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Microscale electrochemical cell using plaster ($CaSO_4$) as liquid junction

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Abstract: A microscale apparatus for electrochemical cell in which plaster ($CaSO_4$) was used as liquid junction has been developed. A glass tube (0.5 cm ID x 5.0 cm) was used to prepare each half-cell. The potentials of the resulting galvanic cells were measured by a multimetre and were compared to those of the galvanic cells in which agar was used as liquid junction. It was found that the potentials produced by the galvanic cells with plaster as liquid junction are not significantly different from those of the cells with agar as liquid junction and close to the theoretical values. In addition, when the developed apparatus was used for the study of electrolysis of potassium iodide solution, it was found that the electrolytic cell made from the microscale apparatus with plaster liquid junction can distinctly separate the reactions occurring at the anode and the cathode. Moreover, the lifetime of the plaster liquid junction is much greater than that of the agar liquid junction.

Keywords: plaster, liquid junction, electrochemical cell

Introduction

Microscale chemistry is a teaching method working with small quantities of chemical substances. It has been widely used both at school and at university levels. The method can be applied to many types of experiments. Pioneering development in this area was carried out by Grey and El-Marsafy in Egypt, and Thompson in the US, among others [1]. There are two main strands of the modern approach [1]. One is based on the idea that many of the experiments associated with general chemistry (acids and bases, oxidation and reduction, electrochemistry, etc.) can be carried out in apparatus much simpler (injection bottles, dropper bottles, syringes, well plates, plastic pipettes) and therefore cheaper than the traditional glassware in the laboratory, thus enabling expansion of laboratory experiences for students in large classes, as well as introduction of laboratory work into institutions too poorly equipped for standard-type equipment. A further application of this idea is to make effective chemical experiments possible for developing countries with schools that lack technical services (electricity, running water) taken for granted in many places. The other strand of idea is the introduction of this approach into synthetic work, mainly in organic chemistry.

There have been many publications [e.g. 2-8] which concern with microscale laboratory. In this work, a microscale apparatus for electrochemistry has been developed. Electrochemistry deals with the production of electricity by chemical reactions (galvanic cell) and with the chemical changes produced by electric current (electrolytic cell). Electrochemical processes require some methods of introducing a stream of electrons into a reacting chemical system and some means of withdrawing electrons. In most applications, the reacting system is placed in a cell and an electric current enters or exits via electrodes [9].

When two miscible aqueous solutions are contacted, they will combine and give a new solution. The way to separate them while some ions can still be transferred from one to the other is to use a liquid junction. In an electrochemical cell, when two half-cells are joined together a liquid junction or salt bridge is used to separate them. Agar has been a material widely used for the liquid junction of the electrochemical cell for many years. The salt bridge serves three functions [9]: 1) it allows electrical contact between the two solutions, 2) it prevents mixing of the electrode solutions, and 3) it maintains the electrical neutrality in each half-cell as ions flow into and out of the salt bridge.

To the best of our knowledge, the use of plaster as liquid junction has not been previously reported. Therefore, a microscale apparatus for electrochemical cells, namely galvanic and electrolytic cells, using plaster as liquid junction is developed and reported in this work, the apparatus being aimed to be used in a first year student laboratory.

Materials and Methods

Apparatus

The micro-electrochemical cell was made from two 3 mm x 5 cm glass tubes. A liquid junction was prepared by mixing 2:1 (by volume) of plaster and saturated (≈ 5 M) potassium chloride solution (Ajax Finechem, AU.) in a 50-ml beaker and stirring. The glass tubes were dipped 0.5 cm into the mixture and left to harden for about 5 minutes, then carefully pulled out. Each tube was then filled with an appropriate solution and an appropriate metal electrode was dipped into the tube. A small cylindrical-shaped vial used as cell container was modified from a capillary tube container and a cell holder was modified from the lid of a plastic bottle (Figure 1). A multimeter (model 972A, Hewlett Packard, USA) was used to measure the potential of the galvanic cell. A 9-volt battery was used as a power supply of the electrolytic cell.

