Membrane-less hybrid flow battery based on low-cost elements

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HIGHLIGHTS

- A novel organic-inorganic flow battery system using low-cost elements.
- For a membrane-less configuration the open-circuit voltage is 1.17−1.59
- The average coulombic efficiency is 71.8% over 20 cycles.
- Voltammetry and dissolution experiments identify the performance limitations.

ARTICLE INFO

ABSTRACT

The capital cost of conventional redox flow batteries is relatively high (>USD$ 200/kWh) due to the use of expensive active materials and ion-exchange membranes. This paper presents a membrane-less hybrid organic-inorganic flow battery based on the low-cost elements zinc (<USD$ 3 Kg^{-1}) and para-benzoquinone (<USD$ 8 Kg^{-1}). Redox potential and voltammetric studies show that the open-circuit voltage of the battery is 1.17−1.59 V over a wide range of pH. Half-cell charge-discharge and dissolution experiments indicate that the negative electrode reaction is limiting due to the presence of chemical side reactions on the electrode surface. The positive electrode redox reactions are not affected and exhibit (half-cell) coulombic efficiencies of >92.7% with the use of carbon felt electrodes. In the presence of a fully oxidized active species close to its solubility limit, dissolution of the deposited anode is relatively slow (<2.37 g h^{-1} cm^{-2}) with an equivalent corrosion current density of <1.9 mA cm^{-2}. In a parallel plate flow configuration, the resulting battery was charge-discharge cycled at 30 mA cm^{-2} with average coulombic and energy efficiencies of c.a. 71.8 and c.a. 42.0% over 20 cycles, respectively.

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1. Introduction

Ambitious targets for cutting greenhouse gas emissions [1] are reliant on the wide-scale deployment of intermittent renewable energy technologies (notably solar and wind) on a grid-scale [2]. To enable the use of such technologies, in particular to provide a stable energy output to end-users, competitive energy storage systems are required to balance load with demand [3–6]. To ensure that energy storage systems are economically competitive in the long term, the US Department of Energy (DoE) has set a long-term capital cost target of USD$ 150/kWh to match the costs of existing physical energy storage technologies [7].

Redox flow batteries have emerged as the most promising energy storage system in terms of cost and safety for applications of a few kW/kWh up to tens of MW/MWh. The main advantage of this technology over conventional rechargeable batteries is the ability to decouple capacity from power effectively by adjusting the electrode size and/or the electrolyte volume [5]. The shelf life of redox flow batteries is theoretically long since most cell components (i.e. plastic and carbon) do not corrode or deteriorate over time, considering that the active redox species can be separated once the battery is charged.

Since the invention of the redox flow battery, various chemistries have been proposed (e.g., all-vanadium [8], zinc-cerium [9] and vanadium-cerium [10]) and most use expensive ion-exchange membranes to separate the negative and positive electrolytes. At the present time, the all-vanadium redox flow battery is the most developed system, due to its high reversibility and large

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power output, as well as the fact that the redox species remain in solution at all times. However, the capital cost of this system (>USD$ 200/kWh) exceeds the proposed DoE target for extensive market penetration. The current cost of vanadium is around USD$ 23—25 Kg^{-1}, which represents around 30% of the overall capital cost of the battery. The costs of the ion-exchange membranes and electrodes are estimated to be *c.a.* 41% in the cost model illustrated in Fig. 1, consistent with existing literature [11].

Aiming to reduce costs and simplify the cell design, several membrane-less systems have been proposed, including the soluble lead acid [13,14], zinc-nickel [15,16], copper-lead dioxide [17], cadmium-chloranil [18], zinc-lead dioxide [19,20] and zinc-cerium [21,22] redox flow batteries. Some of these proposed systems make use of the slow dissolution processes of deposited metals in the presence of certain active species in the electrolytes. For certain chemistries, the capacities of the batteries are still limited by the positive electrode reactions, particularly those relying on a solid-

phase transformation within the electrode materials (e.g., chloro-benzoquinone/chloro-hydroquinone [18], $PbO_2/PbSO_4$ [13,14], $NiOOH/Ni(OH)_2$ [15,16]). In order to address these issues, it is preferable to use soluble active species rather than species undergoing a solid-phase transformation for both of the electrode reactions and should exhibit low corrosion rates at the anode. The chemistry should be based on low-cost active materials (<USD$ 10 Kg^{-1}) and should lead to a voltage of >1.0 V.

