

Short Communication

Effect of silicate and phosphate additives on the kinetics of the oxygen evolution reaction in valve-regulated lead/acid batteries

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Abstract

Effect of sodium silicate and phosphoric acid additives on the kinetics of oxygen evolution on PbO_2 electrodes in sulfuric acid has been studied in gelled and flooded electrolytes with relevance to valve-regulated lead/acid batteries. A comparison of the open-circuit potential versus time transients, with and without these additives, indicates that the additives suppress self-discharge of the electrodes. Tafel polarization studies also suggest that the addition of phosphoric acid attenuates the rate of oxygen evolution reaction. These findings have been supported with cyclic voltammetric data. © 1998 Elsevier Science S.A.

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1. Introduction

To obtain valve-regulated lead/acid (VRLA) batteries with long deep-discharge cycle life, it is desirable to incorporate suitable additives in the electrolyte in order to: (i) increase the hydrogen overpotential of lead and lead alloys in sulfuric acid electrolyte; (ii) decrease the corrosion rate of lead and lead alloys in sulfuric acid electrolyte, and (iii) electrocatalyze the desired electrode reactions at the positive and negative electrodes of the battery [1].

Although there have been several studies on the effect of additives on the kinetics of lead electrodes [2–4], information on possible effects on the kinetics of PbO_2 electrodes is sparse. For example, the use of silica gel in the electrolyte showed [5] to bring a 5–10% improvement in capacity of the PbO_2 electrode, but the exact mechanism is not clear. Furthermore, the increase in utilization of the active material also brings about desirable morphological changes, but how this, either alone or in combination with other additives like phosphoric acid, causes fine-grained secondary structures is not clearly understood. Oxygen evolution on the PbO_2 electrode occurs as a side reaction during charging and also as a partial anodic reaction during self-discharge [6,7]. Surprisingly, the influence of

these additives on the kinetics of the oxygen evolution reaction on PbO_2 electrode has not been studied despite its significance for oxygen recombination in VRLA cells.

This communication reports studies of the effect of sodium silicate and phosphoric acid additives on the kinetics of oxygen evolution on PbO_2 electrodes in sulfuric acid electrolyte. The use of sodium silicate additive as a gelling agent in VRLA free batteries is of particular interest. To this end, steady-state Tafel polarization, open-circuit potential (OCP) versus time transients, and cyclic voltammetry (CV) are used to examine the effects of the additives including changes in the interfacial reaction rates and the ohmic drop. The correlation between the kinetic data from Tafel polarization and CV results indicates a distinct inhibiting influence of silicate and phosphoric acid additives on oxygen gas evolution.

2. Experimental

2.1. Cyclic voltammetric studies

Cyclic voltammetry experiments were carried out in 0.1 M H_2SO_4 using a lead alloy electrode (Pb–0.08wt.%Ca–0.5wt.%Sn) of geometrical area 0.02 cm^2 in a three-electrode, single-compartment set-up with a pre-calibrated $\text{Hg}/\text{Hg}_2\text{SO}_4$, H_2SO_4 (0.1 M) reference electrode (MMS)

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and a platinum-foil counter electrode. Prior to measurements, the electrolyte was kept at a potential of +1.2 V versus MMS for several hours to form a PbO_2 surface electrochemically and this was used as the working electrode. The electrolyte was immobilized using a sodium silicate gelling agent (5 g/l) and a phosphoric acid additive was employed in the normal ratio, viz., 20 g/l [2,8,9].

2.2. Potential–time transients studies

Potential–time transients were recorded using a three-electrode cell with a PbO_2 working electrode, a platinum-foil counter electrode, and a MMS reference electrode in 4.8 M H_2SO_4 . The potential was measured with an accuracy of ± 1 mV by connecting a buffer amplifier with unit gain and substantially high input impedance ($10^{12} \Omega$) between the reference and working electrodes. The PbO_2 electrode was anodically polarized with an arbitrarily selected current density of 1 mA cm^{-2} for few seconds and then the OCP–time transients were recorded until the original rest potential was reached. The experiments were also conducted with sodium silicate and phosphoric acid additives.

