Influence of electrode reactions on electroosmotic flow and ion transport in a microchannel

Runze Sun  
Hebei University of Technology

Chicheng Ma  
Hebei University of Technology

Bader Al-Anzi  
University of Alberta

Emilie Sauret  
Queensland University of Technology

Yuantong Gu  
Queensland University of Technology

Zirui Li (lizirui@gmail.com)  
Hebei University of Technology

Research Article

Keywords:

Posted Date: April 10th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2791621/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Additional Declarations: No competing interests reported.
Influence of electrode reactions on electroosmotic flow and ion transport in a microchannel

Runze Sun¹, Chicheng Ma¹, Bader Al-Anzì²,³, Emilie Sauret⁴, Yuantong Gu⁴ and Zirui Li¹,*

¹ School of Mechanical Engineering, Hebei University of Technology, Tianjin, China.
² Agricultural, Life and Environmental Sci - Ag, Food & Nutri Sci Dep, University of Alberta, Canada
³ Department of Environment Technologies and Management, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait
⁴ School of Mechanical, Medical and Process Engineering, Faculty of Engineering, Queensland University of Technology, Brisbane QLD 4001, Australia

* Correspondence: lizirui@gmail.com

Abstract

Electroosmotic flow (EOF) is a universal phenomenon in most microfluidic systems when an external electric field exists along charged channel walls. The mechanism of ion transport and fluid flow in such systems has been extensively studied, largely based on simplified models without consideration of electrode reactions and water dissociation. In order to study the effects of these electrochemical reactions, we build an electrokinetic model with full consideration of these processes, namely electrochemistry (EC) model, and compare its performance with that of the traditional electrokinetic (EK) model. Our results show that electrode reactions alter the electric potential and reduce the current, causing a significant reduction in EOF velocity. These potential changes and EOF reduction are driven almost entirely by electrode reactions because the difference between the results from the EC model and those from the EK model with potential adjustment induced by chemical reactions is slight. In addition, the participation of ions in electrode reactions leads to notable alterations in their concentration within the microchannel and significant pH change, which are totally ignored in the traditional EK model. It is found that at a typical applied electric field of 50 V/cm, the EOF velocity in the EC model is 64% of that in the EK model. This difference in velocity decreases to only 1.9%
as the EK model considers electric potential shifts caused by electrode reactions. In the microchannel, the Cl\(^{-}\) concentration drops by approximately 50% while the OH\(^{-}\) increases, leading to a pH growth of 3.5. The results presented in this work can improve the understanding of electrode effects on the physicochemical properties of EOF systems, providing essential guidance for manipulating fluid flow and amphoteric molecular transport in various microfluidic systems.

1. Introduction

Microfluidic technology is a rapidly emerging field, providing an excellent method for handling and manipulating fluid samples, suspended cells, and charged particles (Niculescu et al. 2021). Because of its unique advantages, including low sample demand, shortened analysis time, high sensitivity, and miniaturization, microfluidic systems have been widely applied to chemical analysis, drug development, and biomedical diagnostics (Ouyang et al. 2018; Papadimitriou et al. 2020; Musah et al. 2017; Kuriu et al. 2020; Han et al. 2019). All of these applications require the control of the movement of the analytes. The key mechanism for manipulating analyte in a microfluidic system is electrokinetic phenomena (Kang and Li 2009), which are the motion of fluids and particles driven by interfacial double-layer charges induced by external forces such as an electric field, concentration gradient, and pressure gradient (Kim et al. 2009). Electroosmotic flow (EOF) is a well-known electrokinetic phenomenon based on an electric double layer (EDL). The formation of the EDL occurs at charged solid-liquid interfaces in microfluidic devices, as the charged surface attracts counter-ions and repels co-ions (Alizadeh et al. 2021). When an external electric field is applied along the microchannel, free charges in the EDL induce a nearly plug-like fluid, producing much smaller sample dispersion than the traditional parabolic pressure-driven flow (Barz and Ehrhard 2005).
The EOF affects fluid transport significantly and has been extensively studied in different microfluidic systems (Nguyen et al. 2021; Feng et al. 2021; Konášová et al. 2021; Chami et al. 2020). Previous studies have shown the effects of EOF on ions and fluid transport in microfluidic systems with different geometry structures or channel surfaces (Deng et al. 2021; Dubov et al. 2021; Jin et al. 2020). The EOF coupled with pressure flow was also studied to improve the separation efficiency in a capillary zone electrophoresis (CZE) separation system (Jarvas et al. 2018). For designing a micromixer, the optimized fractal curve structure and efficiency DC electric field for controlling the EOF were investigated to enhance the mixing efficiency to achieve a thorough mixing performance (Xiong and Chen 2021; Basati et al. 2019). In isotachophoresis (ITP) sample focusing, the dissimilar conductivity of the leading (LE) and trailing electrolytes (TE) alters the axial distribution of the electric field, resulting in non-uniform EOF velocities. These velocities generate a pressure gradient at the LE-TE interface, causing analyte dispersion strongly affects the sensitivity and resolution of ITP-based focusing. (Garcia-Schwarz et al. 2015; Gopmandal and Bhattacharyya 2015).

However, most microfluidic systems overlook the electrochemical processes occurring on the electrode surface under an electric field. Electric current flow leads to oxidizing reactions at the anode and reduction reactions at the cathode, resulting in variations in the pH and conductivity of the background electrolyte (Persat et al. 2009). A region of modified pH is observed near the electrode, which spreads over time due to thermal convection (Macka et al. 1998). Similar pH changes can be detected in the inlet reservoir using an ion-sensitive field effect transistor (ISFET) and can be suppressed by injecting an acid solution (Oki et al. 2002). In addition to pH alterations, changes in the buffer composition of background electrolytes induced by electrode reactions can significantly decrease analyte mobility by up to 80%. This decrease leads to prolonged analyte migration time with growing analyte diffusion, ultimately reducing the separation resolution of the CZE system. (Stoyanov and Pawliszyn 2004). Suss et al. (Suss et al. 2011) conducted an experimental study on water
electrolysis. The results show that there is both a concentration enrichment and a low pH zone relative to the initial electrolyte near the anode. The electrode reactions change the background electrolyte conductivity, affecting the electric field and the EOF velocity. However, experimentally observing the comprehensive and accurate impact of electrodes on system physicochemical properties is complex. An accurate description of mechanisms relies on numerical simulation.

