SYNTHESIS OF PAPER-BASED Ag/AgCl REFERENCE ELECTRODE ON Ag NANOWIRES BY INKJET PRINTING AND DIPPING METHODS

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REPORT

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INTRODUCTION:

One of the most important components of electrochemical sensors is the reference electrode. Among the reference electrodes studied, the Ag/AgCl is so far the most common type of Reference Electrode used for miniaturization, mainly due to the simplicity of construction, safety, and great stability. The solid-state reference electrode has been known to reduce the problems associated with conventional reference electrodes relating to mass-production, maintenance, contamination by the internal solution, and miniaturization [1].

There are several methods of fabricating electrodes, such as electrochemical deposition, screen-printing, and sputter coating. It is known that the electrodes fabricated by electrochemical deposition consist of amorphous films with varying levels of hydration and relatively high internal micro porosities. The screen-printing technique, which has been used to synthesize a few types of electrodes, including disposable ones, is a useful method owing to its simplicity and low-cost nature. However, the screen-printing technique is limited in that only a few metals can be deposited on the substrate. On the other hand, the electrodes fabricated by sputter coating are known to be chemically stable. Sputter coating is thus widely used for electrode fabrication. In addition, this method is also compatible with the micro fabrication processes involved in the fabrication of micro total analysis systems [2].

One of the most promising alternatives is the ink-jet printing technology, by which the conductive lines can be drawn (i.e. printed), onto the substrate. All devices, organic thin film transistors, LEDs, and solar cells, require conductive structures as part of larger circuits that integrate them. Sensors and detectors are an integral part of many aspects of modern life, such as light detectors, bio-sensors, safety, and security applications such as toxic gas sensors, etc. Many of these

applications require inexpensive, often single-use devices that are ideally suited to inkjet printing [3]. Inkjet printing is a material-conserving deposition technique used for liquid phase materials. These materials, or inks, consist of a solute dissolved or otherwise dispersed in a solvent. Inkjet-printing jets the single ink droplet from the nozzle to the desired position, therefore, no waste is created, resulting in an economical fabrication solution [4] and the printing is uniform throughout the substrate.

Paper-based sensors are a new alternative technology for fabricating simple, low-cost, portable and disposable analytical devices for many application areas including clinical diagnosis, food quality control and environmental monitoring. The unique properties of paper which allow passive liquid transport and compatibility with chemicals/bio chemicals are the main advantages of using paper as a sensing platform. These analytical devices can be integrated in a manner that is flexible, disposable and easy to operate [5].

Regardless of the fabrication methods used, the potential of the reference electrode should remain stable during electrochemical sensing. However, when the electrode is dipped in the test solution, the AgCl present on the thin Ag film gradually dissolves at high chloride-ion concentrations. This can lead to the potential of the reference electrode becoming unstable and thus cause the working electrode to give erroneous readings [2]. So, proper concentration of the solutions is maintained.

In this work, solid state Ag/AgCl reference electrodes are fabricated by inkjet printing of Ag nanowires on paper followed by printing or dipping in KCl. The electrode is checked for the stability of its potential by open circuit potential test and the stable electrode is used for the cyclic voltammetry test of the standard ferrocyanide redox couple.

MATERIALS USED:

1. CHEMICALS
    - Silver Nitrate
    - Potassium Bromide
    - Potassium Iodide
    - Potassium Chloride
    - Isopropyl Alcohol
    - Sodium Sulphite
    - Metol
    - Quinol
    - Borax
    - Sodium hypochlorite
    - Potassium Nitrate
    - Potassium ferrocyanide
    - Deionized water
2. APPARATUS
    - Inkjet printer (HP 1010 series)
    - Black Ink Cartridges (HP 802 small)
    - Halogen Lamp (Crompton Greaves J240V 500 W R7S, 9500 Lumens)
    - Laminar Hood (Esco)
    - Sonicator (Bransonic® Ultrasonic Cleaner)
    - Syringe Filter (Millex ® GV Filter unit)
    - 4 point meter (RCHEK-model RC2175)
    - Electrochemical Analyzer (CHI 608D)
    - Hot Air Oven

3. SOFTWARE

- Microsoft Office PowerPoint 2013
- CHI 608D

4. PREPARATION OF SOLUTIONS

All the chemicals used were used as received from SDFCL, Fisher Scientific and Merck Chemicals and are of higher purity. All the solutions were prepared using DI water. 0.25M $AgNO_3$ and 0.5M KX solutions were prepared to print on paper. KX is a mixture of KBr and KI in the ratio 95: 5.KI was added to enhance the photosensitivity [6]. The molar ratio of $AgNO_3$ to KX is always 1:2, to ensure complete conversion of AgX on paper [6]. 0.5M KCl solution was prepared to print over the silver nanowires to get AgCl layer on paper. The developer solution was prepared by dissolving 20g Sodium Sulphite, 0.4g Borax, 1g Quinol and 0.4g Metol in 100mL deionized water [6]. 3M KCl was prepared to be used as an electrolyte for the working electrode [7].

EXPERIMENTAL METHODS:

