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공학석사학위논문

Rheological and adhesive properties of Li-ion
battery slurry from capillary suspension

모세관 현탁액 기반의 리튬 이온 배터리 수계 음극
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Abstract

Rheological and adhesive properties of Li-ion battery slurry from capillary suspension

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Mechanical properties of Li-ion battery slurry applying the concept of capillary suspension were investigated with regard to the interaction between a binder and the secondary fluid. Capillary suspension, which exploits capillary force induced by small amount of the secondary fluid, provides an innovative alternative for battery material offering advantageous features for processing and end use properties. This concept could be properly applied under an adequate understanding of the influence of the secondary fluid in industrial paste.

In this study, the interaction between styrene–butadiene rubber (SBR) binder of Li–ion anode battery slurry and the secondary fluid octanol was determined by altering mixing protocol and binder content. Consequential variation in mechanical properties such as rheological properties and adhesion characteristics were measured. The role and the distribution of the binder in the capillary suspension were examined by microscopy and interfacial tension measurement. An accurate understanding of this interaction may enable us to optimize targeting mechanical properties of the materials through the concept of capillary suspension.

Key words: capillary suspension, battery anode slurry, adhesive properties

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Chapter 1.

Introduction

Li-ion battery, which has advantages of high energy capacity, long cycle life and better power capability, has taken an important position in the field of energy storage technology. In accordance with the requirements from the future application such as smart devices and electric vehicle, enhancing properties of Li-ion battery have been a significant issue for industry [1, 2]. The factors which determine battery performance are not restricted only to the materials. Fabrication process strongly affects electrochemical performances and stability of the battery [3, 4].

Typical composition of battery electrodes contains active material for anode or cathode electrode, solvent, conductive agent and additives. Active material and conductive agent determine electrochemical characteristics. Additives play a role of binding agent for cohesion and adhesion among particles and rheology control agent [1]. Elaboration of the battery slurry has to be conducted with proper mixing protocol since the dispersion of materials and the microstructure after sample preparation are closely connected with the battery performance in the end [5-7]. Another attempt to control the microstructure of the slurry has been performed in the name of capillary suspension. Capillary suspension is a ternary system composed of particles and two immiscible fluids [8]. A small amount of the secondary fluid increase yield stress and make network structure in the suspension [9, 10].

Employing these unique characteristics of capillary suspension, industrial applications such as printable paste [11], porous materials [12, 13] and even food processing [14] have been tried. Li-ion battery anode slurry is also applied by Bitsch *et al.* This novel concept provides battery slurry with several advantages. Adjusting rheological properties, improvement of sedimentation stability and superior coating behavior are achieved only by several drops of secondary fluid [15]. Besides, porous characteristic by sample spanning network can be utilized to develop ultra-thick electrode with porosity gradient for facile transport of electron [16]. However, a side effect is also appeared by the adoption of external material that is the secondary fluid. Bitsch *et al.* have found the fact that the secondary fluid impedes adhesive properties of the battery slurry to the current collector [15]. Adhesive characteristic is one of the crucial mechanical properties determining cycle life of the battery [17, 18]. Loss of contact between electrode and current collector caused by mechanical stress from expansion and shrinkage of the electrode due to lithium intercalation and de-intercalation leads to capacity fading on cycling [19]. Adhesion is mainly affected by the distribution of the binder in the suspension and the binder migration phenomenon during drying [20–22]. The reason for different adhesive responses under the same drying condition can be inferred distribution difference of binder induced by the secondary fluid. To complement the unexpected side

effect occurred from the capillary suspension, a correlation between the secondary fluid and the binder has to be conscientiously examined.

In this present study, we analyzed mechanical properties of battery electrode based on capillary suspension varied by the interaction between the secondary fluid and a binder. Aqueous anode battery slurry made up of water, graphite particles, Carboxymethyl cellulose (CMC) and Styrene butadiene rubber (SBR) was utilized to develop capillary suspension. Adding a small amount of the secondary fluid completely changed the flow properties of the graphite suspension as known in the theory of capillary suspension. Rheological properties depended also on a mixing order of the secondary fluid and SBR binder. SBR binder is a stabilizer and adhesive agent for aqueous anode battery slurry. The formation or the strength of a capillary suspension have changed by the production process which could influence the interaction between the secondary fluid and SBR binder. The addition of SBR after octanol to the graphite suspension considerably reduced the low shear viscosity of the capillary suspension compared to the samples with adding octanol after SBR. This tendency continued to the adhesion strength of the electrode on the current collector. Superior adhesion strength was obtained from the samples with octanol after SBR mixing method. Microscopic images and interfacial tension measurement denoted microstructure change induced by mixing protocol of SBR and the secondary fluid. The study of

capillary suspension in the perspective of structure and processing design could offer an opportunity to enhance mechanical properties as well as controlling flow behavior for the further industrial application.

Chapter 2.

Experimental methods

2.1 Materials

Synthetic graphite (SMGPA, China Steel Chemical Corporation, Kaohsiung, Taiwan) with a density of 2.2 g/cm^3 , average volume-based diameter D_{50} of $8.92 \mu\text{m}$ and a specific surface area of $2.24 \text{ m}^2/\text{g}$ was used as particles. Carboxymethyl cellulose (CMC)–water solution and glycerol were used as bulk fluids. CMC (CMC2200, Daicel Corporation, Osaka, Japan) with a degree of substitution of > 0.8 , average molecular weight of $1,400,000 - 1,500,000 \text{ g/mol}$ and a density of 1.59 g/cm^3 was added to water to prepare CMC–water solution. Another bulk fluid glycerol (Carl Roth GmbH, Karlsruhe, Germany) with a density of 1.26 g/cm^3 and a viscosity of $1.4 \text{ Pa}\cdot\text{s}$ at 20°C was also used. 1-octanol (Merck Millipore Corporation, Darmstadt, Germany) with a density of 0.83 g/cm^3 was selected as a secondary fluid. Aqueous styrene–butadiene rubber (SBR) latex (JSR Corporation, Tokyo, Japan) with a density of 1.0 g/cm^3 and 48 wt% solid mass fraction was supplied as a binder which plays as a dispersing and adhesive agent. Sodium chloride (NaCl) (Carl Roth GmbH, Karlsruhe, Germany) with a density of 2.17 g/cm^3 was used as a salt to screen the surface charge on the SBR.

