Investigations of a large-capacity medium-power saline aluminium–air battery

E. BUDEVSKI, I. ILIEV, A. KAISHEVA

Central Laboratory for Electrochemical Power Sources BAN, Sofia 1040, Bulgaria

A. DESPIĆ

Institute of Electrochemistry ICTM, Njegoševa 12, 11000 Belgrade, Yugoslavia

K. KRSMANOVIĆ

Department of Industrial Design, Faculty of Applied Arts, University of Arts, 7 jula, 11000 Belgrade, Yugoslavia

This paper describes the development and operation of a medium-power (24 W) aluminium–air battery with saline electrolyte or sea water. The battery consisted of two packs of 10 cells, each connected in series with a projected aluminium anode capacity of 2590 Ah. The anodes were made of a Ga–Sn–Mg alloy capable of giving 89% material efficiency, with an open circuit voltage of 13.4 V. The specific energy based on aluminium was calculated at $577\,\mathrm{Wh\,kg^{-1}}$.

1. Introduction

Aluminium–air batteries are a relatively recent development [1, 2] based on specially designed aluminium alloys [3–5] with a very low content (below 0.3%) of alloying elements (Ga, Sn, In), which enable the use of the very large energy of oxidation of aluminium in an electrochemical process. The batteries are characterized by high specific energies and, if constructed in such a way that aluminium plates can be refilled, they can be considered as (solid) fuel cells or mechanically rechargeable secondary batteries. Two types are being developed oriented towards different targets: (1) alkaline batteries of significant power densities for electric vehicles [6] and (2) saline batteries for special applications such as emergency lighting, reserve power, long-lasting silent power for communication equipment and lighting on yachts and other marine objects, lighting for camping etc. The latter are based on simple neutral salt (NaCl) electrolyte, which is easily accessible (sea water at sea) or easily prepared, is harmless for an ordinary user and is ecologically acceptable without restrictions. Another major advantage is the infinite shelf-life in the inactive state with easy activation by the addition of water.

The saline battery is essentially an energy battery suitable for use with low power requirement. It was shown [7] that changes in specific energy and specific power with the quantity of aluminium in the cell (plate thickness) oppose each other. Hence, optimization of power capacity and energy capacity can be achieved. For high-power applications, however, they should be used in a hybrid combination with some typical power

battery (e.g. lead–acid or Ni–Cd). Unlike other batteries whose capacity is limited by the amount of electrochemically active substance, in the aluminium–air battery and especially the saline type, it is the acceptance of the reaction product by the electrolyte which is limiting the use. Hence, while using one and the same set of anodes, the electrolyte has to be replaced several times, depending of the ratio of aluminium capacity to the electrolyte acceptance capacity. Thus, as well as the specific energy calculated on the basis of the metal content in the battery ('aluminium range' [8]), one also has to take into account the specific energy density based on one filling of the electrolyte ('electrolyte range') which is usually significantly lower. However, in marine applications, where the sea water can be easily replenished, or even caused to flow through the battery, it is only the aluminium-based specific energy which counts.

So far only a few types of the saline battery have been developed to the stage of commercial production and only those produced by Alupower (USA) have appeared on the market. Hence, it was considered useful for the assessment of the potentials of the saline aluminium–air system to present results of an investigation of the performance of an experimental model of a battery run on sea water, satisfying power and energy requirements of a medium-size yacht designed for long times at sea.

This model was produced for a particular purpose by a cooperation between the Serbian Academy of Science and Arts (Yugoslavia) and the Bulgarian Academy of Science (Bulgaria), being designed and manufactured by one of the authors (K.K.).
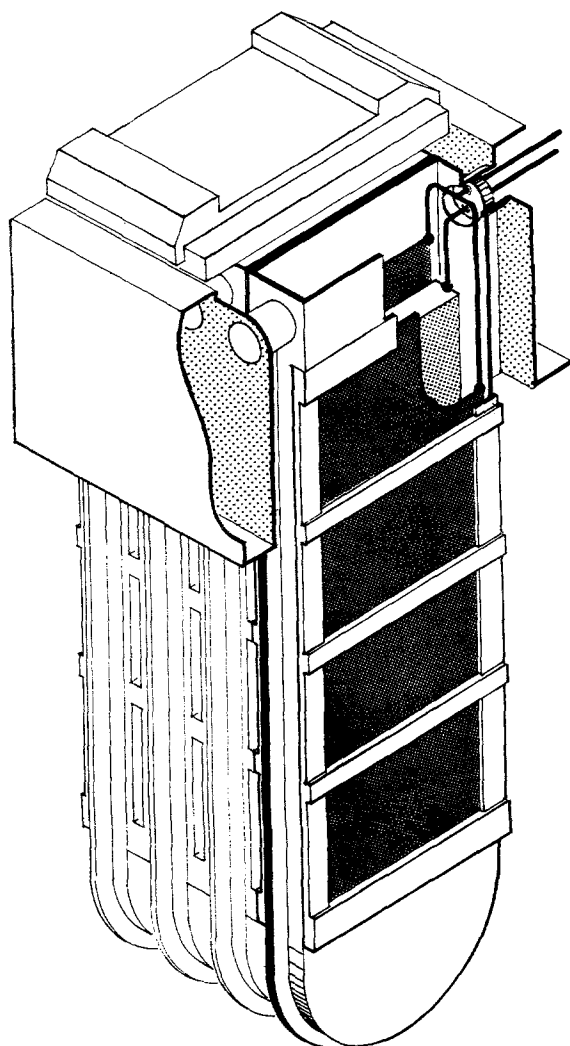
Fig. 1. Representation of one module of the battery.

