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EFFECT OF ELECTROLYTE IMPURITY ON THE ELECTROCHEMICAL PERFORMANCE OF THE LEAD/TETRAFLUOROBORIC ACID/LEAD DIOXIDE CELL

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Summary

Electrolyte composition influences the activation response of and the maximum voltage achieved by the lead/tetrafluoroboric acid/lead dioxide reserve battery. In this study the optimum concentrations of tetrafluoroboric acid, boric acid and glycerol were established from voltage/concentration relationships and the effect of analyzed impurities on electrochemical performance investigated over a range of concentrations at 242, 293 and 333 K. Silicon and iron impurities had little effect on performance but chloride and sulphate ions decreased the cell efficiency particularly at 242 K. Fluctuations in voltage/time records from cells with solutions containing chloride ion or sulphate ion are discussed.

Introduction

The satisfactory performance characteristics of the lead/tetrafluoroboric acid/lead dioxide ($Pb/HBF_4/PbO_2$) electrochemical system over a wide temperature range have led to applications of the cell as a reserve battery. Recent investigations have reported improvements in the plate material; high compressive stress in β-PbO_2 electrodeposited onto a nickel/steel substrate has resulted in superior discharge characteristics [1]; bonded PbO_2 electrodes have been developed and are claimed to have greater capacities, better mechanical properties [2], longer activated open-circuit life and improved low temperature performance [3]. The performance of the electrolyte solution has been investigated at various concentrations of HBF_4 with the Pb/PbO_2 couple and compared with the results from hexafluorosilicic and perchloric acids [4].

In this study, samples of commercial and laboratory-prepared HBF_4 solutions were analyzed using chemical methods; HBF_4 solutions containing a range of concentrations of each constituent were made up and subjected to

single cell electrochemical activation tests with the Pb/PbO_2 couple at 242, 293 and 333 K.

Experimental

HBF_4 solution was prepared by adding stoichiometric quantities of boric acid to concentrated hydrofluoric acid solution [5]; a more concentrated commercial sample was used for experiments in which the effect of varying the HBF_4 concentration was investigated. Analysis of the acid solutions was based on a combination of titrimetric (HBF_4 and H_3BO_3 acids), spectrophotometric (silicon and iron) and absorptiometric (chloride and sulphate ions) techniques. The titrimetric and spectrophotometric methods described in British Standard 2657 were found to be suited to the requirements of this study. The absorptiometric method was based on turbidity measurements of finely divided precipitates of silver chloride and barium sulphate.

The anode material was freshly prepared by electrodepositing lead from lead tetrafluoroborate solution onto nickel sheet and the lead dioxide cathode material was obtained from the Ionic Plating Co., Birmingham. Preliminary tests on random samples of electrode material gave consistent electrochemical performance. Electrode pairs, each with an active surface area of 1.0 cm^2, were mounted 0.3 cm apart on a test jig (Fig. 1). Prepared electrodes were tested on the same day as a precaution against contamination or deterioration. Series of electrolyte solutions were prepared by dilution of the more concentrated HBF_4 solution and by adding H_3BO_3, glycerol, silica, iron, hydrochloric and sulphuric acids usually to the laboratory-prepared solution. The volume changes resulting from these additions were compensated for when the increase in volume exceeded 1%.

The electrochemical measurements were made at 242, 293 and 333 K with the test jig in an environmental cabinet. Following an aclimatization period of 3 hours each cell was activated in turn by an electrical pulse which released the raised arm allowing the electrodes to drop into the electrolyte solution. A 56 ohm resistor was incorporated into the cell circuit and voltage/time profiles were recorded using a u.v. recorder. The cell circuit was disconnected after 120 seconds.

