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Review article

Recent developments in organic redox flow batteries: A critical review

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HIGHLIGHTS

- Future opportunities for organic redox flow batteries are reviewed.
- Advantages, disadvantages and challenges are discussed.
- Organic redox couples are classified (aqueous & non-aqueous chemistries).
- The performance of systems are discussed against benchmarks.
- Critical areas requiring further R & D are highlighted.

GRAPHICAL ABSTRACT

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ABSTRACT

Redox flow batteries (RFBs) have emerged as prime candidates for energy storage on the medium and large scales, particularly at the grid scale. The demand for versatile energy storage continues to increase as more electrical energy is generated from intermittent renewable sources. A major barrier in the way of broad deployment and deep market penetration is the use of expensive metals as the active species in the electrolytes. The use of organic redox couples in aqueous or non-aqueous electrolytes is a promising approach to reducing the overall cost in long-term, since these materials can be low-cost and abundant. The performance of such redox couples can be tuned by modifying their chemical structure. In recent years, significant developments in organic redox flow batteries has taken place, with the introduction of new groups of highly soluble organic molecules, capable of providing a cell voltage and charge capacity comparable to conventional metal-based systems. This review summarises the fundamental developments and characterization of organic redox flow batteries from both the chemistry and materials perspectives. The latest advances, future challenges and opportunities for further development are discussed.

1. Introduction

One of the hurdles to achieving an increased share of intermittent renewables at the grid scale is the need to provide a stable

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energy output to end-users. This will require robust energy storage devices, to deliver stable and flexible electricity that adheres to accepted standards for voltage and frequency, whether grid-connected or off-grid [1–8]. Over the last 30 years, a number of energy storage technologies have been introduced and successfully demonstrated, including thermal (i.e. latent or sensible heat), mechanical (i.e. pump hydro, compressed air) and chemical/electrochemical (i.e. fuel cells and rechargeable batteries). Amongst these technologies, electrochemical devices are attractive because they can be installed anywhere, free from the geological/geographical restrictions [3,4]. To ensure that energy storage devices are economically viable in the long term, the US Department of Energy (DoE) has set a system capital cost target of USD$ 150 $(\mathrm{kW\ h})^{-1}$ by 2023, alongside a target of USD$ 100 $(\mathrm{kW\ h})^{-1}$ to match with existing physical energy storage technologies [9]. This is expected to be in line with the requirements of the EU [10].

With regards to both economic and safety considerations, redox flow batteries (RFBs) are recognized as one of the most realistic candidates amongst electrochemical technologies for energy storage in the range of several kW/kW h up to tens of MW/MW h [3,4]. In contrast to conventional rechargeable batteries, redox flow batteries store all or part of the charge in electrolytes recirculated through the cell, while in conventional batteries such as lead acid and lithium-ion batteries, charge is stored entirely within the cell (as active materials in the electrode structures) and the electrolyte remains in the cell at all times [3,4]. This method of charge storage enables redox flow batteries to be scaled more easily, economically and safely than conventional batteries. In RFBs, the electrolytes are typically stored in separate reservoirs and circulated through the batteries during charge and discharge (Fig. 1a); exceptions include the soluble lead acid battery, which operates in an undivided cell, with an electrolyte common to both half-cells, in one reservoir [11]. In contrast, a fuel cell (FC) is a galvanic cell, in which catalytic oxidation of an externally stored fuel and reduction of an oxidant (typically oxygen from an air-breathing cathode) take place continuously. As in a fuel cell, an ion exchange membrane is usually required in an RFB to minimize losses associated with cross-contamination of the two half-cell electrolytes (internal currents). In a few cases, undivided cells are possible, subject to the stability of highly oxidised species in contact with the electrode materials [3].

Redox flow batteries can be more readily scaled than conventional batteries without incurring losses in the power density. Scale-up of power can be achieved by increasing the electrode active surface area, the number of electrodes in a cell stack and the number of stacks in a system. The storage capacity of conventional RFBs can be increased by increasing the volume of the electrolytes and/or the concentrations of active species.

The overall cost per kW h of the redox flow battery not only depends on the costs of the cell components but also on the molar mass and the corresponding chemistries of the electroactive species. For example, higher concentrations of electrolytes are desired for active species with lower molar mass. If the selected chemistry is reversible and yields a higher cell voltage and/or multi-electron transfers, a larger energy capacity is expected for a given electrolyte concentration [1–8]. A high solubility of the redox couple is needed to maintain a high current while minimizing mass transport losses; ideally, the majority of charge and discharge should take place under charge transfer control at both electrodes.

