The effect of wetting area in carbon paper electrode on the performance of vanadium redox flow batteries:

A three-dimensional lattice Boltzmann study

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Abstract

The vanadium redox flow battery (VRFB) has emerged as a promising technology for large-scale storage of intermittent power generated from renewable energy sources due to its advantages such as scalability, high energy efficiency and low cost. In the current study, a three-dimensional(3D) Lattice Boltzmann model is developed to simulate the transport mechanisms of electrolyte flow, species and charge in the vanadium redox flow battery at the micro pore scale. An electrochemical model using the Butler-Volmer equation is used to provide species and charge coupling at the surface of active electrode. The detailed structure of the carbon paper electrode is obtained using X-ray Computed Tomography(CT). The new model developed in the paper is able to predict the local concentration of different species, over-potential and current density profiles under charge/discharge conditions. The

simulated capillary pressure as a function of electrolyte volume fraction for electrolyte wetting process in carbon paper electrode is presented. Different wet surface area of carbon paper electrode correspond to different electrolyte volume fraction in pore space of electrode. The model is then used to investigate the effect of wetting area in carbon paper electrode on the performance of vanadium redox flow battery. It is found that the electrochemical performance of positive half cell is reduced with air bubbles trapped inside the electrode.

Keywords: Vanadium redox flow battery, Lattice Boltzmann method, Pore scale, Micro-CT tomography, Wetting surface area

Nomenclature

α	Transfer coefficient
$\mathbf{a}$	Acceleration
$\mathbf{e}_\alpha$	Particle velocity in the α_{th} direction
$\mathbf{F}_1$	Fluid-fluid cohesion force
$\mathbf{F}_2$	Fluid-solid adhesion force
$\mathbf{F}_3$	Body force
$\mathbf{v}$	Time step
δt	Time step
η_{act}	Activation overpotential
κ	Electrical conductivity of the solid fibers
Ω	Ohm
ϕ	Electrical potential
ϕ	Local potential
$\psi(\mathbf{x})$	Effective mass
ρ	Density
σ	Surface tension
τ	Single relaxation time
ν	Viscosity
c	Species concentration

c_s	Lattice sound speed
CFD	Computational fluid dynamics
D	Diffusivity
E^0	Standard equilibrium potential of positive electrode
EOS	Equation of state
F	Faraday's constant
f_α	Particle distribution along the α_{th} direction
f_α^{eq}	Equilibrium distribution
FDM	Finite difference method
FEM	Finite element method
FVM	Finite volume method
G_w	Fluid-solid interaction potential parameter
J	Current density
k	Reaction rate constant for reaction
N	Number of discrete particle velocities
P_c	Capillary pressure
R	Universal gas constant
r_j''	Rate of generation and consumption of different species
R_{ave}	Mean pore diameter of porous electrode
Re	Reynolds number

SRT	Single relaxation time
T	Temperature
$VRFB$	Vanadium redox flow battery
w_α	Weighting Factor
WSP	Wetting surface percentage
z	Charge of species

1 Introduction

The utilization of renewable and sustainable energy, such as solar and wind, has been rapidly expanded in many countries around the world in response to climate changes. However, it is very challenging to integrate large-scale renewable energy sources into an electric grid due to their intermittent nature [1]. The vanadium redox flow battery, originally proposed by Skyllas-Kazacos, has drawn increasing attention world-wide owing to its long cycle life, high reliability, independent tunable power and capacity, and low cost of operation and maintenance [2–4]. In the VRFB system, VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox couples are employed as the positive and negative active species respectively, which are separated by an ion-exchange membrane.

During the operation, the performance of the VRFB is highly determined by the electrode microstructure. This microstructure along with material properties could be tuned to increase the performance of batteries and promote the VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions at the electrode surface [5, 6]. A variety of carbon materials, including carbon felt, cloth and paper are widely used as the electrodes due to their large specific surface area, high thermal and electrical conductivity, high stability and low cost [7, 8]. The wettability of carbon-based electrode materials plays an important role in redox flow battery operation [9], and the electrochemical activity may be increased by increasing

the carbon electrode wetting surface with electrolyte. Generally, carbon electrodes have low electrochemical activity and poor wettability originating from its hydrophobic nature, which result in poor electrolyte accessibility and inadequate active sites [10, 11]. Therefore, a number of surface modification methods, including acid [12, 13] and thermal treatment [14, 15], electrochemical activation [16, 17] and other new strategies [18, 19], have been reported to enhance the electrochemical performance of electrodes. In these investigations, increased electrocatalytical activity of the electrode surface is not only attributed to oxygen functional groups introduced onto the surface of the electrode, but also to the improved wettability of the electrodes. In Ref. [20], it is claimed that changes in the surface chemistry are not sufficient to explain the performance enhancements induced by electrode treatments, and the electrochemically wetted surface area is an important factor that must also be considered. It was shown in [21]’s research that, after some of the oxidation treatments, the enhancement of chemical reaction on the surface of electrodes is almost entirely due to the effective wetting of the porous carbon paper rather than any electro-activation effect of surface functional groups on the intrinsic kinetics reaction. Therefore, the effect of wetted surface area on performance of VRFB needs further investigation.

