Synthesis of Ag NANOWIRES on paper by inkjet printing and using them as solid state Ag/AgCl Reference Electrode in GLUCOSE CENSOR

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Material Used:

1. Chemicals

    i. Potassium Bromide (KBr)
    ii. Potassium Chloride (KCl)
    iii. Potassium Iodide (KI)
    iv. Silver Nitrate ($AgNO_3$)
    v. Isopropyl Alcohol (IPA)
    vi. Hydroquinone (Quinol)
    vii. Metol
    viii. Sodium Sulphite
    ix. Borax
    x. De-ionized Water (DI water)

2. Instruments

    i. HP Deskjet 1010 Printer
    ii. HP 802 Black ink cartridges
    iii. CH Instruments Electrochemical Analyzer 600D
    iv. Zeiss Ultra 500 SEM
    v. Desiccator

3. Softwares

    i. Corel Draw X7©
    ii. Electrochemical Analyzer CHI608D

1) INTRODUCTION

Conventional Electrodes used in electrochemical cells are basically the substances in particular shape that could be used for the conduction of electrons through them. The systems studied in electrochemistry are generally good conductors. These may be divided into three main categories, **Gaseous, Metallic and Electrolytic.** [1]

Gases conduct electricity with difficulty and only under the influence of high potentials or if exposed to the action of certain radiations. [1]

Metals are the best conductors, in general, and the electricity is carried exclusively by the electrons. Metallic conduction or electronic conduction, as it is often called, is not restricted to pure metals, for it is a property possessed by most alloys, carbon and certain solid salts and oxides.[1]

Electrolytic conductors, or electrolytes, are distinguished by the fact that passage of an electric current through them results in an actual transfer of matter. Electrolytic conductors are of two main types; there are, first, substances which conduct electrolytically in the pure state, such as fused salts and hydrides, the solid halides of silver, barium, lead and some other metals, and the a-form of silver sulfide. Water, alcohols, pure acids, and similar liquids are very poor conductors, but they must be placed in this category. The second class of electrolytic conductors consists of solutions of one or more substances; this is the type of conductor with which the study of electrochemistry is mainly concerned. The most common electrolytic solutions are made by dissolving a salt, acid or base in water; other solvents may be used, but the conducting power of the system depends markedly on their nature. [1]

Electrochemical Cell:

Most Common type of an electrochemical cell is the one in which two metallic conductors and one electrolytic conductor is used for its construction and since, Silver being one of the best conductors, Ag/AgCl electrode is very common in use mainly due to the simplicity of construction, safety, and great stability. [2] Conventional Ag/AgCl electrode is an electrode in which an Ag wire coated with AgCl at the bottom is dipped in the Solution of normally 1 M KCl. [3]

Paper Based Electrodes:

Paper is rapidly emerging as a substrate of choice for the fabrication of disposable electronic circuits[4, 10] and point-of-care diagnostic devices[5, 10] Batteries[6, 10], sensors[7, 10] and solar cells[8, 10] have been fabricated on paper-based substrate, wherein paper functions primarily as a mechanical support and sometimes as an active part of the device[9, 10]. Some studies have been dedicated to obtain a micro-fabricated Ag/AgCl RE with filling solution [19-21] or all solid-state reference electrodes (SSREs) that have a gel or solid junction. [22-24] As far as paper based Ag/AgCl electrodes are concerned, these are without solid junction SSREs[2] which are made by inkjet printing the Ag base over a specific area of the paper and then coating the further specific area of the base area with the AgCl electrochemically with inkjet printing. [10] For printing Ag over the paper, an ink is required and this functional Ag ink can be divided into 3 categories, namely organometallic inks [10-12], complexed silver salt-based ink formulations [10, 13-15], and nanoparticle-based inks [10, 16-18]. Silver nanoparticle inks are the most widely prevalent form of conductive inks that are also commercially available. Curing of these inks to form conductive traces by chemical or physical processing is a crucial step in obtaining conductive traces. The inkjet printing technique can be considered as a great alternative for Ag/AgCl reference electrodes fabrication due to its low cost, simplicity, reduced material wastage, noncontact technique, mask-less approach, rapid prototyping, applicability to various substrates, and the use of inks with low viscosity. [2, 25-27]

