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Effect of Carboxymethyl Cellulose on Aqueous Processing of Natural Graphite Negative Electrodes and their Electrochemical Performance for Lithium Batteries

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Suspensions of natural graphite particles were prepared in an aqueous medium using carboxymethyl cellulose (CMC) and emulsified styrene-butadiene copolymer latex as part of an environmentally friendly fabrication process for graphite anodes (negative electrodes) intended for application in Li-ion batteries. Suspensions were characterized by adsorption isotherms, electroacoustic measurements, rheology and sedimentation tests, at two different degrees of carboxymethyl substitution (DS) on CMC. A lower DS value (0.7) resulted in greater uptake of CMC on graphite compared with a higher DS value (1.28). This was attributed to attractive hydrophobic interactions associated with the lower carboxymethyl substitution. The greater adsorption for DS = 0.7 correlates with lower relative viscosity in concentrated graphite suspensions, a higher adhesion strength with a copper substrate, and a greater retention of discharge capacity after cycling. The effect of DS is attributed to differences in the aqueous dispersion properties and stability of graphite suspensions. Based on these results, we fabricated high-capacity graphite negative electrodes characterized by gravimetric and volumetric energy densities of greater than 340 mAh/g and 560 mAh/cm^3, respectively. This formulation also led to improved adhesion strength, giving the as-fabricated cell an attractive cycle life greater than 90% of initial discharge capacity after 200 cycles.
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Graphite is now a commonly used anode (negative electrode) material for fabrication of Li-ion secondary batteries. It became an attractive alternative to Li electrodes, which suffer from serious problems with, for example, dendritic growth of Li during repetitive charge-discharge cycling.[1] Graphite has excellent electrochemical characteristics as well as significant cost effectiveness. However, graphite has an inherent limitation with a theoretical gravimetric capacity estimated at 370 mA h/g, compared with 3000 mA h/g for Li electrodes.[2] To increase the specific capacity of Li-ion batteries, researchers have concentrated on development of new negative electrode systems, such as carbon-coated Si,[3] SnO_2-based,[4] and Mg_2Si.[5] However, these developments are not immediately applicable to industrial fabrication, because they place new requirements on the whole system and must be coupled with a compatible cathode, electrolyte, and separator.

Alternatively, it is useful to focus on reformation of the present processing scheme, for example, by transitioning to environmentally friendly manufacturing, but without degrading the existing electrochemical performance. We previously demonstrated that graphite-based suspensions could be successfully prepared in an aqueous system for the fabrication of graphite negative electrodes.[6-8] This was accomplished by preparing a stable slurry using organic additives, namely, carboxymethyl cellulose (CMC) and emulsion polymerized styrene-butadiene copolymer latex (SB latex). SB copolymer, a common latex binder, was used to enhance the handling strength of the green graphite negative electrode sheet following aqueous coating (tape casting). The SB latex used in this study was stabilized in aqueous suspension by residual fatty acid (anionic) surface groups.[9] CMC played a key role as a thickening agent to prevent graphite particles from settling out during processing. It was found that CMC also contributed to the development of surface charge on the graphite particle. The as-assembled battery exhibited improvements relative to less environmentally friendly manufacturing processes in the areas of charge-discharge efficiency and rate capability.[6-8] However, limited information is available on the effect of these polymers, particularly CMC, on graphite suspensions or their effect on the dispersion stability of graphite particles.

CMC is a linear polymeric derivative of cellulose, consisting of β-linked glucopyranose residues with varying levels of carboxymethyl ($-CH_2COO^-$) substitution.[10] The presence of the carboxymethyl groups is responsible for the aqueous solubility of CMC relative to insoluble cellulose. CMC is therefore a weak polyacid that dissociates to form carboxylate anionic functional groups. The degree of substitution (DS) is most commonly in the range of 0.6-0.95 derivatives per monomer unit, but derivatization is not evenly distributed along the chain, and regions of high and low substitution are known to exist.[11] The other predominant functional group on CMC is the hydroxyl, which is replaced by the carboxymethyl group during derivatization.

In the present study, we examined the effect of CMC DS on the suspension stability of graphite and its interaction with other components in the suspension. The physicochemical properties of polyelectrolytes like CMC in aqueous solution are intimately associated with their conformation.[12] A primary factor affecting the conformation of CMC is the degree of substitution. The cellulose backbone has a relatively rigid molecular structure due the nature of the pyranose linkages. The less substituted CMCs, however, are more hydrophobic and have a less extended conformation in water. Similarly, changes in pH affect protonation of the derivative sites on CMC, which in turn impacts conformation as demonstrated by potentiometric titration experiments.[13] The charge density of CMC can be varied as a function of DS, which directly influences the macroscopic properties of solutions. To investigate the effect of carboxymethyl substitution on the dispersion properties of graphite in an aqueous medium, we determined the adsorption isotherms for CMC on graphite, and we measured both the electrokinetic and the rheological behavior of suspensions. Additionally, the sedimentation behavior after 3 months of incubation at room temperature was observed. Finally, we quantified the electrochemical performance of a 1800 mAh-class Li-ion cell containing a $LiCoO_2$ cathode and employing a graphite negative electrode fabricated from our aqueous suspension formulation at different DS values. From the charge-discharge cycling test, the cycle life (retention of capacity) is discussed in relation to the adhesion strength of the electrode as a function of carboxymethyl substitution on CMC.

