Probing space charge and resolving overlimiting current mechanisms at the micro-nanochannel interface

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We present experimental results demonstrating that a primary mechanism for the over-limiting conductance in micro-nanochannel devices is the structure of the extended space charge developing at the depleted interface under high currents. This is correlated with a distinctive maximum in the differential dc resistance. At high voltage, a local minimum is observed in some cases. Based on numerical simulations, this minimum appears to result from surface conduction. Lastly, anomalously sharp resistance minima are observed in devices with shorter nanochannels. These results indicate electroconvective instability plays a minimal role in driving the over-limiting current in these devices.

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The non-linear dc response of electrochemical systems containing ion-selective interfaces, e.g. with electrodes, electro-deposition, shock electrolysis, ion exchange membranes, or fabricated nanochannels, has been the subject of a tremendous amount of research [1–17]. Much of this work has focused on understanding how the canonical phenomenological picture of dc current-voltage response emerges from a variety of possible mechanisms [8–11, 13–15, 18]. At very low voltages, the response appears essentially Ohmic even though concentration polarization (CP) begins to develop salt gradi- ents across the system in an attempt to maintain electroneutrality. For cation-selective interfaces, the inter face adjacent to the anode becomes depleted and that adjacent the cathode becomes enriched. At a sufficiently high (limiting) current [10], the depleted salt concentration approaches zero at the interface, corresponding to an approach to infinite resistance. Electroneutrality cannot be maintained and a region of extended space charge (ESC) develops [11]. This transition occurs just above the Ohmic response and is identified with a deflection of the I-V slope, corresponding to the increased resistance of the system due to depletion and subsequent ESC development (see Fig. 1 and caption). Depending on the geometry of the system, particularity the degree of confinement in shallow microchannels [20, 21], a second transition typically occurs at even higher voltages marked by an inflection of the slope. Both cases can be seen in Fig. 1.

A number of mechanisms have been proposed to account for the over-limiting currents (OLC) in a variety of contexts. Rubinstein and Zaltzman put forth a theory of electrokinetic instability-driven electroconvection to explain chaotic fluctuations in over-limiting current-time plots for membrane systems with large interfaces [12, 13]. This effect was experimentally demonstrated to contribute to the OLC in planar ion-selective membrane systems [14] and nanoslot-reservoir interfaces [13]. Micro-nanochannel devices show similar I-V characteristics with evident micro- and nano-channel geometry-dependence [20, 22]. Dydek et. al proposed a model for microfluidic systems with fluid-impermeable membranes which predicts the dominant mode of OLC based on microchannel depth [18]. The shallowest channels are dominated by a surface-conduction effect [23], intermediate depth channels by EOF and/or pressure-driven backflow vortices [18, 24], and deep channels, or unconfined systems by the aforementioned electrokinetic instability. Khair [25] considered the effects of fluid-flow through the ion-selective region on instability, which can be significant in nanochannels but generally not membranes. But the earliest proposed mechanism for sustaining OLC was the existence and structure of the ESC itself [11], where results are obtained for an ideally-selective membrane system. Nanochannels and sufficiently porous membranes can be sufficiently nonideal [32] which can have a considerable effect on the structure of the ESC [29].

Experimental evidence for suppression of current in shallow micro-nanochannel systems [20] and increase of the critical voltage for instability due to microchannel confinement [21] corroborates the general picture put forth in the paper by Dydek et. al. [18]. However, vortex arrays have been observed to develop in intermediate-depth channels with dynamics similar to those associated with the loss of stability [30, 31]. This seems to indicate some presence of the instability even in microchannels shallow enough that stability should not be the dominant OLC mode. The present paper aims to better clarify both the respective roles of these various mechanisms, and the questions yet to be addressed. Specifically, we provide evidence which indicates that the electrokinetic instability does not appreciably contribute to the OLC in microchannel depths up to approximately 50 μm, and that a large contribution to the OLC response is directly from the ESC itself.

To that end, we employ electrochemical impedance spectroscopy (EIS) along with current-voltage and chronoamperometric measurements to study the OLC in three different micro-nanochannel device geometries.
FIG. 1: Slow (S) and fast (F) -sweep I-V (top) for each of the devices tested with rates of 300 and 20 seconds per voltage step, respectively. The bottom figure shows sample I-t plots for 5 (black, lower OLC) and 12 Vdc (blue, higher OLC) bias used to obtain the slow I-V for the 50 µm 1 mm case. The inset shows a schematic of the micro-nanochannel device.

Two have 50 µm-deep microchambers and a third has a much shallower 3 µm microchamber. The connecting nanochannels are 190 nm deep and approximately 2 mm wide in all cases. One of the 50 µm devices and the 3 µm device have 1 mm long nanochannels and the other has a nanochannel approximately 0.5 mm long. The fabrication of the devices are similar to those used in our previous studies and discussed in detail elsewhere [20]. The results here were obtained using a KCl electrolyte at a concentration of about 2 × 10⁻⁵ M and the preparatory procedure for the channels is described in the supplementary materials [37]. We employ potentiostatic EIS with a 50 mV perturbation voltage applied to the preconditioned system under dc bias using a Gamry 3000. EIS spectra are taken from 1 MHz down to about 0.5 Hz. Thus no appreciable Warburg behavior appears in the Nyquist plots [37].

