Future perspective on redox flow batteries: aqueous versus nonaqueous electrolytes

Lina Tang[1], Puiki Leung[1], Qian Xu[2], Mohd Rusllim Mohamed[3], Shuyang Dai[1], Xun Zhu[1], Cristina Flox[4] and Akeel A. Shah[1]

The unique architecture of redox flow batteries enables energy and power to be decoupled and scaled up more easily than conventional batteries. With the objectives of achieving the cost target (USD\$ < 100 (kW h)$^{-1}$) and superior performances, significant developments of redox and hybrid flow batteries have been made using various organic and inorganic redox couples in aqueous and nonaqueous electrolytes. To further improve the energy and power densities, desirable properties of these electrolytes are essential. In this article, comparisons and latest advances of these electrolytes in terms of stabilities, redox potentials, solubilities, viscosities, conductivities, opportunities, and economic prospects are discussed.

Addresses
[1] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, MOE, Chongqing University, Chongqing 40030, China
[2] Institute for Energy Research, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, China
[3] Sustainable Energy & Power Electronics Research Group, Faculty of Electrical & Electronics Engineering, University Malaysia Pahang, Pekan, Pahang 26600, Malaysia
[4] Institut de Ciencia de Materials de Barcelona, CSIC, Campus UAB, Barcelona 08193, Spain

Corresponding authors: Puiki Leung (leungpuiki@hotmail.com), Cristina Flox (crisflox@gmail.com), Akeel A. Shah (akeelshah@cqu.edu.cn)

Introduction

Redox flow batteries store all or part of their energies in liquid electrolytes instead of electrodes within the cells. This unique architecture enables energy and power to be decoupled and scaled-up more easily than conventional batteries [1–3]. The storage capacities can be increased readily with the amount (or higher concentrations) of the electrolytes, while power rating can be scaled by using larger electrode (active surface) areas or/and number of cells/stacks in the systems. Taking account of this scalability, improved redox flow batteries are considered as one of the most promising technologies in the range of kW/kW h–MW/MW h [2].

In the past decades, various redox flow batteries have been introduced in aqueous and nonaqueous electrolytes. To date, only a few redox and hybrid flow batteries (i.e. V–V, Zn–Br, and Zn–Fe) have been successfully commercialized at MW/MW h scale [1]. Early developments have focused on the uses of metallic redox couples in aqueous electrolytes, which are often stable and reversible reactions. At present, the costs of these systems (i.e. USD\$ > 300 (kW h)$^{-1}$) are still far higher than the future cost targets of USD\$ 100 (kW h)$^{-1}$[4]. For aqueous systems, decreasing active materials' costs by inexpensive materials are recent approaches to reduce the costs effectively, considering that the costs of water and its salts are negligible (USD\$ 0.1 kg^{-1}) [5–7]. The main challenges of aqueous systems are obtaining high voltage and solubilities simultaneously, considering that voltage windows are often limited to < 2.0 V caused by water electrolysis [5].

Various nonaqueous systems enable wider windows of electrochemical stability, multielectron transfers, and increased solubilities [8,9]. For instance, some recent organic molecules can deliver up to 6 electron transfers and provide highly positive electrode potentials in alternative solvents [10••]. Despite the lower ionic conductivities, some nonaqueous systems have demonstrated comparable current densities (15–100 mA cm^{-2}) to their aqueous counterparts [11••]. Considering the higher cost of these nonaqueous electrolytes (USD\$ > 20 kg^{-1}), increasing power density in order to use fewer cells and necessary parts appears to be the most effective approach in cost reduction [8].

