Redox Flow Batteries: Fundamentals and Applications

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Additional information is available at the end of the chapter

Abstract

A redox flow battery is an electrochemical energy storage device that converts chemical energy into electrical energy through reversible oxidation and reduction of working fluids. The concept was initially conceived in 1970s. Clean and sustainable energy supplied from renewable sources in future requires efficient, reliable and cost-effective energy storage systems. Due to the flexibility in system design and competence in scaling cost, redox flow batteries are promising in stationary storage of energy from intermittent sources such as solar and wind. This chapter covers basic principles of electrochemistry in redox flow batteries and provides an overview of status and future challenges. Recent progress in redox couples, membranes and electrode materials will be discussed. New demonstration and commercial development will be addressed.

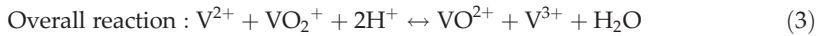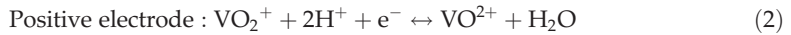**Keywords:** electrochemical energy storage, redox couples, electrolytes, electrodes, membranes

1. Introduction

Global economic growth with the increasing release of carbon dioxide disrupts our ecosphere and causes significant impacts on climate change. An environmentally friendly route to generate electricity from renewable sources such as wind and solar is desirable. To promote the utilization of renewable and sustainable energy and to enhance the stability of grid networks, energy storage systems are needed to store surplus electricity. The stored energy can be then delivered to end customers or to power grids upon need. It is becoming clear that the electrochemical energy storage using rechargeable batteries based on redox chemistry can provide a central solution to tackle such an issue. Through storing energy in recirculating liquid electrolytes, redox flow batteries have merits of decoupled energy density (tank size, electrolyte concentration, cell voltage and number dependent) and power generation capability (electrode size and reaction kinetics dependent). In terms of cost, system flexibility, quick response and

safety concerns for large-scale applications, redox flow batteries show great advantages over other types of batteries such as lead-acid and lithium-ion batteries and are expected to have increasing commercial space through technological development in future. Therefore, the redox chemistry and technical fundamentals of flow batteries, which determine the technological success and market penetration, need to be well understood.

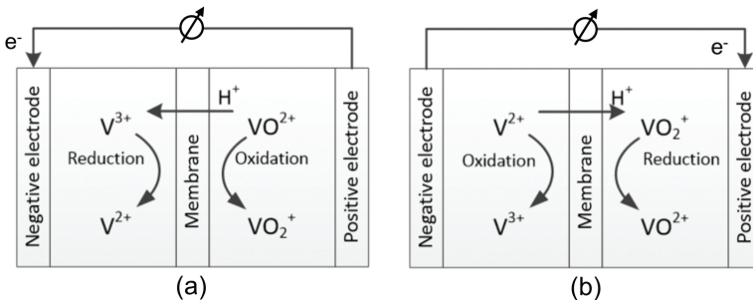## 2. Classic vanadium redox flow batteries

Among various flow batteries, vanadium redox flow battery is the most developed one [1]. Large commercial-scale vanadium redox flow batteries are currently in construction. The structure and charge-discharge reactions of vanadium redox flow batteries are schematically shown in **Figure 1**. During discharging, reduction occurs at the cathode and oxidation occurs at the anode as shown in Eqs. (1)–(3) (discharge: →, charge: ←). While these redox reactions occur, proton ions diffuse across the membrane and electrons transfer through an external circuit.

$$\text{Negative electrode}: V^{2+} \leftrightarrow V^{3+} + e^- \tag{1}$$

$$\text{Positive electrode}: VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O \tag{2}$$

$$\text{Overall reaction}: V^{2+} + VO_2^+ + 2H^+ \leftrightarrow VO^{2+} + V^{3+} + H_2O \tag{3}$$

