ELECTROCHEMISTRY

The electron dynamics involved in the oxidation or reduction of an atom , molecule or solid is closely related to the electronic structure. In atomic systems the highest occupied atomic orbital is relevant .In molecules or solids the highest occupied molecular orbital and lowest unoccupied molecular orbital are relevant. In solids the Fermi energy level or chemical potential of the electron at the most accesible level,the Fermi energy level is applicable.When joining different metals,because the Fermi energy levels are not the same , current instantly and briefly flows and a contact potential is established.Take the case of a piece of Zn and a piece of Cu seperated the Cu being dipped into a solution of $CuSO_4$ / *KCL* / H_2O and the Zn dipped into a KCl / H_2O solution then if you place a salt bridge into the 2 solutions and make elctrical connection between the Cu rod and the Zn rod you will measure a current flow between the Zn and the Cu If you measure the voltage between the Cu rod and Zn rod with a high input impedance Voltmeter so that you don't draw current you will measure an EMF . The reason for the seperate 2 half cells is that if only a solution of $CuSO_4$ / *KCL* / H_2O is used and the Zn and Cu rods are dipped into that same solution the Cu^{2+} will plate out on the Zn rod and short the Cu rod out.The salt bridge is to provide ions to maintain electrical neutrality.

If we set up the cell described below for different elements M as in $M^{n+} + ne^- = M$

Electrolyte Containing M^{n+}

Standard Hydrogen electrode
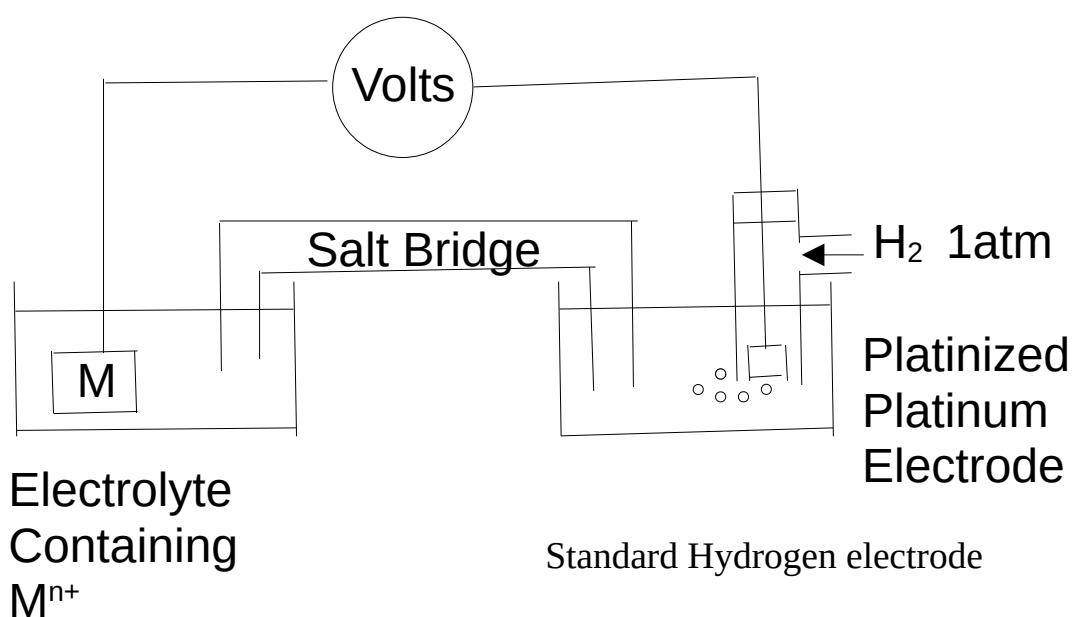
    We find that different M's establish different standard EMF's all in a range of+- 3 Volts.These values are given in Standard reduction potential tables an extract of which is given below.

	E^o Volts
$F_2 + 2H^+ + 2e^- = 2HF$	3.06
$Cu^{2+} + 2e^- = Cu$	0.337
$2H^+ + 2e^- = H_2$	0
$Zn^{2+} + 2e^- = Zn$	-0.763
$Li^+ + e^- = Li$	-3.05

For those half reactions with a positive E^o the spontaneous reaction is reduction with the SHE undergiong oxidation.For those half reactions with E^o negative the cell reaction in the above assembly is oxidation with the SHE undergoing reduction. Take a couple like Rio Tinto

$$Zn = Zn^{2+} + 2e^-$$ 0.763

$$\underline{Cu^{2+} + 2e^- = Cu}$$ $\underline{0.337}$

$$Cu^{2+} + Zn = Cu + Zn^{2+}$$ 1.1 Volts

The condition for a spontaneous reaction is that the free energy change ΔG must be negative.Since $\Delta G = -nF\Delta E$ ΔE must be positive. The higher up in the Std. Red. Table the stronger the stronger the oxidizing agent,while Li would be the strongest reducing agent.So far we have considered the electrochemical cell as a battery.Consider replacing the Volt meter with a power supply.Something with which you can dial up the Fermi energy level of a we , and also be able to measure the current.

The value of a voltammetric electrochemical analytical procedure is that if you obtain a weak solution of even mixed metal salts and the we is made suficiently negative to plate out the same portion of all the positive metal ions these metals will be concentrated as a deposit or plate out on the surface of the we.Now a positive anodic scan will strip or reverse the plating and give peaks in current characteristic in a unique way for every metal present.The strength of the peak is a quantitative measure and can be related to concentration by using standard solutions. If we can measure both the voltage and the current at the we simultaneously during the coarse of the scan we would be in a fine position. If we had computer control we could have a voltammogram with a print option on the screen immediately.

Before we get into the construction of the Linear Scan and Square Wave Voltammeters I want to discuss a model for the interface which will help to understand polarzabiliy of the interface.Polarizabiliy is important because in the 2 electrode situation the ae must be non-polarisable while in the 3 electrode system the re must be non polarizable .

