

Short Communication

Preliminary Studies on a Rechargeable Acidic Lead/Mercury Battery

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Summary

The charge/discharge and cycle-life characteristics of a cell consisting of a Pb/PbSO₄ and a Hg/Hg₂SO₄ electrode in aqueous H₂SO₄ (7 N and 14 N) have been studied. The charging curves show two plateau regions at ~1.0 and ~1.6 - 1.8 V. The discharge curves are fairly rectangular in shape with a plateau around 0.95 V and the efficiency goes beyond ~90% under favourable conditions. The cell can be cycled at ~80% depth of discharge without significant loss in capacity. However, on open circuit storage the cell loses half of its initial charge within 3 - 4 days.

Introduction

Despite the development of new electrochemical devices for energy storage, the lead/acid accumulator still occupies the most important position among the various secondary battery systems available except, perhaps, in applications involving miniaturised devices [1]. Lead/acid technology is backed up by the vast experience gathered over 130 years since its invention by Planté. Nevertheless, the system suffers from two major inherent drawbacks. First, the discharge process involves consumption of the electrolyte, H₂SO₄, and this sets a lower limit for the electrolyte volume at a fixed capacity. Second, the charging process involves a side reaction, *i.e.*, electrolysis of water, and thus a major portion of the charge given to the system is wasted. Moreover, the associated loss of water from the electrolyte requires frequent topping-up of the battery. At present, considerable efforts are being directed towards overcoming the latter problem in particular, *i.e.*, towards developing a maintenance-free lead/acid battery.

With respect to maintenance aspects, it is considered worthwhile to investigate the behaviour of an alternative system in which the positive electrode of a conventional lead/acid battery is replaced by a mercury/mercurous-sulphate electrode. The expected advantages of this modification are two-fold. First, as the overall process, *i.e.*,



does not involve the electrolyte there is no limit on the electrolyte volume. Second, because Hg_2SO_4 is an insulator, water electrolysis is less likely to occur on recharge. The charge-transfer kinetics of the $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode, which is widely used as a reference electrode, are also expected to be fairly rapid and comparable with those of the $\text{PbO}_2/\text{PbSO}_4$ electrode. These considerations gave rise to the present study on the charge/discharge and cycle-life characteristics of a lead/mercury system in aqueous H_2SO_4 .

Experimental

The experimental cell was constructed by coupling a cast lead rod (99.99% pure) with a mercury pool in 7 N and 14 N H_2SO_4 (AnalaR, Glaxo). The lead rod was cycled several times between the hydrogen evolution and PbSO_4 formation regions to form spongy lead prior to the measurements. The surface area of the lead electrode is thus kept at a much higher value than that of the mercury pool ($\sim 2 \text{ cm}^2$), so that the operational characteristics of the cell could be taken to reflect the behaviour of the mercury electrode alone. A constant-current source (DB-300, D.B. Electronics, India) and a digital multimeter (DM 6104 B, Electronics Corporation, India) were used to record voltage-time profiles. All measurements were conducted at room temperature ($30 \pm 2^\circ\text{C}$).

Results and discussion

The charging curves (Fig. 1) for the system under study show two distinct regions; a feature that occurs independent of the acid concentration. This behaviour has been found to be due to the $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode by charging the electrodes separately. The low top-of-charge region ($\sim 1.0 \text{ V}$) should represent the expected overall process (1) as the voltage observed more or less agrees with the calculated value. By similar reasoning, the high

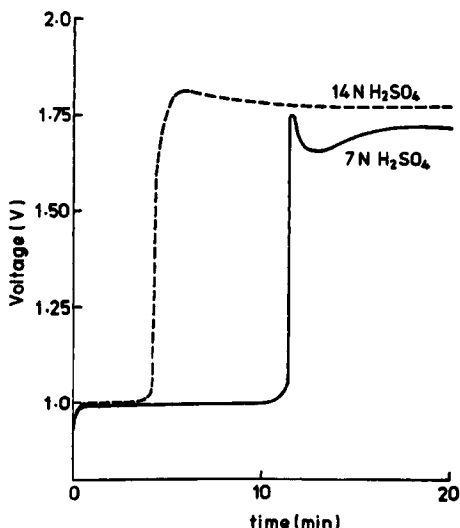


Fig. 1. Charging curves at 1 mA in 7 N (solid line) and 14 N (broken line) H_2SO_4 .

