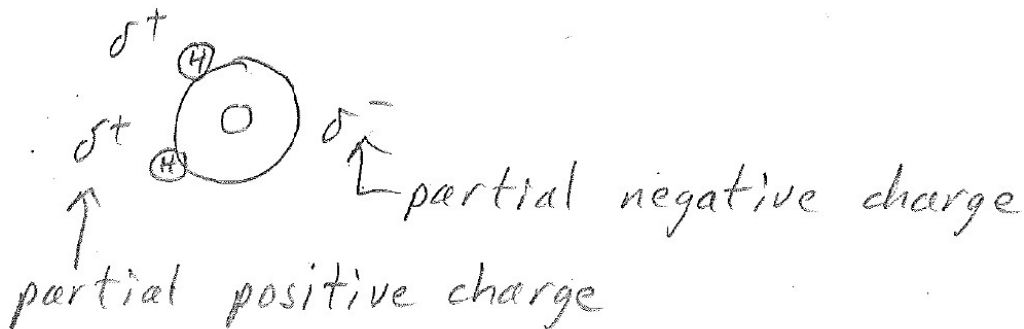Lecture 9/19/24

Resistive Sensing of Aqueous Solutions

1. Background

Water: $H_2O \rightarrow$ a molecule with a polar covalent bond

Physically:

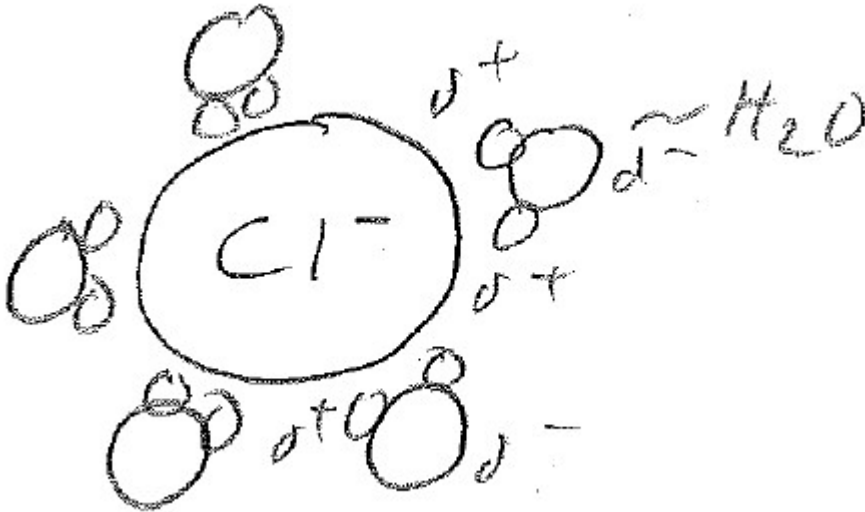Therefore, as a polar compound, H_2O has a permanent dipole, which causes ionic compounds (salts) to dissolve in it.

Example: table salt: $NaCl \rightarrow Na^+ + Cl^-$

        Na^+ is a cation and Cl^- is an anion

        In water: $NaCl + H_2O \rightarrow Na^+(aq) + Cl^-(aq)$

        $Na^+(aq)$ and $Cl^-(aq)$ are hydrated ions

Cl⁻(aq) → hydrated anion:

Observe that the partial positive charge on the H_2O molecules is drawn to the Cl⁻ anion in the exaggerated drawing. The resulting composite structure is called a hydration shell or a hydration sphere.

Similarly, the partial negative charge on the H_2O molecules is drawn to the Na⁺ cation in the exaggerated drawing below, also forming a hydration shell. Na+(aq) → hydrated cation:
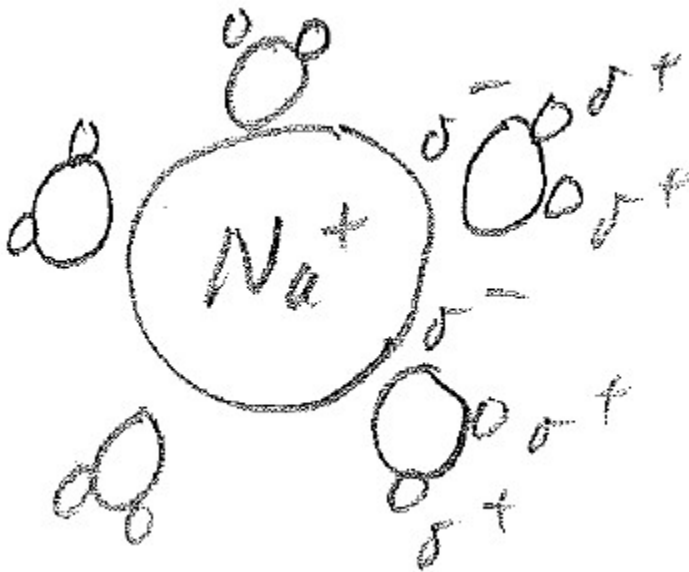
Note: atom sizes are NOT to scale

2. Applying an electric field across the solution

Na^+(aq) and Cl^-(aq) act as mobile charge carriers, like electrons and holes in a semiconductor.

However, ion charge carriers are slow compared to electrons and holes. Therefore, an aqueous solution is a much lower frequency electrical system.

The higher the NaCl concentration, the higher the number of mobile charge carriers, and the higher the electrical conductivity.

The symbol for electrical conductivity is σ, the same symbol used for tensile stress in mechanical systems.

