Inexpensive Alkaline Fuel Cell for Introductory Chemistry Classes

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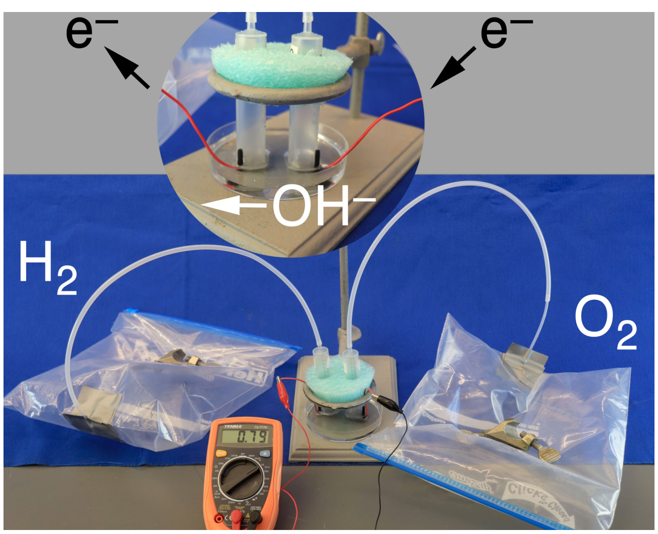
ABSTRACT

Chemical energy storage and use is a critical part of a sustainable world. In this laboratory experiment students construct and use an inexpensive hydrogen fuel cell to power a calculator or a clock. The reusable cells are prepared from plastic syringes and a nickel mesh that is coated with a palladium metal catalyst by electroless deposition. One syringe is filled with hydrogen gas and the other with air. A sodium hydroxide solution is the bridge between the cells. Students measure the produced voltage and combine two fuel cells to power electronics requiring 1.5 V. A goal is for students to make the connection between theory and practice for symbolic representations of redox reactions and their macroscopic and atomic/molecular interpretations.

GRAPHICAL ABSTRACT



KEYWORDS

First-Year Undergraduate/General, Laboratory Instruction, Analogies/Transfer, Hands-on Learning/Manipulatives, Inquiry-Based/Discovery Learning, Catalysis, Electrochemistry, Electrolytic/Galvanic Cells/Potentials, Oxidation/Reduction

INTRODUCTION

The use of fossil fuels is decreasing while wind and solar energy supplies are increasing. Since it is not always sunny or windy, these renewable forms of power generation are intermittent and require energy storage. One energy storage method is to electrolyze water to create hydrogen and oxygen gas.[1,2] These gases can then be used in fuel cells to produce power through carbonless means with water as the only product. Compared to internal combustion engines, fuel cells are more efficient and avoid NO_x production. In this shift for the future, the chemistry that occurs in fuel cells becomes an opportunity to illustrate the role of catalysts and to introduce basic redox chemistry.[3-5]

Fuel cells are redox devices that use a fuel, such as hydrogen, and an oxidant, such as oxygen, to produce electrical energy without combustion.[6-12] Instead of directly combining the fuel and oxidant, the fuel is oxidized at one electrode and the oxidant is reduced at another electrode. The electrons being transferred in the overall redox reaction can be made to travel through a wire between the cells if ion conduction through a salt bridge or membrane is used to complete the circuit. A catalyst, such as palladium, can be used to increase the rate of reaction. A fuel cell will continue to generate electricity as long as it is supplied with fuel and oxidant.

Ion transport can limit fuel cell performance. Much research has been done using proton exchange membranes (frequently a fluorinated polymer with sulfonic acid sites) to selectively conduct hydrogen ions or solid oxides (frequently a high temperature sample of lanthanum-doped zirconium dioxide) to conduct oxide ions.[10-12] An aqueous KOH solution absorbed in an asbestos sheet can also be used for ion transport between the cells. Such an alkaline cell was used by NASA in the Apollo moon landings and in the Space Shuttle.[7,13]

