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DEVELOPMENT OF GELLED ELECTROLYTE FOR LEAD-ACID BATTERY USING POLYACRYLAMIDE AND SULFATE SALTS

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อิเล็กโทรไลต์แบบเจลที่ใช้ในแบตเตอรี่ชนิดตะกั่ว-กรดแบบวาล์วได้ถูกศึกษาในงานวิจัยนี้ อัตราส่วนที่เหมาะสมของสารในการเตรียมเจล ผงซิลิกาและ กรดซัลฟิวริก ถูกเลือกโดยอ้างอิงจากค่าการนำไฟฟ้า สารเติมแต่งพอลิแอคริลาไมด์ โซเดียมซัลเฟต แมกนีเซียมซัลเฟต และโพแทสเซียมซัลเฟต ถูกนำมาใช้เพื่อเพิ่มลักษณะเฉพาะของอิเล็กโทรไลต์ รวมถึงสมรรถนะของแบตเตอรี่ ผลจากการทดลองพบว่า ในอิเล็กโทรไลต์ที่เติมพอลิแอคริลาไมด์จะมีค่าการนำไฟฟ้าที่สูงขึ้น มีความแข็งของเจลมากขึ้น และมีเวลาในการเกิดเจลที่สั้นลง ในขณะที่สารเติมแต่งประเภทเกลือซัลเฟตและสารเติมแต่งผสมระหว่างพอลิแอคริลาไมด์และเกลือซัลเฟตนั้นให้ผลตรงข้ามทั้งในส่วนของค่าการนำไฟฟ้า และเวลาในการเกิดเจล อย่างไรก็ตาม แบตเตอรี่ที่เติมอิเล็กโทรไลต์แบบเจลที่ใช้โซเดียมซัลเฟตเป็นสารเติมแต่งนั้น แสดงเวลาในการจ่ายประจุไฟฟ้าของแบตเตอรี่ยาวนานที่สุด มีความจุไฟฟ้าสูงที่สุดและมีประสิทธิภาพดีที่สุด (98.01%)

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Gelled-electrolyte used in valve-regulated lead-acid (VRLA) battery has been studied. Optimum ratios of the gelling agents, fumed silica and sulfuric acid, were chosen based on the electrical conductance. Polyacrylamide (PAM), sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$) and potassium sulfate (K_2SO_4) were examined as a possibly additive to improve the electrolyte characteristic including the battery performance. Results from these studies showed that adding PAM into the electrolyte resulted in a higher conductance, better the gel strength and shorter the gelling time while all single sulfate salt additives and mixed additives; PAM and sulfate salt, gave opposite results on conductance and gelling time. However, on the performance of the VRLA battery, the battery filled with a gelled electrolyte that had Na_2SO_4 as an additive provided the longest battery discharging period, the highest improvement in the battery capacity and the greatest presenting battery efficiency (98.01%).

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Academic year ………………….2008………………..Advisor's Signature.N. Ngamrojanavan
Co-Advisor's Signature……

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LIST OF ABBREVIATIONS

A	Ampere
AGM	Absorbent glass mat
Ah	Ampere hour
AFM	Atomic Force Microscopy
C	Capacitant
I	Current
CSGE	Colloid silica gel electrolyte
e^-	Electron
SOL	Liquid gel
PAM	Polyacrylamide
PBGE	Polysiloxane-based gel electrolyte
rpm	Round per minutes
t	Time
V	Volt
VRLA	Valve-regulated lead-acid
XRD	X-ray diffraction

CHAPTER I

INTRODUCTION

The recent boom of economic has given rise to a need of powerful and reliable power supplier. Battery is a choice to consider as a power source for vehicles and solar energy storage [1]. The development of lead-acid battery is further step in continuing evolution. Began in 1859, a battery was developed to a rechargeable battery, by alternately charging and discharging lead plates which immersed into sulfuric acid solution [2]. The conventional lead-acid battery is called “flooded” type. Its main disadvantage is that the cell has to be vented to release gases liberated during charging: oxygen gas at the positive electrode and hydrogen gas at the negative electrode. At that time, the lead-acid batteries were operated in open jars and the plates could easily be exchanged. Much water lost constantly occurs through an evaporation [3].

Limitations of flooded lead-acid battery

1) Acid stratification

Stratification of the electrolyte is caused by that the sulfuric acid in electrolyte participates in the electrode reaction of the lead-acid battery [5]. It means that the concentration changes during charging and discharging processes along the vertical side of electrodes. In flooded lead-acid battery, acid stratification can cause severe problems.

Figure 1.1 illustrates the origin of acid stratification [6]. When the battery is discharged, the concentration of the acid reduced, since sulfate (SO_4^{2-}) ions are absorbed by both electrodes and natural convection is caused by the fact that the electrolyte between plates attains a lower weight than the electrolyte beside and above the plates. At the end of discharge, the concentration of the electrolyte is uniform again, except for that share of the electrolyte localized below the plates, which remains at the original concentration. Diffusion would equalize this concentration difference but diffusion occurs at a slow process.

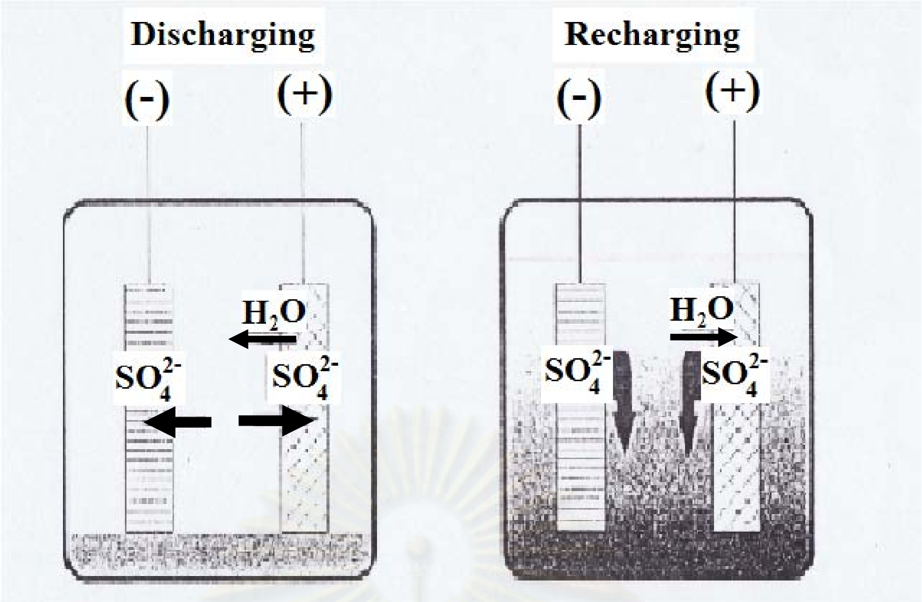

Figure 1.1 The origin of acid stratification, when the lead-acid battery is discharged and recharged. (Picture from Berndt, D. J. Power Sources 100 (2001): 29-46)

When the battery is recharged, sulfuric acid is released from the active material in the plates and the concentration of the acid increases between the plates. So the highest acid concentration is achieved between the plates. At the end of charging process, the battery is filled with slightly increased acid concentration to the upper edge of the plates. The acid above the plates remains diluted and there is no reason for convection, because of the low weight of this acid.

Acid stratification causes uneven current distribution and reduces the efficiency mainly of the charging but also of the discharging process. Furthermore, acid stratification may become dangerous, because the concentration differences between the top and bottom parts of the cell are growing from the cycle to cycle.

2) Overcharge reaction

Overcharge reaction limits the shelf life of flooded lead-acid battery [7]. As the cell approaches 85 to 90% state-of-charge, the recharge reactions become less efficient, and the positive electrode begins to evolve oxygen [8], equation 1.1:

$$\text{Positive electrode: } 2H_2O \rightleftharpoons 4e^- + O_2 + 4H^+ \qquad (1.1)$$

At the negative electrode, hydrogen ions react to form hydrogen gas:

$$\text{Negative electrode: } 4H^+ + 4e^- \rightleftharpoons H_2 \qquad (1.2)$$

The net reaction is water electrolysis:

$$2H_2O \rightleftharpoons O_2 + 2H_2 \tag{1.3}$$

Thus, hydrogen and oxygen are released from the cell and water loss is an effect from overcharge reaction. It means that water loss limits the life of the battery. So that flooded lead-acid battery required a water filling during usability.

In the 20th century, a new design of spill-proof lead-acid battery called valve-regulated lead acid (VRLA) battery was invented, to correct the problem in flooded lead acid battery. The cells were provided with cover to reduce a maintenance expenditure on refilling water into batteries. Only a little gas outlet through a small hole with a plug was provided. Immobilized electrolyte was also developed and proved to be suitable.

1.1 Valve-regulated lead acid battery

Valve-regulated lead acid (VRLA) batteries usually are characterized by a fast running "internal oxygen cycle" which means that almost all the gaseous oxygen (O_2), generated at the positive electrode, passed to the negative electrode and recombine with H^+ ion to form water, according to:

O_2 evolution at positive electrode: $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$ (1.4)

O_2 reduction at negative electrode: $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ (1.5)

The overcharge reaction at the positive electrode is thus compensated by its reversal at the negative electrode, and overcharging does not cause chemical changes in the cell.

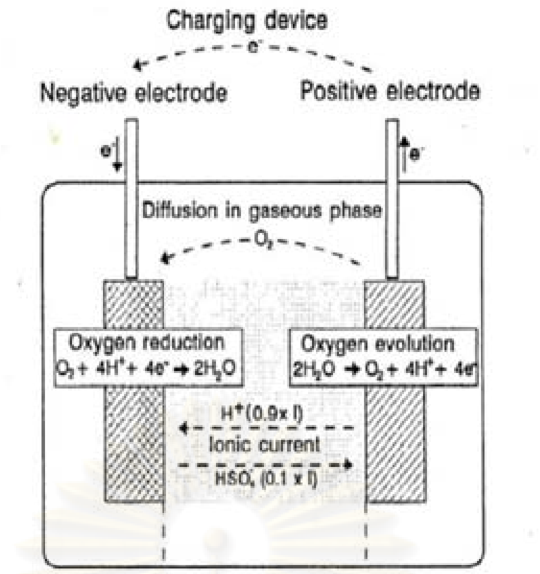

Figure 1.2 The principle of the overcharging reaction in VRLA battery (Picture from Berndt, D. Research Studies Press Ltd. (2003))

In Figure 1.2, the immobilized electrolyte is indicated as a bloc between the electrodes. Oxygen transport from the positive to the negative electrode was fast enough to carry the overcharging current. So that hydrogen evolution is reduced to a small value. Water loss correspondingly reduced, and there is no direct relation between water loss and overcharging.

In the VRLA batteries, immobilized electrolyte is required to provide open space for the fast transport of the oxygen gas between the electrodes, often called dry batteries. Otherwise, the internal oxygen cycle is hindered by the too slow diffusion rate of the dissolved oxygen. Nowadays, two types of the immobilized electrolyte have been used.

1. Absorbed-glass-mat (AGM): sulfuric acid solution electrolyte is immobilized in fiberglass or polymeric fiber separators.
2. Gelled electrolyte: electrolyte is immobilized by addition of a gelling agent as silica (SiO_2) in sulfuric acid solution.

The AGM battery is an extremely reliable energy-storage device, however, it can suffer from the acid stratification. In general, gelled electrolyte battery has less electrolyte-stratification under deep-discharge [3] and highly improved cycle-life [1].

1.2 Gelled electrolyte

Gelling is one method to immobilize the electrolyte. Attempts were made to gelatinize the sulfuric-acid electrolyte in lead-acid batteries using inorganic and organic thickeners prevent the acid from leaking out of defective cell containers. Nowadays, highly dispersed mixture of sulfuric acid with specially prepared silicon dioxide (or fumed silica, SiO_2) is used. It stables over a long term, even to the powerful oxidizing effects of the positive electrode and is environmentally safe and technically easy to handle [9]. Adding fumed silica in sulfuric acid yields a thixotropic gel that can be kept highly liquid by intensive agitation, which is taken advantage of when filling the battery. Convection of the electrolyte is almost repressed in gelled electrolyte and ion movement is restricted to migration and diffusion. Moreover, the stratification effects are not observed with gelled electrolyte.

Fumed silica is the main substance to immobilize sulfuric acid in gelled electrolyte. Fumed silica is made from evaporating silicon chloride in an oxygen-hydrogen flame at temperature above 1500^{o}C to form SiO_2 molecule, as shown in Figure 1.3. Around 10,000 SiO_2 molecules strongly bond in siloxane group (Si-O-Si), bind together to spherical primary particles of 10 nm size. As the particles move to colder areas, they bind together to chain-like aggregates with a length of approximately 1 μm. By further cooling down, they form agglomerates with a diameter of 10 to 250 μm. Figure 1.4 shows the binding force between the primary particles that is the hydrogen bridge linkage. The silanol groups (Si – O – H) of two particles come in contact and create the bridge linkage by exchange of their hydrogen molecules.

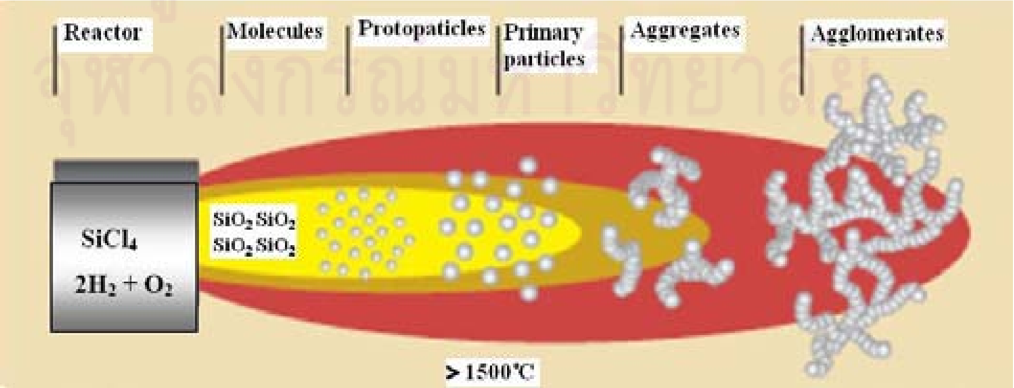

Figure 1.3 Manufacturing process of fumed silica (Picture from Rush, W.; Vassallo, K.; and Hart, H. BATTON 2006: 12(1) -12(8))

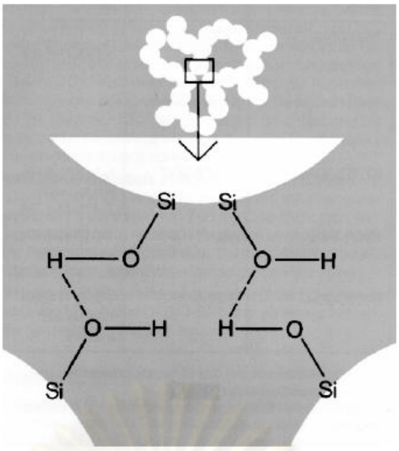

Figure 1.4 Hydrogen bridge linkage between particles (Picture from Rush, W.; Vassallo, K.; and Hart, H. BATTON 2006: 12(1) -12(8))

These agglomerated aggregates of SiO_2 particles are mixed with acid and water, forming a liquid GEL (SOL) as seen in the left part of Figure 1.5. After keeping it for several hours, on sitting, the hydrogen bridge linkages form a three-dimensional structure. This is the GEL, seen in the right hand side of Figure 1.5. Water and sulfuric acid are trapped in the structure [10].

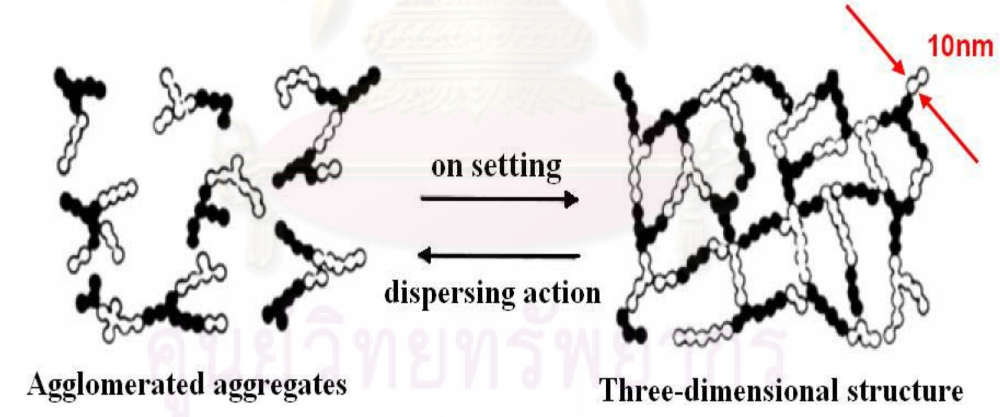

Figure 1.5 The GEL structure is at the beginning reversible, by dispersing SOL and by setting GEL. (Picture from Rush, W.; Vassallo, K.; and Hart, H. BATTON 2006: 12(1) -12(8))

1.3 Literature review: Development of gelled electrolyte

The gelled electrolyte is the key factor affecting the performance of gel batteries which the gel has been obtained by introducing particles of silica into sulfuric acid solution. To form a good electrolyte, the optimum ratios of reagents should be considered.

Hernandez *et al.* [11] prepared gelled electrolyte with different silica types. Colloidal silica was compared the electrolyte formulation with fumed silica. It was found that gelled electrolyte based on fumed silica maintain the structure throughout battery operation whereas colloidal silica gel lose gel strength along cycling although it needed less time to form gel. Moreover, results showed that the gelling time was shorter when an increase of the silica or sulfuric acid concentration and reducing the initial acid temperature was possible to reduce the gelling rate. Wu *et al.* [12] reported that the silica content had the influences on capacity and self-discharge of lead-acid batteries. The result showed that the resistance increased as an increase of silica content and structure of the gel also became more compact which reduced the capacity of batteries. The lower amount of silica in gelled electrolyte had porous structure which was benefit to H^+, SO_4^{2-} and O_2 transportations.

To improve the performance of the VRLA batteries, various additives were investigated. Wei *et al.* [13] studied the effect of adding $SnSO_4$ to sulfuric acid electrolyte on deep discharge capacity of lead-acid batteries. It was found that this battery capacity improved under deep-discharge process. Since, tin (II) would be reduced to tin (0) on the negative plates during the recharged process and would be oxidized to tin (IV) on the positive plates during the discharge process. Thus, the charge-discharge capacity could be improved by tin metal formation on the negative plate.

Torcheux *et al.* [14] developed a new electrolyte by mixing liquid colloidal silica in sulfuric acid solution and added phosphoric acid as additive. The new modified electrolyte batteries were tested. The results showed that using colloid silica decreased acid stratification and using phosphoric acid improved the textural evolution of positive active material due to a delay softening during cycling. Moreover, the cycle life increased with this new electrolyte.

Bhattacharya *et al.* [15] examined a performance of electrode and the battery in 5 M sulfuric acid with the mixed additives such as mixtures of phosphoric acid and boric acid, phosphoric acid and tin sulfate and phosphoric acid and picric acid. Based on their studies, the mixed additives of phosphoric acid and boric acid, and phosphoric acid and tin sulfate improved the cycle life of the lead–acid battery. The corrosion on both negative and positive plates was also reduced.

Chen *et al.* [16] investigated the optimal concentration and particle size of fumed silica in sulfuric acid solution using phosphoric acid additive to improve the performance of gelled electrolyte. The high concentration of fumed silica exhibited an increase of battery resistance. For particle size of fumed silica, it was found that a diameter of 10 nanometer was aggregate easily while aggregation for diameter over 20 nanometer was more difficult. Moreover, the agitation time of 10 minutes at high stirring rate (2000-4000 rpm) in preparing electrolyte gave high capacity and low resistance in battery testing.

