

Rheological characterization and optimization of gelled electrolyte for sealed lead–acid batteries by small amplitude dynamic oscillation measurement

Jin Park ^a, Seung Bin Park ^{a,*}, Seung-Man Yang ^a, Won Hi Hong ^a,
Chun Rak Choi ^{a,b}, Jeong Heon Kim ^{a,c}

^a Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1, Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

^b R&D Center, Korea Storage Battery Co. Ltd., 40-42, Daehwa-dong, Daeduk-gu, Daejeon 306-802, Republic of Korea

^c R&D Center, Hankook Tire Co. Ltd., 23-1, Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

Received 12 May 2004

Available online 5 July 2005

Abstract

Rheological behavior of silica gel in sulfuric acid was investigated with a small amplitude dynamic oscillation measurement method in which storage modulus was monitored with time. For the purpose of quantitative discussion, gelation rate was defined as the time required for the storage modulus to be 1000 Pa, and denoted as t_{1000} . The storage modulus was defined as ‘gel strength’. As silica content, sulfuric acid concentration, or the amount of added polyacrylamide increased, the gel strength and gelation rate were increased at the same time. While the increase of gel strength is desirable for long service life of a gel battery, the increase of gelation rate makes it difficult to fill the gel into the battery. However, this increase of gelation rate was found to be compensated by lowering the gelation temperature. A phase plane plot of gelation time (t_{1000}) against gel strength (G') was proposed to optimize the gel in terms of gel strength and gelation time. By using this phase plane plot, the gel strength was found to be increased by 40% without sacrificing the gelation rate. This was possible because the slopes on the phase plane plot are different depending on the independent variables.

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PACS: 83.60.Pq; 83.80.Kn; 83.85.Cg; 83.85.Vb

1. Introduction

In deep-discharge applications of lead–acid batteries, such as electric vehicle propulsion, load leveling, and solar energy storage, adding water to the battery is prohibitively expensive. The cost of adding water throughout the battery’s life is as high as the cost of the initial battery [1]. Acid stratification leads to overcharging, gassing, and failure in deep-cycling applications unless

acid circulation is incorporated into the cell design [2–4]. To solve this problem, a gel battery was developed over a number of years for stationary applications.

In a gel battery, sulfuric acid is mixed with finely divided silica and forms a gel. The recombination reaction of oxygen and hydrogen takes place by the rapidly diffused oxygen from the positive to the negative plate through a network of micro-cracks in the gelled electrolyte. The batteries can, therefore, operate in a fully sealed manner without any requirement for routine maintenance.

However, gelled electrolyte experiences shrinkage and expansion during cyclic operation of a battery.

* Corresponding author. Tel.: +82 42 869 3928; fax: +82 42 869 3910.

E-mail address: seungbinpark@kaist.ac.kr (S.B. Park).

The repeated physical stress generates macro-cracks. These macro-cracks reduce the service life of the gel battery while micro-cracks help to transfer oxygen gas and enhance the service life. It is proposed that the resistance to deformation from repeated shrinkage and expansion, can be improved by increasing the content of silica in a gel [5].

Addition of extra silica to the gel battery, however, increases the gelation rate. In the battery manufacturing process, a suspension of electrolyte is injected into a battery cell. Gelation rate should be slow enough for the electrolyte to be filled into the whole space between electrodes. If gelation proceeds and the electrolyte no longer has fluidity before the electrolyte is filled into the whole volume of the battery cell, some area on the electrodes is left not in contact with electrolyte, which prevents the battery from achieving its desired performance in operation. Therefore, a method of improving the gel strength without sacrificing the gelation rate should be proposed.

So far, however, there have been few quantitative investigations on gel strength and gelation rate of gelled electrolyte. Lambert et al. investigated the gel strength of the gelled electrolyte by measuring the penetration depth of a falling lead sphere [7]. This method is simple, but the structure of the gel specimen is destroyed after being measured. The destructive method shows the state at the point where gel property is measured, but it does not show the whole behavior of suspension or gel during the gelation process.

