Investigation the Effects of Boehmite and Gibbsite on the Electrochemical Behaviours of Gel-VRLA Batteries

Metin GENÇTEN

Yildiz Technical University, Faculty of Chemical and Metallurgical Engineering, Department of Metallurgy and Materials Engineering, TR34210 Istanbul, Turkey.
E-mail: mgencten27@gmail.com

In this work, gibbsite and boehmite were used as additives of gel valve regulated lead acid battery for the first time in the literature. Optimum amounts of additives were determined as 0.6wt% for each species by using of cyclic voltammetric and electrochemical impedance spectroscopic methods. While anodic peak currents and capacities increased by using of additives, charge transfer resistances decreased. Polarization curves were obtained to determine the effects of additives on the corrosion behaviors of fumed silica based gelled electrolytes. Gel systems consisting of additives showed lower corrosion tendency than those of non-gelled electrolyte and fumed silica based gelled electrolyte. The surface changes of lead electrodes were also analyzed at the end of the 100 voltammetric cycle by scanning electron microscopy. The pictures also supported anti-corrosion (anti-sulfation) effects of additives. These novel additives can be used for manufacturing of fumed silica based gelled electrolyte of valve regulated lead acid batteries.

Keywords: Gel electrolyte, lead acid battery, gibbsite, cyclic voltammetry, electrochemical impedance spectroscopy

1. INTRODUCTION

The valve-regulated lead–acid (VRLA) battery is the one of the most important energy storage device and used in many application areas such as telecommunication, automotive, renewable energy systems, and etc. [1–4]. Since the VRLA batteries have many important advantages such as low cost, high energy efficiency, high safety, high reliability and long cyclic life, they have taken great attention by many researcher [3,5–9].

VRLA batteries mainly consists of electrodes, separators and electrodes [10]. While the electrodes are lead based materials, separators are usually polymeric materials [11,12]. Electrolyte part (sulfuric acid) is crucial for the VRLA battery system and it can be immobilized by two different

methods. One of these methods is the using of adsorbed glass mat (AGM) [13,14]. The electrolyte is adsorbed in this type of the VRLA battery. In other system known as GEL electrolyte a gel agent is used to the immobilize the ions of electrolyte [2,3,5]. Although some gel agents such as polysiloxane, colloidal silica, etc. are used for the formation of three-dimensional gel structure, fumed silica is usually used as gel agent due to its great advantages such as good thixotropy, good three-dimensional web structures, low internal resistance with high capacity and relatively low cost [2,15,16]. Although fumed silica has created a three-dimensional gel structure for mobile ions of the electrolyte, some additives can be used for increasing the structure of the gel and improving the performance of the electrolyte. Sodium sulfate, magnesium sulfate, titanium(IV)oxide, polyols, polyaspartate, propanetriol, and etc. type substance were used to improve the performance of the gel part of the battery [8,9,17–19]. However, some inorganic additives are still needing to obtain a development on electrochemical performance of the fumed silica based gelled electrolyte.

In this work, gibbsite and boehmite were used as additives for the fumed silica based gelled electrolyte to improve the electrochemical behaviors of the gelled system. The optimum amounts of additives were determined by using of electrochemical methods such as cyclic voltammetry and electrochemical impedance spectroscopy. Corrosion behaviors of the non-gelled, gelled and additives including gelled electrolytes were determined by Tafel curves. The morphological changes on the electrodes surface during the cyclic voltammetric analysis were investigated by scanning electron microscopic analysis.

2. MATERIALS AND METHODS

2.1. Preparation of Electrolytes

Non-gelled electrolyte was 30wt% sulfuric acid (Sigma-Aldrich ≥95-98%) solution. Fumed silica (Sigma-Aldrich, 7 nm) based gelled electrolytes were prepared by mixing of 30wt% sulfuric acid solution and 6wt% fumed silica with 500 rpm at 30 min. [2,3,20]. Different amount (as 0.2, 0.4, 0.6 and 0.8 wt%) of additives (gibbsite, Sigma-Aldrich ≥99%; boehmite, Nabaltec ≥99%) were added in the fumed silica based gelled system to preparation of additive including gelled electrolytes. Each gelled system was stored for one hour at room temperature to complete the formation of gelled electrolytes.

2.2. Electrochemical Experiments

A classical three electrode system was used in electrochemical analysis. Metallic lead (0.5 cm^2 geometrical surface area) was used as working and counter electrodes in cyclic voltammetric, electrochemical impedance spectroscopic and corrosion experiments. Cyclic voltammetric analysis were done from -0.9 to -0.1 V versus Ag/AgCl (in 3 M KCl) with 50 mV.s^{-1}. Electrochemical impedance spectroscopy analysis were carried out over a $10^5 – 10^{-2}$ Hz frequency range at 10 mV of amplitude voltage and open circuit potential. EIS data were fitted to an equivalent circuit model given

