Emerging Aqueous Flow Batteries and Perspectives on Future Development

Jiayi Zhang\textsuperscript{1, a}

\textsuperscript{1}China University of Geosciences, No. 29, Xueyuan Road, Haidian District, Beijing, China
\textsuperscript{a}1003171319@cugb.edu.cn

\textbf{Abstract.} Flow battery, as a promising energy storage system, has been interested by researchers for a long time which reveals that the capacity and performance of flow battery is crucial for the usage of inherently intermittent clean energy resources. This work briefly compares three kinds of flow battery which are the most prevailing methods to achieve energy storage. Meanwhile, China is the largest energy producer and consumer in the world, and for this reason, China’s supply chain of raw material and demand for flow battery is critical for development of flow battery. Most of current researches on flow battery are modification on electrolytes, so tailoring on the structure design of flow battery is also a method for performance improvement. At last, a new design of the structure of flow is provided for further researches.

\section{Introduction}

As human society developing from various technology revolutions, huge amount of energies from all kinds of natural resources are required for manufacture and transportation. Resulting from arbitrarily usage of fossil fuels, a great amount of carbon has been emitted in our atmosphere in the shape of carbon dioxide. Carbon dioxide is not a toxic gas, however, due to its ability to absorb infrared ray and as a result, the global temperature will be raised. Climate change, especially global warming, has been a severe issue which encourages the clean energies acquired from renewable resources. In order to have a conspicuous conception of the global energy consumption, China, which has the largest energy consuming and electricity generating and biggest carbon dioxide emission in the world, needs to be studied. The fact that China is the biggest energy consuming country so China’s energy policy makes the world’s energy market fluctuates and will influence the world’s climate change dramatically. If human beings wants to restrict the trend of global warming, redesign of the world’s energy consuming structure bonds to be a promising way, and for this reason, the retrofit of China’s energy policy weights more important in environment protection.

China is currently the world’s largest energy consumer and producer in the world. In 2017, China consumed 3,105 Mtoes (million tonnes of oil equivalent, 1 Mtoe = 1.16×10\textsuperscript{10} kWh) which is 1.4 times higher than the United States with 2,200 Mtoes. When compared with China’s consumption of the largest amount of energy, the China’s production of energy is 2,499 Mtoes, which is 606 Mtoes less than that of consumption. However, the consumption and production of energy of the USA is 2201 Mtoes and 2018 Mtoes, which are relatively balanced than China’s energy structure. And this discrepancy between consumption and production of China is due to the increase of China’s energy production capacity is not synchronized to the fast GDP growth rate. The fast growth of economy is in the cost of environment because China’s mean energy sources is coal, which omits ashes, invisible particles and toxic gases such as SO\textsubscript{3}, NO\textsubscript{2} when it is heated, resulting severe haze in winter around the
whole country and ancient building corrosion caused by acid rains. There are three reasons contributing to this largest energy consuming, global industrial transfer, growing city scale and largest population scale. China is the world’s largest cargo trading country so China needs energy for production and, with the urbanization, more energy is demanded for powering the cities and people’s daily life. China has been trying to diversify the structure of its energy supply when government realized the adverse impact of energy shortage and environmental pollution to both its citizens and human beings. Under the so-called New Policy Scenario, lots of efforts have been made to increase the install capacity of renewable sources. The installed electricity power generated from renewable energy sources, such as solar and wind, has been kept increasing by 40 Gigawatts and 20 Gigawatts per year, respectively.\(^{11}\) In order to be the game changer of the world energy economy, China launched an aggressive policy to accelerate the development of renewable energy industries like photovoltaics and electric vehicles. China subsidies both the consumption and production ends of the zero emission car program and supports the creative companies with policy and loan with little interest. For these policies, China currently has the largest market of electric cars, much more than Europe and the USA.

