JOURNAL OF APPLIED ELECTROCHEMISTRY 4 (1974) 1–6

The discharge capacity of the lead-lead dioxide couple in fluoboric and hydrofluosilicic acid

N. A. HAMPSON

Department of Chemistry, University of Technology, Loughborough, Leics.

C. J. BUSHROD*

Chloride Industrial Batteries Limited, Swinton, Manchester

Results of an investigation of the behaviour of primary cells, based on the PbO_2/Pb couple operating in lead dissolving acids, are presented.

Specifically fluoboric and fluosilicic acids have been examined in detail and the results compared with established data from perchloric acid based systems.

As expected, the performances of the fluoridic electrolytes were somewhat inferior: however some interesting observations are reported, namely the occurrence of maxima in concentration/performance curves and the detailed form of these curves. The characteristics do not depend on the electrode/electrolyte balance within the cell.

Theories are advanced to account for the observed behaviour.

1. Introduction

Desirable properties of high rate–high performance reserve batteries include the following major ones:

1. The battery must be capable of delivering power at a high and specified rate for a period also specified.
2. The battery must be light in weight.
3. The battery must not be bulky.
4. The battery must be self-contained.
5. The battery must be capable of supplying the power almost instantly on demand.
6. For obvious reasons the battery must have excellent storage characteristics such that, depreciation over a period of years should be only marginal.

The selection of an appropriate couple has to take into account a number of factors but, transcending all others is the basic specification which a particular final production battery has to meet. The particular design requirement to be discussed in the context of this paper is as follows:

(a) The battery must yield a current of 750 A for 3·25 min at a voltage of at least 16 V (initially 18 V).
(b) The battery must not weigh more than 50 Kg (i.e. 10·8 Wh Kg^{-1} at the 3-min rate).
(c) The volume of the battery must not be greater than 30 l (0·018 Wh ml^{-1}).
(d) The battery must be capable of 5 years' storage without appreciable loss of performance.

A comprehensive survey of the literature indicated that, with one significant exception, it would be necessary to use couples which were only capable of high rate performance at the expense of very great bulk or weight, or alternatively high cost; the silver oxide/zinc couple is an admirable example, of the latter. The exception is the couple based on electrodeposited lead dioxide operating against a negative of

---

* Present address: Department of Chemistry, University of Manchester, Manchester.

metallic lead in an electrolyte of lead-dissolving acid, such as perchloric, fluoboric, fluosilicic or nitric. In addition to the data which suggested that cells based on this system were capable of delivering energy at high current density, whilst maintaining reasonable potential, it also seemed that the production of the electrodes for such cells might conceivably be developed to a point where it was a more than feasible commercial operation. In short, from *a priori* considerations it seemed that in this system it would be possible to produce high performance batteries capable of meeting the desired specifications using production methods similar to those conventionally used in the battery industry.

This in fact proved to be the case for the PbO_2/Pb couple operating in perchloric acid electrolyte. However, the use of this acid has some disadvantages. The principal one is the explosion risk when perchloric acid comes into contact with organic materials.

It was realized that it was unlikely that any other electrolyte would permit a cell performance comparable with that obtained with perchloric acid, on account of the outstanding solubility of lead perchlorate. The lead salts of fluoboric and fluosilicic acids were known to be very soluble, however, and it was decided to test these acids, in various concentrations, in order to establish whether or not one or other could be used instead of perchloric acid without a serious reduction in the electrical output of the cell. Cells based on the lead/lead dioxide couple and using fluoboric acid as the electrolyte, have found use in more than one field: nothing closely comparable with this present requirement has yet been met by this system however [1].

The present paper describes our results.

2. Experimental

A cell for the study of single plate discharges was devised, in which a positive plate (having rubber bands positioned on it so as to act as separators) situated between two negative plates was discharged through a selected resistance under controlled conditions.

The vessels in which these discharges were carried out were constructed of hard rubber (i.e. rubber which has been fully vulcanized with sulphur) sheet as this material was found to be quite resistant to the acids used under the conditions of the test discharges. Sheets of lead 0·025 cm thick, containing 0·08% calcium as alloying addition, were inserted in the outer slots and were connected through resistances of Nichrome wire cooled in baths of glycerol, so that, on filling the vessel with an appropriate electrolyte, the discharge begins and each side of the positive plate can be tested independently.