Numerical modeling is an useful and efficient tool for optimization of electrodes, which can provide a better understanding of the coupled fluid flow, ion transport, electron conduction, and electrochemical reactions that occur in VRFB electrodes [22]. The numerical models that have been developed for the VRFB can be classified into macroscopic continuum models and pore-scale models. In macroscopic continuum models [23–27], volumetric averaging conservation equations, such as mass, momentum, charge and energy, are solved in each elementary volume and the porous electrode is assumed as continuum with isotropic or anisotropic transport properties. A 2D model for VRFB was developed by Ref. [23] to investigate the effects of applied current density, electrode porosity and local mass transfer coefficient on the performance. In addition, the formation of oxygen and hydrogen bubbles due to the side reactions and their effects on the performance of VRFB

were studied in Ref. [24,25] by a multi-phase mixture model. However, because the influence of porous structures of the electrode is neglected in macroscopic models, the active wetting surface area available for electrochemical reactions is not based on measurement of the actual electrode geometry and there is no detail information is provided about how this parameter affect on the performance of VRFB. Alternatively, the pore-scale models provide an efficient way for in-depth understanding of transport phenomena in porous media [28–30]. Lattice Boltzmann method has successfully been applied at pore scale simulation where detailed of the porous structure of the domain is required. Comparing with traditional CFD method(FDM, FEM, FVM), there are many native advantages for the lattice Boltzmann model. It is easy to apply for complicated boundaries in the pore structure of a porous medium, easy to handle complex flows such as multi-phase and multi-component flows without needing to trace the interfaces between different phases. Hao and Cheng [31] investigated the effect of wettability on liquid transport in porous carbon paper using the multi-phase free-energy LBM approach. Recently, Qiu [32, 33] adopted the lattice Boltzmann method to model the flow of electrolyte through the porous electrode which is obtained using X-ray computed tomography, while the finite volume method(FVM) is used to solve the coupled species and charge transport and predict the performance of the VRFB. Most recently, multi-phase flow and reactive transport in the fibrous electrodes of VRFB is simulated using the LBM [34]. In the work of Ref. [34], liquid-gas two phase flow without reaction is simulated to study the effects of porosity, fibre diameter, wettability of the fibre surface and saturation of the porous electrode on gas bubble migration and reduction of reactive surface area due to coverage of bubbles on solid surface. Moreover, single phase liquid flow coupled with electrochemical reaction is simulated to predict the V^{2+}/V^{3+} transport in the porous electrode, assuming constant electronic potential throughout the porous electrode. However, the effect of reactive surface area of electrode on electrochemical performance requires further study. To the best of our knowledge, there are no study presented in the literature that investigate the effect of wetted surface area on the performance of flow battery with the exception of

other factors.

In this paper, a three-dimensional lattice Boltzmann model is developed to simulate the species/charge/fluid transport processes at a 3D, isothermal, positive half cell where the electrode geometry is based on an X-ray computed tomography reconstructed porous carbon paper electrode material. The electrolyte penetration process in porous electrode is investigated by using a LBM multi-phase flow model and different wetting surface area is achieved with various capillary pressure. Then, the proposed LBM model is adopted to study the effect of wetting surface area in porous electrode on the electrochemical performance of VRFB with flow through design. Different from previous LBM research [34] which assumed a constant electronic potential across the electrode, the simulations of charge transport in electrode and electrolyte are included in our model. The rest of the paper is organized in five sections. In Section 2, the lattice Boltzmann methods for simulation of multi-phase flow, flow of electrolyte, charge and species transport along with electrochemical reaction on the surface of electrode are presented. The developed model is validated in Section 3. In Section 4, the method to obtain detailed geometry of the porous carbon paper electrode is introduced. Model results are discussed in Section 5 followed by conclusions and recommendations for further study in Section 6.

2 Numerical model

2.1 Simulation of multi-phase flow

In this paper, a three-dimensional single-relaxation-time(SRT) pseudopotential Lattice Boltzmann model with Guo's forcing scheme [35] is adopted to simulate the wetting process of the carbon paper electrode. The model has been validated in our previous work [28, 36, 37].

2.1.1 Incorporation of the force term

The fluid flow in porous media can be described by Navier-Stokes equations.

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} - \nu \nabla^2 \mathbf{u} = 0. \quad (1)$$

In the LBM model, the motion of a fluid is described by a set of discrete single-particle density distribution functions and the particle distribution function with single relaxation time can be written as [35].

$$f_\alpha(\mathbf{x} + \mathbf{e}_\alpha \delta t, t + \delta t) = f_\alpha(\mathbf{x}, t) - \frac{1}{\tau} [f_\alpha(\mathbf{x}, t) - f_\alpha^{eq}(\mathbf{x}, t)] + \mathbf{F}_\alpha, \quad (2)$$

where $\mathbf{e}_\alpha$ is the particle velocity in the α_{th} direction, f_α is the particle distribution along the α_{th} direction and f_α^{eq} is the equilibrium distribution, τ is the single relaxation time and δt is the time step. The forcing term $\mathbf{F}_\alpha$ is given by

$$\mathbf{F}_\alpha = (1 - \frac{1}{2\tau}) w_\alpha [\frac{\mathbf{e}_\alpha - \mathbf{v}}{c_s^2} + \frac{(\mathbf{e}_\alpha \cdot \mathbf{v})}{c_s^4} \mathbf{e}_\alpha] \cdot \mathbf{F}, \quad (3)$$

where $\mathbf{v}$ is the velocity, $c_s = c/\sqrt{3}$ is the lattice sound speed and $c = \delta x/\delta t$ is the ratio of the lattice spacing δx and time step δt . The equilibrium distribution function $f_\alpha^{eq}(\mathbf{x}, t)$ in Eq. (2) can be described as

$$f_\alpha^{eq} = \rho w_\alpha [1 + \frac{\mathbf{e}_\alpha \cdot \mathbf{v}}{c_s^2} + \frac{(\mathbf{e}_\alpha \cdot \mathbf{v})^2}{2c_s^4} - \frac{\mathbf{v}^2}{2c_s^2}], \quad (4)$$

where w_α is the weighting factor. In this paper, the D3Q19 model is used for the 3D simulations. Fig. 1 shows the D3Q19 lattice models. The discrete velocities and weighting factors for D3Q19 are given by

$$\left[\mathbf{e}_0, \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3, \mathbf{e}_4, \mathbf{e}_5, \mathbf{e}_6, \mathbf{e}_7, \mathbf{e}_8, \mathbf{e}_9, \mathbf{e}_{10}, \mathbf{e}_{11}, \mathbf{e}_{12}, \mathbf{e}_{13}, \mathbf{e}_{14}, \mathbf{e}_{15}, \mathbf{e}_{16}, \mathbf{e}_{17}, \mathbf{e}_{18} \right] =$$

$$\begin{bmatrix} 0 & 1 & 0 & 0 & -1 & 0 & 0 & 1 & 1 & 0 & -1 & -1 & 0 & 1 & 1 & 0 & -1 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 & 0 & 1 & 0 & 1 & -1 & 0 & -1 & -1 & 0 & 1 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 & 0 & -1 & 0 & 1 & 1 & 0 & -1 & -1 & 0 & -1 & -1 & 0 & 1 & 1 \end{bmatrix} \quad (5)$$

and

$$w_\alpha = \begin{cases} 1/3, & \alpha = 0; \\ 1/18, & \alpha = 1, 2, \dots, 6; \\ 1/36, & \alpha = 7, 8, \dots, 18; \end{cases} \quad (6)$$