in Fig.1. Polarization curves were obtained between 0-(-0.6) V with 2 mV.s^{-1} scan rate. Each electrochemical analysis was done with Reference 3000 series Gamry instrumentation at room temperature.
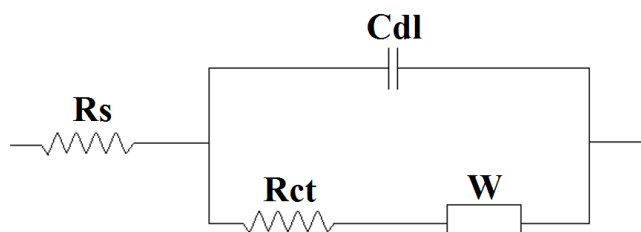
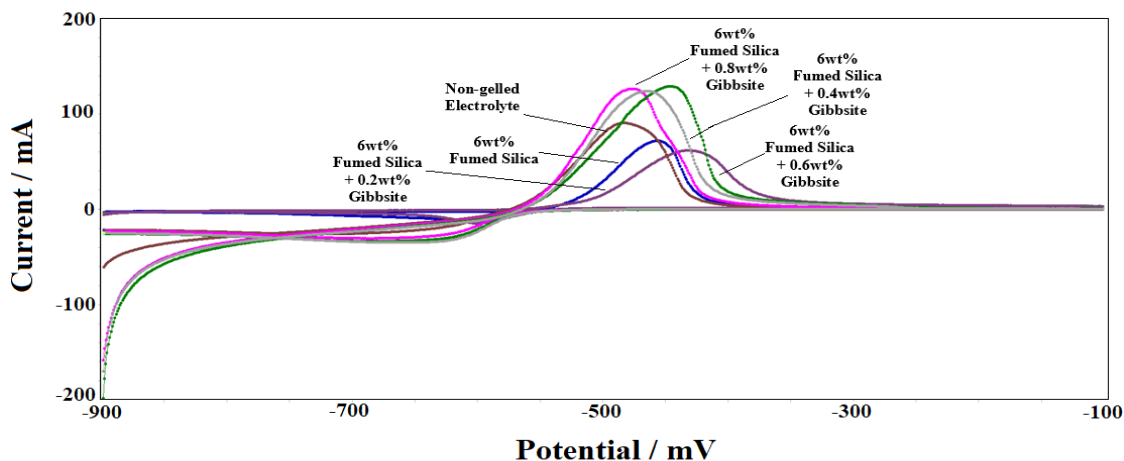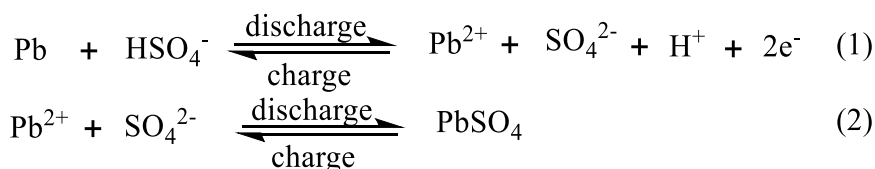**Figure 1.** Used equivalent circuit model in fitting of EIS data

2.3. Morphological Analysis

Morphological changes on the surface used lead electrodes were determined by using of Zeiss EVO® LS 10 instrument. The magnification of each electrodes was 20000×. Scanning electron microscopy (SEM) analysis were carried out without Au coating.

3. RESULT AND DISCUSSION

3.1. Optimization the amounts of gibbsite and boehmite

Cyclic voltammetry and electrochemical impedance spectroscopy are useful methods to determine the effects of additive on the electrochemical behaviors of gelled systems and optimization the amount of additives [2]. Fig. 2 shows the cyclic voltammograms of non-gelled, fumed silica based gelled and gibbsite including gelled electrolytes. Obtained anodic (at around of -500 mV) and cathodic (at around of -650 mV) peaks represent the formation of lead sulfate from the metallic lead and the formation of metallic lead from lead sulfate, respectively (Eq. 1 and Eq. 2) [2,3,15,21]. These reactions were also known as corrosion (sulfation) reactions of lead acid batteries and occurred on the lead electrode during the cyclic charge/discharge [7,22,23]. Used additives had any different reaction in studied potential range (Fig. 2). Since only discharge reaction was investigated in this work, anodic peak currents and peak redox capacities were determined [2]. When the amount of additive was 0.6wt% in fumed silica based gelled system, the highest anodic peak current and capacity were determined (Fig. 3) [2,3,9,20]. Since the hydrolyzed particles of gibbsite combined well with the hydrolyzed fumed silica particles in the gelled system at this amount of additive, the highest peak current and capacity were determined. The interactions of electrodes and mobile ions (H^+, SO_4^{2-}) of electrolyte had highest level according to obtained anodic and cathodic peaks values (Fig. 3) [2,3,9,20]. The result showed that using of gibbsite can increase the capacity and performance of the battery.