Enzymatic Electrochemical Glucose Sensors:

The history of glucose enzyme electrodes began in 1962 with the development of the first device by Clark and Lyons of the Cincinnati Children's Hospital.[28,29] Their first glucose enzyme electrode relied on a thin layer of GOx entrapped over an oxygen electrode via a semipermeable dialysis membrane. Measurements were made based on the monitoring of the oxygen consumed by the enzyme-catalyzed reaction [28-30]

$$\text{glucose} + O_2 \xrightarrow{\text{glusoce oxidase}} \text{gluconic acid} + H_2O_2 \tag{1}$$
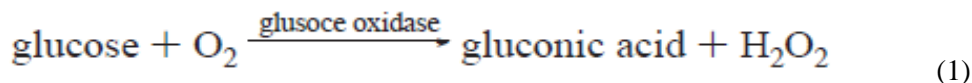
A negative potential was applied to the platinum cathode for a reductive detection of the oxygen consumption. [28-30]

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \tag{2}$$
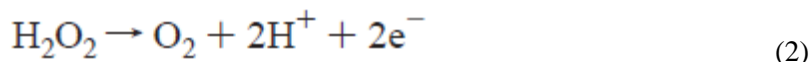
Many other advancements were also made to make better enzymatic glucose sensors like use of Non-Physiological Electron Acceptors [29, 31-33], Wired Enzyme Electrodes [34, 35] or nanomaterial electrical connectors [36-39] and to use them in wide range of applications. [29, 40-44]

Non-Enzymatic Electrochemical Sensors:

There are some disadvantages of the enzyme-modified electrodes, for instance, the instability of the electrode and unsatisfactory reproducibility, the immobilization procedure is complicated, and the enzymes are expensive and easily lose activation. Therefore, it is important to develop novel electrode materials with high sensitivity and stability and that are interference-free in glucose non-enzymatic determination. [45] As an important p-type semiconductor metal oxide with a narrow band gap (1.2 eV), copper oxide (CuO) with virtue of natural abundance, low production cost, good electrochemical and catalytic properties is of particular interest. [45]

## Using Paper Electrodes in Non-Enzymatic Electrochemical Sensors:

The inkjet printed electrodes with the Ag base are further printed with some Nano Particles ink where these are used as working electrodes, the inkjet printed Ag/AgCl is used as Reference Electrodes and Pt wire is used as counter electrode. All these electrodes are dipped in some electrolyte with some sample of Glucose in it. [45]

2) LITERATURE REVIEW

A lot of work has been done in past to make Glucose sensors and to make them perform even better with more reliability and stability. It all started in 1962, when Clark and Lyon [28, 29] proposed the idea of Glucose Electrodes and since them we have witnessed a lot of efforts directed towards this area for the betterment of devices used for diabetes monitoring and controlling. [29] They formed the basis of what we call as the 'First Generation Sensors'. It was their idea only that laid the foundation for synthesis of First Generation Sensors which rely on the use of the natural oxygen cosubstrate and generation and detection of hydrogen peroxide (eqns 1 and 2). The biocatalytic reaction involves reduction of the flavin group (FAD) in the enzyme by reaction with glucose to give the reduced form of the enzyme (FADH2)

$$GOx(FAD) + Glucose \rightarrow GOx(FADH_2) + Gluconolactone \tag{3}$$
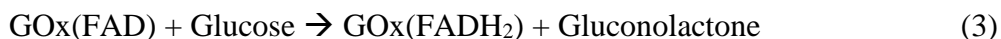
followed by reoxidation of the flavin by molecular oxygen to regenerate the oxidized form of the enzyme GOx(FAD).

$$GOx(FADH_2) + O_2 \rightarrow GOx(FAD) + H_2O_2 \tag{4}$$
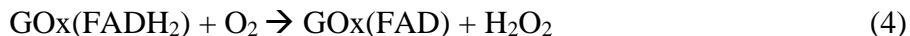
Clark's technology was subsequently transferred to Yellow Spring Instrument (YSI) Company, which launched in 1975 the first dedicated glucose analyzer (the Model 23 YSI analyzer) for direct measurement of glucose in 25 μL whole blood samples. [29]

Updike and Hicks [47, 29] further developed this principle by using two oxygen working electrodes (one covered with the enzyme) and measuring the differential current in order to correct for the oxygen background variation in samples.

