Effects of gold on the structure and electrochemical behavior of lead-gold composite in different temperatures sulfuric acid

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Abstract. Lead is still dominantly used as the main material for lead-acid batteries electrodes and active materials. Lead-gold composites were made in efforts to improve the performance of the active materials component for lead-acid batteries. The electrochemical behavior of Pb-Au composite in sulfuric acid solution (H₂SO₄) were investigated. Au was chosen as the reinforcement material for lead composite because of its high electrical conductivity and its resistance to chemical reaction which is important to resist the formation of lead sulfate (PbSO₄) crystal on the surface of electrodes. Lead-gold composite were made by mixing lead powder and auric chloride (AuCl₃) solution. The fabrication of Pb-Au composites was done by mixing Pb powders and auric chloride (AuCl₃) solution and using hot-press method. Material characterizations were performed using X-ray fluorescence technique to investigate material composition and X-ray diffraction technique to investigate material structure. The electrochemical properties of Pb-Au composites were investigated by electrochemical polarization testing, specifically linear sweep voltammetry technique (LSV) in H₂SO₄ solution with various solution temperature at 10°C, 25°C, and 40°C to simulate common active vehicle condition. The results show that the crystal structure of lead-gold composites is face-centered cubic (FCC) structure. Also, the addition of Au lower the Icorr and shift the Ecorr to a more cathodic potential.

1. Introduction
The advance of energy storage is of the utmost importance in modern times. Lead-acid batteries is still the most used battery for automotive application in the last 100 years because of its cheap production cost and recyclability[1]. The most general lead-acid battery works using the principle of electrochemical reaction between lead (Pb) and lead oxide (PbO) electrodes immersed in H₂SO₄ solution as the electrolyte to create direct electrical current[2]. While having cheap production cost, lead acid batteries generally need to be replaced every 3 to 5 years before failure occurs[3]. One of the main reasons lead-acid batteries lost its capacity which lead to failure is the formation of lead sulfate crystal (PbSO₄) on the electrodes’ surface[4,5]. The formation of amorphous lead sulfate can be reversed by applying reverse direct current, but if it’s not reversed for too long it will grow into crystallized form. Lead sulfate crystal cannot conduct electricity and it will hinder the flow of current which reduce the battery ability to store energy, and lead to battery failure[6,7]. Gold is an inert metal that is used in many electrodes application because it can resist most chemical reaction, also it has the third highest conductivity of pure metals[8,9]. By creating a composite electrode material with gold as a reinforcement phase and lead as the base, it is expected to be able to decrease the effect of lead sulfate formation on electrode. In this study, the crystal structure of Pb-Au was observed using XRD method.
The electrochemical behavior of Pb-Au composite with various composition of gold in H2SO4 solution at 10°C, 25°C, 40°C was observed.

2. Experimental

2.1. Material and preparation
The Au addition to Pb were prepared by mixing Pb powder and AuCl₃ solution and stirred by a magnetic stirrer (Bante Instrument MS300) with a speed of 150 rpm for 10, 20, 30, 40, and 50 minutes at 165°C to reach the temperature needed for AuCl₃ decomposition[10]. The powder then filtered and collected from the solution to be pressed with 1 ton of force and heated again at 165°C. The samples acquired will be cut to plates of similar size for testing.

2.2. Crystallographic orientation
The crystal structure of the Pb-Au composites was identified by using XRD technique (Rigaku RINT 2000 with Cu-Kα radiation). The XRD patterns were scanned from 20° to 80° with a step size of 0.01°. The software used to refine XRD pattern and calculate the full-width half maximum (FWHM) of the Pb-Au composite samples was X’Pert HighScore Plus.

