FlowFETs consisting of drain and source contacts to liquids in microfluidic channels and an isolated gate electrode were used to analyze the ionic content (H\(^+\) and Cu\(^{2+}\)) of fluids for the first time. Compared to ion-selective electrodes, a flowFET is faster and its gate region acts as a programmable membrane with its selectivity determined by the gate potential. Both DC and AC measurement results using aqueous solutions of NaCl and CuSO\(_4\) in the 10\(^{-3}\)-10\(^{-7}\) molar range are discussed.

I. Introduction

Field effect fluidic devices were introduced in [1] to control the electro-osmotic flow (EOF) by controlling the Zeta-potential inside the channel using the gate voltage (V\(_{GS}\)) in these devices, the drain and source electrical contacts to fluids inside the channel were simply accomplished by using exposed electrodes and the gate contact was isolated from the channel fluids by a thin insulator such as silicon dioxide or parylene [2,3]. The majority of reported results in the literature describe the use of flowFETs as valves and microfluidic pumps. To pump fluids in a given direction, the drain-source electrodes are used to apply a voltage to the channel (V\(_{DC}\)) to produce the EOF. When V\(_{DS}\) becomes large, electrolyses occurs in the drain/source electrodes and bubbles form. To prevent bubble formation \(V_{DS}\) and \(V_{GS}\) are switched from large positive values to negative values or they are sinusoidally varied. The reversal of the EOF due to the reversal of the \(V_{DS}\) is cancelled when \(V_{GS}\) is also switched with the same frequency and phase as \(V_{DS}\). The role of \(V_{GS}\) is to invert the channel charges when the drain current is reversed so that the flow is always in the same direction. Here we propose to use flowFETs as ion-sensitive and selective sensors by noting that different ions in the channel have different charges and mobility. Thus, we explore both the dc and ac components of drain-source current (I\(_{DS}\) and i\(_{ds}\)) and the impedance of flowFET’s gate electrode as a function of frequency to detect and quantify ions and their concentrations in the channel.

The drain-source contacts in the flowFETs can be readily used to perform cyclic voltametry, differential pulse voltametry (I-V), potentiometry (V at I=0), amperometry (I at V=0), chrono-amperometry (I-t at a fixed V), and other variations of these techniques. The presence of the gate electrode with narrow channels at the gate region can be additionally used to increase/decrease ionic concentrations near the source contact (the drain contact is connected to the fluid reservoir while the source contact is separated by the gate region.

In flowFETs the gate voltage modifies the Zeta potential (\(\zeta\)). The change in \(\zeta\) due to the gate voltage (V\(_{g}\)) is given by [1,2]:
\[ \Delta \zeta = \frac{C_{\text{wall}}}{C_d} V_g \]  

(1)

where \( C_{\text{wall}} \) is the wall capacitance and \( C_d \) is the capacitance of the electrical double-layer (immobile charge layer underneath the gate). Furthermore, \( C_{\text{wall}} = \frac{\varepsilon_{\text{wall}}}{d_{\text{wall}}} \) (F/cm²) where \( \varepsilon_{\text{wall}} \) is the permittivity of the gate dielectric material (in our case it is parylene) and \( d_{\text{wall}} \) is its thickness. \( C_d \) is given by the ratio of the permittivity of the fluid (\( \varepsilon_m \)) and the Debye screening length (\( 1/\kappa \)),

\[ C_d = \frac{\varepsilon_m}{1/\kappa}, \quad \text{and} \quad 1/\kappa = \frac{\varepsilon_m kT}{\sum_i z_i e^2 C_i} \]

where \( kT/e \) is the thermal voltage, \( e z_i \) is the charge of the \( i^{th} \) ion, and \( C_i \) is its concentration. The \( C_{\text{wall}} \) does not change as a function of gate voltage but \( C_d \) is affected because of its dependence on the ionic concentrations \( C_i \) that in microfluidic channels can be considerably altered by the gate voltage. Moreover, the pore size in the gate can be very small and comparable to the Debye screening length. Thus, the double-layer capacitance can be affected considerably using the gate voltage.