Posch [17] used polyacrylamide as an additive in gelled electrolyte. It improved the gelled electrolyte stiffness and reduced the use of SiO_2 for about 40%w/w when compared with electrolyte containing SiO_2 only. Jang *et al.* [18] studied the sol-gel reaction of tetrathoxysilane (TEOS) in polyacrylamide (PAM) which a function of the TEOS content was observed by atomic force microscopy (AFM). It was found that the PAM-silica hybrid materials presented the hydrogen bonding between the carbonyl group of amide (AAM) and the silinols of the silica gel. Moreover, in the PAM-silica hybrid had the hydrogen bonding between two particles. Additionally, the amide groups of the PAM formed inter- or intramolecule hydrogen bonds. So the silica gel is more compact with interconnected structure.

Alter development was done by adding an additive into the electrodes during plates making. Karimi *et al.* [19] presented the effect of sodium sulfate as an additive in negative plate on the performance of the lead-acid battery. Results showed that the negative electrode containing 0.1%w/w sodium sulfate increased the discharge capacity more than 3 and 12%w/w with respect to the negative electrode without additive before and after cycling test, respectively. Addition of sodium sulfate also increased the time of reaching to a cut off voltage and the cycle life up to 18%. Moreover, using new agent instead of silica in electrolyte has been studied. Tang *et al.* [20] prepared polysiloxane-based gel electrolyte (PBGE) for valve-regulated lead-acid batteries by mixing organically modified polysiloxane with hydrophilic group, methyl silicone oil, tetramethoxy silane and de-ionized water in a high speed mixer. In comparison with AGM-CSGE (Colloid silica gel electrolyte) reference batteries, the PBGE is good fluidity, low viscosity and long gel time to be filled into batteries. Moreover, it improved the efficiency of positive active material in batteries and enhanced battery capacity. It was also found that PBGE had the higher charge efficiency, good conductivity to enhance electrochemical performance.

To investigate the efficiency of the gelled electrolyte, the following parameters have been considered.

1) Gel strength and gelling time: in the battery filling process, electrolyte injected into a battery has to be in suspension form. So the electrolyte gelling time should be slow enough. After filling, electrolyte should become gel which the gel strength is an important requirement of the gelled electrolyte in battery. Thus, a method for improving the gel strength should be optimized with gelling time.

Lambert *et al*. [21] investigated the gel strength of gelled electrolyte with a simple method using penetration depth of a falling lead sphere. However, the structure of the gel sample is destroyed after being measured.

Park *et al.* [22] investigated the rheological behavior of silica gel using fumed silica (diameter 12 nm) and polyacrylamide (MW = 6 x 10^6) as additive in sulfuric acid with a non-destructive technique; small amplitude dynamic oscillation measurement, in which storage modulus was monitored with time and defined as gel strength. Results illustrated that the gel strength and gelation rate increased as silica content, sulfuric acid concentration and the amount of adding polyacrylamide increased.

2) Conductivity: it is an important parameter of an electrolyte system which strongly affects the performance of electrochemical devices.

Grishima *et al.* [23] studied the electrical conductivity of the suspensions of silica in aqueous solution of sulfuric acid with a conductometric cell. The electrical conductivity of 5-70%w/w sulfuric acid solution increased with an increase in the concentration of sulfuric acid and had the maximum conductivity at 33-35%w/w was obtained while higher these concentrations, the conductivity decreased.

Lassegues *et al.* [24] prepared new compound of the polymer electrolyte by choosing polyacrylamide (PAM) with sulfuric acid mixtures. The structural and dynamical properties were reviewed by impedance, infrared and neutron spectroscopies. Results showed that NH_2 group of PAM was transformed into NH_3^+ cation as $–C\text{-}NH_3^+$ when sulfuric acid was added into PAM solution. So that the polymer blend indicated and presented the conductivity up to 10^{-2} S/cm.

3) Capacity of battery: electrical performance such as conductivity and capacity of a battery increases with the concentration of sulfuric acid in the electrolyte.

Pavlov *et al.* [25] observed the influence of sulfuric acid concentration on lead-acid batteries with different concentrations between 1.15 to 1.33 gcm^{-3}. The 12V/32Ah batteries were investigated for the initial capacity and the changes in battery capacity on cycling test. For sulfuric acid concentration less than 1.24 gcm^{-3}, the initial capacity of the battery was low but the cycle life was longer than 100 cycles. For sulfuric acid concentration over than 1.24 gcm^{-3}, the initial capacity of the battery was high but the life of battery was short in maximum of 100 cycles. Therefore, the usage is up to the requirement which need a high capacity or long cycle life.

Lastly, in batteries filling process, Toniazzo [26] studied gel preparing and filling technique onto batteries. The similar technique was mixing sulfuric acid and fumed silica to form the thixotropic gel, still having low viscosity under stirring, and then, electrolyte was pumped to fill under pressure into the container. The advantage was that the gel was very homogeneous because of mixing the agents under stirring. Also this process allowed a precise control of the temperature.

1.4 Objective and scope of this thesis

This research aims to develop gelled electrolyte for VRLA battery. The thesis contains three parts. First, the optimum ratios of sulfuric acid and fumed silica for gelled electrolyte were studied. Second, the gelled electrolyte used with various additives such as polyacrylamide, sulfate salt; Na_2SO_4, $MgSO_4$ or K_2SO_4, and mixed additive; polyacrylamide and sulfate salts, were characterized on conductivity, gelling time and gel strength. Conductometer was used to measure the conductance values. Gelling time and gel strength were indicated by penetration depth of 0.3-g of Pb balls. At least, different gel formations in the VRLA batteries were monitored and the performance of battery in term of capacity, period of usage and battery efficiency was studied.

CHAPTER II

THEORY

2.1 Chemical reactions in lead-acid battery

All types of lead-acid batteries have the same chemical reactions during charging and discharging processes. Chemical reactions in lead-acid battery include the exchange of electrical charges between ions. For the direct conversion into electrical energy, the reaction has to be spilt up into two separate electrode reactions, one that releases electrons, and the other one that absorbs electrons. The electron exchange can be transformed into a current that flows through the charging device.

The reaction products at the electrodes on charge and discharge of a lead storage battery are given in the "double sulfate theory" and this reaction is also reversible reaction. At the positive electrode, lead dioxide reacts with sulfuric acid to form lead sulfate and water (equation 2.1) while at the negative electrode, lead reacts with sulfate ion to form lead sulfate (equation 2.2):

$$\text{Positive electrode: } PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_4 + 2H_2O \quad (2.1)$$

$$\text{Negative electrode: } Pb + SO_4^{2-} \rightleftharpoons PbSO_4 + 2e^- \quad (2.2)$$

The overall reaction in the battery is represented by the equation:

$$Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O \quad (2.3)$$

Discharge reactions in Figure 2.1 reveal that at the negative electrode, oxidation of lead (Pb) to divalent lead ions (Pb^{2+}) continuously reacts with sulfate (SO_4^{2-}) from sulfuric acid (H_2SO_4) electrolyte and means formation of lead sulfate ($PbSO_4$) and two electrons are released. At positive electrode, the two electrons enter and are absorbed: to reduction of PbO_2 (Pb^{4+}) to divalent lead ion (Pb^{2+}) and means conversion of lead dioxide (PbO_2) into lead sulfate ($PbSO_4$):

$$\text{Negative electrode: } Pb \rightleftharpoons Pb^{2+} + 2e^- \quad (2.4)$$

$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4 \quad (2.5)$$

Positive electrode: $PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$ (2.6)

$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4$ (2.7)

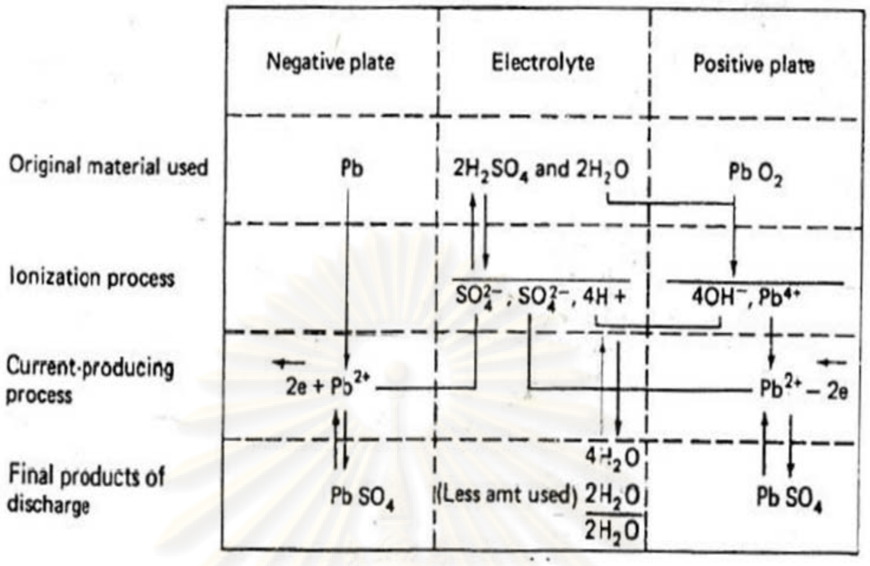

Figure 2.1 Discharge reactions of lead acid battery (Picture from Berndt, D. Research Studies Press Ltd (2003))

During charging as shown in Figure 2.2, both reactions are reversed from discharge reaction. $PbSO_4$ are called reactants while Pb and PbO_2 are the primary products at the negative and positive electrodes, respectively:

Negative electrode: $PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$ (2.8)

$Pb^{2+} + 2e^- \rightleftharpoons Pb$ (2.9)

Positive electrode: $PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$ (2.10)

$Pb^{2+} + 2H_2O \rightleftharpoons PbO_2 + 4H^+ + 2e^-$ (2.11)

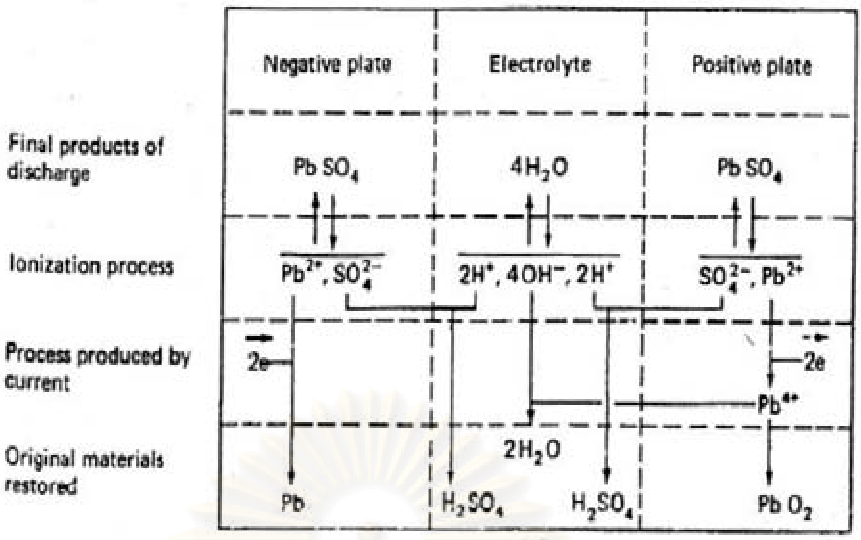

Figure 2.2 Charge reactions of lead acid battery (Picture from Berndt, D. Research Studies Press Ltd (2003))

2.2 Performance characteristics for the VRLA Battery

2.2.1 Charging lead acid battery

Figure 2.3 shows charging curves for the VRLA battery. At the beginning, the float voltage depends on the concentration of electrolyte. During charging period, the cell is charged with a constant current and the resistance drops remain nearly constant [6]. Equations (2.8) - (2.11) present that the cell voltage increases due to an increase in sulfuric acid concentration while the initial current is constant in high level. After the voltage reached a maximum, the current decreases to 0 A when the charging period is long enough.

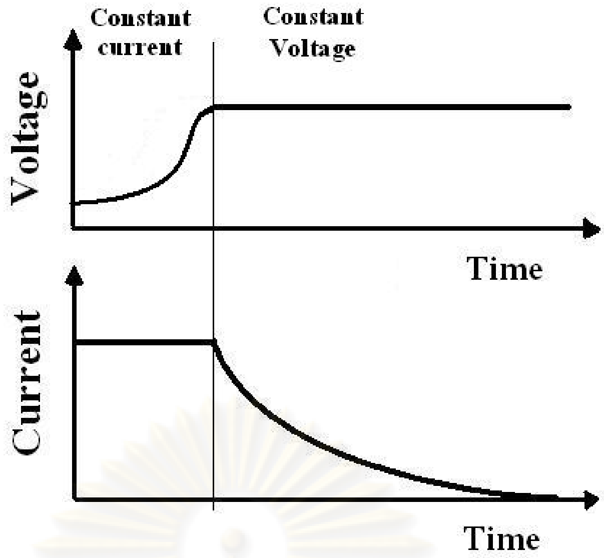

Figure 2.3 Typical charging schedule for VRLA batteries (Picture from Berndt, D. J. Power Sources 100 (2001): 29-46)

2.2.2 Discharging lead acid battery

At the beginning of the discharge, the voltage and the current decline slightly. Afterwards, they are constant for some time, until they suddenly decrease within a couple of seconds [4] as shown in Figure 2.4.

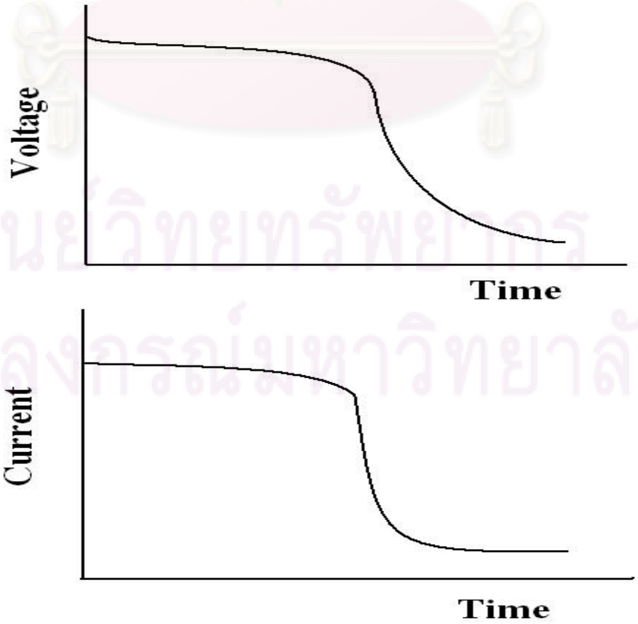

Figure 2.4 Typical discharging schedule for VRLA batteries (Picture from Berndt, D. J. Power Sources 100 (2001): 29-46)

2.2.3 Battery capacity

The capacity is the amount of current that can be taken within a cell. Lead acid batteries are designated by the nominal capacity in ampere hour (Ah) and by the nominal voltage, which has been standardized at 2.0 V/cell for the 12-volt battery (6 cells).

The capacity depends on the charge/discharge current and time. Practically discharge capacity depends on many factors and can be given unequivocally under fixed conditions. The discharge capacity $C = \int_0^t I\,\mathrm{dt}$ is determined in laboratory, usually with a constant discharge current (*I*); therefore $C = It$. Capacity determination with a constant resistance is performed only in special cases. The discharge time (*t*) is defined as the time to reach a specified end or cut off voltage. Figure 2.5 shows the plot of *I* versus *t* where the region under the curve between the start of the measurement and the point where the battery is practically cut off voltage is highlighted. The 'integral' for the marked area is the discharge capacity.

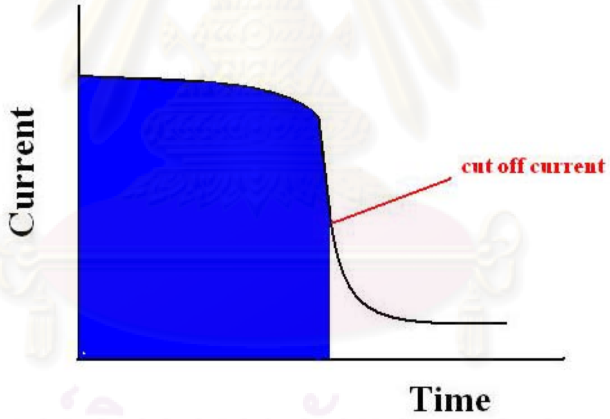

Figure 2.5 The area of the discharge current versus time of a VRLA battery

The capacity of charged battery is obtained in a similar way. It is calculated by integration of the charge current (*I*) over the charge time and represented by the appropriate area below the appropriate plot.

2.2.4 Battery efficiency

The efficiency of battery refers to an amount of power used from battery. It is calculated by dividing a discharge capacity with a charge capacity and its yield percent is obtained from multiplying the efficiency by 100:

$$\text{Battery efficiency} = \frac{\text{Discharged capacity}}{\text{Discharged capacity}} \times 100 \qquad (2.12)$$

CHAPTER III

EXPERIMENTAL

3.1 Instruments and apparatus

The following is a list of instruments and apparatus used in this research.

- Glove box (custom made)
- 0.3-g lead ball
- S70-K sevenMulti conductivity meter (Mettler Toledo GmbH, Switzerland)
- InLab 730 Multi pH-conductivity probe S47 (Mettler Toledo GmbH, Switzerland)
- 628 Rotating disk electrode (Methrom, Switzerland)
- Micropipette 5.00 mL (Eppendorf, Germany)
- Micropipette 1.00 mL (Eppendorf, Germany)
- Beaker 100 mL (Schott Durant, Germany)
- Beaker 150 mL (Schott Durant, Germany)
- Beaker 250 mL (Schott Durant, Germany)
- Beaker 1000 mL (Schott Durant, Germany)
- Volumetric Flask 100 mL (Schott Durant, Germany)
- Volumetric Flask 250 mL (Schott Durant, Germany)
- Volumetric Flask 1000 mL (Schott Durant, Germany)
- Test tubes 10 mL (Schott Durant, Germany)
- Digital clamp multimeter UT 200 series (UNI-TREND Group Ltd., Hong Kong)
- Standard digital multimeter UT 51 (UNI-TREND Group Ltd., Hong Kong)
- Helium lamp 35 Watt (Philips electronic (Thailand) Co. Ltd., Thailand)
- CP 1210 charger (N.V. Battery Ltd., Thailand)
- Electrolyte filling machine (N.V. Battery Ltd., Thailand)
- VRLA battery (N.V. Battery Ltd., Thailand)

3.2 Chemicals

All chemicals used in this research were AR grade. Concentrated sulfuric acid (H_2SO_4), fumed silica (12 nm diameter) [22], polyacrylamide (MW = 6 x 10^6 g/mol) [22], magnesium sulfate ($MgSO_4$) and conductivity standard solution were obtained from Merck (Germany), Fluka (USA), Degassa, Scharlau Chemie S.A. (Spain) and Mettler Toledo Thornton, Inc (USA), respectively. Sodium sulfate (Na_2SO_4) and potassium sulfate (K_2SO_4) were received from Ajax Finechem (Australia). All reagents were used as received.

3.3 Preparation of gelled electrolyte

This section explains procedures of gelled electrolyte preparation.

3.3.1 Preparation of electrolytes containing fumed silica and sulfuric acid

1) A 0.5-g fumed silica was weighted and dissolved in 4.25 mL concentrated sulfuric acid. The total volume was adjusted to 50 mL with deionized (DI) water in 100-mL beaker. The mixture was, then, agitated with a high speed stirrer for 10 min at 3000 rpm [16] at room temperature. Electrolyte containing 1%w/v fumed silica in 15%w/v sulfuric acid was finally obtained.

