

Fabrication of Jello-Based Ag/AgCl Reference Electrode from Recyclable Resources to Enhance Undergraduate Laboratory Student Experience and its Promising Utilization in Corrosion and Electrochemical Sensing

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Abstract. This paper presents a realistic approach to experience electrochemical principles in the context of an upper undergraduate research course where students will learn how to fabricate and calibrate a reference electrode (RE) which is an essential component of an electrochemical system. Among many commercially available REs, Ag/AgCl RE is one of the most employed REs in teaching laboratories and research. However, the REs fabrication and assembly pose technological challenges in addition to their cost especially for large quantities procurement for undergraduate laboratories. To circumvent these constraints, one alternative is to fabricate them in the lab, however, the use of harmful chemicals and complicated techniques limits their practical fabrication in teaching laboratories. Therefore, this study, devised a simple and cost-effective method for fabricating a homemade Ag/AgCl RE assembly where jello is used instead of a glass frit (referred as JRE) from recyclable and obsolete items available in common undergraduate laboratories. The as-fabricated jello RE exhibited excellent sensitivity and accuracy as compared to a commercially available BASi RE from the cyclic voltammetric (CV) studies. Subsequently, JRE showed its potential in two distinct electrochemical experiments, including potentiodynamic Tafel corrosion scans and electrochemical sensing and detection of Ascorbic Acid (AA). In addition to outstanding reproducibility, JRE demonstrated higher stability even after four months of storage in the refrigerator.

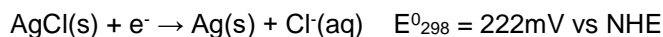
Keywords: Undergraduate laboratories, Homemade reference electrode, recyclable wastes, corrosion, electrochemical detection.

INTRODUCTION

Reference electrodes (RE) play a major role in electrochemistry research and education for the measurement of reference potentials that allows the

comparison of redox properties of electrochemical systems (Smith, 2007). A typical RE is made up of phases of constant composition and is considered as an ideal non-

polarized electrode which has an unchanged potential which is independent of the small current withdrawn by the potentiostat in a typical electrochemical experiment (Bard, 1980). The Ag/AgCl reference electrodes are one of the most commonly used reference electrodes and they are generally preferred due to their simple composition, ease of preparation, and maintenance. The Ag/AgCl electrodes are based on an equilibrium between a silver chloride coated silver wire in contact with typically 3 to 3.5 M KCl³. The redox reaction in the Ag/AgCl reference electrode is shown below.



An Ag/AgCl electrode is typically made of a glass tube filled with concentrated 3-3.5M KCl salt solution with the Ag/AgCl wire immersed in it. The tip of the tube has a junction like vycor or fritted glass that ensure an electrical contact with the electrolyte solution while limiting the diffusion of the inner components. RE can be designed as per the objective of the experiments to be carried out and hence there exist many geometrical commercial designs 4-7. Although there are many available commercial REs, however, they are technologically challenging and costly especially for large quantities purchase for undergraduate laboratories. In addition, replacing obsolete and redundant REs with a new one is costly. Therefore, it is essential that a cheap and facile method to be developed to fabricate REs within the lab (i.e. homemade) using readily available obsolete and cheaper materials. Using materials available in the laboratory, a simple hydrogen reference electrode has been reported⁸. Many papers were published in an attempt to develop reference electrodes as part of undergraduate chemistry laboratories, however, most require chemical modification and some complexity in procedures, in addition to the use of strong acids and toxic solvents (Inamdar *et al.*, 2009; Schmidt *et al.*, 2018; Randle and Kelly, 1984; Kasuda, 1989; Massé and Gerken, 2015).

Here in, in the context of a graduation research course, students were assigned to fabricate their own customized jello-based Ag/AgCl reference electrode (JRE) that students can assemble a priori at home or in the lab from simple and used recyclable parts with minimum cost. The tested JRE electrodes worked well for four months from the start of preparation and it is possible to extend their life span if kept stored dry and sealed with parafilm in the refrigerator. However, the core intent of this paper is to train students on the basic concept of RE preparation and calibrating their own electrode using cyclic voltammetry (CV) in one lab session.

