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RESEARCH ARTICLE

EFFECT OF A PHENYL VINYL KETONE INHIBITOR ON ELECTROCHEMICAL BEHAVIOR OF Pb-Sb ALLOY AS NEGATIVE GRID IN LEAD–ACID BATTERY

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ABSTRACT

Effects of phenyl vinyl ketone (PVK) inhibitor on electrochemical behavior of Pb-3%Sb alloy electrode have been studied by linear sweep voltammetry (LSV), cyclic voltammetry (CV) and Tafel polarization measurements. The alloy surface morphology after discharge/charge reactions was studied by using scanning electron microscopy (SEM). Results show that PVK additive may strongly suppress hydrogen evolution even at a low concentration of 20μL.L^{-1} and reduce the rate of corrosion reaction which occurs on negative electrode grids of the lead- acid battery. The value of inhibition efficiency of PVK additive for corrosion of negative electrode grids is 40.89% to 83.26% with PVK concentrations of 20 to 280μL.L^{-1}. The presence of PVK in electrolyte solution significantly impedes the conversion reactions of negative grid material and makes them more reversible. The effect of PVK additve on conversion coefficients of negative electrode grids is maintained after hundred of CV cycles. The addition of PVK changed surface morphology of alloy electrode. The formed $PbSO_4$ and porous Pb crystals are smaller in size and more compact. The results showed that PVK additieve is promising for use as suitable additives for lead- acid batteries.

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INTRODUCTION

Lead acid battery is a long-standing traditional source of power, with many outstanding features such as high electrity, stable operation, small inert resistance, simple structure, low cost… Lead acid batteries are widely used for starting, lighting, ignition (SLI batteries), backup power supply, etc, resulting in annual turnovers of lead acid battery industry reached tens of billions of US dollars on a worldwide basis (Detchko Pavlov, 2011). The performance of lead acid batteries significantly affected from grids which are used in battery electrodes. It is known that the grids of lead-acid batteries were usually made of lead- (3-11%) antimony alloy because of their good mechanical strength and castability. However, antimony decreases hydrogen evolution overpotenial at the negative plates, which leads to early decomposition of water and the premature loss of lead acid batteries capacity. Many reseach directions have been to overcome this disadvantage.

Various metals have been added to minimize or replace antimony such as calcium, tin, arsence, and selenium. However, at the sametime with the hydrogen evolution overpotential at negative plates was increased, the beneficial effect of antimony on cycle life and capacity of lead-acid battery was lost and the production process was changed. Another method that increases hydrogen overpotential and keep beneficial characteristics of antimony is using electrolyte additives. (Böhnstedt, 1987), studied aromatic ring alcohols, aldehydes and acids as additives for electrolyte solution to determine their effect on hydrogen evolution. They found that methoxy-benzene group does not negatively influence the discharge reaction and aldehydes suppress the hydrogen evolution current. S. Gust and E. Hameenoja (Gust, 1990), indicated that the addition of certain organic compounds such as 2-methoxybenzaldehyde to electrolyte can affect profoundly the rate of the hydrogen evolution and the discharge capacity of lead. H. Dietz and et al. (Dietz, 1993 and Dietz, 1995), proposed aldehydes and acetophenone as promising compounds for the inhibition of hydrogen evolution, because of the presence of these inhibitors in flooded lead-acid batteries can reduce hydrogen evolution durring cycling by 50%. Phenyl vinyl ketone **(**PVK) is an organic compound in

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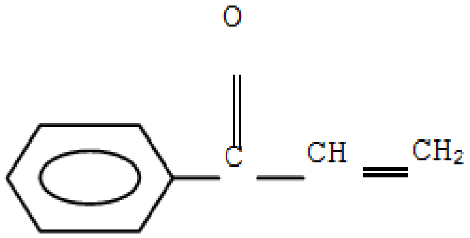
the benzaldehyde family with high temperature resistance. PVK containing unsaturated oxygen α-alkenylphenone in its molecule is new inhibitor that has the ability to protect metals against corrosion in acidic environments. The corrosion-inhibiting ability of this compound is predicted to result from the presence of the free electron pair of oxygen and the л electron system of the double bonds in the molecular structure to increase its adsorption ability on the metal surface. On the other hand, due to double coupling, PVK has the ability to polymerize with molecular weight, enhancing the coverage of metal surface. PVK has the following composition:



This paper studied the effect PVK as electrolyte additive on hydrogen evolution, corrosion of grid, specials conversion of alloy materials and surface morphology of Pb-3%Sb alloy.

