

INVESTIGATION OF THE TEMPERATURE EFFECT ON ELECTROCHEMICAL BEHAVIORS OF TiO₂ FOR GEL TYPE VALVE REGULATED LEAD-ACID BATTERIES

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ABSTRACT

In this study, the effect of temperature on the electrochemical behaviors of gel electrolyte systems was investigated for valve regulated lead-acid battery at $0 \leq T \leq 50$ °C. Fumed silica and mixture of fumed silica and TiO₂ were used as gel electrolytes. TiO₂ has a good combination with fumed silica. They were characterized by cyclic voltammetry, electrochemical impedance spectroscopy and battery tests. The anodic peak currents and redox capacities of the gel electrolytes increased with increasing of temperature. The highest anodic peak current and redox capacity were observed at 30 °C in fumed silica and at 40 °C in fumed silica: TiO₂ based gel systems. The solution and charge transfer resistance values decreased in fumed silica:TiO₂ gel system by increasing temperature. In battery tests, discharge curves were obtained for each gel system at 0, 25 and 50 °C. The discharge time of mixture gel electrolyte system was higher than that of fumed silica based gel electrolyte at low (0 °C) and high (50 °C) temperatures. The best performance was obtained in fumed silica based gel electrolyte at 25 °C.

Keywords: Lead-acid battery, Temperature, Titanium(IV)oxide, Electrochemical impedance spectroscopy, Cyclic voltammetry

1. INTRODUCTION

Valve regulated lead-acid (VRLA) battery is one of the most important energy storage devices in the world since they were introduced in early 1970s. Since they have advantages like high energy efficiency, lower cost and long cyclic life, VRLA batteries have large application areas in many industrial sectors such as; automotive industry, renewable energy systems, portable vehicles, etc. [1-5]. VRLA battery systems consist of three main components; electrodes, membrane and electrolyte. Each component affects significantly the capacity and cyclic life of the system [6].

Regarding the electrolyte part, two main electrolyte technologies have been developed by researchers such as gel electrolyte and adsorbed glass mat (AGM) systems. Sulfuric acid is adsorbed into a kind of glass mat in AGM electrolyte system and this system is called as AGM-VRLA battery [7]. The gelled electrolyte system is obtained by the mixing of gel agent (fumed silica) and optimum concentration of sulfuric acid, called as GEL-VRLA battery. The performance of gel electrolyte system is better than the AGM electrolyte system especially at low and high temperature application. Operating temperature affects AGM and flooded type lead acid batteries more than gel type lead acid batteries. Corrosion rate of positive grids in the GEL-VRLA is also lower than both AGM-VRLA and flooded batteries. Besides, stratification of electrolyte lowers in gelled electrolyte systems under deep-discharge cyclic application than AGM systems [8-13]. Most of studies focused on the improving the capacity and cyclic life of the gelled system, due to its advantages. Some additives have also added into the gel electrolyte such as sodium sulfate, magnesium sulfate, aluminum oxide, boron oxide, titanium oxide, etc. to obtain a better gel structure and increase the capacity for long cyclic life [7, 13, 14]. The performance of fumed silica based gelled system was improved by most of these additives at

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room temperature. However, there is limited number of studied about the effects of these additives on electrochemical behaviors of fumed silica based gelled systems at a temperature range of 0-(+50) °C. Operation temperature is an important parameter for lead acid batteries since temperature of battery is affected by ambient temperature. As the most of batteries are produced for using at room temperature, capacities of batteries are influenced by high (> 40 °C) and low (< 0 °C) temperature. Lead acid batteries show poor performance at high temperature due to high corrosion rate of positive active material, water loss and formation of large quantity of oxygen [8, 10, 15]. In addition, closed oxygen cyclic is decreased by increasing temperature [16-18]. On the other hand, discharge time and cycle life of lead acid batteries reduce at low operating temperature by reason of rising internal resistance of the battery [19]. GEL-VRLA batteries could be more useful especially extreme climate conditions. For this purpose, composition of gel is very important in lead acid battery. Additives could bring a new perspective into fumed silica based gelled system for application at a relatively large temperature range, i.e., 0-(+50) °C. In our previous study, effects of some additives on performance of gel electrolyte were investigated at room temperature [13, 14]. However, some of these additives could show good performance at $0 \leq T \leq 50$ °C.

In this study, the effects of temperature on the electrochemical behaviors of gel electrolyte systems, consisting of fumed silica and the mixture of fumed silica and titanium(IV)oxide, was investigated. The experiments were performed at varying temperatures in the range of 0-50 °C. The gelled systems were characterized by electroanalytical methods such as cyclic voltammetry, electrochemical impedance spectroscopy and battery test. The values of anodic peak current and peak redox capacity were investigated by cyclic voltammetry. In electrochemical impedance spectroscopy, solution resistance (R_s) and charge transfer resistance (R_{ct}) parameters were studied. Discharge curves were obtained by battery test for each gel system at 0, 25 and 50 °C.

