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Modeling the Transient Effects of Pore-Scale Convection and Redox Reactions in the Pseudo-Steady Limit

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We introduce theory to study the convection of active species with redox reactions at solid/solution interfaces within porous media, motivated by applications in energy storage devices where cyclic charge and discharge with recirculating flow requires the consideration of transient mass transfer. We show that under pseudo-steady conditions the coupled mass transfer problem involving redox of active species can be simplified to a linear, time-independent auxiliary problem. The proposed model is then solved numerically for porous media containing periodically spaced cylinders in crossflow. The results show three transport mechanisms depending on Péclet number Pe. Interactions between solid surfaces induced either by diffusion or advection produce spatial variation of surface flux. With Pe increasing from unity, advection initially causes diffusive flux to redistribute, causing a rise in Sherwood number Sh (non-dimensional mass transfer coefficient). The locations of flux maxima coincide with those of vorticity and strain rate for Pe above a certain "saturation" value. The variations of Sh with porosity and Pe are interpreted using a regime map that is defined based on the spatial variance of solute concentration. The auxiliary problem introduced provides a framework to predict mass transfer coefficients for arbitrary microstructures to guide the design of high-performance electrodes.

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Solute transport in porous media impacts many engineering and natural processes. Past studies¹⁻⁴ have shown that the microstructure of porous substrates and flow fields affect heterogenous catalytic and mixing controlled chemical reactions. One application of emerging importance for energy storage and conversion involves reactive flow through the porous electrodes of electrochemical devices, including redox flow batteries (RFBs)⁵⁻⁷ that use dissolved molecules to store and release electrons by way of faradaic electrochemical reactions. Such heterogeneous electrochemical reactions are driven by overpotential at the solid/solution interface, while also creating concentration gradients within pores during the production and consumption of active species. Similar processes arise in numerous engineering applications where pore-scale transport is important, including water purification^{8,9} and desalination,¹⁰ catalytic purification of industrial and vehicle exhaust,^{11,12} and transport of reactive minerals and biodegradation of living cells.^{13–15} Among these applications RFBs exhibit unique mass transfer characteristics owing to the inherently transient nature of charge/discharge cycles that ultimately impact feasible cycling rates. Attempts to increase RFB rate capability and efficiency have targeted enhancing pore-scale mass transfer using modified macroscopic flow fields,^{16,17} material selection^{18–20} and electrochemical aging of porous substrates,²¹ and functionalization of porous electrodes to increase active surface area by attaching nano-particles, 22-24 -rods, 25,26 -fibers, 20 tubes,²² and -walls²⁷ to micron-scale fibers. Building on earlier work,²⁸ recent attempts have been made to measure the pore-scale mass transfer coefficient h_m of RFB porous electrodes by fitting the variation of polarization with current density to predictions from transport models of varying fidelity.^{29–31} These reports have shown conflicting correla-tions for h_m versus flow velocity,^{29–31} as well as non-dimensional masstransfer correlations that are flow-field dependent.²⁹ Furthermore, the advent of alternative battery-electrode fabrication techniques (including additive manufacturing,³² templating,^{33–35} and biomineralization processes³⁶) motivates understanding the impact of porous electrode microstructure on solute transport "from the bottom up."

Understanding of connections between macro-homogenous/upscaled transport coefficients with the microstructure of porous media requires analysis of pore-scale transport phenomena. Early studies in this regard focused on the calculation of these coefficients by either homogenization/volume averaging³⁷ or percolation theory³⁸ for ordered and disordered porous structures. Later, application of the "method of moments" for curvilinear velocity fields enabled their calculation for more complex geometries.^{39,40} Another approach was proposed by decomposing pore scale concentrations into volume averaged and pore level variations.^{41,42} Both such approaches require the solution of characteristic eigenvalue problems, or closure problems, with validity only in the long-time limit with $t \gg b^2/D$, where b is the characteristic pore length and D is diffusivity of active species. For RFBs the temporal variation of electrode potential during charge/discharge cycling causes temporal concentration variation at the solid/solution interface. This concentration variation leads to time-varying local diffusion rates and affects the reaction rate at solid/electrolyte interfaces. To capture this unsteady effect, recently a model has been reported where diffusion of active species alone is considered in the absence of advection and migration.²¹ To the best of our knowledge, no model capable of capturing such transient effects, together with diffusion and advection, has previously been reported in the literature. In this study we introduce theory that not only captures such transient effects but also simplifies the corresponding conjugate masstransfer problem into an auxiliary problem. Here, the auxiliary problem transforms the associated unsteady partial differential equations (PDEs) of the conjugate problem into a steady PDE, while the coupled non-linear boundary conditions (BCs) that define the conjugate problem on the basis of redox-reaction stoichiometry/kinetics are decoupled into linear Dirichlet-type BCs. The validity of the proposed model is analyzed analytically and is presented through nondimensional parameters. In this analysis we also model porous media using a repetitive unit cell with periodic BCs that eliminates finite-size effects.

The developed mathematical model is then solved numerically to obtain the interstitial concentration field and the overall mass transfer coefficient for flow through reactive arrays of circular cylinders. The results are presented by correlating overall Sherwood number $\langle Sh \rangle$ with Péclet number *Pe*. Péclet number and overall Sherwood number are expressed based on cylinder diameter *d* respectively as $Pe = |\mathbf{u}_s|d/D$ and $\langle Sh \rangle = \langle h_m \rangle d/D$, where $\langle h_m \rangle$ is the average mass transfer coefficient. The superficial velocity \mathbf{u}_s is defined in terms of porosity ε (i.e., fluid volume fraction) and the local pore-scale velocity \mathbf{u}^{-} as $\mathbf{u}_s = (\varepsilon/V_f) \int \mathbf{u}^{-} dV_f$, where V_f is interstitial fluid volume. These results provide insights into mass transfer at low flow velocity, where past work has reported conflicting trends. In particular, many previous studies⁴³⁻⁴⁵ argued that at low Reynolds number (Re < 1) mass transfer rate is only a function of Pe, while $\langle Sh \rangle$ approaches a fixed, non-zero value for $Pe \rightarrow 0$. On the contrary, power law correlations, obtained by fitting experimental data, suggest a vanishing trend of $\langle Sh \rangle$ with decreasing $Pe.^{29,30,46}$

We also use the proposed model to study the effect of porous electrode microstructure on mass transfer coefficient by simulating different porosities, array arrangements, and inlet flow angles for regular arrays of cylinders in crossflow. The interactions between adjacent solid cylinders are classified by inspecting correlations between concentration, velocity, and flux fields. The results show three different transport regimes with a dramatic improvement in $\langle Sh \rangle$ for a specified range of *Pe*, as demonstrated on regime map in the *Pe* – ε plane that correlates the microscopic transport mechanisms with *Pe* and porosity ε (medium microstructure). The regime map not only rationalizes the scaling of $\langle Sh \rangle$ with *Pe*, but it also provides design guidelines for optimizing the performance of porous media with electrochemical reactions.

The organization of this article is as follows. We first present theory for the transient production of redox reactions facilitated by the diffusion and the flow of redox-active solution through periodic porous media. We subsequently define an auxiliary problem posed in terms of a single time-independent partial differential equation with linear boundary conditions, and we derive conditions for its validity based on non-dimensional parameters. Secondly, we describe the numerical methods used to simulate *Sh* and the concentration field that produces it for two-dimensional periodic porous media. Finally, we present results using this model to simulate pore-scale transport for crossflow through an array of cylinders with varied porosity, flow orientation, and Péclet number. These results are then used to predict overall mass transfer coefficients.

Mathematical Model: Auxiliary Problem Definition

In this work we simulate the transient pore-scale transport of active species using an auxiliary problem by which mass transfer coefficients can be determined by solving for the time-independent contribution $c_{h,i}(\mathbf{r})$ to the time- and space-dependent concentration field $c_i(\mathbf{r}, t)$ for solute i subject to a homogeneous Dirichlet condition at solid/solution interfaces. Here, r is position vector while t represents time. Further, we define this problem for a periodic microstructure to eliminate finitesize effects. In this section we present the governing equations for this auxiliary problem and derive conditions for its validity. Inspired by the transport processes that facilitate energy storage in redox flow batteries (RFBs), this auxiliary problem replicates a conjugate mass transfer problem under certain conditions of relevance to the RFB application. In the porous electrodes of an RFB the consumption of oxidized solute O is coupled to the production of reduced solute R by electron transfer from the solid electrode surface to the oxidized solute at the solid/solution interface (i.e., reduction), while the reverse process occurs when an electron is transferred from species R into the solid electrode. While such a conjugate problem is principally governed by a set of mass conservation equations (MCEs) with nonlinear boundary conditions (BCs), we show that an auxiliary problem governed by a single MCE with linear BCs can be used to obtain equivalent solutions in the limit of facile electrochemical kinetics and equal diffusion coefficients for O and R species. The details of this auxiliary problem are discussed subsequently to establish it with rigor in the context of pore-scale mass transport in RFB porous electrodes. In this analysis we assume that the reactive electrolyte is isochoric^a in which case the molar-volume averaged fluid velocity $\boldsymbol{u}^{\blacksquare} = \sum_{i} \bar{V}_{i} N_{i}$ is divergence free^{47,48} at the pore scale (i.e., $\nabla \cdot \boldsymbol{u}^{\blacksquare} = 0$). Here \bar{V}_{i} and N_{i} are the partial molar volume and flux of species *i* in the fixed reference frame.