Experimental

Preparation of working electrode

The working electrode is a flat plate made of Pb-Sb (3% wt. Sb) alloy. Except that working surface area of electrodes were exposed, the sides and other parts of them were covered with an epoxy to avoid any contact with electrolyte solution. Then, electrodes were polished with smooth paper.

Materials and electrolytes

The 98% concentrated sulfuric acid is the pure chemical from China. The H_2SO_4 electrolyte (d=1.27g.cm^{-3}) is prepared from concentrated H_2SO_4 and double distilled water. The PVK additive which used in this study have been synthesized and prepared at the Institute of Chemistry and Materials - Science Institute of Military Technology with components of 40% Phenylvinyl Ketone, 40% Isopropylic and 20% a surfactant. Electrolyte solutions containg 20, 40, 60, 80, 120, 160, 200, 240 and 280μL.L^{-1} of PVK additive were prepared by adding an appropriate calculated amount of PVK additive to the electrolyte.

Electrochemical measurements

Electrochemical measurements were carried out with a potentiostat/galvanostat equipment (AUTOLAB PGSTAT 302N-Netherlands) using the three electrode system. Working electrodes were Pb-3%Sb. The counter electrode and reference electrode were a pure lead sheet and Al/AgCl electrode, respectly. Before every mesurement, the working electrode was mechanically polished with emery paper and cleaned with acetone and double distilled water. Cyclic voltammograms were obtained at a 50mV.s^{-1} scan rate, between -0.9 and -0.2V (Ag/AgCl). The used working electrode has a surface area of 0.47cm^2.

For evaluation of the effect of PVK additives on hydrogen evolution, polarization measurements were performed with 5mV.s^{-1} scan rate in the potential range of -1.4 to -0.9V (Ag/AgCl), using 0.49cm^2 working electrode. Tafel polarization measurements were carried out in potential range of -0.8 to -0.5V (Ag/AgCl) with 5mV.s^{-1} scan rate, using 0.47cm^2 working electrode.

SEM imaging

Micrographs of lead-antimony alloy electrode were obtained with JSM 6610- LA scaning electron microscopy (Jeol- Japan). In order to determine the microstructure of $PbSO_4$ or porous Pb formed on alloy electrode surface, before taking SEM imaging, electrodes were polarized in 10minutes at –0.72V (Ag/AgCl) or 10 minutes at -0.72V and 10 minutes at -0.52V (Ag/AgCl), respectively.

RESULTS AND DISCUSSION

Hydrogen evolution

Figure 1 shows LSV of Pb-3%Sb alloy in H_2SO_4 solution without and with various PVK concentrations in the region of hydrogen gas evolution. It is seen that in the presence of PVK, polarization curves shift to more negative potential direction. This indicates that the addition of PVK in electrolyte increases hydrogen evolution overpotential, thus decreases the hydrogen evolution.

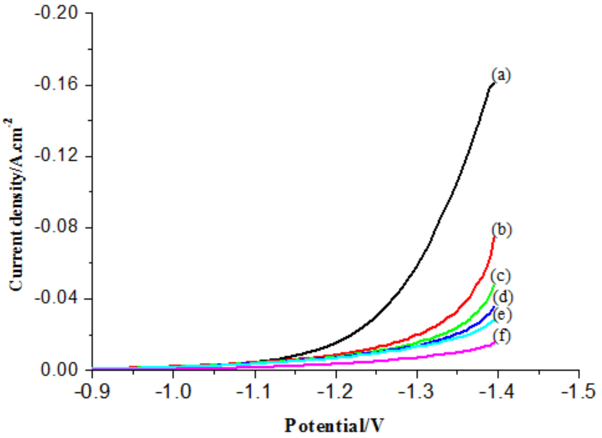


Figure 1. The linear sweep voltammograms (LCV) of Pb-3%Sb alloy in H_2SO_4 solution (1.27 g.cm^{-3}) without (a) and with various concentrations of PVK additives: 20μL.L^{-1} (b), 40μL.L^{-1}(c), 80μL.L^{-1}(d), 120μL.L^{-1}(e) and 140μL.L^{-1}(f). Scan rate: 5mV.s^{-1}

