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Teaching the Nernst equation and Faradaic current through the use of a *designette*: An opportunity to strengthen key electrochemical concepts and clarify misconceptions

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ABSTRACT

An engaging designette based on the assembly of Zn and Cu electrodes into a voltaic array is presented. The aims of this hands-on classroom activity, termed the *OCP Designette*, are to facilitate instruction on the Nernst equation and Faradaic current and clarify misconceptions therein. The designette highlights the importance of identifying redox reactions, the application of the Nernst equation, and Faradaic current dependency on electrolyte concentration while at the same applying *design thinking* to optimize harnessed electrochemical power. The implementation of the designette, with a duration of 60 minutes, is suitable for high school students with a background in chemistry and physics, for undergraduate engineering and architecture students enrolled in a general science course, and for general undergraduate students enrolled in an introductory chemistry course.

KEY WORDS

Electrochemistry, Electrolytic/Galvanic Cells/Potentials, High School/Introductory Chemistry, Hands-on Learning/Manipulative, First-year Undergraduate

TOC SYNOPSIS

INTRODUCTION

Electrochemical concepts are of importance to all students majoring in science and engineering fields, as electrochemistry is a gateway to the understanding of energy storage (batteries), energy production (fuel cells), and materials selection (corrosion). Due to its usefulness, a series of classroom activities, demonstrations and laboratories have been previously introduced for the purpose of demonstrating electrochemical applications in real life situations using easily accessible materials.¹⁻¹¹

Although pivotal, grasping electrochemical concepts correctly has been traditionally difficult for students in high school and introductory courses at the university level. Several reports have demonstrated that there are well-established electrochemical misconceptions among students. These misconceptions in electrochemical cells are related but not limited to instrumental voltage and current measurements, chemical vs. electrochemical equilibrium, half-cell vs. cell potentials, ionic conduction, current flow in electrolyte solutions, the role of the salt bridge in an electrochemical cell, and over-potentials.¹²⁻¹⁵ Generally, the causes for these misconceptions have been attributed to (i) lack of explicit information in textbooks¹⁵, and (ii) inadequate interpretation of scientific language by the students.⁴ One proposed solution to minimize misconceptions has been the use of computer animations to supplement lecture instruction and demonstrations.⁴

We recently presented the *electrochemistry designette* as a platform that uses a mixed method approach to evaluate student performance, student learning, and student creativity,¹⁶

but the *OCP designette* (Open Circuit Potential) aims to accompany the instructors while teaching the following key electrochemical principles:

- (i) identification of redox reactions,
- (ii) the application of the Nernst equation,
- (iii) voltage loss, and
- (iv) Faradaic current.

IMPLEMENTATION OF THE *OCP DESIGNETTE*

The *OCP designette* is a designette since (a) there are minimal instructions on how to accomplish the design brief or task, and (b) there are more than one solution to the design brief. The design brief of the designette read as follows: *Use the materials provided to (1) assemble a voltaic device that ensures maximum power ($W = \text{voltage} \times \text{current}$) and (2) calculate the Faradaic current as a function of Cu^{2+} concentration in a single voltaic cell.*

Students should work in groups and be given 40 min to accomplish the design brief or task, followed by a 20 min discussion addressing the pertinent electrochemical principles. During the designette, instructors have the chance to visualize students' misconceptions and can choose to either correct right away or wait for student inquiries. We encourage instructors to answer all inquiries students can pose during the designette, allowing students to learn on the spot. There are 4 main steps to the implementation of the designette:

- (1) fabrication of the electrodes and preparation of materials and solutions,
- (2) assembly of the voltaic array,
- (3a) acquisition of DC current and voltage readings on the voltaic array,
- (3b) acquisition of current vs Cu^{2+} concentration profiles using a single voltaic cell, and
- (4) discussion on the Nernst equation and Faradaic current.

Fabrication of the electrodes and materials preparation.

