EFFECT OF Cd, Ni, Zn and Co IONS ON ELECTRODE REACTIONS OF THE LEAD–ACID BATTERY

HUGO SANCHEZ, YUNNY MEAS*, IGNACIO GONZALEZ and MARCO A. QUIROZ

Universidad Autónoma Metropolitana - Iztapalapa, Departamento de Química, Apartado Postal 55 - 534, 09340 México, D.F. (Mexico)

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Summary

The influence of metallic ions Cd(II), Ni(II), Zn(II) and Co(II) on gassing and maintenance behaviour of both lead and lead dioxide electrodes has been studied using linear potential sweep voltammetry and charge and discharge curves. The experiments were made using a Pb–0.6%Ca alloy and commercial electrodes in 5 M H_2SO_4 electrolytic solution. Charge efficiencies were enhanced and a lower maintenance was required when the battery contained Cd(II) and Zn(II) ions, but the opposite occurred with Ni(II) and Co(II) ions.

Resumé

L'influence de la présence des ions métalliques Cd(II), Ni(II), Zn(II) et Co(II) sur les réactions de dégagement d'hydrogène, d'oxygène et d'oxydoréduction du plomb et de l'oxyde de plomb est étudiée par voltampérométrie cyclique et de balayage linéaire de potentiel, ainsi que par tracé des courbes de charge et décharge de chaque électrode.

Les électrodes étudiées sont, d'une part, d'origine commerciale, et d'autre part, constituées d'un alliage Pb–0.6%Ca l'électrolyte utilisé est une solution d'acide sulfurique (5 M).

En présence des ions Cd(II) et Zn(II), l'efficacité de la charge est améliorée et la consommation d'eau est moindre. En présence des ions Ni(II) et Co(II), des effets contraires sont obtenus.

1. Introduction

The performance and cycle life of lead–acid batteries can be improved by using additives or lead alloys in manufacturing the grids of the electrodes.

*Author to whom correspondence should be addressed.

The Pb/Sb alloy is the most used lead alloy in the construction of lead–acid battery plates. However, in normal operation of lead–acid cells, antimony is dissolved in the positive plate and this causes some negative effects [1 - 3] for the cell: hydrogen overpotential and charge efficiency are diminished, self-discharge and maintenance are increased [4 - 8], and the toxic gas SbH_3 is liberated in the overcharge of the cell [9, 10]. The negative effects of antimony can be reduced by using lead alloys with a low content of Sb [11, 12 - 16] and 0.02% Se [17]. Because of these problems, several lead alloys have been tested [18, 19] and the best results have been obtained by using a Pb/Ca alloy [18].

The use of a Pb/Ca alloy in manufacturing the grids of lead–acid batteries permits the construction of low or maintenance-free batteries [20 - 22] with long cycle life [23].

Mahato and Tiedemann [24], by means of linear potential sweep (LPS) voltammetry, studied the effect of the metallic ions Te, Sb, As, Co and Ni on the gassing behaviour of lead and lead dioxide battery electrodes. Their work showed the detrimental effect of these ions on charge efficiency, maintenance and cycle life of the lead–acid battery. Other workers [25 - 29] recommend the use of metallic ions of Cd and Zn to improve the efficiency of charge–discharge processes and to reduce the maintenance of lead–acid batteries.

In this work we compare the influence of Cd(II) and Zn(II) ions with Co(II) and Ni(II) ions on gassing and maintenance behaviour of both lead and lead dioxide electrodes prepared from Pb–0.6%Ca alloy, or commercial electrodes. Finally, galvanostatic charge and discharge curves were obtained in the case of commercial electrodes.

