Dramatic performance gains of a novel circular vanadium flow battery

Qiong Zheng [a, b, c], Feng Xing [b], Xianfeng Li [b], Tao Liu [b], Qinzhi Lai [b], Guiling Ning [a, *], Huamin Zhang [b, *]

[a] School of Chemical Engineering, Dalian University of Technology, Dalian 116023, PR China
[b] Division of Energy Storage, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China
[c] Graduate University of the Chinese Academy of Sciences, Beijing 100039, PR China

HIGHLIGHTS

- A novel circular vanadium flow battery (CFB) was firstly proposed.
- CFB presents improved mass transport and reduced concentration polarization.
- CFB gains improved utilization of electrolyte and energy storage capacity.
- The performance advantage of CFB is more evident at high current densities.

GRAPHICAL ABSTRACT
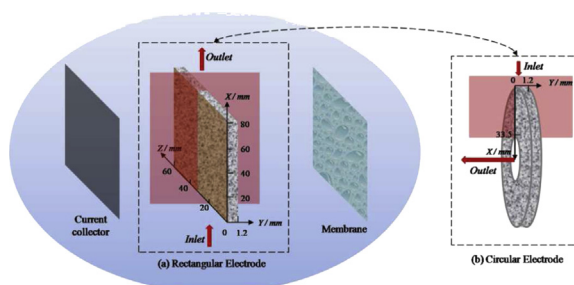
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ABSTRACT

Vanadium flow battery (VFB) holds great promise for use in large scale energy storage applications. However, one major issue that limits the battery performance is the energy storage capacity loss due to insufficient use of electrolyte. The battery structure design is flexible and acceptable to solve the issue. Based on the mass transport limitation of the conventional rectangular vanadium flow battery (RFB), a novel circular vanadium flow battery (CFB) was firstly proposed in the research. Without increasing pump consumption, the new structure of CFB is effective to achieve mass transport enhancement and concentration polarization reduction. The charge—discharge test confirmed the performance advantage of CFB, presenting a significant increment of 10.52% at 40 mA cm^{-2} and 30.46% at 160 mA cm^{-2} in the utilization of electrolyte and improved energy storage capacity by 12.56% at 40 mA cm^{-2} and a 2.55 times of that for RFB at 160 mA cm^{-2}. The performance advantage of CFB becomes exceptionally evident at high current densities.

1. Introduction

Vanadium flow battery (VFB), invented and pioneered by Skyllas-Kazacos and co-workers at the University of New South Wales in the 1980s, is one of the most promising energy storage technologies [1–5]. Unlike conventional energy storage technologies, VFB has a unique design for independent scaling of power output and energy storage capacity, which therefore holds great promise for use in large scale energy storage applications [6–10]. While the unique design offers numerous key advantages, one major issue that limits the battery performance is the energy storage capacity loss due to insufficient use of electrolyte. A lower utilization of electrolyte usually relates to more electrolytes required for specified energy storage capacity, which can be an obstacle for the VFBs' broad market

* Corresponding authors.
  E-mail addresses: ninggl@dlut.edu.cn (G. Ning), zhanghm@dicp.ac.cn (H. Zhang).

penetration due to the increased cost of the VFB system. In order to meet the cost requirement, it is necessary to improve the utilization of electrolyte for the capacity loss reduction of the VFBs.

There are mainly two factors influencing the utilization of electrolyte. On one side, VFB initiates side reactions primarily due to the undesired active materials (vanadium ions) crossover through the membrane, which would reduce the utilization of electrolyte [11]. To alleviate the crossover issue, a majority of studies have been focused on exploring new membranes that can effectively suppress vanadium ions crossover while providing reasonable proton conductivity [12,13]. On the other side, the utilization of electrolyte is significantly affected by the battery polarization, including activation polarization, ohmic polarization and concentration polarization. A lower polarization is usually associated with a higher utilization of electrolyte. In this regard, great progress has been made to reduce the activation polarization and ohmic polarization by the key materials exploitation and development [14,15]. Considering that the mass transport would be a major performance limitation for the VFBs' operation at high current densities, some efforts have been made to enhance the mass transport by raising the flow rate [16–18]. It is effective to reduce the concentration polarization, however achieved with increased pump consumption, leading to reduced system efficiency. Hence, how to reduce concentration polarization without increasing pump consumption is essential for the VFB's efficient operation, especially at high current densities. Actually, the battery structure innovation is flexible and acceptable to solve the issue. Whereas, there are rarely literature reported on the structure innovation for VFBs.

In this paper, the mass transport and mass transport enhancement theory along with numerical simulations was employed as the basis for VFBs structure design. Based on the mass transport limitation in space (weak mass transport near the outlet) and in time (weak mass transport at high state of charge/discharge of electrolyte) of the conventional rectangular vanadium flow battery (RFB), a novel circular vanadium flow battery (CFB) was firstly proposed. Without increasing pump consumption, the mass transport enhancement and concentration polarization reduction of the new structure, CFB, was verified by the polarization curve and the electrochemical impedance spectroscopy (EIS) experiments. Finally, the advantage of battery performance especially utilization of electrolyte and energy storage capacity of CFB was confirmed via the charge–discharge test.

