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공학석사학위논문

**Effect of pH on the dispersion stability of water-based
cathode slurry with poly(acrylic acid) as a binder**

Poly (acrylic acid)를 바인더로 사용하는 수계 양극재
슬러리의 분산 안정성에 미치는 pH 의 영향

2017년 2월

서울대학교 대학원

화학생물공학부

김 도 훈

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Abstract

Effect of pH on the dispersion stability of water-based cathode slurry with poly (acrylic acid) as a binder

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In this study, the effect of pH on the microstructure and dispersion stability of aqueous cathode slurry was investigated. LiFePO_4 , CB and PAA were used as model systems for the cathode slurry. Although the neutralization degree of PAA has been found to affect the electrode performance, few researches about its effect on microstructure has been conducted. So far, we focused on the pH effect on the microstructure and dispersion stability of aqueous cathode slurry. In this study, we present that the neutralization degree has a crucial effect on the dispersion stability of the slurry. The pH condition was set at 3.0, 6.0, 7.7 and 12. To understand the slurry characteristics containing both LiFePO_4 and carbon black, we analyzed the structure and dispersion stability of LFP/PAA and CB/PAA in each pH condition first. In the case of LFP/PAA, the storage modulus at $\text{pH} = 6.0$ was decreased nearly three orders of magnitude compared to $\text{pH} = 7.7$ and liquid-like behavior was observed at pH from 3.0 to 7.7 except at $\text{pH} = 12$ in the case of CB/PAA. Among the pH conditions used in this experiment, LFP/PAA appeared to be most stable at $\text{pH} = 6.0$ and the most

unstable at $\text{pH} = 3.0$ once diluted. In the case of CB/PAA, it remained most stable at $\text{pH} = 7.7$ and unstable at $\text{pH} = 12$. The aqueous cathode slurry containing two particles was most stable at $\text{pH} = 6.0$ and it was confirmed that the large amount of active materials dominantly affected the overall structure of aqueous cathode slurry. Ionization degree of PAA has a large effect on the structure of aqueous cathode slurry, as evidenced by rheological properties and various methods, and the subtle pH difference near the equivalence point was found to have a significant influence on the structure change. Structure changes at each pH were attributed to the adsorption and desorption of PAA as well as the charge density and conformational change of the adsorbed PAA. These factors were investigated through the measurement of adsorption amount of PAA on both particles and the zeta potential. From our experimental results, we could expect that controlling the adsorption amount of PAA, the charge density and conformation alteration of adsorbed PAA should be taken into consideration seriously to obtain the enough dispersibility. This study indicates the importance of pH control when manufacturing the homogeneous water-based cathode slurry and ensuring sufficient dispersibility, especially when the preparation of uniform water-based battery slurry in mass production is considered

Key words: li-ion battery, Poly(acrylic acid), dispersion stability, adsorption, desorption, rheological property, microstructure

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Contents

Abstract.....	i
List of Figures.....	v
Chapter 1 Introduction.....	1
Chapter 2 Experimental.....	5
2.1. Experiments.....	5
2.2. Sample Characterization.....	7
2.2.1. FT-IR.....	7
Chapter 3 Results and Discussion.....	9
3.1. Rheological properties of LFP/PAA.....	9
3.2. Optical micrographs of LFP/PAA.....	12
3.3. Dispersion stability of LFP/PAA.....	13
3.3.1. Sedimentation test.....	13
3.3.2. Turbiscan.....	14
3.4. Surface properties of LFP/PAA.....	17
3.4.1. Adsorption amount of LFP/PAA.....	17
3.4.2. Zeta potential of LFP/PAA.....	18

3.5. Rheological properties of CB/PAA.....	21
3.5.1. Rate sweep & Frequency sweep.....	22
3.5.2 Scaling behavior.....	22
3.6. Optical micrographs of CB/PAA.....	24
3.7. Dispersion stability of CB/PAA.....	25
3.7.1. Sedimentation test.....	25
3.7.2. Turbiscan.....	26
3.8. Surface properties of CB/PAA.....	28
3.8.1. Adsorption amount of LFP/PAA.....	28
3.8.2. Zeta potential of LFP/PAA.....	29
3.9. Rheological properties of LFP/CB/PAA.....	31
 Chapter 4 Conclusion.....	34
 Reference.....	35
 국문초록.....	40

List of Figures

Figure 2.1.	FT-IR of CB /LFP.....	7
Figure 3.1.	Effect of the amount of PAA on the viscosity of LFP 20 vol% slurry at pH = 6.0.....	9
	(a) Viscosity with LFP 20 vol% and various amount of PAA	
	(b) Low shear viscosity with 20 vol% and various amount of PAA	
Figure 3.2	Effect of pH on (a) the viscosity, (b) the storage and loss modulus for a suspension of 20 vol% LFP with 2 wt% PAA.....	10
Figure 3.3.	Optical microscopy of LFP/PAA at various pH, containing LFP 2 vol% / PAA 0.2 wt%. (a) pH = 3.0 (b) pH = 6.0 (c) pH = 7.7(d) pH =12...12	12
Figure 3.4.	Photos of LiFePO ₄ / Poly (Acrylic acid) suspension at different pH All suspensions contain 10 ⁻¹ vol% of LFP and 10 ⁻² wt% of PAA.....	13
Figure 3.5.	Transmittance curves for 10 ⁻¹ vol% of LiFePO ₄ and 0.10·10 ⁻² wt% of PAA suspension.....	14
Figure 3.6.	The adsorption amount of PAA on the LFP surface at each pH conditions.....	17
Figure 3.7.	Zeta potential of LFP in aqueous suspension in the absence and presence of PAA	18
Figure 3.8.	Effect of the pH on the viscosity and storage modulus and loss modulus of CB 1.3 vol% with PAA 1 wt%.....	21
	(a) Viscosity of CB 1.3 vol% with PAA for each pH conditions	

	(b) Low shear viscosity with 20 vol% and various amount of PAA	
Figure 3.9.	Power-law scaling of storage modulus with volume fraction of CB with PAA at pH = 12 and without any polymer.....	22
Figure 3.10.	Optical microscopy of CB/PAA at various pH, containing CB 0.2 vol% / PAA 0.1 wt% (a) pH = 3.0 (b) pH = 6.0 (c) pH = 7.7(d) pH = 12..	24
Figure 3.11.	Photos of CB / PAA suspension at different pH. All suspensions contain 10^{-3} vol% of CB and $0.5 \cdot 10^{-3}$ wt% of PAA.....	25
Figure 3.12.	Transmittance curves for CB and PAA system. All suspensions contain 10^{-3} vol% of CB and $0.5 \cdot 10^{-3}$ wt.....	26
Figure 3.13.	The adsorption amount of PAA on the CB surface at each pH conditions.....	28
Figure 3.14.	Zeta potential of CB in aqueous suspension in the presence of PAA	29
Figure 3.15.	(a) Viscosity for a suspension of 20 vol% LFP with 2 wt% PAA at pH = 6.0 with and without CB (b) Low shear viscosity of 20 vol% LFP with 2 wt% PAA with and without CB at pH = 6.038.....	31
Figure 3.16.	(a) Effect of pH on the storage & loss modulus for a suspension of 20 vol% LFP ,1.3 vol% CB with various amount of PAA(b) Storage & loss modulus value of each and mixed slurries at 6.03 rad/s.....	32

