The Dependence of Mass Transfer Coefficient on the Electrolyte Velocity in Carbon Felt Electrodes: Determination and Validation

Xin You, Qiang Ye,* and Ping Cheng

Ministry of Education Key Laboratory of Power Machinery and Engineering, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People’s Republic of China

In a flow battery, the salient impact of the electrolyte velocity on the mass transfer coefficient in carbon felt electrodes is demonstrated and quantified. A lab-scale flow battery, fed with identical electrolyte solutions containing Fe^{2+}/Fe^{3+} as active substances in both the anode and the cathode, is used to realize stable tests free from side reactions in a broad range of current densities. The electrolyte velocities ranging from 2.5 to 15 mm s\(^{-1}\) are selected in this work, which are typical in flow through electrodes in most flow batteries. By measuring limiting currents at various flow rates, a correlation between the mass transfer coefficient and the velocity in dimensionless form is obtained as \(Sh = 1.68 \cdot Re^{0.9}\). Meanwhile, a 2-D numerical model incorporating this correlation and the experimentally measured electrolyte conductivity is proposed. Voltage losses of the battery fed with adequate reactants at different velocities are both experimentally measured and numerically simulated. The agreement between simulated results and experimental data verifies the applicability of this correlation under normal operating conditions below limiting currents.

Owing to the exclusive advantage of decoupling power generation and energy storage, redox flow batteries (RFBs) have been considered as a critical candidate for large-scale electrical energy storage (EES). Unlike the electrodes of conventional secondary batteries, the electrodes of RFBs do not participate in reactions but only provide electrochemical reaction sites for active ions and support electrons transfer. For numerous kinds of developed RFBs, the porous carbon felts, composed of randomly interlaced carbon fibers, are generally selected as electrodes.

Obtaining high voltage efficiency at high current densities is one of the major challenges in the commercialization of RFBs. Much efforts have been devoted to diminishing the activation loss by modifying the carbon fiber surface. In addition, ohmic loss and mass transfer loss also lead to the reduction of the voltage efficiency. It is generally recognized that supplying high flow rate of electrolyte for the RFB is the most feasible method to minimizing mass transfer loss, but more pumping power is inevitably required for increasing flow rates. Tang et al. and Ma et al. carried out special research on optimizing the operating strategy of electrolyte flow rate for kilowatts class all-vanadium flow battery (VFB) systems, in which the significant impact of flow rate on cell voltage was detected during the whole charge/discharge process. In a carbon felt electrode, the mass transfer loss is caused by the species transport between the bulk solution in the pore and the carbon fiber surface, which is usually quantified by the mass transfer coefficient \(k_{m}\). For cells operating under high current densities, the mass transfer loss also contributes a significant proportion to the voltage loss, especially when approaching the end of charge/discharge process. Considering the dilemma between enhancing mass transport and reducing pumping power, it is essential to quantitatively figure out the dependence of mass transfer capability on the electrolyte velocity.

According to previous studies on mass transfer for porous materials such as metal nets and packed beds, the mass transfer coefficient can be evaluated by the following expression:

\[ k_m = b \left( \frac{v}{1 \text{ m/s}} \right)^n \cdot 1 \text{ m/s} \]  \[1\]

where \(b\) and \(n\) are empirical constants. By transforming specific parameters into dimensionless numbers, the expression can be written as:

\[ Sh = m \cdot Re^n \]  \[2\]

where \(m\) is also an empirical constant.

For carbon felt electrodes, although some attention has been paid to the dependence of mass transfer coefficient on the electrolyte velocity, correlations between these two parameters are not consistent. Moreover, it is rarely verified whether the mass transfer correlation obtained by measuring limiting currents is applicable in the condition of supplying adequate reactants. The importance of electrolyte velocity for the mass transfer in carbon felt electrodes has been qualitatively demonstrated in our previous work. This research was motivated by the demand for quantifying this importance and verifying the obtained correlation, especially at frequently operational velocity range between 2.5 and 15 mm s\(^{-1}\). To minimize activation loss and highlight mass transfer issues, a symmetric flow battery utilizing the redox couple Fe\(^{2+}/Fe^{3+}\) as active substances at both anode and cathode was used as the testing cell. With the extremely fast reaction kinetics, this redox couple has been regarded as an ideal reactant in positive electrodes and received more and more attention. The correlation between the mass transfer coefficient and the electrolyte velocity was derived from the experimentally measured limiting currents at various flow rates. Subsequently, polarization behaviors of the cell fed with adequate reactants were tested at various velocities. In addition, a 2-D numerical model incorporating this obtained correlation and the experimentally measured electrolyte conductivity was proposed. The applicability of this obtained correlation under normal conditions below limiting currents was investigated by comparing the numerically predicted and experimentally measured voltage losses. The experimental approaches and model formulations are detailed in next sections, which are followed by explanations and discussions of results. Finally, conclusions of this study are summarized.

**Experimental**

**Electrode pretreatment and electrolyte preparation.**—Carbon felts produced by Hunan Jiuhua Carbon Hi-Tech Inc., China, were used as electrodes in this study. To improve their wettability and electrochemical activity, heat-pretreatment is required. The raw carbon felts were submerged in the solution of isopropyl alcohol and deionized water (\(V_{C_{2}H_{5}OH}/V_{H_{2}O} = 1:10\)) firstly to remove organic
impurities, and then rinsed in deionized water several times to purge the residual isopropyl alcohol. After this step, cleaned felts were heated to 400°C in an electrical resistance furnace filled with air at a heating rate of 3°C min⁻¹. The constant temperature heating process lasted for 5 hours. Finally, treated felts were cooled down in the air and stored in deionized water before testing.

