Short Communication

Studies on an aluminium–carbon cell

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Abstract

The current–voltage behaviour of an electrochemical cell that consists of an aluminium anode and a carbon cathode in a medium containing aqueous NH_4SCN has been studied, both in the presence and in the absence of a coating on the carbon electrode. It is found that activation polarization is the main factor that limits the current output when using an untreated carbon electrode. This problem is eliminated by coating the carbon electrode with an *in situ* deposition of HgI_2. In this condition, the current output is reduced mainly by ohmic polarization. Further studies with a coated HgI_2–carbon cathode and an aluminium anode, in a medium containing SCN^- and Cl^- ions together with a complexing agent (EDTA, sodium salt), revealed that a cell performance close to ideal, (i.e, showing no appreciable polarization) can be obtained at currents up to 0.6 mA/cm² and above.

Introduction

The application of electrochemical cells in portable power sources has been the subject of extensive investigation [1–5]. Apart from the obvious advantage of serving as localized power sources, electrochemical cells provide pollution-free conversion of chemical to electrical energy that is direct and, therefore, does not involve an intervening heat cycle. This considerably increases the efficiency of the power sources. The work reported here concerns experimental studies that are directed towards the development of aluminium/air cells.

Aluminium is the most abundant element after oxygen and silicon. It is used widely as a constructional material. Following World War II, the production of aluminium rose sharply (Fig. 1) and, concomitantly, the price fell to a level that became acceptable for a large range of uses of the metal [6, 7].

Although aluminium is inherently a highly corrodable metal, it is protected from corrosion through the deposition of a passive oxide film. The film is not attacked by OH^-, Cl^- or SCN^- ions. The last named ions yield a positive corrosion current, while OH^- and Cl^- promote a negative corrosion current. The order of current yield at a given voltage is OH^-, Cl^- and SCN^-. With OH^- and Cl^- ions, however, although the corrosion is very fast, *in situ* production of $Al(OH)_3$ (through hydrolysis in the
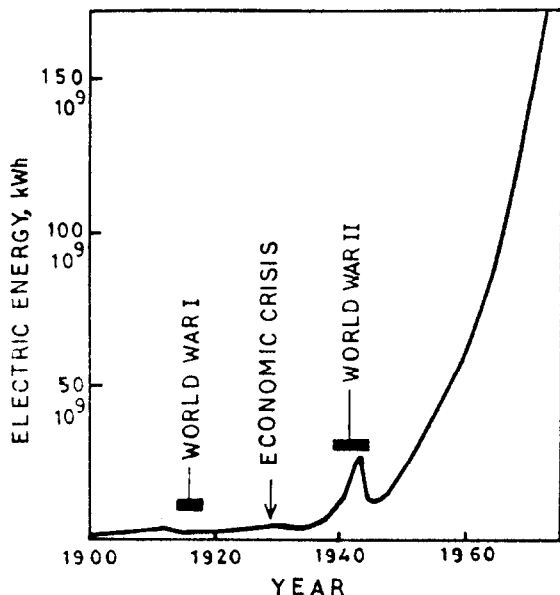
Fig. 1. World production of aluminium in terms of energy consumption.

case of Cl⁻ ions) results in erratic current outputs. This behaviour is unlikely to occur in a SCN⁻ medium because the low rate of corrosion limits the current output. Therefore, it is reasonable to expect that a synergistic effect may occur in a medium that contains appropriate proportions of Cl⁻ and SCN⁻ ions, together with a complexing agent (e.g., EDTA solution) that can prevent the deposition or formation of $Al(OH)_3$.

Zaromb [8] was the first to attempt the development of an alkaline aluminium/air cell. The research showed that the open-circuit potential at room temperature was − 1.75 V against a Hg/HgO reference electrode in the same solution; this is a shift of only 0.67 V away from the thermodynamic reversible potential. The battery system offers significant promise for relatively large power applications, such as electric vehicle propulsion [9]. Vielstich and co-workers [10] showed that satisfactory performance could be obtained in a citrate electrolyte, while Valand [11] used an electrolyte with an undisclosed composition but stated to contain fluoride. Despic *et al.* [12] developed an aluminium/air cell with a sodium chloride electrolyte. This is a cheap electrolyte in which aluminium ions are not hydrolyzed to form alumina. Sodium chloride promotes local activation of the anodic dissolution of the metal, and, thereby, causes severe pitting corrosion [13]. The anodic dissolution of pure aluminium and its alloys has been studied [14, 15] and found to provide the basis of an environmentally acceptable electrical power source. The cost of metal consumed per kWh of energy is given in Table 1 for a variety of metals [16]. The results indicate clearly the economic advantage of using aluminium.

One disadvantage of using aluminium as an anode is the fact that the metal cannot be electrodeposited from a medium containing aluminium ions because aluminium salts are hydrolysed in aqueous media. Therefore, an aqueous-medium-based aluminium anode can only be used for the construction of secondary cells.

