

# The Aluminium-Air Cell: A Hands-on Approach to the Teaching of Electrochemical Technology

RICHARD K. MORRIS, GERRY A. OTTEWILL and B. DES BARKER

*Applied Electrochemistry Group, Centre for Chemistry, University of Portsmouth, St Michael's Building, White Swan Road. Portsmouth PO1 2DT, (UK).*

FRANK C. WALSH

*Electrochemical Engineering Group, Department of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY (UK); Email: f.c.Walsh@bath.ac.uk*

*It is possible for any 16+ or undergraduate student to construct an aluminium-air battery relatively easily and safely. This system makes only minimal demands on materials and financial resources but offers the potential for a comprehensive, hands-on characterisation of a modern electrochemical cell. This paper describes an experimental program and presents typical results. Investigations include measurement of anode, cathode and cell potentials and current together with an examination of the influence of electrolyte concentration. The paper also examines the effect of air-sparging at the cathode.*

## INTRODUCTION

THERE IS A NEED for modern chemistry teaching programmes to reflect the importance of electrochemical cells for technology today. Many undergraduate electrochemistry experiments approach the subject using the principles of thermodynamics. This presents to the student a highly mathematical aspect that an increasing number of students find intimidating, if not totally incomprehensible. Moreover, the use of equilibrium thermodynamics relates to idealised non-practical conditions.

Students often find electrochemistry difficult. Barral and others [1] report the interpretations of a group of 15 and 16 year old secondary students concerning the processes occurring within an electrochemical cell. It became apparent during their study that only a small percentage of students mastered such fundamental concepts as the correct direction of electron flow. Traditionally, studies of electrochemical cells employ either Daniell cells, LeClanche cells or a commercial battery such as the lead-acid cell. Martins [2] used the Daniell cell instructively, for example, to convey the thermodynamics of cells and to explore the influence of atomic packing arrangements and bond strength in electron transfer. Smith and Vincent [3, 4] have illustrated clearly various elements of essential battery chemistry including cycling, energy storage and energy and power density by means of commercial zinc-silver oxide button cells. All

experiments centred on either Daniell cells or sealed commercial batteries share the disadvantage that a 'black box' closed package conceals the internal operation of the cell.

The primitive, easily assembled, 'lemon' battery [5] provides a very direct, hands-on approach to the relationship between electrical and chemical energy. However, it is not sufficiently sophisticated to demonstrate concepts of battery science such as capacity or theoretical energy density.

Roffia and others [6] have demonstrated the interconversion of electrical and chemical energy using the coupled pair, the H<sub>2</sub>/O<sub>2</sub> fuel cell and the electrolysis of water. This is an excellent experimental programme for the experienced physical chemistry student but, in practical terms, quite demanding for the novice. In addition, the use of hydrogen-oxygen mixtures poses potential hazards that are explosive in certain proportions. Lehman, Renich and Schmidt [7] adopt a proactive, student-centred approach to battery electrochemistry, in which the student constructs a cell from an everyday aluminium beverage can and copper wire. This enables students to illustrate for themselves the use of a cell as a source of electrochemical energy. These cells are capable of generating sufficient power to drive a small motor or illuminate a lamp.

The aluminium-air system offers the opportunity to take a hands-on non 'black box' approach with a cell that is not only relatively simple but also relatively safe and inexpensive. It is unfortunate that many high performance batteries contain toxic metals. For example, the commercial car accumulator contains lead and often uses a

\* Accepted 20 October 2000.

cadmium anode to determine the transport number of  $H^+$  in HCl while commercial button cells often contain mercury. Coupled with the possible chemical hazards is the expensive nature of many electrodes.

Use of the aluminium-air cell used with a saline electrolyte addresses all of these problems. It is inherently safe, fabricated from aluminium and metal and contains a safe electrolyte. The electrodes are easy to handle and alleviate the difficulty of instrumenting a commercial electrolyte with a reference electrode. By instrumenting the cell itself with an additional set of reference electrodes the program also avoids the 'black box' problem. Since it requires only aluminium, metal and air for the electrodes and a saline (or sodium hydroxide) electrolyte, none of the aluminium-air system components is expensive. Additionally, commercial battery systems have a fixed interelectrode distance that offers no possibility of change. In an open-topped aluminium-air cell, easy variation of the interelectrode separation enables the student to study its relationship to the cell potential.

Finally, introduction to the student of the use of an air electrode becomes possible using the aluminium-air system. This is an important gas diffusion electrode commonly used in certain fuel cell and electrochemical sensor applications.

The original development of this work began as a project for one student, a 4th year BSc Applied Chemistry student and for use in corrosion education short courses. It is now being introduced to 2nd year Chemical Engineering students taking practical classes in Electrochemical Technology, where students work in small groups, (typically 3 students per group). The experiment runs for 3 hours.