2.2 Sample preparation

CMC–water solution, pure glycerol and glycerol with NaCl were employed as bulk fluids according to the purpose of the experiment. CMC–water solution was prepared by dissolving 3 wt% CMC in water

with propeller type stirrer at 1000 rpm (rounds per minute) for 3 hours. Prepared CMC–water solution and additional water were mixed with 18.85 vol% graphite particles. To assure the slurry homogeneity and deagglomeration of the graphite particles, mixing was performed in a stepwise manner. Graphite particles and 3 wt% CMC solution were mixed for 10min at first. Water was added to the slurry 3 times in every 10 min to raise the water content in the slurry. The slurry was stirred with dissolver type stirrer at 1400rpm for 40min in total. Homogeneous graphite suspension with 0.68 vol% CMC was prepared in the end.

Samples with glycerol and NaCl–glycerol bulk fluids were produced in a slightly different way. NaCl–glycerol was prepared by mixing pure glycerol and 2.17 wt% NaCl using magnetic stirrer at 50°C for 1 hour. Glycerol or NaCl–glycerol bulk fluids were mixed with 18.85 vol% graphite particles and stirred with dissolver type stirrer at 1400 rpm for 40 min. The secondary fluid (2 vol% of octanol) and binder SBR were added to the graphite suspension as follows. Two different mixing protocol were applied as shown in Figure 2.1. Mixing was performed by dissolver type stirrer in the following mixing steps. In the mixing method 1, SBR binder was mixed with graphite suspension before octanol. Octanol was added to the slurry at the end to form a capillary suspension. On the other hand, octanol was added to the graphite suspension ahead and made a capillary suspension in the mixing method 2. SBR was mixed with capillary suspension later. Samples with different SBR contents were prepared for the experiment.

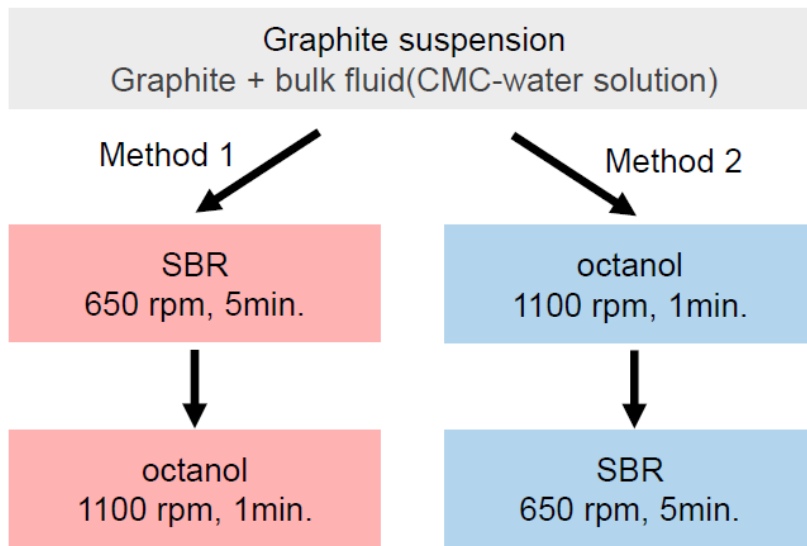


Figure 2.1. Two different mixing protocol have used in this study. Addition order of SBR (binder) and octanol (secondary fluid) was varied. In the method 1, SBR was added first to the graphite suspension and then octanol was added. In the method 2, octanol was mixed before SBR.

2.3 Rheological characterization

Rheological characterization was performed by RheoStress 1 (Thermo Scientific, Karlsruhe, Germany) rotational rheometer at 20°C with a parallel plate of 35 mm in diameter. All slurries were taken 120s of a rest time before starting measurement to exclude shear history that could appear during loading of the slurry to the rheometer plate. Viscosity was determined by steady–shear rate sweep test from shear rate 0.01s^{-1} or 0.1s^{-1} to 1000s^{-1} . To obtain the modulus of the slurry, frequency sweep test was performed from frequency 0.1 rad/s to 100 rad/s in linear viscoelastic regime which was identified by the stress sweep test.

2.4 Adhesion force measurement

To measure adhesion strength of dried electrode, prepared battery slurries were coated on the $10\ \mu\text{m}$ copper foil (Itochu Corporation, Tokyo, Japan) current collector with 50 mm/s speed by ZAA 2300 automatic coater (Zehntner GmbH, Sissach, Switzerland) and ZUA 2000 doctor blade (Zehntner GmbH, Sissach, Switzerland) with a coating width of 60 mm and a coating gap of $300\ \mu\text{m}$. The coated wet electrode film was dried for a day at room temperature. Adhesion force between the dried electrode and the current collector was measured by 90° peel test using TA.XT plus Texture Analyzer (Stable Micro Systems, Godalming, UK). The dried electrode was split into small pieces with a

width of 25mm and a length of 60mm and measured by the peel test at a pre-defined peel velocity of 5 mm/s. For all measurement, a 5kg load cell force sensor which has maximum force of 5kg and force sensitivity of 0.1g was used.

2.5 Investigation through microscopy

To observe the distribution and the role of SBR binder between a bulk fluid and the secondary fluid more clearly, a sample without graphite particles and CMC polymer was prepared. 70vol% water, 28vol% octanol and 2vol% SBR binder were shaken vigorously by hand for 1 min. Microscopic image (Axio Observer, Zeiss, Oberkochen, Germany) of this sample was taken a week later. A long distance (0.75 DIC), x100 lens was selected for the observation.

