A Student-Made Silver–Silver Chloride Reference Electrode for the General Chemistry Laboratory: 10 min Preparation

ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · APRIL 2014

Impact Factor: 1.11 · DOI: 10.1021/ed400722e

6 AUTHORS, INCLUDING:

Rebecca Barlag

Ohio University

15 PUBLICATIONS **28** CITATIONS

SEE PROFILE

Frazier Nyasulu

Ohio University

33 PUBLICATIONS **143** CITATIONS

SEE PROFILE

Phyllis Arthasery

Ohio University

7 PUBLICATIONS **21** CITATIONS

SEE PROFILE

Lauren E. H. Mcmills

Ohio University

12 PUBLICATIONS **65** CITATIONS

SEE PROFILE

JOURNAL OF CHEMICAL EDUCATION

Communication

pubs.acs.org/jchemeduc

A Student-Made Silver–Silver Chloride Reference Electrode for the General Chemistry Laboratory: ∼10 min Preparation

Rebecca Barlag,* Frazier Nyasulu, Rachel Starr, Jenna Silverman, Phyllis Arthasery, and Lauren McMills

Department of Chemistry and Biochemistry, Ohio University, Athens, Ohio 45701, United States

Supporting Information

ABSTRACT: A student-prepared silver–silver chloride reference electrode is described. The chemical deposition of AgCl(s) onto Ag(s) is accomplished in 30–50 s by placement of a Ag(s) wire in laundry bleach. An autopipettor tip with an agarose gel plug serves as the electrode housing; the agarose gel contains predissolved KNO_3. Reference electrode preparation is completed in about 10 min, allowing enough time for laboratory exercises that utilize the electrode. Preparation and operation of the electrode and recovery of the Ag(s) are designed to teach a number of important chemistry principles.

KEYWORDS: *First-Year Undergraduate/General, Laboratory Instruction, Physical Chemistry, Hands-On Learning/Manipulatives, Electrochemistry, Electrolytic/Galvanic Cells/Potentials, Laboratory Equipment/Apparatus*

Commercial reference electrodes are typically either calomel or silver–silver chloride. At $50 to $100 each, the cost of equipping general chemistry laboratories with commercial reference electrodes can be prohibitive, especially considering limited use (typically one laboratory exercise a year) and a short shelf life (less than six months in some cases). For many, the only meaningful option is to have students make their own reference electrodes; the majority of these are standard half-cells (E^o). Because the E^o half-cells typically use toxic heavy metal solutions, it is important to miniaturize the reference electrode to minimize waste. Riyazuddin has proposed a student-made $Cu|Cu^{2+}$ reference electrode housed in a soft-drink straw with an agarose plug at the bottom.[1] Kvittingen et al. miniaturized the Riyazuddin setup by housing the electrode in a small polyethylene pipet.[2] Regarding reference electrodes not based on E^o, Thomas has described a student-made $Ag(s)|AgCl(s)|Cl^-(3.0\ M)$ reference electrode housed in glass tubing in which the solution is a 3.0 M KCl–agar mixture.[3] The Ag(s)|AgCl(s) electrode is made by electrochemical oxidation of Ag(s) in a chloride solution at a fixed-potential; fixed-potential methods are superior to fixed-current methods to electrodeposit AgCl(s).[4] Other versions of $Ag(s)|AgCl(s)|Cl^-$ reference electrodes that have been published are less suitable because of construction complexity.[5,6] Utilizing the ideas described above, we have devised a student-made $Ag(s)|AgCl(s)|Cl^-(3.0\ M)$ reference electrode that is much easier to prepare. The steps to make the electrode and associated advantages are as follows: (i) Autopipettor tips are used; these are readily available and inexpensive and are used without any modification. (ii) Autopipettor tips are placed upright into a solution of hot agarose containing predissolved KNO_3. Upon gelation, the agarose holds the solution and functions as the salt bridge. The use of an autopipettor tip is advantageous because, with its decreasing diameter, the gel cannot fall out as it does with tubes that have a constant diameter. (iii) Instead of being electrodeposited, which requires additional equipment, AgCl(s) is chemically deposited onto Ag(s) in a 30–50 s process. Students prepare the electrode in about 10 min, leaving plenty of time for the rest of the laboratory work. In addition to preparing a reliable reference electrode, students learn chemical principles involved in its preparation and operation and in recovery of the Ag(s). These principles are described in the Theory section below. We do not provide this information to students; each aspect is derived in either the pre- or post-laboratory exercises. Further details can be found in the Supporting Information.

PREPARATION OF THE ELECTRODE

Electrode Body and the Salt Bridge

The electrode is housed in an autopipettor tip. The salt bridge consists of an agarose gel with predissolved inert electrolyte. The gel composition consists of 7 g of agarose, 500 mL of water, and 25 g of KNO_3. This mixture is heated and stirred to dissolve the agarose. The hot mixture is transferred to a large beaker; the depth of the solution in the beaker is 1–2 cm. The autopipettor tips are placed upright in the beaker and the mixture is allowed to cool and gel for a minimum of 24 h. Hundreds of autopipettor tips containing agarose are prepared prior to the laboratory session and made available to students.

The chemical deposition of AgCl(s) onto Ag(s) by use of laundry bleach has been described.[7,8] In a small beaker, equal volumes of the laundry bleach and $AgNO_3(aq)$ are mixed. Silver wires (5–6 cm in length and about 1 mm in diameter) are placed vertically into this solution, which is in contact with about $^2/_3$ of the bottom of each wire. Chemical deposition takes approximately 30–50 s to give a coating of AgCl (s). The AgCl(s)|Ag (s) wire is placed into the autopipettor tip with ∼1 mL of 3.0 M (aq) KCl, so that the wire is in contact with the KCl(aq) but not the agarose gel; see Figure 1. A small cork is fitted into the autopipettor tip to keep the wire in a fixed position and to allow easy connection to the voltmeter.