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Experimental

A proprietary natural graphite powder formulation (SL-20, Superior Graphite Company, Japan)[d] was used in this study; the morphology of this material is known to be plate-like, based on electron microscopy. The physical and chemical data for the graphite, provided by the manufacturer, were as follows: density is 2.245 g/cm^3, particle diameter is 5-20 μm, and specific surface area [Brunauer-Emmett-Teller N_2-gas adsorption] is 4.74 m^2/g. Sodium CMC with an average relative molecular mass of 330,000 was obtained from Daicel FineChem, Ltd. (Tokyo, Japan) with two different degrees of substitution: DS = 1.28 and DS = 0.7. Emulsified SB copolymer latex suspension containing a solid mass fraction of 40% was used as the binder (SB131, Zeon Corporation, Tokyo, Japan). The particle size for this latex, as provided by the manufacturer, is 0.19 μm. Unless otherwise stated, concentrations given for CMC and SB latex are on a mass basis relative to the graphite phase. The final pH value for all suspensions prepared in this study was between 7.3 and 7.8. The estimated uncertainty in all experimental data is expressed as one standard deviation.

Adsorption isotherms for CMC on graphite were determined at 25 ± 1 °C via the solution-depletion method using a total organic carbon (TOC) analyzer (5000A, Shimadzu Corp., Kyoto, Japan). Samples were prepared in deionized water containing a graphite mass fraction of 2% and ultrasonicated for 3 min using a high-intensity (760 W) ultrasonicator (vcx 760, Sonic & Materials, Inc., USA). An ice bath was used to prevent overheating of suspensions during ultrasonication. After treatment, samples were equilibrated for 24 h under stirred conditions. Each sample was then centrifuged and the supernatant analyzed in triplicate for TOC. Results were averaged for each sample, and corrected for background TOC using a solution blank derived from a native graphite suspension in the absence of organic additives. The root-sum-of-squares method was used to combine the uncertainty components (standard deviations) for each data point. TOC values were converted to polymer mass using an experimentally determined calibration curve. Adsorption isotherms were derived from the difference between the amount added and the amount remaining in the supernatant.

For electrokinetic measurements, suspensions containing a graphite mass fraction of 5% were prepared in deionized water, with or without CMC, and subsequently treated ultrasonically for 3 min. The treated suspensions were then allowed to equilibrate at room temperature for 12 h with magnetic stirring, after which they were ultrasonicated for an additional 3 min. The required amount of SB latex was then added and the suspensions were equilibrated for an additional 12 h, for a total equilibration time of 24 h. Electrokinetic curves were determined using an electroacoustic analyzer (model ESA-9800, Matec Applied Sciences, Hopkinton, MA). The electrokinetic sonic amplitude (ESA) was measured in response to an applied AC electric field at a nominal frequency of 1 MHz and converted to dynamic mobility (average particle velocity per unit applied field strength uncorrected for particle inertia). Dynamic mobility is the AC analog to the DC electrophoretic mobility, and, as such, is an indirect determination of surface-related charge phenomena. Further details on the ESA technique and its application can be found in the literature.[14,15]

The rheological behavior of graphite suspensions containing a mass fraction of 35% solids was determined at 20 ± 0.1 °C using a controlled-stress rheometer (MCR 300, Paar Physica, Stuttgart, Germany) with a concentric cylinder geometry (CC 27, bob radius 13 mm and cup radius 14 mm). Sample preparation followed the same procedure previously described for ESA measurements. The apparent viscosity of graphite suspensions was measured as a function of shear rate, and relative viscosity was then calculated by normalizing to the viscosity of the liquid medium (including dissolved polymer), which was measured separately following removal of the solid phase by centrifugation.

[d]Certain trade names and company products are mentioned in the text or identified in illustrations in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

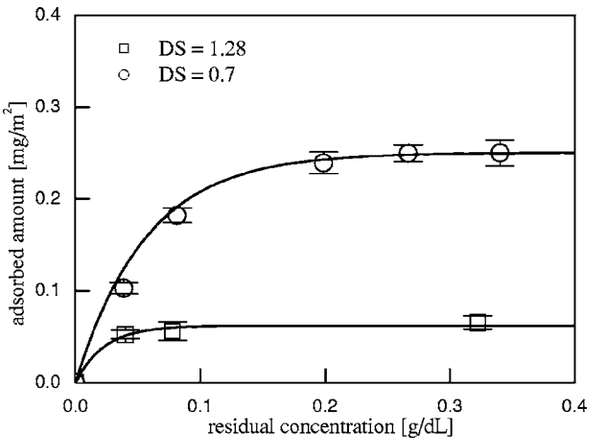


Figure 1. Room temperature adsorption isotherms for CMC on graphite for two different DS. Error bars represent the calculated standard deviation for the experimental data.