2.6 Interfacial tension measurement

Pendant drop method was conducted to investigate the interfacial tension between two immiscible fluids, that is the bulk fluid(water) and the secondary fluid(octanol). The secondary fluid which has a lower density than the bulk fluid was filled in a glass cuvette for interfacial tension measurement. A drop of the bulk fluid was injected into the secondary fluid through a hollow needle with a diameter of 1.65 mm. A shape of the bulk fluid droplet inside the secondary fluid was taken with a camera (AVT Stingray F-033B, Allied Vision Technology: 1/2 CCD,

656 492 square pixels) in every 10s for 20min. Obtained droplet images were analyzed using commercial software (drop shape analysis, Kruss GmbH, Hamburg, Germany) to calculate interfacial tension between two fluids.

Chapter 3.

Results and discussion

3.1 Rheological measurement

Before investigating rheological properties of battery slurry based on capillary suspension, battery slurry without secondary fluid was observed in Figure 3.1 in advance. Slurry which contained graphite, water, CMC and SBR showed the same flow behavior despite increasing the amount of SBR. Both viscosity and modulus graphs were not changed according to SBR content. Lim *et al.*[23] already investigated the effect of SBR on the anode battery slurry and discovered the fact that SBR cannot affect to the flow behavior of the slurry in the presence of comparatively high content of CMC. Figure 3.1 corresponds to the Lim's results. However, SBR could be an altering factor for rheological properties of battery slurry based on capillary suspension. Capillary suspension based slurry included graphite, CMC and SBR same as preceding slurry samples but this time 2 vol% of octanol was added as a secondary fluid. Two different mixing methods (SBR→octanol, octanol→SBR) in Figure 2.1 were applied with 5 different SBR content (0.47vol%, 0.94vol%, 1.41vol%, 1.88vol%, 2.35vol%) to investigate the rheological behavior originated from the interaction between SBR and octanol. Figure 3.2 (a) displayed the viscosity as a function of shear rate of the slurries based on capillary suspension. SBR→octanol mixing samples were marked with red symbol and octanol→SBR mixing samples were marked with blue symbol in the graph. Drastic increase in low shear viscosity due to the secondary fluid is the nature of capillary suspension.

The secondary fluid makes bridges between particles and creates a sample-spanning network exploiting capillary force. This can be observed from SBR→octanol mixing samples in Figure 3.2 (a). Octanol added at the end induces suspension to have higher low shear viscosity. SBR content has an impact on the rheological properties since low shear viscosity was slightly decreased as increasing the amount of SBR. While SBR→octanol samples follow typical characteristics of the capillary suspension, octanol→SBR mixing samples show different flow behavior. It was clearly observed that octanol→SBR mixing samples showed an abrupt decrease in low shear viscosity depending on SBR content in spite of the existence of the secondary fluid. Sample from octanol→SBR mixing with 2.35 vol% SBR content even has similar low shear viscosity to samples without the secondary fluid. The sample-spanning network formed from the secondary fluid collapsed with the appearance of SBR. To examine the flow properties regarding SBR content and a mixing protocol at a glance, shear stress at shear rate 0.1s^{-1} as a function of the amount of SBR was plotted in Figure 3.2 (b). Shear stress was lowered as SBR content increased in both mixing methods but more steep decrease was detected with octanol→SBR samples. SBR tends to lower the shear stress of the capillary suspension and this tendency appears more obviously with octanol→SBR samples. For additional rheological analysis, storage and loss modulus of capillary suspension with different mixing method as a function of frequency were measured in Figure 3.3 Modulus value at 1 rad/s was selected. Modulus of SBR→

octanol samples were displayed with red symbol and modulus of octanol →SBR samples were denoted with blue symbol. Flow behavior became totally different from 0.94 vol% SBR content. SBR content below 0.94% samples had higher storage modulus(G') than loss modulus(G'') in the both samples. From 0.94 vol%, trend in modulus values changed depending on mixing protocol. In the case of SBR→octanol samples, G' was higher than G'' until they reached 2.35 vol% SBR content. In the case of octanol→SBR samples, G' and G'' became the same.

To visualize the difference in flow behavior depending on mixing methods, images of capillary suspension with 1.41vol% SBR produced from different mixing methods were taken in Figure 3.4 Difference in flow properties could be noticed with the naked eye. Octanol→SBR sample in Figure 3.4 (b) shows more liquid-like behavior than SBR→octanol sample in Figure 3.4 (a). Destruction of capillary network by virtue of the addition of SBR afterwards leads to suspension to have liquid-like properties.

Battery slurry prepared up to here contained not only SBR but also CMC. CMC is another polymer widely used in aqueous anode battery slurry industry. CMC plays a role as a thickener and adsorbing polymer on the graphite surface in the battery slurry [24, 25]. The effect of CMC on the strength of capillary suspension is indefinite. Therefore, to clarify the effect of SBR itself and mixing methods on the flow properties of a capillary suspension, rheological properties of the capillary suspension excluding CMC polymer should also be investigated. Bulk fluid has to be

reselected for making samples without CMC polymer. Capillary suspension can be produced readily with viscous bulk fluid. Water is inappropriate as a bulk fluid without CMC. Glycerol was selected as an alternative bulk fluid owing to its viscous nature and wetting properties which is a key factor for capillary suspension. Figure 3.5 showed viscosity data from capillary suspension which consisted of graphite, glycerol, octanol and SBR. Low shear viscosity declined as increasing SBR content and different flow behavior depending on mixing methods were detected as the result before in Figure 3.2 (a). Without CMC, only a half of the SBR was needed to decrease the low shear viscosity by an order of magnitude compared to samples including CMC. SBR content of 0.94 vol% was enough to make such a big difference without CMC but when CMC solution was used as a bulk fluid, CMC interfered this to happen up to 1.88 vol%. SBR changes flow properties easily when there is no CMC in the suspension. This result confirms that altering low shear viscosity depending on the mixing process of SBR and octanol is only contributed from one component, SBR.

