries:

(A) Organic – Quinine powders
(B) Organic –
  a. Hydrogenated molecules
  b. Radicals and polymers
(C) Organic – Polymer suspension

Organic base is used for one electrolyte reaction or two electrode reactions. In most cases active species is dissolved in either aqueous or non-aqueous electrolyte and some organic materials are also used in the form of polymer. Metals are incorporated in organic mixture to increase the cell voltage. e.g., Zn (Ɛ° = -0.76 V), Li (Ɛ° = -3.00 V).

Recent research and development in redox flow battery has focussed on synthesis and modification of new organic active molecule [7, 8, 9]. In non-aqueous electrolyte active molecule include transition metal complex achieve high overall cell voltage but these are restricted due to use of expensive metal such as Nickel, Ruthenium and Cobalt [10,11,12], limited solubilities of complexes and low efficiency.

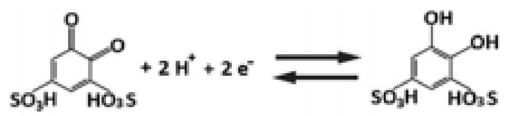
(1) Orgnic Molecules in aqueous electrolyte: Aqueous electrolytes have advantages in terms of cost and ionic conductivities. Aromatic compounds have higher redox (reduction) potential, suitable for positive electrode Organic compound, Quinine containing hydroxyl gp exhibit high reversibility for energy storage application [13, 14, 15]. These hydroxyl gp of quinone serves as liquid carrier of hydrogen in aqueous electrolyte. In this case energy is released by oxifising the hydroxyl group into corresponding aldehyde/ ketone.
Six membered ring compound containing N as hetero-atom ashow increase in redox potential relative to its carbocyclic analogue. Similar effect is indicated in five membered ring [16].
In aqueous solution, pH of the solution is a significant factor that influences electrochemical performance, water solubility of molecule as well as chemical stability of reaction products [17, 18, 19].
  (a) Quinone is used in RFB due to its reversible & stable nature in aqueous media [20]

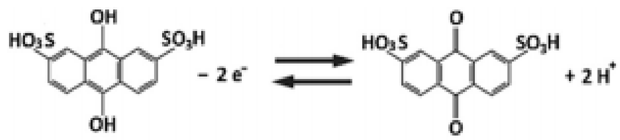



When protons are freely available in aqueous electrolyte, reduction of quinone molecule occurs. This feature of reduction of quinone enables RFBs to achieve high energy density and also enhance solubility in aqueous electrolyte [21]. Other members like benzoquinone, naphthaquinones and anthraquinone also show quinone type behavior in aqueous electrolyte [22]. The hydrogen bonding ability, polarity and acidity of these group helps in achieving high solubility. The formation of protonated hydroquinone through the reduction proves takes place over a range of pH (0.5, -9.5) in p-benzoquinone 82, 6-dihydroxy anthraquinone.

(II) Acidic Anthraquinone – benzoquinone RFB:

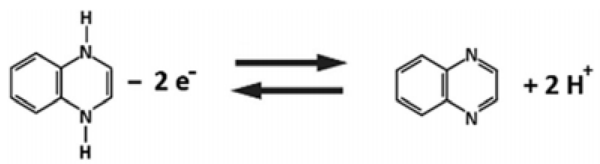
The first all organic RFB was introduced by Yang & Coworkers [23, 24, 25]





Anthaquinone& 1,2 benzoquinone are nearly soluble. Their solubility is increased by adding sufuric acid and hydroxy acid.

(III) Quinonaline acidic benzoquinone RFB:



Brushett and coworkers studied the use of quinonaline in aqueous system. The derivative of quinonaline have been used in dye sensitized solar cells and non-aqueous RFB [26]. It has high solubility in water because of its polar

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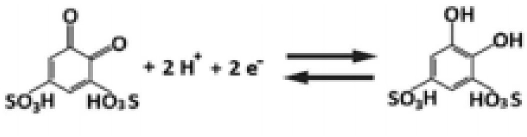
346 – 350

nature. The capacity of 2 $e^-$ transfer and low molecular weight lead to theoretical high specific energy Influence of pH, cation and anion were studied with the help of electrolytes composition.



Recent studies show use of 1,2dihydrobenzoquinone 3,5-disulfuric acid in acidic electrolyte at positive electrode and quinonaline at negative electrode in and alkaline electrolyte yields high cell voltage.

(IV) Methyl viologen – hydroxyl TEMPO Redox flow batteries:

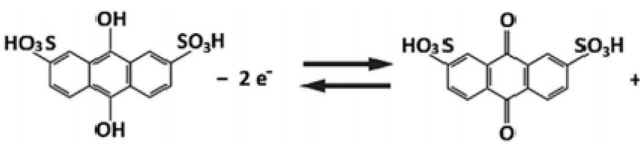
Lics& coworkers suggested the use of such system where similar active species can easily dissolve in aqueous electrolyte [27]. Viologens are organic compound having molecular formula $(C_5H_5NR)^{n+}$ R -> alkyl group Tempo (2,2,6,6Tetramethylpiperidinyl)

2) **Organic-Inorganic RFB:-**

To enhance cell voltage, inorganic active material is mixed with organic active material at electrodes. The inorganic metal species such as zinc, bromine are of low cost introduced in organic active mixture to increase specific energy. This hybrid RFB has high energy density than all organic system.

