

EFFECT OF SOME ELEMENTS ON OXYGEN REDUCTION AND HYDROGEN EVOLUTION AT LEAD-ACID BATTERY NEGATIVE PLATES

M MAJA* and N PENAZZI

Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Turin (Italy)

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Summary

The effects which the impurities As, Bi, Cd, Co, Cr, Ni, Sb, Se, Sn and Te have on the processes of hydrogen evolution and oxygen reduction on the negative plates of lead-acid batteries have been tested. This was done by measuring the gas pressure in sealed vessels containing cycled, wet, negative plates. The addition of As, Co, Ni, Sb and Te to the electrolyte used during the cycling increases the hydrogen ion discharge rate, whereas Cr, Bi and Sn have the opposite effect. In the case of oxygen, As, Bi, Ni, Sb, Se, Sn, and Te promote its reduction while Co and Cr suppress it. The effect of impurity concentration has also been considered.

Introduction

The behaviour of maintenance-free batteries and the performance of gas recombination cells based on the "oxygen cycle" markedly depend on the H₂ evolution and O₂ reduction rates at the negative plates. Therefore, materials which modify these processes must be considered in detail.

The effects exerted by the most common impurities are already known, at least from the application viewpoint. Vinal [1] and Dasoyan *et al* [2] reported that the hydrogen evolution rate is increased by contaminants with low hydrogen overpotential.

Pierson *et al* [3] evaluated the behaviour of 24 different elements by means of a constant current overcharge test. They showed that Sb, As, Co, Mn, Ni and Te influence gas evolution at the negative plate when present in the electrolyte, even at concentrations lower than 10 ppm. According to Vinal [1] cycling can, in some cases, reduce the effect of the inorganic contaminants; they may be covered by the newly deposited Pb or PbSO₄ or eliminated as hydride (As, Sb).

* Author to whom correspondence should be addressed

More recently Mahato *et al* [4] studied the effect of Te, Sb, As, Co, and Ni by examining linear sweep voltammetry curves using pasted and unpasted lead electrodes. The results show that Te affects hydrogen discharge by promoting a catalytic reaction involving the H_2Te_2 species. The influence of Sb and As has been explained as being due to the lower H_2 overpotential of these elements.

Chartier *et al* [5] proved that Cd, deposited onto the lead electrode in underpotential condition, increases the rate of reduction of O_2 with maximum effect at a Cd^{2+} concentration of 1.12 ppm. The same amount of cadmium ions reduced the rate of H_2 evolution to a corresponding minimum value.

Bismuth is often present in the lead oxide used to prepare the active material. Kilmnik and Rotinyan [6] and Drotschmann [7] found that this element should not have any harmful effect on the performance of the negative plates.

In this paper we have considered the effects of Sb, Te, As, Co, Ni, Bi, Cr, Sn, Cd, and Se on the negative plate, taking into account the whole lead-acid system. The experiments were concerned with hydrogen evolution and oxygen consumption taking place at negative plates after cycling in electrolyte with added impurity. The elements considered can be present in lead-acid batteries as electrolyte impurities, as contaminants of the active material, or as alloying elements in the grid metal.

In a previous study of the behaviour of conserved charge batteries during storage [8] and the inhibition of lead sulphation in acid media [9], we monitored the pressure change in a sealed system in consequence of H_2 evolution and O_2 consumption. This method was very sensitive to small variations of the gas partial pressure in the system under test and is, therefore, suitable for the investigation of electrochemical reactions involving gas. The same experimental technique has been used in the present work.

Experimental

The negative plates used in the tests were obtained from Pb-Ca-Sn expanded grids, pasted following a standard procedure starting from pure lead oxide. Chemical analysis of the paste gave the results reported in Table 1. After curing at low temperature, the plates were formed using a pure lead sheet anode in a high purity, dilute sulphuric acid (density 1.06 kg l^{-1}). The conversion was with 45 A h per negative plate (approx. 10 A h capacity) at a constant current over 46 h. After formation the plates were washed in distilled water and dried in argon.

The negative plates were then cycled using a similar pure lead sheet counter electrode but with sulphuric acid having a density of 1.28 kg l^{-1} and containing a known amount of the impurity under investigation. Analytical grade reagents were used and the impurities were added as sulphate salts or oxides dissolved in sulphuric acid. The concentrations of the impurities in the electrolyte ranged from 25 to 200 p.p.m.

TABLE 1

Chemical analysis of the negative inert material

Impurity	Maximum content in the inert material (p p m)
Fe	1
Ni	0.8
Cr	1.2
Mn	0.1

Every plate underwent 30 cycles at a constant current corresponding to the $C/10$ rate, the discharge was for 2.5 h to obtain a depth of discharge equal to 25% of the plate capacity. After cycling, the plate, in charged condition, was removed from the cell, drained for one minute and sealed in a glass vessel.

