



The effect of binders on the rheological properties and the microstructure formation of lithium-ion battery anode slurries

Sanghyuk Lim ^a, Sunhyung Kim ^b, Kyung Hyun Ahn ^{a,*}, Seung Jong Lee ^a

^a School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Seoul 151-744, Republic of Korea

^b Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute Technology, Gotthard-Franz-Straße 3, Building 50.31, 76131 Karlsruhe, Germany

HIGHLIGHTS

- The effect of binders on the microstructure in anode slurry is investigated.
- The microstructure is analyzed by viscoelastic properties and cryo-SEM images.
- CMC and SBR influence the microstructure formation of the slurry in different ways.

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ABSTRACT

There have been many efforts to enhance the performance and the stability of Li-ion battery. It is crucial to develop a new material as well as to understand the mechanism of microstructure formation of the electrode in order to enhance the performance of the battery. In this study, the effect of sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) on the microstructure formation as well as on the rheological properties in the aqueous anode slurries is investigated. The graphite particles aggregate with each other due to their hydrophobicity and form a gel structure in an aqueous slurry. Both CMC and SBR induce the dispersion of the graphite particles by adsorbing onto the graphite surface. In the graphite/CMC/SBR slurry, the SBR can affect the dispersion of the graphite particles at low CMC concentration, while the microstructure is not changed regardless of added SBR at high CMC concentration because the SBR cannot adsorb on the graphite surface due to the presence of CMC. The microstructure of the slurry is also confirmed by the cryo-SEM images. Understanding the role of the binders on the microstructure formation will be helpful for the effective design of the battery slurries.

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1. Introduction

Li-ion battery has been widely used in industries due to many advantages such as high operating voltage, long life cycle, and high storage characteristic, and so on [1,2]. The use of battery has been expanded to portable devices such as smart phone and laptop computer, and even to huge equipment such as electric vehicle. With this trend of battery application, it is a hot issue to enhance the performance and the stability of the battery. Thus, there have been many efforts to solve various issues such as improvement of energy density, electrical stability, and safety problems.

Previously, poly(vinylidene difluoride) (PVDF) has been used as

a binder in the organic solvent for anode slurry. However, an aqueous system is preferred over the non-aqueous system due to high cost and safety problems. The advantages of the aqueous anode slurry are low cost, environment-friendly, and fast drying during manufacturing process of the electrode [3]. So, it is a recent trend to move from the PVDF in non-aqueous system to the sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) in aqueous system.

CMC has been used as a thickening agent, binder, stabilizer, etc. in various industries [4–8]. It is a linear polymeric derivative of cellulose which contains two anhydroglucose units (β -linked glucopyranose residues) with each anhydroglucose unit having three hydroxyl groups. The hydrogen in hydroxyl group is substituted by carboxymethyl group, and the average number of hydroxyl groups substituted per anhydroglucose unit is defined as a degree of substitution (DS). When all hydroxyl groups are substituted, the DS is

* Corresponding author.

E-mail address: ahnnet@snu.ac.kr (K.H. Ahn).

three. The CMC shows a variety of characteristics depending on the concentration, molecular weight, pH, DS, and so on [7–14]. Lee et al. [8] investigated the effect of DS of CMC on the electrokinetic behavior and the electrochemical performance of the anode. At low DS, the CMC became adsorbed more on the graphite particles than at high DS. The adsorption amount of CMC affected the dynamic mobility and dispersion stability of graphite particles in the suspension. It also affected the electrochemical performance of the anode such as charge–discharge capacity and adhesion strength.

SBR has been used as a reinforcing agent, binder, flexibility enhancer in many industries [15–20]. It is a kind of synthetic rubber consisting of styrene and butadiene units. The SBR in the anode slurry is used as a binder to enhance the adhesion force between the film and the current collector. The effect of SBR distribution in the thickness direction of the film on the electrochemical performance of the cathode and anode has been investigated [19,20]. When the SBR is distributed non-uniformly, the adhesion force between the film and current collector diminishes, leading to poor performance of the battery.

The battery slurry is a typical particulate system which consists of graphite or carbon black as a particle, PVDF or CMC as a binder, and organic or aqueous medium as a solvent. A variety of microstructure in a particulate system can be formed due to the interaction between the particle and polymer such as bridging, depletion attraction or electrostatic repulsion [21–24]. The influence of the microstructure of the anode slurry on the latex migration during drying has also been reported [24]. The microstructure in the anode slurry was dependent on the ratio of CMC and graphite. When the ratio of CMC to graphite was low, the graphite particles were dispersed in the slurry due to steric repulsion by the adsorbed CMC on the graphite surface. However, when the ratio of CMC to graphite was high, the graphite particles formed aggregates due to depletion attraction by non-adsorbed CMC in the medium. Different microstructure of the film was formed according to the microstructure of the slurry due to the latex migration during drying. Likewise, the microstructure of the slurry affects the battery performance as well as the microstructure of the film after drying [25–32]. Nguyen et al. [26] investigated the effect of polymer not only on the particle dispersion in the silicon based anode slurry but also on the dried film together with the battery performance. Poly (acrylic-co-maleic acid) (PAMA) which was used as a dispersant affected the dispersion of carbon black in the slurry as well as in the film. It also played a role to enhance the battery performance such as cyclability and coulombic efficiency. In addition, Lee et al. [27] studied the microstructure of the slurry as well as of the dried film according to the mixing protocol, and the effect of the microstructure on the battery performance. When the active material and the carbon black were well dispersed in the slurry and the film, the battery showed better performance. Therefore, it is crucial to understand the mechanism of microstructure formation of the slurry as well as the film in order to enhance the performance of the battery.

The graphite particles tend to get aggregated in an aqueous solvent due to non-polar surface and hydrophobicity, and the dispersion of carbon particles in an aqueous solution is one of the crucial issues. It is also important to understand the effect of CMC and SBR on the dispersion of graphite particles as well as on the microstructure formation of the slurry in the aqueous anode slurry. However, there is a lack of studies about the mechanism of microstructure formation by the binders in the aqueous anode slurry. In this study, we investigate the effect of CMC and SBR on the microstructure formation in three anode slurries; graphite/SBR, graphite/CMC and graphite/CMC/SBR slurries. The microstructural change depending on the concentration of CMC or SBR can be confirmed through the rheological measurements and cryo-SEM

images.