2. Theory of mass transport and mass transport enhancement

In VFBs, mass transport is one of the most important steps for the electrochemical reactions, which proceeds as following: the reactants are firstly transferred from the bulk electrolyte to the electrode; after the electrochemical reactions on the electrode surface, the products are then transferred to the bulk electrolyte. The process repeats and forth and over again. If the reactant transferred to the electrode surface is not enough for the reactions, that is, the reactant concentration on the electrode surface, c_s, is not high enough, the concentration polarization comes up. If c_s is as low as 0, there will be a completely mass transport control on the electrochemical reaction, correspondingly, the concentration polarization becomes dominated in the battery polarization. Hence, the concentration polarization and the reactant concentration on the electrode surface c_s are strongly coupled. An investigation on the mechanism of mass transport and mass transport enhancement is in need to reduce the concentration polarization in VFBs.

According to the hydrodynamics theory, the electrolyte flow on the electrode surface can be assumed to be laminar flow on flat plate (Re < 2000). As seen in Fig. 1(a), a boundary layer with a thickness of δ will be formed on the surface. A velocity gradient (the
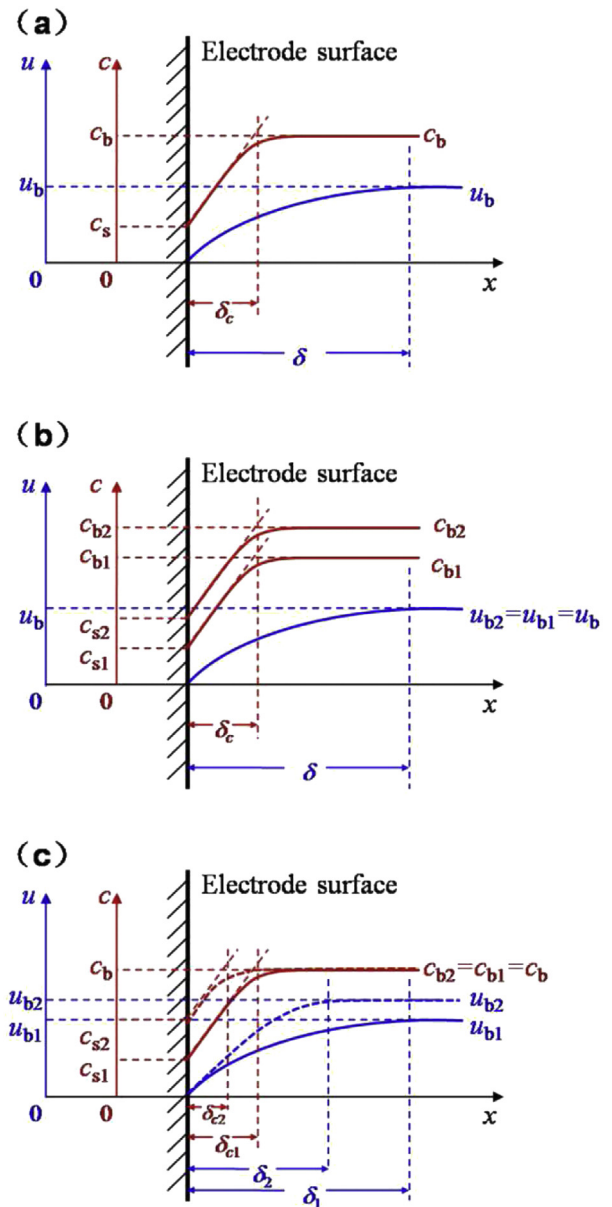

Fig. 1. (a) Mass transport and mass transport enhancement by improving (b) the concentration, c_b, (c) the velocity, u_b, of the bulk electrolyte.

velocity is 0 at the surface and u_b at the bulk electrolyte) can be found in the boundary layer, which motivates the momentum transfer in the electrolyte. Similarly, there will be a diffusion layer, δ_C, near the electrode surface. A concentration gradient (the concentration is c_s at the surface and c_b at the bulk electrolyte) can be found in the diffusion layer, which drives the mass transfer in the electrolyte. Generally, the diffusion layer, δ_C, is thinner than the boundary layer, δ. The mass transport is caused by convection when the distance from the electrode surface, x, is larger than δ_C, while a comprehensive effect of convection and diffusion, especially the latter one, when x is smaller than δ_C. Different from the theoretical mass transport by diffusion, where the concentration gradient, dc/dx, keeps constant, the gradient, dc/dx, in the actual diffusion layer is changing as x changes. The concentration gradient presents approximately constant near the electrode surface and gets smaller when x is close to the diffusion layer δ_C, where the momentum transport facilitates the mass transport. Based on the mass