Structure and electrochemical behaviour of composite Pb-nano ZnO in sulfuric acid solution for different temperature

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Abstract. Lead is one of the important materials used as an electrode for battery application. With a good performance at the lowest price possible, using lead as an active material for lead-acid battery still high even though the fact that lead waste is very dangerous for the environment. Lead must be optimized to reduce lead waste with adding new material to the lead for the electrode. For this research lead and nano zinc oxide became a composite Pb-Nano ZnO and this composite tested into sulfuric acid solution with various solution temperature 10°C, 25°C, and 40°C. The structure and electrochemical behaviour were analysed with X-Ray Diffraction (XRD) and Potentiostat (LSV and CV) respectively. Detected phase from the spectrum shows lead phase with cubic FCC crystal structure. Linear Sweep Voltammetry and Cyclic Voltammetry test used to see is the composite can be used as an electrode for a battery and is the performance different than lead electrode. The result shows that the composite is electrochemically reversible and corrosion rate decrease when nano ZnO added with lowest corrosion rate 0.011852 mm/year in ZnO 20% wt composition on temperature variation 10°C.

1. Introduction

Battery is a storing energy device where the work principle is changing chemical energy into electrical energy with electrochemical reaction. Battery consists of electrode which anode where oxidation reaction takes place and cathode where reduction reaction takes place. Battery can be divided into two different categories based on the electrochemical reaction that occur in the electrode.[1] Primary battery is a battery that is not rechargeable because the electrochemical reaction that occurs is just one way and cannot be reversed. Meanwhile secondary battery is a battery that is rechargeable because the electrochemical reaction that occurs is two way from anode to cathode and vice versa. This makes the reaction reversible thus the battery can be undergoing discharging process or charging process. Lead acid battery is one of the rechargeable batteries that is cheap and easy to produce and become more attractive to be optimized.

Lead acid batteries, invented in 1859, are the oldest and most widely used rechargeable electrochemical devices. A lead acid battery consists of (in the charged state) electrodes of lead metal and lead oxide in an electrolyte of sulfuric acid. In the discharged state both electrodes turn into lead sulphate and the electrolyte loses its dissolved sulfuric acid and becomes primarily water.[2] Lead sulphate is isolator. Lead sulphate that failed to turn back to lead and lead oxide when the charging process occur will make the battery less conductive in will fail eventually. Sulfation in lead acid battery can be observe when battery capacity is decreasing, loss of voltage, increase in internal resistance, and sulfuric acid concentration is decreasing.[3] Using ZnO as the reinforcement for lead electrode hopefully can tackle this sulfation problem to make the lead acid battery last longer.
Addition of another material to lead electrode has been done before. Antimony and Calcium were added to lead electrode to see if there is improvement or drawback from it. For the lead-antimony electrode there is an increasing strength in mechanical properties of electrode, good cycling, increasing charge acceptance of battery. The drawback is higher water loss & maintenance and battery goes flat quicker. For the lead-calcium electrode there is decreasing in battery water loss, battery last longest when not in use. The drawback is the cycling not as good as lead-antimony, higher corrosion rate in higher temperature, sulfation occur more frequently. [4] The improvement and drawback from adding reinforcement to lead electrode can be see and tested for different material. For this work the material that will be used is zinc oxide nano particle. Zinc oxide is used for the reinforcement because it is a good semiconductor, high breakdown voltage, lower noise produced, can work in higher temperature and power output. [5] The nanoparticle one is used to increase the surface area of zinc oxide in lead electrode. Nano particle zinc oxide has diameter less than 100 nanometer. [6]

The objective of this work is to study the structure and electrochemical behavior of the Pb-Nano ZnO for different wt% composition and for different solution temperature using data from x-ray diffraction and electrochemical corrosion test.

2. Methods

2.1. Material
Lead powder and nano ZnO powder is mixed with ZnO wt% composition 4%, 8%, 12%, 16%, and 20%. The composite then grinded for thirty minutes. After grinding process, Pb-Nano ZnO composite then pressed to become a plate 2 cm in length and 1 cm in width. There are 6 samples of composite Pb-Nano ZnO.

2.2. X-ray diffraction (XRD)
Samples were tested in x-ray diffractometer to see the diffraction pattern of x-ray that were going through the sample. Data from the spectrum then used to determine whether adding more ZnO to lead electrode change the crystal structure or not. X-ray diffraction can also be used to search crystallite size and used to determine whether adding more ZnO to lead electrode change the crystallite size.