Finally, a 1800 mAh-class cylindrical Li-ion battery was assembled using a graphite negative electrode and $LiCoO_2$ cathode and its electrochemical performance quantified. For the purpose of measuring adhesion strength between copper substrate and graphite sheet, the peel test (Hounsfield Test Equipment, Ltd., Redhill, U.K.) was used. A graphite sheet with a width of 25.4 mm and a length of 20-30 mm was cut and uniformly attached to a glass plate with a width of 25.4 mm and a length greater than 50 mm. The charge-discharge cycle test was carried out galvanostatically at a current of 1.8 A with a nominal capacity of 1800 mAh between 3.0 and 4.2 V, using a TOSCAT-3000U battery testing unit (Toyo System Co., Ltd., Fukushima, Japan).

Results and Discussion

Figure 1 shows the aqueous adsorption isotherms for CMC on graphite for the two DS values. Adsorption of CMC on graphite particulate surfaces increases and reaches a plateau level of approximately 0.24 and 0.06 mg/m^2 for DS of 0.7 and 1.28, respectively. These saturation levels correspond to polymer mass fractions (relative to the solid phase) of 3 and 1.2%, for low and high DS, respectively. The plateau coverage for CMC having a low DS value is a factor of four greater than that for the more substituted polymer. This is likely driven by the difference in hydrophobicity, which affects the interaction of CMC with both the solid phase and the solvent medium. A high DS value permits stronger interaction with the aqueous phase and reduces the driving force for adsorption onto hydrophobic graphite. This results in reduced uptake and a more extended adsorption conformation with fewer attachment points on the graphite surface.[16] In contrast, a lower level of substitution results in a stronger, more compact interaction with the graphite surface through hydrophobic moieties.

Figure 2 shows the pH-dependent electrokinetic behavior of graphite suspensions prepared at different CMC concentrations for DS values of (a) 0.7 and (b) 1.28. SB latex has not been added to these suspensions. The electrokinetic curves indicate that graphite particles in the presence of CMC exhibit a negative potential across the normal pH range. This is attributed to the presence of the carboxylate functional groups within the adsorbed layer of CMC, which contribute to an effective surface layer charge on graphite. The relatively low magnitude of the dynamic mobility values reported in Fig. 2 is due to inertial dampening of the oscillatory motion of the charged particles in the applied high-frequency electric

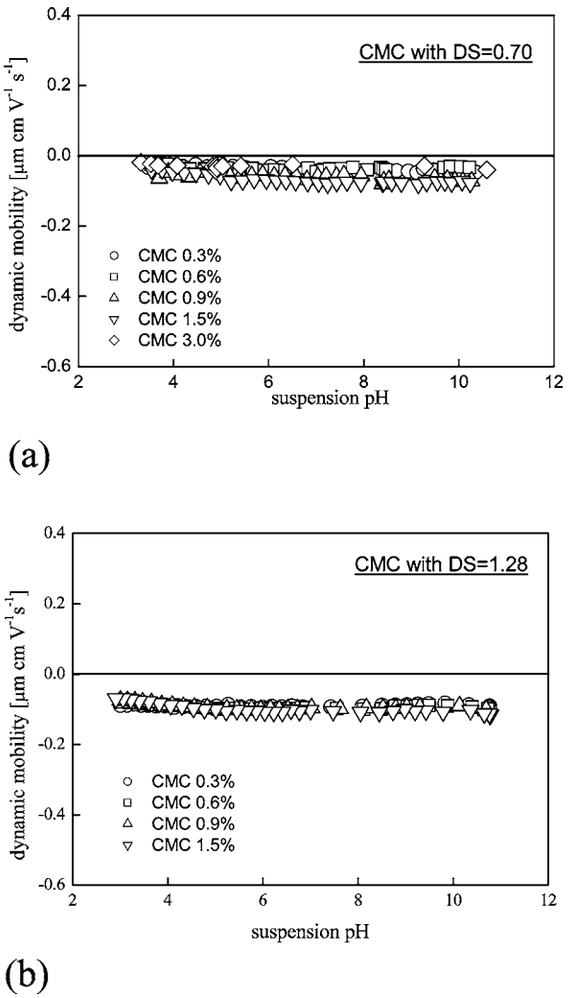


Figure 2. Effect of CMC concentration (mass fraction relative to graphite) on the electrokinetic behavior of graphite suspensions prepared at a mass fraction of 5% solids: (a) with DS equal to 0.7 and (b) with DS equal to 1.28.