$$Pb \ + \ HSO_4^- \ \xrightleftharpoons[charge]{discharge} \ Pb^{2+} \ + \ SO_4^{2-} \ + \ H^+ \ + \ 2e^- \quad (1)$$

$$Pb^{2+} \ + \ SO_4^{2-} \ \xrightleftharpoons[charge]{discharge} \ PbSO_4 \qquad\qquad\qquad (2)$$
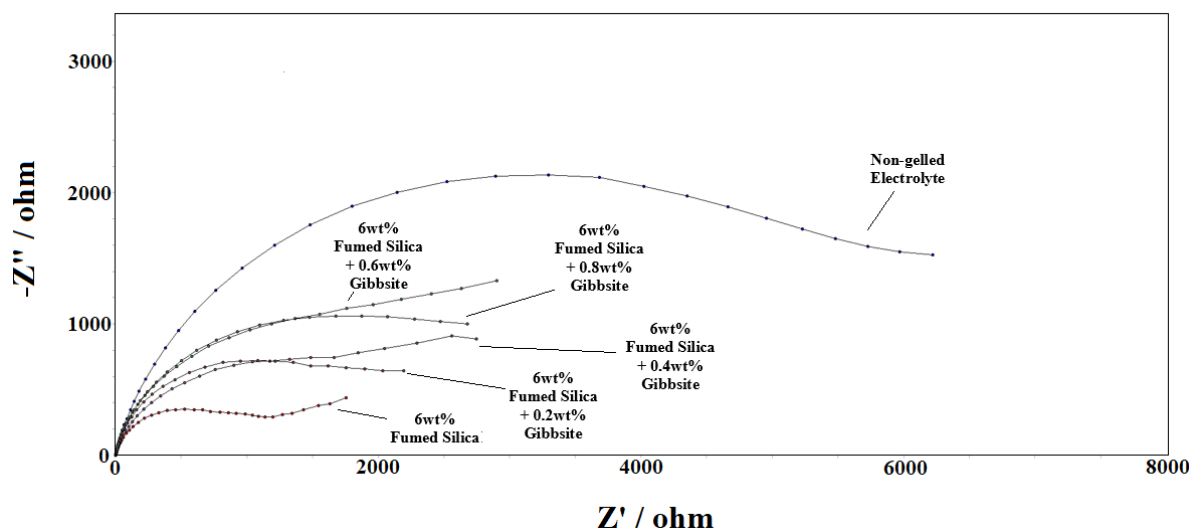

Figure 2. Cyclic voltammograms of non-gelled, fumed silica based gelled and gibbsite including gelled electrolytes (obtained from -0.9 to -0.1 V versus Ag/AgCl in (3 M KCl) with 50 mV.s^{-1} scan rate at room temperature)
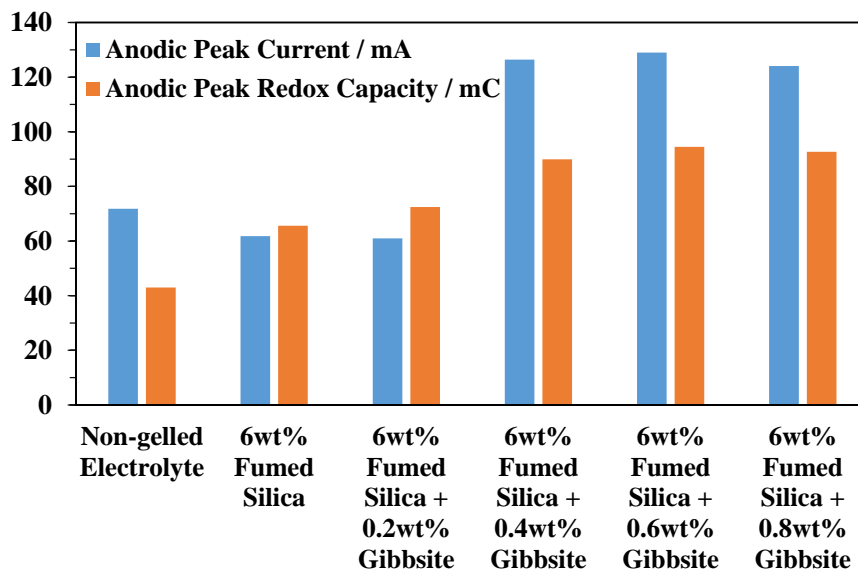
Figure 3. Anodic peak currents and capacities of non-gelled, fumed silica based gelled and gibbsite including gelled electrolytes

Electrochemical impedance spectra of non-gelled and fumed silica based gelled systems were given in Fig. 4. Here, solution resistance (Rs) is also known as ohmic resistance which is mainly related with the conductivity of the solution [24–31]. Charge transfer resistance (Rct) is related with the resistance of rate-controlling reaction in the corrosion process [24–28]. The diffusion of mobile