While the resistor obeys Ohms Law $V = iR$ so that when a current goes through the resistor there is a voltage drop, the capacitor is different.A capacitor consists of 2 conducting plates seperated by a non conducting insulator or dielectric.Whe a dc voltage source is connected across the capacitor the voltage acoss the capacitor quickly ramps up to the value of the voltage source and further current is stopped.For an ac voltage source the capacitor is conducting.The model for an interface can be made with a resistor and capacitor
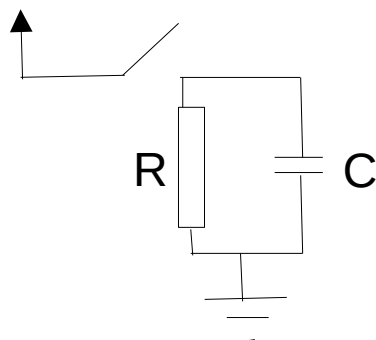
When the switch is closed current is divided between the resistor and the capacitor. The capacitor integrates the current allowed it by the resistor.R represents the leakage of charge through and from the capacitor after charging when the switch is open. . The bigger R the lesser is the current drawn and the more polarizable the interface.if we should wind in with technicalities we would use an argument about the exchange current density i_0 and how it relates to polarizability.Here I assume that you know the Butler Volmer equation for positive overpotential η

$i = i_0 (e^{(1-\beta)F\eta/RT} - e^{-\beta F\eta/RT})$ Consider that if x is small then to a good approximation $e^x = 1 + x$. So $e^{(1-\beta)F\eta/RT} = 1 + (1-\beta)F\eta/RT$ and $e^{-\beta F\eta/RT} = 1 - \beta F\eta/RT$ using the low field approximation. Then substituting into the Butler Volmer   we have

$i = i_0 F\eta/RT$ and $$\frac{d\eta}{di} = \frac{RT}{i_0 F}$$ and this is the polarizability of an interface.

i_0 is a measure of the fierce electronation and de-electronation current that exists at the interface.In the limit of i_0 going to infinity the derivative above goes to zero and the interface is non polarizable. In the limit of i_0 going to zero the interface is highly polarizable. The derivative goes to infinity.

Electronics:-

The Operational Amplifier or OA is made from some 14 transistors which can present quite a challenge in resolving the teamwork they process.We are going to rely in some places on the simple formula for V_{out} of the std configuration shown below
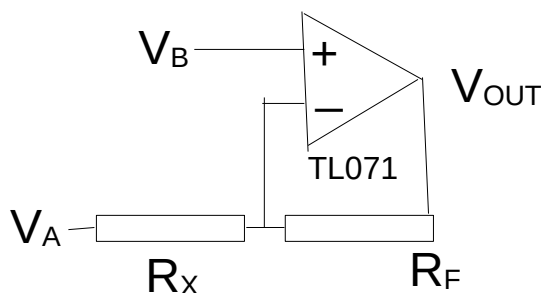
$$V_{OUT} = \left(\frac{R_F}{R_X} + 1\right) V_B - \left(\frac{R_F}{R_X}\right) V_A$$

Also 2 assumptions are made when calculating V_{OUT} as a function of the various input parameters.The first is that the OA computes till the voltage at the noninverting input, + equals the voltage at the inverting input- and the second assumptionis that both + and − inputs are very high impedance and thus draw negligable current

Consider the configuration below:

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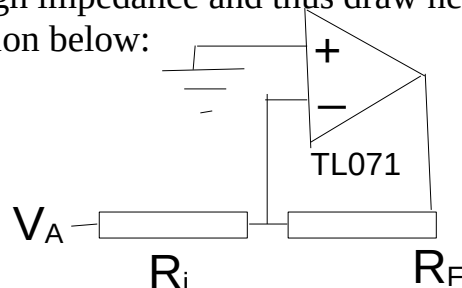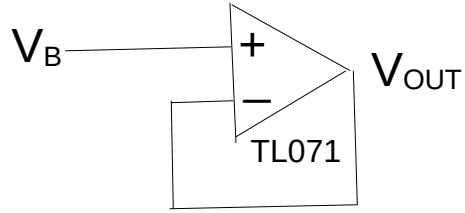
.Here $V_B = 0$ So $V_{OUT} = -\{R_F/R_X\} * V_A$

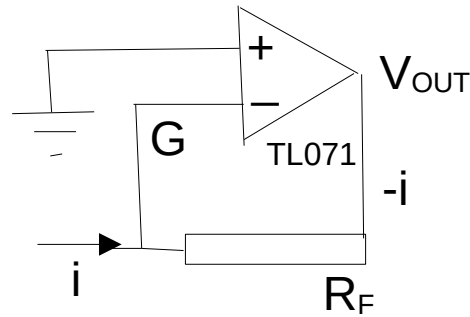$R_F < R_X$ inverting division

$R_F = R_X$ invertor

$R_F > R_X$ inverting amplifier

consider the config below
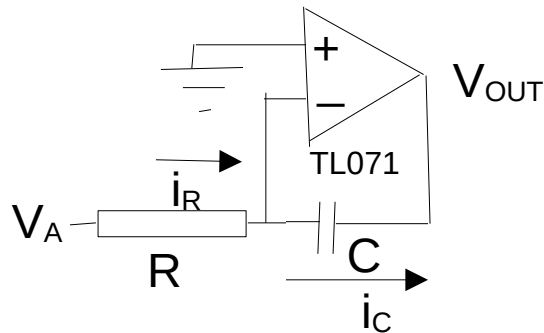

$R_F = 0$ So $V_{OUT} = V_B$

this is a high input impedance voltage follower

consider :-

Point G is a virtual earth since the + input is grounded , so the output must supply current i = input current and $V_{OUT} = - R_F i$

For oxidation ae <0 thus i is <0 so V_{OUT} is>0   i.e. positive current for oxidation

    Consider

For the current through the cap , C=q/V so C=dq/dV and dq =idt

so CdV= idt or i =CdV/dt

then $i_R = i_C$ since the – terminal is a virtual earth and $i_C = -C \, dV_{OUT} \, dt = i_R = V_A/ R$

$dV_{OUT} = -V_A / RC \quad dt$

$$V_{OUT}(t) - V_{OUT}(0) = -\int_0^t \frac{V_A}{RC} dt$$ so if V_A is constant and $V_{OUT}(0) = 0$

$V_{OUT}(t) = -1/RC *$ constant $* t$ and it can be seen that under these conditions the output voltage is a linear ramp in t .