2) The process in 1) was repeated with different volumes of the concentrated sulfuric acid; 4.43 mL, 5.66 mL, 7.08 mL, 9.91 mL, 11.32 mL, 12.74 mL, 14.16 mL, 15.58 mL, 16.99 mL, 18.40 mL, 19.82 mL and 21.23 mL, to obtain electrolytes containing 1%w/v fumed silica in 20%w/v, 25%w/v, 30%w/v, 35%w/v, 40%w/v, 45%w/v, 50%w/v, 55%w/v, 60%w/v, 65%w/v, 70%w/v and 75%w/v sulfuric acid, respectively.

3) The process in 1) and 2) were repeated with different amounts of fumed silica; 1.0 g, 1.5 g, 2.0 g, 2.5 g, 3.0 g, 3.5 g, 4.0 g, 4.5 g, 5.0 g, 5.5 g, 6.0 g, 6.5 g, 7.0 g and 7.5 g to obtain electrolytes containing 2%w/v, 3%w/v, 4%w/v, 5%w/v, 6%w/v, 7%w/v, 8%w/v, 9%w/v, 10%w/v, 11%w/v, 12%w/v, 13%w/v, 14%w/v and 15%w/v fumed silica, respectively, in various percentages of sulfuric acid.

3.3.2 Preparation of electrolytes containing fumed silica, sulfuric acid and polyacrylamide (PAM) as an additive

A 1%w/v stock solution of PAM was prepared by dissolving 1.0 g PAM in 80°C DI water and the total volume was adjusted to 100 mL with DI water in a 100-mL volumetric flask.

1) A 0.5-g fumed silica was weighted and dissolved in 9.91 mL concentrated sulfuric acid. A 0.05 mL of 1%w/v PAM stock solution was added and the total volume was adjusted to 50 mL with DI water in 100-mL beaker. The mixture was, then, agitated with a high speed stirrer for 10 min at 3000 rpm at room temperature. Electrolyte containing 1%w/v fumed silica and 0.001%w/v PAM in 35%w/v sulfuric acid was finally obtained.

2) The process in 1) was repeated with different volumes of the concentrated PAM stock solution; 0.10 mL, 0.15 mL, 0.20 mL, 0.25 mL, 0.30 mL, 0.35 mL, 0.40 mL, 0.45 mL, 0.50 mL, 0.60 mL, 0.70 mL, 0.80 mL, 0.90 mL, 1.00 mL, 1.50 mL, 2.00 mL, 2.50 mL, 3.00 mL and 3.50 mL to obtain electrolytes containing 1%w/v fumed silica with 0.002%w/v, 0.003%w/v, 0.004%w/v, 0.005%w/v, 0.006%w/v, 0.007%w/v, 0.008%w/v, 0.009%w/v, 0.010%w/v, 0.012%w/v, 0.014%w/v, 0.016%w/v, 0.018%w/v, 0.020%w/v, 0.030%w/v, 0.040%w/v, 0.050%w/v, 0.060%w/v and 0.070%w/v PAM in 35%w/v sulfuric acid, respectively.

3) The processes in 1) and 2) were repeated with different amounts of fumed silica 1.0 g, 1.5 g, 2.0 g and 3.0 g to obtain electrolytes containing 2%w/v, 3%w/v, 4%w/v and 6%w/v fumed silica, respectively, in various percentages of PAM and in 35%w/v sulfuric acid. All the mixings were done at room temperature unless otherwise indicated.

3.3.3 Preparation of electrolytes containing fumed silica, sulfuric acid and sulfate salts as an additive

A 30%w/v stock solution of sodium sulfate (Na_2SO_4) was prepared by dissolving 30.0 g Na_2SO_4 with 60°C DI water in 100-mL volumetric flask.

A 20%w/v stock solution of magnesium sulfate ($MgSO_4$) was prepared by dissolving 20.0 g of $MgSO_4$ with 60°C DI water in 100-mL volumetric flask.

A 10%w/v stock solution of potassium sulfate (K_2SO_4) was prepared by dissolving 10.0 g of K_2SO_4 with 60°C DI water in 100-mL volumetric flask.

3.3.3.1 Preparation of electrolytes containing fumed silica and sulfate salts in 35%w/v sulfuric acid

1) A 0.5-g fumed silica was weighted and dissolved in 9.91 mL concentrated sulfuric acid. A 0.33 mL of 30%w/v Na_2SO_4 stock solution was added and the total volume was adjusted to 50 mL with DI water in 100-mL beaker. The mixture was, then, agitated with a high speed stirrer for 10 min at 3000 rpm at room temperature. Electrolyte containing 1%w/v fumed silica and 0.20%w/v Na_2SO_4 in 35%w/v sulfuric acid was finally obtained.

2) The process in 1) was repeated with different volumes of the Na_2SO_4 stock solution; 0.67 mL, 1.00 mL, 1.33 mL, 1.67 mL, 2.00 mL, 2.33 mL, 2.67 mL, 3.00 mL, 3.33 mL, 3.67 mL, 4.00 mL, 4.17 mL, 4.33 mL, 4.67 mL and 5.00 mL to obtain electrolytes containing 1%w/v fumed silica with 0.40%w/v, 0.60%w/v, 0.80%w/v, 1.00%w/v, 1.20%w/v, 1.40%w/v, 1.60%w/v, 1.80%w/v, 2.00%w/v, 2.20%w/v, 2.40%w/v, 2.50%w/v, 2.60%w/v, 2.80%w/v and 3.00%w/v Na_2SO_4 in 35%w/v sulfuric acid, respectively.

3) The processes in 1) and 2) were repeated by using 20%w/v $MgSO_4$ stock solution, instead of 30%w/v Na_2SO_4 stock solution. Different volumes of the $MgSO_4$ stock solution; 0.50 mL, 1.00 mL, 1.50 mL, 2.00 mL, 2.50 mL, 3.00 mL, 3.50 mL, 4.00 mL, 4.50 mL, 5.00 mL, 5.50 mL, 6.00 mL, 6.25 mL, 6.50mL, 7.00 mL and 7.50 mL was added to obtain electrolytes containing 1%w/v fumed silica with 0.20%w/v, 0.40%w/v, 0.60%w/v, 0.80%w/v, 1.00%w/v, 1.20%w/v, 1.40%w/v, 1.60%w/v, 1.80%w/v, 2.00%w/v, 2.20%w/v, 2.40%w/v, 2.50%w/v, 2.60%w/v, 2.80%w/v and 3.00%w/v $MgSO_4$ in 35%w/v sulfuric acid, respectively.

4) The processes in 1) and 2) were repeated by using 10%w/v K_2SO_4 stock solution, instead of 30%w/v Na_2SO_4 stock solution. Different volumes of the concentrated K_2SO_4; 1.0 mL, 2.0 mL, 3.0 mL, 4.0 mL, 5.0 mL, 6.0 mL, 7.0 mL, 8.0 mL, 9.0 mL, 10.0 mL, 11.0 mL, 12.0 mL, 12.5 mL, 13.0 mL,14.0 mL and 15.0 mL was added to obtain electrolytes containing 1%w/v fumed silica with 0.20%w/v, 0.40%w/v, 0.60%w/v, 0.80%w/v, 1.00%w/v, 1.20%w/v, 1.40%w/v, 1.60%w/v, 1.80%w/v, 2.00%w/v, 2.20%w/v, 2.40%w/v2.50%w/v, 2.60%w/v, 2.80%w/v and 3.00%w/v $MgSO_4$ in 35%w/v sulfuric acid, respectively.

5) The processes in 1) to 4) were repeated with different amounts of fumed silica; 1.0 g and 1.5 g, to obtain electrolytes containing 2%w/v and 3%w/v

fumed silica, respectively, in various percentages of sulfate salt in 35%w/v sulfuric acid.

3.3.3.2 Preparation of electrolytes containing 8%w/v fumed silica and sulfate salt in 35%w/v sulfuric acid

1) A 4.0-g fumed silica was weighted and dissolved in 4.43 mL concentrated sulfuric acid. A 0.83 mL of 30%w/v Na_2SO_4 stock solution was added and the total volume was adjusted to 50 mL with DI water in 100-mL beaker. The mixture was, then, agitated with a high speed stirrer for 10 min at 3000 rpm at room temperature. Electrolyte containing 8%w/v fumed silica and 0.5%w/v Na_2SO_4 in 15%w/v sulfuric acid was finally obtained.

2) The process in 1) was repeated with different volumes and different sulfate salts. A 5.00 mL of the Na_2SO_4 stock solution, 1.25 mL and 7.50 mL of $MgSO_4$ stock solution, and 2.50 mL and 15.00 mL K_2SO_4 stock solution was added, instead of 0.83 mL Na_2SO_4 stock solution, to obtain electrolytes containing 8%w/v fumed silica with 3.0%w/v Na_2SO_4, 0.5%w/v $MgSO_4$, 3.0%w/v $MgSO_4$, 0.5%w/v K_2SO_4 and 3.0%w/v K_2SO_4 in 15%w/v sulfuric acid, respectively.

3.3.4 Preparation of electrolytes containing fumed silica, sulfuric acid using PAM and sulfate salts as additives

3.3.4.1 Preparation of electrolytes containing fumed silica using PAM and sulfate salts in 35%w/v sulfuric acid

1) A 0.5-g fumed silica was weighted and dissolved in 9.91 mL concentrated sulfuric acid. A 0.05 mL of 1%w/v PAM stock solution and 0.33 mL of 30%w/v Na_2SO_4 stock solution was added and the total volume was adjusted to 50 mL with DI water in 100-mL beaker. The mixture was, then, agitated with a high speed stirrer for 10 min at 3000 rpm at room temperature. Electrolyte containing 1%w/v fumed silica, 0.001% PAM and 0.20%w/v Na_2SO_4 in 35%w/v sulfuric acid was finally obtained.

2) The process in 1) was repeated with different volumes of the Na_2SO_4 stock solution; 0.67 mL, 1.00 mL, 1.33 mL, 1.67 mL, 2.00 mL, 2.33 mL, 2.67 mL, 3.00 mL, 3.33 mL, 3.67 mL and 4.00 mL, to obtain electrolytes containing 1%w/v fumed silica with 0.40%w/v, 0.60%w/v, 0.80%w/v, 1.00%w/v, 1.20%w/v,

1.40%w/v, 1.60%w/v, 1.80%w/v and 2.00%w/v Na_2SO_4 in 0.001%w/v PAM, 35%w/v sulfuric acid, respectively.

3) The processes in 1) and 2) were repeated by using 20%w/v $MgSO_4$ stock solution, instead of 30%w/v Na_2SO_4 stock solution. Different volumes of the $MgSO_4$ stock solution; 0.50 mL, 1.00 mL, 1.50 mL, 2.00 mL, 2.50 mL, 3.00 mL, 3.50 mL, 4.00 mL, 4.50 mL and 5.00 mL was added to obtain electrolytes containing 1%w/v fumed silica with 0.20%w/v, 0.40%w/v, 0.60%w/v, 0.80%w/v, 1.00%w/v, 1.20%w/v, 1.40%w/v, 1.60%w/v, 1.80%w/v and 2.00%w/v $MgSO_4$ in 0.001%w/v PAM, 35%w/v sulfuric acid, respectively.

4) The processes in 1) and 2) were repeated by using 10%w/v K_2SO_4 stock solution, instead of 30%w/v Na_2SO_4 stock solution. Different volumes of the K_2SO_4 stock solution; 1.0 mL, 2.0 mL, 3.0 mL, 4.0 mL, 5.0 mL, 6.0 mL, 7.0 mL, 8.0 mL, 9.0 mL and 10.0 mL was added to obtain electrolytes containing 1%w/v fumed silica in 0.20%w/v, 0.40%w/v, 0.60%w/v, 0.80%w/v, 1.00%w/v, 1.20%w/v, 1.40%w/v, 1.60%w/v, 1.80%w/v and 2.00%w/v K_2SO_4 in 0.001%w/v PAM, 35%w/v sulfuric acid, respectively.

5) The processes in 1) to 4) were repeated with different amounts of fumed silica; 1.0 g and 1.5 g, to obtain electrolytes containing 2%w/v and 3%w/v fumed silica, respectively, in various percentages of sulfate salt in 0.001%w/v PAM, 35%w/v sulfuric acid.

3.3.4.2 Preparation of electrolytes containing 8%w/v fumed silica using PAM and sulfate salt in 35%w/v sulfuric acid

1) A 4.0-g fumed silica was weighted and dissolved in 4.43 mL concentrated sulfuric acid. A 1.00 mL of 1%w/v PAM stock solution and 0.83 mL of 30%w/v Na_2SO_4 stock solution was added and the total volume was adjusted to 50 mL with DI water in 100-mL beaker. The mixture was, then, agitated with a high speed stirrer for 10 min at 3000 rpm at room temperature. Electrolyte containing 8%w/v fumed silica, 0.5%w/v Na_2SO_4 and 0.001%w/v PAM in 15%w/v sulfuric acid was finally obtained.

2) The process in 1) was repeated with different volumes and different sulfate salts. A 5.00 mL of the Na_2SO_4 stock solution, 1.25 mL and 7.50 mL of $MgSO_4$ stock solution, and 2.50 mL and 15.00 mL K_2SO_4 stock solution was added, instead of 0.83 mL Na_2SO_4 stock solution, to obtain electrolytes containing

8%w/v fumed silica with 3.0%w/v Na_2SO_4, 0.5%w/v $MgSO_4$, 3.0%w/v $MgSO_4$, 0.5%w/v K_2SO_4 and 3.0%w/v K_2SO_4 in 0.001%w/v PAM, 15%w/v sulfuric acid, respectively.

3.4 Measurement of conductivity, gelling time and gel strength

The electrolyte conductivity was measured by S70-K sevenMulti conductrometer in connected with InLab 730 conductivity probe.

The measurement of gelling time was done by penetrating of 0.3-g lead ball into the suspension every 15 minutes [11]. The depth of the falling ball was monitored and an acceptable gel texture is defined when the penetrated depth is about 2-3 mm.

Gel strength is indicated through the penetrated depth of the falling lead ball [21]. After the electrolyte was mixed and left still for 24 hours, the 0.3-g lead ball was drop into the gel and the penetrated depth was noted to indicate the gel strength.

3.5 Battery performance using modified gelled electrolyte

A 264-mL selected gelled-electrolyte was filled into a 12-volt VRLA battery using the electrolyte filling machine at N.V. Battery Ltd., Figure 3.1. The battery was, then, investigated for its charge capacity, discharge capacity, discharge period and efficiency.

Figure 3.1 Electrolyte filling machine (N.V. Battery Ltd., Thailand)

3.5.1 Charging of the battery

The prepared battery was charged with a constant current of 1 A using a CP 1210 charger. Changes in voltage (*V*) and current (*I*) were monitored every 15 minutes until the current dropped to zero A, where battery was fully charged, using a standard digital multi-meter and digital clamp multimeter, respectively, as shown in Figure 3.2. Then, the charge capacity was calculated from an area under the curve of current versus time. The voltage versus time was also plotted. An example of these plots was demonstrated in Figure 3.3.

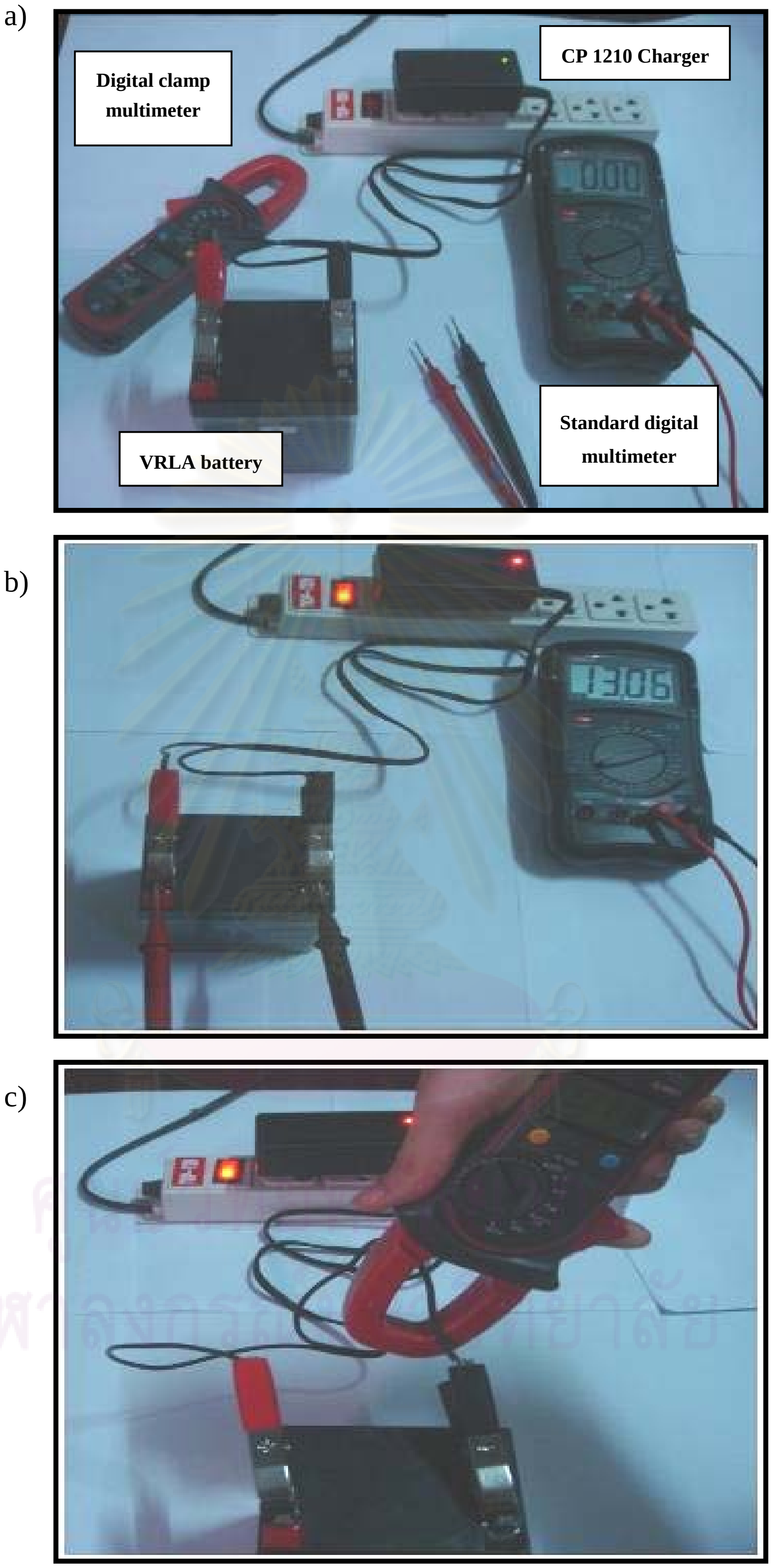

Figure 3.2 a) Instrument for battery charging,
b) Demonstration of voltage measurement using a multimeter
c) Demonstration of current measurement using a digital clamp multimeter

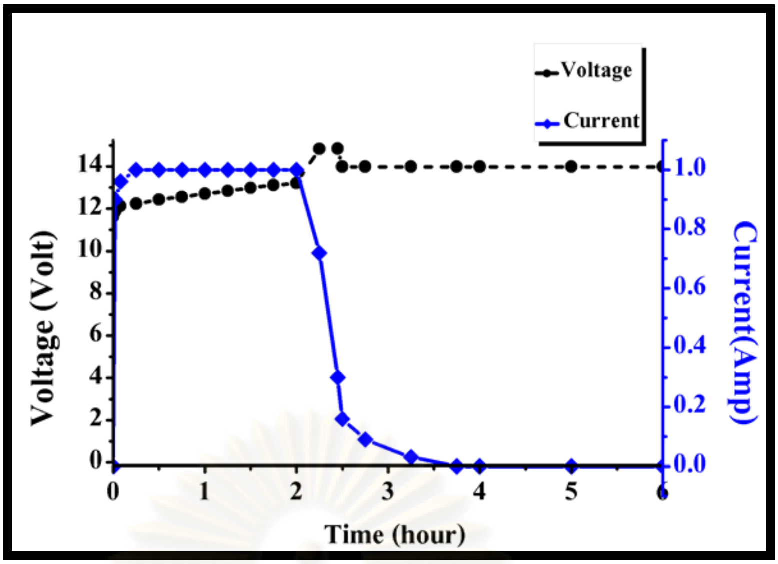

Figure 3.3 The voltage and the current at the first charging of a VRLA battery containing 1%w/v SiO_2 in 35%w/v H_2SO_4 as electrolyte

3.5.2 Discharging of the battery

After the charging process, the battery was discharged through a 35-Watt halogen lamp. Changes in voltage (*V*) and current (*I*) were monitored every 2 minutes until the voltage dropped to 9 V. Total period, from the beginning of discharging until the cut off voltage 9 V, was reported as discharging period. The instrument set for battery discharging is shown in Figure 3.4. The discharge capacity of battery was calculated from the area below current versus time curve. The voltage versus time was also plotted. An example of these plots was demonstrated in Figure 3.5.