Periodic concentration condition for periodic microstructures.— Because we seek to model porous microstructures that are periodic in space, BCs are imposed at the boundaries of the primary image of a given microstructure's periodic repeat unit to enable the simulation of an infinitely periodic system. For the present auxiliary problem, we invoke periodic BCs on the concentration field specified by $c_i(\mathbf{r}, t) = c_i(\mathbf{r} + \mathbf{R}, t)$ where **R** is an integer multiple of any combination of lattice vectors that define the microstructure's periodicity. This periodic BC inherently neglects macro-scale streamwise concentration gradients by enforcing them to be absent altogether. This assumption has certain conditions that assure its validity, and thus we derive those by introducing simplified analysis of RFB cycling dynamics. For this analysis we consider a fluid circuit connecting an electrode to a tank, such that electrolyte recirculates between the electrode and tank with a constant volumetric flow rate \dot{V} while electric current I is simultaneously applied to the electrode. Positive I induces the oxidation of redox-active molecules, while negative I induces their reduction. We assume that this electrode is separated from a counter-electrode by a membrane that selectively isolates redox-active molecules to the fluid circuit of interest. We subsequently apply mass conservation for each species *i* to the electrode (reactor) with volume V_r and to the tank with volume V_t . This analysis produces two coupled ordinary differential equations that govern the average concentrations in the reactor $\langle c \rangle_{i,r}$ and in the tank $\langle c \rangle_{i,t}$:

Reactor:
$$\frac{d}{dt} \left(V_r \langle c \rangle_{i,r} \right) = \dot{V} \langle c \rangle_{i,t} - \dot{V} \langle c \rangle_{i,r} + \frac{Is_i}{F}$$
 [1a]

Tank:
$$\frac{d}{dt} \left(V_t \langle c \rangle_{i,t} \right) = \dot{V} \langle c \rangle_{i,r} - \dot{V} \langle c \rangle_{i,t}$$
 [1b]

where s_i is the stoichiometric coefficient for species *i* with $s_0 = 1$ and $s_R = -1$ for a single electron-transfer reaction and *F* is Faraday's constant. We obtain solutions to the above equations using the Laplace transform subject to the initial conditions $\langle c \rangle_{i,r}(t = 0) = \langle c \rangle_{i,r}^0$ and $\langle c \rangle_{i,t}(t = 0) = \langle c \rangle_{i,t}^0$ (see derivation in Appendix A):

$$\langle c \rangle_{i,r}(t) = \langle c \rangle_{i,r}^{0} \left[v_r + v_t e^{-t/\tau} \right] + \langle c \rangle_{i,t}^{0} \left[v_t \left(1 - e^{-t/\tau} \right) \right] + \frac{Is_i}{F} \left[\frac{t}{V_r + V_t} + \frac{v_t^2}{\dot{V}} \left(1 - e^{-t/\tau} \right) \right]$$
 [2a]

$$\langle c \rangle_{i,t} (t) = \langle c \rangle_{i,r}^{0} \left[v_r \left(1 - e^{-t/\tau} \right) \right] + \langle c \rangle_{i,t}^{0} \left[v_t + v_r e^{-t/\tau} \right]$$

$$+ \frac{Is_i}{F} \frac{1}{(V_r + V_r)} \left[t + \tau \left(1 - e^{-t/\tau} \right) \right]$$
 [2b]

Here, τ is the harmonic mean residence time for flow through the tank and the reactor $\tau^{-1} = (1/V_t + 1/V_r)\dot{V}$. v_r and v_t are the fractions of total electrolyte volume in the reactor and tank, respectively: $v_r = V_r/(V_r + V_t)$ and $v_t = V_t/(V_r + V_t)$.

To satisfy the periodic BCs in the auxiliary problem of our ultimate interest streamwise concentration differences across the microstructure $(\Delta c)_{i,\parallel}^m$ should vanish in comparison with pore-scale concentration differences transverse to the mean flow $(\Delta c)_{i,\perp}^m$. The above solutions enable us to analyze the macroscopic streamwise concentration difference $(\Delta c)_{i,\parallel}$ across the electrode by recognizing its scaling $(\Delta c)_{i,\parallel} \sim (\langle c \rangle_{i,r} - \langle c \rangle_{i,t})$. Microscopic streamwise concentration

^aWe define a reactive isochoric fluid presently as having fixed partial molar volume \bar{V}_i for all species *i* (including solvent), while simultaneously requiring that solution volume be preserved during reactions that occur. In the context of an RFB using the reaction $O^{e_O} + n_e e^- \rightarrow R^{e_R}$, the latter condition requires that $\bar{V}_O = \bar{V}_R$. Such fluids are not necessarily incompressible because mass density can vary with solution composition.

gradients are assumed to equal macroscopic ones such that streamwise concentration differences at the pore-scale $(\Delta c)_{i,\parallel}^m$ can be expressed in terms of the corresponding macroscopic concentration difference $(\Delta c)_{i,\parallel}: (\Delta c)_{i,\parallel}^m \sim (\Delta c)_{i,\parallel}(b/L_r) \sim (\langle c_{i,r} \rangle - \langle c_{i,l} \rangle)(b/L_r)$, where *b* and L_r are the relevant microscopic and macroscopic length scales. For $(\Delta c)_{i,\perp}^m$ we consider the characteristic difference in concentration across a pore as $(\Delta c)_{i,\perp}^m \sim (c_{s,i} - \langle c_i \rangle)$, where $c_{s,i}$ is the local concentration at the solid/solution (electrolyte) interface, $\langle c_i \rangle = (1/V_f) \int c_i dV_f$ is the volume-averaged concentration within the microstructure, and V_f is interstitial fluid volume. Using these scaling relationships, we express a non-dimensional parameter defined as the characteristic ratio of the streamwise and transverse concentration gradients at the pore scale $(\Delta c)_i^*$:

$$(\Delta c)_{i}^{*} = \frac{b}{L_{r}} \cdot \frac{\langle c \rangle_{i,r} - \langle c \rangle_{i,t}}{c_{s,i} - \langle c \rangle_{i}} \sim \frac{(\Delta c)_{i,\parallel}^{m}}{(\Delta c)_{i,\perp}^{m}}$$
[3]

Thus, for $(\Delta c)_i^* \ll 1$ streamwise concentration gradients are negligible.

To determine how $(\Delta c)_i^*$ varies with Péclet number and other nondimensional parameters we consider that the RFB initially has uniform concentration such that $\langle c \rangle_{i,r}^0 = \langle c \rangle_{i,l}^0$. After substitution of the timedependent solutions for $\langle c \rangle_{i,r}$ and $\langle c \rangle_{i,l}$ into $(\Delta c)_i^*$ and subsequent simplification, we find the following expression for $(\Delta c)_i^*$:

$$(\Delta c)_i^* = (a \cdot b) \frac{\langle Sh \rangle}{Pe} \left[\frac{1 - 1/\alpha}{(1 + 1/\alpha)^2} \right] \left(1 - e^{-(1 + 1/\alpha)(b/L_r)Pe \cdot Fo} \right) \quad [4]$$

 $(\Delta c)_i^*$ is expressed in terms of the following non-dimensional parameters:

• $\alpha = V_t / V_e$ is the tank-to-electrode electrolyte volume ratio.

• $Pe = |\mathbf{u}_s|b/D_i$ is the Péclet number expressed in terms of the superficial velocity \mathbf{u}_s and the diffusion coefficient D_i .

• $\langle Sh \rangle = \langle h_m \rangle b/D_i$ is the overall Sherwood number expressed in terms of the average pore-scale mass transfer coefficient $\langle h_m \rangle$.

• $Fo = D_i t/b^2$ is the Fourier number.

• $a \cdot b$ is the product of volumetric surface area a and the characteristic microscopic length-scale b.