Before we can discuss the Potentiostat we must discover the 3 electrode system as used in Voltammetry.Historically the 2 electrode system came first but it just did not do the job.
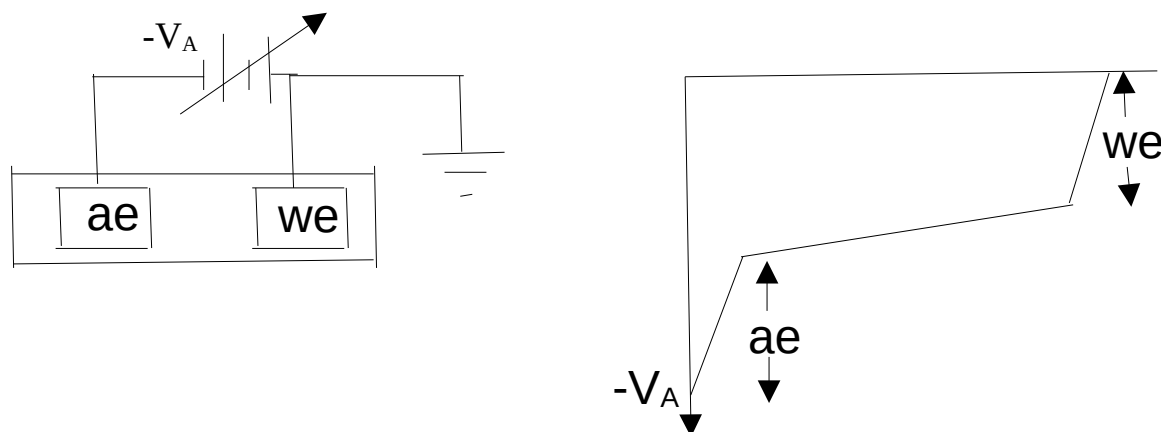