Further in 1973, Guilbault and Lubrano [46, 29] described an enzyme electrode for the measurement of blood glucose based on amperometric (anodic) monitoring of the hydrogen peroxide product

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \tag{5}$$

The resulting biosensor offered good accuracy and precision in connection with 100 μL blood samples. A wide range of amperometric enzyme electrodes, differing in electrode design or material, immobilization approach, or membrane composition, has since been described. [29]

Gough's Group [48, 49, 29] designed a 2-D electrode that has been particularly attractive for addressing the oxygen deficit by allowing oxygen to diffuse into the enzyme region of the sensor from both directions while glucose diffuses only from one direction (of the exposed end).

Electrochemical biosensors are well suited for addressing the needs of personal (home) glucose testing and have played a key role in the move to simple one-step blood sugar testing. Since blood glucose home testing devices are used daily to diagnose potentially life-threatening events they must be of extremely high quality. The majority of personal blood glucose monitors rely on disposable screen-printed enzyme electrode test strips. [50, 51, 29] The screen-printing technology involves printing patterns of conductors and insulators onto the surface of planar solid (plastic or ceramic) substrates based on pressing the corresponding inks through a patterned mask. Each strip contains the printed working and reference electrodes, with the working one coated with the necessary reagents (i.e., enzyme, mediator, stabilizer, surfactant, linking, and binding agents) and membranes (Figure 1). [29] The reagents are commonly dispensed by an ink-jet printing technology and deposited in the dry form.

For non-enzymatic glucose sensors, Tripathy N. and group [45] published in their paper that they used CuO NPs as ink for the inkjet printing of the CuO over the Ag/Si Base v/s the Ag/AgCl electrode, which showed tremendous results as the fabricated sensor presented a number of attractive analytical features such as high sensitivity, good stability, reproducibility, selectivity, and wide linear range as well as fast response time.
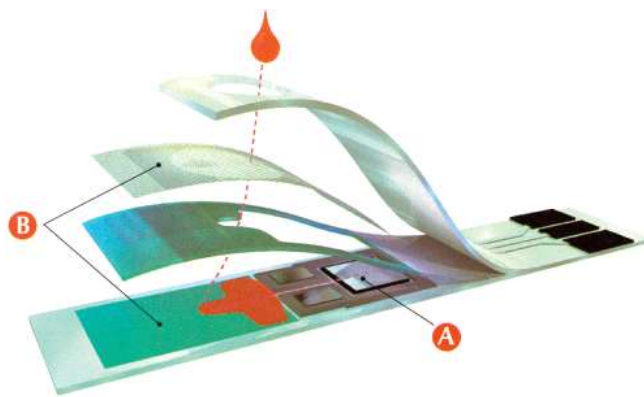
Figure 1: Cross section of a commercial strip for self-testing of blood glucose (based on the Precision biosensor manufactured by Abbott Inc.): (A) electrode system; (B) hydrophobic layer (drawing the blood). [29]

The data from glucose determination in blood serum samples were in accordance with the calculated ones. This inkjet printing method can easily be used for the mass-production of electrodes using CuO NPs-ink not only on the Si/Ag electrode but also on the variety of electrodes material to use for long-term as an amperometric sensor for routine analysis of glucose in real blood serum samples as well as in agricultural products or foods. [45]

As far as other electrode materials are concerned, we can use paper also by inkjet printing the Ag base [10] and then coating part of the Ag base with CuO ink as was done by Tripathi N. and group [45] and cover the other part with AgCl electrochemically as was done by Parmar S.K. and Venugopal S. [10] or Miserere S. et al [2].

Parmar S.K. and Venugopal S. [10] printed $AgNO_3$ and KX alternatively over a particular pattern and then exposing it to the light resulted in formation of latent clusters of Ag metal due to reduction of AgX. Further, dipping it in the developer solution D-76, resulted in formation of Ag nanowires. Hence, the formation of Ag base.

Miserere S. et al [2] used the same technique of inkjet printing but with different chemicals. They used a silver nanoparticle ink (20 wt % in ethylene glycol from Sigma-Aldrich) for Ag base and then dipped the patterns in the bleach solution and washing it with water resulted in formation of AgCl layer.