Traditionally, simulations of EOF have relied on electrokinetics (the EK model), which solves coupled Navier-Stokes, Nernst-Planck, and Poisson (NPN) equations to illustrate ion transport, fluid movement and electric field distribution in the microchannel (Rubinstein and Zaltzman 2000). This model has been widely used to study various microfluidic systems (Shen et al. 2010; Schiffbauer et al. 2021; Rybalkina et al. 2022). Based on this research, the surface charge density is used to describe surface charge effects, accurately demonstrating the changes in EOF under non-uniform electric fields and various ion concentrations (Gong et al. 2018). To investigate chemical reactions in microfluidic systems, Hlushkou et al. simulated buffer reactions and water dissociation in an isoelectric focusing (IEF) system, demonstrating the influence of buffer reactions on EOF velocity and ion enrichment (Hlushkou et al. 2009). Recently, electrolysis phenomena in electrophoresis have been analyzed by numerical calculation (Novotný and Gaš 2020). A uniform electric field and constant EOF mobility are used to calculate ions’ velocity and concentration changes. The quantity of transported charged ions under a uniform electric field indicates the number of charged ions attracted to the electrode. These assumptions will become invalid when electrode reactions result in the enrichment or depletion of ions and the variation of the electric field. Eden et al. conducted a more accurate numerical model to simulate faradic reactions and electrokinetic phenomena at bipolar electrodes (BPEs). This model demonstrates, for the first time, the complex transport and reaction mechanisms at the surface of a BPE in microscopic detail (Eden et al. 2019). However, to the best of our knowledge, the electrodes used to apply an
external electric field have not been investigated. During the electrokinetic manipulation of electrolyte solutions, such as electrophoresis, electrodialysis, and EOF, variations in ion transport, electrolyte pH, electric field, and EOF velocity induced by electrochemical reactions are inevitable but poorly understood. Moreover, the influence of concentration polarization, which refers to changes in the electrolyte concentration resulting from the passage of current through the electrode-electrolyte interface, has not been well studied.

The purpose of this paper is to study the effects of electrode reactions on the physicochemical properties of the EOF system through multi-physics modeling. We have constructed an EC model that integrates electrokinetics and electrochemistry. Our model simultaneously includes electrode reactions, hydrolysis equilibrium, fluid flow, ionic migration, and diffusion. To further understand the impact of reactions and

![Fig. 1](a) Schematic sketch of the EOF system. (b) The simulation model. Cutline A-A’ is located at x = 200 μm

The purpose of this paper is to study the effects of electrode reactions on the physicochemical properties of the EOF system through multi-physics modeling. We have constructed an EC model that integrates electrokinetics and electrochemistry. Our model simultaneously includes electrode reactions, hydrolysis equilibrium, fluid flow, ionic migration, and diffusion. To further understand the impact of reactions and
concentration polarization on the EOF process, the electric potential distribution, electrode kinetic parameters changes, EOF velocity, ion concentration, and pH changes are analyzed under different electric fields and electrolyte concentration and compared with the EK model. Specifically, we present the ion transport behavior and significant concentration changes around the electrode through ion flux vectors and concentration distributions. The results provide insights for better understanding electrode effects on EOF and guide the design and optimization of various forms of microfluidic devices.

2. Methods

2.1 System setup

Fig. 1(b) shows a schematic of the two-dimensional model with electrode reactions. The critical component of the system is the microchannel of length \( L \) and wide \( H \). Connected to the microchannel are two wider compartments representing part of the reservoirs with length \( L_s \) and wide \( H_s \). The microchannel walls are negatively charged, while the walls of wider compartments are uncharged. An electric field is applied by placing a silver electrode at the anode and a platinum electrode at the cathode in the reservoirs. These two electrodes with width \( H_d \) are placed in the center of the reservoir boundary. The voltage on the left electrode is \( V_L \), and the voltage on the right electrode is \( V_R \). Voltages \( V_L \) and \( V_R \) (\( V_L > V_R \)) generate a leftward electric field, which induces a rightward EOF. The solution inside the system is potassium chloride (KCl) with the concentration \( C_0 \). Pressure at both the left and right boundaries are set to zero, so the transport of ions and fluids results from electrokinetic phenomena only.

2.2 Governing equations

The transport of ions and particles in our system is governed by a statement of mass conservation with Nernst-Plank fluxes (Rubinstein and Zaltzman 2000):

\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{J}_i + R_i, \quad (1)
\]
\[ \mathbf{J}_i = -(D_i \nabla C_i + Z_i(D_i F / RT)C_i \nabla \phi_i) + \mathbf{U} C_i, \]  

(2)

where \( C_i \) and \( \mathbf{J}_i \) are the concentration and flux of species \( i \), \( D_i \) and \( Z_i \) are its diffusion coefficient and valency, respectively. For convenience, we set \( i = 1 \) for \( K^+ \), \( i = 2 \) for \( Cl^- \), \( i = 3 \) for \( H^+ \), and \( i = 4 \) for \( OH^- \). \( \phi_i \) is the local electric potential of the electrolyte; \( F \), \( R \), and \( T \) represent the Faraday constant, molar gas constant, and temperature, respectively. \( \mathbf{U} \) is the flow velocity, and \( R_i \) is the homogeneous reaction source term.

In the Nernst-Plank equation, we include reaction source terms for the association/dissociation reactions of water and the electrode reactions of cathode and anode. The water association and dissociation reactions are

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- . \]  

(3)

The reaction source terms in Eq. (1) for \( i=3 \) and \( i=4 \) can be represented as

\[ R_3 = k_f C_{\text{H}_2\text{O}} - k_b C_3 C_4, \]  

(4)

\[ R_4 = R_3 = k_f C_{\text{H}_2\text{O}} - k_b C_3 C_4, \]  

(5)

where \( k_f \) and \( k_b \) denote the rate constants for the forward and backward reaction of water self-ionization (Hlushkou et al. 2009).

