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Flow field design and optimization based on the mass transport polarization regulation in a flow-through type vanadium flow battery

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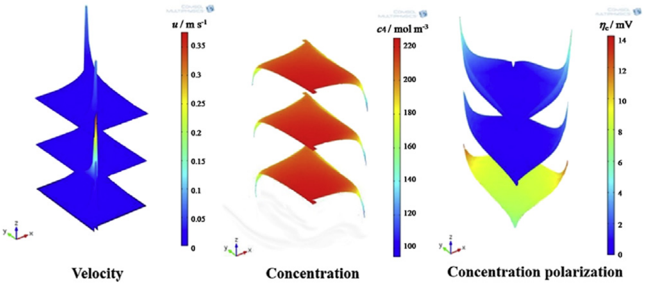
HIGHLIGHTS

- The mass transport polarization distribution in space and time in RDFB was studied.
- Flow field was designed by improving the uniformity of mass transport polarization.
- Flow field was optimized by reducing the mass transport polarization.
- RPFB with a plug flow and short path is effective to improve the mass transport.

GRAPHICAL ABSTRACT



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ABSTRACT

Vanadium flow battery holds great promise for use in large scale energy storage applications. However, the power density is relatively low, leading to significant increase in the system cost. Apart from the kinetic and electronic conductivity improvement, the mass transport enhancement is also necessary to further increase the power density and reduce the system cost. To better understand the mass transport limitations, in the research, the space-varying and time-varying characteristic of the mass transport polarization is investigated based on the analysis of the flow velocity and reactant concentration in the bulk electrolyte by modeling. The result demonstrates that the varying characteristic of mass transport polarization is more obvious at high SoC or high current densities. To soften the adverse impact of the mass transport polarization, a new rectangular plug flow battery with a plug flow and short flow path is designed and optimized based on the mass transport polarization regulation (reducing the mass transport polarization and improving its uniformity of distribution). The regulation strategy of mass transport polarization is practical for the performance improvement in VFBs, especially for high power density VFBs. The findings in the research are also applicable for other flow batteries and instructive for practical use.

1. Introduction

Over the last few years, intense attention has been paid on large scale energy storage technology due to its urgent need in grid management, load leveling and peak shaving, backup power, utilization and integration of renewable energy sources. Vanadium

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flow battery (VFB) with the attractive features of independently tunable power and capacity, long cycle life, high safety, high efficiency and environmental friendliness has become one of the most promising technologies for large-scale energy storage applications [1,2]. In contrast to the conventional energy storage technologies, VFB can independently scale the power and energy components of the system by storing the redox-active species outside the battery container itself. In a VFB, the power is generated in a device resembling a fuel cell, which contains electrodes separated by an ion conductive membrane. Liquid electrolytes of redox-active species are pumped into the cell, where they can be charged and discharged, before being returned to storage in an external tank. Scaling the amount of energy to be stored thus involves simply making larger tanks. This unique trait has therefore made VFBs hold great promise for use in large scale energy storage applications [3,4]. While VFBs offer a number of advantages, challenges with the relatively low energy density and low power density far have prevented their large-scale commercialization [5–8]. Although low energy density is a significant problem for electric vehicle applications, it is not necessarily a primary issue for stationary use with a VFB system, where the mass and volume constraints are much less important. However, larger-size cells must be employed to satisfy the power demand for the low power density VFBs, which correspondingly introduces a significant increase in the system cost. Therefore, any appreciable improvements in power density can yield significant cost-savings, making VFBs more competitive for grid-scale applications.