Furthermore, the JRE were tested for different applications where the utilization of a high quality RE is essential for the generation of stable and reproducible signals. Therefore, the robustness and effectiveness of the as-produced JRE is investigated in two different scanning potential experiments including potentiodynamic Tafel

corrosion scans and electrochemical sensing.

Materials and Equipment

Materials and reagents

Potassium ferricyanide (K₃FeCN₆), potassium chloride (KCl), ascorbic acid (AA) were used from common laboratory stock. The commercial water coolant containing corrosion inhibitors were purchased from the local market. The Ag/AgCl wire was extracted from an obsolete pH meter in the laboratory. The used and disposed siphon tube of liquid soap container was taken out from a liquid soap disposal container, washed out and used for the assembly of the homemade RE components. The jello powder was purchased from the local market.

The appropriate amount of sodium phosphate dibasic dihydrate (Na₂HPO₄•2H₂O), sodium phosphate monobasic monohydrate (NaH₂PO₄•H₂O) and sodium chloride (NaCl) were dissolved in deionized (DI) water to prepare 0.1 M phosphate-buffered saline (PBS) buffer solution with pH value of 7.2. The electrochemical studies were conducted using a Gamry 3000 potentiostat-galvanostat in which a three-electrode system was used where the working electrode was a platinum disk from BASi. A Keithley multimeter was employed for potential difference measurements. Deionized water was used for all the solutions preparations.

Preparation of the Ag/AgCl Reference Electrode (JRE)

The procedures were carried out in three steps and can be carried out in laboratory setup and it requires jello powder, plastic tube from used sources such as the liquid soap dispenser in this case, used Ag/AgCl wire, and KCl salt as shown in Figure 1.

Step 1: Ag/AgCl wire extraction

The Ag/AgCl wire was extracted from obsolete pH electrodes as shown in the Figure 1(A). Although it is possible to prepare a silver wire coated with AgCl using acid solutions or electrochemically, however, this would teach undergraduate students the importance of recyclability and the creativity in using obsolete items instead of just disposing them.

Step 2: Preparing the filling tube

In this step, the study used the siphon tube of liquid soap container (an inner plastic pen barrel may and was also used) after draining and cleaning the ink as shown in Figure 1 (B). Both worked well, however the siphon tube

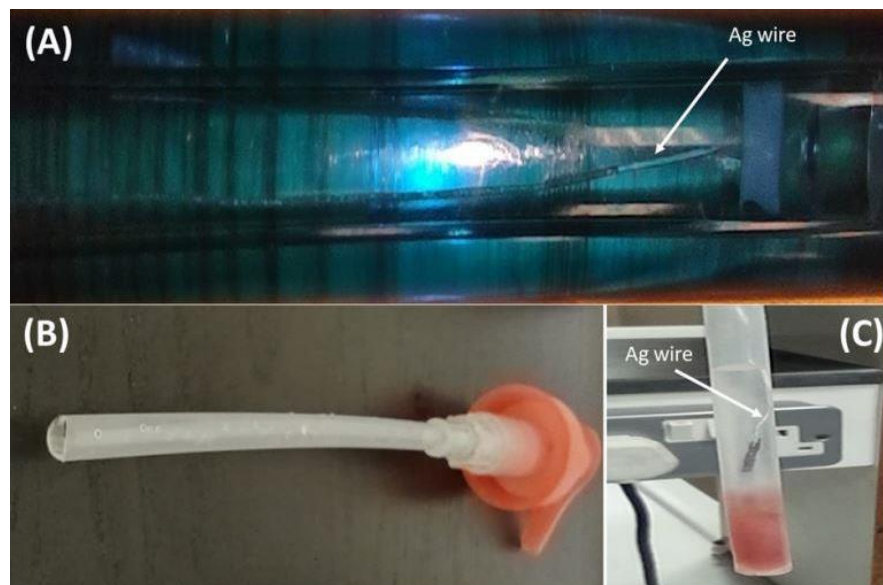


Figure 1. (A) An obsolete pH electrode showing the Ag/AgCl inside the glass compartment; (B) siphon tube is removed from a used liquid soap bottle; (C) the as-prepared Ag/AgCl electrode (JRE) showing the outer plastic tube casing, the bottom jello layer, the Ag/AgCl wire in 3M KCl