2. The battery

The battery was designed for a continuous supply of 24 W of power (12 V, 2 A) with periodic replacements of electrolyte. It was composed of 20 modules of the type shown in Fig. 1. A flat plate aluminium alloy electrode was placed between two air electrodes of 200 cm² area each. The interelectrode distance at the

start was about 2 mm. Significant space for excess electrolyte was left at the bottom of the cell. Electrical connections were taken from the top of the electrodes on one side of the module. The other side has a circular opening at the top, through which the electrolyte could be admitted from an outside channel connecting all cells stacked in the battery. The latter was so designed that, after all cells were filled it could be emptied so as to break any electrolyte connection between the cells in the stack. The cells could be emptied of the used electrolyte containing the reaction product through the same channel by tilting the entire battery on a central axis by 90°.

The casting of the modules was done by incorporating a standard air electrode frame in production in Bulgaria, made of ABS resin, into a fiber-glass carrier. The (double layer) air electrodes were made of active carbon catalyst and a special porous hydrophobic material pressed on a lead-plated metal net. Details of their structure and performance were published earlier [9, 10].

The aluminium electrodes (supplied by courtesy of Alupower Inc., Bernardsville, USA) were in the form of flat plates 20 × 10 × 0.8 cm in size, made of an aluminium–tin–gallium–magnesium alloy. The polarization characteristics of the alloy in 2 M NaCl and the corrosion rate (expressed as hydrogen evolution current density) as functions of anodic dissolution current density are shown in Fig. 2. It is seen that the alloy exhibits very low corrosion at open circuit (of only 0.3 mA cm⁻²) and a relatively low so-called negative difference effect, i.e. increase in the rate of hydrogen evolution with increase in anodic current density, promising a material efficiency in anodic dissolution of 89%. The flat polarization plateau up to 200 mA cm⁻² indicates that the limitations in the power density are not on the side of the aluminium electrode.

The battery was composed by stacking the 20 cells inbetween two end-plates in a steel frame with a possibility of a 180° tilt around a central axis, fixed at the two ends into bearings on a steel carrier. The total weight of the empty battery was 27 kg.
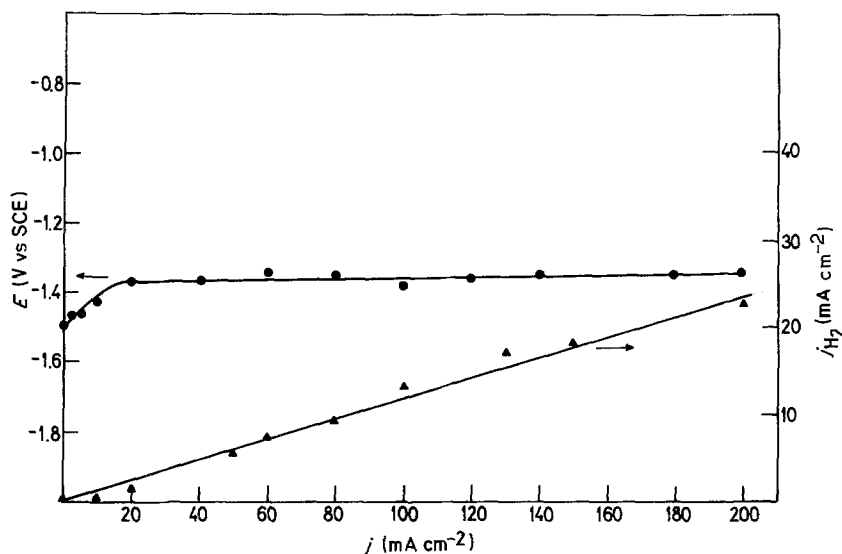