2.3. Electrochemical characterization
The electrochemical behavior of Pb-Au composite samples were investigated with linear sweep voltammetry technique using potentiostat instrument Digy-Ivy DY2311. The linear sweep voltammetry was carried using a three-electrode system and a beaker glass containing 36% H2SO4 solution (100 mL) as electrolyte at various temperature of 10°C, 25°C, and 40°C to imitate the working condition of automotive lead-acid battery. The samples of the Pb-Au composites were mounted with an exposed area of 1.2cm² for linear sweep voltammetry testing. The linear sweep voltammetry data was obtained at a scan rate of 50 mV s⁻¹ between -1.4 and +2 V. A Pt wire was used as a counter electrode (CE), while a silver chloride electrode (Ag/AgCl) was used as a reference electrode (RE). The Tafel extrapolation method was employed for the calculation of the corrosion current density (Icorr) and the potential of corrosion (Ecorr). The corrosion rates were calculated from the following equation[11]

\[
\text{Corrosion Rate} = \Sigma C \frac{M I_{corr}}{n \rho A}
\]

where C is corrosion rate constant (3.27 mmpy (mm years⁻¹)), M is the atomic weight (g mol⁻¹) of the material, Icorr is the corrosion current density (A cm⁻²), n is the number of electrons involved, ρ is the density (g cm⁻³), and A is the exposed area on the material for testing (cm²). Each sample was fully immersed in the H2SO4 electrolyte for testing.

3. Results and Discussion

3.1. Material composition
Table 1 presents the composition of each sample obtained through XRF analysis. The number in the sample name indicate the amount of time Pb powders were mixed with AuCl₃ solution in ascending order i.e. Pb-Au1 for 10 minutes of mixing, Pb-Au2 for 20 minutes of mixing, and so on. From the table, it was found that the longer the mixing time of Pb powder and AuCl₃ solution, the larger Au concentration on the created sample.
Table 1. Chemical concentration of Pb-Au composites (wt%), determined from the X-Ray Fluorescence measurement.

| Sample  | Element Concentration | Au (wt%) | Pb (wt%) |
|---------|-----------------------|----------|----------|
| Pb-Au0  |                       | 0        | Balance  |
| Pb-Au1  |                       | 0.17     | Balance  |
| Pb-Au2  |                       | 0.35     | Balance  |
| Pb-Au3  |                       | 0.61     | Balance  |
| Pb-Au4  |                       | 0.84     | Balance  |
| Pb-Au5  |                       | 0.98     | Balance  |

3.2. Crystallographic orientation

Figure 1 presents the XRD patterns of Pb-Au1, Pb-Au3, and Pb-Au5 samples. The XRD analyses revealed that the peaks positions of all samples are identical at 31.3°, 36.3°, 52.3°, 62.2°, 65.3°, 77.0°, 85.5°, and 88.2° which are corresponding to the planes of (111), (002), (022), (113), (222), (004), (133), and (024). The XRD Analysis by HighScore Plus software revealed that all peaks correspond to the reflection from the face-centered cubic (FCC) crystallographic planes. By using Rietveld refinement, it was found that all peaks shown in Figure 1 correspond to the phase of lead with ICSD 98-064-8341 as the reference pattern. The gold phase was not detected because of its low composition in the samples (below 1wt%) which caused its diffraction peaks intensity to merge with the intensities of noise.

The crystallite size of the materials strongly affect their physical and mechanical properties[12]. Therefore, the determination of the crystallite size is necessary. In this study the Debye-Scherrer equation has been used to estimate he crystallite size of the samples[13];

$$D = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)
where $\lambda$ is the wavelength of Cu-K\(\alpha\) radiation (0.1541874 nm), \(\theta\) is the Bragg angle of the X-ray, and \(D\) is the average crystallite size. By using the Debye-Scherrer equation, crystallite size is obtained. The resulting average crystallite sizes from Equation (2) are shown in Table 2. In general, the structure of lead phase with gold addition as reinforcement material does not change the lattice arrangement (FCC), while the crystallite size of Pb-Au samples increases with higher gold composition.