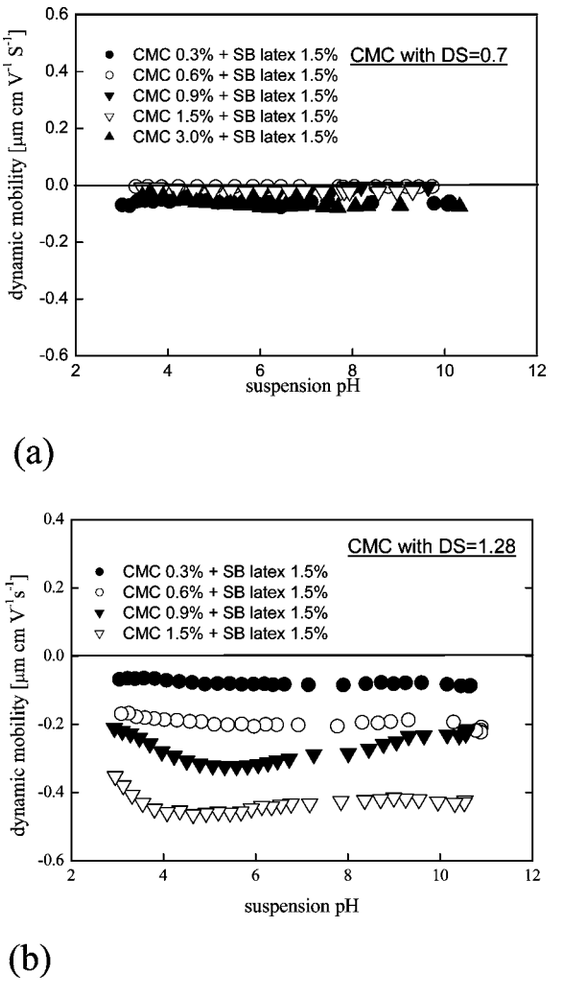


Figure 3. Electrokinetic behavior of graphite suspensions prepared at a mass fraction of 5% solids and containing both CMC and SB latex, as a function of CMC concentration (mass fraction relative to graphite) (a) with DS equal to 0.7 and (b) with DS equal to 1.28. SB latex concentration is fixed at a mass fraction of 1.5% relative to graphite.

field as a result of their large mass. The inertial effect on electroacoustic measurements becomes significant for particle diameters larger than roughly 0.1 μm and is maximized at sizes above about 10 μm.[15]

Carboxymethyl substitution has a small but significant influence on the magnitude of the dynamic mobility, which increases with increasing DS due to the higher density of anionic carboxylate groups present. The dependence on CMC concentration is within the experimental error for this measurement, which we estimate at ±0.05 μm cm V^{-1} s^{-1}.[17] This weak dependence on DS and the lack of an obvious concentration dependence can be explained with respect to the electrokinetic shear-plane. Only the near-surface fraction of carboxylate sites contribute to the shear-plane potential that is responsible for the ESA (dynamic mobility) response; polymer chains dangling from the surface or only loosely attached extend beyond the shear-plane and do not contribute to the electrokinetic charge. Once the graphite surface is saturated, any additional CMC remains in solution and does not influence the measurement, except through its contribution to the bulk electrolyte concentration and the resulting screening of charge. To some degree, the reduced charge density associated with a lower value of DS is compensated by the concurrent increase in adsorption, and this partially explains the similarity in electrokinetic curves for the two DS values examined here.

Aqueous suspensions of native (untreated) graphite are unstable with respect to their dispersion, as described previously.[6] Even in the presence of moderate stirring, graphite particles in an aqueous medium settle out within a few minutes due to their hydrophobic nature and large particle size. Consequently, we were unable to obtain reliable ESA measurements on the native graphite. Similarly, we were unable to measure electrokinetic curves for graphite suspensions prepared with SB latex in the absence of CMC. SB latex exists as an insoluble latex particle with a negative surface charge due to fatty acid emulsifiers[9] and is therefore unlikely to interact directly with the hydrophobic graphite particles. Thus, a suspension prepared with SB latex was, like its native counterpart, unstable and the graphite phase settled out during the measurement. Only in the presence of CMC were graphite suspensions sufficiently stable for ESA analysis.

Figure 3 shows pH-dependent electrokinetic curves for graphite suspensions prepared with SB latex and CMC as a function of CMC concentration for DS values of (a) 0.7 and (b) 1.28. The concentration of SB latex was fixed at a mass fraction of 1.5% relative to the graphite phase; this value was selected as optimal based on the results of a previous study.[6] The dynamic mobility of the graphite suspension prepared with SB latex and CMC having a DS of 0.7 is essentially the same as with CMC alone. In stark contrast, the dy-

namic mobility of graphite suspensions in the presence of CMC with a DS of 1.28 increases remarkably with CMC concentration when SB latex is subsequently added. Additional measurements (data not shown) indicate that mobility also increases with increasing SB latex concentration up to a point, then decreases somewhat at higher SB latex loadings. In order to eliminate possible contributions to the ESA signal from solution-phase macroions and inert electrolytes, pure solutions of SB latex and CMC (without graphite) were analyzed at concentrations equal to those added in the graphite formulations. The results of these analyses (data not shown) indicate that the magnitude of the ESA signal for SB latex is very weak and can be considered insignificant. The weak signal can be attributed to the low density-contrast for SB latex in water, which produces a weak acoustic signal, combined with the low solids concentration relative to graphite. Similarly, CMC, even at the highest concentrations used in this study, does not contribute a significant background ESA signal in this system. Therefore, the apparent influence of SB latex on the electrokinetic behavior of graphite with adsorbed CMC (DS = 1.28) is likely a real effect and not a measurement artifact.