The action of the gate voltage in the gate region with pore sizes on the order of Debye screening length, can be viewed as modifying the thickness of the double-layer and affecting the charge content of the diffusive layer near the Stern layer. For example, a negative gate voltage attracts positive charges in the channel and immobilizes (although not completely) these charges near the gate region while a positive gate voltage attracts negative charges. Very similar to the MOSFET, it is also possible to deplete the channel from positive or negative charges using appropriate gate voltages. Thus, all the different operation regimes of accumulation, depletion and inversion are possible. The notable difference between the flowFET and MOSFET is the lack of fixed charges (ionized dopants) in the flowFET. We note that the charge and potential pictures are related through the Poisson’s equation and present the same phenomena. But to understand the ion-selectivity of the flowFET, it is easier to think in terms of channel charges.

Another important parameter that determines the flowFET drain-source current is the EOF velocity given by:

\[ v_{\text{EOF}} = \frac{\varepsilon_m}{\eta} \zeta \cdot E \]  

(2)

where \( \eta \) is the viscosity and \( E \) is the electric field in the channel generated by \( V_{DS} \). Clearly when \( \zeta \) is reversed, the velocity reverses too.

It is possible to use flowFETs both in the DC and AC modes to sense ions. The DC mode of operation is easier to analyze than the AC mode. In the AC mode, the “electronic” process dominates the conductivity measurements down to very low frequencies, and it is difficult to decouple the electronic conductivity from ionic conductivity and signal “mixing” is required to eliminate capacitive coupling effects between the gate and drain/source contacts. We discuss these different modes of the operation after discussing the basic structure and fabrication of flowFETs below.
II. Design and Fabrication of FlowFETs

Figure 1 shows the flowFET used in our studies. Its fabrication process and operation characteristics are given in [2]. The device has a 20-µm high, 200-µm wide main channel. The gate electrode was formed by electroplating nickel through a 20-µm thick photoresist mold. The mold had 10 openings, 10-µm wide, 100-pin long, separated by 10-µm. The structure was over electroplated so that grown pillars with mushroom structures forming closed channels forming 20-µm high, 10-µm wide 10 parallel channels. The electroplated channel array structure is conformally coated with 0.5-µm thick parylene [2]. The measured gate capacitance was around 2 pF at 100 KHz.

![Figure 1](image1.jpg)

(a) Schematic of the FlowFET. b) Optical image of the FlowFET used as ion-sensitive sensor.

III. Modes of FlowFET Operation for Ion Detection

FlowFETs can be operated in various modes to perform ion spectroscopy. These operation modes can be broadly divided into DC and AC operation regimes. In the DC mode, the $I_{DS}$ is monitored as a function of $V_{DS}$ at different $V_{GS}$. The experimental setup used in the dc measurements is very simple as schematically shown in Fig. 2a. The flowFET is connected to a semiconductor parameter analyzer. The flowFETs have symmetric drain-source regions except that the drain contact is closer to the fluidic input channel while the source contact is near the discharge end. Thus, the physical fluidic flow is from the drain to source.

At DC and low frequencies, there are two main contributions to the $I_{DS}$: the charge (electron/hole) transfer between drain/source electrodes and the ions in the channel and the charge transfer inside the channel from drain to source. The charge transfer from electrodes to the ions in the channel depends on the oxidation/reduction potentials, and it is voltage dependent. The charge transfer in the channel is essentially Ohmic at low gate voltages and may exhibit saturation behavior (similar to MOSFET) when the channel is pinched-off.

The oxidation/reduction process at the drain electrode does not deplete the ions in the vicinity of the drain electrode because the external fluid reservoir is near the drain contact and can supply unlimited amount of ions on demand. However, near the source electrode,
the oxidation/reduction process depletes the ions owing to the very small volume of the fluids near the source junctions. The gate electrode controls the rate at which the ions can be replenished near the source contact. Thus, the gate voltage can be viewed as a parameter that controls the effective volume near the source contact.