3) EXPERIMENTAL SECTION

In this work, a 6x8 cm^2 pattern was drawn on the COREL DRAW X7© and was printed alternatively with 1 M $AgNO_3$ and 2 M KCl and 1 M $AgNO_3$ and 2 M KBr/KI in the ratio of 19:1 in three separate HP 802 black ink cartridges with the help of HP 1010 Deskjet Printer. For putting the chemicals in the cartridges, first the cartridges were emptied by removing the sponge holding the ink and to remove the leftovers, it was placed under the running tap. It was found that 4 printings of $AgNO_3$ and 2.67 printings of KCl and 4 printings of $AgNO_3$ and 3 printings of KBr deposited 1 mg/cm^2 of Ag base over the A4 size paper. The method used to measure the deposition was, first the empty cartridge was weighed and then after 1 printing, it was again weighed and the amount used for printing the printed area was calculated. Assuming that the printing was uniform, the average value of no. of printings for depositing 1 mg/cm^2 was calculated. For proper formation of Ag base, 5 printings of $AgNO_3$ and 3 printings of KCl/KBr were done, so that $AgNO_3$ could react properly with KCl/KBr. After all the printings, the printed area was kept under the halogen lamp for approximately 15 minutes. Keeping the sample for prolonged time under the lamp showed no appreciable effect. The color of the sample changed from colorless to shaded purple, indicating the formation of Ag latent clusters. [10] After

putting the sample in the light, it was dipped in the developer solution D-76 for half an hour. The D-76 was made by dissolving 20 gm of Sodium Sulphite, 0.4 gm of Borax, 1 gm of Quinol and 0.4 gm of Metol in 200 mL water at 29 °C. After half an hour, the sample was taken out from the developer solution, and a dark yellowish-brown color was seen. It was put in the DI water for another half an hour and was shaken intermittently for removal of any unreacted ions. DI water was used for preparation of all the chemicals.
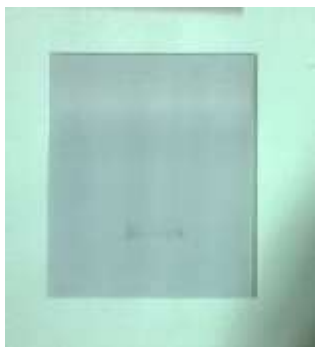

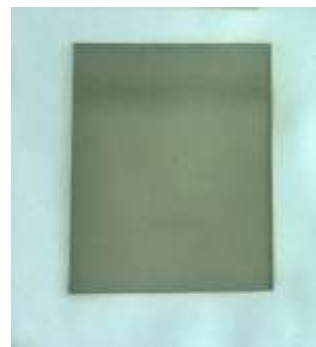Figure 2.a)   Figure 2.b)   Figure 2.c)

Figure 2:
   a) Electrode sample right after printing (colorless)
   b) Electrode sample after exposure to the light (shaded purple)
   c) Electrode Sample after dipping in the D-76 (yellowish-brown)

After the formation of Ag base, it was further coated with printings of 1 M $AgNO_3$ and 2 M KCl at an area of 18 cm^2. Different numbers of printings were done for different samples, which are shown in the table 1.

Amount of AgCl (mg/cm^2)	No. of Printings	
	KCl	AgNO$_3$
1	2	3
2	4	6
3	6	8
3.5	7	9
4	8	10

