Redox flow cells for energy conversion

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Abstract

Energy storage technologies provide an alternative solution to the problem of balancing power generation and power consumption. Redox flow cells are designed to convert and store electrical energy into chemical energy and release it in a controlled fashion when required. Many redox couples and cell designs have being evaluated. In this paper, redox flow systems are compared in the light of characteristics such as open circuit potential, power density, energy efficiency and charge-discharge behaviour. The key advantages and disadvantages of redox flow cells are considered while areas for further research are highlighted.

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Keywords: Electrochemical power; Energy storage; Redox flow batteries; Redox flow cells; Regenerative fuel cells

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1. Introduction

The relatively new technologies able to store large quantities of energy have the potential to increase the flexibility of power systems and improve the response to a sudden demand of energy minimising environmental damage. The use of energy storage technologies provides some advantages to electric power transmission systems such as; effective use of existing plant investment, flexibility in operation and better response to price changes. Stored electricity can be made readily available to meet immediate changes in demand allowing effective operation of base load units at high and essentially constant levels of power. An energy storage facility that responds quickly and efficiently to provide or store energy over a wide range of loads could displace less-efficient and more-expensive facilities. Energy storage systems have additional benefits by using off-peak power for pumping and/or charging, maximising operations and flexibility for buying or selling electricity during on-peak or off-peak periods.

Battery technologies can be distinguished in the way energy is stored; lead-acid cells, store energy within the electrode structure whereas redox flow cells systems store the energy in the reduced and oxidised species that recirculate through the cell. Fuel cells, on the other hand, store energy in the reactants externally to the cell. Table 1 provides a comparison among these three systems. Table 2 shows other strategies for energy storage and their main characteristics.

The advantages and disadvantages of conventional, developmental and redox flow cell systems are listed in Table 3. The main electrochemical storage systems at present are the flooded lead-acid battery, the oxygen-recombinant valve-regulated lead-acid (VRLA) battery and redox flow cells. These systems are briefly described below, followed by a review of redox flow cells storage systems.

Flooded lead-acid batteries [1,2] are by far the most developed technology used for large scale electrochemical energy conversion in the transport industry. These batteries have a long life span and good reliability under extreme working conditions. Their limitations include the relatively frequent maintenance required to replace the water lost during operation, high cost compared to other non-storage options and their heavy weight. These limitations reduce their profitability and transport flexibility. Oxygen recombination catalyst and the valves of VRLAs prevent venting hydrogen gas and the entrance of air into the cells. VRLA batteries are significantly more-expensive than flooded lead-acid batteries and their expected life span is shorter. The major advantage of VRLAs over flooded lead-acid batteries is the low maintenance necessary to keep the battery in operation. Also, VRLA cells are smaller than flooded cells, reducing the size and weight of the battery.

The advantages of redox flow cells can be summarised in four features: moderate cost, modularity, transportability and flexible operation. Due to their modular design its construction and maintenance costs could be the lowest of any of the storage systems mentioned above. The redox flow batteries are well-suited for transmission and distribution deferral applications, where batteries might be transported from substation to substation or load centre in order to provide local capacity needed to defer expensive upgrades. The modular nature of these batteries simplifies

<table>
<thead>
<tr>
<th>Electrochemical device</th>
<th>Site of reactants/products</th>
<th>Electrolyte conditions</th>
<th>Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static battery</td>
<td>Active electrode material</td>
<td>Static and held within cell</td>
<td>Microporous polymer separator</td>
</tr>
<tr>
<td>Redox flow cell</td>
<td>Aqueous electrolytes in reservoirs</td>
<td>Electrolyte recycles through the cell</td>
<td>Ion exchange membrane (cationic or anionic)</td>
</tr>
<tr>
<td>Fuel cell</td>
<td>Gaseous or liquid fuel plus air</td>
<td>Solid polymer or ceramic acts as solid electrolyte within cell</td>
<td>Ion exchange membrane polymer or ceramic</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy storage system</th>
<th>Type of process</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed air</td>
<td>In this technology energy is stored as compressed air and can be withdraw by a combustion turbine-generator</td>
<td>Special terrain required</td>
</tr>
<tr>
<td>Pumped hydro</td>
<td>In this technology, water is pumped up into a reservoir during off-peak hours; the water generates electricity by gravity through a reversible turbine-generator during on-peak hours</td>
<td>Special terrain required</td>
</tr>
<tr>
<td>Redox systems (batteries)</td>
<td>This technology refers to the conversion of electrical energy into chemical that can be recovered by reversing the electrochemical reaction</td>
<td>No special requirements</td>
</tr>
<tr>
<td>Superconducting magnetic energy</td>
<td>In this technology, electricity is stored on a superconductor material and is discharged directly as dc power</td>
<td>Very low temperatures required</td>
</tr>
<tr>
<td>Flywheels</td>
<td>This technology stores electricity into kinetics energy and can be taken back by an electrical generator</td>
<td>Vacuum is required</td>
</tr>
</tbody>
</table>

Table 1: General comparison of static battery, redox flow cells and fuel cells

Table 2: Strategies for energy storage
Table 3
Advantages and disadvantages of storage systems compared to redox flow cells

<table>
<thead>
<tr>
<th>Battery energy storage system</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Redox system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional systems</td>
<td>Well-known technology</td>
<td>Frequent maintenance</td>
<td>Flooded lead-acid battery</td>
</tr>
<tr>
<td></td>
<td>Low maintenance</td>
<td>Heavy</td>
<td>Valve-regulated lead-acid (VRLA)</td>
</tr>
<tr>
<td></td>
<td>Low size</td>
<td>High construction cost</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expensive technology</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Short life span</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not portable</td>
<td></td>
</tr>
<tr>
<td>Developmental systems</td>
<td>Transportability</td>
<td>Thermal management</td>
<td>Sodium/sulfur battery</td>
</tr>
<tr>
<td></td>
<td>High energy (charging) efficiency</td>
<td>Difficult maintenance</td>
<td>Zinc/bromine redox flow cell</td>
</tr>
<tr>
<td></td>
<td>Flexible operation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Redox flow cells</td>
<td>Low cost</td>
<td>Newer technology</td>
<td>Bromine/polysulphide redox flow cell</td>
</tr>
<tr>
<td></td>
<td>Modularity</td>
<td></td>
<td>Vanadium redox flow cell</td>
</tr>
<tr>
<td></td>
<td>Transportability</td>
<td></td>
<td>Iron/chromium redox flow cell</td>
</tr>
<tr>
<td></td>
<td>Flexible operation</td>
<td></td>
<td>Zinc/cerium redox flow cell</td>
</tr>
<tr>
<td></td>
<td>High efficiency</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Large scale</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4
Characteristics of lead-acid battery compared with the all vanadium redox system, adapted from Ref. [3]