Table 1 shows hydrogen evolution potentials on Pb-3%Sb alloy recorded from LSV at a current density of 5mA.cm^{-2} in H_2SO_4 solution, without and with PVK additive in concentration range from 20 to 280μL.L^{-1}. In order to evaluate the effect of PVK additive on hydrogen evolution inhibitation, the I(%) coefficient is calculated and presented in Table 1.

$$I(\%) = \frac{Q_{H0} - Q_{H\,Add}}{Q_{H0}} \times 100\% \qquad \text{………….(1)}$$

Here, Q_{H0} and $Q_{H\ add}$, which are obtained from Fig.1 (the area under the LSV curves for hydrogen evolution), indicate the amount of charge used during hydrogen evolution on Pb-Sb alloy electrode without and with PVK additives in H_2SO_4 solution, respectively. Thus, I(%) characterize for decreased amount of hydrogen gas evolution in the presence of PVK additive at a certain concentration.

Table 1. Dependence of the hydrogen evolution potential E(V) and inhibit coefficient I(%) on Pb-3%Sb electrode on PVK additives concentrations

C_{pvk} μL.L^{-1}	0	20	40	80	120	160	200	240	280
E(V)	-1.10	-1.11	-1.13	-1.14	-1.14	-1.23	-1.24	-1.21	-1.21
I(%)	0	59	69	72	75	85	86	84	84

According to the results which are observed from table 1, the addition of PVK additive makes hydrogen evolution potential shifts to more negative values. This means that the presence of PVK additive in electrolyte solution increases the hydrogen evolution overvoltage. With increasing PVK additive concentration of up to 20μL.L^{-1}, hydrogen evolution potential decreases and then remains constant. The minimum value of hydrogen evolution potential is -1.24V (vs.Ag/AgCl) at PVK concentration of 200μL.L^{-1}. The obtained I(%) values in table 1 reveal that PVK additive strongly suppresses hydrogen evolution even at a low concentration of 20μL.L^{-1}. With increasing PVK additive concentration, the I(%) increases and then remains constant. The maximum I(%) value of 86% is obtained at the PVK additive concentration of 200μL.L^{-1}.

Corrosion of negative grid

Figure 2 shows polarization curves of Pb-3%Sb alloy in the absence and presence of various concentrations of PVK additive. The E_{corr} corrosion potential and i_{corr} corrosion current density obtained from fig.2 by extrapolation of linear parts of anodic and cathodic branches is presented in table 2. The P(%) corrosion inhibition coefficient is calculated using the following equation:

$$P(\%) = (1 - \frac{i_{corr,PVK}}{i_{corr,0}}) \times 100\% \qquad \text{.............(2)}$$

where $i_{corr,PVK}$ and $i_{corr,0}$ are corrosion current densities of Pb-3%Sb alloy in H_2SO_4 solution without and with PVK additive, respectively.

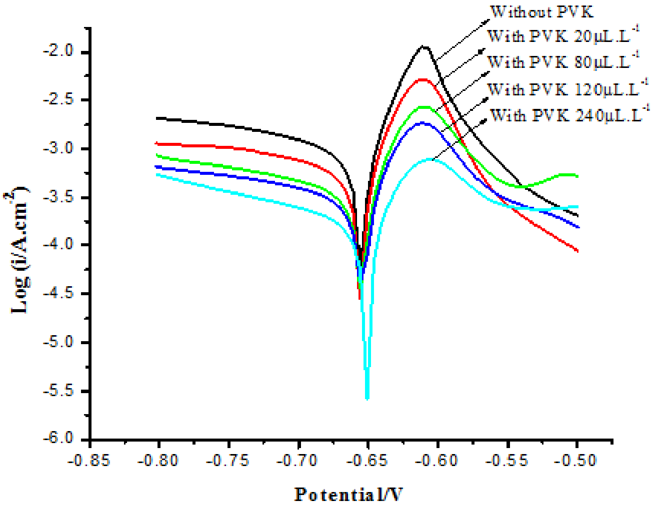


Figure 2. Polarization curves of Pb-3%Sb alloy in H_2SO_4 (d=1,27g.cm^3) solution without and with PVK additive, scan rate: 5mV.s^{-1}