Chapter 1 Introduction

The development of environmentally friendly and cheaper rechargeable batteries is regarded as important energy storage technology these days, since they provide solutions to our issues of environment and energy. However, preparation of the electrodes for the rechargeable battery necessitates the use of organic solvents such as N-methyl-2-pyrrolidone (NMP) which are toxic and high cost. The usage of such harmful organic solvents has been considered as a disadvantage of rechargeable lithium ion batteries. Recently, many researchers have tried to replace the solvent and binder used to manufacture the electrode to achieve cost reduction and eco-friendly processing. In recent times, water has attracted much attention as an alternative for the electrode processing due to its low cost.[1] The difference in economic viability between NMP-based and water-based processing has been considerably increased when the environmental issues are being considered. Therefore, usage of water-soluble binders for graphite based anodes is already being applied in the industrial field [2–4]. Thanks to the successful replacement of aqueous processing for anode, a new trend is now being developed to replace the NMP-soluble PVDF binder in the cathode. Attempting to change the solvent and the binder in this way, not only electrical or mechanical properties of the electrode but also the dispersion problem of the battery slurry should be taken into consideration seriously. Recently, many kinds of cathode materials have been used to manufacture the electrode. [1,5] Among them, LiFePO_4 [LFP] has attracted much attention due to its low cost, eco-friendly, high stability and long cycle life. [6,7] However, studies have been reported that the carbon layer on the coated surface for overcoming the drawback of LFP's low conductivity becomes the reason of aggregation in water due to its hydrogen bonding. [8,9] Carbon black, widely used as a conductive agent, also causes serious aggregation in water due to its hydrophobicity. [10] Aqueous cathode slurries have considerable problems

such as agglomeration and viscosity control due to agglomeration of these particles, and these factors have an important influence on achieving uniform product quality on industrial scale. [11,12] Heterogeneous distribution of the components weakens not only the mechanical properties of the electrodes but also shortens the cycle life. [13] Thus, some binder materials have been suggested for the process of aqueous battery slurry. Water-soluble binders such as CMC, SBR [14,30] and PAA [15,16] have been proposed as candidates for the aqueous cathode processing. Especially, PAA has been extensively studied as a dispersant and a binder of positive and negative electrodes of a lithium ion battery. It plays a role as a dispersant in the water-based slurries when it has smaller molecular weight, thereby reducing the viscosity of the slurry and improving the cycle life of the cell. [17,18] On the other hand, weakly cross-linked PAA composed with higher molecular weight have been reported as a binder for aqueous processing. This is because it shows an improvement of cycle life in a silicon based anode due to superior shifting between shrinkage and expansion to other binders. [19-21] Also, it is well known to have better performance than NMP-based slurries containing PVDF binder. [22-24] One of the unique behavior of PAA is reversible conformation transition depending on slurries pH, and researchers have carried out to control the state of dispersion using PAA's property. [25] At low pH, PAA is less protonated and found to have coiled conformation due to intramolecular hydrogen bonding otherwise exhibits highly extended conformation by electrostatic repulsion force by increment of PAA's negative charge density at high pH. It gives us crucial implication in the preparation of the electrode slurry. As previous studies present that the dispersibility of the carbon nanoparticles using PAA would vary significantly depending on slurries' pH [26-29], we can expect that dispersibility of the electrode slurry would also be sensitive to pH. Serious problems such as agglomerate formation, phase heterogeneity, precipitation would occur if PAA couldn't play any role in dispersing the slurry.

Even it doesn't lead to a significant effect on the performance of the electrode manufactured in the laboratory scale, they could be a crucial deficiency on the process considered on industrial scale. Recently, it is reported that the performance of the electrode is found to be improved by simply adjusting the pH.[20] This performance improvement may be induced from the change in the microstructure of the electrode due to the alteration of charge density and conformation of PAA. However, although the interactions of SBR and CBC with LFP particles have been studied previously, the effect of pH on the dispersion and change in microstructure of aqueous cathode slurry containing PAA as a binder is rarely studied. Understanding and considering interaction between the component and its role in the battery slurry should be primary to explain and deal with the change in the whole system since the electrode slurry is a very complex system containing conductive agent, active materials, binder or any surfactant. Our study focuses on the change in interaction between each particle and the polymer while considering the adsorption of polymer on the particles which provides dispersibility of slurry. There is an experimental difficulty due to the formation of a microgel when using weakly-crosslinked PAA. As a strategy, a simplified slurry model was designed by using a linear PAA polymer. In this study, we have investigated the particle-polymer interaction depending on the pH using linear PAA as a model system of aqueous cathode slurry. We characterized the microstructure of aqueous cathode slurry from the rheological properties and dispersion stability at each pH, further suggesting the role of polymer on the dispersibility of aqueous cathode slurry by measuring the adsorption amount and zeta potential. We confirmed that the subtle difference of neutralization degree of PAA near the equivalence point induces the microstructure change rapidly and that the electrode slurry should be dealt with carefully while considering the structure change of the slurry. We could notice that our results show the importance of the binder's role in the battery slurry. It is closely related to

adsorption and desorption kinetic of PAA with alteration of ionization degree depending on pH and it also shows that the pH of aqueous battery slurry system affects its microstructure extensively.

Chapter 2 Experimental

2.1 Experiments

Carbon black [Conductex-7067 Ultra] were provided by Columbian Chemicals, containing less than 0.1 % Ash. We purchased LFP [Carbon coating, 2~3 wt%] from GELON LIB Co. We used carbon blacks and LFP without any refinement process. PAA ($M_w = 250,000$ g/mol) was purchased from Aldrich. The weight fraction of aqueous cathode slurry containing LFP/CB/PAA/DI water is 46/1.6/5.6/46.6. Suspension's PH was adjusted by using 1M sodium hydroxide or Hydrogen chloride and measured by pH meter. Both particles CB and LFP suspensions were mixed respectively, using rotor stator homogenizer for 10 min at 8000 rpm. For CB/LFP/PAA slurry, CB was pre-dispersed for 5 minutes with a rotor-stator disperser at 8000 rpm, followed by LFP particles with a mechanical stirrer for 10 minutes. Before measurements, we disperse slurry with homogenizer for 30 seconds to remove agglomerated and sediment. Rheological properties were measured using a stress controlled type rheometer [AR-G2, TA Instruments] at 25 °C. Pre-shear at 2000 s^{-1} for 40 s & 1 s^{-1} for 10 s and equilibrium time for 5 min were performed to obtain reproducible results, removing shear history. Viscoelastic properties were measured in linear viscoelastic region. Viscosity of the suspension was measured in descending order of shear rates from 1000 /s to 0.01 /s. In this study, all measurements were implemented after 24 hours. This is quietly reasonable duration for manufacturing and processing of Li-Ion battery slurries. Also, it is enough times for equilibrate adsorption and desorption of PAA the particle surface. Not only rheological properties but various methods were used for characterizing and understanding the structure and dispersion stability. Sedimentation test was conducted to investigate and compare the dispersion

stability for each pH conditions. Turbidimetric method [Turbiscan LAB-EXPERT, Formulaction] was used, quantifying the sedimentation tendency. It was measured during 12 hours, which data was collected every 5 mins for 1 hour, followed by every 30 mins for 11 hours. Zeta potential was determined through an electrophoretic light scattering [ELS-8000, Otsuka Electronics]. Zeta potential was measured by applying a electric field to sample and measuring the mobility of the particles. Samples were manufactured, equilibrated for 24 hour and centrifuged. And then, the supernatant concentration was analyzed by measuring the weight percent of supernatant, using electronic microbalance. Cross-linked PAA isn't suitable as a model system to understand the interaction between particles and PAA because of strong yield stress produced by neutralized and swelled PAA itself. Therefore, in this study, linear PAA was used to characterize and quantify the interaction.

2.2 Sample characterization

2.2.1 FT-IR

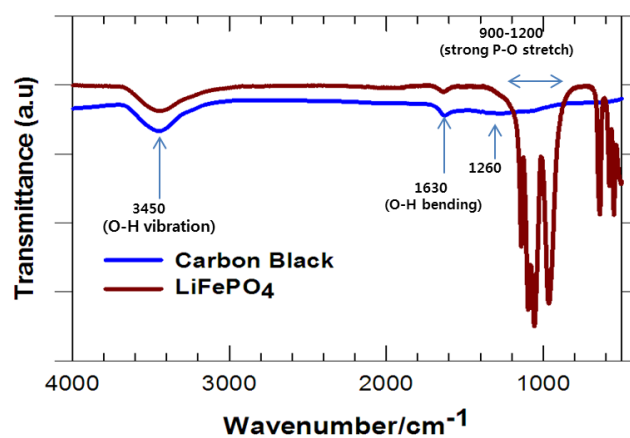


Fig. 2.1. FT-IR of CB and LFP

Fig. 2.1 is the FT-IR graph. As mentioned above, LFP particle's surface is coated with carbon on part of its surface. The surface of the LFP particle is found to be composed with two parts. Surface of LFP particles is partially covered with metallic component, which could be confirmed by P-O stretch peaks. Also, we could identify that the remaining portion of LFP surface covered with carbon have a similar surface properties with CB, proved by same wavenumber peaks with CB and LFP.

