Ion Fluxes and Electro-osmotic Fluid Flow in Electrolytes around a Metallic Nanowire Tip under Large Applied ac Voltage

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ABSTRACT: Motivated by the analysis of electrochemical growth of metallic nanowires from solution, we studied ion fluxes near nano-electrodes in a binary symmetric electrolyte on the basis of the modified Poisson–Nernst–Planck equations in the strongly nonlinear region at large applied ac voltage. For an approximate calculation of the electric field near the nanowire tip, concentric spherical blocking electrodes were considered with radius of the inner electrode being of typically a few ten nanometers. The spatiotemporal evolution of the ion concentrations within this spherical model was calculated numerically by using the finite element method. The potential drop at the electric double layer, the electric field enhancement at the electrode surface, and the field screening in the bulk solution were determined for different bulk concentrations, ac voltages, and frequencies. The appearance of ac electro-osmotic fluid flow at the tip of a growing metallic nanowire is discussed, based on an estimation of the body force in the liquid near the nanowire tip, which was modeled by a cylinder with hemispherical cap. Electric field components tangential to the electrode surface exist near the contact between cylinder and hemisphere. Our analysis suggests that ac electro-osmotic flow causes an additional convective transport of metal complexes to the tip of the growing metal nanowire and thus affects the nanowire growth velocity.

INTRODUCTION

In the recent years, metal nanowires have attracted great interest because of their versatile applicability in electronic and optical devices, and particularly in sensing. Examples of successful applications include electrical interconnects,7 and optical resonators,2,3 as well as chemical,4,5 biochemical6 and gas7,8 sensors. Fabrication of metal nanowires by lithographic methods,9,10 electromigration,5 cluster assembly,10,11 template-controlled,12 and field-assisted electrochemical growth13–15 (electrodeposition) from solution has been successfully demonstrated. Field-assisted wire growth from solution between two electrodes is especially interesting, as it is a cheap, fast, and high-yield fabrication technology. It has been reported for, example, the metals Au,10,11,13 Pd,14,16 In,13 and Pt.13,17 The corresponding growth velocities of micro-11 and nanowires13,14 were observed to depend strongly on the applied ac frequency and the concentration of ions in the solution.

Recently, we investigated the growth velocity of platinum nanowires growing from a K2PtCl4 solution, both experimentally and theoretically.17 The simple convection-diffusion model, used to describe the dielectrophoretic wire growth in an ac field, included the deposition of platinum from neutral platinum complexes at the wire tip. Although screening of the electric field by ions in the solution was neglected, the predicted growth velocities were found to be more than 1 order of magnitude smaller than the measured values. As a possible explanation for this discrepancy, it was presumed that, owing to the presence of ions, an additional ac electro-osmotic (ACEO) fluid flow near the nanowire tip causes an enhanced mass transport of platinum complexes to the tip. This conjecture is supported by the observation that the growth velocity changes by the addition of KCl to the solution.17 On the microscale, such an ACEO flow near a microtip has been used for bacterial cell capturing.10 The flow exhibits vortices in the vicinity of the tip which lead to a concentration of cells at the tip.

Determination of the ACEO fluid flow generally requires the solution of the Navier–Stokes equation. To this end, the body force in this equation has to be derived which, in turn, requires the calculation of the charge density and the electric field around the wire tip in the solution. In the dc case, static ion distributions have been studied based on the Poisson–Boltzmann theory.19–21 To capture the ion dynamics in electrolytes at large applied ac voltages Poisson–Nernst–Planck equations are typically used, see for example refs 21–24. At low frequencies and high ion concentration, ion crowding at the electrode surface occurs, which has been taken into account with appropriate modifications of the chemical potential or by extended approaches beyond mean field theory.25 The dynamically changing charge layer near the electrode is usually very thin compared to characteristic lengths of the electrode configuration. In those cases, a slip velocity in the tangential direction to the electrode surface is calculated, which then

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serves as a boundary condition for the calculation of the ACEO flow based on the Stokes equation.\textsuperscript{26–29} This approach is commonly referred to as slip approximation. Calculations of the ACEO flow beyond the slip approximation, where the body force is included in the Navier–Stokes equation, have been reported, for example, in refs 20 and 30. Such extended calculations become necessary with miniaturization of the electrodes. In the present work, we consider spherical nanoelectrodes with radius of a few ten nanometers, which is of the same order of magnitude as the double layer thickness so that the slip approximation is not applicable.

The aim of this work is to assess the occurrence of ACEO flow near a nanowire tip in order to elucidate whether this flow causes considerable additional mass transport of metal complexes to the metal wire tip, which could explain experimentally observed wire growth velocities. The paper is outlined as follows. First, we describe our model to analyze the effects in the solution in dependence on the frequency of the voltage and voltages. Second, we present results of the calculated flows near a spherical nanoelectrode at high applied ac frequencies.\textsuperscript{20,22} The value of the maximum concentration of cations (charge number \(z_c\)) and anions (−\(z_a\)), respectively. The ion concentration within the bulk of the solution is denoted by \(c_0\). The diffusion coefficient \(D\) is assumed to be equal for both ion species. The value of \(D\) is estimated by employing the Einstein–Stokes equation \(D = \frac{\kappa T}{6 \pi a \eta}\) where \(\eta\) is the viscosity of water (chosen as \(\eta = 1\) mPa s) and \(a\) is an effective radius of the ion including its hydration shell.\textsuperscript{31} As an upper estimate we used \(a = 0.5\) nm which yields \(D = 4.3 \times 10^{-10}\) m\(^2\)/s at a temperature of \(T = 293\) K.