Nafion 115 membrane was selected as the separator and also pre-treated before assembling into the cell. Firstly, the membrane was soaked in 3 wt% H₂O₂ at 80°C, and then put into deionized water at 80°C. Following this step, the membrane was submerged in 0.5M H₂SO₄ at 80°C, and then rinsed in deionized water at 80°C. Each of preceding steps lasted for 30 min, and the pretreated membranes were immersed in deionized water before testing.

Ferrous chloride (FeCl₂•4H₂O, aladdin, 99% purity) and ferric chloride (FeCl₃•6H₂O, SCR, 99% purity) were dissolved in degassed hydrochloric acid to form final electrolytes including desired concentration of Fe²⁺/Fe³⁺ and 2 M HCl. In preparing electrolyte, the solution was isolated from air by purging nitrogen through the solution to prevent the oxidation of Fe²⁺. And during electrochemical testing, the space above electrolyte surface in the reservoir was also filled with nitrogen.

**Figure 1.** (a) Schematic of the RFB setup adopting full flow-through mode; (b) schematic of the electrolyte flow circuit in the testing RFB system; (c) modeling domains.

**Symmetric cell construction.—** A symmetric cell configuration, feeding an identical redox couple to both the anode and the cathode, is usually used to effectively minimize crossover issues and to realize long stable state operating conditions. All the tests in this study were also conducted using a symmetric cell which consisted of a membrane, two carbon felt electrodes, two composite graphite electrolyte distributors and two gold-plated current collectors as shown in Fig. 1a. The electrode had a geometric area of 5 cm × 5 cm, of which the position and the compressed thickness were fixed by Teflon gaskets. Carbon felts with uncompressed thickness of 2.5, 5 and 7.5 mm were employed, and the compression rate of each felt was fixed at 20% in the assembled cell. The carbon felt porosity was calculated according to the weight of a carbon felt sample and the density of carbon fiber. The porosity of the uncompressed sample was about 0.93, which reduced to 0.9125 when the sample was assembled and compressed in the cell.

In our design, the electrolyte was forced to flow through the porous electrode directly. To realize a uniform inlet velocity at the electrode entrance, the electrolyte stream was divided into several tributaries by the forked flow channels added on the carbon plate as the close-up shown in Fig. 1a, and then flowed through a buffer slot before entering...
the porous electrode. The flow circuit of electrolyte is illustrated in Fig. 1b. The electrolyte was stored in a single reservoir and circulated through the two electrodes in parallel. Owing to the opposite reacting direction of one redox couple in the two electrodes, the composition and concentration of the electrolyte at the inlets of anode and cathode remained identical and invariant all the time, which ensured steady state operating conditions.

**Electrochemical measurements.**—All measurements in this study were performed with a battery testing equipment Arbin BT2000 (Arbin Instrument). To ensure the membrane getting equilibrated with the liquid electrolyte solution, the newly assembled cell was continuously fed with the solution for about 30 minutes at open circuit and then charged at a small current density of 20 mA cm\(^{-2}\) for five minutes. In the experiments of measuring limiting currents, polarization curves at specific flow rates were recorded by charging the cell at a stepwise potentiostatic mode. The applied cell voltage was increased in 20 mV steps, and each step lasted for 30 s to exclude capacitive currents. The cell was considered to be operated at a limiting state when the maximum variation of the current became lower than 1.5% with 100 mV increment of the applied voltage. In these experiments, the cell was fed with electrolyte containing 0.05M Fe\(^{2+}\) and 0.75 M Fe\(^{3+}\). Since the inlet concentration of Fe\(^{3+}\) was 15 times higher than that of Fe\(^{2+}\), the limiting currents were only determined by the oxidation of Fe\(^{2+}\).

In addition, polarization characterizations of cells fed with electrolyte containing adequate Fe\(^{2+}\) and Fe\(^{3+}\) were also tested to verify the applicability of mass transfer correlation under normal operating conditions below limiting currents. In this part, cell voltages were measured galvanostatically at current densities ranging from 0 up to 400 mA cm\(^{-2}\). Each galvanostatic step lasted for at least 30 s to reach a steady voltage.

The electrolyte conductivity was measured using a precision lab conductivity meter MP515 (Shanghai San-Xin Instrument Inc.), and the electrolyte viscosity was measured using an Ubbelohde type viscometer. To keep the temperature of measured electrolyte constant and the electrolyte viscosity was measured using an Ubbelohde type viscometer. To keep the temperature of measured electrolyte constant and the electrolyte viscosity was measured using an Ubbelohde type viscometer. To keep the temperature of measured electrolyte constant and the electrolyte viscosity was measured using an Ubbelohde type viscometer. To keep the temperature of measured electrolyte constant and the electrolyte viscosity was measured using an Ubbelohde type viscometer. To keep the temperature of measured electrolyte constant and the electrolyte viscosity was measured using an Ubbelohde type viscometer.

To focus our attention on the concerned issues, the model was constructed based on the following additional assumptions for simplicity: 1) Electrolyte flow is incompressible; 2) The electrolyte velocity in porous electrode is constant and the influence of water crossover is neglected; 3) Diffusivity of ions and physical properties of porous electrode are isotropic; 4) Except for protons, no ions permeate the membrane; 5) The membrane conductivity is constant at a given concentration of the feeding electrolyte solution.