Short course delegates in the areas of electrochemical technology, fuel cells and corrosion protection have appreciated the simplicity of the system. Undergraduate students report favourably on the simplicity of the cell and instrumentation construction. Constructive comments on the advantages of a 'pre-wired cell' enabled the update of the experimental arrangement.

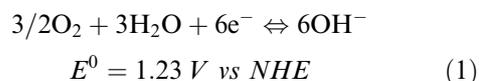
### METAL-AIR CELLS

A metal-air cell comprises a metal anode, an air cathode and an aqueous electrolyte. The use of an air cathode leads to a high theoretical energy density, as shown:

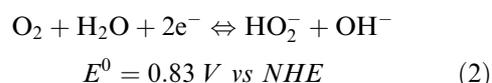
1. Zn-air: around  $100 \text{ J kg}^{-1}$
2. Al-air: with a saline electrolyte— $100 \text{ J kg}^{-1}$
3. Al-air: with a sodium hydroxide electrolyte— $360 \text{ J kg}^{-1}$

These compare very favourably with the  $30 \text{ J kg}^{-1}$  average obtained from a lead-acid cell. The cathode reaction is an oxygen reduction reaction. The air electrode comprises a conducting component that brings relatively unreactive oxygen and the electrolyte into contact with a catalyst, typically

carbon or silver. Use of a porous, hydrophobic membrane such as PTFE prevents leakage of electrolyte. Atmospheric oxygen diffuses into the electrolyte through the cathode material (thickness 0.4mm). Oxygen reduction then occurs within the porous structure of the cathode:



Although equilibrium could theoretically occur at 1.23 V, measurement in practice reveals a potential of around 1.00 V, which reduces further due to loss of voltage through polarisation. The observed voltage loss occurs, in part, because the electrode process is not exclusively direct oxygen reduction but also involves a two step process proceeding by way of a peroxide intermediate:



The peroxide species decomposes at the electrode surface to give a hydroxyl ion and oxygen:



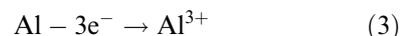
The observed potential of 1.00 V, i.e., 0.83–1.23 V, indicates the simultaneous occurrence of reactions (1) and (2).

Formation of either metal ions or metal oxide in solution is possible through electrochemical oxidation of the metal anode of a metal-air cell. Generally, a metal anode gives the theoretical standard potential of the metal on open circuit and then polarises when current is drawn. Although polarisation of the air cathode does not vary with time, polarisation of the anode increases as discharge continues.

The electrolyte serves as an ionic conductor, as are aqueous electrolytes, which are non-volatile and stable in contact with air.

### THE EXPERIMENTAL ALUMINIUM-AIR CELL

Although the aluminium-air cell was first developed by Zaromb [8], (see Fig. 1a), they are now marketed by Alupower Inc., at Bernardsville, New Jersey, USA. The anode is of aluminium alloy with the approximate composition, 99% aluminium (by weight) plus magnesium, tin and gallium at 0.6, 0.1 and 0.04 wt%, respectively. Dissolution of aluminium metal occurs at the anode:



The air cathode is a reactive layer of carbon contained between a nickel grid current collector and a porous, hydrophobic PTFE film that serves to prevent leakage of electrolyte. This results in a three-phase contact electrode. Gas, liquid and