The ae is non polarisable so any change of voltage across the cell is ideally to be found at the we. So we measure $-V_A$ vs current through the cell for different values of $-V_A$. There is however a changing voltage drop through the bulk solution which reaches a maximum at the equilibrium potential of the we.Sadly it is at that point that we need an accurate measure of $-V_A$ and current.This failure is overcome in the 3 electrode system.This system places a non polarisable reference electrode in close proximity to the we. The ae need not be non polarisable.
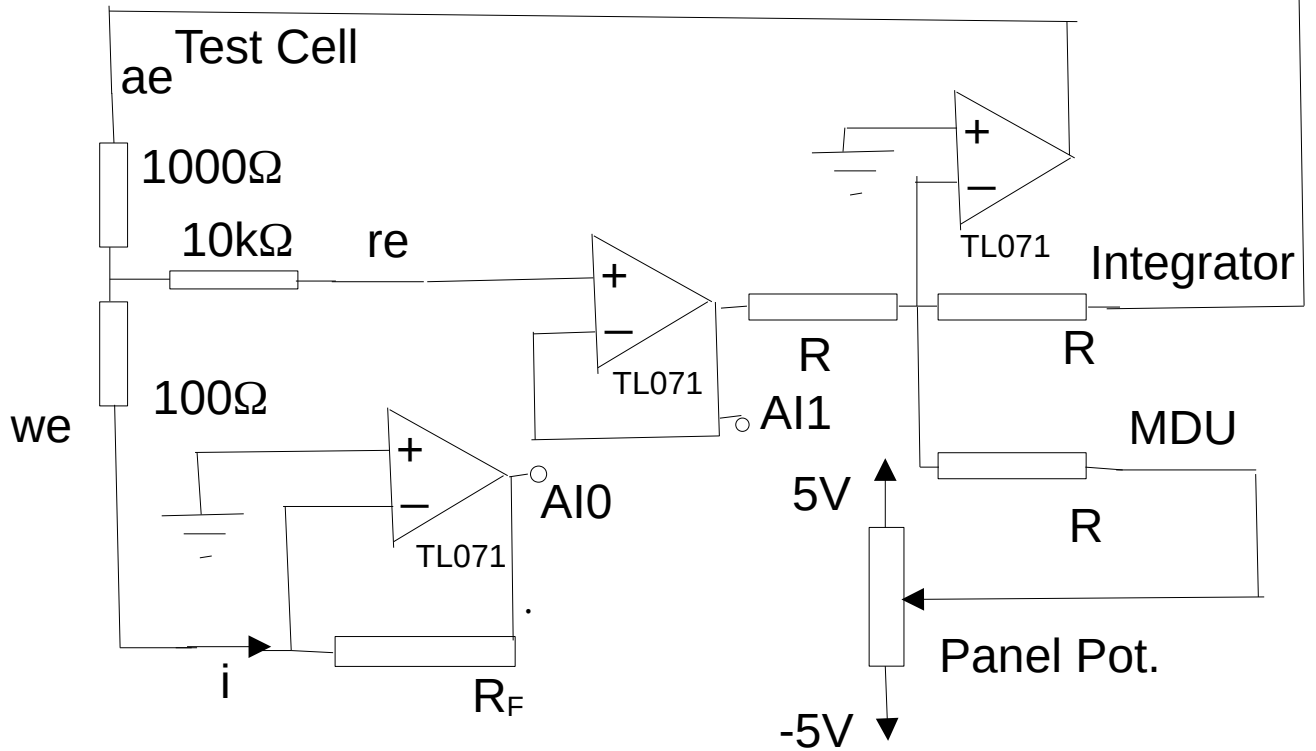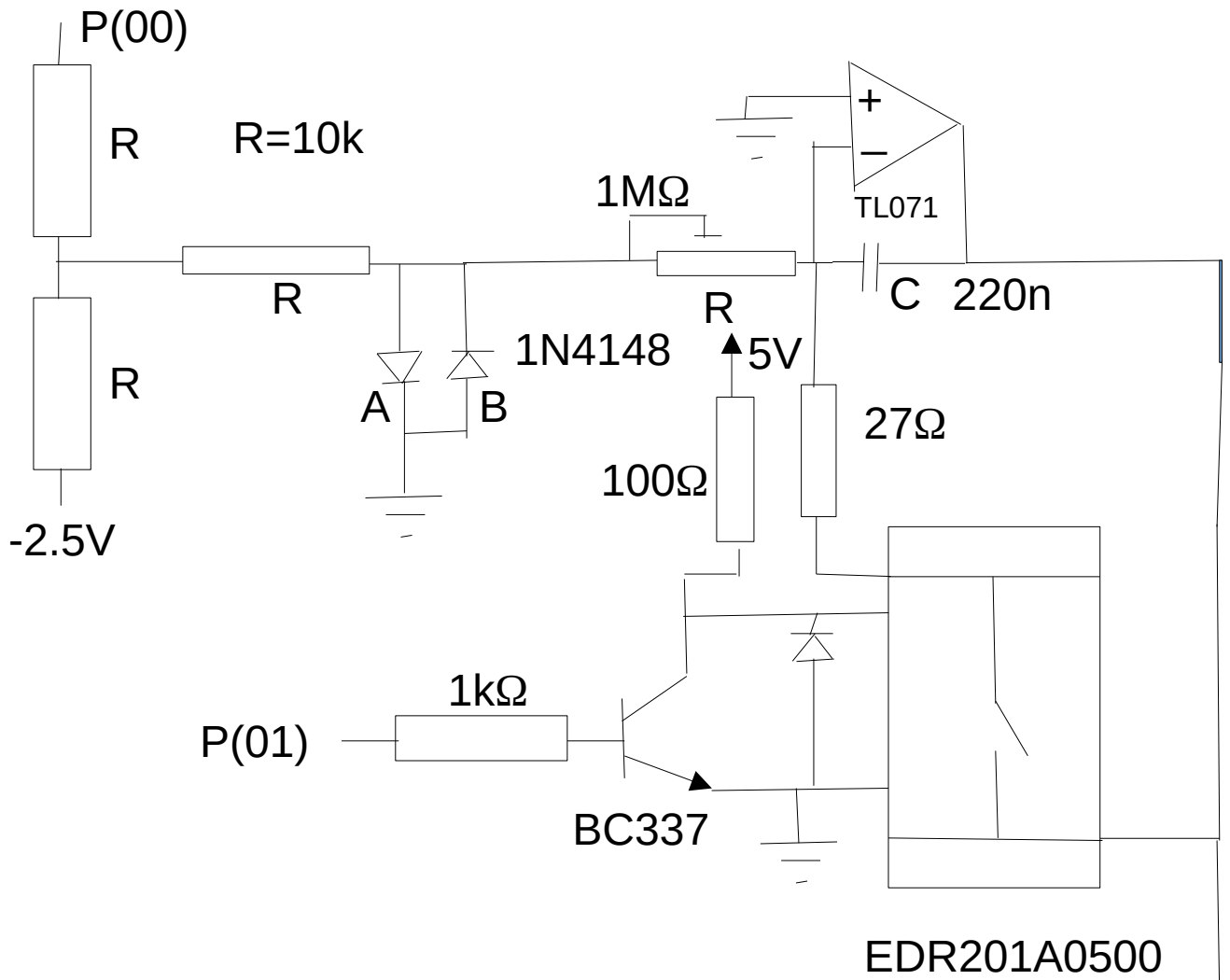The Test cell used in linear scan voltammetry is composed of resistors
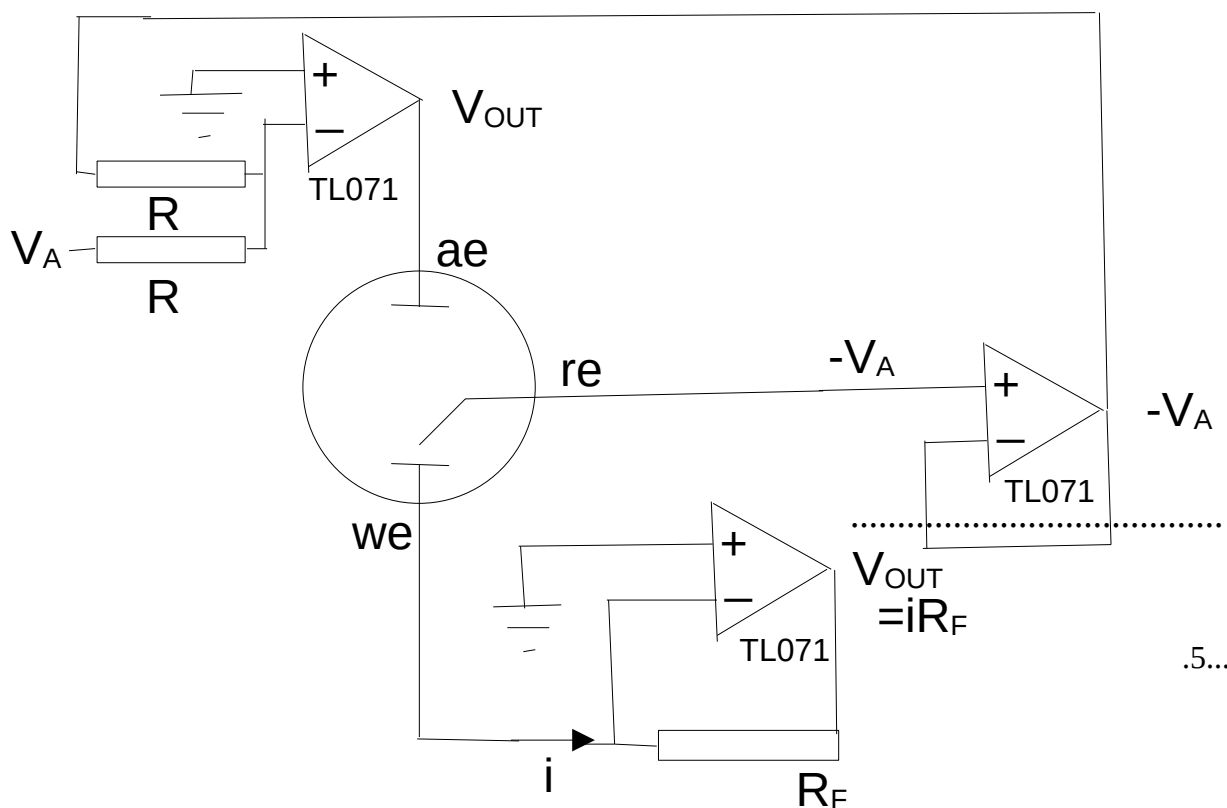
The we has been potentiostated to -V_A volts.
Practically the SHE is difficult to make and maintain.So we use other non polarisable electrodes like the Standard Calomel Electrode -SCE.The SCE is 242mV positive of the SHE.When the ae is made positive the voltage follower measures 0.242_+ Vwe.In interpreting this as -0.242 -Vwe we recover -Vwe by adding 0.242.When the ae is made negative the Voltage follower measures -Vwe +0.242 and in interpreting this as Vwe – 0.242 we recover Vwe by adding 0.242.
In the adder potentiostat the Integrator and MDU are added as follows
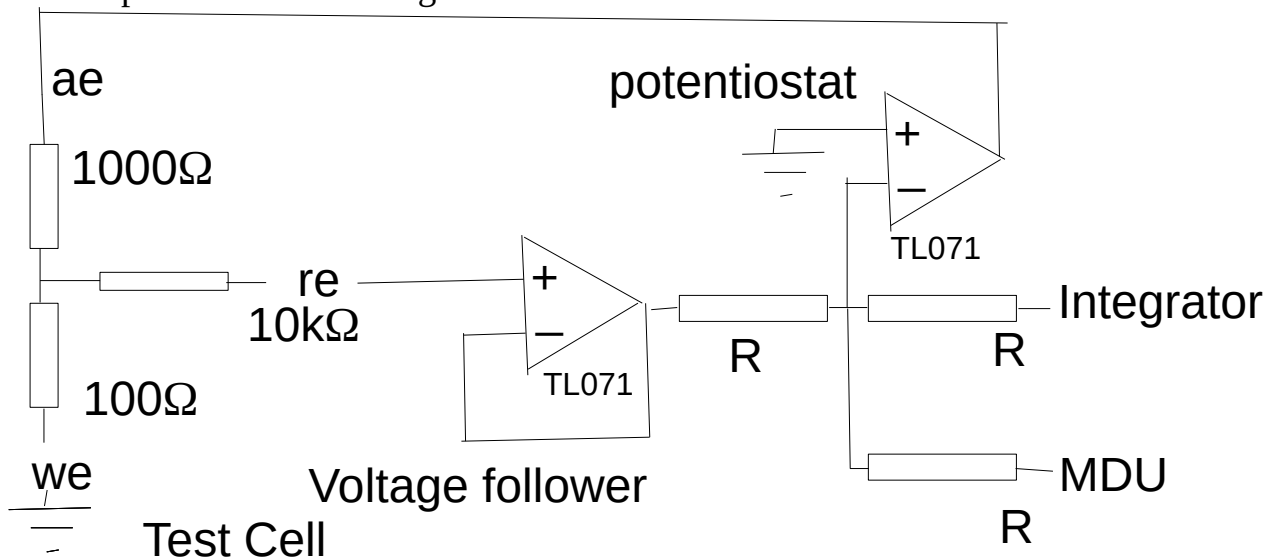
.This now brings us prepared to discuss the computer controlled Linear Scan Voltammeter.