Table 1: No. of Printings required for different amount of AgCl.
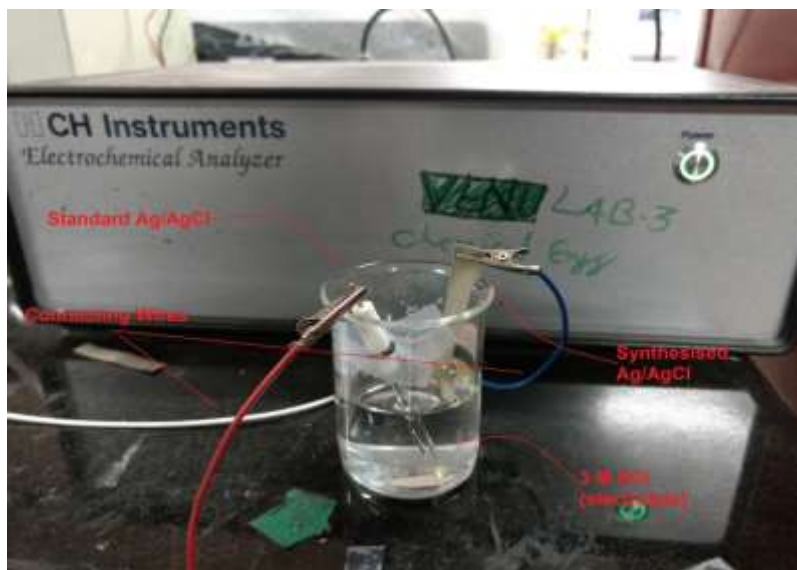
These paper based electrodes were used as working electrodes with the conventional glass tube Ag/AgCl electrode as the reference electrode and these two were dipped in 3 M KCl solution as electrolyte. Hence, the Open Circuit Potential was determined with the help of the Electrochemical Analyzer 600D by CH Instruments. The setup is shown in the Figure 3.

Figure 3: Electrochemical Cell Setup

4) RESULTS AND DISCUSSIONS

During Open Circuit Potential determination, it was found that the potential of the cell was negative continuously no matter what the deposition of AgCl was, indicating that the reaction was not spontaneous. Although, during the first run of the experiments, the Cell Potential started to move towards the zero value, as the deposition of AgCl was increased, which shows that the concentration of AgCl has certainly some role to play to define the stability of the electrode. Apart from this, a very interesting thing came out that when KCl was used to form the Ag base in place of KBr, instead of Ag nanowires, Ag nanoparticles did form even after going through the same process that was confirmed by the FESEM images as shown in Fig 3. As can be seen from the figure 3a and 3b, Ag nanoparticles of size roughly between 250-450 nm are formed when KCl was used along with $AgNO_3$ to form the Ag base. When KBr was used along with $AgNO_3$, it gave rise to the Ag nanowires, Fig 3c. This may have occurred because of size of the lattices of AgBr and AgCl. Since size of lattice of AgBr is larger than that of AgCl, the Ag ions would have been able to grow in the AgBr, which would have not been possible in the AgCl lattice, hence, the formation of nanoparticles and not the nanowires.
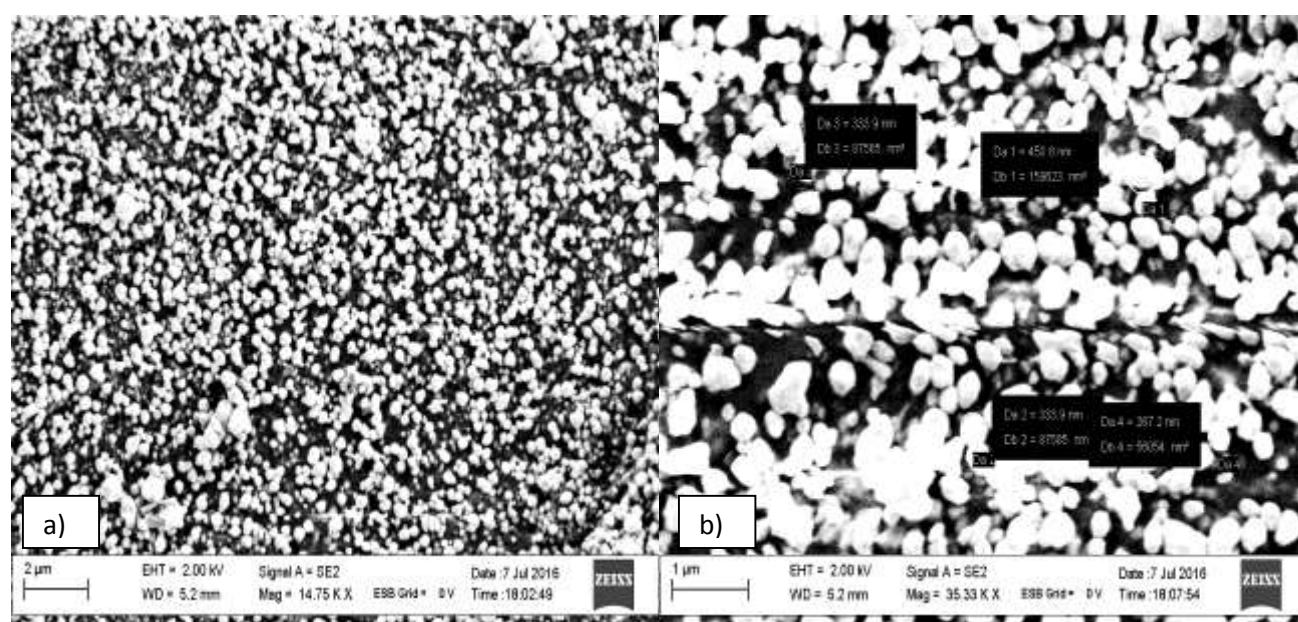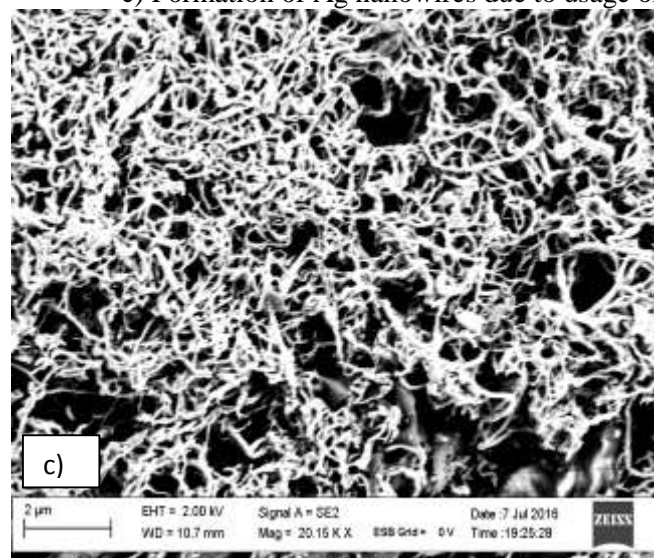