The reason for different flow behavior from different mixing samples were examined through another approach using rheological analysis. At this time, mixing time of the sample was considered. Samples were elaborated with the mixing process illustrated in Figure 2.1. Graphite suspension composed of graphite particles and CMC–water solution were prepared at first. SBR was added in the graphite suspension at 650 rpm for 5 minutes. According to supplier, SBR latex is vulnerable to high

mixing rate so that it might not properly working as a binder after severe mixing. Therefore, mixing rate was selected with a comparatively low value. Instead, enough mixing time of 5 min was applied to ensure complete mixing. Octanol was added at 1100 rpm for 1 min. Capillary suspension can be formed with high mixing rate and this is the reason for relatively higher mixing rate for the octanol. Mixing rate and time was chosen in accordance with the nature of the components. However, as shown in Figure 3.6, this could be another factor determining the strength of capillary suspension. In Figure 3.6, additional mixing was applied after completely developing the samples with the 2 mixing method in Figure 2.1 Additional mixing rate was 650 rpm and time was varied from 0 to 10 min. Shear stress at shear rate 0.1s^{-1} was measured for samples and illustrated as a graph. As a reference, shear stress of graphite suspension with only octanol and graphite suspension with only SBR were measured. As can be seen in Figure 3.6, it is apparent that mixing time affects to the strength of capillary suspension when SBR is included.

Longer mixing time lowered the shear stress of the capillary suspension. It seemed that longer mixing time could render more possibility for SBR binder to contact with the interface between water and octanol. SBR binder trapped on the interface could not escape from that position for a thermodynamic reason. Therefore, the more SBR binder might locate on the interface when longer mixing was applied. As we already know from interfacial tension data, the more SBR binder on

the interface, the lower interfacial tension would become. This might be the reason for the decline in shear stress. The different flow behavior from mixing protocol might also related to mixing time.

Network structure developed by the secondary fluid was deteriorated by SBR binder on the interface. When octanol was added earlier than SBR binder, a secondary bridge by octanol was exposed longer to the SBR binder than the other mixing protocol. Exposure time of the secondary bridge to the binder could be a key factor determining the strength of a capillary suspension in this case.

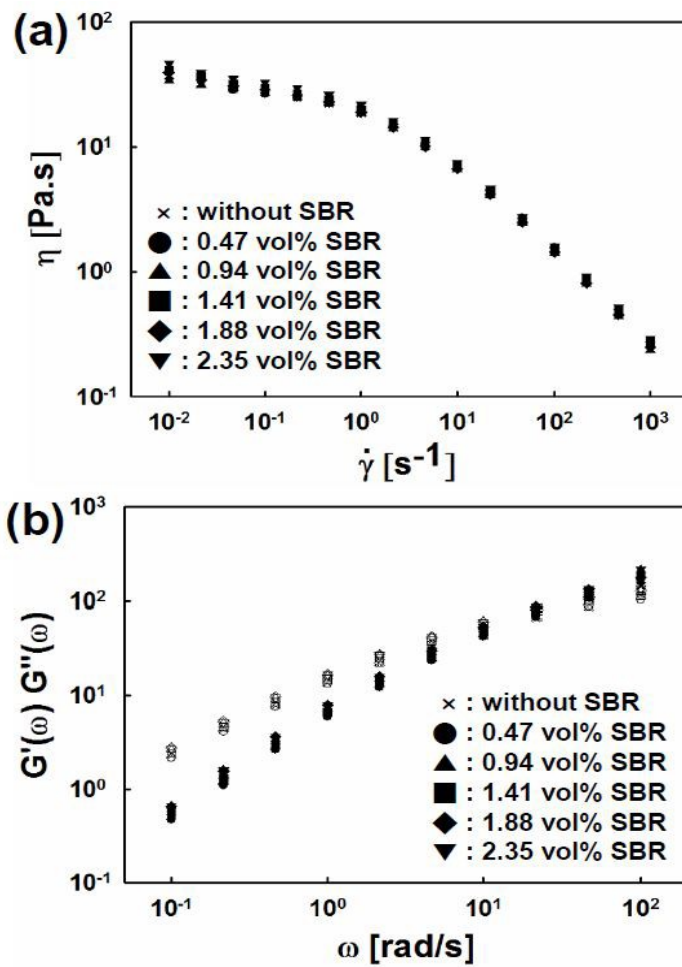


Figure 3.1. (a) Viscosity as a function of shear rate and (b) storage modulus (closed symbol) and loss modulus (open symbol) as a function of frequency for anode battery slurry without secondary fluid.

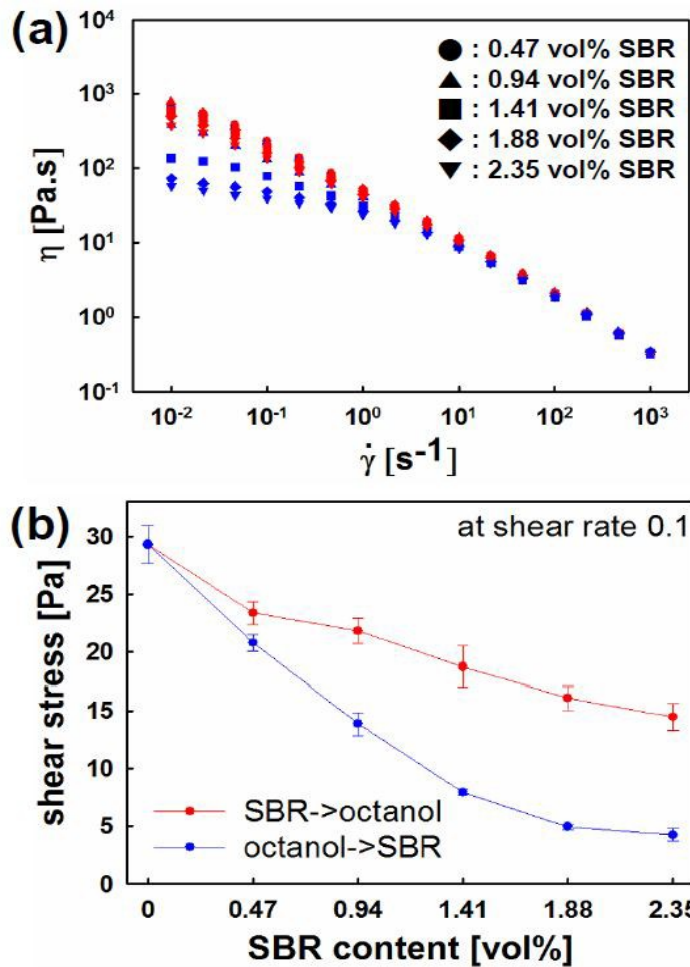


Figure 3.2. (a) Viscosity as a function of shear rate and (b) shear stress at shear rate 0.1 s^{-1} as a function of SBR content of battery slurry based on capillary suspension. Red symbol indicated samples made from mixing method 1 (SBR→octanol) and blue symbol indicated samples made from mixing method 2 (octanol→SBR) in Figure 2.1 in both graphs.