P(00)

R

R=10k

1MΩ

TL071

R

R

C 220n

1N4148

A   B

27Ω

5V

100Ω

-2.5V

1kΩ

P(01)

BC337

EDR201A0500

Test Cell

ae

1000Ω

10kΩ   re

Integrator

TL071

we 100Ω

R   R

TL071

AI1

MDU

TL071

AI0

R

5V

i

R_F

Panel Pot.

-5V

For computer control we use the USB6008.It is addressed using Visual Basic and has 8 simultaneous ADC's of which we use AI0 to capture voltage related current and AI1 to capture Volts of the we.We also use 2 digital I/O lines PO0 to switch the integrator feed and PO1 to turn the relay on and off.
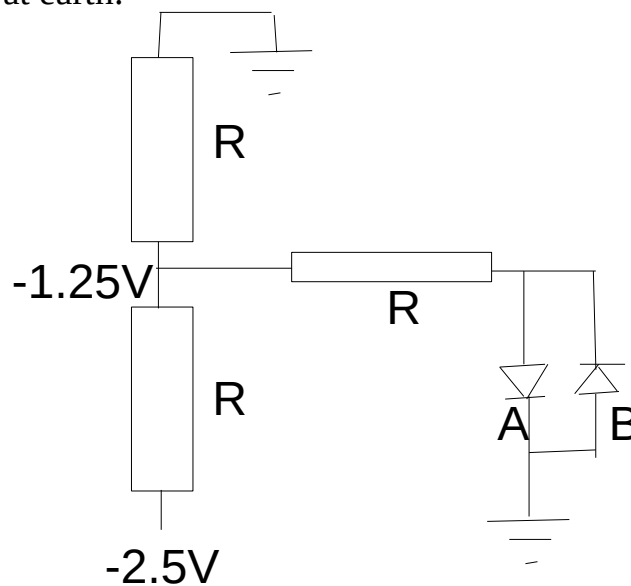
The signal feeding the Integrator is from

P(00)

R   R=10k

R

A   B

-2.5V

When P(00) = 5 V   we have

5V

R

R

R

A   B

-2.5V

=

2.5V

R

1.25V

R

A   B
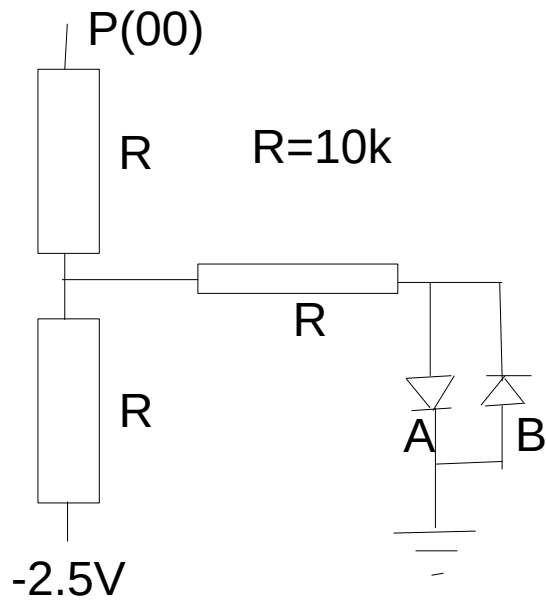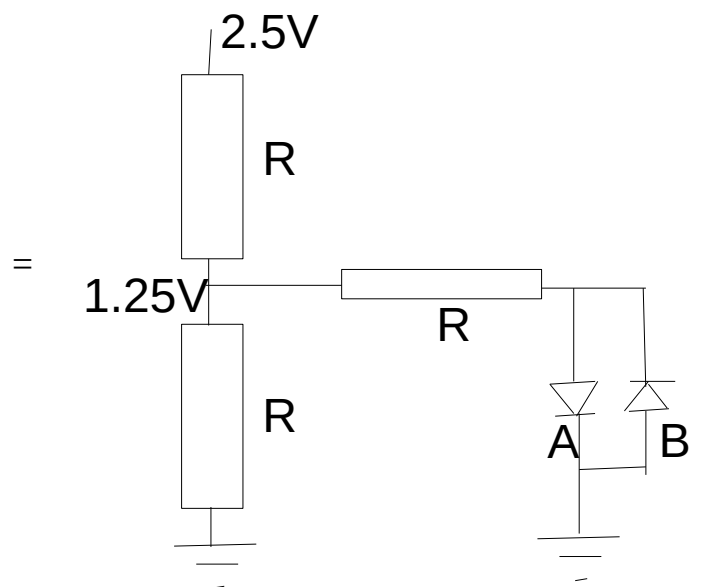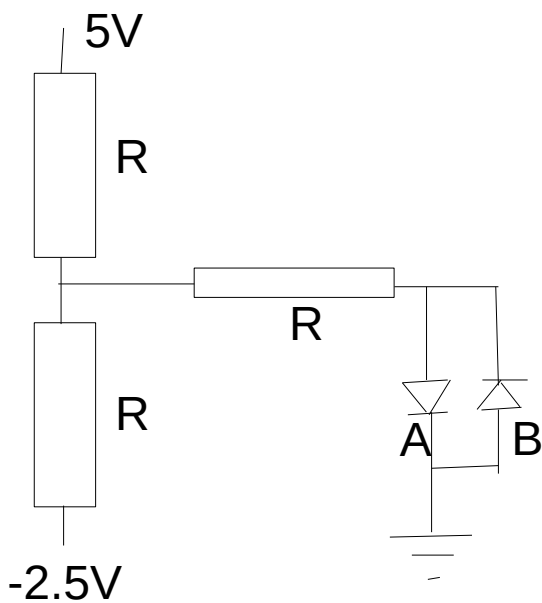
Here diode A is on and has an anode voltage of 0.8V which feeds the integrator.