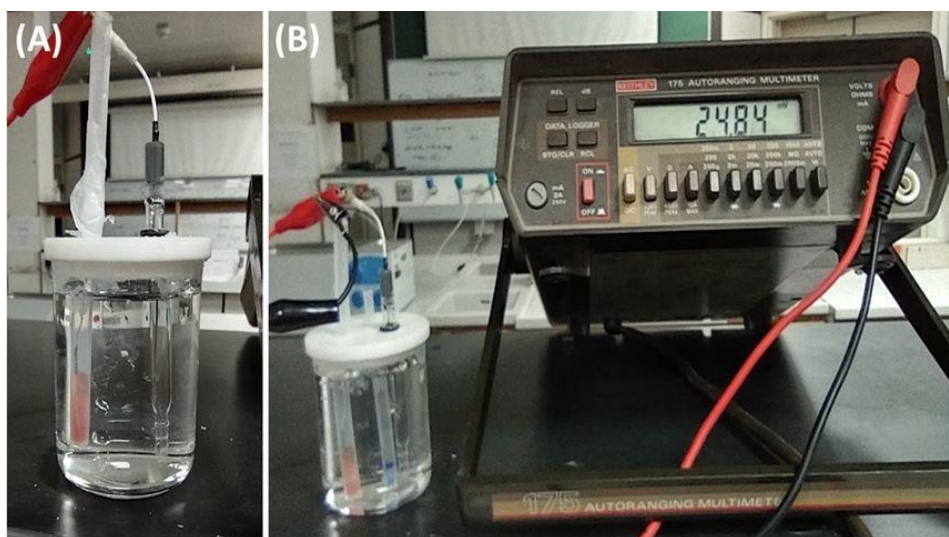


Figure 2. The prepared jello electrode (a) in 3M KCl and (b) potential difference vs BASi Ag/AgCl after the fresh fabrication.

had a wider diameter and it was easier to handle and to work with. The tip is heated and melted gently and shrank until a small hole opening is left out. Around 45 g jello powder from commercial food sources was dissolved in 25 ml water and 5 g KCl and boiled gently for 30 minutes until very viscous. The duration of heating and the final viscosity of the solution is of vital importance in order to adhere well inside the tube. Once the required viscosity is determined visually as suitable, the heat is turned off and the jello is left to cool until warm. Little amount of the jello is sucked up inside the tube at approximately two centimeters from the bottom. The tip is immediately wrapped with parafilm and stored in the refrigerator to cool. After around thirty

minutes, the tube is taken out, filled with 3M KCl and the Ag/AgCl wire is inserted just above the jello layer as shown in Figure 1 (C).

Step 3: Calibration of the prepared RE vs BASi Ag/AgCl

The prepared JRE was immersed in 3M KCl solution containing a commercial Ag/AgCl RE made by BASi. The startup potential difference measured by a digital multimeter is usually in the range of 25-40 mV as shown in Figure 2.