Fig. 2. Electrode potential and hydrogen corrosion current as functions of anodic dissolution current density of the Alupower anodes in the battery.
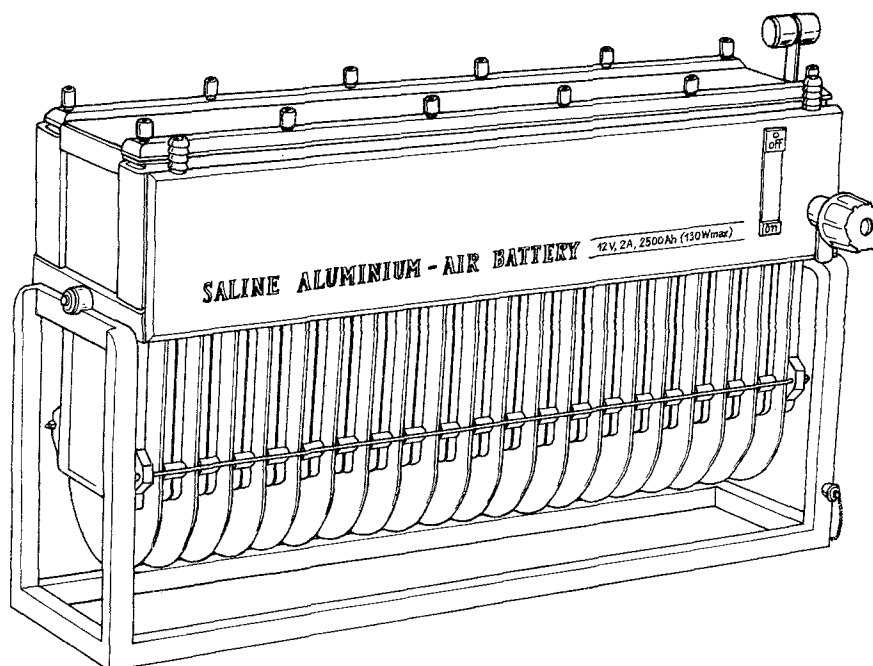
Fig. 3. View of the battery ready for operation.

The cells were divided into two groups. Each group contained 10 cells connected in series. The two groups were connected in parallel to the battery terminals. The air was provided by convective flow between the air electrodes through a 3 mm gap secured by plastic spacers separating the cells.

A view of the battery ready for operation is shown in Fig. 3. All cells were covered by a common lid lined with an elastic pad and pressed against the cell top edges by a set of screws.

3. Experimental details

Experiments were carried out first on a cell module filled with 3% NaCl solution. Continuous runs at constant current were performed with periodic measurements of the cell voltage. Current–voltage curves were taken at the beginning and at the end of the experiments.

The battery was tested with NaCl solutions of five different concentrations (1.5, 3, 6, 9 and 12%). Solutions were prepared from analytical grade salt and distilled water. The cells accommodated 13 dm³ of electrolyte.

With each electrolyte the battery was tested under different constant current regimes using a constant current source capable of delivering up to 20 A. The voltage of the battery was measured at the terminals by a digital voltameter. The voltage of individual cells could also be measured at the contacts between adjacent cells.

The battery was operated at ambient temperature which was around 22° C. The temperature inside the cells was measured by inserting a thermometer into the electrolyte of a cell in the middle of the battery after a steady-state voltage had been reached.

The testing procedure consisted of filling the battery with a fresh electrolyte, applying the desired current and observing the change in voltage with time. In experiments carried out at the nominal current of 2 A, in electrolytes of different concentrations, current–voltage characteristics were taken after a steady–state voltage had been reached. After running for a certain predetermined period of time (usually 8 or 24 h) the battery was emptied and the cells washed several times by filling them with fresh water, tilting back and forth and draining the water and the reaction product out in the same way as the electrolyte. In some runs difficulties were encountered in getting the reaction product out, so that the lid had to be taken off and the product accumulated between the electrodes removed mechanically. Hot water rinsing also was found to help.

4. Results

The results of testing the module are shown in Figs 4 and 5. Figure 4 exhibits the voltage change with time at several constant currents. It is seen that the operation at the nominal cell current of 1 A does not affect the voltage during the 24 h period. The electrolyte could be easily drained and the cell washed free of reaction product. Contrary to that at 10 A the cell worked only for 4 h before voltage breakdown. Initial polarization and power characteristics are seen to be relatively good, with the power maximum at 6.5 W. They are, however, significantly reduced at prolonged operation, even when the cell is washed free of reaction product and filled with fresh electrolyte.

The results of the first two 24 h runs of the battery in 3% NaCl at the nominal current of 2 A are shown in Fig. 6. They are seen to be very reproducible with virtually no change in voltage during the run. Still, a loss of about 70 mV was observed.