In the past five years, a number of review articles have been published summarizing the latest advances of redox flow batteries [1], regarding cell engineering [12], mathematical modeling [13], and specific systems (e.g. zinc [14], organic [4], and lithium-based [15]). The main contribution of this work focuses on the pros and cons of using aqueous and nonaqueous electrolytes with the discussions of their stabilities, redox potentials,

Figure 1
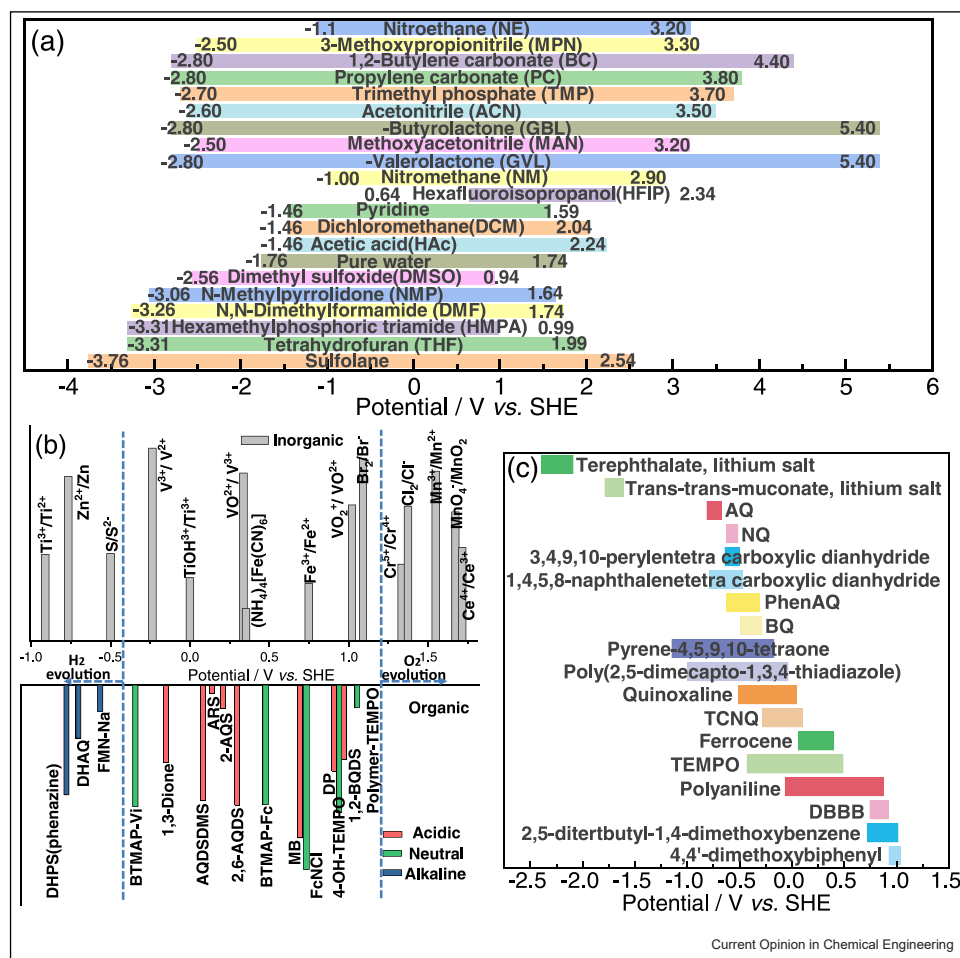
Stabilities and redox potentials. **(a)** Potential stability windows of various electrolytes potentially used in redox flow batteries (DMSO: dimethyl sulfoxide and ACN: acetonitrile) [16]; **(b)** the redox potentials of different active materials (inorganic and organic) in aqueous electrolytes (DHAQ: 1.8-dihydroxy-9,10-anthraquinone; FMN-Na: flavin mononucleotide sodium salt; BTMAP-Vi: bis (3-trimethylammonio) propyl viologen tetrachloride; AQDSDMS: anthraquinone-2,6-disulfonate dimethyl sulfide; ARS: 3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid; 2-AQS: anthraquinone-2-sulfonic acid; 2 , 6-AQDS: anthraquinone-2,6-disulfonate; Fc: ferrocene; DP: dopamine, TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy) [21]; **(c)** the redox potential of organic or organometallic active material in nonaqueous electrolytes (AQ: anthraquinone; NQ: naphthoquinone; BQ: benzoquinone; TCNQ: 7,7,8,8-tetracyanoquinodimethane; DBBB: di-tert-butyl-1,4-bis-(2-methoxyethoxy) benzene) [2].

solubilities, viscosities, conductivities, opportunities, and economic prospects.