2. EXPERIMENTAL

2.1. Preparation of Electrolyte and Electrodes

The gelled electrolytes were prepared by the mixing of fumed silica (Sigma-Aldrich, 7 nm)-TiO₂ (AppliChem, 99%) and sulfuric acid (J. T. Baker % 95-97). The optimum concentration of fumed silica and sulfuric acid were determined in our previous studies as 6 wt% and 30 wt%, respectively [13]. 3 wt% (0.06 g/mL) of TiO₂ is added to gelled system consisting of fumed silica and sulfuric acid. The different amount of TiO₂ was studied our previous studies and the value of 3 wt% of TiO₂ was chosen to perform temperature experiments [13, 14]. The mechanic dispersion parameters are also important to obtain a good gel structure [13, 14, 20]. The best gel structure was obtained in 30 min. agitation time and 500 rpm stirring rate, at 25 °C [13]. The lead electrodes were prepared by cutting from metallic lead (Alfa-Aesar, > 99%) as geometrical area 0.5 and 0.6 cm² for working and counter electrode, respectively. The electrode were polished in each electrochemical experiments.

2.2. Electrochemical Experiments and Thermal Stabilizing

The electrochemical impedimetric spectroscopic (EIS) and cyclic voltammetric (CV) measurements were performed with a system, consisting of three electrodes. The working and counter electrodes were polished before the electrochemical experiment and then the working electrode was polarized at -1.4 V versus Hg/Hg₂SO₄, K₂SO₄ (saturated) (MSE) to remove impurities.

CHI Potentiostat/Galvanostat Model 660 D (CH Instruments, USA) was used as equipment for cyclic voltammetric and electrochemical impedimetric measurements. The cyclic voltammetric studies were done at a 20 mV.s⁻¹ scan rate, between -1.4 and -0.8 V versus RE for all the gel electrolytes, using lead working electrode, lead counter electrode and Hg/Hg₂SO₄, K₂SO₄ (saturated) as reference electrode. Anodic peak currents and peak redox capacities were investigated by cyclic voltammetry.

Redox capacities were determined via integration of the peaks recorded in the cyclic voltammetric analysis.

EIS experiments were carried also with the electrochemical three electrode cell system at open circuit potential over a $10^5 - 10^{-2}$ Hz frequency range at amplitude of 10 mV and the Figure 1 represents an equivalent circuit model for fitting process each impedance spectrum [13, 14]. Here, R_s , R_{ct} , C_{dl} and W show the solution resistance, charge transfer resistance, double layer capacitance and Warburg impedance, respectively. R_s is related the ohmic resistance consisting of the resistance of the electrolyte, the resistance of the corrosion products placed on the electrode surface, and the resistance of the electrical connections to the electrode. R_{ct} is also representing the charge transfer resistance of the rate-controlling electrochemical reaction of corrosion process [21-23]. All of the samples were studied at temperatures, between 0 °C and 50 °C with 10 °C intervals.

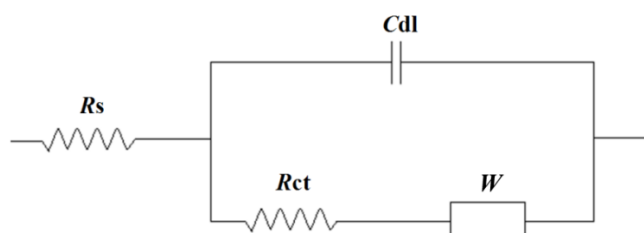


Figure 1. Equivalent circuit model

Thermal stabilizing of gel systems during the electrochemical analysis were done by refrigerated and heating circulator (Jeio Tech, RW-0525G).

2.3. Battery Test

To determine the effects of temperature on battery performance, discharge curves of gel systems were obtained for the first cycle at 0, 25 and 50 °C. Reference 3000 series Gamry instrumentation was used for each test. All battery system was obtained on one cell of a lead acid battery with two negative electrodes and one positive electrode with 7.5 cm² active area for each electrode and separated by micro-porous membrane. Discharge curves were obtained for one cell with the potential range 1.75 - 2.15 V at 0, 25 and 50 °C. Each electrodes were positioned with 0.5 cm spacing. The gel systems were charged and discharged at constant currents at 0.025 A and 0.01 A, respectively.

2.4. Scanning Electron Microscopy

The structural features of lead electrodes were examined with field emission scanning electron microscope using Carl Zeiss Ultra Plus FESEM. The surfaces of electrodes were investigated after one voltammetric cycle in fumed silica and fumed silica-TiO₂ based gel electrolyte system at 0, 20 and 50 °C with 5000× magnitude.

3. RESULTS AND DISCUSSION

3.1. Optimum Concentration of Fumed Silica, Sulfuric Acid and Titanium (IV) Oxide

The concentration of gel agent is a significant parameter to obtain a three dimensional web structure. In our previous study, the optimum concentration of fumed silica was determined as 6 wt%. In the case of lower amount of fumed silica than 6 wt%, the gel structure couldn't be obtained. The viscosity of the

system was like that of water. If the concentration of fumed silica was higher than 6 wt%, the peak currents and peak redox capacities decrease radically while the R_s and R_{ct} values were increasing [13]. In the process of preparing a good gel structure, electrolyte concentration is also other important parameters [13, 24]. In this study, all of gel system was prepared using 30 wt% sulfuric acid. If the concentration of sulfuric acid is lower or higher than 6 wt%, anodic peak current, peak redox capacities decrease through R_s and R_{ct} , increase dramatically [13].