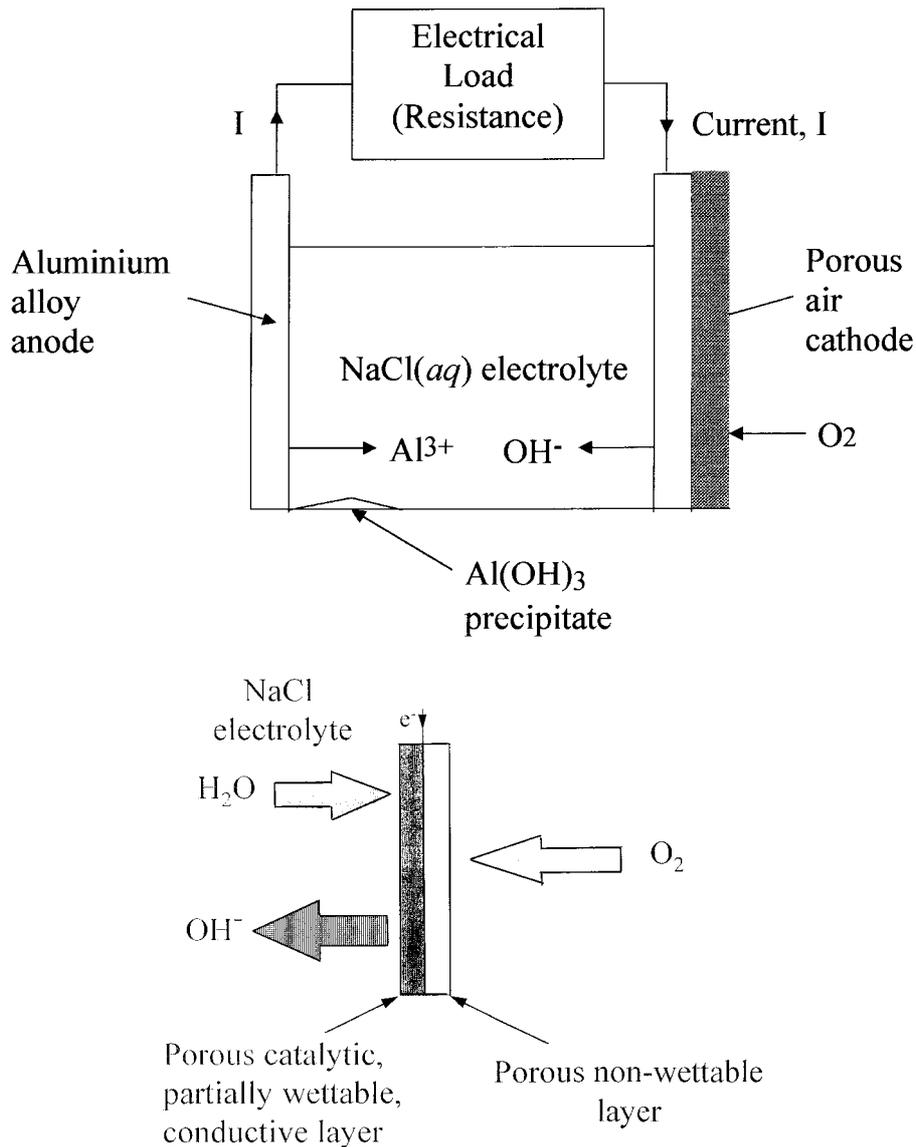


Fig. 1. The aluminium-air cell. a) the essential components of the cell and the species involved in the electrode reactions; b) the structure of the porous air cathode.

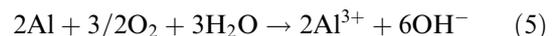
solid phases are all in contact as illustrated schematically in Fig. 1b.

The electrolyte (except when changed specifically to investigate the effects of composition) is aqueous sodium chloride (3 wt%). A perspex box of rectangular cross-section designed to give an interelectrode separation of 45mm contains the entire system, which uses silver or silver chloride reference electrodes. After gentle abrasion, immersion of the silver wire in concentrated nitric acid took place for about 30 seconds, followed by thorough rinsing with doubly distilled water. Immersion of a silver wire (the anode) in hydrochloric acid ( $0.1 \text{ mol dm}^{-3}$ ) using a platinum cathode achieves chloridation of the silver electrode. A current of 2 mA for 30 minutes enables the process of electrolysis:



to take place and the finished electrode is rinsed with doubly distilled water. One electrode is placed as close as possible to the anode, (but not touching), and the other as close as possible to the cathode. A pipette placed at the cathode allows the use of a pump to pass air over it.

Add reaction equations (1) and (3) to obtain a simplified overall cell reaction:



The type of electrolyte used, NaCl or NaOH, results in the formation of aluminium hydroxides (as shown in Fig. 1a):



For longer term use of aluminium-air batteries these hydroxides may be precipitated out by the

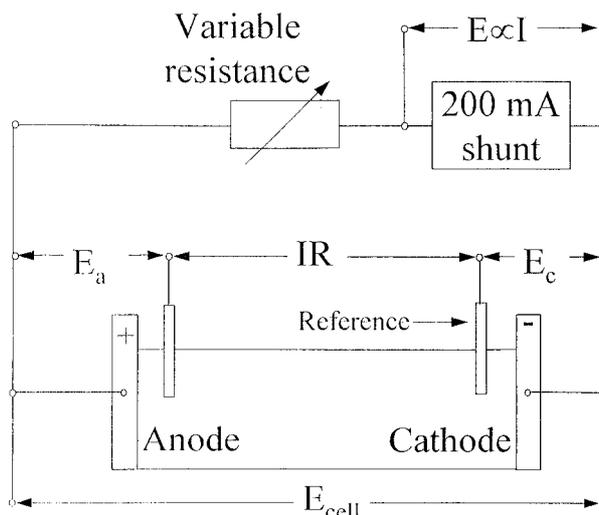


Fig. 2. The electrical circuit arrangement.

addition of appropriate organics [9] to minimise reduction in the charge capacity.

### EXPERIMENTAL DETAILS

Figure 2 shows, in schematic form, the electrical circuit arrangement used. Variation of the current passing through the aluminium–air cell took place using a resistance box, (range 1–9999  $\Omega$ ), to vary the load on the circuit. Use of a resistive shunt enable measurement of the current. All the experiments took place at an ambient temperature of 22°C.