2. Experiments

2.1. Sample preparation

Graphite (SG-BH8, Ito Graphite Co., Ltd., Japan) is used as an active material. The diameter, density, and specific surface area are 8.11 μm , 2.23 g/cm^3 , and 12.12 m^2/g , respectively (provided by manufacturer). CMC and SBR are provided by SK innovation. The average molecular weight (M_w) and the degree of substitution of CMC are 330,000 g/mol and 0.7, respectively. The SBR is a spherical shape and the diameter was 140 nm.

The CMC powder is dissolved in deionized water using a magnetic stirrer for 12 h. The graphite particles are added to the CMC solution and are dispersed using a homogenizer (Ultra-Turrax® T18 basic, IKA® Works, Inc.), followed by mixing with a magnetic stirrer for 12 h. Then 40 wt% SBR suspension is added to the graphite slurry and is mixed using a planetary centrifugal mixer (ARM-310, Thinky Corporation) at 2000 rpm for 5 min, and the slurry is finally mixed on a magnetic stirrer for 12 h.

2.2. Characterization of rheological properties of the anode slurry

The rheological properties of the anode slurry are measured by two types of rheometers, stress controlled (AR-G2, TA instruments) and strain controlled (ARES, TA instruments). The viscosity at low shear rates is measured through the stress sweep test by using the stress controlled rheometer with parallel plates of 25 and 40 mm in diameter. In addition, the viscosity at high shear rates is measured through the rate sweep test by using the strain controlled rheometer with parallel plates of 25 and 50 mm in diameter. The dynamic properties of the slurry are measured by the strain controlled rheometer with parallel plates. The frequency sweep test is conducted in linear viscoelastic regime which is confirmed from the strain sweep test. All rheological measurements are performed at 25 °C. The anode slurries are allowed to take a rest time for 120 s without pre-shear before conducting rheological measurements in order to remove shear history which can appear when the slurry is loaded on the lower plate in the rheometer.

2.3. Cryogenic-SEM

The scanning electron micrographs are obtained using the FE-SEM (Mira3 LMU FEG, Tescan) with the sample preparation system for cryo-SEM (PP3000T, Quorum Technologies). The slurry is loaded on the specimen shuttle with cryo-stubs. Then, the slurry is fast frozen by plunging into liquid nitrogen. The frozen slurry is transferred to the cryo-preparation system, and the samples are fractured in the cross sectional direction. The fractured samples are sublimated at –100 °C for 10 min, and then are coated with platinum at –140 °C for 120 s. All images are captured at –140 °C.

3. Results and discussion

3.1. Graphite/SBR slurry

Fig. 1 shows the viscosity and the storage and loss moduli of the anode slurries which contain 50 wt% of graphite and SBR concentration ranging from 0 to 30 wt%. In the slurry with only graphite particles without SBR, the yielding behavior is observed. The behavior can be confirmed clearly by analyzing the viscosity as a function of shear stress (inset in Fig. 1(a)). The viscosity remains constant at low shear stress indicating the slurry shows a solid-like behavior. The viscosity drops steeply after a critical point, which is

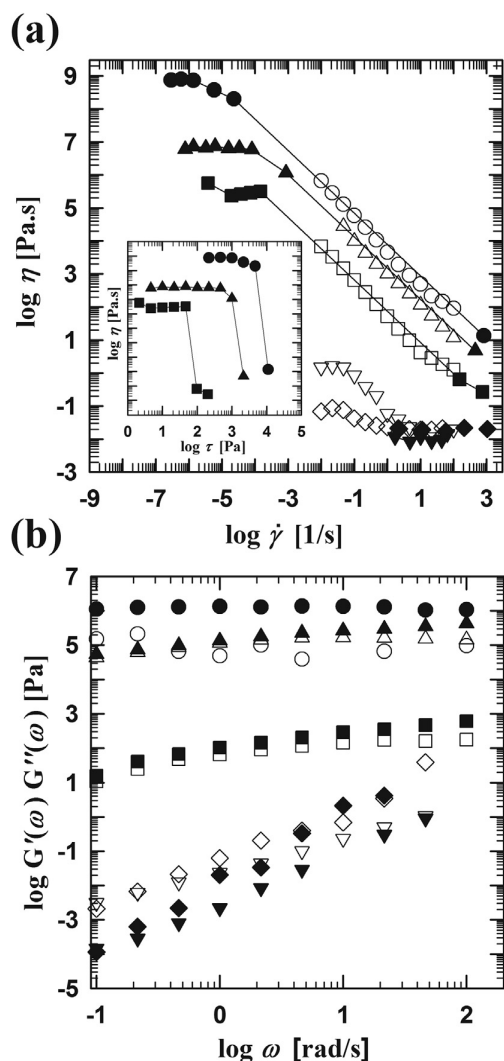


Fig. 1. Rheological properties of anode slurries containing 50 wt% of graphite and various concentration of SBR. (a) Viscosity as a function of shear rate and as a function of shear stress (inset in (a)); obtained from stress controlled (closed symbol) and rate controlled (open symbol) rheometer. (b) Storage (closed symbol) and loss (open symbol) moduli as a function of frequency. SBR concentration in (a) and (b): (●○) 0 wt%, (▲△) 3 wt%, (■□) 8 wt%, (▼▽) 15 wt%, (◆◇) 30 wt%.

defined as the yield stress [33]. In addition, the storage modulus, G' , is larger than the loss modulus, G'' , and the moduli remain constant regardless of frequency. This behavior is often observed in a particulate system which forms the gel structure in particular. The graphite particles have a tendency to form aggregates in an aqueous solution due to their hydrophobicity [34]. Therefore, it can be confirmed that the graphite particles form a gel structure with percolated networks in an anode slurry without SBR. The gel structure in the slurry is not changed even though small amount of SBR is added to the slurry. Both viscosity and moduli are slightly decreased, indicating the gel strength is decreased as the SBR is added to the slurry. However, when the SBR concentration is increased to 15 wt%, the yielding behavior disappears and the shear thinning behavior occurs. In addition, the G'' is larger than the G' and the moduli depend on the frequency, indicating the gel structure in the slurry does not exist anymore. It means that the gel

structure from the aggregation of graphite particles is changed to the liquid-like structure due to the dispersion of graphite particles at high SBR concentration.