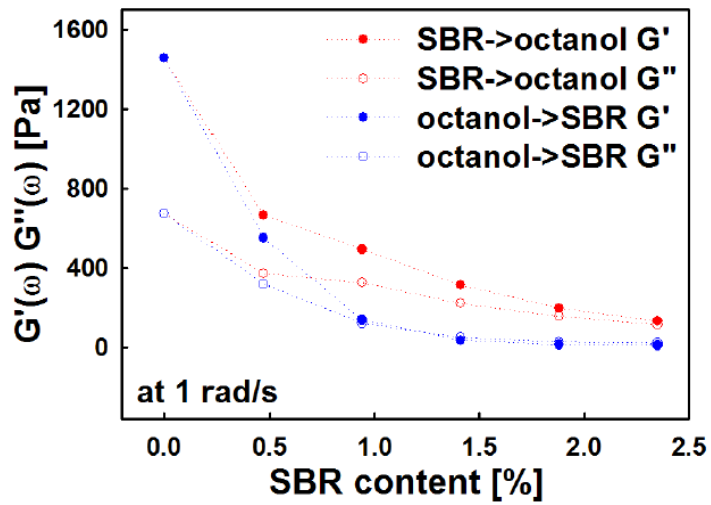


Figure 3.3. Storage modulus (closed symbol) and loss modulus (open symbol) as a function of frequency of the slurry based on capillary suspension. Red symbol indicated samples from SBR→octanol mixing method and blue symbol indicated samples from octanol→SBR mixing method.

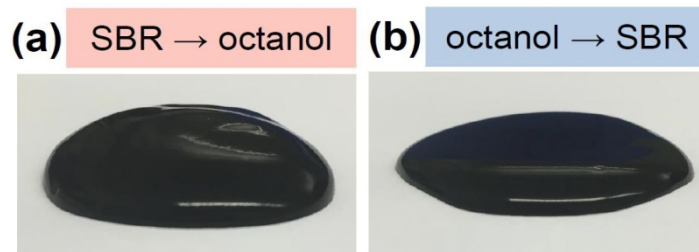


Figure 3.4. Capillary suspension made from different mixing method with 1.41vol% SBR. (a) SBR→octanol method and (b) octanol→SBR method were conducted.

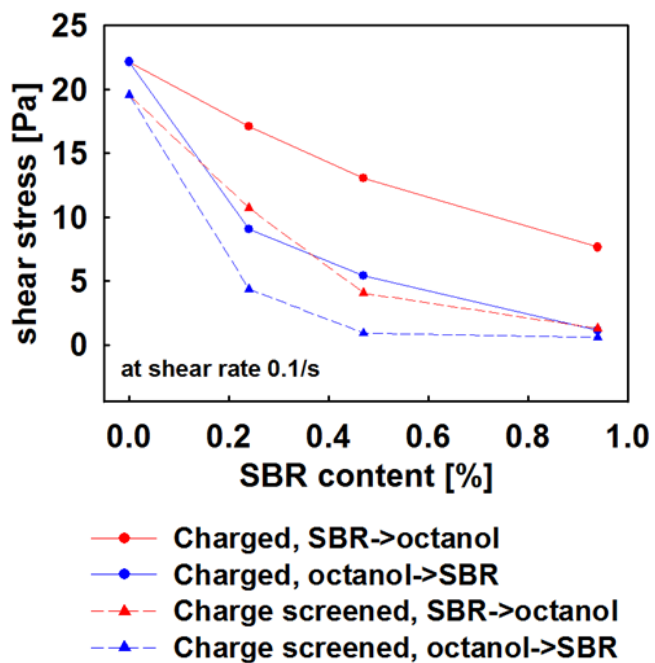


Figure 3.5. Shear stress at shear rate 0.1s^{-1} of capillary suspension made from glycerol as a bulk fluid with increasing the amount of SBR. SBR→octanol samples were colored with red and octanol→SBR samples were colored with blue in the graph.

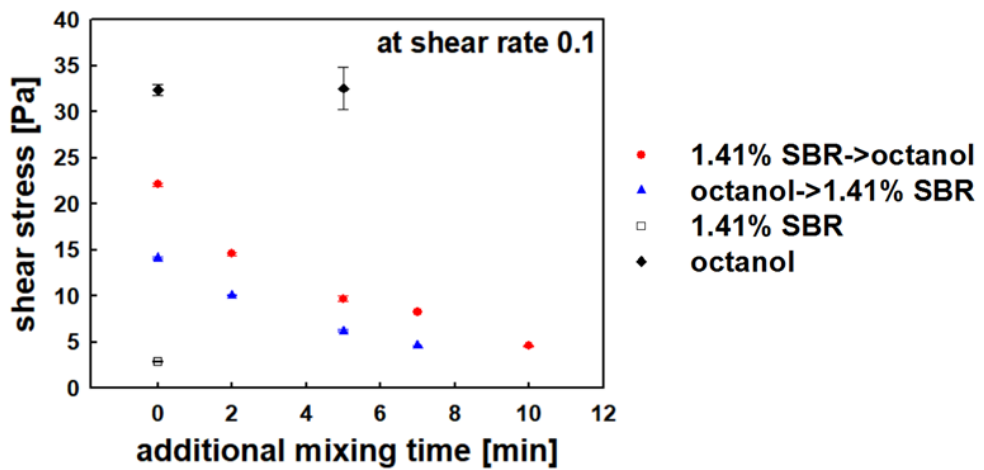


Figure 3.6. Shear stress at shear rate 0.1s^{-1} of capillary suspension according to additional mixing time was plotted. Additional mixing time in a x axis indicated mixing time applied after preparing the samples with the mixing method in Figure 2.1. Additional mixing was applied at a mixing power of 650 rpm.