The standard cell voltage for the all-vanadium redox flow batteries is 1.26 V. At a given temperature, pH value and given concentrations of vanadium species, the cell voltage can be calculated based on the Nernst equation:
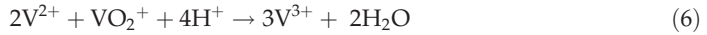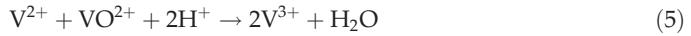
$$E = 1.26\ V - RT/F \ln\left(\left[VO^{2+}\right] \cdot \left[V^{3+}\right]\right) / \left(\left[VO_2^+\right] \cdot \left[H^+\right]^2 \cdot \left[V^{2+}\right]\right) \tag{4}$$

where R, T and F are the universal gas constant, absolute temperature and Faraday constant, respectively. The crossover of vanadium ions through the membrane may occur, resulting in self-discharge with the unwanted mixing of vanadium species at both sides of the cell, as following [2]:
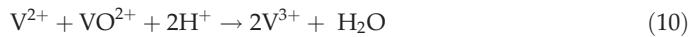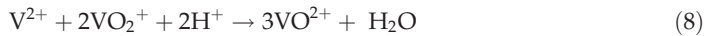

Figure 1. A schematic of a vanadium redox flow battery: (a) charge reaction and (b) discharge reaction.

At the negative electrode:

$$V^{2+} + VO^{2+} + 2H^+ \rightarrow 2V^{3+} + H_2O \tag{5}$$

$$2V^{2+} + VO_2^+ + 4H^+ \rightarrow 3V^{3+} + 2H_2O \tag{6}$$

$$V^{3+} + VO_2^+ \rightarrow 2VO^{2+} \tag{7}$$

At the positive electrode:

$$V^{2+} + 2VO_2^+ + 2H^+ \rightarrow 3VO^{2+} + H_2O \tag{8}$$

$$V^{3+} + VO_2^+ \rightarrow 2VO^{2+} \tag{9}$$

$$V^{2+} + VO^{2+} + 2H^+ \rightarrow 2V^{3+} + H_2O \tag{10}$$

Side reactions such as hydrogen evolution due to water decomposition and CO_2 evolution due to the oxidation of carbon-based electrode may occur during operation [3]. The battery performance is generally evaluated with three efficiencies: coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE), which are defined as following:

$$CE = \frac{\text{discharge capacity}}{\text{charge capacity}} \times 100\% \tag{11}$$

$$VE = \frac{\text{average discharge voltage}}{\text{average charge voltage}} \times 100\% \tag{12}$$

$$EE = CE \times VE \tag{13}$$

The CE reduces because of crossover of vanadium ions during cell operation and side reactions. The VE is related to the operation current density, ionic conductivity of membrane, electrode materials, flow rate and mass transport of electrolyte. As current density increases, the VE reduces due to the increase in polarization.

3. Types and configurations of redox flow batteries

Conventional redox flow batteries have two divided electrolyte reservoirs (**Figure 2a**). Catholyte and anolyte are separated by a membrane, which permits ions to pass through it. The most common working ions in aqueous media, H^+ (349.8 S cm^2 mol^{-1}) and OH^- (198.0 S cm^2 mol^{-1}), have the highest limiting molar conductivity among all known cations and anions, respectively [4]. All-vanadium redox flow batteries, for instance, have V^{3+}/V^{2+} redox reactions on the negative side (anolyte) and VO_2^+/VO^{2+} on the positive side (catholyte). Such battery uses the same metal ions on both sides. Crossover of metal ions through the membrane will then not cause contamination of the electrolyte. In contrast, for redox flow batteries with different metal ions such as Fe^{3+}/Fe^{2+} and Cr^{3+}/Cr^{2+} in an iron-chromium flow battery, the cross-contamination via ion penetration may cause irreversible performance loss.
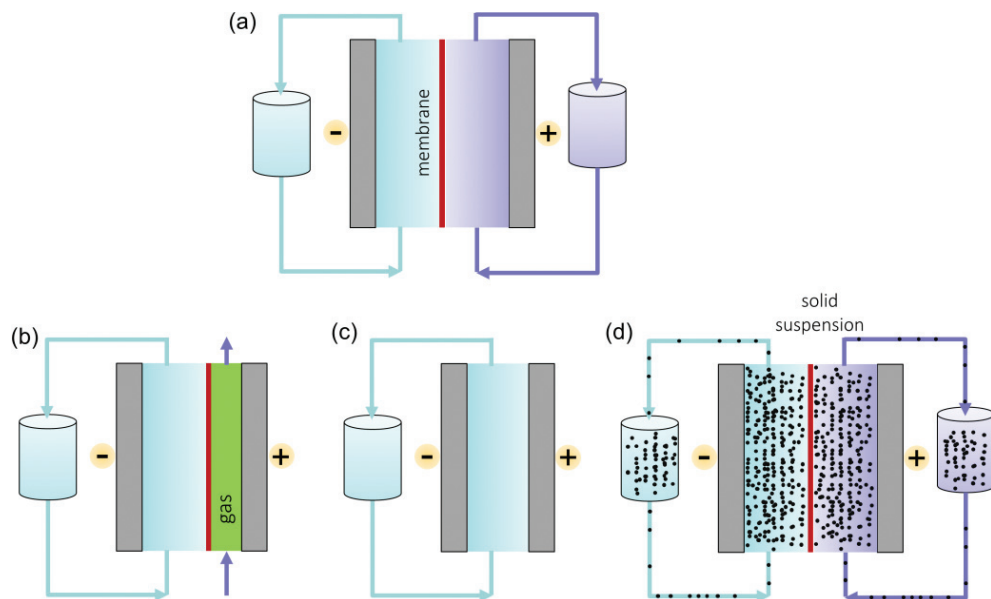
Figure 2. Configurations of (a) a conventional redox flow battery with two divided compartments containing dissolved active species, (b) a hybrid redox flow battery with gas supply at one electrode, (c) a redox flow battery with membrane-less structure and (d) a redox flow battery with solid particle suspension as flowing media.