It is seen from table 2 that corrosion potential values of Pb-3%Sb alloy electrode in presence of PVK additive are slightly more positive than that of without additive. With increasing PVK additive concentration, first corrosion current density decreases and its' value is minimum in electrolyte solution with PVK additive concentration of 240μL.L^{-1}. Then, i_{corr} slightly increases with continuous adding of additive. The calculated results of P(%) in table 2 also pointed that the inhibition effect obtains from 40.89% to 83.26%. This indicates that PVK additive has a good inhibition for the corrosion of Pb-3%Sb alloy.

Table 2. Dependence of corrosion E_{corr} potential and I_{corr} current density, and P(%) inhibition coefficient of Pb-3%Sb alloy on PVK additive concentrations (C_{PVK})

C_{PVK} (μL.L^{-1})	E_{Corr} (V)	I_{corr} (A.cm^{-2})	P (%)
0	-0.654	1.01x10^{-3}	
20	-0.654	5.97x10^{-4}	40.89
40	-0.653	3.76x10^{-4}	62.77
80	-0.654	3.56x10^{-4}	64.75
120	-0.653	3.15x10^{-4}	68.81
160	-0.652	1.91x10^{-4}	81.09
200	-0.651	1.82x10^{-4}	81.98
240	-0.650	1.69x10^{-4}	83.26
280	-0.652	2.3x10^{-4}	77.23

The conversion of specials in negative grids

Figure 3 shows cyclic voltammograms recorded at 50 mV.s^{-1} scan rate on a Pb-3%Sb alloy electrode in H_2SO_4 (d=1.27 g.cm^3) without and with PVK various additive concentrations of, in the potential region from -0.9 to -0.2V (Ag/AgCl). It is seen that there are two peaks in CVs. The anode peak relates to the oxidation of lead to lead sulfate and the other peak relates to the reduction of lead sulfate to lead metal corresponding to the following reaction equation:

$$Pb + SO_4^{2-} \leftrightarrow PbSO_4 + 2e \qquad \text{..................(3)}$$

The obtained datas from Fig. 3 represents in table 3. In there, E_{pa} and E_{pc} (mV) are anode and cathode potentials, respectively. ΔE_p (mV) is the difference between anode and cathode potential values, which is characteristic for reversise level of electrode reaction. Q^+_{add} / Q^+_0 and Q^-_{add} / Q^-_0 are coefficients used to evaluate the conversion level of lead to lead sulfate and vice versa, respectively. They are quotient of charge amount (the area under peaks) used for lead oxidation (Q^+) or lead sulfate reduction (Q^-) in 20th cycle. It can be seen from table 3 that ΔE_p values of Pb-Sb alloy electrode in presence of PVK additive is smaller than that in absence PVK additive.

This indicates that the addition of PVK additive makes conversion reactions on alloy electrode become more reverse. However, the more PVK additive concentration from 20 to 200 μL.L^{-1}, the more decreasing reversible degree of reactions on the electrode is. Then, with continued increase in PVK additive concentration of over 200μL.L^{-1}, the reversible degree of electrode reactions increases again.