ions to the porous electrode surface was related with Warburg impedance (W) value [24–28]. Since the mobility of the H^+ and SO_4^+ ions were higher than those of gelled systems, the lowest solution resistance was determined in non-gelled system (Table 1). However, there were no big differences at solution resistances between non-gelled and gelled electrolyte systems due to high acid concentration (30wt% sulfuric acid) (Table 1). Charge transfer resistance was the lowest in the fumed silica based gelled system (Table 1). The value increased when the amount of additive increased. However, a certain decrease was determined in the gelled system consisting of fumed silica and 0.6wt% gibbsite (Table 1). This also supported a good combination of gibbsite and fumed silica to form a gel structure in sulfuric acid solution. Since the interactions of ions (H^+ and SO_4^+) and electrode surface had the highest level, the redox reaction occurred easier in this amount of additive [2,3]. Warburg impedance value was the highest in the gel system consisting of 0.6wt% boehmite including gelled electrolyte (Table 1). This showed that the diffusion of mobile ions to the electrode surface was the highest at this amount of additive [2,3]. According to the CV and EIS analysis, optimum amount of gibbsite as additive was determined as 0.6wt% for fumed silica based gelled system.
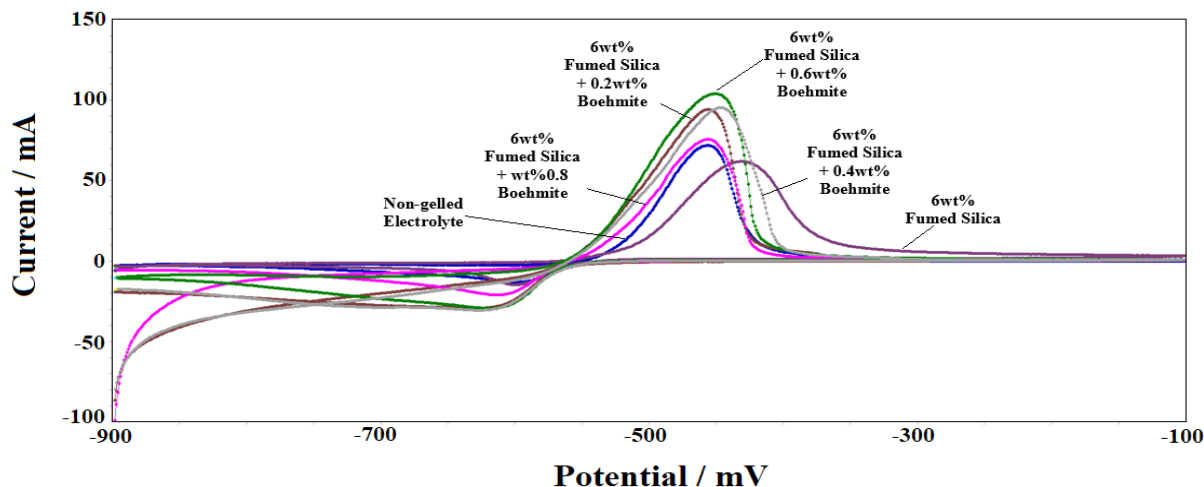

Figure 4. EIS spectra of non-gelled, fumed silica based gelled and gibbsite including gelled electrolytes (obtained over a $10^5 - 10^{-2}$ Hz frequency range at 10 mV of amplitude voltage and open circuit potential)

Table 1. Rs, Rct and W values of non-gelled, fumed silica based gelled and gibbsite including gelled electrolytes

Electrolyte	Fitted impedance values		
	Rs (ohm)	Rct (ohm)	W
Non-gelled electrolyte	0.287	4718	0.00057
6wt% fumed silica	0.575	924.8	0.00166
6wt% fumed silica + 0.2wt% Gibbsite	0.823	1757	0.00250
6wt% fumed silica + 0.4wt% Gibbsite	0.323	2167	0.00100
6wt% fumed silica + 0.6wt% Gibbsite	0.475	1720	0.00273
6wt% fumed silica + 0.8wt% Gibbsite	0.495	2500	0.00210

Cyclic voltammograms of non-gelled and boehmite including fumed silica based gelled electrolytes can be seen in Fig. 5. When the amount of boehmite was 0.6wt%, the determined anodic peak current and capacity were higher than those of non-gelled electrolyte, fumed silica based gelled electrolyte and the gelled electrolyte consisting of different amount of boehmite (Fig. 6).
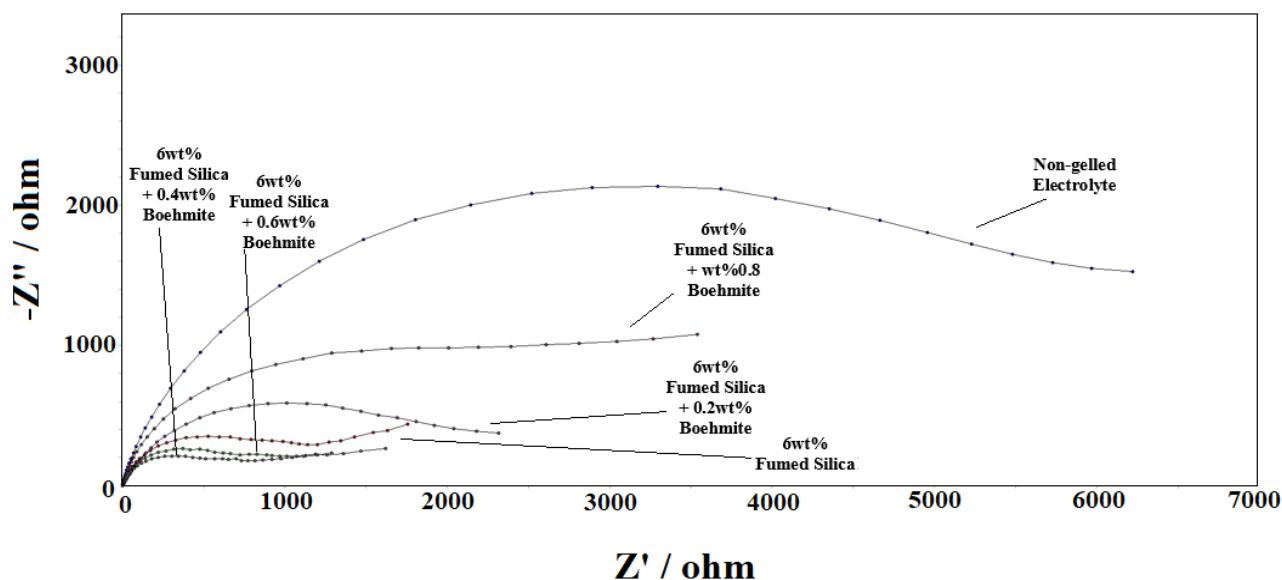