The corresponding macroscopic density and velocity are calculated by

$$\rho(\mathbf{x}, t) = \sum_{\alpha=0}^N f_\alpha(\mathbf{x}, t), \quad (7)$$

$$\rho \mathbf{v}(\mathbf{x}, t) = \sum_{\alpha=0}^N \mathbf{e}_\alpha f_\alpha(\mathbf{x}, t) + \frac{\mathbf{F}}{2}, \quad (8)$$

where N is the number of discrete particle velocities. The total force on each particle $\mathbf{F}$ includes the fluid-fluid cohesion $\mathbf{F}_1$, the fluid-solid adhesion force $\mathbf{F}_2$ and the body force $\mathbf{F}_3$.

2.1.2 Fluid-fluid cohesion

Interaction forces for liquid-liquid, liquid-gas, gas-gas are described as follows. It is commonly accepted that the segregation of different phases is microscopically due to the long-range interaction force between the particles at site $\mathbf{x}$ and the particles at neighbour sites $\mathbf{x}'$ [38]. The interaction force is defined as:

$$\mathbf{F}_1(\mathbf{x}) = -\psi(\mathbf{x}) \sum_{\mathbf{x}'} G(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') (\mathbf{x}' - \mathbf{x}). \quad (9)$$

where $G(\mathbf{x}, \mathbf{x}')$ is Green's function and satisfies $G(\mathbf{x}, \mathbf{x}') = G(\mathbf{x}', \mathbf{x})$. It reflects the

intensity of the interparticle interaction and it is given by

$$G(\mathbf{x}, \mathbf{x}') = \begin{cases} g', & |\mathbf{x} - \mathbf{x}'| = 1, \\ g'/2, & |\mathbf{x} - \mathbf{x}'| = \sqrt{2}, \\ 0, & \text{otherwise.} \end{cases} \quad (10)$$

where g' is a constant equal to 1/18 in the current work. In Eq. (9), $\psi(\mathbf{x})$ is the effective mass, which is a function of the local density and can be varied to reflect different fluid and fluid mixture behaviors, as represented by various equations. The equation of state (EOS) of the system is given by

$$p = c_s^2 \rho + \frac{c_0}{2} g[\psi(\rho)]^2, \quad (11)$$

and then the effective mass can be defined as:

$$\psi(\rho) = \sqrt{\frac{2(p - c_s^2 \rho)}{c_0 g}}, \quad (12)$$

where $g=g'$ and $c_0=6.0$ for the D3Q19, and p is the pressure. In Yuan and Schaefer's study [39], five different EOS were compared, and it was found that the Carnahan-Starling (CS) EOS provided the maximum density ratio while maintaining small spurious currents around the interface. Hence, the C-S EOS was adopted in our multiphase flow research, which is expressed as:

$$p = \rho RT \frac{1 + b\rho/4 + (b\rho/4)^2 - (b\rho/4)^3}{(1 - b\rho/4)^3} - a\rho^2, \quad (13)$$

with $a = 0.45724R^2T_c^2/p_c$ and $b = 0.0778RT_c/p_c$, where a is the attraction parameter, b is the volumetric or repulsion parameter, and ω is the acentric factor. T_c and P_c are the critical temperature and critical pressure respectively. The density ratio and surface tension of the liquid are governed by the temperature T and parameters a and b respectively. Substituting Eq. (13) into Eq. (12), we get

$$\psi(\rho) = \sqrt{\frac{2(\rho RT^{\frac{1+b\rho/4+(b\rho/4)^2-(b\rho/4)^3}{(1-b\rho/4)^3}} - a\rho^2 - c_s^2\rho)}{c_0 g}}. \quad (14)$$

Unlike in the original pseudopotential two-phase LB model developed by Shan and Chen [38], the value of the coefficient of interaction strength g becomes unimportant. Indeed, it is canceled out when Eq. (12) is substituted into Eq. (9). The only requirement for g is to ensure that the term inside the square root in Eq. (12) is positive, (i.e $g = \text{sgn}(p - c_s^2\rho)$ has to be stored when computing Eq. (12)).

2.1.3 Fluid-solid adhesion and body force

At the fluid-solid interface, the interaction between the fluid and the solid needs to be considered. The force applied on a particle that comes in contact with the solid wall is:

$$\mathbf{F}_2 = -\psi(\mathbf{x}) \sum_{\mathbf{x}'} G_w(\mathbf{x}, \mathbf{x}') \rho_w(\mathbf{x}') (\mathbf{x}' - \mathbf{x}), \quad (15)$$

where $G_w(\mathbf{x}, \mathbf{x}')$ denotes the intensity of the fluid-solid interaction. For the D3Q19 model, it is defined as:

$$G_w(\mathbf{x}, \mathbf{x}') = \begin{cases} G_w g', & |\mathbf{x} - \mathbf{x}'| = 1, \\ G_w g'/2, & |\mathbf{x} - \mathbf{x}'| = \sqrt{2}, \\ 0, & \text{otherwise.} \end{cases} \quad (16)$$

G_w is the fluid-solid interaction potential parameter, and different contact angles can be obtained through its adjustment G_w . The term $\rho_w(\mathbf{x}')$ in Eq.(15) is the wall density, which equals one at the wall and zero in the fluid. In addition to the interparticle and wall forces, the body force can be simply defined as:

$$\mathbf{F}_3(\mathbf{x}) = \rho(\mathbf{x}) \mathbf{a}. \quad (17)$$

where $\mathbf{a}$ is the acceleration.