Chapter 3 Results and Discussion

3.1 Rheological properties of LFP /PAA

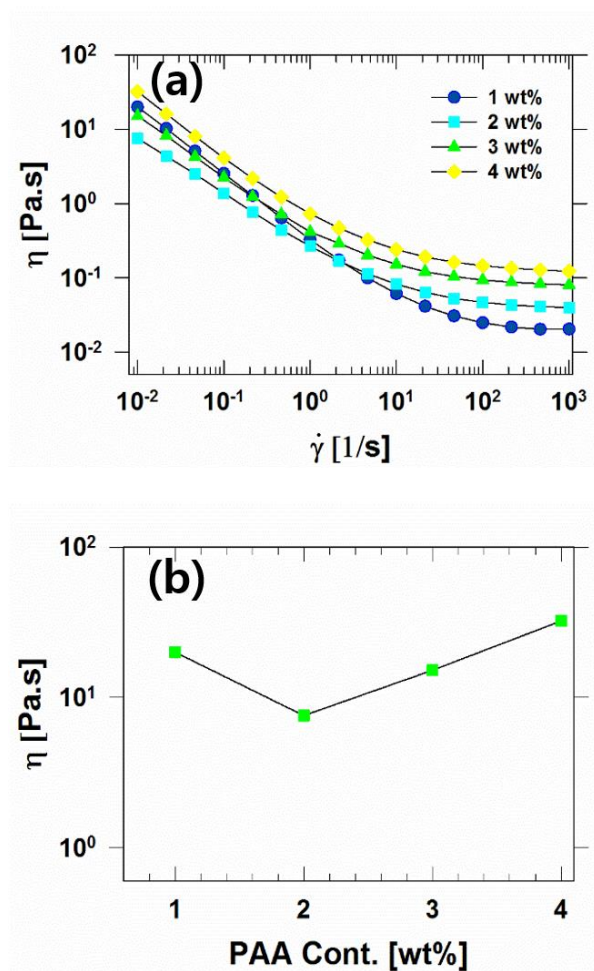


Fig. 3.1. Effect of the amount of PAA on the viscosity of LFP 20 vol% slurry at pH = 6.0.

(a) Viscosity with LFP 20 vol% and various amount of PAA

(b) Low shear viscosity with 20 vol% and various amount of PAA

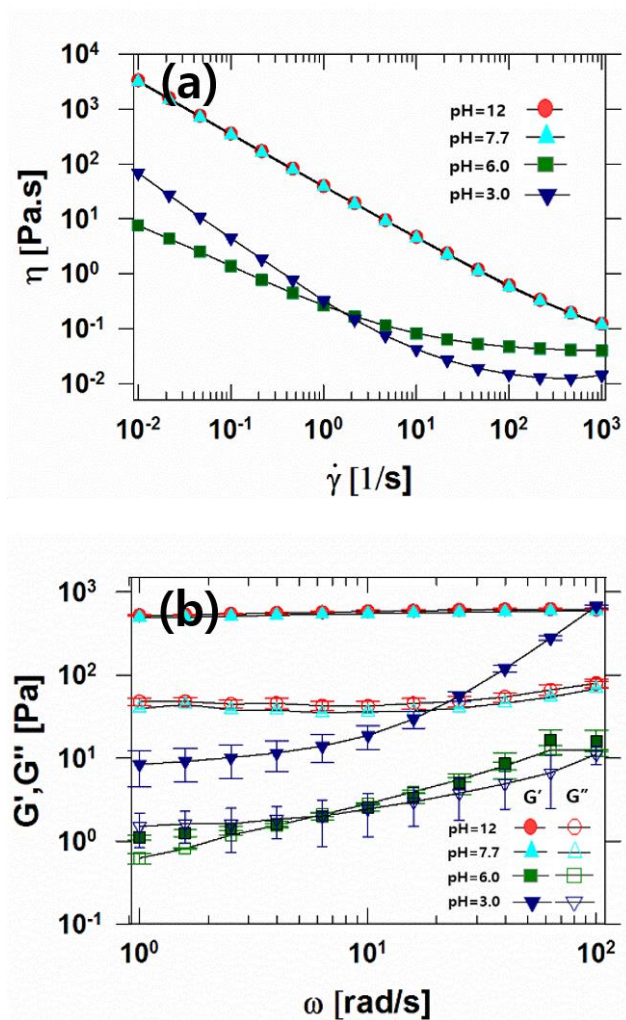


Fig. 3.2. Effect of pH on (a) the viscosity, (b) storage and loss modulus for a suspension of 20 vol% LFP with 2 wt% PAA.

Fig. 3.1 shows the effect of the amount of PAA on the viscosity of LFP slurry at pH = 6.0. To investigate the appropriate amount polymer, we measured the viscosity with changing the content of the PAA shown in Fig. 3.1 (a). In Fig. 3.1(b), decrease of low shear viscosity was observed as the amount of PAA was increased from 1 wt% to 2 wt%, meaning that 1 wt% wasn't sufficient content to disperse the 20 vol% of LFP at pH = 6.0. In other words, 2 wt% of PAA was found to be minimum appropriate value for dispersing slurry at pH = 6.0. And then, viscosity increases with increment of PAA. This increment of viscosity may be induced from the increase of medium viscosity and depletion effect etc. After noticing the proper range of PAA with LFP, we conducted an experiment by dividing the range of pH into four intervals based on pH = 7, in order to figure out the difference in interaction between PAA and LFP near neutralization point. PAA chain was reported to have charge density nearly 0%, 30%, 70%, 100% at each pH conditions 3.0, 6.0, 7.7, 12. [31] Fig. 3. 2. presents the rheological properties of LFP slurry with PAA at each pH condition. Subtle pH difference near the equivalence point affects the interaction between LFP and PAA significantly. Especially at pH = 7.7, storage modulus was increased almost three orders of magnitude compared pH = 6.0. Even in strong basic conditions at pH=12, there was no change in structure compared with pH = 7.7. In addition, weak gel-like behavior and shear thinning also occurs severely at pH = 3.0. In this study, optical microscopes and sedimentation experiment have been conducted to investigate the effect of microstructure change on the dispersibility in each pH conditions.

3.2 Optical Micrographs of LFP/PAA

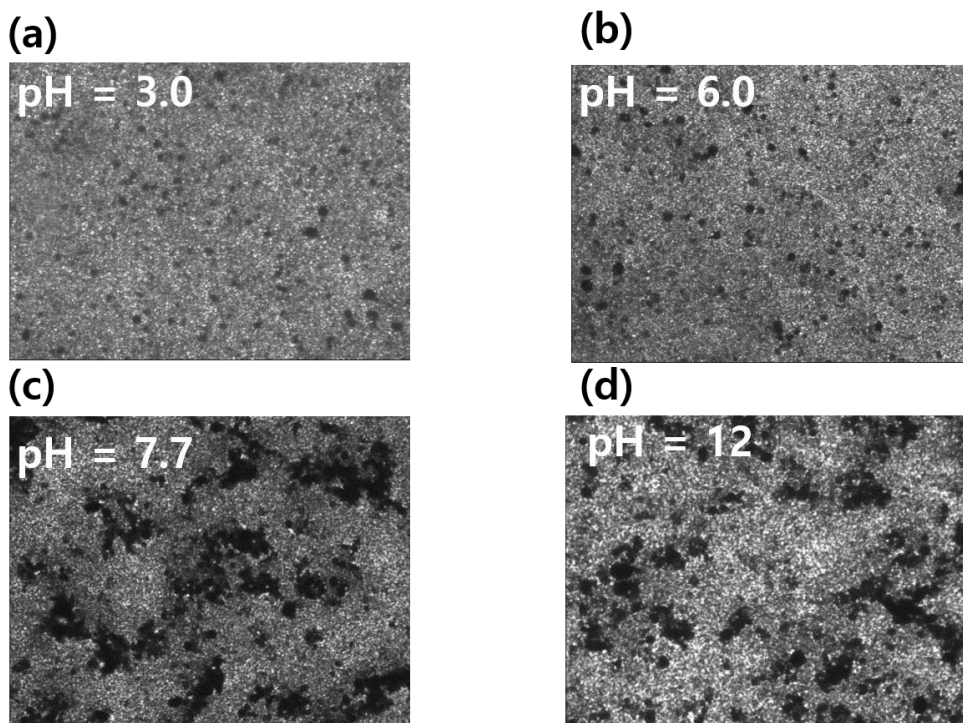


Fig. 3.3. Optical microscopy of LFP/PAA at various pH, containing LFP 2 vol% / PAA 0.2 wt%. (a) pH = 3.0 (b) pH = 6.0 (c) pH = 7.7 (d) pH = 12