2.3. Corrosion test
Corrosion tests data were collected out using Potentiostat. The Working Electrode and the Reference Electrode are used to quantify the current and the voltage, where Ag/AgCl was used as the reference electrode in this experiment [7]. All of the samples were connected with the wire so the samples can be dipped into the solution to collect the data. These electrodes were soaked into sulfuric acid solution. The corrosion rate of each samples had been calculated after all data were collected from Potentiostat.

3. Result and Discussion

3.1. XRD analysis
The XRD plots of all composite Pb-Nano ZnO sample can be seen in Figure 1 and the data of the characterization is served in Table 2. There were eight demonstrated peaks, namely, (111), (002), (022), (113), (222), (004), (133), and (024) which are clearly visible for lead phase. For the Pb-ZnO 0% sample, eight peaks were identified with angle positions of 31.30°, 36.30°, 52.25°, 62.17°, 65.30°, 77.00°, 85.44°, and 88.00°. For Pb-ZnO 4% sample, eight peaks were identified with angle positions of 31.33°, 36.32°, 52.27°, 62.12°, 65.28°, 77.00°, 85.45°, and 88.2°. For Pb-ZnO 8% sample, eight peaks were identified with angle positions of 31.34°, 36.3°, 52.27°, 62.18°, 65.29°, 77.00°, 85.46°, and 88.24°. For Pb-ZnO 12% sample, eight peaks were identified with angle positions of 31.36°, 36.4°, 52.30°, 62.20°, 65.31°, 77.09°, 85.49°, and 88.00°. For Pb-ZnO 16% sample, eight peaks were
Figure 1. XRD plot of composite Pb-Nano ZnO.

identified with angle positions of 31.34º, 36.33º, 52.00º, 62.20º, 65.31º, 77.04º, 85.48º, and 88.26º. For Pb-ZnO 20% sample, eight peaks were identified with angle positions of 31.30º, 36.30º, 52.30º, 62.15º, 65.30º, 77.00º, 85.43º, and 88.21º.

All samples have a little difference at each peak which states that there was a slight peak shift caused by adding ZnO to the lead. Adding more ZnO does not change the crystal structure which can be shown from the Figure 1. This can happen because the nanoparticles of zinc oxide that has been used not crystalizing properly due to high melting point temperature of zinc oxide thus the crystal structure formed by ZnO is amorphous and there is no difference between lead electrode without ZnO and lead electrode with 20% wt ZnO.

Using program Highscore, XRD plot compared with lead XRD plot reference from Crystallography Open Database and can be determined that the crystallite system of these samples is cubic, so the lattice parameters have the same value for a, b, and c. For lead reference, the lattice parameter of all sample does not change extremely when ZnO added more. Crystallite size changed but not in a linear fashion. This maybe can occur because of the production of the sample using powder. ZnO of the sample does not distribute evenly at micro level.

By considering the crystallite size, the various composition of ZnO added to lead electrode believed can change the grain size when the ZnO is produced ideally and distributed evenly to all of the surface. For different crystallite size, it has commonly assumed that there are deformation and grain growth that depend on the strain.

Table 1. Crystallographic parameters of the composite Pb-Nano ZnO.

| Sample | 0%  | 4%  | 8%  | 12% | 16%  | 20%  |
|--------|-----|-----|-----|-----|------|------|
| Crystallite Size (Å) | 687.08 | 740.08 | 638.04 | 533.07 | 649.99 | 554.88 |
| Lattice Parameter (Å) | a = 4.950  | a = 4.951  | a = 4.950  | a = 4.950  | a = 4.951  | a = 4.949  |
|                    | b = 4.950  | b = 4.951  | b = 4.950  | b = 4.950  | b = 4.951  | b = 4.949  |
|                    | c = 4.950  | c = 4.951  | c = 4.950  | c = 4.950  | c = 4.951  | c = 4.949  |
| Volume (Å³)         | 121.30    | 121.41    | 121.32    | 121.35    | 121.36    | 121.23    |
3.2. Potentiodynamic curves analysis

By analysing the corrosion mechanism and understanding the change in corrosion rate, electrochemical behaviour of the composite Pb-Nano ZnO samples in this experiment are observed. The outcome potentiodynamic curves test in sulfuric acid solution for samples with different temperature are shown on Figure 2. For all samples, similar trend are displayed in potentiodynamic polarization curves. I_{corr} and V_{corr} are obtained by applying Tafel plotting exploration. The reactions that represent for corrosion in lead electrode in sulfuric acid electrolytes are shown below.

Anodic reaction \[ Pb \rightarrow Pb^{2+} + 2e \] (1)

Cathodic reaction \[ PbO_2 + 4H^+ + 2e \rightarrow Pb^{2+} + 2H_2O \] (2)

In cathodic reactions, electrons from anodic reaction are absorbed to do some reduction of oxygen in solution.