The internal pressure of the vessel, maintained at a constant temperature of $40\text{ }^{\circ}\text{C}$ ($\pm 1\text{ }^{\circ}\text{C}$), was monitored and the data logged automatically for at least 150 h. Additional information was obtained from the chemical analysis of both the active material and the electrolyte after cycling. The results for plates cycled in electrolyte containing 100 p.p.m. of impurity are shown in Table 2.

TABLE 2

Chemical analysis of the active mass of negative plates cycled in H_2SO_4 solutions containing 100 p.p.m. of the elements investigated

Element	Content in the active mass (p p m)
As	12
Bi	60
Cd	40
Co	23
Cr	14
Ni	33
Sb	150
Se	1
Sn	600
Te	280

Results and discussion

Figure 1 shows some of the experimental curves involving the change of pressure, P , in the sealed container (initially at atmospheric pressure) with time, for negative plates after cycling in pure and doped electrolytes. It can be seen that the general trend is similar in all cases: the pressure, after an

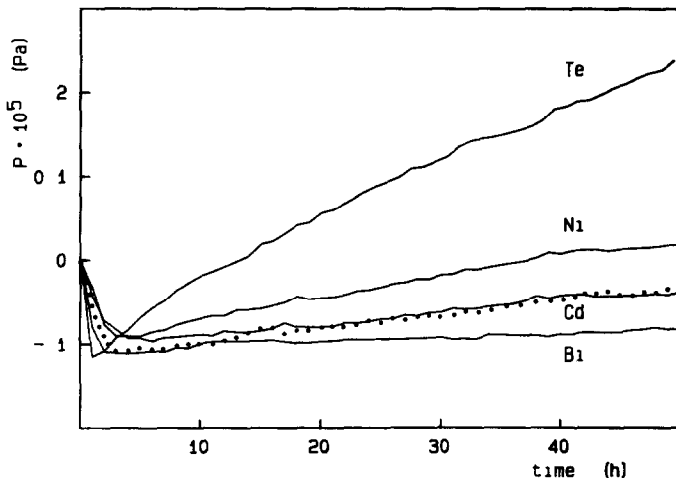


Fig 1 Plot of the gas pressure, P , vs time in sealed vessels containing wet negative plates which had been cycled in pure H_2SO_4 (dotted line), and with 200 p p m of Te, Ni, Cd, and Bi added

initial fast decrease corresponding to oxygen consumption, rises as hydrogen is evolved. The contaminants modify both the negative and the positive slopes.

The features of the overall process have already been discussed [8, 9].

The experimental results satisfactorily fit the expression

$$P = P_0 (\exp(-D/P_0 t) - 1) + B (t + t_0)^{1/2}$$

The parameters D , B , t_0 and P_0 depend on the experimental conditions. D and B are related to the rates of oxygen consumption and hydrogen evolution, respectively. Figure 2 shows how the expression fits the experimental curves obtained for negative plates cycled in 50 p p m. Co, 100 p p m. Sn, and 50 p p m Cr-sulphuric acid solutions.

The effect of the various impurities has been evaluated by means of the parameters

$$KO = (D - D_0)/D_0 \text{ relative to } \text{O}_2 \text{ consumption}$$

$$KH = (B - B_0)/B_0 \text{ relative to } \text{H}_2 \text{ evolution}$$

where D_0 and B_0 are the D and B values for plates cycled in pure electrolyte. A positive value of KO or KH therefore indicates enhancement of the processes involving O_2 reduction and H_2 evolution, respectively, while a negative value corresponds to an inhibiting effect.

Table 3 gives the KO and KH values referred to an impurity concentration of 100 p.p.m. in the electrolyte. The elements have been placed in one of four groups, according to their action towards O_2 consumption and H_2 evolution.

Group I consists of elements having a "strong" positive, *i.e.*, enhancing, effect.

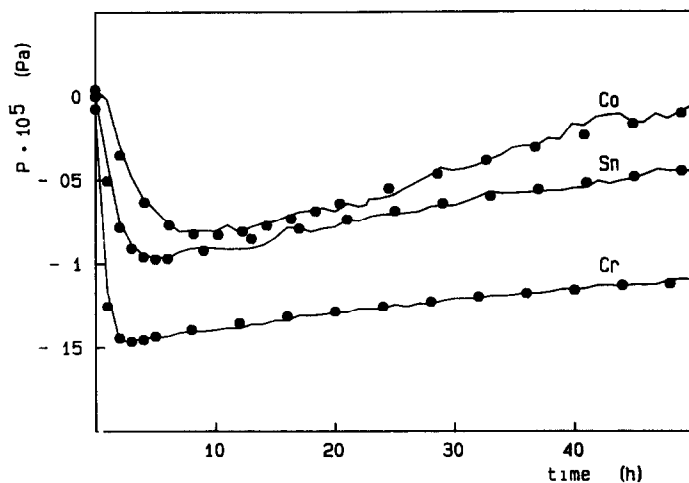


Fig 2 Experimental (continuous line) and theoretical points (●) for the gas pressure, P , vs time in sealed vessels containing wet negative plates which had been cycled in H_2SO_4 with 50 p p m Co, 100 p p m Sn and 50 p p m Cr added

