

Assembly of a Robust and Economical MnO₂-Based Reference Electrode

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S Supporting Information

ABSTRACT: There is a dearth of base-stable reference electrodes that are suitable for use by students in a teaching laboratory or undergraduate research context. To remedy this, we have developed a technique to produce reference electrodes suitable for alkaline environments. By utilizing components of a commercially available alkaline-type battery, an engineered MnO₂/MnO(OH) cathode that is both stable and reproducible is readily obtained. The electrode potentials are quite stable with respect to time and depend on the state of charge of the battery used to make the electrode. The assembly and use of such reference electrodes easily lends itself to introductory electrochemistry lab experiments at a fraction of the cost of traditional electrodes.

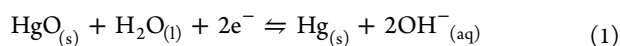
KEYWORDS: Electrochemistry, Laboratory Equipment/Apparatus, Analytical Chemistry, Hands-On Learning/Manipulatives, Upper-Division Undergraduate, Graduate Education/Research, Electrolytic/Galvanic Cells/Potentials, Undergraduate Research



INTRODUCTION

Reference electrodes are necessary for most electrochemical experiments and are a good demonstration of concepts such as reversible electrochemical equilibria and half-cells. As a result, diverse methods for construction of reference electrodes have been reported, usually for the Ag/AgCl electrode.^{1,2} However, few reference electrodes have been reported for use under basic conditions, with fewer still that are also readily produced or available. The academic and industry standard reference electrodes, such as the saturated calomel electrode (SCE) or Ag/AgCl electrodes, exhibit all the hallmarks of a good reference electrode: they have reproducible redox equilibria that exhibit rapid kinetics and stability over time.³ However, these electrodes also display poor potential stability in alkaline media due to formation of HgO or Ag₂O, which have different electrochemical potentials than do the chlorides.

It is possible to construct reference electrodes from these base-stable species, but each has inherent complications. For example, the HgO/Hg electrode, which uses the reaction in eq 1, has been used as a base-stable reference. It is effective provided that one takes into account the pH-dependence of the relevant equilibrium^{3–5} as per the Nernst eq 2:



$$E = E^\circ - \frac{RT}{nF} \ln Q \approx E^\circ - 0.059 \text{ V} \times \text{pH} \quad (2)$$

where $T = 25 \text{ }^\circ\text{C}$, and the other quantities have their usual meanings.

Nonetheless, the toxicity hazards of mercury add to its difficulties and make it suboptimal as a pedagogical tool.⁶ Furthermore, cost is a significant factor that teachers and lab directors must overcome. The costs of most commercially available SCE and Ag/AgCl electrodes make them less appealing at the undergraduate or high school general chemistry instructional level where large numbers of electrodes may be needed.⁷

As an example of a situation that would benefit from an inexpensive, alkali-stable reference electrode, we have recently reported an electrochemical assay designed to screen mixed-metal oxides in alkaline media for potential use as electrocatalysts for the oxygen-evolution reaction.⁸ An analogous screen for photoelectrocatalysts had previously been developed and has been adapted to an undergraduate general chemistry laboratory curriculum.⁹ To do likewise with an electrochemical project requires that the equipment and procedures be streamlined to accommodate a teaching lab's requirements.

To avoid the inherent expense of silver and achieve stability under alkaline conditions, we eschewed mercury and investigated the use of other redox couples. After fruitless preliminary experiments on Cu/CuO and Cu/Cu₂O electrodes, our attention turned to manganese. The Pourbaix diagram of manganese shows several usable redox couples (Figure 1).^{10,11} Redox processes that involve solid species are desirable for a reference electrode since the potential is not dependent on, for example, the Mn²⁺ concentration. Of these, the equilibrium indicated by the bold line is well-defined over a wide pH range,