Table 2. The crystallite size of samples.

| Structure Parameters | Pb-Au 1 | Pb-Au 3 | Pb-Au 5 |
|----------------------|---------|---------|---------|
| Lattice Parameters   |         |         |         |
| a (Å)                | 4.9506  | 4.9507  | 4.9507  |
| b (Å)                | 4.9506  | 4.9507  | 4.9507  |
| c (Å)                | 4.9506  | 4.9507  | 4.9507  |
| Volume (Å\(^3\))     | 121.33  | 121.33  | 121.34  |
| Crystal Structure    | Cubic (FCC) | Cubic (FCC) | Cubic (FCC) |
| Crystalline Size (nm)| 63.31 | 72.55 | 76.20 |

3.3. Electrochemical characterization

Linear sweep voltammetry is used to examine the corrosion current density and the corrosion potential. The current density obtained from the testing is processed into log | \(I\) | in which the resulting graph can be extrapolated using Tafel extrapolation to obtain corrosion current density. The Tafel plot can also be used to find the corrosion potential. The resulting Tafel plot is shown in Figure 2. and the corrosion rate of the samples is shown in Table 3. With gold addition, the corrosion potential of samples tends to be more cathodic than pure lead. this is due to gold’s half-cell potential which is more cathodic compared to lead’s half-cell potential[14]. The corrosion rate of Pb-Au samples tends to decrease with higher amount of gold addition due to the property of gold which is inert to chemical reaction. Also, the the corrosion rate tends to increase with higher temperature except in Pb-Au 4 and Pb-Au 5 because higher temperature system acquire more energy which leads to easier electron transfer[15].

![Figure 2. Linear sweep voltammetry Tafel plot at (a) 10°C. (b) 25°C. and (c) 40°C.](image-url)
4. Conclusions
In summary, the phase detected in all Pb-Au samples is lead phase with fcc structure. Gold phase was not detected because of its low concentration in the samples (<1wt%). The corrosion potential of lead shifted to be more cathodic when added with gold, because gold’s half-cell potential is more cathodic than lead. The corrosion rate of Pb-Au samples decreases with more gold addition because of gold inert characteristic. The corrosion rate of Pb-Au samples also increased with higher temperature because higher energy in the system allows for easier electrons transfer.

Acknowledgements
The author thanks for the financial support from the Ministry of Research, Technology and Higher Education of Indonesia (RISTEK-DIKTI), under grant Penelitian Dasar Unggulan Perguruan Tinggi (PDUPT) No. NKB-2797/UN2.RST/HKP.05.00/2020).

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Table 3. $E_{\text{corr}}$, $I_{\text{corr}}$, and corrosion rate of samples.

| Temperature | Sample  | $E_{\text{corr}}$ (V) | $I_{\text{corr}}$ (A) | Corrosion Rate (mm/year) |
|-------------|---------|-----------------------|-----------------------|--------------------------|
| 10°C        | PbAu0   | -0.607                | 8.69E-05              | 0.1298                   |
|             | PbAu1   | -0.395                | 5.50E-05              | 0.0686                   |
|             | PbAu2   | -0.408                | 4.04E-05              | 0.0507                   |
|             | PbAu3   | -0.434                | 2.77E-05              | 0.0348                   |
|             | PbAu4   | -0.429                | 6.48E-06              | 0.0081                   |
| 25°C        | PbAu0   | -0.612                | 1.70E-04              | 0.2126                   |
|             | PbAu1   | -0.624                | 7.53E-05              | 0.0944                   |
|             | PbAu2   | -0.552                | 7.45E-05              | 0.0929                   |
|             | PbAu3   | -0.309                | 2.44E-05              | 0.0305                   |
|             | PbAu4   | -0.421                | 2.29E-05              | 0.0288                   |
| 40°C        | PbAu0   | -0.608                | 2.17E-04              | 0.2706                   |
|             | PbAu1   | -0.601                | 9.40E-05              | 0.1173                   |
|             | PbAu2   | -0.593                | 9.30E-05              | 0.1166                   |
|             | PbAu3   | -0.284                | 3.33E-05              | 0.0196                   |
|             | PbAu4   | -0.423                | 8.56E-06              | 0.0108                   |
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