Factors affecting cell performance in aqueous and nonaqueous electrolytes
Stabilities

The stabilities of aqueous and nonaqueous flow batteries depend on the selections of suitable supporting electrolytes, redox chemistries, and battery components. Aqueous systems use water as solvent that has a narrower-potential stability window (often < 2.0 V) but subjected to the overpotentials of hydrogen and oxygen evolutions, which could vary with electrolyte compositions and electrode surfaces [6]. In addition to gas evolutions, some metal anodes (e.g. zinc) used in hybrid

systems have the tendency to dissolve in acidic/alkaline electrolytes, resulting in energy losses (as a self-discharge/corrosion process) [14]. Other than active materials, exposure of metallic components/parts to corrosive acid or alkaline shall be avoided, which may lead to unstable redox potentials during cycling.

Compared with aqueous flow batteries, there are various solvents available for nonaqueous systems and tend to provide wider potential stability window (up to 8.2 V as shown in Figure 1a) [16], also subjected to kinetics, materials involved, and durations of the required reactions [17]. Solvent decompositions may also take place with its electrochemical window by their interactions with corresponding active species and electrolyte

salts [18]. However, nonaqueous electrolytes are usually based on nonpolar solvents, for example, acetonitrile. Unlike metal complexes, many organic active molecules exist as free radicals. They are often reactive and short-lived but can be stabilized by steric and/or resonance effects through functionalization with substituents. Among carbonyls, amide molecule exhibits relatively high stability due to their high-resonance stabilization effect between carbon–oxygen and carbon–nitrogen [19]. Stabilizing radicals are essential in long-term cycling and maintaining storage capacities, which have been major hurdles in exploiting increased concentrations of many nonaqueous systems. For instance, phenothiazine radicals have been successfully stabilized for up to 7 weeks in acetonitrile [20•]. Nonaqueous electrolytes are also corrosive on most polymer (plastic)-based components/parts. Thus, higher material stabilities are required for components from electrolyte tubing to reservoirs, that also increase the overall costs of most nonaqueous systems [9].

Redox potentials

Redox potentials of the active species in redox flow batteries depend on the selected chemistries for a given solvent. Increasing the potential difference is a cost-effective approach to reduce the electrolyte cost per kW h and to involve fewer cells for the same power output. The redox chemistries can be very different in nonaqueous electrolytes compared with their aqueous counterparts, which also vary with their electrolyte compositions (e.g. pH and anions) [19]. Figure 1b and c show the electrode potentials of the reported redox couples in aqueous and nonaqueous flow batteries, respectively. It is obvious that the redox potentials of most active materials in aqueous electrolytes are restricted by the stability window of water (between –1.0 and +1.75 V vs. SHE) [3]. The use of alkaline electrolyte can suppress hydrogen evolutions and realize electrode potentials of < -0.5 V vs. SHE [2].