In our previous study, we proposed a charge developing mechanism for graphite with adsorbed CMC having a DS of 1.28, in regard to the reorientation of carboxymethyl units and the location of the electrokinetic shear-plane.[6] However, we do not yet have a clear understanding of the underlying mechanism(s) responsible for the observed increase in dynamic mobility (and by inference, the electrokinetic potential) when SB latex is added to the graphite suspension containing high-DS CMC, and conversely the lack of this effect in the low-DS system. Because the DS value is central to this phenomenon, it seems obvious that the carboxymethyl groups on CMC must play a central role in the observed increase in mobility, whether directly or indirectly, through an interaction with the negatively charged SB latex in solution. In this context, we can suggest three possible scenarios that might explain this phenomenon: (*i*) The negatively charged SB latex displaces the weakly bound high-DS CMC from the graphite surface, resulting in a higher density of charged groups on graphite due to adsorbed latex particles. What the driving force for such a displacement might be, however, is not obvious to the authors, and we have no direct evidence for displacement of CMC by SB latex. (*ii*) The presence of SB latex in the solution influences the conformation of adsorbed CMC such that a greater number of the deprotonated carboxylate groups on CMC lie behind the shear-plane and thus contribute to the measured electrokinetic potential. The driving force for this mechanism would be principally electrostatic. At the relatively dilute concentrations used in the present ESA measurements, where the medium accounts for slightly more than 97% of the total suspension volume, it is difficult to rationalize this type of "forced" interaction. A related effect to consider is a salting out of the CMC by the presence of the SB latex in solution, in which the actual adsorbed amount of CMC increases. We currently have no direct evidence for either a conformational change or an increase in CMC adsorption in the presence of SB latex. (*iii*) The SB latex interacts attractively with the graphite-bound CMC via hydrogen bonding between COOH and COO- groups on SB latex and CMC, respectively, resulting in the effective coadsorption of SB latex onto graphite, with a concomitant increase in the shear-plane charge due to the surface carboxylate groups on the latex. This mechanism seems plausible, particularly if there are large differences between the average pK_a (negative log of the dissociation constant) for the carboxyl groups on CMC and those on SB latex, resulting in significantly different ratios of protonated-to-deprotonated sites for each polymer. Such variations in pK_a are well known for polyprotic carboxylic acids,[18] where the deprotonation of the first carboxyl group reduces the acidity (i.e., increases pK_a) for adjacent groups due to unfavorable electrostatic repulsive interactions. Because the carboxyl groups on CMC are expected to be fairly isolated, due to the relatively low number and randomness of the substitution reaction, the pK_a of these sites would be less affected and therefore more acidic overall. For SB latex the carboxyl sites are constrained primarily to the surface layer, and are thus more likely to be influenced by the electrostatic fields of adjacent groups. Certainly, these ideas warrant further research in order to more fully resolve this issue; however, as is subsequently shown, the apparent increase in surface-bound negative charge on graphite in the case of DS = 1.28 does not translate into a more stable suspension or better negative electrode properties.

Figure 4 shows log-log plots of apparent (a, b) and relative (c, d) viscosity for graphite suspensions at different CMC concentrations as a function of the shear rate. Relative viscosity is presented in order to help differentiate the particle-particle interactions from the collective contribution of all solution components. The curves corresponding to DS = 0.7 are shown in (a) and (c), while those for DS = 1.28 are shown in (b) and (d). CMC is a commonly used thickening agent, so the primary macroscopic effect of unadsorbed (free) CMC is to increase the apparent viscosity and produce pseudoplastic behavior.[19] Overall, the apparent viscosity of graphite suspensions with DS of 0.7 was higher than those with DS of 1.28. The corresponding supernatant polymer solutions followed this same trend, with solutions containing CMC with a DS of 0.7 showing the higher overall viscosity. Therefore, the relative viscosity curves are inverted with respect to the apparent viscosity, with DS = 0.7 exhibiting the overall lower values. This result lies in contrast to conventional wisdom, which states that with everything else being the same, an increase in DS should increase viscosity because of the greater chain extension afforded by electrostatic repulsion between charged carboxyl groups on CMC. The different behavior observed here may be attributed to the complexity of a multicomponent system or the effects of the associated counterions (primarily Na^+).