Results and Discussion

Analytical results obtained from the HBF_4 solutions are contained in Table 1. The mean HBF_4 and H_3BO_3 acid concentrations were determined from 10 titrations and the standard deviation for both found to be 0.05 mol/dm^3. Lange [6] has reported that, in the absence of interfering anions, nitron–HBF_4 complex precipitation occurs quantitatively and Wamser [7] has established that the principal hydrolysis product of the acid, the hydroxy-
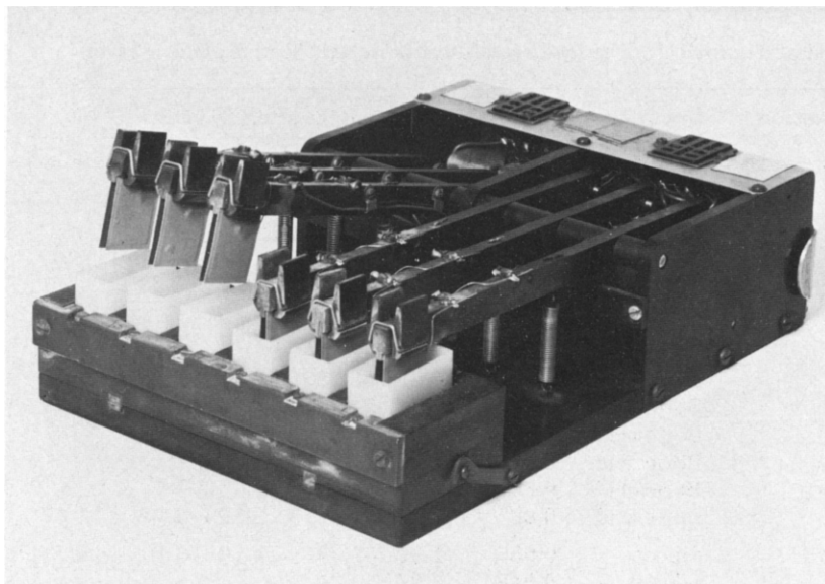
Fig. 1. Lead/tetrafluoroboric acid/lead dioxide cell test jig.

TABLE 1

Analytical results for tetrafluoroboric acid solutions

Species	Commercial sample (mol/dm^3)	Laboratory sample (mol/dm^3)
Tetrafluoroboric acid*	6.52	5.50
Tetrafluoroboric acid**	6.15	5.45
Boric acid	0.57	–
Silicon	0.003	0.023
Iron	0.0033	0.0001
Fluoride ion	–	0.20
Chloride ion	0.0003	0.0011
Sulphate ion	0.001	0.024

*Titrimetric.
**Nitron complex.

trifluoroborate ion, is not precipitated by nitron. The HBF_4 solutions were approximately 3 (laboratory) and 20 (commercial) months old when the analyses were carried out. Comparison of the titrated values of HBF_4 in each sample (representative of the total fluoride ion content) with the amount of unhydrolyzed HBF_4 calculated from the nitron–HBF_4 complex precipitations gave a measure of the rate of hydrolysis. The respective percentage of hydrolyzed HBF_4 in the 3 and 20 months old samples were about 1 and 6.

The voltages obtained using various electrolyte solutions in the electrochemical experiments are presented in Table 2. Six identical activation experiments were carried out consecutively to provide the mean values and the

TABLE 2

Electrochemical performance of the lead/tetrafluoroboric acid/lead dioxide system