#### Results and discussion

A load resistance of 1  $\Omega$  was selected since this best typifies the possible magnitude of load found in many ‘real’ electrochemical applications.

#### Potential vs time

In a series of four separate experiments, monitoring of the cathode potential,  $E_c$ , anode potential,  $E_a$ , potential drop across the solution,  $IR_{\text{soln}}$ , and cell potential,  $E_{\text{cell}}$ , occurred for 300 minutes, (see Fig. 3).

1. The cathode potential, initially about  $-390$  mV, rises to  $-375$  mV during the first 10 minutes indicating the necessity of an induction time to activate the catalyst on the air cathode.
2. The anode potential shows an initially rapid rise from about  $-1160$  mV to about  $-1120$  mV, as the passive oxide film breaks down under the effect of the activating elements, tin and gallium. A decrease in potential begins after 150 minutes as the anode surface begins uneven dissolution. A scanning electron micrograph showed evidence of pitting. Surface pits accumulate corrosion products such as aluminium hydroxide causing a decrease in effective anode area.

3. The potential drop across the solution maintains a steady 710 mV for 150 minutes then rises in response to the heating effect of the current.
4. The cell potential,  $E_{\text{cell}}$ , represents the difference between cathode and anode potential less the potential drop across the solution:

$$E_{\text{cell}} = E_c - E_a - IR_{\text{soln}} \quad (7)$$

Both calculation and measurement gave a result of a steady value of about 40 mV for  $E_{\text{cell}}$ .

#### Current vs time

Figure 4 shows the variation in current with time. Observation shows a rise from about 30–35 mA over a period of 150 minutes. Initially, the rise is rapid, corresponding to:

1. Activation of the cathode
2. Chloride ions in the electrolyte causing breakdown of the passive oxide film on the surface of the aluminium alloy anode.

A more gradual rise follows, arising from the heating effect of the current, which results in an increased conductivity and, therefore, reduced resistance in the electrolyte. Corrosion products accumulate in the anode as the surface begins to pit, indicated by observing the currents starting to fall after 150 minutes.

#### Potential vs resistance

Figure 5 shows plots of  $E_c$ ,  $E_a$ ,  $IR_{\text{soln}}$  and  $E_{\text{cell}}$  against resistance (logarithmically). Plots show conditions with and without air sparging in each case:

1. The cathode potential,  $E_c$ , increases as the resistance increases, rising from about  $-350$  mV at 1  $\Omega$  resistance to  $-180$  mV at a resistance of 500  $\Omega$ . At a value of 100  $\Omega$ ,  $E_c$  is invariant with air flow. The maximum effect of air sparging is observed at extreme values of R