Positive plates (10 cm × 5 cm × 0·01 cm) were prepared as described elsewhere [2, 3] by depositing lead dioxide (at a current rate equivalent to 0·043 g cm^{-2}) until a mean deposit weight of 26·4 g had been obtained.

Three single plate test cells, which differed only in the spacing between the negative auxiliary electrodes, were used; these spacings were 0·34 cm, 0·58 cm and 1·19 cm respectively and corresponded with volumes of electrolyte of 59 ml, 85 ml and 150 ml. The choice of the two larger cell dimensions was somewhat arbitrary, but the smallest was based on the electrode spacings and electrolyte volumes, which could be accommodated assuming that *twelve cells* each having 23 positive and 24 negative plates would be near optimal in meeting the high rate electrical performance specified for the battery.

A number of positive plates were tested in the smallest cell using 55% w/v perchloric acid as the electrolyte. Resistances of 0·08 Ω were used which, at a final cell voltage of 1·33 V, correspond with the current required to give 750 A from a cell embodying 23 such positives. Twelve cells connected in series and discharging to a final voltage of 1·33 would, in this regard, conform to the battery-specified final voltage of 16 V at the high rate of discharge. In addition the choice of this method of test rather than pure galvanostatic discharge had the advantage of more nearly corresponding to service conditions.

Under these conditions, and at a temperature of 15°C*, it was found that the initial voltage on discharge was always between 1·52 and 1·58 V, therefore the selected parameters for the cell and battery design were thus far consistent with the specifications for the high rate discharge. These test discharges of single plates were initiated by

---

*All data in this paper were obtained at a temperature of 15°C.

pouring the electrolyte into the cell after electrical connection had been made. This eliminated the need for switching heavy currents (with all its attendant problems) and indeed simulated the eventual battery-operating mode.

Typical discharges gave durations of 4 min ± 20 s. It was observed that significant variations in the duration of the discharge from each side of the positive plate were frequent; this was attributed to small variations from symmetry in the arrangement caused by the plates not being truly planar. The end point of the discharge is brought about by passivation but there is of course some convection which serves to delay the onset of film formation. Even slight variations in the gap between the tested positive plate surface and the negatives, would have a profound effect on the convection process.

3. Results

Fluoboric and fluosilicic acid electrolytes

Using the single plate test equipment described, a number of tests were made on standard positive plates discharging in fluoboric and fluosilicic acids of various concentrations. Most of the experimental discharges were made in the cell having a 0·34 cm electrode spacing. A few, however, were carried out in the larger cells. In all these tests the currents were maintained constant using a large battery and series resistor.

The results of discharging plates in fluoboric acid of varying concentrations using a range of current densities are shown in Fig. 1.

Results from discharges carried out in fluosilicic acid over a range of concentrations and current densities are shown in Fig. 2.

It will be remarked that, at the higher current densities, the curves of output (in Ah) against acid concentration pass through maxima; the relevant figures are entered in Table 1. (Data are

Table 1. Values of capacity, initial voltage and acid concentration at the maxima of the curves in Figs. 1 and 2 (Perchloric acid data included for comparison)

Current (A)	*Fluoboric acid*			*Fluosilicic acid*		
	Ah	*Volts*	*Conc. (mol l^{-1})*	*Ah*	*Volts*	*Conc. (mol l^{-1})*
15	2·40	1·52	6·7	2·35	1·63	4·05
20	1·85	1·51	6·75	1·90	1·57	3·60
30	1·55	1·44	5·7	1·00	1·48	2·93

Current (A)	*Perchloric acid (55%)*	
	Ah	*Volts*
15	3·4	1·70
20	2·9	1·66
30	2·43	1·56

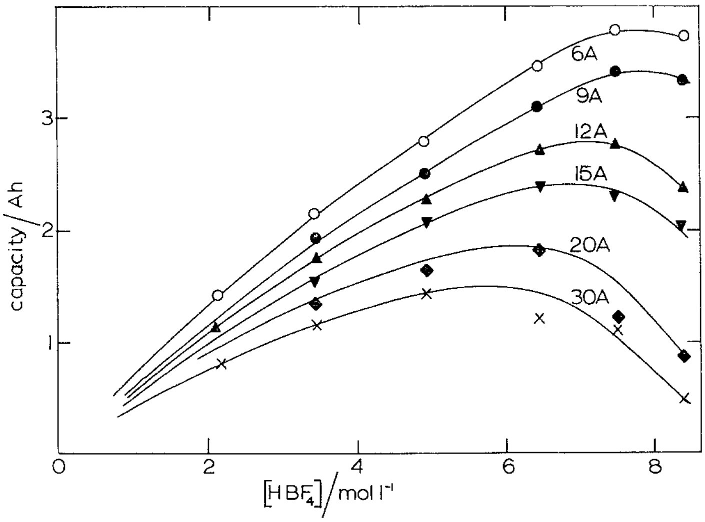

Fig. 1. Single plate discharges in HBF_4. Capacity-concentration data at various discharge rates.