Rheological measurement is useful for the investigation of the gelation behavior. The viscosity and the dynamic modulus are directly related to the physical and mechanical properties of the gel during the battery manufacturing process. However, the structure of the gelled electrolyte is weak and easily disrupted by just a small shear, which makes the investigation difficult. Therefore, the shear strain should be kept low. The small amplitude dynamic oscillation measurement technique is non-destructive, as compared with the steady shear measurement, since the level of deformation is kept low. In the measurement the moduli are monitored as a function of time at constant frequency by a dynamic time-sweep test [6,7]. No previous rheological investigation of colloidal suspension and gel was reported at strongly acidic conditions such as gelled electrolyte for lead–acid batteries.

In this work, gelled electrolytes were prepared from fumed silica and sulfuric acid, and their rheological behaviors during gelation were investigated by small amplitude dynamic oscillation measurement. The gel strength and the gelation rate were measured from the time evolution of the storage modulus during gelation. The effects of the processing variables, such as silica content, sulfuric acid concentration, temperature, and polymer addition, on the gel properties were inspected. The effective variables were used for controlling the gel strength and the gelation rate.

The goal of this paper is to define the gelation rate and gel strength, and to propose a method of enhancing the gel strength without sacrificing the gelation rate.

2. Experimental procedures

Aerosil 200 (Degussa) was used to prepare gelled electrolyte [8,9]. It has a surface area of $200 \text{ m}^2/\text{g}$ and the diameter of a primary particle is about 12 nm. The silica and sulfuric acid were dispersed and diluted in water, respectively. The prepared silica suspension and sulfuric acid aqueous solution were mixed and formed the suspensions containing 2–15 wt% of silica, where the concentration of sulfuric acid was 15 or 38 wt%. The concentrations of silica and sulfuric acid are in the range of those in general lead–acid batteries using gelled electrolyte. Then the suspension was agitated at 2000 rpm.

In gel batteries, polymer additives are used for suppression of the formation of macro-crack during battery operation, and polyacrylamide is a well-known polymer additive. In this work, polyacrylamide ($\text{MW} = 6 \times 10^6$) was prepared as aqueous solution. The prepared polyacrylamide solution was added to the suspension after the sulfuric acid solution was mixed with the silica suspension, and then the mixed suspension was agitated at 2000 rpm. After agitation, the mixed suspension was loaded into the rheometer for measurement.

Dynamic rheological measurements were performed with ARES (advanced rheometric expansion system, Rheometric ScientificTM) to measure the storage and loss moduli of silica–sulfuric acid suspensions and gels. The measurements were performed by applying an oscillatory strain of 1% for 1 rad/s of frequency.

3. Results

3.1. Three regions of time evolution of storage modulus

Time evolution of storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$) for the suspension containing 8 wt% of silica and 38 wt% of sulfuric acid solution is shown in Fig. 1. The general trends of the curves are similar to those of other suspensions of different concentrations of silica and sulfuric acid, although their details are different. Storage modulus is a property representing the elasticity of a material: higher storage modulus means higher gel strength [10]. The storage modulus is an indicator that a real three-dimensional network is formed by aggregation or gelation of colloidal particles [11]. The increase of storage modulus reflects extensive interactions among particles and formation of network structure, and the increase of the loss modulus indicates an increase of the aggregates sizes and of polydispersity [12].

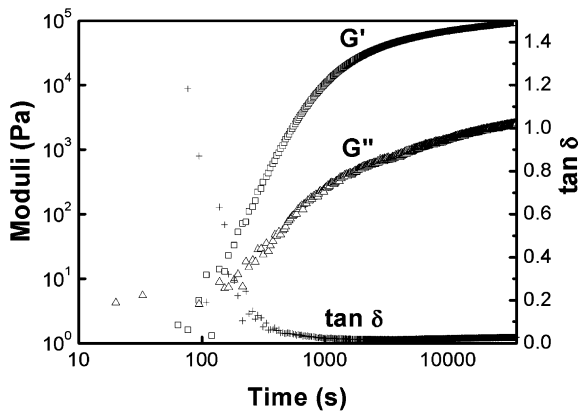


Fig. 1. Time evolution of storage modulus (G'), loss modulus (G''), and loss tangent ($\tan\delta$) of the silica-sulfuric acid gel with 8 wt% of silica and 38 wt% of sulfuric acid.