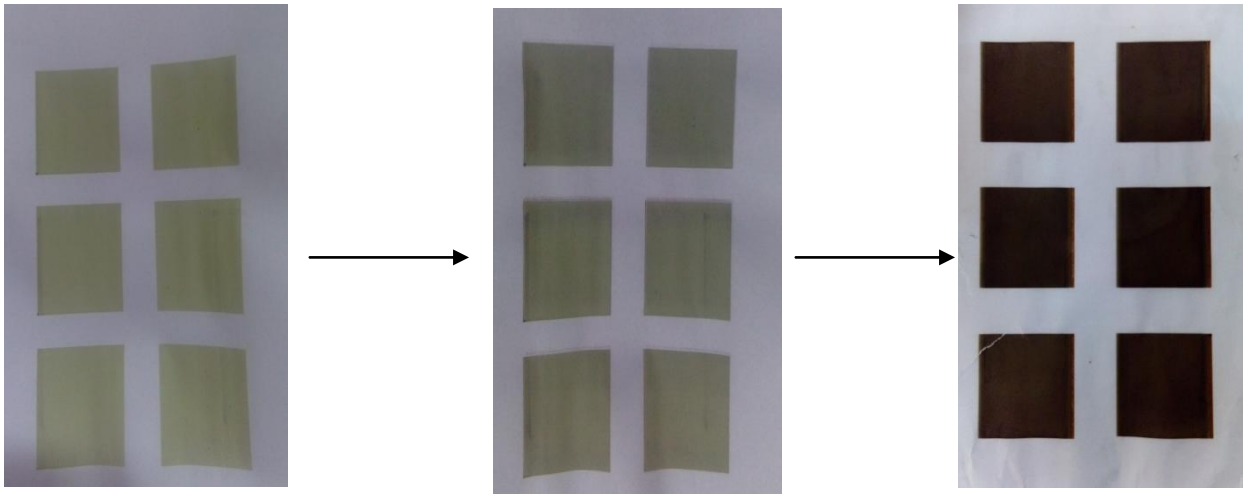
An inkjet printer was used to print the salt solutions on paper(A4 copier paper, 80 gsm). Three separate ink cartridges were used to print the different solutions. The black ink cartridge was opened and the sponge holding the black ink was removed. The cartridge was washed under the running tap and finally with DI water. Then the cartridge was used to print DI water and free prints for rough patterns were made on the paper surface to make sure it is printing properly and no black ink is left in the cartridge.

The loading of the cartridge was found out by weighing the cartridge before and immediately after printing with DI water. This was repeated for five printings and the average of difference in their weights was noted. Knowing the density of water, the volume to be used per print could be found out. The loading of $AgNO_3$ was found to be 0.05mg/cm^2.

In this work, print-expose-develop process was followed. Six squares of 4.5cm side each were drawn on Microsoft Office PowerPoint 2013 and printed alternatively with 0.25M $AgNO_3$ and 0.5M KX for six times. The reducing agent KX was printed on paper at first because it enhances the conductivity and $AgNO_3$ does not stick well to paper. The number of printings was increased to ensure uniform printing of the solutions on the paper [6] and to increase the conductivity of silver on the printed area. As a result of alternate printings, AgX layers were formed on the paper. This is identified by the greenish tint on the printed surface. The paper should be dried properly between each print. Printing on wet paper may block the print head and lead to cartridge failure.

After printing, the pattern was exposed under halogen lamp for 15minutes. This leads to the formation of Ag clusters on paper. It is then dipped for 10 minutes in the developer solution, which is a source of electrons to form Ag ions [6]. These ions on reduction change its lattice structure by breaking the clusters and forming Ag nanowires on paper. The colour of the printed area was green and greenish brown after exposure to halogen lamp and development respectively. Developing the solution immediately after exposure showed higher conductivity compared to the exposed prints which were developed after few days. The developed print was then washed in DI water to remove the unreacted silver ions on the surface of paper. It was put in a laminar hood for complete drying. The resistance values in all the six squares were measured using the four-point meter and found to be 9 Ω,

8 Ω, 12 Ω,11 Ω,18 Ω and 29 Ω. Since the resistance is less, their conductivity will be more.



(a) (b) (c)

Figure 1: (a) After printing alternative layers of KX and $AgNO_3$

(b) After exposing under halogen lamp

(c) After development of the Ag nanowires

The reference electrode was fabricated on the silver base by printing with KCl, dipping in KCl and NaOCl and the results were compared and discussed.

1. PRINTED WITH KCl

After the formation of the silver base, an area of 3x4.5 cm^2 was printed with 0.5M KCl to form AgCl layer on paper. A separate cartridge was used to print KCl on paper. The loading of KCl was found out to be 0.0455mg/cm^2 . The number of prints in every square was varied to get different amounts of AgCl on paper.

Number of prints of KCl	Amount of AgCl printed (mg/cm^2)
10	0.4
14	0.6
18	0.8
22	1.0
26	1.2
30	1.4

Table 1: No. of Printings required for different amount of AgCl.

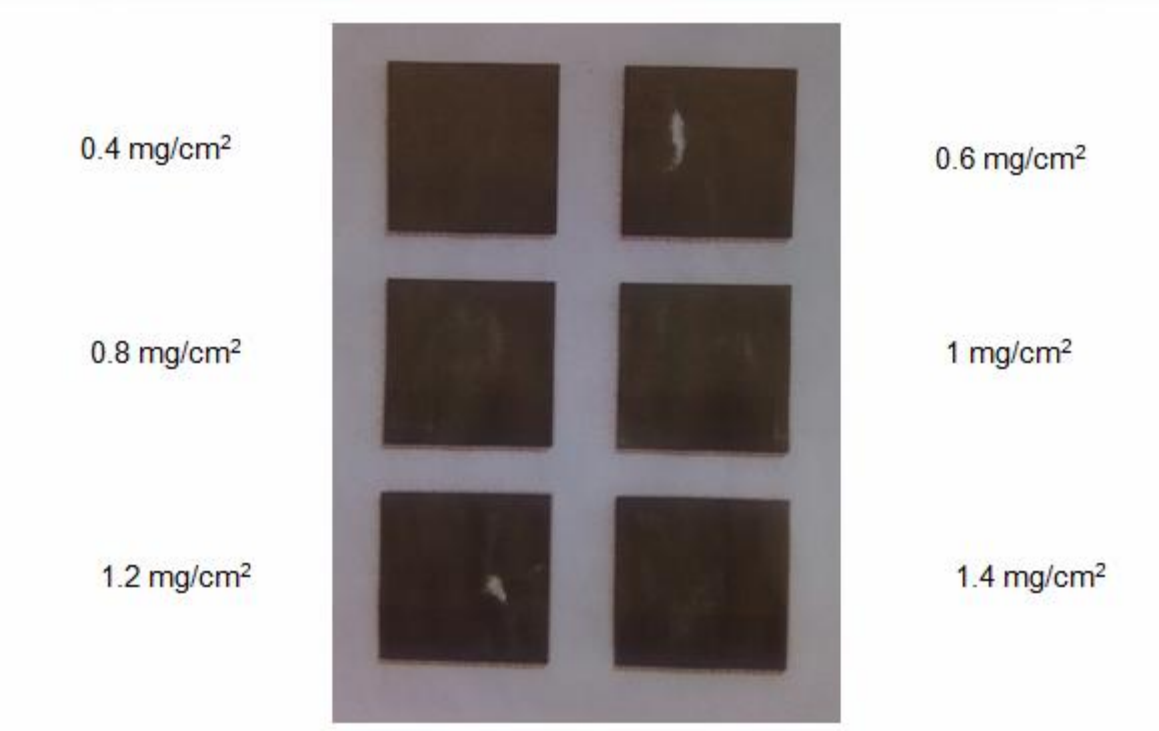
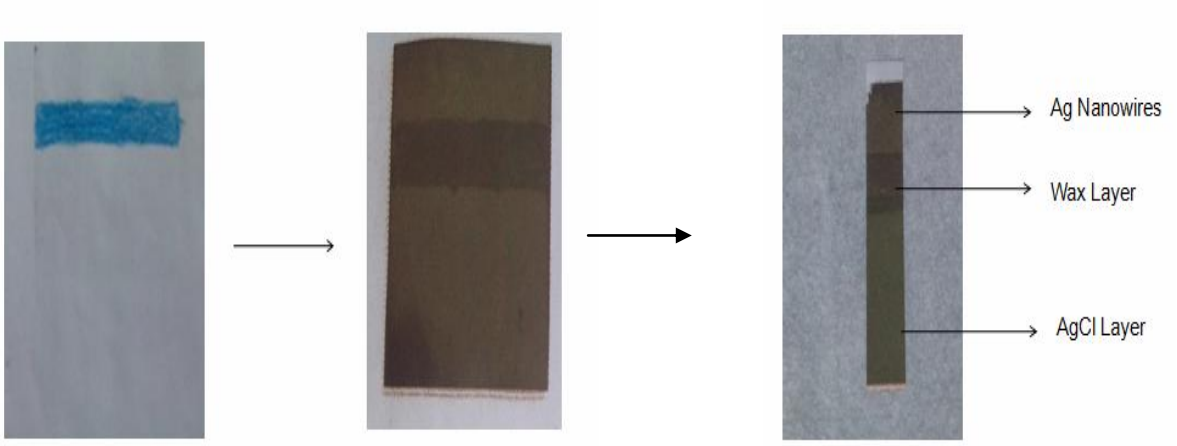