HBF$_4$ concentration (mol/dm^3)	Impurity concentration (mol/dm^3)		Mean voltage after 0.1 and 120's at					
			242 K		293 K		333 K	
5.05[a]	Boric acid	0.57	1.28	1.34	–	–	–	–
5.48	Boric acid	0.57	1.28	1.34	–	–	–	–
5.87	Boric acid	0.57	1.33	1.37	1.61	1.63	1.73	1.74
6.19	Boric acid	0.57	1.31	1.35	–	–	–	–
6.53	Boric acid	0.57	1.27	1.32	1.59	1.62	1.72	1.75
5.50[b]	Boric acid	0.05	1.23	1.28	1.60	1.64	1.73	1.75
5.50	Boric acid	0.04	1.34	1.37	–	–	–	–
5.50	Boric acid	0.22	1.32	1.37	–	–	–	–
5.50	Boric acid	0.45	1.32	1.37	–	–	–	–
5.50	Boric acid	0.68	1.31	1.36	–	–	–	–
5.50	Boric acid	0.82	1.29	1.34	1.59	1.62	1.69	1.71
5.50[c]	Silicon	0.035	1.30	1.35	1.60	1.61	1.71	1.74
5.50	Silicon	0.048	1.28	1.34	–	–	–	–
5.50	Silicon	0.084	1.29	1.33	–	–	–	–
5.50	Silicon	0.125	1.29	1.32	1.60	1.61	1.69	1.73
5.50[c]	Iron	0.005	1.30	1.35	1.61	1.62	1.72	1.74
5.50	Iron	0.012	1.28	1.34	–	–	–	–
5.50	Iron	0.049	1.29	1.37	–	–	–	–
5.50	Iron	0.092	1.26	1.36	1.58	1.62	1.70	1.73
5.50[c]	Chloride	0.005	1.24	1.39	1.59	1.63	1.70	1.74
5.50	Chloride	0.009	1.23	1.35	1.57	1.62	1.68	1.72
5.50	Chloride	0.026	1.27	1.37	1.56	1.63	1.67	1.72
5.50	Chloride	0.041	1.19	1.38	1.56	1.63	1.66	1.72
5.50	Chloride	0.064	1.13	1.38	1.55	1.63	1.66	1.74
5.50	Chloride	0.081	1.04	1.35	1.55	1.63	1.65	1.72
–	Chloride	0.080	1.11	0.35	–	–	–	–
5.50[c]	Sulphate	0.030	1.29	1.33	1.60	1.62	1.72	1.74
5.50	Sulphate	0.037	1.29	1.32	1.59	1.61	1.72	1.73
5.50	Sulphate	0.072	1.29	1.31	1.59	1.60	1.76	1.72
5.50	Sulphate	0.094	1.29	1.33	1.60	1.60	1.72	1.70
5.50	Sulphate	0.112	1.29	1.31	1.60	1.60	1.71	1.70
5.50	Sulphate	0.129	1.27	1.30	1.62	1.59	1.68	1.68
–	Sulphate	0.130	1.11	0.00	–	–	–	–
5.48[a]	Glycerol	0.020	1.31	1.37	–	–	–	–
5.48	Glycerol	0.056	1.30	1.38	1.61	1.63	1.72	1.74
5.48	Glycerol	0.100	1.30	1.36	–	–	–	–

[a]Commercial solution with 0.57 mol/dm^3 H$_3$BO$_3$ added.
[b]Laboratory-prepared solution.
[c]Laboratory-prepared solution with 0.3 mol/dm^3 H$_3$BO$_3$ added.

standard deviation over the range of mean voltages was 0.01 V. Since the electrochemical performance of each cell was worst at the lowest test temperature, more data were collected at 242 K than at 293 or 333 K. At 242 K

a broad maximum was detected at approximately 5.8 mol/dm^3 HBF$_4$ when the acid concentration was varied between 5.05 and 6.50 mol/dm^3. Hampson and Bushrod [4] have identified maxima in the range 2 to 8 M HBF$_4$ at 288 K, the precise position being dependent on current density. The maxima were explained in terms of the opposing effects of electrolyte concentration and reaction product solubility. Variation of the H$_3$BO$_3$ concentration in HBF$_4$ solution in the range 0.04 to 0.50 mol/dm^3 had little effect on the activation response of and maximum voltage attained by the electrochemical cell. However, a deficiency of H$_3$BO$_3$ (*i.e.* excess fluoride ion) had a detrimental effect on performance at 242 K. Addition of glycerol to the electrolyte improved the low temperature performance of the Pb/HBF$_4$/PbO$_2$ cell by a small amount. This was attributed principally to an improvement in conductivity at 242 K resulting from freezing point depression of the solution and perhaps also to an increase in the acid strength of H$_3$BO$_3$ caused by complex acid formation thus:

$$H_3BO_3 + CH_2OH.CHOH.CH_2OH \rightarrow CH_2OH.\underset{\underset{\underset{BO^-H^+}{\diagdown\diagup}}{O\quad O}}{CH-CH_2} + 2H_2O$$
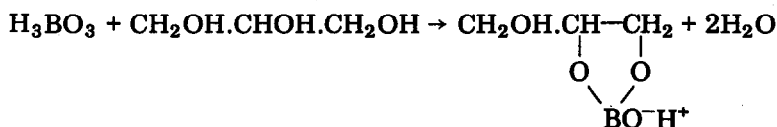
At the highest concentrations investigated, the presence of elemental iron and silicon in solution at 242 K had a small effect on the activation response and maximum voltage achieved respectively, although these concentrations were about an order of magnitude greater than the maximum levels of impurity found on analysis of the HBF$_4$ solutions.