Fig. 1 shows that there are three regions in modulus evolution, depending on the slope.

In the first region of the increasing curve, the silica suspension has very low storage modulus and loss modulus, and the storage modulus is lower than the loss modulus. Therefore, the suspension behaves as a fluid. The fluidity of the suspension in this region makes it possible that gelled electrolyte fills the empty space between the electrodes in a battery cell during the manufacturing process.

In the second region, the storage modulus and the loss modulus begin to increase rapidly. The storage modulus increases faster than the loss modulus so that the storage modulus becomes higher than the loss modulus. According to definition of gelation point, the point at which the storage modulus and the loss modulus intersect, that is, at which the loss tangent ($\tan\delta$) becomes unity, is defined as gelation point, since at this point the elastic property related to solid-like behavior becomes superior to the viscous property related to liquid-like behavior [12]. In this region, the network between the silica particles expands to the whole volume in the suspension [13]. The rapid increase of the storage modulus implies that an extensive three-dimensional network structure develops rapidly.

The storage modulus settles in the pseudoplateau third region, where the moduli are nearly invariant, compared with that in the second region, although the moduli increase continuously [14].

It is important that the loss tangent decreases to 0.02 in the third region. It implies that the gel in this system is highly elastic.

3.2. Effect of silica and sulfuric acid contents on storage modulus

Fig. 2 is the relationship between silica content and storage modulus which is the value in the pseudoplateau

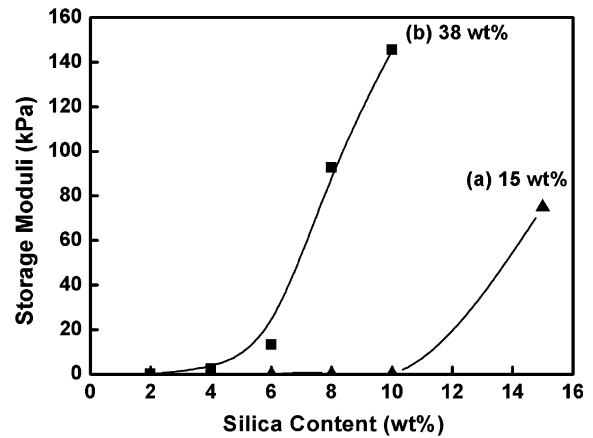


Fig. 2. Storage moduli of silica-sulfuric acid gels containing (a) 15 and (b) 38 wt% of sulfuric acid with the content of silica.

third region in Fig. 1. In this figure, we chose 15 and 38 wt% of sulfuric acid concentration because the sulfuric acid concentration is 15 wt% when the electrolyte is filled and the concentration increases to 38 wt% after charging the battery. Fig. 2 shows that the storage moduli of the gels with 15 wt% of sulfuric acid are always lower than those with 38 wt% at the same content of silica. This explains why the gel strength increases in the course of charging the battery.

The storage moduli increase abruptly above about 10 and 6 wt% of silica for 15 and 38 wt% of sulfuric acid, respectively. It is reasonable that silica content in gelled electrolyte for commercial lead-acid battery is in the range of 6–20 wt%. This is because gel with silica content less than about 6 wt% has low gel strength and is easily destroyed by just a small shock or stress from repeated charging and discharging.

The trend that the storage modulus increases with the silica content, is the same as the result obtained by the destructive method [7]. But the quantitative result obtained by the non-destructive method provides continuous information and is more useful for optimizing the gel property as shown in Section 4 of this paper.

3.3. Effect of silica and sulfuric acid content on gelation rate

In this work, the time at which storage modulus reaches a critical value, after which the penetration of the gelled electrolyte into the empty space in a battery cell is no longer possible, was defined as the value representing the gelation rate. This type of definition of gelation time is not new. Calloni et al. defined and used the time, at which the storage modulus reaches 10^4 Pa, as the gelation time in their work [15]. For practical reasons, the time at which storage modulus reaches 1000 Pa is defined as the gelation rate and denoted as t_{1000} . The value, 1000 Pa, has significant meaning in

