Additional file 1 for

Dynamic analysis of the Extended Space Charge Layer using Chronopotentiometric Measurement

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**1. Voltage-current characteristics in both shear-flow assisted- and no shear- system.**

Voltage-current (*V*-*I*) characteristics in the ion concentration polarization (ICP) system was the unique and peculiar form, since it exhibited the overlimiting conductance (OLC) at larger current far beyond the limiting current that classical theory predicted. Numerous studies on both theory and experiment verified the OLC mechanisms in large part, especially regarding the electro-convection (EC). Much ICP platforms, coupled with the shear flow, has been actively investigated so far in order to characterize the convectional ED system in detail. Recently, we developed another form of shear-flow assisted ICP system, which was mainly consisted of the external flows from the tangential direction to the electric field, forming a sheath ICP layer. In the previous research, we controlled all the parameters including flow-rate, voltage and geometry) and revealed out the relevant-electrokinetics (flow-pattern, streamline, current and OLC).

Here, we utilized the voltage-sweeping method with a voltage sweep rate at 3.33 mV/sec, characterizing the *V*-*I* behaviors when Q = 20 nL/min and Q = 0 from the side channel respectively. In the present work, we also confirmed that the unique voltage-current characteristics in accordance with our previous research, regarding both (1) limiting current value (*Ilim*) and (2) OLC. When Q = 0, the micro-/nano-fluidic platform could be regarded as the conventional 1D ICP system, resulting in the ohmic-limiting-overlimiting regime as shown in SI Figure 1. Here, the limiting currents reached the value *Ilim,Q*=0 as 2nA. The convective flows with Q = 20 nL/min restricted the propagation of the ion depletion zone, (or confining the diffuse layer from the end of microchannel into the shear-flow boundary), the limiting current was dramatically enhanced since *Ilim* is inversely proportional to the system dimension. Hence, the *Ilim,Q*=20 was obtained to be 12nA in our experiments.



Figure S1. In order to obtain the limiting current values, we conducted the voltage-sweeping method in our systems. Under the 20nL/min flows was applied near the Nafion membrane, the limiting current value reaches 12 (nA).

**2. Overlimiting conductance via chronopotentiometry**

Valenca and co-workers already validated the voltage behaviors by electro-osmotic instability (EOI) using the chronopotentiometric measurement. They revealed that the applied current density has the linear response to the 2nd voltage responses (*V2nd*) times the conductance of EOI regime. Here, we collapsed *V2nd* with respect to the various current values in OLC regime, ranging from 12 to 29 nA as shown in below SI Figure 2. The results demonstrated that *flow* has a constant value as 0.21 nS, which leading to the linear relationships between *jconv* and *V2nd*.



Figure S2. The *V2nd* from the measurement has been obtained with the applied current, *I*. This result showed that the slope of *V2nd* – *I*, which is the overlimiting conductance (OLC) by electro-osmotic flows (EOF) have the constant values as 0.21 nS.

**3. The onset time of the electro-osmotic flows during chronopotentiometry**

In order to figure out the onset time of EOF (*C*), we obtained the collapsed data of *tEC* as shown in Figure 3.

Here, *tEC* represented the electro-convective time scale, which is defined as

 …(X)

where *LEOF* is the size of the fully developed electro-osmotic flows of the second kind from the Nafion membrane, and (*∂LEOF* / *∂t*) is the growing rate of EOF. Recently, Valenca and co-workers investigated the microvortices dynamics induced by the ICP and the electrical responses using two equations:

 …(X)

 …(X)

They revealed the interesting results that the conductivity during same external current should be constant as *EOF, saturated* = *EOF, growing*. Thus, *tEC* has the form as

 …(X)

Since *V2nd* is *O*(10-1) and (*∂V2nd* /*∂t*)|*t*=*tEC* is *O*(10-2) if *j* ~ 1 and *V2nd* is *O*(100) and (*∂V2nd* /*∂t*)|*t*=*tEC* is *O*(10-1) if *j* > 1 in our experiments, the time scale should lie in the order of *O*(101), which satisfied the graph in SI Figure 3.



Figure S3. The onset time (*C*) of electro-convective flows was obtained from the chronopotentiometric measurement. The *C* values are between 10 and 30, which result is coincided our scaling theory, *C* ~ O (101).

**4. The potential, resistance and capacitance of the electrical double layer (EDL) and the extended space charge layer (ESC)**

Since the electrical double layer (EDL) possessed both the resistance and the capacitance, the time-varying potential during the chronotpotentiometry is solely accounting for the electrical double layer. Thus, *V1st* was collected in the Ohmic current values between 0 to 9 nA, and was plotted as shown in SI Figure 4(a). In addition, the experiments revealed out that the potential of the EDL has the linear relation to the applied current. Here, the slope represented the resistance of the EDL (*REDL* = *VEDL* / *I)*, which value is 3 ± 0.7 M in our experiments. The RC delay time of the *V1st* was also collected as shown in SI Figure 4(b) for calculating the capacitance of the EDL. Thus, one can obtain the capacitance values by the simple calculation (*CEDL* = *RC* / *REDL*), which value is 6 ± 1.2 F



Figure S4. The *V1st*, which was time-varying potential reflected by the electrical double layer, was obtained from the chronopotentiometric measurement. From this result, the resistance can be calculated by Ohm’s law (*REDL* = *VEDL* / *I*). (b) The RC delay time caused by the electrical double layer was collected in Ohmic current regime. The RC delay times is almost constant as the value of 18 seconds in our experiments. From this result, the capacitance can be calculated by (*CEDL* = *tEDL* / *REDL*).

In addition, one can calculate the resistance, capacitance of the extended space charge layer from the equivalent circuit model. From the experimental data, we were able to calculate each component as shown in SI Table 1.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R*bulk* (M) | R*EDL* (M) | C*EDL* (F) | R*ESC* (M) | C*ESC* (F) |
| 240±42 | 3±0.7 | 6±1.2 | 1.09(*I*- *Ilim*) | 2.23 (*I*- *Ilim*) |

Table S1. The electrical components of the equivalent circuit model were calculated by simple calculation. Note that *REDL* and *CEDL* remains same regardless of the applied current (*I*), while *RESC* and C*ESC* are linearly proportional to the current values (*I* – *Ilim*), where *Ilim* is the limiting current values.