The power density is mainly governed by the electrodes, which are responsible for hosting the redox reactions and for facilitating the transport of both electrons (through the solid phase) and chemical reactants (through the pore phase) to the reaction sites in a VFB. Thus, the major factors limiting the power density of a VFB are kinetic, ohmic, and mass transport losses associated with the electrodes [6,7]. These factors are separately determined by the electrode surface functionality, electronic resistance of the electrode, and the flow field (including the cell architecture and pore structure). In recent decades, significant work has been done to improve the electrodes of the VFB systems in order to increase the power density and thence lower the system cost [9–22]. The main emphasis in these studies has been placed on increasing the available surface area, surface chemistry and the electronic conductivity of the material to reduce the activation polarization and the ohmic polarization. A major aspect of the electrode design which has been largely ignored in previous studies is the mass transport strength of the reactants or products between the available reaction sites on the electrode surface and the bulk electrolyte, which needs more attention for the high current density operations in VFBs. Recently, much progress has been achieved through the mass transport enhancement by the flow field design and optimization. The serpentine, parallel and interdigitated flow channels (Fig. 1 (c)), designed commonly on the bi-polar plate and derived from fuel cells, have been employed to enhance the mass transport in VFBs. For example, Zawodzinski and Mench et al. [18] reported a 'zero-gap' flow battery prototype design, which uses a serpentine flow channel along with the electrode as the flow field and demonstrates good performance at a higher current density and power density in contrast to flow batteries without flow channels. Other similar work can be found in the related references [23–27]. Instead of the serpentine flow channel design, Mayrhuber et al. [28] used a laser perforation approach to generate holes among the structures of the carbon fiber paper electrodes in VFBs based on the research of Manahan [29,30]. The results show that the holes can help to enhance the electrolyte flow and consequently mass transport and penetration in the porous electrode and a higher power density can be achieved. Nevertheless, the serpentine, parallel and interdigitated flow channels or the excessive holes will result in smaller active surface area, which would finally lead to performance degradation. In addition, the flow channels design on the bi-polar plate will lead to a poor mechanical performance of VFBs. Hence, the flow field with a flow-through type (Fig. 1(d)) is still the most desirable for the widespread applications of VFB system. Considering this point, some work has taken the strategy of increasing the electrolyte flow to minimize the mass transport polarization, but it is achieved with the compensation of increased energy consumption. In this regard, some control strategies for flow rate during VFB operations [31,32] have been proposed to optimize the relationship between the mass transport enhancement and the energy consumption, however, it is not so advisable for the variable operation conditions and accordingly of limited significance in practical applications of VFBs. Therefore, better ways to improve the mass transport is still necessary to further increase the power density and reduce the cost of the VFB systems. One important aspect which is the most advisable for achieving the above goal is performing the flow field design and optimization in a flow-through type VFB.

For the electrochemical reactions in VFBs, the mass transport polarization and the electrolyte flow and reactant concentration are strongly coupled. Hence, a deeper understanding of the relationship between the mass transport polarization and the electrolyte flow and the reactant concentration involved in VFBs must be key to successful design of the flow field in a flow-through type VFB. To better understand the mass transport limitations, the spatial and time distribution of mass transport polarization should be clarified to show where and when the mass transport is limited and thence how to optimize the flow field. However, the research on the spatial and time distribution of mass transport polarization cannot be performed effectively by experiments. Herein, the modeling method is more efficient and time-saving than experiments. Motivated by this and based on the previous studies on the modeling improvements and applications [33–37] in our team, the three-dimensional flow battery model [36] was again employed to probe into the mass transport polarization inside flow batteries. Thus, the space-varying and time-varying characteristic of mass transport polarization inside the conventional rectangular diagonal flow battery (RDFB) was investigated by modeling firstly based on the analysis of the electrolyte flow and the reactant concentration in the bulk electrolyte. Subsequently, a new structure of rectangular plug flow battery (RPFB) with a plug flow field was designed and optimized according to the mass transport polarization regulation. The regulation strategy of mass transport polarization is of great significance for the performance improvement in VFBs, especially for high power density VFBs. The findings in the research are also applicable for other flow batteries and instructive for practical use.

2. Model geometry and calculation

A conventional rectangular diagonal flow battery (RDFB) (Fig. 1(a),(b)), which is fabricated by clamping a membrane (Nafion 115) with two carbon-felt electrodes (XF-30, installed in the frames), hold tightly by two bi-polar plates and current collectors (Graphite plate), was used as the initial research object. All the parts are installed between two stainless end plates. Herein, the frame along with the electrode installed forms the flow field for the electrolyte flow [36], shown in Fig. 1(d). The frame is usually designed with an inflow channel and an outflow channel, where the electrolyte flows in and out from the electrode. 60 mL of a solution containing 1.5 M VO^{2+}, 3 M H_2SO_4 and 60 mL of a solution containing 1.5 M V^{3+}, 3 M H_2SO_4 were employed as the positive and negative electrolyte, separately.

In the research, a three-dimensional model was proposed to