The current–voltage and power characteristic of the first two runs are shown in Fig. 7. Although designed
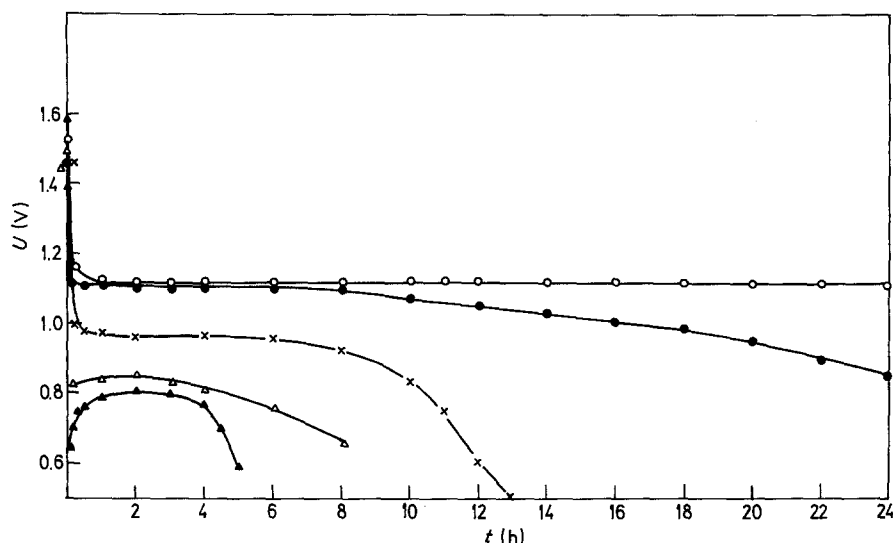
Fig. 4. Change in the voltage of a single cell module with time at different current densities: O, 1 A; ●, 2 A; ×, 5 A; △, 7 A; ▲, 10 A.

for a nominal power of 24 W, the battery is seen to be capable of delivering a maximum power of 80 W, exhibiting a good capacity for overload.

After a number of runs some sluggishness was observed in establishing the steady-state voltage as seen in Figs 8 and 9. However, at low currents, around the nominal value, initial voltages were never less than 95% of the steady-state value and the latter was established within 1 h. At higher currents the rise in voltage took a longer time but was due to an increase in cell temperature rather than to activation problems, since the latter are known to decrease with increasing current density.

It was observed that keeping the battery without the electrolyte for a longer period (48–400 h) led to somewhat lower initial voltage and it took up to 24 h to recover the last 5% of the voltage normally obtained in subsequent runs repeated every day with a fresh electrolyte.

The current–voltage characteristics of the battery in

electrolytes of different concentration, recorded after 4 h of operation at 2 A, are shown in Fig. 10. It is seen that the voltage was almost independent of concentration up to 1 A indicating the electrode polarization control over the operation. At higher currents it was the ohmic resistance of the electrolyte which took over the control. The slope of 1 ohm at the concentration of 3% is compared with 0.6 ohms at 12% NaCl which is not unexpected for concentrated electrolytes, in which deviations from linear dependence of specific conductivity on concentration are normally found.

The individual cell response to the load is exemplified in Fig. 11. A fairly large variation in the slopes, between 0.05 and 0.1 ohm, is probably due to different degrees of clogging of the cells with the reaction product. Indeed, when the battery lid was removed after some hours of operation, considerable differences in the appearance of the electrolyte in different cells could be seen. In some cells the electrolyte was quite clear, in others milky, while in a third group
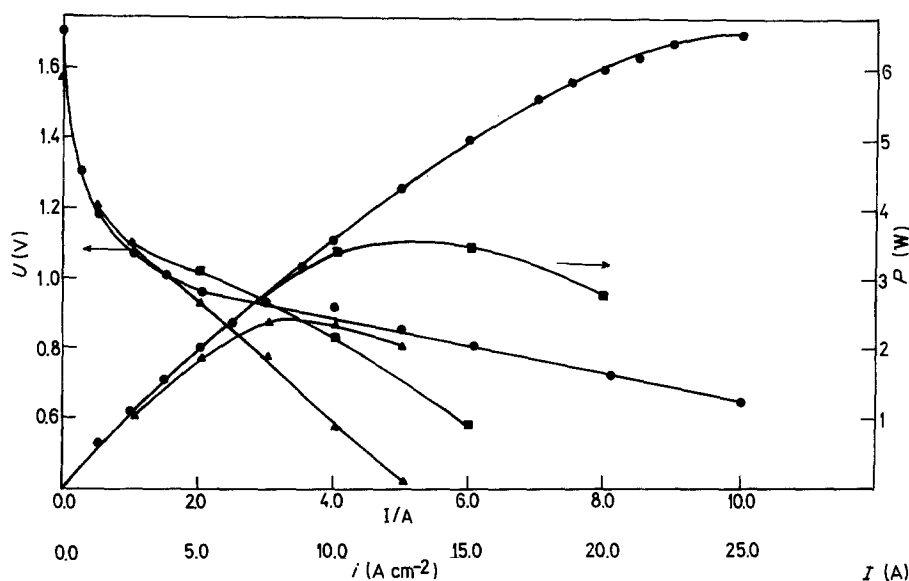