Here, the dependence on applied current *I* is eliminated by using the film theory of mass transport: $(c_{s,i} - \langle c \rangle_i) = Is_i/(\langle h_m \rangle F)$.

Henceforth, we assume a large RFB tank (i.e., $\alpha \to \infty$) to produce the following expression:

$$(\Delta c)_i^* = (a \cdot b) \left(\langle Sh \rangle / Pe\right) \left(1 - e^{-(b/L_r)Pe \cdot Fo}\right)$$
[5]

For $(b/L_r)Pe \cdot Fo \rightarrow \infty$ this expression approaches $(\Delta c)_i^* = (a \cdot b)(\langle Sh \rangle / Pe)$. Conversely, in the limit of $(b/L_r)Pe \cdot Fo \rightarrow 0$ Eq. 5 approaches $(\Delta c)_i^* = (a \cdot b)(b/L_r)Pe \cdot Fo$ by application of L'Hospital's rule. In summary we find the following result for $(\Delta c)_i^*$ in these asymptotic limits:

$$(\Delta c)_i^* = \begin{cases} (a \cdot b) (b/L_r) \langle Sh \rangle Fo, & \text{for } (b/L_r) Pe \cdot Fo \to 0\\ (a \cdot b) (\langle Sh \rangle / Pe), & \text{for } (b/L_r) Pe \cdot Fo \to \infty \end{cases}$$
[6]

Assuming that $a \cdot b$ is of order unity, the effect of streamwise concentration gradients becomes negligible (i.e., $(\Delta c)_i^* \ll 1)$ for $\langle Sh \rangle \ll (L_r/b)/Fo$ and $\langle Sh \rangle \ll Pe$ in the respective limits of low and high *Pe*.

Sufficient supporting electrolyte approximation.—Active species transport in electrolyte within porous electrodes occurs by advection, diffusion, and electromigration (i.e., drift). However, the contributions of these driving forces relative to total species flux depend on electrolyte composition. Electromigration is a transport process driven by electric potential gradients in solution. For the present theory we neglect electromigration contributions to flux by assuming that a sufficient concentration of highly mobile supporting ions is dissolved in addition to active species. Such a condition is satisfied by requiring that the transference number $t_j = z_j^2 m_j c_j / \sum_i z_i^2 m_i c_i$ for active species *j* is small (i.e., $t_j \ll 1$), where z_i and m_i are the mobility and charge number of ion *i*.

Decoupling conjugate transport in the pseudo-steady limit.—The assumptions that were qualified in the two preceding sub-sections enable the specification of an advection-diffusion transport problem (i.e., neglecting electromigration) with a periodic microstructure having a periodic concentration field. Here, we also assume that Fickian diffusion prevails with a constant diffusion coefficient, such that flux can be written in the fixed reference frame as $N_i = u^{\blacksquare} c_i - D_i \nabla c_i$. Thus, the governing equations for the oxidized and reduced species can be expressed under these assumptions as:

$$\frac{\partial c_o}{\partial t} + \nabla \cdot \left(\boldsymbol{u}^{\blacksquare} \boldsymbol{c}_O - \boldsymbol{D}_O \nabla \boldsymbol{c}_O \right) = 0$$
 [7a]

and

$$\frac{\partial c_R}{\partial t} + \nabla \cdot \left(\boldsymbol{u}^{\blacksquare} c_R - D_R \nabla c_R \right) = 0$$
 [7b]

The dynamics embodied by these equations evolve in a coupled manner as a result of the conjugate production and consumption of active species when electron transfer occurs at solid/electrolyte interfaces. These processes occur subject to reaction stoichiometry: $O^{z_0} + e^- \rightleftharpoons R^{z_R}$. In equation form conjugation is facilitated by constraining the local fluxes along the normal direction *n* of surface *s* to be equal in magnitude and opposite in direction:

$$D_O \left. \frac{\partial c_O}{\partial n} \right|_s = -D_R \left. \frac{\partial c_R}{\partial n} \right|_s \tag{8}$$

where D_i is the Fickian diffusion coefficient of species *i*. Furthermore, we assume fast reaction kinetics, such that reaction overpotential $\eta = \phi_s - \phi_e - \phi_{eq}$ is small ($\eta \approx 0$). Here, solid $\phi_s(t)$ and electrolyte $\phi_e(t)$ potentials are assumed to be time-dependent but uniform in space.^b Under such conditions the applied half-cell potential $E_{cell}(t) = \phi_s - \phi_e$ is equal to the equilibrium potential ϕ_{eq} , which is expressed in terms of active species concentrations $c_{O/R}$ using the Nernst equation.⁴⁹

$$E_{cell}(t) = \phi_{eq}(t) = \phi_{eq}^{0} + (RT/F)\ln(c_{O}/c_{R})$$
[9]

Here we show that, under certain limiting conditions of high relevance to RFBs, the preceding *time-dependent, conjugate* mass transport problem can be solved using a *time-independent* auxiliary problem defined by a *single* MCE subjected to homogeneous Dirichlet boundary conditions and having a certain volumetric source term. For this auxiliary problem we posit the following decomposition of the concentration field $c_i(\mathbf{r}, t)$, where surface concentration $c_{s,i}(t)$ takes on a uniform but time-dependent form: $c_i(\mathbf{r}, t) = c_{s,i}(t) + c_{h,i}(\mathbf{r}, t)$.^c Here, $c_{h,i}(\mathbf{r}, t)$ is defined as the homogeneous contribution to the concentration field. Using this approach, we express the MCE for species *i* in terms of $c_{h,i}$ as:

$$\frac{\partial c_{h,i}}{\partial t} + \nabla \cdot \left(\boldsymbol{u}^{\bullet} \boldsymbol{c}_{h,i} - \boldsymbol{D}_i \nabla \boldsymbol{c}_{h,i} \right) = -\sigma_i$$
[10]

where σ_i is the rate of change of surface concentration, i.e., $\sigma_i = dc_{s,i}/dt$. Together with this MCE, a homogeneous Dirichlet boundary condition for $c_{h,i}|_s \equiv c_i|_s - c_{s,i} = 0$ enforces the uniformity of surface concentration at solid/electrolyte interfaces at each instant in time. If σ_i varies slowly enough and enough time elapses for solute molecules to diffuse across streamlines, $c_{h,i}$ becomes a time-independent field. This limit, which we refer to as pseudo-steady, is satisfied for $t \gg b^2/D_i$, and it enables the specification of $c_{h,i}(\mathbf{r})$ using a time-independent equation:

$$\nabla \cdot \left(\boldsymbol{u}^{\blacksquare} \boldsymbol{c}_{h,i} - \boldsymbol{D}_i \nabla \boldsymbol{c}_{h,i} \right) = -\sigma_i$$
[11]

Until this point we have assumed that the surface concentration of either active species is uniform in space at any given instant in time, but

^bThese potentials are uniform in space when the representative conductivity for that phase is large.

^cWe note that this decomposition is different than that used in Ref. 41. For the present auxiliary problem we decompose solute concentration using a spatially uniform surface concentration, whereas the decomposition in Ref. 41 uses the average concentration inside the pore with surface concentration varing subject to a Robin-type BC.

	Conjugate Problem	Auxiliary Problem
MCEs	$\frac{\partial c_O}{\partial t} + \nabla \cdot (\boldsymbol{u}^{\blacksquare} c_O - D_O \nabla c_O) = 0$	$\nabla \cdot (\boldsymbol{u}^{\blacksquare} \boldsymbol{c}_{h,O} - D\nabla \boldsymbol{c}_{h,O}) = -\sigma$
	$\frac{\partial c_R}{\partial t} + \nabla \cdot (\boldsymbol{u}^{\blacksquare} c_R - D_R \nabla c_R) = 0$	$\nabla \cdot (\boldsymbol{u}^{\blacksquare}c_{h,R} - D\nabla c_{h,R}) = +\sigma$
BCs	$D_O \frac{\partial c_O}{\partial n} _s = -D_R \frac{\partial c_R}{\partial n} _s$	$c_{h,O} _s = 0$
	$\phi_{eq}^0 + \frac{RT}{F} \ln(\frac{c_0}{c_R}) _s = \phi_{eq}(t)$	$c_{h,R} _s = 0$
Coupling	Coupled by BCs	Decoupled

Table I. Summary and comparison of equations governing the conjugate and auxiliary mass transfer problems.

in general there is no such mathematical support for this assumption. Here we examine the set of MCEs and BCs that govern $c_{h,i}$ to reveal the particular conditions under which its solution is equivalent to the conjugate problem. Defining the variable $c'_{h,i} = c_{h,i}/\sigma_i$ we have:

MCE:
$$\nabla \cdot \left(\boldsymbol{u}^{\bullet} \boldsymbol{c}_{h,O}^{\prime} - D_{O} \nabla \boldsymbol{c}_{h,O}^{\prime} \right) = -1$$

BCs: $\boldsymbol{c}_{h,O}^{\prime} |_{s} = 0$ and periodic [12a]

MCE:
$$\nabla \cdot (\boldsymbol{u}^{\bullet} \boldsymbol{c}_{h,R}^{\prime} - D_R \nabla \boldsymbol{c}_{h,R}^{\prime}) = -1$$

BCs: $\boldsymbol{c}_{h,R}^{\prime}|_{c} = 0$ and periodic [12b]

Inspection reveals that $c'_{h,O} = c'_{h,R} = c'_{h}$ is satisfied when $D_O = D_R = D$. Thus, we choose σ_i to determine $c_{h,O}$ and $c_{h,R}$ that also satisfy the conjugate condition at the solid/electrolyte interface in the pseudo-steady limit:

$$D\left.\frac{\partial c_O}{\partial n}\right|_s = -D\left.\frac{\partial c_R}{\partial n}\right|_s = \sigma_O D\left.\frac{\partial c'_h}{\partial n}\right|_s = -\sigma_R D\left.\frac{\partial c'_h}{\partial n}\right|_s \qquad [13]$$

From this expression we deduce that $\sigma_O = -\sigma_R = \sigma$ enforces the conjugate condition exactly. Furthermore, the uniform surface concentrations $c_{s,O}(t)$ and $c_{s,R}(t)$, chosen *a priori*, satisfy the condition that equilibrium potential (ϕ_{eq} from the Nernst equation) is uniform on solid/electrolyte interfaces, thus satisfying the second BC of the conjugate mass transport problem. Therefore, this analysis proves that, in the pseudo-steady limit, the present auxiliary problem posed separately for R and O species decouples the conjugate problem when kinetics are facile and when redox-active species possess identical diffusion coefficients. A summary of the governing partial differential equations, boundary conditions, and coupling conditions is shown in Table I.

Numerical Solution to the Auxiliary Problem

Model domain.—In this section, we describe the numerical methods used to solve the auxiliary problem described in the preceding section for a two-dimensional microstructure. Since the auxiliary problem decouples the heterogenous redox reaction for the oxidized and reduced species, only the production of R (reduction of O) due to electron transfer to the electrode is considered. For brevity the subscript R, which indicates reduced species, is dropped hereafter. The porous medium simulated here is a regular array of unconsolidated cylinders that are infinitely long along the z-axis (Figure 1a). A unit cell is selected to represent the array of circular cylinders as shown in Figure 1b. Figure 1c shows dimensions and the angular direction θ about the unit cell's centroid where the center of the primary solid cylinder coincides. All angles are measured from the negative x-axis, and counterclockwise rotation is taken as positive. Two different array configurations of the cylinders (square and rectangular) are studied along with different superficial velocity orientations θ_{f} .

The porosity ε of the unit cell is defined as the ratio of interstitial fluid volume V_f to the volume of entire unit cell V_{cell} as $\varepsilon = V_f/V_{cell}$. Five different porosity values are simulated by changing cylinder diameter, ranging from $\varepsilon = 0.446$ to 0.874. Fifteen different superficial velocities are studied with *Pe* ranging from 0.01 to 840. For rectangular arrays, the *L/H* ratio is varied from 1.5 to 2.5 by keeping the *y*-dimension *H* unchanged, while using a common flow with *Pe* = 420 that is aligned with either of the coordinate axes ($\theta_f = 0$ or $\pi/2$). For inclined flows, the least porous microstructure of rectangular arrays ($\varepsilon = 0.446$) is subjected to a constant superficial velocity (*Pe* = 420) while θ_f is varied between 0 and $\pi/4$.

Numerical discretization and solution methods.--We model the interstitial velocity field u^{\blacksquare} assuming a Newtonian, isochoric solution with constant viscosity in the creeping flow limit, where inertial effects are negligible ($Re \leq 0.05$, where Re is Reynolds number). To ensure the conservation of fluid volume and momentum in the present isochoric flow, we pose the vorticity transport equation (derived by application of the curl operator, $\nabla \times$, to the Navier-Stokes equations) in terms of a stream function ψ to enforce linear momentum conservation: $\nabla^4 \psi = 0$. The stream function ψ defines the components of velocity as $u_x^{\bullet} = \partial \psi / \partial y$ and $u_y^{\bullet} = -\partial \psi / \partial x$, thus automatically satisfying volume conservation for the isochoric flow $(\nabla \cdot u^{\blacksquare} = 0)$. Periodic jump/fall BCs are applied at unit-cell boundaries using the following expression: $\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R}) + (\mathbf{R}/|\mathbf{R}|) \cdot \Delta \psi$. Here $\Delta \Psi = \Delta \Psi_x \hat{i} + \Delta \Psi_y \hat{j}$ represents the jump/fall in Ψ across unit cell boundaries in the x and y directions. The components of $\Delta \psi$ are chosen to produce a certain volumetric flow rate of the solution. No slip $(\partial \psi / \partial n = 0)$ and impermeability $(\partial \psi / \partial s = 0)$ conditions are applied at the surface of solid cylinders. An additional boundary condition is applied at the cylinder surface by considering that no lift is generated perpendicular to u_s . Using the Kutta-Joukowski⁵⁰ theorem this condition is expressed mathematically using the definitions of the circulation Γ and the stream function ψ as $\Gamma = \oint_c u^{\blacksquare} \cdot ds = -\oint_c \nabla^2 \psi dA_s = 0$.



Figure 1. Geometry of domain. (a) Flow through regular array of reactive circular cylinders, (b) selection of a repetitive unit cell, and (c) a repetitive unit cell with geometric parameters labeled.



Figure 2. Contour plot of non-dimensional diffusive flux j_d for flow with $\theta_f = 0$ and either (a) $\varepsilon = 0.446$ or (b) $\varepsilon = 0.874$. The numerical values at the middle of contours show *Pe* values. Variation of diffusive flux on the particle surface $j_{d,s}^*$ with *Pe* for (c) $\varepsilon = 0.446$ and (d) $\varepsilon = 0.874$.

The vorticity transport equation and its associated boundary conditions were discretized spatially using a 2^{nd} order accurate finite difference method, where ψ was solved at each node of a rectangular grid overlaid on the unit cell. A direct linear solver was used to solve the resulting discretized system of algebraic equations.

For the auxiliary problem governing pore-scale mass transfer, we discretized the MCE for species R using the finite volume method (FVM), where fluxes at mesh faces are approximated using central differencing. A direct linear solver was used to solve for c_h . To ensure numerical stability subject to the Courant–Friedrichs–Lewy condition,⁵¹ mesh spacing parameters (Δx and Δy) were selected such that the magnitude of the grid level Péclet numbers ($Pe_x = u_x^{-} \Delta x/D$ and $Pe_y = u_y^{-} \Delta y/D$) were less than 0.5. Verification of the implemented model and its validation based on analytical theory is included in Appendix B.

Results and Discussion

Here, we present and analyze simulations of transient mass transfer in periodic porous media comprised of cylinders in crossflow through the use of the auxiliary problem introduced in the preceding sections. From our analysis of the auxiliary problem we recall that the auxiliary problem is valid for $t >> b^2/D$ in the respective limits of creeping flow, fast redox kinetics, and equal diffusivity of oxidized and reduced species. The effects of varying porosity, Péclet number, and flow inclination on local concentration and diffusive flux distributions are explored in the first sub-section. In the subsequent sub-section we analyze the statistical variance of concentration fields to construct a transport regime map that we ultimately use to interpret the variations of non-dimensional mass transfer coefficient with *Pe* and porosity.

Analysis of diffusive flux and concentration distributions.—Bulk flow through porous microstructures causes interstitial concentration and diffusive flux fields to redistribute spatially. In this section we investigate the redistribution of these fields and how they are affected by porosity, Péclet number, and flow direction. Figures 2a, 2b show the distribution of the diffusive flux magnitude normalized by its maximum value within the fluid for $\varepsilon = 0.446$ and 0.874 with different *Pe* values. Here, diffusive flux is $j_d = |-D\nabla c|$. In Figs. 2c, 2d the diffusive flux distribution on cylinder surfaces is shown as $j_{d,s}^* = j_{d,s}/\langle j_{d,s} \rangle$, where $\langle j_{d,s} \rangle$ is the area-averaged diffusive flux defined by $\langle j_{d,s} \rangle = -1/A_s \int D\nabla c \cdot dA_s$.