Without the concern of solvent breakdown, nonaqueous electrolytes tend to offer larger potential difference (i.e. > 4 V) in flow batteries. However, suffering from the interaction with solution species and redox molecules, organic solvents usually have not enough wide effective potential window [22••]. Early investigations focused on the uses of metal–ligand complexes [9] to yield relatively high cell voltages (> 2 V), but suffer from poor solubilities and low efficiencies. To address this, recent works have considered a wide range of organic and organic–metallic materials (Figure 1c) that may also provide multielectron transfers and high solubilities for high-energy-density systems. However, low ionic conductivities of these nonaqueous systems are still the major hurdle for future commercialization.
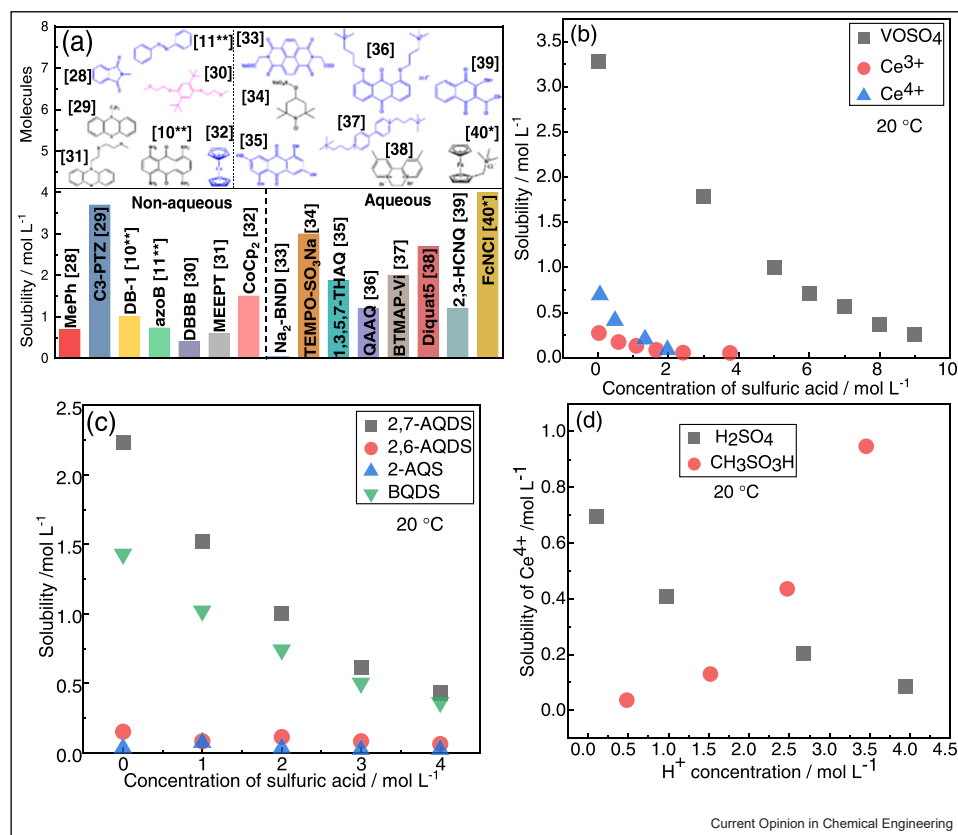
Solubilities

Solubility is the ability to dissolve active materials, in particular, electrolytes at the highest concentrations, which are proportional to the theoretical capacities and hence the energy densities. Figure 2a summarizes the solubilities of different active materials in aqueous and nonaqueous electrolytes [10••,11••,28–40]. Regardless of electrolytes, active species with larger molecular mass tend to have lower solubilities. The law of "like dissolves like", polar active compounds/molecules (i.e. metal ions and organic molecules with polar groups) dissolve easier in aqueous electrolytes, while nonaqueous electrolytes are more prone to dissolve nonpolar active molecules (such as free radicals and organic molecules with nonpolar groups) [19]. For metallic active species, solubilities are associated with ion-pair formation effect, which can be improved with suitable complexations/supporting electrolytes. Their organic or organometallic counterparts can achieve higher solubilities in aqueous and nonaqueous electrolytes by grafting ionic ($-SO_3^-$, $-CO_2^-$, $-PO_3^{2-}$ and $-N^+R$, etc.) and polar substituents (carbonyls and ethers, etc.), respectively [23–25]. For instance, when ferrocene is functionalized with ammonium-cation group, solubilities could reach up to 4 M in water (neutral) at the expense of the slight increase in molar mass [40•]. Instead, nonpolar groups (i.e. benzene rings) may decrease the solubility in polar solvents and water.