This experiment describes a reusable, low-cost alkaline fuel cell. Once the cells have been created, either as part of a longer experiment or prepared beforehand, they can be set up and tested within an hour-long class period. Similar experiments have been described in this *Journal* using Nafion™ as the membrane,[3] alcohol as the fuel,[3,14] or the reaction of Fe(III) and Zn on a cation exchange resin[15] or an enzyme mediated glucose oxidation.[16] Other experiments have used $NaBH_4 + H_2O$, or Zn + HCl, or $MgH_2 + H_2O$ as the hydrogen source[3,17] or Cl_2(aq) produced during electrolysis as the oxidant.[18] Hydrogen fuel cell model cars are commercially available and have been used in teaching laboratories,[5] but present costs are at least $100 USD each. Our cell uses electroless deposition of palladium on nickel as the catalyst and does not require electrolytic reduction of platinum. It does require a tank of hydrogen gas. The initial one-time cost of this fuel cell is under $4 USD with the largest expense being the disposable syringes, and one electrode can be refreshed for $0.05 USD of palladium. See the supporting information for a cost breakdown. Because of the inherent carbonless energy production, this experiment would be suitable for courses with an environmental focus as well as chemistry courses.

EXPERIMENTAL OVERVIEW

This procedure was adapted from Projekt Brændselscellen (see acknowledgements) where students assembled their own fuel cells from medical supplies. Our procedure replaces urine bags with slider storage bags, plastic droppers, and matching tubing to contain the gases as seen in Figure 1. These bags are then used to supply hydrogen gas and air in the assembly shown in Figure 2.

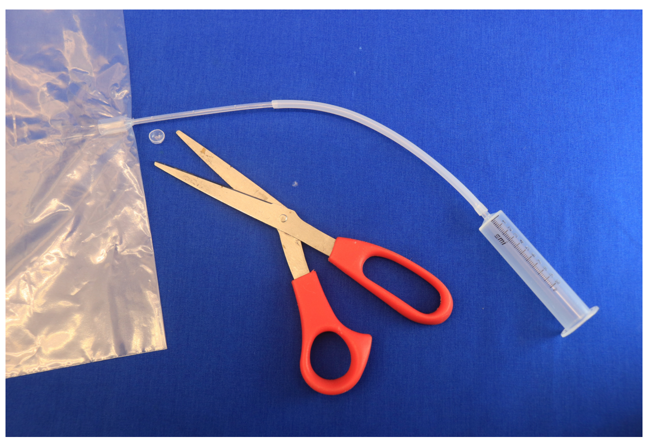


Figure 1: Gases are stored in a slider storage bag and connected using 3mm ID x 5mm OD polyethylene tubing that matches both a thin stem disposable transfer pipet with the top cut off and the luer-slip syringe tip.

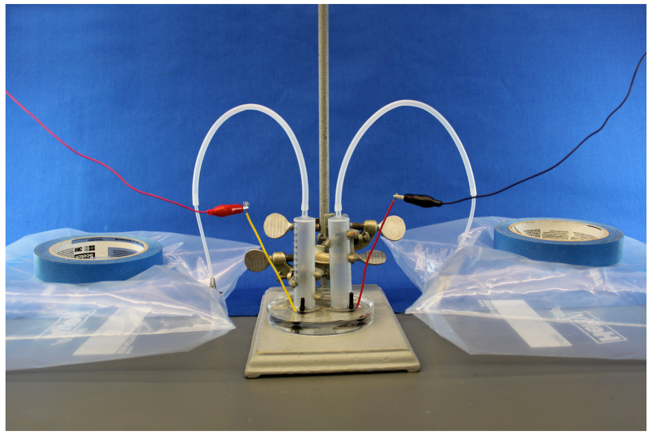


Figure 2: The assembled student fuel cell. The electrodes are held in place by a ring stand and clamps adjusted so that the mesh is located at the gas and hydroxide solution interface. Constant pressure is maintained by resting something on the bags (a roll of tape is shown in the photograph.) The wires extending beyond the image are connected to a voltmeter.

The fuel cell operates on two electrode reactions (Scheme 1) with a hydroxide solution for ion transport between the cells.

$$2\ H_2(g) + 4OH^-(aq) \xrightarrow{Pd/Ni} 4e^- + 4\ H_2O \qquad E° = 0.828$$
$$O_2(g) + 4\ e^- + 2\ H_2O \xrightarrow{Pd/Ni} 4\ OH^-(aq) \qquad E° = 0.401$$

$$2\ H_2 + O_2 \rightarrow 2\ H_2O \qquad E° = 1.229V$$

Scheme 1. E° values for electrode reactions under standard conditions of 25°C, 1 M solution concentration and 1 atm gas partial pressure. 1 M NaOH would be pH 14.