When P(00) is low at earth:-



-1.25V

R

R

R

-2.5V

A   B

Now diode B is on with a cathode voltage of -0.8V which feeds the integrator.
 A relay (EDR201A0500) is used to short circuit the integrator capacitorand switch the integrator capacitor off.The 27Ω resistor is to prevent a spark when discharging the capacitor.To swith the integrator on the relay must be open P(01) must be high.AI0 captures the voltage of the we while AI1 captures the current related voltage. The voltammeter is switched on by closing the relay.
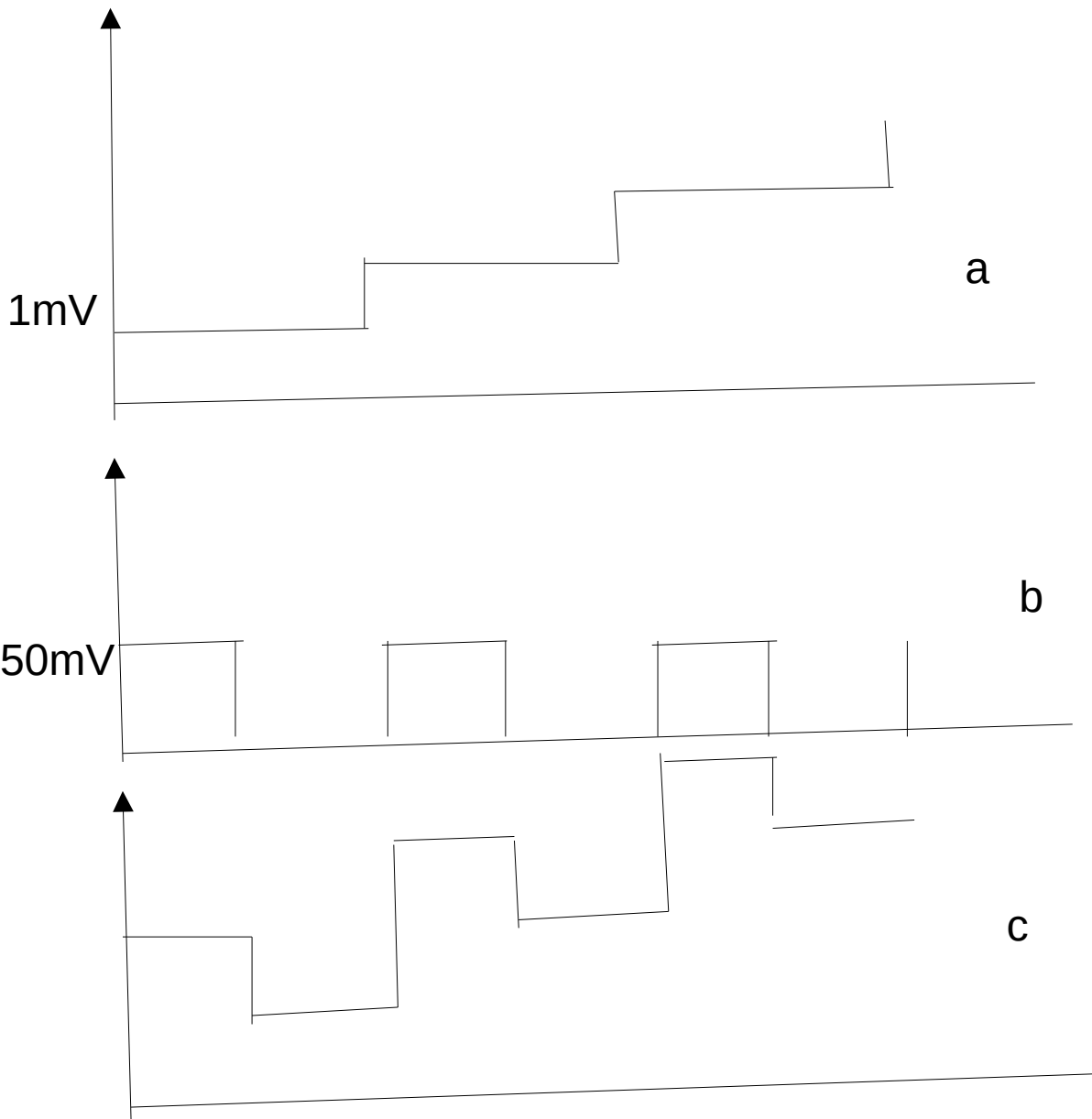Square wave voltammetry SWV is more powerful than linear scan because it removes the charging current.
The SWV waveform is as in c below the addition of b and a.One step shown below