Two types of I-V are shown in Fig. 1. The fast sweep I-V is taken in 100mV steps taken at 20 seconds per step, and the slow sweep is obtained from the last few seconds of an I-t for the 300 s conditioning voltage step prior to each EIS frequency sweep. The slow I-V is more representative of the steady-state response of the system, corresponding to a well-developed CP and thus provides an accurate measure of the transition between regimes. Note that the difference between fast and slow is small in the Ohmic regime, and becomes pronounced at voltages corresponding to the limiting depleted condition and consequent emergence of ESC. However the difference is not very pronounced in the 3 µm case, suggesting that field-focusing effects play an important role in governing the transient development of the ESC. The departure from Ohmic response occurs between 1.5-2 V for both 50 µm cases, and slightly lower for the 3 µm device, around 1 V. In all cases, there are distinctly different qualitative and quantitative OLC responses at different voltages. Hence there are lower- and higher- OLC regimes, denoted 1 and 2 respectively. OLC1 has a lower slope—hence one expects higher resistance—than either the Ohmic or OLC2 regimes. OLC2 is denoted by an increase in slope. This is most apparent in the 50 µm devices, where the dramatic difference between the slow and fast I-V accentuates this feature. Like the Ohmic-to-limiting regime, the transition voltage between the two apparent OLC regimes increases with increased field-focusing. However, the length of the nanochannel affects the OLC response more profoundly than the Ohmic response.

The chronoanperometric response used to obtain the slow I-V does not show any evidence of chaotic fluctuations in the current associated with the strong role of electro-convective instability at any voltage (see Fig. 1). This agrees with the predictions of [18] for sufficiently shallow channels.

Fig. 2 shows a typical series of Nyquist plots for the 50 µm 0.5 mm device, which represent the general trend in all the devices. Both imaginary and real impedance components increase with increasing voltage through the Ohmic regime and into the OLC1 regime. Curiously, at a given voltage, the impedance reaches a local maximum and is observed to decrease with subsequent increase in
voltage, corresponding roughly to the OLC1-2 transition. An impedance minimum is observed with a subsequent rise upon further increase in the voltage in some cases. While the details of the impedance maxima and minima depend on the details of the device geometry, particularly microchannel height and nanochannel length—as well as the preparation procedure and age of the nanochannel itself [30]—these seem to be general features of the micro-nanochannel response. We will consider the 1 mm long channels in greater detail first.

The low-frequency $\text{Re}(Z)$, effectively the differential dc resistance, is plotted versus dc voltage in Fig. 3 for the 1 mm long channels. These are obtained by averaging over the lowest 10 frequencies of the EIS spectra at each voltage. In the data shown, the Ohmic region is nearly flat. Then the resistance increases with increasing voltage and reaches a maximum value above the Ohmic-to-OLC1 transition. For the 50 $\mu$m 1 mm channel, the maximum resistance is lower than the 3 $\mu$m channel [33], occurs at higher voltage, and the resistance generally appears to decrease after the maximum [39]. In the 3 $\mu$m channel (and in the 50 $\mu$m 0.5 mm device as discussed separately below), a resistance minimum is observed at yet higher voltages.

Figure 4 shows phase vs. frequency data for a sequence of voltages on a 3 $\mu$m channel. The phase drops from 0 to around −85 degrees with increasing frequency more rapidly as the voltage increases. Previous work concerning the changes in the dc conductance of nanochannels due to bulk concentration [27, 28] suggests this corresponds to development of CP. In such non-ideal systems this occurs both inside and outside the nanochannel [32, 34]. Compare this with Figs. 3 and 4. The change in $\text{Re}(Z)$ is relatively small in the Ohmic region (see Fig. 3), resulting from increased depletion near the interface and corresponding to the resistive-to-capacitive shift below a few kHz. However, the more substantial changes in resistance seen above the Ohmic-to-OLC1 transition corresponds to a slight shift back towards resistive response above 10 kHz. Because shifts in this range occur only above the Ohmic region and do not appear to be either significantly suppressed or enhanced by microchannel height (additional cases in [30]), the shift is likely due to the development of the ESC.