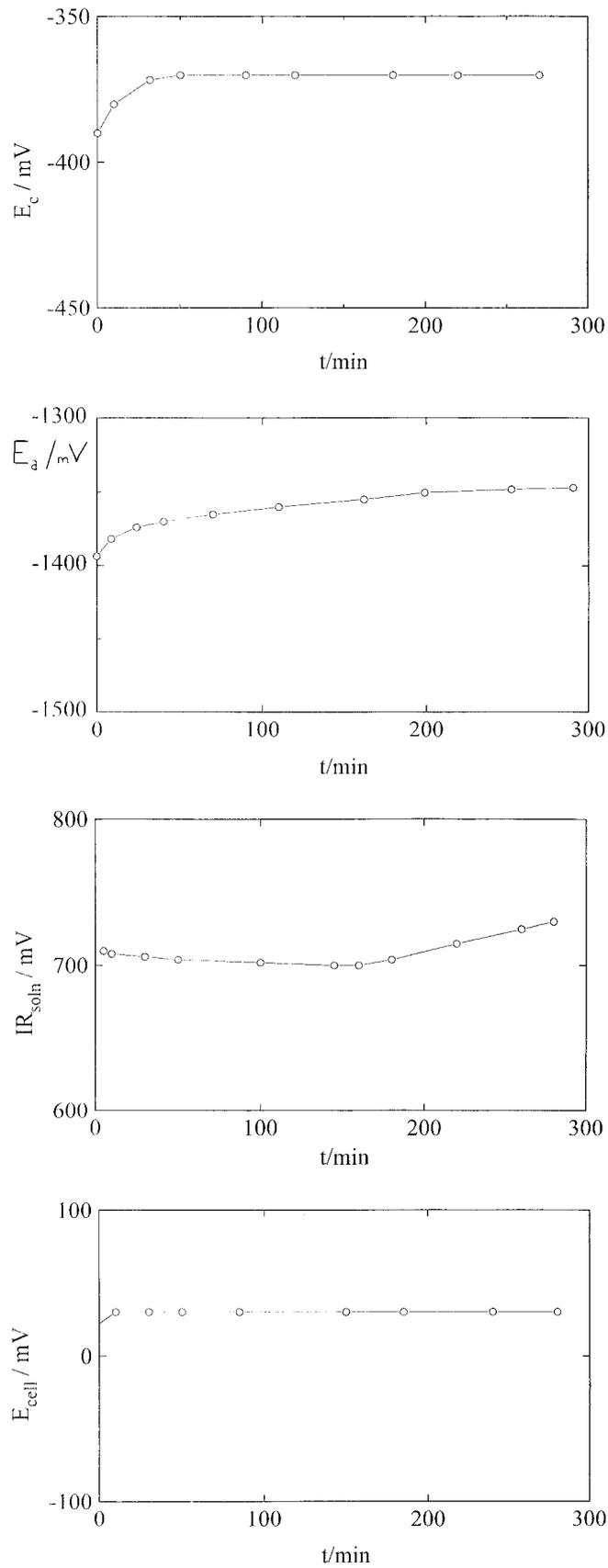


Fig. 3. Potential vs time; 30 wt% NaCl electrolyte; load 1  $\Omega$ ; 22°C.

1. cathode potential ( $E_c$ ) vs. time
2. anode potential ( $E_a$ ) vs. time
3. potential drop across the solution ( $IR_{soln}$ ) vs. time
4. cell potential ( $E_{cell}$ ) vs. time

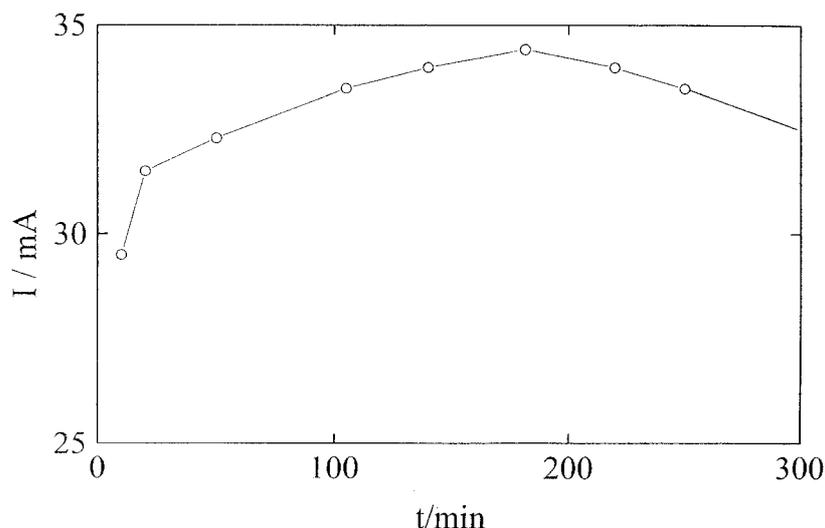


Fig. 4. Cell current vs time; 30 wt% NaCl electrolyte; load 1  $\Omega$ ; 22°C.

but only small differences appear to occur in response to air treatment. At low resistance (1  $\Omega$ )  $E_c$  decreases by around 2%. At 500  $\Omega$  an increase occurred of around 3%.

- The low degree of influence of air sparging suggests that the cathodic process is not rate determining. Aeration has the effect of agitating the solution, reducing the extent to which polarisation occurs and so enhancing the rate that hydroxyl ions transferred from the cathode into the bulk solution.
- A decrease in anode potential,  $E_a$ , occurs as  $R$  increased, falling from approximately  $-1000$  mV at 1  $\Omega$  to approximately  $-1250$  mV at 500  $\Omega$ . Over the entire range of resistance the effect of air sparging is to increase the potential by 30–40 mV (3–4%), ie, some inactivation of the anode is apparent. As the resistance increases the potential drop across the solution,  $IR_{\text{soln}}$ , decreases from about 640 mV at 1  $\Omega$  to 30 mV at 1000  $\Omega$ . The effect of sparging is to reduce the potential by approximately 7% due to the agitating effect of aeration.
- The cell potential,  $E_{\text{cell}}$ , rises with increasing resistance. At a value of 1  $\Omega$ ,  $E_{\text{cell}}$  is around 30 mV increasing to almost 1300 mV when  $R$  is 5000  $\Omega$ . Sparging of the cathode by air decreases the cell potential over the entire resistance range but has a proportionately greater effect at low resistance (approximately 7% at 1  $\Omega$ , compared to <1% at 5000  $\Omega$ ).

#### Current vs log resistance

Figure 6 shows a plot of current against log resistance with and without air sparging. At low resistance values a drop in current of 5–10% occurs on aeration indicative of loss of anode activity. The effect of aerating the electrolyte is to encourage competition between the dissolution of aluminium ions and the formation of aluminium oxide ( $\text{Al}_2\text{O}_3$ ). The sparging, therefore,

promotes deactivation of the anode by facilitating oxide formation. With increasing resistance the influence of aeration diminishes until, at 500  $\Omega$ , the current remains constant irrespective of rate of air flow.