In aqueous flow batteries, solubilities vary significantly with acid or base at different concentrations (Figure 2). As shown in Figure 2b and c, the solubilities of selected metal ions (V^{4+}, Ce^{3+}, and Ce^{4+}) and organic molecules (BQDS, AQDS) tend to decrease at higher sulfuric acid concentrations, but this trend may not be valid for the same metallic ions at different oxidative states in other acids [26]. In some cases, the solubility trends of certain metal ions in different acids can be completely opposite. For instance, solubility of both Ce^{3+} and Ce^{4+} decreases with higher concentrations of sulfuric acid. In contrast, the solubility of Ce^{4+} increases at higher methanesulfonic acid concentrations (Figure 2d) [14]. This indicates that mixed electrolytes of two acids may enhance the solubilities of certain active species in aqueous electrolytes. For the case of vanadium, the mixed electrolytes of sulfuric and hydrochloric acids are known to minimize the issues associated with the precipitation of V^{5+} at elevated temperatures and overcome low solubilities of V^{4+} at low temperatures [27].

Viscosities

High concentration of active species could mean more energy to be stored in a given electrolyte volume. However, it is inevitable to increase the viscosities [42] that hinder the mass-transport processes, particularly through the porous electrodes or at high current densities [43]. It also has influences on electrolytic

Figure 2

Solubilities. (a) The solubilities of reported organic active species (anode in blue, cathode in black, and bipolar electrode in red) in aqueous and nonaqueous electrolytes (MePh, DB-1 DBBB, and CoCp$_2$ dissolved in nonaqueous DME: methoxymethane, DMSO, carbonate, and DOL: 1,3-dioxolane, respectively. Besides, MEEPT: N-[2-(2-methoxyethoxy) ethyl] phenothiazine, azoB, and C3-PTZ all dissolved in ACN.) [10••,11••,28–40]; **(b)–(d)** show the relationships between solubilities of active materials and acid concentrations in aqueous flow batteries [14,26,41]. **(b)** Selected metal active species (VOSO$_4$, Ce^{3+}, and Ce^{4+}) in sulfuric acid solution; **(c)** Organic active molecules (2,7-AQDS: Anthraquinone-2,7-disulfonate, 2,6-AQDS, 2-AQS, and BQDS: 1,2-ihydroxybenzene-3,5-disulfonic acid) in sulfuric acid; **(d)** Ce^{4+} in sulfuric and methanesulfonic acid.

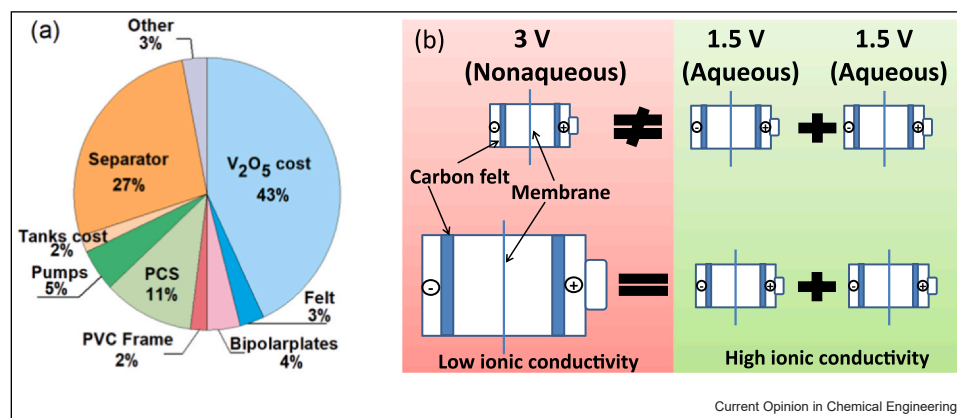conductance and pump losses while recirculating the electrolytes [44].