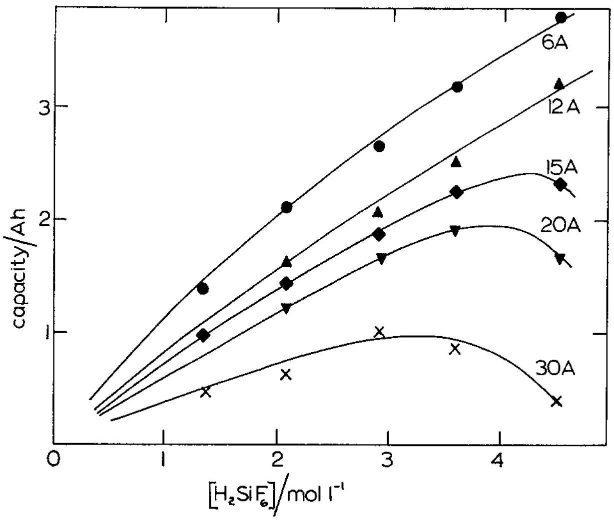

Fig. 2. Single plate discharges in H_2SiF_6. Capacity-concentration data at various discharge rates.

included for comparison with the perchloric acid system.) It is of interest to speculate on the reason for this general effect and this will be discussed later.

A few discharges were made using the two larger test cells and the results of these experiments are entered in Tables 2 and 3 for fluoboric acid and 4 and 5 for fluosilicic acid.

Table 2. Discharges in fluoboric acid with auxiliary electrodes spaced at 0·58 cm (85 ml electrolyte)

Fluoboric acid concentration ($mol\ l^{-1}$)		*Current in amperes*	
		12	30
3·45	I.V.	1·52	1·38
	Ah	2·1	1·25
4·01	I.V.	1·53	1·41
	Ah	2·5	1·4
4·95	I.V.	1·54	1·42
	Ah	2·9	1·75
6·09	I.V.	1·56	1·43
	Ah	3·4	2·15

I.V. denotes initial voltage

Table 3. Discharges in fluoboric acid with auxiliary electrodes spaced at 1·19 cm (150 ml electrolyte)

Fluoboric acid concentration ($mol\ l^{-1}$)		*Current in amperes*		
		9	15	30
3·45	I.V.	1·55	1·50	1·33
	Ah	4·12	3·25	1·75
4·01	I.V.	1·55	1·50	—
	Ah	4·90	4·5	—
4·95	I.V.	1·57	1·52	—
	Ah	5·7	5·25	—
5·45	I.V.	1·55	1·52	1·43
	Ah	4·35	4·7	2·9
6·09	I.V.	—	—	1·33
	Ah	—	—	2·9
6·47	I.V.	—	—	1·33
	Ah	—	—	2·7
8·37	I.V.	—	—	1·22
	Ah	—	—	0·5

Table 4. Discharges in fluosilicic acid with auxiliary electrodes spaced at 0·58 cm (85 ml electrolyte)

Fluosilicic acid concentration (*mol l^{-1}*)		*Current in amperes*	
		12	30
1·88	I.V.	1·53	1·38
	Ah	1·3	0·25
2·40	I.V.	1·56	1·40
	Ah	1·8	0·35
2·93	I.V.	1·57	1·41
	Ah	1·9	0·5
3·71	I.V.	1·58	1·45
	Ah	2·6	0·7

Table 5. Discharges in fluosilicic acid with auxiliary electrodes spaced at 1·19 cm (150 ml electrolyte)

Fluosilicic acid concentration (*mol l^{-1}*)		*Current in amperes*	
		12	30
1·88	I.V.	1·51	1·31
	Ah	2·1	0·25
2·40	I.V.	1·51	1·35
	Ah	2·6	0·35
2·93	I.V.	1·53	1·36
	Ah	3·0	0·5
3·71	I.V.	1·54	1·36
	Ah	3·4	0·75

4. Discussion

In assessing the potentialities of these two acids, as electrolytes for batteries to meet the specification, the difficulties stem from the number of variables involved. Volume, weight, current and ampere hours have all to be reconciled with each other and with the minimum design requirements. Some simplification results from concentrating on the high rate requirement of 750 A for 3·25 min, to a final voltage of 16 V, equal to 40·6 Ah.