The world has made lots of efforts to the exploitation of renewable energy which will both contribute to mitigate the discrepancy of energy production/consumption and alleviate the severe environmental pollution resulting from combustion of fossil fuels. Moreover, researches on electricity generated from renewable resources starting from 1980s, the usage of versatile renewable resources has been continuously increasing, although, coal, oil and gas-based generation still occupies the majority in present. Since the beginning of 21th century, the percentage of coal in total energy sources continues to decline; on the contrary, the percentage of clean energy generated from renewable sources has been increasingly playing an important role. As anticipated, electricity generated from renewable resources is undergoing a boom, and by 2050s, only one sixth of the electricity will be generated by fossil fuels. In addition, as the statistics provided by international renewable energy agency (IRENA), the cost range of electricity from renewable resources, compared with fossil fuels, has declined, particularly after hydro-power boomed in 2009 when the largest hydroelectric gravity dam finishing its construction, the cost of hydro-power and photovoltaic-based electricity has decreased by \(~72\%) in the past decade. Multiple resources have been used to generating electricity, such as solar, wind and geothermal energy. However, electricity generated from those renewable resources is intrinsically intermittent and its production peak is continuously fluctuating, which does not match users’ regular demands (stable and regular peak). In order to balance the production and the demand of the grid, a suitable energy storage system is called. An electricity-storage system can collect and store electricity generated from renewable resources, then release the electricity when at peak electricity demand. For example, four general approaches are applied now for energy storage, which are thermal, hydrogen, electro-mechanical and electro-chemical storage. However, all of them suffer from either poor duration, or high cost, or limited power capacity. At present, the most popular large scale (> 100 MW) renewable energy storage technique is pumped hydro energy storage (PHES)\(^{3}\). Although these facilities are widely applied in the world, requiring a suitable geology and huge amount of water limits its further deployment\(^{3}\). A lithium-ion based energy storage sector of Arizona public service built on 2017 has a compromised energy efficiency of \(~55\%) due to the parasitic cooling system. Moreover, the expensive lithium-ion based organic electrolyte is highly flammable, leading to its explosion in 2019 with a service time less than two years. The reason behind the explosion is that lithium ion tends prone to deposit on the lithium site during charging process and gradually grows up and forms middle-like lithium metal dendrites, those sharp lithium metal dendrites can penetrate separator and contact cathode, the short circuit then leads to thermal runaway, overheated electrolyte gets ignited, leading to explosion. Furthermore, owing to very thin electrodes used in lithium-ion batteries, its scale has also been concerned.

Alternatively, redox flow battery has been proposed, it not only greatly increases the longevity and capacity of the battery but replaces the flammable organic electrolyte with nonflammable aqueous electrolyte. The stunning point of this system is that it decouples the energy and power scaling by independently adjusting sizes of cell stack or electrolyte tanks. It is because the current speed can be controlled by the power of pump, and the contact area between electrolyte and electrodes can be exactly
controlled by the area of electrodes, so that the power and current density are decoupled, moreover, low battery would be adjustable for customer’s usage, therefore, enhanced the commercial potential. The present work focuses on comparing and evaluating three types of flow batteries, *i.e.*, vanadium redox flow battery, anthraquinone redox flow battery, and metal complex redox flow battery in terms of chemistry, merits, and challenges. Furthermore, a novel flow battery architecture design is also proposed to increase energy efficiency.

**Vanadium Redox Flow Battery.** In order to increase the deployment of intermittent renewable resources for electricity generation, redox flow batteries have been becoming more and more compelling for large-scale electricity storage. Among various redox flow batteries, vanadium redox flow battery (VRFB) is the most promising system for commercial applications[4]. However, VRFB has several problems, in particular, such as cross-contamination and high capital cost for electrolytes, etc. Before discussing aforementioned concerns, we first describe the characteristics and properties of VRFB.

![Figure 1](image_url)

**Figure 1** There are two electrolyte tanks, *i.e.*, $V^{4+}/V^{5+}$ in catholyte and $V^{2+}/V^{3+}$ in anolyte and these two tanks are separated by an ion-selective membrane, which serves to keep the charge balance of the two electrodes.

