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Laser-perforated carbon paper electrodes for improved mass-transport in high power density vanadium redox flow batteries

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HIGHLIGHTS

- Laser-perforated carbon paper electrodes are tested in vanadium flow batteries.
- Effects of perforation size, spatial density, and flow rate are investigated.
- Power density of perforated electrodes is improved (30%) compared to raw electrodes.
- Performance improvement is attributed to the enhanced electrolyte accessibility.

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ABSTRACT

In this study, we demonstrate up to 30% increase in power density of carbon paper electrodes for vanadium redox flow batteries (VRFB) by introducing perforations into the structure of electrodes. A CO_2 laser was used to generate holes ranging from 171 to 421 μm diameter, and hole densities from 96.8 to 649.8 holes cm^{-2}. Perforation of the carbon paper electrodes was observed to improve cell performance in the activation region due to thermal treatment of the area around the perforations. Results also demonstrate improved mass transport, resulting in enhanced peak power and limiting current density. However, excessive perforation of the electrode yielded a decrease in performance due to reduced available surface area. A 30% increase in peak power density (478 mW cm^{-2}) was observed for the laser perforated electrode with 234 μm diameter holes and 352.8 holes cm^{-2} (1764 holes per 5 cm^2 electrode), despite a 15% decrease in total surface area compared to the raw un-perforated electrode. Additionally, the effect of perforation on VRFB performance was studied at different flow rates (up to 120 mL min^{-1}) for the optimized electrode architecture. A maximum power density of 543 mW cm^{-2} was achieved at 120 mL min^{-1}.

1. Introduction

Redox flow batteries (RFBs) are emerging as a promising energy storage technology for a broad range of applications. These batteries can be used as medium- to large-scale energy storage systems, which are implemented into the electrical grid to store or deliver energy based on demand. Furthermore, this technology can be used for emergency back-up applications to replace diesel generators as uninterruptible power supplies (UPS), or as a stand-alone device to store and deliver electric power in remote areas and micro-grids [1–3]. The key advantage of flow battery systems is that their energy capacity and power output are decoupled, unlike conventional secondary batteries. Accordingly, the energy capacity of a RFB is determined by the size of the electrolyte reservoirs, while the power output is determined by the electrochemical cell stack (size and number of cells) [1–3]. Other advantages of this technology are fairly long cycle-lifetimes, and the ability to deep-discharge the system without adversely affecting its lifetime. Additionally, the need for cell balancing is eliminated, unlike other secondary battery technologies, because all cells in the stack are supplied from the same storage tanks. Many redox chemistries can be applied in

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RFB systems, however the ‘all-vanadium’ chemistry is among the most extensively studied [1–4] due to the advantages of using the same, but differently charged, active species in both half cells.

Although vanadium redox flow batteries (VRFBs) offer a number of advantages, there are several limitations which hinder their widespread implementation. One disadvantage is the relatively low energy density (40 Wh L^{-1}) [1–3]. Although low energy density is a significant problem for transportation applications, it is not necessarily a major issue for stationary use of a VRFB system, where mass and volume constraints are much less important. Similarly, the power density of a VRFB cell is relatively low compared to lead-acid and lithium-ion batteries. As a result, larger cells must be used to satisfy the power demand, leading to a significant increase in cost. Therefore, any appreciable improvements in power density can yield significant cost-savings, making VRFBs more competitive for grid-scale applications.

The power generated by a VRFB is primarily governed by the electrodes. The electrodes in a VRFB 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. Thus, the major factors limiting the power density of a VRFB are kinetic, ohmic, and mass transport losses associated with the electrodes [2,3]. These factors are primarily determined by surface functionality, electronic resistance, cell architecture and pore structure of the electrode material.

Recently, significant work has been done to improve the electrodes of the VRFB systems in order to increase power density and lower system cost [5–18]. The main emphasis in these studies has been placed on improving the surface area, surface chemistry, pore size distribution and conductivity of the material to improve the reaction kinetics and mass transport ability and reduce the areal series resistance (ASR). Until recently, carbon felts were the most commonly employed electrode materials in VRFBs [6]. Although no catalyst is necessary to facilitate the redox reactions, reaction kinetics still play an important role on system performance, and much work has been done to understand and improve the surface chemistry of carbon felts [6–11]. To-date, thermal treatments, similar to those described by Sun et al. [9], are considered to be the most common practice employed to functionalize carbon felt electrodes and improve their electrochemical performance.