Figure 5. Cyclic voltammograms of non-gelled, fumed silica based gelled and boehmite including gelled electrolytes (obtained from -0.9 to -0.1 V versus Ag/AgCl in (3 M KCl) with 50 mV.s^{-1} scan rate at room temperature)
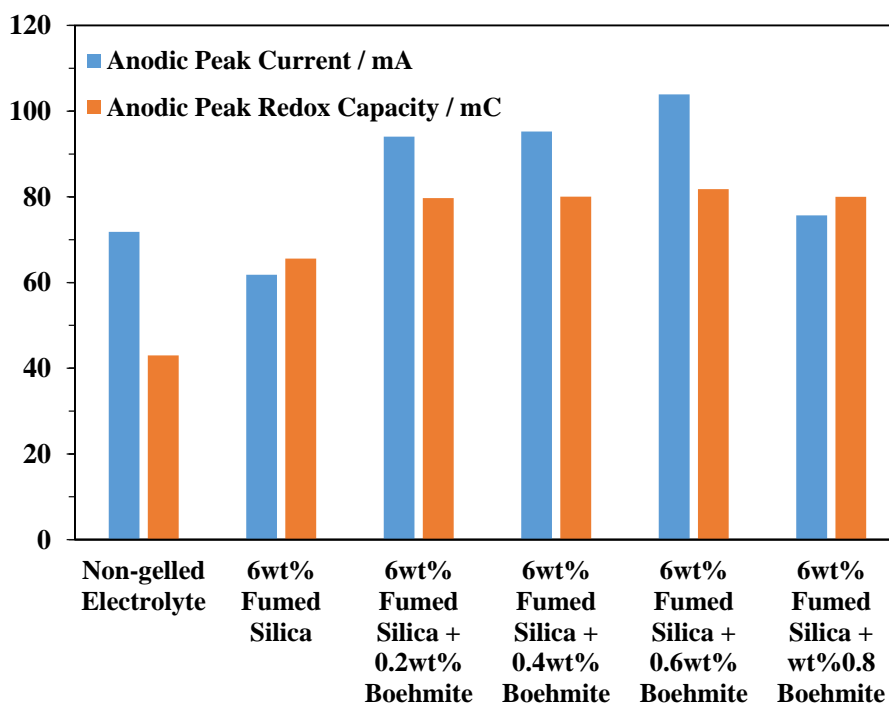
Figure 6. Anodic peak currents and capacities of non-gelled, fumed silica based gelled and boehmite including gelled electrolytes

Since the hydrolyzed particles of boehmite combined well with hydrolyzed silica particles, anodic peak current and capacity increased in the gelled system consisting optimum amount (0.6wt%) of additive. When the amount of additive was higher/lower than optimum amount of boehmite, the three-dimensional web structure of fumed silica based gel probably couldn't be obtained. Hence, investigated parameters in cyclic voltammetric analysis decreased [2,8]. Boehmite can be used an effective additive for improving capacity and performance of GEL-VRLA battery according to the cyclic voltammetric analysis (Fig. 6).

Fig. 7 shows the EIS spectra of electrolyte systems. The lowest solution resistance was determined in non-gelled electrolyte, as expected, due to free mobilities of ions (Table 2) [2]. Since the amount of solid particles increased in the gelled system and the mobility of mobile ions was prevented, solution resistance value increased (Table 2). Charge transfer resistance was the lowest in the gelled system consisting of fumed silica and 0.6wt% of boehmite. Since the hydrolyzed particles of additive and fumed silica in the sulfuric acid solution combined well to form a three-dimensional gel structure, the interactions of electrolyte ions and electrode had the highest level and charge transfer resistance decreased in the gelled system consisting of optimum amount of boehmite (Table 2) [2,3]. The Warburg impedance value was the highest in gel system consisting of 0.6wt% of boehmite as additive (Table 2). This result also supported cyclic voltammetric analysis and charge transfer resistance value. The highest diffusion of mobile ions to the porous electrode surface was determined in the gel electrolyte system consisting of optimum amount of boehmite as 0.6wt% (Table 2) [2,3,20].