Figure 3: a) & b) Formation of Ag nanoparticles due to usage of KCl along with $AgNO_3$
c) Formation of Ag nanowires due to usage of KBr and $AgNO_3$

As can be seen from the figures, clearly, the base made by reaction of 1 M $AgNO_3$ and 2 M KBr was more conducting as compared to the base made by reaction of 1 M $AgNO_3$ and 2 M KCl. This is because of large void spaces in case of formation of Ag nanoparticles. It could be seen in the results given by the Electrochemical Analyzer too. It was observed that the electrode made by using the Ag base synthesized by KBr showed much lesser deflection (roughly 75 mV) from the standard electrode potential as compared to the electrode which was made by using the Ag base synthesized from the KCl which showed deflection of about 240 mV for same amount of deposition.

Graph 1: Potential v/s Time for Ag/AgCl synthesized by KCl and AgNO$_3$
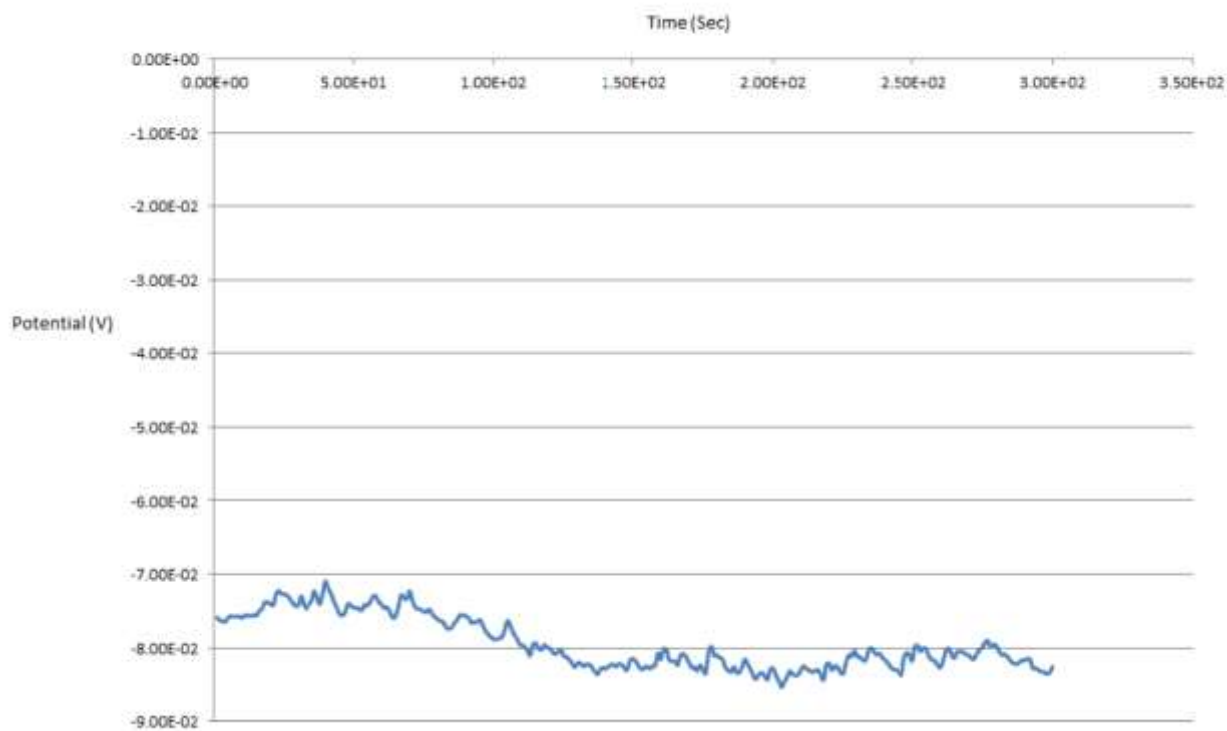
Graph 2: Potential v/s Time for Ag/AgCl synthesized by KBr and AgNO$_3$

As can be seen the Potential of the cell of the Graph 2 is less deflected from 'zero' as compared to that in Graph 1. Moreover, it can be seen that the potential of Graph 2 is more stable also as the range of scattering is just 10 mV whereas the potential of Graph 1 is showing some unwanted peaks, which may be due to the non-uniform deposition as well.

From Graph 3, it can be said that as the amount of AgCl was increased, the deviation of the electrode potential from the standard Ag/AgCl electrode decreased.
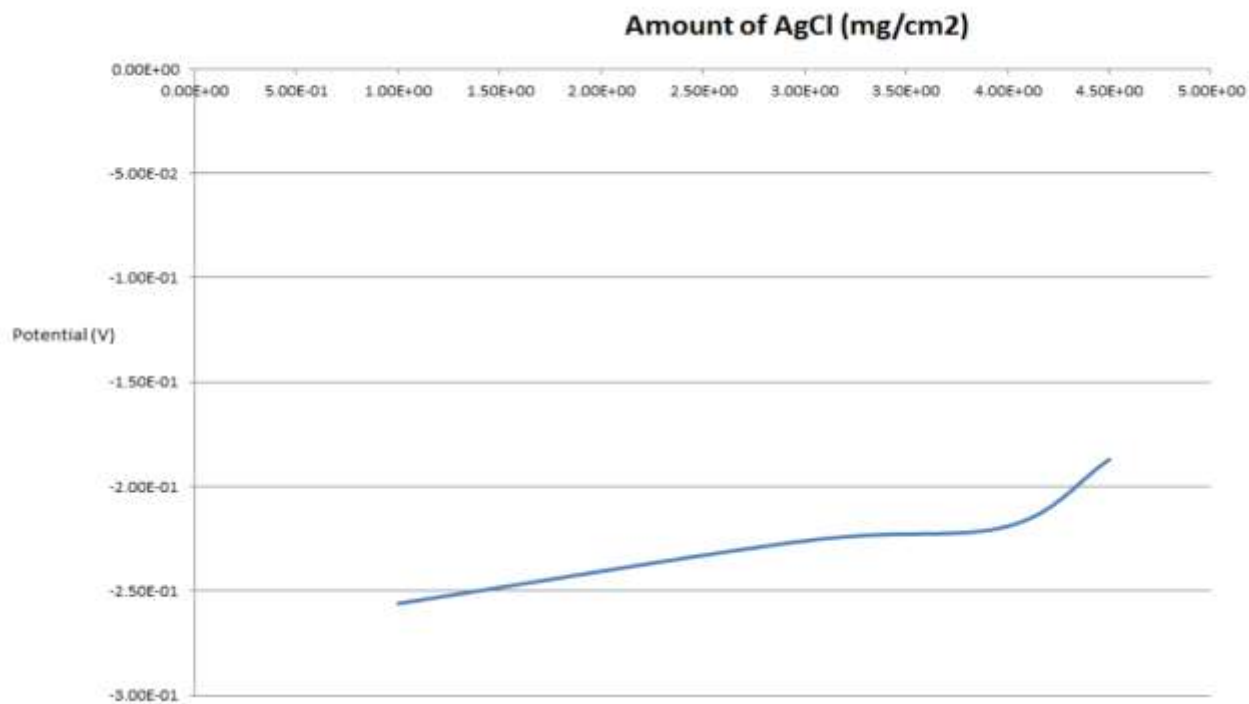
Graph 3: Comparison between electrode potentials for different amount of AgCl in the Ag/AgCl electrode