Hybrid redox flow batteries such as zinc-bromine and zinc-cerium systems use metal stripping/plating reactions (Zn^{2+}/Zn, -0.76 V vs. [standard hydrogen electrode] SHE) on one of the electrodes inside the cell and the other side with normal soluble flowing electrolyte. Similarly, redox flow lithium batteries in non-aqueous electrolytes have been explored to make use of the low redox potential of Li^+/Li couple (-3.04 V vs. SHE). During charging, zinc or lithium is deposited from the electrolyte and during discharging, Zn^{2+} or Li^+ dissolves into the solution again. A shortcoming of such hybrid redox flow battery is that the energy storage capability is limited by the free space inside the cell accommodating the metal deposits.

A second-type hybrid redox flow batteries use gas such as Cl_2, O_2 and H_2 as the reaction medium or with gas evolution reaction at the cathode or anode (**Figure 2b**). For instance, oxygen reduction reaction ($O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$) with high positive potential can be used as the cathode. The cell capacity is then only determined by the capacity of anolyte. Oxygen reduction reaction in non-aqueous electrolytes with the presence of lithium ions can proceed through: $O_2 + 2Li^+ + 2e^- \rightleftarrows Li_2O_2$. Moreover, oxygen reduction and oxidation during discharging and charging can be catalysed chemically with redox mediators [5]. Interestingly, the use of electrocatalysts for the oxygen reduction and oxidation as in a conventional system can be avoided. Note that the formation and deposition of Li_2O_2 proceed at porous matrix, which can be held statically in a gas diffusion tank over charging/discharging. Such a concept may maintain the character of decoupled energy and power for flow batteries.

For aqueous electrolytes, oxygen and hydrogen gas evolution reactions by electrolysis of water take place during charging at very positive and negative electrode potentials, respectively.

Hydrogen evolution reaction has been observed as a parasitic side reaction at the anode for some flow battery systems. Such behaviour has been used to store electricity and to generate hydrogen simultaneously ($2V^{2+} + 2H^+ \rightarrow H_2 + 2V^{3+}$) as demonstrated in a vanadium-cerium flow battery [6]. Hydrogen generated can be then used to produce electricity in fuel cells.

The ionic conductivity and selectivity of membranes often significantly affect the overall cell performance for many redox flow batteries. High area resistance of membrane restricts the practical operation only at low current densities. Crossover of active species through membrane leads to performance loss over cycling. Redox chemistry of active species with formation of electrodeposits leads to another type of cell configuration without membranes and with only one electrolyte reservoir [7] (**Figure 2c**). Some selected membrane-free redox flow batteries are listed in **Table 1** [8–14]. Reasonable energy efficiencies and cycling stability have been observed. Considering the high cost of most commercial ion exchange membranes, such membrane-free cell configuration could enable simple operation and cost-effective applications.

Deposited anodic species should have slow dissolution rate in the presence of oxidized catholyte species as a self-discharge reaction. A direct reaction between the deposited metal and the other electroactive species in the electrolyte should be negligible or inhibited. Self-discharge effects must be minimized compared to a targeted rapid charging/discharging reaction. Acidic-supporting electrolyte is not suitable for anodic metal deposition. Solid-phase reactions in general have poor kinetics, in comparison with those in liquid electrolytes. The voltage efficiencies in most of the membrane-free flow batteries are relatively low (60–80%) restricted by mass transport and charge transfer kinetics. Compared to the flow-by configuration, an undivided battery with flow-through electrodes may assure enhanced mass transport. However, the flow rate will be largely limited.