The local concentrations of the charged species and the local electric potential of the electrolyte are related by the Poisson equation (Rubinstein and Zaltzman 2000):

\[ -\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \phi) = \rho_s, \]  

(6)

where \( \varepsilon_0 \) and \( \varepsilon_r \) are the vacuum permittivity and dielectric constant, respectively. \( \rho_s = e \sum_{i=1}^{4} Z_i C_i \) is the free space charge density, with \( e \) being the elementary charge.

Governing equation for the incompressible fluid flow is described by the Navier-Stokes equation (Li et al. 2017):

\[ \rho \left[ \frac{\partial \mathbf{U}}{\partial t} + (\mathbf{U} \cdot \nabla) \mathbf{U} \right] = -\rho \nabla \phi + \eta \nabla \cdot \nabla \mathbf{U} - \nabla P, \]  

(7)
where $\rho$ and $\eta$ are the mass density and dynamic viscosity of the liquid, and $P$ is the hydrostatic pressure.

### 2.3 Boundary conditions

The boundary conditions of the system are as follows.

At the anode (silver electrode): in the model based on electrokinetics (EK model), the boundary condition of the electric potential is $\phi = V_L$. However, the electric potential of the electrode $\phi_s$ is different from the local electric potential of electrolyte $\phi_l$ at the electrode-electrolyte interface. We implement the Butler-Volmer equation to describe the relationship between applied voltage $V_L$, electric potential $\phi_l$, and local Faradaic current density $i_{loc}$ (Davies and Crooks 2020):

$$i_{loc} = i_{0,a} \left[ \exp\left(\frac{\alpha \eta_a}{RT}\right) - \exp\left(-\frac{\beta \eta_a}{RT}\right) \right],$$  

$$\eta_a = \phi_s - \phi_l - E_{eq,a},$$  

$$\phi_s = V_L,$$

where $i_0$ is the exchange current density, $\alpha$ and $\beta$ are the dimensionless transfer coefficient for anodic and cathodic reactions. $\phi_s$ is the electric potential of the electrode. $\eta_a$ and $E_{eq,a}$ are the overpotential and the equilibrium electrode potential for the anode.

The electrode reactions of the anode is

$$\text{Ag} + \text{Cl}^- \rightleftharpoons \text{AgCl}.$$  

The $E_{eq,a}$ is calculated by the Nernst equation (Bagotsky and Vladimir 2005):

$$E_{eq,a} = E_{0,a} - RT / nF \ln(C_i / C_{0,i}), \ i = 2,$$

where $n$ is the number of electrons in the reaction’s elementary act, $E_{0,a}$ is standard electrode potential of the anode. $C_{0,i}$ is the standard concentration condition for $E_{0,a}$.

According to Faraday’s Law, the reaction source term of anode reactions can be represented as
\[ R_i = v_i i_{loc} / nF, \quad i = 2 \]  \hspace{1cm} (14)

where \( v_i \) and \( i_{loc} \) denote the stoichiometric coefficients of species \( i \) and the local Faradaic current density.

At the cathode (platinum electrode): the Butler-Volmer equation and Faraday’s Law are also adopted to describe electrochemical kinetics:

\[ i_{loc} = i_{0,c} \left[ \exp \left( \frac{\alpha \eta_c}{RT} \right) - \exp \left( \frac{-\beta \eta_c}{RT} \right) \right], \]  \hspace{1cm} (15)

\[ \eta_c = \phi_s - \phi_i - E_{eq,c}, \]  \hspace{1cm} (16)

\[ \phi_s = V_g, \]  \hspace{1cm} (17)

\[ R_i = v_i i_{loc} / nF, \quad i = 4 \]  \hspace{1cm} (18)

where \( E_{eq,c} \) is the equilibrium electrode potential of the cathode.

The relevant Faradaic reactions in our system is the hydrogen evolution and oxidation reaction (HER and HOR):

\[ 2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- . \]  \hspace{1cm} (19)

For HER, it is found that one \( OH^- \) ion is generated in the reaction per electron. When there are changes in the form of products with solution pH, the values of \( E_{eq,c} \) and the pH dependence of electrode potential will change accordingly. These changes are illustrated by Pourbaix diagrams (Bagotsky and Vladimir 2005).

Therefore, the \( E_{eq,c} \) is calculated by following the simplified equation:

\[ E_{eq,c} = E_{0,c} - 0.059(\text{pH} - 14), \]  \hspace{1cm} (20)

where \( \eta_c \) and \( E_{eq,c} \) are the overpotential and the equilibrium electrode potential for the cathode.

At the left reservoir boundary (Zaltzman and Rubinstein 2007): (i) concentration of all ions are the same as those in the left reservoir; (ii) zero charge; (iii) The pressure is zero:

\[ C_i = C_{i,0}, \quad i = 1, 2, 3, 4, \quad \phi_l = 0, \quad \nabla \mathbf{U} \cdot \mathbf{n} = 0, \quad P = 0 \]  \hspace{1cm} (21)
At the right reservoir boundary: (i) concentration of all ions are the same as those in the right reservoir; (ii) zero charge; (iii) The pressure is zero:

\[ C_i = C_{i,0}, \ i = 1,2,3,4, \ \phi_i = 0, \ \nabla \mathbf{U} \cdot \mathbf{n} = 0, \ P = 0. \]  (22)

At the microchannel walls, the boundary conditions: (i) The computational model is greatly simplified for the flow equations if one does not have to resolve the velocity field in the EDL. This situation may be avoided when the thickness of the EDL is small relative to the channel height and width. Thus, a slip boundary condition can be applied on the microchannel walls with minimal impact on the accuracy of the flow solution. The slip velocity is calculated from the Helmholtz-Smoluchowski equation (Dasgupta et al. 2008); (ii) zero charge; (iii) Impermeability to ions and particles:

\[ \mathbf{U}_{\infty} = -\zeta \varepsilon_0 \varepsilon_r \mathbf{E} / \eta = \zeta \varepsilon_0 \varepsilon_r \nabla \phi_i / \eta, \ \nabla \phi_i \cdot \mathbf{n} = 0, \ \mathbf{J}_i \cdot \mathbf{n} = 0, \ i = 1,2,3,4, \]  (23)

where \( \mathbf{U}_{\infty} \) is the electroosmotic velocity, \( \zeta \) is the zeta potential and \( \mathbf{E} \) is the electric field.