Viscosities of the selected aqueous (all-V, and all-organic) and nonaqueous (e.g. Li-based) flow batteries are illustrated in Figure 3a and b at higher concentrations of active materials (V^{n+}, BQDS, and AQDS in H$_2$SO$_4$) and supporting salts (LiTFSI and TEABF$_4$ in acetonitrile) [26,45]. In conventional all-vanadium systems, the viscosities are not the same at different oxidative states in sulfuric acids (viscosities of 1.6 M V^{2+}, V^{3+}, VO$_2$$^{2+}$, and VO$_2$$^+$electrolytes are 4.7, 3.7, 3.0, and 2.8 mP s, respectively). For organic molecules, despite larger molecular size of AQDS, its viscosities are even higher in sulfuric acid than that of BQDS. In nonaqueous electrolytes, the use of some organic conductive salts (e.g. TEABF$_4$) may lead to lower viscosities than using conventional LiTFSI in acetonitrile [45]. However, the viscosities of nonaqueous solvents could vary significantly and are summarized in Figure 3d. Nonaqueous solvents, particularly

those amides and carbonates, tend to have higher viscosities (i.e. N-methylacetamide, ~4 mPa s), while most ether, ketones, and nitriles have lower viscosities than water (ca. 0.89 mPa s) at ambient temperatures [19].

Conductivities
The ionic conductivities of the supporting electrolytes are the ability to transfer supporting ions for electrical conduction, which are directly related to ohmic losses in the charge–discharge processes. Conductive electrolytes are essential for larger power outputs that lead to drastic saving in electrode areas and number of cells/stacks. Supporting electrolytes having high degrees of ionization are often referred as strong electrolytes. Enhanced conductivities are often expected with smaller sizes of free ions at increased concentrations [8]. In aqueous systems, the ions used in supporting electrolytes are usually small ions, such as H$^+$, OH$^-$, and Na$^+$, that transfer rapidly and lead to relatively high ionic conductivities (i.e. > 140 mS cm^{-1}) [19]. The ionic

Figure 3

Viscosities and conductivities. The influences of **(a)** concentration of active materials (V^{3+} and VO^{2+} at 0% SOC, V^{2+} and VO_2^+ at 100% SOC, as well as 2,7-AQDS, BQDS at 0% SOC, SOC: state of charge) on electrolyte viscosities in aqueous 1 M and 4 M H_2SO_4 solutions [26]; **(b)** the concentration of supporting electrolyte (LiTFSI: bis(trifluoromethane) sulfonimide lithium and $TEABF_{4: \text{ tetraethylammonium tetrafluoroborate}}$) on viscosities in nonaqueous acetonitrile [45]; **(c)** the concentration of active materials (V^{2+}, V^{3+}, VO^{2+}, VO_2^+, 2,7-AQDS, and BQDS) on ionic conductivities in aqueous 1 M and 4 M H_2SO_4 solutions [26]; **(d)** a concise relationship between ionic conductivity and viscosity of typical solvents used in aqueous and nonaqueous redox flow battery systems [8,19].

conductivities in nonaqueous electrolytes are often lower and associated with viscosities, dielectric, and dissociation constants [8,42], although $100\,\text{mA}\,\text{cm}^{-2}$ has been achieved with suitable membranes/separators (e.g. Daramic) [11••].

In nonaqueous electrolytes, some organic salts (e.g. BF_4^-, PF_6^-, and $TFSI^-$) are preferred over halide salts due to their higher solubilities and stabilities [46]. Figure 3d summarizes the ionic conductivities of typical aqueous and nonaqueous electrolytes used in several flow batteries. The ionic conductivities of most aqueous electrolytes (e.g. $2\,\text{M}\,H_2SO_4/H_2O$: 630 mS cm^{-1}) are an order of magnitude higher than those of their nonaqueous counterparts (e.g. $1.5\,\text{M}$ $TEABF_4/ACN$: 60 mS cm^{-1}) [19]. In general, ionic conductivities tend to increase with supporting electrolyte concentrations, but the influences of active material concentrations on conductivities can be very different, depending on the

electrolytes. However, additions of organic molecules, BQDS and 2,7-AQDS, in aqueous electrolytes, tend to decrease ionic conductivities, but still with comparable values of conventional vanadium species (Figure 3c) [47].