**Governing equations.**—In each half-cell, four kinds of ions (i.e. Fe\(^{2+}\), Fe\(^{3+}\), H\(^{+}\), Cl\(^{-}\)) are considered. Unlike the other three kinds of charged ions, the concentration of chloride ions is calculated by the electroneutrality equation:

\[ \sum z_i c_i = 0 \]  

where \( c_i \) is the bulk concentration of species \( i \) \((i=Fe^{2+}, Fe^{3+}, H^{+}, Cl^{-})\) in pores, and \( z_i \) denotes the valence of species \( i \). The conservation of ions is defined in the following equation:

\[ \nabla \cdot \vec{n}_i = -S_i \]  

where \( \vec{n}_i \) is the flux of species \( i \) in the electrolyte, and \( S_i \) denotes the source term related to ion production/consumption in electrochemical reactions. Apparently, both \( S_{H^+} \) and \( S_{Cl^-} \) are equal to zero. The source term of Fe\(^{2+}\) and Fe\(^{3+}\) are given as follows:

\[ S_{Fe^{2+}} = \frac{j}{F} \]  

\[ S_{Fe^{3+}} = -\frac{j}{F} \]  

where \( j \) represents the volume-based local current density, and \( F \) is the Faraday constant. The movement of charged ions in electrolyte is dominated by three mechanisms: diffusion, migration and convection. And the resultant flux of each kind of ions is defined by the Nernst-Planck equation:

\[ \vec{n}_i = -D_i^{eff}\nabla c_i - z_i u_i c_i F \phi_i + \vec{v}_i \]  

where \( \phi_i \) represents the ionic potential; \( \vec{v}_i \) is the superficial velocity of electrolyte, which is averaged over the volume of both matrix-phase and pore-phase in the porous electrode; \( D_i^{eff} \) denotes the effective diffusion coefficient of species \( i \) in the porous electrode, which is obtained by modifying the diffusion coefficient in bulk solution with Bruggemann correlation:

\[ D_i^{eff} = \varepsilon^{1.5} D_i \]  

where \( \varepsilon \) is the porosity of the carbon felt. In Eq. 7, \( u_i \) is the ionic mobility, which denotes the movement ability of ions in response to an electric field. As a result, it determines the electrolyte conductivity as follows:

\[ \sigma_i = F^2 \sum z_i^2 u_i c_i \]  

Under the infinite dilution solution approximation, the ionic mobility can be evaluated by Nernst-Einstein equation:

\[ u_i = \frac{D_i^{eff}}{k T} \]  

The moving charged ions generate ionic current, the density of which can be described in the following equation:

\[ \vec{i}_i = F \sum_i z_i \vec{n}_i \]  

According to the conservation of charge, the ionic current density in the liquid electrolyte is correlated to the electronic current density in the solid electrode in the following equation:

\[ \nabla \cdot \vec{i}_i = -\nabla \cdot \vec{j} = j \]  

And the electronic current density is associated with electronic potential by Ohm’s law:

\[ \vec{i}_e = \sigma_e \nabla \phi_e \]  

where \( \sigma_e \) is the electronic conductivity of the porous electrode.

The volume-based local current density \( j \) resulted from electrochemical reaction is calculated by the Butler-Volmer equation. Both
of the B-V equation at anode and cathode are given in the following form:

\[ j = a F k (c_{Fe^{2+}})^{n} (c_{Fe^{3+}})^{m} \left[ \left( \frac{c_{Fe^{3+}}}{c_{Fe^{2+}}} \right) \exp \left( \frac{(1 - \alpha) F \eta}{RT} \right) - \left( \frac{c_{Fe^{2+}}}{c_{Fe^{3+}}} \right) \exp \left( -\alpha F \eta \right) \right] \]  

where \( k \) is the reaction rate, and \( \alpha \) denotes the charge transfer coefficient. The quantity \( \alpha \) represents the specific surface area of the porous electrode, which can be calculated by the following expression for the electrode composed of carbon fibers:

\[ \alpha = \frac{4 (1 - \epsilon) d_f}{d_f} \]  

where \( d_f \) is the diameter of carbon fiber. This formula is actually calculating the whole flank areas of cylinders in a certain volume of porous media, which is therefore a good prediction of the specific surface area of highly porous materials composed of slender cylindrical fibers with smooth surface, such as carbon felts. The overpotential \( \eta \) in Eq. 14 is defined in the following equation:

\[ \eta = \phi_i - \phi_f - E_{eq} \]  

The term \( E_{eq} \) represents the equilibrium potential of each half-cell calculated using Nernst equation:

\[ E_{eq} = E_0 + \frac{RT}{F} \ln \left( \frac{c_{Fe^{3+}}}{c_{Fe^{2+}}} \right) \]  

where \( E_0 \) is the standard equilibrium potential for reaction Fe^{2+}/Fe^{3+).

As described in previous sections, there is a mass transfer resistance between the bulk solution in the pore and the carbon fiber surface. In Eq. 14, \( c_{Fe^{2+}} \) and \( c_{Fe^{3+}} \) denote the concentrations of ferrous and ferric ions at carbon fiber surface respectively, which are different from those in bulk solution. Considering the localized conservation of species at steady state, the amount of reactant/product consumed/produced at the electrode surface by the reaction is balanced with that transferring from/to the bulk solution to/from the electrode surface. Accordingly, the transfer rate and reaction rate of reactant/product can be coupled by the following equations:

\[ F k_{m,Fe^{2+}} (c_{Fe^{2+}} - c_{Fe^{3+}}) = \frac{j}{a} \]  

\[ F k_{m,Fe^{3+}} (c_{Fe^{3+}} - c_{Fe^{2+}}) = -\frac{j}{a} \]  

The mass transfer coefficients \( k_{m,Fe^{2+}} \) and \( k_{m,Fe^{3+}} \) are correlated with velocity by Eq. 1. And the detailed information of Eq. 1 will be discussed later on the basis of experimental results.