For low salt concentrations:

$$\sigma \propto ion\ concentration:$$

$$\sigma = \sum_{i=1}^{n} \lambda_i C_i$$

where: σ = solution electrical conductivity (EC)

λ_i = ionic conductivity of the ith ion type

C_i = molar concentration of the ith ion type

For high concentrations: ions will interact with each other, invalidating this equation:

By measuring EC, the concentration of dissolved salts can be determined.

3. Temperature effects

EC is affected by temperature nonlinearly. However, for $0°C \leq T \leq 30°C$, a linear model is:

$$\sigma_T = \sigma_{25}[1 + a(T - 25)]$$

Where: σ_{25} is the EC at 25°C

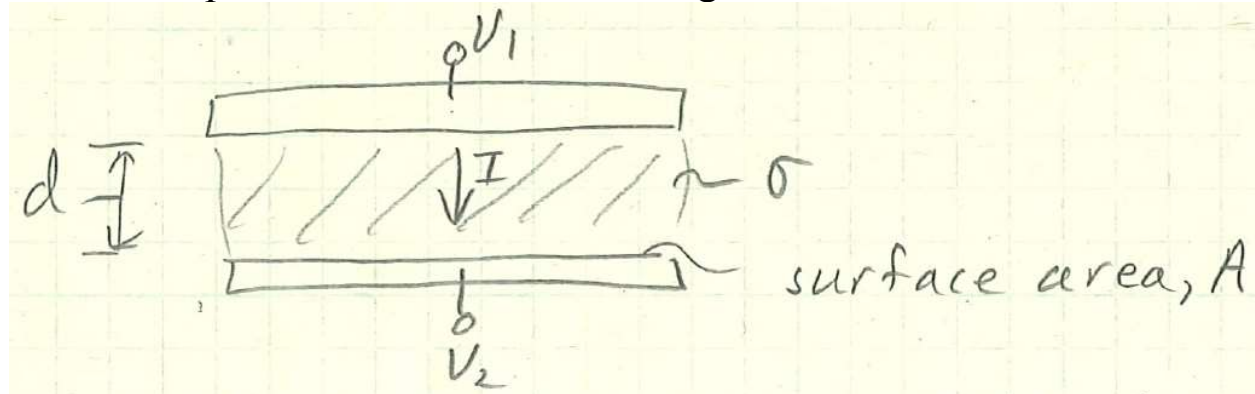"a" is a temperature compensation factor, $[a] = 1/°C$

Various values for "a" are found in publications: 0.0191, 0.02, 0.025, 0.0187, etc. However, all are approximately a = 0.02.

Often, σ_{25} is calculated and used for comparison.

4. Measuring EC of an aqueous solution

Consider 2 parallel electrodes in a homogeneous solution:

Assumptions: A $\gg$ d^2, and a uniform current density

Therefore: $R = \dfrac{d}{\sigma A}$

Conductance: $G = \dfrac{1}{R} = \dfrac{\sigma A}{d} = \sigma \kappa$

The sensor's cell constant, κ, is a function of the sensor's geometry, and is independent of concentration or temperature.
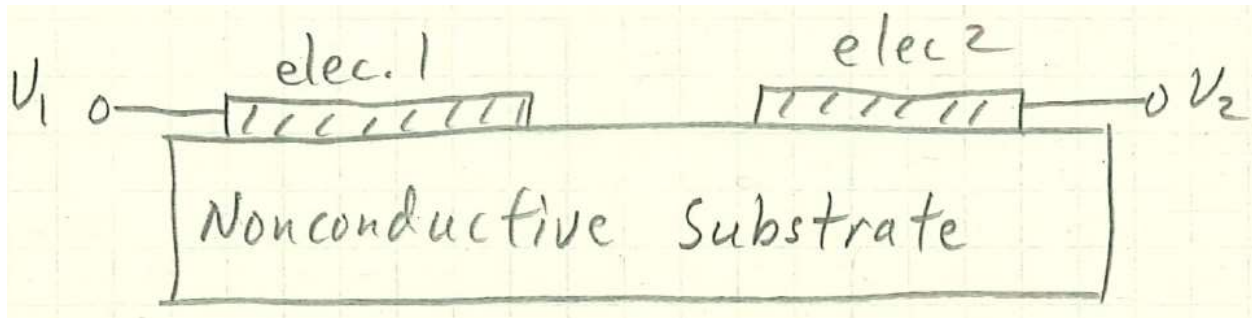
$[\kappa] = m$

$[G] = S$

$[\sigma] = S/m$

If κ is known, you can measure G (or R) and calculate σ.

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    a. Flat electrode sensor

Consider:

This type of electrode structure is easy to build in MEMS or on a PCB.

However, it has a non-uniform current density. Therefore, κ is difficult to calculate.

But, you can use an EC sensor of known κ and measure EC with it. Then measure G with the flat electrode sensor. Then calculate κ for the flat electrode sensor:

$$\kappa = \frac{G}{\sigma}$$

With now knowing κ for the flat electrode sensor, the sensor can be used to determine σ from any G measurement.