3.2 Adhesion force measurement

Adhesion force was measured utilizing 90° peel-test to investigate variation of adhesive characteristics resulted from the addition of octanol and different mixing methods. Peel test enabled to determine adhesion strength between anode battery layer and copper foil. Adhesion force was defined as averaged (20 mm length) peel force divided by sample width. Adhesion force of battery slurry without secondary fluid showed stepwise increase as increasing the SBR content in Figure 3.7. SBR obviously renders adhesion between battery layer and copper foil. The influence of interaction between SBR and octanol arised from two mixing methods on adhesion force was analyzed in Figure 3.8 through adhesion force difference. Adhesion force difference was defined as adhesion force of battery slurry without secondary fluid subtracted from adhesion force of capillary suspension. Force difference over 0 signifies improved adhesive properties of electrode layer due to the addition of the secondary fluid. In Figure 3.8 (a), SBR→octanol slurry had negative force difference at 0.47vol% SBR sample, whereas it had positive force difference from 0.94vol% SBR content. Different tendency was observed with octanol→SBR sample in Figure 3.8 (b). In all range, octanol→SBR samples had lower force difference than SBR→octanol samples which illustrated inefficient SBR performance owing to mixing process resulting in microstructural change. When sample contained 2.35 vol% SBR, depending on mixing protocol, octanol became either

enhancement or deterioration additive for adhesion force. Adhesion force ratio in Figure 3.9 which was defined as adhesion force of capillary suspension over adhesion force of suspension without octanol facilitated straightforward comparison between the results from two different mixing samples. Data marked in red indicated SBR→octanol sample and data marked in blue indicated octanol→SBR sample. The disparity of force ratio between red and blue symbol became pronounced from 1.41 vol% to 2.35 vol% SBR content. In this region, mixing methods permitted samples to have completely different adhesion force. Steep decline in force ratio of octanol→SBR sample denoted severe degradation of adhesive characteristic. This adhesion data was correlated with rheology data in Figure 3.3. Octanol→SBR mixing samples having 1.41 vol%, 1.88 vol% and 2.35 vol% SBR showed exceptional tendency of modulus in Figure 3.3. They had the same G' and G'' values contrary to the modulus of common capillary suspension. From 1.41vol% SBR content, Octanol→SBR sample showed both liquid-like properties and deterioration of adhesion force. In other words, destroyed capillary network owing to the addition of high content of SBR after octanol induced not only transition of flow behavior but also degeneracy of adhesion properties.

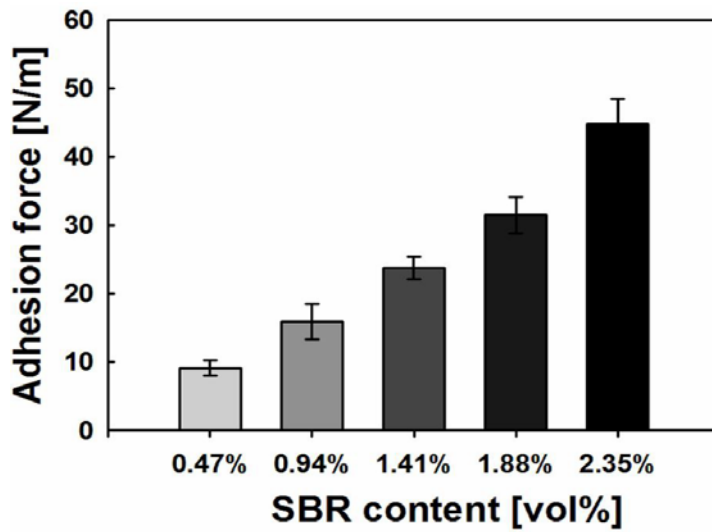


Figure 3.7. Adhesion force measured from battery slurry without secondary fluid as increasing the amount of SBR.

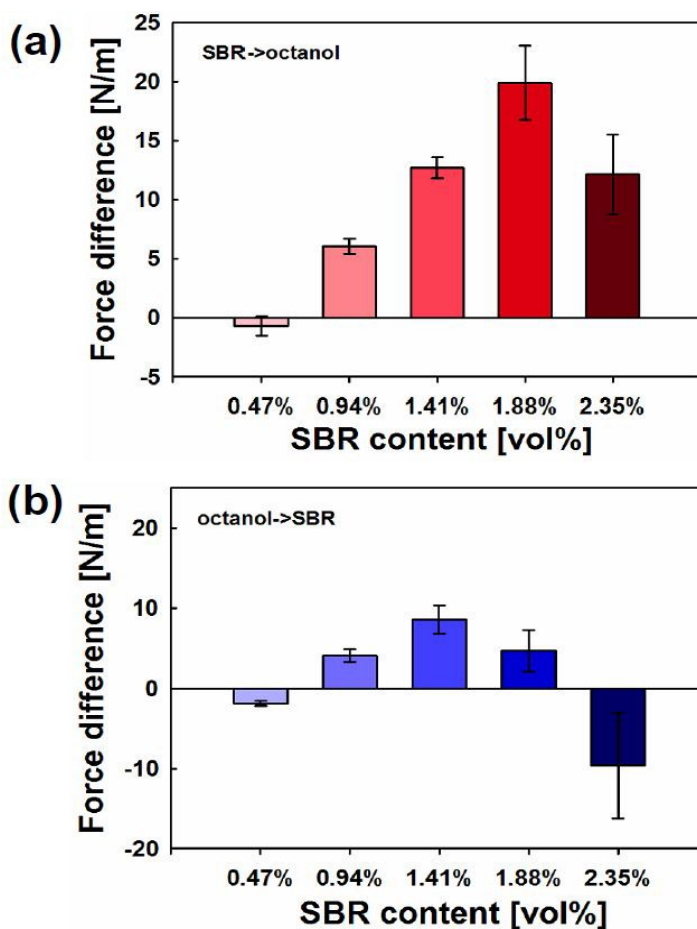


Figure 3.8. Adhesion force differences defined as 'adhesion force of capillary suspension – adhesion force of suspension without octanol' with varied SBR content were plotted. Two mixing methods, (a) SBR→octanol and (b) octanol→SBR, were applied.

