Short Communication

Metallized graphite as an improved cathode material for aluminium/air batteries

Ambick Mukherjee and Indra N. Basumallick*
DENS Battery Project, Department of Chemistry, Visva Bharati, Santiniketan 731235 (India)

(Received November 6, 1992; accepted January 15, 1993)

Abstract

This paper reports the fabrication of metallized (Pt, Ni, Cu, Fe, Co) graphite cathodes by an electrodeposition method from an appropriate electrolytic bath, together with the performance characteristics of specially-designed aluminium/air cells that utilize these cathodes. In these cells, the aluminium electrodes were separated by a glass-jacket separator. The latter prevents mixing of hydrogen gas evolved due to the corrosion of the aluminium electrode. While the open-circuit voltage of the cells is virtually invariant, the short-circuit current and discharge behaviour are markedly dependent upon the choice of catalytic metal. The discharge profiles are improved markedly for cells with a Pt-, Ni- or Cu-coated graphite air cathode, but the reverse is found for Fe- and Co-coated cathodes. The behaviour is explained in terms of chemisorption and the better catalytic activity of Pt, Ni and Cu. These results suggest that Ni- and Cu-coated graphite air cathodes are promising low-cost and efficient electrodes for aluminium/air batteries.

Introduction

Aluminium/air batteries are being investigated both as economical and potential power sources for electric vehicles and as primary batteries for standby-power applications [1–5]. In simple terms, the cell consists of an aluminium or aluminium alloy anode and a graphite air cathode immersed in a suitable electrolyte, preferably alkaline solution. Although significant progress has been reported [6, 7] for the anode material, there is still much scope to improve fabrication methods for the cathode.

Previously, we have reported [8] the development of a depolarizer for aluminium batteries. The principle objective of the present study is to explore suitable catalytic materials that can enhance the efficiency of graphite air cathodes.

In fuel cells [9, 10], metallized graphite has sometimes been found to act as a good catalyst for fuel oxidation. Indeed, the emergence of new cathode materials from attempts to develop better oxygen electrocatalysts has given improved diffusion conditions for practical aluminium/air batteries [11]. For example, platinum has been used as a cathode catalyst in air batteries. Here, an identical approach, i.e., studies on metallized graphite air cathodes, is reported. In summary, the goal is to produce low-cost, metallized

0378-7753/93/$6.00

graphite to be used as an effective catalyst for electronation of oxygen in aluminium/air batteries.

Experimental

Graphite electrodes were collected from dry cells (Nippo, Japan), washed free of electrolytes, leached in alkali and acid, and finally washed with distilled water. For electrodeposition of the metals, appropriate salt solutions along with other chemicals, as prescribed in the literature [12], were used as electrolytic bath. A platinum wire served as the anode. Electrolysis was performed with a 6 V d.c. source and a current of 2 to 5 mA was passed for 15 to 20 min. The metal-coated carbon electrodes were washed several times with distilled water and then dried in hot air. Johnson–Mathey aluminium rod was used as supplied; the outer surface was polished to remove any oxide layers.

The design of the aluminium/air cell is shown in Fig. 1. The cell was housed in an all-glass, two-inlet, inverted conical flask. This was filled with 50 cm^3 of 1 M KOH (E. Merck, India). The cathode and anode were introduced via the cell inlets. The anode was shrouded in a glass-jacket separator. Air was passed into the cell via a side tube. The glass-jacket separator prevented the diffusion of hydrogen gas that arise from corrosion of the aluminium in the alkaline solution. Although the glass-jacket separator has a high impedence value, the present study is concerned with the relative, not absolute, behaviour of different cathodes and thus the high impedence can be ignored. The effective area of the metallized graphite electrodes was estimated from the values of the cell constant of a specially-designed conductivity cell that used these electrodes. The results of the area correction are given in Table 1.

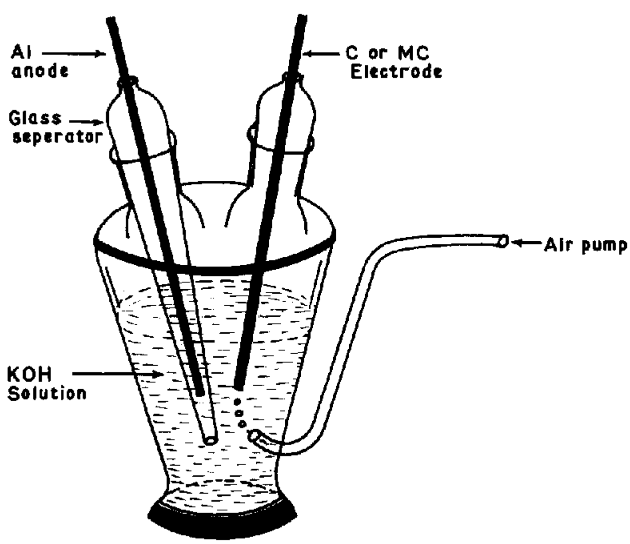

Fig. 1. Cell design for aluminium/air battery with glass-jacket separator.