The small footprint and easy construction of the *OCP designette* allows instructors or laboratory technicians to fabricate the Zn and Cu electrodes and solutions needed beforehand. The tools required are not specialized and commonly found in chemistry and physics labs. Figure 1 shows materials, solutions and tools needed to implement the designette. Further details for the construction can be found in Figures S1 and S2 in the supporting information (SI). Importantly, before the next steps, students must become acquainted with the use of the eyelet puncher for the fabrication of the Zn-Cu electrode pairs and the multipurpose meter to acquire voltage and current measurements.

Assembly of the voltaic array (20 min)

Groups of 4 students assembled the electrochemical device by using eyelets to connect Zn and Cu electrodes in-series. This is the first step implemented by the students, which main tasks consisted in electrically connecting the electrodes and setting up an in-series configuration of the voltaic array to subsequently take current and voltage measurements. Further details in three potential types of electrical connectivity of the electrodes are shown in Figure S2 in SI. However, there were other solutions presented by the students for the electrical connectivity of the Zn and Cu electrodes. For instance, the use of conductive wire between Zn and Cu electrodes knotted on holes created by using the eyelet puncher.

Figure 1: Representative list of materials and tools required for the implementation of the *OCP design*.

Figure 2: Panel A shows the various components assembled in a voltaic array, such as metal electrodes, connecting eyelets and electrolyte. Panel B shows the location of the anode (-) and cathode (+) and the in-series configuration of the individual cells. The red arrows point to the direction of the electron flow, from the Zn electrodes to Cu electrodes, in the voltaic array.

Acquisition of current and voltage readings (20 min)

The Zn-Cu 6-cell voltaic array, shown in Figure 2, and a single Zn-Cu voltaic cell were tested with a wireless data logger (Multimeter/datalogger, EX500, Extech Instruments) capable of reading current and voltage in DC mode separately and relaying the data directly to a laptop via bluetooth. The current and voltage differential between the Zn and Cu electrodes were measured for 20 s in DC mode. We noticed that this time frame was reasonable for students to take current and voltage measurements during the designette. Zn and Cu electrodes were sanded (Boson, waterproof sandpaper, P60) for 30-60 s each followed by a thorough water rinse and dried with Kimwipes (KimTech). Only two electrolytic solutions were used in the designette as they provided different voltage and current outcomes: rice wine and 100 mM CuSO_4 (aq). Rice wine was used because it is readily available, conductive (20 % ethanol by

volume and 0.27 M NaCl), and easily disposable. ZnSO_4 (aq) can be used instead of CuSO_4 (aq) but the current output was only half while the *emf* decreased to < 1 V per single cell. Using both salts simultaneously was not considered because it will complicate the interpretation of the results further.

*Current density (*j*) and voltage profiles of the Zn-Cu 6-cell voltaic array.* The current density curves for both, rice wine and 100 mM CuSO_4 (aq) electrolytes, are shown in Figure 3A. When rice wine was used as the electrolyte, the current density in the Zn-Cu voltaic array was $j = (2.0 \pm 1.1) \times 10^{-4} \text{ A/cm}^2$ ($n = 3$) at $t = 20 \text{ s}$. The decrease in current density as a function of time can be attributed to the physisorption of acetic acid dimers and other organic matter on the Zn surface left behind from the fermentation process.¹⁷ When 100 mM CuSO_4 was used as the electrolyte, the current observed showed no exponential decay, but instead exhibited a stable output culminating with a current density of $j = (4.0 \pm 0.028) \times 10^{-5} \text{ A/cm}^2$ ($n = 3$) at $t = 20 \text{ s}$. These values indicate that current density increased by a factor of 20 when copper sulfate was used as an electrolyte versus rice wine.

The voltage profiles for both rice wine and 100 mM CuSO_4 (aq) electrolytes are shown in Figure 3B. The Zn-Cu 6-cell voltaic array exhibited a stable voltage over the time range when rice wine was the electrolyte of choice, with a value of 4.78 V at $t = 1 \text{ s}$ and average and standard deviation values of $4.81 \pm 0.01 \text{ V}$ ($n = 3$) at $t = 20 \text{ s}$. Similarly, a stable profile was observed when 100 mM CuSO_4 (aq) was the electrolyte, with a value of 6.19 V at $t = 1 \text{ s}$ and average and standard deviation values of $6.20 \pm 0.05 \text{ V}$ ($n = 3$) at $t = 20 \text{ s}$. In other words, an additional 1.39 V was observed when 100 mM CuSO_4 (aq) was selected as the electrolyte versus rice wine.