At reservoir walls: (i) no-slip condition for fluid velocity and zero-gradient condition for pressure; (ii) zero charge:

\[ \mathbf{U} = 0, \ \nabla P \cdot \mathbf{n} = 0, \ \nabla \phi_i \cdot \mathbf{n} = 0. \]  (24)

Here \( \mathbf{n} \) is the normal vector perpendicular to the boundary pointing out of the fluid domain.

2.4 Numerical methods

This study used the commercial finite element software COMSOL Multiphysics 5.6 to carry out the numerical simulation. Based on symmetries in geometry and physics setup, only the lower half of the channel was modeled with symmetric boundary conditions at the upper boundary of the calculation model (the central line of the channel). Concentration and potential fields were implemented in physics interfaces of Tertiary Current Distribution. Navier–Stokes (NS) and continuity equations were implemented in the Creeping Flow interface. The computational domain was meshed using quadrilateral elements. 34000 quadrilateral elements were utilized for meshing. Finer meshed are adopted at the charged walls, electrode surfaces, inlet and outlet
boundaries of the reservoirs, and the microchannel. At these wall regions, a minimum of one mesh layer per micrometer is required. Coupled governing equations are solved by MUMPS with Newton’s method. In particular, we seek steady-state solutions, which describe the system state after the system runs for sufficiently long time. To obtain a converged solution under particular conditions or to study the effect of specific parameters, the auxiliary sweep of parameters is frequently used.

3. Results and discussion

In our simulation, the geometric parameters of the microfluidic system are $L = 800 \mu m$, $H = H_d = 20 \mu m$, and $L_s = H_s = 100 \mu m$ (see Fig. 1). The zeta potential of polydimethylsiloxane (PDMS) microchannel walls is $\zeta = -0.1 \text{ V}$ (Liu et al. 2020). The density, viscosity, and relative permittivity of the solution are $\rho = 1000 \text{ kg/m}^3$, $\eta = 0.001 \text{ Pa\cdot s}$, and $\varepsilon_r = 78.5$, respectively (Li et al. 2017). The absolute temperature is fixed at $T = 300 \text{ K}$. The parameters regarding each ion in the electrolyte are provided in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (unit)</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{1,0}$</td>
<td>1 (mM)</td>
<td>Initial ion concentrations of K$^+$</td>
<td>(Li et al. 2017)</td>
</tr>
<tr>
<td>$C_{2,0}$</td>
<td>1 (mM)</td>
<td>Initial ion concentrations of Cl$^-$</td>
<td>(Li et al. 2017)</td>
</tr>
<tr>
<td>$C_{3,0}$</td>
<td>$1 \times 10^{-4}$ (mM)</td>
<td>Initial ion concentrations of H$^+$</td>
<td>(Hlushkou et al. 2009)</td>
</tr>
<tr>
<td>$C_{4,0}$</td>
<td>$1 \times 10^{-4}$ (mM)</td>
<td>Initial ion concentrations of OH$^-$</td>
<td>(Hlushkou et al. 2009)</td>
</tr>
<tr>
<td>$C_{H_2O}$</td>
<td>$55.5 \times 10^3$ (mM)</td>
<td>Concentration of water</td>
<td>(Femmer et al. 2015)</td>
</tr>
<tr>
<td>$D_1$</td>
<td>$1.96 \times 10^9$ (m$^2$/s)</td>
<td>Diffusion coefficients of K$^+$</td>
<td>(Buffle et al. 2007)</td>
</tr>
<tr>
<td>$D_2$</td>
<td>$2.03 \times 10^9$ (m$^2$/s)</td>
<td>Diffusion coefficients of Cl$^-$</td>
<td>(Buffle et al. 2007)</td>
</tr>
<tr>
<td>$D_3$</td>
<td>$9.31 \times 10^9$ (m$^2$/s)</td>
<td>Diffusion coefficients of H$^+$</td>
<td>(Buffle et al. 2007)</td>
</tr>
<tr>
<td>$D_4$</td>
<td>$5.27 \times 10^9$ (m$^2$/s)</td>
<td>Diffusion coefficients of OH$^-$</td>
<td>(Buffle et al. 2007)</td>
</tr>
</tbody>
</table>
3.1 Influence of electrode reactions on electric potential and current

Previous investigations into numerical simulations of electro-osmotic flow were based on electrokinetics (Rubinstein and Zaltzman 2000). However, the electrokinetic (EK) model fails to account for the electric potential and concentration disparities that emerge due to electrode reactions. It assumes that the potential difference between the electrode and the electrolyte is uniform. To illustrate the electrochemical kinetics inherent in the EOF system, we simulate the steady-state behavior of the EK model and the EC model at $V_L = 5$ V and $V_R = 0$ V without applying external pressure. The parameters used to simulate electrode reactions and water self-ionization are given in Table 2. In this case, electric field drives all processes, including the fluid flow, transport of ion species, and distribution of electric potential.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (unit)</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{0,a}$</td>
<td>$1.3$ (A/m$^2$)</td>
<td>Anode exchange current density</td>
<td>(Ha and Payer 2011)</td>
</tr>
<tr>
<td>$i_{0,c}$</td>
<td>$4 \times 10^{-4}$ (A/m$^2$)</td>
<td>Cathode exchange current density</td>
<td>(Wang et al. 2021)</td>
</tr>
<tr>
<td>$E_{0,a}$</td>
<td>$0.222$ (V)</td>
<td>Anode standard electrode potential</td>
<td>(Bagotsky and Vladimir 2005)</td>
</tr>
<tr>
<td>$E_{0,c}$</td>
<td>$-0.822$ (V)</td>
<td>Cathode standard electrode potential</td>
<td>(Bagotsky and Vladimir 2005)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$0.5$</td>
<td>Dimensionless transfer coefficient for anodic reaction</td>
<td>(Bagotsky and Vladimir 2005)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$0.5$</td>
<td>Dimensionless transfer coefficient for cathodic reaction</td>
<td>(Bagotsky and Vladimir 2005)</td>
</tr>
<tr>
<td>$k_f$</td>
<td>$2 \times 10^{-5}$ (s$^{-1}$)</td>
<td>Forward reaction rate constants of water self-ionization</td>
<td>(Hlushkou et al. 2009)</td>
</tr>
</tbody>
</table>
The profile of the electrolyte potential displays potential shifts caused by electrode reactions. As shown in Fig. 2(a), one may find that the potential drop experienced by the EC model is smaller than that of the EK model. At the anode, at \( x = 0 \mu m \), the electric potential of the electrolyte \( \phi_l \) of the EC model is 4.02 V, which is lower than the \( \phi_l \) of the EK model, which is 5 V. The trend is the opposite for the cathode. The \( \phi_l \) of the EC model exhibits an elevation of 0.82 V relative to the EK model. This situation arises from concentration polarization. Within the electrolyte, oxidation-reduction reactions occurring at the electrode surfaces result in the accumulation and depletion of charged ions, thereby affecting the electric field applied and the distribution of \( \phi_l \). More specifically, when current passes through the anode, the speed of electrons flowing out of the electrode is greater than the speed of the oxidation reaction, which results in the accumulation of positive charges and renders the anode potential more positive. Similarly, there is a negative electrode potential shift at the cathode. These electrode potential changes consume applied voltage, reducing the electric potential of the electrolyte in the system. For a detailed illustration of the concentration changes induced by electrode reactions, refer to Fig. 9.