For $Pe \leq 1$ the diffusive flux field is symmetric about both axes in the bulk (Figures 2a, 2b) and on surfaces (Figures 2c, 2d), resembling that of pure diffusive transport when Pe = 0. This finding indicates that the effect of advection is insignificant for $Pe \leq 1$ and that diffusion dominates solute transport in that regime. For Pe > 1 advection distorts the diffusive flux field, and it becomes asymmetric with respect to the axis perpendicular to bulk flow. Figure 2a ($\varepsilon = 0.446$) shows that the initial effect of advection (i.e., for Pe = 4.2 to 84) causes j_d to redistribute locally. As Pe increases from 84 to 840, diffusive flux increases in magnitude throughout the interstitial fluid volume without substantial redistribution. Similar results are obtained for cases with $\varepsilon \leq 0.678$ that are not shown for brevity. A more gradual, yet similar, transition in the j_d field is observed for $\varepsilon \geq 0.788$ (Figures 2b). We note that, in all instances, the maximum local diffusive flux is always obtained on cylinder surfaces and not in the bulk of the solution.

Further, on the solid surface a non-uniform distribution of diffusive flux $j_{d,s}$ is evident for all *Pe* and ε values that are shown in Figures 2c, 2d. The surface diffusive fluxes $j_{d,s}$ were calculated based on local solute flow rates through each finite stair-stepped surface and by dividing each flow rate by a corresponding curved surface area as $j_{d,s} = -D\nabla c \cdot \Delta A_s / \{(d/2)\Delta \theta\}$. Here, *d* is the diameter of solid cylinders and $\Delta \theta$ is the angular span of each stair-stepped surface. Here, $j_{d,s}$ is normalized as in Figures 2a, 2b $(j_{d,s}^* = j_{d,s} / \langle j_{d,s} \rangle)$. Due to the approximation of stair-stepped fluid/solid interfaces, the distribution of $j_{d,s}^*$ can show artificial fluctuations. To eliminate such fluctuations the local fluxes were averaged by conserving net molar flow over circular segments with angular span $\approx 6^\circ$ to preserve the topology of $j_{d,s}^*$ distributions (i.e., maxima and minima). This smoothing technique conserved total solute mass flow rate within $10^{-11}\%$ of $\langle j_{d,s} \rangle \pi d$.

The variations of diffusive flux with increasing *Pe* at solid surfaces are accompanied by variations in concentration within the interstitial fluid volume. To classify the effect of interactions between adjacent cylinders on surface flux distributions we attempt to find correspondence between concentration and velocity fields. Using this approach we ultimately classify interactions as either strong or weak, where strong interactions produce more nonuniformity in surface flux. In addition to the strength of interactions, we also classify the transport mechanism by which such interactions are produced (i.e., by diffusion or advection).



Figure 3. Contour of \tilde{c} at different *Pe* for (a) $\varepsilon = 0.446$ and (b) $\varepsilon = 0.874$. Variation of c^* with *Pe* for (c) $\varepsilon = 0.446$ and (d) $\varepsilon = 0.874$ along the *y* (left panel), downstream-*x* (middle panel), and upstream-*x* (right panel) directions.

For $\varepsilon = 0.446$ and $Pe \leq 1$, the distribution of $j_{d,s}^* = j_{d,s}/\langle j_{d,s} \rangle$ shows four peaks comprising local maxima at $\theta = \pi/4$, $3\pi/4$, $5\pi/4$ and $7\pi/4$. This nonuniform distribution results from the diffusive interactions between cylinders, and the peaks correspond to the angular positions of points with most extreme (lowest) concentrations. For $\varepsilon = 0.874$ and $Pe \le 1$, the distributions of $j_{d,s}^*$ are more uniform due to the diminishing interactions between the concentration fields around adjacent solid cylinders when cylinders are separated by sufficient distance. Thus, we conclude that, for diffusion-dominated transport, the cylinders in low porosity media experience strong diffusive interactions (SDIs), while cylinders in high porosity media experience weak diffusive interactions (WDIs). For both low and high porosity media (Figures 2c, 2d) the $j_{d,s}^*$ distribution becomes more nonuniform with increasing Péclet number. During this transformation $j_{d,s}^*$ decreases weakly upstream of the cylinder, whereas in the downstream region $j_{d,s}^*$ decreases significantly. In the midstream regions (i.e., between upstream and downstream regions) $j_{d,s}^*$ increases substantially with increasing *Pe*. A gradual shift occurs for the location of $j_{d,s}^*$ maxima toward $\theta = \pi/2$ and $3\pi/2$ with increasing *Pe* (Figures 2c, 2d). Further, we observe that for both low and high porosity media advection influences the distribution of $j_{d,s}^*$ to a diminishing degree for very large *Pe*, showing an insignificant shift of $j_{d,s}^*$ maxima.

To identify the effect of advection on interactions between cylinders for Pe > 1, we analyze the variations of concentrations by examining the concentration deviations between cases simulated at non-zero Pe with that simulated at Pe = 0 for the same microstructure. To do this we define the following non-dimensional concentration deviation \tilde{c} in terms of local c, surface c_s , and volume-averaged $\langle c \rangle$ concentrations: $\tilde{c} = c^*|_{Pe>0} - c^*|_{Pe=0}$, where $c^* = (c - c_s)/(\langle c \rangle - c_s)$ is nondimensionalized local solute concentration. \tilde{c} can be interpreted as a change in the driving force for diffusion relative to pure diffusion (Pe = 0) that is induced by advection with non-zero Pe. Hence, regions with negative \tilde{c} promote diffusion away from solid surfaces, while regions with positive \tilde{c} suppress it. Accordingly, we refer to these regions as positively (PAZs) and negatively (NAZs) affected zones, respectively. The location of NAZs downstream of the solid shows that solutes accumulate there. For low-porosity media advection causes solute accumulation where pore dimensions are largest in the downstream region (i.e., along $\theta \approx 3\pi/4$ and $5\pi/4$), as shown in Figure 3a. For higher porosity media (Figure 3b), larger pores allow solute to accumulate downstream of the cylinder along $\theta \approx \pi$. This local accumulation of solute, which results from advection, retards the flux at the next downstream cylinder surface (Figure 2d, Pe = 200 for example) by increasing the surrounding solute concentration (Figure 3b, Pe = 200

for example). We refer to this correspondence of reduced flux and solute accumulation at high Pe as an advective interaction. For high porosity media the accumulation of solute immediately upstream of the next downstream cylinder reduces surface flux. Further, for high porosity media solute transport at the location of solute accumulation is retarded by the low flow velocity there, resulting in a strong advective interaction (SAI) between adjacent cylinders. For low porosity media the flow velocity at the location of solute accumulation transports solute more effectively compared to high porosity media. The enhanced flow velocity in regions of accumulation is a result of two factors: (1) the location of solute accumulation is far from stagnation points (defined by $u^{\blacksquare} = 0$) located on the cylinder surface and (2) low porosity media show higher mean interstitial velocity than high porosity media for the same superficial velocity. This advective transport limits interactions between adjacent cylinders, resulting in a weak advective interaction (WAI) between them.

Evidence for the interactions described above is also reflected by the axial and transverse variations of concentration c^* in space at various *Pe* values (Figures 3c, 3d). We examine these profiles along the particular paths shown by red dashed lines in Figure 3b (Pe = 0.01) within the simulated fluid domains. We note that the definition of c^* results in negative correlation between c^* and c (i.e., an increase in c^* corresponds to a decrease in c). An exponential concentration variation with position is observed in the transverse direction (i.e., y direction) for all cases (left panels in Figures 3c, 3d). At the pore center corresponding to $(y - d/2)/b_y = 1$, the concentration gradient vanishes due to the symmetry of the porous medium. A significant increase in surface concentration gradient is produced with increasing Pe that ultimately increases diffusion on the midstream surfaces of cylinders. From the axial (x-direction) variation of c^* it is evident that, for low-porosity media, up- and down-stream regions are relatively unaffected by advection due to the WAI between adjacent cylinders (middle and right panels in Figures 3c). In contrast, high-porosity media show reduced diffusion rates with increasing Pe in both the up- and down-stream directions because of a SAI between cylinders (middle and right panels in Figures 3d).