Hydrogen gas is oxidized at the anode to produce water. Oxygen gas is reduced at the cathode to produce hydroxide ion. The overall reaction produces water and has a theoretical maximum voltage of 1.229V for 1 atm of oxygen or 1.219V for 0.21 atm of oxygen in air. In NASA applications, the produced water was vacuum distilled and used as a potable water supply.[13]

For the initial pre-assembly, see the cell pre-assembly directions and images in the supporting information. A 10 mL plastic syringe is melted onto a Monel 400 nickel/copper fine mesh. The alloy is about two-thirds Ni and corrosion resistant to acid, alkalis, and seawater.[19] This mesh can be coated in palladium by submerging the mesh in a solution of 0.010 M $PdCl_2$ for four minutes. This electroless deposition is shown to be successful by SEM and EDS analysis of the uncoated and coated mesh as seen in Figure 3. The same 1.5 mL of solution can be used to coat four or five cells (see Figure 4.)

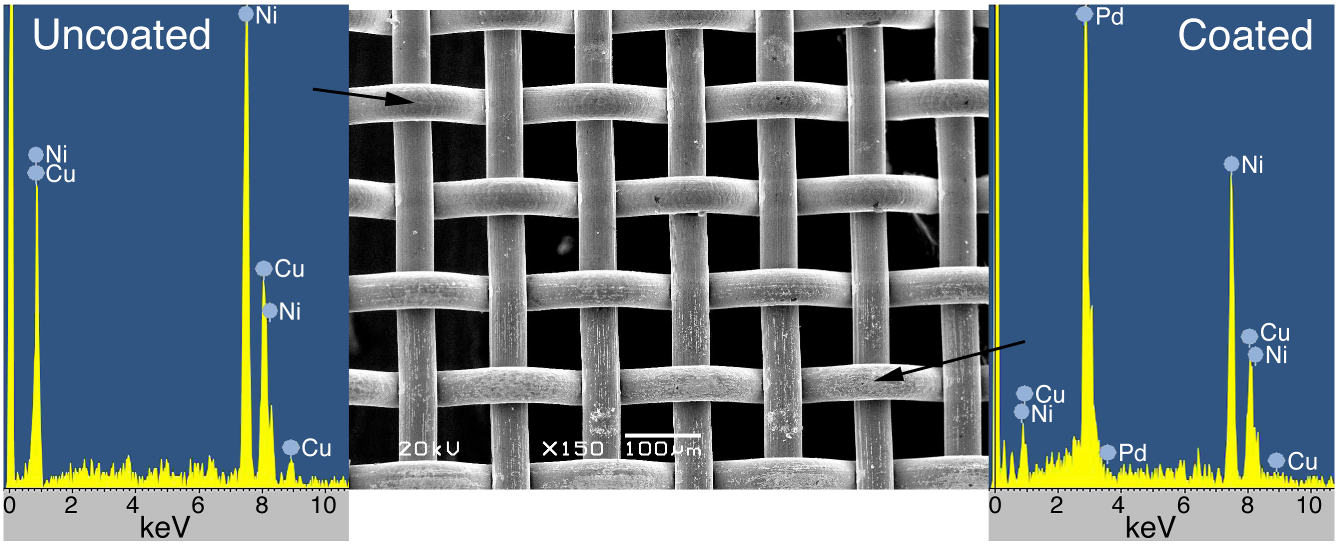


Figure 3. Uncoated nickel/copper mesh (top portion of the SEM image) shows energy dispersive x-ray spectroscopy (EDS) peaks at left corresponding to copper and nickel. Electroless deposition of palladium on the mesh (bottom portion of the SEM image) is confirmed by the appearance of palladium in the EDS spectrum at right. EDS vertical scale is 118 counts for both.

