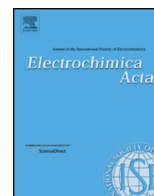




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# Numerical studies of carbon paper-based vanadium redox flow batteries

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## ABSTRACT

This study analyzed theoretically the effects of a carbon paper (CP)-based electrode on the performance of a vanadium redox flow battery (VRFB). Compared to conventional carbon felt-based electrode materials, the CP-based electrode showed superior characteristics in facilitating the redox reactions of  $\text{VO}^{2+}/\text{VO}_2^+$  and  $\text{V}^{2+}/\text{V}^{3+}$  couples, such as better electrochemical activity and higher electronic conductivity. A three-dimensional, non-isothermal VRFB model developed in a previous study was applied to a range of single cell structures equipped with CP-based electrodes and flow channels in the current collectors. The model was then validated using the experimental data measured under the CP- and channel-based VRFB geometries. The model successfully captured the experimental trend that showed a higher discharging performance with increasing number of CP layers used for each electrode. The simulation results clearly showed that the activation overpotentials in the electrodes were reduced significantly using more CP layers, which dominated over the effects of increased mass transport limitation of vanadium ions due to the thicker electrode.

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## 1. INTRODUCTION

Redox flow batteries (RFBs) are critical technologies that enable the cost effective and reliable storage of renewable energy resources on a grid scale. Leung et al. [1] published a comprehensive overview of RFB technologies. Among the various types of RFBs, all-vanadium redox flow batteries (VRFBs) have attracted considerable interest, and megawatt-class VRFB systems have been demonstrated [1–5]. VRFBs utilize the same species (i.e. vanadium) but with different oxidation states in the anolyte and catholyte, resulting in excellent electrochemical reversibility. A loss of capacity that inevitably occurs during multiple charge/discharge cycles can be recovered easily by simply rebalancing the vanadium electrolytes, whereas other RFBs using different anolyte and catholyte species involve expensive electrolyte separation and reactant recovery. Despite this, the cost of vanadium is one of main concerns in the VRFB community. The cost of  $\text{V}_2\text{O}_5$  electrolyte is around 18 \$/kg and 16 Ah/\$, which is much more expensive than the bromine electrolyte (1 \$/kg and 335 Ah/\$) [6,7]. Because the cost of the vanadium electrolyte comprises a significant fraction of the VRFB system cost, the VRFB stack cost needs to be reduced to compensate. Therefore, the key to the commercialization of VRFB

technologies is to increase the powder density of VRFB stacks. This allows for the use of a lower number of cells and/or reducing the area of the cell and membrane, which results in a lower overall system cost.

To achieve high power density and efficiency, irreversible voltage losses comprising kinetic, ohmic and concentration polarization losses need to be reduced during VRFB charging and discharging. Because kinetic, ohmic and concentration polarization occur in the negative and positive electrodes, the successful design of these electrodes is key to improving the VRFB performance and efficiency. Carbon felt (CF) materials are commonly used as the electrode for VRFBs. Typical CF has a porosity of approximately 0.8–0.9, a fiber diameter of 10  $\mu\text{m}$ , permeability of around 1 darcy ( $\sim 10^{-12} \text{ m}^2$ ), good stability, high surface area, wide operation potential range, and reasonable cost. [8–10] Several groups have improved the electrocatalytic activity and conductivity of the CF electrode further by depositing metal particles on the CF surface [11–13] or through various surface treatments [14–16]. High power densities and energy efficiencies have been reported using these treated CF electrodes. [13,15,17–20] In particular, Chen and Kumbur [20] achieved an outstanding power density of 311  $\text{mW cm}^{-2}$  and high energy efficiency of approximately 90% at 40  $\text{mA cm}^{-2}$ .

Recently, carbon paper (CP) has been recognized as a suitable electrode material for VRFBs. Significant improvement in power density and efficiency has been reported [21–23]. In particular,

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## Nomenclature

$A$	cross-sectional area, $\text{m}^{-2}$
$a$	effective catalyst area per unit electrode volume, $\text{m}^{-1}$
$C$	molar concentration, $\text{mol m}^{-3}$
$C_{KC}$	Kozeny-Carman constant
$D$	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$E_0$	thermodynamic equilibrium potential, V
$F$	Faraday's constant, $96487 \text{ C mol}^{-1}$
$h$	heat transfer coefficient $\text{W K}^{-1}$
$I$	current, A
$j$	transfer current density, $\text{A m}^{-2}$
$K$	effective permeability, $\text{m}^2$
$k$	reaction rate/coefficient, $\text{m s}^{-1}$ and thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
$M$	molecular weight, $\text{kg mol}^{-1}$
$\bar{N}$	species flux, $\text{mol m}^{-3} \text{s}^{-1}$
$P$	pressure, Pa
$Q$	volumetric flow rate, $\text{m}^3 \text{s}^{-1}$
$R$	universal gas constant, $8.314 \text{ J mol}^{-1} \text{K}^{-1}$
$r_p$	pore radius, m
$S$	source/sink term
$s$	entropy, $\text{J K}^{-1} \text{mol}^{-1}$
$T$	temperature, K
$\bar{u}$	fluid velocity, $\text{m s}^{-1}$
$V$	volume, $\text{m}^3$
$v$	velocity, $\text{m s}^{-1}$
$v_{f_i}$	volume fraction of species $i$