Figure 3: Panel A shows average ($n = 3$) current density vs. time curves for the Zn-Cu 6-cell voltaic array when both rice wine and 100 mM CuSO_4 (aq) are utilized as the electrolyte. Panel B displays average ($n = 3$) voltage vs. time curves for the Zn-Cu voltaic array under rice wine and 100 mM CuSO_4 (aq) electrolytes.

Student results for Zn-Cu 6-cell voltaic arrays. A total number of 20 groups comprised of 4 students each and spread over two years enrolled in the Integrated Learning Programme chemistry (ILP-Chemistry 2) participated in the designette. Representative average voltage, current, and power values obtained by the students are shown in Table S1. We observed that the presence of Cu^{2+} sped up the redox reactions and harnessed superior power as shown in Table S1. Furthermore, the choice of electrical connectivity in-series of the electrodes varied from group to group, which is an attribute of the designette, objectively determining overall performance via achieved power (voltage $\times$ current). Students used either eyelets, conductive wires, staples, and combinations in various forms to electrically connect the Zn and Cu electrodes.

Ion concentration effects on current density and voltage measured using a single Zn-Cu voltaic cell. These measurements were cleaner and faster when using a single Zn-Cu voltaic cell. Current density profiles for 1, 10, and 100 mM CuSO_4 electrolyte are displayed in Figure 4A. A plot of current density after 20 s versus Cu^{2+} concentration is displayed in Figure 4B. A least square fitting provided a linear relationship with an equation of the line $y = 4 \times 10^{-5} x + 0.0003$ with $R^2 = 0.9948$. Voltage vs time plots are shown in Figure 4C, while the behaviour of voltage as a function of Cu^{2+} concentration is exhibited in Figure 4D. Average current density and voltage values for a single Zn-Cu voltaic cell are shown in Table S2 in SI.

Figure 4: Panel A shows average ($n = 3$) current density vs. time curves for a single Zn-Cu voltaic cell under 1, 10, and 100 mM CuSO_4 (aq) electrolytic solutions. Panel B exhibits a plot of current density after 20 s vs CuSO_4 concentration and a trendline fitting. Panel C displays average ($n = 3$) voltage vs. time curves for a single Zn-Cu voltaic cell under 1, 10, 100 mM CuSO_4 (aq) electrolytic solutions. Panel D shows a plot of voltage after 20 s vs. CuSO_4 (aq) concentration.

HAZARDS.

No electrical shock hazard occurred when building and implementing the Zn-Cu voltaic array due to low observed voltage and currents. Gloves are highly recommended to be worn at all times to avoid unnecessary contact with the CuSO₄ solution and minimize the risk of injuries/cuts to the fingers due to the metal sharp corners. CuSO₄ solution can cause respiratory irritation and is harmful if swallowed. Although rice wine appears harmless to the skin, contact is discouraged.

DISCUSSION (20 min)

Identification of redox reactions

Given the following overall equilibrium $a X + b Y \rightleftharpoons c X^+ + d Y^-$, the Nernst equation in the forward direction can take the following form:

$$E_{cell} = (E_{Cathode}^{o,red} - E_{Anode}^{o,red}) - \frac{RT}{nF} \ln\left(\frac{[X^+]^c [Y^-]^d}{[X]^a [Y]^b}\right) \quad (1)$$

where $E^{0,red}$ are the standard half-cell reduction potential values at the cathode and anode electrodes, respectively, R is the ideal gas constant, F is the Faraday constant, T is temperature in Kelvins, n is the stoichiometric number of moles of electrons transferred, and the natural logarithms terms refers to the concentrations of the redox reactants (X , Y , X^+ , Y^-) with their corresponding exponential. The first term on the right is the electrostatic potential contribution and refers to the voltage difference between the anode/solution potential interface and cathode/solution potential interface, while the second term is the chemical potential contribution and refers to the voltage difference driven by a concentration gradient between the two half-cell reactions. When the electrostatic and chemical contributions are highlighted in the Nernst equation, students grasp that the choice of materials for anode and cathode contribute via electrostatic potential, while the initial ion concentrations in the cells contribute via chemical potential.