The AC modes of operations include a) monitoring the modulation of the AC drain-source current ($i_{ds}$) by an AC gate voltage ($v_{gs}$), b) monitoring drain-source conductance ($G_{ds}$) as a function of frequency and DC gate bias, c) measuring the gate impedance as a function of frequency and DC drain-source current, d) by monitoring $i_{ds}$ at $2\omega$ where $\omega$ is the radial frequency of $v_{gs} (=v_0\cos(\omega t))$ and $V_{DS}$ is a constant dc voltage (Fig. 2c.). The advantage of $2\omega$ measurement is that only gate voltage modulation of ionic current in the channel is detected (at low enough frequencies).

It is also possible to operate the FlowFET in the large-scale signal regime, for example by pulsing both the $V_{DS}$ and $V_{GS}$. In our FlowFETs the gate capacitance with de-ionized water in the channel was around 2 pF. Thus, performing gate impedance spectroscopy was challenging specially at low frequencies (<1 kHz) where the ionic conductivities become important and add to the electronic conductivities.

![Diagram](image1.png)

Figure 2: a) Schematic of the experimental setup for DC $I_{ds}-V_{ds}$ measurements. b) Schematic of the one of the experimental setups for AC measurements. The gate voltage controls the $I_{ds}$ through the transconductance ($g_m$). c) $2\omega$ AC measurement to eliminate the gate-channel parasitic coupling effects.
IV. DC Operation

The $I_{DS}$-$V_{DS}$ measurements in the microfluidic channel exhibit classical oxidation-reduction peaks that are routinely observed in cyclic voltametry as shown in Fig. 3. The total current is composed of anodic and cathodic currents. For reversible oxidation/reduction couples, the peak current ($I_{DSP}$) is given by [3]:

$$I_{DSP} = 2.68 \times 10^5 n^{3/2} A D^{1/2} C_{ox}^{1/2}$$

(3)

where $n$ is the number of electrons transferred from the electrode to the ions and is equal to $z_i$ for the $i^{th}$ ion in the solution, $A$ is the electrode area, $D$ is the diffusion coefficient, $C_{ox}$ is the concentration of the oxidized (positively charged ions) specie, and $v$ is the volume. In principle a different peak can occur corresponding to the reduction of different positively ionized species in the solution. The reverse process of electron transfer from the reduced species to the electrode (oxidation process) also occurs when the voltage is reversed. In the reversible process the negative peak corresponding to the oxidation process is just negative of the above equation.

The voltage at which the peak current occurs ($V_{DSP}$) is given by [3]:

$$V_{DSP} = E^0 + \frac{0.056}{n}$$

(4)

where $E^0$ is the standard electrode potential, also called standard half-cell potential, that is measured against a hydrogen electrode ($E_{H^0}^0 = 0$). $E^0$ for different metals are tabulated and can be found in standard reference sources.

Figure 3 shows $I_{DS}$-$V_{DS}$ at different gate voltages in our flowFET with different fluids that included de-ionized water, DI-water with different concentrations of NaCl and CuSO$_4$. The peaks in $I_{DS}$ are shown with arrows. The reduction of Cu$^{++}$ occurs at $V_{DSP} \sim 4V$ while that of H$^+$ (in the solution with NaCl) occurs at $V_{DSP} \sim 3V$. When both these ions are present in the solution, two peaks are observed as shown in Fig. 3d.

The main reason for asymmetry in $I_{DS}$-$V_{DS}$ curves shown in the above figures is that the drain region is directly connected to the reservoir while the source region is isolated from the reservoir by the gate region with narrow channels. Thus, the ions near the source regions are easily depleted upon reduction (ie, charge transfer from the source electrode) while the ions in the drain region are readily supplied from the reservoir and the current increases without a bound (at $V_{DS} \sim -3V$ or -4V). The main reason for the shift in $V_{DSP}$ as a function of gate voltage is that the potential at source is the sum of the channel potential due to $V_{DS}$ and $V_{GS}$. Thus, we note that in the DC mode, the flowFET can be used as an ion-sensitive sensor. To quantify the ionic concentrations, Eq. 3 can be used or a calibration procedure can be devised to relate the $I_{DSP}$ to $C_{ox}$, $V_{DS}$ ramp rate and other relevant device parameters.