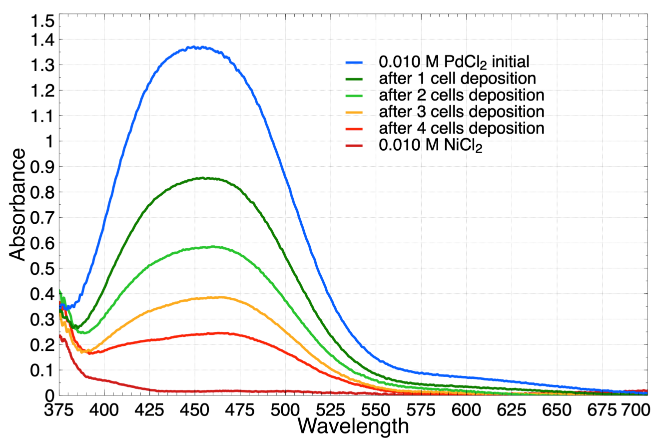


Figure 4: Visible spectrum of a $PdCl_2$ coating solution after successive electroless depositions of palladium on a nickel mesh electrode. All electrodes have approximately the same mesh area. Some solution is lost with each coating but the 1.5 mL of 0.010 M $PdCl_2$ solution can be used at least four times. For reference, the spectrum of 0.010 M $NiCl_2$ is also shown indicating that the less strongly colored $NiCl_2$ product does not interfere with observing the remaining $PdCl_2$ color.

A pilot hole is melted through the flange of the syringe using a hot paper clip, the hole is drilled to size and threaded, and a plastic bolt is added to attach a wire to the mesh. Two of these pre-assemblies are used, one for the anode and another for the cathode. Students can prepare this step themselves or re-use previous samples to construct a fuel cell.

A thin stem disposable transfer pipet with a portion of the bulb tip removed is used to make a connector between plastic tubing and slider storage gallon bags containing hydrogen or atmospheric oxygen gas. (See Figure 1 and Figure S2.) The syringe assemblies are clamped or supported above a Petri dish as in Figure 2. See the graphical abstract or Figure S1 for another method of support using two-hole closed-cell foam stoppers carved from packing materials. The 3mm ID x 5mm OD polyethylene tubing, pre-stretched by forcing it over the tip of a spare syringe, is slid onto the luer-slip syringes and the filled bags slightly depressed in order to flush out the syringes. The volume of gas in the bag needs to be decreased at least as much as the volume of the syringe. *Flushing the syringe with hydrogen is important and skipping this step is one of the main causes of cells not working.*

A Petri dish is filled with enough 1.0 M NaOH to just barely reach the coated mesh. The head of the plastic screw serves as a spacer and permits lowering the cell to the bottom of the dish without blocking the mesh. It is important that the mesh is located at the interface between the hydroxide solution and the gas. See Scheme 1 where both gas and hydroxide must be in contact with the Pd coated mesh. Wires are connected to a voltmeter to measure the cell's voltage. Combining two of these fuel cells in series can power a clock (see Figure 5 and Figure S3), a calculator, or a piezoelectric buzzer. If 0.10 M NaOH is used instead of 1.0 M NaOH, the same voltage is produced but the power generated is only enough to run a calculator and not the clock.

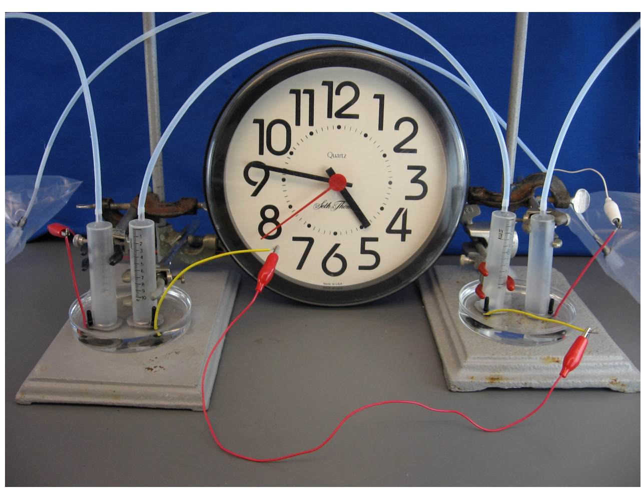


Figure 5: Two cells connected in series to provide enough voltage and current to power a clock.

The electrodes can be rinsed with water and stored for reuse in later classes. If the performance of the electrodes drops, the mesh can be recoated to refresh as needed. Over a period of five years, we have recoated after about every 5 uses when using 0.06 M $PdCl_2$ for the depositions but the SEM images (see Figure S4) when using our now recommended 0.010 M $PdCl_2$ show less flaking and we expect longer life at lower cost.

HAZARDS

Hydrogen gas is flammable so keep it away from flame. Gas cylinders should be equipped with the correct regulator and be firmly secured to prevent tipping. Hydrogen should be dispensed by someone who is familiar working with compressed gas.

Wear safety glasses since sodium hydroxide is corrosive and can severely damage eyes. Chemical gloves should be used to prevent prolonged or repeated skin contact with 1.0 M NaOH.