3.3 Dispersion Stability of LFP/PAA

3.3.1 Sedimentation test

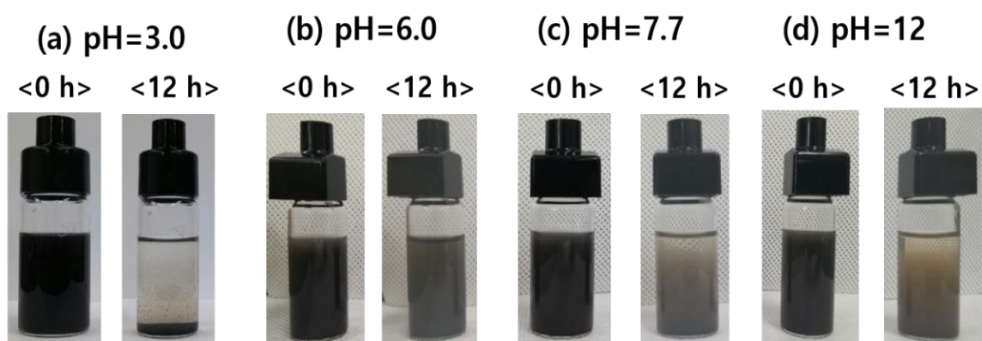


Fig. 3.4. Photos of LFP / PAA suspension at different pH. All suspensions contain 10^{-1} vol% of LFP and 10^{-2} wt% of PAA

3.3.2 Turbiscan

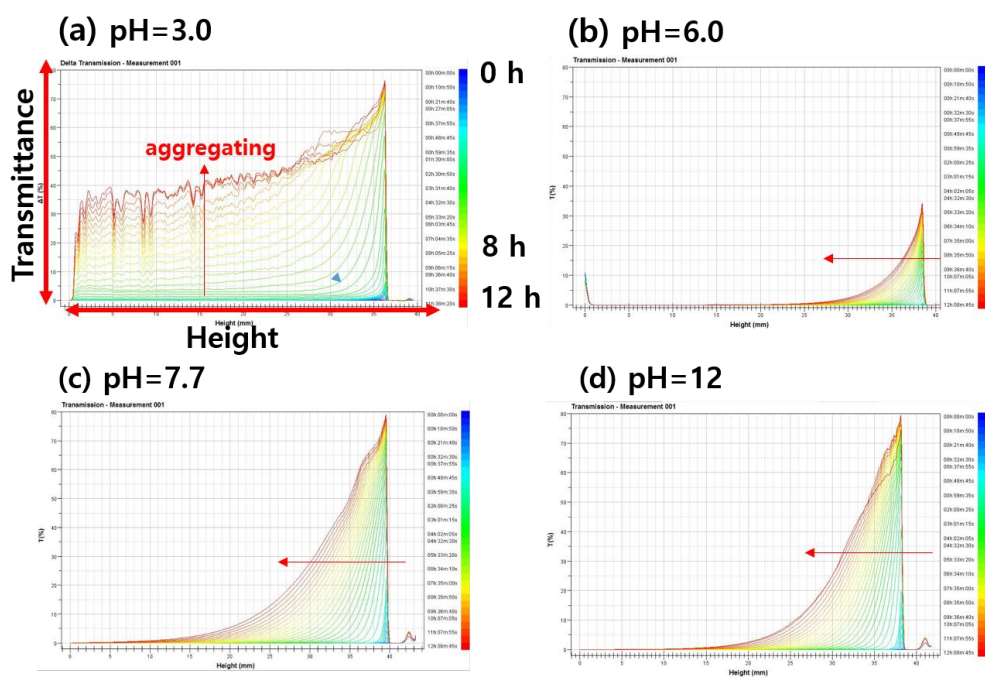


Fig. 3.5. Transmittance curves for 10^{-1} vol% of LFP and 10^{-2} wt% of PAA suspension.

Fig. 3.3 shows an optical microscopy image of LFP/PAA slurry at each pH conditions. At pH = 3.0, LFP/PAA slurry seems to be well dispersed compared to pH = 7.7, 12. However, once diluted more, we could easily observe the particle being aggregated severely. At pH = 7.7, 12, as presented in Fig 3.3, aggregated particle exists. At pH = 6.0, slurry was found to have the most well dispersed slurry among our pH conditions. Fig. 3.4 presents the sedimentation experiment to figure out the dispersion stability of slurry containing 10^{-1} vol% of LiFePO_4 and 10^{-2} wt% of PAA. As expected, sedimentation would occur most rapidly at pH = 7.7, 12 due to agglomeration of the LFP particle according to the fact that slurry forms strong gel-like structure. However, slurry at pH = 3 seems the most unstable and particle sediments quickly. Aggregates of LFP particle lead to a full sedimentation and deteriorates stability significantly. The most stable dispersion state was observed at pH=6.0. Turbiscan-LAB experiments were done to quantify the sedimentation tendency as well as kinetic phenomena occurring in the dispersion system in each pH condition. Fig. 3.5 shows transmittance and backscattering curves for the LFP with PAA in each pH condition during 12 hours. The sedimentation tendency of four investigated suspensions were totally different depending on each pH. LFP particle settled sequentially from the upper part of phial at pH=6.0, 7.7, 12 while sedimentation occurred overall at each position and time at pH = 3.0, which is proved by the increment aspect of transmittance value. It means that slurry at pH =3.0 undergoes destabilization significantly compared with other pH conditions. At pH = 6.0, the transmittance increased slowest and sedimentation proceeded slowly. When pH was 7.7 and 12, sedimentation proceeded in a similar way, but was found to be proceeding faster than the condition when pH was 6.0. We believe that the influence of pH on the structure shown in Fig. 3.1, Fig. 3.2 and the dispersion stability shown in Fig. 3.3., Fig. 3.4, Fig. 3.5 would have close relationship with interaction alteration between the LFP particle and PAA. In order to quantify the interaction between the polymer and the particles, we directly measured the adsorption amount of the polymer

on the LFP surface in Fig. 3.6.

3.4 Surface Properties of LFP with PAA

3.4.1 Adsorption amount

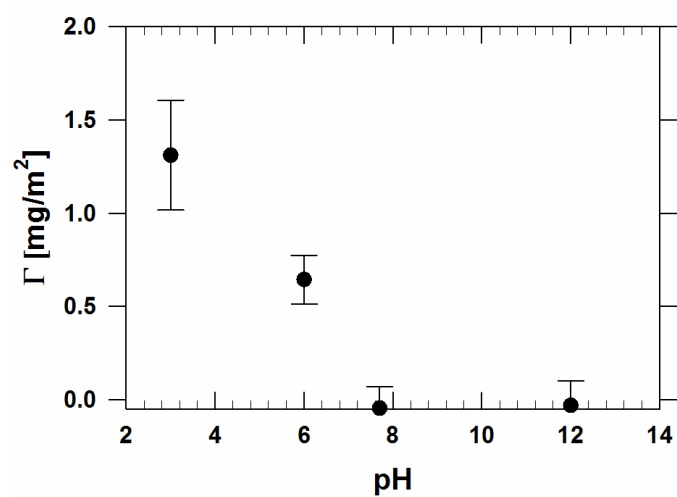


Fig. 3.6. Effect of pH on the adsorption amount of PAA on the LFP surface

3.4.2 Zeta potential

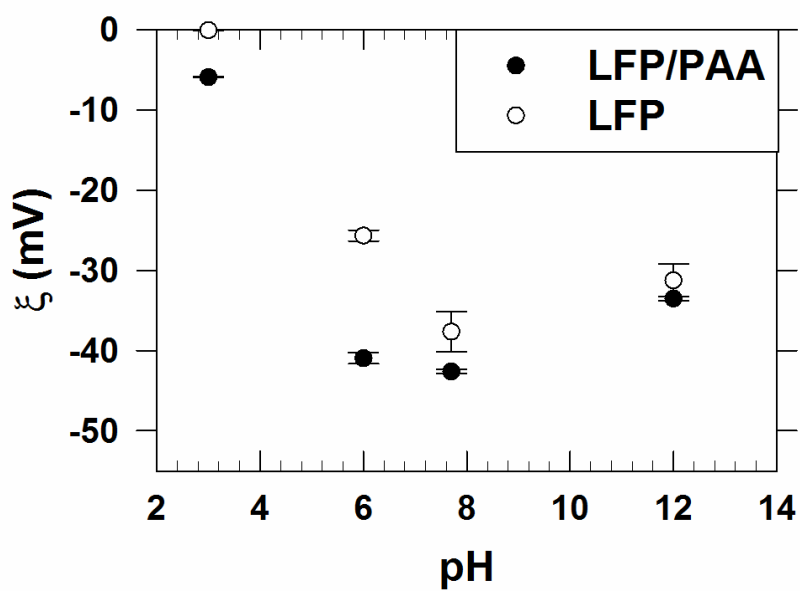


Fig. 3.7. Zeta potential of LFP in aqueous suspension in the absence and presence of PAA