<table>
<thead>
<tr>
<th>Lead-acid battery (deep cycle)</th>
<th>Vanadium redox flow cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage efficiency 70–80% depending on age</td>
<td>Storage efficiency expected to reach 90% under favourable, low current density conditions</td>
</tr>
<tr>
<td>Storage capacity and power rating are interrelated by chemical energy storage in the electrodes</td>
<td>Non-participating electrodes allow storage capacity and power rating to be designed independently</td>
</tr>
<tr>
<td>Battery voltage varies 10% between charged and discharged states</td>
<td>Voltage is constant through charging and discharging processes</td>
</tr>
<tr>
<td>Easily damaged by excessive charge or discharge</td>
<td>No damage from complete discharge; but overcharging must be prevented</td>
</tr>
<tr>
<td>Can only be charged slowly</td>
<td>Can be charged at any rate by electric current or by replacing the electrolytes</td>
</tr>
<tr>
<td>Damaged by rapid discharging</td>
<td>Can be discharged at any rate</td>
</tr>
<tr>
<td>Lifetime reduced by microcycles (rapid fluctuations in charging rate as in wind and solar applications)</td>
<td>Not affected by microcycles</td>
</tr>
<tr>
<td>Requires regular maintenance</td>
<td>Very low maintenance is expected</td>
</tr>
<tr>
<td>Life rarely exceeds five years (because phase changes deteriorate electrodes)</td>
<td>Life expected to be at least 20 years (no phase changes in the battery and use of durable membrane technology)</td>
</tr>
<tr>
<td>Cost and size of battery per kilowatt is constant as storage capacity increases</td>
<td>Cost per kilowatt decreases as storage capacity increases and size is smaller that lead-acid battery</td>
</tr>
</tbody>
</table>
Fig. 1. Unit redox flow cell for energy storage.

cells where the electrochemical reactions (reduction and oxidation) take place. Fig. 1 shows the basic concept of a redox flow cell; the reactor consists of two compartments separated by the ion exchange membrane, each compartment is connected to a reservoir tank and a pump through an electrolyte circuit loop. In practice, such a unit cell can be multiplied and form stacks of 10–200 cells containing bipolar electrodes. Scale-up can be achieved by increasing the size of the electrodes, adding more electrodes in each stack or by connecting the stack in either parallel or series configuration. Fig. 2 shows a stack of four power-producing cells connected in series in a bipolar manner.

The main attractions of electrically rechargeable redox flow systems, as opposed to other electrochemical storage batteries are: simplicity of their electrode reactions, favourable exchange currents (for some redox couples), low temperature, no cycle life limitations (for the redox couples), electrochemically reversible reactions (some redox couples), high overall energy efficiency, no problems in deep discharge of the system and no inversion of polarity if one cell of the system fails.

One of the most important features of these batteries is that the power and energy capacity of the system can be separated. The power of the system is determined by the number of cells in the stack and the size of the electrodes whereas the energy storage capacity is determined by the concentration and volume of the electrolyte. Both energy and power can be easily varied from just a few hours (as in emergency uninterruptible power supplies or load-leveling applications) to several days or weeks (as needed for remote area stand-alone applications employing photovoltaic or wind generating systems).

2.2. Reactive species and electrode properties

The electrode reactions must be reversible and both the oxidised and reduced species must be soluble with their redox potential as far apart as possible. The cost of reactants must be reasonable and the electrolytes must be chemically stable and easy to prepare at high concentrations.

2.3. Membrane considerations

The membrane must reduce the transport of reactive species between the anode and cathode compartments to a minimum rate and to allow the transport of non-reactive species and water to maintain electroneutrality and electrolyte balance. In a typical redox cell system such as

Anode compartment : \( A^n - e^- \rightarrow A^{n+1} \) (1)
Cathode compartment : \( C^{n+1} + e^- \rightarrow C^n \) (2)
the membrane should be an impermeable barrier for A and C ions in both states of charge. Typical strategies are proton transport in acid electrolytes or Na⁺ transport in the presence of sodium salts. Other considerations include: low electric resistivity, long life span, easy manufacture and handling and moderate cost.

2.4. Design considerations

Major challenges to the development of redox flow batteries include:

(a) Shunt (bypass or leakage) currents [6]: these self-discharge currents of the electrolyte are best reduced by increasing the ionic resistance of the flow ports by making the length of the manifold longer or by reducing the cross-sectional area of the ports. However, increasing the manifold length of the cell ports increases the electrolyte flow resistance demanding more pumping power complicating cell design and increasing costs. A compromise must be reached between the energy saved by reducing the shunt currents and the additional energy needed to recirculate the electrolyte.

(b) Flow distribution in the stack [7]: ideally, the face of each electrode should “see” a constant mean linear flow electrolyte velocity (typically 0.05–1 ms⁻¹) in a plug flow electrolyte regime. In practice, uneven flow distribution occurs and stagnant zones are formed in certain areas of the electrode surface.

(c) Reactant back mixing: partially depleted reactant leaves the cell and return to their respective tanks mixing with more concentrated reactant. At any time, the reactants entering the cell are at lower concentration than they would be if the...
mixing had not occurred causing a gradual drop in the cell potential. The problem could be avoided using two tanks for each reactant; one for new reactants going towards the cell and other for depleted reactants coming out from the cell.

(d) Compensation for ionic migration: the water transferred across the membrane by osmosis or electro-osmosis changes the concentration of ionic species during the operation of the battery. Therefore, the electrolyte must be treated by a suitable method such as reverse osmosis, water evaporation or electrodialysis to remove unwanted formed species and to maintain the redox couple concentrated and pure.

**Figures of merit**: The main figures of merit defined for a redox flow cell systems are: voltage efficiency; the ratio of cell voltage between discharge and charge cycles

\[ \eta_V = \frac{V_{cc}(\text{discharge})}{V_{cc}(\text{charge})} \]  

where \( V_{cc} \) (discharge) and \( V_{cc} \) (charge) are the discharge and charge cell voltages, respectively at certain time or state of charge during the operation of the cell.