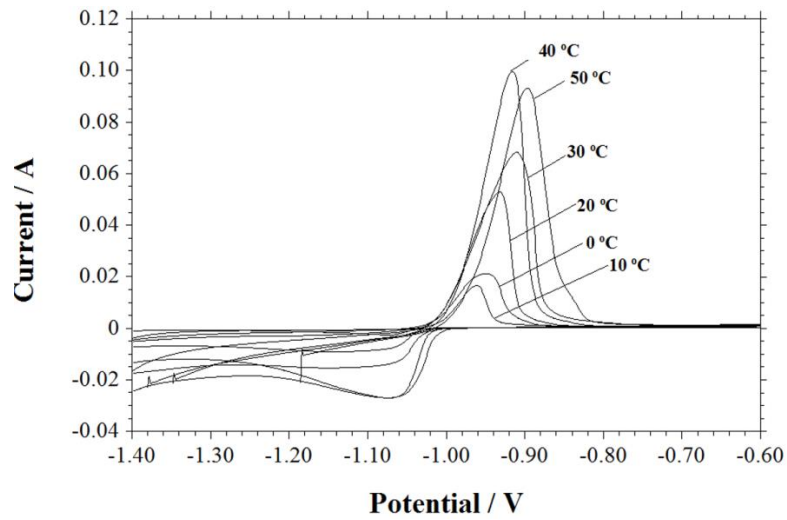
Some additives were added into the fumed silica based gelled system to improve the cyclic life and the discharge capacity of the gel VRLA battery. Titanium (IV) oxide made a good combination with fumed silica based system [14]. The gelled electrolytes consisting of fumed silica and different amount of titanium (IV) oxide had same electrochemical behaviors with fumed silica based gel system. When 3 wt% (0.06 g/mL) of TiO_2 was added into the 6 wt% fumed silica based gelled system, anodic peak current and peak redox capacity increased. This result can be explained by structure of titanium (IV) oxide. Titanium (IV) oxide has same physical properties with fumed silica. When the fumed silica dispersed into the sulfuric acid solution, it hydrolysis and isolated silanol groups combined with each other. These interactions led to obtain a three dimensional gel structure. Titanium (IV) oxide could be dispersed into the sulfuric acid solutions and hydrolyzed TiO_2 molecules combined with each other and other silanol groups. The interactions between the silanol groups and hydrolyzed TiO_2 groups obtained a three dimensional gel structure. In electrochemical impedimetric studies, R_s value was the lowest when 3 wt% (0.06 g/mL) of TiO_2 added into the gel system. These results were compatible with the anodic peak currents and peak redox capacities [14]. According to these experimental results, the effects of temperature investigated fumed silica and fumed silica- TiO_2 based gelled systems in this study.

3.2. Temperature Effect on Electrochemical Behaviors of Gelled Systems

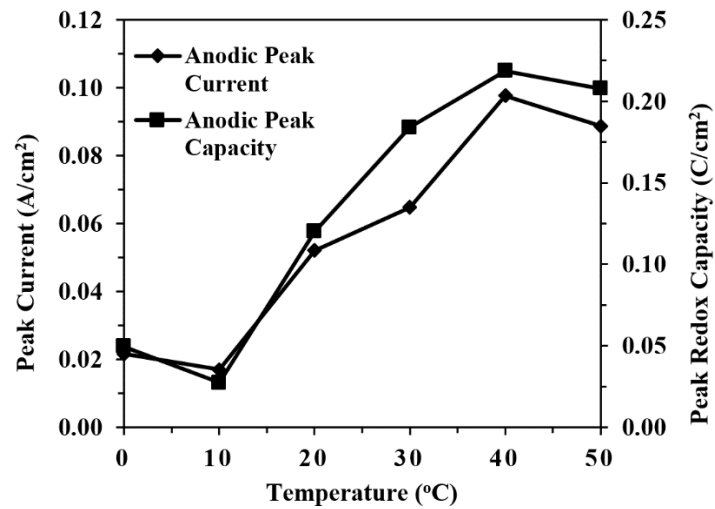
Electrochemical behaviors of gel systems, consisting of fumed silica and fumed silica: TiO_2 , were investigated by cyclic voltammetry and electrochemical impedance spectroscopy. Figure 5a shows cyclic voltammograms of fumed silica based gel system, performed at different temperatures (0, 10, 20, 30, 40 and 50 °C). Obtained peak between -1.0 – (- 0.9) V in given voltammograms represents the formation of lead sulfate from metallic lead (Figure 2a) [25-27]. When operation temperature was increased, the reaction between lead and sulfate occur faster [28]. By the increasing of operation temperature, anodic peak currents and peak redox capacities increased radically until 40 °C (Figure 2b). Since hydrogen evolution begins at lower potential, the performance of battery at high temperature (> 40 °C) may be affected negatively. By the time operation temperature was 50 °C, hydrogen evolution potential was the lowest and forms of anodic peak and cathodic peaks were changed.