The microstructural change of the graphite/SBR slurry can also be confirmed by cryo-SEM images (Fig. 2). Fig. 2(a) and (b) show the microstructure of the slurry containing 50 wt% of graphite and 3 wt% of SBR. In the image with low magnification, the network structure by the aggregated graphite particles can be verified (Fig. 2(a)). In addition, the SBR particles are adsorbed on the surface of graphite particles as can be verified in the image with high magnification (Fig. 2(b)). There is a study about the adsorption of SBR on the graphite surface. Li and Lin [35] investigated the interaction of SBR and CMC with graphite particles by measuring the zeta potential of the slurry and the sedimentation test. They figured out that the SBR as well as CMC could be adsorbed on the graphite particles although the interaction of the binders with the graphite particles was different with each other. Fig. 2(c) and (d) show the microstructure of the slurry consisting of 50 wt% of graphite and 30 wt% of SBR. In the image with low magnification, it can be confirmed that the graphite particles are well dispersed in the medium (Fig. 2(c)). The SBR exists on the surface of the graphite particles as well as in the medium as shown in the image with high magnification (Fig. 2(d)). Through the rheological properties and the cryo-SEM images for the graphite/SBR slurry, the microstructural change of the slurry from gel to dispersion by the SBR can be confirmed. The graphite particles form the gel structure by hydrophobic attraction. The SBR is adsorbed on the graphite surface when the low concentration of SBR is added to the slurry, where the gel strength is decreased but the gel structure is still maintained in the slurry. However, as the SBR is further added to the slurry, the graphite particles are dispersed by electrostatic repulsion due to anionically charged surfactant which exists on the SBR. As a result, the slurry shows a liquid-like behavior at high SBR concentration.

3.2. Graphite/CMC slurry

In this section, the microstructure of the graphite/CMC slurry will be discussed through the analysis of the rheological properties and cryo-SEM images.

Fig. 3(a) and (b) shows the viscosity of the slurries containing 50 wt% of graphite and various concentration of CMC. The graphite slurry without CMC shows a yielding behavior, as mentioned in the section of graphite/SBR slurry. As the concentration of CMC is increased to 0.1 wt%, both the viscosity and the yield stress decrease but the yielding behavior is still observed (Fig. 3(a)). When the CMC concentration is increased above 0.4 wt%, the behavior is totally changed. The yielding behavior disappears and the shear thinning behavior appears. In addition, the viscosity increases as the concentration of CMC is increased unlike at low CMC concentration (Fig. 3(b)). As the CMC concentration is further increased to 1.4 wt%, the yielding behavior appears again.

Fig. 3(c) and (d) shows the viscoelastic behavior of the graphite slurries depending on the concentration of CMC. The G' is larger than G'' and the moduli remain constant independent of frequency in the graphite slurry without CMC. As the concentration of CMC is increased to 0.1 wt%, the moduli decrease, similar to the viscosity decrease at low CMC concentration. The trend of frequency-independent modulus is maintained even when the CMC is added to the slurry, indicating the gel structure still exists in the slurry although the gel strength is decreased.

The viscoelastic behavior is changed at 0.4 wt% of CMC, after which the moduli increase with CMC concentration like the viscosity. In addition, the G'' is larger than G' and the moduli increase with frequency. It means that the gel structure which is formed at low CMC concentration is changed to dispersion state as the CMC is

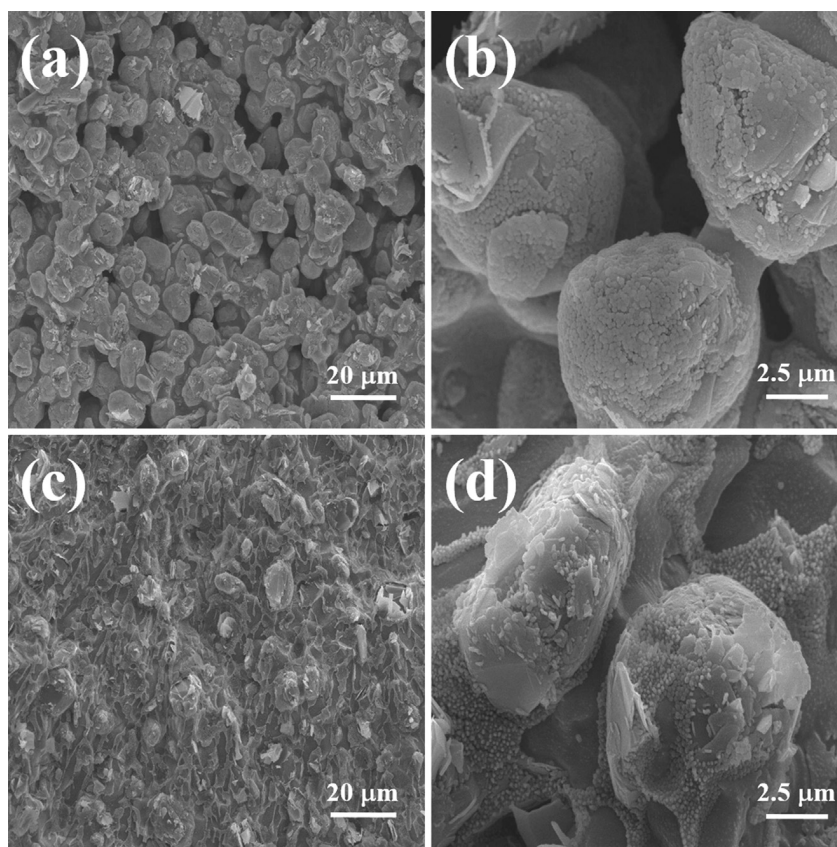


Fig. 2. Cryo-SEM images of anode slurries containing 50 wt% of graphite and different concentrations of SBR; (a)&(b) graphite 50 wt% + SBR 3 wt%, (c)&(d) graphite 50 wt% + 30 wt %.

further added to the slurry. The moduli increase as the concentration of CMC is increased. However, when the CMC concentration is increased to 1.4 wt%, the trend is changed again. The G' is larger than G'' and the moduli show a power-law behavior with frequency, which means that the dispersed graphite particles form the gel structure again at high CMC concentration. Therefore, the microstructure of the slurry heavily depends on the CMC concentration, and there exist two transitions; one from gel to liquid and the other from liquid to gel structures.

