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Evaluation of redox flow batteries goes beyond round-trip efficiency: A technical review

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ABSTRACT

The flow battery is a promising technology for large-scale storage of renewable energy owing to its unique advantages such as independence of power and energy capacity, scalability and versatility. The evaluation method is extremely important for the developments of both researches and applications of flow batteries. However, there is a lack of clear and uniform evaluation criteria in the open literature. The round-trip energy efficiency is commonly used to evaluate cell performance, whereas other different evaluating criteria may be suitable for different situations, with respective emphases. This paper reviews the development of performance evaluation criteria for redox flow batteries and clarifies the selection principle of evaluation criteria, stating that the system energy efficiency is the primary criterion, and power density or/and energy density are also vital evaluation criteria on the premise of maintaining high system energy efficiency for diverse types of redox flow batteries. The recent applications of these evaluation criteria on flow batteries are demonstrated afterwards. Finally, some exceptional conditions under what the system energy efficiency criterion is unsuitable are discussed, and emphasis is addressed on the new types of flow batteries. Applying a proper evaluation criterion helps to circumvent the remaining challenges of redox flow batteries, therefore, this review paper will be a useful guideline for the technology development and practical deployment of flow batteries.

Contents

1. Introduction

With the increasing demands on the electricity generation from renewable energy resources and construction of distributed smart grids, the redox flow batteries (RFBs) which serve as cost-effective,

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reliable, and longer-lived energy storage technologies, are receiving more and more concerns [1–6]. A typical RFB consists of two electrolyte tanks for storing energy, a cell unit for energy conversion, and pumps for circulating the electrolytes between the cell units and electrolyte reservoirs. Unlike in other battery systems, in RFBs the energy is stored in the electrolyte solutions and the capacity of the system is determined by the concentration of the active redox couple species and the volume of electrolyte reservoirs, while the power rating of the system is determined by the electrode area of a cell and the number of cells in the stack. As such, the power and energy capacity of an RFB system can be designed separately, offering the flexibility to construct battery systems according to various working conditions. The electrodes of RFBs only provide a platform for charge transfer, so there are no significant physical or chemical changes on the electrodes, which is a factor that contributes to a long cycle life [2,3]. With these advantages, the RFBs exhibit a promising market perspective. Till now, RFB systems ranging from a few kWh to several MWh have been developed and demonstrated, e.g. sodium polysulfide/bromine, all-vanadium and zinc/bromine redox flow batteries [4,5]. However, the low energy density ($<50\,\mathrm{Wh\,L^{-1}}$), low stability and high-cost of separators as well as the cross over contaminations of active materials still hinder the wide commercialization of RFBs [6].

Rational evaluation criteria for cell performance are the necessities to advance the researches on RFBs. Currently, there are various indexes for performance evaluation, e.g. coulombic efficiency (the ratio of the average discharging capacity to the average charging capacity), voltage efficiency (the ratio of the average discharging voltage to the average charging voltage), energy efficiency (the ratio of the average discharging energy to the average charging energy), utilization of electrolyte (the ratio of the actual discharging capacity to the theoretical discharging capacity), capacity decay rate (cycling times) and power density (current density multiplies cell voltage) [7–13]. As a secondary cell, the charging-discharging test is the most typical evaluation method for RFBs, which is reflected as energy efficiency. Recently, with the involvement of some fuel cell research groups in the area of RFBs, polarization curves and the associated power density curves, which are widely used for performance evaluation of fuel cells, have come into use for RFBs' performance evaluation. These researchers have been chasing higher power densities [14–19]. Houser et al. found that optimal flow field design for RFBs was not simply related to the best architecture, but was instead a more complex interplay between architecture, electrode properties, electrolyte properties, and operating conditions [16]. They took discharge capacity and power density as evaluation criteria for the cell performance, while missed the charge-discharge cycling curves. In their another work, they compared the effect of several kinds of flow fields, i.e. the serpentine flow field, the equal path length (EPL) flow field, and the aspect-ratio design (ARD) flow field. At the current density of $200\,\mathrm{mA\,cm^{-2}}$, the energy efficiency of an all-vanadium RFB with electrode area of $9\,\mathrm{cm^2}$ can reach 68%. But if the energy consumption by pump was taken into consideration, the system energy efficiency was only 54% even for the optimal flow field design (the ARD) [17].