Fig. 5. Current–voltage and power characteristics of a single cell module: ●, initial performance; ▲, performance after 380 Ah without changing the electrolyte; ■, same, after washing the cell, scrubbing the electrode and refilling with fresh electrolyte.
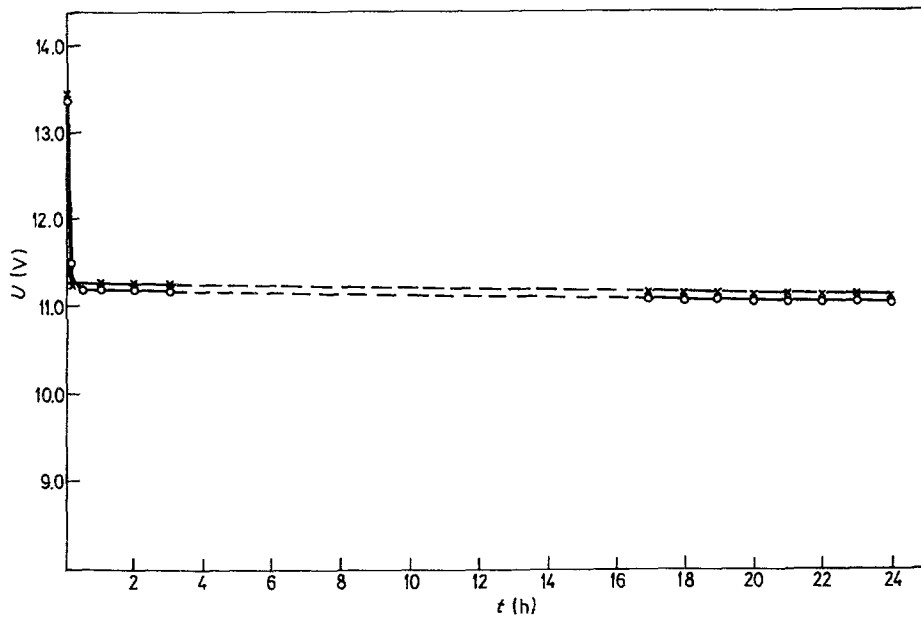
Fig. 6. Change in the battery voltage with time during the first two 24 h runs.
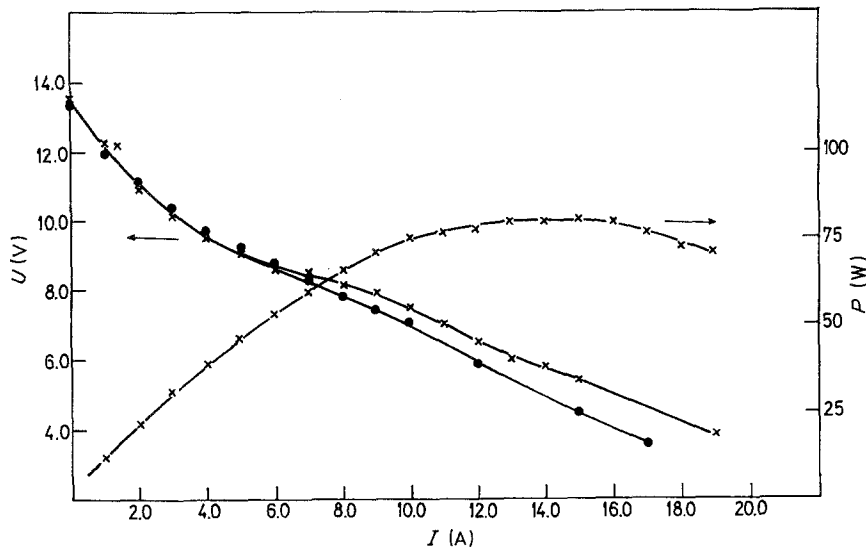