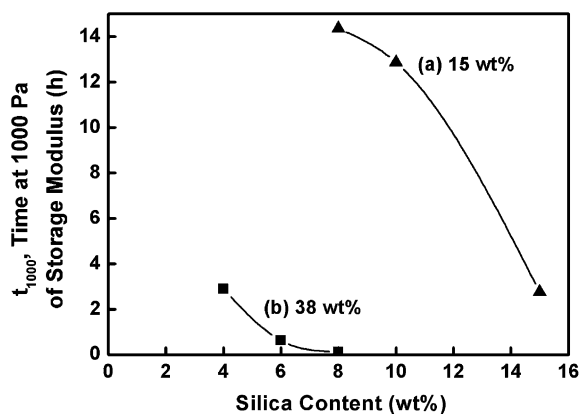


Fig. 3. Gelation rate presented as time (t_{1000}) at 1000 Pa of storage moduli of silica–sulfuric acid gels containing (a) 15 and (b) 38 wt% of sulfuric acid.

battery manufacturing. If the storage modulus is higher than 1000 Pa, fluidity is so low that the filling of silica gel becomes difficult. Although the crossover point of the storage modulus and the loss modulus designates the gelation point in Fig. 1, it is not available in the practical battery manufacturing process, since the point appears in the region of excessively low modulus.

t_{1000} was plotted against silica content in Fig. 3. t_{1000} becomes shorter as the silica content is increased at a fixed sulfuric acid concentration. When the sulfuric acid concentration is increased from 15 wt% to 38 wt%, t_{1000} is decreased dramatically. This result explains why the electrolyte with low sulfuric acid concentration is injected into a battery cell and then the sulfuric acid concentration is increased by charging the battery.

As shown in Fig. 2, gel strength increases as the silica content is increased. This is desirable for the prolonged service life of a gel battery. However, as shown in Fig. 3, the gelation rate becomes faster as the silica content is increased. Therefore, the silica content has to be optimized so that the gelation rate is slow enough for the gel to fill the cell space of the battery while the gel strength is high enough to resist the formation of macro-cracks.

Since, typically, sulfuric acid of 15 wt% is filled in the battery cell and becomes 38 wt% after being fully charged, the gelation rate measured in the sulfuric acid of 15 wt% is meaningful whereas the gel strength should be in 38 wt% sulfuric acid.

3.4. Temperature dependence of the gelation rate

Gels were prepared with 8 wt% of silica in sulfuric acid of 15 or 38 wt%, and t_{1000} and storage modulus were measured at 15, 20, 25, and 45 °C for the two sets of gels, respectively. Fig. 4 confirms the report that the gelation is accelerated as temperature increases [16], and shows that the gel strength is increased with increasing temperature.

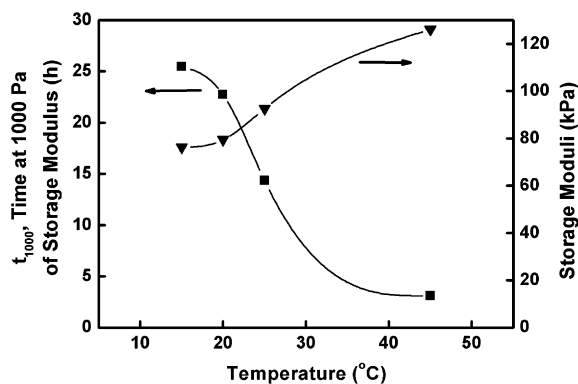


Fig. 4. Times (t_{1000}) at 1000 Pa of storage of the 15 wt% sulfuric acid gel and storage moduli of the 38 wt% sulfuric acid gel with temperature.

The fact that gelation rate becomes slower at lower temperature, is significant and useful for controlling gelation rate. When the gel strength should be increased by increasing the silica content, the shortened t_{1000} can be compensated by decreasing the temperature. This idea will be discussed quantitatively in Section 4 of this paper.

3.5. Addition of polyacrylamide

The amount of silica should be minimized in order to maximize the amount of sulfuric acid in the electrolyte, since electrical performance such as electric conductivity and capacity of a battery increases with the amount of sulfuric acid in the electrolyte. That is, the strength of the gel and the electrical performance of the battery go against each other as the silica content increases.