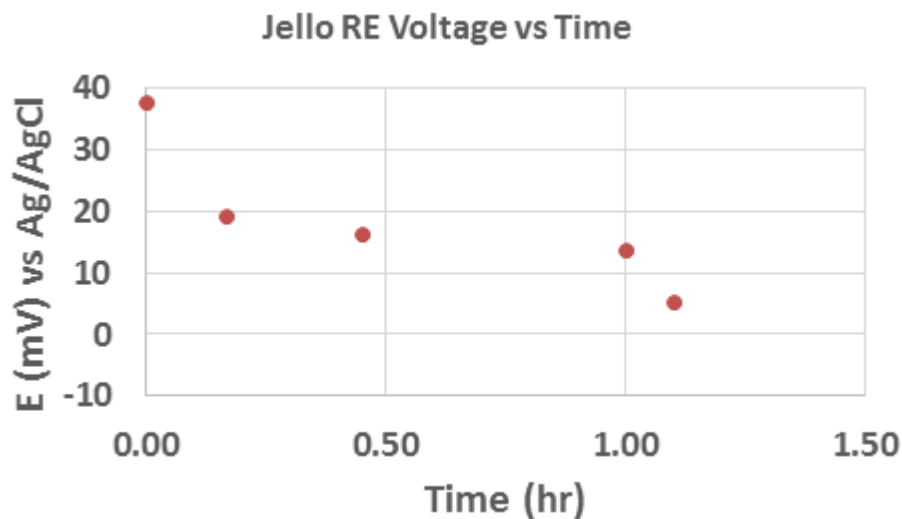


Figure 3. Potential difference between the freshly prepared JRE vs the BASi RE in 3M KCl solution.

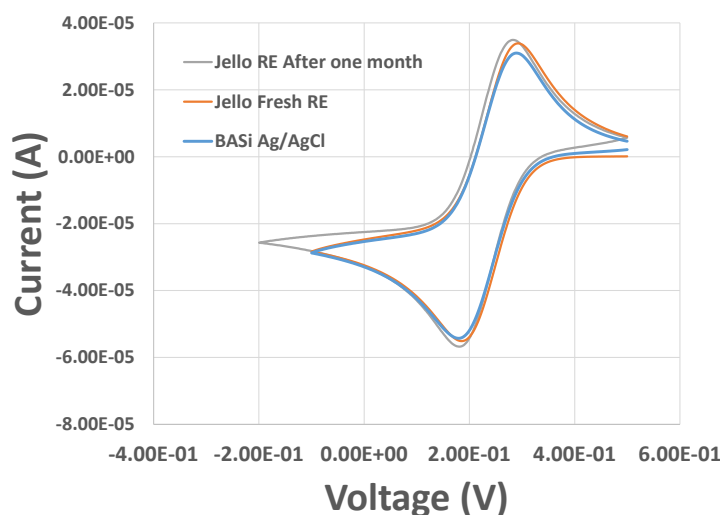


Figure 4. Cyclic voltammograms of 0.080M M potassium ferricyanide in 0.10 M KCl using the BASi as a reference electrode and compared the prepared the JRE, fresh and after one month with a scan rate of 20 mV/s.

RESULTS AND DISCUSSION

Potential measurement between commercial and JRE

The potential of the fabricated RE was measured at different intervals of times vs BASi RE and voltages recorded in Figure 3 which shows that it took around 1.5 hours to reach a voltage difference of 5 mV vs the BASi RE. However, if the amount of the jello inside the tube is less, then it is possible to reach the 5 mV difference in less than 30 minutes. Therefore, it is possible to work with this RE shortly after preparation.

Potassium ferricyanide ($[\text{K}_3\text{Fe}(\text{CN})_6]^{3-/4}$) is a reference benchmark reagent that is commonly used for electrode testing as well defined voltammograms are produced

when electrodes are working properly (Kariuki, 2012; Mistry *et al.*, 2015; Elgrishi *et al.*, 2018). Thus, cyclic voltammetry (CV) was carried out using a three electrodes cell as shown in Figure 4. The measured CVs showed a good correlation between the prepared JRE and the BASi RE. Table 1 shows the peak anodic E_{pa} and cathodic E_{pc} peak potentials for the three CVs.