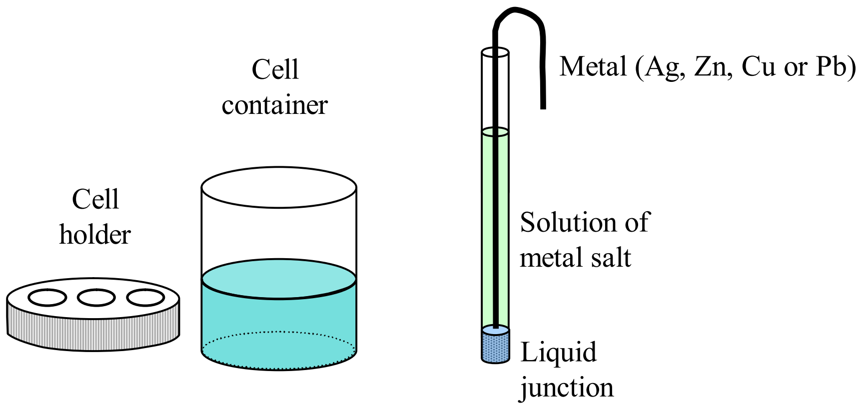

Figure 1. Apparatus used for micro-electrochemical cell

Chemicals

All solutions were prepared from laboratory grade reagents and distilled water. A 0.10 M solution of each metal salt was prepared by dissolving 0.0170 g of $AgNO_3$ (Merck, Germany), 0.0160 g of $Cu(NO_3)_2$ (Merck, Germany), 0.0331 g of $Pb(NO_3)_2$ (Merck, Germany), and 0.0189 g of $Zn(NO_3)_2$ (Merck, Germany) in a portion of water and transferring to a 100-mL volumetric flask before making up to a volume of 100 ml. A 0.1 M solution of KNO_3 (Ajax Finechem, AU) was prepared by dissolving 0.101 g KNO_3 in a portion of water before making up to a volume of 10 ml. A 0.1 M solution of KI (Ajax Finechem, AU) was similarly prepared using 0.17 g KI. Phenolphthalein and starch solution were used as indicators for testing the final products generated from each-half cell.

Study of galvanic cell

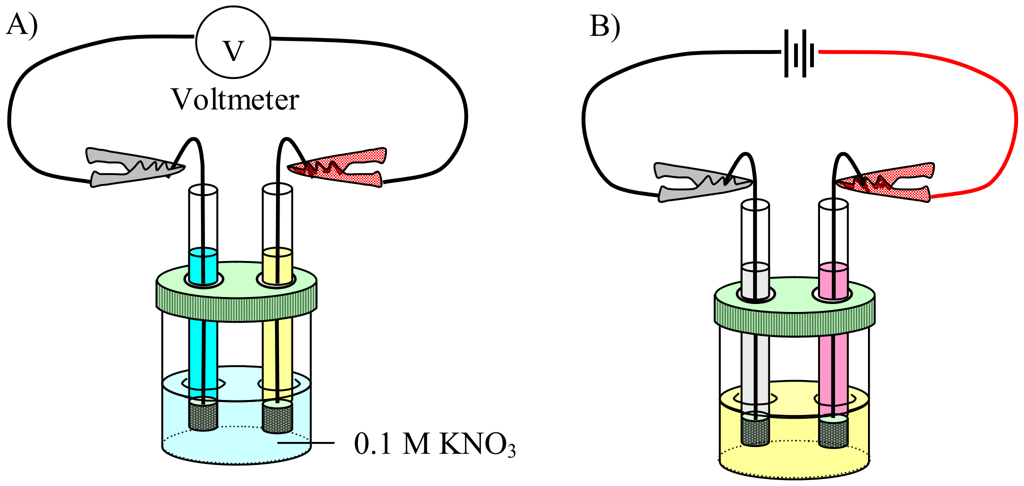

Figure 2. Setup of A) galvanic cell and B) electrolytic cell

The glass tubes with agar and plaster liquid junction were filled with a solution of a metal salt [$AgNO_3$, $Cu(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$] to about ¾ of the tube. An appropriate metal was dipped into the glass tubes and the tubes were put into the cell holder as illustrated in Figure 2A. The cell container was filled up with 1 ml of 0.1 M KNO_3 before the cell holder was placed on. The potential produced by each pair of the half-cell was measured using the multimeter.

Study of electrolytic cell

A solution of 0.1 M KI (5 mL), 2 drops of starch solution and 2 drops of phenolphthalein was placed in two glass tubes (about ¾ of the tube) with plaster liquid junction. Graphite rods were dipped into the tubes, which were inserted in the cell holder as shown in Figure 2B. The cell container was filled with 0.1 M KI (1.0 mL) before the cell holder was put in. Each half-cell was connected to a 9-volt battery. The reaction on each half-cell was observed during a period of 5 minutes.

Results and Discussions

Galvanic cell

The potential of each pair of the galvanic cells with plaster and agar as liquid junction was measured and compared to the theoretical value which was calculated from Nernst's equation as follows:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where E^0 is the standard reduction potential of each half-cell:

$$Ag^+ + e^- \longrightarrow Ag \quad E^0 = -0.76\ V$$
$$Pb^{2+} + 2e^- \longrightarrow Pb \quad E^0 = -0.13\ V$$
$$Cu^{2+} + 2e^- \longrightarrow Cu \quad E^0 = +0.34\ V$$
$$Ag^+ + e^- \longrightarrow Ag \quad E^0 = +0.80\ V$$

The results of the potential measured from different types of galvanic cell were shown in Table 1. From the results it was found that the E_{cell} values produced by the galvanic cells with plaster liquid junction and agar liquid junction were close to the theoretical values, and the relative accuracy of the average values of E_{cell} ($n = 3$) was in the range of 94.3-99.9 % and 93.6-100.1% respectively. The precision of the triplicate measurements indicated by the relative standard deviations (%RSD) of the E_{cell} values was in the range of 0.2-3.0 % and 0.4-5.8 % respectively. Furthermore, it was found that the E_{cell} values produced by both types of the galvanic cell were not significantly different by paired t-test at 95% confidence level ($t_{cal} = 0.1495$).