2. Experimental

In all the experiments, a conventional 50 ml capacity spherical cell (five entries) designed to work in deaerated medium was used. Deaerating of the solution was accomplished by bubbling purified nitrogen gas. The electrochemical treatments and all the experiments were realized in 50 ml of 5 M H_2SO_4 electrolyte solution using a platinum gauze counter electrode. The use of lead, lead dioxide or a carbon rod as counter electrode does not change the obtained results. In the charge–discharge experiments, lead or lead dioxide electrodes were used as counter electrodes. The $Hg/Hg_2SO_4/K_2SO_4$ (saturated) electrode (MSE) was used as reference electrode and all potentials are given with respect to this electrode.

The electrodes studied were a Pb–0.6%Ca alloy, potentiostatically prepared, and electrodes formed from commercial battery plates.

Using an industrial Pb–0.6%Ca alloy, two disc electrodes of 0.100 and 0.44 cm^2 geometric area were constructed and imbedded in a cylindrical Teflon base of 1.0 cm diameter and connected to the exterior by a copper wire. These wires were protected by glass tubes of 0.6 cm external diameter and 20 cm length.

Before each experiment, the electrodes were polished mechanically using 600 grade sandpaper followed by alumina (0.05 μm) until a mirror surface was obtained. After this, the electrodes were subjected to an electrochemical treatment which consists in maintaining the electrode at -1150 mV *versus* MSE to obtain a minimum constant current due to the evolution of small quantities of hydrogen gas. This treatment enables preparation of an electrode surface relatively free of oxidized species [30 - 32].

For gassing behaviour and cyclic voltammetry (CV) studies of negative and positive electrodes based on Pb/Ca 0.6% alloy, the stabilized electrode was obtained by a procedure similar to that of Mahato and Tiedemann [24].

In the gassing behaviour experiments of the negative electrode, the Pb–0.6%Ca alloy electrode was stabilized by cycling between -1075 and -1470 mV at 5 mV/s scan rate until a constant response called 'control' was obtained due to hydrogen gas evolution. In the case of the commercial negative electrode (1.8 × 0.7 cm), the plate was subjected to a fixed potential of -1080 mV and then it was cycled between -1070 and -1370 mV at 5 mV/s scan rate to obtain the 'control' curve. For cyclic voltammetry studies on the negative electrode Pb–0.6%Ca alloy, 0.044 cm^2 geometric area), the potential was cycled between -903 and -1203 mV at 2 mV/s scan rate to obtain the constant response called the 'control' curve.

In the study of the gassing behaviour of the positive electrode, the active material was formed on Pb–0.6%Ca alloy (0.100 cm^2 geometric area) by applying a potential of -950 mV until a minimum and constant current was obtained (a $PbSO_4$ layer was obtained), then a current density of 0.5 mA/cm^2 was applied to obtain the lead dioxide. The electrode was cycled between 1110 and 1500 mV at 5 mV/s scan rate to obtain the 'control' curve due to oxygen gas evolution. For the commercial positive electrode, lead dioxide was formed by galvanostatic charge (34.4 mA/cm^2) and then the plate was cycled between 1110 and 1500 mV (5 mV/s scan rate) to obtain the 'control' curve. Cyclic voltammetry studies on the positive electrode were made by preparing the active material on Pb–0.6%Ca alloy (0.044 cm^2 geometric area) by direct cycling between 900 and 1425 mV, at 2 mV/s scan rate, until the constant response ('control' curve) was obtained.

Galvanostatic charge–discharge experiments with commercial negative electrodes were realized by using 1.8 × 1.2 cm plates, which were charged at -28.7 mA/cm^2 for 80 min and discharged by reversing the direction of the current (potential electrode reaches -975 mV, indicative of its discharged state). A 1.8 × 1 cm commercial lead dioxide plate was used as counter electrode. Charge–discharge experiments of commercial positive electrodes were realized by using 1.8 × 1 cm plates, charged at 34.4 mA/cm^2 for 2 h and discharged at -55.5 mA/cm^2 until the electrode potential diminished to 860 mV. A large area (5 cm^2) commercial lead plate was used as counter electrode. In the charge–discharge experiments, a deaerated medium is not required.