Charge efficiency; the ratio of electrical charge used during discharge compared to that used during charge

\[ \eta_C = \frac{Q(\text{discharge})}{Q(\text{charge})} \]  

Energy efficiency; the ratio of energy between the discharge and charge processes

\[ \eta_e = \frac{E(\text{discharge})}{E(\text{charge})} \]  

Power efficiency; the ratio of power between discharge and charge processes

\[ \eta_p = \frac{IV_{cc}(\text{discharge})}{IV_{cc}(\text{charge})} \]

It is important to refer these figures of merit to electrolyte volume, reactant conversion, and state of charge as well as considering practical design and operational factors.

3. Types of redox flow cells

3.1. Bromine/polysulphide flow battery

In these batteries, the electrolytes during the discharge cycle are: sodium bromide in the positive side, and sodium polysulphide on the negative side [8–12]. These chemical species are abundant, their cost is reasonable and they are very soluble in aqueous media. During the charging cycle shown in Fig. 3a, the bromide ions are oxidised to bromine and complexed as tribromide ions. The following half-cell reactions are involved: at the positive electrode, bromide ions are transformed to tribromide ions

\[ 3\text{Br}^- - 2e^- \rightarrow \text{Br}_3^- \]  

\[ \text{E}^0 = +1.09 \text{ V versus SHE} \]  

At the negative electrode the sulfur present as soluble polysulphide anion, is reduced to sulphide ion in the charge cycle; the reactions being simplified to

\[ \text{S}_4^{2-} + 2e^- \rightarrow 2\text{S}_2^{2-} \]  

\[ \text{E}^0 = -0.265 \text{ V versus SHE} \]  

The electrolyte solutions are separated by a cation selective membrane to prevent the sulfur anions reacting directly with bromine and the electrical balance is achieved by the trans-
Table 5
Nominal Module Sizes of Regenesys® Cells [12]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Module series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Individual electrode cross-sectional area (m$^{-2}$)</td>
<td>S (small)</td>
</tr>
<tr>
<td>Number of bipolar electrodes</td>
<td>&lt;60</td>
</tr>
<tr>
<td>Total electrode area (m$^{-2}$)</td>
<td>&lt;6.6</td>
</tr>
</tbody>
</table>

Port of sodium ions across the membrane. On discharge, the sulphide ion is the reducing agent and the tribromide ion the oxidising species. The open circuit cell potential is around 1.5 V and varies depending on the concentration of the electrochemically active species. Challenges with this system include: (a) the nature of the different electrolytes causes cross-contamination of both electrolyte solutions over a period of time, (b) the difficulty in maintaining electrolyte balance, i.e., a fixed composition, (c) the possibility of deposition of sulfur species in the membrane and (d) the need to prevent H$_2$S(g) and Br$_2$(g) formation.

This system was successfully evaluated by the former Innogy Technologies; Regenesys Ltd. [9,10] in 1 MW test facility. Tables 5 and 6 show the sizes of the modular cells developed by this company and the specifications for the plant constructed at the Little Barford site, respectively. The next step in process development was to build a 15 MW h utility scale energy storage plant [13]. A typical 100% charged sulfur-bromine redox battery consist of 1 mol dm$^{-3}$ NaBr satu rated with Br$_2$, and 2 mol dm$^{-3}$ Na$_2$S in contact with a graphite and porous sulphide nickel electrodes, respectively separated by a Nafion$^\text{®}$ 125 membrane. Electrode area of 35 cm$^2$ and 0.25 cm interelectrode gap [12].

Table 6
Outline specification planned for the Regenesys$^\text{®}$ energy storage plant at Little Barford, UK [10]

<table>
<thead>
<tr>
<th>Overall plant parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum rated power output</td>
<td>15 MW</td>
</tr>
<tr>
<td>Energy storage capacity</td>
<td>120 MW h</td>
</tr>
<tr>
<td>Discharge duty cycle</td>
<td>10 h</td>
</tr>
<tr>
<td>Design turnaround efficiency</td>
<td>60–65%</td>
</tr>
<tr>
<td>Predicted lifetime</td>
<td>&gt;15 years</td>
</tr>
<tr>
<td>Site area</td>
<td>&lt;3000 m$^2$</td>
</tr>
<tr>
<td>Design availability</td>
<td>95%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Power conservation system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Power rating</td>
<td>15 MW, 18 MV A</td>
</tr>
<tr>
<td>Design response time</td>
<td>&lt;100 ms</td>
</tr>
<tr>
<td>dc link operating voltage</td>
<td>±2400 V</td>
</tr>
<tr>
<td>Design ramp rate</td>
<td>+15 to –15 MW in &lt;100 ms</td>
</tr>
<tr>
<td>Inverter ac output voltage</td>
<td>6600 V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Nafion$^\text{®}$ cationic</td>
</tr>
<tr>
<td>Nominal cell voltage</td>
<td>1.5 V</td>
</tr>
<tr>
<td>Electrode area</td>
<td>0.67 m$^2$</td>
</tr>
<tr>
<td>Electrolytes</td>
<td>NaBr and Na$_2$S (15 m$^3$ of each per MWh)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XL module</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical number of cells perm stack</td>
<td>200</td>
</tr>
<tr>
<td>Nominal discharge power rating</td>
<td>100 kW</td>
</tr>
<tr>
<td>Operating voltage range</td>
<td>150–360 V</td>
</tr>
<tr>
<td>Module open circuit voltage</td>
<td>300 V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Module layout</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of XL modular stacks</td>
<td>120</td>
</tr>
<tr>
<td>Number of stacks in electrical series</td>
<td>12 (each string)</td>
</tr>
<tr>
<td>Number of parallel strings</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 4. Cell voltage vs. a range of charge and discharge current densities for a 50% charged sulfur-bromine redox battery. About 1 mol dm$^{-3}$ NaBr saturated with Br$_2$, and 2 mol dm$^{-3}$ Na$_2$S in contact with a graphite and porous sulphide nickel electrodes, respectively separated by a Nafion$^\text{®}$ 125 membrane. Electrode area of 35 cm$^2$ and 0.25 cm interelectrode gap [12].