The performance of RFBs has improved remarkably in the last decades. Fig. 1 shows the battery performances that are achieved in several major flow battery research groups. As can be found, the power density increased from $50\,\mathrm{mW\,cm^{-2}}$ to $200\,\mathrm{mW\,cm^{-2}}$, while the energy efficiency deceased from 87% to around 60% (except for the work by Zhao's group, in which the all-vanadium RFB adopting the dual-scale carbon paper electrodes can keep an energy efficiency as high as 82% when charging and discharging the battery at $200\,\mathrm{mW\,cm^{-2}}$) [10–14,20]. Some other research results on RFBs simply showed the current density-voltage polarization curves and current density-power density curves, where the maximum discharge current density can reach as large as $1.0\,\mathrm{A\,cm^{-2}}$, and the maximum output power density can approach $800\,\mathrm{mW\,cm^{-2}}$ [18,19]. Power density, maximum discharge current density or other criteria have advanced the flow battery technology. However, there is a lack of clear and uniform evaluation criteria in practical application of RFBs. To address such issue, in 2014 Zheng and Zhang clarified that using the polarization curve was not a comprehensive method for evaluation of performance of RFBs, and the peak power density was even of limited significance in practical usages [11]. They concluded that the charging-discharging test was optimal for RFBs' performance evaluation.

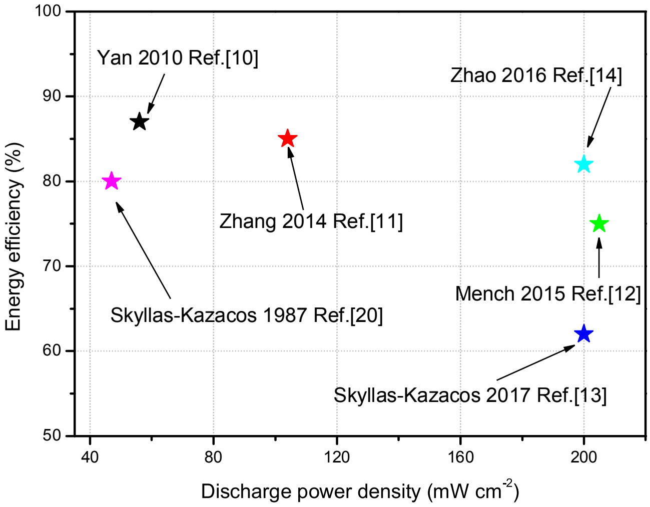

Fig. 1. Battery performance criteria commonly adopted by several major research groups on flow batteries.

In this review paper, we will further deepen the understanding of the evaluation criteria for RFBs based on Zheng et al.'s work. The primary criterion is analyzed in the viewpoint of practical applications, and the selection of other criteria is clarified based on diverse types of RFBs. Finally, some exceptive conditions are discussed in which the energy efficiency is not appropriate to serve as the evaluation criterion of RFBs.

2. Further discussions on the evaluation criterion of energy efficiency

2.1. Energy efficiency as the criterion for the design and operation of practical large-scale RFBs

Currently, RFBs are mainly used in these application: load-balancing for electric grid, storing energy from renewable sources such as wind or solar for discharge during periods of peak demand, and stand-alone power system. These large stationary applications usually have no constraint on site area, such that the different power demands can be met by adjusting the cell number in the RFB stack (i.e. adjusting the electrode area of a RFB system). The energy efficiency is commonly selected as the design and operation criterion for the RFBs.

Skyllas-Kazacos et al. summarized the operation parameters of some representative large-scale all-vanadium RFBs set up during last decades [21]. It can be found that the total power of these RFBs system increases gradually with the development of membrane and system integration, while the energy efficiency is kept being higher than 80%. The Cellstrom GmbH (Austria) built an all-vanadium RFB system in 2008 with the power/capacity of 10 kW/100 kWh. It worked as an off-grid charging station by storing the energy from photovoltaic devices [22].