Figure 2: Fabricated Electrode Sample after printing with KCl

2. DIPPED IN KCl

The paper printed with silver nanowires was dipped in 2M KCl solution to form AgCl layer. Only 2/3rd of the paper should be dipped in the solution, because conducting Ag nanowires are needed to be used as a reference electrode. AgCl is formed on the paper to maintain the constant potential of the electrode sample, as the potential depends on the concentration of AgCl. To avoid the upward movement of the solution through the capillaries in the paper, crayon wax was applied on the paper and melted by heating in a hot air oven at 100°C to form a hydrophobic layer on paper. This hydrophobic layer was also helpful while performing the electrochemical studies of the electrode to prevent the movement of the electrolyte solution. The printed paper was dipped in the KCl solution for 15 and 30 minutes for the comparison of electrode samples.



(a) (b) (c)

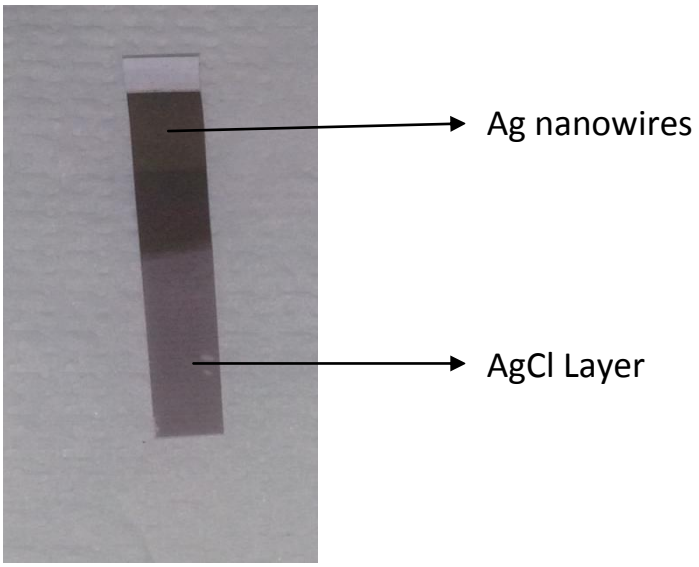
Figure 3: (a) Crayon wax was applied on the back side of the printed paper

(b) After the formation of hydrophobic layer by wax

(c) After dipping in 2M KCl solution

3. DIPPED IN NaOCl

After the formation of hydrophobic layer on the paper surface by coating with wax, the paper printed with Ag nanowires was dipped in the sodium hypochlorite solution for 5, 10, 20 and 30 minutes. The fabricated electrodes were immersed in old and fresh 3M KCl solution as an electrolyte while performing the electrochemical studies and were compared.



. **Figure 4:** After dipping in NaOCl Solution

RESULTS AND DISCUSSIONS:

An electrochemical analyzer was used to study the electrochemical behavior of the analyte species present in the electrolyte solution using the fabricated paper-based Ag/AgCl reference electrode and standard Ag/AgCl reference electrode samples.

1. OPEN CIRCUIT POTENTIAL

The paper based electrodes dipped in 3M KCl as electrolyte were used as working electrodes along with the standard Ag/AgCl glass electrode and the open circuit potential was determined.