Above critical concentration levels, the anion impurities in the electrolyte produced characteristic waves in the voltage/time curves (Figs. 2 and 3). Complete sets of data were collected at all three temperatures and the phenomenon was noted at 242 K for Cl$^-$ ion concentrations in excess of 0.035 mol/dm^3 and at 242 and 333 K for SO$_4^{2-}$ ion above 0.11 mol/dm^3. Under the conditions where the wave effect was not observed (Cl$^-$ ion at 293 and 333 K and SO$_4^{2-}$ ion at 293 K) the activation response deteriorated with increasing Cl$^-$ ion concentration at 293 and 333 K. For comparison Pb/PbO$_2$ electrodes were also discharged in aqueous solutions of either 0.13 mol/dm^3 sulphuric acid or 0.08 mol/dm^3 hydrochloric acid only (Figs. 4d and 5d).

Linear potential sweep techniques have been used by Fleming *et al.* [8] to investigate the electrochemistry of lead in perchloric and sulphuric acids. In HClO$_4$ solution lead dissolved directly as the solvated Pb^{2+} ion and in HClO$_4$/H$_2$SO$_4$ mixtures the ClO$_4^-$ ion occupied the first hydration shell of the Pb^{2+} ion in preference to the HSO$_4^-$ ion. In H$_2$SO$_4$ solution at low current densities the anodes was considered to dissolve as a lead-containing species (PbSO$_4$ or PbHSO$_4^+$) whereas at higher anodic potentials PbSO$_4$ formed directly on the electrode surface by a solid state nucleation and growth mechanism. These conclusions are in general agreement with earlier work by Archdale and Harrison [9] favouring a solution/precipitation reaction mechanism controlled by the solubility product of PbSO$_4$.
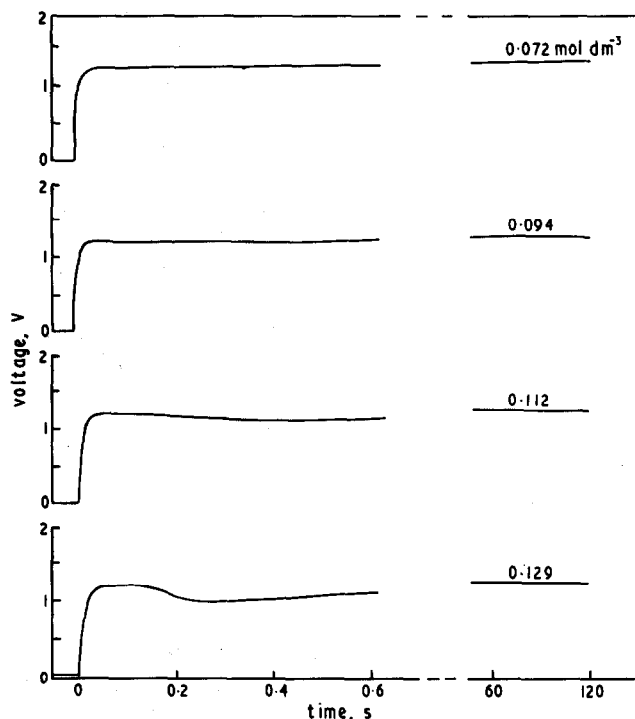
Fig. 2. Effect of sulphate ion concentration on the voltage performance of the Pb/HBF$_4$/PbO$_2$ cell at 242 K.