Copper sulphate electrolyte. In order to apply the Nernst equation, we first need to identify the corresponding anode and cathode reactions. For 100 mM CuSO₄ (aq) as the electrolyte, the corresponding electrostatic potential reactions at room temperature are shown below, whereby the cell potential is driven by the initial concentrations of Zn²⁺ and Cu²⁺.

Anode:

Cathode:

Overall reaction:

Therefore, the cell potential for a single cell can be calculated by applying the Nernst equation using concentrations and known half-cell reduction potential values at 25 °C.¹⁸

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log \left(\frac{[\text{Zn}^{2+}/1\text{M}]}{[\text{Cu}^{2+}/1\text{M}]} \right) \quad (5)$$

$$E_{\text{cell}} = +1.103 - \frac{0.0592}{2} \log \left(\frac{[\text{Zn}^{2+}]}{[10^{-1}]} \right) \quad (6)$$

We note that as soon as the Zn electrode was placed in solution, Zn metal dissolved and the Zn surface was polarized. Similarly, we note that although the initial concentration of Cu^{2+} was 100 mM, Cu^{2+} had a strong affinity to chemisorb to the electron-rich Zn surface, indicating its concentration decreased rapidly. If given a difference of concentrations between Zn^{2+} and Cu^{2+} of 100-times, for instance, the chemical potential contribution would have been in the order of 59.2 mV or 5.4 % with respect to the electrostatic potential contribution of 1.103 V, and zero if the concentrations of Zn^{2+} and Cu^{2+} were equal, for example at 1 mM. Hence, it is reasonable to simplify the theoretical value of the Nernst equation to:

$$E_{\text{cell}} = E^\circ_{\text{cell}} = +1.103 \text{ V}. \quad (7)$$

The electromotive force (*emf*) of a single Zn-Cu voltaic cell in 100 mM CuSO_4 (aq) was measured to be $1.056 \pm 0.011 \text{ V}$ ($n = 3$), closely in agreement with the theoretical Nernstian value of 1.103 V, indicating that the *emf* ($E_{\text{right}} - E_{\text{left}}$ at open circuit potential difference) of each Zn-Cu voltaic cell was mostly driven by the electrostatic potential difference between the terminals, with negligible contribution by chemical potential.

Rice wine electrolyte. When using rice wine as the electrolyte, a consistent student misconception was to assign the Cu/Cu^{2+} reduction reaction to the cathode terminal. However, there were no significant source of Cu^{2+} ions in the rice wine solution. The electrochemical reactions at the corresponding electrodes are shown in the equilibrium reactions below, whereby the Cu surface at the cathode terminal acts as an inert electrode on which reaction 9 occurs, producing hydrogen gas which was visually observed as bubbles:

Anode:

Cathode:

Overall reaction:¹⁸

The cell potential for a single Zn-Cu voltaic cell with rice wine as the electrolyte is obtained by considering the Nernst equation and the solution $pH = 6.49$:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log \left(\frac{\left[\text{Zn}^{2+} / 1M \right] P_{\text{H}_2}}{\left[\text{H}^+ / 1M \right]^2 {}^\circ P} \right) \quad (11)$$

$$E_{\text{cell}} = +0.7628 - \frac{0.0592}{2} \log \left(\frac{\left[\text{Zn}^{2+} / 1M \right] P_{\text{H}_2}}{\left[3.2 \times 10^{-7} / 1M \right]^2 1 \text{ atm}} \right) \quad (12)$$

where P_{H_2} and ${}^\circ P$ represent the partial pressure of H_2 dissolved in solution measured in atmospheres and standard partial pressure at 1 atmosphere, respectively. Therefore, for equations 11 and 12, each logarithmic term is dimensionless as the numerator and denominator terms are each divided by their corresponding standard quantities: that is, 1 M for solutions and 1 atmosphere for gases.