All reagents were AR grade and the electrolyte solution, 5 M H_2SO_4, was prepared from concentrated H_2SO_4 and tridistilled water. Metallic

ions were added as the sulphate salt: cadmium sulphate ($3CdSO_4 \cdot 8H_2O$), nickel sulphate ($NiSO_4 \cdot 6H_2O$), zinc sulphate ($ZnSO_4 \cdot 7H_2O$) and cobalt sulphate ($CoSO_4 \cdot 7H_2O$). The concentration of metallic salt used in all the experiments was 400 ppm.

All measurements were made by using a PAR model 173 potentiostat-galvanostat with a PAR model 179 digital coulometer. These instruments were coupled to a PAR model 175 universal programmer. An X-Y-T Houston instrument or type TRP SEFRAM plotter was used to record all the curves.

3. Results and discussion

Figure 1 shows the effect of metallic ions Cd(II), Ni(II), Zn(II) and Co(II) on LPS of a Pb–0.6%Ca electrode (0.10 cm^2) between −1075 and −1470 mV *versus* MSE at 5 mV/s scan rate. The observed effect was obtained after the addition of the corresponding metallic salt and 2 h of continuous cycling. The presence of Cd(II) and Zn(II) ions in the electrolytic solution caused a hydrogen gas evolution decrease of 63% and 46%, respectively. The presence of Ni(II) and Co(II) ions has a contrary effect: an increase of 67% and 14%, respectively, was found. The percentages of variation in hydrogen gas evolution, with respect to the 'control' curve, were measured at −1450 mV.

The observed increment in hydrogen gas evolution due to the presence of Co(II) and Ni(II) ions can be attributed to a catalytic effect of these sub-
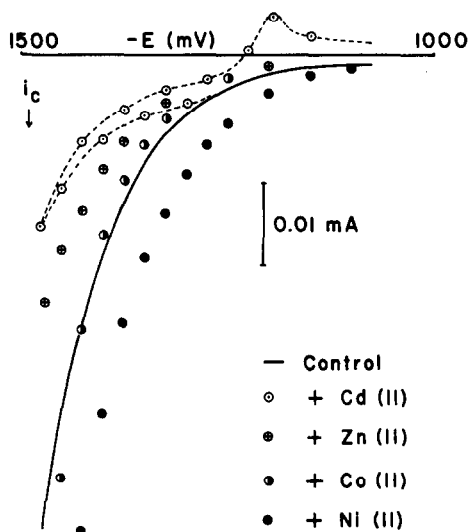

Fig. 1. LPS of the hydrogen gas evolution reaction on the Pb/Ca electrode. Electrolyte: 5 M H_2SO_4, counter electrode: Pt, reference: MSE, scan rate: 5 mV/s, without agitation. Observed effects after 2 h.

stances because, in the potential range of Fig. 1, the ions can already be deposited on the electrode surface (the deposition potentials of Co(II) and Ni(II) in the experimental conditions of this work were -920 and -870 mV, respectively). In the case of Cd(II) and Zn(II) ions, their deposition potentials (-1245 and -1380 mV, respectively) are between the potential limits of Fig. 1 and a non-massive deposit could be formed, which explains the observed negative catalytic effect on hydrogen gas evolution.

The CV of the Pb/Ca 0.6% electrode (0.044 cm^2) from -903 to -1203 mV, obtained at 2 mV/s scan rate, is shown in Fig. 2. The anodic peak current is due to the oxidation reaction of lead to lead sulphate and the cathodic peak current corresponds to the reverse reaction. The 'control' curve of the stabilized electrode is modified by the presence in the electrolyte solution of the metallic ions Cd(II), Ni(II), Zn(II) and Co(II). The effect of these substances after 8 h of continuous cycling is shown with a dashed line. The area under the anodic and cathodic peaks gives the charge involved in anodic (Q_a) and cathodic (Q_c) reactions, respectively on the lead electrode.