**Boundary conditions.**—The \( x \) and \( y \) coordinates of the computational domain are illustrated in Fig. 1c. The species flux is assumed to be zero at the external boundaries except for the inlets and outlets:

\[ -\vec{n} \cdot \vec{N}_i = \begin{cases} 0 & \text{at : } x = 0, \ x = x_3 \\ \text{except inlet and outlet} \end{cases} \]  

\[ -\vec{n} \cdot \vec{N}_o = \begin{cases} 0 & \text{at : } x = 0, \ x = x_3 \\ \text{at : } y = 0, \ y = L_e \end{cases} \]  

The negative dot product of the flux vector and the normal vector represents the ion flux entering the simulated domain at the specified boundary. At the inlet of porous electrode, the electrolyte with a constant concentration is supplied at a constant velocity:

\[ -\vec{n} \cdot \vec{D}^{\text{el}} / \nabla c_i = 0 \text{ at : } y = L_e (\text{inlet}) \]  

To provide a reference potential for the cell, the electronic potential at the left external boundary of the anode is set as zero:

\[ \phi_i = 0 \text{ at : } x = 0 \]  

When the cell is simulated under a potentiostatic condition, a fixed electronic potential is applied on the right external boundary of the cathode:

\[ \phi_f = V \text{ at : } x = x_3 \]  

In contrast, a specific total current is given at this boundary instead when the cell is simulated under a galvanostatic condition:

\[ -W_e \int_{L_e}^{L_e} \nabla \cdot \vec{I} \, dl = I \text{ at : } x = x_3 \]  

In this model, it is assumed that the current in the membrane is carried only by the movements of protons. Thus, the proton flux at the electrolyte-membrane interface should be calculated by the following equation:

\[ -\vec{n} \cdot \vec{N}_{H^+} = \begin{cases} \frac{I_{H^+}}{H} & \text{at : } x = x_1 \\ \frac{I_{H^+}}{F} & \text{at : } x = x_2 \end{cases} \]  

And the ionic current density is considered to be continuous at the electrolyte-membrane interface:

\[ i_{H^+}^m = i_{H^+} \text{ at : } x = x_1, \ x = x_2 \]  

However, the ionic potential has a jump at this interface, since the proton concentration in the electrolyte is different from that in the membrane. This jump is known as Donnan potential and calculated by the following equation:

\[ \phi_{H^+} = \phi_f + \frac{RT}{F} \ln \left( \frac{c_{H^+}}{c_{H^+}^m} \right) \text{ at : } x = x_1, \ x = x_2 \]  

As the assumption stated at the beginning of this section, the proton concentration in the membrane \( c_{H^+}^m \) is treated as a constant, the value of which is equal to the fixed charge site concentration \( c_f \) in the membrane. Even though the Eq. 28 is fundamentally valid in predicting the Donnan potential,\(^\text{28}\) the accuracy of which has not been verified experimentally in typical flow battery systems. Fortunately, this uncertainty does not impair the output in this work due to the fact that the mass transfer coefficient correlation was obtained at limiting current conditions.

The components properties and model parameters are listed in Table I. The system of equations listed above was solved using the finite element software COMSOL Multiphysics. The built-in tertiary and secondary current distribution options were applied to the porous electrode and the membrane domain respectively. On this basis, we considered the difference between the bulk and surface concentrations, and employed the mass transfer coefficient to correlate these two concentrations. The grid number of computational domain was around 9000, and the relative tolerance was set as \( 1 \times 10^{-6}\).

**Results and Discussion**

**The correlation between mass transfer coefficient and velocity.**—The mass transfer capability in these flow through porous electrodes were evaluated by measuring limiting current densities at various flow rates. To ensure that only one direction of the reaction \( \text{Fe}^{2+}/\text{Fe}^{3+} \) is controlled by the mass transfer, electrolyte containing 0.05 M \( \text{Fe}^{2+} \) and 0.75 M \( \text{Fe}^{3+} \) was supplied in this part of experiments. The electrolyte flow rate varied from 15 to 90 mL min \(^{-1}\) corresponding to superficial velocities ranging from 2.5 to 15 mm s \(^{-1}\) in the 2 mm-thick carbon felt electrode. The polarization curves obtained from the experiments are shown in Fig. 2, in which it is clear that current densities reach plateaus with the increase of the cell voltage. The final limiting current was obtained by averaging the last five points of each plateau, which was used for the following calculation.

The purpose of measuring limiting current densities at various velocities is to explore the dependence of mass transfer coefficient
Table I. Physical properties and model parameters.