Figure 7. EIS spectra of non-gelled, fumed silica based gelled and boehmite including gelled electrolytes (obtained over a $10^5 - 10^{-2}$ Hz frequency range at 10 mV of amplitude voltage and open circuit potential)

Table 2. Rs, Rct and W values of non-gelled, fumed silica based gelled and gibbsite including gelled electrolytes

Electrolyte	Fitted impedance values		
	Rs (ohm)	**Rct (ohm)**	**W**
Non-gelled electrolyte	0.287	4718	0.00057
6wt% fumed silica	0.575	924.8	0.00166
6wt% fumed silica + 0.2wt% Boehmite	0.605	1948	0.00656
6wt% fumed silica + 0.4wt% Boehmite	0.423	693	0.00173
6wt% fumed silica + 0.6wt% Boehmite	0.682	563	0.00285
6wt% fumed silica + 0.8wt% Boehmite	0.338	2206	0.00263

3.2. Corrosion behaviors of lead electrodes in non-gelled and fumed silica based gelled electrolytes

Corrosion behavior of lead electrodes in lead acid battery is an important parameter which radically effects the performance of the battery [32,33]. Fig. 8 shows the polarization curves of lead electrodes in different type electrolytes. Here, obtained peaks between -0.4 V and -0.2 V were related with the corrosion reactions of lead with sulfuric acid to form lead sulfate (Eq. 1 and Eq. 2) [34,35]. Corrosion potential (E_{corr1}) shifted more negative potential in the additives including gelled systems (Fig. 8). This also showed lower corrosion tendency in the additive including gelled electrolytes. Formed gelled structure with hydrolyzed fumed silica particles and hydrolyzed particles of additives probably caused a controllable interaction with electrodes and ions of electrolyte [34,35]. Corrosion rates in non-gelled and fumed silica based gelled system were also higher than those of gelled systems consisting fumed silica and additives according to the corrosion currents (Table 3). Corrosion tests supported to use of boehmite and gibbsite as additives in gelled electrolytes.
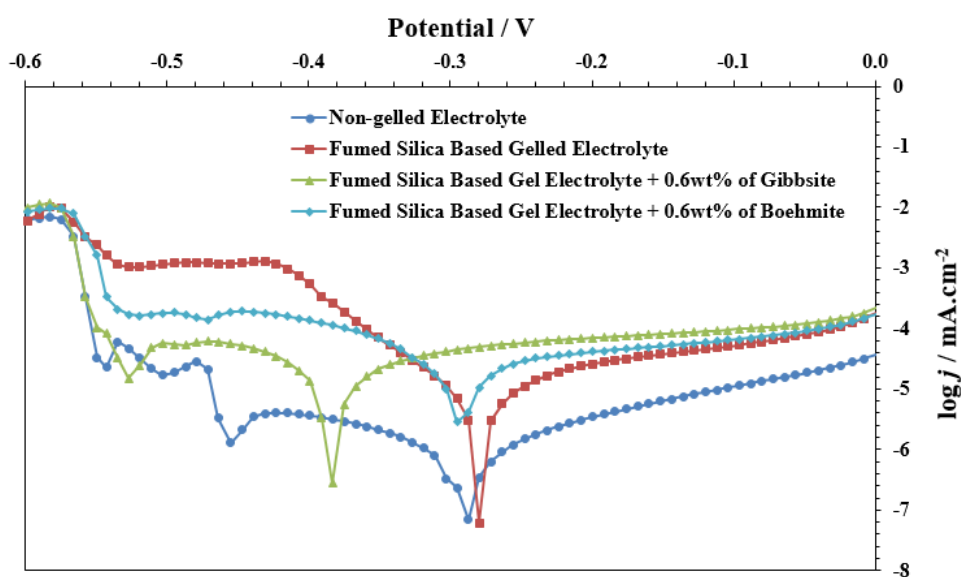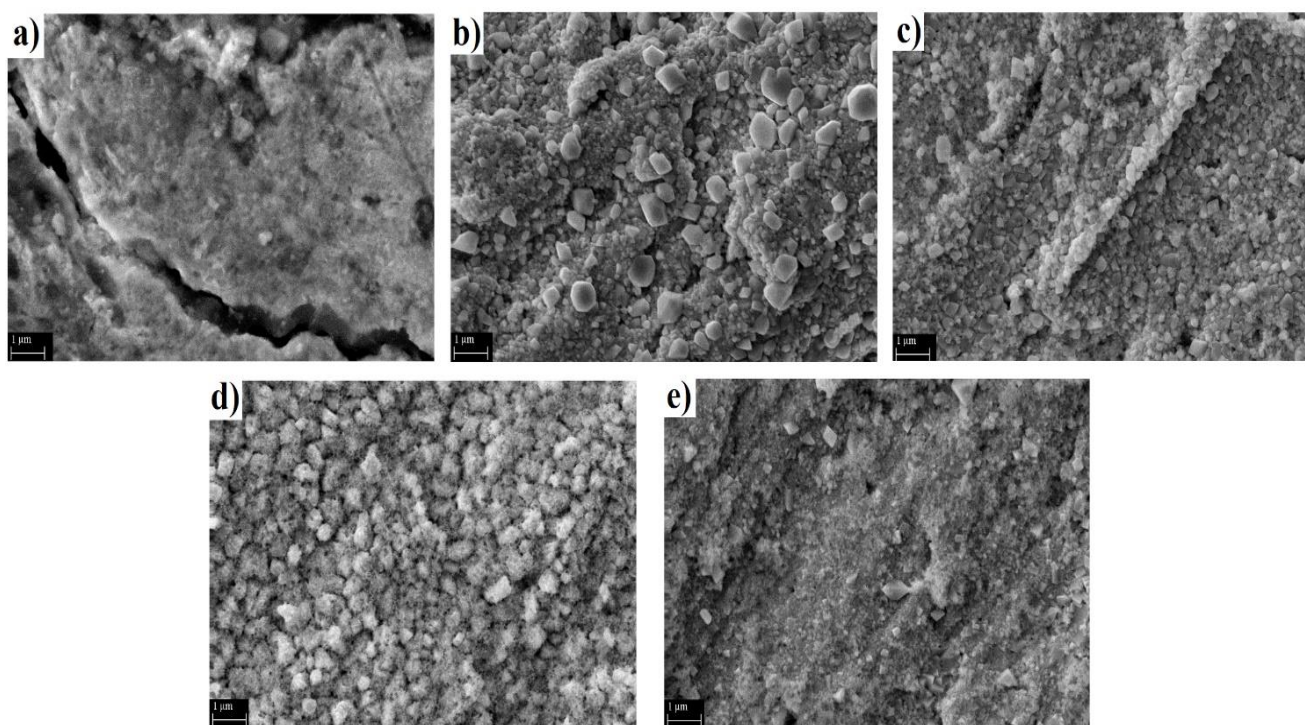