A laminar flow battery using two-liquid flowing media, pumped through a slim channel without lateral mixing or with very little mixing, enables membrane-free operation. H_2 (flowing across anode with pumped liquid hydrobromic acid) aqueous bromine laminar flow

Flow batteries	Energy efficiencies	Cycling stability	Ref.
Pb/PbO$_2$	65%	Limited by the dendrite growth of Pb and formation of unwanted phase of β-PbO$_2$	[8]
Zn-NiOOH	86%	Stable over 1000 cycles with ~600% Zn excess	[9]
Cu-PbO$_2$	About 83% at 20.8 mA cm^{-2}	Stable over 450 cycles	[10]
Zn-Ce	About 75% at 20 mA cm^{-2}	Limited by Zn negative electrode, Zn residual on electrode after discharge	[11]
Zn-Quinone	About 40–70% at 30 mA cm^{-2}	Stable for low concentration quinone (50 mM)	[12]
H$_2$-Br$_2$	High round-trip efficiency at high current density up to 1 A cm^{-2}	Not given	[13]
Symmetric Ru(acac)$_3$	About 20% at about 2 mA cm^{-2}	Low coulombic and voltage efficiencies	[14]

Table 1. Membrane-free redox flow batteries.

battery demonstrated herewith allows high concentration reactants, fast reaction rates and a high peak power density (0.795 W cm^{-2}) [13].

Among various electrical energy storage technologies, redox flow batteries generally have relatively low energy density (for instance about 30 Wh L^{-1} for all-vanadium redox flow batteries). Thus, although recharging the electrolyte can be done by replacing the depleted one within a few minutes of transportation applications, redox flow batteries are only considered to be used in stationary energy storage. To increase the energy density, highly water-soluble species for instance LiI (solubility up to 8.2 M) and ZnI (7 M) can potentially enhance the volumetric energy density. The use of concentrated ZnI electrolyte leads to a high theoretical energy density of 322 Wh L^{-1} [15], which may even rival batteries based on lithium-ion chemistry (LiFePO$_4$ cathode, 223 Wh L^{-1}).

Another successful development is the redox flow lithium batteries. Pulverized energy-dense solid electrode materials such as LiCoO$_2$ and LiFePO$_4$ can be suspended in a flowable slurry, which is then circulated like a liquid-soluble electrolyte (**Figure 2d**). Due to the high molar concentration of lithium in the solid materials (for instance about 51.2 M for LiCoO$_2$ and 22.8 M for LiFePO$_4$, compared to about 1.6 M for vanadium species in conventional vanadium redox flow batteries), such flow batteries allow high volumetric energy density (about 580 Wh L^{-1} have been achieved [16]). Thus, redox flow batteries may find applications even in portable electronics and electric vehicles.

4. Redox electrochemistry of flow batteries

The overall system performance and cost for redox flow batteries depend largely on the flow cell redox electrochemistry. Great efforts have been made in search of alternative battery chemistry from electrolytes to electrodes [4, 17, 18]. The possible cell voltage depends on the selected redox couples (**Table 2**) and is limited by the electrochemical window of a given solvent-electrode system, stability of the supporting cation or anion and stability of the bipolar plate materials (**Figure 3**).

Table 2 summarises the electrochemical redox reactions at cathode and anode and cell open circuit voltage (OCV) for various reported redox flow batteries. For aqueous electrolytes, the typical cell voltage is below 1.5 V. To achieve high cell voltage, organic solvents with a broad electrochemical window such as acetonitrile (6.1 V) and propylene carbonate (6.6 V) are needed [4]. However, most of the used active species have poor solubility in organic solvents. High cell voltage in this case comes at the expense of low concentration of active species. A compromise among the solubility, cell voltage, reaction kinetics and suitable working temperature should be reached for selecting a suitable electrolyte. Ce^{4+}/Ce^{3+} redox reaction (from 1.44 to 1.70 V vs. SHE, depending on the type of supporting acidic electrolyte), occurring at potential beyond the stability limit of bipolar plate (**Figure 3**), needs special electrodes such as catalyst-coated titanium plate or mesh.