The redox peak potentials for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple from the CV with the constructed RE showed a shift of maximum 13 mV in the positive direction compared to BASi Ag/AgCl, which is within typical experimental limits of REs. The peak potential difference and peak heights were reproducible up to one month from the preparation. Hence, CV tests showed no statistically significant differences in the CV's peak potentials. After one month of keeping the

Table 1. Anodic and cathodic peak potentials from the CVs of potassium ferricyanide using BASi RE and the JRE fresh J1, and after seven days J7.

RE	E_{pa} (mV)	E_{pc} (mV)
BASi	287	182
J1	290	190
J7	285	180

Table 2. The corrosion parameters extracted from the Tafel region.

RE Type	E_{corr} / mV'	β_a V/decade	β_c V/decade	$i_{corr}/\mu A$	CR/mpy
BASi RE	-146.0	0.501	100.2e-3	0.262	119.0e-3
JRE	-176.0	0.657	135.1e-3	0.247	113.5e-3

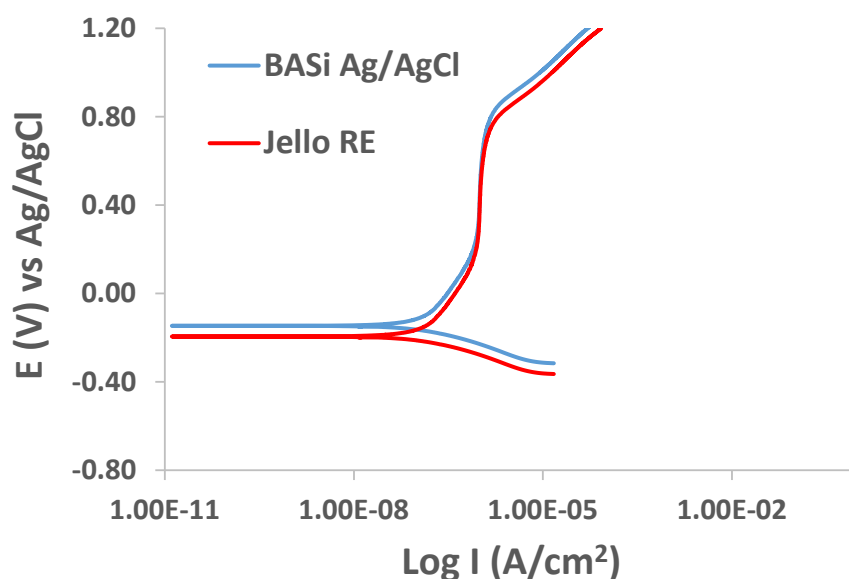


Figure 5. Tafel experiments of steel sample using BASi and JREs in a solution containing a commercial corrosion inhibitor.

JRE in the 3M KCl, it was noticed that the jello started to break down in chunks and leaked outside the filling tube. However, to prolong the lifespan of the RE and get around this, the KCl solution was removed from the JRE, and the bottom and top of the tube was wrapped with parafilm and stored in the refrigerator.

Potentiodynamic Tafel Corrosion Experiments

Typical electrochemical corrosion experiment involves the variation of the potential below and above the corrosion potential and monitor the current which reflect the kinetics of the electron transfer¹⁷. The voltage applied during a very slow scan of 0.166 mV/s for long period would be a significant test of the reliability, accuracy and robustness of the reference electrode built as it will remain under testing for around three hours. A Tafel experiment was carried out in a 3-electrodes cell to investigate the

corrosion of steel specimen. The results of Tafel scans are shown in Figure 5. It can be seen the two scans are pretty close to each other and hence reflect good performance of the JRE electrode. Furthermore, this was verified by extracting the Tafel parameters using Gamry Analyst software as shown in Table 2.

A negative shift of 20mV is observed for the E_{corr} of the JRE while a 5% change in corrosion rate is recorded between the two runs. These changes are within expected variation in typical electrochemical corrosion experimental results. Hence, the JRE can be considered reliable for prolonged electrochemical experiments under slow scans and high voltage conditions.