TABLE 3

KO and KH values for negative plates cycled in H_2SO_4 solutions containing 100 p p m of the elements investigated

O ₂ reduction		H ₂ evolution	
Element	KO	Element	KH
Group I			
Sb	3	Sb	5
Te	1.7	Te	1.1
Sn	0.86	Co	0.85
Group II			
As	0.55	Ni	0.65
Ni	0.33	As	0.35
Bi	0.12		
Se	0.1		
Group III			
Cd	-0.08	Se	-0.05
		Cd	-0.09
Group IV			
Cr	-0.35	Cr	-0.14
Co	-0.6	Bi	-0.3
		Sn	-0.4

Group II contains those showing a "medium" positive effect

Group III includes the impurities whose effect can be considered practically negligible

Group IV consists of those elements with a "medium" negative, i.e., inhibiting, effect

It can be seen that, while some of the impurities are strong promoters of electrochemical reactions involving gas at the negative plate (Group I elements) there is no inhibitor of comparable efficacy among the elements considered. A strong inhibiting action could only occur if most of the active reaction centers of the lead sponge could be eliminated, such as by selective covering of the surface.

Considering the experimental findings with reference to sealed cells the marked increase of O_2 recombination caused by Sb and Te appears to be particularly interesting. Unfortunately, this effect is counterbalanced by the simultaneous strong enhancement of H_2 evolution. The influence of Bi, Se, and Sn is more important because these elements appear to enhance O_2 reduction and suppress H_2 evolution.

The results obtained generally confirm the findings reported in the literature. In the case of Cd our data are not comparable with those of Chartier *et al* [5] which are for a lower Cd concentration and a smaller quantity of oxygen reaching the electrode. With regard to Bi, while some authors [6, 7] did not observe any significant effect, our tests show that it enhances O_2 reduction and reduces H_2 evolution.

Our tests also show that the effect of the impurities in most cases depends, to a more or less degree, on their concentration in the electrolyte used for cycling. The influence of Sb and Te increases with the amount of impurity, Fig. 3, while the KO and KH values for As, Co, and Se, Fig. 4, show either a maximum or a minimum before tending to a constant value. The influence of Bi, Cd, Cr, and Sn on the electrochemical reactions appears to be independent of the impurity level. Finally, the increase in Ni concentration causes a slight lowering of the KO values, leaving KH unchanged.

Quantitative analysis of the impurities present in the sponge lead of the plates after cycling allowed us to evaluate the "specific activity" of the various elements considered. For this purpose the values $KOC = (KO/C) \times 100$ and $KHC = (KH/C) \times 100$, where C is the impurity concentration in the active material, have been calculated. It must be stressed, however, that the information given by the parameters KOC and KHC is of limited significance as the distribution of the deposited contaminant in the lead sponge is not known, and because of the inherent limitations of the analytical method used in the case of some of the elements considered.

In Table 4 the values of KOC and KHC are found for plates cycled in an electrolyte containing 100 p.p.m. of the impurity. The elements appear to be ordered almost in the same sequence as that suggested by the KO and KH values given in Table 3. The main differences are for the oxygen reaction, Se and As exhibit the highest activities while Sb, Te, and Sn appear to have

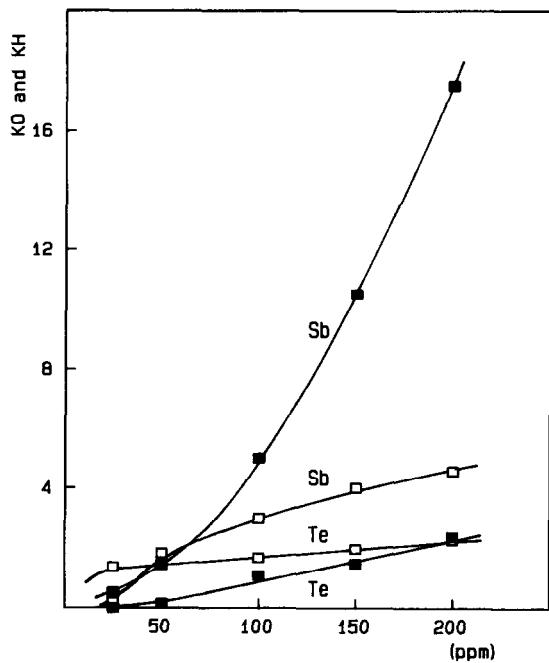


Fig 3 Influence of the Sb and Te impurity levels in the electrolyte on the KO (□) and KH (■) values