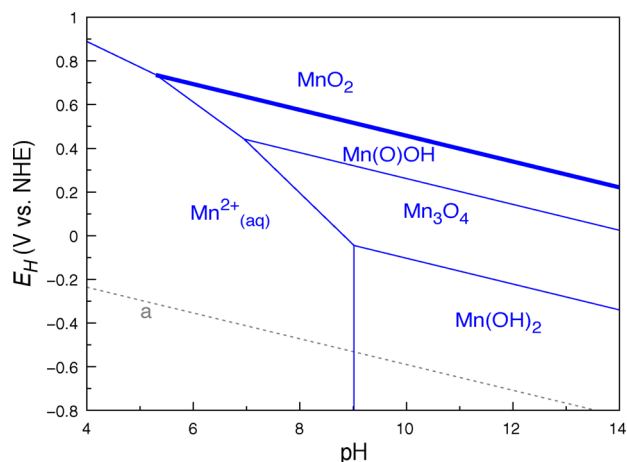


Figure 1. Simplified Pourbaix diagram of manganese. All species other than $\text{Mn}^{2+}_{(\text{aq})}$ are in the solid state. Line (a) indicates the potential of the equilibrium $2 \text{H}^{+}_{(\text{aq})} + 2 \text{e}^{-} \rightleftharpoons \text{H}_{2(\text{g})}$, for reference. The bold line indicates the equilibrium in eq 3, which sets the cathode potential in an alkaline battery.

reversible, and stable to the presence of oxygen and light. The $\text{MnO}_2/\text{MnO}(\text{OH})$ couple has been used as a potential reference in the field of concrete chemistry to monitor the rate of galvanic corrosion of steel reinforcing rods.¹² As described in the literature, these electrodes are generally unwieldy for laboratory use and rely on skill in making a dense, conductive manganese dioxide paste that is in electrical contact with the electrode wire.

To avoid this preparation issue, we have utilized materials obtained from the cathode of commercial alkaline batteries. These devices are modified to produce a robust, reproducible, and inexpensive reference electrode whose potential is set by the $\text{MnO}_2/\text{MnO}(\text{OH})$ redox couple in eq 3:



The widely available alkaline battery is a $\text{Zn}/\text{Zn}(\text{OH})_2/\text{MnO}_2/\text{MnO}(\text{OH})$ cell in aqueous KOH electrolyte (Figure 2). Considerable engineering effort has been expended in optimizing these cells for high capacity, steady voltage, and low environmental impact. Disassembly of such a cell is an expeditious route to obtain an electrochemical half-cell composed of a pressed mixture of manganese dioxide and carbon powder (added for increased electrical conductivity) in

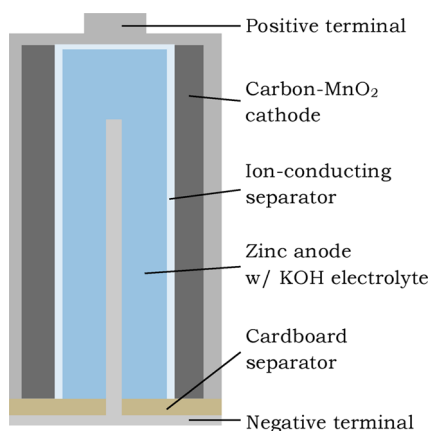


Figure 2. Cross-sectional diagram of an alkaline battery (not to scale).

an electrically conductive container that can be attached to a potentiostat. By removing the Zn side of the cell and adding a salt bridge, this half-cell can be placed in contact with other redox couples and used as a reference electrode to measure their potentials.

Once the reference electrode has been constructed, it can be used in various experiments in the classroom and research laboratory. The experiments on water electrolysis and photo-electrolysis in refs 8 and 9, which inspired this work, can be performed with substitution of this electrode for the previously used reference electrode or addition of the reference electrode to a two-electrode configuration. Two-electrode experiments can be modified either by attaching the reference electrode to the appropriate potentiostat lead (e.g., ref 9e) or by using a high-impedance multimeter to measure the potential between the working electrode and a reference electrode (e.g., ref 9d). Other experiments where this electrode would be suitable for classroom use include the measurement of hydrogen evolution kinetics, Nernst equation verification, and voltammetric determination of solutes.^{13–16}