Low E limit (V)	-1
High E limit (V)	1
Run Time (sec)	1800
Sample Interval (sec)	1

Table 2: Parameters used for open circuit potential test

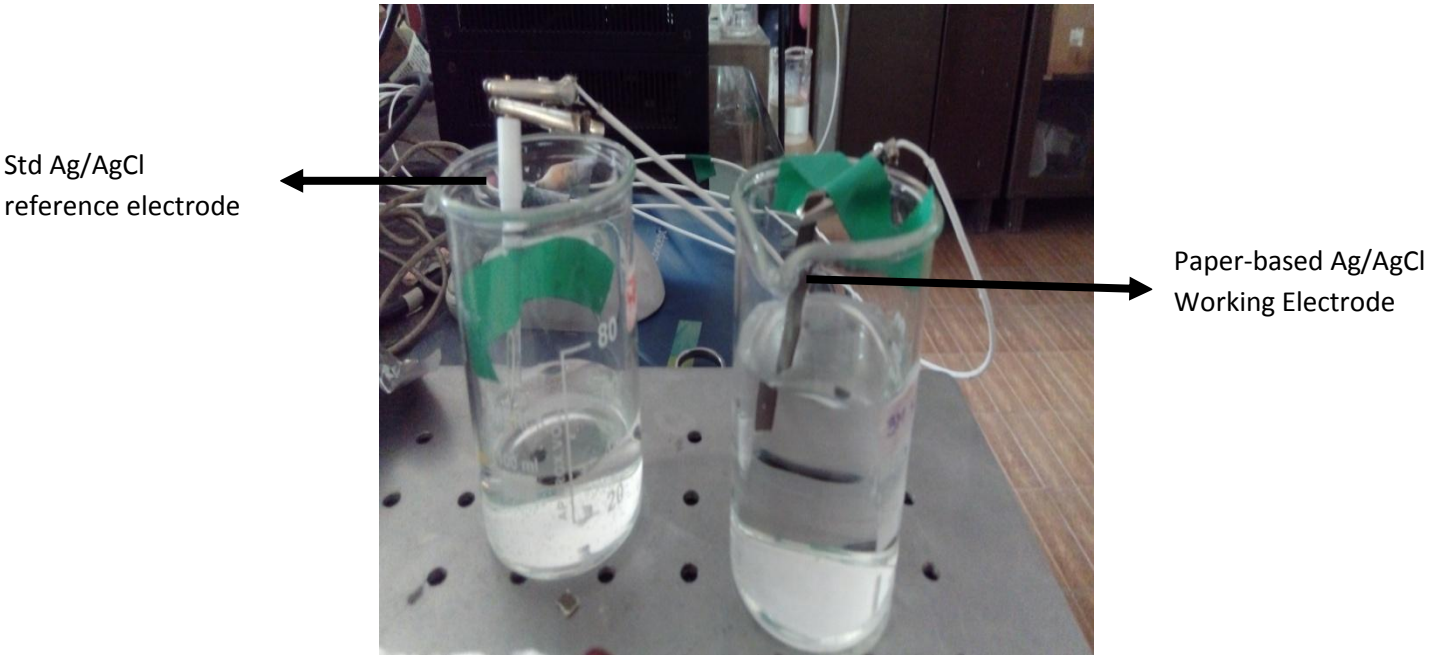
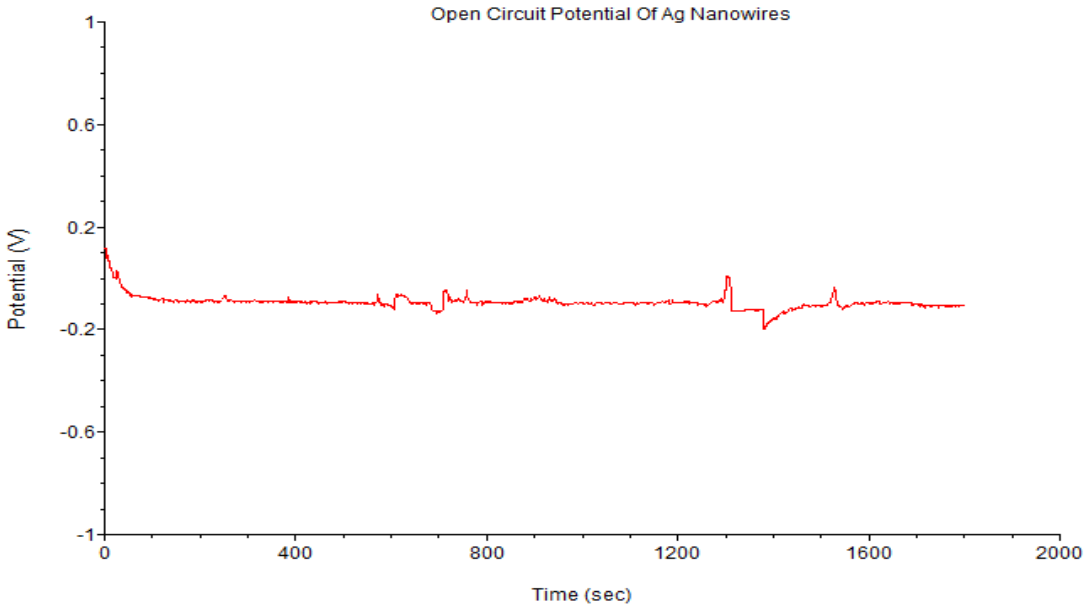


Figure 5: Electrochemical cell setup for the determination of open circuit potential

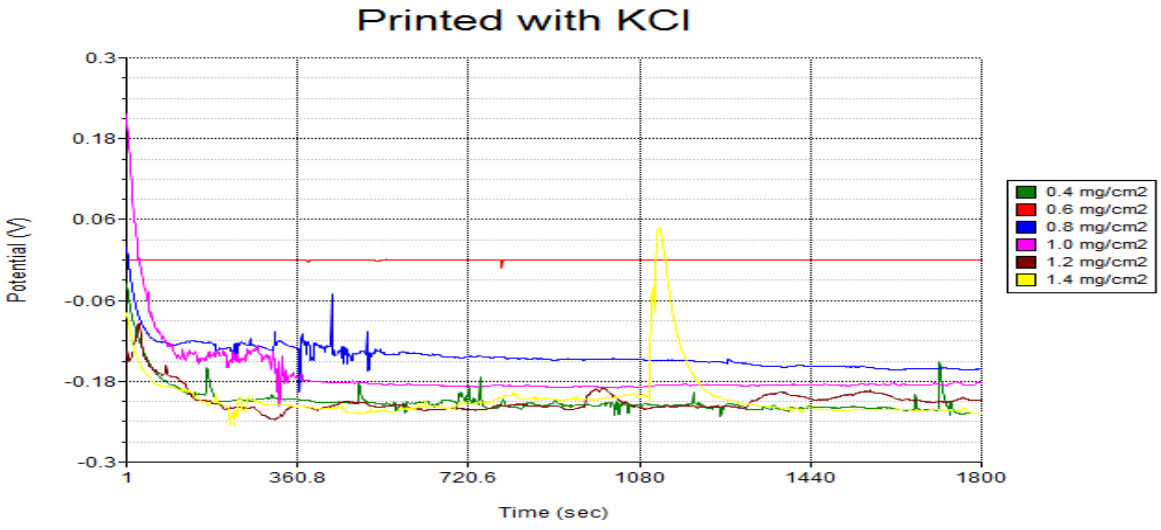
- Ag NANOWIRES

The open circuit potential technique showed a very less deflection indicating the stability of the silver nanowires printed on paper.