| Symbol | Description                                   | Value              |
|--------|-----------------------------------------------|--------------------|
| $L_e$  | Electrode length (cm)                        | 5                  |
| $W_e$  | Electrode width (cm)                         | 5                  |
| $\varepsilon$ | Electrode porosity                     | 0.9125 a          |
| $d_f$  | Carbon fiber diameter (μm)                   | 10 b               |
| $\sigma_s$ | Electronic conductivity of electrode       | 500 (S m$^{-1}$) |
| $H_m$  | Membrane thickness (μm)                      | 127                |
| $c_f$  | Fixed charge site concentration in the membrane (mol m$^{-3}$) | 199030 c          |
| $D_{Fe^{2+}}$ | $Fe^{2+}$ diffusion coefficient (m$^2$ s$^{-1}$) | $7.2 \times 10^{-10}$ 31 |
| $D_{Fe^{3+}}$ | $Fe^{3+}$ diffusion coefficient (m$^2$ s$^{-1}$) | $6.1 \times 10^{-10}$ 31 |
| $D_{H^+}$ | $H^+$ diffusion coefficient (m$^2$ s$^{-1}$)   | $9.312 \times 10^{-9}$ 31 |
| $D_{Cl^-}$ | $Cl^-$ diffusion coefficient (m$^2$ s$^{-1}$)  | $2.032 \times 10^{-9}$ 31 |
| $k$    | Reaction rate constant (m s$^{-1}$)          | $1.6 \times 10^{-5}$ 32 |
| $a$    | Charge transfer coefficient                  | 0.5                |
| $E_0$  | Standard equilibrium potential of $Fe^{2+}/Fe^{3+}$ (V) | 0.771              |

*aCalculated.  
bEstimated based on Reference 33.

don velocity. There are two approaches to solving for mass transfer coefficient according to the measured limiting currents in published literatures. In Kinoshita et al.’s study, the mass transfer coefficient is solved using the following equation:

$$k_m = \frac{I_{lim}}{zF \varepsilon a W_e H_e L_e}$$  \[29\]

In fact, this equation is based on the assumption that the reactant concentration is equal to $c_i^{\text{in}}$ at each point in the porous electrode. This supposition is approximately valid only when the electrolyte flows through the porous electrode extremely fast, whereas the electrolyte velocities applied in our study fall within the typical operating range. Due to the continuous consumption by electrochemical reaction, the reactant concentration at downstream of the electrolyte flow is significantly lower than that near the entrance. As a consequence, the mass transfer coefficient obtained from Eq. 29 is underestimated.

Another frequently-used solving method of the mass transfer coefficient is derived from the mass conservation in the electrode. Because the reactants at carbon fiber surfaces are exhausted at limiting currents, the mass conservation equation in the electrolyte flow direction is given as follow:

$$k_m a c_i = -v \frac{d c_i}{dy}$$  \[30\]

And then, the concentration of reactant at outlet of the porous electrode can be obtained by integrating Eq. 30 over the electrode length $L_e$ and is expressed as follow:

$$c_i^{\text{out}} = c_i^{\text{in}} \exp\left( - \frac{k_m a L_e}{v} \right)$$  \[31\]

Since the correlation between the limiting current and the variation of reactant concentration can be expressed as:

$$I_{lim} = zF H_e W_e \left( c_i^{\text{in}} - c_i^{\text{out}} \right)$$  \[32\]

the mass transfer coefficient can be calculated on the basis of the measured limiting current and basic parameters, which is given as:

$$k_m = -\frac{v}{a L_e} \ln \left( 1 - \frac{I_{lim}}{zF H_e W_e c_i^{\text{in}} v} \right)$$  \[33\]

As mentioned previously, the symbol $v$ represents the superficial electrolyte velocity in the porous electrode. Considering the fact that the mass transfer coefficient correlation describes the dependence of reactant transfer on the electrolyte velocity in micro-scale pores, the pore-phase velocity $v_p$ ($v_p = v/\varepsilon$), instead of the superficial velocity, was used in the dimensional form correlation and the definition of Reynolds number. Fig. 3 shows the mass transfer coefficients calculated from the measured limiting currents. The correlation between the mass transfer coefficient and velocity can be obtained by fitting a linear curve for the discrete points in the logarithmic plot and is given.

Figure 2. Polarization curves showing the limiting current densities at various flow rates. The electrolyte containing 0.05 M $Fe^{2+}$ and 0.75 M $Fe^{3+}$ was fed into the cell with (a) 2 mm-thick; (b) 4 mm-thick; (c) 6 mm-thick electrode.
Fig. 4 presents the bulk concentration of reactant Fe\(^{2+}\) in the anode when the cell is charged at (a) 0.1 V (non-limiting state); (b) 0.4 V (limiting state). The cell using 4 mm-thick electrode is fed with electrolyte containing 0.05 M Fe\(^{3+}\) and 0.75 M Fe\(^{3+}\) at a flow rate of 45 mL min\(^{-1}\).

It should be noted that values of limiting currents are determined by mass transport capability of Fe\(^{2+}\) and independent of the cell ohmic resistance. However, when simulating voltage losses below limiting currents, it is important to accurately predict ohmic loss owing to its dominant role in the total voltage loss. Considering the influence of ion concentration on the electrolyte conductivity, conductivities of the electrolytes used in this study were measured using a conductivity meter (MP515-03, SANXIN, Shanghai, China), and the results are listed in Table II. It is obvious that there are significant differences between calculated and measured electrolyte conductivities, especially when the ion concentration is high, which is attributed to the increase of interaction among ions with concentration. The overestimate of calculated electrolyte conductivity will make the simulated ohmic loss disaccord with the actual situations. For instance, when the symmetric cell with 4 mm-thick electrode is fed with electrolyte containing 0.4 M Fe\(^{2+}\) and 0.4 M Fe\(^{3+}\), the predicted ohmic loss based on measured conductivity is 123 mV at the current density of 200 mA cm\(^{-2}\), accounting for nearly 74 percent of the total voltage loss. However, using the calculated electrolyte conductivity lead to a 34 mV reduction in the simulated voltage loss owing to the underestimated ohmic resistance. Consequently, to provide persuasive simulated results, the experimentally measured electrolyte conductivities are utilized in the simulations of this study.