Figures 3a and 3b show that the mean location of PAZs gradually moves toward $\theta = \pi/2$ and $\theta = 3\pi/2$ with increasing *Pe*. Similar observations can be made from the surface flux distributions in Figures 2c and 2d, where the locations of flux maxima do not move with further increase in *Pe* after moving to $\theta = \pi/2$ and $3\pi/2$. The diminishing effect of bulk flow on j_d redistribution with increasing *Pe* and the termination of flux maxima locations indicates that the effect of bulk flow gradually saturates. The minimum *Pe* correspond-



Figure 4. Contour of (a) strain rate λ^* and (b) vorticity ω^* for flow through square array of cylinders with different porosity ($\theta_f = 0, Pe = 100$).

ing to this saturation is called Pe_{sat} , a parameter that we quantify in the next sub-section. Here, we seek to understand what factors influence the locations of flux maxima after saturation. To do this we calculated two components of fluid deformation: (i) strain rate $\lambda = 1/2(\partial u_x^{T}/\partial y + \partial u_y^{T}/\partial x)$ describing the rate of fluid element stretching and (ii) vorticity $\omega = 1/2(\partial u_x^{T}/\partial y - \partial u_y^{T}/\partial x)$ describing the rotation rate of fluid elements. Figures 4a, 4b show the contours of λ^* and ω^* for horizontal flow through a square array with $Pe > Pe_{sat}$, where "*" indicates normalization by a maximum value. We observe that the locations of maximum λ^* and ω^* occur at $\theta = \pi/2$ and $\theta = 3\pi/2$, corresponding to the same locations of flux maxima observed earlier (see Figures 2a, 2b).

While the maxima of λ^* and ω^* coincide with flux maxima for horizontal flow through cylinder arrays, these results alone do not guarantee their correlation for other mean flow orientations and microstructures. To test whether this correlation of extrema holds generally we varied the mean flow orientation θ_f and simulated concentration and flux fields with *Pe* above *Pe_{sat}*. The contours of j_d , λ^* , and ω^* are shown in Figures 5a–5c respectively for three different mean flow orientations. In all three cases the locations of global maxima in diffusive flux coincide with those of fluid deformation. The variations of j_d^* , λ^* , and ω^* are also shown on the solid surface as a function of angular position θ_r for five different mean flow orientations (Figures 5d–5f). The angular position θ_r is defined relative to the mean flow orientation θ_f such that the stagnation point is always at $\theta_r = \theta - \theta_f = 0$. We observe that the distribution of surface diffusive flux in Figure 5d is symmetric about the mean flow direction for horizontal flow ($\theta_f = 0$), but it becomes asymmetric for other flow inclinations excluding $\theta_f = \pi/4$. For $\theta_f = \pi/4$ the distribution becomes symmetric again due to the symmetry of the microstructure about u_s . Similar symmetries are exhibited by the global maxima of λ_s^* and ω_s^* in Figures 5e, 5f with coincidence of the location of maximum values.

Aside from varying mean flow orientation, we also varied the arrangement of cylinders in the array in order to test whether the locations of global maxima for diffusive flux coincide with those of fluid deformation when microstructure is changed. To do this we simulated mass transfer in rectangular arrays of cylinders where the distance between neighboring cylinders was different in the x and y directions. Such microstructure allows the location of maximum fluid deformation to be different from the location of minimum separation between adjacent solid surfaces, unlike cylinders arranged in square arrays where these locations coincide. The contours of j_d , λ^* , and ω^* are shown for two different array arrangements in Figure 6 subjected to flows with two different mean orientations ($\theta_f = 0$ and $\pi/2$). These contours show that for horizontal flow ($\theta_f = 0$) the locations of maximum j_d , λ^* , and ω^* are $\theta = \pi/2$ and $3\pi/2$. Changing the flow direction from $\theta_f = 0$ to $\theta_f = \pi/2$, the locations of maximum j_d , λ^* , and ω^* changes to $\theta = 0$ and $\theta = \pi$, while the angular locations of minimum separation between nearest-neighbor cylinders remain at $\theta = \pi/2$ and $3\pi/2$. These results further confirm our conclusion that the locations of global maxima for diffusive flux are determined by those of fluid deformations.⁵² While this conclusion is valid for regular arrays of cylinders, we note that further study is needed to confirm this conclusion for arbitrary microstructures.

Pore-scale transport regime map and mass transfer coefficient.— In this section, we present a pore-scale transport regime map that correlates microscopic solute transport mechanisms with external flow conditions given by *Pe* and porous medium microstructure given by porosity ε . We subsequently use this map to interpret the variations of Sherwood number with *Pe* and ε . The spatial variations of each solute concentration field are quantified using the volume-averaged variance of c^* , defined as $\operatorname{Var}(c^*) = (1/V_f) \int (c^* - \langle c^* \rangle)^2 dV_f$. A contour map of $\operatorname{Var}(c^*)$ versus *Pe* and ε in Figure 7a was constructed using 75 different simulations with various ε and *Pe* values by using the piecewise



Figure 5. Contour of dimensionless (a) diffusive flux, (b) strain rate, and (c) vorticity at different θ_f (Pe = 420, $\varepsilon = 0.446$). Variation with $\theta_r = \theta - \theta_f$ on solid surfaces of dimensionless (d) diffusive flux, (e) strain rate, and (f) vorticity.



Figure 6. Contour of (a) diffusive flux, (b) strain rate, and (c) vorticity for Pe = 420 and two mean flow direction ($\theta_f = 0$ and $\pi/2$) in rectangular array of cylinders. The arrows at the middle of each sub-figure indicate mean flow direction. The first two columns show results for L/H = 1.5 ($\epsilon = 0.631$) and the second two columns show results for L/H = 2.5 ($\epsilon = 0.778$).

cubic Hermite interpolating polynomial (PCHIP) scheme to preserve the monotonicity and shape of the data.

For a specified porosity, $Var(c^*)$ shows non-monotonic variation with Pe. For low Pe transport is diffusion dominated, and thus $Var(c^*)$ is independent of bulk flow conditions in that regime. The minimum *Pe* where $Var(c^*)$ decreases 2.5% from its value at Pe = 0 we define as the boundary for this diffusion-dominated regime, denoted as Pe_{diff} . For $Pe > Pe_{diff}$, $Var(c^*)$ initially decreases due to the redistribution of local flux vectors, and it eventually reaches a minimum value as redistribution terminates. In this regime solute transport is strongly dependent on both porosity and Péclet number. The particular Péclet number Pe_{sat} corresponding to the minimum value of Var(c^*) (also called the saturation Péclet number) was thus calculated to determine the boundary of this transport regime for each porosity ε . For Pe >Pesat advection is the dominant transport mechanism, and, while the locations of flux extrema remain fixed with increasing Pe, the flux at extreme locations shows greater variation from the mean flux $j_{d,s}$. The obtained values of Pe_{diff} and Pe_{sat} for different ε are listed in Table II.

We use the values of Pe_{diff} and Pe_{sat} calculated from Figure 7a to identify boundaries for the different regimes of solute transport in the $Pe - \varepsilon$ plane that are marked as the diffusion and saturation lines in Figure 7b, respectively. These lines divide the $Pe - \varepsilon$ plane into three regimes: (i) a diffusion dominated regime for $Pe < Pe_{diff}$, (ii) a transition regime for $Pe_{diff} < Pe < Pe_{sat}$ where j_d undergoes re-

distribution, and (iii) an advection dominated regime for $Pe > Pe_{sat}$ where j_d shows increased variation from the mean but has negligible redistribution. This map reveals that, for low porosity media, advection causes the redistribution of flux until extrema approach their terminal locations with increasing *Pe*. Based on the interaction classifications discussed in the preceding sub-section, we deduce that such a transformation with increasing *Pe* at low porosity results in a transition from strong diffusive (SDI) to weak advective (WAI) interactions. On the contrary, for high porosity media the transition with increasing *Pe* from weak diffusive (WDI) to strong advective (SAI) interactions causes there to be no apparent transition between diffusion and advection dominated transport regimes. As a result, *Pe_{sat}* coincides with *Pe_{diff}* for high porosity media, as shown in Table II.

Next, we present results for the scaling of Sherwood number (i.e., the non-dimensional mass transfer coefficient) with Péclet number and

Table II. Values of Pe_{diff} and Pe_{sat} for square array of cylinders at different porosities.