On activation of the Pb/PbO$_2$ couple in 0.13 mol/dm^3 H$_2$SO$_4$ solution direct nucleation and growth of PbSO$_4$ on the anode surface is considered to take place causing rapid passivation of the electrode (Fig. 4d). Since Pb(BF$_4$)$_2$, like Pb(ClO$_4$)$_2$, is very soluble in aqueous solution an analogy may be made between the HBF$_4$/H$_2$SO$_4$ solutions investigated in this work and the HClO$_4$/H$_2$SO$_4$ mixtures studied by Fleming et al. With SO$_4^{2-}$ ion present as impurity in concentrated HBF$_4$ solution the direct dissolution of lead as Pb^{2+} solvated by BF$_4^-$ ions dominates PbSO$_4$ formation at the anode. However, above critical concentrations of SO$_4^{2-}$ ion impurity fluctuations were noted in the voltage/time curves at approximately 0.2 s after activation at 242 and 333 K (Figs. 4a and 4c). On activating the cell, SO$_4^{2-}$ ions migrate from the diffusion layer and absorb on the anode surface at nucleation sites (Figs. 4a1 and 4c1) participating in the electrochemical step:

$$Pb_{(s)} + SO_{4(sol)}^{2-} \rightarrow PbSO_{4(ads)} + 2e$$
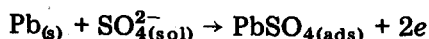
As PbSO$_4$ crystals grow on the electrode surface the cell voltage falls (Figs. 4a2 and 4c2) until the supply of SO$_4^{2-}$ ions in the diffusion layer becomes depleted (Figs. 4a3 and 4c3). At 242 K the migration rate of SO$_4^{2-}$ ions from the bulk solution was insufficient to maintain the reduced voltage level which recov-
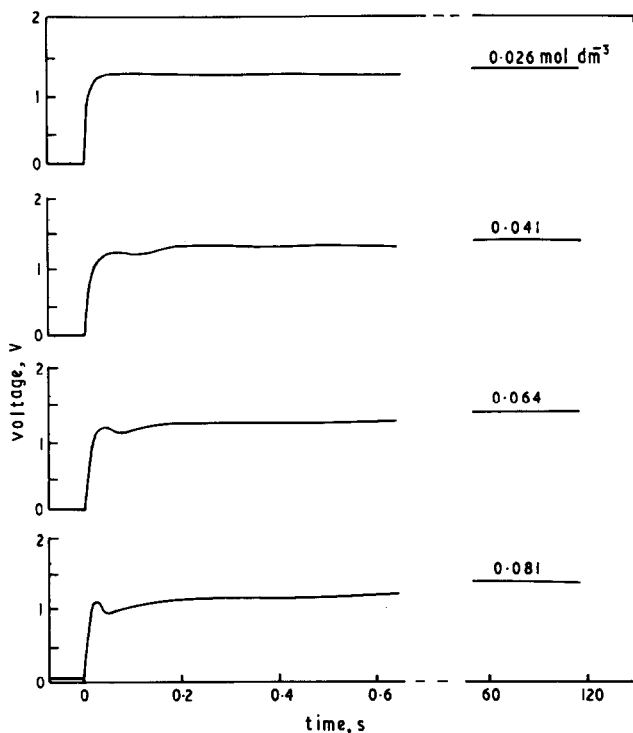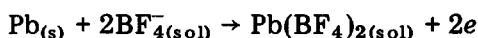
Fig. 3. Effect of chloride ion concentration on the voltage performance of the Pb/HBF$_4$/PbO$_2$ cell at 242 K.

ered towards the original value (Fig. 4c4) attributed to the principal electrode reaction:

$$Pb_{(s)} + 2BF_{4(sol)}^- \rightarrow Pb(BF_4)_{2(sol)} + 2e$$

The PbSO$_4$ initially precipitated onto the anode was removed by erosion of the actively dissolving lead around the crystal sites rather than by direct solution of PbSO$_4$. At 333 K the improved migration of SO$_4^{2-}$ ions to the electrode from the bulk solution resulted in an extended period at the lower voltage level (Fig. 4a4). The times between activation of the cell and the voltage fall at 242 and 333 K were 0.15 and 0.13 s respectively which compare favourably with the corresponding period of 0.18 s in the 0.13 mol/dm^3 H$_2$SO$_4$ solution investigated at 283 K (Fig. 4d). The voltage/time curves obtained at 293 K did not show the fluctuations found at the other temperatures (Fig. 4b). The reason for this is not clear although the absence of a voltage drop shortly after activation suggests that growth of PbSO$_4$ on the anode surface had been inhibited.