The ion fluxes \(j\) are driven by the gradient of the chemical potentials \(\mu_i\) and the electrical potential \(\varphi\). For the chemical potential, we adopt the simple form

\[
\mu_i = k_B T \ln \frac{c_i}{c_0} - \frac{e_i \varphi}{\varepsilon} - \frac{e_i}{\varepsilon} \left( \frac{c_i}{c_0} - \frac{c_a}{c_0} \right)
\]

\[\text{(2)}\]

The term in the denominator (introduced by Bikerman\textsuperscript{32}) takes into account in a simple manner steric effects at high ion concentration, which limit the concentration. Crowding of attracted counterions at the electrode surface occurs at high electric fields and low ac frequencies.\textsuperscript{20,22} The value of the maximum concentration \(c_{i,max}\) in eq 2 is not well-known. The mean spacing of crowded ions \(a_i = c_{i,max}^{1/3}\) could be chosen as ion diameter or as diameter of an ion with its solvation shell. However, as discussed in ref 22 because of ion–ion correlations, the Bjerrum length \((\kappa = \epsilon^2/(4\pi\kappa T))\) could be also appropriate, which is about 0.7 nm in water at room temperature with relative permittivity \(\varepsilon_r = 80\). This length could be even larger if the permittivity \(\varepsilon_r\) considerably diminishes at large electric fields. In the following calculations, we used the value \(\varepsilon_r = 93\), corresponding to the solubility of potassium chloride at 293 K.\textsuperscript{33} The respective mean ion spacing is about 0.6 nm.

In the case of a growing nanowire, the nanowire tip moves relative to the fluid. Thus, an additional convection term with the nanowire growth velocity as fluid flow velocity should be added in the flux (eq 1b). The tip velocity is however very small compared to typical ion velocities driven by the electric field. The ion velocity \(v\) can be estimated from the balance of the electric field force and the drag force: \(z_e e E = 6 \pi \eta a v\). For an electric field of \(1 \times 10^8\) V/m, \(z = 1\), and the other parameters as above, one obtains \(v = 17\) mm/s, which is at least 2 orders of magnitude larger than typical tip velocities in the range from 10 to 50 000 nm/s.\textsuperscript{13,17}

The electric potential \(\varphi\) obeys the Poisson equation, eq 1c, with \(\rho\) as charge density. It is subject to the boundary conditions

\[
\varphi(r_1, t) = V(t), \quad \varphi(r_2, t) = 0
\]

\[\text{(3)}\]

These conditions differ from those used in several other studies.\textsuperscript{24,28,29} Usually, a mixed boundary condition was chosen to account for an additional capacity owing to the presence of a compact or oxide layer on the electrode surface. In the case of a noble metal nanowire, we think that the formation of an oxide layer during growth is unlikely. Moreover, expecting the thickness of a possible compact layer to be very small (of the order of one monolayer), the corresponding capacity would be very high and thus should be omitted in series circuit with the electrolyte volume.

For the permittivity \(\varepsilon = \varepsilon_r \varepsilon_0\) in the Poisson equation, an approximately constant value \((\varepsilon_r = 80, \varepsilon_0\) vacuum permittivity) was assumed. Note however that for large electric field strength \(2 \times 10^8\) V/m the value of \(\varepsilon_r\) decreases.\textsuperscript{24,33} Also with regard to the relatively simple modeling of steric effects in the chemical potential, eq 2, the following results have to be considered with caution in the limiting cases of large electric fields and high ion concentrations.

Since we suppose blocking electrodes, that is, the absence of chemical reactions of the ions at the electrodes, the boundary condition for the continuity equation, eq 1a, read

\[
j = - \frac{D}{k_B T} \frac{\partial}{\partial x} c_i - \frac{1}{\varepsilon} \epsilon_i \varphi
\]

\[\text{(1a)}\]

\[
j = - \frac{D}{k_B T} \frac{\partial}{\partial x} c_i - \frac{1}{\varepsilon} \epsilon_i \varphi
\]

\[\text{(1b)}\]

\[
\frac{\partial}{\partial x} \varphi = - \frac{\rho}{\varepsilon}
\]

\[\text{(1c)}\]
where \( j_i \) is the radial component of the ion fluxes. Starting from some initial condition for the concentration profiles, for example, \( c_i(t=0) = c_0 \), the system approaches after some transient time an asymptotic periodic regime which is characterized by

\[
c_i(r, t) = c_0(r, t = T/2)
\]

where \( T = 1/f \) is the oscillation period. In our calculations, discussed in the following section, we have always determined this asymptotic regime.