At higher shear rates, the apparent viscosity becomes mostly independent of DS and can be attributed to the growing importance of dilatant behavior associated with the platelet-shaped graphite particles. The dilatancy is more evident in the relative viscosity curves, especially in the case of DS = 1.28, and the lowest CMC concentration for DS = 0.7. Pseudoplasticity, as seen in the apparent viscosity curves, is frequently observed in ceramic particulate suspensions at high solids loadings and its mechanism is well described in the literature;[6,20] however, it appears that in the present case most of the observed pseudoplastic contributions come not from particle interactions but from the dissolved polymer phase. Hence, the relative viscosity for both DS values exhibit Newtonian-like behavior over extended shear rate ranges after normalizing against the corresponding supernatant solution to produce relative viscosity curves.

The moderate reduction in relative viscosity for the lower DS value, relative to the higher DS value, at CMC concentrations greater than 0.3% can possibly be attributed to an improvement in the dispersion stability, because the effects of dissolved polymer have presumably been removed by normalization. If we consider the adsorption data for CMC shown in Fig. 1, less substitution contributes to a stronger interaction with the graphite surface, which in turn may reduce particle agglomeration and thus lower the relative viscosity. Certainly, the effect is rather subtle here, as are the differences in relative viscosity shown in Fig. 4c and d. Another possibility to consider is that the normalization against the supernatant polymer solution may not be entirely appropriate. It has been shown that solution-phase polyelectrolytes at the same concentration can respond differently to an applied shear depending on whether or not a concentrated solid phase is also present.[21,22] This difference has been attributed to restriction of polymer motion when the persistence length of an extended polymer chain is on the order of the average separation distance between adjacent particles in solution. For high-molecular-mass polyelectrolytes like the CMC used in the present study, the persistence length can be quite large (on the order of 100 nm).[12] By removing the solid phase during centrifugation, the polymer solution rheology may change because the polyelectrolyte is no longer constrained between solid interfaces. In this case, one would predict a higher relative viscosity for the higher DS value