The applicability of the obtained correlation is firstly verified by comparing the numerically predicted limiting current densities with the experimental data. As shown in Fig. 5, in all cases, simulated limiting current densities on the basis of correlation \(Sh = 1.68 Re^{0.9}\) agree well with the experimental data. In contrast, the simulations based on the commonly used correlation \(Sh = 7 Re^{0.418}\) overestimated the mass transport capability especially at high liquid velocities.

To verify if the above obtained correlation is capable of predicting the influence of velocity on mass transfer under normal conditions below limiting currents, performances of the symmetric cell feeding with adequate reactants on both the anode and the cathode were

![Figure 3. Dependence of calculated mass transfer coefficient on velocity.](image)

\[
k_m = 8.85 \times 10^{-4} \left( \frac{v_p}{1 \text{ m/s}} \right)^{0.9} \cdot 1 \text{ m/s} [34]
\]

This correlation is usually transformed into the following dimensionless form to generalize its applicability:

\[
Sh = 1.68 Re^{0.9} [35]
\]

It should be mentioned that Eq. 33 is derived based on the assumption that the reactant concentration is invariable along the through-plane direction, the validity of which was demonstrated in the following discussion. Taking the cell using 4 mm-thick electrode as an example, Fig. 4 presents the bulk concentration of reactant Fe\(^{2+}\) in the anode at non-limiting state (cell voltage = 0.1 V) and limiting state (cell voltage = 0.4 V) respectively when the electrolyte containing 0.05 M Fe\(^{2+}\) and 0.75 M Fe\(^{3+}\) was fed to the cell at a flow rate of 45 mL min\(^{-1}\). When the cell current was far below the limiting current, as shown in Fig. 4a, the Fe\(^{2+}\) concentration was significantly lower in the region near the membrane due to the fact that the carbon felt conductivity is much higher than that of the liquid electrolyte. When the cell was operated at the limiting current, as shown in Fig. 4b, the distribution of Fe\(^{2+}\) concentration became one dimensional, i.e. invariable along x-direction, which is a basis in deriving Eq. 33.

Applicability of the correlation.—After the correlation of mass transfer coefficient is obtained, the accuracy of predicting the influence of velocity on mass transfer by this correlation should be investigated. Therefore, in addition to the experiment of measuring limiting currents, polarization behaviors of the cell fed with adequate reactants were also tested at various electrolyte velocities. And the corresponding simulations were conducted using the numerical model incorporating this obtained correlation.

| Electrolyte composition (mol L\(^{-1}\)) | Density (g mL\(^{-1}\)) | Viscosity (mPa s) | Measured conductivity (S m\(^{-1}\)) | Calculated conductivity \(^a\) (S m\(^{-1}\)) |
|----------------------------------------|--------------------------|-----------------|----------------------------------|---------------------------------|
| FeCl\(_2\)                              | FeCl\(_3\)               | HCl             |                                  |                                 |
| A                                      | 0                        | 0               | 2                               | 52.8                            | 73.1                           |
| B                                      | 0.05                     | 0.75            | 2                               | 1.249                           | 39.0                           | 102.1                          |
| C                                      | 0.4                      | 0.4             | 2                               | 1.13                            | 1.329                          | 43.0                           | 96.9                           |
| D                                      | 0.8                      | 0.8             | 2                               | 1.21                            | 1.737                          | 32.9                           | 120.8                          |

\(^a\)Based on infinitely dilute solution theory.
tested and simulated. Considering the fact that the ohmic resistance in the cell is insensitive to the electrolyte velocity, the cell voltage differences resulting only from tripling electrolyte flow rate were calculated and compared in the following discussion. Taking the cell with 4 mm-thick electrode as an example, Fig. 6a shows the predicted decrease of voltage loss at current densities ranging from 0 to 400 mA cm$^{-2}$ when the flow rate is increased from 30 to 90 mL min$^{-1}$. The experimentally measured decreases of voltage loss are presented as hollow squares in this figure. When the supplied electrolyte containing 0.4 M Fe$^{2+}$ and 0.4 M Fe$^{3+}$, the stoichiometry of reactant is about 2 at the current density of 400 mA cm$^{-2}$ and the flow rate of 30 mL min$^{-1}$. Apparently, the simulated decreases of voltage loss using the correlation $Sh = 1.68 \text{Re}^{0.9}$ are closer to the experimental data than those based on $Sh = 7 \text{Re}^{0.4}$ especially at high current densities. In further validation tests, the concentrations of both Fe$^{2+}$ and Fe$^{3+}$ were doubled to 0.8 M in the electrolyte, while keeping other testing conditions unchanged. As shown in Fig. 6b, the correlation $Sh = 7 \text{Re}^{0.4}$ underestimates the impact of electrolyte velocity on mass transfer in the electrode. In contrast, the simulated results based on $Sh = 1.68 \text{Re}^{0.9}$ again shows better agreements with the experimental data. As a result, the correlation $Sh = 1.68 \text{Re}^{0.9}$ is recommended in modeling mass transport in carbon felt electrodes when the superficial electrolyte velocity falls in the range from 2.5 to 15 mm s$^{-1}$.