Figure3.4 Instrument for battery discharging through a 35-Watt helium lamp

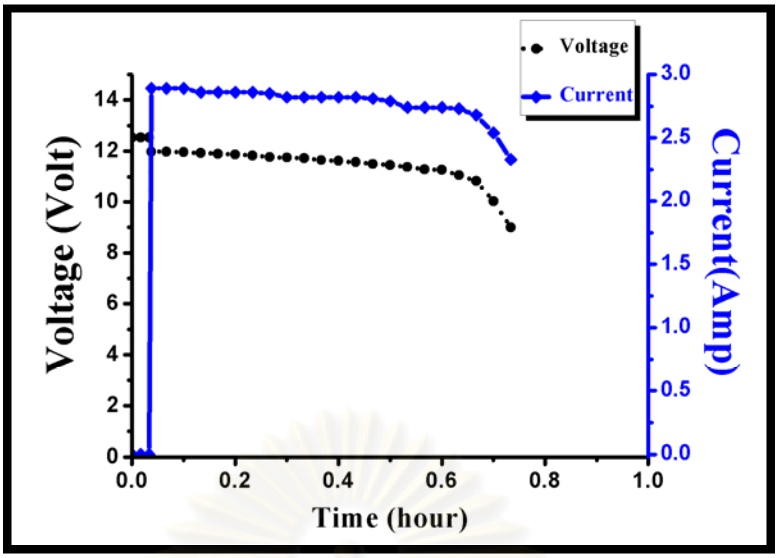

Figure 3.5 The voltage and the current at the first discharging of a VRLA battery containing 1%w/v SiO_2 in 35%w/v H_2SO_4 as electrolyte

3.5.3 Efficiency of battery

The charge capacity from section 3.5.1 divided by the discharge capacity from section 3.5.2 is obtained as the battery efficiency (equation 2.12).

CHAPTER IV

RESULTS AND DISCUSSION

This chapter describes a characteristic of prepared-gelled electrolytes and effects of polymer and sulfate salt additives in term of conductivity, gel strength and gelling time. Performances of valve-regulated lead-acid battery filled with the developed-formula gelled electrolyte will also be discussed.

4.1 Silica-based electrolyte

4.1.1 Selection of silica-based gelled electrolyte

Various silica-based electrolytes were prepared by mixing 1-15%w/v fumed silica and 15-75%w/v sulfuric acid, Table 4.1. Two forms of the electrolyte were observed. One was a suspension which was a homogeneous liquid form in white color. The other was a gel which had a look of solid-like structure that form could not be changed even the container was tripped over. The suspended-form electrolyte represented as S in Table 4.1 was observed in the electrolyte with silica content lower than 10%w/v. The gel-form electrolyte, represented as G in Table 4.1, first appeared at 4%w/v fumed silica in 75%w/v sulfuric acid. In silica content of 5-9%w/v, the gel-form electrolyte occurred in high percentage sulfuric acid. Results in Table 4.1 suggest that the more fumed silica presents, the least the acidic condition required for gelled electrolyte formation. Once the fumed silica content was higher than 9%w/v, gel-form electrolyte appeared in every percentage sulfuric acid.

In practical, the preferred electrolyte should not promptly form gel prior to be filled into a battery. Thus, the gelled electrolyte suddenly forms in high silica content would not be considered for a further development.

Table 4.1 Characteristic of electrolytes at various ratios of fumed silica and sulfuric acid

H_2SO_4 (%w/v) / SiO_2 (%w/v)	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**	**75**
1	S	S	S	S	S	S	S	S	S	S	S	S	S
2	S	S	S	S	S	S	S	S	S	S	S	S	S
3	S	S	S	S	S	S	S	S	S	S	S	S	S
4	S	S	S	S	S	S	S	S	S	S	S	S	G
5	S	S	S	S	S	S	S	S	S	G	G	G	G
6	S	S	S	S	S	S	S	G	G	G	G	G	G
7	S	S	S	S	S	S	G	G	G	G	G	G	G
8	S	S	S	G	G	G	G	G	G	G	G	G	G
9	S	G	G	G	G	G	G	G	G	G	G	G	G
10	G	G	G	G	G	G	G	G	G	G	G	G	G
11	G	G	G	G	G	G	G	G	G	G	G	G	G
12	G	G	G	G	G	G	G	G	G	G	G	G	G
13	G	G	G	G	G	G	G	G	G	G	G	G	G
14	G	G	G	G	G	G	G	G	G	G	G	G	G
15	G	G	G	G	G	G	G	G	G	G	G	G	G

"S" refers to suspended-form and "G" refers to gel-form electrolyte.

4.1.2 Effect of sulfuric acid on the electrical performance of the electrolyte

Electrical performance of the electrolyte was reported through a conductance value (σ). Only suspended-form electrolytes reported in Table 4.1 were selected for this study. The results are shown in Figure 4.1. Figure 4.1 (a) – (c) show plots of conductance values measured from suspended electrolytes containing 1-3%w/v silica content, respectively, in 15-75%w/v sulfuric acid which the maximum conductance of these electrolytes obtained at 35%w/v sulfuric acid. Figure 4.1 (d) – (i), the maximum percentage of sulfuric acid used in the electrolyte containing high silica content, was less than 75%w/v. This dues to a limit of suspended-electrolyte formation. Figure 4.1 (d) – (i) show the conductance data obtained form electrolyte containing 4-9%w/v fumed silica in various sulfuric acid concentrations up to the limit of the suspended-electrolyte formation. Plots in Figure 4.1 express an influence of sulfuric acid concentration on electrical property of the electrolyte. Though, this is not clear in the Figure 4.1 (i) where the gelled electrolyte was easily form in the lowest percentage sulfuric acid, 15%w/v, at 9%w/v fumed silica. Consider from Figure 4.1 (a) - (h), it is simply seen that the electrolyte conductance rises with higher percentage of sulfuric acid until it reaches a maximum. This could due to an increment of free ions, H^+ and SO_4^{2-}, in the electrolyte. Beyond the maximum point, the electrolyte conductance, however, decreased when more sulfuric acid involved. This behavior appears at all silica contents and it could be explained by a charge on a silica surface [21]. That is, in high percentage of sulfuric acid, silica molecule is protonated at a silanol group to form a positive charge ($SiOH_2^+$) on the surface. This positive-charge surface, then, attracts the SO_4^{2-} ion and consequently results in a limitation of ion movement in the electrolyte. Therefore, the electrolyte conductance decreases.

According to the result in Figure 4.1, the percentage of sulfuric acid that maximized the electrolyte conductance in each silica content was selected and listed in Table 4.2. These data imply that electrolyte contained high silica content requires less percentage of sulfuric acid for its maximum conductivity. In the other word, if all plots from Figure 4.1 were overlayed onto a single scale, a shift of the maximum point to a lower acid concentration would be expected when silica content increased. Moreover, from Table 4.2, the maximum conductance value trends to decrease with increase of silica content, except that of the electrolyte containing 1%w/v fumed silica.

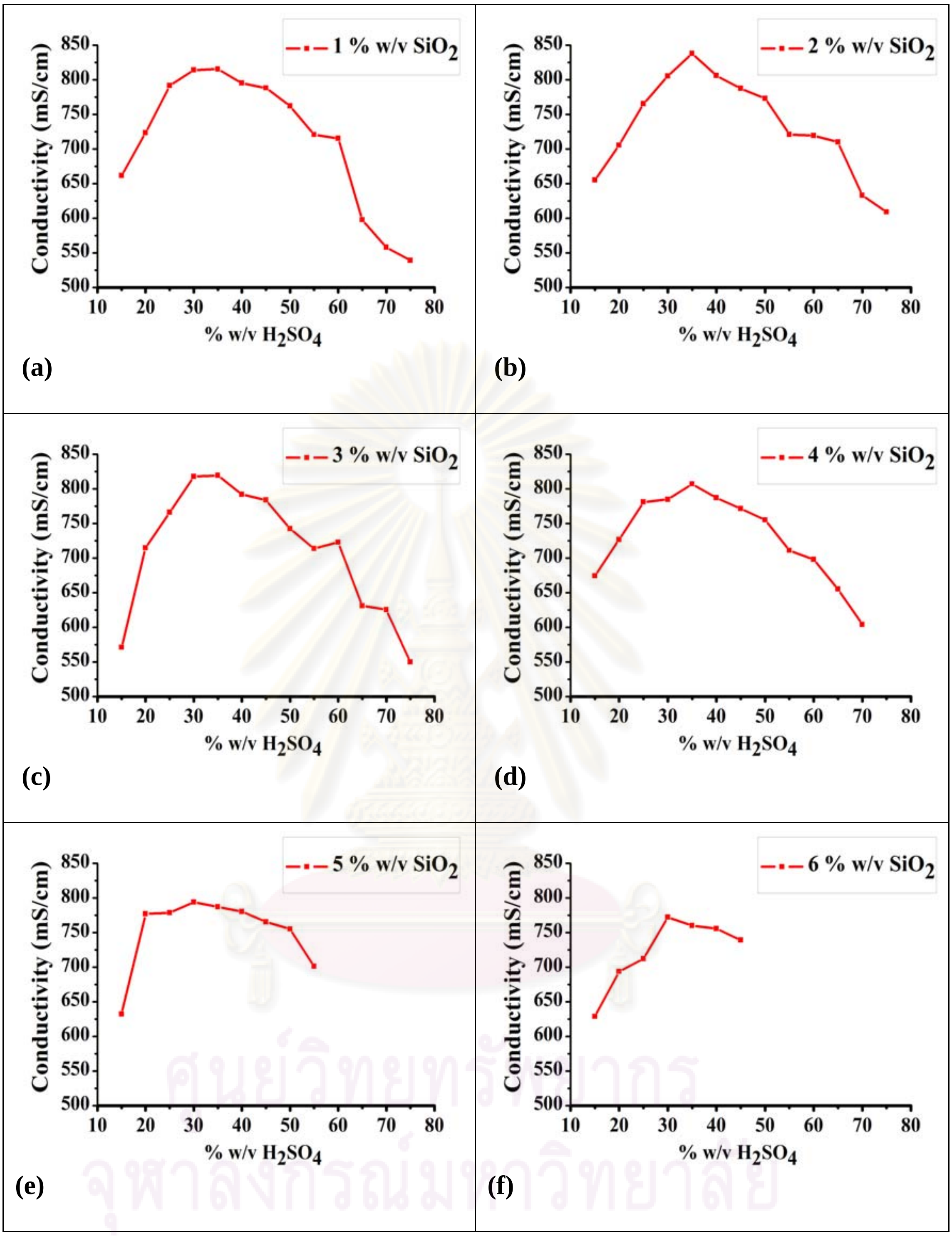

Figure 4.1 Conductivity of electrolytes containing (a) 1%w/v fumed silica, (b) 2%w/v fumed silica, (c) 3%w/v fumed silica, (d) 4%w/v fumed silica, (e) 5%w/v fumed silica and (f) 6%w/v fumed silica in different sulfuric acid concentrations from 15 to 75%w/v

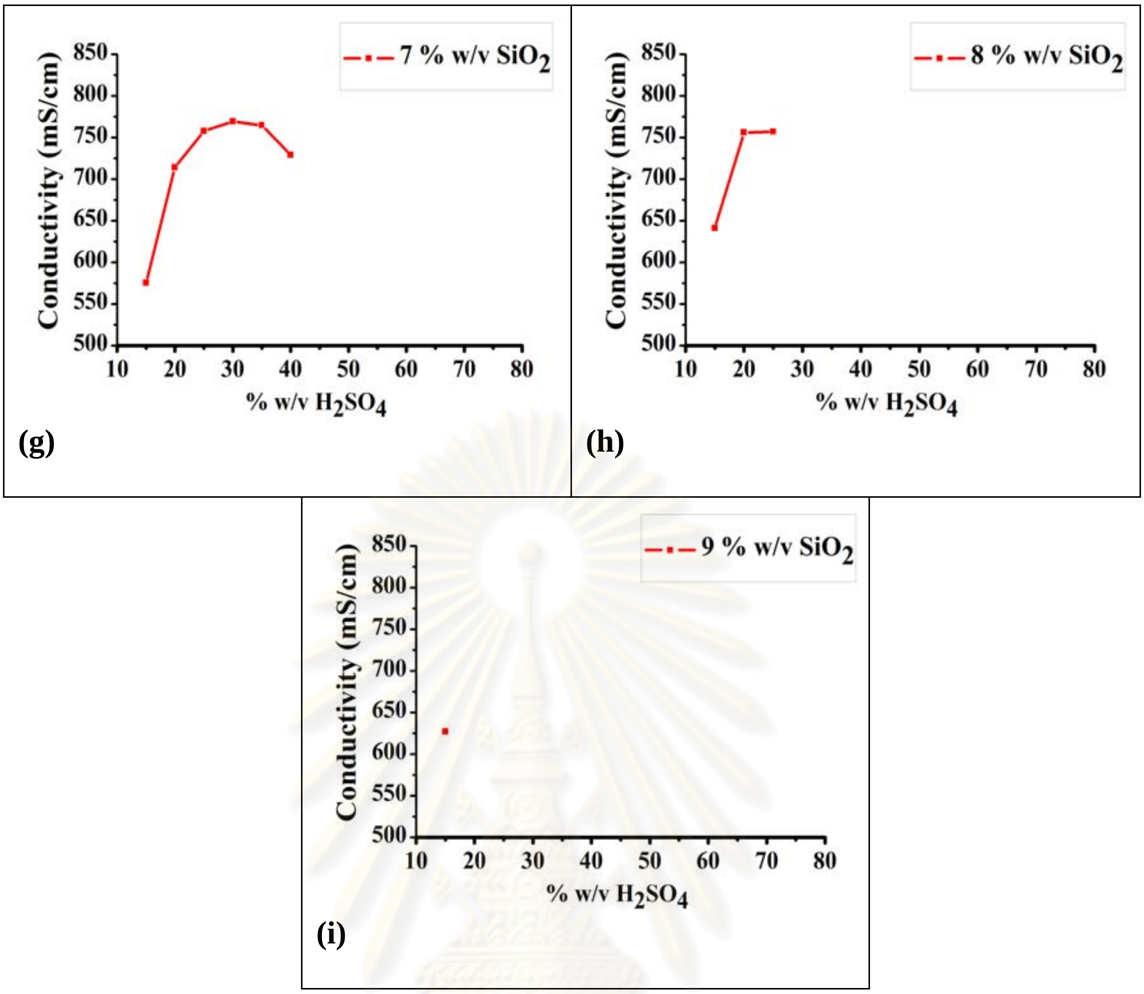

Figure 4.1 (continue) Conductivity of electrolytes containing (g) 7%w/v fumed silica, (h) 8%w/v fumed silica and (i) 9%w/v fumed silica in different sulfuric acid concentrations from 15 to 75%w/v

Table 4.2 Maximum conductivity (σ) of suspended-form electrolytes at each silica content

SiO_2 (%w/v)	H_2SO_4 (%w/v)	σ (mS/cm)
1	35	815 ± 2
2	35	838 ± 2
3	35	819 ± 3
4	35	807 ± 2
5	30	794 ± 2
6	30	772 ± 4
7	30	769 ± 4
8	25	757 ± 3
9	15	627 ± 3

Since high conductivity reflects good electrical performance, the electrolyte component of 1-4%w/v silica content in 35%w/v sulfuric acid that provides a high conductivity, over than 800 mS/cm, would further be investigated in the next section.

4.2 Addition of polyacylamide as an electrolyte additive

According to the result in Table 4.2, the electrolytes containing 1-4%w/v fumed silica in 35%w/v sulfuric acid that provide high conductivity value would be developed. Polyacrylamide (PAM) was used as a possibly electrolyte additive in this section.

4.2.1 Electrolyte formation

Appearances of the electrolyte were altered by to not only the percentage of fumed silica but also the percentage of PAM. Electrolyte containing 1%w/v fumed silica and 0.001%w/v PAM in 35%w/v sulfuric acid appeared in a suspended form, Figure 4.2. An increase of the PAM percentage beyond the 0.001%w/v value, a heterogeneous appearance occurred. Figure 4.3 represents a mixture containing 1%w/v fumed silica and 0.010%w/v PAM in 35%w/v sulfuric acid. A precipitation-like occurred in the solution; white precipitate fell on the bottom of the container and separated from the solution.

For electrolyte containing 2%w/v fumed silica and PAM in 35%w/v sulfuric acid, suspended form was found when less than 0.020%w/v PAM was added and the precipitation-look appeared in the electrolyte containing more than 0.020%w/v PAM. Similar to the 2%w/v silica-based electrolyte, the electrolyte containing 3%w/v fumed silica and PAM in 35%w/v sulfuric acid appeared in suspended-form when less than 0.030%w/v PAM was added and appeared in the precipitation-look when more than 0.030%w/v PAM was included. Unlike all of the above, the 4%w/v silica-based electrolyte appeared in suspended form at all percentages of PAM added (0.020–0.040%w/v). These data were summarized in Table 4.3.