The discharge of lead in aqueous HCl solution has been studied recently by Klepinina et al. [10] and Barradas et al. [11]. The former group established that at high anodic potentials and low Cl$^-$ ion concentrations PbCl$_2$ was formed in preference to higher complex chlorides. The dissolution
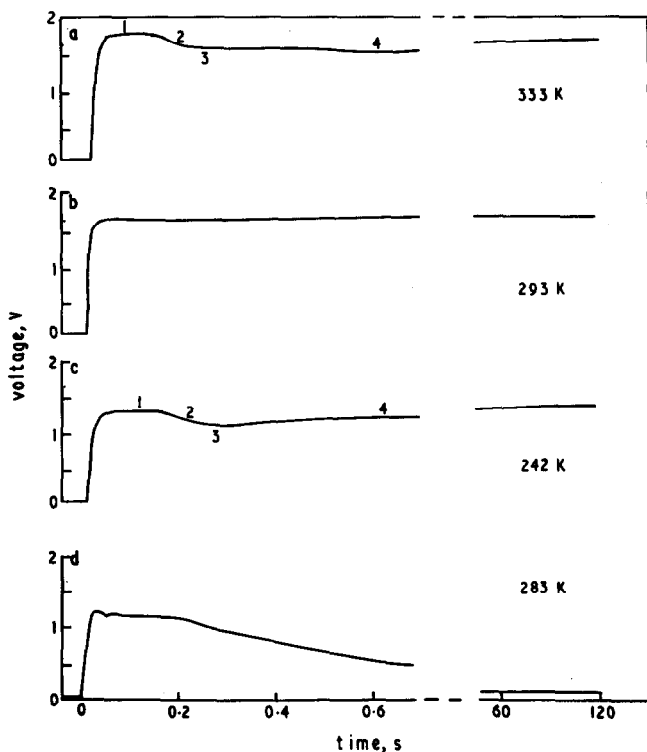
Fig. 4 (a, b, c). Effect of temperature on the voltage performance of the Pb/HBF$_4$/PbO$_2$ cell containing 0.129 mol/dm^3 sulphate ion and (d) the Pb/PbO$_2$ couple discharged in 0.13 mol/dm^3 H$_2$SO$_4$ solution.

reaction of the anode was diffusion controlled and passivation of the electrode by a PbCl$_2$/PbO film occurred above 0.05 mol/dm^3 Cl$^-$ ion concentration. Barradas *et al.* attributed the rapid passivation of the lead electrode at high anodic potentials to a high degree of supersaturation at the electrode/electrolyte interface followed by the rapid formation of large numbers of nucleation sites. At low Cl$^-$ ion concentrations diffusion was again recognised to be a significant factor.

The voltage/time curves obtained from the Pb/HCl/PbO$_2$ cells at 283 K showed rapid activation followed by a gradual fall in voltage as the anode surface became passivated by an insulating PbCl$_2$ layer. In the cells containing HBF$_4$/HCl electrolyte solutions the fluctuations in the voltage/time curves at 242 K and the higher Cl$^-$ ion concentrations may be explained in a similar way to the HBF$_4$/H$_2$SO$_4$ solutions discussed above. On activating the cell, the principal reaction mechanism is again the direct dissolution of lead solvated by BF$_4^-$ ions with PbCl$_2$ formation influencing the voltage/time curve profile above 0.035 mol/dm^3 Cl$^-$ ion concentration. PbCl$_2$ crystals grow at nucleation sites on the anode directly or precipitate from the supersaturated electrolyte adjacent to the electrode (Fig. 5c1) until the Cl$^-$ ion concen-
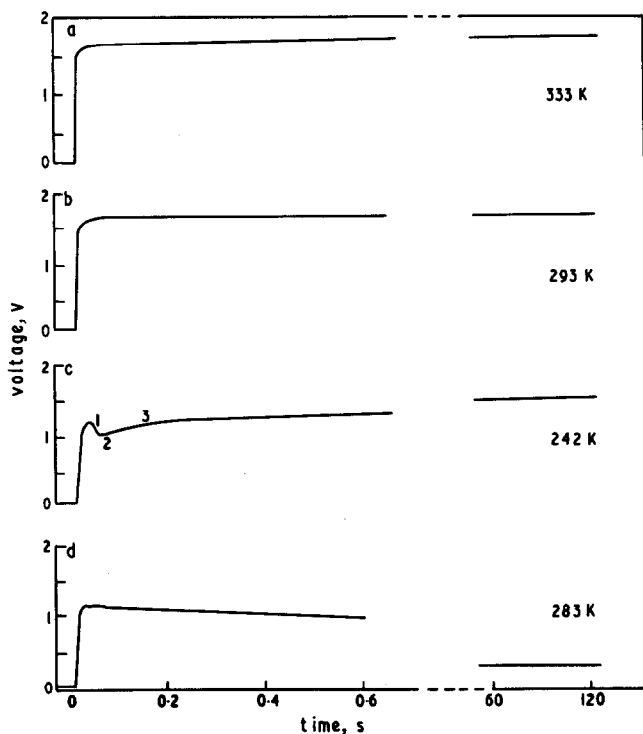
Fig. 5 (a, b, c) Effect of temperature on the voltage performance of the Pb/HBF$_4$/PbO$_2$ cell containing 0.081 mol/dm^3 chloride ion and (d) the Pb/PbO$_2$ couple discharged in 0.08 mol/dm^3 HCl solution.