    5. Frequency effects

When a metal electrode is put in water, a water molecule making contact with the metal will transfer an electron to the metal, leaving the water molecule with a positive charge.
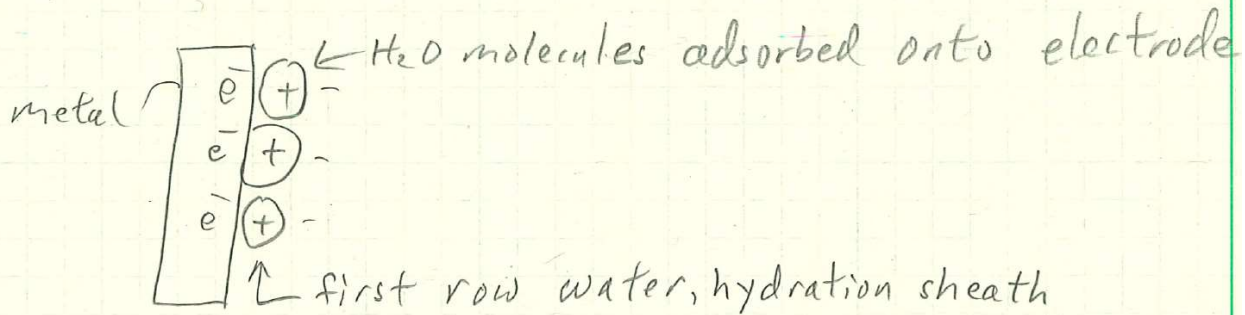
Other water molecules (dipoles) will be attracted to the H_2O molecules on the electrode, and will align with them.
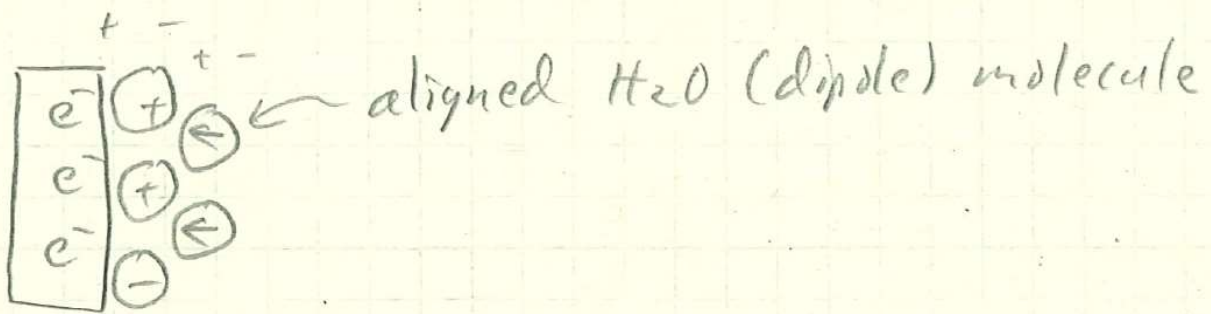
Cations will be attracted to the aligned dipoles and will form hydrated cations there:
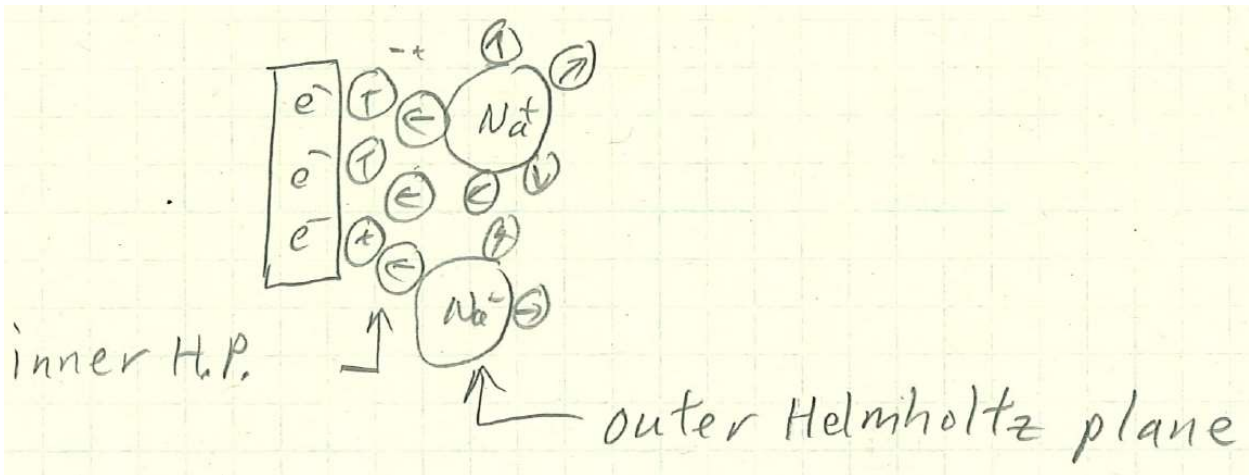

Some Na^+ ions will also chemically bond to the metal, forming an inner Helmholtz plane.

The 2 Helmholtz planes together form the "electrical double layer," or EDL, which is two capacitors in series (C_{H1} and C_{H2}), and in parallel with

the resistance (R_F) between the electrode and the water when a voltage is applied. The subcircuit consisting of C_{H1}, C_{H2}, and R_F is called the Faradaic impedance.