Fig. 5 shows the overall cell voltage of a monopolar cell with activated carbon/polyolefin pressed electrodes divided by a Nafion$^\text{®}$ 115 membrane containing 5 mol dm$^{-3}$ NaBr as anolyte and 1.2 mol dm$^{-3}$ Na$_2$S as a catholyte [14]. During the charging cycle for 30 min at 40 mA cm$^{-2}$ the cell voltage climbed sharply from 1.7 to 2.1 V. This behaviour could be explained by the different overpotentials created within the cell and the adsorption of bromine on the activated carbon. During the discharge cycle at the same current, the curve shows a characteristic critical point at which the voltage drops, indicating complete discharge. Activated carbon adsorbs bromine providing readily available reactant and the discharge process only becomes mass transport controlled at high reactant conversion levels. Operation of redox flow cells under deep discharge high fractional conversions conditions necessitates mass transport conditions. Under these circumstances, high electrolyte flow velocity, effective turbulence promoters and roughened electrode surfaces become important factors in achieving a satisfactory performance.
3.2. All vanadium redox flow battery (VRB)

The vanadium redox battery shown in Fig. 3b employs vanadium ions to store energy in both half-cell electrodes and uses, e.g., graphite felt electrodes [16]. The V(II)/V(III) redox couple is employed at the negative electrode while the positive electrode uses the V(IV)/V(V) redox couple [17,18]. Electrical balance is achieved by the migration of hydrogen ions across a membrane separating the electrolytes. All of the reactants and products of the electrode reactions remain dissolved in one or other of the two electrolytes and, if solution crossover occurs, the vanadium half-cell electrolytes can be recycled and the system brought back to its original state, albeit with a loss of energy efficiency. No significant phase change reactions or electrocrystallization processes occur in the VRB system.

The following half-cell reactions are involved in the all vanadium redox cell. At the positive electrode, vanadium (IV) ions are transformed to vanadium (V) ions:

\[
\text{VO}^{2+} + \text{H}_2\text{O} - \text{e}^- \rightarrow \text{VO}_2^{+} + 2\text{H}^+ \quad \text{(charge)}
\]

At the negative electrode, vanadium (III) cations are transformed to vanadium (II) cations:

\[
\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+} \quad \text{(charge)}
\]

Using 1 mol dm\(^{-3}\) concentrations at 25 °C, the standard open circuit cell potential of this system is 1.26 V. The relatively fast kinetics of the vanadium redox couples allow high coulombic and voltage efficiencies to be obtained but the value of these efficiencies also depends on the internal resistance of the cell.

It is claimed that the VRB is not damaged by fluctuating power demand or by repeated total discharge or charge rates as high as the maximum discharge rates [3,19–29]. It can also be rated to ensure that gassing is eliminated during the high charge rates associated with rapid charging cycles. In addition, VRB cells can be overcharged and overdischarged, within the limits of the capacity of the electrolytes, and can be cycled from any state of charge or discharge, without permanent damage to the cells or electrolytes. There is the problem that the strong activity of a certain kind of vanadium ion, V(V), degrades the ion exchange membrane. Such batteries are being studied in detail by the group of Skyllas-Kazacos at the University of New South Wales [16–40] and by various industrial organisations [3,41].

Fig. 6 shows the second charge and discharge cycles for a cell using vanadium solutions in 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) when two different membranes separated the electrolyte [28]. For a sulfonated polyethylene cation selective membrane in 0.5 mol dm\(^{-3}\) vanadium solution (charged at 15 mA cm\(^{-2}\) current density and discharged across 1 Ω resistor) the open circuit voltage was 1.47 V and the coulombic efficiency was 87%. This indicates a small amount of cross mixing and self-discharge. Better results were obtained when a polystyrene sulfonic acid cation selective membrane was used in a 1.5 mol dm\(^{-3}\) vanadium electrolyte. The cell was charged at a higher current density of 40 mA cm\(^{-2}\) and discharged across a 0.33 Ω resistor to obtain a coulombic and voltage efficiency of 90% and 81%, respectively, over 10–90% state of charge. The overall energy efficiency with this membrane was 73% which compares well with most redox flow systems [30].

Fig. 7 shows another example of a charge/discharge curve for an all vanadium redox flow system [25]. The cell consisted of two 6 mm thick felt electrodes (of 132 cm\(^2\) surface area) bonded to a graphite impregnated polyethylene plate (of 0.26 mm thickness) separated by a polystyrene sulfonic acid membrane. The electrolyte was 2 mol dm\(^{-3}\) vanadium sulphate in 2 mol dm\(^{-3}\) H\(_2\)SO\(_4\) at 35 °C with a charge/discharge current density of 30 mA cm\(^{-2}\). The coulombic, voltage and overall efficiencies at several temperatures for this cell are shown in Fig. 8.
The coulombic efficiency decreased slightly with temperature due to vanadium being transported preferentially through the membrane while as expected the voltage efficiency increased slightly with temperature. The combined effect of coulombic and voltage efficiencies produced the highest overall efficiency at 23 °C. The resistance values of the cell during the charge and discharge cycles were 4.5 and 5.4 Ω cm⁻², respectively, which were obtained from the current potential curves showed in Fig. 9 [25].

A small vanadium redox fuel cell utilising the laminar flow characteristics of two electrolytes operating at very low Reynolds numbers to reduce the convective mixing in a membraneless flow cell has been considered [42]. The two ele-
trolytes containing V(V)/V(IV) and V(III)/V(II), respectively are stored separately and flow-through the cell generating a current density of 35 mA cm\(^{-2}\) at 1.1 V. Although the kinetics of each electrode reactions is rapid, contact between the two electrolyte systems (and very rapid solution redox reaction) drastically reduces the fuel utilization to around 0.1%. The redox fuel cell is interesting from the point of view that eliminates ohmic losses but the very small Reynolds numbers in a laminar fluid flow channel would not be sustainable in larger cell operating at higher Reynolds numbers.

### 3.3. The vanadium-bromine redox system

The all vanadium redox flow cell has a specific energy density of 25–35 Wh kg\(^{-1}\) which is considered low for energy vehicle applications \[43\]. Due to this limitation systems such as vanadium-bromide redox flow cell have long been considered and recently revisited \[44, 45\]. The energy density is related to the concentration of the redox ions in solution, on the cell potential and the number of electrons transferred during the discharge per mol of active redox ions. All vanadium redox flow cells have a maximum vanadium concentration in the region of 2 mol dm\(^{-3}\), which limits energy density and represents the solubility limit of V(II) and V(III) ions in sulfuric acid at temperatures from 5 up to 40 \(^\circ\)C at which the V(V) ions are still stable.