Inspection of Table 1 enables us to make trial calculations as follows:

At 15 A per positive plate in fluoboric acid of concentration 6·7 mol l^{-1} the capacity per plate is 2·5 Ah. Fifty plates would be necessary to yield the 750 A discharge current but the capacity of the cell would be 125 Ah or three times the requirement. The initial voltage of 1·52 V would be satisfactory for the twelve-cell battery but each cell would be more than twice as large as the provisional design based on perchloric acid.

At 20 A per plate the capacity of 1·85 Ah per plate is again more than adequate but 38 plates would be necessary for each cell and, though a twelve cell battery would meet the initial voltage requirement the margin would be small.

At 30 A per plate only 25 plates per cell would be necessary but the capacity at 38·75 Ah (25 × 1·55) is inadequate. Moreover the initial voltage at 1·44 V would involve the use of 13 cells in order to meet the initial battery voltage of 18 V specified for the 750 A rate of discharge.

It will be seen from Table 1 that, although the initial voltages using fluosilicic acid are somewhat higher than with fluoboric, the difference is not sufficient to offset the further reduction in capacity.

The maxima shown by the curves relating to the higher current densities in Figs. 1 and 2 may be explained as follows:

1. Although the vertical attitude of the electrodes in these single plate test cells permits some convection, at sufficiently high current densities the discharge will be terminated by the formation of a passive film of reaction product.
2. The greater the acid concentration the less will be the solubility of the reaction product.
3. Since the capacity is measured by the time taken, at a fixed current, to reach an arbitrary final voltage, the high resistivity of dilute electrolytes will tend to restrict the discharge.

Considering these three factors we should expect the measured capacity at a given current to increase with increasing electrolyte concentration until the advantages of reducing resistivity are overtaken by the declining solubility of the reaction product. Increasing the current would merely displace the curve downwards as is seen in Figs. 1 and 2.

Using greater electrode separations, and incidentally more electrolyte, permits much freer convection and thus delays the onset of passivation. One would therefore anticipate that the general shape of the curves would be the same but that, at any given current and electrolyte concentration, capacities would increase with the electrode separation. An inspection of Tables 1, 2, 3 and 4 reveals that this is generally so and in Fig. 3 typical results have been plotted for fluoboric acid electrolyte at the 30 A rate of discharge for the three separations. In the case of fluosilicic acid at the 30 A rate, passivation occurs so rapidly that the convection process has little modifying effect.

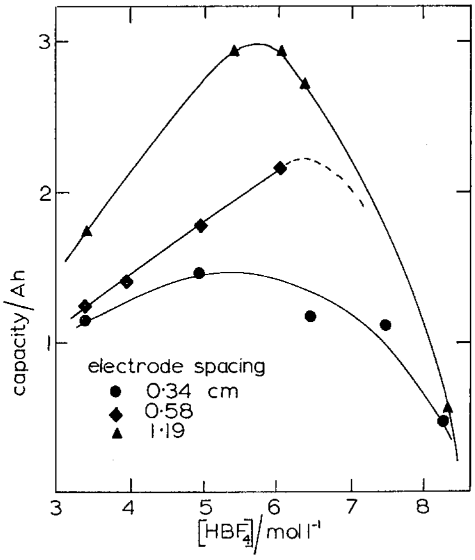

Fig. 3. Performances of single plate cells (HBF_4 electrolyte) at various concentrations and electrode separations.

Acknowledgements

We are grateful to Professor R. F. Phillips for provision of laboratory facilities and to the directors of Chloride Industrial Batteries Limited for permission to publish this paper.

References

[1] G. D. McDonald, E. Y. Weissman and T. S. Roemer, *J. Electrochem. Soc.*, **119** (1972) 660.

[2] C. J. Bushrod and N. A. Hampson, *Trans. Inst. Metal Finishing*, **48** (1970) 131.

[3] C. J. Bushrod and N. A. Hampson, *Br. Corros. J.*, **6** (1971) 129.