Many anodic reactions have low negative potential; the applications in aqueous batteries can be hindered by H$_2$ evolution due to the electrolysis of water with unwanted energy loss and an

Cathode redox reactions	Anode redox reactions	Cell OCV/V
$Br_2 + 2e^- \rightleftarrows 2Br^-$ or $Br_3^- + 2e^- \rightleftarrows 3Br^-$	$AQDSH \rightleftarrows AQDS^- + H^+ + e^-$	0.86
$[Mn(acac)_3]^+ + e^- \rightleftarrows Mn(acac)_3$	$[Mn(acac)_3]^- \rightleftarrows Mn(acac)_3 + e^-$	1.10
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	$Cr^{2+} \rightleftarrows Cr^{3+} + e^-$	1.19
$VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{2+} + H_2O$	$V^{2+} \rightleftarrows V^{3+} + e^-$	1.26
$I_3^- + 2e^- \rightleftarrows 3I^-$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	1.30
$PbO_2 + 4H^+ + SO_4^- + 2e^- \rightleftarrows PbSO_4 + 2H_2O$	$Cu \rightleftarrows Cu^{2+} + 2e^-$	1.35
$ClBr_2^{2-} + e^- \rightleftarrows 2Br^- + Cl^-$	$VBr_2 + Br^- \rightleftarrows VBr_3 + e^-$	1.35
$Br_2 + 2e^- \rightleftarrows 2Br^-$ or $Br_3^- + 2e^- \rightleftarrows 3Br^-$	$2S_2^{2-} \rightleftarrows S_4^{2-} + 2e^-$	1.36
hydroquinone $\rightleftarrows$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	1.40
para-benzoquinone $+ 2H^+ + 2e^-$		
$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	$V^{2+} \rightleftarrows V^{3+} + e^-$	1.49
$[Fe(CN)_6]^{3-} + e^- \rightleftarrows [Fe(CN)_6]^{4-}$	$Zn + 4OH^- \rightleftarrows [Zn(OH)_4]^{2-} + 2e^-$	1.58
$PbO_2 + 4H^+ + 2e^- \rightleftarrows Pb^{2+} + 2H_2O$	$Pb \rightleftarrows Pb^{2+} + 2e^-$	1.69
$2NiOOH + 2H_2O + 2e^- \rightleftarrows 2Ni(OH)_2$	$Zn + 4OH^- \rightleftarrows [Zn(OH)_4]^{2-} + 2e^-$	1.70
$TEMPO^+ + e^- \rightleftarrows TEMPO\bullet$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	1.70
$VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{2+} + H_2O$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	1.76
$[Ru(acac)_3]^+ + e^- \rightleftarrows Ru(acac)_3$	$[Ru(acac)_3]^- \rightleftarrows Ru(acac)_3 + e^-$	1.77
$Br_2 + 2e^- \rightleftarrows 2Br^-$ or $Br_3^- + 2e^- \rightleftarrows 3Br^-$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	1.82
$Cl_2 + 2e^- \rightleftarrows 2Cl^-$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	2.12
$ClBr_2^- + 2e^- \rightleftarrows 2Br^- + Cl^-$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	2.16
$[V(acac)_3]^+ + e^- \rightleftarrows V(acac)_3$	$[V(acac)_3]^- \rightleftarrows V(acac)_3 + e^-$	2.18
$Ce^{4+} + e^- \rightleftarrows Ce^{3+}$	$Zn \rightleftarrows Zn^{2+} + 2e^-$	2.20–2.46
$[Fe(bpy)_3]^{3+} + e^- \rightleftarrows [Fe(bpy)_3]^{2+}$	$[Ni(bpy)_3] \rightleftarrows [Ni(bpy)_3]^{2+} + e^-$	2.30
$Rubrene\bullet^+ + e^- \rightleftarrows Rubrene$	$Rubrene\bullet^- \rightleftarrows Rubrene + e^-$	2.30
$[Ru(bpy)_3]^{3+} + e^- \rightleftarrows [Ru(bpy)_3]^{2+}$	$[Ru(bpy)_3]^+ \rightleftarrows [Ru(bpy)_3]^{2+} + e^-$	2.60
$[Cr(acac)_3]^+ + e^- \rightleftarrows Cr(acac)_3$	$[Cr(acac)_3]^- \rightleftarrows Cr(acac)_3 + e^-$	3.40
$[Fe(CN)_6]^{3-} + e^- \rightleftarrows [Fe(CN)_6]^{4-}$	$Li \rightleftarrows Li^+ + e^-$	3.40
$OFN\bullet^+ + e^- \rightleftarrows OFN$	$BP\bullet^- \rightleftarrows BP + e^-$	4.52
$4Ce^{4+} + 2H_2O \rightarrow 4Ce^{3+} + 4H^+ + O_2$	$2V^{2+} + 2H^+ \rightarrow H_2 + 2V^{3+}$	Cell is chemically discharged [6]