2.2 Simulation of species transport

In the present study, only the positive half cell is simulated. So, only the transport of species $j \in \{VO_2^+, VO^{2+}, H^+, H_2O\}$ is considered. The transport of species j within the electrolyte is governed by the convection-diffusion equation.

$$\frac{\partial C_j}{\partial t} + \nabla \cdot (C_j \mathbf{u}) = \nabla \cdot (D_j \nabla C_j) + \nabla \cdot \left[\frac{z_j C_j D_j}{RT} \nabla \phi \right] \quad (18)$$

where D_j is the diffusivity of species j , z_j is the charge of species j , R is the universal gas constant, T is the absolute temperature and ϕ is the electrical potential. In previous publication [23, 32, 33], it claims that the effect of migration on the species transport is not significant in redox flow batteries, so that the migration term in the right-hand side of Eq. (18) is neglected. The concentration of SO_4^{2-} is obtained via the electroneutrality condition, $\sum z_j C_j = 0$. Assuming the sulfuric acid completely dissociates into sulfate SO_4^{2-} and protons H^+ . For species transport, the evolution of lattice Boltzmann model is described by Dawson et al. [40]

$$c_{j,\alpha}(\mathbf{x} + \mathbf{e}_\alpha \delta t, t + \delta t) = c_{j,\alpha}(\mathbf{x}, t) - \frac{1}{\tau_{D_j}} [c_{j,\alpha}(\mathbf{x}, t) - c_{j,\alpha}^{eq}(\mathbf{x}, t)], \quad (19)$$

where $c_{j,\alpha}$ is the concentration distribution function and τ_{D_j} is the dimensionless relaxation time. For porous media with high porosity such as the fibrous electrodes used in current work, the D3Q7 lattice model without lattice velocity $i=7 \sim 18$ is sufficient to accurately simulate species transport in electrolyte [29, 34]. The equilibrium function is specified as:

$$c_{j,\alpha}^{eq} = C_j [A_\alpha + 0.5 \mathbf{e}_\alpha \cdot \mathbf{v}], \quad (20)$$

where C is the species concentration which is obtained by

$$C_j(\mathbf{x}, t) = \sum_{\alpha=0}^N c_{j,\alpha}(\mathbf{x}, t), \quad (21)$$

and A_α in Eq. (20) is given by [41]

$$A_\alpha = \begin{cases} A_0, & \alpha = 0 \\ (1 - A_0)/6, & \alpha = 1 \sim 6 \end{cases} \quad (22)$$

where A_0 is equal to 0.25 and $D_j = (1 - A_0)(\tau_{D_j} - 0.5)/3$. The Dirichlet boundary condition is applied on the wall concentration boundary condition which can be described as $D_j \frac{\partial C_j}{\partial n} = r_j''$. Where r'' is the reaction rate per unit area for different species. It will be explained in section 3.3. To implement this boundary condition with LBM, the distribution function entering from wall $c_{j,\alpha}^-(\mathbf{x}, t + \delta t)$ should be determined as [42]

$$c_{j,\alpha}^-(\mathbf{x}, t + \delta t) = -c_{j,\alpha}^+(\mathbf{x}, t) + 2A_\alpha C_{j,w}. \quad (23)$$

2.3 Electrochemical reaction

The electrochemical reaction at the positive half cell of VRFB only takes place at electrode-electrolyte active surfaces. The reaction occurs as follows

The reaction is represented by boundary condition at the surface of the electrode where contact with the electrolyte as

$$D_j \frac{\partial C_{j,w}}{\partial n} = r_j'', \quad (25)$$

where r_j'' represents the rate of generation and consumption of different species at active surface. The mole flux for VO_2^+ and VO^{2+} at positive electrode during charge will be

$$r_{IV}'' = -r_V'' = k(C_{IV})^\alpha (C_V)^\alpha [\exp(-\frac{\alpha F \eta_{act}}{RT}) - \exp(\frac{\alpha F \eta_{act}}{RT})]. \quad (26)$$

where k is reaction rate constant for reaction. F is the Faraday's constant. α is the transfer coefficient. The local activation overpotential η_{act} at the interface of elec-

trode/electrolyte is defined as follows [23, 32, 33]:

$$\eta_{act} = \phi_s - \phi_e - E^0 - \frac{RT}{F} \ln\left(\frac{C_V}{C_{IV}}\right). \quad (27)$$

where ϕ_s and ϕ_e are local potential for electrode and electrolyte and E^0 is the standard equilibrium potential of positive electrode.

2.4 Simulation of charge transport

Inside the solid carbon fibers, the governing equation for the potential field can be written as

$$\nabla \cdot (\kappa_s \nabla \phi_s) = 0. \quad (28)$$

where κ_s is the electrical conductivity of the solid fibers.