It is common practice to use polymer additives to increase the gel strength without the loss of electrical performance in gelled electrolyte [17]. Since a small amount of additive is used, it has no effect on the electrical performance. Polyacrylamide is a well-known polymer additive to gelled electrolyte for lead–acid batteries [18]. It is known that nitrogen in polyacrylamide side group plays the role of a bridge between silica particles so that the structure of a gel becomes strong [19].

To perform quantitative investigation of the effects of polyacrylamide, the storage moduli of gels were measured by varying the amount of polyacrylamide. Gel samples were prepared with 8 wt% of silica in sulfuric acid of 15 or 38 wt%.

Fig. 5 shows that the storage moduli increase with the amount of added polyacrylamide. The added polyacrylamide increases the storage modulus, and it supports that polyacrylamide is used in gelled electrolyte for increased gel strength. The drastic increase of the storage modulus is observed at the polyacrylamide concentration of 0.015 wt% in the gel containing 38 wt% of sulfuric acid. The addition of polyacrylamide is no longer effective for increasing the storage modulus when

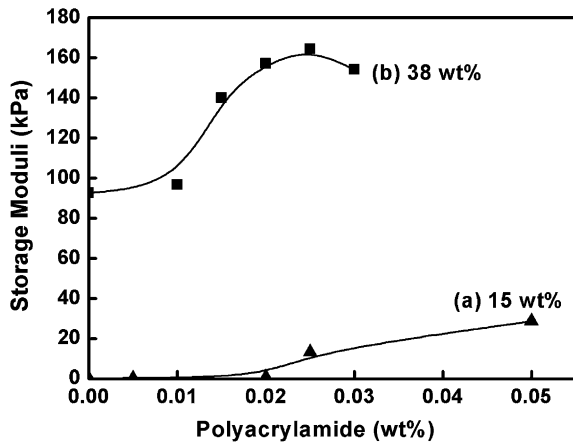


Fig. 5. Storage moduli of silica-sulfuric acid gels with a small amount of polyacrylamide, 8 wt% of silica, and (a) 15 and (b) 38 wt% of sulfuric acid.

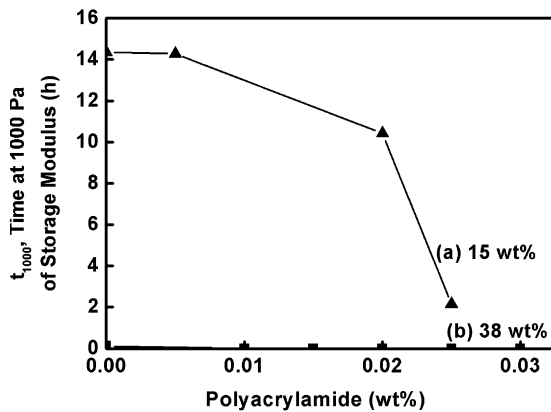


Fig. 6. Gelation rate represented as time (t_{1000}) at 1000 Pa of storage moduli of silica-sulfuric acid gels with a small amount of polyacrylamide, 8 wt% of silica, and (a) 15 and (b) 38 wt% of sulfuric acid.

the polyacrylamide concentration is higher than 0.025 wt% for the sulfuric acid concentration of 38 wt%.

Fig. 6 is the plot of t_{1000} against the amount of polyacrylamide. Since the gelation rate of the suspension containing polyacrylamide in 38 wt% sulfuric acid was fast, its t_{1000} cannot be measured. It shows that the gelation rate of the suspension containing polyacrylamide in 15 wt% sulfuric acid increases as the polyacrylamide content increased. While polyacrylamide enhances the strength of gelled electrolyte, it also accelerates gelation rate. Therefore, the key conclusion is that the amount of polyacrylamide additive should be optimized.