The structure is displayed on Fig. 1. Despite from the redox active materials in the electrolytes, mixed acids are added to the electrolyte in order to increase the solubility of the vanadium ion, as a result, to improve the energy density of the battery. Both positive and negative electrodes are porous carbon materials and they can output a theoretically voltage of 1.26 V. The positive electrolyte is composed of $V^{2+}/V^{3+}$ in mixed acids of $H_2SO_4$ and $HCl$. The negative electrolyte is composed of $V^{2+}/V^{3+}$ in $H_2SO_4$[5]. The main issues that hindered the commercial application are the source of voltage loss, tailoring the design to reduce ohm resistance, maximize the transport of electrolytes and boost the surface area and activity of electrodes. The largest vanadium flow battery is being constructed by Dalian Rongke Power and supported by local government in Dalian, China, however, the vanadium element is usually coexisting with magnesium and aluminum elements, vanadium refining is thus becoming expensive and uncertain, resulting in a fluctuating $V_2O_5$ price[6]. There are some advantages and disadvantages associated with VRFBs. The advantages contains: high efficiency, low solution contamination, and long cycle life[7]. On the contrary, VRFB has some disadvantages, such as, electrolytes are highly sensitive to temperature variation so that the temperature has to be controlled within 10 °C to 40 °C in order to prevent precipitation[4,7]. However, above 50 °C, the V (vanadium) ions readily precipitate in the form of $V_2O_5$ at 1.8 M[8]. Moreover, the crossover of ions limits the efficiency of the battery. With the concentration of electrolytes in each tank decreasing, the voltage loss will become higher[5]. The construction of VRFBs always associates of high capital cost for the vanadium based electrolytes and the mean reason for this dilemma is that vanadium based electrolytes can only acquired from $VO_2^+$ in $H_2SO_4$[8] and $V_2O_5$ employs $[9,10]$ electrolytic dissolution, which are neither a efficient way for industrial production. On the other hand, the energy density of vanadium based electrolyte seriously curbed the development of VRFBs. As researchers believed, the energy density and
stability of battery determined by the chemical activity, concentration and stability of the vanadium ion. For this reason, it is worth taking research on the modification of solution for electrolytes.

Membrane, another crucial component of VRFB, prevents negative and positive electrolytes from mixing[11]. Nafion 112, Nafion 1135, Nafion 115, and Nafion 117 are several kinds of cation exchange membranes (CEMs) which is currently the most popular polymer membranes that are applied in VRFBs[12]. However, Nafion membranes are usually expensive because of its fluorinated polymer structure; they also suffer from fast crossover of vanadium ion. The focus of research has gradually shifted to non-fluorinated polymers, such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(ether sulfone) (SPES), sulfonated poly(imide) (SPI) and poly benzimidazole (PBI)[13-17]. Structural modifications including tethering different charging groups was employed to adjust permeability of vanadium ion, i.e., the cross over rate of ions over membranes. Although PBI membrane can prevent ion transportation and reduce the self-discharging, it also suffers from the high cell resistance and hinders proton transportation, as a result, it leads to high a coulombic efficiency but an extremely low voltage efficiency[5].

Secondly, electrodes are subject to transport electrons in each side of the battery. There are many kinds of treatments of the electrodes to improve the electrode behavior including increasing the active sites, expanding the surface area, reducing the ohm resistance and stabilizing the electrodes from chemical reaction. The treatment of electrodes includes heat treatment, design enhancement, compression, surface treatment and chemical treatment. In most cases, treatment combined with each others will generate better performance. To enhance the active sites of the electrodes, Jiang et al., [5] came up with a novel multiscale porous electrode with primary, secondary and tertiary pores. In some aspects, these pores are impurities caused by defects in processing. But what is creative is that by using relatively rough processing, it can both multiple the active sites in graphite fibers (GFs) and make it suitable for mass manufacturing. Research on the electrochemistry reveals, under relatively low current density of 200 mA cm\(^{-2}\), that battery with the multiscale GF containing bismuth nanoparticles (BiNPs) explicit poor performance than battery with multiscale but without BiNPs. However, when the current density surpasses 200 mA cm\(^{-2}\), the electrochemistry performance has greatly improved, which is owing to the polarization of the functional groups in the electrodes. A. Bhattarai et al., [18] designed a porous electrode with channels for electrolyte to flow. Adding flow channels to the electrode can improve system efficiency by reducing the pumping power requirement, improve flow distribution over the reactive area, and lower flow resistance of electrolyte through the system [18]. Bhattarai et al., [18] found overall efficiency increases by 2.7% after testing multiple flow path designs on the full name (PAN) based carbon felt.