The vanadium-bromine redox flow cell shown in Fig. 3c employs the VBr\(_2\)/VBr\(_3\) redox couple at the negative electrode

\[
\text{VBr}_3 + e^- \rightarrow \text{VBr}_2 + \text{Br}^- \quad \text{(charge)} \tag{15}
\]

\[
\text{VBr}_3 + e^- \leftarrow \text{VBr}_2 + \text{Br}^- \quad \text{(discharge)} \tag{16}
\]

and the redox couple Cl\(^-\)/BrCl\(_2\)\(^-\) at the positive electrode

\[
2\text{Br}^- + \text{Cl}^- \rightarrow \text{ClBr}_2^- + 2e^- \quad \text{(charge)} \tag{17}
\]

\[
2\text{Br}^- + \text{Cl}^- \leftarrow \text{ClBr}_2^- + 2e^- \quad \text{(discharge)} \tag{18}
\]

Preliminary studies were carried out using 3–4 mol dm\(^{-3}\) vanadium-bromide solution by Magnam Technologies \[44\]. For this concentration of active ions, it is possible to reach energy densities up to 50 Wh kg\(^{-1}\).

Fig. 10 shows the charge and discharge time versus the number of cycles of a typical vanadium-bromide redox flow cell at a current of 1 A. The cell contained a Nafion\(^{\circledast}\) 112 cationic membrane. Electrolyte concentration: [V] = 1 mol dm\(^{-3}\), [Br\(^-\)] = 3 mol dm\(^{-3}\), [HCl] = 1.5 mol dm\(^{-3}\). The charge/discharge current was 1 A. Adapted from Ref. [44].

![Fig. 10. Charging and discharging time vs. number of cycles for a vanadium-bromine redox flow cell using carbon material bonded to conductive plastic sheets separated by a Nafion\(^{\circledast}\) 112 cationic membrane. Electrolyte concentration: [V] = 1 mol dm\(^{-3}\), [Br\(^-\)] = 3 mol dm\(^{-3}\), [HCl] = 1.5 mol dm\(^{-3}\). The charge/discharge current was 1 A. Adapted from Ref. [44].](image)

A variation of the vanadium-bromide cell is the vanadium/polyhalide \[46\] cell in which the polyhalide presents higher oxidation potential and exists as a result of the interaction between halogen molecules and halide ions such as Br\(_2\)Cl\(^-\) or Cl\(_2\)Br\(^-\) equivalent to the species I\(_3\)\(^-\) or Br\(_3\)\(^-\). This system has been tested in a small laboratory scale redox flow cell with two glassy carbon sheets current collectors and graphite felt electrodes separated by a Nafion\(^{\circledast}\) 112 membrane and VCl\(_2\)/VCl\(_3\) electrolyte in the negative side and Br\(^-\)/ClBr\(_2\)\(^-\) in the positive side of the cell. At charge/discharge current of 20 mA cm\(^{-2}\) the cell lead to 83% and 80% coulombic and voltage efficiencies, respectively. Fig. 11 shows the charge/discharge curve for this V/polyhalide redox flow cell. The reactions of this cell are; at the negative electrode

\[
\text{VCl}_3 + e^- \rightarrow \text{VCl}_2 + \text{Cl}^- \quad \text{(charge)} \tag{19}
\]

![Fig. 11. Charge/discharge response of a vanadium polyhalide redox cell. 1 M VCl\(_3\) in negative half-cell and 1 mol dm\(^{-3}\) NaBr in positive half-cell, both in 1.5 M HCl electrolyte at a current density of 20 mA cm\(^{-2}\) \[43\].](image)
3.4. The iron-chromium redox system

This system was one of the first studied. The positive reactant is an aqueous solution of ferric-ferrous redox couple while the negative reactant is a solution of the chromous-chromic couple, both acidified with hydrochloric acid. Their charge and discharge reactions involve simple one-electron transfer as is schematically shown in Fig. 3d and e. At the positive electrode, ferrous ion is transformed to ferric ion

\[
\text{Fe}^{2+} - e^- \rightarrow \text{Fe}^{3+} \quad \text{(charge)}
\]

\[
E^0 = +0.77 \text{ V versus SHE} \quad (21)
\]

\[
\text{Fe}^{2+} - e^- \rightarrow \text{Fe}^{3+} \quad \text{(discharge)}
\]

\[
E^0 = +0.77 \text{ V versus SHE} \quad (22)
\]

while at the negative electrode, chromic ions are converted to chromous

\[
\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+} \quad \text{(charge)}
\]

\[
E^0 = -0.41 \text{ V versus SHE} \quad (23)
\]

\[
\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+} \quad \text{(discharge)}
\]

\[
E^0 = -0.41 \text{ V versus SHE} \quad (24)
\]

In this redox flow cell the flow rate of each reactant is always higher than the stoichiometric flow requirement, which would result in total reactant utilization in a single pass through the cell. In each cell, an anionic [47] or cationic [48,49] ion exchange membrane separates the two flowing reactant solutions. In an ideal situation the membrane prevents cross diffusion of the iron and chromium ions, permitting free passage of chloride and hydrogen ions for completion of the electrical circuit through the cell. These early cells have been studied by NASA [47,50–59], by a research group of the University of Alicante [48,49,60–66] and by other workers [67].

An investigation of the effect of carbon fibres electrodes on the performance of a Fe–Cr redox flow cell was reported by Shimada et al. [68]. The redox flow cell consisted of two carbon fibre electrodes of 10 cm² geometrical area, separated by a cation exchange membrane. The electrolyte was 1 mol dm⁻³ chromic chloride in the negative half-cell and 1 mol dm⁻³ of both ferric and ferrous chloride, both in 4 N hydrochloric acid in the positive side. It was reported that the coulombic efficiency increased when the structure of the carbon fibbers changed from amorphous to graphite and that 95% coulombic efficiency can be maintained if the average space of carbon layer analysed by X-ray was kept under 0.37 nm. The authors reported that the addition of boron into the carbon fibbers help to achieve high energy efficiency.