During preassembly, a Bunsen burner is used for heating a paper clip to create a pilot hole so be cautious around the open flame. A power drill can be dangerous so supporting the syringe in a jig while drilling is recommended; a 2x4 block of wood with a syringe-sized hole is an inexpensive support.

Palladium chloride is a toxic salt if ingested and should be disposed of properly.

RESULTS AND DISCUSSION

These cells typically reach a voltage between 0.75V and 0.85V within minutes if the palladium coated mesh is at the gas-solution interface and if the syringe has been flushed with hydrogen. Achieving these two requirements takes some students longer than others. The presence of the palladium catalyst decreases the amount of time needed for the fuel cell to reach this voltage; the nickel mesh on its own takes significantly longer (tens of minutes). A slowly increasing voltage may be indicative of a need to recoat.

Coating the mesh with platinum by electrochemical reduction[3] gave similar results to the palladium coating but is more expensive and requires more time for the pre-assembly.

When a fuel cell measures between 0.75V and 0.85V, that group is encouraged to join together with another group measuring a similar voltage. When two such cells are connected in series (“a fuel cell stack”), the requisite 1.5V is produced that can power a clock, a calculator, or a piezoelectric buzzer. Using a gallon of gaseous hydrogen for each fuel cell, the stack runs for about four hours, as determined by letting the clock run until it stops.

A typical coal-fired power plant is about 33% efficient and a natural gas power plant is about 42% efficient at turning chemical energy into electricity.[20] Higher efficiencies can be achieved when use is made of the waste heat. Fuel cells are about 60% efficient.[10] Comparing the observed voltage of this fuel cell with the theoretical voltage gives 0.80/1.22 = 65% voltage efficiency. Operating the fuel cell under load would give a lower thermodynamic efficiency. There are many possible causes for observing less than the theoretical voltage including ohmic losses and concentration gradients.[6,11]

Alkaline electrolytes are sensitive to carbon dioxide exposure and the formation of carbonate precipitates that can block the interface when their solubility is exceeded.

$$CO_2(g) + 2\ OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O$$

$$2\ Na^+(aq) + CO_3^{2-}(aq) \rightarrow Na_2CO_3(s)$$

Some alkaline fuel cells use KOH rather than NaOH because the solubility of K_2CO_3 is larger than that of Na_2CO_3.[6] We have not found carbonate formation to be a problem during a lab period, so the less expensive NaOH is used instead of KOH.

STUDENT LEARNING

A pedagogically insightful realization is that chemists use three different languages to describe or explain: an atomic/molecular language concerning the arrangement or motion of atoms, a macroscopic language concerning observable properties of matter, and a symbolic language of formulas and equations that can represent either of the other two languages.[21-23] Electrochemical concepts can be difficult because the use of all three languages is expected.[24] A goal of this experiment would be for students to make the connection between symbolic representations of redox reactions happening at the catalyst as shown in Scheme 1, the atomic language for the movement of electrons in the wires and the movement of ions in solution, and the macroscopic positioning of the solid palladium catalyst in contact with both liquid and gas. Students were asked to report the function of each part of the fuel cell by following the path of the charge carriers through the complete circuit. Almost all could follow the electrons in the wires but some had trouble conceptualizing the hydroxide ions traveling between the electrodes in the solution to complete the circuit. A known electrochemical misconception is a belief that electrons travel through an electrolyte solution.[23-29]

During pre-assembly, cells were often ruined by a wandering drill bit when trying to drill through the finely-woven metal mesh. This problem was solved by using a hot paperclip to quickly melt through the plastic to prepare a pilot hole. Once we had enough cells pre-assembled we have used those cells repeatedly. Most students were able to produce a working fuel cell from the pre-assembly syringes.

We do this experiment concurrently with classwork on clean energy. Our students have previously measured heats of combustion by soda can calorimetry[30] and performed bond energy calculations on common fuels to illustrate that it takes energy to break bonds and that energy is released when bonds are formed. This experiment serves as our introduction to redox chemistry. Production of energy from hydrogen without combustion was new to most students. They gained an appreciation that the volume of hydrogen required to accomplish useful work was large.

If students are familiar with the Nernst equation, an interesting question is to calculate the expected voltage difference if pure oxygen was used instead of air or the effect of changing the hydroxide concentration from the 10 M KOH used by NASA.