3	0.446	0.546	0.678	0.788	0.874
Pe _{diff}	2.01	2.01	2.01	2.01	2.01
Pe _{sat}	42.01	19.01	16.01	13.01	2.01



Figure 7. (a) Contour plot of variance $Var(c^*)$ of local nondimensional concentration c^* and (b) the corresponding transport regime map on the $Pe - \varepsilon$ plane. (c) Variation of $\langle \langle Sh \rangle \rangle$ with Pe for different porosity values.

porosity of the cylindrical porous media already discussed. We use the regime map to explain the observed variations in Sherwood number with *Pe*. The overall Sherwood number $\langle Sh \rangle$ is calculated from each simulated concentration field as $\langle Sh \rangle = \langle h_m \rangle d/D$, where the overall mass transfer coefficient $\langle h_m \rangle$ is calculated using the film theory of mass transport $\langle j_{d,s} \rangle = \langle h_m \rangle (c_s - \langle c \rangle)$. The variation of *Sh* with *Pe* is shown in Figure 7c for various porosity values. (Sh) varies with Pe in different ways depending on the prevailing transport mechanisms. In the diffusion-dominated regime ($Pe \leq Pe_{diff}$), $\langle Sh \rangle$ remains constant with Pe, and in the limit of $Pe \rightarrow 0$ Sherwood number is minimum and non-zero. In the transition regime $(Pe_{diff} < Pe < Pe_{sat}, marked by$ the shaded area in Figure 7c) a dramatic rise in (Sh) is observed with increasing Pe due to the redistribution of local diffusive flux. In the advection dominated regime ($Pe > Pe_{sat}$) a slower increase in $\langle Sh \rangle$ is observed with increasing Pe. The $\langle Sh \rangle$ – Pe variations in Figure 7c thus show that (Sh) does not follow a power law with Pe. Rather a power law respectively under- or over-predicts mass transfer coefficients in the limits of low and high Pe. Further, our results show that high porosity media produce lower values of $\langle Sh \rangle$ at the same Pe values. This trend of $\langle Sh \rangle$ variation agrees with experimental observations.⁵³ Thus, low porosity media are preferred as porous substrates for heterogenous electrochemical reactions over high porosity media on the basis of mass transfer consideration alone. On the contrary, low porosity media possess low hydraulic permeability⁵⁴⁻⁵⁶ and high tortuosity for ion transport.^{57–59} Such competing effects, together with pore-scale mass transfer, should be considered to design optimized RFB electrodes.

Conclusions

In this article we introduce theory to study pore-scale mass transport where heterogeneous redox reactions convert solute molecules between oxidation states. Such processes should be facile to enable efficient cycling of electrochemical energy storage devices, including redox flow batteries (RFBs). While prior RFB studies were restricted to measuring mass transfer coefficients under different flow conditions and with different electrode microstructures, microscopic understanding of the effect of electrode microstructure on surface flux in RFBs has not been established. In the broader chemical engineering literature mathematical models that capture the inherently transient effects of electrolyte charging and discharging do not exist. The auxiliary problem introduced here shows that transient effects can be captured by a time-independent mass conservation equation with linear boundary conditions with minimal loss in generality in the pseudo-steady limit. The decomposition of pore concentrations $c(\mathbf{r}, t)$ into time-dependent surface concentration $c_s(t)$ and a time-independent pore concentration $c_h(\mathbf{r})$ results in a Dirichlet-type BC that automatically satisfies actual BCs arising from fast reaction kinetics and stoichiometry when active species have identical diffusivity and the electromigration flux of active species transport is negligible. The auxiliary problem decouples the conjugate problem into uncoupled problems for individual active species and, thus, provides an efficient numerical method to study redox-active solute transport with heterogeneous reactions. We also show that the auxiliary problem can be applied readily to periodic microstructures by invoking periodic boundary conditions for the concentration field, a condition whose validity depends on the magnitudes of Péclet, Sherwood, and Fourier numbers.

We solved the auxiliary problem numerically for crossflow through a regular array of circular cylinders using the finite-difference and finite-volume methods. Primary results showed that advection causes local diffusive flux fields to redistribute spatially, a process that gradually terminates with increasing Péclet number. The termination of this redistribution process is guided by the locations of maximum fluid deformation components (i.e., strain rate λ and vorticity ω). Investigation of local concentration fields reveals that adjacent solid surfaces in the array experience diffusive interactions for low *Pe*, and this interaction is weakened as porosity increases. With increasing *Pe* for the same microstructure, the interaction between solid cylinders switches to advective-dominated after the termination of redistribution, a process that results from the downstream accumulation of solute.

Furthermore, the limits of *Pe* for diffusion- (Pe_{diff}) and advectiondominated (Pesat) convection mechanisms are identified using the spatial variance of solute concentration. For $Pe < Pe_{diff}$ solute transport is diffusion dominated and is followed by a transition regime $Pe_{diff} < Pe < Pe_{sat}$ where flux redistribution occurs. At high Pe $(Pe > Pe_{sat})$ advection dominates solute transport throughout the interstitial fluid volume. We use a transport regime map to synthesize these concepts together by plotting the obtained values of Pe_{diff} and Pe_{sat} on a $Pe - \varepsilon$ plane that correlates the micro-transport mechanisms with flow conditions and the microstructure of porous media. This map shows that for low porosity media the pore-scale transport mechanism changes from diffusion dominated to advection dominated with substantial redistribution of local diffusive flux. During this change the interaction between adjacent cylinders changes from strong diffusiveto weak-advective interaction (SDI to WAI) as well. For high porosity media the transport mechanism changes without substantial redistribution, where weak diffusive interaction changes gradually to strong advective interaction (WDI to SAI).

The overall Sherwood number (Sh) is finally calculated and its dependence on *Pe* and porosity is investigated. The results show that $\langle Sh \rangle$ does not increase continuously with Pe, and it attains an asymptotic non-zero value for $Pe \rightarrow 0$. The regime map is used to rationalize the dependence of (Sh) on *Pe*. Three different mechanisms result in three distinct variations with *Pe* with a significant increase of $\langle Sh \rangle$ in the transition regime. Thus, the empirical correlation of Sh using powerlaw functions of Reynolds/Péclet number, as is common practice in the RFB literature, fails to capture the variations of (Sh) that arise from the transition between diffusion- and advection-dominated regimes. The creation of transport regime maps based on concentration field variance can be used as a tool to interpret the variations of (Sh) with Pe and microstructure. Thus, these analytical tools, together with the auxiliary problem posed, can provide guidelines for the optimal design of efficient porous substrates for electrochemical reactions, including redox flow batteries. For example, based on mass transfer alone, low porosity media are shown to produce three to four-fold increased (Sh) with porosity decreasing from 87% to 45%. However, due to the competing effects of decreasing permeability and increasing tortuosity with decreasing porosity, further investigation is required to assess the multi-functional performance of arbitrary porous microstructures beyond two-dimensional circular cylinders. We also note that the effect of finite reaction kinetics can be included by considering spatial and temporal variations of the interface overpotential.

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Appendix A: Simplified Analysis of RFB Cycling Dynamics

Here we present the solution procedure for the simplified analysis of RFB cycling dynamics. We consider a fluid circuit that recirculates electrolyte at a constant volumetric flow rate \dot{V} between tank and electrode of volumes V_r and V_t respectively, as shown in Figure A1. Building on our previous numerical modeling of coupled transport between RFB tanks and reactors,^{60–63} here we derive a closed form analytical model for the average concentration within both compartments during cycling.

The obtained MCEs are shown in Equation 2 in terms of average concentrations of species *i* in the reactor $\langle c \rangle_{i,r}$ and tank $\langle c \rangle_{i,t}$. Considering that the volume of the reactor and the tank are constant in time, Eq. 2 can be simplified to:

$$\frac{d}{dt}\left(\langle c \rangle_{i,r}\right) = \delta_r \langle c \rangle_{i,t} - \delta_r \langle c \rangle_{i,r} + \gamma_i$$
[A2a]

$$\frac{d}{dt}\left(\langle c \rangle_{i,t}\right) = \delta_t \langle c \rangle_{i,r} - \delta_t \langle c \rangle_{i,t}$$
 [A2b]

Here, γ_i is expressed as $\gamma_i = (Is_i)/(V_r F)$. $\delta_r = \dot{V}/V_r$ and $\delta_t = \dot{V}/V_t$ are the inverse of mean residence times of the electrolyte flow inside reactor and tank respectively. Solving Eqs. A2a, A2b using Laplace transformation with initial conditions as $\langle c \rangle_{i,r}(t=0) = \langle c \rangle_{i,r}^0$ and $\langle c \rangle_{i,t}(t=0) = \langle c \rangle_{i,t}^0$ provides the solution in the Laplace domain, where *s* is the



Figure A1. Fluid circuit connecting electrode and tank to recirculate electrolyte in an RFB.