Various metal-based redox flow battery chemistries have been proposed with the use of aqueous and non-aqueous electrolytes [12–29]. Some successful systems have received significant industrial investment and have reached the stage of commercialization, mainly for grid-scale applications due to their relatively low energy densities ($<40\ \mathrm{W\ h\ dm^{-3}}$) [3]. At present, the all-vanadium redox flow battery is the most developed system, primarily as a consequence of the active species remaining in solution at all times during charge/discharge cycling, its high reversibility and its relatively large power output. Compared to the DoE target, however, the capital cost of these systems (USD$ 300–800 $(\mathrm{kW\ h})^{-1}$) remains far too high for deep market penetration [30,31]. For example, the cost of vanadium redox flow battery electrolytes is as high as USD$ 80 $(\mathrm{kW\ h})^{-1}$, while the ion-exchange membrane can account for up to 40% of the total cost of the battery [32,33].

In order to meet the proposed cost target of USD$150 $(\mathrm{kW\ h})^{-1}$ [9], recent investigations have highlighted the use of organic active materials in solid-state organic batteries [34–38], in which energy is stored within the cell, mainly in the form of a radical polymer. In general, the advantages of using organic molecules are their abundance and the possibility of their extraction from diverse sources. Even in the early stages of development, the electrolyte cost of some organic-based flow batteries has been demonstrated to be lower than USD$ 35 $(\mathrm{kW\ h})^{-1}$ (based on half-cell estimatations) [39–42]. With advances in synthetic chemistry, the properties of these organic molecules can be further tailored to provide fast kinetics and high solubility, and to yield high cell voltages in batteries [43–47]. The electrolyte cost per kW h can be lowered further by selecting active species based on the cell voltage and/or on multi-electron transfers. In the presence of non-aqueous electrolytes, the operating cell voltage is no longer limited to 1.5 V due to the evolutions of hydrogen and oxygen in the water electrolysis. In contrast, the electrochemical stability window of typical non-aqueous solvents, such as acetonitrile and propylene carbonate, can exceed 5 V [48]. As suggested by their fundamental electrochemical behaviour, some redox couples exhibit better electrochemical performance at more negative potentials than is possible in aqueous electrolytes [49,50], and a cell voltage of 4.5 V might be achieved by the use of a suitable pair of organic redox couples [43]. During charging of the battery, organic electrolytes can afford the opportunity to minimize solvent electrolysis due to their wider potential window compared to water.

Organic electroactive species can provide the possibility of a higher solubility in both aqueous and non-aqueous electrolytes. Before the introduction of all-organic redox flow batteries, organic molecules contained in aqueous electrolytes (with reasonable solubilities ($>1\ \mathrm{mol\ dm^{-3}}$)) were used in early studies of regenerative fuel cells [51] and organic fuel cells [52,53]. In the case of quinoxaline, the solubility is up to 4.0 $\mathrm{mol\ dm^{-3}}$ in potassium hydroxide solution (0.9 $\mathrm{mol\ dm^{-3}}$ potassium chloride + 0.1 $\mathrm{mol\ dm^{-3}}$ potassium hydroxide, pH 12.9) and the redox potential in such an electrolyte is more negative than − 0.70 V *vs.* SHE [54], although the addition of salts and solvents could reduce the solubility significantly (e.g., solubilities of quinoxaline: 4.5 $\mathrm{mol\ dm^{-3}}$ at *ca.* 1.0 $\mathrm{mol\ dm^{-3}}$ potassium chloride and 0.01 $\mathrm{mol\ dm^{-3}}$ potassium hydroxide; 0.5 $\mathrm{mol\ dm^{-3}}$ *ca.* 0.5 $\mathrm{mol\ dm^{-3}}$ potassium sulphate and 0.01 $\mathrm{mol\ dm^{-3}}$ potassium hydroxide). High solubilities of organic compounds have been reported in selected non-aqueous electrolytes [43]. For instance, methyl-para benzoquinone (molar mass: 122.12 $\mathrm{g\ mol^{-1}}$) has a solubility of up to 6 $\mathrm{mol\ dm^{-3}}$ in acetonitrile [55].

In an ideal scenario, these organic compounds could function as reversible redox species in a rechargeable battery and the specific energy of 150 $\mathrm{W\ h\ kg^{-1}}$ or energy density of 210 $\mathrm{W\ h\ dm^{-3}}$ could be comparable with that in conventional lithium-ion batteries (120 $\mathrm{W\ h\ kg^{-1}}$; 270 $\mathrm{W\ h\ dm^{-3}}$ in Table 1).

This assumption is based on a realistic performance scenario for an existing flow battery, namely, a molecular weight of 120 $\mathrm{g\ mol^{-1}}$, a 2-electron transfer, a cell potential of 1.5 V and a 75% round trip energy efficiency [56]. To obtain these desirable properties for all-organic flow batteries, tremendous improvements need to be made in existing systems, considering that the energy densities are