METHODS

Duracell AAA batteries were discharged via a simple circuit (Figure 3) at a rate of ~ 50 mA until they were approximately

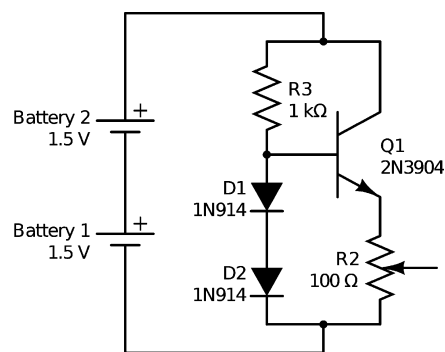


Figure 3. Circuit used to discharge batteries to as low as 25% SOC.

25%, 50%, and 75% discharged, assuming a capacity of 1150 mAh.¹⁷ In contrast, batteries whose states of charge (SOC) were 100% and 0% were either used as received (100%) or discharged by another method (0%). For simplicity, cells at 0% SOC were first discharged with a resistor such that the rate of discharge was near that of the other cells and afterward were short-circuited to ensure that they were in fact fully discharged.

After discharge, the battery was opened up by removing the anode terminal and end-cap (see Supporting Information). Care should be taken in this step to not short-circuit the battery while the terminal is removed. The paper separator was then removed with forceps, still wrapped around the zinc powder anode material. CAUTION: the zinc powder and cell separator are saturated with a caustic concentrated KOH solution. Use appropriate protective equipment consisting of at minimum: splash resistant goggles and alkali-resistant gloves. Note that as the depth of discharge increases, the zinc within the cell is consumed to form zinc hydroxide, which has a higher molar volume than does zinc metal. This in turn makes the removal of the swollen anode materials more difficult and considerably messier. At 0% and 25% SOC, the vigorous use of forceps that is required to remove the anode materials may dislodge some of

the cathode materials, which can indelibly stain clothes, paper, laboratory benches, and other surfaces.

The solid, black cathode materials within the steel can were rinsed twice with 0.1 M NaOH solution, allowing the solution to equilibrate for at least 10 min each time. The can is then sealed onto either a 1 mL plastic syringe barrel or 1 mL pipet tip using rubber tubing (see Figures S2–S4, Supporting Information). A glass eyedropper tip was also successfully used, but it offered no special advantage. Although not necessarily required, the tubing was further wrapped with Parafilm to prevent leakage. Finally, the assembly was filled with 0.1 M NaOH and stopped with a small wad of cotton wool.¹⁸

A three-electrode setup was used to test the electrochemical stability of the electrodes using a BASi Epsilon potentiostat. The previously assembled electrode was used as the reference, a Pt disc electrode was used as the working electrode, and graphite mechanical pencil lead was used as the counter electrode. In the interest of minimizing cost, graphite was also considered as the working electrode, but ultimately was not feasible because of slow charge transfer kinetics with ferricyanide.¹⁹ Cyclic voltammograms of $K_3[Fe(CN)_6]$ in 0.1 M NaOH were taken, and the $E_{1/2}$ voltage was recorded for each electrode.^{20,21} Electrodes were stored between uses with the tip immersed in a 0.1 M NaOH solution, and cyclic voltammetry (CV) experiments were periodically performed to monitor the electrode stability over time. To study the effect of the buffer solution, the 0.1 M NaOH solution in select electrodes was replaced by 1.0 M NaOH or 0.1 M KOH solutions.

RESULTS AND DISCUSSION

Consistent CV data and $E_{1/2}$ values were both used to demonstrate the stability of the reference electrodes over time (Figure 4). A greater degree of discharge was correlated with a greater $E_{1/2}$ potential (Table 1). This is to be expected as the discharge process reduces Mn^{4+} to Mn^{3+} , that is, the Mn redox couple is shifted to a less oxidizing, or more negative, potential.