A) Acidic Anthraquinone-bromide RFB:-

Redox flow batteries can also yield high cell voltage without involvement of metal in hybrid system. This type of example is studied by Aziz Efal. Anthraquinone is a low cost organic molecule which is prepared from anthracene that is abundant in crude oil [28]. Anthraquinone have low electrode potential, it is better for negative electrode.



**At positive electrode: -**

$$Br_2 + 2H^+ + 2e^- \quad \_ \quad 2HBr + \quad E^0 = +1.09V$$

2) Organic material in non-aqueous electrolyte: -

Redox flow batteries in non-aqueous electrolyte operate at higher cell voltage. Many researches have been done for selecting such a redox system that has higher energy density & system efficiency. Matgudaetal in 1988 demonstrated the first non-aqueous RFB based on Ruthenium Bipyridine complex with cell voltage 2.6 Volt [29]. Since then many such systems containing metal coordination complex have been studied [29, 30]. Low ionic conductivity in non-aqueous electrolyte is one of the limitations suffered by it as compared to aqueous system which has high ionic conductivity. This low ionic conductivity is due to higher viscosity of organic solvent. In such case ionic conductivity can be enhanced by addition of salts containing cations e.g. tetraethyl ammonium perchlorate etc [31].

In some cases, propylene, diethyl carbonates also increase ionic conductivity & solubility of active species.

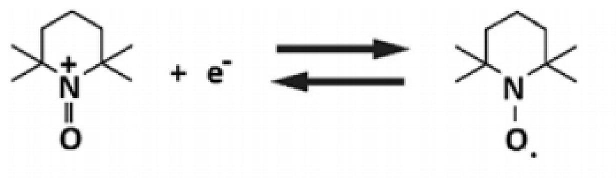
A) All organic redox flow batteries:

This system involves active organic species at both electrode reactions. The active molecules were mainly derivative of quinoxaline, anthraquinone&thiophene. Non aqueous solvents are mainly aprotic. Electron transfer in reaction involve formation of charged radicals, indicating fast reaction but long term poor stability of chemicals is a major concern.

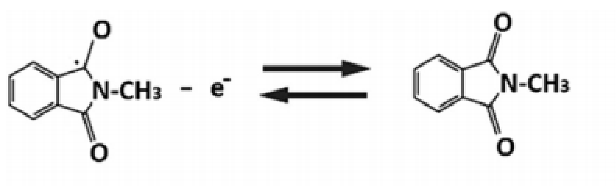
1) N-methyl Thalidomide - TEMPO Redox flow battery

The first non-aqueous all organic RFB was proposed by Li & coworkers using N-methyl phthalimide& TEMPO for negative & positive electrode reaction respectively [32]. This mixture has also been used in traditional Lithium ion battery to prevent over charge.

**At positive Electrode**

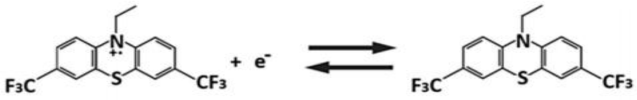


At negative Electrode



**2 Trimethyl p-quinoxaline-Trifluoro methyl-ethyl phenothiazine RFB**

ISSN: 2454-4248
346 – 350


**Polymer organic molecules RFB**

Organic molecule in polymer form exhibit some attractive properties like high charge discharge rates, high capacity and long cycle life.

1. Zinc polymeric TEMPO hybrid RFB
   Polymeric tempo at positive electrode and cheap cost zinc at negative electrode produce hybrid flow battery. During charging process, TEMPO is oxidized and forms an Oxo ammonium cation [TEMPO+] in positive electrode and metallic zinc is deposited on negative electrode. During discharge process reverse process takes place.
2. Lithium organic flow batteries
   This system combines the advantage of RFB and Li ion batteries. Electronegative Li present at negative electrode and liquid phase redox reaction occur at positive electrode.
   Since the number of other combinations were studied to increase voltage. The lithium TEMPO redox battery was demonstrated to get higher energy density by Takcchi and Coworkers [33]. Modified TEMPO was mixed with Lithium Trifluoro Methane salt to liquefy active molecule. The redox potential of resulting methoxy TEMPO was 3-6 volt vs. lithium. This Li organic hybrid RFB has highest columbic and energy efficiency than other organic based RFBs.

**Conclusion and future perspectives**

Number of research has been done for expending area of RFB in both aqueous and non-aqueous electrolyte but there is lot more to do. These aqueous and non-aqueous electrolyticsystems have many advantages resulting in higher cell voltage but there are many limitations, which must be solved to reach at high level of market penetration. In aqueous electrolyte, low solubility is a major challenge and in non-aqueous system high electrolyte resistance, chemical instability cross over of active material is the limitations. To get full use of these organic based RFB, these limitation have to overcome first and their cost should be low as of conventional batteries. This over all cell cost can be minimized only by increasing cell voltage.

Organic molecules are unstable in aqueous and non-aqueous electrolyte so the reason of their instability find first as a result of this their stability can be improved by some substitution and by addition of some salts. Organic based RFB is a very good method amongst different electrochemical methods but need some improvement including cost and efficiency.

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