This explains the reason why the structure and colloidal stability of LFP aqueous slurry was observed different at each condition. At pH = 7.7, 12, PAA doesn't adsorb on the LFP surface. As a result, the Van der Waals force between LFP particles become dominant and finally gelation occurred. The deprotonated backbone of polymer at pH = 7.7, 12 may cause electrical repulsion between chains and subsequently prevents it from adsorbing on the surface of LFP particles. Dispersion stability become worse due to aggregated particles, confirmed by optical microscopy shown in Fig. 3.3. We figured out the reason that drastic change of microstructure and dispersion stability occurs near the equivalence point. The decrease in PAA adsorption with increasing pH from 3.0 to 6.0 is originated from reasons related with repulsion force between PAA chain. However, the dispersion stability increases dramatically even if the amount of adsorbed PAA decreases at pH= 6.0. In this work, the reasons why the dispersion stability increases sharply at pH = 6.0 have been investigated, using zeta potential measured by dynamic light scattering. We believe that zeta potential of LFP particles is a crucial indicator, noticing the polymer's degree of charge and conformation on the particle surface. We expected that deprotonated PAA adsorbed on the particle surface affects significantly the electro-steric repulsion force closely related with structure and dispersions stability since the increase in the ionization of degree induces not only the polymer conformation more stretched but the polymer charged more negative. Fig. 3.7 indicates the zeta potential of LFP particles at each pH with and without PAA. From Fig. 3.7, isoelectric point(IEP) of LFP particle is about pH = 3.0, which means the charge on the particle surface is zero. Also, this provides the reasonable explanation about the reduction of the amount of adsorbed PAA shown in Fig 3.6. when it changed from pH = 3.0 to pH = 6.0. That may be attributed to the repulsive force from the charge of the polymer and particle surface as well as the charge of the polymer chain each other, preventing PAA from adsorbing on the surface of LFP. At pH = 3.0, not significant variation of zeta potential was observed with and

without PAA. It would be sensible results since PAA isn't nearly deprotonated even if it strongly adsorbed at $\text{pH} = 3.0$. Not sufficient electro-steric repulsion force would be produced since -5.93 mV of zeta potential and highly coiled conformation state don't satisfy the conditions generating both coulombic and steric force enough for dispersion. Thus, resultant force isn't enough and leads to shear thinning behavior and gel-like structure as well as the poorest dispersion stability. However, it is seen that the value of zeta potential changed to more significantly negative from -25.69 mV to -40.96 mV at $\text{pH} = 6.0$ with addition of PAA, revealing that negatively charged PAA successfully adsorbs on the LFP surface. At $\text{pH} = 6.0$, such a Van der Waals forces between LFP particle were canceled out and ultimately dominated by electro-steric repulsion force, proved by adsorption amount and zeta potential. In other words, partially deprotonated PAA chain has not only extended conformation but negatively charge, leading to increment of electro-steric repulsion force which improves the dispersion stability remarkably compared to $\text{pH} = 3.0$. Because PAA didn't adsorb at $\text{pH} = 7.7$ and 12 , zeta potential on the particle surface was not significantly different depending on the presence of absence of PAA. From these results, we conclude that aggregation could not be prevented only by the charge of the particle surface but many factors should be considered such as the amount of polymer adsorption on the particle surface, surface charge change of the particle by the adsorbed polymer and adsorbed polymer's conformation to ensure sufficient dispersibility by the electro-steric repulsion force.

3.5 Rheological properties of CB /PAA

3.5.1 Rate sweep & Frequency sweep

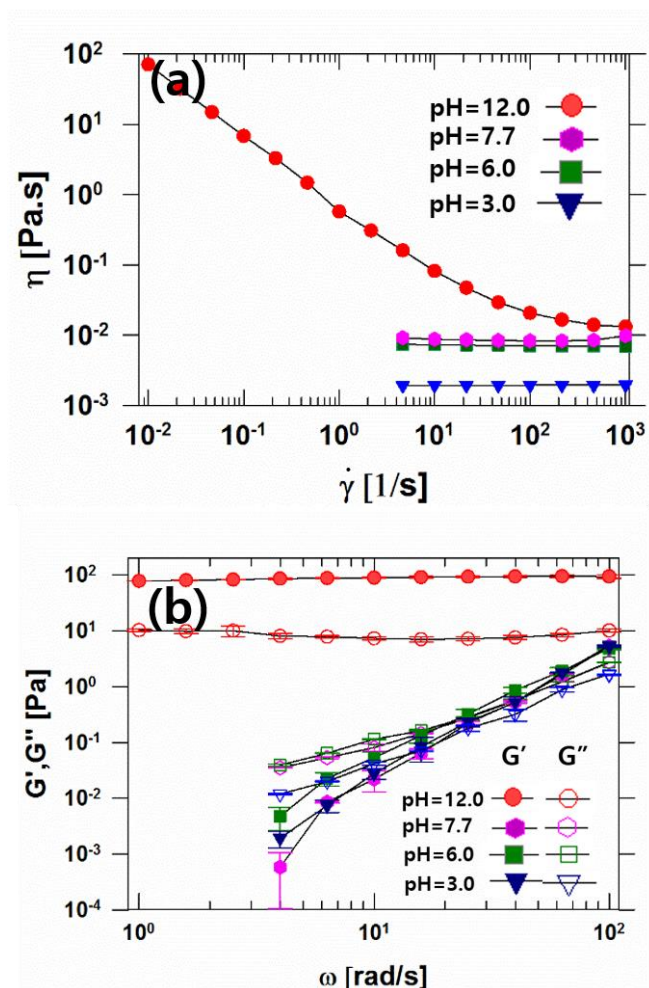


Fig. 3.8. Effect of the pH on the viscosity and storage modulus and loss modulus

of CB 1.3 vol% with PAA 1 wt%

(a) Viscosity of CB 1.3 vol% with PAA for each pH conditions

(b) Low shear viscosity with 20 vol% and various amount of PAA

3.5.2 Scaling behavior

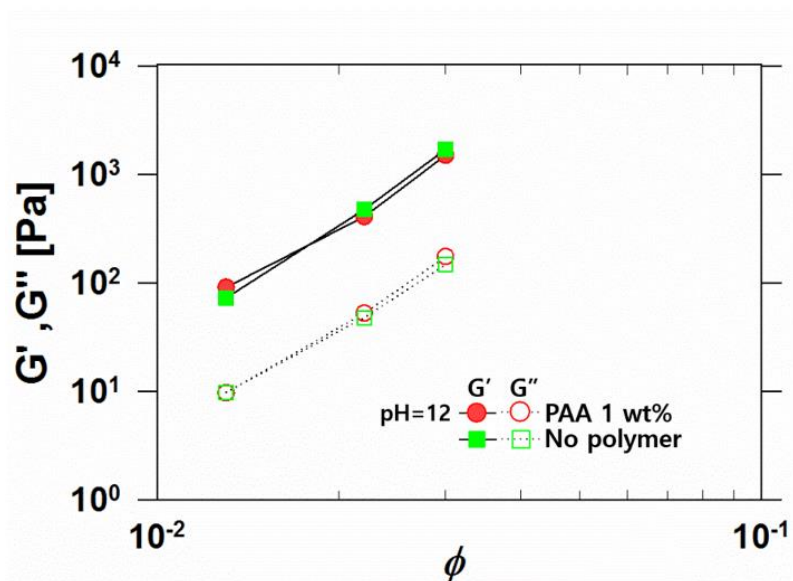


Fig. 3.9. Power-law scaling of storage modulus with volume fraction of CB with PAA at pH = 12 and without any polymer.