In the electrolyte, the potential field is obtained

$$\nabla \cdot [\kappa_e \nabla \phi_e + F \sum z_j D_j \nabla C_j] = 0. \quad (29)$$

where the effective electrical conductivity of electrolyte κ_e is defined as

$$\kappa_e = \frac{F^2}{RT} \sum z_j^2 D_j C_j. \quad (30)$$

The LBM is used to solve Eq.(28) and Eq.(29). The LB equation is written as follows:

$$g_\alpha(\mathbf{x} + \mathbf{e}_\alpha \delta t, t + \delta t) = g_\alpha(\mathbf{x}, t) - \frac{1}{\tau_\kappa} [g_\alpha(\mathbf{x}, t) - g_\alpha^{eq}(\mathbf{x}, t)] + W \delta t. \quad (31)$$

where W is equal to zero for Eq.(28), g_α^{eq} is the equilibrium distribution. The Dirichlet boundary condition is applied at the electrode-electrolyte active surface

$$\kappa \frac{\partial \phi_w}{\partial n} = J, \quad (32)$$

where J is the current density that can be calculated by Faraday's law

$$r'' = \frac{J}{F}. \quad (33)$$

To implement this boundary condition with LBM, the distribution function entering from wall $g_{\alpha}^{-}(\mathbf{x}, t + \delta t)$ should be determined as [42]

$$g_{\alpha}^{-}(\mathbf{x}, t + \delta t) = -g_{\alpha}^{+}(\mathbf{x}, t) + 2A_{\alpha}g_w. \quad (34)$$

2.5 Units conversion

To relate the parameters in LBM simulation with the real physical parameters, the lattice unit in base si unit such as length scale l_{LB} , time scale t_{LB} , mole scale mol_{LB} , current scale C_{LB} and mass scale m_{LB} are specified firstly. Then the other parameters and units in LBM simulation can be computed through the equations given below:

$$D_{LB} = \frac{D_P t_{LB}}{l_{LB}^2}. \quad (35)$$

where the D_{LB} is diffusivity in LBM and D_P is physical diffusivity.

$$k_{LB} = \frac{k_P t_{LB}}{l_{LB}}. \quad (36)$$

where the k_{LB} is standard reaction rate constant in LBM and k_P is standard reaction rate constant in real physics.

$$\Omega_{LB} = \frac{m_{LB} l_{LB}^2}{t_{LB} C_{LB}^2}. \quad (37)$$

where Ω_{LB} is the Ohm in LBM simulation.

$$J_{LB} = \frac{C_{LB}^2 \Omega_{LB}}{t_{LB} l_{LB}}, \quad (38)$$

$$E_{LB} = \frac{E_P J_{LB}}{C_{LB}}. \quad (39)$$

where E_{LB} is the potential in LBM simulation and E_P is the potential in real physics.

$$F_{LB} = \frac{96485 mol_{LB}}{C_{LB}}. \quad (40)$$

where F_{LB} is the Faraday's constant value in LBM simulation.

3 Model verification

In this section, the 3D half-cell model developed based on LBM model is verified by comparing the result with the study from positive electrode in vanadium redox flow battery [23] based on a volume-averaged model and the experimental data. Table 1 summarizes the parameters that are adopted for this verification study. A simplified fin geometry which has been used in previous research [32, 33] is adopted here in order to preserve the geometric parameters used in [23]. In Fig. 2(a), the simple electrode geometry is shown in XY-cross section and all features are identical along the Z-axis. Solid electrode and liquid electrolyte phases are denoted by yellow and blue respectively. Electrolyte flow is through the blue areas and coming out of the page. The following assumptions are made during the simulations in current work: the VRFB is assumed to be operating at steady-state; the ionic species do not influence the flow field in any manner; the flow is driven by a constant pressure gradient along the Z-axis; the species do not interact with each other in the bulk fluid; side reactions such as hydrogen and oxygen evolutions are not considered. Fig. 2(b) and Fig. 2(c) show the averaged solid electrode potential and the positive electrode over-potential as a function of the inlet state of charge(SOC) during charging as compared to the results of Ref. [23]. The predictions from pore-scale model based on LBM show good agreement with macroscopic models and experimental data indicating the validity of the LBM model in predicting the VRFB performance.

4 3D electrode microstructure

The 3D microstructure of the carbon felt sample was imaged using a laboratory X-ray CT system (Phoenix Nanotom 180, GE, USA). With an X-ray tube voltage and current setting of 75 kV and 100 A respectively, 1600 projection images of the sample were captured over a 360 rotation range. The felt sample and X-ray detector (CMOS flat panel, Hamamatsu Photonics, Japan) were positioned to provide an effective pixel size of 0.6 μm . Tomographic reconstruction of the acquired projection images was performed with datos—x -reconstruction software (GE), which uses a cone-beam filtered backprojection algorithm based on the Feldkamp-Davis-Kress (FDK) algorithm [43].

Image pre-processing and segmentation of the resulting reconstructed volume was carried out using commercial image processing software (Avizo v9.3, Thermo Fisher Scientific). In here, a Gaussian smoothing filter was applied to the reconstructed volume to reduce

Table 1: Operating parameters for the verification study [23].

Quantity	Value
Porosity	0.929
Specific surface area	16200 m^{-1}
Half-cell width	0.003 m
Average velocity v	0.014 m s^{-1}
Initial vanadium concentration	1500 mol m^{-3}
Equilibrium potential, E^0	1.004 V
External current density, J_{ext}	-400 A m^{-2}
Operating temperature, T	298 K
Universal gas constant, R	$8.314\text{ J mol}^{-1}\text{ K}^{-1}$
Faraday's constant, F	96485 C mol^{-1}
Electrolyte density, ρ	1000 kg m^{-3}
Electrolyte viscosity, ν	$1.0 \times 10^{-6}\text{ m}^2\text{ s}^{-1}$
Solid electrode conductivity, κ_s	1000 S m^{-1}
Initial proton concentration	6000 mol m^{-3}
Transfer coefficient, α	0.5
Standard reaction rate constant, k	$6.8 \times 10^{-7}\text{ m s}^{-1}$
Diffusivity of VO^{2+}	$3.9 \times 10^{-10}\text{ m}^2\text{ s}^{-1}$
Diffusivity of VO_2^+	$3.9 \times 10^{-10}\text{ m}^2\text{ s}^{-1}$
Diffusivity of H^+	$9.312 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$
Diffusivity of SO_4^{2-}	$2.2 \times 10^{-10}\text{ m}^2\text{ s}^{-1}$

the image noise. Threshold-based segmentation of the volume was then performed to isolate the carbon fibres from the pore/electrolyte phase.