Figure 8. Polarization curves of lead electrodes in non-gelled electrolyte, fumed silica based gelled electrolyte, fumed silica based gelled electrolyte consisting of 0.6wt% of gibbsite, and fumed silica based gelled electrolyte consisting of 0.6wt% of boehmite (obtained between 0 and -0.6 V versus Ag/AgCl (in 3 M KCl) with 2 mV.s^{-1} scan rate)

Table 3. Polarization parameters of lead electrodes in different types of electrolyte

Electrolyte	Parameters		
	E_{corr} (V)	I_{corr} (µA)	Corrosion Rate (mpy)
Non-gelled electrolyte	-0.289	1.89	3.28
6wt% fumed silica	-0.279	9.86	4.51
6wt% fumed silica + 0.6wt% Gibbsite	-0.383	50.30	23.00
6wt% fumed silica + 0.6wt% Boehmite	-0.295	50.60	23.11

SEM pictures of pure lead and lead electrodes which were used in different electrolyte systems for 100 voltammetric cycles. Since the lead sulfate crystals formed on the surface of lead electrodes during voltammetric analysis, a non-porous surface of pure lead changed (Fig. 9a) [20]. The electrodes which were used in non-gelled electrolyte and fumed silica based gelled electrolyte (Figs. 9b and 9c) had more lead sulfate crystals than others (Figs. 9d and 9e). Indeed, the nanosized crystals formed in additive including gelled electrolytes indicating less sulfation for a GEL-VRLA battery [20]. This result also supported to use of additives for gel component of GEL-VRLA batteries.

Figure 9. SEM pictures of a) lead electrodes, and lead electrodes after 100 voltammetric cycles in b) non-gelled electrolyte, c) fumed silica based gelled electrolyte, d) fumed silica based gelled electrolyte consisting of 0.6wt% of gibbsite, e) fumed silica based gelled electrolyte consisting of 0.6wt% of boehmite

4. CONCLUSION

In this study, inorganic based two different additives (gibbsite and boehmite) were used as additives for gel part of VRLA battery. Amount optimizations of additives were done by electrochemical methods. Optimum amounts for gibbsite and boehmite were determined as 0.6wt% for fumed silica based gelled electrolyte (prepared by mixing of 6wt% of fumed silica and 30wt% of sulfuric acid). Anodic peak currents and capacities of gel systems increased by adding optimum amount of additives indicating enhanced battery performance for battery. Corrosion potentials were also lower in the additives including gelled electrolytes. This result also supported the low corrosion (sulfation) effects of additives for gel VRLA battery. When SEM pictures were analyzed after 100 voltammetric cycle in non-gelled and different gelled systems, the size of formed lead sulfate crystals decreased in the gelled systems consisting fumed silica and optimum amounts of additives. This also showed lower corrosion effects of formed novel gel formulations of battery. These additives can be used to produce the gel part of VRLA batteries according to electrochemical and microscopic analysis.