But it was observed that these values were not remaining constant i.e. after some continuous runs, the deviation from the standard electrode potential increased which may be encountered because of the reduction of AgCl due to continuous use and deposition of Ag metal over the paper electrode surface.
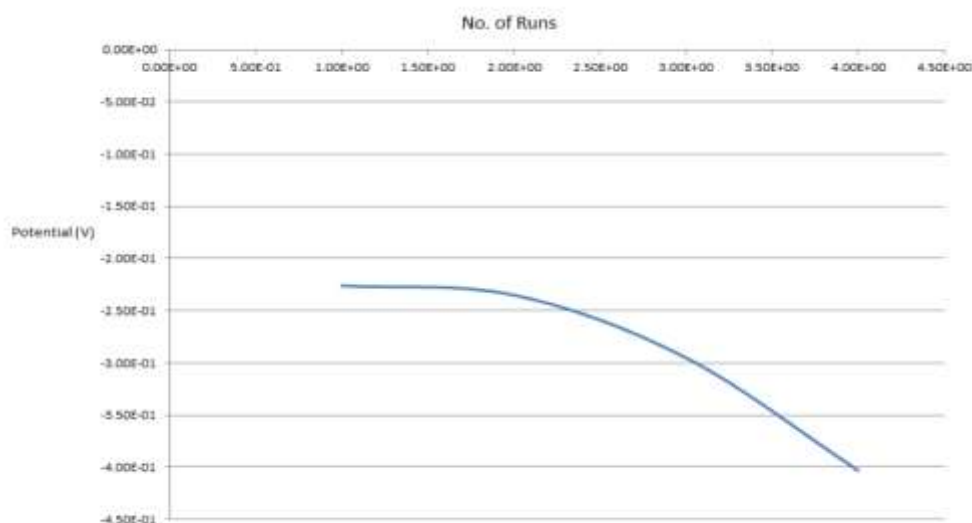
As can be seen from the Graph 4, the Cell Potential is decreasing exponentially after being run 4 times.

Graph 4: Deflection from Standard Potential due to being used continuously.

5) <u>CONCLUSION</u>

After performing all the experiments, it can be concluded that in order to make the synthesized Ag/AgCl electrodes as similar to the standard Ag/AgCl electrode as possible, the Ag base used should be synthesized from the $AgNO_3$ and KBr only and not with KCl as with KBr, much more conducting nanowires are formed.

As far as the amount of AgCl or the concentration of the Cl⁻ ions is concerned, it should also be optimized according to the standard electrode in order to make the deflections as nil as possible. Apart from all this stuff, one major problem that I encountered was during usage of the cartridges. It was observed that the amount of the chemicals in the cartridges should be as low as possible as more be the amount in it, more are the chances of the leakage of the chemicals which may spoil the samples as the cartridges are designed to hold the ink which is way too viscous as compared to the chemicals we used. Another such problem was the blockage of the cartridge pores after few printings. It could be stopped by continuously wiping off the printing portion of the cartridges with iso-propyl alcohol (IPA) and after all the printings are done, dipping the printing portion of the cartridge in hot water after properly washing off the chemicals and filling some hot water inside the ink holding area of the cartridge as well.

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