In another study, the Fe–Cr redox system was evaluated using 1/8 in. carbon felt electrodes [69]. Since the reduction of chromium is slow in most surfaces, traces of lead (100–200 μg cm⁻²) and gold (12.5 μg cm⁻²) were deposited on the electrode used for chromium but no catalyst was used for the iron reaction. The area of each electrode was 14.5 cm² and they were separated by an ion exchange membrane (Ionics Inc. series CD1L) the electrolytes were 1 mol dm⁻³ CrCl₃ and FeCl₂ in 2 mol dm⁻³ HCl in the negative and positive sides of the cell, respectively. The open circuit response of this system is shown in Fig. 12 as a function of the percentage of electrolyte charge at a charge/discharge current of 21.5 mA cm⁻². The curves show that there is a higher polarization during the charging cycle in comparison to the discharge cycle that will cause lower energy storage efficiency. The reason for the different open circuit voltages was attributed to the fact that different chromium complexes predominate during the charge and discharge cycles. Three main chromium species predominate in aqueous HCl solutions: Cr(H₂O)₆Cl₂³⁺, Cr(H₂O)₅Cl₂⁺, and Cr(H₂O)₆Cl³⁺. The equilibrium and electrochemical reactions between these complexes is slow but the chromatography and spectrophotometry studies showed that only Cr(H₂O)₅Cl₂⁺ and Cr(H₂O)₆Cl³⁺ species exist in a discharged solution. During charge the concentration of the Cr(H₂O)₅Cl₂⁺ species decreases faster than Cr(H₂O)₆Cl³⁺ indicating that this is the chromium species being reduced. During the discharge cycle the concentration of the Cr(H₂O)₅Cl₂⁺ species rises rapidly while the concentration of Cr(H₂O)₆Cl³⁺ only increases after certain amount

![Fig. 12. Open circuit voltage response of an Fe–Cr redox system at 25°C in 1 mol dm⁻³ CrCl₃ and 1 mol dm⁻³ FeCl₂ in 2 mol dm⁻³ HCl. Charge/discharge cycles at current density of 21.5 mA cm⁻² and reactant volume to membrane area ratio of 0.65 cm³ cm⁻² [69].](image)
of the pentahydrate species has being produced. This shows that the equilibrium between these two species is slow and that their behaviour can be explained in base of their equilibrium potentials.

3.5. Zinc/bromine redox flow cells

The zinc/bromine redox flow battery received much interest as a rechargeable power source because of its good energy density, high cell voltage, high degree of reversibility, and abundant, low cost reactants. As in the case of other redox flow cells, the aqueous electrolyte solutions containing reactive species are stored in external tanks and circulated through each cell in the stack. Each cell contains two electrodes at which reversible electrochemical reactions occur. Sometimes, a porous layer or flow-through porous region is used for the bromine electrode. The electrochemical reactions are as follows: at the positive electrode, bromide ions are converted to bromine

$$3\text{Br}^- \rightarrow 2\text{e}^- + \text{Br}_3^- \quad \text{(charge)}$$

$$\mathcal{E}^\circ = +1.09 \text{V versus SHE} \quad \text{(25)}$$

$$3\text{Br}^- \rightarrow 2\text{e}^- \rightarrow \text{Br}_3^- \quad \text{(discharge)}$$

$$\mathcal{E}^\circ = +1.09 \text{V versus SHE} \quad \text{(26)}$$

At the negative electrode, zinc is reversibly deposited from its ions

$$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn} \quad \text{(charge)}$$

$$\mathcal{E}^\circ = -0.76 \text{V versus SHE} \quad \text{(27)}$$

$$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn} \quad \text{(discharge)}$$

$$\mathcal{E}^\circ = -0.76 \text{V versus SHE} \quad \text{(28)}$$

To avoid the reduction of Br$_2$ at the zinc electrode during charge, the gap between the positive and the negative electrodes is usually divided by a porous separator. A second liquid phase is circulated with the electrolyte to capture the bromine and further prevent it for reaching the zinc electrode. The organic phase contains complexing agents, such as quaternary ammonium salts, with which the bromine associates to form an emulsion. This emulsion is insoluble in water, has different density than water and travels with the electrolyte to the storage tank where it is separated by gravity.

In order to optimise the zinc/bromine battery, various mathematical models have been used to describe the system [70–73]. The problems with the Zn/Br$_2$ battery include high cost electrodes, material corrosion, dendrite formation during zinc deposition on charge, high self-discharge rates, unsatisfactory energy efficiency and relatively low cycle life. Another disadvantage of this system is that the Zn/Zn$^{2+}$ couple reacts faster than the bromine/bromide couple causing polarization and eventually battery failure. To overcome this, high surface area carbon electrode on the cathode side is normally used however, the active surface area of the carbon eventually decreases and oxidation of the carbon coating occurs.

Despite the drawbacks of this system, a Zn/Br$_2$ battery with an energy efficiency of 80% has been constructed with two carbon electrodes of 60 cm$^2$ and 5 mm interelectrode gap separated by a Nafion® 125 or polypropylene microporous membranes [74]. The electrolyte was an aqueous solution of 1–7.7 mol dm$^{-3}$ zinc bromide ZnBr$_2$ with an excess of Br$_2$ with additives such as potassium or sodium chloride at a flow rate of 0.5–3.2 mL s$^{-1}$. Initially, the concentration of bromine Br$_2$, in the negative electrode was in excess of 0.05 mol dm$^{-3}$ to promote total discharge. The polarization of both electrodes and the potential drop across the separators were measured with a calomel reference electrode; Fig. 13 shows that the polarization of the bromine and zinc electrodes was very low even at charge/discharge current densities above 100 mA cm$^{-2}$ and at concentrations of zinc bromide of 1–6 mol dm$^{-3}$. Most of the potential drop across the cell was due to the IR drop of the electrolyte and the separator as it can be seen from the figure. Zinc dendrites were observed at current densities of 15 mA cm$^{-2}$ but they were cut off as they touched the separator without perforate it and hydrogen evolution was observed at this electrode at pH below 3. Fig. 14 shows that constant cell potential is maintained during the charge and discharge cycles followed by sharp potential decrease after ten hours discharge at 15 mA cm$^{-2}$ current density. The voltage efficiency was over 80% at a current density of 30 mA cm$^{-2}$ but drop just over 45% at 100 mA cm$^{-2}$. This type of battery was proposed for load level applications especially because of its low electrode polarization, low cost, and wide availability of the active materials and electrodes.