## Greek symbols

$\alpha$	transfer coefficient
$\varepsilon$	porosity
$\eta$	overpotential, V
$\kappa$	ionic conductivity, $\text{S cm}^{-1}$
$\mu$	dynamic viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
$\rho$	density, $\text{kg m}^{-3}$
$\sigma$	electronic conductivity, $\text{S cm}^{-1}$
$\tau$	viscous shear stress, $\text{N m}^{-2}$
$\Phi$	potential, V
$\delta$	electrode thickness

## Subscript

0	equilibrium or initial value
amb	ambient
cc	current collector domain
ch	charged species
dis	discharged species
e	electrolyte domain
elec	electrode
$i$	species index
in	channel inlet
mem	membrane domain
NE	negative electrode
out	channel outlet
PE	positive electrode
s	solid electrode domain

## Superscript

0	equilibrium or initial value
e	bulk electrolyte
eff	effective value
s	electrode surface

Aaron et al. [22] achieved a power density of  $557 \text{ mW cm}^{-2}$ , using three layers of CP for each electrode, i.e. more than five times higher than that published elsewhere. Table 1 lists the basic electrode properties of these two carbon materials. Compared to CF, CP is thinner and features lower porosity and higher density. Therefore, the electronic resistance can be reduced using a CP electrode and electrolyte transport through the electrode can also be facilitated, reducing the concentration overpotential. In addition, Blasi et al. [23] reported that the electrocatalytic activity of CP was improved greatly by a chemical treatment, whereas treated CF exhibited poorer electrochemical performance than the untreated CF. According to their test results, the use of a CP electrode generally resulted in higher discharging voltages and better energy efficiency than the CF electrode (e.g., 1.48 V startup voltage and 80% efficiency for the CP electrode compared to 1.40 V and 73% for the CF electrode at a discharging current density of  $40 \text{ mA cm}^{-2}$ ). Previous studies clearly showed that the use of a CP as the electrode material was beneficial and might reduce activation, ohmic and concentration overpotentials during VRFB operations. On the other hand, detailed analysis of its beneficial impacts was not clearly reported.

The present study aims to conduct a numerical comparative study of CF- and CP-based VRFB designs during charging and discharging processes. The focus is mainly on a quantitative estimation of the improvement in VRFB charging and discharging performance using the CP-based electrodes and further on elucidating the effects of designing multiple CP layers for VRFB electrodes. In the following, a 3-D transient VRFB model developed in previous studies [28–31] is first assessed in terms of the model assumptions, governing equations and corresponding source/sink terms. The model is then applied to various VRFB configurations with CF or CP electrodes. Subsequently, numerical simulations are conducted during a single charging/discharging process. In particular, various voltage losses associated with cell polarization are analyzed precisely under different electrode configurations. In addition, the overall performance and multidimensional distribution of the species concentration and transfer current density are analyzed to provide greater insight into the operating characteristics of the VRFBs equipped with CF or CP electrodes. Finally, major conclusions are drawn and a basic strategy for designing a VRFB electrode using CP is evaluated.

## 2. NUMERICAL MODEL

The present three-dimensional (3-D), transient VRFB model accounts for the redox reactions of the  $\text{VO}^{2+}/\text{VO}_2^+$  and  $\text{V}^{2+}/\text{V}^{3+}$  couples during charging and discharging and the resulting species and heat transport through the various components of a VRFB cell, which is described schematically in Fig. 1. A detailed description of the 3-D transient VRFB model was reported elsewhere [28–31]; therefore, only a brief summary of the model equations and assumptions have been repeated. The conservation equations in Table 2, Eqs. (1), (3), (4), (7), and (10) represent the five principles of conservation (i.e. mass, momentum, species, charge, and thermal energy) and constitute the present transient non-isothermal VRFB model. These transport equations are then coupled with electrochemical processes through the source/sink terms in Table 3 to describe the reaction kinetics in the positive and negative electrodes. While the species conservation equations based on Eq. (4) are solved numerically for the species of vanadium ions ( $\text{V}^{2+}$ ,  $\text{V}^{3+}$ ,  $\text{VO}^{2+}$ , and  $\text{VO}_2^+$ ) and protons ( $\text{H}^+$ ), the charge conservation equations in Eq. (7) are solved to predict the solid and electrolyte potential distributions, i.e., a combined result of activation, ohmic and concentration polarization. The conservation equation of heat energy in Eq. (10) is to predict the temperature distribution inside a VRFB, i.e., driven by various heat generation

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