CMC is a polyelectrolyte which separates into a sodium cation and a polymer anion in an aqueous solution. These ions in a medium interact with each other by electrostatic forces and affect the polymer conformation [36]. Fig. 4 shows the specific viscosity of CMC solution depending on the CMC concentration. The specific viscosity is defined as $\eta_{sp} = (\eta - \eta_s)/\eta_s$, where η is the zero shear viscosity of CMC solution and η_s is the viscosity of the solvent. The specific viscosity increases as the concentration of CMC increases. It shows a power law behavior with the concentration of CMC, $\eta_{sp} \sim c^\nu$, and three transition concentration thresholds of CMC can be defined. (1) For $c < c^*$, the polymer chains begin to overlap, and it is defined as the semidilute unentangled regime. In this regime, the specific viscosity follows the Fuoss law, $\eta_{sp} \sim c^{1/2}$ [11–14]. (2) For $c^* < c < c^{**}$, the polymer chains form entanglements, and it is defined as the semidilute entangled regime. In this regime, the specific viscosity follows $\eta_{sp} \sim c^{3/2}$ [11–14]. (3) For $c^{**} < c < c^{***}$, it is defined as the concentrated regime and the specific viscosity follows $\eta_{sp} \sim c^{3.75-5.5}$ [12–14]. (4) For $c > c^{***}$, the polymer solution shows a gel-like behavior, and the c^{***} is defined as the sol–gel transition concentration [14]. As shown in Fig. 4, the power indices of the specific viscosity are obtained as $\nu \sim 0.58, 1.53, 4.36$, and 7.82

at each regime, respectively. These values are similar to the predictions obtained by the scaling theory in previous researches. In addition, the transition concentration thresholds are obtained as $c^* \sim 0.1$ wt%, $c^{**} \sim 0.4$ wt%, and $c^{***} \sim 1.6$ wt% of CMC.

The viscoelastic behavior of the CMC solution according to the CMC concentration is shown in Supplementary Information Fig. S1. When the concentration of CMC is below 1.4 wt%, the G'' is larger than G' and the typical viscoelastic behavior of polymer solution is observed. However, when the concentration of CMC is above 2.0 wt%, the G' is larger than G'' and the moduli exhibit power-law behavior, indicating that the CMC forms the polymeric networks, that is the gel structure [37]. The gel behavior is observed above the sol–gel transition concentration, c^{***} , as mention in Fig. 4.

Fig. 5 shows the $\tan\delta$ for the anode slurry and the CMC solution as a function of CMC concentration. The $\tan\delta$ is defined as the ratio of G'' and G' , and is obtained at $\omega = 0.1$ rad/s. The $\tan\delta$ of the anode slurry at low concentration of CMC is below unity, and it increases above unity after a critical concentration of CMC, $\phi_{LC} \sim 0.28$ wt%. When the CMC concentration is below 0.28 wt% in the anode slurry, the moduli are independent on the frequency (Fig. 3(c)). It means that the gel structure is formed by graphite particles when the low concentration of CMC is added to the slurry. As mentioned in the section of graphite/SBR slurry, the gel structure is formed by hydrophobic attraction of graphite particles, and the graphite particles are dispersed by adsorbed SBR on the graphite surface. Like SBR, the CMC molecules tend to adsorb on the graphite surface, and the adsorption amount of CMC increases as the CMC concentration is increased [8,24]. Thus, both the viscosity and the moduli decrease as the CMC is added to the slurry until the concentration less than 0.28 wt%, meaning that the gel strength decreases due to the

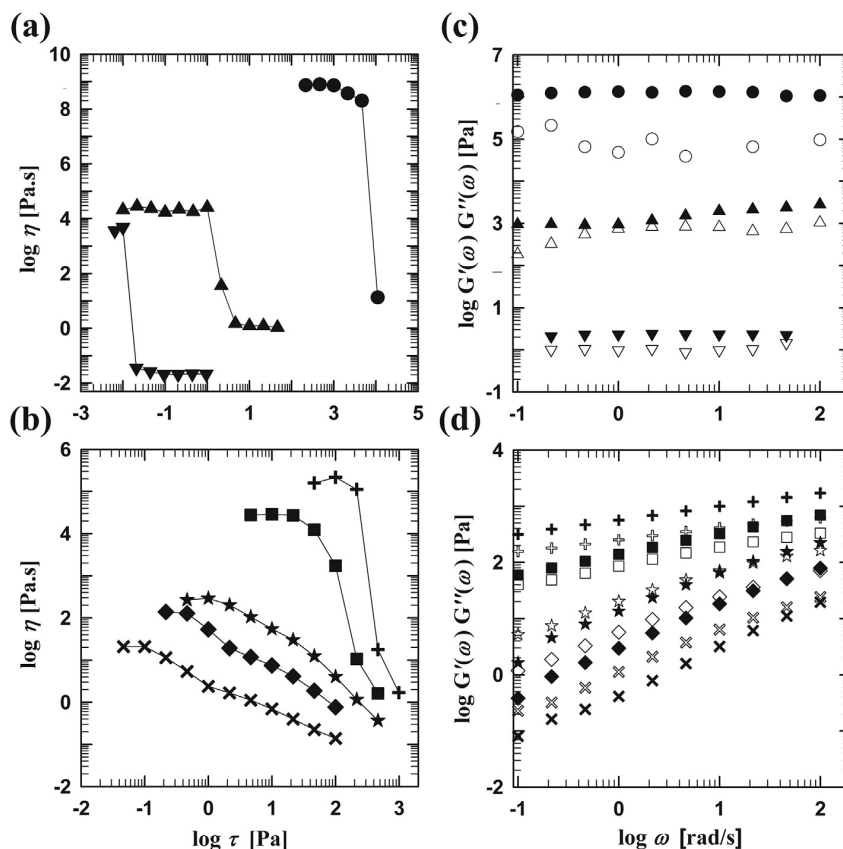


Fig. 3. Viscosity as a function of shear stress (a) & (b) and storage (closed symbol) and loss (open symbol) moduli as a function of frequency (c) & (d) for anode slurries containing 50 wt% of graphite and various concentration of CMC; (●) 0 wt%, (▲) 0.07 wt%, (▼) 0.1 wt%, (×) 0.4 wt%, (◆) 0.7 wt%, (★) 1.0 wt%, (■) 1.4 wt%, (+) 1.7 wt%.