Table 2. Selected redox reactions and cell OCV for redox flow batteries.

imbalance in the state of charge between two sides of the batteries. Through using concentrated electrolytes of water-in-ionic liquid (water in 1-butyl-3-methylimidazolium chloride, BMImCl) [19, 20] or water-in-salt (water in lithium, bis(trifluoromethylsulphonyl)imide, LiTFSI) [21], the onset of oxygen evolution and hydrogen reactions can be shifted to more positive and negative potentials, respectively. Broad electrochemical window of about 3 V has been achieved accordingly (**Figure 3**). It is considered that the amount of free water molecules reduces at such
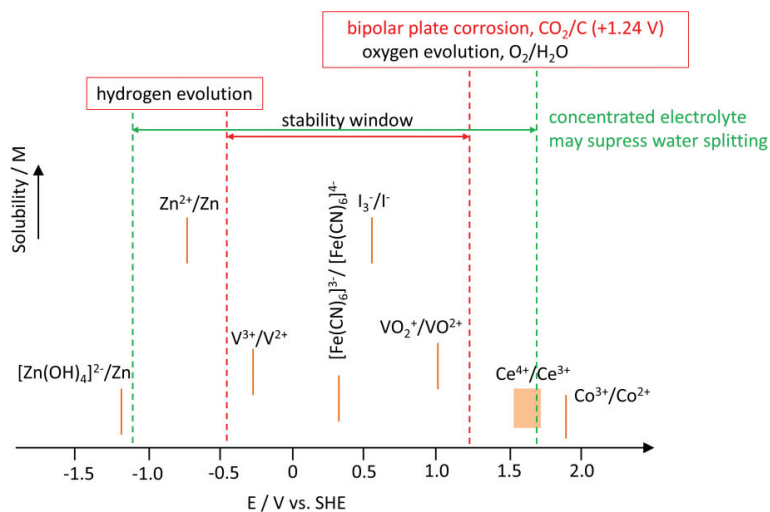
Figure 3. Potentials and relative solubility of selected inorganic and organic redox couples for redox flow batteries. Dotted lines show the electrochemical stability limit of typical aqueous electrolytes. Dashed lines show the possibility to extend the stability limit for aqueous electrolytes using concentrated electrolytes [19, 21].

concentrated mixtures. The inner Helmholtz layer close to the electrode surface is mostly occupied by the $[BMIm]^+$ cation or $TFSI^-$ anion, respectively. Water decomposition is then largely inhibited. The redox potentials for hydrogen and oxygen evolution reactions are pH dependent. Individual control in the pH values of the anolyte and catholyte with a multi-membrane system leads to high cell operation voltage of about 3 V [22].

In contrast to the electrochemical stability of the redox species and solvents, chemical stability of electroactive species and cell components is also critical for long-term operation. Vanadium electrolytes form solid precipitates at a temperature above 40 or below 10°C at concentrations above 1.6 M for all-vanadium redox flow batteries. Oxidizing V^{5+} and Ce^{4+} may cause degradation of membrane and the graphite electrode materials. Complexing agents are needed to store bromine, whereas phase separation (formation of water-insoluble emulsion) occurs for bromine complexes during charging for bromine-based flow batteries. Cross-contamination in bromine-polysulphide batteries may generate heat and release toxic Br_2 and H_2S.