**RESULTS AND DISCUSSION**

**Evolution of Ion Concentrations.** The PNP equations, eq 1, were solved numerically to analyze the spatiotemporal behavior of the ion concentrations and the electric potential within the electrolyte. Details of the numerical procedure to determine the asymptotic periodic behavior, defined by eq 5, are presented in Appendix A. For an illustration of the calculated concentration evolution, concentration profiles at the inner nanoelectrode are shown in Figure 2 at different times for a frequency of 100 kHz and bulk concentrations \( c_0 = 0.1 \) and 1 mM. During cation attraction at the times \( t = 5/8T \) and \( 7/8T \) \((T = 1/f)\), the curves reveal an extreme increase of the concentration of several orders of magnitude within a very thin layer of a few angstrom thickness (for \( c_0 = 0.1 \) mM) at the electrode surface. On the other hand, during ion repulsion, a long-range ion depletion up to about 200 nm is observed. For the higher ion concentration \( c_0 = 1 \) mM, crowding of ions at the electrode surface occurs as shown in Figure 2c. The thickness of the corresponding high concentration layer reaches about 1 nm. At the outer electrode with large radius of 2 \( \mu \)m, the electric field is much smaller than at the inner nanoelectrode. Thus, only small ion fluxes develop.

Figure 1 schematically shows the formation of the dynamically charged regions near the electrode surfaces. The boundaries of the charged layers are denoted by \( r_3 \) and \( r_2 \), respectively. The bulk zone between these radii is practically charge neutral since both ion species have a concentration very close to the bulk concentration. The inner charged region \( r_1 < r < r_3 \) consists of a very thin inner layer with a high concentration of attracted ions and an outer layer with depletion of the repelled ions. For comparatively low frequency, the concentration in the inner layer can be several orders of magnitude larger than the bulk value. When the concentration reaches \( c_{\text{max}} \), this layer grows in thickness until a quasi-stationary state is reached within one-half oscillation period (c.f. Figure 2c), similar to the dc case.

The high space charge density \( \rho \) near the electrodes causes a strong screening of the electric field in the bulk zone. Commonly, this effect is expressed by a voltage drop at the electric double layer. To analyze this voltage drop, the solution of the Poisson equation, eq 1c, subject to the boundary conditions eq 3 is expressed by the following integral representation

\[
\varphi(r, t) = V(t) - \frac{1}{\varepsilon} \int_0^r dr' \rho(r', t)
\]

By differentiation of eq 6, one can easily show that the Poisson equation in spherical coordinates, \( (r^2 \varphi'(r')) = -r^2 \rho/\varepsilon \), is fulfilled. Because of charge conservation (electrical neutrality of whole electrolyte), the integral

\[
\int_0^{r_1} dr' r^2 \rho(r', t)/\varepsilon = 0
\]

vanishes so that the boundary condition \( \varphi(r_1) = 0 \) is also fulfilled. The first term on the right hand side of eq 6 is referred to as the external potential. The other two terms are due to the induced charge density. Both first and second term of the potential behave as \( 1/r \), while the last term exhibits a complex radial dependence. We are particularly interested in the potential near the inner electrode outside the charge layer, that is for \( r_3 < r < r_2 \). Supposing \( r_2 \approx r_1 \) and taking into account that \( \rho = 0 \) for \( r > r_2 \), one can simplify the potential in eq 6. As result one obtains the asymptotic expression

\[
q_{\text{sym}}(r, t) = \frac{r}{r_1} (V(t) - V_0(t))
\]

with the time-dependent voltage drop

\[
V_0(t) = \int_0^{r_1} dr' \frac{\rho(r', t)}{\varepsilon} - \frac{r_0 - r_1}{r_1}
\]

Correspondingly, the potential outside the charge layer behaves like the external potential, but with lower voltage, reduced by the potential drop \( V_0 \). The spatial dependence of the potentials in eq 6 and eq 8 at time \( t = 3/8T \) are compared in Figure 3a. The electric field, \( E(r) = -\varphi'(r) \), which drives the ion fluxes, is obtained from the potential eq 6 as

\[
E(r) = E_{\text{exc}}(r) + E_{\text{emb}}(r) + E_{\text{sci}}(r)
\]

\[
E_{\text{exc}}(r) = \frac{r r_0}{r^2 (r_2 - r_1)} V(t)
\]

\[
E_{\text{emb}}(r) = \frac{r r_0}{r^2 (r_2 - r_1)} \int_0^{r_1} dr' \rho(r')/\varepsilon
\]

\[
E_{\text{sci}}(r) = \frac{r r_0}{r^2 (r_2 - r_1)} \int_0^{r_1} dr' \rho(r')/\varepsilon
\]
At very high frequency of the ac field, the increase in the permittivity of water of \(\varepsilon_r\) due to additional charges on the electrode, which according to eq 6, results in a nearly linear decay at low frequencies immediately near the electrode, which reveals a nearly linear decay within the corresponding ion crowding zone (Figure 3a). The curves practically agree for \(r > r_b = 200\) nm (cf. also Figure 2). Parameters: \(t = 3/8\) \(\times 10^{-6}\) s, \(c_b = 0.1\) mM, \(V_0 = 5\) V, \(r_1 = 20\) nm, \(f = 100\) kHz. (b) Radial dependence of the electric field strength for various frequencies. At high frequency \(f = 1\) MHz, the induced charge is very small so that the curve practically agrees with the external electric field. The inset reveals a nearly linear decay at low frequencies immediately near the electrode, which reflects a plateau in the counterion concentration and corresponding charge density due to ion crowding.