It was observed that the presence of the mentioned metallic ions in the electrolyte solution caused a small increase in the charge involved in the oxidation and reduction reactions of the lead electrode. The major effect was obtained in the case of the Zn(II) ion, in which Q_a is increased by 18% and
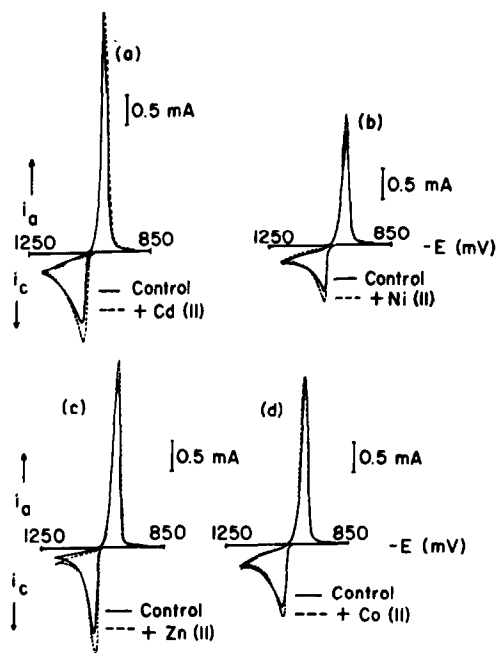

Fig. 2. CV of the Pb/Ca electrode between -903 and -1203 mV. Electrolyte: 5 M H$_2$SO$_4$, counter electrode: Pt, reference: MSE, scan rate: 2 mV/s. Dashed curve: observed effect after 8 h continuous cycling.
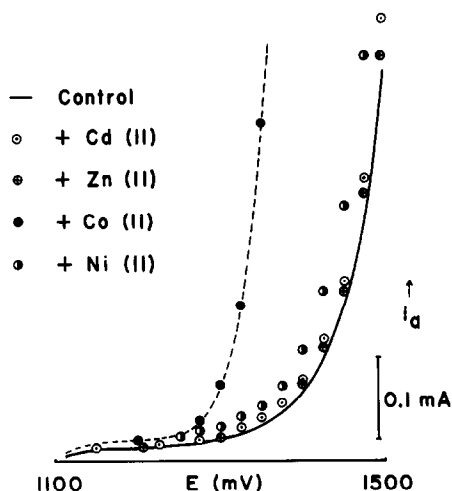
Fig. 3. LPS of the oxygen gas evolution reaction on the lead dioxide electrode (supported on Pb/Ca). Electrolyte: 5 M H_2SO_4, counter electrode: Pt, reference: MSE, scan rate: 5 mV/s, without agitation. Observed effects after 2 h.

Q_c by 27% (with respect to the 'control' curve). The presence of Zn(II), Co(II) and Ni(II) ions in the electrolyte solution caused the ratio Q_a/Q_c to be closer to unity because the percentage variation is higher in Q_c than in Q_a, so the reversible behaviour of the lead electrode is enhanced by these substances. Intersection of the dashed curve with the 'control' curve on the cathodic scan in Fig. 2(b) and (d) may be due to electrochemical deposition of Ni(II) and Co(II), respectively.

Figure 3 shows the effect of the metallic ions Cd(II), Ni(II), Zn(II) and Co(II) on LPS of a lead dioxide electrode (0.10 cm^2), which was supported on a Pb–0.6%Ca alloy base. LPS was obtained at a 5 mV/s scan rate between 1110 and 1500 mV. The observed effect, due to the presence in the electrolyte solution of the mentioned metallic ions, after 2 h of continuous cycling, is shown for each ion. The rate of the oxygen gas evolution reaction is significantly raised due to the presence of Co(II) and Ni(II) ions (1275% and 59%, respectively), but Cd(II) and Zn(II) produce a smaller but similar effect. The percentages were estimated at 1400 mV and are given with respect to the 'control' curve. In the case of the Co(II) ion, the percentage of variations was estimated by graphic extrapolation of the corresponding curve. Taking the anodic oxygen evolution increment as a measure of charge inefficiency [24], we estimate that Cd(II) and Zn(II) do not decrease the charge efficiency of the positive electrode by an appreciable amount.