Current is one of the crucial parameters reflecting the system behavior. It is assumed that if the depth of the model \( l_z \) is 1 m, then the equivalent current \( I \) can be obtained by the following Eq. (25)

\[
I = \int_{-A}^{A} F (J_1 + J_3 - J_2 - J_4) dy.
\]

As demonstrated in Fig. 2(b), both models exhibit a linear current growth with respect to the applied voltage. The potential drop in the EC model considerably reduces the current flow. At \( V_L = 2 \) V, the current in the EC model is noticeably lower than in the EK model, having decreased by \( 5.91 \times 10^{-3} \) A. This disparity further

\[
1.11 \times 10^8 \quad \text{Backward reaction rate constants of} \quad (\text{Hlushkou et al. 2009})
\]

\[
k_b \quad \text{(m}^3 \text{/(mol·s))} \quad \text{water self-ionization}
\]
increases as the voltage rises, reaching a difference of $10.21 \times 10^{-3}$ A at $V_L = 5$ V. Furthermore, it can be observed that the slope of the current-voltage curve in the EC model is lower than that in the EK model, implying that the system's conductivity is compromised by the concentration changes induced by electrode reactions. The depletion and enrichment regions of concentration and the overall concentration changes in the system, can be observed in Fig. 10(a), which is discussed in section 3.4.

The influence of electrode reactions on the electric potential shifts at the electrode interface depends on the overpotential $\eta$ and the equilibrium electrode potential $E_{eq}$ (Haber and Russ 1904). The relationship between these potentials and the applied voltage and the electrolyte potential can be described by Eqs. (10) and (16). To demonstrate these potential changes during electrode reactions, we set $V_L$ values between 2 V and 5 V while maintaining $V_R$ at a constant 0 V. This voltage range corresponds to the typical external electric fields in microfluidic systems (20 V/cm~50 V/cm). The $\eta$ and $E_{eq}$ for the cathode and anode, as shown in Fig. 3 (a), vary with the applied voltage $V_L$. For the anode, the oxidation reaction produces solid salt AgCl and electrons to reduce the Cl$^-$ concentration. Note that the dissolution of AgCl is much smaller than its deposition,
so the impact of its dissolution is ignored in our model. As the voltage and current increase, the oxidation reaction rate rises, leading to a decrease in the concentration of Cl\(^{-}\). Meanwhile, the equilibrium electrode potential of the anode \(E_{eq,a}\) displays an exponential increase with \(V_L\), as described by the Nernst equation [Eq. (12)]. Fig. 3(a) shows that as \(V_L\) increases from 2 V to 5 V, the \(E_{eq,a}\) increases from 0.41 V to 0.51 V. Consequently, the anode overpotential \(\eta_a\) escalates by 0.17 V with the rising voltage, ranging from 0.28 V to 0.45 V.

Fig. 3 Dependence of the equilibrium electrode potential \(E_{eq}\) and the overpotential \(\eta\) on the applied voltage \(V_L\). (a) anode (b) cathode

In the case of the cathode, the OH\(^{-}\) ion is involved in the reaction to transfer electrons; hence, the electrode potential becomes more negative when the pH is raised. As the \(V_L\) increases, the production of OH\(^{-}\) through the HER undergoes an upsurge, resulting in a decrease in the equilibrium electrode potential of the cathode \(E_{eq,c}\) from \(-0.617\) V to \(-0.657\) V. The overpotential of the cathode \(\eta_c\) also experiences a similar reduction, dropping from \(-0.150\) V to \(-0.163\) V [see Fig. 3(b)].

### 3.2 Influence of electrode reactions on EOF velocity

Fig. 4 shows the fluid flow field calculated from the two models. It is worth noting that although the zeta potential and the applied electric field are the same for both models, the velocity of the EK model is significantly greater than that of the EC model. In the EK model, the EOF velocity inside the microchannel is
approximately 0.4 mm/s. In comparison, that in the EC model is about 0.256 mm/s decreased by 36%. The underlying reason for this phenomenon is that electrode reactions reduce the electric potential. Thus, the effective electric field imparted to the electrolyte is diminished compared to the applied electric field, reducing the EOF velocity.