An electromotive force (E_{cell}) is the difference in electrode potential which can be expressed by the following equation:

$$E_{cell} = E_{cat} - E_{an} + E_j$$

E_{cat} = Potential of the cathode half-cell

E_{an} = Potential of the anode half-cell

E_j = Junction potential

Table 1. Potential of each pair of galvanic cells

Galvanic cell	E_{cell} (V)			Relative accuracy and % RSD	
	Theoretical value	Plaster junction	Agar junction	Plaster junction	Agar junction
Pb//Cu	0.466	0.465	0.466	99.9 / 3.0	100.1 / 5.8
Pb//Zn	0.637	0.614	0.598	96.3 / 2.6	93.9 / 4.6
Pb//Ag	0.925	0.894	0.895	96.7 / 1.2	96.8 / 3.0
Zn//Cu	1.103	1.079	1.080	97.9 / 0.2	97.9 / 0.4
Cu//Ag	0.459	0.433	0.430	94.3 / 2.1	93.6 / 0.4
Zn//Ag	1.562	1.508	1.509	96.6 / 0.3	96.6 / 0.4

From the equation, the important factor which affects the E_{cell} value is the junction potential. However, the results show that the E_{cell} measured from both types of the galvanic cell are not different. This indicates that the junction potentials produced by both plaster and agar liquid junction are quite small and do not affect the E_{cell} value. As a consequence, the material used in both types of liquid junction or the composition of ions in the liquid junction does not affect the E_{cell} value.

It was also observed that the plaster liquid junction was harder and more durable than the agar liquid junction. The latter was soft and easy to be penetrated by the metal wire. Besides, the former has a much longer lifetime than the latter after preparing and leaving to contact with air.

Electrolytic cell

The setup for electrolysis of 1.0 M KI solution using the microscacale apparatus for electrolytic cell is shown in Figure 3. From the result of the electrolysis it could be clearly seen that the reactions at both electrodes were different. When the circuit of the electrolytic cell was connected, at the half-cell of the anode, oxidation of the iodide ions occurred as indicated by the dark blue colour of iodine-starch complex:

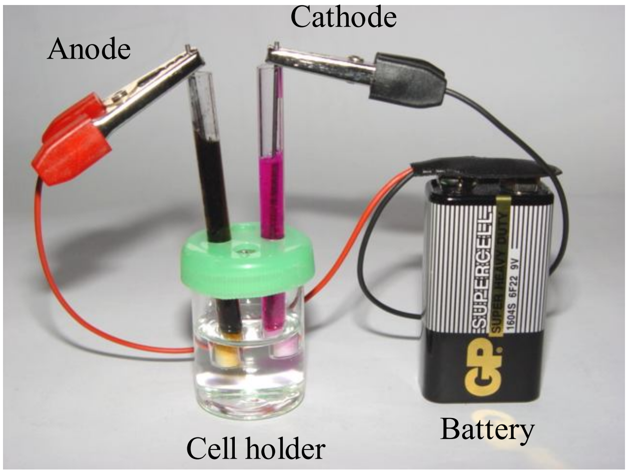

Figure 3. Electrolysis setup of KI using small scale apparatus

$$2I^- \longrightarrow I_2 + 2e^-$$

At the half-cell of the cathode, reduction of water took place and hydroxide ions were produced:

$$H_2O + 2e^- \longrightarrow OH^- + H_2$$

The generation of hydroxide ions at the cathode half-cell was indicated by the change of colour of phenolphthalein indicator, which turned to pink in the basic solution. In addition, it could be seen that some gas bubbles were also produced at the cathode half-cell.

Conclusions

A microscale apparatus for electrochemical cells has been developed and successfully applied to galvanic and electrolytic cells. It was found that the developed apparatus can reduce the consumption of the solutions involved to less than 5 mL per experiment. This apparatus is environmentally friendly as it produces less amount of waste to the laboratory. Besides, the apparatus works efficiently as the results obtained from the microscale apparatus are not different from those obtained from a large-scale one. The developed apparatus is also inexpensive and can be further applied to small-scale experiments in general chemistry for first-year undergraduate students.

Acknowledgements

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