The CV of the lead dioxide electrode (0.044 cm^2 geometric area) between 900 and 1425 mV, at 2 mV/s scan rate, is shown in Fig. 4. The cathodic part corresponds to the reduction reaction of lead dioxide and the anodic to PbSO$_4$ oxidation. The observed effect (dashed curve) due to the presence in the electrolyte solution of the metallic ions Cd(II), Ni(II), Zn(II)
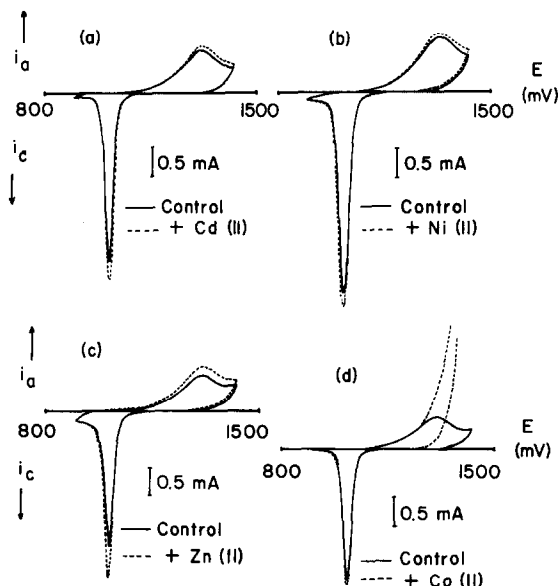
Fig. 4. CV of the lead dioxide electrode (supported on Pb/Ca) between 900 and 1425 mV. Electrolyte: 5 M H_2SO_4, counter electrode: Pt, reference: MSE, scan rate: 2 mV/s. Dashed curve: after 4 h continuous cycling.

and Co(II), after their addition and 4 h of continuous cycling, is shown in Fig. 4. In the presence of Cd(II), Ni(II) and Zn(II) ions, the anodic and cathodic parts of the voltammogram are raised. The presence of Co(II) only modifies the anodic part and the cathodic part is slightly increased; this means that the increment in the oxidation current is not due to a probable oxidation of Co(II).

The charge associated with the anodic (Q_a) and cathodic (Q_c) reactions for a stabilized lead dioxide electrode ('control' curve) in the presence of metallic ions (dashed curve) was evaluated by integration of corresponding areas in Fig. 4. It was discovered that Q_a was increased by the presence of Cd(II) and Zn(II) ions in the electrolyte solution (10% and 29%, respectively). This effect cannot be attributed to contributions by the oxygen gas evolution reaction, because the effect of these ions on this reaction is minimal, as was shown in Fig. 3. In the case of Cd(II), the percentage of variation in Q_c is similar to that of Q_a, and the presence of the Zn(II) ion causes the anodic part of Fig. 4(c) to grow more than the cathodic part (Q_c is increased by 15%), thus the $PbSO_4$ oxidation reaction can be favoured by this ion.

As was shown in Fig. 3, the presence of the Ni(II) ion causes the oxygen gas evolution reaction to be increased, and so the major increment in Q_a (11%) with respect to Q_c can be due to an important contribution of this reaction on $PbSO_4$ oxidation. The anodic part of Fig. 4(d) is rapidly (15 min) modified in the presence of the Co(II) ion and this modification increases to give the corresponding curve for 4 h shown in the Figure. How-

ever, the cathodic zone is only slightly modified with respect to the 'control' curve. A similar result of the effect of Co(II) on the lead dioxide electrode was obtained by Mahato and Tiedemann [24].