SUMMARY

An inexpensive reusable hydrogen fuel cell is created from slider storage bags, syringes, a nickel-palladium catalyst and a sodium hydroxide solution as an ion membrane. Hydrogen gas is required to operate the fuel cell. Students should be able to make the connection between theory and practice for the reactions shown symbolically in Scheme 1 with their macroscopic and atomic/molecular interpretations. By powering a calculator or clock, students see tangible examples of the potential that fuel cell technology has in the future.

Associated Content

Supporting Information

Complete experimental protocol including student directions, a materials list and pre-assembly directions, laboratory questions and answer key, additional figures, and a cost breakdown.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Dinga, G. P. Hydrogen: the ultimate fuel and energy carrier. *J. Chem. Educ.* **1988**. *65(8)*, 688. DOI: 10.1021/ed065p688.
2. Roffia, S.; Conciallni, V.; Paradisi, C. The Interconversion of Electrical and Chemical Energy: The Electrolysis of Water and the Hydrogen-Oxygen Fuel Cell. *J. Chem. Educ.* **1988**. *65(8)*. 725-726. DOI: 10.1021/ed065p725.
3. D'Amato, M. J.; Lux, K. W.; Walz, K. A.; Kerby, H. W.; Anderegg, B. Introducing New Learning Tools into a Standard Classroom: A Multi-Tool Approach to Integrating Fuel-Cell Concepts into Introductory College Chemistry. *J. Chem. Educ.* **2007,** *84*, 248-252. DOI: 10.1021/ed084p248
4. Shultz, M. J.; Kelly, M.; Paritsky, L.; Wagner, J. A Theme Based Course: Hydrogen as the Fuel of the Future. *J. Chem. Educ.* **2009**, *86(9)*, 1051-1053. DOI: 10.1021/e086p1051.
5. Young, G. L; Rozelle, R. B. Fuel Cells. *J. Chem. Educ.* **1959**, *36(2)*, 68. DOI: 10.1021/ed063p68

6. Cifrain, M.; Kordesch K. Hydrogen/oxygen (Air) fuel cells with alkaline electrolytes. *Handbook of Fuel Cells – Fundamentals, Technology and Applications*; Vielstich, W.; Lamm, A.; Gasteiger, H. A., Eds.; Volume 1: Fundamentals and Survey of Systems; John Wiley & Sons: Chichester, 2003; pp 267-280. ISBN: 0-471-49926-9
7. Sammells A. F. Fuel cells and electrochemical energy storage. *J. Chem. Educ.* **1983**, *60(4)*, 320-324. DOI: 10.1021/ed060p320.
8. Weissbart J. Fuel cells – Electrochemical converters of chemical to electrical energy. *J. Chem. Educ.* **1961**, *38(5)*, 267. DOI: 10.1021/ed038p267.
9. U. S. Department of Energy. Fuel Cells. https://www.energy.gov/sites/prod/files/2015/11/f27/fcto_fuel_cells_fact_sheet.pdf (accessed Mar 7, 2021.)
10. Haile, S. M. Materials for fuel cells. *Materials Today* **2003** *6(3)*, 24-29. DOI: 10.1016/S1369-7021(03)00331-6. https://www.sciencedirect.com/science/article/pii/S1369702103003316
11. Ramani, V. Fuel Cells. *The Electrochemical Society Interface,* Spring 2006, 41-44. https://www.electrochem.org/dl/interface/spr/spr06/spr06_p41-44.pdf
12. National Aeronautics and Space Administration (NASA). Fuel Cell Power Plants (2002). https://web.archive.org/web/20200229065410/https://spaceflight.nasa.gov/shuttle/reference/shutref/orbiter/eps/pwrplants.html Accessed March 7, 2021.
13. Klara, K.; Hou, N.; Lawman, A.; Wu, L.; Morrill, D.; Tente, A.; Wang, L. Developing and Implementing a Simple, Affordable Hydrogen Fuel Cell Laboratory in Introductory Chemistry. *J. Chem. Ed.* **2014**, *91*, 1924-1928. DOI: 10.1021/ed4007875.
14. Zerbinati, O.; Mardan, A.; Richter, M. M. A Direct Methanol Fuel Cell. *J. Chem. Educ.* **2002**, *79(7)*, 829-831. DOI: 10.1021/ed079p829.
15. Rawat, J. P.; Ansari, A. A. Redox Ion Exchanger Fuel Cell. *J. Chem. Educ.* **1990**, *67(9)*, 808-809. DOI: 10.1021/ed67p808.
16. Ge, J.; Schirhagl, R.; Zare, R. N. Glucose-Driven Fuel Cell Constructed from Enzymes and Filter Paper. *J. Chem. Educ.* **2011**, *88*, 1283-1286. DOI: 10.1021/ed100967j.
17. Bailey, A.; Andrews, L.; Khot, A.; Rubin, L.; Young, J.; Allston, T. D.; Takacs, G. A. Hydrogen Storage Experiments for an Undergraduate Laboratory Course – Clean Energy: Hydrogen/Fuel Cells. *J. Chem. Educ.* **2014**, *92*, 688-692. DOI: 10.1021/ed5006294.
18. Shirkhanzadeh, M. Thin-Layer Fuel Cell for Teaching and Classroom Demonstrations. *J. Chem. Educ.* **2009**, *86(3)*. 324-329. DOI: 10.1021/ed086p324.
19. McMaster-Carr. Acid resistant 400 Nickel Wire Cloth. https://www.mcmaster.com/9225T321/ (accessed Mar 7, 2021.)
20. The National Academy of Sciences. Our Energy Sources, Natural Gas. http://needtoknow.nas.edu/energy/energy-sources/fossil-fuels/natural-gas/ (accessed Mar 7, 2021.)
21. Johnstone, A. H. The development of chemistry teaching: A changing response to changing demand. *J. Chem. Educ.*, **1993**, *70(9*), 701–705. DOI: 10.1021/ed070p701