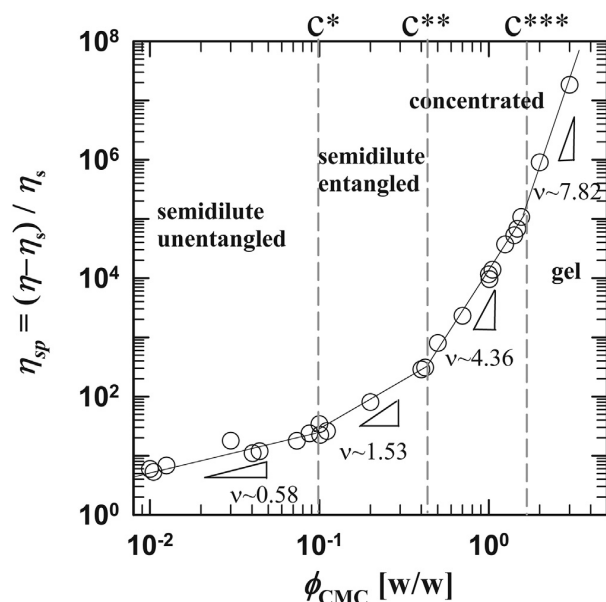


Fig. 4. The specific viscosity of CMC solution as a function of CMC concentration.

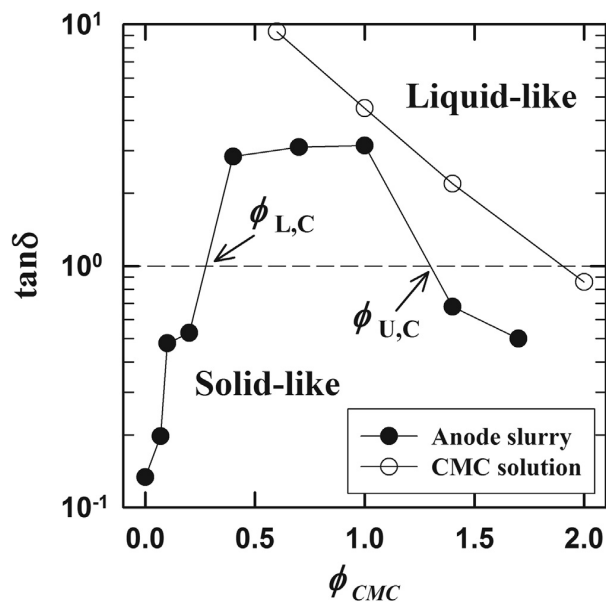


Fig. 5. $\tan \delta$ as a function of CMC concentration for anode slurries containing 50 wt% of graphite (●) and CMC solution (○).

adsorbed CMC on the surface of the graphite. However, the frequency-independent behavior of the moduli is observed, indicating that the gel structure by graphite particles is still maintained in the slurry. The formation of gel structure by graphite can also be confirmed by the cryo-SEM images (Fig. 6(a) and (b)).

The $\tan\delta$ increases with CMC concentration, and it is larger than unity after $\phi_{L,C}$. It means that the gel structure at the low CMC concentration disappears and the slurry shows a liquid-like behavior. The dependence of microstructure on the CMC concentration can be explained by the characteristic of CMC which can adsorb on the graphite surface. The carboxymethyl unit in the CMC molecule is dissociated to COO unit in aqueous solution. And the adsorption amount of CMC on the graphite surface increases as the

CMC concentration is increased, and the graphite particles are dispersed by electrosteric repulsion between the adsorbed CMC molecules. The well-dispersed graphite particles by CMC can be confirmed by cryo-SEM images (Fig. 6(c) and (d)).

As the concentration of CMC is further increased, the $\tan\delta$ remains above unity until a critical concentration where it starts to decrease to below unity. The critical concentration is defined as the upper critical concentration, $\phi_{U,C}$, and it is approximately 1.3 wt%. That is, the liquid-like behavior in the slurry is changed to the solid-like behavior from 1.3 wt% of CMC. The microstructure change can be explained by the characteristic of CMC solution which forms the gel structure at high CMC concentration. The $\tan\delta$ of CMC solution is above unity, and it decreases with the CMC concentration. The