Main reaction \[ Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \] (3)

**Figure 2.** (a) Potentiodynamic polarization curves of the composite Pb-Nano ZnO in 10°C. (b) Potentiodynamic polarization curves of the composite Pb-Nano ZnO in 25°C. (c) Potentiodynamic polarization curves of the composite Pb-Nano ZnO in 40°C.
Potential corrosion $E_{\text{corr}}$ (V) and corrosion current $I_{\text{corr}}$ (A) affect changes in the corrosion rate. Table 2 shows that if the more ZnO added, the corrosion rate will decrease further. It is expected because zinc oxide does have high corrosion resistant.

Table 2. Data from the corrosion test of the composite Pb-Nano ZnO in sulfuric acid solution at 10°C, 25°C, and 40°C.

| Temperature | Sample   | $E_{\text{corrosion}}$ (V) | $I_{\text{corrosion}}$ (A) | Corrosion Rate (mm/year) |
|-------------|----------|---------------------------|-----------------------------|--------------------------|
| 10°C        | Pb-ZnO 0% | -0.606                    | 8.693 $\times 10^{-5}$      | 0.0834                   |
|             | Pb-ZnO 4% | -0.622                    | 2.793 $\times 10^{-5}$      | 0.0261                   |
|             | Pb-ZnO 8% | -0.621                    | 2.059 $\times 10^{-5}$      | 0.0188                   |
|             | Pb-ZnO 12%| -0.624                    | 1.695 $\times 10^{-5}$      | 0.0150                   |
|             | Pb-ZnO 16%| -0.612                    | 1.556 $\times 10^{-5}$      | 0.0134                   |
|             | Pb-ZnO 20%| -0.619                    | 1.406 $\times 10^{-5}$      | 0.0118                   |
| 25°C        | Pb-ZnO 0% | -0.612                    | 1.704 $\times 10^{-4}$      | 0.1636                   |
|             | Pb-ZnO 4% | -0.615                    | 8.979 $\times 10^{-5}$      | 0.0841                   |
|             | Pb-ZnO 8% | -0.618                    | 4.643 $\times 10^{-5}$      | 0.0424                   |
|             | Pb-ZnO 12%| -0.623                    | 3.856 $\times 10^{-5}$      | 0.0343                   |
|             | Pb-ZnO 16%| -0.593                    | 2.428 $\times 10^{-5}$      | 0.0210                   |
|             | Pb-ZnO 20%| -0.610                    | 1.923 $\times 10^{-5}$      | 0.0162                   |
| 40°C        | Pb-ZnO 0% | -0.608                    | 2.171 $\times 10^{-4}$      | 0.2085                   |
|             | Pb-ZnO 4% | -0.614                    | 1.113 $\times 10^{-4}$      | 0.1042                   |
|             | Pb-ZnO 8% | -0.612                    | 7.866 $\times 10^{-5}$      | 0.0718                   |
|             | Pb-ZnO 12%| -0.614                    | 5.287 $\times 10^{-5}$      | 0.0470                   |
|             | Pb-ZnO 16%| -0.610                    | 3.466 $\times 10^{-5}$      | 0.0300                   |
|             | Pb-ZnO 20%| -0.467                    | 2.926 $\times 10^{-5}$      | 0.0246                   |

4. Conclusion

Adding zinc oxide to lead electrode cause some changes in structure and corrosion rate. The more zinc oxide added to lead, corrosion resistant of the electrode becoming higher. Increasing the temperature generally increase the corrosion rate of the electrode. Best corrosion rate of sample is at 10°C with 20 wt% ZnO composition with corrosion rate 0.0118 mm/year.

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References

[1] Schmidt-rohr K 2018 J. Chem. Educ. 95 pp. 1801–10
[2] Chen H, Ngoc T, Yang W, Tan C and Li Y 2009 Prog. Nat. Sci. 19(3) pp. 291–312
[3] Catherino H A, Feres F F and Trinidad F 2004 Sulfation in lead – acid batteries 129 pp. 113–120
[4] Pavlov D 2017 Lead-acid batteries: science and technology: a handbook of lead-acid battery technology and its influence on the product, 2nd ed
[5] Özgür U et al 2005 Appl. Phys. Rev. 041301 no. August, 2005
[6] Piccinno F and Gottschalk F 2012 Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world
[7] Vats A 2017 Corrosion measurement, friction testing and XRD analysis of single layer CrN coatings on AISI 304 stainless steel no 5 pp. 435–45