2.3. Tafel polarization studies

Tafel polarization was carried out with a PAR 173 galvanostat. Prior to measurements, the working-electrode compartment was de-aerated by purging the cell with pure argon. The steady-state potential for the highest current density was recorded first and, subsequently, steady-state potentials for other current densities were monitored by decreasing the current densities in descending steps. This procedure was adopted to avoid any experimental complications due to hysteresis [6]. The experiments were also performed with gelled electrolyte.

3. Results and discussion

Fig. 1 shows the steady-state anodic Tafel-polarization curves for the PbO_2 electrode in sulfuric acid electrolyte and also with sodium silicate and phosphoric acid additives. For the sake of brevity, only the linear portions of the curves are presented. Although the Tafel slopes are not affected by the addition of sodium silicate, an appreciable difference in exchange current densities for the oxygen evolution reaction (OER) is observed, i.e., the value changes from 1.9×10^{-5} to $8.5 \times 10^{-5} \text{ A cm}^{-2}$. Also, a significant change is observed in the limiting current values. This difference can easily be explained in terms of slower diffusion of oxygen through the silicate network due to gelling, together with an increased ohmic overpotential. A direct comparison of the Tafel slopes and exchange current densities obtained from Fig. 1 with reported values indicates a good agreement [6]. It is noteworthy that

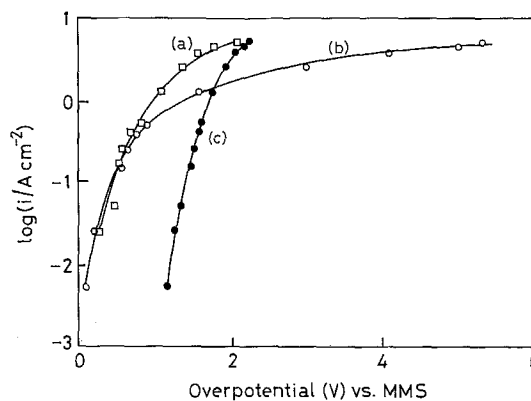


Fig. 1. Steady-state anodic Tafel polarization curves for PbO_2 electrodes: (a) sulfuric acid (flooded electrolyte); (b) phosphoric acid, and (c) sodium silicate (gelled).

the Tafel slopes vary from 70 to 140 mV/decade depending on the amounts of α - and β - PbO_2 in the electrode and the oxygen stoichiometry [10].

More significant changes are observed with phosphoric acid additives. The Tafel slopes are lower while the exchange current densities are found to decrease from 8.5×10^{-5} to a value as low as $2 \times 10^{-9} \text{ A cm}^{-2}$. There is also a large increase in the oxygen overpotential even in the low current density region (not included in Fig. 1). The suppression of the kinetics of the OER is evident from both the exchange current density as well as the Tafel slope data. This is contrary to the known effects of phosphoric acid on the negative electrode at which both the Tafel slopes and the corrosion potential remain unaffected by the addition of phosphoric acid [11].

The OCP–time transients following the interruption of a pre-anodic polarization corresponding to the oxygen evolution region for the PbO_2 electrode in flooded, gelled and phosphoric-acid-containing electrolyte are presented in Fig. 2. An instantaneous variation in the electrode potential caused by the ohmic drop makes these transients quite steep at the onset. Subsequently, however, the potential

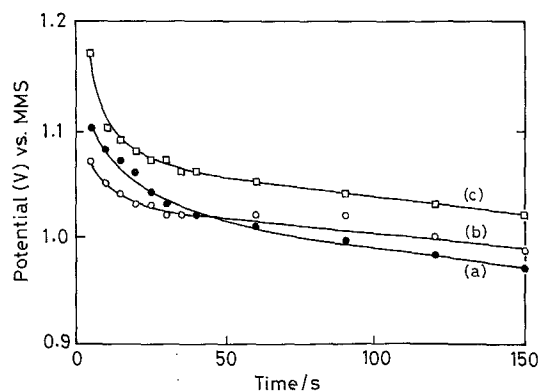


Fig. 2. Open-circuit potential–time transients for PbO_2 electrodes: (a) sulfuric acid (flooded electrolyte); (b) phosphoric acid, and (c) sodium silicate (gelled).