V_A

i_A

Plot V_A vs I_A - I_B
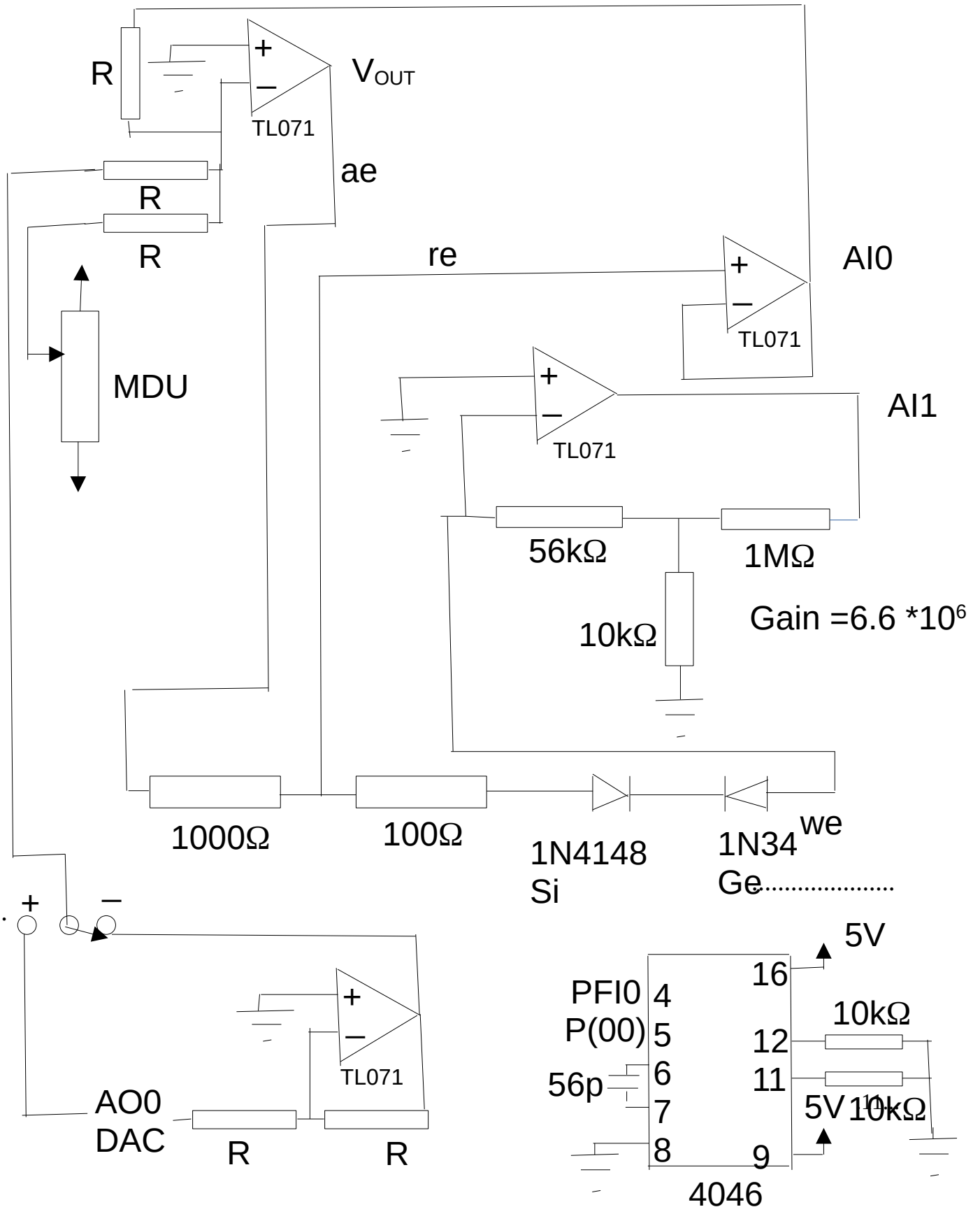
Faradaic

i_B

Charging current

a

1mV

b

50mV

c
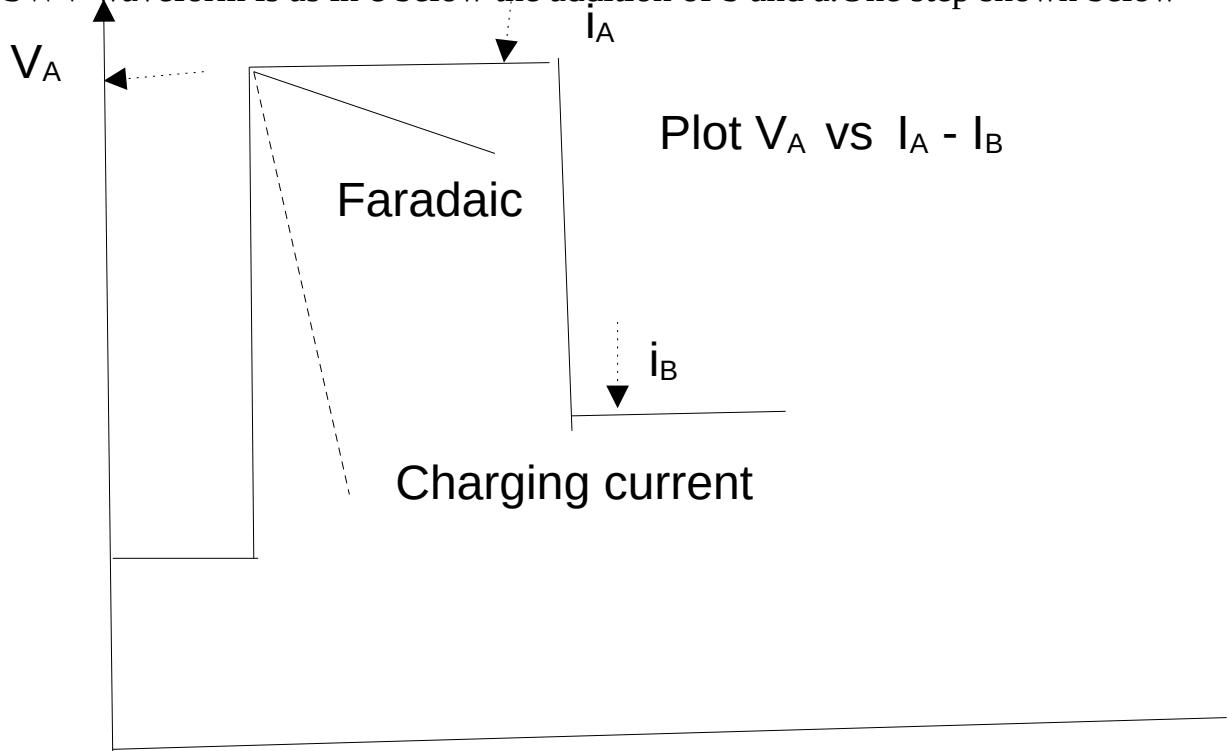
a can be produced by a clocked counter feeding a DAC

b can be produced by dividing the same clock down to maximum amplitude of 50mV

c is produced by adding a and b
Practically we use the USB DAC to produce c in one go by repeatadly adding 50mV
making a measure of Voltage I_A and I_A then subtracting 49mV and measuring I_A at
every tick of the Timertick procedure of visual basic