Electrochemical sensing

Electrochemical sensing has shown its tremendous potential for various important analytes (Zaidi, 2017;

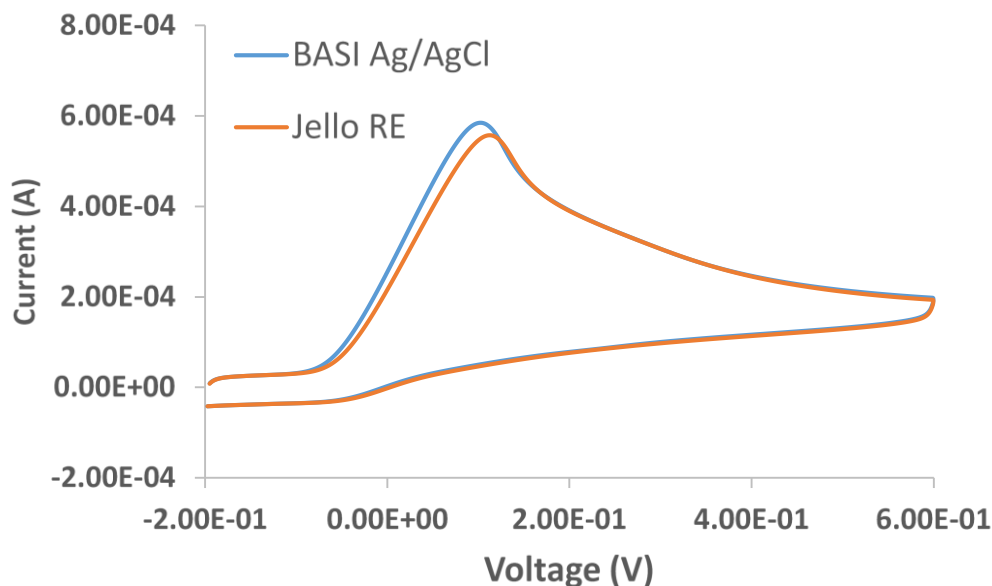


Figure 6. A CV profile of 10 mM Ascorbic acid at a scan rate of 0.1 V/s in 0.1 M PBS (pH-7.2).

Shezad *et al.*, 2017; Hussian *et al.*, 2019). For the proof-of-concept, ascorbic acid (AA) was chosen as the analyte of interest owing to its inherent electrochemical behavior. Figure 6 depicts the behavior of JRE, after four months storage dry in the refrigerator, in electrochemical sensing of AA as compared to commercial RE. It clearly reveals that the ascorbic acid oxidation occurs at comparable peak potentials of 105 mV and 110 mV for BASi Ag/AgCl and JRE, respectively, with a difference of nearly $\sim 4.75\%$. Moreover, the current responses are very close to one another. The obtained results substantiate that the JE performs well and there is no significant difference between commercial and homemade JRE.

Stability and reproducibility

As discussed in the previous section, a JRE stored in 3M KCl could be effectively utilized for over a month for various electrochemical applications without any notable variations in performance. It was experienced that proper storage extended the performance beyond one month if the JRE was drained and carefully wrapped with a parafilm and kept in refrigerator. Finally, the as-developed method is highly reproducible. Nevertheless, the as-proposed method is found to be exhibiting good stability and reproducibility.

Conclusion

It has been shown that it is possible to construct a fully functional RE from available laboratory materials and obsolete items in the context of an undergraduate graduation research Chemistry course. The difference

between the fabricated Ag/AgCl reference jello electrode and the commercial BASi RE electrode was not statistically significant. The results demonstrated that there was good correlation in the performance of JRE in electrochemical corrosion experiments and electrochemical detection of ascorbic acid in comparison to a commercial RE. The electrode showed good stability and reproducibility and it may be adopted for qualitative and quantitative training for undergraduate students both at the theoretical and experimental levels. The as-developed simple and facile method is promising and cost-effective to produce REs for diverse undergraduate laboratory electrochemical systems.

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