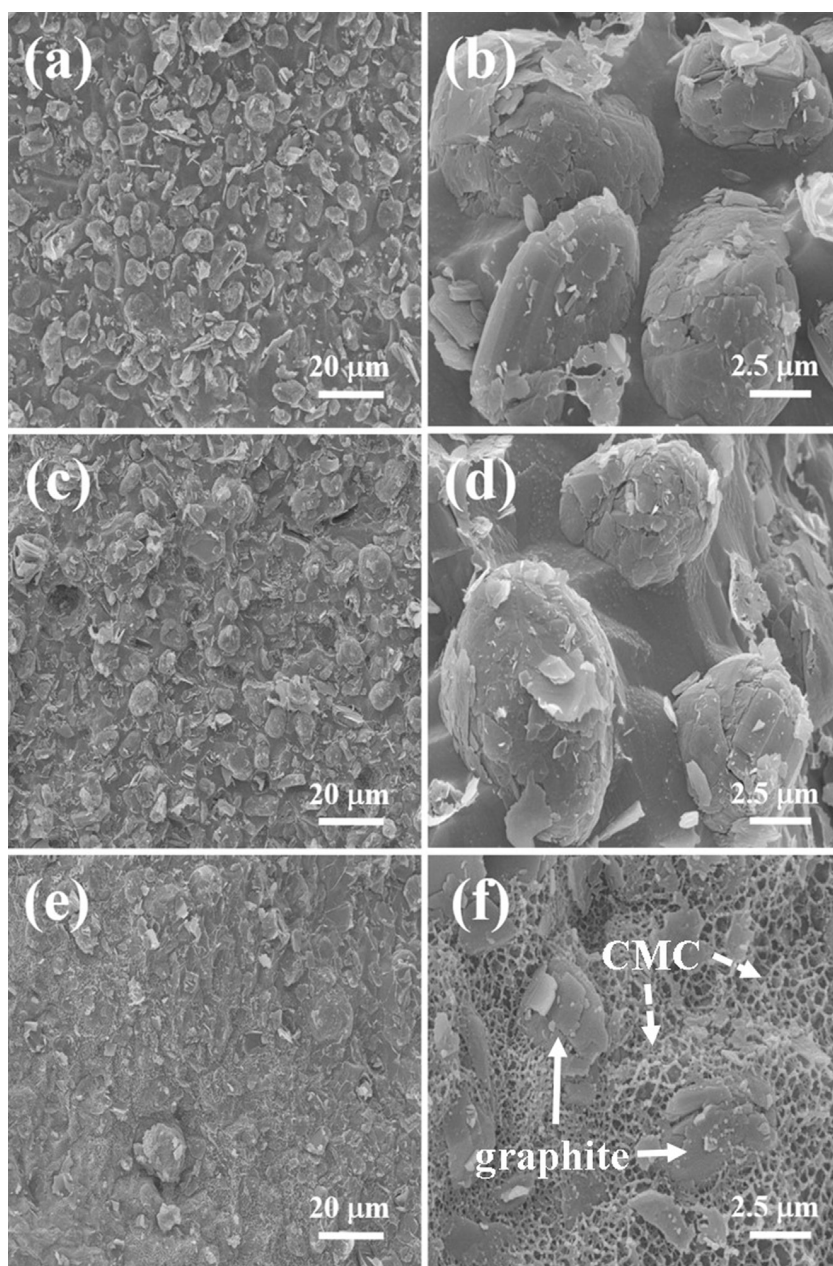


Fig. 6. Cryo-SEM images of anode slurries containing 50 wt% of graphite and different concentrations of CMC; (a)&(b) graphite 50 wt% + CMC 0.07 wt%, (c)&(d) graphite 50 wt% + CMC 0.7 wt%, (e)&(f) graphite 50 wt% + CMC 1.7 wt%.

$\tan\delta$ is less than unity after 1.9 wt% of CMC (Fig. 5). In addition, it is already confirmed that the CMC molecules formed the gel structure above 1.9 wt% of CMC concentration, as shown in Fig. 4. Therefore, the gel structure of CMC above $\phi_{U,C}$ has an effect on the solid-like behavior of the anode slurry. The microstructure of the slurry containing high CMC concentration is also observed by cryo-SEM (Fig. 6(e) and (f)). The microstructure of the slurry with high CMC concentration is different from that of the slurry with low CMC concentration as shown in Fig. 6(d) and (f). For the slurry with high CMC concentration, the network structure is formed, in which the graphite particles are embedded (Fig. 6(f)). The network is the gel structure formed by the polymeric network of CMC molecules and the size of hexagon lattice is less than 500 nm in the anode slurry. The cryo-SEM images for the 2 wt% of CMC solution are taken in order to confirm whether the network structure is formed by CMC or not (see Supplementary Information Fig. S2). The honeycomb-like structure is observed in Supplementary Information Fig. S2(a), but the structure may include the artifact which results from free water crystallization when the aqueous solution is frozen in a liquid nitrogen [38]. In addition, as the size of the hexagon lattice for frozen water is about a micron scale, it disagrees with the size of network structure appearing in the anode slurry in Fig. 6(f). However, when the cryo-SEM image is enlarged with high magnification, the network structure can be clearly observed (see Supplementary Information Fig. S2(b)). The size of the structure is about a few hundred nanometer scale, and the network size is the same as in the anode slurry. In addition, there exists another evidence that the CMC molecules form the network structure [39]. So, it can be argued that the network structure in anode slurry at high concentration of CMC is originated from the CMC molecules.

Therefore, the CMC molecules form the network structure as the concentration is increased, and the graphite particles which are well dispersed at intermediate concentration, $\phi_{L,C} < \phi < \phi_{U,C}$, are trapped in the network structure of CMC. So, the anode slurry behaves solid-like above $\phi_{U,C}$. At both concentrations below $\phi_{L,C}$ and above $\phi_{U,C}$ of the CMC, the gel behavior is observed in the slurry, but the gel structures are different from each other. In other words, the gel structure is formed by the aggregation of graphite particles due to hydrophobic attraction below $\phi_{L,C}$, while the polymeric network induces the gel structure above $\phi_{U,C}$. In addition, we also check the microstructural change of the anode slurry depending on the CMC concentration by the flowability test (see Supplementary Information Fig. S3). The gel structure is formed for the slurries with low and high CMC concentration and it does not flow in the upturned vials. On the other hand, the slurry with an intermediate concentration, $\phi_{L,C} < \phi < \phi_{U,C}$, flows in the upturned vial.

3.3. Graphite/CMC/SBR slurry

Fig. 7 shows the rheological properties of the slurries containing various concentration of CMC and SBR, from 0.07 to 1.7 wt % and 2 to 5 wt%, respectively. As mentioned in the previous sections, the CMC as well as the SBR which can be adsorbed on the graphite surface affects the dispersion of the graphite particles. As shown in Fig. 7(a) and (b), when the slurry contains the low concentration, 0.07 wt%, of CMC without SBR, the graphite particles form the gel structure inducing yielding and frequency-independent modulus. As 2 or 5 wt% of SBR is added to the slurry, both the viscosity and the moduli decrease. The rheological properties decrease as the SBR is added to the slurry because the graphite particles are dispersed due to the adsorbed SBR on the graphite surface. The microstructure of the slurry can be confirmed by cryo-SEM images (Fig. 8(a) and (b)). While the graphite particles form the gel structure in the slurry containing only 0.07 wt% of CMC without SBR (Fig. 6(b)), the graphite

particles are dispersed by adsorbed SBR on the graphite surface in the slurry containing 0.07 wt% of CMC and 5 wt% of SBR (Fig. 8(b)). That is, in the slurry with low concentration of CMC, the SBR can be adsorbed on the graphite surface because the adsorption amount of CMC on the graphite is very small. So, the SBR adsorbed on the graphite surface forces the graphite particles to disperse, causing the decrease of both viscosity and modulus.