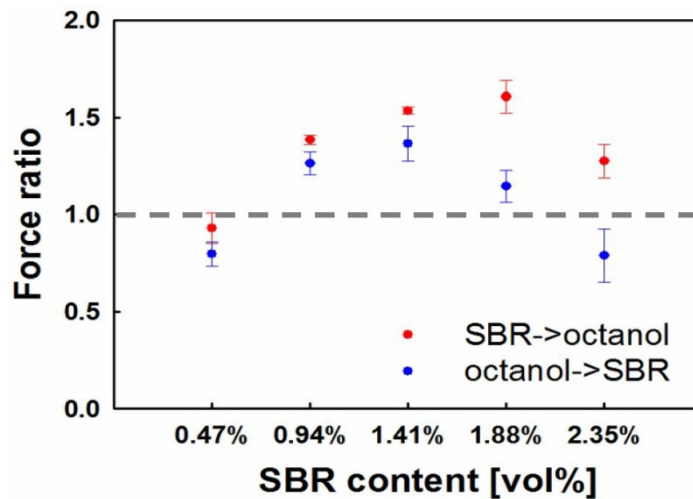


Figure 3.9. Adhesion force ratio defined as 'adhesion force of capillary suspension / adhesion force of suspension without octanol' with respect to different mixing methods was calculated. SBR→octanol samples were plotted as red symbol and octanol→SBR samples were plotted as blue symbol in the graph.

3.3 Microscopy and interfacial tension analysis

Observing distribution and determining the role of the binder are crucial to thoroughly understand the alteration of mechanical properties in the capillary suspension. Microscopic observation and interfacial tension analysis were employed to confirm the location and the action of the binder between two immiscible fluids, that is to say a bulk fluid and the secondary fluid. SBR binder with two immiscible fluids was prepared in Figure 3.10 (a). Left picture in Figure 3.10 (a) represented fluids which was separated into SBR–water suspension(white part) and octanol(transparent part). SBR is a white polymer particle dispersed in water in a latex form, thereby SBR–water suspension has white color. Before shaking, octanol and water were separated due to fluid immiscibility. After intense shaking by hand for 1 minute, on the right side in Figure 3.10 (a), stable emulsion was formed and maintained over 3 weeks. SBR undoubtedly hindered two immiscible fluids to be separated. This emulsion was investigated under a microscope in Figure 3.10 (b). Emulsion formed by particles instead of surfactant was already named as Pickering emulsion [26] and emulsion in Figure 3.10 (b) followed the same formation principle. Particles which were partially wetted by both bulk and secondary fluid tried to locate on the interface between two immiscible fluids so that they were in an energetically favorable state [27–29]. This implied that the addition of immiscible secondary fluid changed the location of SBR particles in the suspension

towards the interface between water and octanol.

Relocated SBR binder affected properties of suspension as shown in section III A. Rheological properties had a strong correlation with interfacial tension of capillary suspension. To Figure out the Interfacial tension between octanol and SBR–water suspension was measured in Figure 3.11. The content of SBR in SBR–water suspension was from 0 to 2.35vol%. The whole measurements were conducted for 1200 seconds. As shown in Figure 3.11, interfacial tension decreased as increasing SBR content. Another distinctive point that could be detected was the interfacial tension change at the beginning of the measurement with the samples having SBR polymer. Interfacial tension between octanol and pure water keep constant value for 1200 seconds. On the other hand, interfacial tension between octanol and SBR–water suspension changed as time goes by. Increasing SBR concentration promoted steeper decrease in interfacial tension during measurement time. The reason for the decline of interfacial tension is related to the appearance and the concentration of SBR. SBR latex is polymerized by emulsion polymerization using emulsifier [30, 31]. Emulsifier remains on the surface of the SBR polymer after the whole polymerization process and has an impact on the properties [24]. SBR polymer particle trapped on the interface and the emulsifier on the SBR might affect to the interfacial tension. Higher SBR concentration in SBR–water suspension induced the more SBR to be located on the interface resulting in decrease in interfacial tension.

Microscopy and interfacial tension results showed the distribution of SBR in the midst of two immiscible fluids and the interfacial tension tendency relying on SBR concentration. These data could be evidences for explaining mechanical properties varied by different mixing methods shown in III A and B. Simplified capillary force F_c from pendular bridge between two shpere particles in contact is given by

$$F_c = 2 \pi r \gamma \cos \theta \quad (1)$$

where r is a particle radius, γ is the surface tension and θ is a wetting angle [32]. Capillary suspension which established by capillary force is strongly connected with surface tension according to equation (1). As we already observed from interfacial tension measurement, SBR concentration trapped on the interface determines capillary force that is, the strength of capillary suspension. SBR is sporadically trapped on the interface between bulk and the secondary fluid during mixing process. As seen in Figure 3.6, the strength of capillary suspension depended on mixing time. It could be inferred that higher concentration of SBR on the interface was induced by longer mixing time and this could be the reason for the decline in interfacial tension and the strength of capillary suspension.

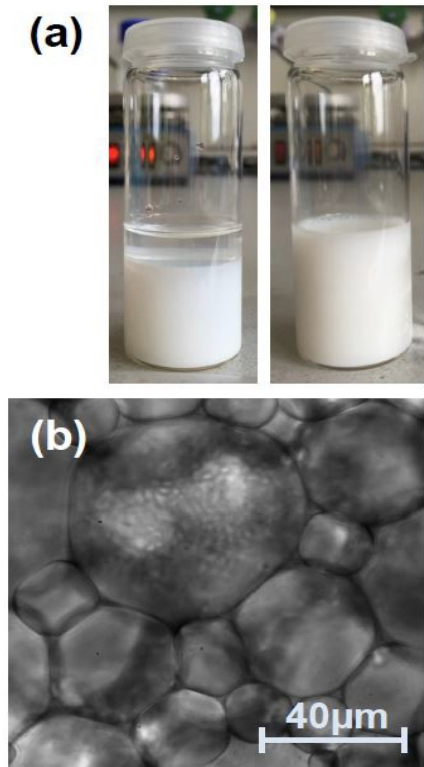


Figure 3.10. (a) Separated octanol and SBR–water suspension (left) and the mixture after vigorous mixing by hand for 1 min which becomes an emulsion (right). (b) Emulsion has been examined by microscopy.