22. Bunce**,** D. M. Enhancing and Assessing Conceptual Understanding. Chapter 7 pp 107-119 in Orna, M. V. Sputnik to Smartphones: A Half-Century of Chemistry Education, *ACS Symposium Series*; American Chemical Society: Washington, DC, 2015. DOI 10.1021/bk-2015-1208.ch007
23. Alexandra R. Brandriet, A. R.; Bretz, S. L. The Development of the Redox Concept Inventory as a Measure of Students' Symbolic and Particulate Redox Understandings and Confidence. *J. Chem. Educ.*, **2014**, *91(8*), 1132-1144. DOI: 10.1021/ ed500051n
24. Tien L.T., Osman K. Misconceptions in Electrochemistry: How Do Pedagogical Agents Help? in Karpudewan M., Md Zain A., Chandrasegaran A., Eds. *Overcoming Students' Misconceptions in Science*. Springer (2017) DOI: 10.1007/978-981-10-3437-4_6
25. Garnett, P.L.; Treagust, D.F. Conceptual Difficulties Experienced by Senior High School Students of Electrochemistry: Electrochemical (Galvanic) and Electrolytic Cells. *J. Res. Sci. Teach.*, **1992**, 29, 1079. DOI: 10.1002/tea.3660291006
26. Ogude A. N.; Bradley, J. D. Ionic Conduction and Electrical Neutrality in Operating Electrochemical Cells. *J. Chem. Educ.*, **1994**, 71, 29-34. DOI: 10.1021/ed071p29
27. Sanger, M. J.; Greenbowe, T. J. Students' Misconceptions in Electrochemistry Regarding Current Flow in Electrolyte Solutions and the Salt Bridge. *J. Chem. Educ.*, **1997**, *74(7*), 819-823. DOI: 10.1021/ed074p819
28. Huddle, P. A.; White, M. D.; Rogers, F. Using a teaching model to correct known misconceptions in electrochemistry. *J. Chem. Educ.*, **2000**, *77(1)*, 104 -110. DOI: 10.1021/ed077p104
29. De Jong, O.; Treagust D. The Teaching and Learning of Electrochemistry, in *Chemical Education: Towards Research-Based Practice*; Gilbert, J. K., De Jong, O., Rosaria, J., Treagust, D., Van Driel, J. H., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002; pp 317–337.
30. For examples see Soda Can Calorimeter: Energy Content of Food, Flinn Scientific, https://www.flinnsci.com/api/library/Download/f9560a5fc7ef4a6b8f4598fea30626eb or Calorimetry: Measuring the Energy in Food, Carolina Biological Supply Company, https://www.carolina.com/images/teacher-resources/essentials/food-calorimetry/Calorimetry-Measuring-Teacher.pdf