Graph 1: Open Circuit Potential Of Ag Nanowires

- PRINTED WITH KCl

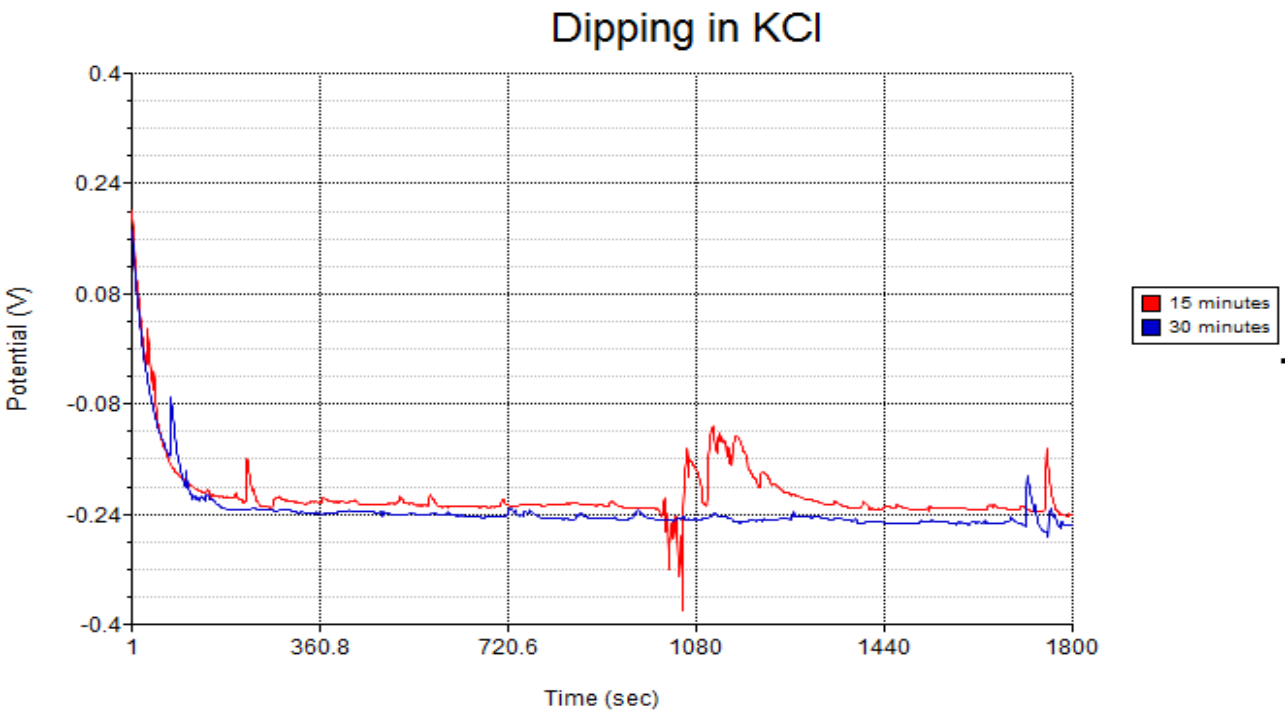


Graph 2: Open Circuit Potential of KCl printed electrodes

The KCl printed electrode samples with different loading of AgCl were tested for its stability.

- DIPPED IN KCl

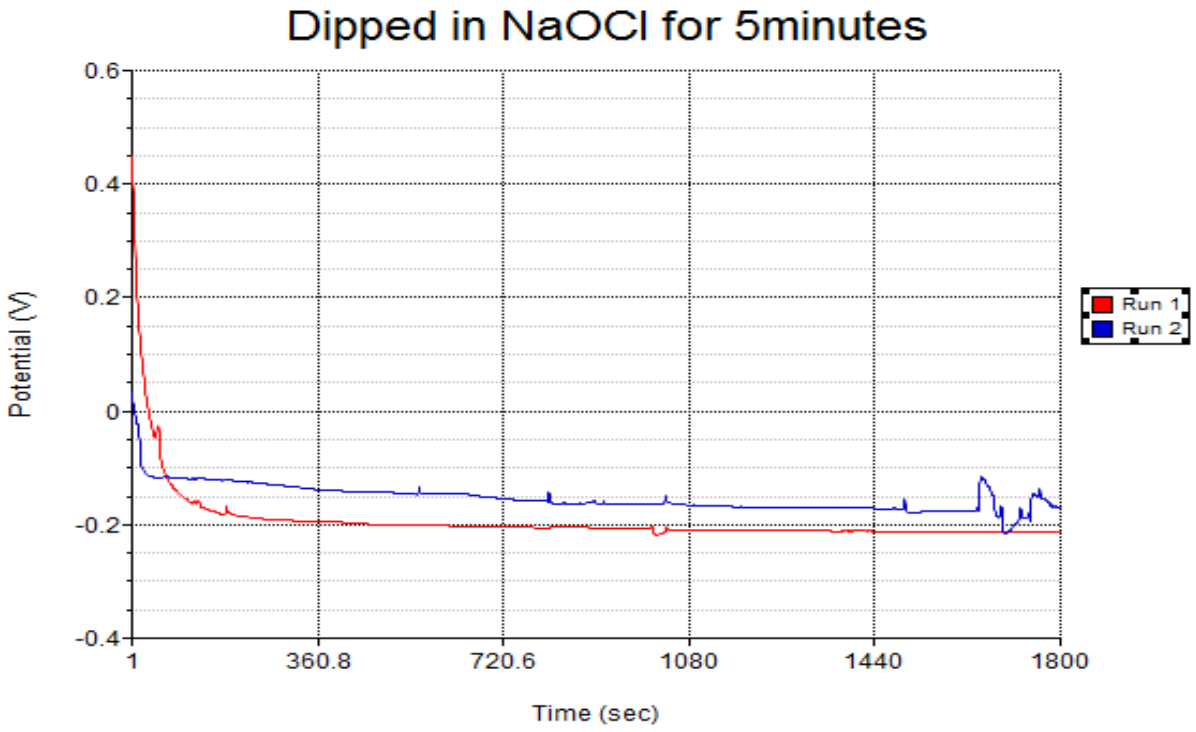
The paper printed with silver nanowires was dipped in 2M KCl solution for 15 and 30 minutes.