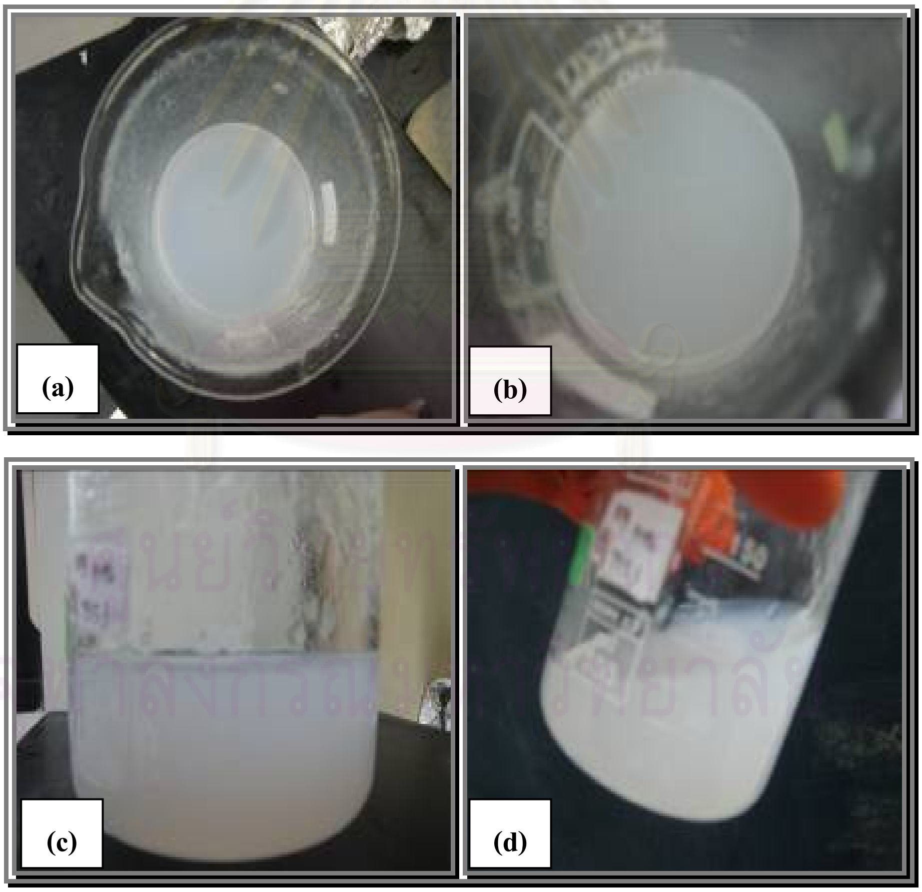

Figure 4.2 Electrolyte containing 1%w/v fumed silica and 0.001%w/v PAM in 35%w/v sulfuric acid; (a) and (b) top view, (c) and (d) side view

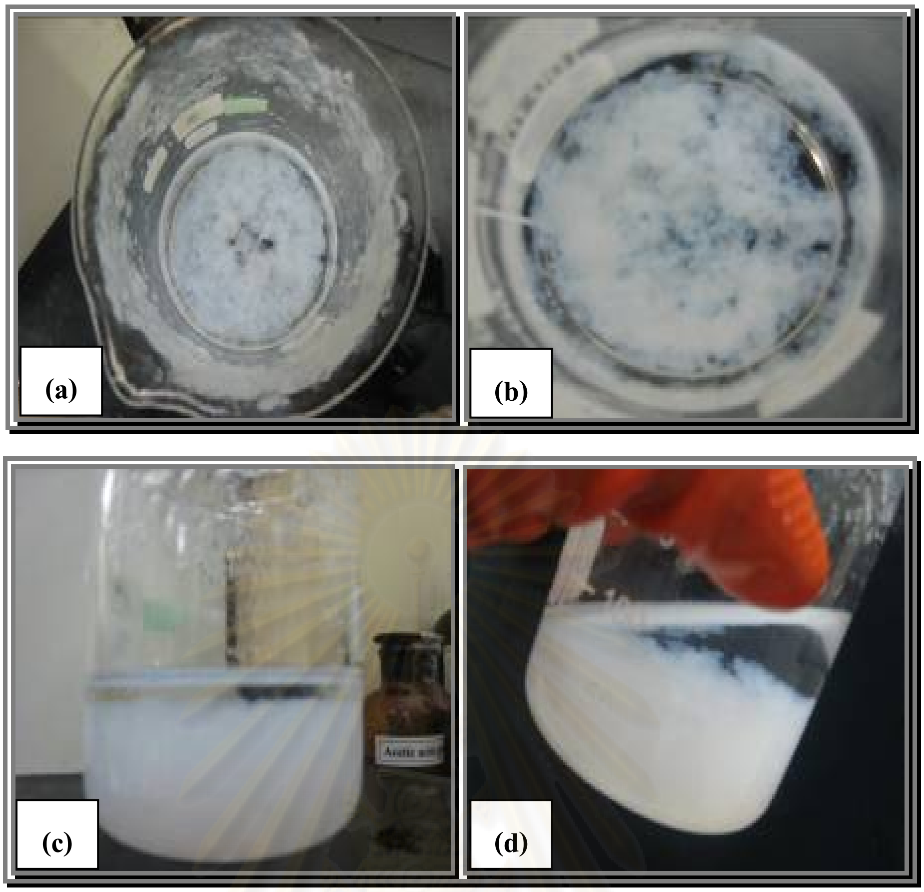

Figure 4.3 Electrolyte containing 1%w/v fumed silica and 0.01%w/v PAM in 35%w/v sulfuric acid; (a) and (b) top view, (c) and (d) side view

Table 4.3 Characteristic of electrolytes at various percentages of fumed silica and PAM in 35%w/v sulfuric acid.

PAM (10^{-2}%w/v) / **SiO_2 (%w/v)**	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**	**1.2**	**1.4**	**1.6**	**1.8**	**2.0**	**3.0**	**4.0**
1	P	P	P	P	P	P	P	P	P	P	P	P
2	S	S	S	S	S	S	S	S	S	S	P	P
3	S	S	S	S	S	S	S	S	S	S	S	P
4	S	S	S	S	S	S	S	S	S	S	S	S

“S” refers to suspended form and “P” refers to precipitation.

4.2.2 Effect of polyacrylamide on the electrolyte conductance

The conductivity of electrolyte containing PAM was studied. Measurements were done in the suspended-electrolytes containing various amounts of PAM, from 0 to 0.02%w/v. Figure 4.4 shows an effect of PAM on the conductivity of electrolytes that was prepared from 1-4%w/v fumed silica in 35%w/v H_2SO_4. The electrolyte conductance trended to increase with more percentage of PAM added. The highest conductivity for most of the electrolyte was found in a mixture containing 0.02%w/v PAM, except the one with 1%w/v fumed silica. In the electrolyte containing 1%w/v fumed silica in 35%w/v sulfuric acid, the highest conductance was found to be 824 mS/cm when 0.001%w/v PAM presented. Adding more percentage of PAM into the 1%w/v fumed silica electrolyte was limited by the texture of precipitation-like. Therefore, the maximum percentage of PAM used in this electrolyte was 0.001%w/v.

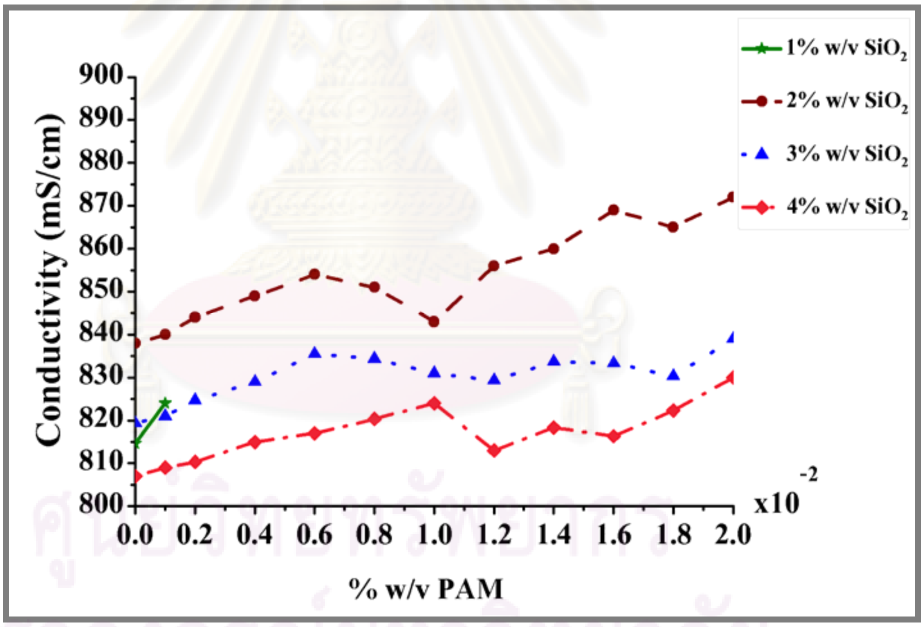

Figure 4.4 Conductivity of electrolytes composed of 1, 2, 3 and 4%w/v fumed silica in 35%w/v H_2SO_4 and different percentages of PAM

Table 4.4 shows a list of percentage of PAM that maximize the electrolyte conductance (σ) in each silica content. These electrolyte conductances are larger than those reported in Table 4.2, compare at the same silica content. This would due to a replacement of the positive charge on the silica-surface ($SiOH_2^+$) under an acidic condition by hydrogen bonding between amide group in PAM and the silanol group

(SiOH) on silica surface [16, 21]. Then, the proton ions (H^+) are released from the silica surface into the solution and cause a rise in the electrolyte conductance. Therefore, these results indicate that PAM could be used to improve the electrolyte conductance.

Table 4.4 Percentage of PAM that maximize the electrolyte conductance at each silica content

SiO_2 (%w/v)	PAM (%w/v)	σ (mS/cm)
1	0.001	824 ± 2
2	0.02	873 ± 3
3	0.02	839 ± 4
4	0.02	830 ± 3

4.2.3 Effect of polyacrylamide on gelling time and gel strength

Gelling time of the electrolyte was monitored in two containers, 10-mL test tube and 50-mL beaker. The beaker was a regular container used to prepare the electrolyte mixture in laboratory. The test tube was included in this study because it represents a tall shape with small open on top which similarly to the battery cell.

The electrolytes containing 1, 2, 3 and 4%w/v fumed silica in 35%w/v sulfuric acid included with difference percentages of PAM were examined. The mixtures of 1 and 2%w/v fumed silica were, unfortunately, not thoroughly form gel with in 36 hours at any percentage of PAM added. Therefore, these electrolyte contents were not included in this study. For the electrolytes containing 3 and 4%w/v fumed silica in 35%w/v sulfuric acid included with PAM, gel-form electrolyte appeared in every percentage of PAM added, up to 0.02%w/v, as shown in Figure 4.5. Therefore, these mixtures would be used to study the effect of gelling time and gel strength.

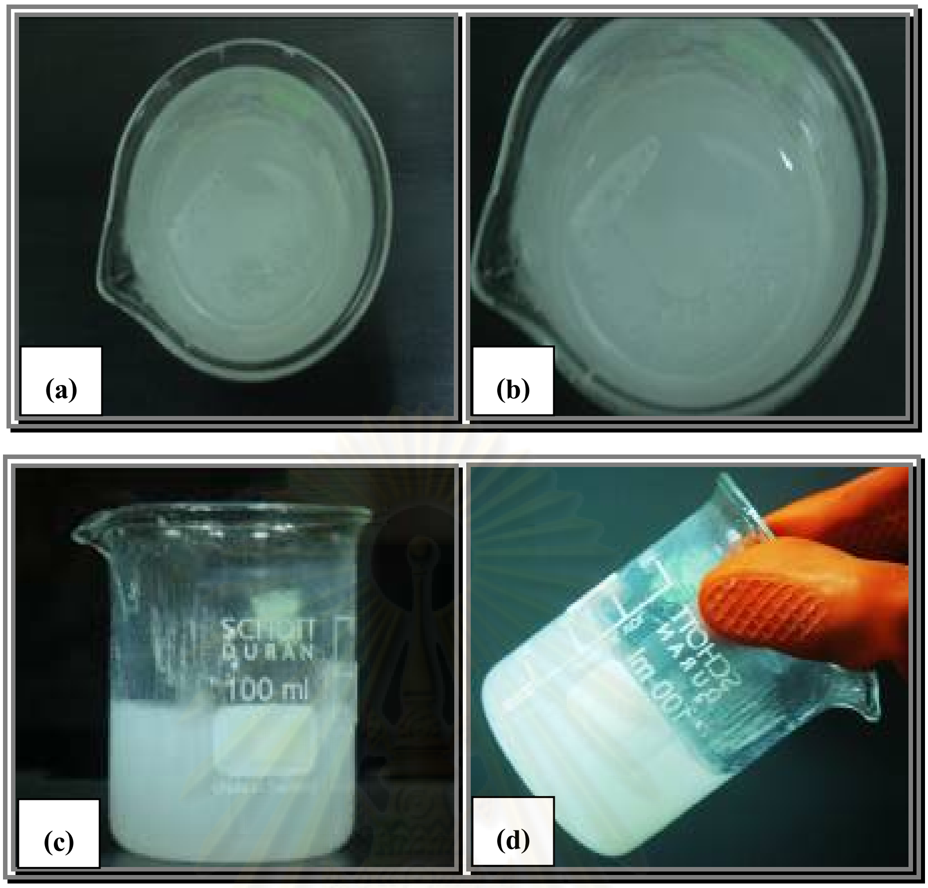

Figure 4.5 A gel formation of electrolyte containing 3%w/v fumed silica and 0.016%w/v PAM in 35%w/v sulfuric acid after prepared and left for 24 hours; (a) and (b) top view, (c) and (d) side view

Figure 4.6 shows a continuously decrease in gelling time when more percentage of PAM was added into the electrolyte. This happened in both containers. In addition, the electrolyte containing higher percentage of silica provided a smaller number in gelling time when compared at the same percentage of PAM.

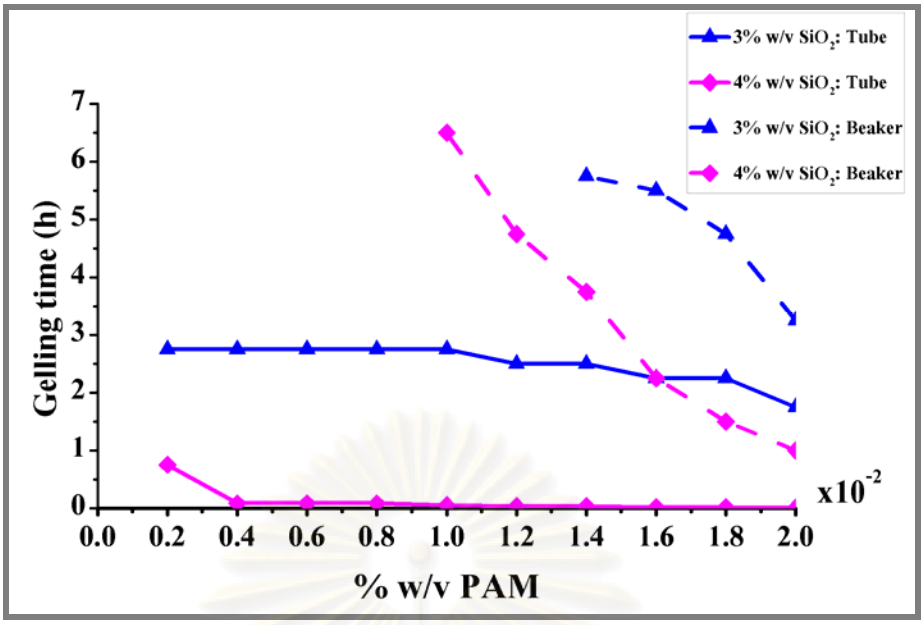

Figure 4.6 Gelling time of electrolytes containing 3 and 4%w/v fumed SiO_2 in 35%w/v sulfuric acid and polyacrylamide in test tubes and beakers

Unlike the gelling time, PAM showed an opposite trend on the gel strength. Figure 4.7 shows that the penetration depth decreased with an increase of PAM percentage in beaker container. The penetration depth, measured at 24 hours right after the electrolyte was thoroughly mixed, is reciprocal to the gel strength. The deeper the penetration indicates the weakness in gel strength. An acceptable of gel structure was determined when the penetration depth of the lead ball is about 2-3 mm [11]. Therefore, Figure 4.7 suggests that the gel strength of the electrolyte could be improved by an addition of PAM. The result agrees with the previous study [16] which revealed that the amide groups in PAM form hydrogen bonding with silica particles and intra-molecular hydrogen bonds form between the amide groups of PAM. This reason indicates that the electrolyte with PAM additive provide a stronger structure. Note here that the constancy of 35-mm penetration depth appeared at the low percentages of PAM added dued to a limited height of the beaker container. The same study was also done in the test-tube container and 0-mm penetration depth was obtained in all electrolyte mixtures. Thus, the data were not considered here.

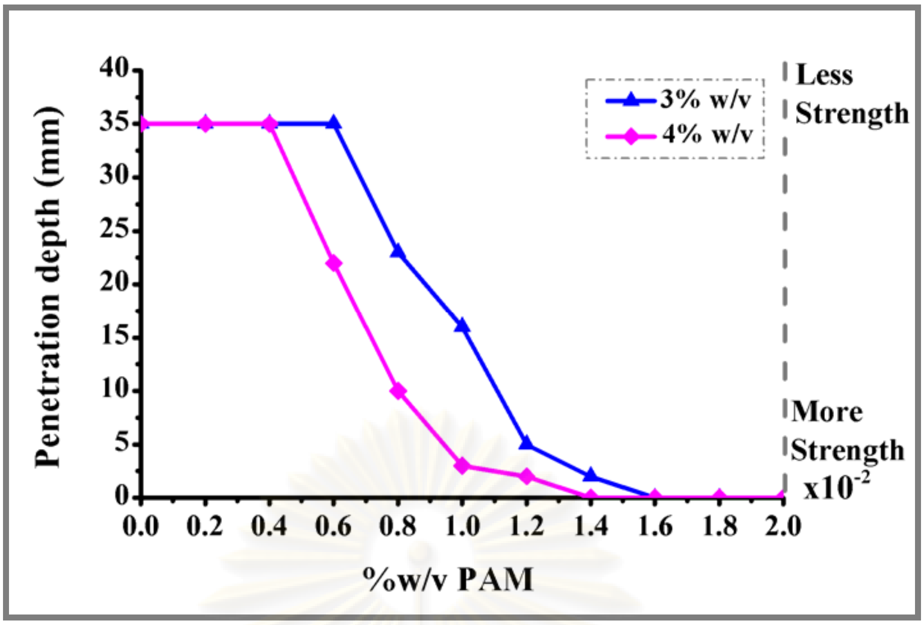

Figure 4.7 Penetration depth of a 0.3-g lead ball in electrolytes containing 3 and 4%w/v fumed silica in 35%w/v sulfuric acid and polyacrylamide

It is clear that to achieve a high gel strength which would consecutively provide a long service life battery [22] with an appropriate gelling time, the amount of PAM added into the silica-based electrolyte should be controlled.

4.2.4 Influence of operating temperature on gelling time

Apart from the influence of silica content on the gelling time, operating temperature was studied. The electrolytes containing 3, 4 and 6%w/v fumed silica in 35%w/v sulfuric acid with various amount of PAM were prepared at different temperatures; 15^{o}C, 24^{o}C, and 80^{o}C. Figure 4.8 shows, at all electrolyte contents, an increase of gelling time with decreasing the operating temperature. For the electrolytes containing 3 and 4%w/v fumed silica prepared at 15^{o}C, their gelling times were over than 36 hours. Therefore, these data were not included on the scale in Figure 4.8. Effect of the operating temperature was obvious in the electrolyte containing high silica percentage. Thus, the electrolyte containing 6%w/v fumed silica was also displayed in Figure 4.8. The results indicated that low operating temperature expanded the gelling time of the electrolyte. This information could be useful in correcting the short gelling time that occurred when high percentage of PAM added.