Rheological results of carbon black slurry with PAA were shown in Fig. 3.8 To manufacture well dispersed cathode slurry, the dispersion efficacy of carbon black with PAA also should be considered importantly. According to Fig. 3.8, PAA disperses carbon black as a liquid state, proved by having a newtonian behavior in the range of pH from 3 to 7.7 except pH = 12. Since PAA wasn't adsorbed on the CB due to electrical repulsion between perfectly deprotonated chains at pH = 12, CB exhibits aggregated structure and forms gel structure. Also, shear thinning behavior was observed because of particle breakage. As mentioned above, at pH from 3.0 to 7.7, CB with PAA presents a newtonian behavior. This is induced from PAA's adsorption which increases dispersibility by electro-steric repulsion force. In order to investigate about PAA's behavior at pH = 12, we measured the value of G' and G'' with presence or absence of PAA shown in Fig. 3.9 As we expected, value of G' and G'' and power law scaling behavior was found to be nearly corresponding with and without PAA at pH = 12. In other words, storage modulus is increased by a factor of 4.1 versus the volume fraction and fitted well to scaling factor from 3 to 5 when forming weakly-attractive gel fractal aggregates. [32-33] In this regard, we could notice that perfectly deprotonated PAA just remains as a fully extended state in medium and doesn't have any effect on dispersibility of CB.

3.6 Optical Micrographs of CB/PAA

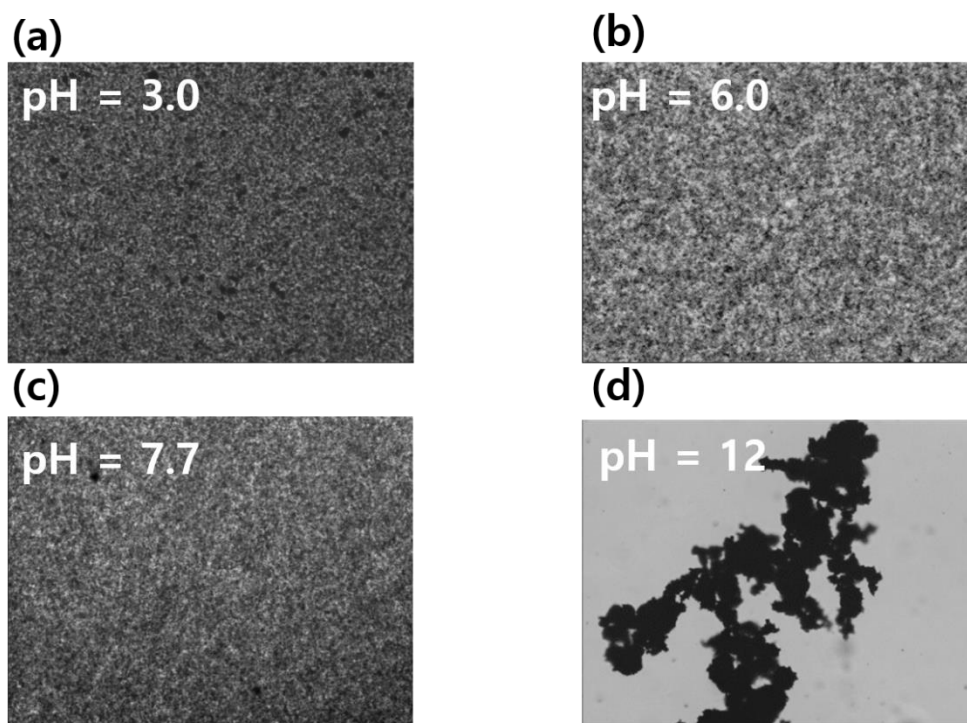


Fig. 3.10. Optical microscopy of CB/PAA at various pH, containing CB 0.2 vol% / PAA 0.1 wt% (a) pH = 3.0 (b) pH = 6.0 (c) pH = 7.7(d) pH = 12

3.7 Dispersion stability of CB/PAA

3.7.1 Sedimentation test

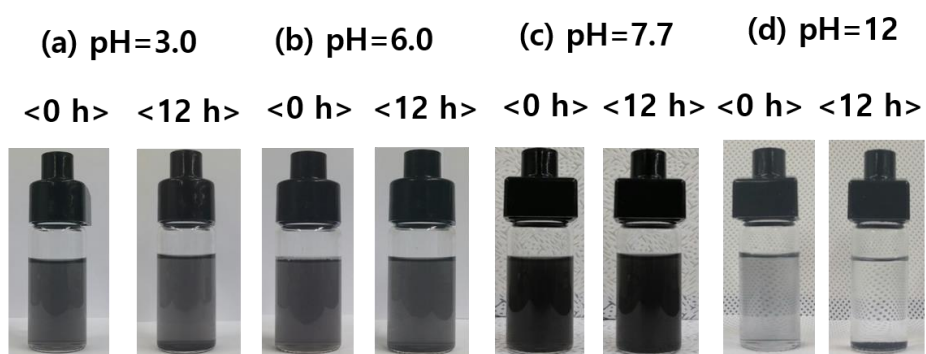


Fig. 3.11. Photos of CB / PAA suspension at different pH. All suspensions contain 10^{-3} vol% of CB and $0.5 \cdot 10^{-3}$ wt% of PAA.

3.7.2 Turbiscan

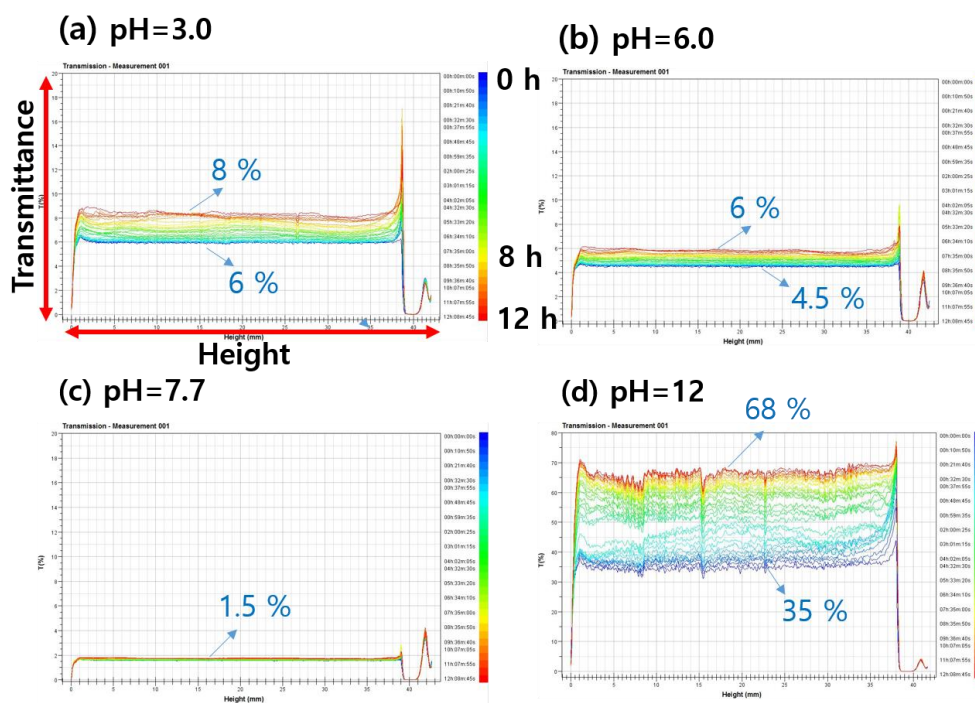


Fig. 3.12. Transmittance curves for CB and PAA system. All suspensions contain 10^{-3} vol% of CB and $0.5 \cdot 10^{-3}$ wt% of PAA.