tration in the diffusion layer becomes depleted (Fig. 5c2) when the dissolution and/or the erosion rate of the precipitated PbCl$_2$ exceeds the diffusion of Cl$^-$ ion from the bulk solution (Fig. 5c3). The initial appearance of the ripple in the voltage/time curves at 242 K at about 0.035 mol/dm^3 Cl$^-$ ion concentration agrees with the reported absence of passivating films on the anode below 0.05 M Cl$^-$ ion concentration [10]. The ripple in the voltage/time curve occurred sooner after activation of the Cl$^-$ ion containing cells (0.03 s) than the SO$_4^{2-}$ ion containing cells (0.15 s) at 242 K suggesting more rapid crystal growth and dissolution of PbCl$_2$. The absence of the wave phenomenon in the voltage/time curves of HBF$_4$/HCl solutions at the higher test temperatures was attributed to the improved diffusion away from the anode region and the increased solubility of the reaction product.

Conclusions

The activation response of and maximum voltage achieved by a simulated reserve-type Pb/HBF$_4$/PbO$_2$ cell were found to be sensitive to the composition of the electrolyte. Over the concentration ranges investigated variation

of the solution constituents influenced the electrochemical performance of the cell. The optimum concentrations of tetrafluoroboric and boric acids were established to be 5.8 and 0.05 mol/dm^3 respectively; glycerol slightly increased the voltage levels whereas chloride and sulphate ions decreased the cell efficiency. Silicon and iron impurities had little effect. Fluctuations in some of the voltage/time curves obtained from solutions containing chloride or sulphate ions were explained in terms of temporary, partial passivation of the anode by $PbCl_2$ or $PbSO_4$.

References

1 J. F. Smith, Trans. Inst. Metal Finishing, 53 (1975) 83.
2 T. J. Kilduff and E. F. Horsey, Proc. 24th A. Power Sources Symp. (U.S.A.), (1970) 30.
3 D. McDonald, E. Y. Weissman and T. S. Roemer, J. Electrochem. Soc., 119 (1972) 660.
4 N. A. Hampson and C. J. Bushrod, J. Appl. Electrochem., 4 (1974) 1.
5 F. Fichter and K. Thiele, Z. Anorg. Allg. Chem., 67 (1910) 302.
6 W. Lange, Ber. Dtsch. Chem. Ges., 59 (1926) 2107, 2432.
7 C. A. Wamser, J. Am. Chem. Soc., 73 (1951) 409.
8 A. N. Fleming, J. A. Harrison and J. Thompson, in D. H. Collins (ed.), Power Sources 5, Academic Press, New York, 1975.
9 G. Archdale and J. A. Harrison, J. Electroanal. Chem. Interfacial Electrochem., 34 (1974) 21.
10 T. N. Klepinina, V. K. Altykhov and E. S. Vorontsov, Sb. Tr. Kafedra Fiz. Obshch. Khim. Voronezh. Politekhn. In-T., (1973) 182.
11 R. G. Barradas, K. Belinko and W. Shoesmith, Electrochim. Acta, 21 (1976) 357.