Economic prospects

To ensure broad market penetration, the capital cost of the overall flow battery systems shall be lower than USD $ 100 (kW h)$^{-1}$ in the long term (e.g. 2030 s) [6,48]. At present, the costs of active materials and membranes contribute about 70% of a commercial all-vanadium flow battery (USD\$300 (kW h)$^{-1}$) (Figure 4a). Hence, cost reductions of aqueous flow batteries can be achieved by decreasing the costs of active materials and membranes through mass productions [6,49]. Furthermore, the real cost shall also consider the lifetime of active materials and interest rate for discounting as in a recent cost model [50**].

Figure 4

Economic analysis of flow batteries. (a) The cost breakdown of "commercial" all-vanadium redox flow batteries (4 MW h) [6]; **(b)** the illustrations of typical aqueous and nonaqueous redox flow batteries for the same power output. Assumption: aqueous flow batteries have lower resistance and single-cell voltage.

By contrast, nonaqueous flow batteries use more expensive solvents and supporting salts, that is, PF_6^- and $TFSI^-$ (USD\$ > 20 kg^{-1} vs. USD\$ 0.1 kg^{-1} of water). These systems are known to have lower ionic conductivities in both electrolytes and membranes, thus larger area resistances (> 5 Ω cm^2) [48]. Some electrolytes are susceptible to the absorption of water and lead to higher resistances/overpotentials. In such cases, it is more cost-effective to enhance the power density by making use of their larger cell voltages, while further increasing current densities with more conductive electrolytes and with fast kinetic reactions (e.g. radicals). The resulting higher power densities imply the use of smaller electrode areas or/and number of cells in the systems for the same power outputs. Owing to the lower current densities (usually < 10 mA cm^{-2}), most nonaqueous flow batteries require much larger electrode areas to deliver the same power than their aqueous counterparts, even with higher voltage of each single cell (Figure 4b). Taking account of the notable aqueous AQ–Br and nonaqueous Li–TEMPO systems, the stack volume per kW h was estimated to be 1.4 and 29 L (kW h)$^{-1}$ based on commercial 2 MW Regenesys® stack. The significant increase in stack volume for nonaqueous Li–TEMPO system results in much higher stack cost (USD\$ 788 (kW h)$^{-1}$compared with USD\$ 44 (kW h)$^{-1}$ for aqueous AQ–Br batteries) that involves the uses of membranes, electrodes, and other cell components [2]. Realizing higher output voltage and volumetric power density, the bipolar manifold stacks are required for both aqueous and nonaqueous RFBs.

Opportunities
In addition to the existing works (past 5 years), there are many other opportunities required for further developments, including

(1) Exploration and design of new active electrolytes with high-energy content and stabilities through computational screenings.
(2) Characterizations of aqueous and nonaqueous electrolytes based on their physical/ chemical properties (e.g. solubilities and conductivities) and stabilities at different compositions (active materials, salts, and solvents) and operating conditions.
(3) Further increase of power density for both aqueous and nonaqueous systems with enhanced mass-transport processes and improved cell architectures.
(4) Development of high-performance electrodes and membranes that catalyze the redox reactions and reduce the area resistance/cross-contamination, respectively.
(5) Addressing durability and stability issues under prolonged cycling at reasonable concentrations and current densities.
(6) Scale-up and mass-transport/rheological studies from lab-scale to practical industrial systems.

Challenges and future perspectives
For both aqueous and nonaqueous batteries, the overall cost per kW h not only depends on the cell components (e.g. electrolytes and cells), but also on the choices of the active materials (molar mass and solubilities), redox chemistries (potentials and electron transfers), and supporting electrolytes (viscosities and conductivities). It is difficult to enhance the energy and power densities of current systems without sacrificing the long-term stability (i.e. radicals). This requires electrolytes with high-energy content that offers competitive cell voltages, stabilities, and multielectron transfers simultaneously. Decreasing molar mass also improves the gravimetric capacity, thus lowering active material cost per unit charge. This is particularly challenging due to lack of

suitable chemistries and the restriction of potential window (< 2.0 V). Meanwhile, high-energy density means smaller size or number of cells can deliver the same power output, resulting in significant cost reduction. This can also be facilitated by efficient mass transport of active species and decreased area resistances with suitable flow fields, which may also result in more complex architectures.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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