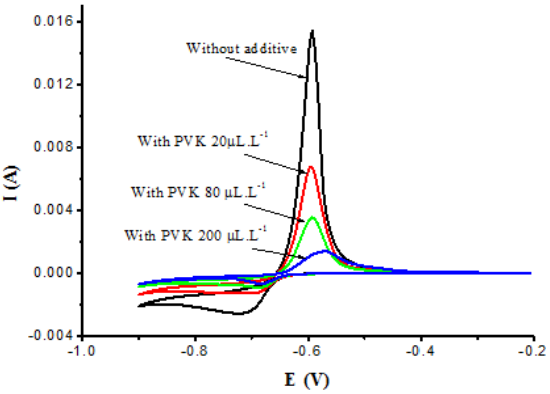


Figure 3. Cyclic voltammograms of Pb-3%Sb alloy electrode in H_2SO_4 ($d=1.27 g.cm^{-3}$) with and without PVK in 20th cycle, Scan rate: $50 mV.s^{-1}$

Table 3. Influence of PVK additive concentration on conversion of Pb to $PbSO_4$ and vice versa on negative grid

C_{PVK} ($\mu L.L^{-1}$)	E_{pa} (mV)	E_{pc} (mV)	ΔE_p (mV)	Q^{+}_{add}/Q^{+}_{0}	Q^{-}_{add}/Q^{-}_{0}
0	-592	-719	127	1	1
20	-597	-685	88	0.546	0.580
40	-592	-685	93	0.360	0.383
80	-592	-685	93	0.323	0.348
120	-592	-685	93	0.285	0.305
160	-587	-685	98	0.268	0.282
200	-568	-685	117	0.225	0.225
240	-573	-680	107	0.205	0.235
280	-583	-685	102	0.269	0.258

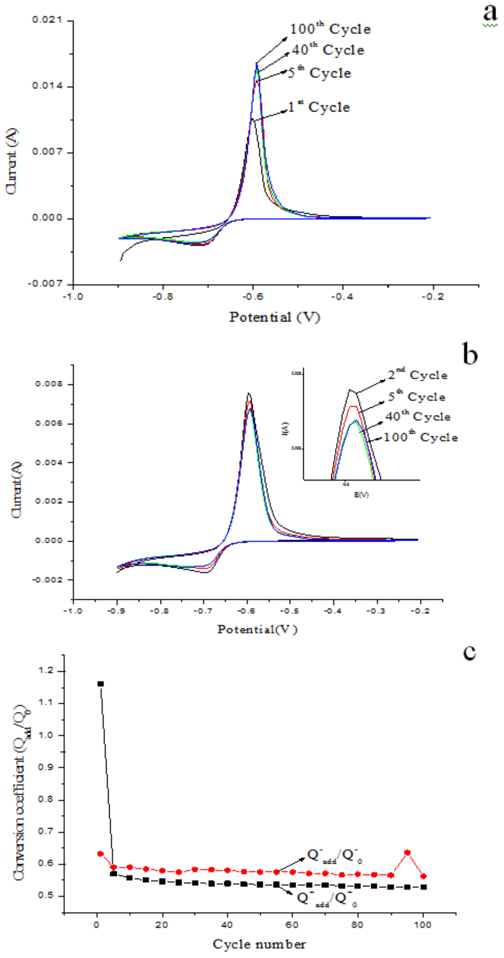
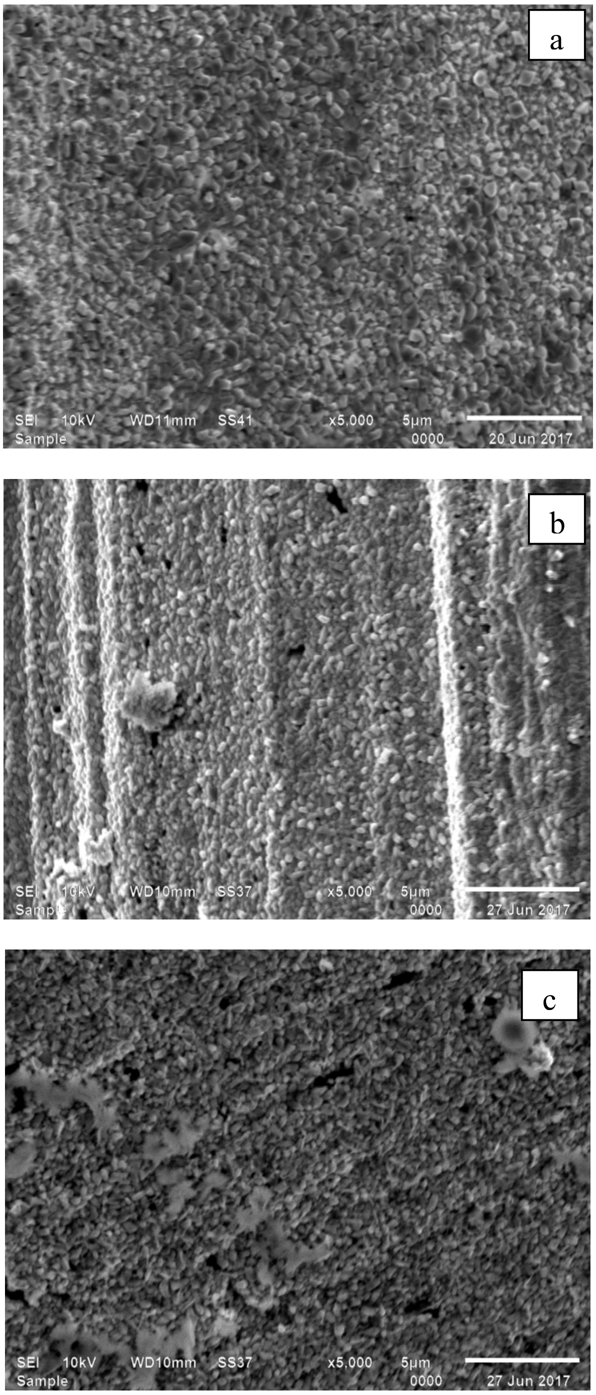