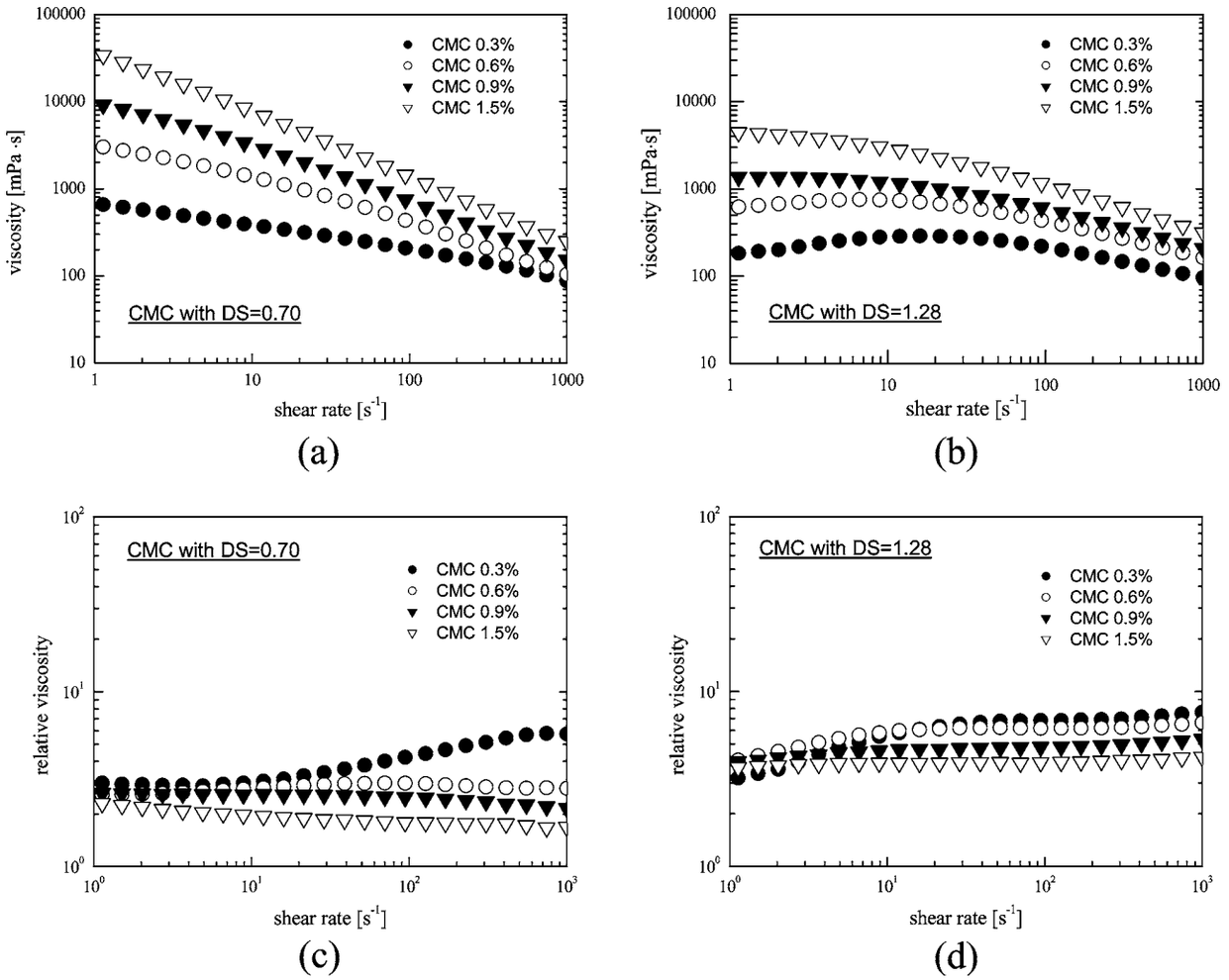


Figure 4. Log-log plots of viscosity as a function of ascending shear rate for graphite suspensions at a mass fraction of 35% solids prepared with CMC at different concentrations (mass fraction relative to graphite) and with two DS values: (a, c) DS equal to 0.7, and (b, d) DS equal to 1.28. Apparent viscosity is shown in (a, b) and the corresponding relative viscosity is shown in (c, d).

because normalization would not account for the increase in viscosity caused by the presence of the solid phase. It is difficult to rule out this possibility in the present system.

Assuming for the moment that the lower relative viscosity for DS = 0.7 can be associated with better stability of the graphite particle phase (and not due to the effects of free polymer), one might be inclined to suggest that steric interactions play a significant role in this stability improvement. This is particularly tempting because electrostatic effects are minimized in the case of low DS. Repulsive steric interactions occur between particles whose surfaces are saturated with a polymer coating, while at the same time polymer solubility in the solution phase is such that chains can extend out into solution away from the particle surface.[23] This certainly describes the situation with respect to CMC on graphite in an aqueous medium. It could also be argued that a thick, somewhat compact, adlayer of CMC simply prevents graphite particles from interacting with each other sufficiently to form any structures other than weak associations that are easily broken by mild shear. As indicated by the adsorption isotherms, only CMC with a low DS value can form such a dense adlayer. The more substituted CMC exhibits a factor of four lower adsorption at the plateau value. It is also likely that the deprotonated carboxyl groups on CMC orient themselves toward the solution phase and away from the particle surface. This is facilitated by the tendency of carboxymethyl derivatives to be unevenly distributed, with unsubstituted and trisubstituted areas coexisting. Reorientation of carboxyl sites would provide for the possibility of both steric and electrostatic contributions to stability, but based on sedimentation results (see below), it would appear that the steric/adlayer effects are more important for increased stability in this system.

In order to compare the long-term dispersing efficiency of CMCs on graphite as a function of DS, suspensions containing a mass fraction of 35% graphite (with 1.5% SB latex and 1.5% CMC) were photographed after 3 months of incubation (see Fig. 5). The dispersion prepared with DS of 0.7 remains homogeneous, while the one prepared with DS of 1.28 has largely sedimented. Clearly, this suggests that a low DS value provides better stability for natural graphite particles in an aqueous medium. This might, in turn, result in a more efficient particle packing during formation of graphite negative electrodes by film-coating methods. More efficient packing should facilitate the fabrication of higher capacity electrodes, but we have not as of yet observed direct evidence for this link. Based on the

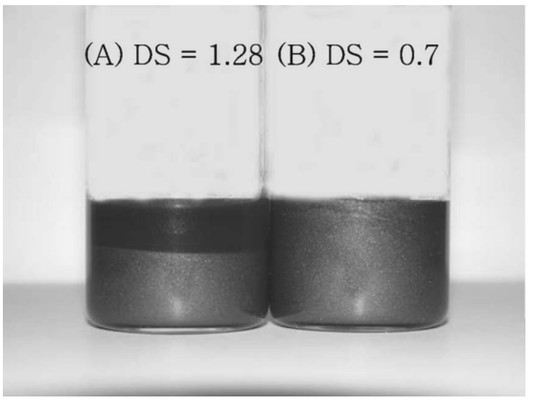


Figure 5. Photograph of suspensions prepared with a mass fraction of 35% graphite, and relative mass fractions (based on graphite phase) of 1.5% SB latex and 1.5% CMC, after 3 months of incubation at room temperature. The effect of the DS of the CMC is demonstrated by the (A) presence or (B) absence of phase separation.