Up to the above discussions, the ohmic resistance of the membrane plays a trivial role concerning mass transport controlled issues. In simulating the overall cell voltage, however, the membrane resistance is not negligible, which are functions of the composition and the concentration of the contacting liquid electrolyte. Due to the lack of first-hand-data, conductivities of the membrane equilibrated with hydrochloric acid solutions containing different amount of ferric/ferrous ions were estimated by fitting the experimentally measured cell voltage. As shown in Fig. 7, the measured cell voltages are compared with the simulated voltage curves at different feeding rates and concentrations. When the cell is fed with 0.4 M reactants, as shown in Fig. 7a, the simulated polarization curves agree well with the experimental data if the membrane conductivity is set as a constant of 6.3 S m$^{-1}$. When the inlet concentration is increased to 0.8 M, a good consistency between simulation results and experimental data is obtained as shown in Fig. 7b if the membrane conductivity is fixed as a constant of 4.6 S m$^{-1}$. The decline of membrane conductivity with the increase of metal ion concentration in the adjacent electrolyte has been reported and explained by Tang et al. In conclusion, the good agreements between measured and simulated voltages at varied flow rates and current densities suggested that the correlation $Sh = 1.68 \text{Re}^{0.9}$ is capable of capturing the influence of electrolyte velocity on mass transport and helpful in improving the accuracy of simulation in carbon felt electrodes, especially at high current densities.

**Conclusions**

In this work, a symmetric flow battery employing Fe$^{2+}$/Fe$^{3+}$ as redox couple at both anode and cathode is used as the testing cell to explore the correlation between the mass transfer coefficient and the electrolyte velocity for the carbon felt electrode by measuring limiting currents. The velocities from 2.5 to 15 mm s$^{-1}$ are selected as the concerned scope of this research, which is a frequently applied range of the electrolyte velocity in typical RFB designs. The dependence of mass transfer coefficient on the velocity is obtained as $k_m = 8.85 \times 10^{-4} \text{v}^{0.9}$, of which the corresponding dimensionless form is $Sh = 1.68 \text{Re}^{0.9}$. In addition, a 2-D steady numerical model incorporating this correlation is proposed to verify the applicability of this correlation. Under limiting conditions, the simulated results based on this correlation are in better agreement with the experimental data compared with those numerical estimations according to $Sh = 7 \text{Re}^{0.4}$. The applicability of the correlation $Sh = 1.68 \text{Re}^{0.9}$ under non-limiting conditions are also validated by comparing the simulated and experimentally obtained variations of voltage loss with the flow rate in the conditions of supplying adequate reactants. The electrolyte conductivities used in our numerical model are from experimental measurements rather than from estimations based on the...
assumption of infinite dilute solution, which are two to four times larger than the experimentally measured values. Such large overestimation of the electrolyte conductivity underestimates the ohmic loss significantly, which in turn strongly affects the accuracy of numerical simulations. According to a series of comparisons between simulated results and experimental data, it is reasonable to conclude that the expression $Sh = 1.68 \ Re^{0.9}$ embodies the dependence of mass transfer on the velocity ranging from 2.5 to 15 mm s$^{-1}$ for the carbon felt electrode.

**Figure 7.** Comparison of the measured and simulated polarization behaviors. The electrode thickness is 4 mm. And the electrolyte fed into the cell contains (a) 0.4 M Fe$^{2+}$ and 0.4 M Fe$^{3+}$; (b) 0.8 M Fe$^{2+}$ and 0.8 M Fe$^{3+}$.

| Symbol | Definition |
|--------|------------|
| $F$    | Faraday’s constant (C mol$^{-1}$) |
| $H_e$  | electrode thickness (m) |
| $i$    | current (A) |
| $i_c$  | current density (A m$^{-2}$) |
| $j$    | volumetric current density (A m$^{-3}$) |
| $k$    | reaction rate constant (m s$^{-1}$) |
| $k_m$  | mass transfer coefficient (m s$^{-1}$) |
| $L_e$  | electrode length (m) |
| $N$    | flux (mol m$^{-2}$ s$^{-1}$) |
| $n$    | unit normal vector of boundary surfaces |
| $R$    | universal gas constant (J mol$^{-1}$ K$^{-1}$) |
| $Re$   | Reynolds number ($Re = \frac{Du}{v}$) |
| $S$    | source term (mol m$^{-3}$ s$^{-1}$) |
| $Sh$   | Sherwood number ($Sh = \frac{k_m d_f}{n}$) |
| $T$    | temperature (K) |
| $u$    | ionic mobility (s mol kg$^{-1}$) |
| $V$    | voltage (V)/volume (m$^3$) |
| $v$    | velocity (m s$^{-1}$) |
| $W_e$  | electrode width (m) |
| $\varepsilon$ | porosity |
| $\phi$ | potential (V) |
| $\sigma$ | conductivity (S m$^{-1}$) |
| $\mu$ | dynamic viscosity (Pa s) |
| $\rho$ | density (kg m$^{-3}$) |
| $\alpha$ | charge transfer coefficient |
| $\omega$ | flow rate (m$^3$ s$^{-1}$) |
| $\eta$ | overpotential (V) |

**List of Symbols**

| Symbol | Definition |
|--------|------------|
| $a$    | specific surface area (m$^2$ m$^{-3}$) |
| $c_f$  | the fixed charge site concentration in the membrane (mol m$^{-3}$) |
| $D$    | diffusion coefficient (m$^2$ s$^{-1}$) |
| $d_f$  | carbon fiber diameter (m) |
| $E_0$  | standard equilibrium potential (V) |
| $E_{eq}$ | equilibrium potential (V) |

**Greek**

| Symbol | Definition |
|--------|------------|
| $\epsilon$ | porosity |
| $\phi$ | potential (V) |
| $\sigma$ | conductivity (S m$^{-1}$) |
| $\mu$ | dynamic viscosity (Pa s) |
| $\rho$ | density (kg m$^{-3}$) |
| $\alpha$ | charge transfer coefficient |
| $\omega$ | flow rate (m$^3$ s$^{-1}$) |
| $\eta$ | overpotential (V) |