Circuit model:
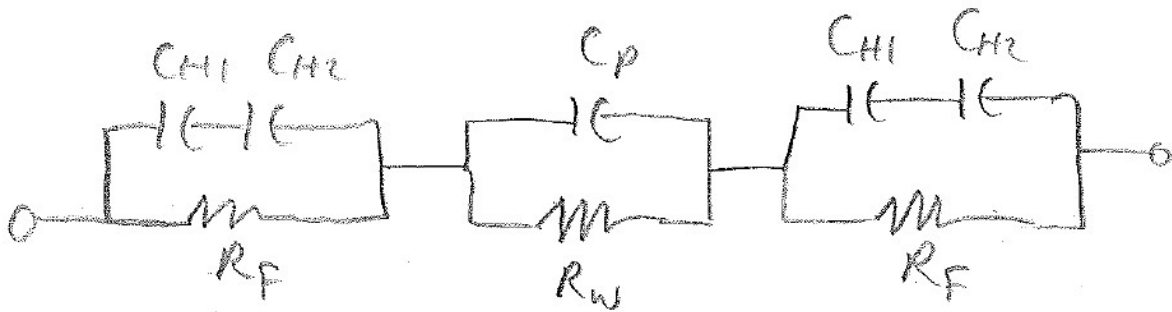
$$\frac{1}{\dfrac{1}{C_{H1}} + \dfrac{1}{C_{H2}}} > C_p$$

The Faradaic impedance of the EDL results in an EC measurement error at DC and low frequencies.

Measuring EC at a sufficiently high frequency shorts across the EDL for a more accurate EC reading.

But too high of a measurement frequency will result in shorting across the small parasitic capacitance, C_p.

Choose some measurement frequency that ~ shorts C_{H1} and C_{H2}, but not C_p. The goal is to measure R_w with the sensor. The exact frequency used depends on the sensor. With the sensors I have developed, 50 kHz to 1 MHz seems to work well.

6. More on hydration shells

A hydrated anion:
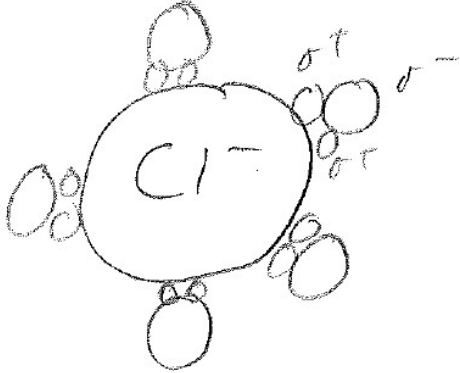
Mechanically, a hydration shell is a SMD with a mechanical ω_n and Q.

The lower the concentration, the larger the hydration shell around each ion: the larger its mass and the lower its ω_n.

If the dipole-like hydration shell is electrically excited at its ω_n, it will vibrate. This is called relaxation and f_n is called the relaxation frequency. Electrically, the solution of hydration shells has a minimum impedance at that frequency, due to its complex permittivity.

A frequency sweep across the liquid can be performed with a network analyzer connected to an appropriate set of electrodes to detect the impedance minima. This information can sometimes be used to estimate the chemical composition and/or contaminant concentration of the aqueous solution. This is called Electrochemical Impedance Spectroscopy (EIS).

In aqueous solutions, the relaxation frequency can be quote low, in the 5 MHz to 10 MHz range.
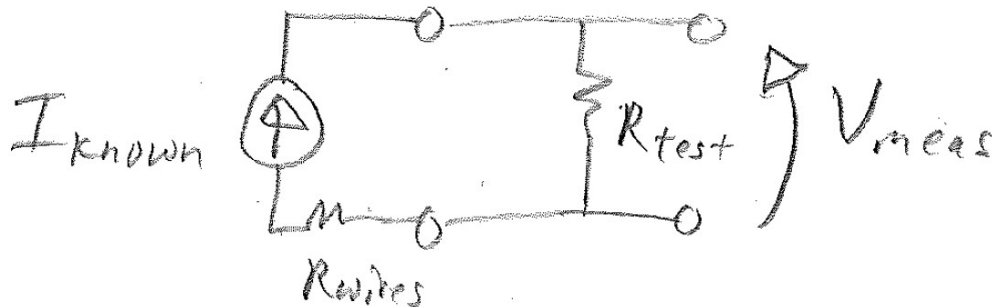
2-Point and 4-Point Resistance Measurements

    1. 2-Point Resistance Measurement
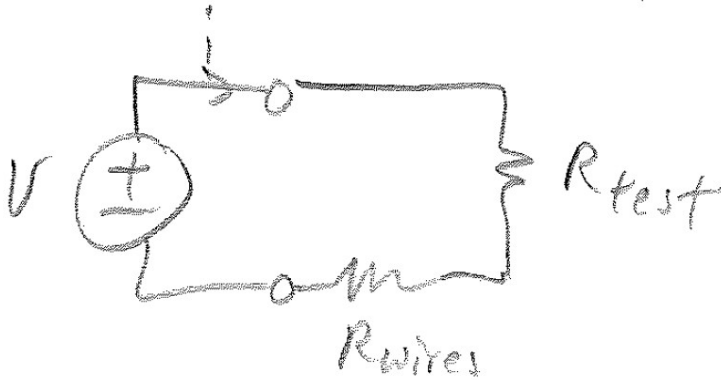
R_{wires} ~ few Ω. If $R_{test} \gg R_{wires}$, then $R_{meas} = \frac{v}{i} \approx R_{test}$

However, if $R_{test} \approx R_{wires}$, then $R_{meas} = \frac{v}{i} = R_{test} + R_{wires}$, and measuring R_{meas} does not yield a good estimate for R_{test}.

    2. 4-Point Resistance Measurement

Apply a known current to the resistance under test, I_{known}. Measure the voltage across R_{test}, V_{meas}, with a high impedance voltmeter. Then compute R_{meas} to determine R_{test}:

$$R_{meas} = \frac{V_{meas}}{I_{known}} = R_{test}$$

This is a more precise resistance measurement technique, but it is also more complicated.