However, this time we cannot assume that the terms in the numerator, initial Zn^{2+} concentration and partial pressure of H_2 , are negligible since the *emf* measured with rice wine as the electrolyte was $0.813 \pm 0.006 \text{ V}$ ($n = 3$), implying there were both, electrostatic and chemical contributions of 0.0502 V (50.2 mV).¹⁹ We also noticed that upon addition of rice wine, bubbles were visible on the Zn electrode surface, suggesting Zn metal had oxidized and dissolved, leaving behind 2 electrons which are collected by protons in solution to form H_2 gas.

Voltage loss in a voltaic array

As per the activity discussion, one optional topic is the introduction of a voltage drop in a multi-cell electrochemical device using already measured voltage values. For such a purpose, we can use a single Zn-Cu voltaic cell measured voltage value and then project the voltage value (E_{cell}) for a Zn-Cu 6-cell voltaic array. Hence, when copper sulphate was used as the electrolyte, we expected a voltage value of $E_{\text{cell}} = 1.056 \text{ V/cell} \times 6 \text{ cells} = 6.336 \text{ V}$. This value was then compared to the experimental voltage value of 6.20 V , showing a voltage loss of 0.136 V (136 mV).

Similarly, when rice wine was used as the electrolyte, we found that based on a single Zn-Cu voltaic array voltage value, $E_{\text{cell}} = 0.813 \text{ V/cell} \times 6 \text{ cells} = 4.88 \text{ V}$ for a Zn-Cu 6-cell voltaic array. Since the experimental cell voltage for a Zn-Cu 6-cell voltaic array was 4.81 V , the comparison indicates a voltage loss 0.07 V (70 mV). The voltage losses in both instances can then be discussed with the students using the following voltage loss phenomena:

a. Ohmic voltage losses – refers to a voltage loss due to the current passing through a resistor, which in the Zn-Cu 6-cell voltaic array context corresponds to the electrical resistivity in the Zn and Cu electrodes, the internal resistance in the multipurpose meter, and the resistance created at the Zn-Cu contacts.²⁰

b. Ion migration voltage losses – refers to the migration of ions in solution towards the electrode surfaces, especially in the absence of hydrodynamic transport in the electrolytic solution.²⁰ Ion migration voltage losses are the sum of mass transfer, adsorption/desorption on the surface of the electrode, and electron transfer at the electrode ($V_{\text{ion migration}} = V_{\text{mass transfer}} + V_{\text{adsorption/desorption}} + V_{\text{electron transfer}}$).^{20, 21}

c. Kinetic voltage losses – refers to a voltage required to overcome the initial activation energy needed to trigger the redox reactions on the surface of the electrodes. This process occurs during electrostatic equilibrium, resulting in the presence of a double layer at the surface of the electrodes.²⁰

d. Diffusion voltage losses – refers to a mass transport of chemical species in solution due to a chemical potential difference (concentration gradient) near the electrode.²¹

Generally, prior knowledge, such as Ohm's law, Coulomb's law, and kinetics, accelerates the student grasp of voltage losses in electrochemical systems.

Faradaic current

A review of undergraduate chemistry texts^{18, 22-24} shows that Faradaic current is not addressed, however, students are repeatedly asked to measure the *power (J/s or watts)* of electrochemical devices, such as energy storage devices and hydrogen fuel cells. Hence, we must address Faradaic current in its basic form and the *OCP designette* can assist.

Faradaic current refers to the rate of the electrochemical reaction at the electrode/solution interface of the electroactive species of interest, and it indicates a series of steps, such as mass transfer reactions, electron transfer reactions at the interface, and chemical reactions coupled with the electron transfer process.²⁵ During a standard electrochemical reaction, current due to non-electroactive species sources is called background current, including electrolysis of impurities, electrode material, as well as charging or capacitive current.²⁵ With the exception of charging current, which is due to the presence of a double layer, the remaining background currents are also Faradaic currents. Hence, it is desirable to minimize the sources of background current or to subtract from the Faradaic current due to the electroactive species of interest whenever possible.