3.6. Zinc/cerium redox flow cells

This system has been developed by Plurion Systems Inc. [75] and successful operation of a cell at current densities as high as
400–500 mA cm\(^{-2}\) has been claimed. The charging reaction is
\[
\text{Zn}^{2+} + 2\text{Ce(III)} \rightarrow \text{Zn}^0 + 2\text{Ce(IV)} \quad (29)
\]
while the discharging reaction is
\[
\text{Zn} + 2\text{Ce(IV)} \rightarrow \text{Zn}^{2+} + 2\text{Ce(III)} \quad (30)
\]
The cell voltage of the Zn/Ce system in comparison with other redox systems during charge is approximately 2.5 V and drops below 2 V on the discharge cycle. A Zn/Ce system with a cell containing carbon plastic anodes and platinized titanium mesh cathodes of 100 cm\(^2\) geometrical area separated by a (non-specified type of) Nafion\(^\circledR\) membrane was patented in 2004 [76]. The gap anode-membrane was 0.4 cm while the cathode-membrane was 0.2 cm with 0.3 mol dm\(^{-3}\) Ce\(_2\)(CO\(_3\))\(_3\) + 1.3 mol dm\(^{-3}\) of ZnO in 70 wt.% methanesulfonic acid as anolyte at a 1.3–1.4 L min\(^{-1}\) flow rate. The catholyte consisted of 0.36 mol dm\(^{-3}\) Ce\(_2\)(CO\(_3\))\(_3\) + 0.9 mol dm\(^{-3}\) of ZnO in 995 g of methanesulfonic acid at a flow rate of 1.4–1.5 L min\(^{-1}\), the cell operated at 60 °C. A series of 30 charge/discharge cycles was performed as follows; during 5 min the cell was charged at constant current of 100 mA cm\(^{-2}\) followed by 134 min charge at 50 mA cm\(^{-2}\). The total charge after this cycle was 1200 Ah m\(^{-2}\) (432 C m\(^{-2}\)). After 1 min rest the cell was discharged at constant voltage of 1.8 V until the current density dropped to 5 mA cm\(^{-2}\). After 5 min rest, this charge/discharge cycle was repeated 10 times and was followed by similar 20 charge/discharge cycles in which the 50 mA cm\(^{-2}\) charge cycle this time was maintained for 243 min to store a total charge of 2110 Ah m\(^{-2}\) (760 C m\(^{-2}\)) in the cell. Fig. 15 shows the discharge capacity of the cell and the calculated coulombic efficiency during this series of cycles. It can be seen that the coulombic efficiency was larger during cycles when the stored charge was 1200 Ah m\(^{-2}\) than when it was 2110 Ah m\(^{-2}\). Also a series of 30 charge/discharge cycles was performed as follows; during 5 min the cell was charged at constant current of 100 mA cm\(^{-2}\) followed by 134 min charge at 50 mA cm\(^{-2}\). The total charge after this cycle was 1200 Ah m\(^{-2}\) (432 C m\(^{-2}\)). After 1 min rest the cell was discharged at constant voltage of 1.8 V until the current density dropped to 5 mA cm\(^{-2}\). After 5 min rest, this charge/discharge cycle was repeated 10 times and was followed by similar 20 charge/discharge cycles in which the 50 mA cm\(^{-2}\) charge cycle this time was maintained for 243 min to store a total charge of 2110 Ah m\(^{-2}\) (760 C m\(^{-2}\)) in the cell. Fig. 15 shows the discharge capacity of the cell and the calculated coulombic efficiency during this series of cycles. It can be seen that the coulombic efficiency was larger during cycles when the stored charge was 1200 Ah m\(^{-2}\) than when it was 2110 Ah m\(^{-2}\). Also
The concept of a soluble lead-acid acid battery.

\[ \text{Pb}^{2+} + 2\text{H}_2\text{O} - 2\text{e}^- \leftrightarrow \text{PbO}_2 + 4\text{H}^+ \text{(discharge)} \]

\[ E^0 = +1.49 \text{ V versus SHE} \quad (32) \]

negative electrode

\[ \text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}^0 \text{(charge)} \]

\[ E^0 = -0.13 \text{ V versus SHE} \quad (33) \]

\[ \text{Pb}^{2+} + 2\text{e}^- \leftrightarrow \text{Pb}^0 \text{(discharge)} \]

\[ E^0 = -0.13 \text{ V versus SHE} \quad (34) \]

The system differs from the traditional lead-acid battery as Pb(II) is highly soluble in the aqueous acid electrolyte. It also differs from the reported redox flow batteries because only requires a single electrolyte, i.e., no separator or membrane is necessary; this reduces the cost and design complexity of the batteries significantly. The electrode reactions involve the conversion of the soluble species into a solid phase during charging and dissolution at the discharging cycles. This introduces complexities to the electrode reactions and might reduce the performance of the battery if growing metal across the interelectrode gap short circuit the battery. Dissolution and deposition of lead should be fast and no overpotential should be required, however if overpotentials occur hydrogen evolution might take place reducing thus storage capacity.

These cells have been studied in several electrolytes; perchloric acid [77–79], hydrochloric acid, hexafluorosilicic acid, tetrafluoroboric acid [80–83] and most recently in methanesulfonic acid [84–87]. Fig. 18 shows the cell voltage versus time response during the charge/discharge cycles of a soluble lead (II) acid battery in methanesulfonic acid at two current densities [87]. The experiments were carried out in an undivided flow cell containing positive and negative electrodes separated by a 4 mm interelectrode gap in 1.5 mol dm$^{-3}$ \( \text{Pb(CH}_3\text{SO}_3\text{)}_2 + 0.9 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{H} + 1 \text{ g dm}^{-3} \text{ Ni(II)} + 1 \text{ g dm}^{-3} \) sodium ligninsulfonate. Mean linear flow rate of 10 cm s$^{-1}$. Adapted from Ref. [87].

The electrolyte contained 1 g dm$^{-3}$ of sodium ligninsulfonate as an additive to decrease the roughness of the lead deposit avoiding the formation of dendrites and to improve the kinetics of the Pb(II)/PbO$_2$ couple. The curves in the figure show constant voltage during charge and slow voltage drop during the discharge cycles. The overpotential was higher when the applied current was 40 mA cm$^{-2}$ in comparison with 20 mA cm$^{-2}$. The charge and energy efficiencies at a current density of 20 mA cm$^{-2}$ were 79% and 60% while at 40 mA cm$^{-2}$ they were 65% and 46%, respectively. Fig. 19 shows the voltage versus time curves for two sets of 15 min charge/discharge cycles at 20 mA cm$^{-2}$. The low overpotentials observed from the second cycle during the charging process was explained by the formation of insoluble Pb(II) remaining in the positive electrode during the reduction of PbO$_2$. During the 79th to the 84th cycles the shape of the curve remains the same but lower overpotentials during the discharge process can be observed.