Capacitive Sensing

1. Simple Parallel Plate Capacitor
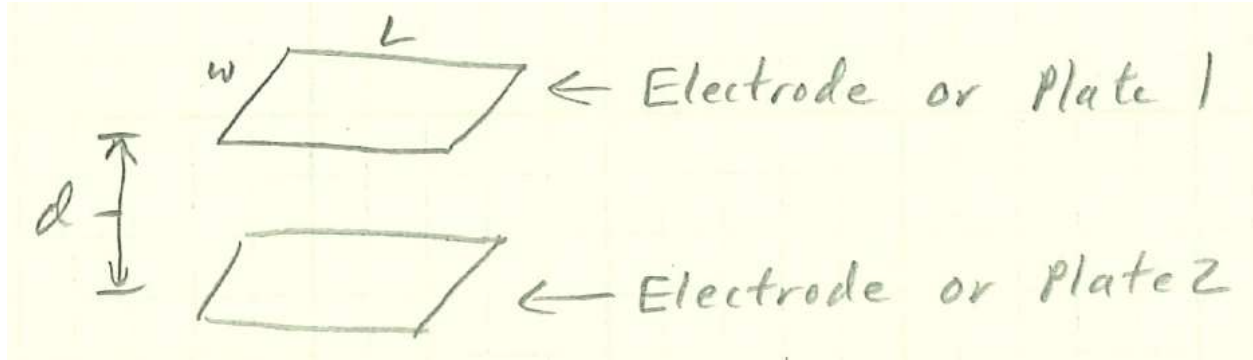
d is the electrode separation distance.

For A >> d²: fringing effects can be ignored and $C = \frac{\varepsilon_o \varepsilon_r A}{d}$

where: ε_o = permittivity of free space = 8.854 pF/m

ε_r = relative permittivity of the dielectric material between the electrodes
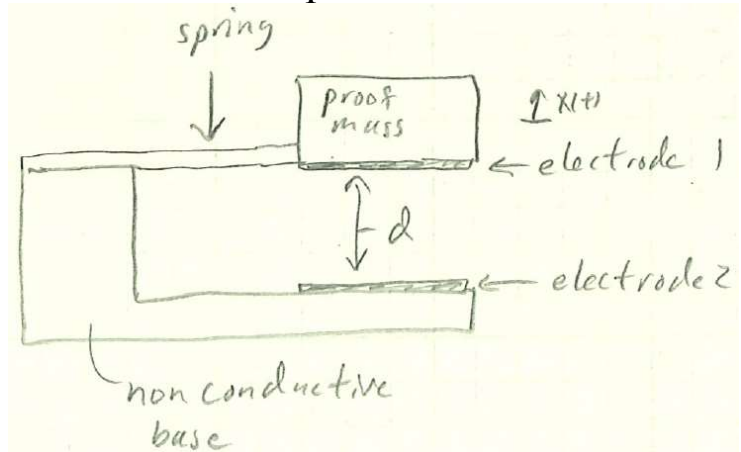For a vacuum ε_r = 1, and for most gases: $\varepsilon_r \approx 1$

A = electrode overlapping surface area = wL here

Ways to detect with a capacitive sensor (non-fringing sensor):

1) Change the dielectric material, i.e. change ε_r → this can be difficult to do.

2) Change the electrode separation distance → easy to do.
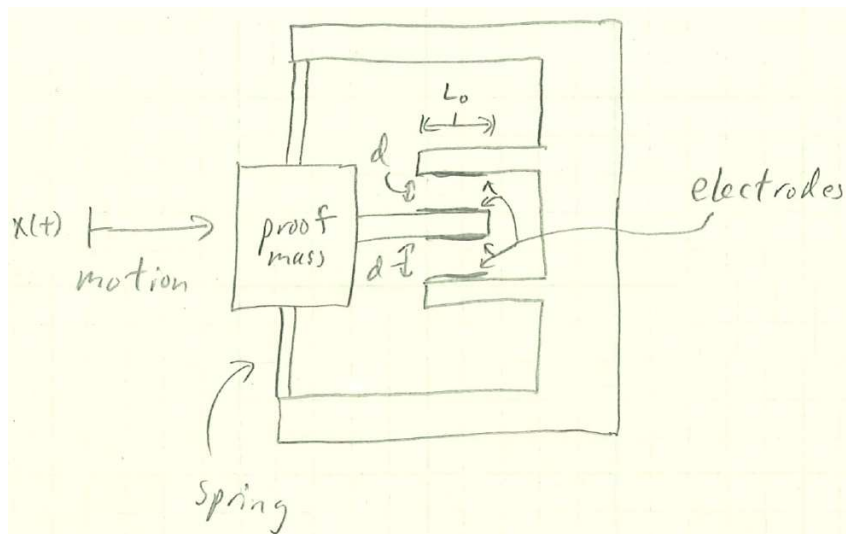
Consider this simple MEMS accelerometer:

$$C = \frac{\varepsilon_o \varepsilon_r A}{d_o + x(t)}$$

where d_o is d when $x(t) = 0$ ("at rest" condition)

3) Change the electrode overlap area → easy to do.