\[
E_{scw}(r) = \frac{1}{r^2} \int_1^r \frac{dr'}{r'} \frac{\rho(r')}{\varepsilon}
\]

(10d)

The first field contribution, \(E_{scw} \propto r^{-2}\), corresponds to the external electric field. The second term \(E_{scw}\) shows the same radial dependence and causes a general enhancement of the field strength. The field enhancement at the electrode surface \(E_{scw}(r_1)\) is due to additional charges on the electrode, which guarantee that the boundary condition for the potential, \(\Phi(r_1,t) = V(t)\), is fulfilled. The presentation of the electric field as a function of the position in Figure 3b shows that a field enhancement is noticeable only in the immediate vicinity of the electrode. At frequencies of 1 and 10 kHz, the nearly linear decay of the field strength within a thin layer of a few nanometer thickness is due to the nearly constant charge density within the corresponding ion crowding zone (Figure 2c). Outside this zone, the last term \(E_{scw}\) in eq 10 causes the field screening within the bulk zone. Note that the present field calculations were done using constant relative permittivity of water of \(\varepsilon_r = 80\). As mentioned above, at the large calculated field strengths \(\geq 5 \times 10^8\) V/m the decrease of the permittivity of water with increasing field should be taken into account within a more accurate analysis. \(^{34,35}\) At very high ion concentration, the present classical description should also be improved by new extended approaches as proposed in refs 25, 37, and 38.

**Frequency Dependence.** At very high frequency of the ac voltage, the time for accumulation or depletion of ions at the electrode surface is very small so that the ion concentration at the electrode surface differs only slightly from the bulk value. In the opposite limit of very low frequency, the time for ion transport is sufficient to reach a quasi-stationary concentration profile near the surface, which is accompanied by a strong field screening within the bulk zone. By Fourier transformation of the electric field \(E(r,t)\), one finds the following relationship between the magnitudes of the Fourier components of the electric field strength within the bulk zone at \(r = r_b\) and at the electrode surface \(r = r_1\) (cf. Appendix B)

\[
|E(r_b, \omega)| = \frac{\omega}{\sqrt{\omega^2 + \omega_c^2}} \frac{r_b^2}{r_1^2} |E(r_1, \omega)|
\]

(11)

The characteristic transition frequency is given by \(\omega_c = \sigma/\varepsilon_r\) where the conductivity of the electrolyte follows as \(\sigma = 2zD\varepsilon_0 / (k_B T)\). The anions and cations have a charge number of \(\pm z\), for KCl \(z = 1\). For high frequencies \(\omega \gg \omega_c\), no screening occurs and the field decays \(\propto r_1^2/r_b^2\) as in vacuum. For low frequencies \(\omega \ll \omega_c\), the field in the bulk is additionally reduced by the factor \(\omega / \omega_c\). The amplitude of the Fourier component of the related voltage drop across the double layer, eq 9, is shown in Figure 4 as a function of the frequency. The curves demonstrate an almost entire voltage drop across the double layer for frequencies \(\omega \leq 0.01\ \omega_c\). The field enhancement at the electrode surface for low frequencies is shown in Figure 5 with the bulk concentration as parameter.

**Figure 3.** (a) Comparison of the electric potentials \(\Phi\) and \(\Phi_{sym}\) according to eq 6 and eq 8, respectively. The potential difference at \(r = r_1\) corresponds to the potential drop \(V_0\). The curves practically agree for \(r > r_b = 200\) nm (cf. also Figure 2). Parameters: \(t = 3/8\) \(\times 10^{-6}\) s, \(c_b = 0.1\) mM, \(V_0 = 5\) V, \(r_1 = 20\) nm, \(f = 100\) kHz. (b) Radial dependence of the electric field strength for various frequencies. At high frequency \(f = 1\) MHz, the induced charge is very small so that the curve practically agrees with the external electric field. The inset reveals a nearly linear decay at low frequencies immediately near the electrode, which reflects a plateau in the counterion concentration and corresponding charge density due to ion crowding.

**Figure 4.** Amplitude of the first Fourier component of the voltage drop across the double layer as a function of the frequency for different amplitudes of applied voltage \(V_0\). Transition frequency \(\omega_c/(2\pi) = 73\) kHz (\(c_b = 0.1\) mM, \(r_1 = 20\) nm, \(r_2 = 2\) \(\mu\)m).

**Figure 5.** Amplitude of the first Fourier component of the electric field at the electrode surface as a function of the frequency for different bulk concentrations (\(V_0 = 5\) V, \(r_1 = 20\) nm, \(r_2 = 2\) \(\mu\)m).