Commercial electrodes

In this case, the LPS results are different from those obtained with Pb–0.6%Ca electrodes. The corresponding cyclic voltammetry experiments could not be obtained because the large area of the electrode caused very high currents. However, galvanostatic charge–discharge curves for individual lead and lead dioxide electrodes were obtained.

Figure 5 shows the effect (after 2 h of continuous cycling, 5 mV/s scan rate) of metallic ions Cd(II), Ni(II), Zn(II) and Co(II) on LPS of the commercial lead electrode. From this Figure, it can be observed that the hydrogen gas evolution reaction is increased (with respect to the 'control' curve) in the presence of Ni(II) (74% at −1300 mV *versus* MSE) and in a minor way by the presence of Cd(II), Zn(II) and Co(II).

The presence of metallic ions in the electrolyte solution caused a variation in some measurable parameters during the charge and discharge processes of both the lead and lead dioxide electrodes. Some of these parameters are the electrode potential, cell voltage (measured just before the charging or discharging current was reversed) and discharge time.
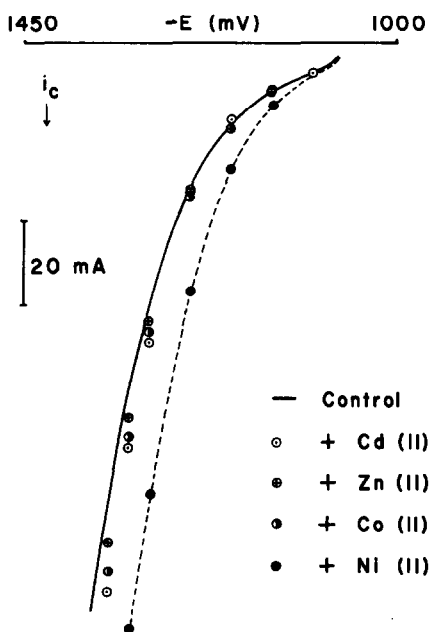

Fig. 5. LPS of the hydrogen gas evolution reaction on the commercial lead electrode. Electrolyte: 5 M H_2SO_4, counter electrode: Pt, reference: MSE, scan rate: 5 mV/s, without agitation. Observed effects after 2 h continuous cycling.

The obtained galvanostatic charge (-28.7 mA/cm^2) and discharge (28.7 mA/cm^2) curves for the commercial lead electrode showed that the discharge time is increased in each cycle because the quantity of active material is increased, but the relation: charge time/discharge time (t_c/t_d) is constant and practically unity, indicating a reversible behaviour of the electrode. The end of charge potential (E_{Pb}) of the lead electrode, the cell voltage (*FEM*) and discharge time (t_d) for continuous charge–discharge processes were measured with and without the presence of metallic ions in the electrolyte solution.

After some charge–discharge cycles, E_{Pb} and *FEM* at the end of the charge process are constant (-1235 mV *versus* MSE and 2640 mV, respectively) and so can be used as comparision criteria between charge–discharge cycles realized with and without the presence of metallic ions. It was observed that the presence of Cd(II) ions in the electrolyte solution shifted E_{Pb} by 30 mV to less negative potentials and *FEM* diminished by approximately 20 mV. In the case of Ni(II) ion, E_{Pb} was slightly increased, but *FEM* was not modified. The end of the charge potential was shifted slightly to less negative values by the presence of Co(II) ions, however, *FEM* was diminished by approximately 100 mV. In all cases, the ratio t_c/t_d was not modified by the presence of the mentioned metallic ions.