Consider this MEMS accelerometer

d, w, and ε_r are constants here.

$$L(t) = L_o + x(t)$$

$$\therefore C(t) = \frac{\varepsilon_o \varepsilon_r w L(t)}{d} = \frac{\varepsilon_o \varepsilon_r w}{d}(L_o + x(t))$$
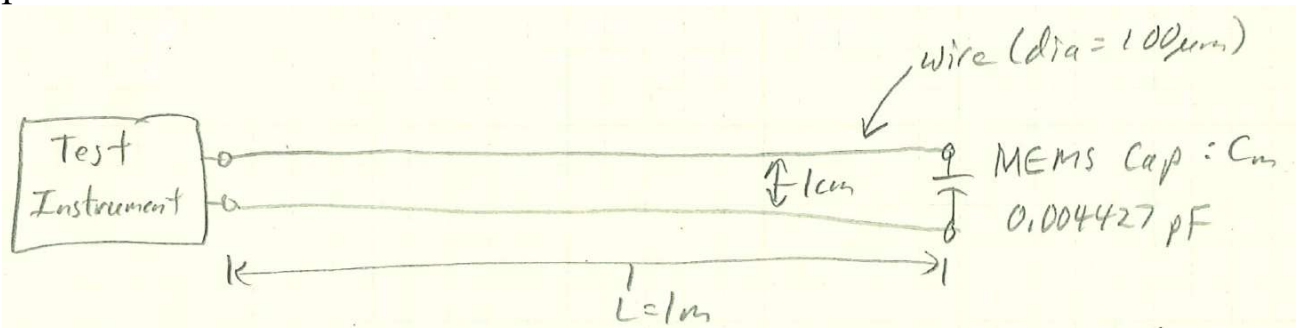
2. Typical Capacitor Sizes in MEMS

For a parallel plate capacitor: let w = 50 μm, L = 100 μm, d = 10 μm, and
$$\varepsilon_r = 1$$

$$\therefore C = \frac{(8.854)(50x10^{-6})(100x10^{-6})}{10x10^{-6}} = 0.004427 \; pF = 4.427 \; fF$$

1 fF = 1x10^{-15} F ! → a <u>very</u> small capacitance!

Consider that a 10% change is C is only 0.4427 fF!

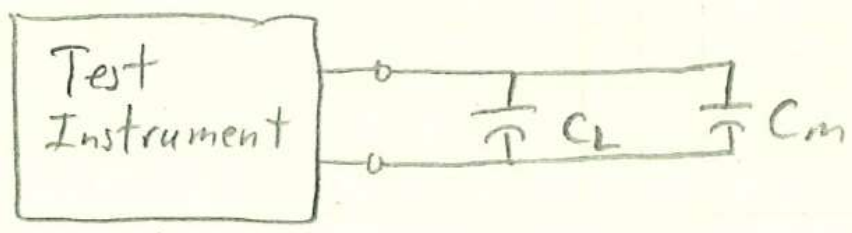With sensor capacitances this small, stray capacitance can be a big problem. Consider this:

For the cable: $C_L \approx \frac{(8.854)(100x1^{-6})(1)}{0.01} = 0.08854pF$

Observe that: $\frac{C_L}{C_m} = 20 \rightarrow C_L = 20C_m!$ or $C_L = 200\Delta C_m|_{10\%\Delta}!$
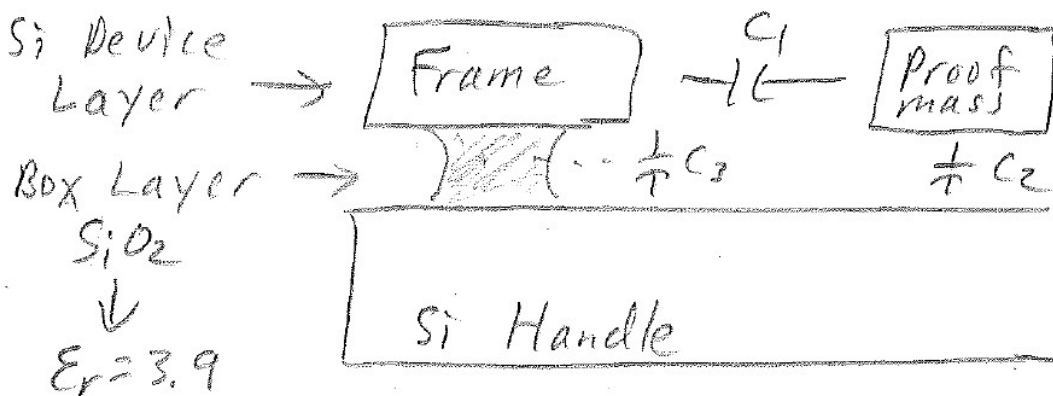
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Instrumentation model:

C_m adds with C_L. Therefore, you need to locate the interface circuitry as close to the MEMS capacitor as possible, such as on the same chip.

Note: stray capacitance can also be an issue on the MEMS chip between different microstructures.

Example: A cross-section of an SOI MEMS device:

$C_1 \rightarrow$ desired capacitance between two microstructures

$C_2 \rightarrow$ stray capacitance in air ($\varepsilon_r \sim 1$)

$C_3 \rightarrow$ stray capacitance in SiO_2 ($\varepsilon_r = 3.9$)

So, C_2 and C_3 may not be able to be ignored, depending on the design, particularly with a typical Box Layer thickness of $0.5\ \mu m$ to $1\mu m$.