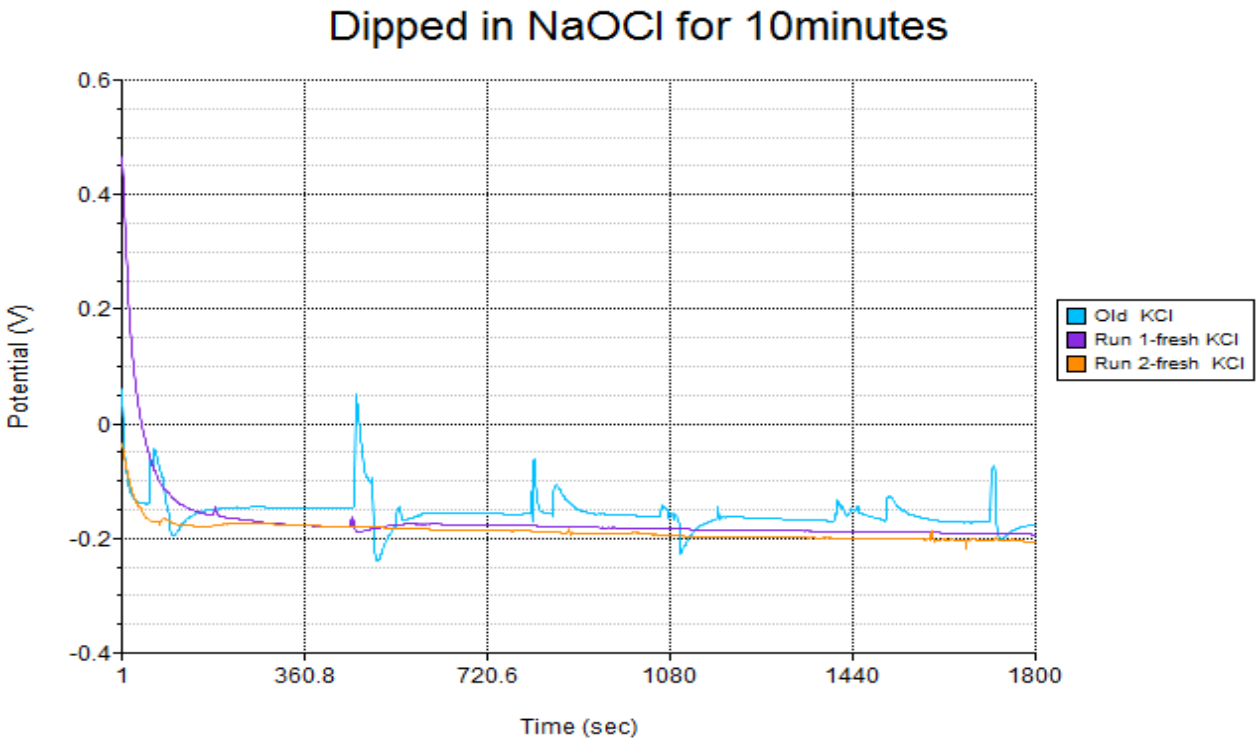
Graph 3: Open Circuit Potential of electrodes dipped in KCl

- DIPPED IN NaOCl

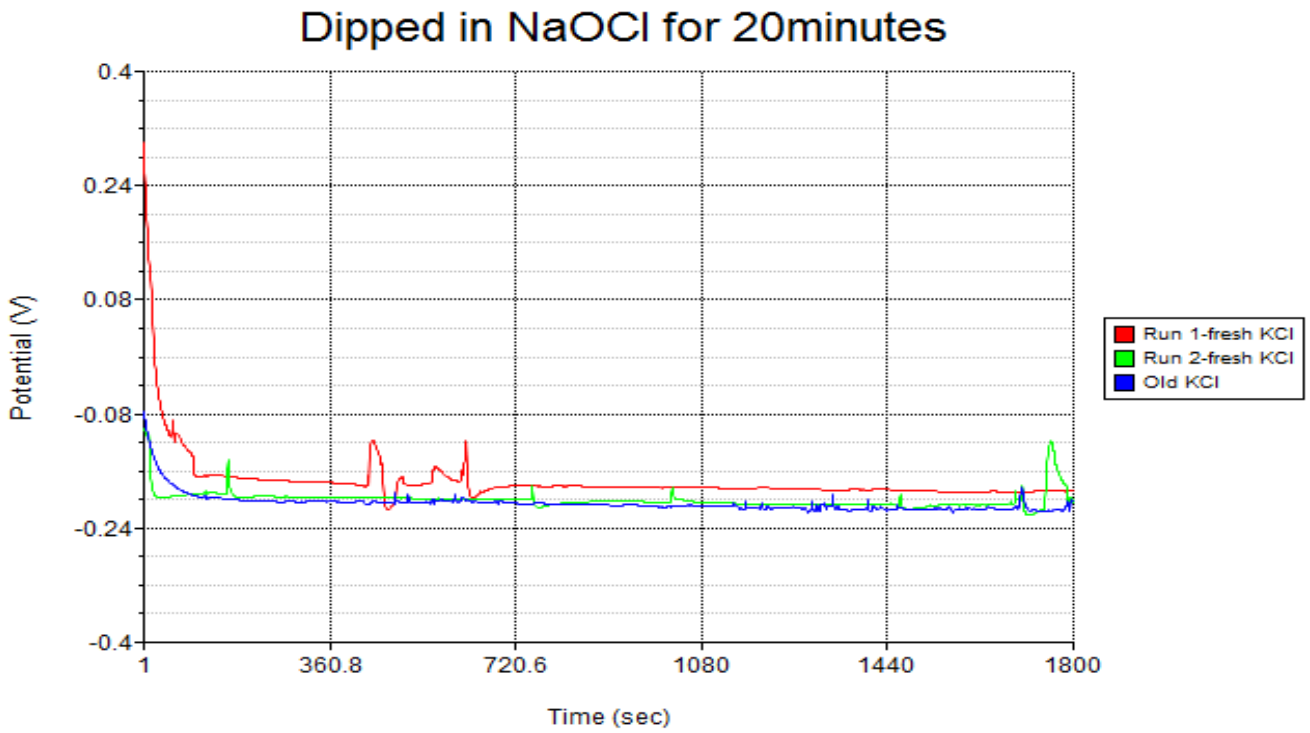
The silver nanowires were dipped in NaOCl solution for 5, 10, 15 and 20 minutes. The fresh and old electrolytes were used for the analysis and were compared.