Mass transfer refers to the transfer of molecules from the bulk solution to the electrode surface and can take the form of diffusion, ion migration and convection.²¹ Mass transfer at the

electrode surface is described by the Nernst-Planck equation, which in one-dimension along the x axis take the following form:

$$J(x) = -D \frac{\partial C(x)}{\partial x} - \frac{zF}{RT} DC \frac{\partial \phi(x)}{\partial x} + Cv(x) \quad (13)$$

where $J(x)$ is the flux density of the species ($\text{mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$) at distance x from the electrodes surface, D is the diffusion coefficient ($\text{cm}^2\cdot\text{s}^{-1}$), $\frac{\partial C(x)}{\partial x}$ is the concentration gradient at distance x , $\frac{\partial \phi(x)}{\partial x}$ is the potential gradient, z is the charge, C is the concentration ($\text{mol}\cdot\text{cm}^{-3}$), $v(x)$ is the velocity of the solution ($\text{cm}\cdot\text{s}^{-1}$), F is Faraday constant, R is the ideal gas constant, and T is temperature in Kelvin. The flux density is then defined as the number of molecules at a unit area on an imaginary plane in a unit time. The negative sign indicates motion away while the positive sign indicates motion towards the imaginary plane. The terms on the right of equation 12 represent diffusion, ion migration, and convection mass transfer, respectively.^{20, 21}

The solution to the Nernst-Planck equation is mathematically difficult, however, it is feasible to restrict the contribution of ion migration and convection near the surface of the electrode to simplify it. For instance, we can work with a relatively high electrolyte concentration to render the ion migration term negligible. Similarly, we can carry out the activity under quiescent conditions to eliminate any forced convection and assume zero solution velocity near the surface of the electrode.

Consequently, given an electrochemical equilibrium reaction $a \text{Ox} + b \text{Red} \rightleftharpoons c \text{Ox}^+ + d \text{Red}^-$, and using a semi-empirical treatment of steady-state mass transfer to simplify the contributions to the Nernst-Planck equation, as discussed above, the observed cathodic current can be expressed only by the diffusion mass transfer contribution at the electrode surface, a phenomenon driven by a concentration gradient (chemical potential). Hence, the solution can be as follows:

$$i_c = nFAm_{red}(C_{red}^b - C_{red}^i) \quad (14)$$

where i_c is cathodic current, n is the stoichiometric number of moles transferred in the electrochemical reaction, F is Faraday's constant, A is the surface area immersed in solution, m_{red} is the mass transfer coefficient for *Red* species, C^b is the bulk concentration of *Red* species and C^i is the initial concentration at distance $x = 0$ from the surface of the electrode of *Red* species. Note, that when the bulk concentration of the *Red* species is much larger than the initial concentration at the electrode surface ($C^b \gg C^i$), the Faradaic current equation simplifies to:

$$i_c = nFAm_{red}C_{red}^b \quad (15)$$

And since n , F and m_{red} are constants, we can rewrite equation 15 as:

$$j = \frac{i_a}{A} = kC_{red}^b \quad (16)$$

where $k = nFm_{red}$ and we can clearly see that Faradaic current density ($j = i/A$) is linearly proportional to C_{red}^b ($[Cu^{2+}]$), provided that temperature and solution viscosity are kept constant.

SUMMARY

The *OCP Designette* consists of a Zn-Cu voltaic array incorporating elements of *design thinking* to reinforce a series of pivotal electrochemical concepts, such as identification of redox reactions, application of the Nernst equation, and measuring Faradaic current dependency on electrolyte concentration. In addition, the designette can address common student misconceptions about the corresponding electrochemical reactions at the terminals, electrostatic and chemical potential contribution to the Nernst equation, and the origins of an observed voltage loss across a voltaic array.

ASSOCIATED CONTENT

Supporting Information. List of materials and tools for the cell potential designette; Information on measuring current density and voltage values; and a Design brief template (DOCX).” This material is available via the internet at <http://pubs.acs.org>

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