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Nonaqueous redox-flow batteries: features, challenges, and prospects

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The increasing concern over climate changes and the limited supply of fossil fuels bring into the general realization that we urgently need to maximize the use of renewable energy resources such as solar and wind. Redox-flow batteries are one of the most promising energy storage technologies, overcoming the intermittency of solar and wind energy. In this review, we focus on nonaqueous redox-flow batteries because of their appealing features in comparison with aqueous based systems, including wider voltage windows, intrinsically faster electron-transfer kinetics, and more extended working temperature ranges. The limitations and challenges of nonaqueous redox-flow batteries are also discussed to provide information for the further development of nonaqueous redox-flow batteries.

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The need for renewable electricity storage

In today's world, the need for energy is ever increasing. The fossil fuel-burning energy-production industry faces serious challenges, including the exhaustion of limited fossil fuels and the threat of climate change [1]. It has been generally realized that we urgently need to minimize the combustion of fossil fuels and maximize the use of renewable energy. Solar and wind are the most promising resources of renewable energy, however, their intermittent nature leads to the mismatch between generation and consumption. The key to achieving a stable supply from the renewable energy resources lies in the development of suitable energy storage systems [2]. As an electrochemical method, redox-flow batteries (RFBs) offer a flexible and versatile means of storing energy [3,4]. RFBs provide users with a variety of benefits including moderate cost, long durability, quick response, and variable load.

Unique features of RFBs

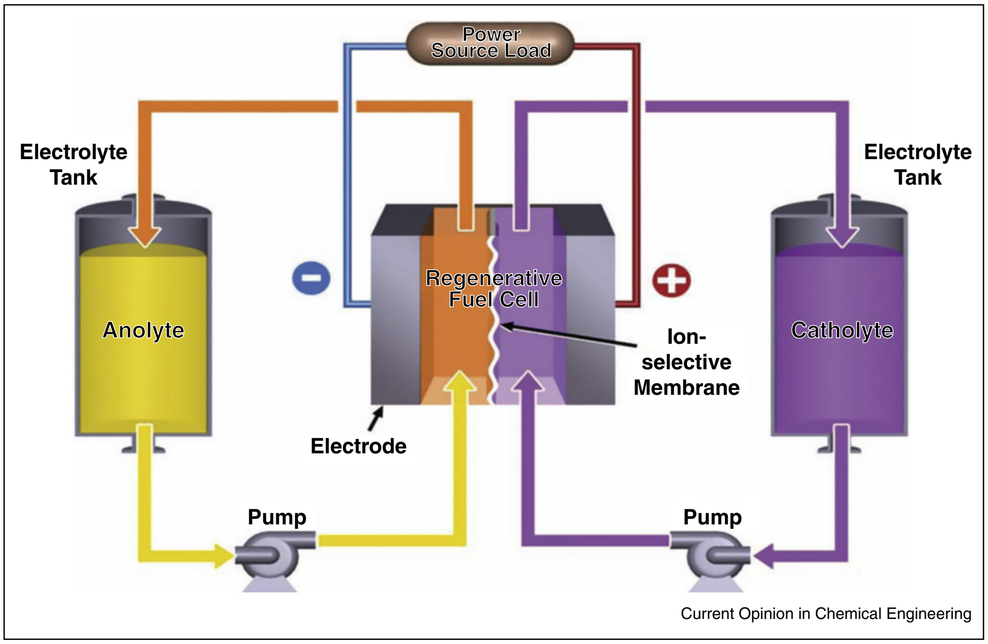
RFBs generally consist of two electrolyte reservoirs from which the electrolytes are circulated (by pumps) through an electrochemical cell, which is comprised of a negative electrode, a positive electrode, and an ion-exchange membrane (IEM) (Figure 1). The chemical energy and electrical energy are inter-converted in the electrochemical cell via utilizing the oxidation and reduction of two soluble redox couples in the electrolytes. The two electrolytes are stored separately in large storage tanks outside the electrochemical cell. The amount of electrolytes determines the energy capacity of RFBs; and the area of electrodes does the power rating of RFBs. The appealing properties of RFBs are unprecedented scalability and flexibility owing to the decoupling between energy storage and power delivery. Increasing the power output of RFBs only requires the addition of more cells/cell areas. Likewise, increasing the energy stored in this system only needs to add the electrolytes.