The presence of metallic ions Cd(II), Ni(II), Zn(II) and Co(II) in the electrolyte solution modified the oxygen gas evolution reaction on the lead dioxide electrode, and the observed effect after 2 h of continuous cycling between 1110 and 1500 mV (5 mV/s, scan rate) is shown in Fig. 6. It can be observed that the oxygen gas evolution reaction is slightly diminished (with
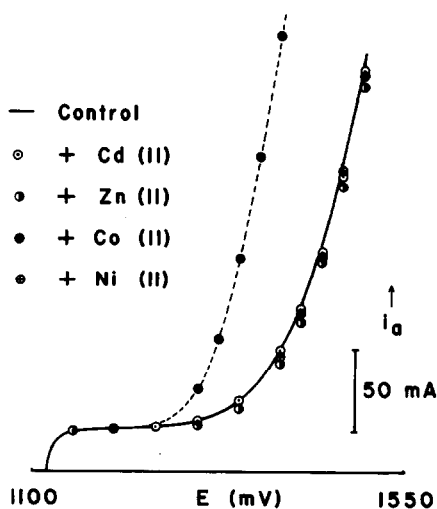

Fig. 6. LPS of the oxygen gas evolution reaction on commercial lead dioxide. Electrolyte: 5 M H$_2$SO$_4$, counter electrode: Pt, reference: MSE, scan rate: 5 mV/s, without agitation. Observed effects after 2 h continuous cycling.

respect to the 'control' curve) when the solution contains metallic ions Cd(II), Ni(II) and Zn(II). However, the presence of Co(II) has a contrary effect (194% at 1450 mV *versus* MSE). This percentage was estimated by graphic extrapolation of the corresponding curve in Fig. 6.

The presence of metallic ions in the electrolyte solution gives rise to some important and measurable effects on the lead dioxide electrode during successive charge and discharge cycles. From galvanostatic charge and discharge curves for a commercial lead dioxide electrode we obtained the electrode potential (E_{PbO_2} *versus* MSE) as a function of time; in this case discharge time was constant for successive cycles, thus the quantity of active material is not altered.

It was observed that the electrode potential (E_{PbO_2}, 1418 mV *versus* MSE) at the end of the charge process, the cell voltage and the discharge time are constant after the first cycle and this fact gives comparison criteria between charge–discharge cycles with and without the presence of metallic ions in the electrolyte solution. From charge–discharge experiments, it was discovered that E_{PbO_2} is displaced about 20 mV to more positive potentials when the Cd(II) ion is present. This observation agrees with Fig. 6 and means that charge efficiency can be enhanced by this ion. The discharge time is altered by a small degree. Similar results are obtained in the case of the Zn(II) ion. The Ni(II) ion shifts the end of the charge potential in a minor way.

The opposite effect is observed in the case of the Co(II) ion at the end of charge. The electrode potential and cell voltage are diminished by about 100 and 70 mV, respectively.

Conclusions

Pb/Ca electrodes

(i) The presence of the ions Cd(II) and Zn(II) in the electrolyte solution of the lead–acid cell causes the hydrogen gas evolution reaction to be shifted to more negative potentials, but the Ni(II) ion provokes a contrary effect. Only at low potentials is hydrogen gas evolution reduced by the presence of the Co(II) ion.

(ii) The oxygen gas evolution reaction on the lead dioxide electrode of the lead–acid cell is shifted to less positive potentials when the electrolyte solution contains the metallic ions Ni(II) and Co(II). However, Cd(II) and Zn(II) ions do not have an important effect on this reaction.

Commercial electrodes

(i) The hydrogen gas evolution reaction on the lead electrode is shifted to less negative potentials when the electrolyte solution contains the metallic Ni(II) ion. The Co(II), Cd(II) and Zn(II) ions have a very small effect on this reaction.

(ii) When the electrolyte solution of the lead–acid cell contains the Cd(II), Ni(II) and Zn(II) ions, the oxygen gas evolution reaction is shifted to slightly more positive potentials.

(iii) In the presence of Co(II), the cell voltage is diminished and an important change in oxygen gas evolution is observed.

(iv) The end of charge potential of the lead electrode is shifted to less negative potentials when the electrolyte solution contains Cd(II) and Ni(II) metallic ions.

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