Fig. 3.10 is an optical microscopy image of CB/PAA suspension according to each pH. As shown in the Figure. 3.10, when the pH is 12, carbon black particles existed in aggregated state was observed, On the other hand, at pH = 3.0 6.0,7.7 carbon black particles seems like well dispersed state. Sedimentation experiments presented in Fig. 3.11. were conducted to investigate the dispersibility of CB/PAA under each pH conditions. There should be importantly noticed that a degree of blackness of CB slurry is influenced by the primary particle size, the primary aggregated size and the degree of dispersion. CB slurry containing finer particles become more darkness because of improvement of effectiveness for adsorbing light due to its large surface area. [34]. At pH = 12, dispersibility of CB/PAA slurry decreased drastically compared to other pH. Based on these results, we could confirm that PAA had nearly no interaction with CB at pH = 12. Except pH = 12, CB with PAA seems well dispersed. As seen in Fig 3.11., the CB/PAA slurry at pH = 7.7 has the darkest state. This is proved, using turbimetric method shown in Fig 3.12 We tried to quantify the darkness and sedimentation tendency by using turbican [Fig 9]. It is noticed that scale bar is different with pH = 3.0, 6.0,7.7 and pH=12, showing difference of dispersibility more obviously in the range of optimum value. Initial transmittance value of CB with PAA slurry was decreased from 6%, 4.5%, 1.5% as pH increased from 3 to 7.7. Also, at pH = 7.7, the most improved dispersion stability was observed, demonstrated by changeless in transmittance with time compared to pH = 3.0 ,6.0. At pH = 12, the initial transmittance value was nearly 35% and increased to near 70 %, which is consistent results presented in Fig. 3.11. Interaction between CB and PAA was thought to be a crucial factor, determining the structure and dispersion stability of CB/PAA like LFP/PAA. Also, the adsorption amount of PAA on CB was measured to quantify the interaction between each other, indicated in Fig. 3.13.

3.8 Surface Properties of CB with PAA

3.8.1 Adsorption amount

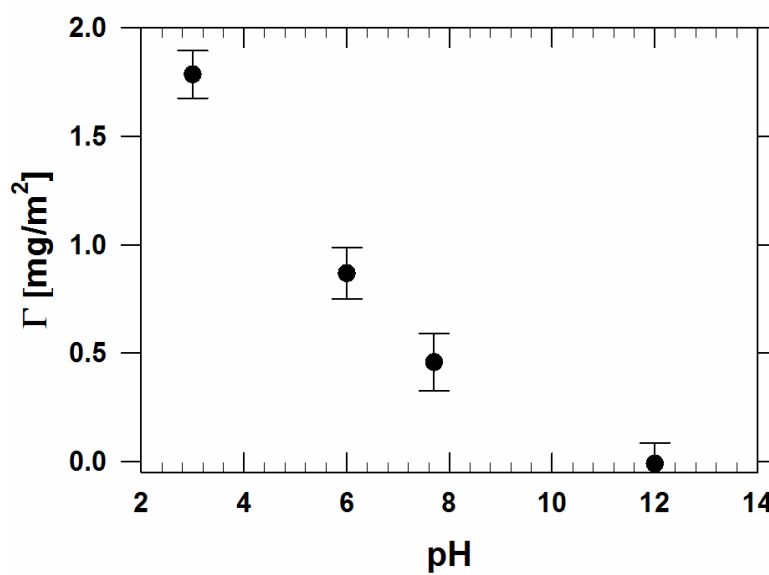


Fig. 3.13. The adsorption amount of PAA on the LFP surface at each pH conditions.

3.8.1 Zeta potential

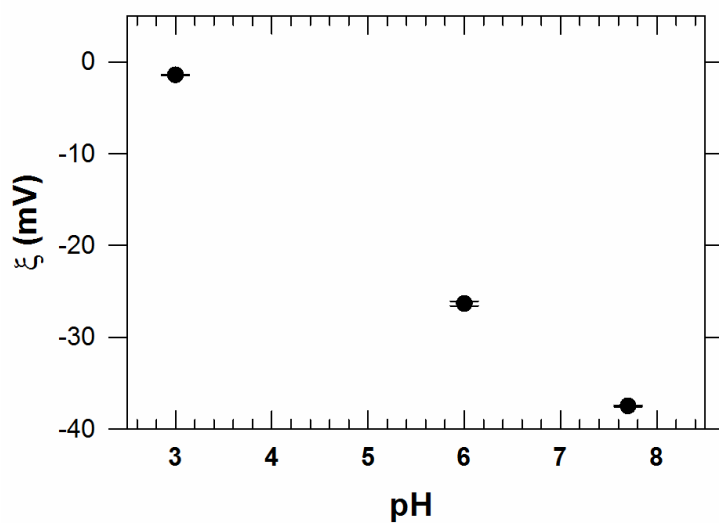


Fig. 3.14. Zeta potential of CB in aqueous suspension in the presence of PAA

The adsorption amount of PAA on CB was decreased continually as pH was came to be near 7.7 and finally became nearly zero at pH = 12. Considering the improvement of dispersion stability even reduction of adsorption amount of PAA on CB, it should be emphasized how the charge density and conformation of PAA has a significant effect on the dispersion state and surface properties of CB. Zeta potential of CB was found to be -1.37 mV, -26.09 mV, -37.41 mV for each pH conditions from 3.0 to 7.7 shown in Fig. 3.14. Thus, it is noticed that the reasons why the dispersion stability was most improved at pH = 7.7 comes from its strongly negative charge of adsorbed PAA and its conformation change as a highly extended state. In other words, charge density and conformation of adsorbed polymer could be one of the most dominant factors determining electro-steric repulsion force influencing the dispersion stability. Except for these conditions, zeta potential of CB couldn't be measured due to critical limitation of brownian motion because of severe aggregation problem of CB. Electro-steric repulsion force should be taken into consideration seriously for preparing homogeneous and dispersed aqueous cathode slurry.

3.9 Rheological properties of LFP/CB/PAA

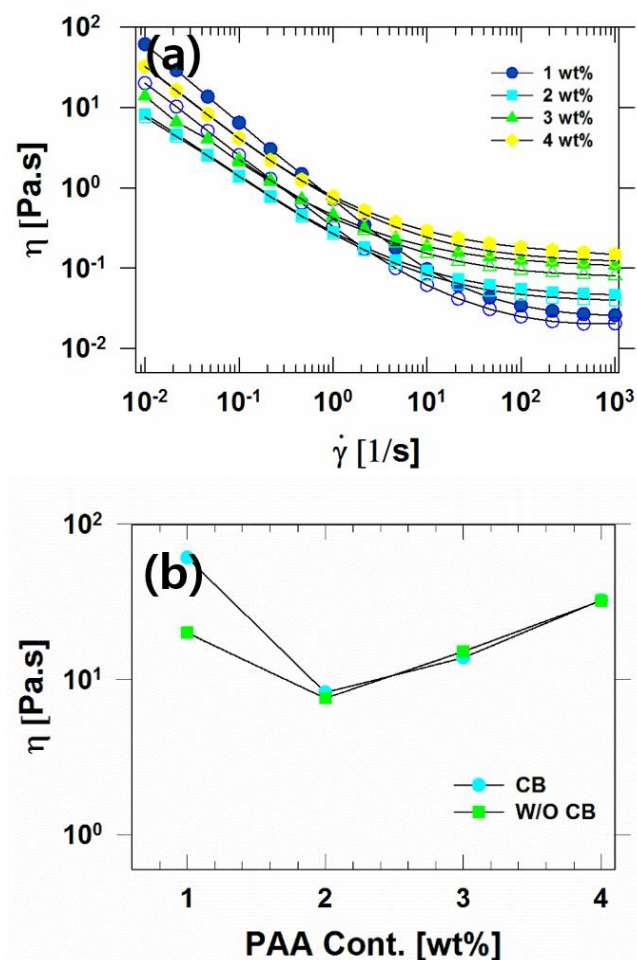


Fig. 3.15. (a) Viscosity for a suspension of 20 vol% LFP with 2 wt% PAA at pH = 6.0 with and without CB (b) Low shear viscosity of LFP slurry with and without CB at shear rate = 0.01 /s.