In the above measurements, the $V_{DS}$ ramp rate was fast enough to prevent EOF from replenishing the fluids near the source contact. But one can perform very precise ion
spectroscopy by adjusting the $V_{DS}$ ramp rate to only permit the “fastest” ionic species to reach the source region. Inevitably, other species will also be “dragged” but at lower concentrations.

**Figure 3:** $I_{DS}-V_{DS}$ characteristics with a) de-ionized water b) with $10^{-5}$ molar NaCl and c) $10^{-5}$ molar CuSO$_4$ in the flowFET channel. d) $I_{DS}-V_{DS}$ at $V_{GS}=-5$ V for 50% CuSO$_4$ and 50% NaCl solutions with different molar concentrations. Arrows show different peaks. At $10^{-7}$ mole/liter concentration two peaks are observed that clearly correspond to the two different ions (H$^+$ and Cu$^{2+}$). These two peaks can also be seen in other concentrations with somewhat reduced clarity. Arrows indicate the location of current peaks.

**V. AC Characteristics**

**a) Gate Impedance Spectroscopy:** The gate conductance (inverse of the real part of the impedance) can be used to identify different ionic species in the channel near the gate region. In MOSFET research, gate conductance spectroscopy is routinely used to find charge states in the gate dielectric [4]. In flowFETs, the same technique can be used. The main idea is that different ionic species having different charge state and mobility will have different relaxation time constant ($\tau$). To successfully perform these measurements, the gate dielectric should be made very thin to increase the gate capacitance and to improve the signal-to-noise ratio. In our flowFETs, the value of gate capacitance was too low to permit reliable conductance spectroscopy. But as discussed in the next section, we have obtained experimental evidence that the gate voltage changes the relaxation time constant of the ionic species that contribute to $i_{ds}$.

**b) Frequency Response of the Drain Current:** The ability of ions to move back-and-forth either in response to an AC drain voltage or an AC gate voltage is determined by
their relaxation time constant in the fluid. A major problem we encountered in these measurements was the capacitive coupling between the gate and drain-source regions that bypasses the ionic conduction in the fluidic channel. To solve this problem, we performed harmonic measurement by modulating the gate voltage at frequency $\omega$ and monitored the drain-source current at $2\times\omega$. The approach seems to work well as shown in the preliminary results of Fig. 4 (for experimental set up see Fig. 2c). In Fig. 4a, DI-water was used in the channel and both +4 V and -4 V dc drain voltages lowered the cut-off frequency of the drain current. The gate voltage was 1 V$_{pp}$. When the drain voltage is at +4 V, the positive ions tend to move in the direction of the source contact while the negative ions move toward drain. The AC gate voltage modulates the ability of these ions in transit through the narrow-channel gate region. It appears that the gate voltage effectively immobilizes the ionic species near the gate region, reducing the fluidic conductivities in the channel. Reduced conductivity results in larger relaxation time constant lowering the cut-off frequency. When we used NaCl and CuSO$_4$ solutions, (both 10$^{-4}$ molar) the cut-off frequencies were also modified as shown in Fig. 4b but in a different manner than before.

We note that the harmonic measurements indicate that above 3-4 kHz, the $i_{ds}$ response is more or less constant while in the AC measurements at $\omega$ the response linearly increased as a function of frequency (these measurements are not shown here). Thus, the $2\times\omega$ measurements were not affected by the capacitive coupling between the gate and the drain-source region.

![Figure 4: a) – c) The $i_{ds}$ at 2xFrequency as a function of gate voltage frequency ($V_{gs}=0.5\cos(\omega t)$). The NaCl and CuSO$_4$ concentrations were 10$^{-4}$ molar.](image)
VI. Conclusion

We showed for the first time that flowFETs can be used as ion-selective sensors. Two modes of sensing were demonstrated. In DC mode sensing, two peaks in $I_{DS}-V_{DS}$ were observed that correspond to H$^+$ and Cu$^{++}$ ionic content of the channel fluid. In AC mode sensing, we showed that the ionic relaxation times can be modified by the gate modulation. In order to perform gate conductance spectroscopy flowFETs with very thin gate dielectrics are needed to increase the gate capacitance and to improve the signal-to-noise ratio. The narrow-channel gate region acts as a programmable membrane with “tunable” transport characteristics that can be altered using the gate voltage.

References