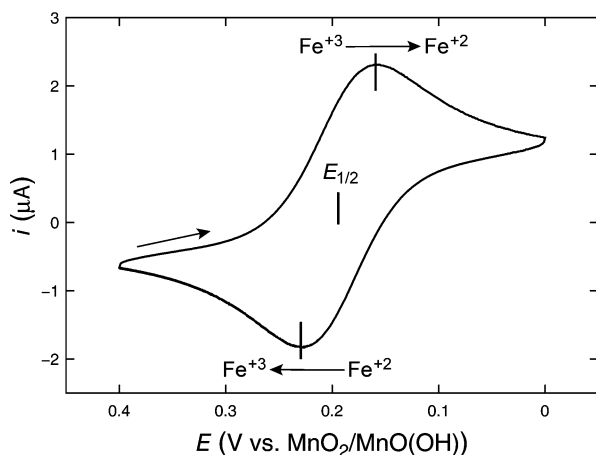


Figure 4. Cyclic voltammogram of 1.0 mM $K_3Fe(CN)_6$ in 0.1 M NaOH at a scan rate of 25 mV/s. The scan starts from the arrow at lower left, and ferricyanide is reduced to ferrocyanide as the electrode potential decreases and is then reoxidized as the potential is raised. The $E_{1/2}$ value is the average of the two peak potentials denoted by tickmarks and is close to E° for a reversible redox process. The smooth, symmetric curve with closely spaced peaks is indicative of a good reference electrode with a low solution resistance between it and the working electrode.

Table 1. Average Steady-State Half-Cell Potentials Obtained from MnO_2 -Based Reference Electrodes at Different Depths of Discharge

State of Charge (%)	Ferricyanide $E_{1/2}$ (mV) at Pt Electrode ($n = 2$)
100	-78 ± 44
75	50 ± 40
50	108 ± 5
25	188 ± 103
0	649 ± 20

This means that the observed redox potential for the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple increases relative to the $Mn^{4+/3+}$ reference. When the ferricyanide reduction potential is converted to give the reference electrode potential versus the normal hydrogen electrode (NHE) (cf. ref 21), the 50% SOC potential aligns with the $MnO_2/MnO(OH)$ potential in Figure 1, and the 0% SOC potential aligns with the $Mn_3O_4/Mn(OH)_2$ potential. A correlation between the observed potential and a simple Nernst's Law model was found within the limits of the accuracy of the degree of discharge of each battery (Figure 5).

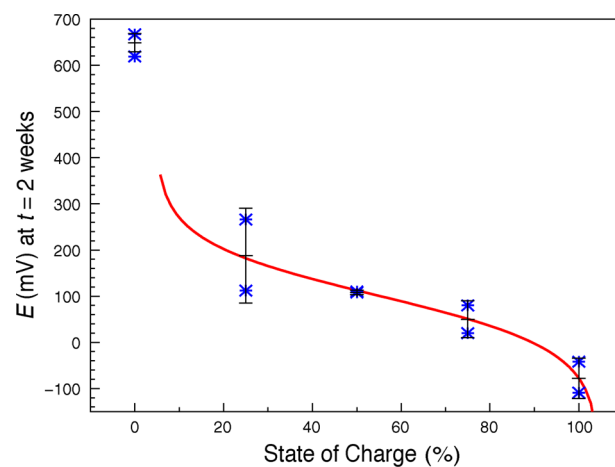


Figure 5. Observed $E_{1/2}$ potential for the ferricyanide redox couple using the manganese dioxide-based reference electrodes. Error bars represent one standard deviation from the mean value. The curve is a fit of $E_{1/2} = a - 59 \times \log((SOC + b)/(100 - SOC - b))$, with values for a and b of 102 ± 4 mV and $-4.6 \pm 0.6\%$, respectively. The points at 0% SOC were excluded from fitting.

The Nernst equation was fit with two parameters, the potential of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple relative to the reference electrode and an adjustment to the nominal state of charge. A good fit was obtained with a potential of 102 ± 4 mV and an adjustment indicating that nominally fully charged batteries are in fact drained by $4.6 \pm 0.6\%$. This result also indicates that the MnO_2 and $MnO(OH)$ are in a solid solution. Selected electrodes were retained and their $E_{1/2}$ values were periodically measured by CV of a ferricyanide solution.