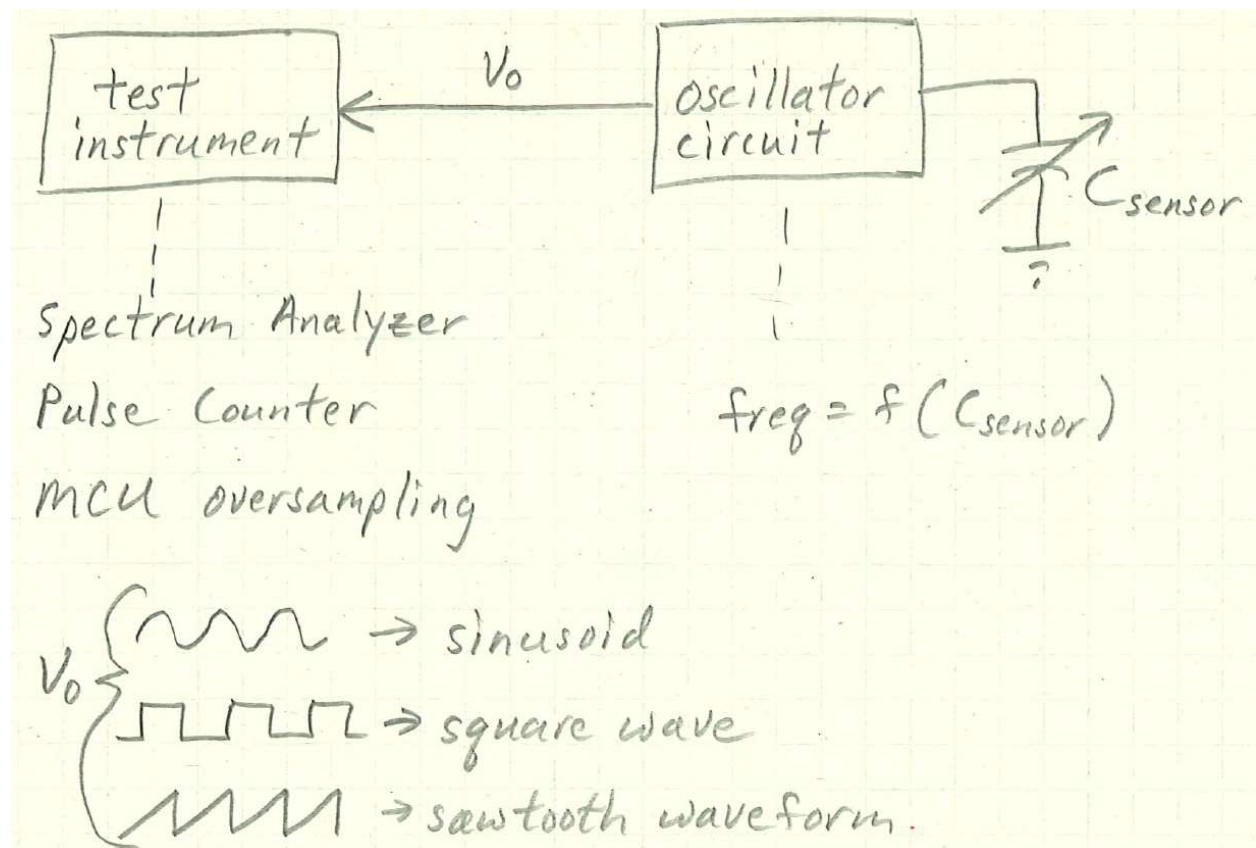Lecture 9/19/24

3. Capacitor Interface Circuity: Oscillator

Consider C: $q = CV$ and $\dot{q} = \dot{C}V + \dot{V}C = i(t)$

In most EE application: $\dot{C} = 0 \rightarrow i(t) = C\frac{dV}{dt}$
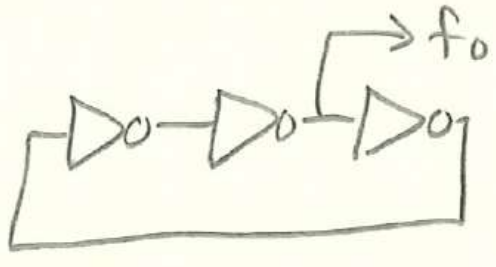
However, with capacitive sensors, $\dot{C} \neq 0$ usually

So, how then do you measure C(t)???

One technique is to place C(t) in an oscillator circuit where freq = f(C):

Spectrum Analyzer
Pulse Counter
mcu oversampling

$freq = f(C_{sensor})$

$V_0 \begin{cases} \text{∿} \rightarrow sinusoid \\ \text{⊓⊔} \rightarrow square\ wave \\ \text{⋀⋀} \rightarrow sawtooth\ waveform. \end{cases}$

Consider a simple CMOS ring oscillator:

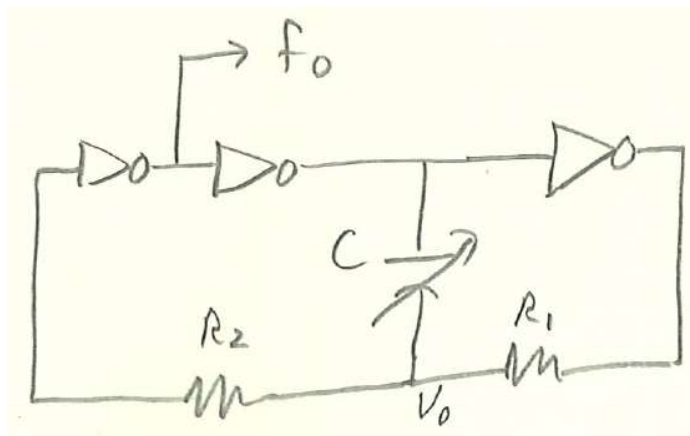It is a closed chain of an odd number of inverter stages $\rightarrow$ unstable

Let τ_d = propagation delay per inverter

N = number of inverters

It take two complete cycles for two state changes (1 period)

Therefore: $f = \dfrac{1}{2\tau_d N}$

Although this oscillator circuit is not useful for a capacitive sensor interface circuit, consider this related circuit:

This oscillator circuit is called a <u>relaxation oscillator</u>, and it is based on an RC time constant that controls when a state change occurs in the unstable chain of CMOS inverters.

