



Sodium hexa meta phosphate impact as electrolyte additive on electrochemical behavior of lead-acid battery



Shadi Hosseini*, Khalil Farhadi, Sepideh Banisaeid

Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran

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ABSTRACT

Sodium hexa meta phosphate (SHMP) is an inorganic salt with a polymeric structure which produces massive branches of hexa meta phosphate anions (HMP^-) in an acidic environment. The main goal of the presented work is to investigate the influence of SHMP as an electrolyte additive on the performance of the lead-acid batteries. To achieve the point, the examinations are done in two separate ways: i) Investigation electrochemical behavior of lead alloy electrode, by studying Hydrogen and Oxygen Evolution Reaction (HER and OER) with electrochemical techniques including; Cyclic Voltammetry and Linear Sweep Voltammetry. Then, Scan of Electron Microscopy (SEM performed to study the surface of the electrode after electrochemical treatments. By increasing SHMP concentration, overpotential of hydrogen and oxygen evolution is increased due to improving particle size of PbSO_4 which consequently lessens water loss. ii) Real battery tests including; water consumption test, capacity measurements and High Rate Partial State of Charge (HRPSoC) as a cycle-life examination. Also, Scan of Electron Microscopy from the surface of the negative electrode and X-Ray Diffraction (XRD) analysis of negative electrode plate at the charge and discharge state after cycle-life test are prepared for study the PbSO_4 particles size and quantity or the morphology of sulfating layer. Addition of SHMP to the electrolyte of the lead-acid battery increases cycle-life numbers and accordingly prolongs battery life. Therefore, SHMP is a promising electrolyte additive and it would be used with a combination of additives to increase the overall performance of a lead-acid battery.

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1. Introduction

During the decades, lead-acid batteries have been one of the most important within reach energy sources due to their wide application including; energy storage, emergency power and electric vehicle. Also, great developments of starting lightening and ignition (SLI) machines made lead-acid batteries one of the important energy storage sources. Low relatively specific energy is the principle issue with the lead-acid battery which using additives as active material can improve it. Also, additives are added to the electrolyte of a battery to increase reversibility of the crystallization during charge and discharge process to guarantee its long cycle-life [1]. Minimizing water loss is another benefit of additives for both VRLA (Valve Regulated Lead Acid) and maintenance free batteries which finally decreases corrosion of the grid, water consumption, electrolyte depletion and danger of explosion of the battery during overcharging state [2]. Additives

should chemically and thermally be stable and the cost of proposed additive should be considered as well. As a result, for a lead-acid battery to meet the standard performance, additives are necessary.

H_3PO_4 is one of the most widely used electrolyte additives in lead-acid batteries [3,4]. H_3BO_3 [5], citric acid [6], SnSO_4 [7], $\text{Al}_2(\text{SO}_4)_3$ [8], NaSO_4 [9], are the other inorganic acids or salts which are added to the electrolyte of the lead-acid batteries. Carbon suspensions [10] and polymer emulsions [11,12] are some other types of electrolyte additives for lead-acid batteries. Each of these additives causes different influence on the performance of the battery, thus a mix of the additives is added to the electrolyte.

For the first time, in the present work, Sodium Hexa Meta Phosphate (SHMP) (Fig. 1) is proposed as an electrolyte additive for lead-acid batteries. It is a nontoxic, colorless polymeric substance and causes no genetic toxicities on bacteria [13]. So, SHMP is environment-friendly substance and doesn't have a hazardous side effect on the environment.

In this study, proposed electrolyte additive (SHMP) is studied from two different aspects; namely inhibitor and expander effect. An inhibitor additive increases the overvoltage of Hydrogen

* Corresponding author.

E-mail address: shadi.hosseini@hotmail.com (S. Hosseini).

Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) so it can reduce the water loss of a battery during overcharging states, while an expander delays progressive agglomeration of lead sulfate on the negative plate [14], subsequently it can increase cycle-life of the battery and prolongs its lifetime. OER is the process of generating oxygen through electrolyzing of water and HER is the process of producing hydrogen by the same process.

Cyclic Voltammetry (CV) [15,16] is used for investigation the expander action of a proposed additive and Linear Sweep Voltammetry (LSV) is used for investigation the inhibitory action of an additive.

Sulfating of the surface of the negative electrode is one reason that causes early failure of a battery due to limiting its cycle-life. For reducing passivation of the electrodes surface, reducing the size of PbSO₄ during discharge process is necessary. In the present work, we investigated the effect of SHMP on PbSO₄ particle size and morphology of the sulfating layer, and then we studied its impact on the performance of the lead acid battery.

2. Methods and materials

Reagent grade of Sulfuric acid and SHMP were purchased (Merck Company, Germany). We used distilled water for the preparation of sulfuric acid solutions as an electrolyte.