As the driving factor that induces EOF, the electric field plays a crucial role in this system. Hence, the variation of electric potential and electric field in microchannels inevitably alters the EOF velocity. Generally, the average velocity at the cutline $A-A'$ (see Fig. 1) represents the EOF velocity within the microchannel. To illustrate the influence of electric potential shifts on the EOF velocity, we compared the velocity of the EK model and EC model under the identical applied electric fields $E_s$, defined as $E_s = (V_L - V_R)/(L+2L_s)$. The ratio of EOF velocities of the two models $\alpha_u$ is used to demonstrate this influence visually. The EOF velocity ratio $\alpha_u$ is defined by the following Eq. (26)

$$\alpha_u = \frac{u_{EC}}{u_{EK}},$$  \hspace{1cm} \text{(26)}

where $u_{EC}$ and $u_{EK}$ are the axial components of the velocity vectors and denote the EOF velocity for the EC and EK models. Notably, although electrode reactions become more pronounced as the external electric field increases, their influence on electroosmotic flow decreases. As shown in Fig. 5(a), the effect of electrode
reactions on electroosmotic flow is most significant at a low external electric field, with the $\alpha_u$ being 0.26 at $E_s = 20 \text{ V/cm}$. This ratio suggests that the EOF velocity in the EK model is roughly three times that in the EC model. As the external electric field grows, the proportion of applied voltage attributed to potential deviation caused by electrode reactions decreases, increasing $\alpha_u$. The velocity ratio increases gradually from 0.26 to 0.63 as $E_s$ rises from 20 V/cm to 50 V/cm. This phenomenon is mainly attributed to the decreasing proportion of the potential shift caused by reactions compared to the elevation in the external electric field (i.e., the increase of $V_L$). Another noteworthy point is that the growth in velocity ratio follows a logarithmic relationship with the increase in $E_s$. This trend is due to the exponential growth of $E_{eq,a}$ and $\eta_a$, which leads to the electric potential difference between anode $\phi_s$ and the electrolyte $\phi_l$ increasing. Consequently, the electric field and EOF velocity in the microchannel rise slowly for the EC model. In addition, when the concentration of Cl$^-$ drops to zero with the $E_s$ surpassing 50 V/cm, the electrode reactions turn to consume H$^+$. This complex electrochemical behavior needs further research to reveal its influence on the EOF system.

In addition to the variation in the applied electric field, the EOF velocity also varies with the concentration of the electrolyte. Fig. 5(b) shows the variation in velocity profile under $V_L = 5 \text{ V}$, corresponding to $E_s = 50 \text{ V/cm}$, for different electrolyte concentrations $C_0$. It can be observed that the EOF velocity falls with increasing $C_0$. As depicted in Fig. 5(b), when $C_0$ is 1 mM, the EOF velocity is approximately 0.256 mm/s, whereas, at the concentration of 10 mM, the EOF velocity decreases to 0.252 mm/s. This decline is attributed to the elevation of system conductivity arising from alterations in electrolyte concentration, thereby augmenting the magnitude of current traversing through the system. The intensification of current increases electric potential shifts, resulting in a growth in overpotential, which reduces the strength of the electric field driving EOF and lowers its velocity.
3.3 Influence of microchannel length on EOF velocity

In addition to the changes mentioned above, in practical systems, the microchannel length varies depending on the specific requirements for sample processing. As the length of the microchannel increases, the voltage applied to the electrodes must also increase to maintain the same external electric field. When the microchannel length $L$ is 800 μm, and the overall system length $L+2L_s$ is 1000 μm, an applied voltage of 5V is required to achieve an external electric field of 50 V/cm. With the reservoir length $L_s$ being constant, when the microchannel length increases to 1300 μm, the same external electric field requires an applied voltage of 7.5V. However, the potential shift caused by the electrode remains almost unchanged. The electric potential difference between the two models decreases, and the velocity ratio between the two models increases. For the same applied electric field $E_s$, the variation of EOF velocity becomes smaller. As depicted in Fig. 6, The disparity in the EOF velocity between the two models gradually diminishes with increasing distance. For the microchannel length of 1300 μm, with the identical applied electric field, the velocity ratio $\alpha_u$ escalates to 0.73. This trend suggests that the effect of electrode reactions on the electric potential decreases with increasing voltage in longer microchannels. If the microchannel length reaches the centimeter level, the potential shifts...
caused by electrode reactions can be ignored. However, electrode reactions significantly alter the electric potential and reduce the EOF velocity in shorter microchannels or lower voltages. Therefore, it is crucial to consider the effect of electrode reactions when designing microfluidic systems for sample processing.

![Fig. 6](image_url)

**Fig. 6** Dependences of the EOF velocity ratio $\alpha_u$ on the length of microchannel $L$ at $E_s = 50$ V/cm.

### 3.4 Influence of electrode reactions on ions concentration and pH

Apart from variations in electric potential, Faraday reactions and dissociation of water also significantly alter ion transport and the pH of the system. The EC model effectively simulates the changes in ion concentration in a microchannel EOF system. Fig. 7(a) and (b) show that the steady state of Cl$^-$ concentration and pH are generally constant. Thus, one can conclude that applying the electric field does not change the concentration of all the charged species. As a comparison, Fig. 7(c) and (d) show the steady-state distribution of Cl$^-$ concentration and pH when electrode reactions [Eqs. (9)-(20)] and water dissociation [Eqs. (4)-(5)] are considered. It is found that the Cl$^-$ concentration is notably reduced by 50%, and the pH is higher than those predicted by the EK model. This variation occurs because that electrical current flow through the system, consuming Cl$^-$ from the oxidation reaction and generating OH$^-$ from HER. In addition to the overall concentration changes within the microchannel at steady-state, another striking feature is that, within 20 μm
around the electrode, the concentration and pH changed the most, and both the concentration and pH gradients were significantly higher than in other regions. These high-gradient regions around the electrode, concentration polarization regions, accelerate the diffusion of ions and thus sustain the transport of ion currents.