Thirdly, there are currently four kind of flow fields, i.e., conventional blank field, parallel field, serpentine field and interdigitated field. Discussion indicates the dimensions of the bipolar plate, the number of channels and the permeability of the electrode all play significant roles in the distribution of electrolyte, which could lead one path to be more effective than the other[19]. The work of Jiang et al.,[5] has compared two kinds of structure of the battery, which is serpentine and interdigitated flow battery field. The charge-discharge curve of 400 and 600 mA cm\(^{-2}\) are shown in the work, and statistically, the battery with interdigitated flow field exhibited higher charge-discharge capacity and lower charge-discharge over-potential. The work of Reed et al.,[20] shows that the interdigitate channels, which could directly insert into the electrolytes, is more effective. However, apart from analysis of systematical design, charge-discharge curve of the designed high-performance VRFB at different current density shows that the battery’s voltage is highly concerned with the polarization of electrodes.

After tailoring the design of VRFB, the beat way to fabricate VRFBs needs to be seriously considered in engineering perspective. Although VRFBs is the most developed device for large scale energy storage, it still suffers from its high capital cost, low energy density of electrolytes and corrosive and toxic electrolyte solution which is harmful for environment.

**Organic Electrolyte Flow Battery.** As raw oil and coal became the blood of modern industries, ramifications of coal and oil have been applied to all realms of chemistry. Due to the fact that chemicals of more than three aromatic rings, such as anthracene and pyrene, could only be obtained from coal, tar
(coked coal) provides raw materials for most of the dyestuff, pharmaceuticacls, synthetic pitches. In the aspect of crude oil and raw natural gas, they can be cracked down to lighter composition and refined to denser composition while benzene, toluene and xylenes (BTX) of the dense composition can be used to synthesize aromatics. Since China’s coal production continues to occupy the first place in the world and China’s crucial role in energy reformation\cite{21}, exploring electrolyte based on coal ramification should be a promising way for commercial application of flow battery.

Coal processing is significant because it is key factor to the efficiency of the usage of the coal. Now, coal coking is the universal applied processing and it can be divided to three stages which is pro-plastic stage (under 350°C, gases and light hydrocarbons are collected via evaporation), plastic stage (350-500°C, degradation to semi-coke and primary tar) and post-plastic stage (1000-1200°C, structural reorganization). After this processing, the carbon content raised from ~70wt% to ~100% and can be used in iron and steel industry as reductant and source of heat\cite{22}. It has to remind that coal plastic stages contains multiple chemical reactions(e.g., dealkylation, thermal cracking, dehydrogenetion, condensation, hydrogen transfer and isomerization) and the formation of aromatics with sp² structure are formed in post-plastic stage. Here we focus on tar, a byproduct of coal coking, which contains hundreds of polycyclic aromatic hydrocarbons (PAHs). Tar is the feed stone of the carbo-chemical industry because of its long chain of aliphatic compounds with alkyl and hydroxyl substituents, alkyl-substituted and unsubstituted aromatics and hetersatom-based compounds.

There are 18 kinds of representative aromatic compounds in typical tar, of which the anthracene is the key composition to our further discussion. To get anthracene, tar distillation is induced to refine tar separately in different temperature. Soft pitch, which is remain of the distillation stage, is added to process furnace to get anthracene oil at the temperature of ~400°C. The byproducts of tar distillation can also be used in various areas. After three anthracene purification processings (crystallization, vacuum distillation and re-crystallization), anthracene can be purified from coal with ~95wt% purity(ACS). Here we assume the transformation efficiency is 100% (all enrichment processes can enrich all favorable matters), the mass fraction of anthracene to coal is 0.0625wt%. According statistics from L. S. Plakitkina\cite{23}, the production of coal in all over the world in 2016 is 7.1 biliontons, of which 1.1biliontons is coking coal and 6biliontons is power-generating coal. As renewable energies generating more electricity, the demand for power-generating coal will continue to decline. Given the demand for coal is undergoing a declination, here we suppose all the power-generating coal can be used to enrich anthracene, we can acquire 443,750t of anthracene. These anthraquinone, as row materials, will help for the inexpensive industrialization of electrolyte. To get a precursor named anthraquinone, there are three synthetic methods in Fig. 2 which are liquid-phase oxidation with CrO₃, gas-phase oxidation with FeVO₄ as catalyst and acylation of benzene with phthalic anhydride.