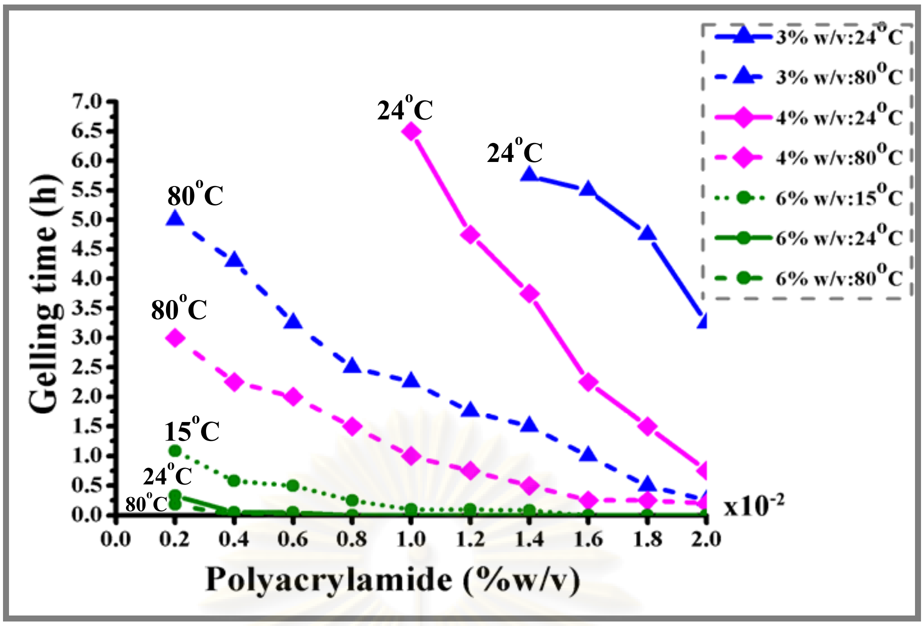

Figure 4.8 Gelling time of electrolytes containing 3, 4 and 6%w/v fumed silica in 35%w/v sulfuric acid and polyacrylamide. The electrolytes were prepared at 15°C, 24°C and 80°C.

4.2.5 Electrolyte formation in cell battery

In an industrial battery filling process, the prepared electrolyte should not form gel prior to be fully filled into a battery. Therefore the percentage of fumed silica in the electrolyte should be kept as low as possible, results discussed in section 4.2.1. Electrolytes containing 1, 2 and 3%w/v fumed silica and PAM in 35%w/v sulfuric acid were, then, considered for this study. According to the electrolyte conductivity, gelling time and gel strength studied in section 4.2.2 and 4.2.3, 0.001%w/v, 0.02%w/v and 0.016%w/v of PAM were selected as an optimum additive percentage that suit for the electrolytes containing 1, 2 and 3%w/v fumed silica, respectively.

The formations of these electrolytes after filled into 12V/4Ah batteries were shown in Figure 4.9 – 4.11. Figure 4.9 demonstrates that a suspended form obtained from the electrolyte containing 1%w/v fumed silica. A perfect gel formation occurred, Figure 4.10, in the electrolyte containing 2%w/v fumed silica and unfully filled electrolyte occurred in the electrolyte containing 3%w/v fumed silica, Figure 4.11.

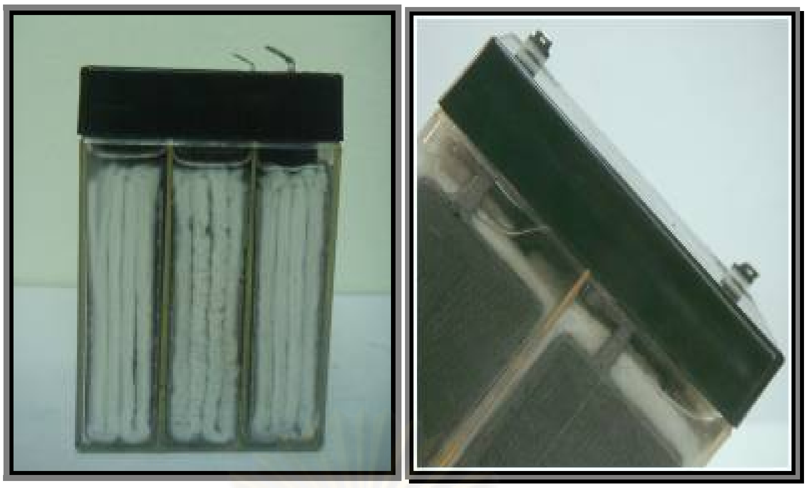

Figure 4.9 A battery filled with electrolyte containing 1%w/v fumed silica and 0.001%w/v PAM in 35%w/v sulfuric acid

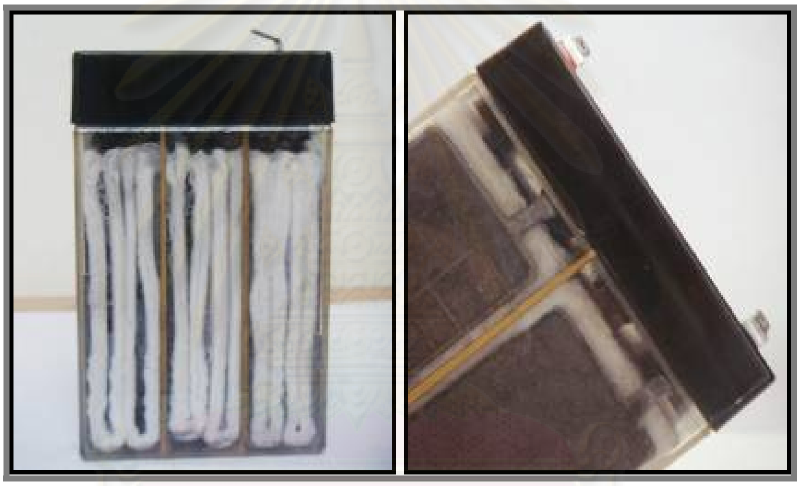

Figure 4.10 A battery filled with electrolyte containing 2%w/v fumed silica and 0.02%w/v PAM in 35%w/v sulfuric acid

Figure 4.11 shows the battery that was filled with the electrolyte containing 3%w/v fumed silica and 0.016%w/v PAM in 35%w/v sulfuric acid. It was found that the electrolyte could not fully be filled into the battery. This could caused by a reaction between the electrolyte and charged electrodes in the battery cell. In general, the electrodes in battery are 80% charged prior to be composed in a battery. When the electrolyte is in contact with these eletrodes, the gel formation process would be accelerated.

From the result, it is noted that the prepared electolyte containing 3%w/v fumed silica is not potentially to be used as an industry product because of the limitation in the battery filling process. Thus, the electrolyte containing 1 and 2%w/v fumed silica should be developed in the further studies.

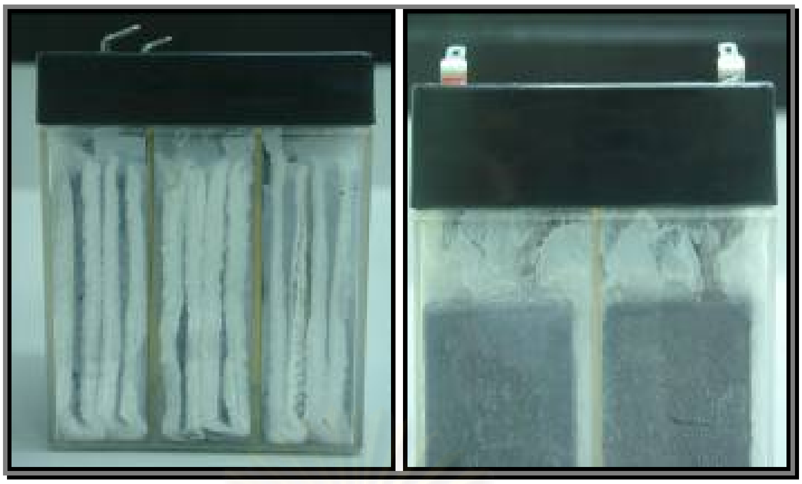

Figure 4.11 A battery filled with electrolyte containing 3%w/v fumed silica and 0.016%w/v PAM in 35%w/v sulfuric acid

4.3 Addition of sulfate salt as an electrolyte additive

The aim of this study is to understand an effect of sulfate salt additive in the silica-based electrolyte and on the battery capacity. Sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$) and potassium sulfate (K_2SO_4) will be used in this study.

Due to a difficulty of filling process in the industrial occurred from the electrolyte containing 3%w/v fumed silica in 35%w/v sulfuric acid, the electrolyte of lower percentage of silica was considered to be developed. Thus, 1 and 2%w/v fumed silica electrolytes will be used in the following investigations.

4.3.1 Effect of sulfate salt on the conductance

The conductivity of electrolytes containing sulfate salt; Na_2SO_4, $MgSO_4$ or K_2SO_4, was studied. Measurements were done in the suspended electrolytes containing various percentages of sulfate salt from 0.2 to 3.0%w/v. Figure 4.12 and 4.13 present the effect of sulfate salt on the conductivity of electrolytes prepared with 1 and 2%w/v fumed silica in 35%w/v sulfuric acid, respectively. Both plots show that the electrolyte conductance decreases as percentage of any sulfate salt increases. Although, the three sulfate salts gave almost the same conductance value at the same percentage of added sulfate salt, electrolyte containing potassium sulfate as an additive provided the highest conductance value among them.

Refer to the results in section 4.1.2, a similar trend observed after the conductance reach the highest point at 35%w/v sulfuric acid for electrolytes containing 1-4%w/v fumed silica. That is the conductance decreases with higher percentage of added sulfuric acid. The similarity from the sulfuric acid, in section 4.1.2, and from the effect of sulfate salt, Figure 4.12 and 4.13, suggest that the decrease in the electrolyte conductivity dues to an excess mole of sulfate ion alone, regardless of cation.

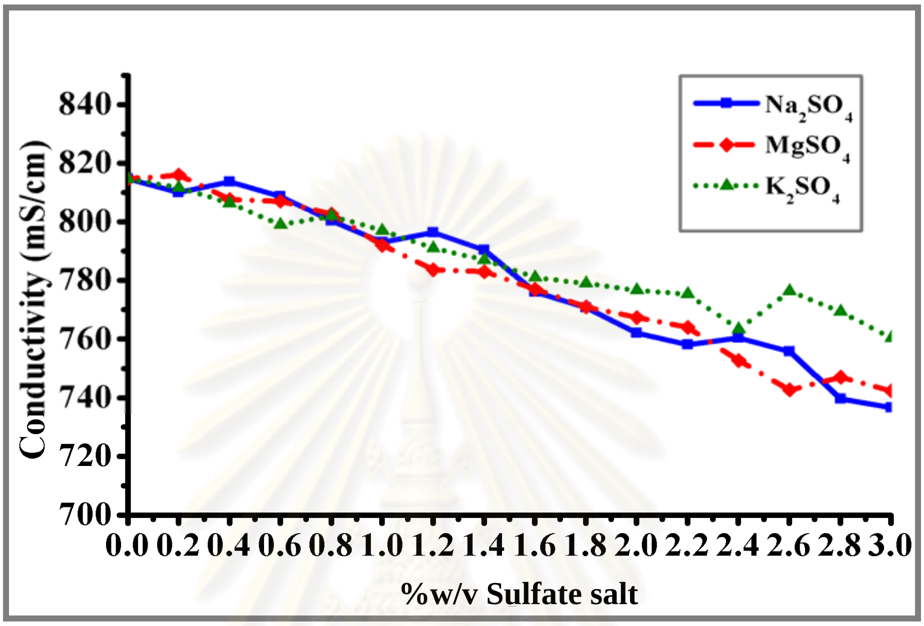

Figure 4.12 Conductivity of electrolytes containing 1%w/v fumed silica in 35%w/v H_2SO_4 and different percentages of sulfate salt additives: Na_2SO_4, $MgSO_4$ and K_2SO_4

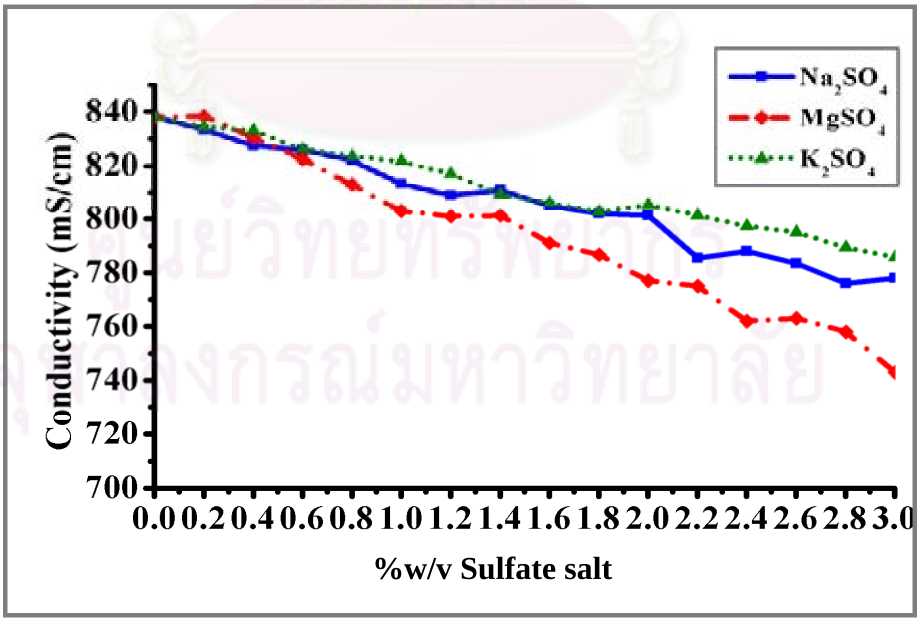

Figure 4.13 Conductivity of electrolytes containing 2%w/v fumed silica in 35%w/v H_2SO_4 and different percentages of sulfate salt additives: Na_2SO_4, $MgSO_4$ and K_2SO_4

4.3.2 Effect of sulfate salt on the gelling time

Due to a slow process of gel formation in laboratory condition, electrolyte containing high percentage silica, 8%w/v fumed silica in 15%w/v sulfuric acid, was chosen to represent a study in the effect of sulfate salt additive on gelling time. The amount of 0.5 and 3.0%w/v of sulfate salt; Na_2SO_4, $MgSO_4$ or K_2SO_4, was added in the electrolyte and the gelling time was monitored. The results were reported in Table 4.5. The comparisons were performed with a controlled electrolyte which no adding salt. These results indicate that sulfate salt additive lengthen the electrolyte gelling time and the more the salt additive added, the longer the time required for gel formation. It is possible that most of the silanol groups (Si–OH) of fumed silica in electrolyte come in contact and create the bridge linkage by exchange of their hydrogen molecules (Figure 1.4). When sulfate salt was added, the cation adsorbed onto the –OH group, on the silica surface, displacing and disrupting the hydrogen-bond network around the silica particles. Therefore, electrolyte took a long time to form gel. In addition, among the three sulfate salts, $MgSO_4$ showed the longest gelling time.

Table 4.5 Gelling time of electrolytes containing 8%w/v fumed silica in 15%w/v sulfuric acid and sulfate salt additive

%w/v Sulfate salt	Gelling time (hour)
None	7.50
0.5% Na_2SO_4	8.00
3.0% Na_2SO_4	8.45
0.5% $MgSO_4$	8.30
3.0% $MgSO_4$	10.00
0.5% K_2SO_4	7.75
3.0% K_2SO_4	9.00

Gel strength of the electrolytes containing 8%w/v fumed silica in 15%w/v sulfuric acid with different sulfate salts were not reported because their penetration depths were all 0 mm after prepared and left for 24 hours.

4.4 Addition of PAM and sulfate salt additives in the electrolyte

PAM and sulfate salt; Na_2SO_4, $MgSO_4$ or K_2SO_4, additives were added in the electrolyte. Then, conductivity and gelling time were investigated.

4.4.1 Effect of mixed additives on the electrolyte conductance

The conductivities of 1 and 2%w/v fumed silica in 35%w/v sulfuric acid electrolytes containing PAM and sulfate salt (Na_2SO_4, $MgSO_4$ or K_2SO_4) additives were studies.

Percentage of PAM that provided the highest electrolyte conductance for each electrolyte component, based on the result in Table 4.4, was selected and fixed. That are 0.001%w/v and 0.020%w/v PAM were added into the electrolyte containing 1%w/v and 2%w/v fumed silica, respectively. Then, percentage of sulfate salt; Na_2SO_4, $MgSO_4$ or K_2SO_4, in the electrolytes was altered in the range of 0.2–2.0%w/v. Figure 4.14 and 4.15 represent an effect of the mixed additives on the electrolyte conductance. The result showed that the conductivity decreased with increasing the percentage of sulfate salt. At the same percentage of added sulfate salt, the electrolyte contained $MgSO_4$ provided the lowest conductivity.

Compare to the conductivity of electrolytes without additive (815 and 838 mS/cm for 1 and 2%w/v fumed silica electrolyte, respectively -Table 4.2) and electrolytes with PAM additive (824 and 873 mS/cm for 1 and 2%w/v fumed silica electrolyte, respectively -Table 4.4), the electrolytes containing the mixed additives gave a higher conductance than those without additive and lower than those electrolytes added PAM. When compare to the electrolytes with a single sulfate salt (Figure 4.12 – 4.13), it was found that the electrolytes with the mixed additive gave the higher conductance in all percentages of sulfate salt.

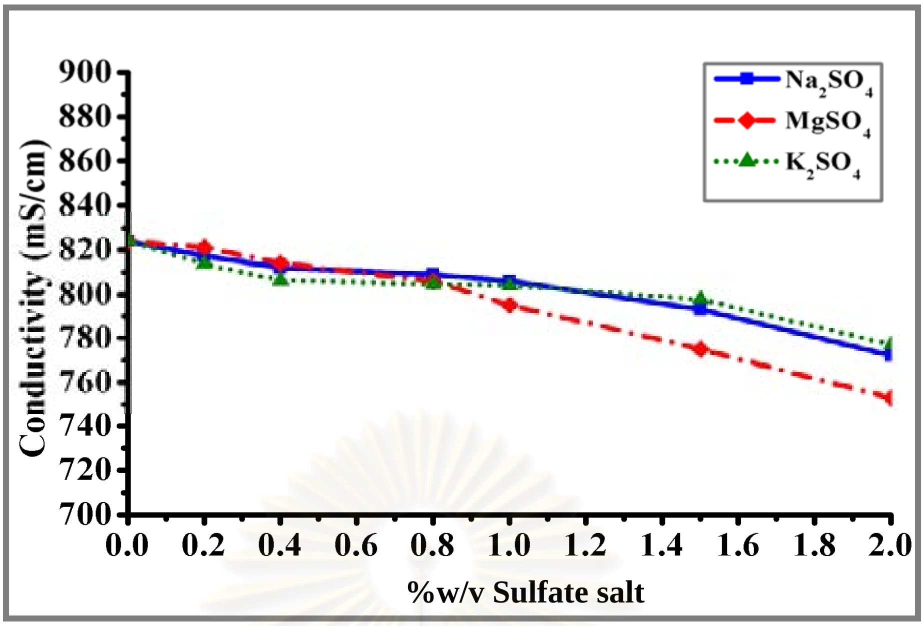

Figure 4.14 Conductivity of electrolytes containing 1%w/v fumed silica, 0.001%w/v PAM and sulfate salt: Na_2SO_4, $MgSO_4$ or K_2SO_4 in 35%w/v H_2SO_4

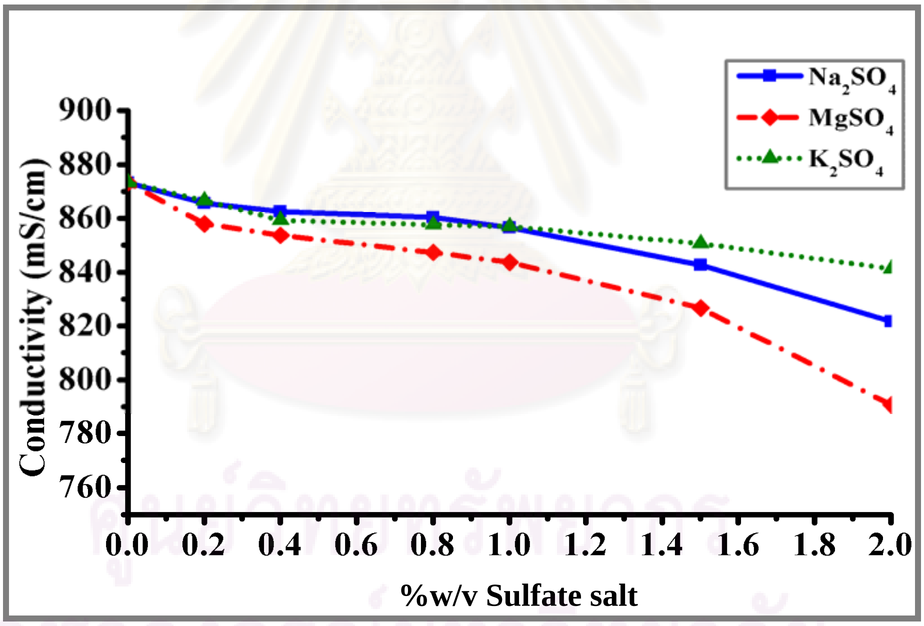

Figure 4.15 Conductivity of electrolytes containing 2%w/v fumed silica, 0.02%w/v PAM and sulfate salt: Na_2SO_4, $MgSO_4$ or K_2SO_4 in 35%w/v H_2SO_4

4.4.2 Effect of mixed additives on gelling time

As stated in section 4.3.2, electrolyte with high percentage silica suit for the gelling time study. Thus, electrolyte containing 8%w/v fumed silica and 0.02%w/v PAM in 15%w/v sulfuric acid was selected for this study by varying the percentage of sulfate salt added, 0.5 and 3.0%w/v. Table 4.6 presents the gelling time of electrolytes containing 8%w/v fumed silica in 15%w/v sulfuric acid with the mixed additives; PAM and sulfate salt. These results showed that the mixed additives lengthen the electrolyte gelling time and the more the sulfate salt added, the longer the time required for gel formation. In addition, among the three sulfate salts, $MgSO_4$ resulted in the longest gelling time.