In order to achieve the low costs required, several studies have investigated the use of abundant organic active materials based on common elements, such as carbon, hydrogen, oxygen and sulfur [23,24]. These organic molecules can be tailored to have certain properties, such as fast kinetics, high solubility and high associated cell voltage in the resulting flow battery [25—28]. They typically dissolve in either aqueous or non-aqueous electrolytes and can be incorporated in polymers [29] or appear as solid electrodes mixed with porous carbon and binders [30].
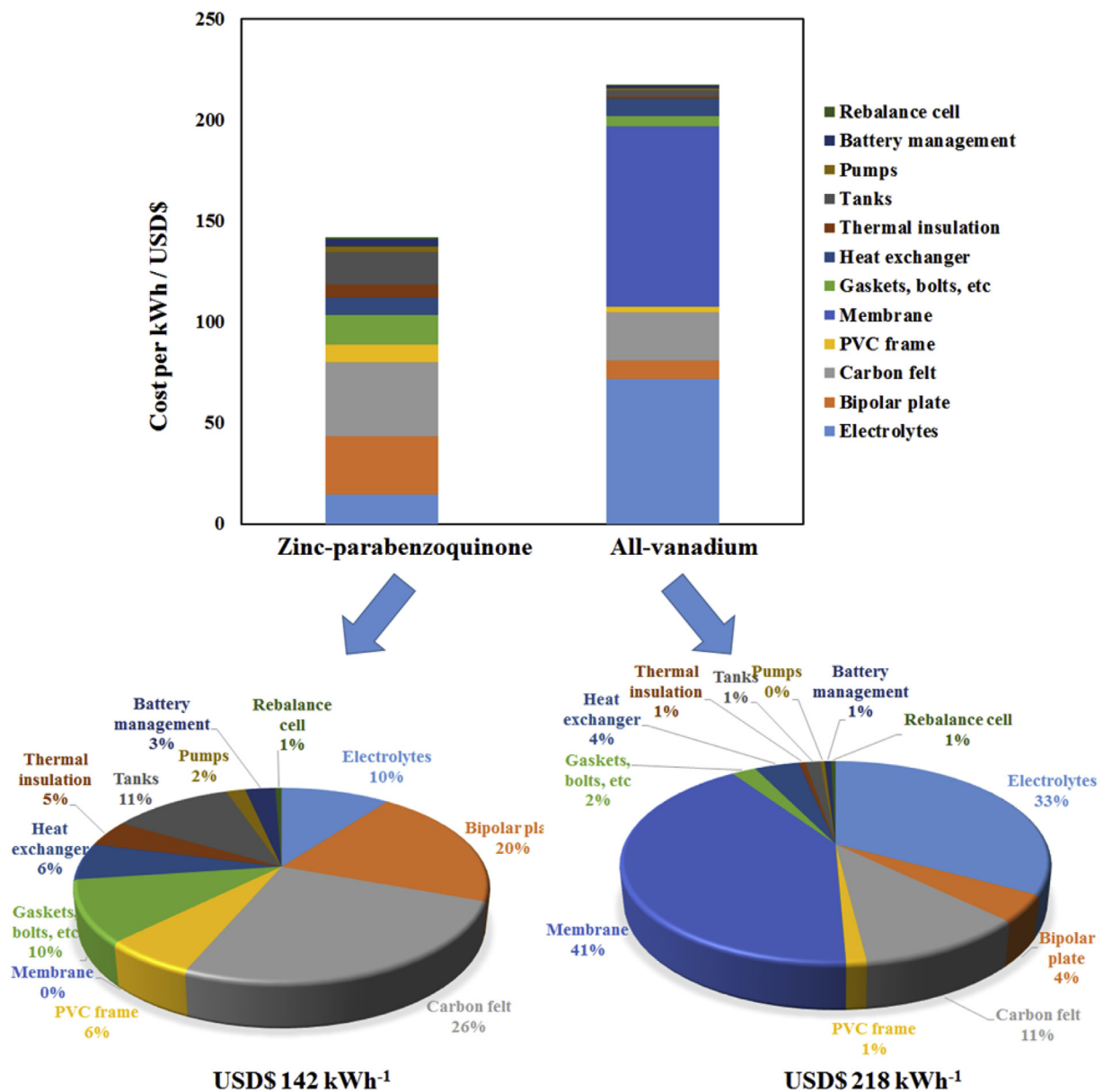

Fig. 1. Capital cost breakdown of 1 MW × 10 h redox flow batteries: (a) comparison between zinc-benzoquinone (pBQ) and all-vanadium chemistries. Detailed descriptions and calculations are available in Supplementary Information. Component costs are based on Ref. [12].