In the electrodes retained for stability testing, slight variations in potential were noticed over weeks (Figure 6). However, the stability is adequate for research purposes, especially if the electrode is calibrated before use when precise potential measurements are performed. A linear fit to the data indicated that at 50% SOC, the electrode drifts at a rate of <1 mV/week.

As depth of discharge increases, the observed difference between the initial and steady-state potential tends to increase. Furthermore, the difference between the two trials is smallest

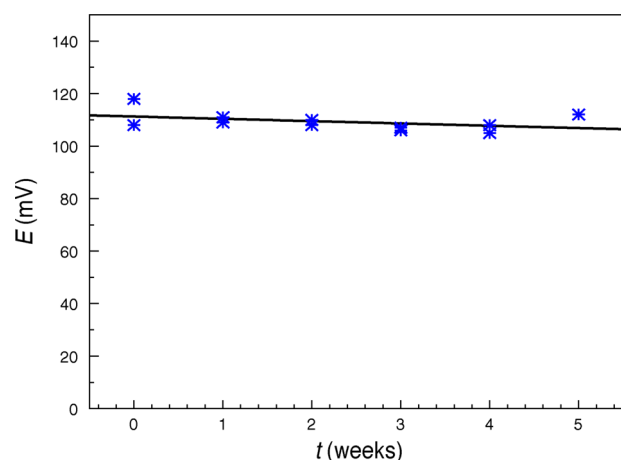


Figure 6. Stability over time for 50% SOC electrodes. A linear fit to the data gives $E_{1/2} = 111(\pm 2) - 0.9(\pm 0.6) \times t$ mV.

for 50% SOC, but each cell tested settled at a stable potential within approximately 1 week of assembly. Although a new battery is presumably filled with MnO_2 , the exact composition is proprietary and may contain a significant amount of $\text{MnO}(\text{OH})$. Partial discharge of the battery ensures that both Mn^{3+} and Mn^{4+} are present in equilibrium, which is necessary to have a well-defined potential. Previous descriptions of this electrode in the literature seem to have neglected this requirement.^{12a} Near-complete discharge of the battery before assembly of the reference electrode can be expected to give a mixture that contains some $\text{Mn}(\text{OH})_2$ or Mn_3O_4 . Here again, the electrode will then have a poorly defined potential set between the $\text{Mn}^{4+/3+}$ or $\text{Mn}^{3+/2+}$ couples. Indeed, there are appreciable voltage differences in the $E_{1/2}$ potential for SOC other than 50%, whereas the cells having been discharged to 50% capacity were found to be at approximately identical potentials (Figure 5). In light of this, we recommend that cells are halfway discharged before assembly.

The equilibrium potential of the $\text{Mn}^{4+/3+}$ couple is pH-dependent and varies by 59 mV/pH (cf. Figure 1). As a result, reference electrodes using this equilibrium should be prepared with an electrolyte that is well buffered, ideally to the pH value of the solution being measured. To avoid pH gradients within the carbon paste, the reference electrode should be allowed to equilibrate until it gives steady readings by CV as described above or by measurement of the potential against a known stable reference, which takes a day or less. A stable electrode will show a very low change in potential versus time as seen in Figure 6. Because of our interest in reactions under alkaline conditions, the electrodes were typically prepared with 0.1 M aqueous NaOH. At pH 13, the hydroxide concentration itself is high enough to buffer the solution. Other possible electrolytes are discussed in the Supporting Information. Use of the pH-dependent potential to measure pH by comparison of the electrode potential to a pH-independent redox couple is left as an exercise for the interested reader.

Replacement of the 0.1 M NaOH buffer solution with 1.0 M NaOH led to a shift in potential as expected. The average $E_{1/2}$ potential for the reaction was shifted by 60 mV after correction for the shift in the ferricyanide potential.²² On the other hand, changing the buffer's counterion from sodium to potassium while maintaining the same pH value led to an observed 6 mV shift in potential, which is within the margin for experimental error.