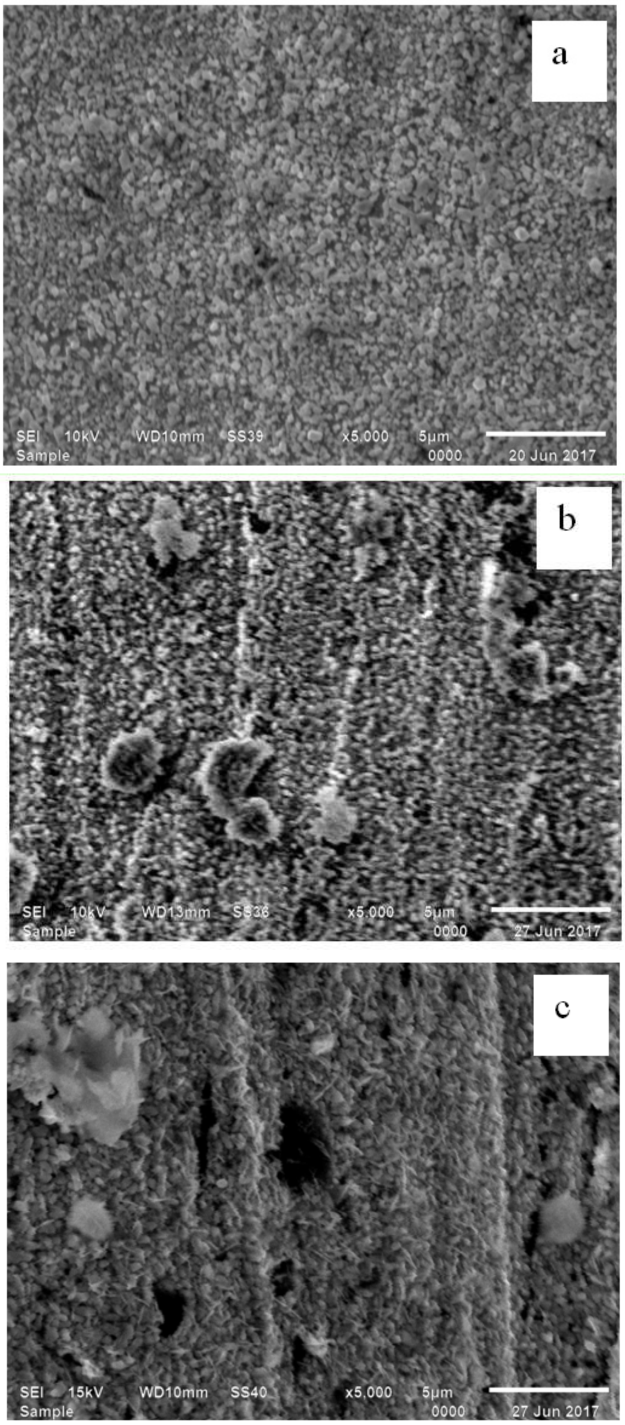
Figure 4. Cyclic voltammograms with various cycle of Pb-3%Sb alloy electrode without PVK additive (a) and with $20\mu L.L^{-1}$ of PVK additive (b), and the dependence of conversion coefficients on the number of scan cycles (c). Scan rate $50mV.s^{-1}$