![Graphical representation of the flux distribution of Cl⁻ and OH⁻](image)

**Fig. 7** The distribution of Cl⁻ concentration and pH calculated from the EK model and EC model at $V_L = 5$ V. (a) Distribution of Cl⁻ concentration in the EK model. (b) The pH distribution of the EK model. (c) Distribution of Cl⁻ concentration in the EC model. (d) The pH distribution of the EC model

To provide a more comprehensive depiction of the transport characteristics of ions participating in reactions around the electrode, a graphical representation of the flux distribution of Cl⁻ and OH⁻ is generated in Fig. 8. Fig. 8(a) shows the flux of Cl⁻. Overall, Cl⁻ migrates from the cathode to the anode under the influence of the external electric field. The maximum flux of Cl⁻ is observed within 20 μm of the anode, with Cl⁻ flowing towards the electrode. However, concentration gradients at a distance of 50 μm cause Cl⁻ to exhibit reverse diffusion. Another ion that participates in the electrode reaction is OH⁻, which migrates under the applied
electric field and participates in electrode reactions and water dissociation [see Fig. 8(b)]. At the cathode, a large amount of OH\(^-\) is generated from HER and migrates to the anode. Meanwhile, OH\(^-\) combines with H\(^+\) to form water during migration. The maximum OH\(^-\) flux location is around 20 μm near the cathode. The spatial scale of the significant concentration changes near the electrode is about 50 μm.

![Fig. 8 The distribution of flux of ions participating in reactions calculated from the EC model at \(V_L = 5\) V. (a) Cl\(^-\) (b) OH\(^-\)](image)

Concentration polarization is the primary factor behind changes in concentration, pH, and flux during electrode reactions. The chloride concentration curve near the electrode illustrates the concentration polarization as the voltage is elevated. According to Fig. 9(a), with an initial concentration of \(C_0 = 1\) mM, the concentration of Cl\(^-\) plummets as the voltage increases in response to the demands of the electrode reactions. At \(V_L = 5\) V, the concentration of Cl\(^-\) is nearly zero. The position of the electrode is from \(y = 40\) μm to \(y = 60\) μm. In the region beyond the electrode, the concentration of Cl\(^-\) remains at a constant value of 1 mM. However, a significant concentration gradient is observed at the electrode boundary (positioned at \(y = 40\) μm and \(60\) μm). This gradient arises from the difference between the rate of Cl\(^-\) consumption by the electrode reaction and the migration rate of Cl\(^-\) ions from the solution to the electrode surface. Consequently, there is a shortage of Cl\(^-\)
supply on the electrode surface. The concentration gradient greatly enhances the diffusion of Cl\(^-\) ions towards the electrode, thus maintaining a balance between their consumption and transport. Determined by electrical neutrality, the consumption of a single ion in the solution results in an overall reduction in the solution concentration in that particular region. This decrease in concentration is accompanied by a growth in electrical conductivity. At the boundary of the electrode, the presence of an extremely high concentration gradient causes a substantial change in electrical conductivity, along with a simultaneous surge in the tangential electric field \(E_x\). At low voltage levels, the alteration in \(E_x\) is negligible, merely a marginal increment in contrast to the ambient solution enveloping the electrode. Specifically, at \(V_L = 3\) V, the \(E_x\) value corresponds to 30 V/cm. Upon elevating the voltage to 4 V, the \(E_x\) augment significantly to approximately 100 V/cm at the electrode's boundary on both sides, which is more than twice the applied electric field \(E_s\). Further raising the \(V_L\) to 5 V, a depletion zone of Cl\(^-\) emerges, and the \(E_x\) increases by a factor of six relatives to the \(E_s\) [see Fig. 9(b)].

**Fig. 9** The profiles of Cl\(^-\) concentration and the tangential electric field \(E_x\) over the cross section near the anode surface at \(x = 0.25\) μm. (a) \(V_L\) (b) \(E_x\)

Fig. 10 shows the variation in concentration of all ions and pH at the centerline of the system at \(V_L = 5\) V. It is clear that there is no concentration gradient within the microchannel. As for K\(^+\), which does not participate in the electrode reaction, its concentration drops slightly compared to the initial concentration \(C_{0,1}\) (1 mM), by
about 0.07 mM. The concentration of Cl\(^-\) decreases by almost half, from 1 mM to about 0.545 mM within the microchannel. The ion with the most concentration change is OH\(^-\), which rises from \(1 \times 10^{-4}\) mM to 0.385 mM, leading to a corresponding pH increase of 3.6 units. These phenomena are attributed to the alteration of ion transport caused by the electrode reactions. What is even more noteworthy is the significant change in ion concentration occurring in the vicinity of the electrode. Near the anode, Cl\(^-\) diffuses towards the electrode and reacts to form precipitates, resulting in a depletion zone of Cl\(^-\). At a distance of 20 μm, an accumulation of chloride ions occurs due to the migration of the current, creating a localized area of high Cl\(^-\) concentration. Hence, diffusion towards both sides is the dominant factor for Cl\(^-\) transport in this region. This diffusion is the reason for the reverse flux of chloride ions observed at \(x = 50\) μm in Fig. 8(a). The migration of OH\(^-\) displays a distinctive pattern. In the left reservoir, the process of water association leads to a gradual decline in the OH\(^-\) concentration. However, near the anode, the attraction of OH\(^-\) by electrostatic forces enlarges its concentration. The combined influence of these two processes yields a minimum concentration of OH\(^-\) at 10 μm, which is 0.1 mM, corresponding to the lowest point in pH, slightly below 10.

For the cathode, generating a large amount of OH\(^-\) from HER increases the OH\(^-\) concentration, with the highest concentration at the electrode reaching 2.2 mM. The variation in K\(^+\) follows to the principle of electrical neutrality. Due to the influence of electrostatic forces, the concentration of K\(^+\) reaches its minimum of 0.22 mM at the anode, and its maximum of 2.56 mM at the cathode. As a result, the pH in the right reservoir is significantly higher than in the microchannel, reaching as high as 11.34. The pH difference between the anode and cathode is about 1.34, which is consistent with the pH shifts observed in a microchip electrophoresis experiment (Hasan et al. 2021). The EK model disregards reactions; hence the fluctuation of ion concentration within the EOF system cannot be accurately depicted. The ion concentration is held steady, thereby sustaining a pH of 7.
At varying electrolyte concentrations, the corresponding electric current passing through the system differs, resulting in more significant ion concentration and pH variations. As the concentration rises, the high concentration zone (at $x = 50 \mu m$) formed by the combined effect of Cl$^-$ diffusion to the anode and Cl$^-$ electric migration will become increasingly conspicuous. The most remarkable feature is that at $C_0 = 10$ mM, the Cl$^-$ concentration reaches a peak of 6.75 mM, which is 1.75 mM higher than the Cl$^-$ concentration in the microchannel [see Fig. 11(a)]. Furthermore, remarkable variations in the concentration can be observed near the anode. As depicted in the inset in Fig. 11(a), there is an increase in the Cl$^-$ concentration on the electrode surface concomitant with the augmentation of the electrolyte concentration. This growth implies that under circumstances of high electrolyte concentration, the voltage required for the electrode reactions to switching from Cl$^-$ consumption to oxygen reduction (ORR) for H$^+$ production is amplified. The cathodic reaction remains unchanged; hence the rise in pH aligns with the upsurge in electrolyte concentration. When $C_0$ is up to 10 mM, the current undergoes a tenfold amplification, and the abundance of OH$^-$ ions also increases tenfold, resulting in an elevation of pH by one unit. In the microchannel, the pH reaches 11.6.