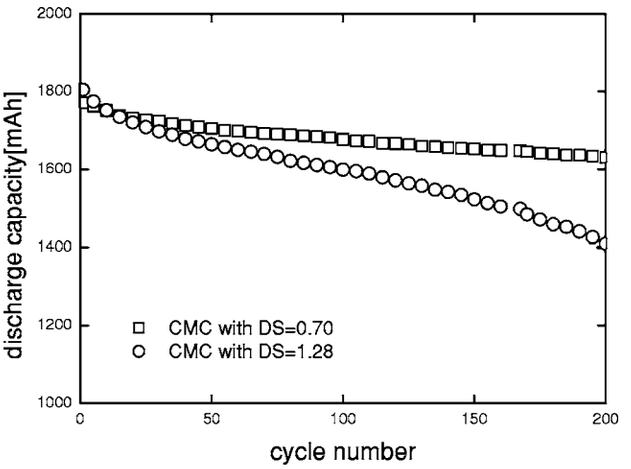


Figure 6. Variation of discharge capacity with the number of cycles for the 1800 mAh-class cylindrical Li-ion cells manufactured from suspensions containing a mass fraction of 35% graphite, and relative mass fractions (based on graphite) of 1.5% SB latex and 1.5% CMC at two DS values.

measured initial discharge capacity, the gravimetric and volumetric energy densities of a fabricated graphite negative electrode, prepared using 1.5% CMC with DS = 0.7 and SB latex at 1.5%, were calculated to be above 340 mAh/g and 560 mAh/cm^3, respectively. This promising energy density makes this graphite negative electrode attractive as part of an innovative rechargeable Li-ion battery system.

The initial charge-discharge capacity of natural graphite electrodes as a function of DS of CMC was measured to evaluate the half-cell characteristics. Table I shows the initial discharge capacity values and the coulombic efficiency obtained from the half-cells with natural graphite electrodes as a function of DS. In the first charge-discharge cycle, both natural graphite negative electrodes showed an initial discharge capacity of $>$340 mAh/g and a coulombic efficiency $>$92%, independent of the DS value. Figure 6 shows the variation of discharge capacity with the number of cycles for 1800 mAh-class cylindrical Li-ion cells fabricated from graphite suspensions with 1.5% SB latex and 1.5% CMC. After 200 charge/discharge cycles at 1 C, the Li-ion cell prepared with the graphite suspension containing CMC with DS = 0.7 retains a discharge capacity of above 90% of the nominal capacity (1630 mAh). In contrast, the Li-ion cell fabricated using CMC with DS = 1.28 produced a discharge capacity of 1400 mAh after the same number of cycles and exhibited a greater rate of capacity loss. Similarly, the results of adhesion strength measurements between the graphite sheet and copper substrate, shown in Table II, indicates that the adhesion strength for graphite prepared with a formulation based on DS = 0.7 is nearly two times greater than that based on the higher DS value. The adhesion strength values of artificial graphite negative electrodes made using the conventional method [poly(vinylidene difluoride) (PVDF)-nonaqueous processing] are very similar to those of natural graphite negative electrodes made using the new technique. However, if the natural graphite negative electrodes are fabricated by the conventional method (PVDF-nonaqueous processing), more than 15 mass % (based on solid contents) PVDF are needed for similar adhesion strength values, compared to the new technique. To a certain extent, adhesion strength is more important than any other negative electrode property, because good electrochemical performance (based, for instance, on lifetime, specific capacity, etc.) cannot be achieved if the adhesion strength is not sufficient to endure multiple charge-discharge cycling. Finally, the graphite negative electrodes, which were prepared using CMC having a low DS, exhibited excellent cell performance, with an initial specific capacity above 560 mAh/cm^3 and improved self-discharging characteristics.

Conclusions

The effect of DS of CMC on the dispersion properties of particulate graphite in an aqueous medium was investigated, and the electrochemical performance of Li-ion cells fabricated using aqueous-based processing was evaluated. From the results obtained for electroacoustic, rheological, and adsorption isothermal data, it was found that suspension properties, as well as the quality of graphite particle dispersion, depends on the value of DS. CMC with a lower DS value has a more hydrophobic nature, which enhances its interaction with the graphite surface in an aqueous medium. These interactions contribute to the increase in plateau adsorption for CMC onto graphite and appear to enhance suspension stability, most likely through a combination of steric and electrostatic interparticle repulsive forces. An analysis of the electrochemical performance of Li-ion batteries fabricated using aqueous formulations with two different DS values showed better adhesion strength with lower DS, and this appears to lead to longer cycle life with higher retention of discharge capacity during operational tests. Furthermore, graphite green sheets made using CMC with DS = 0.7 shows improved energy density and specific capacity in fabricated Li-ion batteries.

Table I. The initial discharge capacity and coulombic efficiency obtained from the cell of Li/1.1 M $LiPF_6$ EC/EMC/DMC (30/60/10 vol %) solution/natural graphite electrodes with the degree of substitution in CMC (graphite:CMC:SB latex = 97:1.5:1.5 mass fraction).

Degree of substitution	Initial discharge capacity (mAh/g)	Coulombic efficiency (%)
1.28	341	92.1
0.7	344	92.7

Table II. The adhesion strength of graphite sheet as a function of degree of substitution in CMC (graphite:CMC:SB latex = 97:1.5:1.5 mass fraction).

Degree of substitution	Strength[a] (mN/mm)
1.28	4.705 ± 0.293
0.7	7.911 ± 0.037

[a] Each value represents the calculated mean and standard deviation of a minimum of five samples.

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