Published: April 10, 2014

Figure 1. Student-made Ag(s)|AgCl(s)|Cl^-(3.0 M) reference electrode.

RECOVERY OF THE Ag(s)

Chemical etching to reclaim the Ag(s) wire is accomplished in stirred 5 M NH_3(aq) solution for 5−10 min. The recovered Ag(s) wire is reused by other students.

ELECTRODE PERFORMANCE

Students compare the performance of their electrode to that of a provided commercial Ag(s)|AgCl(s)|Cl^-(3.0 M) reference electrode. Ideally, the potential difference between their electrode and the commercial version should be 0 mV. The potential difference between five student-made electrodes and a given commercial Ag(s)|AgCl(s)|Cl^-(3.0 M) electrode is typically |3.1 ± 1.1| mV. The potential difference between five commercial electrodes is similar: |2.3 ± 0.8| mV. As long as the gel is kept moist, the electrode continues to perform well for weeks. The reference electrode has a potential of 0.210 V versus SHE.

HAZARDS

The ammonia solution is corrosive and should be handled in the fume hood. Laundry bleach should be handled with care.

THEORY

The reaction between OCl^-(aq) and Ag(s) can be formulated by consideration of the following reduction half-reactions:

$$OCl^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq) \qquad E^o = 0.89\ V \tag{1}$$

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \qquad E^o = 0.22\ V \tag{2}$$

With ΔE^o equal to 0.67 V, the overall cell reaction is

$$OCl^-(aq) + H_2O(l) + 2Ag(s) + Cl^-(aq) \rightarrow 2AgCl(s) + 2OH^-(aq) \qquad K = 4 \times 10^{22} \tag{3}$$

According to eq 3, Cl^-(aq) is a reactant. Clorox bleach (5−10% m/m NaClO) is used and students confirm the presence of Cl^-(aq) by adding $AgNO_3$(aq) and observing precipitation of AgCl(s). We also have previously used a solution consisting of 0.40 M $Ca(ClO)_2$(aq) and 0.25 M NaCl(aq).

The reduction potential of AgCl(s) (eq 2) is controlled only by the Cl^-(aq) concentration as indicated in eq 4. This being a reference electrode, it is critical to make the Cl^-(aq) concentration constant, which is accomplished by using a high concentration of Cl^-(aq), 3.0 M.

$$E_{AgCl(s)|Ag(s)} = E^o{}_{AgCl(s)|Ag(s)} - \frac{RT}{F}\ln[Cl^-(aq)] \tag{4}$$

Chemical etching with NH_3(aq) can be understood if one considers eqs 5 and 6, which add to give eq 7.

$$AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10} \tag{5}$$

$$Ag^+(aq) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2{}^+(aq) \qquad K_f = 1.7 \times 10^7 \tag{6}$$

$$AgCl(s) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2{}^+(aq) + Cl^-(aq) \qquad K = K_{sp} \times K_f = 3.0 \times 10^{-3} \tag{7}$$

Although K is 10^{-3}, the reaction goes essentially to completion because the concentration of NH_3(aq) is high (5 M) and the concentration of $Ag(NH_3)_2{}^+$(aq) formed close to the electrode is practically zero because it is swept away by stirring.

CONCLUSION

In this communication, a student-prepared Ag(s)|AgCl(s)|Cl^-(3.0 M) reference electrode is described. Its performance is satisfactory for general chemistry laboratory purposes. Students not only prepare a reliable reference electrode and compare it to a commercial counterpart, they also learn the chemical principles involved in its preparation and operation, and in the recovery of the expensive component, Ag(s). With a short preparation time (10 min), it leaves plenty of time for other laboratory exercises to be performed.

ASSOCIATED CONTENT

Supporting Information

Instructor notes and student handout. This material is available via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: barlag@ohio.edu.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Riyazuddin, P. Low-Cost Reference Electrode for Potentiotitrimietry. *J. Chem. Educ.* **1994**, *71*, 167.

(2) Eggen, P.; Kvittingen, L.; Gronnebberg, T. Small-Scale and Low-Cost Electrodes for "Standard" Reduction Potential Measurements. *J. Chem. Educ.* **2007**, *84*, 671−673.

(3) Thomas, J. Student Construction of a Gel-Filled Ag/AgCl Reference Electrode for Use in a Potentiometric Titration. *J. Chem. Educ.* **1999**, *76*, 97−98.

(4) Brewer, P. J.; Leese, R. J.; Brown, R. J. C. An Improved Approach for Fabricating Ag/AgCl Reference Electrodes. *Electrochim. Acta* **2012**, *71*, 252−257.

(5) East, G. A.; del Valle, M. A. Easy-to-Make Ag/AgCl Reference Electrode. *J. Chem. Educ.* **2000**, *77*, 97.

(6) Inamdar, S. N.; Bhat, M. A.; Haram, S. K. Construction of Ag/AgCl Reference Electrode from Used Felt-Tipped Pen Barrel for Undergraduate Laboratory. *J. Chem. Educ.* **2009**, *86*, 355.
(7) How to Make a Reference Electrode. http://www.youtube.com/watch?v=JOR8DWH2PXE (accessed Mar 2014).
(8) Electrodes and Potentiometry. http://webs.wofford.edu/splawnbg/Chem_411_files/Chem%20411_Lecture%201_Electrodes%20and%20Potentiometry.pdf (accessed Mar 2014).

dx.doi.org/10.1021/ed400722e | *J. Chem. Educ.* 2014, 91, 766−768