The curves reflect that the transition frequency \(\omega_c\) between the low and high frequency regime is proportional to the bulk ion concentration \(c_b\). Remarkably, the curves at higher bulk concentrations tend to the same field strength with lowering of the frequency, independent of the concentration. Obviously, the oscillation period becomes long enough to reach a quasi-stationary ion concentration profile.

**Estimation of Fluid Flow.** The present investigation of the ion dynamics near spherical nanoelectrodes is a prerequisite for the analysis of ACEO flow in the vicinity of the electrodes. The
flow of an incompressible fluid is determined by the Navier–Stokes equation

$$\rho m \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \eta \Delta \mathbf{v} + \mathbf{f}$$

(12)

where \( \mathbf{v} \) is the fluid velocity field, \( p \) is the pressure, and \( \mathbf{f} \) is the body force, which drives the fluid flow (\( \rho_{\text{av}} \), mass density; \( \eta \), fluid viscosity). Because of the incompressibility, we have additionally \( \nabla \cdot \mathbf{v} = 0 \). The present flow problem is characterized by a small Reynolds number \( Re = \rho_{\text{av}} v l / \eta \lesssim 10^{-4} \), where \( l \approx 100 \) nm was used as characteristic system length, and for the velocity we supposed \( v \lesssim 10^{-3} \) m/s. The body force in the present context is given by the charge density and the electric field: \( \mathbf{f} = \rho \mathbf{E} \). Within a purely spherical model, the body force would be balanced by the pressure gradient and, consequently, no fluid flow would evolve. Therefore, we extend in this section the geometry of our model as shown in Figure 6. The nanowire tip is approximated by a cylinder with a hemispherical cap. At the contact between cylinder and sphere, the symmetry changes from cylindrical to spherical-symmetric. Outside this transition region, the electric field near the electrode is directed in the radial direction. Omitting the presence of ions, the electric field within water around such an idealized nanowire tip was calculated using the software Matlab. The simulation cell for the calculation ranged from \( z = -0.85 \) μm to \( z = 2.15 \) μm and up to \( r = 3 \) μm. As result, the normal and tangential components of the axial-symmetric field are compared in Figure 7, where the normal component is the radial component in the respective cylindrical and spherical coordinate system. The tangential component, which is crucial for the ACEO flow, is the corresponding orthogonal component, that is, \( E_z \) and \( E_\theta \) respectively.

As expected, the tangential field component is mainly localized near the contact plane between cylinder and hemisphere (Figure 7). Because of the dominant normal field component and its moderate change along the surface of the spherical cap (Figure 7a), we expect that the radial dependence of the charge density does not dramatically change near the transition region. Thus, for the following rough estimate of the order of magnitude of the body force, we use the charge density calculated above for the mere spherical-symmetric case also within the transition region close to the contact plane \( z = 0 \) highlighted in Figure 7b. For an illustration of the spatiotemporal behavior of the body force, we first consider the body force within the contact plane \( z = 0 \). There, the tangential component of the body force is parallel to the axial \( z \)-direction

$$f_z(r, t) = \rho(r, t) E_z(r, t)$$

(13)

As reasoned above, for a crude estimate of the charge density in eq 13, we use our spherical-symmetric solution of the PNP equations without taking into account fluid flow. The corresponding spatiotemporal behavior of the charge density is shown in Figure 8 at frequencies 10 kHz and 1 MHz, that is, below and above the transition frequency \( \omega_T/(2 \pi) = 73 \) kHz. The plots reveal a phase shift between the oscillation of the applied voltage and the charge density. For the frequency of 10 kHz, the shift of the zero crossings of the charge density depends only slightly on the radius, whereas for the high frequency of 1 MHz the phase shift increases with distance from the electrode surface.

The tangential electric field component in eq 13 is actually affected by the induced charge density. To simplify matters, we consider in the following the limiting case where this effect is small and the electric field is almost equal to the external field. Choosing a bulk concentration of 0.1 mM, this is fulfilled for frequencies \( f > 300 \) kHz (cf. Figure 5). The electric field is then
in phase with the applied voltage, but not with the space charge. An important consequence is that charge density and electric field in eq 13 exhibit different signs during certain time intervals or, in other words, the body force changes sign with time. As an example, Figure 9a shows the $z$-component of the body force within the plane $z = 0$ as a function of time at different radial distances for a frequency of 1 MHz. All curves exhibit two zero crossings within one-half oscillation period. For determining the ACEO flow, the time-averaged body force is usually used. Figure 9b shows the $z$-component of the time-averaged body force as a function of the radial position. Remarkably, this curve reveals a change in sign of the body force, suggesting fluid flow near the nanowire to occur in a direction opposite to the wire growth direction, and a back-flow at distances beyond 90 nm.