5 Simulation results and discussion

5.1 Characterization of electrode microstructure

In order to keep a reasonable computational cost, the resolution of the simulation geometry of electrode is coarsened from $0.6\mu m \text{ voxel}^{-1}$ to $3\mu m \text{ voxel}^{-1}$. This is done by traversing through every voxel in the original high-resolution geometry and every $5 \times 5 \times 5$ voxels are merged into one voxel. The low resolution structure exhibits the same geometric properties as the original XCT geometry. The geometric parameters for the simulation structure is tabulated in Table 2. The grid effect is tested by performing additional simulations for fully wetting case with 600 Am^{-2} external current density in a finer grid with $l_{LB} = 2\mu m$ and a coarser grid with $l_{LB} = 4\mu m$. The result show similar concentration and overpotential distribution for the grid sizes of $l_{LB} = 2\mu m$ and $l_{LB} = 3\mu m$, and the difference of half cell overpotential between them is below %2 as shown in Table 3. However, the half cell overpotential for the grid size with $l_{LB} = 4\mu m$ has %10 higher than the result from $l_{LB} = 3\mu m$. Considering that the $l_{LB} = 3\mu m$ grid size gives similar results to that of $l_{LB} = 2\mu m$ but has significantly reduced computational cost(as shown in Table3), the resolution of $3\mu m \text{ voxel}^{-1}$ in current work can ensure the accuracy of results. Fig.

Table 2: Characterization of simulation structure.

Quantity	Value
Lattice size[x,y,z]	$86 \times 196 \times 88$
Grid resolution	$3\mu m \text{ voxel}^{-1}$
Cell dimensions	$258\mu m \times 588\mu m \times 264\mu m$
Porosity	0.9042
Specific surface area	72.1 mm^{-1}
Mean pore diameter	$35.2 \mu m$
Mean fiber diameter	$5.2 \mu m$

3 shows the porous electrode used in the 3-D LBM simulation and the pore size distribution of porous electrode. The pore size distribution can be characterized through the computation of the density of the spherical contact distribution. The distance of each pore voxel to the solid phase is determined by inserting discrete spheres with increasing diameters until they touch the solid phase. As a voxel close to the wall can nevertheless be an element of a large sphere centered at another position, the size of each pore voxel could be computed as the diameter of the largest sphere that includes this pore voxel.

5.2 Computational details

The LBM model used in simulation work is developed by C language and the implementation of parallel computation is based on OpenMP technology. It will take about 15h to complete one simulation case on the workstation with 20 processor. A three-dimensional computational domain is shown in Fig. 3(a). The flow of electrolyte takes place through

Table 3: Grid test.

	$4\mu m$	$3\mu m$	$2\mu m$
Overpotential	$47.4mV$	$42.3mV$	$41.7mV$
Computation time	$\approx 6.5h$	$\approx 15h$	$\approx 50h$

Table 4: Boundary conditions.

	Boundary conditions
Species in electrolyte	$C_j _{x=0} = C_j^{in}$
	$\frac{\alpha C_j}{\alpha x} _{x=96} = 0$
Charge in electrode	$-\kappa_s \frac{\alpha \phi}{\alpha z} _{z=101} = J_{ext}$
	$\kappa_s \frac{\alpha \phi}{\alpha x} _{x=0} = 0$
	$\kappa_s \frac{\alpha \phi}{\alpha x} _{x=96} = 0$
	$\kappa_s \frac{\alpha \phi}{\alpha y} _{y=0} = 0$
	$\kappa_s \frac{\alpha \phi}{\alpha y} _{y=196} = 0$
Charge in electrolyte	$-\kappa_e \frac{\alpha \phi}{\alpha z} _{z=0} = J_{ext}$
	$\kappa_e \frac{\alpha \phi}{\alpha x} _{x=0} = 0$
	$\kappa_e \frac{\alpha \phi}{\alpha x} _{x=96} = 0$
	$\kappa_e \frac{\alpha \phi}{\alpha y} _{y=0} = 0$
	$\kappa_e \frac{\alpha \phi}{\alpha y} _{y=196} = 0$

the pore space of the electrode. Indeed, to save computational cost, the computational domain is much smaller than a typical size of VRFB. Nevertheless, the chosen computational domain is still sufficiently large to represent the VRFB electrode, according to our previous studies [44]. The advantage of the pore-scale model compared to the macroscopic model is its ability to provide understanding of the microscopic physical and chemical processes, and that it can be used as a design tool to design the electrode microstructure. The pore-scale model can be linked with macroscopic model by providing more accurate structural information including effective diffusivity, permeability, porosity, active surface area, which are necessary input parameters to macroscopic models. Such structural information is important to obtain accurate prediction of VRFB performance by the macroscopic model. However, they are often taken from literature or derived from empirical relations, which are not necessarily accurate and representing the particular VRFB systems. So the pore-scale model can help improve the accuracy of the macroscopic model.

The half bounce back scheme in LBM is applied on the wall boundary in this study. Constant pressure boundary conditions are imposed on the plane of $X=0$ and $X=96$.

Table 5: Operating parameters used in simulation [33].

Quantity	Value
Initial vanadium concentration, C^0	2000 mol m^{-3}
Initial proton concentration, $C_{H^+}^0$	4000 mol m^{-3}
State of charge, C_{VO_2}/C^0	0.5
Equilibrium potential, E^0	0.991 V
Operating temperature, T	298 K
Electrolyte density, ρ	1000 kg m^{-3}
Electrolyte viscosity, ν	$1.0 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$
Solid electrode conductivity, κ_s	1000 S m^{-1}
Transfer coefficient, α	0.5
Standard reaction rate constant, k	$6.8 \times 10^{-7} \text{ m s}^{-1}$
Diffusivity of VO^{2+}	$3.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
Diffusivity of VO_2^+	$3.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
Diffusivity of H^+	$9.312 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
Diffusivity of SO_4^{2-}	$2.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

The detail boundary conditions for species and charge transport are shown in Table 4. Table 5 illustrates the operating parameters used in the simulation. The concentration expressions of any species at inlets are given by

$$\begin{cases} C_{VO_2^+}^{in} = C^0 \cdot SOC \\ C_{VO^{2+}}^{in} = C^0 \cdot (1 - SOC) \\ C_{H^+}^{in} = C_{H^+}^0 + C^0 \cdot SOC \end{cases} \quad (41)$$

The Reynolds number is equal to 0.0008 in current work, which can be calculated by

$$Re = v_{ave} R_{ave} / \nu \quad (42)$$

where R_{ave} is the mean pore diameter of porous electrode and v_{ave} is average superficial velocity of electrolyte. The ν is kinetic viscosity of electrolyte. It should be noted here that the difference in flow rate results in a change in the performance of VRFB, which has been pointed out in previous studies [32, 33]. The effect of flow rate on battery performance is not included in current work, so that the Reynolds numbers are equal to 0.0008 in all cases.