top-of-charge region ($\sim 1.6 - 1.8$ V) can be associated with water oxidation at the mercury surface under the passive layer of Hg_2SO_4 . The observation that nearly 70% charge can be recovered even if the system is operated in this region indicates, however, that the oxidation product, O_2 or H_2O_2 , can oxidise mercury via a secondary chemical process known to occur in acid solutions [2]. Figure 1 also shows that an increase in the electrolyte concentration hastens the transition from the low-voltage region to the other. This possibly indicates that the porosity of the Hg_2SO_4 layer formed decreases with increasing H_2SO_4 concentration, thus somewhat restricting the movement of SO_4^{2-} ions towards the underlying 'virgin' mercury surface. The slightly higher value of the high-voltage plateau in the case of more concentrated electrolyte supports the speculation of water oxidation being the primary electrochemical process in this region, as the activity of water decreases significantly with increasing H_2SO_4 concentration [3].

The discharge curves for the system are fairly rectangular in shape. If the charging is limited to the low top-of-charge region, around 90% discharge efficiency can be obtained. As mentioned earlier, however, on charging the system at the high-voltage region at most 70% of the input charge can be recovered on discharge. The discharge efficiencies, as usual, decrease with increasing discharge rates (Fig. 2), the decrease being more rapid in 14 N H_2SO_4 . The voltage obtained from the cell during discharge is around 0.95 V, whereas the theoretical e.m.f. has been calculated to be 0.97 V. The shelf life has been found to be not so good (Fig. 3). The cell loses half of its initial charge within 3 to 4 days on open-circuit storage.

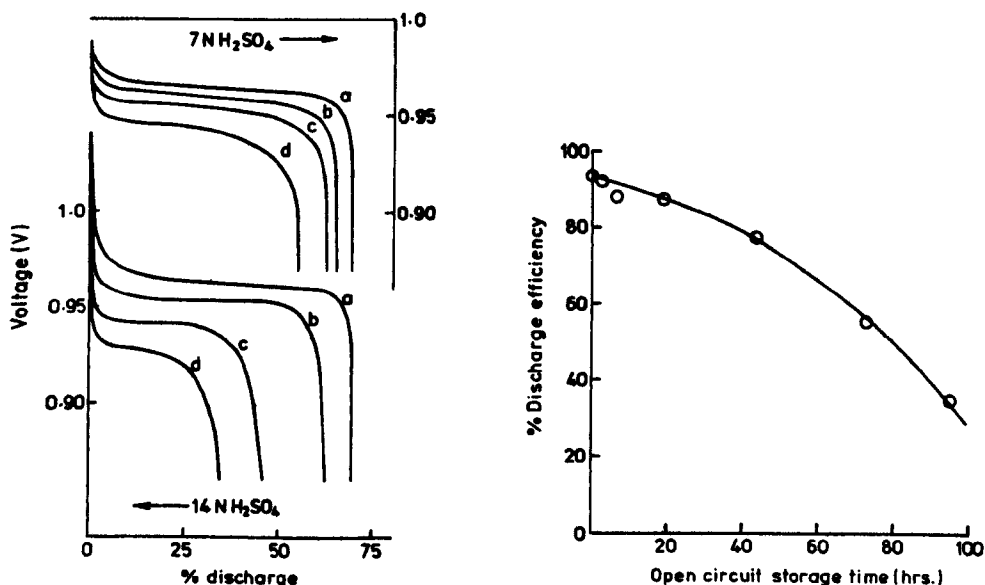


Fig. 2. Discharge curves at (a) 0.5, (b) 1, (c) 2, (d) 4 mA for a cell charged at 1 mA.