**Subscripts**

| Symbol | Definition |
|--------|------------|
| $i$    | species $i \in \{Fe^{2+}, Fe^{3+}, H^+, Cl^-\}$ |
| $l$    | liquid or ionic |
| $lim$  | limiting state |
| $p$    | pore-phase |
| $s$    | solid or electronic |
| $x$    | x-direction |

**Superscripts**

| Symbol | Definition |
|--------|------------|
| $\text{eff}$ | effective value |
| $\text{in}$ | inlet |
| $\text{out}$ | outlet |
| $\text{m}$ | membrane |
| $\text{s}$ | electrode surface |

**References**

1. W. Wang, Q. T. Luo, B. Li, X. L. Wei, L. Y. Li, and Z. G. Yang, *Adv. Funct. Mater.*, 23, 970 (2013).
2. Z. G. Yang, J. L. Zhang, M. C. W. Kintner-Meyer, X. C. Lu, D. W. Choi, J. P. Lemmon, and J. Liu, *Chemical Reviews*, 111, 3577 (2011).
3. A. Z. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, and Q. Liu, *Journal of Applied Electrochemistry*, 41, 1137, (2011).
4. M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli, and M. Saleem, *Journal of the Electrochemical Society*, 158, R55 (2011).
5. Q. Xu, X. S. Zhao, and C. Zhang, *Electrochimica Acta*, 142, 61 (2014).
6. A. Tang, J. Ban, and M. Skyllas-Kazacos, *Journal of Power Sources*, 248, 154 (2014).
7. X. K. Ma, H. M. Zhang, C. X. Sun, Y. Zou, and T. Zhang, *Journal of Power Sources*, 203, 153 (2012).
8. D. J. Suarez, Z. Gonzalez, C. Blanco, M. Granda, R. Menendez, and R. Santamaria, *ChemSusChem*, 7, 914 (2014).
9. B. Li, M. Gu, Z. M. Nie, Y. Y. Shao, Q. T. Luo, X. L. Wei, X. L. Li, J. Xiao, C. M. Wang, V. Sprenlde, and W. Wang, *Nano Letters*, 13, 1330 (2013).
10. E. Agar, C. R. Dennison, K. W. Knehr, and E. C. Kumbur, *Journal of Power Sources*, 225, 89 (2013).
11. B. Sun and M. Skyllas-Kazacos, *Electrochimica Acta*, 37, 2459 (1992).
12. B. Sun and M. Skyllas-Kazacos, *Electrochimica Acta*, 37, 1253 (1992).
13. A. Storck, P. Robertson, and N. Ibl, *Electrochimica Acta*, 24, 373 (1979).
14. P. W. Appel and J. Newman, *AIChE Journal*, 22, 979 (1976).
15. P. S. Fedkiw and J. Newman, *International Journal of Heat and Mass Transfer*, 25, 935 (1982).
16. N. Vatistas, P. Marconi, and M. Bartolozzi, *Electrochimica Acta*, 36, 339 (1991).
17. B. Delanghe, S. Tellier, and M. Austruc, *Electrochimica Acta*, 35, 1369 (1990).
18. D. Schmal, J. Van Erkel, and P. Van Duin, *Journal of applied electrochemistry*, 16, 422 (1986).
19. K. Kinoshita and S. Leach, *Journal of The Electrochemical Society*, 129, 1993 (1982).
20. X. You, Q. Ye, and P. Cheng, *ECS Transactions*, 72, 187 (2016).
21. Y. K. Zeng, X. L. Zhou, L. An, L. Wei, and T. S. Zhao, *Journal of Power Sources*, 324, 738 (2016).
22. M. C. Tucker, K. T. Cho, and A. Z. Weber, *Journal of Power Sources*, 245, 691 (2014).
23. W. Wang, S. Kim, B. W. Chen, Z. M. Nie, J. L. Zhang, G. G. Xiu, L. Y. Li, and Z. G. Yang, *Energy & Environmental Science*, 4, 4068 (2011).
24. A. M. Pezeshki, R. L. Sacci, F. M. Delnick, D. S. Aaron, and M. M. Mench, *Electrochimica Acta*, 229, 261 (2017).
25. R. M. Darling and M. L. Perry, *Journal of the Electrochemical Society*, 161, A1381 (2014).
26. R. M. Darling and M. L. Perry, *ECS Transactions*, 53, 31 (2013).
27. R. Cartu, S. Palmaa, A. Polcario, and G. Tola, *Journal of applied electrochemistry*, 21, 793 (1991).
28. K. W. Knehr and E. C. Kumbur, *Electrochemistry Communications*, 13, 342 (2011).
29. Z. Tang, R. Svoboda, J. S. Lawton, D. S. Aaron, A. B. Papandrew, and T. A. Zawodzinski, *Journal of The Electrochemical Society*, 160, F1040 (2013).
30. K. W. Knehr, E. Agar, C. R. Dennison, A. R. Kalidindi, and E. C. Kumbur, *Journal of the Electrochemical Society*, 159, A1446 (2012).
31. W. M. Haynes, *CRC handbook of chemistry and physics*, CRC press (2014).
32. D. Stephenson, S. Kim, F. Chen, E. Thomsen, V. Viswanathan, W. Wang, and V. Sprenkle, *Journal of the Electrochemical Society*, 159, A1993 (2012).
33. L. Zhang, Z.-G. Shao, X. Wang, H. Yu, S. Liu, and B. Yi, *Journal of Power Sources*, 242, 15 (2013).