Figure 2c shows the electrochemical impedance spectra of gel systems consisting of fumed silica and sulfuric acid. Solution resistance (R_s) and charge transfer resistance (R_{ct}) parameters were studied in these spectra at a range temperature scale (0-(+50) °C). It has been shown that, while operation temperature increases, R_s values don't show a radical change. This result can be explained by structure of the gel system. Gel electrolyte is obtained by three dimensional networks of silanol groups. Moving ions enter the free space of this network. When operating temperature increases, the mobility of the ions don't change significantly. However, charge transfer resistance decreases by increasing temperature (Figure 2d). While operation temperature rises, the reaction between lead and sulfate occur easier [28]. This reaction is also the reason for self-discharge at high temperature [29]. If this reaction is controlled well by three dimensional network of the gel, self-discharge rate of VRLA batteries could be reduced. For this reason, additives play an important role for application of VRLA batteries at extreme climate conditions.

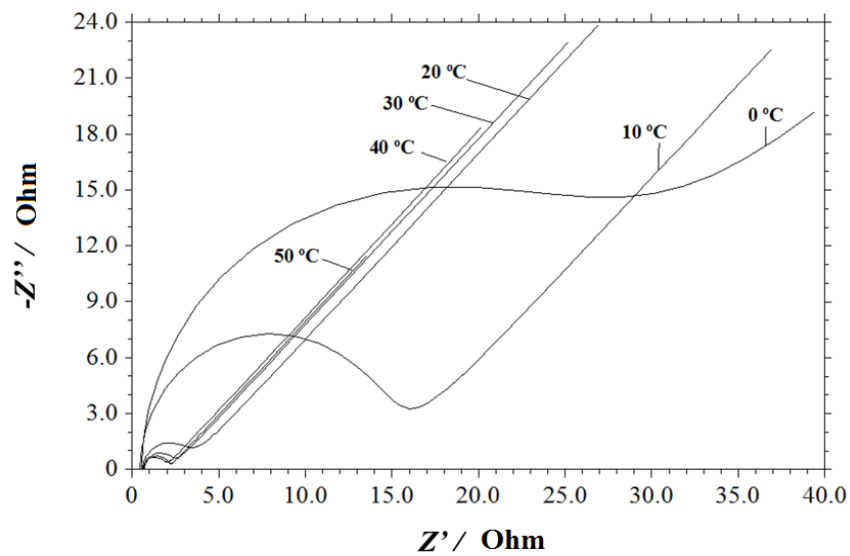
a)



b)



c)



d)

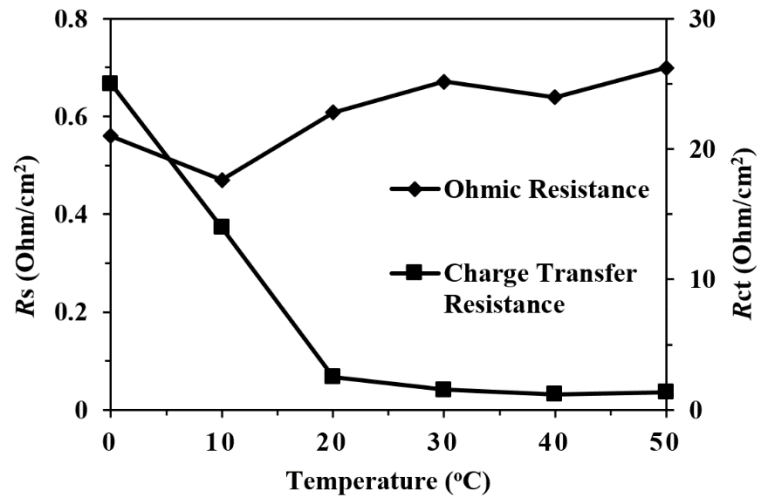


Figure 2 Cyclic voltammetric behaviors of gel electrolytes having consisting of fumed silica and sulfuric acid solutions **a)** cyclic voltammograms **b)** the anodic peak capacities and currents **c)** impedance spectra and **d)** R_s and R_{ct} values (at 0; 10; 20; 30; 40 and 50 °C)

Figure 3 shows the SEM pictures of lead electrode which was used as working electrode in cyclic voltammetric analysis for fumed silica based gel electrolyte system. The morphological evaluation of electrode can be seen easily as function of operating temperature. Since the sulfation reaction (Eq. 1) increased by increasing temperature, the amount of lead sulfate increased on the surface of electrode and the morphology of sulfate crystals were changed (Figure 3b and 3c).