Fig. 3. Variation of discharge efficiency with open-circuit storage time.

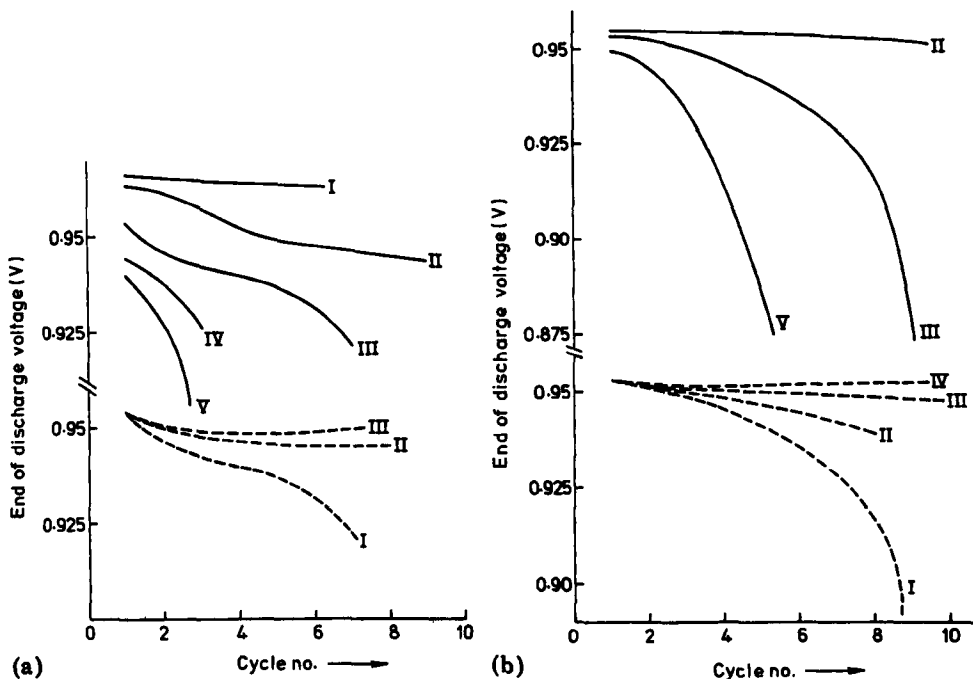


Fig. 4. Variation of end-of-discharge voltage with cycle number: (a) 7 N H₂SO₄, (b) 14 N H₂SO₄. Solid lines: discharge up to different fractions of initial charge at 100% depth-of-discharge: (I) 0.1, (II) 0.3, (III) 0.5, (IV) 0.6, (V) 0.7. Broken lines: discharge up to 50% of initial charge at different depths-of-discharge: (I) 100%, (II) 91%, (III) 83%, (IV) 77%.

This behaviour may be improved, however, by suitably altering the method of electrode preparation, particularly the mercury electrode.

To study the cycling characteristics of the system, the cell is first activated by giving a fixed quantity of initial charge. The subsequent discharge/charge cycles are carried out with variation in both discharge capacity and depth-of-discharge. The former is the quantity of charge withdrawn during discharge and the latter quantity is given by the relation: % depth-of-discharge = $100 \times (\text{discharge capacity}) / (\text{quantity of charge passed during recharge})$. The results are depicted in Fig. 4(a) and (b). Under a 100% deep-discharge mode, the end-of-discharge voltage decreases with the number of cycles. This fall in voltage becomes faster as the discharge capacity chosen is increased to progressively higher fractions of the initial charge. However, reduction in the depth-of-discharge is found to improve the cycling behaviour. With a depth-of-discharge of $\sim 80\%$, the end-of-discharge voltage remains practically unchanged with cycling at a discharge capacity of half the initial charge (broken curve III, Fig. 4(a) and (b)). This shows that only $\sim 20\%$ overcharge is necessary to make the system completely rechargeable. One can, therefore, conclude that the acidic lead/mercury cell has a potential to be developed into a practical secondary battery.

References

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