Fig. 7. Current–voltage and power characteristic of the battery in the first two runs. x, The first run; ●, the second run.
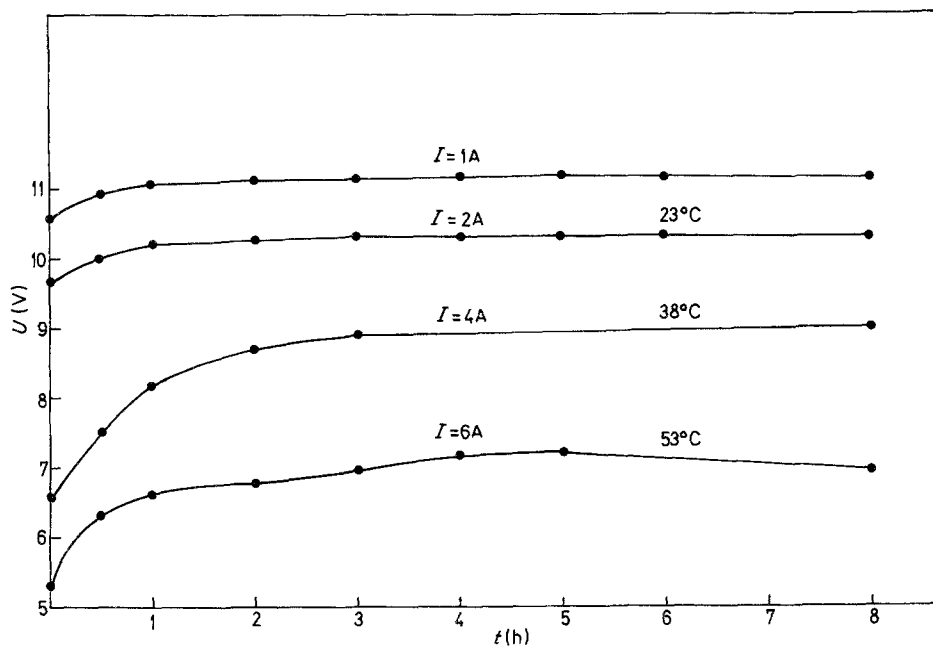

Fig. 8. Change in battery voltage with time at different current drains in 3% NaCl solution. Temperatures after 6 h of operation are noted.
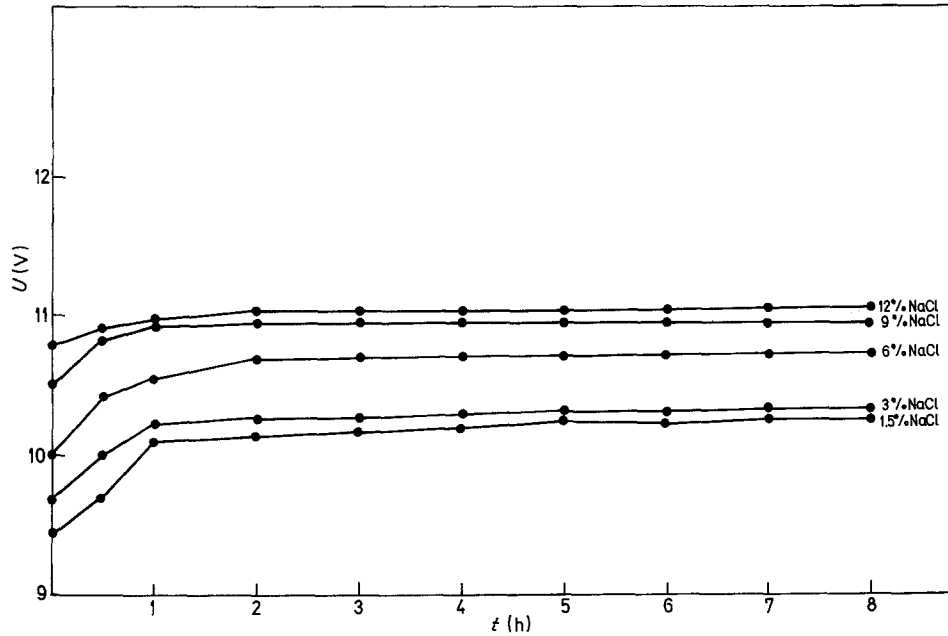
Fig. 9. Change in battery voltage with time at a current of 2 A for electrolytes of different salt concentrations.

chunks of a gel were seen to be stuck between the electrodes. This is reflected in significant differences in cell voltages, shown in the diagram of Fig. 12, which were particularly pronounced at high currents (6 A).

Inspection of the cells with the open lid showed very little hydrogen bubbling, which reflects the good corrosion resistance of the alloy even after a significant quantity of electricity (about 550 Ah) was drained from the battery.