RFBs are considered one of the most promising electrochemical technologies for the large-scale storage of renewable electrical energy. They are capable of storing large amount of energy up to megawatt-hours (MWh). The flexible modular design allows the RFBs to be sized for a wide range of energy storage and power delivery. Unlike conventional batteries, the energy-bearing chemicals in RFBs are not stored in the solid electrodes inside the electrochemical cell but in the liquid electrolytes outside of it. As such there is no fundamental cycle-life limitation that is often associated with morphological changes at the electrodes during charge–discharge cycle. Moreover, RFBs are of high reliability and good safety since the electroactive materials are stored separately and the flow of electrolytes can also quickly bring the heat out of the electrochemical cell. Due to their simple modular design and inexpensive material, the cost for their construction and maintenance could be the lowest among electrochemical storage technologies [5].

Nonaqueous RFB technology

Since the first invention by Thaller in 1974, many RFBs have been designed and studied, and most of the RFBs in commercial development are based on aqueous chemistries. At present, all-vanadium RFB [6,7] and Zn–Br RFB [8] are the two most developed RFB technologies. Despite

Figure 1



Schematic illustrating the general structure of a typical redox-flow battery.
Source: Reprinted with permission from Ref. [4].

of the tremendous success, however, RFBs employing aqueous electrolytes have a generally low energy density of 20–50 Wh/L [5]. The energy density of an RFB is proportional to both cell voltage and the solubility of redox compounds. The cell voltage of aqueous RFBs is fundamentally limited by the narrow electrochemical window (1.23 V, standard conditions) of water which practically breaks down with less than 1.5 V [9,10]. By contrast, nonaqueous RFBs with organic electrolytes offer much wider electrochemical window (e.g., over 5 V) and potentially higher solubility for redox compounds, both of which can lead to high energy density. In addition, the working temperature of RFBs can also be extended since organic solvents can provide low freezing point and/or high boiling point.

The basic concept of nonaqueous RFBs was first proposed by Singh in 1984 [11]. Then Matsuda *et al.* first demonstrated an experimental nonaqueous RFB based on tris(bipyridine)ruthenium(II) tetrafluoroborate complex [$Ru(bpy)_3(BF_4)_2$] in acetonitrile (CH_3CN) with tetraethylammonium tetrafluoroborate ($TEABF_4$) as the supporting electrolyte in 1988 [12]. The expected open circuit voltage (OCV) of this system is approximately 2.6 V, which is higher than those of most aqueous RFBs. Three types of membranes (anion-exchange membrane, AEM; cation-exchange membrane, CEM; and non-ion-selective membranes) were examined in an H-cell with carbon fiber cloth as electrodes, in which AEM was studied under the optimal circulation rate of the electrolyte. Since then, the study on nonaqueous RFBs has attracted more attention (Figure 2) [13••].

Chakrabarti *et al.* reported an OCV of 1.8 V for ruthenium acetylacteonate [$Ru(acac)_3$] based nonaqueous RFB in CH_3CN as solvent with $TEABF_4$ as supporting electrolyte, and also examined the charge–discharge performance of tri(2,2′-bipyridine) iron(II) perchlorate [$Fe(bpy)_3$]$(ClO_4)_2$ based RFB in CH_3CN [14]. Yamamura *et al.* pioneered the nonaqueous RFBs based on various uranium beta-diketonates, obtaining a cell voltage of around 1 V [15]. It was shown that a larger OCV might be achieved if ligands with higher basicity are used. Thompson and co-workers studied three redox systems: vanadium acetylacetonate [$V(acac)_3$] [16•], chromium acetylacetonate [$Cr(acac)_3$] [17], and manganese acetylacetonate [$Mn(acac)_3$] [18], in CH_3CN with $TEABF_4$. Charge–discharge performances were evaluated in an H-cell using an AEM as separator. Kim *et al.* reported a nonaqueous RFB employing tri(2,2′-bipyridine) nickel(II) tetrafluoroborate [$Ni(bpy)_3(BF_4)_2$] and tri(2,2′-bipyridine) iron(II) tetrafluoroborate [$Fe(bpy)_3(BF_4)_2$] in propylene carbonate and $TEABF_4$ [19]. Its kinetics and reactivity on different electrodes were examined by cyclic voltammetry method. Zhang *et al.* developed another new single-metal nonaqueous RFBs based on cobalt bis(acetylacetone)ethylenediamine redox system [Co(acacen)] in CH_3CN with $TEAPF_6$, showing an OCV of around 2.0 V for one electron