2.1. Electrochemical technique analyzes

CV and LSV analyses were carried out by using Auto Lab. (Metrohm, Germany). The working electrode was a lead alloy that was prepared by casting machine and the alloy of the electrode was the exact alloy of the lead-acid battery grid (2.0% Sb, 0.2% Sn) (Azar Battery Company, Iran). Every side of the electrode except certain area (0.07 cm²) of the electrode surface was covered by resin epoxy to prevent any undesirable electrical connection between electrode and electrolyte.

In all experiments 5.0 M Sulfuric acid was used as an electrolyte which is the same concentration of H₂SO₄ solution in the real lead-acid battery electrolyte. The concentration of SHMP was varied from 0.5 to 2.5 mg ml⁻¹. CV and LSV voltammograms were obtained with a potential sweep from -1.5 V to +2.5 V at a scan rate of 50 mV S⁻¹ for lead alloy vs. Saturated Calomel Electrode (SCE) as a reference electrode. Before every scan of CV and LSV, electrode surface was polished by soft emery paper then it was washed with acetone and distilled water to remove any possible oxides away from the electrode surface.

After CV and LSV analyses, the surface of electrodes was coated by a thin film of gold to prevent oxidation on their surface and then Scan of Electron Microscopy (MIRA3 FEG-SEM, Tescan) characterized electrode surface.

2.2. Real battery test

Real battery tests were performed by charge/discharge instrument (Mersan, Turkey). 2 V lead-acid batteries were prepared with grid alloy (2.0% Sb, 0.2% Sn) in size of 20 × 20 cm (height and width) with a thickness of 2.7 and 2.3 mm for positive and negative electrodes respectively (casted in Azar Battery Company). Grids were pasted with the typical, positive and negative paste of lead-acid battery, containing PAM (Positive Active Material) and NAM (Negative Active Material), respectively. Absorptive Glass Membrane (AGM) with a thickness of 1.65 mm with 93% porosity (Sinoma international) was used as a separator between positive and negative plates to eliminate any possible physical connection between electrodes. Finally, charged plates immersed in 5 M sulfuric acid.

2.2.1. Water consumption

Two 2 V batteries with and without SHMP were prepared for water consumption test. The initial weight of each battery was recorded as W₁. Batteries were placed in 40 °C water bath and then charged with constant 2.45 V for 240 h (10 days) to imitate overcharging state. Batteries weight was recorded every 24 h as W₂. (W₁-W₂) equals to the weight of the lost water.

2.2.2. Capacity

The capacity of 2 V lead-acid batteries was investigated in a water bath maintained at 25 °C during the test. Batteries were discharged at a current of C₁₀ (1.6 A) until the terminal voltage decreased to 1.7 V, and the discharge time was recorded as t (h). The capacity was calculated by the following equation:

$$C(Ah) = t \times C10$$

The capacity of three battery groups was investigated to ensure the repeatability of the results. Also, after first and second HRPSoC cycle profile, the capacity of batteries was investigated.

2.2.3. Cycle-life

For the cycle-life test, two 2 V lead-acid battery with and without SHMP were assembled as explained previously. Also, this test was repeated three times on three different battery groups to investigate the repeatability of the results.

In order to imitate micro-hybrid driving mode, a simplified High Rate Partial State of Charge (HRPSoC) regime was designed [17–19]. Before starting the life cycling test, the tow batteries with and without SHMP were discharged by I = 1C A to 50% state of charge (SOC) (where C is the capacity after 1 h discharge that determined by Peukert equation), then the following steps were performed:

1. Charge 2C 90 s (with upper voltage limit 2.54 V)
2. Rest 10 s
3. Discharge 2C 60 s
4. Rest 10 s

The batteries were placed in 25 °C water bath during the test and voltage between positive and negative terminals of the battery was monitored during the test. The cycling was stopped when the voltage between two terminals decreased to 1.70 V as End of Discharge (EOD) state.

At the end of the cycling test, the batteries fully recharged, and their C₁₀ capacity was evaluated, then the batteries performed the same HRPSoC cycling test (second cycle).

The samples of negative plate surface after cycling were covered by a thin film of gold and then were investigated by Scan of Electron Microscope (MIRA3 FEG-SEM, Tescan). furthermore, XRD analysis was carried out on powdered NAM with a Siemens D5000 diffractometer under the following conditions: Cu Ka radiation (λ = 1.54 Å), tube voltage of 40 kV, a tube current of 30 mA and the samples were scanned in the range of 2θ = 10–80° at scanning speed of 2/min.

3. Results and discussion

Investigation of the electrochemical reactions of lead alloy electrode in sulfuric acid is complicated because electrode surface composition is changing continually while voltage changes during the potential sweep. On the other hand, electrochemical behavior of the lead electrode in H₂SO₄ solution strongly depends on H₂SO₄ concentration, potential sweep rate and existing impurities like additives. Researchers proposed CV and LSV as simple and reliable electrochemical techniques for studying ups and downs of the lead

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