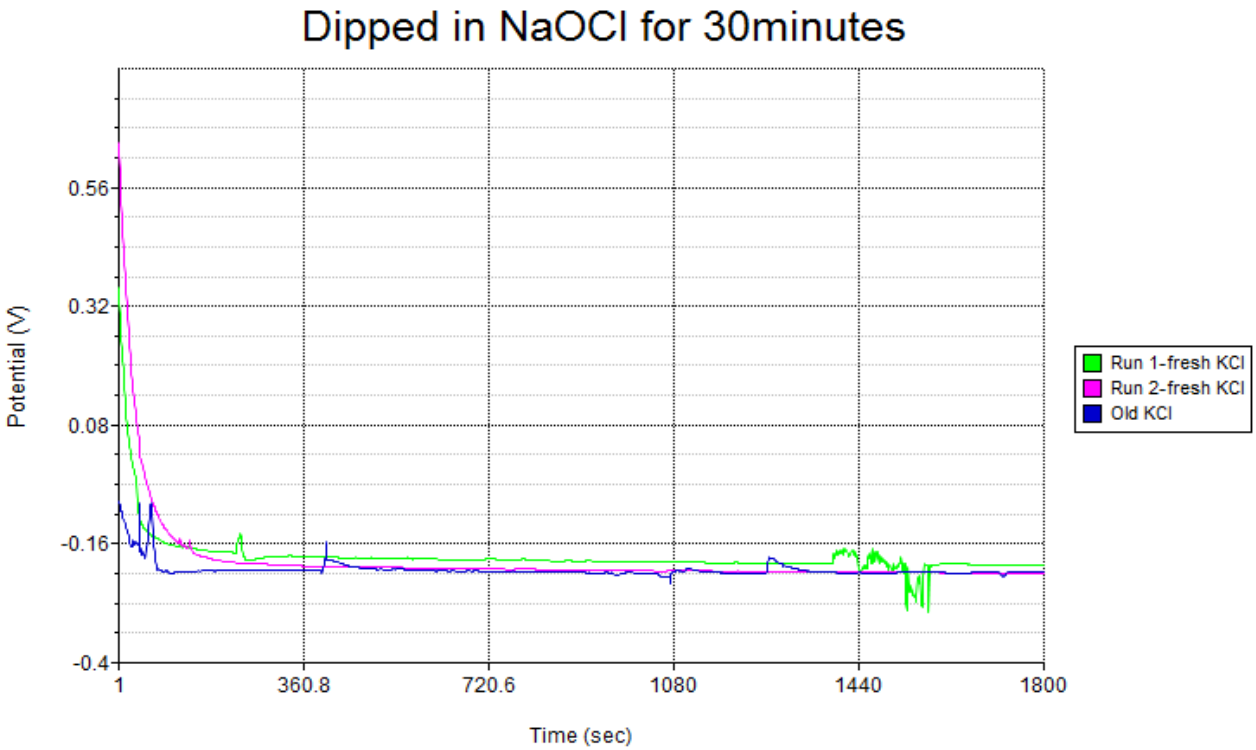
Graph 4: Open Circuit Potential of electrodes dipped in NaOCl for 5minutes



Graph 5: Open Circuit Potential of electrodes dipped in NaOCl for 10minutes



Graph 6: Open Circuit Potential of electrodes dipped in NaOCl for 20minutes



Graph 7: Open Circuit Potential of electrodes dipped in NaOCl for 30minutes

2. CYCLIC VOLTAMMETRY

Cyclic voltammetry is the most versatile electro analytical technique for the study of electro active species, and it is widely used in industrial applications and academic research laboratories [8]. This technique was performed to study the potential of potassium ferrocyanide which undergoes redox reaction easily. It was added to 1M Potassium Nitrate electrolyte [15]. The technique was performed for both the standard Ag/AgCl and paper-based Ag/AgCl electrode.

Init E (V)	-0.1	**Sweep segments**	20
Final E (V)	0.5	**Quiet time (sec)**	1
Low E (V)	-0.1	**Init P/N**	P
High E (V)	0.5	**Sample Interval (V)**	0.001
Scan Rate (V/s)	0.01	**Sensitivity (A/V)**	$1*e^{-4}$