Table 4.6 Gelling time of electrolytes containing 8%w/v fumed silica and 0.02%w/v PAM in 15%w/v sulfuric acid with sulfate salt additive

%w/v Sulfate salt	**Gelling time (min)**
None	5
0.5% Na_2SO_4	8
3.0% Na_2SO_4	12
0.5% $MgSO_4$	13
3.0% $MgSO_4$	20
0.5% K_2SO_4	7
3.0% K_2SO_4	15

Gel strength of the electrolytes containing 8%w/v fumed silica and 0.02%w/v PAM in 15%w/v sulfuric acid with different sulfate salts were not reported because their penetration depths were all 0 mm after prepared and left for 24 hours.

4.5 Battery performance

In this section, selected electrolytes with and without additive studied previously were filled into 12V/4Ah VRLA batteries using electrolyte filling machine, Figure 3.1. Each battery was named according to the electrolyte composition and they were listed in Table 4.7. All batteries will be examined in term of capacity, discharge time and battery efficiency.

Table 4.7 Batteries filled with different electrolyte compositions

Battery	**Electrolyte composition**		
	SiO_2 (%w/v)	**H_2SO_4 (%w/v)**	**Additive (%w/v)**
1Si	1	35	None
1SiP	1	35	0.001% PAM
1SiNa	1	35	2.5% Na_2SO_4
1SiMg	1	35	2.5% $MgSO_4$
1SiK	1	35	2.5% K_2SO_4
1SiPNa	1	35	0.001% PAM and 2.5% Na_2SO_4
1SiPMg	1	35	0.001% PAM and 2.5% $MgSO_4$
1SiPK	1	35	0.001% PAM and 2.5% K_2SO_4
2Si	2	35	None
2SiP	2	35	0.02% PAM
2SiNa	2	35	2.5% Na_2SO_4
2SiPNa	2	35	0.02% PAM and 2.5% Na_2SO_4

4.5.1 Discharge capacity

The prepared batteries were charged and discharged for 50 cycles. A discharge capacity for each cycle was calculated from an area under a curve of current versus time. Then, the calculated-discharge capacity was plots against the number of cycle. Figure 4.16 represents plots of discharge capacity of batteries containing silica-based gelled electrolyte with 0.001%w/v PAM additive (Figure 4.16 battery 1SiP) and without additive (Figure 4.16 battery 1Si). Both plots show a nearly consistence of the discharge capacity thorough out the first fifty cycles. The same behavior was also found in the other batteries. Average discharge capacity values for the first twenty-five and fifty cycles of each battery were concluded in Table 4.8.

In Table 4.8, the average discharge capacity values for the first 25 and 50 cycles of batteries containing 1%w/v silica-based electrolyte were compared. Less than 3% differ between the two averaged values were observed for all batteries.

These results confirm a consistency in discharge capacity of the VRLA battery. From this consistency, all batteries containing 2%w/v silica-based electrolyte were run for 25 cycles and the discharge capacities were calculated, as listed in Table 4.8.

At each percentage of silica-based electrolyte, all batteries containing electrolyte with additive provided higher capacity than the one that containing the electrolyte without additive. Among the batteries that contained single-additive electrolyte, battery 1SiNa and 2SiNa provided the highest capacity in the battery set containing 1 and 2%w/v silica-based electrolytes, respectively. Moreover, the batteries containing single-additive electrolyte trended to have a higher capacity than those containing the mixed-additive electrolyte, when compared under similar conditions. These results suggested that the mix-additive electrolyte does not enhance the battery capacity as powerful as the single-additive electrolyte and among additives in this study, Na_2SO_4 improved the battery capacity the most.

In comparison between the battery 1SiNa and 2SiNa when Na_2SO_4 was added equally as an additive into the 1 and 2%w/v fumed silica electrolytes, respectively, the battery containing 2%w/v silica-based electrolyte provided a higher capacity than the one with 1%w/v silica-based electrolyte and this was true for all batteries containing 2%w/v silica-based electrolyte when compared at the same additive.

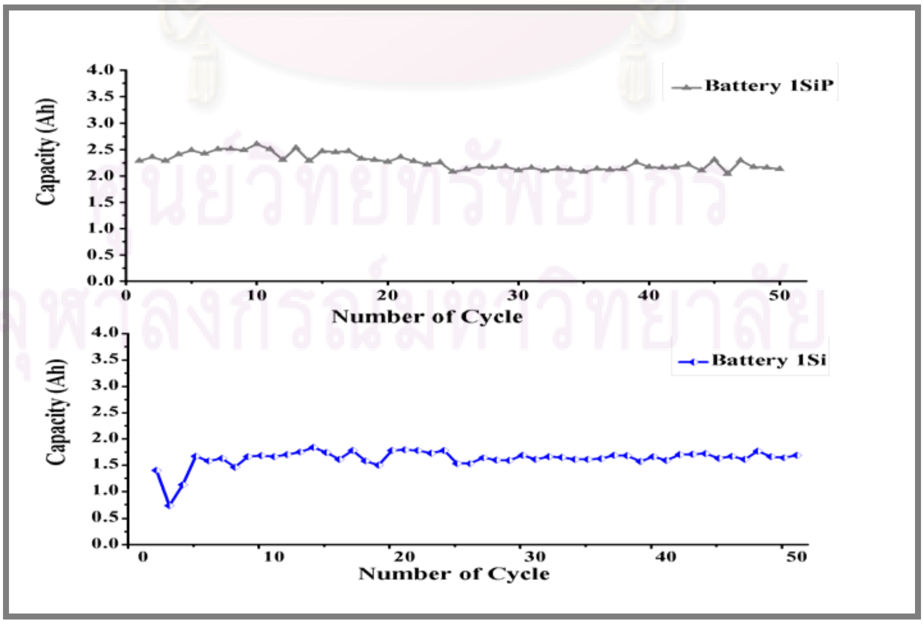

Figure 4.16 Discharge capacity during 50 test cycles of VRLA batteries containing (Battery 1Si) 1%w/v SiO_2 in 35%w/v H_2SO_4 and (Battery 1SiP) 1%w/v SiO_2 and 0.001%w/v PAM in 35%w/v H_2SO_4

Table 4.8 Average discharge capacity value for the 25 and 50 cycles of 12V/4Ah VRLA batteries containing different electrolytes

Battery	**Additive**	**Average discharge capacity (Ah)**	
		25 cycles	**50 cycles**
1Si	None	1.93	1.88
1SiP	0.001% PAM	2.29	2.22
1SiNa	2.5% Na_2SO_4	2.42	2.36
1SiMg	2.5% $MgSO_4$	2.19	2.12
1SiK	2.5% K_2SO_4	2.15	2.09
1SiPNa	0.001% PAM + 2.5% Na_2SO_4	2.25	2.18
1SiPMg	0.001% PAM + 2.5% $MgSO_4$	2.14	2.11
1SiPK	0.001% PAM + 2.5% K_2SO_4	2.02	1.96
2Si	None	2.35	-
2SiP	0.02% PAM	2.44	-
2SiNa	2.5% Na_2SO_4	2.57	-
2SiPNa	0.02% PAM + 2.5% Na_2SO_4	2.38	-

*All batteries were named upon the contained electrolyte composition as listed in Table 4.7

4.5.2 Discharge time

The period of battery usage usually results in discharge time and this can deteriorate the discharge performance of batteries. Figure 4.17 represents plots of discharge time of batteries containing silica-based gelled electrolyte with 0.001%w/v PAM additive (Figure 4.17 battery 1SiP) and without additive (Figure 4.17 battery 1Si). Both plots show a nearly consistence of the discharge time thorough out the first fifty cycles. The same behavior was also found in the other batteries. Average discharge time values for the first twenty-five and fifty cycles of each battery were concluded in Table 4.9.

In Table 4.9, the average discharge time values for the first 25 and 50 cycles of batteries containing 1%w/v silica-based electrolyte were compared. Less than 5% differ between the two averaged values were observed for all batteries. These results confirm a consistency in discharge time of the VRLA battery. From this consistency, all batteries containing 2%w/v silica-based electrolyte were run for 25 cycles and the discharge times were calculated, as listed in Table 4.9.

At each percentage of silica-based electrolyte, all batteries containing electrolyte with additive provided longer discharge time than the one that containing the electrolyte without additive. Among the batteries that contained single-additive electrolyte, battery 1SiNa and 2SiNa provided the longest discharge time in the battery set containing 1 and 2%w/v silica-based electrolytes, respectively. Moreover, the batteries containing single-additive electrolyte trended to have a longer discharge time than those containing the mixed-additive electrolyte, when compared under similar conditions. These results suggested that the mix-additive electrolyte does not enhance the battery usage period as much as the single-additive electrolyte and among additives in this study, Na_2SO_4 improved the battery discharge time the most.

In comparison between the battery 1SiNa and 2SiNa when Na_2SO_4 was added equally as an additive into the 1 and 2%w/v fumed silica electrolytes, respectively, the battery containing 2%w/v silica-based electrolyte provided a longer discharge time than the one with 1%w/v silica-based electrolyte and this was true for all batteries containing 2%w/v silica-based electrolyte when compared at the same additive.

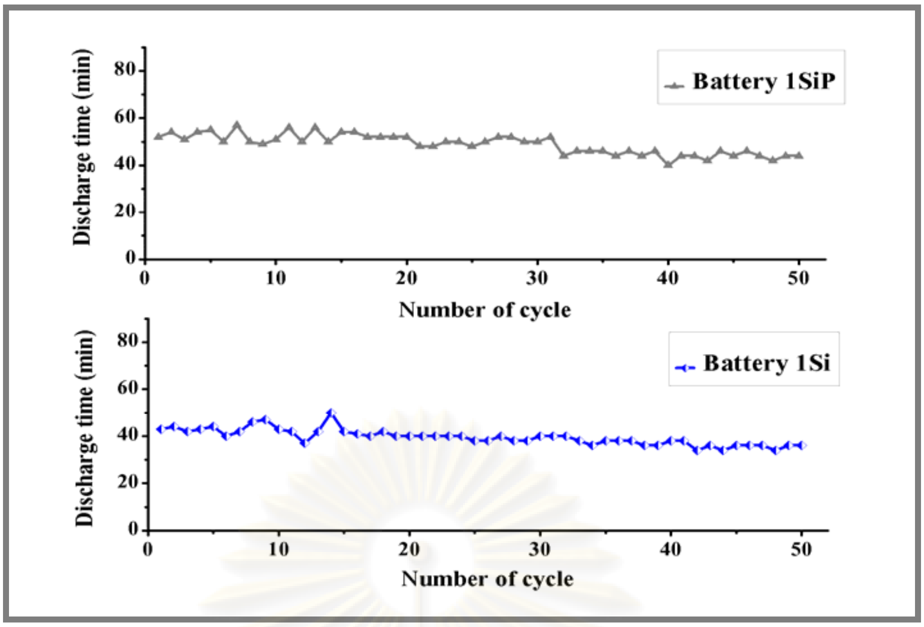

Figure 4.17 Discharge time during 50 test cycles of VRLA batteries containing (Battery 1Si) 1%w/v SiO_2 in 35%w/v H_2SO_4 and (Battery 1SiP) 1%w/v SiO_2 and 0.001%w/v PAM in 35%w/v H_2SO_4

Table 4.9 Average discharge time value for the 25 and 50 cycles of 12V/4Ah VRLA batteries containing different electrolytes

Battery	**Additive**	**Average discharge time (min)**	
		25 cycles	**50 cycles**
1Si	None	42	40
1SiP	0.001% PAM	52	49
1SiNa	2.5% Na_2SO_4	52	51
1SiMg	2.5% $MgSO_4$	47	45
1SiK	2.5% K_2SO_4	46	44
1SiPNa	0.001% PAM + 2.5% Na_2SO_4	49	47
1SiPMg	0.001% PAM + 2.5% $MgSO_4$	46	45
1SiPK	0.001% PAM + 2.5% K_2SO_4	43	42

Table 4.9 (continue) Average discharge time value for the 25 and 50 cycles of 12V/4Ah VRLA batteries containing different electrolytes

Battery	**Additive**	**Average discharge time (min)**	
		25 cycles	**50 cycles**
2Si	None	49	-
2SiP	0.02% PAM	52	-
2SiNa	2.5% Na_2SO_4	54	-
2SiPNa	0.02% PAM + 2.5% Na_2SO_4	50	-

*All batteries were named upon the contained electrolyte composition as listed in Table 4.7

4.5.3 Efficiency of battery

The prepared batteries were charged and discharged for 50 cycles. The charge and discharge capacities for each cycle were calculated from an area under a curve of current versus time. Then, the battery efficiency was calculated using equation 2.12. Table 4.10 presents average charge capacity, average discharge capacity and the calculated battery efficiency for the first twenty-five and fifty cycles of each battery.

In Table 4.10, the battery efficiency values for the first 25 and 50 cycles of batteries containing 1%w/v silica-based electrolyte were compared. Less than 2% differ between the two averaged values were observed for all batteries. These results, again, confirm a consistency in charge capacity and discharge capacity of the VRLA battery. From this consistency, all batteries contained 2%w/v silica-based gelled electrolyte were run for 25 cycles and the battery efficiencies were calculated, as listed in Table 4.10.

At each percentage of silica-based electrolyte, all batteries containing electrolyte with additive provided greater battery efficiency than the one that containing the electrolyte without additive. Among the batteries that contained single-additive electrolyte, battery 1SiNa and 2SiNa provided the greatest battery efficiency in the battery set containing 1 and 2%w/v silica-based electrolytes, respectively. Moreover, the batteries contain single-additive electrolyte trended to have a greater battery efficiency than those containing the mixed-additive electrolyte, when compared under similar conditions. These results suggested that the mix-additive electrolyte does not enhance the battery efficiency as much as the single-additive electrolyte and among additives in this study, Na_2SO_4 improved the battery efficiency the most.

In comparison between the battery 1SiNa and 2SiNa when Na_2SO_4 was added equally as an additive into the 1 and 2%w/v fumed silica electrolytes, respectively, the battery containing 2%w/v silica-based electrolyte provided the greater battery efficiency than the one with 1%w/v silica-based electrolyte and this was true for all batteries containing 2%w/v silica-based electrolyte when compared at the same additive.

Table 4.10 Battery efficiency for the 25 and 50 cycles of 12V/4Ah VRLA batteries containing different electrolytes

Battery	**Additive**	**Average charge capacity (Ah)**		**Average discharge capacity (Ah)**		**Battery efficiency (%)**	
		25 cycles	**50 cycles**	**25 cycles**	**50 cycles**	**25 cycles**	**50 cycles**
Si	No	2.50	2.47	1.93	1.88	77.49	76.22
1SiP	PAM	2.52	2.46	2.29	2.22	90.96	90.34
1SiNa	Na_2SO_4	2.61	2.56	2.42	2.36	92.62	92.19
1SiMg	$MgSO_4$	2.63	2.58	2.19	2.12	83.42	82.07
1SiK	K_2SO_4	2.65	2.60	2.15	2.09	81.11	80.23
1SiPNa	PAM + Na_2SO_4	2.54	2.50	2.25	2.18	88.64	87.08
1SiPMg	PAM + $MgSO_4$	2.62	2.58	2.16	2.11	82.62	81.93
1SiPK	PAM + K_2SO_4	2.55	2.46	2.02	1.96	79.35	79.12
2Si	No	2.50	-	2.35	-	94.15	-
2SiP	PAM	2.51	-	2.44	-	97.29	-
2SiNa	Na_2SO_4	2.62	-	2.57	-	98.01	-
2SiPNa	PAM+Na_2SO_4	2.49	-	2.38	-	95.34	-

*All batteries were named upon the contained electrolyte composition as listed in Table 4.7

CHAPTER V

CONCLUSIONS

In this thesis, gelled electrolyte for valve-regulated lead-acid (VRLA) battery has been developed. The ratio of gelling agents; fumed silica and sulfuric acid, were optimized. After mixing, the electrolytes were observed in two forms. One was a suspension at low percentage of sulfuric acid and fumed silica and the other was a gel at high percentage of the reagents. The electrolytes contained 1-4%w/v fumed silica in 35%w/v sulfuric acid provided high conductance over than 800 mS/cm. Polyacrylamide (PAM) and sulfate salt; Na_2SO_4, $MgSO_4$ or K_2SO_4 were used as additives to improve the gelled electrolyte performance. Increasing in conductance, improving in gel strength and shortening in gelling time were observed when PAM was included into the electrolyte. The gelling time, in addition, could be extended by using a low operating temperature. Therefore, addition of PAM into the electrolyte at controlled low temperature would give a strengthen-gelled electrolyte that has an appropriate gelling time. Unlike the PAM additive, addition of sulfate salt or mixed additive; PAM and sulfate salt, in the electrolyte caused a decrease in conductivity and increase the gelling time. However, addition of sulfate salt or mixed additive in the electrolyte enhanced the performance of battery in term of capacity, usage period and battery efficiency.

On performance of the VRLA battery filled with the developed electrolyte, electrolyte containing additive gave a higher capacity, longer discharge time and greater battery efficiency than the battery filled with electrolyte without additive. Moreover, the batteries containing single-additive electrolyte trend to have higher capacity, longer discharge time and greater battery efficiency than those containing the mixed-additive electrolyte, when compare under similar conditions. Compare between batteries that contained the same additive species and volume, the battery containing 2%w/v silica-based electrolyte provided a higher capacity, longer discharge time and greater battery efficiency than the one with 1%w/v silica-based electrolyte.

The best performance battery was found in battery filled with electrolyte containing 2%w/v SiO_2 and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 which provides 2.57 Ah capacity, 54 min usage time and 98.01% battery efficiency.