High rate performance of redox flow batteries means high power generation capability. Ideally, two active species at both sides of the cell are expected to have close rate constants. However, mismatches in reaction rates are often observed. For many electrode reactions with sluggish kinetics, catalysts are needed to reduce the polarization (i.e. to improve the voltage efficiencies) and to improve the reaction rate (**Table 3**) [23]. Catalysts are generally applied onto a porous material, which offers high contact area for electrolytes. The supporting materials should have high electrical conductivity, mechanical stability, reasonable cost and high levels of oxygen and hydrogen evolution overpotential for aqueous system. Carbon-based materials are commonly used for this purpose [24].
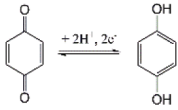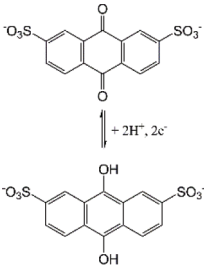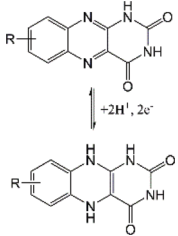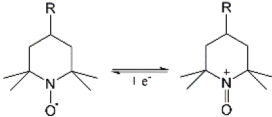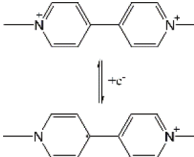
Electrode reactions	Catalysts
$VO_2^+ + 2H^+ + e^- \rightleftarrows VO^{2+} + H_2O$	Mn_3O_4/carbon fibre
	ZrO_2
	Bi_2O_3
	Nanorod Nb_2O_5
	Ir-modification of carbon felt
	WO_3
	PbO_2
$V^{3+} + e^- \rightleftarrows V^{2+}$	Mn_3O_4/carbon fibre
	ZrO_2
	Bi_2O_3
	Nanorod Nb_2O_5
	TiC
$Cr^{3+} + e^- \rightleftarrows Cr^{2+}$	Noble catalysts
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	Platinized titanium
$Cl_2 + 2e^- \rightleftarrows 2Cl^-$	RuO_2
$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	Pt/Ir mixed oxide

Table 3. Catalysts used for redox couple reactions.

5. Redox active organic electrolytes

Compared to the metal-based electrolytes for redox flow batteries with limited number and resource, organic molecules with unlimited chemical space allow low-cost (for instance, from $5–10 kg^{-1} vs. $27 kg^{-1} for vanadium) and high-performance operation. Fast reaction kinetics of organic compounds permit high power generation. High solubility can be realized by controlling the solubilizing functional groups. Redox potentials can be adjusted by varying the electron-donating ($-OH$, $-NH_2$) or -accepting ($-SO_3H$, $-NO_2$, $-PO_3H_2$) properties of the functional groups. By tuning the molecule size or grafting polymer chains, low membrane crossover can be obtained. High-performance organic-based aqueous redox flow batteries have been demonstrated recently (**Table 4**) [25–30].

Quinone-based organic compounds have received great attention, ranging from simple hydro-quinone to large anthraquinone. These materials have merits of low cost and fast reaction rates. A peak power density of 1 W cm^{-2} has been observed for a 9,10-anthraquinone-2,7-disulfonic acid (AQDS)-bromide system [31], which is close to a reported peak power density of 1.34 W cm^{-2} for vanadium redox flow batteries. Compared to the relative small molecules such as hydroquinone and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), large molecules such as AQDS and methyl viologen (MV) are expected to have low-membrane crossover rates. Functionalization of these active organic compounds with polymer backbone chains further enables the battery operation with low-cost size-exclusion membranes [32]. The development

Reaction mechanisms	Redox reactions	Redox potential/V vs. SHE	Ref.
$2e^-$, $2H^+$ redox reactions		pH dependent, ranging from 0.56 to 0.75	[25]
$2e^-$, $2H^+$ redox reactions		0.2	[26]
$2e^-$, $2H^+$ redox reactions		−0.73 for R = OH	[27]
Organic radicals		About 0.5 V in carbonate electrolyte	[28]
Organic radicals		−0.45 V	[29]
Organodisulfide	R–S–S–R ⇌ 2 R–S⁻	About −1 V	[30]

Table 4. Selected redox active organic compounds used for redox flow batteries.

of organic active materials for redox flow batteries holds great promise for stationary electro-chemical energy storage.

6. Semi-solid redox flow batteries

To overcome the restrictions in solubility of active species in liquid electrolytes, suspensions with energy-dense solid materials have been introduced for redox flow batteries. The concept

was first demonstrated with intercalation materials by Chiang et al. [33], which are typically used for lithium ion batteries. Such semi-solid lithium redox flow batteries combine the merits of high energy density for lithium ion batteries and the decoupled character of conventional redox flow batteries. In order to form a percolation network for charge transfer, several strategies have been proposed: (i) dispersing conductive additive such as carbon into the electrolytes, (ii) adding redox mediators and (iii) inserting a metal wire as a current collector [34]. It has been found that the conductive electrolytes encounter the issue of shunt current between cells in a stack.

Energy-dense batteries, based on lithiation chemistry and intercalation chemistry of abundant elements (such as Na, Mg and Al etc.), contribute significantly to the transportable applications of various electronic devices and revolution of our modern societies. The successful development in these materials raises opportunities in new applications for flow batteries. Li-, Na- and organic molecule-based semi-solid redox flow batteries have been developed recently (**Table 5**) [33–37]. For a pumping system with solid suspension, the rheological properties of suspension need to be considered.