As indicated from Table 3, values of conversion coefficients with the presence of PVK in electrolyte solution are much smaller than one. This exhibits that PVK additive strongly hinders conversion reactions of negative grid material, especially at PVK concentration range of 200 to $240\mu L.L^{-1}$. It is well known that, the corrosion of negative grids is derived from non-recoverable conversion of grid material. In this respect, PVK additive with the ability to significantly impede the conversion of negative grid material and make this reaction more reversible is suitable for use as a corrosion inhibitor for negative grids. This result is consistent with the results discussed in 3.2 section.



Figue 5. The scanning electron micrographs (SEM) of Pb-3%Sb after 10 minutes of discharge in H_2SO_4 without PVK (a) and with PVK concentration of $200\mu L.L^{-1}$ (b) and $280\mu L.L^{-1}$ (c)

Figure 4 shows electrochemical effect of PVK additive on conversion of Pb and $PbSO_4$ with various cycles. It can be seen from figure 4a and b that CVs without PVK additive become stable after 5th cycle while those with 20µL.L^{-1} become stable after 2nd cycle. This reveals that the presence of PVK additive in electrolyte solution makes the surface of electrode more stable. It is also kown that a cycle of cyclic voltammetry measurement can be considered as a discharge and charge cycle for surface material layer of electrode. The stable effect of PVK additive on conversion coefficients of grid alloy after a hundred cycles of CV, as indicated from figue 4c, demonstrates that PVK additive is durable under the operating conditions of the lead-acid battery.



Figue 6. The scanning electron micrographs (SEM) of Pb-3%Sb after 10 minutes of charge in H_2SO_4 without PVK (a) and with PVK concentration of 200µL.L^{-1} (b) and 240µL.L^{-1} (c)

The surface morphology of alloy electrode

Figure 5 and 6 shows SEM images of Pb-3%Sb alloy surface after discharge or charge in H_2SO_4 solution without and with PVK various concentrations of, respectively. Durring the discharge, the conversion of Pb to $PbSO_4$ occus on the surface of negative grids arcording to reaction (3). As indicated from Fig. 5, formed $PbSO_4$ crystals on the lead alloy electrode surface in the present of PVK additive are smaller in size and more compact. It seem that PVK additives adsorbed on electrode surface, hence, change the structures of crystals formed on the electrode surface.

Conclusions

The effects of PVK as an electrolyte additive on electrochemical behavior of Pb-3%Sb alloy grids were investigated. The following conclutions were drawn:

- The PVK additive may strongly suppress hydrogen evolution even at a low concentration of 20µL.L^{-1} and reduces the rate of corrosion reaction which occurs on negative electrode grids of the lead- acid battery.
- The PVK additive reduces the rate of corrosion reaction which occurs on negative electrode grids of the lead- acid battery. The values of inhibition efficiency of PVK additive for corrosion of negative electrode grids is 40.89% to 83.26% with PVK concentrations of 20 to 280µL.L^{-1}.
- The presence of PVK in electrolyte solution significantly impede the conversion reactions of negative grid material and make them more reversible. The effect of PVK additve on conversion coefficients of negative electrode grids is maintained after hundred of CV cycles.
- The addition of PVK changed surface morphology of alloy electrode. The formed $PbSO_4$ and porous Pb crystals are smaller in size and more compact.
- The electrochemical behavior of Pb-3%Sb depends on PVK concentration in the electrolyte. The PVK additive is promising for use as suitable additives for lead- acid batteries.

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