References

1. G.J. May, A. Davidson, B. Monahov, *J. Energy Storage,* 15 (2018) 145.
2. M. Gençten, K.B. Dönmez, Y. Şahin, K. Pekmez, E. Suvacı, *J. Solid State Electrochem.,* 18 (2014) 2469.
3. K.B. Dönmez, M. Gençten, Y. Şahin, *Ionics*, 23 (2017) 2077.
4. D. Pavlov, Fundamentals of Lead–Acid Batteries, in: Lead-Acid Batter. Sci. Technol., (2017) 33.
5. T. Tantichanakul, O. Chailapakul, N. Tantavichet, *J. Power Sources*, 196 (2011) 8764.
6. D. Pavlov, V. Naidenov, S. Ruevski, *J. Power Sources*, 161 (2006) 658.
7. D. Pavlov, G. Papazov, B. Monahov, *J. Power Sources*, 113 (2003) 255.
8. M. Gencten, K.B. Dönmez, Y. Şahin, *Anadolu Univ. J. of Sci. and Technology A– Appl. Sci. and Eng.*, 18 (2017) 146.
9. M. Gencten, K.B. Dönmez, Y. Şahin, *Anadolu Univ. J. of Sci. and Technology A– Appl. Sci. and Eng.*, 17 (2016) 882.
10. D.A.J. Rand, J. Garche, P.T. Moseley, C.D. Parker, Valve-Regulated Lead-Acid Batteries, 2004.
11. K. Ihmels, W. Böhnstedt, Separator Materials for Valve-regulated Lead-Acid Batteries, in: Valve-Regulated Lead-Acid Batter., (2004) 183.
12. D.A.J. Rand, P.T. Moseley, Energy Storage with Lead–Acid Batteries, in: Electrochem. Energy Storage Renew. Sources Grid Balanc., (2015) 201.
13. D.W.H. Lambert, P.H.J. Greenwood, M.C. Reed, *J. Power Sources*, 107 (2002) 173.
14. R.D. Prengaman, Improvements to active material for VRLA batteries, *J. Power Sources*, 144 (2005) 426.
15. H. Li, H. Liu, Q. Wang, H. Chen, A. Ren, J. Hu, *Electrochim. Acta*, 56 (2010) 663.
16. M.Q. Chen, H.Y. Chen, D. Shu, A.J. Li, D.E. Finlow*, J. Power Sources*, 181 (2008) 161.
17. M. Chen, W. Guo, M. Zhang, F. Cheng, P. Liu, Z. Cai, Y. Zhang, *Electrochim. Acta*, 164 (2015) 243.
18. P. Tundorn, O. Chailapakul, N. Tantavichet, *J. Solid State Electrochem.*, 20 (2016) 801.
19. C.F. Sun, F.L. Cheng, M.Q. Chen, M. Zhang, Z.Q. Cai, *Mech. Aerosp. Eng. Pts*., 110–116 (2012)

514.

20. K.B. Dönmez, M. Gençten, Ş. Yücel, Ionics, (2018) doi: 10.1007/s11581-018-2551-1
21. E. Hämeenoja, T. Laitinen, G. Sundholm, A. Yli-Pentti, *Electrochim. Acta,* 34 (1989) 233.
22. K.R. Bullock, *J. Power Sources*, 195 (2010) 4513.
23. X. Muneret, V. Gobé, C. Lemoine, *J. Power Sources*, 144 (2005) 322.
24. M. Gençten, H. Gürsu, Y. Şahin, *Int. J. Hydrogen Energy*, 41 (2015) 9868.
25. M. Gencten, H. Gursu, Y. Sahin, *Int. J. Hydrogen Energy*, 42 (2017) 25608.
26. M. Gencten, H. Gursu, Y. Sahin, *Int. J. Hydrogen Energy*, 42 (2017) 25598.
27. K. Pan, G. Shi, A. Li, H. Li, R. Zhao, F. Wang, W. Zhang, Q. Chen, H. Chen, Z. Xiong, D. Finlow, *J. Power Sources*, 209 (2012) 262.
28. M.P. Vinod, K. Vijayamohanan, *J. Power Sources*, 89 (2000) 88.
29. H. Gürsu, M. Gençten, Y. Şahin, *Ionics*, (2018) doi:10.1007/s11581-018-2547-x.
30. H. Gürsu, M. Gençten, Y. Şahin, *Int. J. Energy Res.*, (2018) doi:10.1002/er.4117.
31. H. Gursu, M. Gençten, Novel chlorine doped graphene electrodes for positive electrodes of a vanadium redox flow battery, *Int. J. Energy Res.*, 42 (2018) 3303.
32. R.D. Prengaman, *J. Power Sources*, 95 (2001) 224.
33. P. Ruetschi, *J. Power Sources*, 124 (2004) 33.
34. S. Salih, A. Gad-Allah, A. Abd El-Wahab, H. Abd El-Rahman, *Turkish J. Chem.*, 38 (2014) 260.
35. S. Khatbi, Y. Gouale, S. Mansour, A. Lamiri, Electrochemical and Metallurgical Behavior of Lead-Aluminum Casting Alloys as Grids for Lead-Acid Batteries, *Portugaliae Electrochim. Acta*, 36 (2018) 133.