4. Other characteristics and comparisons

A number of redox flow battery systems are considered in Table 7 (other redox flow cells include: sodium or potassium sulphide-poly sulphide species in the anodic reaction and iodide-polyiodide or chloride-chlorine in the cathodic reaction [12], bromine/chromium [88] and uranium [89]). From the systems listed in Table 7, a number of features can be highlighted:

(a) the size of the cells is generally small with the exception of the bromine/poly sulphide system of the Regenesys cells; the installed power is in the range kW for most systems and MW for the bromine/poly sulphide system,
Table 7: Comparison of different redox flow cell systems

<table>
<thead>
<tr>
<th>System</th>
<th>Electrodes</th>
<th>Membrane</th>
<th>$E_{cell}$ (V)</th>
<th>Current density (A m$^{-2}$)</th>
<th>$K_A$ ($\Omega$ m$^2$)</th>
<th>Voltage efficiency (%)</th>
<th>Current efficiency (%)</th>
<th>Energy efficiency (%)</th>
<th>Installed power</th>
<th>Installed energy</th>
<th>Temperature (°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Cr</td>
<td>Fe: Carbon felt</td>
<td>Cr: Carbon felt + catalyst</td>
<td>1.03</td>
<td>9</td>
<td>0.04</td>
<td>1.1 $\times$ 10$^{-1}$</td>
<td>90</td>
<td>81.6</td>
<td>81.2</td>
<td>10 W</td>
<td>10 kW h</td>
<td>30–55</td>
</tr>
<tr>
<td>Br/PS</td>
<td>Carbon polymer composite</td>
<td>Cationic membrane Nafion®</td>
<td>0.77</td>
<td>64.5</td>
<td>0.031</td>
<td>1.2 $\times$ 10$^{-2}$</td>
<td>73</td>
<td>99</td>
<td>72</td>
<td>2.6 $\times$ 10$^{-3}$</td>
<td>75</td>
<td>80–98</td>
</tr>
<tr>
<td>V/V</td>
<td>Graphite felt</td>
<td>Selemion CMV</td>
<td>1.54</td>
<td>600</td>
<td>0.67</td>
<td>2.6 $\times$ 10$^{-3}$</td>
<td>75</td>
<td>90</td>
<td>60</td>
<td>98.2</td>
<td>82</td>
<td>85</td>
</tr>
<tr>
<td>Soluble Pb/LA</td>
<td>Carbon composite</td>
<td>None</td>
<td>1.70</td>
<td>800</td>
<td>0.15</td>
<td>2.1 $\times$ 10$^{-2}$</td>
<td>73.2</td>
<td>98.2</td>
<td>71.9</td>
<td>73.2</td>
<td>82</td>
<td>80</td>
</tr>
<tr>
<td>Lead-acid</td>
<td>Microporous separator</td>
<td>None</td>
<td>1.78</td>
<td>100–600</td>
<td>0.0002</td>
<td>1.00 $\times$ 10$^{-3}$</td>
<td>72</td>
<td>98.2</td>
<td>73.2</td>
<td>80</td>
<td>80.50</td>
<td>70–75</td>
</tr>
</tbody>
</table>

(b) the majority of the systems use a cationic membrane to separate the two electrode reactions except the soluble lead-acid battery system,

(c) most systems use carbon and carbon composite electrodes, three-dimensional and carbon felt electrodes are also used, and

(d) efficiencies are generally high but are dependent on the state of charge and process conditions, the values are; 73–62% voltage efficiency, 80–98% current efficiency and 66–75% energy efficiency.

The energy density of redox flow batteries in comparison with other battery systems is shown in Fig. 20 [91]; specific energy density of flow cells varies within the range of 18–28 kW h t$^{-1}$ and volumetric energy density within 21–35 kW h t$^{-1}$. As it is shown in the figure, the energy density of redox flow cells is below the energy density of batteries such as metal-air, lithium-ion, Na$_2$S, Ni–Cd and lead-acid. These values show that redox flow cells systems can compete with Ni–Cd, super-capacitors, flywheels and lead-acid batteries for energy storage, rather than for portable applications.

As in the case of many batteries, it is important to consider health and safety; many electrolytes require careful manipulation during storage and transport due to their corrosion and toxicity. Another important aspect is the compatibility of the electrolytes; in the case of membrane failure for example, vanadium cells will lose power as the homogeneous reaction will be thermodynamically favourable, however, in other systems the incompatibility of the electrolytes in case of membrane failure can cause more problems and health and safety issues should be considered carefully.
5. Summary and further work

Modular technologies such as redox flow systems offer the capability of high power rating; long energy storage time and excellent response time, full power can be delivered in few seconds. Such characteristics are important for better use of power generation in the competitive electricity market. At the generation level, energy storage can be used to increase the load factor of base load and mid merit plant, thereby reducing the need to dispatch less-efficient peaking plant, as well as providing benefits such as meeting load increases and covering operating and contingency reserve.

Electricity transmission companies should be able to increase the load factor of their transmission lines and other assets, while distribution companies can use energy storage to replace or defer investment in generating and other plant, such as static Var compensators, on their electrical network. There is hence, a significant potential market for energy storage products in the range of several hundred MW and several hours storage down to the multi MW level that is presently unsatisfied by existing technology.

Other future markets for these systems are their use in conjunction with renewable energy sources, such as wind power and photovoltaics energy generation systems. A characteristic of renewable sources is their lack of predictable availability at any given time. The redox flow batteries can be used to store energy during periods when conditions favour production, then continuing dispatching the stored electricity at periods of low productivity. In this mode, the redox flow batteries can significantly increase the value of renewable energy sources and represent an efficient energy supply in remote power applications. Table 8 shows some potential applications for redox flow cell storage systems.

The performance of a redox flow cells indicated by the volumetric energy density (kW h m$^{-3}$) figures of merit [92,93] can be enhanced by means of porous, three-dimensional electrodes, highly catalytic electrodes, high linear velocities and good turbulence promoters.

Further work is required in the areas of: (a) reactor characterisation, (b) catalysis by composite (carbon-polymer) electrodes, (c) membrane performance and its effect on electrolyte housekeeping, (d) large scale engineering of redox flow cell systems.
and their integration with other energy systems and (e) the time-dependence of cell components and their performance. Improvements in redox flow cell technology can be anticipated due to developments in: modular electrochemical reactor and stack design, the engineering of electrode structures, improved electrocatalysis of electrode surfaces, tailoring of the reaction environment in filter-press cells and intelligent control systems to maximise voltage power efficiency.

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