The 50 $\mu$m 0.5 mm devices (see Fig. 4) have a distinctly different behavior. As the dc bias increases, the low-frequency $\text{Re}(Z)$ increases through the sub-limiting voltages, even though the response appears essentially Ohmic in the current-voltage plot up to around 1.5 Vdc. Around the knee region, the resistance begins to saturate. Comparing the 50 $\mu$m devices at voltages around this knee, there is not as much of a difference between fast and slow I-V in the 0.5 mm long nanochannel as the 1 mm nanochannel (see Fig. 1b). The classical limiting condition on the salt flux density is governed by the geometry of the microchamber region itself [33]. Thus the limiting depletion and ESC development should occur at roughly the same voltage. Indeed the Ohmic-to-OLC1 knee appears at approximately the same voltage for both 50 $\mu$m channels in Fig. 1. The 1 mm case has a gradual change in I-V slope occurring just above 6 V, just below the (broad) resistance maximum while the 0.5 mm case has a resistance plateau from about 3 V until the occurrence of an anomalous, discontinuous jump (just above 8.5 V for channel 1 as seen in Fig. 5). This seems to imply that the nanochannel has some influence also over both the evolution and ultimate structure of the ESC.

Upon further increase of the dc bias, the resistance begins to decrease with a sharp minimum around 8.5 V before jumping back up to a nearly constant value. The depth and position of the minimum appeared to depend somewhat on the degree of use of a given channel, but the character—the well-defined minimum and rapid rise—were consistent features. In cases where a minimum was observed in the longer channels—i.e. the 3 $\mu$m case—the increasing resistance following the minimum was consid-
FIG. 5: Low-frequency Re(Z) vs. applied voltage response for two different 50 µm 0.5 mm micro-nanochannel devices. Channel 1 data is shown in Fig. 1 [2]. The two channels were subjected to pre-conditioning cycles of different lengths (see [30]). Note the higher resistance following the minima in both cases.

erably slower than in the 0.5 mm nanochannel cases. Notice that there is a corresponding bump visible in the slow I-V (≈ 8.5 V, see Fig. 1), indicating that this is not a transient response. Notice also that the slope in the I-V is higher above this voltage, which should correspond to a lower resistance. However, the EIS-determined resistance is in fact higher here.

From a comparison to the 1D theory [22, 35] and 2D PNP simulations [30], the ESC itself is responsible for the appearance of the prominent resistance maximum. Accordingly, however, beyond this maximum, the resistance of the ESC drops monotonically in the absence of any other effects. However, by modeling charged microchannel walls, the 2D electro-diffusion simulations show a high-voltage resistance minimum. The appearance of the resistance-voltage curve (Fig. 8 [30]) is similar to the 3 µm case in Fig. 3. This suggests that the surface-conduction mechanism is indeed making a very large contribution to the OLC, particularly at higher voltages in the 3 µm case. In comparing the 3 and 50 µm 1 mm channels, the most apparent distinction is the lower resistance of the 50 µm channel due primarily to the larger microchannel cross-section. However, we can anticipate that both field-focusing and convection effects contribute as well. The reason for the differences between the 50 µm 1 mm and 0.5 mm apparent in both OLC regimes is unclear.

In summary, we have demonstrated that the ESC itself is responsible for a significant component of the OLC and provided experimental evidence confirming the basic picture of depth-dependent regimes of OLC [18]. In this picture, the EOF backflow mechanism should be the dominant OLC mode in the 50 µm device. Indeed, vortex rolls have been observed in the device [30]. We cite the distinct absence of chaotic fluctuation in the 1-t signatures, indicative instability-driven OLC, as evidence that the instability is not dominant in depths up to 50 µm. Vortex-like patterns and dynamics characteristic of the instability have nonetheless been observed in devices of similar design [30, 36]. Furthermore, it has previously been shown that the threshold voltage instability increases [21] while the maximum growth rate of critical perturbations and the overall range of unstable perturbations decreases [33] with decreasing channel depth. Accordingly, any fluctuations due to vortex dynamics may be relatively small, slow, and thus difficult to observe in shallow channels. So while the vortices due to instability may be present [21, 30], they do not seem to contribute strongly to the OLC. However, the present body of theoretical and numerical work on instability is based on models which more closely resemble interfaces with membranes rather than nanochannels. This raises two questions: what, if not the instability, is responsible for the abrupt change in slope between the lower and higher OLC regimes evident in the 50 µm current-voltage response and why is this feature subdued in the shallower channel? Lastly, it has been shown that Dukhin-type vortices at a geometrically-modulated membrane interface can interact with the instability and in some cases dominate the OLC response [31]. Similar vortices have been observed to dominate the flow pattern in micro-nanochannel devices at long times [36]. It is plausible that these could interact with the EOF-backflow mechanism as well as the instability.

So a number of questions persist. In addition to clarifying the roles of EOF-backflow, Dukhin vortices, and nature of instability in a micro-channel, field-focusing [22, 35], and non-ideality [29, 32, 34] also require further study. Most curious, however, is the response of the 0.5 mm long nanochannel with the previously unobserved sharp minimum and anomalous jump to higher Re(Z) compared to the increase in OLC2 slope. These phenomena are currently being investigated.

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[39] In some cases, there are smaller subsequent local maxima [30]