TABLE 1

Cost of metal consumption per kWh of energy produced

Metal	$M \times 10^{-3a}$ (kg/mol)	$Q_m{}^b$ ($/kg)	ΔG^c (kWh/mol)	Q_e^{0d} ($/kWh)	$\eta_v{}^f$ (%)	$Q_e{}^g$ ($/kWh)
Li	6.94	44.150	0.1250	2.450	0.65	0.77
Na	23.00	2.052	0.1160	0.407	0.58	0.70
Mg	24.32	2.958	0.1580	0.455	0.51	0.89
Al	26.97	1.660	0.2190	0.204	0.44	0.46
Zn	65.38	1.324	0.0884	0.979	0.60	1.63

^aM = mol. wt.
^bQ_m = price of metal ($) on world market (1982–1984).
$^c\Delta G$ = molar free energy change in the cell reaction.
$^dQ_e^0$ = theoretically achievable cost ($) of unit energy.
$^f\eta_v$ = achievable voltage efficiency (%) of cell operation.
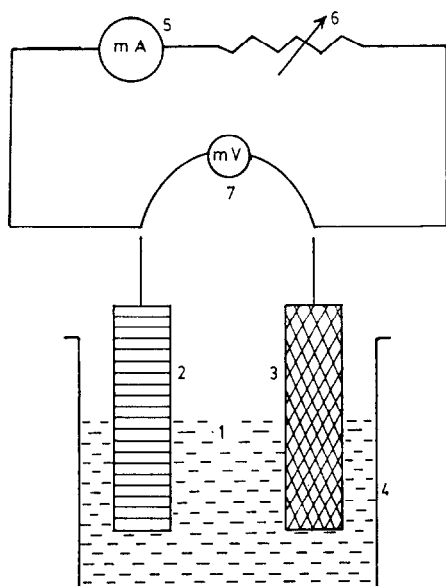^gQ_e = practical achievable cost ($) of unit energy.

Fig. 2. Schematic of aluminium electrochemical cell: (a) saturated NH$_4$SCN solution; (2) graphite cathode; (3) aluminium anode; (4) Pyrex glass beaker; (5) milliameter; (6) resistance box, and (7) millivoltmeter.

Experimental

Solutions with different concentrations of ammonium thiocyanate (NH$_4$SCN) were prepared, namely: saturated solution, 1 M, 0.5 M, 0.2 M and 0.1 M. A 100 cm^3 portion of solution was placed in a 250 cm^3 beaker. The experimental setup is shown in Fig. 2.

The current–voltage behaviour of the different solutions showed that the voltage was not a function of the concentration of the ammonium thiocyanate solution.

The current–voltage behaviour of saturated NH₄SCN was studied with an untreated graphite cathode and an aluminium anode (Fig. 3) (I)). The graphite electrode was then washed, cleaned, and placed in a 0.1 M HgCl₂ solution for 1 h. It was then removed and put into an ammonium hydroxide solution for 1 min, followed by immersion in 0.1 M KI solution for 30 s, and then washed and dried. This treated graphite electrode was again used as the cathode and the current–voltage response was re-examined using the apparatus shown in Fig. 2. The results are given as curve II in Fig. 3.

With the same experimental setup, saturated NH₄SCN solution was saturated with KCl and then with the sodium salt of EDTA. The resulting current–voltage behaviour are shown as curve III in Fig. 3. It can be seen from this curve that the incorporation of Cl⁻ ions along with SCN⁻ ions in presence of a complexing agent such as EDTA raised the cell performance to near ideal conditions, in as much as no appreciable polarization was observed, even on drawing current up to 0.6 mA/cm² at about 0.8 V.

Preliminary experiments were conducted with a treated graphite cathode and an aluminium anode in KCl solution alone, or in saturated NH₄SCN containing only the sodium salt of EDTA. The data are presented, respectively, as curves IV and V in Fig. 3. In both cases, there is a rapid decline in battery performance with current output.
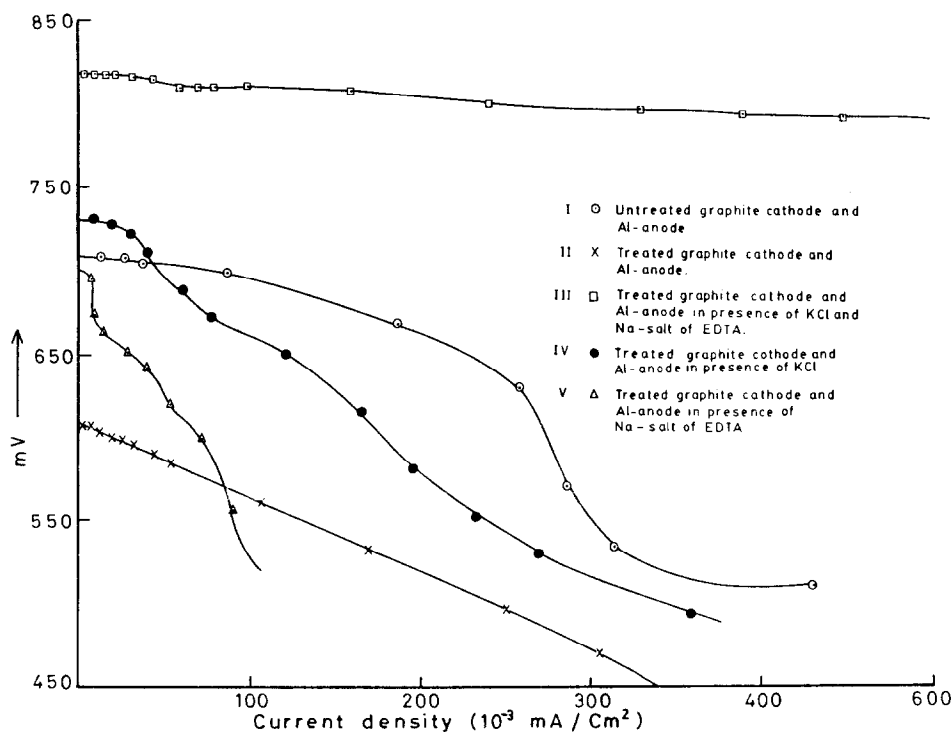