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APPENDIX

APPENDIX

Table A1 Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1Si) 1%w/v SiO_2 in 35%w/v H_2SO_4 and (Battery 1SiP) 1%w/v SiO_2 and 0.001%w/v PAM in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1Si**		**Battery 1SiP**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
1	2.16	1.65	2.42	2.29
2	2.22	0.98	2.59	2.36
3	2.3	1.38	2.51	2.29
4	2.52	1.92	2.58	2.41
5	2.41	2.04	2.54	2.44
6	2.49	1.96	2.55	2.43
7	2.42	1.91	2.57	2.45
8	2.51	2.04	2.54	2.42
9	2.53	1.93	2.48	2.39
10	2.46	1.92	2.47	2.41
11	2.48	1.95	2.57	2.46
12	2.53	2.00	2.51	2.31
13	2.55	2.09	2.55	2.44
14	2.52	1.99	2.57	2.29
15	2.47	1.96	2.64	2.42
16	2.53	2.03	2.62	2.45
17	2.46	1.83	2.71	2.42
18	2.42	1.93	2.42	2.17
19	2.48	2.03	2.44	2.15
20	2.49	2.04	2.39	2.10
21	2.54	2.03	2.34	1.96
22	2.51	1.98	2.39	1.88
23	2.55	2.05	2.50	2.16
24	2.41	1.96	2.61	2.26
25	2.43	1.97	2.35	2.01
26	2.49	1.88	2.39	2.13
27	2.46	1.85	2.44	2.15

Table A1 (continue) Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1Si) 1%w/v SiO_2 in 35%w/v H_2SO_4 and (Battery 1SiP) 1%w/v SiO_2 and 0.001%w/v PAM in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1Si**		**Battery 1SiP**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
28	2.45	1.84	2.50	2.16
29	2.54	1.83	2.44	2.11
30	2.43	1.88	2.49	2.11
31	2.51	1.71	2.45	2.16
32	2.49	1.91	2.37	1.97
33	2.46	1.86	2.21	2.14
34	2.4	1.86	2.40	2.12
35	2.29	1.67	2.28	2.05
36	2.54	1.94	2.34	2.14
37	2.5	1.93	2.41	2.12
38	2.45	1.82	2.32	2.13
39	2.53	1.91	2.61	2.16
40	2.46	1.84	2.20	2.17
41	2.55	1.93	2.39	2.16
42	2.51	1.78	2.40	2.17
43	2.49	1.78	2.21	2.22
44	2.46	1.89	2.19	2.11
45	2.48	1.92	2.43	2.31
46	2.45	1.86	2.57	2.14
47	2.48	1.97	2.74	2.25
48	2.5	1.91	2.38	2.12
49	2.46	1.89	2.40	2.11
50	2.55	1.99	2.44	2.03
Average	**2.47**	**1.88**	**2.46**	**2.22**

Table A2 Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1SiNa) 1%w/v SiO_2 and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 and (Battery 1SiMg) 1%w/v SiO_2 and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1SiNa**		**Battery 1SiMg**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
1	2.60	2.27	2.80	2.22
2	2.75	2.27	2.60	2.15
3	2.69	2.27	2.58	2.20
4	2.68	2.78	2.45	2.35
5	2.48	2.34	2.57	2.32
6	2.59	2.37	2.46	2.31
7	2.52	2.45	2.42	2.27
8	2.59	2.49	2.67	2.33
9	2.63	2.42	2.62	2.34
10	2.62	2.48	2.50	2.38
11	2.59	2.51	2.63	2.42
12	2.69	2.53	2.66	2.21
13	2.66	2.7	2.71	2.28
14	2.83	2.44	2.84	2.29
15	2.92	2.9	2.91	2.37
16	2.68	2.9	2.88	2.35
17	2.66	2.34	2.43	2.12
18	2.63	2.3	2.83	2.11
19	2.56	2.28	2.57	2.09
20	2.60	2.31	2.66	1.96
21	2.54	2.28	2.65	1.95
22	2.46	2.13	2.68	1.75
23	2.64	2.42	2.79	2.04
24	2.32	2.18	2.33	2.15
25	2.40	2.15	2.52	1.90
26	2.44	2.15	2.56	2.13
27	2.50	2.29	2.65	2.09
28	2.51	2.31	2.57	1.92
29	2.64	2.29	2.45	1.91
30	2.55	2.3	2.67	2.11

Table A2 (continue) Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1SiNa) 1%w/v SiO_2 and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 and (Battery 1SiMg) 1%w/v SiO_2 and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1SiNa**		**Battery 1SiMg**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
31	2.52	2.46	2.78	2.06
32	2.48	2.4	2.55	1.96
33	2.42	2.13	2.63	2.11
34	2.47	2.21	2.58	2.03
35	2.47	2.32	2.31	2.00
36	2.39	2.14	2.28	1.95
37	2.38	2.19	2.48	1.98
38	2.44	2.21	2.52	1.96
39	2.71	2.7	2.77	2.08
40	2.52	2.23	2.71	2.15
41	2.55	2.24	2.58	2.12
42	2.49	2.26	2.12	2.14
43	2.44	2.19	2.36	2.10
44	2.46	2.12	2.47	2.11
45	2.60	2.41	2.39	2.06
46	2.54	2.43	2.56	2.04
47	2.57	2.31	2.79	1.97
48	2.60	2.46	2.81	1.95
49	2.38	2.26	2.20	2.01
50	2.44	2.32	2.37	2.01
Average	**2.56**	**2.36**	**2.58**	**2.12**

Table A3 Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1SiK) 1%w/v SiO_2 and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4 and (Battery 1SiPNa) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1SiK**		**Battery 1SiPNa**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
1	2.65	2.04	1.77	2.26
2	2.86	2.17	2.38	1.44
3	2.32	2.08	3.11	2.31
4	2.23	2.14	2.56	2.29
5	2.47	2.44	2.58	2.44
6	2.29	2.16	2.58	2.29
7	2.19	2.22	2.46	2.17
8	2.20	2.22	2.73	2.36
9	2.19	2.27	2.54	2.35
10	2.59	2.39	2.50	2.26
11	2.48	2.30	2.48	2.32
12	2.43	2.06	2.50	2.33
13	2.53	2.15	2.68	2.35
14	2.76	2.29	2.44	2.34
15	2.66	2.23	2.41	2.35
16	2.59	2.47	2.51	2.36
17	2.87	1.92	2.42	2.25
18	2.87	2.11	2.27	2.24
19	2.75	2.12	2.79	2.31
20	2.61	1.98	2.51	2.35
21	2.82	1.97	2.80	2.33
22	2.77	1.90	2.42	2.17
23	2.78	2.05	2.72	2.28
24	2.47	2.15	2.68	2.10
25	2.59	2.04	2.73	2.10
26	2.69	2.07	2.46	2.16
27	2.58	2.12	2.52	2.14
28	2.61	2.04	2.56	2.08
29	2.62	1.90	2.52	2.16
30	2.77	1.98	3.26	2.27

Table A3 (continue) Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1SiK) 1%w/v SiO_2 and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4 and (Battery 1SiPNa) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1SiK**		**Battery 1SiPNa**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
31	2.66	2.09	2.88	2.40
32	2.99	1.93	2.30	2.01
33	2.49	2.02	2.33	2.05
34	2.72	1.91	2.16	2.10
35	2.50	2.01	2.68	2.28
36	2.67	1.99	2.27	2.08
37	2.70	1.97	2.27	2.04
38	2.72	2.13	2.53	2.30
39	2.50	2.10	2.21	2.05
40	2.63	2.02	2.46	2.09
41	2.51	2.09	2.76	2.20
42	2.62	2.20	2.15	2.11
43	2.74	2.13	3.05	1.98
44	2.60	2.14	2.33	2.03
45	2.66	1.88	2.36	1.97
46	2.75	2.10	2.38	2.02
47	2.63	1.96	2.47	2.05
48	2.77	1.75	2.09	1.99
49	2.53	2.00	2.33	1.97
50	2.51	2.01	2.24	2.02
Average	**2.60**	**2.09**	**2.50**	**2.18**

Table A4 Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1SiPMg) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 and (Battery 1SiPK) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1SiPMg**		**Battery 1SiPK**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
1	2.57	2.15	2.83	2.04
2	2.66	2.08	2.48	1.98
3	2.50	2.07	2.44	1.90
4	2.73	2.25	2.15	2.07
5	2.46	2.30	2.29	2.21
6	2.52	2.34	2.33	2.00
7	2.39	2.32	2.30	2.00
8	2.28	2.20	2.08	2.00
9	2.37	2.28	2.36	2.21
10	2.59	2.30	2.38	2.24
11	2.69	2.33	2.39	2.12
12	2.50	2.07	2.44	1.95
13	2.58	2.02	2.51	2.04
14	2.75	2.29	2.78	2.38
15	2.56	2.25	2.85	2.12
16	2.60	2.24	2.73	2.23
17	2.56	1.95	2.72	1.86
18	2.07	2.08	2.92	2.02
19	2.34	1.98	2.66	1.93
20	2.46	1.93	2.74	1.86
21	2.53	1.91	2.84	1.89
22	2.46	1.93	2.83	1.83
23	2.54	2.07	2.98	1.96
24	2.45	2.17	2.34	1.95
25	2.46	2.04	2.46	1.86
26	2.59	2.14	2.66	1.88
27	3.06	2.10	2.19	1.93
28	2.78	2.13	2.26	1.86
29	2.81	2.12	2.28	1.81
30	2.86	2.11	2.76	1.92

Table A4 (continue) Charge and discharge capacities of batteries filled with electrolytes containing (Battery 1SiPMg) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 and (Battery 1SiPK) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Battery 1SiPMg**		**Battery 1SiPK**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
31	2.84	1.96	3.06	1.93
32	2.43	2.15	2.67	1.76
33	2.76	2.13	2.34	1.74
34	2.47	2.12	2.31	1.84
35	2.53	2.07	2.26	1.83
36	2.67	2.08	2.32	1.83
37	2.60	2.01	2.28	1.81
38	2.82	2.06	2.36	1.89
39	2.46	2.17	2.31	1.86
40	2.92	2.22	2.28	1.84
41	2.98	2.20	2.20	1.83
42	2.52	2.15	2.32	1.89
43	2.77	2.11	2.26	1.84
44	2.42	2.08	2.31	1.83
45	2.53	2.07	2.24	1.78
46	2.89	1.98	2.31	1.81
47	2.92	1.88	2.34	1.69
48	2.61	1.99	2.44	1.60
49	2.56	2.13	2.15	1.64
50	2.81	2.05	2.25	1.71
Average	**2.58**	**2.11**	**2.46**	**1.92**

Table A5 Charge and discharge capacities of batteries filled with electrolytes containing (Battery 2Si) 2%w/v SiO_2 in 35%w/v H_2SO_4 and (Battery 2SiP) 2%w/v SiO_2 and 0.02%w/v PAM in 35%w/v H_2SO_4 during 25 cycles

Number of cycle	**Battery 2Si**		**Battery 2SiP**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
1	1.41	2.82	1.44	3.02
2	2.74	2.32	2.49	2.35
3	2.41	2.30	2.47	2.41
4	2.54	2.40	2.53	2.43
5	2.47	2.35	2.5	2.41
6	2.49	2.35	2.51	2.42
7	2.5	2.38	2.54	2.41
8	2.44	2.29	2.5	2.4
9	2.51	2.43	2.59	2.55
10	2.49	2.38	2.52	2.46
11	2.5	2.36	2.48	2.43
12	2.54	2.40	2.49	2.44
13	2.48	2.35	2.45	2.41
14	2.51	2.36	2.49	2.42
15	2.48	2.33	2.51	2.44
16	2.49	2.35	2.52	2.45
17	2.44	2.32	2.54	2.48
18	2.45	2.33	2.52	2.46
19	2.53	2.38	2.55	2.51
20	2.55	2.40	2.53	2.48
21	2.51	2.37	2.46	2.43
22	2.5	2.35	2.48	2.44
23	2.46	2.32	2.54	2.46
24	2.51	2.34	2.47	2.42
25	2.48	2.35	2.49	2.43
Average	2.50	2.35	2.51	2.44

Table A6 Charge and discharge capacities of batteries filled with electrolytes containing (Battery 2SiNa) 2%w/v SiO_2 and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 and (Battery 2SiPNa) 2%w/v SiO_2, 0.02%w/v PAM and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 during 25 cycles

Number of cycle	**Battery 2SiNa**		**Battery 2SiPNa**	
	Charge capacity (Ah)	**Discharge capacity (Ah)**	**Charge capacity (Ah)**	**Discharge capacity (Ah)**
1	1.49	3.14	1.36	2.81
2	2.74	2.6	2.49	2.40
3	2.54	2.54	2.45	2.37
4	2.63	2.58	2.50	2.42
5	2.6	2.56	2.48	2.38
6	2.57	2.52	2.46	2.35
7	2.62	2.57	2.49	2.37
8	2.68	2.54	2.48	2.36
9	2.65	2.56	2.50	2.38
10	2.68	2.6	2.53	2.41
11	2.69	2.62	2.52	2.40
12	2.64	2.58	2.49	2.38
13	2.63	2.56	2.47	2.35
14	2.58	2.57	2.52	2.36
15	2.59	2.55	2.50	2.35
16	2.61	2.54	2.48	2.36
17	2.59	2.56	2.47	2.38
18	2.64	2.58	2.49	2.37
19	2.65	2.6	2.54	2.40
20	2.6	2.58	2.50	2.36
21	2.61	2.58	2.52	2.39
22	2.63	2.61	2.48	2.35
23	2.61	2.60	2.50	2.39
24	2.6	2.55	2.47	2.36
25	2.58	2.56	2.48	2.38
Average	2.62	2.57	2.49	2.38

Table A7 Discharge time of batteries filled with electrolytes containing (Battery 1Si) 1%w/v SiO_2 in 35%w/v H_2SO_4, (Battery 1SiP) 1%w/v SiO_2 and 0.001%w/v PAM in 35%w/v H_2SO_4, (Battery 1SiNa) 1%w/v SiO_2 and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 and (Battery 1SiMg) 1%w/v SiO_2 and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Discharge time (min)**			
	Battery 1Si	**Battery 1SiP**	**Battery 1SiNa**	**Battery 1SiMg**
1	43	52	51	50
2	44	54	51	50
3	42	51	53	51
4	43	54	53	53
5	44	55	54	47
6	40	50	54	52
7	42	57	55	47
8	46	50	55	52
9	47	49	55	47
10	43	51	54	54
11	42	56	53	48
12	37	50	49	43
13	42	56	53	46
14	50	50	48	50
15	42	54	52	45
16	41	54	52	46
17	40	52	53	46
18	42	52	54	44
19	40	52	54	44
20	40	52	52	46
21	40	48	50	44
22	40	48	50	38
23	40	50	50	44
24	40	50	52	46
25	38	48	49	42

Table A7 (continue) Discharge time of batteries filled with electrolytes containing (Battery 1Si) 1%w/v SiO_2 in 35%w/v H_2SO_4, (Battery 1SiP) 1%w/v SiO_2 and 0.001%w/v PAM in 35%w/v H_2SO_4, (Battery 1SiNa) 1%w/v SiO_2 and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 and (Battery 1SiMg) 1%w/v SiO_2 and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Discharge time (min)**			
	Battery 1Si	**Battery 1SiP**	**Battery 1SiNa**	**Battery 1SiMg**
26	38	50	49	46
27	40	52	52	46
28	38	52	51	42
29	38	50	50	42
30	40	50	52	46
31	40	52	51	46
32	40	44	52	42
33	38	46	51	46
34	36	46	50	44
35	38	46	52	44
36	38	44	49	42
37	38	46	50	44
38	36	44	52	44
39	36	46	49	40
40	38	40	51	38
41	38	44	49	44
42	34	44	50	44
43	36	42	47	44
44	34	46	51	46
45	36	44	48	44
46	36	46	52	46
47	36	44	49	44
48	34	42	52	38
49	36	44	48	44
50	36	44	49	44
Average	**40**	**49**	**51**	**45**

Table A8 Discharge time of batteries filled with electrolytes containing (Battery 1SiK) 1%w/v SiO_2 and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4, (Battery 1SiPNa) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4, (Battery 1SiPMg) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 and (Battery 1SiPK) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Discharge time (min)**			
	Battery 1SiK	**Battery 1SiPNa**	**Battery 1SiPMg**	**Battery 1SiPK**
1	47	47	47	36
2	49	30	47	22
3	47	54	48	42
4	48	52	50	42
5	49	53	48	44
6	44	49	44	42
7	46	47	48	40
8	46	49	46	45
9	46	47	46	44
10	48	49	46	45
11	46	49	47	42
12	41	50	42	44
13	47	50	47	47
14	50	53	50	45
15	44	49	47	44
16	50	50	46	45
17	44	47	44	42
18	46	47	46	40
19	46	49	44	45
20	44	50	44	45
21	44	53	44	48
22	44	53	44	44
23	44	54	44	47
24	46	46	46	42
25	44	50	44	41

Table A8 (continue) Discharge time of batteries filled with electrolytes containing (Battery 1SiK) 1%w/v SiO_2 and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4, (Battery 1SiPNa) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4, (Battery 1SiPMg) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v $MgSO_4$ in 35%w/v H_2SO_4 and (Battery 1SiPK) 1%w/v SiO_2, 0.001%w/v PAM and 2.5%w/v K_2SO_4 in 35%w/v H_2SO_4 during 50 cycles

Number of cycle	**Discharge time (min)**			
	Battery 1SiK	**Battery 1SiPNa**	**Battery 1SiPMg**	**Battery 1SiPK**
26	46	50	46	43
27	44	48	46	43
28	44	50	46	43
29	42	48	46	44
30	46	44	46	40
31	42	44	42	40
32	42	46	46	38
33	44	46	46	40
34	42	44	46	44
35	44	46	44	40
36	44	48	46	40
37	44	44	46	40
38	42	44	42	40
39	40	48	40	43
40	42	46	46	40
41	44	44	46	42
42	42	40	44	39
43	44	44	46	40
44	42	46	44	39
45	40	46	46	40
46	42	42	44	40
47	44	42	38	42
48	38	44	44	40
49	42	44	46	38
50	40	42	44	40
Average	**44**	**47**	**45**	**42**

Table A9 Discharge time of batteries filled with electrolytes containing (Battery 2Si) 2%w/v SiO_2 in 35%w/v H_2SO_4, (Battery 2SiP) 2%w/v SiO_2 and 0.02%w/v PAM in 35%w/v H_2SO_4, (Battery 2SiNa) 2%w/v SiO_2 and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 and (Battery 2SiPNa) 2%w/v SiO_2, 0.02%w/v PAM and 2.5%w/v Na_2SO_4 in 35%w/v H_2SO_4 during 25 cycles

Number of cycle	**Discharge time (min)**			
	Battery 2Si	**Battery 2SiP**	**Battery 2SiNa**	**Battery 2SiPNa**
1	52	54	57	51
2	49	49	53	48
3	49	51	53	49
4	49	51	53	50
5	49	51	53	50
6	49	51	53	50
7	49	51	54	50
8	48	50	52	49
9	50	53	54	51
10	50	52	54	51
11	49	51	53	50
12	49	52	53	50
13	49	52	54	50
14	49	52	54	50
15	50	53	54	51
16	49	52	54	50
17	49	51	54	50
18	49	51	53	49
19	49	52	52	50
20	50	52	54	50
21	49	53	54	50
22	50	52	54	51
23	49	52	53	50
24	49	53	54	50
25	49	52	54	50
Average	**49**	**52**	**54**	**50**

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