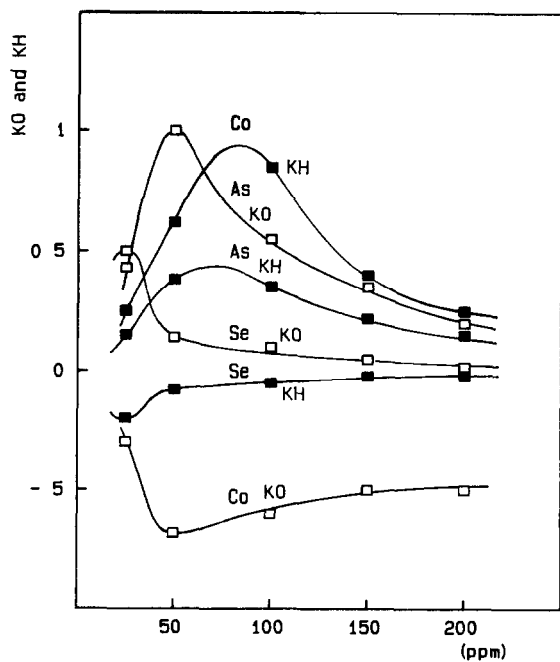


Fig 4 Influence of the As, Co, and Se impurity levels in the electrolyte on the KO (□) and KH (■) values

TABLE 4

KOC and *KHC* values for negative plates cycled in H_2SO_4 solutions containing 100 p p m of the elements investigated

O ₂ reduction		H ₂ evolution	
Element	<i>KOC</i>	Element	<i>KHC</i>
Se	11	Co	3.5
As	5	Sb	3.3
Sb	2	As	3
Ni	1	Ni	2
Te	0.6	Te	0.4
Bi	0.2		
Sn	0.15	Sn	-0.1
		Cd	-0.25
Cd	-0.2	Bi	-0.5
Cr	-2.5	Cr	-1
Co	-2.6	Se	-5.6

much less influence. Regarding the hydrogen process, Co and Se show, respectively, the most positive and the most negative activity.

As far as hydrogen evolution is concerned, a possible relation between this process and the reported *KHC* values can be suggested. Consider the values, reported in the literature [10], of the exchange current density for hydrogen discharge on the various elements considered (i_o)_i and the one on pure lead (i_o)_{Pb}. It can be seen that the ratio (i_o)_i/(i_o)_{Pb} is, for the impurities exerting a marked positive specific activity, generally higher than 10 000. On this basis, however, the relationship between H₂ evolution and impurity influence is, for the remaining elements, not so straightforward.

As the concentration of impurity in the electrolyte was increased, it was found that the amount of impurity in the active material after cycling also increased linearly. If, therefore, *KO* and *KH* change proportionally to the concentration of the impurity (as is the case of Sb and Te), *KOC* and *KHC* remain constant. In all other cases *KOC* and *KHC* decrease with increasing impurity content above 50 - 100 p.p.m. as the *KO* and *KH* values tend towards zero.

Conclusions

In terms of the H₂ evolution these tests confirmed the marked deleterious influence exerted by Sb, Te, and Co. Arsenic and Ni were also shown to promote H₂ evolution whereas Bi, Sn, and Cr inhibited it markedly. Conversely, O₂ reduction on sponge lead is enhanced, in diminishing order, by Sb, Te, Sn, As, Ni, Bi, and Se, and inhibited by Co and Cr. Examination of these results suggests, therefore, that gas recombination in lead-acid

batteries, using the oxygen cycle, could improve their performance by the presence of Bi, Sn, and Se

The process by which metallic additives influence hydrogen ion generation during discharge cannot be fully explained in terms of the reaction overpotential. It is not clear, for instance, why tin, antimony, and tellurium, having different specific activities, Table 4, have similar values for H_2 exchange current. As for oxygen reduction, the literature reports few data suitable for a direct comparison with the obtained KO values.

A better understanding of the reaction mechanisms may be obtained by taking into account the characteristics of the active centers on which the electrochemical reactions take place. One can suggest that the elements acting as inhibitors exhibit a decreasing specific activity with an increasing impurity level because some of the active centers in the lead sponge remain uncontaminated. Conversely, the behaviour of elements showing an initial positive specific activity which then decreases with an increasing impurity level, agrees with the idea that the number of new active centers increases up to a limit beyond which the specific activity returns to zero.

Further investigations will be carried out on complete cells (positive and negative electrodes with absorbent separators) to evaluate the effect of metallic additives in practical battery operating conditions. In the meanwhile, experimental work on single plates is continuing to obtain a more thorough understanding on the action of metallic impurities.

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