In contrast to the flow batteries with both (de)lithiation and electron transfer reactions occurring inside the electrochemical cells (**Figure 2d**), a new concept using redox shuttle molecules has been introduced [38], wherein solid active materials are kept statically in the tank and only the shuttle molecules are circulated in the electrochemical cell (**Figure 4**). Electrochemical redox reactions of the shuttle molecules go on at the electrode inside the cell, whereas chemical (de)lithiation of the active solid materials in the tank occurs through the reactions between the solid materials and the shuttle molecules. Since the active solid materials are not involved in the electrochemical reaction, conductive additives (such as carbon black) are not necessary in such a system. In addition, low concentration shuttle molecules of only several mM are sufficient to induce the (de)lithiation reaction of a large amount of solid materials.

Semi-solid flow batteries	Suspension	Remarks	Ref.
$LiCoO_2/Li_4Ti_5O_{12}$	26 vol% $LiCoO_2$, 0.8 vol% Ketjen; 25 vol% $Li_4Ti_5O_{12}$, 0.8 vol% Ketjen	C/3 to C/8 rate, high energy efficiency	[33]
$LiCoO_2/Li_4Ti_5O_{12}$	Carbon-free 0.5 vol% $LiCoO_2$, 1 vol% $Li_4Ti_5O_{12}$	Low current density from 0.002 to 0.008 mA cm^{-2}, low coulombic efficiency of about 11.5%	[34]
P2-type $Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O_2/$ $NaTi_2(PO_4)_3$	Active material with 1.3 wt% conductive additive	Current density below 0.5 mA cm^{-2}, low voltage efficiency of about 40%, energy density of about 9 Wh L^{-1}	[35]
Symmetric battery with polythiophene	Polythiophene (8.41 g L^{-1}), Ketjenblack (2 g L^{-1})	Low current density (<1 mA cm^{-2}), energy efficiency of 60.9% at 0.5 mA cm^{-2}	[36]
Zn/polyaniline	10 wt% polyaniline powder in suspension	0.28 V overpotential at 20 mA cm^{-2}	[37]

Table 5. Selected examples for semi-solid redox flow batteries.
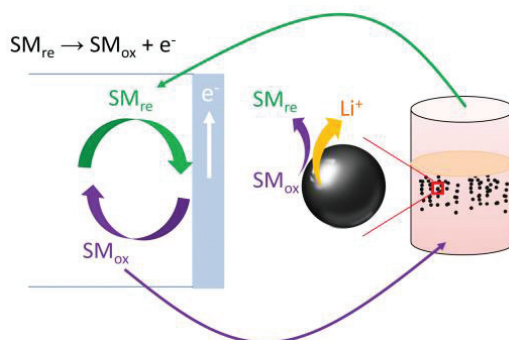
Figure 4. An illustration of a semi-solid redox flow battery with solid materials stored statically in the tank, and redox shuttle molecule (SM) circulated with electrolyte.

7. Conclusions and perspectives

Redox flow battery technology is relatively new and not yet well-developed. Rational electrolyte management and cell design can lead to the enhancement of energy storage capability and a reduction in construction cost. Novel electrolyte chemistry and development of a new configuration of flow batteries will create high system flexibility. Physiochemical and electrochemical redox properties of active couples, stability window of supporting electrolyte, selection of supporting ions, stability of electrode materials and cell components are key factors for successful applications. Future market penetration of flow batteries needs low cost, high energy density and high power density. The pace of recent development in the active organic molecules as electrolytes opens new strategies of cost-effective and sustainable solutions for large-scale stationary energy storage. The application of energy-dense solid materials in suspension for redox flow batteries may largely enhance the energy density of flow battery systems.

Acknowledgements

Abbreviations

AQDS	9,10-Anthraquinone-2,7-disulphonic acid
BMImCl	1-Butyl-3-methylimidazolium chloride
BP	Biphenyl
$BP^{\bullet-}$	Biphenyl radical anion
LiTFSI	Lithium bis(trifluoromethylsulphonyl)imide

MV	Methyl viologen dichloride
OCV	Open circuit voltage
OFN	Octafluoronaphthalene
OFN$^{\bullet+}$	Octafluoronaphthalene radical cation
SHE	Standard hydrogen electrode
TEMPO	2,2,6,6-Tetramethylpiperidine 1-oxyl

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