The utility of the reference electrode was tested for the voltammetric determination of ascorbate. In this technique, a glassy carbon working electrode was used to oxidize different concentrations of ascorbate in aqueous 0.1 M NaOH electrolyte (Figure 7). The peak current density is correlated

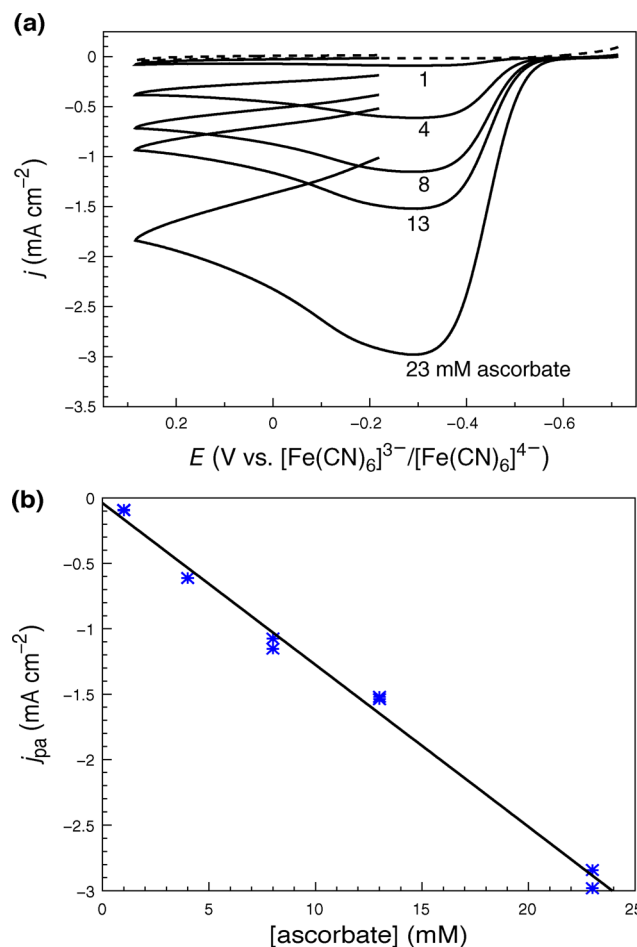


Figure 7. (a) CV scans at 25 mV/s of different concentrations of sodium ascorbate in 0.1 M aqueous NaOH using a glassy carbon electrode. (b) Peak current density of the irreversible ascorbate oxidation wave versus concentration shows a linear dependence.

to the ascorbate concentration, and this phenomenon has been used for an undergraduate analytical chemistry experiment on measurement of the vitamin C content of orange juice.¹⁵ After the CV scans of the ascorbate solutions were complete, ferricyanide was added to the solution, and the reference electrode was calibrated by CV as above. This step is not strictly necessary, since the peak current is independent of the reference electrode potential, and can be omitted if desired to save class time.

CONCLUSION

Research-grade reference electrodes can be expeditiously assembled from materials that are available in any laboratory classroom and even in most homes.²³ The $\text{MnO}_2/\text{MnO}(\text{OH})$ redox couple is stable at all states of charge under alkaline aqueous conditions and has minimal hazard relative to SCE or HgO electrodes. In addition, this reference electrode design takes advantage of the careful engineering of modern alkaline batteries as a source of preassembled manganese oxide/carbon

paste cathodes.²⁴ This half-cell, designed to supply high current, ensures that the electrode can supply the minuscule amount of charge drawn by the potentiostat without voltage drift. First discharging the cell to ~50% SOC ensures that the cell contains both MnO₂ and MnO(OH), a necessary condition for a well-defined electrode potential. Physically disassembling an inexpensive battery to make a reference electrode is also a powerful demonstration of connections between redox chemistry and batteries, the idea of electrochemical half-cells, and reversible redox processes. Once the electrode has been assembled and characterized, it can be readily substituted for other reference electrodes in research projects, classroom experiments, or demonstrations.

■ ASSOCIATED CONTENT

● Supporting Information

Documentation for the step-by-step assembly of the electrodes. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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