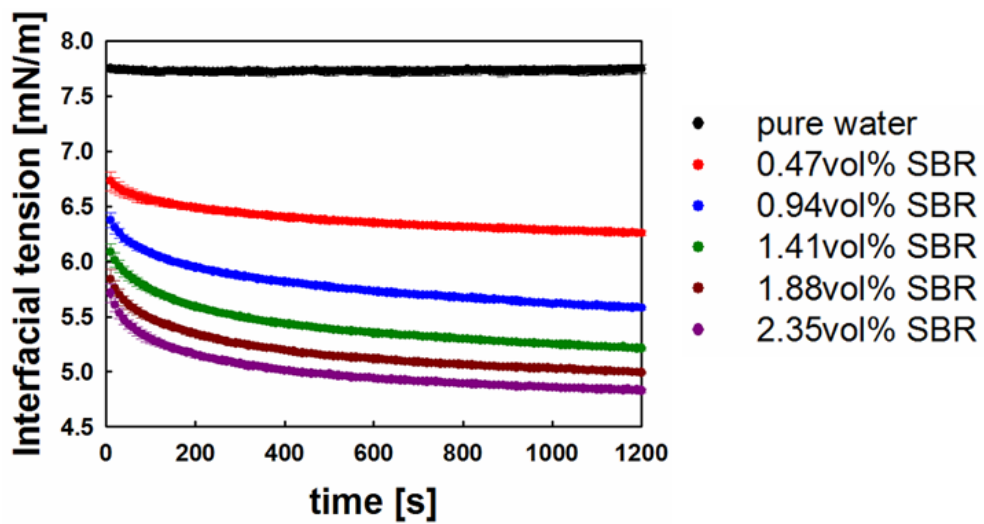


Figure 3.11. Interfacial tension of SBR–water suspension against octanol. Concentration of SBR in SBR–water suspension was varied from 0vol% to 2.35vol%.

Chapter 4.

Conclusion

Capillary suspension is an innovative concept for enhancing processing and mechanical properties of the material. To apply this concept to industrial field, precise understanding of the interaction between secondary fluid and additives for industrial materials has to be preceded. In this study, Li-ion battery anode slurry based on capillary suspension was selected to investigate the interaction of common binder SBR and a secondary fluid octanol and the consequential change in mechanical properties. Different sample preparation methods which induced interaction change between SBR and octanol were employed for thorough investigation.

Rheological properties and adhesive properties were varied by mixing protocol and SBR content. When SBR binder was added before octanol to the graphite suspension, rheological and adhesion properties were both enhanced compared to the other protocol. Higher SBR content lowered rheological properties of capillary suspension with both mixing protocol. Proper content of SBR were revealed to develop adhesive properties using capillary suspension.

Addition of the secondary fluid relocates SBR binder to the interface between bulk and the secondary fluid. SBR on the interface alters interfacial tension resulting in change of capillary force. Mixing time was critical factor since longer mixing induced more SBR to be trapped on the interface. Mixing time could be adjusted by mixing methods. Different mixing methods result in distribution variation of SBR in the

capillary suspension and those cause changes in mechanical properties such as flow behavior and adhesive properties.

Investigating the interaction between the secondary fluid and additive and the consequences revealed by changes in mechanical properties enable effective application of capillary suspension concept to industrial materials. This study suggests the way to improve mechanical properties of battery slurry based on capillary suspension with simple process control and relates this phenomena to structural point of view.

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국문요약

모세관 현탁액을 기반으로 한 리튬 이온 전지 음극 슬러리의 유변 물성 및 접착 특성에 대하여 알아보았다. 모세관 현탁액은 현탁액에 소량의 2차 유체를 첨가하여 현탁액의 흐름 특성을 크게 변화시킨다는 개념이다. 첨가된 2차 유체는 입자 사이에 위치하여 입자 사이에 모세관 힘을 유도하고 이로 인하여 입자의 네트워크가 형성된다. 형성된 네트워크 구조로 인하여 유변 물성이 크게 변화하는 것이다. 모세관 현탁액은 다양한 산업 슬러리에 적용될 수 있으며, 다양한 이점들을 제공해줄 수 있다. 그러나 이 개념을 부작용 없이 산업 슬러리에 올바르게 적용하기 위해서는 첨가되는 2차 유체와 산업 슬러리에 물성 조정을 위하여 첨가되는 바인더간의 상호작용에 대하여 정확하게 이해하고 있어야 한다.

이 연구에서는 수계 음극 배터리 슬러리에 첨가되는 바인더 SBR과 2차 유체인 옥탄올 간의 상호작용에 대하여 알아보고, 2차 유체 첨가로 인한 미세 구조 변화를 믹싱 조건을 변경함으로써 조정하고자 하였다. 2차 유체와 바인더간의 상호작용은 바인더의 함량과 바인더와 2차 유체의 믹싱 순서를 변경하고, 이에 따른 유변 물성과 접착 특성 변화를 관찰하여 알아보고자 하였다. 모세관 현탁액에서의 바인더의 영향과 분포는 에멀전 형성 실험과 계면 장력 측정 실험으로 알아보았다. 유변 물성과 접착 특성이 크게 증진될 수 있는 바인더의 함량과 믹싱 조건을 찾을 수 있었고, 이에 대한 원인에 대해서도 파악하였다.

모세관 현탁액에서의 바인더와 2차 유체간의 상호작용에 대한 이해와 믹싱

공정을 통한 미세 구조 조정을 통하여 여러 물성이 향상된 산업 슬러리를 제조할 수 있기를 기대한다.