To quantify the effect of wetting on the performance of the electrode, a wetting factor WSP (WSP =wetting surface area of electrode/the total surface area of electrode) is defined to describe the wetting conditions of porous electrode. When $WSP = 0$, the surface of the electrode is completely hydrophobic and the liquid electrolyte will just flow through the porous space without wetting the surface of the electrode, meaning no electrochemical reactions could happen. When $WSP = 1$, the surface of the electrode is completely hydrophilic and the liquid electrolyte will be able to wet all the surface of the electrode, meaning there will be maximum surface available for electrochemical reactions. In practice, most of the current state-of-art VRFB electrodes have partially wetting, with WSP in between 0 and 1, meaning not all the electrode surface is available

for electrochemical reactions. This affects the performance of VRFB and is the subject of the following investigation.

5.3 Performances of fully wetting electrode with different external current density

For the fully wetting electrode($WSP = 1$), it assumes that the pore void space inside porous electrode is filled with electrolyte and all of surface of electrode is reactive. The local distributions of concentration, activation overpotential and current density for the positive half cell with different external current density are shown in Fig. 4. Fig. 4(a) shows the concentration distribution for one slice at Y-middle plane($Y=294\mu m$), the concentration near the inlet($X=1\mu m$) remains unchanged as Dirichlet concentration boundary condition is used. Along the X-direction, the concentration of both species in the electrolyte changes steadily from the specified value($SOC = 0.5$) at the inlet. The value of SOC decrease at the outlet($X=258\mu m$) with the increase of external current density. The corresponding averaged profiles of distribution of concentration, activation overpotential and current density are illustrated in Fig. 5. The average concentration profile along the Z-direction of electrode shown in Fig. 5(a) reveals that the concentration of VO_2^+ in the middle of Z is larger than that close to the current collector and membrane. This observation can be explained by the fact that it has stagnant region induced by the low flow velocity near the current collector and membrane(wall boundary condition). A 3-D distribution of the activation overpotential at the active surface for a small part(from $x=93\mu m$ to $x=123\mu m$) of simulated porous electrode is shown in Fig. 4(b). The local distribution is dependent on the physical distribution and local connectivity of the carbon fibers. Overall, the activation overpotential is higher on the surface of fibers that are closer to the current collector, and tends to decrease along the Z direction of the electrode. It is interesting to note that near the current collector where the high concentration gradient is observed from Fig. 5(a), activation overpotential tends to be smaller. In contrast,

in the direction of X, the overpotential tend to decrease with decreasing concentration of VO_2^+ . Average distributions of the current density on the surface of fibers along the Z and X directions are illustrated in Fig. 5(c). The surface current density is obtained directly from the Butler-Volmer equation(Eq. (26)) and Faraday's law(33), so that the trend in current density is identical in shape to the trend observed for overpotential on the surface of fibers.

It can be seen from Fig. 5(c) that the magnitude of average current density on the surface of fiber is proportional to the value of the external current density to satisfy charge conservation. The activation overpotential increases by nearly $5mv$ when the external current density increases from $300A\ m^{-2}$ to $600A\ m^{-2}$, while the difference in activation overpotential is $10mv$ when the external current density increases from $600A\ m^{-2}$ to $1200A\ m^{-2}$. The activation overpotential almost doubled as the external current density increases twofold, which will increase the concentration gradient and leads to a higher concentration polarization inside the porous electrode. From the concentration distributions in Fig. 5(a), there are significantly larger consumption rates of VO_2^+ in electrolyte with larger external current density. Similar results were presented in finite volume method(FVM) model [32] and experimental study [23] for fully wetting electrode, which further confirms the validity of the LBM simulated results obtained in this paper.

5.4 Effect of wetting surface area on half cell performance

During electrolyte penetration into porous electrode, as driven by the pressure difference between inlet and outlet, electrolyte front start to invade through the pores and forms convex electrolyte fronts due to hydrophobic carbon-based electrode. Then electrolyte selects preferential paths to the flow direction of in-plane and through-plane which has lower resistance force because of relatively large pore size and less tortuous path, while the air bubbles are trapped into the relatively small pores. At last, several invading fronts break through from porous electrode. The liquid in the porous electrode finds its own flow path and the distribution and wetting surface area inside the electrode only varies

marginally with time after breakthrough. The trapped air bubbles inside porous electrode will reduce the active surface area of fibers, resulting in a decrease in the performance of the electrode. In order to evaluate the effect of wetting surface area on half cell performance, a partially wetting electrode caused by the trapped bubbles during electrolyte penetration process is used in current work.