R

V_{OUT}

TL071

ae

R

R

re

AI0

TL071

MDU

AI1

TL071

56kΩ

1MΩ

10kΩ

Gain =6.6 *10⁶

1000Ω

100Ω

1N4148
Si

1N34
Ge

we

5V

+   −

PFI0 4
P(00) 5

16

10kΩ

56p   6
7

12
11

AO0
DAC

R   R

8

5V 10kΩ

9

5V

4046

TL071

+

−

A digital I/O P(00) is used to switch the 4046 clock on.The output of the 4046 on pin 4 goes to the PFIO input on the USB6008 and now we can time anything to an accuracy of 1.2uS.

This test cell produces a peak of about 300nA at about 300mV

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.As a final touch the let us discuss some of the math involved in Voltammetry and why peaks are produced. The Nernst equation is vital where

$E = E^o - 0.059/n \log [Red_o]/[Ox_o]$

where the subscrit o signifies that the concentration applies to the thin film adjacent to the electrode surface-the zeroth concentration.

$_d$The reaction is $O_X + ne^- = Red$ $EMF = E^O$

We are going to use the 2 electrode system with an nonpolarizable SCE as the anode and a highly polarizable mercury cathode .The layer of electrolyte containing Ox and Red immediately adjacent to the electrode surface is considered to be thin enough so that Ox and Red may be considered to be in instantaneous equilibrium with the electrode surface

Eappplied = E cathode – E anode

The current in reducing $[Ox_O]$ is $i = k([Ox] - [Ox_O])$ where $[Ox]$ =bulk concentration

As the potential gets more negative so $[Ox_O]$ goes down to a diminishing level till i reaches a maximum level $i_d = k[Ox]$ diffusion controlled current in a quiescent solution no stirring

$(i_d - i)/k = [Ox] - ([Ox] - [Ox_O]) = [Ox_O]$

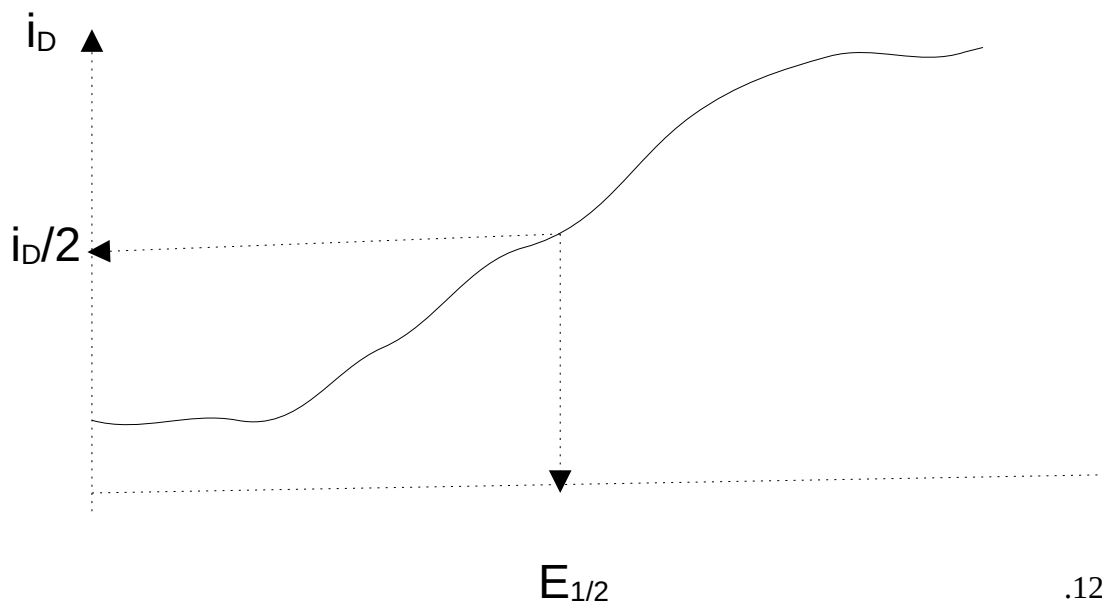The surface concentration of Red_O will also be proportional to the current

$i = k_R [Red_O]$.

Now we can write Eapplied = E^O -Esce – 0.059/n log [$(i/k_R)/(i_d - i)/k$]

=E-Esce - 0.059/n * $(\log k/k_R - \log(i/(i_d - i))$

at $i = i_d$ *2 when i* /$(i_d - i)$ =1

Eapplied = $E_{1/2}$ = E^O – Esce - 0.059/n * $\log k/k_R$

Then Eapplied =$E_{1/2}$ – 0.059/n * log i /$(i_d - i)$ and we plot i vs Eapplied

On a slow DC scan there is no interfacial strain and equilibrium is quickly established at every incremental change of potential and the curve looks as above. Note that $E_{1/2}$ is independent of concentration and will be dependant only of the identity of the chemicals involved so it can be used in a qualitative way. Quantitative analysis rests on the fact that the diffusion current (max) is proportional to the concentration .
In a rapid scan on the time scale of diffusion there is no time to establish thermodynamic equilibrium and all the action is accumulated.There is an increase in measured current.At Eapplied = $E_{1/2}$ i reaches a maximumand tapers off as the zeroth layer becomes deplete of Ox_0 this creates a peak in the current response.
In the case of SWV we use The Evaluation of Analytical Pulse Polarography by Perry and Osteryoung in Analytical Chemistry Vol 37 number 13 Dec 1965 p1634-1637 where he comes up with the following equation

$$\frac{di}{dE} = \frac{n^2 F^2}{RT} AC \sqrt{\frac{D}{\pi t}} \frac{P}{1+P^2}$$

P = exp((E-$E_{1/2}$) nF/RT)

Then we see that at E = $E_{1/2}$ P = 1 and P/(1 + P^2) = 0.5
and at E − $E_{1/2}$ = 0.1   P = 47.94 and   P/(1+ P^2)   = 0.02
and at E − $E_{1/2}$ = - 0.1 P= .021 and   P/(1+ P^2)   =0.02

So we see that the function P/(1+ P^2) will force the function for di/dE into quite a sharp peaked response.

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