#### Cell potential vs current

Figure 7 shows the relationship between  $E_{\text{cell}}$  and current and its variation with electrolyte concentration. Over the entire range of electrolyte concentrations used (360 wt% NaCl) the cell potential decreases linearly with an increase in current. The plot shows that a larger current occurs with the use of a more concentrated electrolyte. A decrease in resistance occurs when an increase in the concentration of sodium chloride, (within the range used), causes an increase in the conductivity of the electrolyte solution. In an ohmic system, (ie, one where current is inversely proportional to resistance), a linear voltage-current curve naturally occurs. In practice, non-linearity of the type seen here, is common.

The rate at which  $E_{\text{cell}}$  decreases as the current increases for all electrolyte concentrations at higher current values. In the case of the 30 wt% electrolyte, for example, an initial fall off of around 45  $\Omega$  is found, decreasing to just 5  $\Omega$  as the current is increased to approximately 15 mA. The initial steep fall in  $E_{\text{cell}}$  is due to activation polarisation, i.e., to the existence of the energy barrier that must be surmounted in the electrode reaction slow step. The slow step is likely to be electron transfer at the active catalyst on the cathode. (The student is able to see reaction kinetics in action.) The slower, linear decrease in  $E_{\text{cell}}$  occurs as ohmic, (resistance), polarisation increases and begins to dominate and the curve becomes ohmic. Although not seen here, concentration polarisation effects may occur which manifest as a tail off in the high current section of the voltage-current curve.

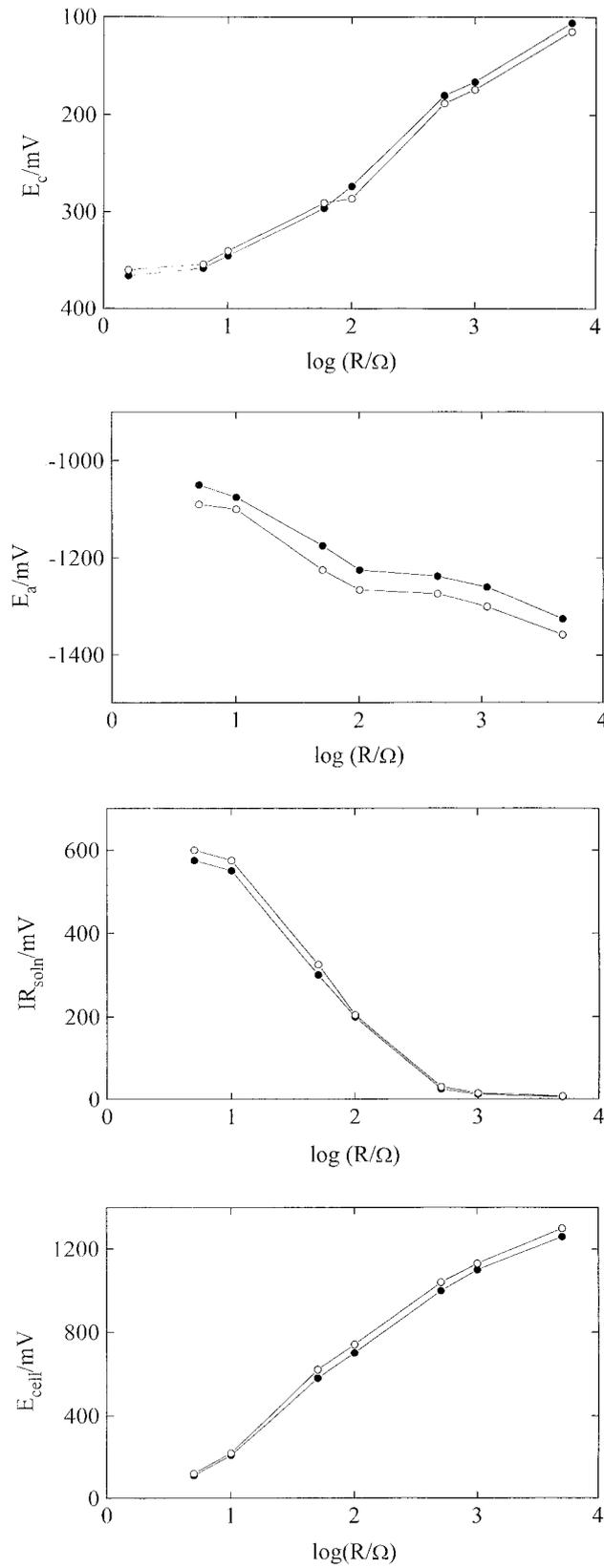


Fig. 5. Potential vs. log resistance; 3 wt% NaCl electrolyte; 22°C.