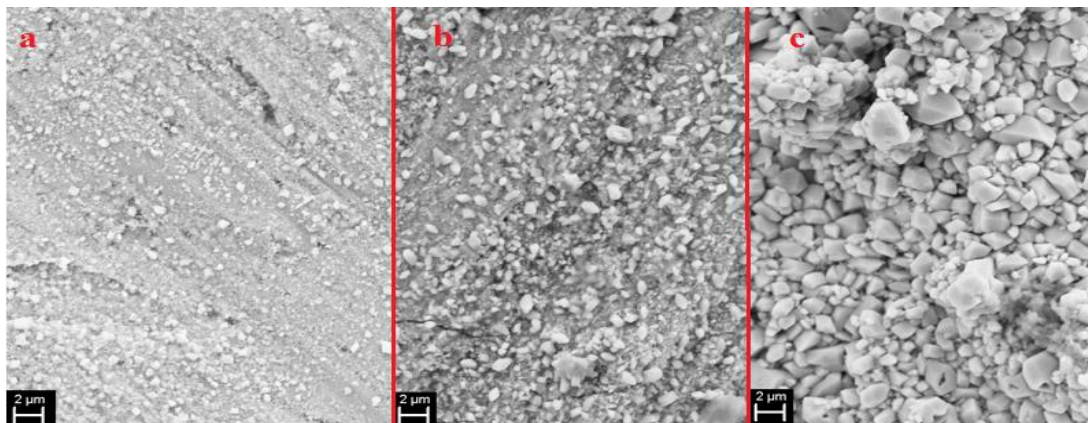


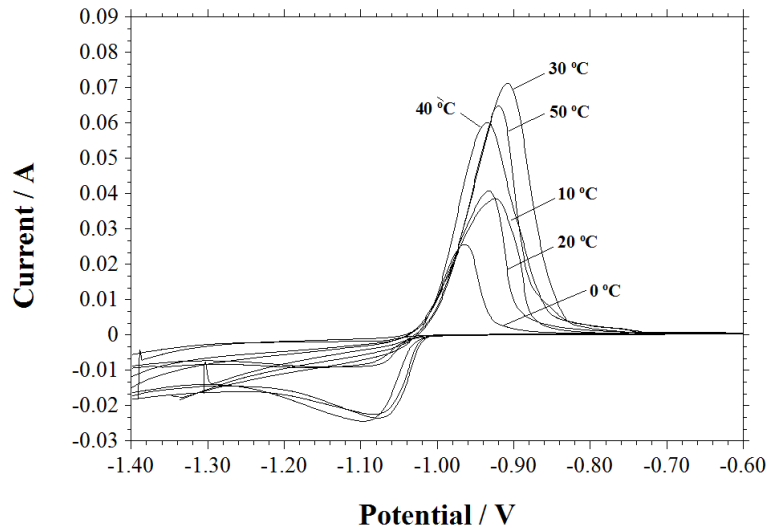
Figure 3. SEM pictures of used lead electrodes after one voltammetric cycle in fumed silica based gel electrolyte **a)** 0 °C **b)** 20 °C and **c)** 50 °C

Figure 4a shows cyclic voltammograms of gel electrolyte consisting of fumed silica:TiO₂ at range temperature scale (0-(+50) °C). Anodic peak currents and peak redox capacities increased, while operation temperature is increasing until 30 °C. Then, these values decrease at 40 and 50 °C (Figure 4b). Since anodic peak current and peak redox capacities are lower than 30 °C, self-discharge effects for VRLA batteries could be lower by the time TiO₂ is added fumed silica based gel as additive. Hydrolyzed TiO₂ was combined with silanols and three dimensional structure of gel was formed. Since amount of sulfate is changed in free spaces of network, the anodic peak currents and peak redox

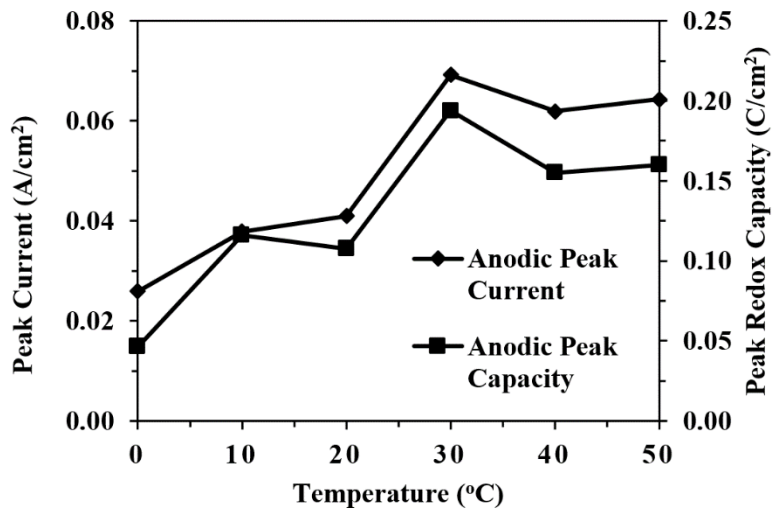
capacities are different in this system than fumed silica based gel system. The differences in electrochemical behaviors of gel systems consisting of fumed silica and fumed silica-TiO₂ could bring a useful application for VRLA battery at high and low temperature.