Fig. 3. Current voltage behaviour of saturated NH₄SCN solution, with and without a treated graphite cathode and an aluminium anode.

Discussion

The corrosion behaviour of aluminium electrodes in the presence of different anions has been studied extensively in connection with the construction of aluminium/air batteries. This behaviour in different anionic media is shown in Fig. 4. It can be seen that the Cl^- ion attack on aluminium occurs at negative potentials, while the SCN^- ion attack takes place at positive potentials. Under a negative potential, the aluminium probably enters into a complex anionic species. (Note, a complex is known to form in an OH^- ion medium.) In an SCN^- ion medium, the aluminium probably exists as a cationic species.

With SCN^- ions alone, and with an untreated graphite cathode, the activation polarization is found to be a serious impediment that limits the current output of the cell (curve I, Fig. 3). Upon treating the graphite cathode with a sparingly soluble mercuric salt, however, the activation polarization is curtailed and concentration polarization limits the current output upon drawing currents of 0.2 mA/cm^2 and above (see curve II, Fig. 3). Evidently, this suggests diffusion limitation of the electrolytic species, probably because of the bulkiness of the diffusing species.

Consequently, it was sought to reduce the concentration of the bulky diffusing species by incorporating some oppositely charged electroactive diffusing species through incorporation of Cl^- ions in the medium. Unfortunately, due to some irreversible reaction, the aluminium is reduced to a non-electroactive form that restricts the voltage output of the cell. In order to confirm this, experiments were conducted using a KCl medium alone, or a medium that comprised the sodium salt of EDTA in a saturated solution of NH_4SCN. In the KCl medium, the current–voltage behaviour follows a rapid pattern that suggests a nucleation in crystal growth at the electrode (curve IV, Fig. 3). This occurs simultaneously with the dissolution of hydrated aluminium oxide as a result of the cell reaction with the Cl^- ions. The incorporation of a sodium salt of EDTA in a medium containing SCN^- ions also shows a rapid downward trend in performance upon drawing an increasing amount of current (curve IV, Fig. 3). This suggests that while any irreversible product is quickly dissolved due to the presence
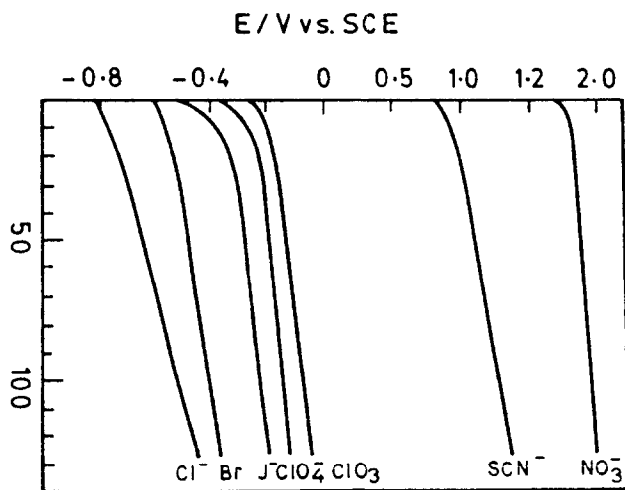

Fig. 4. Polarization plateaux of aluminium in the presence of different anions in the electrolyte.

of the complexing agent, the resulting species diffuse only slowly to register at the electrodes.

By contrast, incorporation of both Cl^- and SCN^- ions and also the complexing agent in the medium, causes the current–voltage behaviour to behave in a nearly optimum manner for an efficient cell performance, as shown in curve III, Fig. 3. This could be due to a synergistic effect where the electroactive nature of the diffusion species remains unaffected and the rate of diffusion becomes adjusted to conditions that promote efficient cell performance.

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