Table 3: Parameters used for cyclic voltammetric test

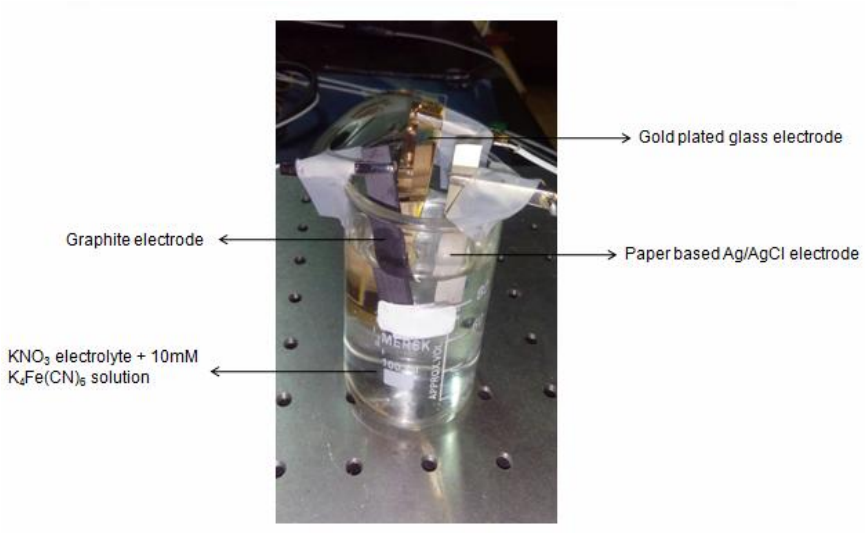
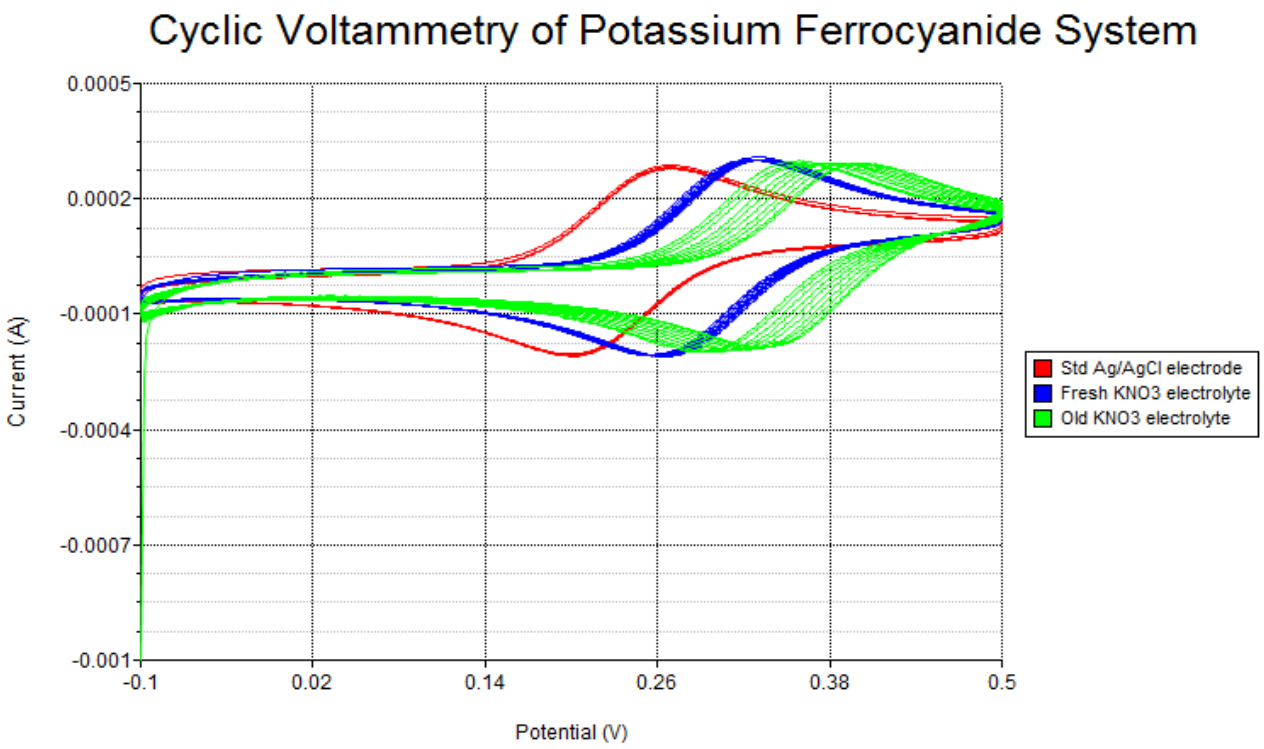


Figure 6: Three Electrode Setup For Cyclic Voltammetric studies



Graph 8: Cyclic Voltammetry Studies of Potassium Ferrocyanide System

From all the experiments conducted using the electrochemical analyzer, the electrode fabricated by dipping the silver nanowires in NaOCl for 10minutes was found to be more stable and was used for the cyclic voltammetry of potassium ferrocyanide system. In the cyclic voltammetric studies, the results of the standard Ag/AgCl electrolyte and the paper-based electrode dipped in fresh electrolyte solution showed a similar graphical data, while there was an undesirable sweep while using the old KNO_3 solution electrolyte for the study. This may be due to the reducing concentration of the AgCl layer on paper because of the dissolution of the nanoparticles in the electrolyte. The contaminations present in the paper surface can also lead to the change in the potential of the analyte.

Though it is not economical, it is better to use fresh electrolytes for the studies to get the appropriate results of the fabricated electrodes.

FUTURE STUDIES:

For the development of electrochemical glucose sensor, the electrodes are modified with glucose oxidase (GOx), which could be used in many areas such as clinical and industrial applications. However, there are some disadvantages of the enzyme modified electrodes, such as, 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 useful in non enzymatic determination of glucose [11]. So, paper-based electrodes can be fabricated because of its low cost and disposable nature.

The main application of this paper based electrode is the non enzymatic detection of glucose in the blood sample. A novel electrochemical cell setup has to be made for this detection. In place of the reference electrode, paper-based Ag/AgCl electrodes can be used. Cupric oxide nanoparticles have to be synthesized and coated over the inkjet printed silver nanowires, which can be used as working electrodes [11]. Platinum wire can be used as a counter electrode and all these electrodes were dipped in an electrolyte with a lesser concentration of glucose in it [13]. By varying the concentration of glucose in the electrolyte solution, different values of current could be obtained by the cyclic voltammetric studies. These values of current are proportional to the glucose concentration [16]. This is almost similar to the working of the commercial glucose test strips in market, in which the glucose gets oxidized by the enzyme, which is then converted to current signal by electrochemical reactions and is displayed as glucose concentration [17-19].

Hence, the paper based Ag/AgCl reference electrodes can be effectively used in the electrochemical biosensor for the non enzymatic detection of glucose.

CONCLUSION:

From the results of open circuit potential test and cyclic voltammetry of potassium ferrocyanide system, it can be concluded that the paper-based Ag/AgCl reference electrodes fabricated by inkjet printing of Ag nanowires and dipping them in sodium hypochlorite solution for 10 minutes can be used as an alternative for the standard Ag/AgCl reference electrode, provided the electrolytes used for the study are fresh. With further development, it could be used as a non- enzymatic glucose biosensor.

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