Electrochemical impedance spectra of gel systems consisting of fumed silica-TiO₂ obtained at different operation temperature are shown in Figure 4c. Charge transfer resistance (*R*_{ct}) and solution resistance (*R*_s) show same behavior and they decrease by increasing operation temperature (Figure 4d). This result can be explained by temperature effect on the reaction between lead and sulfate. *R*_s value decreased in fumed silica-TiO₂ based gel system by increasing temperature but it was almost same in fumed silica based gel system (Figure 2d). This is also related with structure of three-dimensional network of these gel systems. *R*_s values show that the mobility of ions is higher in fumed silica-TiO₂ gel system than that of fumed silica based gel system. Charge transfer resistance (*R*_{ct}) also decreased until 40 °C. After this operation temperature, it continued to decrease. The structure of gel changes with changing temperature. The reaction between lead and sulfate occurs slower at 40 °C, since the interacted surface of lead electrode and sulfate ions is lower at 40 °C than 30 °C.

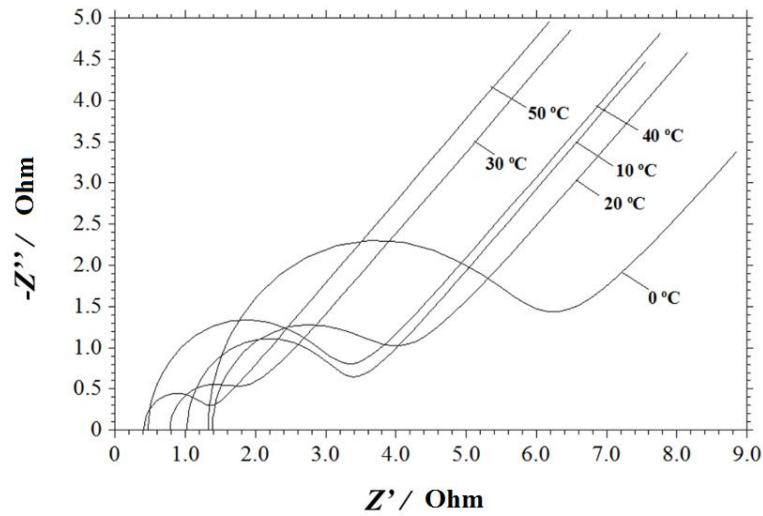
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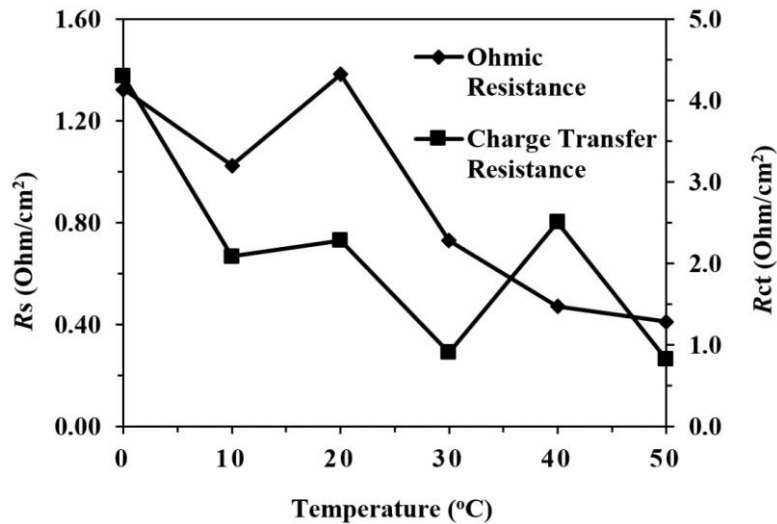


Figure 4 Cyclic voltammetric behaviors of gel electrolytes consisting of fumed silica, TiO₂ and sulfuric acid solutions **a)** cyclic voltammograms **b)** the anodic peak capacities and currents **c)** impedance spectra and **d)** R_s and R_{ct} values (at 0; 10; 20; 30; 40 and 50 °C)

The change of the lead electrode surface were shown in Figure 5. The sulfation of electrodes after one voltammetric cycle in fumed silica-TiO₂ based gel system increased with increasing operating temperature (Figure 5b and 5c). When the temperature increased, the reaction between lead and sulfate occurred easier and the amount of formed lead sulfate increased. While the formed amount of lead sulfate on the electrode surface in fumed silica based gel system was higher than that of fumed silica-TiO₂ based gel system at 20 °C (Figure 3b and 5b), it was lower at 0 °C and 50 °C. This result may be caused by the differences of obtained gel structure with fumed silica and fumed silica-TiO₂.