Laplace transformed variable related to time coordinate t: $\mathcal{L}(f(t)) = \overline{f}(s)$.

$$s\langle \overline{c} \rangle_{i,r} (s) - \langle c \rangle_{i,r}^{0} = \delta_r \langle \overline{c} \rangle_{i,t} (s) - \delta_r \overline{c}_{i,r} (s) + \gamma_i / s$$
[A3a]

$$s\langle \overline{c} \rangle_{i,t}(s) - \langle c \rangle_{i,t}^{0} = \delta_t \langle \overline{c} \rangle_{i,r}(s) - \delta_t \langle \overline{c} \rangle_{i,t}(s)$$
 [A3b]

We obtained the Laplace transformed solution for $\langle \overline{c} \rangle_{i,r}(s)$ and $\langle \overline{c} \rangle_{i,t}(s)$ by solving the above algebraic equations:

$$\overline{c_i^r}(s) = \frac{(s+\delta_t)}{s(s+\delta)} \langle c \rangle_{i,r}^0 + \frac{\delta_r}{s(s+\delta)} \langle c \rangle_{i,t}^0 + \frac{(s+\delta_t)}{s^2(s+\delta)} \gamma_i$$
 [A4a]

$$\overline{J}_{i}(s) = \frac{\delta_{t}}{s(s+\delta)} \langle c \rangle_{i,t}^{0} + \frac{(s+\delta_{e})}{s(s+\delta)} \langle c \rangle_{i,t}^{0} + \frac{\delta_{t}}{s^{2}(s+\delta)} \gamma_{i}$$
 [A4b]

Here, δ is expressed as $\delta = (\frac{1}{V_l} + \frac{1}{V_r})\dot{V} = \tau^{-1}$, where τ is the harmonic mean residence time of the electrolyte flow. To obtain expressions for average concentrations as a function of time, the inverse Laplace transformation was performed after partial factorization of each term to yield the following:

 $\langle c$

$$\begin{split} \lambda_{i,r}(t) &= \langle c \rangle_{i,r}^{0} \left[v_{r} + v_{t} e^{-t/\tau} \right] + \langle c \rangle_{i,t}^{0} \left[v_{t} \left(1 - e^{-t/\tau} \right) \right] \\ &+ \frac{Is_{i}}{F} \left[\frac{t}{V_{r} + V_{t}} + \frac{v_{t}^{2}}{\dot{V}} \left(1 - e^{-t/\tau} \right) \right] \end{split}$$
[A5a]

$$\begin{aligned} \langle c \rangle_{i,t}(t) &= \langle c \rangle_{i,r}^{0} \left[v_r \left(1 - e^{-t/\tau} \right) \right] + \langle c \rangle_{i,t}^{0} \left[v_t + v_r e^{-t/\tau} \right] \\ &+ \frac{Is_i}{F} \frac{1}{(V_r + V_t)} \left[t + \tau \left(1 - e^{-t/\tau} \right) \right] \end{aligned}$$
[A5b]

where v_r and v_t are the fractions of total electrolyte volume in the reactor and tank, respectively: $v_r = V_r/(V_r + V_t)$ and $v_t = V_t/(V_r + V_t)$.

Appendix B: Model Verification and Validation

To verify the numerical implementation of the present theory we analyzed convergence with mesh size, global mass conservation, and the stability of the obtained interstitial velocity fields for flow over cylinder arrays. For flow over a circular cylinder array with Pe = 105 and $\varepsilon = 0.446$, $\langle Sh \rangle$ approaches a fixed value with increasing number of finite volumes simulated N_{grid} with a variation of approximately 0.05% observed for $N_{grid} \ge 10^6$ (Figure B1). To minimize computational effort $N_{grid} = 10^6$ cells (10³ in each axial direction) was used for all square arrays for cases with Pe < 300. For higher Pe and for rectangular arrays a finer mesh was used to ensure numerical stability. Three types of cases were subsequently simulated for further verification: (i) horizontal flow ($\theta_f = 0$) through a square array, (ii) horizontal flow ($\theta_f = 0$) through a rectangular array, and (iii) inclined flow ($0 \le \theta_f \le \pi/4$) through a square array. The contour plots of streamlines and iso-concentration lines of three representative cases with highest Pe and lowest porosity were inspected for the appearance of sub-grid fluctuations (Figure B1). All the contour lines obtained appear smooth, confirming the stability of simulated flow and concentration fields. For each case studied, we calculated the total solution volume and individual redoxactive species mass residuals by integrating local residual values over the entire interstitial fluid volume. For all cases studied the volume of solution was conserved within 10^{-15} % and the mass of redox-active species was conserved within 10-11%, which are respectively normalized by the advected flow rates of solution volume and active species mass along the mean flow direction.

Validation of the model was performed using analytical solutions for flow between reacting parallel plates with constant surface concentration (Figure B1). To minimize entrance effects plate lengths were taken as one order of magnitude larger than the gap between them (i.e., L/H = 10). To enable validation of the presently implemented model, a 3% gap between plates was used. A case with Pe = 100 (based on inter-plate distance, H_d) was numerically solved using the proposed model. The transverse velocity distribution along a vertical line at x = 0 inside the duct (Figure B1) shows a maximum 0.001% deviation at $y/H_d = 0$, confirming that the theoretical velocity distribution for Poiseuille flow is reproduced numerically. Further, the pressure difference along the duct deviates from analytical theory by less than 1%. The interstitial concentration profile (Figure B1) shows a maximum deviation from the analytical solution that is less than 0.5% at y = 0.



Figure B1. (a) Variation of $\langle Sh \rangle$ with number of finite volumes (N_{grid}) for $\theta_f = 0$, Pe = 105, and $\varepsilon = 0.446$. (b) Contour plot of stream function ψ (upper row) and concentration c^* (lower row) for: (left panel) horizontal flow through a square array ($\theta_f = 0$, Pe = 840, $\varepsilon = 0.446$), (middle panel) inclined flow through a square array ($\theta_f = \pi/4$, Pe = 840, $\varepsilon = 0.446$), and (right panel) horizontal flow through a rectangular array ($\theta_f = 0$, Pe = 420, $\varepsilon = 0.778$) of circular cylinders. (c) Geometry for flow through reacting parallel plates. Comparison of (d) velocity and (e) concentration profile along the *y* axis at x = 0 with analytical solutions. *u* in sub-figure (d) is the mean velocity for the cross-section located at x = 0.

List of Symbols

Bold case represents vector quantities and $\langle \rangle$ represents either a volume- or area- averaged quantity.

a	volumetric surface area of electrode, m ² /m ³
	2

- A area vector, m²
- b characteristic pore dimension, m
- minimum pore dimensions in x and y directions, m b_x, b_y
- concentration, mol/m3 С
- time-independent contribution to c, mol/m³ C_h diameter of solid cylinder, m d
- Fickian diffusion coefficient, m²/s D
- electron
- e^{-} E_{cell}
- half-cell potential, V Faraday's constant, C/mol F
- FoFourier number, (Dt/b^2)
- mass transfer coefficient, m/s
- $\langle h_m \rangle$ Η height of unit cell, m
- H_d gap between parallel plates, m
- electric current, A I
- diffusive flux vector, mol/m²s j
- L length of unit cell, m
- L, macroscopic length of reactor electrode, m
- m_i mobility of species j, m²/s-V
- п normal unit vector
- number of electrons transferred n_e
- Ν molar flux, mol/m²s
- Ngrid number of finite volumes in entire unit cell
- Péclet number Pe
- r position vector, m
- R gas constant, J/mol-K
- R combination of lattice vectors, m
- Re Revnolds number
- tangential direction S
- coefficient of chemical stoichiometry of species i Si
- overall Sherwood number $\langle Sh \rangle$
- time, s t
- transference number of species j
- t_j Tabsolute temperature, K
- superficial velocity vector, m/s u_s
- u[®] molar-volume averaged interstitial fluid velocity, m/s
- fraction of total electrolyte volume in an RFB component v
- \bar{V} partial molar volume, m³/mol
- V volume, m³
- Ņ volumetric flow rate of electrolyte, m³/s
- oxidation state Ζ.

Greek

- tank-to-reactor volume ratio α
- Γ circulation, m²/s
- δ inverse of mean residence time, 1/s
- porosity of porous media ε
- overpotential at solid/solution interface, V η
- θ angular position variable, radians
- λ strain rate, 1/s
- temporal rate of c_s variation, mol/m³-s σ
- harmonic mean residence time for electrolyte flow, s τ
- electric potential, V φ
- ψ stream function, m²/s
- vorticity, 1/s ω

Superscripts

- 0 initial/standard value
- diffusive quantity d
- microscopic quantity т
- non-dimensional quantity

Subscripts

d	diffusive quantity
diff	diffusion limit
e	electrolyte (liquid) phase
eq	equilibrium quantity
f	fluid quantity
i	<i>i</i> th species
max	maximum value
0	oxidized species
r	reactor/electrode quantity
R	reduced species
S	surface/solid-phase quantity
sat	saturation limit
t	tank quantity
	stream wise quantity
i i	

transverse quantity \bot

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