TABLE 1

Electrochemical parameters of aluminium/air cells with a glass-jacket separator

Serial no. of cell	Coated metal	OCV (V)	SCC after correction for effective area (mA)	SCC per unit area (mA cm^{-2})
1	C (blank)	1.29	10.6	1.38
2	Fe	1.38	10.4	1.35
3	Co	1.31	10.1	1.31
4	Ni	1.54	11.8	1.53
5	Pt	1.58	14.5	1.89
6	Cu	1.42	11.3	1.47

Results and discussions

The open-circuit voltage (OCV) and short-circuit current (SCC) of the different aluminium cells were determined at 25 °C with a digital multimeter (Mic-6000Z, Taiwan). The values are listed in Table 1. All potentials are reported with respect to a saturated calomel electrode (SCE). The OCV values are only slightly perturbed for these cells and are close to the literature value. However, the observed SCC values of the cells are less than those reported in the literature. This is because of the high impedence of the glass jacket used here as the separator.

The performance characteristics of the cells were evaluated by discharging the cells at 2 mA for 1 h. The discharge curves are given in Fig. 2. It is interesting to note that two distinct categories of discharge behaviour have been found. In the first case (Pt, Cu, Ni on graphite) the discharge behaviour is markedly improved compared with unmetallized graphite. By contrast, the discharge behaviour of cells with Fe- and Co-coated graphite is less satisfactory. The observed lower working potential for the cells with Fe- and Co-coated electrodes is shown in Fig. 2. The relative sequence of catalytic behaviour for the electronation of oxygen appears to follow the order: $Pt > Ni > Cu \gg Fe > Co$.

A considerable amount of work has been devoted to the theoretical treatment of heterogeneous catalysis in terms of the structure of solids. Such treatments deal with the nature of the chemisorptive bond. Studies of the percentage of d-band character and number of holes in the d-band of these metals [13] support the results obtained in the present study.

In conclusion, it appears that Ni- or Cu-coated graphite may serve as efficient, low-cost, air cathodes for aluminium/air batteries.

Acknowledgement

The authors are grateful to the Ministry of Energy, Government of India (DENS) for providing financial support for this work.

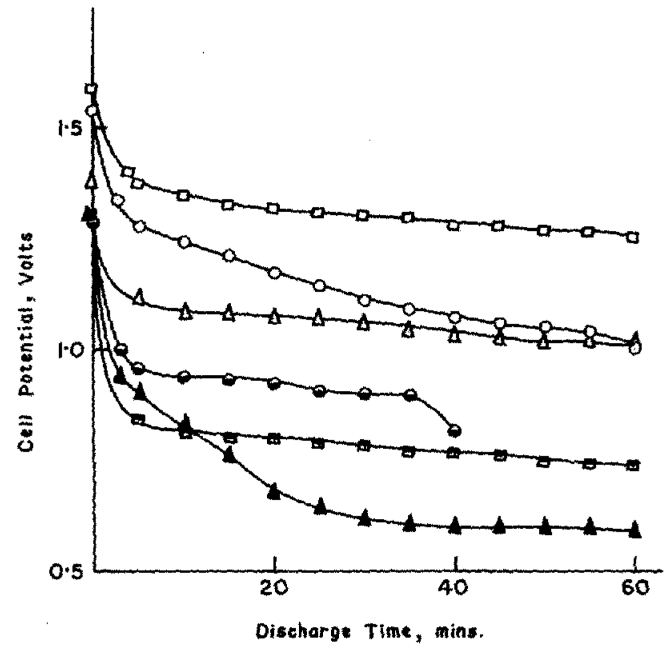

Fig. 2. Discharge profiles for cells: Al|1 M KOH| metallized graphite air: (□) Pt; (○) Ni; (△) Cu; (◒) (blank) C; (⊡) Fe; (▲) Co. Performance at 25 °C and 2 mA rate.

References

1 G. Scamans, J. Hunter, C. Tuck, R. Hamlen and N. Fitzpatrick, in T. Keily and B. W. Baxter (eds.), *Power Sources 12, Research and Development in Nonmechanical Electrical Power Sources*, International Power Sources Symposium Committee, Leatherhead, UK, pp. 363–378.
2 Current Titles in Electrochemistry, *Soc. Adv. Electrochem. Sci. Technol., 23* (7) (1991) A29.
3 S. Real, M. Urquidi-Macdonald and D. D. Macdonald, *J. Electrochem. Soc., 135* (1988) 2397.
4 E. Behrin and J. F. Cooper, *Proc. Fall Meet. Electrochemical Society, Pittsburg, PA, USA, 1978*, Proc. Vol. 78-2, The Electrochemical Society, Pennington, NJ, USA, 1978, p. 281.
5 J. F. Cooper, R. V. Homsy and J. H. Landrum, *Proc. 15th Intersoc. Energy Conv. Eng. Conf., Seattle, WA, USA, Aug. 18–22, 1980*, Vol. 2, pp. 1487–1495.
6 S. Real, M. Urquidi-Macdonald, D. D. Macdonald, *J. Electrochem. Soc., 135* (1988) 1633.
7 D. D. Macdonald and S. English, *J. Appl. Electrochem., 20* (1990) 405.
8 A. Mukherjee and I. Basumallick, *J. Power Sources, 37* (1992) 411.
9 L. K. Verma and D. Guha, *J. Electrochem. Soc. India, 39* (1990) 257.
10 R. D. Ghosh and D. Guha, *J. Electrochem. Soc. India*, 39 (1990) 260.
11 D. A. J. Rand, *J. Power Sources, 4* (1979) 101.
12 K. I. Vasu, *Refresher Course in Metal Finishing*, Electrochemical Society of India, Bangalore, 1974.
13 L. Pauling, *Phys. Rev., 54* 899 (1938); *J. Am. Chem. Soc., 69* (1947) 542; *Proc. Roy. Soc. London, Ser. A, 196* (1949) 343.