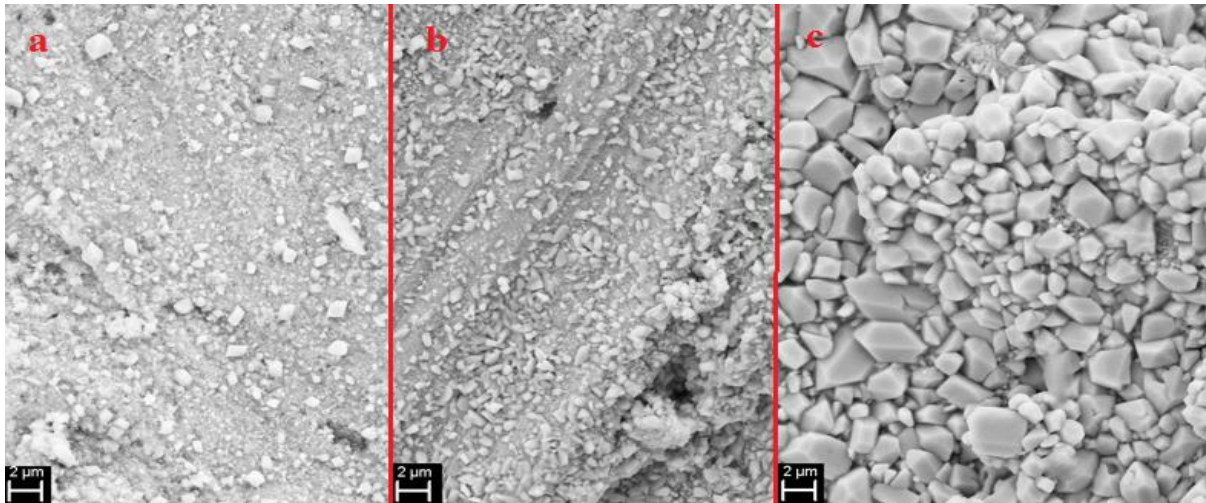


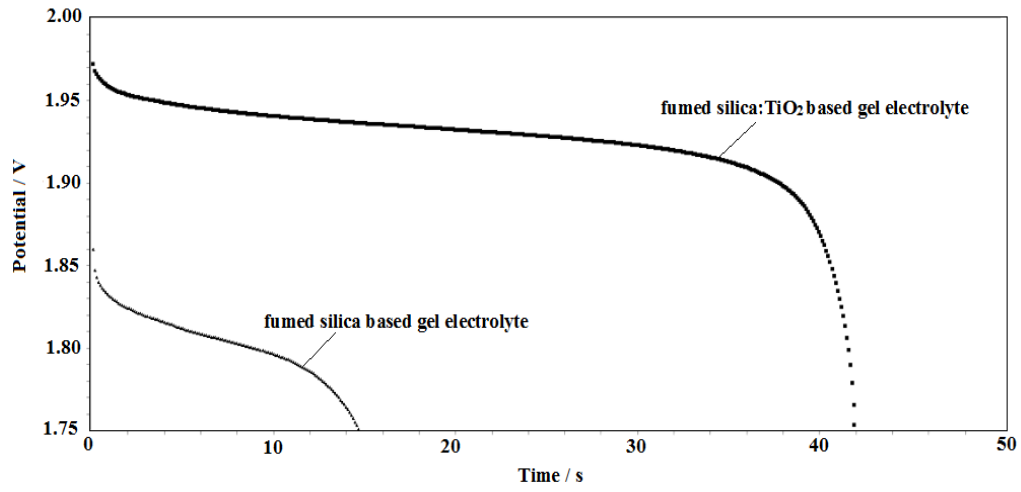
Figure 5 SEM pictures of used lead electrodes after one voltammetric cycle in fumed silica-TiO₂ based gel electrolyte **a)** 0 °C **b)** 20 °C and **c)** 50 °C

Operation temperature is a key parameter for application areas of GEL-VRLA batteries. TiO₂ added fumed silica based gel system has some significant electrochemical properties such as lower solution resistance and charge transfer resistance at high temperatures. Some novel additives could bring new perspective for application of GEL-VRLA batteries at extreme climate condition.