Two-phase displacement is performed by simulating the electrolyte drainage the gas in the 3D porous electrode. The contact angle of electrolyte is assumed to have a uniform value of 120° to represent the hydrophobic nature of carbon-based electrode. A non-wetting phase and a wetting phase reservoirs with 10 lattices size are added to the front end and back end of the porous electrode, respectively. Pressure boundary conditions are imposed at the two reservoirs and the drainage process is simulated by increasing the non-wetting phase reservoir pressure gradually while keeping the pressure in the wetting phase reservoir unchanged as was done in [45]. The capillary pressure p_c , defined by the difference of non-wetting phase pressure and wetting phase pressure, increases gradually and drives the electrolyte into the porous electrode which is initially filled by air. By increasing the pressure, more gas is exhausted and the pore space becomes partially gas filled. The gas is replaced by electrolyte if the applied pressure is higher than or equal to the size dependent capillary forces. The electrolyte saturations are obtained at different capillary pressures and the wetting surface area of electrode increases with increasing saturation. The saturation is defined by the volume electrolyte inside electrode divided by the volume of pore space inside electrode. Fig. 6(a) shows the LBM simulated capillary pressure versus the electrolyte saturation during the drainage process in porous electrode with 120° contact angle, while the wetting surface area curve is illustrated in Fig. 6(b). The distribution of electrolyte and wetting surface inside simulated porous electrode after electrolyte breakthrough under a capillary pressure of $15kPa$ are visualized in Fig. 7. The distribution and wetting surface area inside the electrode only varies marginally with time after breakthrough. The electrolyte saturation level steeply decreases along the X-direction from 1 near $X=120\mu m$ to about 0.2 near the outlet of porous electrode. This

steep decrease results from an invasion-percolation process in the porous electrode that merges transport paths therein. As shown in Fig. 6(b), only 74 percent of the carbon fiber surface ($WSP = 0.74$) is wetted by electrolyte when capillary pressure is equal to $15kPa$, corresponding to 76% saturation of electrolyte. The operating parameters and boundary conditions are consistent with that used in the case of fully wetting electrode, which are shown in Table 1 and Table 4.

The effect of wetting surface area on both local and averaged species concentration, activation overpotential, and current density are investigated, and the results are compared to those of the fully wetting electrode presented in the above section. Fig. 8 shows the averaged spatial distribution of concentration, activation overpotential and current density for fully wetting electrode and partially wetting electrode under a constant discharge current density of $600A\ m^{-2}$. As air bubbles trapped inside porous electrode, a part of surface becomes unavailable for electrochemical reactions, and as a result higher local current densities are required to satisfy charge conservation as the same external current density is applied in two cases. So, it can be seen from Fig. 8(b) and Fig. 8(c) that the overall magnitudes of average activation overpotential and current density on the surface of fibers are greater for partially wetting electrode, while lower concentrations of VO_2^+ are observed from Fig. 8(a). The concentration gradient tends to be smooth after $X=150\mu m$ due to the steep reduction in active surface as shown in Fig. 7(b), so that more electrochemical reaction occurs before $X=150\mu m$. The local concentration inside electrode is dependent on the mass transfer condition and consumption rate caused by electrochemical reaction. Since the same current density is applied in the partially wetting and fully wetting electrode, the reaction rate associated with the discharge rate should remain the same for two cases in accordance with Faraday's law. However, as a part of pore space used for electrolyte transport is occupied by trapped air bubbles, it has higher spacial average value of fuel consumption rate for partially wetting electrode due to the decrease of volume occupied by electrolyte. In addition, the existence of air bubbles in porous electrode will block the species transport path and prevent the reac-

tant species from reaching active surface. So, more concentration polarization of species is observed in partially wetting electrode.

Fig. 9(a) and Fig. 9(b) illustrate the overall results of half-cell voltage and total overpotential of positive electrode as a function of external current density for partially wetting and fully wetting electrode. It is obvious that the electrochemical performance of positive half cell is reduced with air bubbles trapped inside electrode. It has lower half-cell voltage and higher total overpotential for partially wetting electrode. On one hand, the air bubbles trapped in electrode will impede the reactant species transport to active surface of fibers, which results in the higher concentration polarization of species for partially wetting electrode. It is expected to contribute to higher concentration overpotential. On the other hand, the air bubbles trapped inside porous electrode leads to the higher activation overpotential as higher local current densities are required to ensure the overall reaction rate is same as that for fully wetting electrode which is applied same external current density. In addition, higher overpotential in partially wetted electrode will lead to lower electrolyte utilisation and the carbon fibres surrounded by air can be oxidised and degraded over a long time of operation.

6 Conclusions

In the current study, a three-dimensional lattice Boltzmann model is developed to simulate coupled multiphase fluid flow, species and charge transport as well as electrochemical reaction in vanadium redox flow batteries (VRFB) based on real carbon paper electrode. The detailed structure of the carbon paper electrode is obtained using X-ray computed tomography. Pore scale multiphase flow simulations were conducted to investigate the electrolyte saturation and wetting surface area in the hydrophobic carbon paper electrode with different capillary pressure during the electrolyte drainage process. It was found that trapped gas bubbles are a common problem which induced by the fact that forced convection is not sufficient for accessing the small pores in the hydrophobic electrode. The

wetting surface area and saturation of electrolyte can be increased with higher capillary pressure. The LBM model is then used to predict the average and local species concentration, activation overpotential, and current density with different external current densities. Both the average current density and activation overpotential on the surface of fiber are proportional to the value of the external current density, which show good agreement with macroscopic model and experimental observations. At last, the effect of active wetted surface area on the performance of positive half cell was evaluated through comparing the results from fully wetting electrode and partially wetting electrode. It was found that the air bubbles trapped inside porous electrode can result in an increase of activation overpotential and concentration overpotential. It can be concluded that the increase in surface area, without other effects, can account for the decrease in local current density and overpotential.

Although the current paper just focus on the effect of the wetting condition on electrode performance, we recognize that both the wetting condition and the flow distribution can affect the accessibility of electrolyte flow through the porous electrode and consequently the electrode performance. It is also important to understand how the flow distribution affects the electrode performance. In a follow-up paper, we will report the investigation of a number of electrode structures which give different flow distributions, and their effects on the performance of flow battery.

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Figure 1

(a)

(b)

(c)

Figure 2

(a)

(b)

Figure 3

Figure 4

(a)

(b)

(c)

Figure 5

(a)

(b)

Figure 6

(a)

(b)

Figure 7

Figure 8

(a)

(b)

Figure 9