![Figure 2 Three synthetic methods of anthraquinone.](image-url)
To get to know the capacity of the electricity storage of the flow batteries we are able to build in a year, we suppose all the anthraquinone could be used to make electrolyte and take 9,10-anthraquinone-2,7-disulphonic acid (AQDS) as an example. In the production of one year, 2500 million molars of AQDS can be produced and the storage capacity under 1V is $1.3 \times 10^8$ kW·h. The electricity consumption of an ordinary family of 4 person in a month on average is 350 kw·h, which means if all the AQDS are applied in flow batteries, there are going to be 40 thousands families at the scale of a city with 1.6 million population using renewable energies stored in the flow batteries. Judging from that, the flow battery is facing a great upsurging demand both in household and industry market in the future. Besides, the energy density of AQDS is relatively higher, so if all these 40 thousands families use flow battery as their household energy station for solar-based or wind-based electricity, there will be about only 0.15 m$^3$ of extra space is needed. Owing to the adequate resources, high energy density, versatile utilities and environment friendliness, flow battery with nonmetallic electrolyte is a promising energy storage method in the future. It’s a promising candidate for a low-costing electrolytes.

Here, there are many researches demonstrating metal-free flow battery based on anthraquinone disulphonic acid (AQDS) and other organic electrolytes. Recently, Huskinson, B. et al.,[24] came up flow battery based on AQDS/AQDSH$_2$ electrolyte in sulphuric acid solution. The addition of two hydroxy groups to AQDS increase the open circuit potential and cell voltage$^{[24]}$. The discharge mechanism of this flow battery has shown below.

There are solution of AQDS in sulphuric acid in negative side and Br$_2$ in HBr in positive side and they are pumped to the porous carbon electrodes, where they will react on the surface of each electrodes. Nafion 212 membrane is applied in the middle of two Toray carbon paper, as two carbon electrodes, and enables the proton coupled electron transport reaction happened between both sides. However, flow battery in this stage still has a disadvantage that electrolyte are in acid solution and the solution will corrode the tank which seriously vitiate the commercial application of flow battery.

Vanadium redox flow battery (VRFB) is a promising solution for large scale energy storage, as the demand ascents, the commercial application of VRFBs is severely limited by high price. For this aspect, organic electrolytes based on coal and row oil is a perfect bypass of high cost.

2. Perspectives

Improvement of redox flow battery undergoes several stages, from VRFBs, organic redox flow battery to metallic coordination complexes flow battery. After recent review the researches on the performance enhancement of flow battery, however, redox flow battery is a energy storage system that will definitely come into application. While tailoring the component of electrolytes with the aim of increasing cell voltage and cyclic stability, retrofits on the fundamental design of flow battery could be another promising path on engineering aspect. Nowadays, the research on finding substitute for flow battery has been prevailed for a long time, with the most relatively viable choices for electrolytes tested not ideal, researchers will have to develop a brand new chemical structure for the commercial application of flow battery. On the other hand, the modification of the structure of the flow battery is a more enduring method for promoting the performance because it can not only escalate the efficiency but can also reduce the investment in the exploitation on new electrolyte.
Figure 3 The schematic of the structure of a flow battery that is able to decouple the different state of electrolytes.

After reviewing these works, apart from exploiting new molecular for flow battery, modification of the structure is getting more important. Here is a model (the schematic of this model in Fig. 3) that decouples the single electrolyte tank into two separate tanks. The separation of the electrolyte tank is very necessary because the battery’s power energy is hampered by the increasing temperature lead by working. This separation of electrolytes could make electrolytes in both sides more isolated and prevent the mixture of oxidation and reduction state electrolytes. By the controlling of pump and other temperature monitoring system, a more stable electrolytes could be provided to electrodes.

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