- air flow on
- air flow off
- 1. cathode potential ( $E_c$ ) vs. log resistance
- 2. anode potential ( $E_a$ ) vs. log resistance
- 3. potential drop across the solution ( $IR_{soln}$ ) vs. log resistance
- 4. cell potential ( $E_{cell}$ ) vs. log resistance

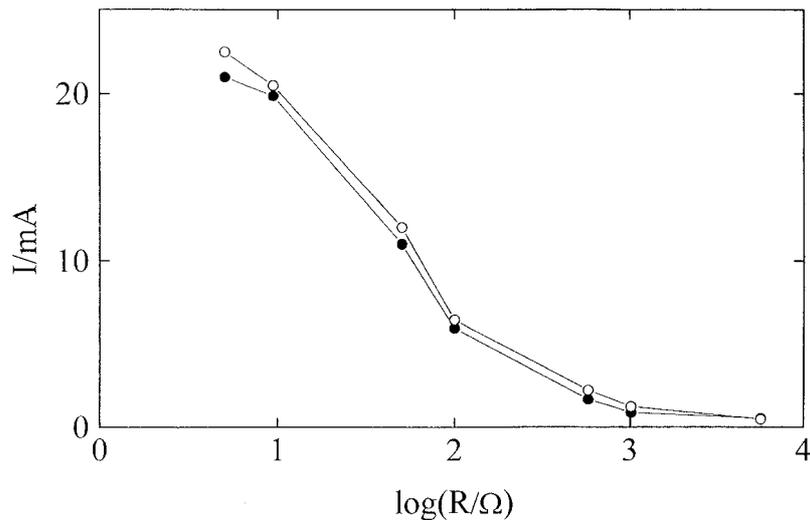


Fig. 6. Cell current vs. log resistance; 3 wt% NaCl electrolyte; 22°C.

● air flow on  
○ air flow off

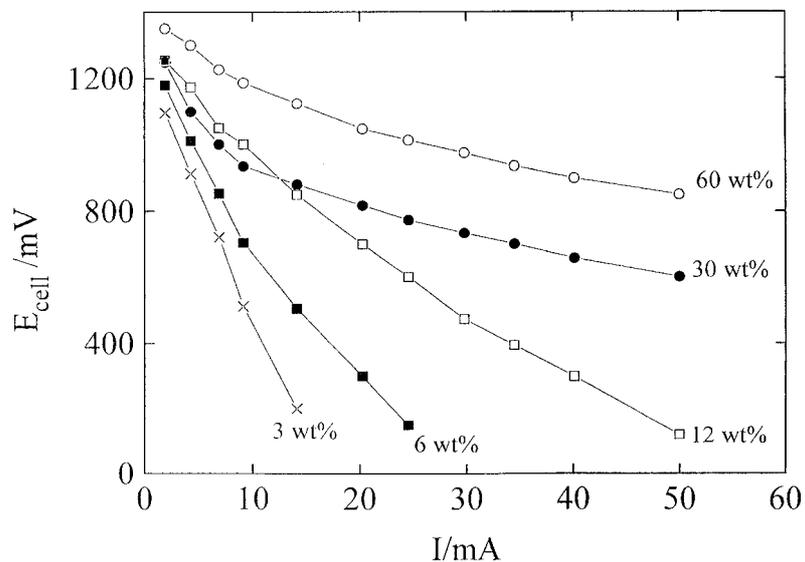


Fig. 7. Cell potential vs. current for various electrolyte concentrations. (3, 6, 12, 30 and 60 wt%); 22°C.

## SUMMARY

Presented here is a hands-on, student-centred, experimental approach to learning the rudiments of battery technology, that moves away from the traditional 'black box' approach, where students experience battery science in a 'packaged' cell. Here, the cell itself is instrumented with an extra set of electrodes affording much better insight to its operation. The aluminium-air cell is a versatile cell that allows an opportunity not only to measure current potential and power but also to demonstrate the effects of different electrolyte concentration.

## CLOSING REMARKS

The relatively simple program of experiments described requires little previous knowledge of electrochemistry and serves as an excellent introduction to battery technology through experiential learning. Furthermore, students are able to investigate the field of metal-air cell technology, an area of increasing importance. Zinc-air cells, for example, are currently under consideration for use in battery powered automobiles.

The program described is not exhaustive. Further experimental projects could examine, for

example, the relationship between potential and interelectrode separation, theoretical capacities, energy densities and the effect of substituting pure aluminium for the aluminium alloy anode and of using electrolyte additives. The aluminium–air cell provides an opportunity to illustrate the similarity between a primary battery and a corrosion cell [10].

This program focuses on learning the principles of ‘how a battery works’. A comparative study examined the similarities and differences between different battery systems [11].

*Acknowledgement*—The authors gratefully acknowledge Alcan International Ltd., Banbury, U.K. for the supply of the aluminium–air cell.