For calculating the ACEO flow, the slip approximation has often been applied; that is, the Stokes equation without the body-force term is solved with the slip velocity at the electrodes as boundary condition for the velocity. Hereby, the slip velocity is derived within the thin double layer approximation by solving the PNP equations without considering ACEO flow. In view of the complex spatiotemporal behavior of the body force found here, the ACEO flow should be derived by fully taking into account the spatiotemporal dependence of the body force. However, to simplify matter, we consider here the case of high frequencies above the transition frequency and replace the body force in the Navier–Stokes equation, eq 12, by its time average over an oscillation period $f$ (time average denoted by a bar). Because the expected fluid flow is characterized by a small Reynolds number, we neglect the nonlinear term in eq 12 and consider stationary flow. Then, eq 12 simplifies to

$$\eta \Delta v = \nabla \bar{p} - \bar{f}$$

(14)

Let us recall that the body force in this equation is approximately derived by extending the charge density $\rho(r,t)$, obtained above for the spherical-symmetric case, into the cylinder region $z < 0$. This is of course a crude approximation, overestimating the charge density in this region. However, in view of the small extension of the tangential electric field in the $z$-direction (cf. Figure 7), this approximation should yield a tentative picture of the fluid flow and an estimate of the order of magnitude of the flow velocity. The Stokes equation, eq 14, has been solved numerically by means of the software Matlab. Along the electrode surfaces and on the edges of the simulation cell ($0 \leq r \leq 3 \, \mu m$, $-0.85 \, \mu m \leq z \leq 2.15 \, \mu m$), the velocity was set to zero. An exception marks the rotational axis $r = 0$, as this is no system boundary. The calculated velocity field of the fluid flow near the nanowire tip is shown in Figure 10. Accordingly, the body force drives the fluid from the nanowire tip along the
nanowire surface in the negative z-direction within a cylindrical shell of about 50 nm thickness. The main back-flow occurs in a cylindrical shell with an inner radius of about 100 nm and outer radius of 150 nm. The magnitude of the estimated velocity reaches values up to 0.6 nm/s. A qualitatively similar flow pattern was reported by Yeo et al.\textsuperscript{18} for a wire geometry on the microscale using a slip boundary condition.

Frequency and bulk concentration in the example in Figure 10 have been chosen such that screening of the external electric field is small, indicated, for example, by the corresponding small voltage drop in Figure 4. With increasing bulk concentration, the charge density and body force should increase, which would result in higher flow velocity. However, depending on the frequency, also the field screening by the induced charge density increases, which additionally leads to a temporal phase shift between voltage and electric field. Thus, the electric field in the electrolyte can strongly differ from the external field. In the limiting case of very small frequencies and high bulk concentrations, strong field screening dramatically lowers the tangential electric field so that ACEO flow becomes very slow.\textsuperscript{26,27} In the frequency and concentration region where highest flow velocity can be expected, it is obviously necessary to solve the PNP equations exactly for the real axial-symmetric nanowire geometry. If the fluid velocity becomes comparable to the ion velocities, the ACEO flow has to be included also in the PNP equations. Solution of the coupled PNP and Navier–Stokes equations for a nanowire electrode geometry is a numerically challenging problem beyond the scope of the present paper.

Regarding the nanowire growth, the appearance of the roll cell in the velocity field shown in Figure 10 leads to an additional convective transport of metal complexes or clusters to the nanowire tip where the metal is deposited. For typical nanowires (e.g., 50 nm radius and 2 μm length) and concentrations of Pt complexes (e.g., 0.1 mM), the region, where the wire forming Pt complexes come from, extends to about 16 μm around the nanowire. This follows from a balance of the number of Pt atoms in the wire and in the solution. According to our simulation, the size of the fluid-flow roll-cell is less than 1 μm. The range of the dielectrophoretic force is even shorter, of the order of the wire radius. Consequently, Pt mass transport outside the ACEO flow region is mainly by diffusion. On the basis of these estimates, the Pt mass transport from the bulk solution to the nanowire tip can be characterized by a series connection of the following processes: diffusion in the outer region, ACEO convection in the middle region, and additional convective transport owing to the dielectrophoretic force near the nanowire (cf. Figure 11).

To get a quantitative assessment of the impact of ACEO fluid flow on the nanowire growth velocity, we compared simulations of nanowire growth in the presence and absence of ACEO flow for the following parameters: \( f = 200 \text{ kHz}, \varepsilon_0 = 0.1 \text{ mM}, V_0 = 5 \text{ V}, \) and \( r_1 = 50 \text{ nm}. \) Further parameters, describing the dielectrophoretic force, were taken as in our previous work.\textsuperscript{17} As a result of our simulations in the case of Pt complexes, we find that the growth velocity increases due to ACEO flow from 0.75 to 1.4 nm/s. The impact of fluid flow on the growth velocity is more pronounced for larger Pt clusters, exhibiting a smaller diffusion coefficient (cf. ref 17). For clusters with 23 nm diameter and concentration of 0.24 mM (=1.4 \times 10^{17} m^{-3}), i.e., the bulk Pt density is the same as for the example with Pt complexes) the growth velocity considerably changes from 0.44 to 8.5 nm/s. It has to be emphasized that these calculated growth velocities are crude estimates because of the used rough approximation of the charge density and due to the finite size of the simulation cell of 6 μm × 6 μm.

To explain the dependence of the nanowire growth velocity on the particle size, we consider the Pt mass transport in analogy to an electric current through a series connection of resistors. The nanowire growth velocity is proportional to the Pt particle current \( I, \) which can be expressed by the concentration difference between the Pt concentration in the bulk, \( c_{\text{Pt}} \), and at the electrode surface, and by a total resistor, \( R_{\text{tot}} \), as \( I = c_{\text{Pt}}/R_{\text{tot}} \) (assuming the particle concentration at the electrode to be considerably smaller than the bulk concentration).