5. Discussion

In the reported experiments only about one-fifth of the projected capacity was used. However, if it is assumed that the entire aluminium capacity of 2590 Ah placed in the battery could be used at 89% material

efficiency and taking into account the total battery weight (including electrolyte) of 40 kg, one arrives at a specific energy value of 577 Wh kg^{-1}, which is a very attractive figure.

The major problem in the work with the saline battery is the gelatinous form of the reaction product which blocks the cells and degrades their performance.

In earlier experiments with the saline battery it was shown [1] that reciprocation (i.e. a slow periodic motion up and down the electrodes) of the electrolyte helps virtually eliminate the problem of gel formation and clogging the battery, as a cause of failure. In such a case the electrolyte can accommodate up to 0.4 Ah cm^{-3}. Hence, in such a case more than one-fifth of the ampere-hour capacity of the present battery could be used with a single electrolyte filling. How-
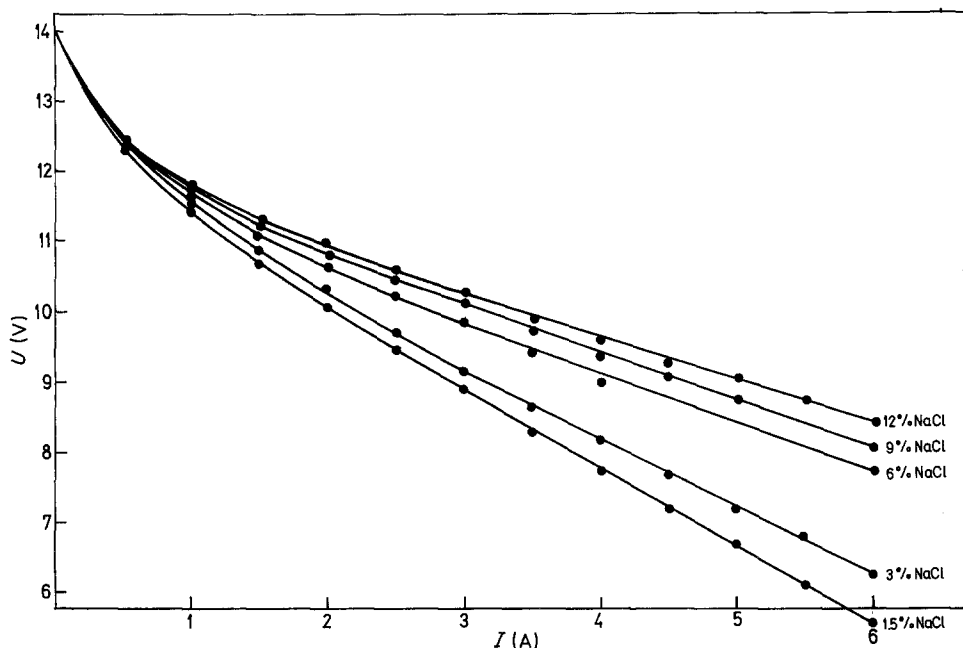