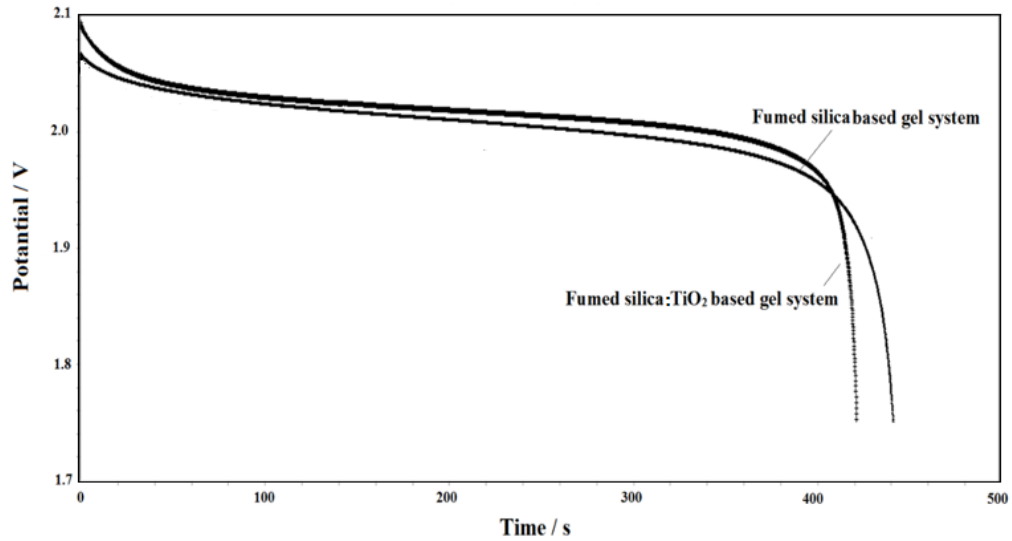
3.3. Battery Tests

Discharge curves of gel systems, consisting of fumed silica and fumed silica-TiO₂, are obtained by high rate charge consisting were performed at 0, 25 and 50 °C. TiO₂ added fumed silica based gel system shows significant capacity behaviors especially at high (50 °C) and low (0 °C) temperatures. Figure 6a and 6c show discharge curves of fumed silica and fumed silica-TiO₂ based gel electrolyte at 0 and 50 °C, respectively. Discharge time of fumed silica-TiO₂ based gel systems is higher than fumed silica based gel electrolyte at high and low temperature. The values were determined as 42 and 700 s at 0 and 50 °C, respectively. Besides, the discharging potential of fumed silica-TiO₂ based gel electrolyte system was higher than other gel system at each studied temperature. However, discharge time of fumed silica based gel electrolyte system (around 420 s) is higher than other gel system (around 410 s) at room temperature (Figure 6b). This result may also be attributed to the structure of three dimensional networks. When TiO₂ is added into fumed silica based gel system, mobility and amount of ions are changed in free spaces of three dimensional systems. Interactions between electrode surface and electrolyte ions are higher at low and high temperature than that in fumed silica-TiO₂ based electrolyte system. The structure of three dimensional networks of gel electrolyte is changed especially at high and low temperature. Since TiO₂ makes a good combination with fumed silica, the structure of gel is maintained well. At room temperature, the performance of fumed silica based gel system is better than the system having fumed silica-TiO₂. This result also shows better network system of fumed silica based gel than the gel consisting of fumed silica-TiO₂ at room temperature. However, the structure of gel system prepared with fumed silica was deformed and discharge time were determined as 15 and 290 s at 0 and 50 °C, respectively.

a)



b)



c)

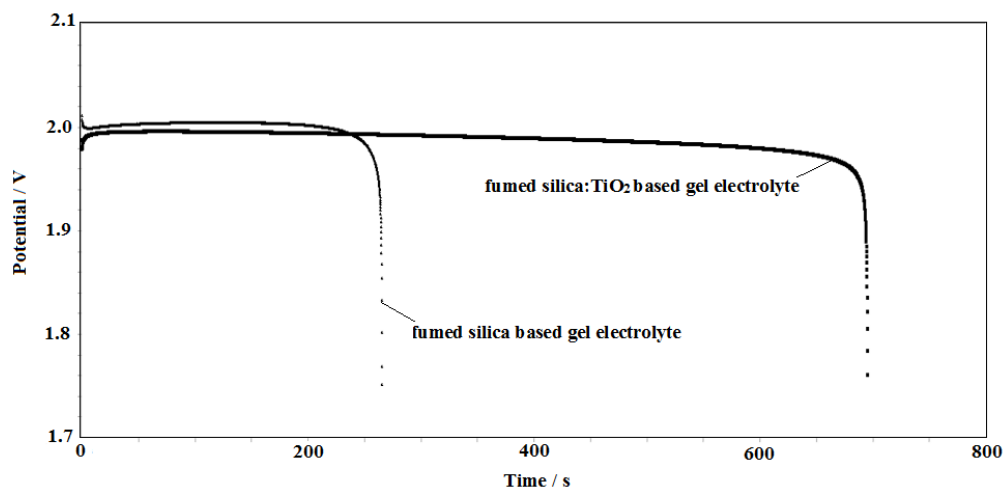


Figure 6. Discharge curves of gelled systems at a 0 °C, b 25 °C and c at 50 °C

4. CONCLUSION

Operation temperature is an important parameter for energy storage devices. Most of batteries are designed to use at room temperature. On the other hand, application of batteries at extremely climate conditions becomes an important study area. Since the application areas of VRLA batteries are large, operation temperature is also significant for these batteries. Electrolyte components affect the performance of VRLA batteries at high (> 40 °C) and low (< 0 °C) temperatures. In this study, fumed silica and fumed silica:TiO₂ added gel electrolytes were prepared and characterized by electrochemical methods such as cyclic voltammetry, electrochemical impedance spectroscopy and battery tests. Anodic peak currents and peak redox capacities increased for each gel system while operation temperature was rising. These values were the highest for fumed silica and fumed silica:TiO₂ based gel systems at 30 and 40 °C, respectively. In electrochemical impedance studies, solution resistance was decreasing in fumed silica-TiO₂ based gel while operation temperature was increasing. However it was almost stable in fumed silica based gel at a range temperature scale (0-(+50) °C). Charge transfer resistance of each system is decreased by the time temperature is high. Cyclic charge-discharge test were performed for each gel electrolyte system at 0, 25 and 50 °C. Here, fumed silica-TiO₂ based gel electrolyte system had a significant performance especially at low (0 °C) and high (50 °C) performance. However, the performance of fumed silica based gel electrolyte was better than the other electrolyte system at room temperature. These results can be attributed to the three dimensional structure of gel systems. TiO₂ has good combination with fumed silica and this combination provides the composition of gel at low and high temperature.

As a result, batteries which could be used at extreme climate conditions are needed for many applications. GEL-VRLA batteries can be modified for this demand by changing gel formulation. Novel additives are still necessary to improve the performance of GEL-VRLA batteries at high and low temperature regimes.

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