## REFERENCES

1. F. L. Barral, E. G. R. Fernandez and J. R. G. Otero, Secondary students' interpretation of the processes occurring in an electrochemical cell. *J. Chem. Educ.* **69**(8), pp. 655–657 (1992).
2. G. F. Martins, Why the Daniell cell works. *J. Chem. Educ.* **67**(6), p. 482 (1990).
3. M. J. Smith and C. A. Vincent, Electrochemistry of the zinc-silver oxide system, Part 1: Thermodynamic studies using commercial miniature cells. *J. Chem. Educ.*, **66**(6), pp. 529–531 (1989).
4. M. J. Smith and C. A. Vincent, Electrochemistry of the zinc-silver oxide system, Part 2: Practical measurements of energy conversion using commercial miniature cells. *J. Chem. Educ.*, **66**(8), pp. 683–687 (1989).
5. J. D. Worley and J. Fournier, A homemade lemon battery. *J. Chem. Educ.*, **67**(2), p. 158 (1988).
6. S. Roffia, V. Concialini, and C. Pardisi, The interconversion of electrical and chemical energy. The electrolysis of water and the hydrogen-oxygen fuel cell. *J. Chem. Educ.*, **65**(3), pp. 272–273 (1988).
7. T. A. Lehman, P. Renich and N. E. Schmidt, The aluminum can as an electrochemical energy source. *J. Chem. Educ.*, **70**(6), pp. 495–496 (1993).
8. S. Zaromb, The use and behaviour of aluminum anodes in alkaline primary batteries. *J. Electrochem. Soc.*, **109**, pp. 1125–1130 (1962).
9. G. Scamans, *Development of the Aluminium Air Battery*. Chemistry and Industry (London), 192–196 17 March 1986.
10. B. D. Barker and F. C. Walsh, Laboratory experiments to demonstrate the principles and practice of corrosion and protection of metals. Paper for the Corrosion Education Session, U.K. Corrosion & EuroCorr 94 Conference, Bournemouth, U.K. 31 October-3 November 1994.
11. X. LeRoux, G. A. Ottewill, and F. C. Walsh, Accepted for publication in *J. Chem. Educ.*, 1995.

### Further Reading

1. Barak (Ed.) *Electrochemical Power Sources; Primary and Secondary Batteries*; Peter Peregrinus, New York (1980).
2. Corey Cahoon and G. W. Heise. *The Primary Battery*; Wiley, New York (1976).
3. P. Gregory. *Metal-Air Batteries*; Mills and Boon, Richmond, Surrey, UK (1972).
4. I. Ismail (Ed.) *Electrochemical Reactors; Their Science and Technology, Part A: Fundamentals, Electrolysers, Batteries and Fuel Cells*; Elsevier, Amsterdam (1989).
5. Pletcher and F. C. Walsh. *Industrial Electrochemistry*, 2nd edn.; Chapman and Hall, New York (1990).
6. C. Shearer and R. F. Jones, The construction and use of commercial voltaic cell displays in freshman chemistry. *J. Chem. Educ.*, **67**(2), 158–159 (1990).
7. O. Tanis, Galvanic cells and the standard reduction potential table. *J. Chem. Educ.* **67**(7), pp. 602–603 (1990).
8. A. Vincent, F. Bonino, M. Lazzori and B. Scrosati. *Modern Batteries, An Introduction to Electrochemical Power Sources*; Edward Arnold, London (1984).
9. Walsh, *A First Course in Electrochemical Engineering*; The Electrochemical Consultancy, Romsey, 1993.

**Richard Morris** is a graduate of the BSc Applied Chemistry course at the University of Portsmouth, Portsmouth, UK. He specialised in corrosion engineering and energy technology during his undergraduate course.

**Gerry Ottewill** is a Senior Lecturer in the School of Pharmacy and Biomedical Sciences at the University of Portsmouth. She lectures in mathematics, chemistry and environmental science and has a number of years experience of teaching science and engineering students at the undergraduate level.

**Des Barker** is a Principal Lecturer in the Centre for Chemistry at the University of Portsmouth. He specialises in corrosion and metals protection and has approximately 30 years experience of teaching these subjects to science and engineering students. Des has held the positions of Chairman of the Institute of Metal Finishing and Educational Secretary to the institution of Corrosion Science and Technology.

**Frank Walsh** is Professor in Electrochemical Engineering and directs the Applied Electrochemistry group at the University of Portsmouth. His previous positions include

a Head of School, Reader and Senior Lecturer at Portsmouth, a lectureship in chemical technology at the University of Strathclyde and an engineering consultancy at the University of Southampton. He has developed or improved over 35 industrial electrochemical processes Frank has had 20 years experience teaching electrochemistry to science and engineering students and to industrial short course delegates. His publications number some 200 papers and 3 books on industrial electrochemistry and electrochemical engineering. Professor Walsh has recently moved to the University of Bath, to occupy a chair in Electrochemical Engineering.