In the slurry containing 0.7 wt% of CMC, the yielding behavior disappears and the viscoelastic behavior is observed, in which the G'' is larger than G' and the moduli increase with frequency (Fig. 7(c) and (d)). However, the rheological properties of the slurry does not change even when the SBR is added, unlike the slurry with low concentration of CMC. Li and Lin [35] investigated the adsorption of the binder on the graphite according to different mixing protocols. One of the mixing protocols was that both CMC and SBR were added and mixed to the slurry simultaneously. Another was that the CMC was added to the slurry first and the SBR was added followed by mixing with the slurry. In the case of split addition of binders to the slurry, the graphite particles were dispersed by the adsorbed CMC on the graphite surface as the CMC was added to the slurry first. And the SBR was added to the slurry, the SBR could not adsorb on the graphite and did not affect the dispersion of the graphite particles. When the binders were added simultaneously, the SBR could not adsorb on the graphite surface because the CMC was adsorbed on the graphite surface in preference to the SBR. That is, when both CMC and SBR exist in the slurry, the CMC adsorbs on the graphite surface more preferably than the SBR, and it plays a dominant role in dispersing the graphite particles. As shown in Fig. 7(c) and (d), the viscosity as well as the modulus remain constant although the concentration of SBR is increased, meaning that the SBR cannot affect the dispersion of the graphite particles any more. Fig. 8(c) and (d) illustrate cryo-SEM images for the slurry containing 0.7 wt% of CMC and 5 wt% of SBR. While the SBR is adsorbed on the graphite surface in the slurry containing low concentration of CMC (Fig. 8(b)), the SBR exists only in the medium, not on the graphite surface (Fig. 8(d)). The adsorption amount of CMC on the graphite surface increases as the concentration of CMC is increased. The SBR cannot adsorb on the graphite due to the CMC which is adsorbed in advance, and stays in the medium. Therefore, the dispersion of graphite particles is influenced mostly by the adsorbed CMC and the SBR which exists in the medium cannot affect the dispersion of the graphite particles. Thus, the rheological properties of the slurry are constant although the concentration of SBR is increased.

The trend, in which the rheological properties of the slurry maintain constant although the concentration of SBR is increased, is also shown in the slurry containing 1.7 wt% of CMC (Fig. 7(e) and (f)). It is already confirmed that the graphite/CMC slurry with 1.7 wt % of CMC shows the gel behavior due to the polymeric network by CMC molecules (Fig. 6(f)). When the SBR is added to the slurry containing 1.7 wt% of CMC, the polymeric network can also be formed in the slurry (Fig. 8(f)). In addition, the SBR does not exist on the graphite surface in the slurry with 1.7 wt% of CMC as in the slurry with 0.7 wt% of CMC. Supplementary Information Fig. S4 shows the enlarged image of the CMC network structure in the slurry with 1.7 wt% of CMC. It can be found that the SBR which cannot adsorb on the graphite particles exists at the polymeric network structure. Therefore, in the slurry with high concentration of CMC, the SBR cannot affect the dispersion of the graphite particles, and only CMC plays a leading role in forming the microstructure in the slurry.

To summarize, when the anode slurry containing low concentration of CMC, the SBR can adsorb on the graphite surface and affects the dispersion of the graphite. As the concentration of CMC is increased, the adsorption amount of CMC is also increased.

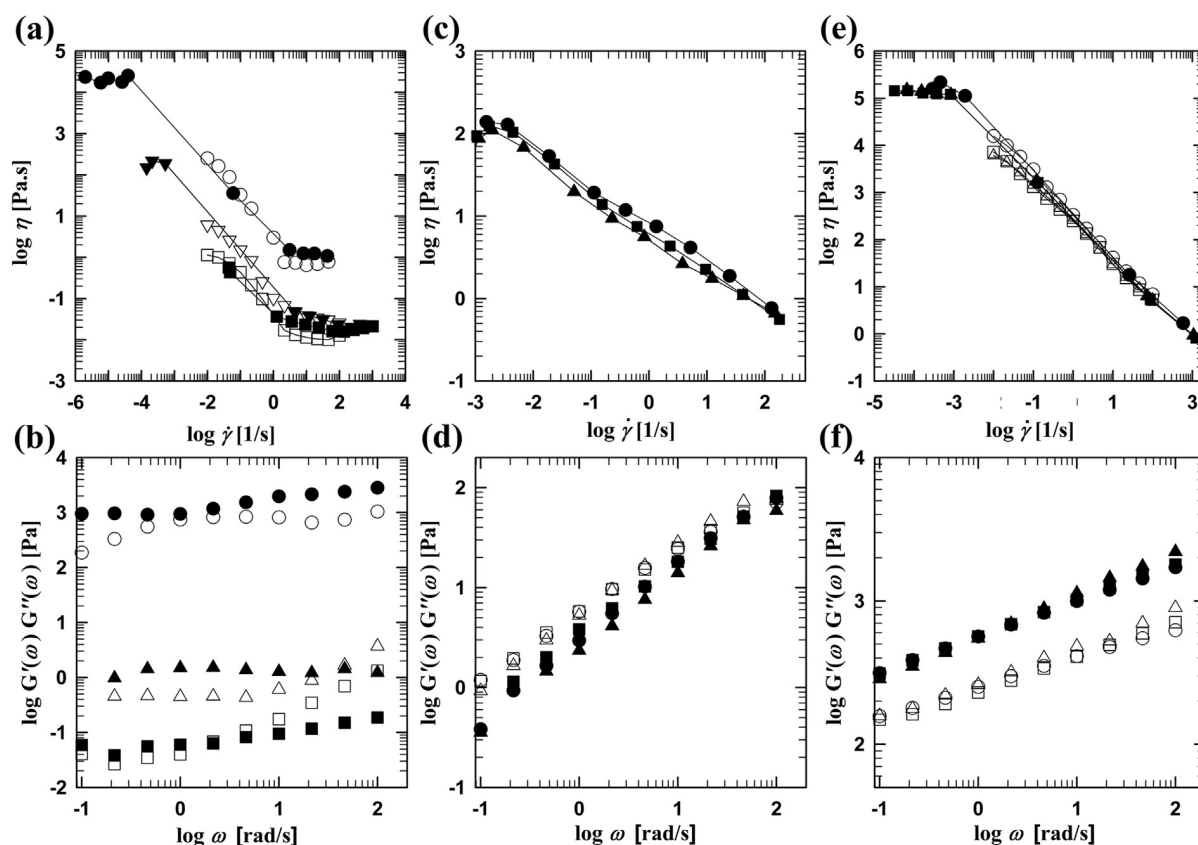


Fig. 7. Rheological properties of anode slurries containing 50 wt% of graphite and various concentration of CMC and SBR; (a)&(b) 0.07 wt% of CMC, (c)&(d) 0.7 wt% of CMC, and (e)&(f) 1.7 wt% of CMC; (a)&(c)&(e) Viscosity as a function of shear rate which is obtained from the stress controlled (closed symbol) and rate controlled (open symbol) rheometer, (b)&(d)&(f) storage (closed symbol) and loss (open symbol) moduli as a function of frequency; (●○) 0 wt%, (▲△) 2 wt%, (■□) 5 wt% of SBR concentration.

Then, the SBR cannot adsorb on the graphite surface and cannot have an influence on the dispersion of the graphite particles. The CMC plays a primary role in forming the microstructure of the slurry.