According to the schematic in Figure 11, the total resistor is the sum of individual resistors \( R_{\text{tot}} = R_1 + R_2 + R_3, \) where \( R_1 \) corresponds to the DEP region, \( R_2 \) to the ACEO region, and \( R_3 \) to the diffusion region. Only resistor \( R_3 \) is affected by the ACEO fluid flow. The resistors \( R_1 \) and \( R_2 \) are proportional to the reciprocal of the particle diffusion coefficient. The convective Pt flux due to ACEO fluid flow, however, is independent of the Pt particle diffusion coefficient since it results from the ion dynamics. Comparing mass transport in the absence and presence of ACEO flow, one finds that additional ACEO flow causes a lowering of resistance \( R_3, \) leading to higher particle current \( I \) and, correspondingly, to higher nanowire growth velocity. For lower diffusion coefficient (larger Pt clusters) the corresponding resistances, describing diffusion and DEP convection, are higher. Thus, the lowering of \( R_3 \) by additional ACEO flow is comparatively higher for larger Pt clusters, leading to a stronger increase of the growth velocity. The calculated ACEO flow pattern suggests that this flow also has impact on the morphology of the growing nanowire. As shown in Figure 11, the fluid flow leads to a preferred transport of Pt complexes or clusters to the nanowire tip where they are attracted by the dielectrophoretic force, and finally incorporated in the wire. Assuming that Pt complexes or clusters attached at the wire tip, are immediately incorporated, the fluid flow along the cylinder surface is depleted of platinum. This could explain why the cylinder practically does not grow in diameter.

\section{CONCLUSIONS}

On the basis of the modified Poisson–Nernst–Planck equations, the complex spatiotemporal behavior of the ion concentrations around a spherical nanoelectrode due to large ac electric fields was calculated for a wide frequency range. A special numerical algorithm was proposed to calculate the asymptotic periodic solution after many oscillation periods in

![Figure 11. Schematic of Pt mass transport in the presence of ACEO fluid flow. The flow approaches the nanowire tip is rich in Pt complexes or clusters. As the flow passes the wire, Pt particles are attracted to the wire by the dielectrophoretic force (DEP), which leads to a depletion of Pt particles within the fluid. During back flow, the fluid is enriched with Pt particles owing to particle diffusion from outside of the fluid roll cell.](Image)
an efficient way, using the finite element method. Regarding the question of the appearance of an ACEO flow around a nanowire tip, this work was focused on calculating electric field and charge density in the electrolyte.

The dynamically changing double layer at the electrode is characterized by a very thin inner layer of attracted counterions of a few angstrom thickness with ion concentration, which can exceed the bulk value by orders of magnitude. For low frequency and high bulk concentration, ion crowding at the electrode surface leads to thickening of this inner layer. The extent of the depleted region of repelled co-ions is typically much larger than this inner layer.

For frequencies below the transition frequency \( \omega_T \), the calculated electric field at the electrode surface is considerably larger than that without electrolyte between electrodes. This field enhancement should be of interest for analyzing field-dependent atomic surface reactions at the electrode, as for example, adsorption and desorption of ions, and presumably also metal deposition from metal complexes during nanowire growth. The field enhancement at the electrode surface is accompanied by strong field screening in the bulk electrolyte. At low frequencies, extremely high ion concentrations and electric field strengths can appear at the electrode surface. Under these conditions, the field dependence of the permittivity of water should be considered. The effect of electrostatic correlations in concentrated electrolytes on electrokinetic phenomena has been studied for example in ref 25.

For nanowire growth at frequencies slightly above the transition frequency, our estimations suggest that, due to small field screening, a noticeable tangential electric field near the nanowire tip drives an ACEO flow. Our approximate derivation of the corresponding body force in the Navier–Stokes equations reveals a complex spatiotemporal behavior of this force. Flow calculations predict a toroidal roll cell-like fluid flow around the tip. This ACEO flow was shown to increase the nanowire growth velocity, particularly for the case of growth from metal clusters.

Finally, it is emphasized that the present prediction of ACEO flow around a nanowire tip is based on rough estimates of the order of magnitude of the charge density and the related body force in the Navier–Stokes equation. Substantiation of this approach is urgently needed by solving the coupled PNP and Navier–Stokes equations for the actual nanowire geometry, where the electro-osmotic flow should be included in the PNP equations.

**APPENDIX A: NUMERICAL SOLUTION**

The PNP equations, eq 1, were solved using the finite element method. To derive the weak form of eq 1a, this equation is multiplied by a test function \( w_i(r) \) and integrated over the entire volume \( \Omega \) between the two electrodes (cf. Figure 1)

\[
\int_{\Omega} dV \left( \frac{\partial}{\partial t} c_i + \nabla \cdot j_i \right) w_i = 0
\]

(15)

Partial integration with consideration of the boundary condition \( n \cdot j_i = 0 \) on the electrode surfaces (\( n \), normal unit vector) yields the weak form

\[
\int_{\Omega} dV \left( w_i \frac{\partial}{\partial t} c_i - j_i \cdot \nabla w_i \right) = 0
\]

(16)

Time integration was performed by the following implicit finite difference scheme with \( \tau \) as time step

\[
\int_{\Omega} dV \left( \frac{c_i^{n+1} - c_i^n}{\tau} - j_i^{n+1} \cdot \nabla w_i \right) = 0
\]

(17)

where the superindex denotes the time step.