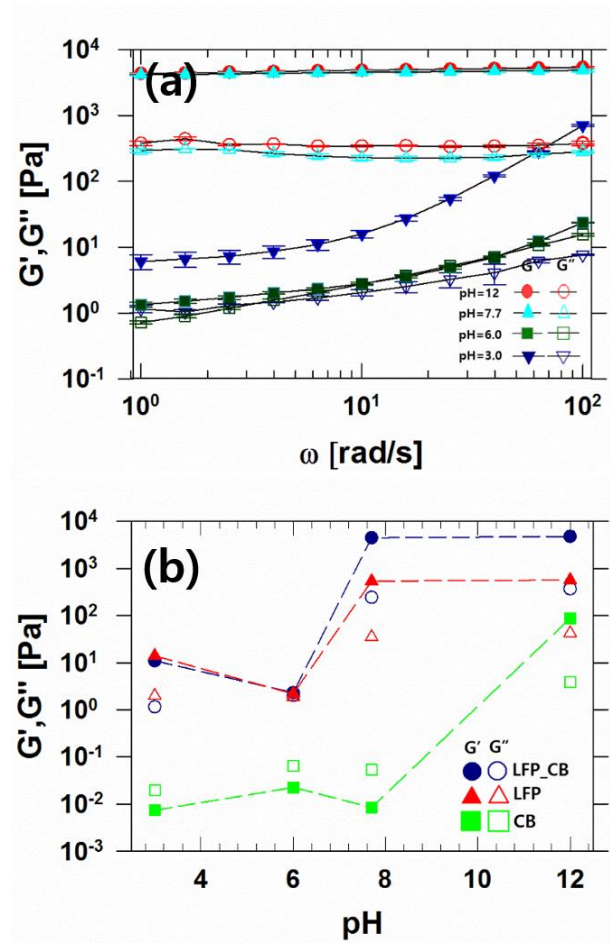


Fig. 3.16. (a) Effect of pH on the storage & loss modulus for a suspension of 20 vol% LFP, 1.3 vol% CB, 2 wt% PAA (b) Storage & loss modulus value of each particles' slurry and mixed slurry at 6.03 rad/s

We measured rheological properties of CB/LFP/PAA at each pH conditions shown in Fig. 3.15, Fig. 3.16. At pH = 6.0, the low shear viscosity wasn't changed with the addition of carbon black except the slurry containing only 1 wt% of PAA. As mentioned above, 1 wt% of PAA wasn't sufficient amount for dispersing 20 vol% of PAA at pH = 6.0. Interaction between CB and LFP would occur due to not sufficient polymer covering the particle at pH = 6.0, which makes slurries' viscosity larger. For slurry containing more than 2 wt% of PAA, at pH = 6.0, viscosity wasn't changed at low shear rate but increases at high shear rate regime, which indirectly confirmed that CB was dispersed in the medium without having any additional effect on the structure. This result indicates that there is no interaction between CB and LFP at pH = 6.0 with sufficient polymer. A little change of pH near 7 has a significant effect on the structure and dispersion stability between PAA and particles when neutralizing the cathode slurry. It was found to be attributed to adsorption and desorption of PAA on both particles CB, LFP surface in aqueous cathode slurry. Structure change also wasn't observed in the structure of LFP/PAA slurry with and without CB addition at pH = 3.0, 6.0. When pH = 7.7, even though CB had a liquid-like structure, dense gel was formed after mixing with LFP. Structure of the aqueous cathode slurry was found to be dominated by a large amount of cathode active material. Measurement results indicated that interaction between particle and PAA has a significant effect on the interplay of both particles. In this study, structure changes were quantified through rheological properties and various methods were used to demonstrate the change of dispersibility related with microstructure. We believe that information on structure changes and its effect on dispersion stability can give a lot of insight for dealing and manufacturing of aqueous cathode slurry. Also, these results present the importance of interaction between binders and particles for manufacturing homogeneous aqueous cathode slurry.

Conclusion

In this study, the effect of pH on the dispersion of aqueous battery slurry was investigated. In particular, we have tried to quantify the dispersion by defining the dispersibility in terms of the interaction between the polymer and particles. At low pH, although the polymer adsorbs on the particles, the dispersibility decreases because of the small charge density and the decrease in chain mobility due to the coiled conformation of the adsorbed polymer, resulting in insufficient electro-steric repulsion force. As pH increases, adsorbed polymer induces a sufficient electro-steric repulsion force and improves dispersion stability by stretched conformation of PAA and charge density. If pH is above a certain value, PAA has a strong negative charge which prevents adsorption on the particles. To obtain electro-steric force, protonation of PAA should be maintained at an appropriate level. Furthermore, we found out that the dispersibility was greatly altered by a subtle difference in pH near $\text{pH} = 7$. Therefore, when neutralizing aqueous slurries containing PAA, fine tuning is essential. The bulk properties of the slurry containing all the components were confirmed to be dominated by LFP. However, the pH dependence of carbon black and LFP was not the same. Moreover, even though the slurry containing both carbon black and LFP has similar value of the apparent rheological behavior at different pH of 7.7 and 12, it may have a difference in dispersibility of carbon black in overall cathode slurry. For example, at $\text{pH} = 7.7$ and 12, the rheological properties of water-based cathode slurry containing carbon black and LFP are all gel-like, but when the carbon black only exists, dispersibility becomes totally different at $\text{pH} = 7.7$ compared to $\text{pH} = 12$. It must be noticed that aggregates of small amounts of particles that are not easily observable in bulk phase could also cause a serious failure in large scale production. In conclusion, pH should be tuned in the appropriate range, preventing aggregation to produce a homogeneous aqueous cathode slurry when the PAA is used as a main binder or a main dispersant.

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국문초록

본 연구에서는, 수계 양극 슬러리의 미세 구조와 분산 안정성에 미치는 pH 영향에 대해 알아보았다. 양극 슬러리의 모델 시스템으로써 LiFePO_4 와 CB 그리고 PAA를 사용하였다. PAA의 중화 된 정도가 수계 전극 성능에 영향을 준다는 결과가 보고 되었듯이, 구조에 미치는 영향에 대해서도 파악해보았다. pH 조건은 크게 3.0, 6.0, 7.7, 12 로 나누어 실험을 진행하였다. 우리는 전체 슬러리에 대해 이해하기 위해, pH 에 따른 LFP/PAA 와 CB/PAA의 구조와 분산 안정성에 대해 각각 분석해보았다. LFP/PAA 의 경우, pH가 6.0 일 때의 G' 값은 pH 가 7.7 일 때의 G' 값 보다 약 1000배 정도 작은 값을 보였고, CB/PAA인 경우 pH 가 12 일 때를 제외 하고는 모든 조건에서 액체의 거동을 보였다. 본 실험에서 사용 된 pH 조건 중, LFP/PAA는 pH = 6.0 에서 가장 안정적인 분산 안정성을 띄었고 pH = 3.0 에서 불안정성을 띄었다. CB/PAA 는 pH = 7.7 에서 가장 안정적인 상태를 유지하였고 pH = 12 에서 불안정성을 띄었다. 두개의 입자를 합친 수계 양극 슬러리는 pH = 6.0 에서 가장 안정적인 상태를 보였

으며, 전체적인 구조를 지배하는 것은 많은 함량을 포함하는 양극 활 물질인 것을 확인하였다. PAA의 ND 값이 양극 활물질과 도전제 등을 포함하는 수계 양극 슬러리의 구조에 미치는 영향이 크고, 특히 당량점 근처의 작은 pH 의 차이가 구조의 변화에 큰 영향을 미치는 것을 확인하였다. 이러한 결과는, 첫 번째로는 고분자의 흡착과 탈착 그리고 흡착된 고분자의 전하와 형태의 차이에 기인하는 것으로 나타났으며 이러한 결과를 흡착량과 제타 포텐셜 값을 통해 확인 하였다. 즉, 고분자가 흡착하는 양 그리고 흡착 된 고분자의 전하량과 형태의 균형이 잘 이루어져야 수계 양극 슬러리의 분산성을 충분히 확보 할 수 있다는 것을 확인하였다. 본 연구에서는, 수계 양극 슬러리를 제조시 pH 조절을 통해 충분한 분산성 확보를 해주어야 하며 산업적 스케일에서 제품을 생산할 때 pH를 통한 슬러리 내 성분간의 상호작용 대해 고려해야 함을 확인하였다.