Fig. 10 (a) The profiles of ions concentration along the centerline of the system calculated from the EC model at $V_L = 5$ V (b) The profiles of pH along the centerline of the system at $V_L = 5$ V.
3.5 Comparison of the EC model, EK model and EK model with potential shifts

While the EK model cannot capture the changes in concentration resulting from chemical reactions, the simulation of electroosmotic flow velocity can be achieved like the EC model, by considering the potential shift at the electrode-electrolyte interface. This modification reduces the difference in the EOF velocity between the two models. In the EK model, the electric potential applied to both boundaries is adjusted to consider the polarization of the electrode. Instead of setting $\phi$ to $V_L$ at the left boundary, it is set to be the same as the $\phi_l$ of the electrode surface. The EOF velocity in the EK model considering the electric potential shifts (0.261 mm/s), is very close to that of the EC model (0.256 mm/s), only slightly higher by $5 \times 10^{-3}$ mm/s, representing a mere 1.9% difference (see Fig. 12). This slight difference is due to the change in the electrolyte concentration within the microchannel caused by the electrode reactions, which decrease from 1mM to 0.93mM. [see Fig. 10(a)].
Fig. 12 The velocity profile for the EC model, the EK model and the EK model with electric potential shifts at $V_L = 5$ V.

We have demonstrated the ability of the EC model to predict the variations of electric potential, EOF velocity, concentration, and pH induced by electrode reactions. While the electric potential changes significantly at a lower voltage, this alteration decreases as the applied voltage rises, ultimately rendering the influence of electrode reactions on the EOF velocity negligible. Nevertheless, the concentration changes cannot be discounted. Although the overall concentration variation of the electrolyte in the microchannel is minor, the concentration of ions participating in electrode reactions experiences substantial fluctuations. The change in ion concentration induced by these reactions inevitably produces a pH gradient. Our approach enhances comprehension of concentration and pH variations, with the potential to mitigate challenges related to cellular, protein, ion, and solvent transport in microchannels. Especially, amphoteric biological molecules such as peptides and proteins experience shift in molecular electrostatic charges based on the pH of their local environment. Such pH-induced adjustments can influence solubility, and the direction of the electrostatic forces exerted upon them, thereby significantly impacting their transport behavior. A more advanced extension could include various forms of electrode reactions. Additionally, in practical systems, HEO and oxygen
reduction reactions (ORR) can generate bubbles, interrupting the contact between the fluid and the electrode. However, the dynamics of this phenomenon require a more detailed simulation to be elucidated.

4. Conclusions

In this paper, we propose a finite-element numerical model to investigate electrode reactions, hydrolysis reactions, and concentration polarization in an EOF system. The influence of these electrochemical processes is studied through the EC model based on electrokinetics and electrochemistry, in terms of ions concentration and pH changes, electric potential distribution, EOF velocity. It is found that the electrode reactions lead to shifts in the electric potential at the electrode-electrolyte interface. The electric potential of two electrodes moves closer, causing a reduction in both the electric field within the electrolyte and the current flowing through the system. The decrease resulted in a decline of the EOF velocity by 35% under the applied electric field $E_s = 50\text{V/cm}$, compared to the prediction by the electrokinetic (EK) model, which overlooks the reactions. As the potential shifts are considered in the EK model, the predicted EOF velocities by both models become similar. The small difference between the predictions is attributed to the concentration decline caused by the electrode and hydrolysis reactions.

According to the comparison, the EC model is capable of predicting the ion concentration and pH changes resulting from chemical reactions. An ion depletion zone is formed at the anode, with the maximum ion concentration gradient occurring at 50 μm from the electrode. In contrast, the cathode forms an ion-rich region with maximum pH growth. In the microchannel, electrode reactions lead to a nearly half decrease in $\text{Cl}^-$ and a pH increase of 3.5 under $E_s = 50\text{V/cm}$. Along with these processes, the water dissociates $\text{H}^+$ and $\text{OH}^-$ ions to maintain electrical neutrality, resulting in 1.3 pH shifts between the anode and cathode.

These findings obtained within the 800 μm microchannel under $E_s = 20$–$50\text{ V/cm}$ reveal that a large portion of the applied voltage is consumed by potential shifts caused by electrode reactions. As the
microchannel length grows, the shifts become relatively inconsequential; hence, the decline in the EOF velocity is negligible at high voltage. Nevertheless, the ions concentration and pH changes remain significant, essential in charged species transport.

The results prove that the EC model gives a good description of the influence of electrode reactions on the EOF system, providing important guidance for designing the devices that transport charged particles, manipulate fluid flow or depress the EOF impact. The further development direction of this research involves simulating the bubbles generated at the electrode and Faraday reaction transformation after ion depletion. Our subsequent work is to gain a comprehensive understanding of the dynamic electrochemical processes and their influence on fluid flow and ion transport in microfluidic systems.
ACKNOWLEDGMENTS

The authors would like to acknowledge support from the National Natural Science Foundation of China (No. 12072100) and Natural Science Foundation of Hebei Province (Nos. A2022202008 and E2022202132). We thank Prof. Jongyoon Han (Massachusetts Institute of Technology) for helpful comments.

Declarations

The authors have no relevant financial or non-financial interests to disclose.

Data availability

All data generated or analysed during this study are included in this published article.
REFERENCES