Fig. 10. Current–voltage characteristics of the battery filled with electrolyte of different salt concentrations, after 4 h of operation at 2 A.
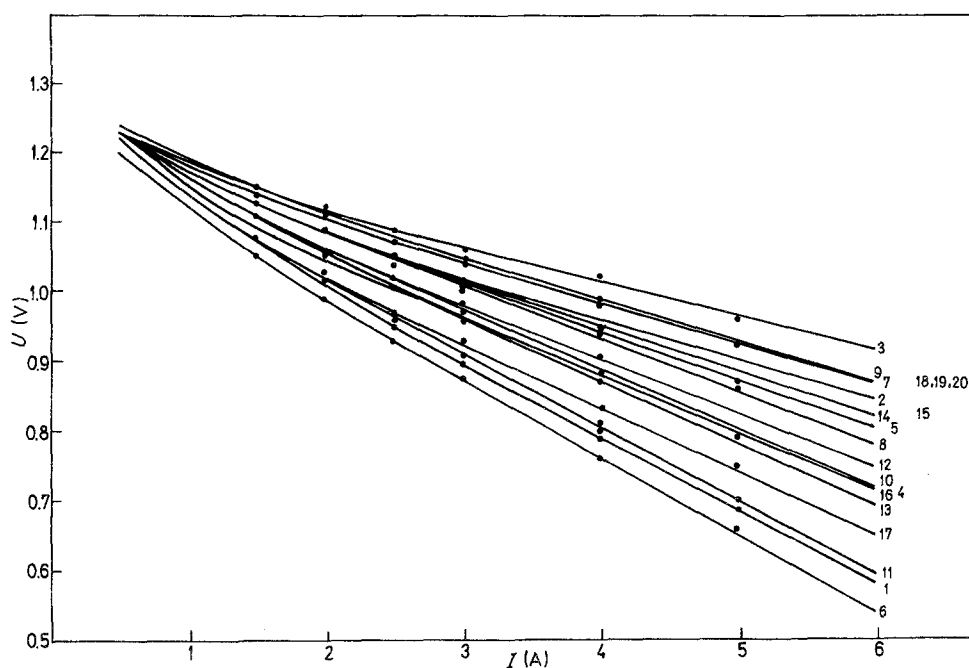
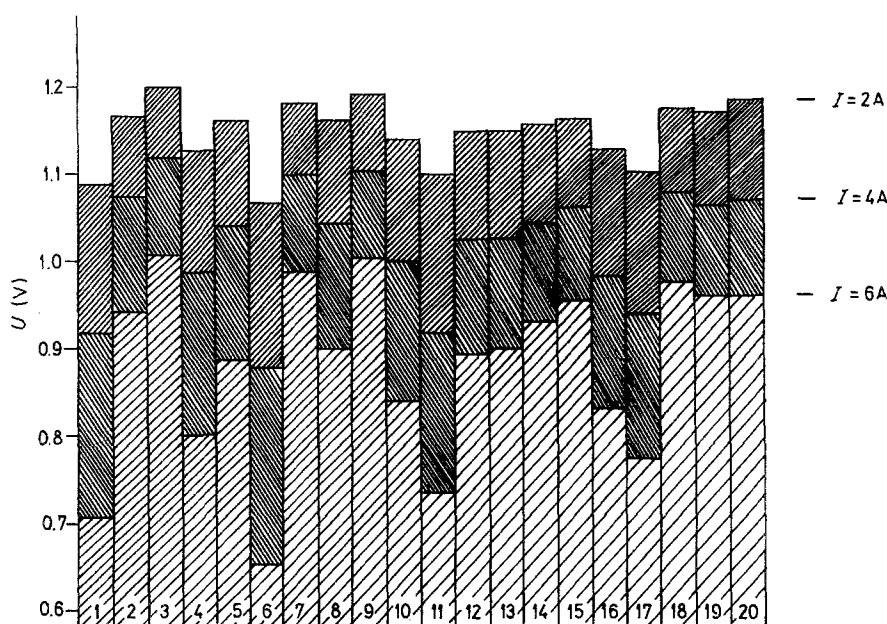Fig. 11. Individual cell current–voltage characteristics after a 4 h run on an electrolyte with 9% NaCl.

Fig. 12. Cell voltages of the cells stacked in the battery at three different currents recorded after 4 h of operation.

ever, in the present experiments the possibilities of operation with a stationary electrolyte were investigated, since it is more useful at sea to have periodic replacements of the sea water in the cells, than a reciprocation device working continuously. Indeed it was established that 24 h runs between electrolyte replacement can be achieved without difficulty.

The present construction is not very suitable for draining the cells, since all the reaction product, most of it accumulating at the bottom of the cells, has to go back between electrodes. Hence, some modifications in the draining system have been made and are being investigated. Also experiments with operation at different ambient temperatures are in progress.

Summarizing, the results demonstrate that saline aluminium–air batteries, supplied with appropriately

active alloy anodes and running on sea water, can serve as reliable large-capacity medium-power sources for sea-going applications.

Acknowledgements

References

[1]   A. R. Despić and D. M. Dražić, Bull. Soc. Chim (Beograd)
        48S (1983) 299.
[2]   G. Scamans, Chem. Ind. 17 March (1986) 192.
[3]   I. T. Reding and J. J. Newport, Mat. Protect. 5 (1966) 15.

[4] A. R. Despić, D. M. Dražić, M. M. Purenović and N. Ciković, *J. Appl. Electrochem.* **6** (1976) 527.

[5] N. Fitzpatrick and G. Scamans, *New Scient.* **111** (1986) 34.

[6] E. L. Littauer and J. F. Cooper, in 'Handbook of Batteries and Fuel Cells' (edited by D. Linden), McGraw Hill, London (1984) p. 30.

[7] A. R. Despić, *J. Appl. Electrochem.* **15** (1985) 191.

[8] A. R. Despić and P. D. Milanović, *Rec. Trav. Inst. Tech. Sci., Acad. Serbe Sci. Arts* **12** (1979) 1.

[9] I. Iliev, S. Gamburzev and A. Kaisheva, 'Air Electrodes for Aluminium–air Saline Batteries', Fall Meeting Electrochem. Soc., Las Vegas, Nevada, 13–18 Oct. (1985) Ext. Abstr., pp. 7–9.

[10] S. K. Zečevic, A. R. Despić, D. M. Dražić, A. Kaisheva and S. Gamburzev, *J. Appl. Electrochem.* **17** (1987) 657.