4. Discussion

The quantitative results can be applied to design the gel properties. The storage modulus G' representing the gel strength and t_{1000} representing the gelation rate are functions of silica content (C_s), temperature (T),

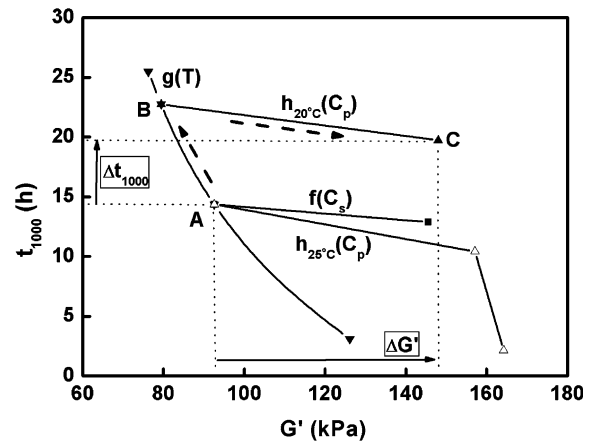


Fig. 7. Phase plane plot of gelation rate (t_{1000}) against storage modulus (G'). The storage modulus G' was increased as much as $\Delta G'$ with adjustment of temperature (A \rightarrow B) and polyacrylamide addition (B \rightarrow C) at the constant silica content without sacrificing t_{1000} .

and the amount of added polyacrylamide (C_p). Their contributions to G' and t_{1000} are expressed as the curves of $f(C_s)$, $g(T)$, and $h(C_p)$, respectively, in a phase plane of G' and t_{1000} in Fig. 7. In the phase plane, the slope ($\frac{dt_{1000}}{dG'}$) of each curve is negative slope and it shows that G' increased by increasing silica content, temperature, or the amount of added polyacrylamide, is accompanied with shortened t_{1000} .

As an example, it will be demonstrated how G' is increased for a fixed 8 wt% of silica without shortening t_{1000} .

When C_s , T , and C_p are 8 wt%, 25 °C and 0 wt%, respectively, G' and t_{1000} are located at the point A on the phase plane. In order to increase G' without change of silica content, there are three choices. The first is to increase temperature and the second is to add polyacrylamide. However, these two methods shorten t_{1000} and, therefore, are not feasible.

The third is to follow the trajectory from A, B, and C on the phase plane in Fig. 7. Line A-B is to follow $g(T)$ by lowering the temperature from 25 to 20 °C. At the point B, G' is decreased instead of increased t_{1000} , compared with the initial state, the point A. Line B-C is to follow $h_{20}(C_p)$ by adding 0.02 wt% of polyacrylamide at 20 °C. As a consequence, the storage modulus G' is increased from 9.3×10^4 Pa to 13.0×10^4 Pa by 40% and t_{1000} is increased from 5.2×10^4 s to 7.1×10^4 s by 37%.

This example shows the usefulness and the possibility of controlling the gel properties by adjusting the processing variables with the quantitative rheological data.

5. Conclusion

Rheological behavior of silica gel electrolyte was investigated by time-sweep method in which small amplitude dynamic oscillation measurement was applied

in order to prevent the destruction of silica gel. For the purpose of quantitative analysis, ‘gel strength’ and ‘gelation rate’ were defined by storage modulus (G') and the time (t_{1000}) required for the storage modulus to be 1000 Pa, respectively.

The dynamic oscillation measurement provided quantitative information on how the gel strength and gelation rate (t_{1000}) were changed as silica content, sulfuric acid concentration, gelation temperature, and the amount of added polyacrylamide were increased. These results were summarized on a phase plane, which is a plot of t_{1000} against G' . The phase plane plot shows that the $\frac{dt_{1000}}{dG'}$ slopes are different depending on the independent variables. This implies that we can improve the gel strength at the fixed silica content without sacrificing the gelation rate (t_{1000}). This idea was tested and found that the gel strength was increased by 40% by decreasing the gelation temperature from 25 to 20 °C and adding polyacrylamide of 0.02 wt%.

It is concluded that the plot of gelation rate (t_{1000}) against gel strength (G') is useful in determining the optimum condition for high gel strength and slow gelation rate. The details of the phase plane would be different depending on the type of gel and experimental conditions. But the methodology developed in this report would still be valid for preparing optimized gel in terms of gel strength and gelation rate.

Acknowledgements

This work was financially supported by Hankook Tire Co. Ltd, Korea Storage Battery Co. Ltd., and ITEP (Korea Institute of Industrial Technology Evaluation

and Planning). Seung Bin Park and Seung-Man Yang would like to thank the BK21 (Brain Korea 21) program and CUPS (Center for Ultramicrochemical Process System) for supporting part of this research.

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