The effect of binders, both CMC and SBR, on the microstructure formation in the anode slurry has been investigated by analyzing the rheological properties and cryo-SEM images. We figure out that the microstructural change of the slurry, such as from gel to dispersion, and vice versa, depends on the concentration of binders. Especially, in the slurry containing both CMC and SBR, the effect of SBR on the microstructure is different depending on the CMC concentration. In the battery industry, excess organic binders such as CMC and SBR have a negative effect on the electrode performance. Therefore, it is crucial to understand the effect of binders on the microstructure formation and to optimize the composition of the ingredient of the slurries.

4. Conclusion

In this study, the effect of CMC and SBR, which are used as binders in the anode slurry, on the microstructure formation is investigated. The microstructure of the slurry is estimated by the rheological measurements, and it is confirmed by the cryo-SEM images.

The graphite particles form the gel structure by hydrophobic attraction in the aqueous solution. When the SBR is added to the slurry, the SBR adsorbs on the graphite surface and decreases the attractive force between the graphite particles. In addition, as the

concentration of SBR is increased further, the graphite particles cannot be aggregated any longer and are well dispersed in the medium, inducing liquid-like behavior of the slurry.

The CMC can also adsorb on the graphite surface like SBR. In the case of graphite/CMC slurry, the microstructure of the slurry is changed depending on the concentration of CMC. For the slurry with low concentration of CMC, the graphite particles form the gel structure by hydrophobic attraction. As the concentration of CMC increases after ϕ_{LC} , the adsorption amount of CMC on the graphite surface is also increased. The graphite particles are dispersed by electrostatic repulsion between the adsorbed CMC. As the CMC concentration is further increased after ϕ_{UC} , the slurry shows a gel behavior again because the CMC molecules form the polymeric network structure at high concentration. The gel structure is formed at low and high CMC concentration, but the structures are different from each other. That is, the gel structure is formed by the aggregation of graphite particles at low CMC concentration, while it is formed by the polymeric network structure of CMC at high CMC concentration.

In the graphite/CMC/SBR slurry, the microstructure of the slurry depends on the concentration of CMC and SBR. For the slurry with low concentration of CMC, the graphite particles are dispersed by adsorbing SBR on the graphite surface. On the other hand, in the slurry with high CMC concentration, the SBR cannot adsorb on the graphite surface due to the CMC which is preferably adsorbed on the particle, and stays in the medium. When the CMC concentration is high enough in the slurry, the CMC plays a leading role in forming the microstructure of the slurry.

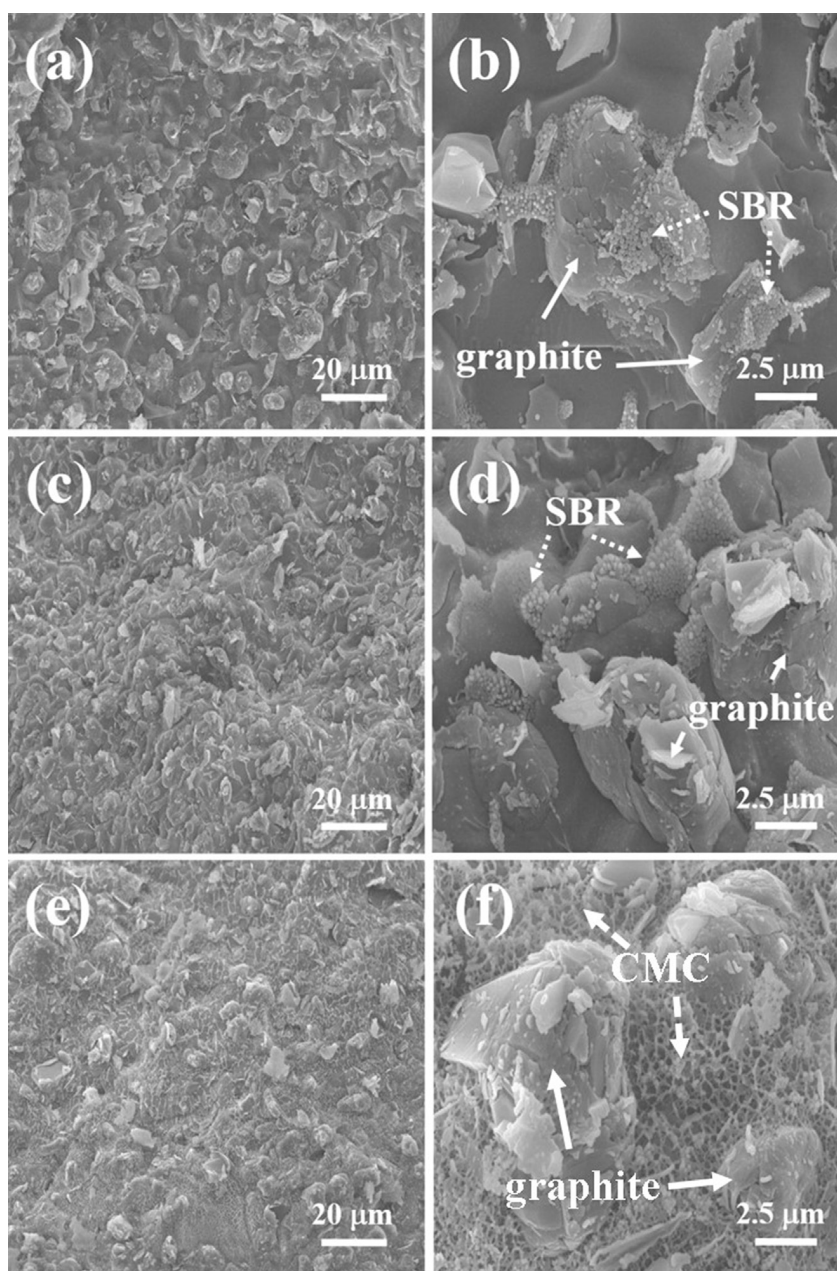


Fig. 8. Cryo-SEM images of anode slurries containing 50 wt% of graphite and different concentrations of CMC and SBR: (a)&(b) graphite 50 wt% + CMC 0.07 wt% + SBR 5 wt%, (c)&(d) graphite 50 wt% + CMC 0.7 wt% + SBR 5 wt%, (e)&(f) graphite 50 wt% + CMC 1.7 wt% + SBR 5 wt%.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2015.09.009>.

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