varies more slowly with time and reaches the steady-state value asymptotically. The attainment of equilibrium is almost complete within 20 s in the pure acid electrolyte, while in the case of gelled electrolyte the relaxation to equilibrium is attained only after 50 s. The latter indicates the increased hindrance of mass transfer. These potential transients can be analysed quantitatively by assuming the OCP to be a mixed potential due to the $\text{PbSO}_4/\text{PbO}_2$ and oxygen evolution reactions. For a PbO_2 electrode in sulfuric acid, potential–time transient analysis was first attempted by Ruetschi [12] with various potential-determining reactions and the present results in Fig. 2 are qualitatively similar to the data reported by Ruetschi for PbO_2 electrodes polarized in the oxygen evolution region. Hence, addition of sodium silicate does not drastically change the nature of potential-determining reactions on the PbO_2 electrode and this along with the results of Tafel polarization suggest similar mechanism for the OER in spite of the slowing down of the oxygen transport. Nevertheless, the self-discharge rate seems to be lower for the gelled electrolyte, as reflected from the slopes of the decay transients. This finding is in agreement with the reported ameliorating effects of the sodium silicate additive.

The OCP–time data in Fig. 2 reflect important features with respect to the phosphoric acid additive. In the time domain corresponding to more than 40 s, a small but distinct step is observed (Fig. 2(c)) in the OCP–time transients. This is probably due to the presence of an insoluble phosphate film at the electrode surface; such a film is known to inhibit oxygen mass transport. Indeed, addition of phosphoric acid is also known to suppress lead corrosion and the formation of plumbous phosphate has been reported during the reduction of PbO_2 in H_2SO_4 containing phosphoric acid [13,14]. Thus, an analysis of OCP–time transients for PbO_2 electrode clearly indicates that both sodium silicate and phosphoric acid additives suppress the kinetics of self-discharge. This behaviour is beneficial in designing VRLA batteries based on the oxygen-recombination cycle.

Cyclic voltammograms of PbO_2 electrodes taken under identical conditions in flooded, gelled and phosphoric-acid-containing electrolyte are given in Fig. 3. These voltammograms show an oxidation peak at a potential around +1.6 V versus MMS and a reduction peak at +0.5 V versus MMS that can be assigned to the $\text{PbO}_2/\text{PbSO}_4$ couple [15]. Addition of sodium silicate as a gelling agent appears to make this couple more irreversible, as demonstrated by the change in shape of both voltammetric peaks. More significantly, the peak currents are substantially reduced, although this is partly due to the increased ohmic drop caused by gelling.

A comparison of the voltammogram obtained with and without phosphoric acid shows a small peak around +1.1 V versus MMS. The peak corresponds to an intermediate faradaic process which does not occur in voltammograms taken with free and gelled electrolytes. Earlier studies

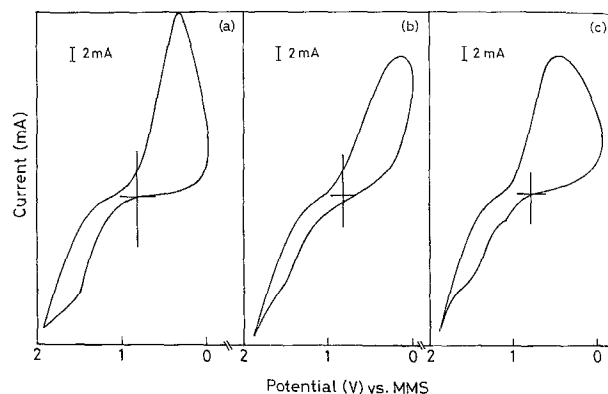


Fig. 3. Cyclic voltammograms for PbO_2 electrodes: (a) sulfuric acid (flooded electrolyte); (b) phosphoric acid, and (c) sodium silicate (gelled).

[13,14] have shown that plumbous phosphate is formed when PbO_2 is reduced in sulfuric acid in the presence of phosphoric acid, and its further oxidation to plumbic phosphate may explain the formation of two steps when phosphoric acid is used as an additive. There is no evidence for the enhancement of the kinetics of PbO_2 formation by phosphoric acid additives. On the contrary, the corresponding currents are smaller than those found in free sulfuric acid electrolyte.

4. Conclusions

This study shows that addition of phosphoric acid in the electrolyte in combination with sodium silicate used for immobilization suppresses the OER on PbO_2 electrodes. It is suggested that the present findings are of value for realizing VRLA batteries with improved characteristics.

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