Beyond kinetics, the effective delivery and removal of reactants is another important consideration, which has not been thoroughly studied. Qiu et al. performed pore-scale simulations utilizing XCT-reconstructed electrode morphologies to predict cell performance and localized phenomena inside carbon felt electrodes [12,13]. The authors investigated electrodes with porosities ranging from 84.5% to 93.2% and observed lower localized current density and overpotential fields with increased pressure drop for the lower porosity electrodes. Under normal operating conditions, however, the performance of the simulated carbon felt electrodes was not found to be limited by mass transport losses.

Recently, Mench and co-workers utilized carbon paper as an electrode material for VRFBs [14–16]. These materials are 5×–10× thinner than carbon felts which enables reduced transport pathlengths for both electrons and ions, resulting in reduced ASR. Moreover, the porosity and pore-size of this material are reduced compared to carbon felt, giving rise to increased specific surface area and thus a higher limiting current density. In a recent study, they demonstrated a VRFB with a peak power of 557 mW cm^{-2}, which is significantly higher than what had previously been reported in literature [14]. They accomplished this by stacking sheets of carbon paper as the electrodes in each half cell. Additionally, they varied the number of sheets stacked in each half cell in order to study the tradeoff between resistance and surface area. They identified an optimal stack height of three sheets of carbon paper per half-cell, corresponding to an uncompressed thickness of 1230 μm per electrode [14].

Manahan et al. expanded on this work by modifying carbon paper electrodes with a thin layer of multi-walled carbon nanotubes (CNTs), and then testing the performance of a VRFB with the CNT-treated layer facing either the membrane or flow field side in both half-cells [15]. Experiments showed that cell voltage and power density improved the most when the CNT layer faced the current collector, especially at the negative side. Based on these findings, they pointed out three important observations: a) the majority of the reactions happen near the current collector, b) CNTs improved electrical contact with the current collectors, and c) the negative electrode is the rate-limiting electrode [14], in agreement with other studies [5].

Liu et al. further improved the performance of a vanadium flow battery using a no-gap architecture by thermal pre-treatment of the carbon paper electrodes in argon and air [16]. The air treatment showed a greater power density improvement (16% compared to raw material) than argon treatment. This result was attributed to an increase in oxygen containing functional groups, which improved the reaction kinetics at the electrode surface. By optimizing the surface area/chemistry, conductivity of the electrodes, and changing the membrane material, the authors demonstrated a power density of 767 mW cm^{-2}, which is the highest power density reported to-date [16].

As these studies show, the most common approach to improving the power density of VRFBs is by increasing the available surface area, decreasing ohmic resistance, and maximizing reaction kinetics. Although significant progress has been achieved through the use of functionalized, high surface area carbon paper electrodes, further improvement of the power density is still necessary to further reduce the cost of these systems. A major aspect of electrode design which has been largely ignored in previous studies is the capability of the electrode to quickly deliver fresh reactant to the available reaction sites. Although the effect of electrode microstructure has previously been explored using numerical simulations [12,13], these simulations were applied primarily to carbon felt materials with very high porosity, and relatively large pores. Here, we hypothesize that mass transport is a limiting factor for more dense, high-power carbon paper electrodes, and by improving the accessibility to the available active surface area it is possible to further increase the power density of existing electrode materials.

Motivated by this hypothesis, our goal in this study was to better understand the mass transport limitations associated with high power density carbon paper electrodes, and to identify mitigation strategies which improve the electrolyte accessibility and further enhance power density of these materials. Specifically, we investigated the effects of macro-scale perforations (“transport channels”), on the power density and performance of the carbon paper electrodes in a VRFB system. These transport channels are expected to provide a more facile route for electrolyte to enter and permeate through the electrode, thus improving the supply of reactants to the active surface area of the material. Our approach is similar to that reported in a study by Manahan et al., where they perforated 300 μm diameter holes into the micro-porous layer of a polymer electrolyte fuel cell to improve the transport of liquid water through the cell [19,20]. Here, we used a CO_2 laser to open transport pathways of varying size and number in the electrode structure. By varying the diameter and density of these transport channels, we studied the effects of perforation size and the critical transport length for electrolyte flowing through the bulk electrode material. Additionally, the flow rate in the cell was varied to better understand the effect of these perforations (i.e., transport channels) under different mass transport conditions.