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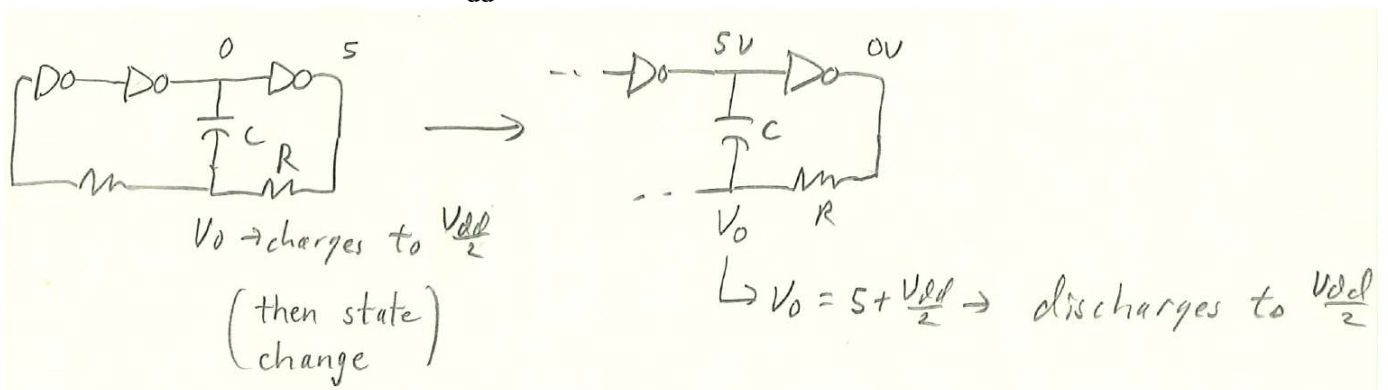Circuit analysis:

Assume: (1) $R_1 = R_2 = R$

(2) $C \gg$ input capacitance on an inverter

(3) The inverter trip voltage: $V_{tr} = \frac{V_{dd}}{2}$

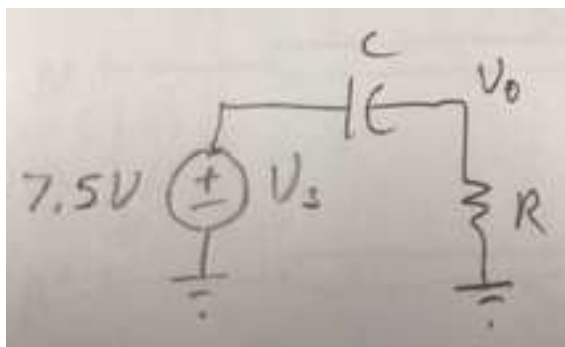Therefore, when V_o crosses V_{tr}, the system changes state.

The RC time constant determines the output frequency, f_o, let's see how:

Examine the circuit with $V_{dd} = 5V$:

$V_o \rightarrow$ charges to $\frac{V_{dd}}{2}$

$\left(\begin{array}{c}\text{then state} \\ \text{change}\end{array}\right)$

$\hookrightarrow V_o = 5 + \frac{V_{dd}}{2} \rightarrow$ discharges to $\frac{V_{dd}}{2}$

With $V_{dd} = 5V$: $V_{tr} = 2.5V$

At switching time, we have this circuit model:

With this model, C is fully discharged initially and $v_o = 7.5V$. We want to find t for $v_o = 2.5V$.

$$\frac{V_o}{V_s} = \frac{R}{R + \frac{1}{sC}} = \frac{s}{s + \frac{1}{RC}}$$

$$V_s(s) = \frac{7.5}{s}$$

$$V_o(s) = V_s(s)\left(\frac{s}{s + \frac{1}{RC}}\right) = \frac{7.5}{s + \frac{1}{RC}}$$

$$v_o(t) = 7.5e^{-\frac{t}{RC}}$$

We want to evaluate t when $v_o(t) = 2.5$ V

$$2.5 = 7.5e^{-\frac{t}{RC}}$$

Solving for t: $t = -RCln\left(\frac{2.5}{7.5}\right) = 1.0986RC$

For the square wave output: T = 2t and f = 1/T, and $f = \frac{0.455}{RC}$

For an actual circuit, the equation for f will be slightly different due to the analysis assumptions. But for low frequency square waves (less than about 1 MHz), it should be close. This also works for fixed C: R-sensor.

For the case where $C = \frac{\varepsilon_o \varepsilon_r A}{d} = \frac{\varepsilon_o \varepsilon_r A}{x(t)} \rightarrow$ plate separation C sensor,

$$f = \frac{0.455}{RC} = \frac{0.455x(t)}{R\varepsilon_o\varepsilon_r A} \rightarrow \text{therefore } f \propto x(t)$$