For the solution of the variational problem eq 17 the concentrations were substituted by the corresponding chemical potentials to avoid numerical problems when the concentration approaches the maximum value \( c_{max} \). According to eq 2, one obtains

\[
c_i = c_{max} \frac{\exp(\mu_i/k_B T)}{1 + \sum c_j \exp(\mu_j/k_B T)}
\]

(18)

For the finite element calculation, a highly nonuniform mesh with very small elements near the electrodes was created with the software Comsol and exported to Matlab. Within the elements, quadratic ansatz functions for the functions \( \mu_i \) and \( w_i \) were chosen. The resulting system of nonlinear algebraic equations for the field variables at the nodes of the finite element mesh was solved by means of the Newton method using the software Matlab.

As initial conditions, uniform ion concentrations \( c_1 = c_2 = c_b \) were chosen. As already mentioned above, after some transient time, the concentrations reach their asymptotic periodic behavior characterized by \( c_j(t) = c_j(t - T/2) \). Especially at intermediate frequencies \( \omega \approx \omega_T \), many oscillation periods must be calculated before this asymptotic stage is reached. To avoid this inefficient long-term calculation, an additional convergence acceleration was implemented. The condition \( c_j(t) = c_j(t - T/2) \) at every node of the finite element mesh reads in the discrete time formulation \( c_j^t = c_j^{t-N} \) with \( N \Delta t = T/2 \). Thus, at every time step, the concentrations were manipulated according to the following rules, where \( c_i^t \) are the manipulated values:

\[
c_1^{t+1} = (1 - 2^{-N})c_1^t + 2^{-N}c_2^{t-N}
\]

(19a)

\[
c_2^{t+1} = (1 - 2^{-N})c_2^t + 2^{-N}c_1^{t-N}
\]

(19b)

For the initial steps, when \( n - N = k < 0 \), the values \( c_i^t = \hat{c}_i \) were taken. This algorithm ensures that the amount of ions is conserved. The asymptotic periodic state is of course unaffected by the manipulation. From the modified concentrations \( \hat{c}_i \) the related chemical potentials according to eq 2 were computed, which were used then to calculate \( c_i^{t+1} \) as described above.

**APPENDIX B: FIELD SCREENING**

In the case of a considerable screening of the electric field by the ions accumulated at the electrode surface, the field strength rapidly decays with increasing distance from the surface. For quantifying the screening, the field strength on the electrode surface was compared with the strength at a distance where the charge density approaches zero. To this end, the change of the total charge \( \partial Q/\partial t \) within a spherical shell \( r_1 \leq r \leq r_2 \) was considered (cf. Figure 1, \( j_i(r_1) = 0 \))

\[
\frac{\partial}{\partial t} Q(t) = -4\pi r_1^2 \varepsilon (z_{j_1}(r_1, t) + z_{j_2}(r_1, t))
\]

(20)

Since at \( r_1 \), the concentrations are practically equal to the bulk concentrations, the diffusive contribution of the ion flux...
vanishes so that $j_z(r_{bl},t) = -j_z(r_{bl},t) = D\kappa_0 E(r_{bl},t)/(k_b T)$ and with $z = z_1 = z_2$.

$$\frac{\partial}{\partial t}Q(t) = -4\pi r_{bl}^2 2\varepsilon_0 c^2 E(r_{bl},t)$$

(21)

On the other hand, denoting the spherical shell volume by $\Omega_b$ and its boundaries by $\partial \Omega_b$, the total charge is given by

$$Q = \int_{\Omega_b} dV \rho = \int_{\Omega_b} dV V \cdot \vec{E} = \int_{\partial \Omega_b} dA \vec{n} \cdot \vec{E}$$

(22)

Thus, one obtains

$$Q(t) = 4\pi \varepsilon_0 \left( E(r_{bl},t)r_{bl}^2 - E(t_1,t)r_1^2 \right)$$

(23)

Combining the time derivative of eq 23 with eq 21 leads to

$$\frac{\partial}{\partial t}E(r_{bl},t) + \omega_r E(r_{bl},t) = \frac{r_1^2}{r_{bl}^2} \frac{\partial}{\partial t}E(t_1,t)$$

(24)

where $\omega_r = 2\varepsilon_0 c^2/(\varepsilon_0 k_b T)$. The Fourier transform of the last equation reads

$$E(r_{bl},\omega) = \frac{10}{10 + \omega^2} \frac{r_1^2}{r_{bl}^2} E(t_1,\omega)$$

(25)

Calculation of the magnitude of $E(r_{bl},\omega)$ eventually yields eq 11.

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**Notes**

The authors declare no competing financial interest.

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