

Short communication

# Effect of poly(acrylic acid) on adhesion strength and electrochemical performance of natural graphite negative electrode for lithium-ion batteries

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## Abstract

High-capacity natural graphite negative electrodes for use in prismatic lithium-ion batteries are fabricated from an aqueous suspension precursor. The effects of poly(acrylic acid) (PAA) on suspension stability and the resulting mechanical properties of the electrodes are investigated. Precursor suspensions consisting of graphite particles, sodium carboxymethyl cellulose (CMC), emulsified styrene-butadiene (SB) copolymer latex and PAA are prepared in an aqueous medium and tape-cast on to a copper foil. The addition of PAA enhances the stability of the suspension at low shear rates without compromising the solvent-thickening effect of CMC. Peel test results showed that the adhesion strength of the graphite electrode on the copper substrate is significantly improved by PAA. Graphite negative electrodes fabricated using PAA are characterized by gravimetric and volumetric energy densities of more than 340 mAh g<sup>-1</sup> and 560 mAh cm<sup>-3</sup>, respectively. The PAA formulation also leads to improved cycle life, with a discharge capacity exceeding 90% of initial capacity after 500 cycles.

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## 1. Introduction

Typically, negative electrode (anode) films for prismatic lithium-ion battery applications are prepared from a stable suspension of graphite particles by the tape-casting method [1]. Mechanical integrity is provided by inclusion of a polymeric binder. The negative electrode must have high energy density and good mechanical stability. The fabrication of an electrode with high energy density is closely tied to the preparation of a graphite sheet with a high packing efficiency, which is in turn dependent on the particle stability and other properties of the precursor suspension [2]. Suspension properties can also exert an impact on the mechanical stability (in particular the adhesion strength) of the fabricated negative electrode, and good adhesion to the substrate is a key factor for achieving increased

cyclability of the battery [1]. In practice, maleic acid, for example, is incorporated into non-aqueous polyvinylidene difluoride (PVDF)-based systems to improve the adhesion strength [3].

In our previous work [2,4,5], natural graphite-based suspensions were successfully prepared in an aqueous system for the fabrication of negative electrodes. Electrodes with high capacity were produced by selecting the degree of substitution of the carboxymethyl cellulose (CMC) additive. Unfortunately, the graphite electrodes fabricated by this aqueous-based technique suffered from relatively weak adhesion strength values compared with conventionally produced products (e.g., PVDF-nonaqueous processing). Therefore, attention has been directed towards improving the adhesion strength of aqueous-processed graphite electrodes cast on a copper foil, and precursor colloidal stability and resulting electrochemical performance has been investigated.

In the present investigation, a stable slurry is prepared with a combination of three organic additives, namely CMC, emulsion polymerized styrene-butadiene copolymer latex (SB latex) and

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polyacrylic acid (PAA). CMC is used primarily as a thickening agent to prevent the relatively massive graphite particles from settling and segregating during processing. SB latex is a commonly used binder, and is employed to enhance the handling strength of the green graphite electrode sheet following tape-casting. PAA is introduced to determine whether this surface-active dispersing agent can contribute to the stability of the precursor suspension, and at the same time improve adhesion strength between the graphite electrode and copper substrate. The effect of introducing PAA to the suspension is evaluated by determining adsorption isotherms for PAA and CMC on graphite, and by measuring the electrokinetic response and shear rheology for the formulated suspensions. The adhesion strength between electrode and copper substrate is determined by the peel test. From charge–discharge of an 800 mAh-class lithium-ion battery, the cycle life is assessed in relation to the adhesion strength of the incorporated electrode. Finally, the temperature performance of an 800 mAh-class lithium-ion battery based on this formulation is evaluated.

## 2. Experimental

A proprietary natural graphite powder (SL-20, Superior Graphite Company, Japan)<sup>1</sup> was used. The physical and chemical data for the graphite, as provided by the manufacturer, were as follows: density, 2.245 g cm<sup>-3</sup>; particle diameter, 5–20 μm; specific surface area (BET N<sub>2</sub>-gas adsorption), 4.74 m<sup>2</sup> g<sup>-1</sup>. CMC with an average relative molecular mass, Mr (formerly molecular weight, MW), of 330,000 and a degree of substitution (DS) of 1.28 was obtained from Daicel FineChem, Ltd. (Tokyo, Japan). An emulsified SB latex suspension containing a solid mass fraction of 40% was obtained from Zeon Corporation (SB131, Tokyo, Japan). The particle size for this latex, as provided by the manufacturer, is 0.19 μm. PAA (50% solution in water) with an average Mr of 5000 was obtained from Polysciences, Inc. (Warrington, PA, USA). Unless otherwise stated, concentrations of organic additives are expressed on a mass basis relative to the graphite phase. In practice, additive concentrations for suspension formulation were constrained by the electrochemical performance of the electrode; total polymer concentrations in excess of 3 wt.% were determined to be detrimental to final properties. Optimal CMC and SB latex concentrations were previously established at levels of 0.9 and 1.5 wt.%, respectively.

All suspensions were prepared with filtered de-ionized water (18 MΩ resistance), and ultrasonicated for 3 min using a high-intensity submersible horn (5000A, Shimadzu Corp., Kyoto, Japan). The final pH value for all suspensions was between 5.2 and 5.6, and was not independently controlled. The uncertainty values presented for experimental data are expressed as the estimated standard deviations determined from multiple measurements or replicate test samples.

<sup>1</sup> 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 the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

Adsorption isotherms for CMC and PAA on graphite were determined at 25 ± 1 °C via the solution-depletion method using a total organic carbon (TOC) analyzer. Samples were prepared with a graphite mass fraction of 2%, equilibrated for 24 h under stirred conditions, centrifuged, and the supernatant analyzed in triplicate for TOC. Results were corrected for background TOC using a graphite suspension without additives. The TOC values were converted to polymer mass by means of 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 as a function of PAA concentration and equilibrated at room temperature for 12 h with magnetic stirring. The required amount of SB latex was then added and the suspensions were equilibrated for an additional 12 h. Electrokinetic curves were determined using an electroacoustic analyzer (Model ESA-9800, Matec Applied Sciences, Hopkinton, MA, USA) operating nominally at 1 MHz. The electrokinetic sonic amplitude (ESA) was measured and converted to dynamic mobility (particle velocity per unit applied field strength), which is the high-frequency a.c. analog to the d.c. electrophoretic mobility (a metric for particle surface charge) [6,7].

The rheological behaviour 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 ascending shear rate.

Negative graphite electrodes were fabricated by tape-casting the precursor suspension on to a 10-μm thick copper substrate (Furukawa, Japan) using a Model STC-20B tape-casting machine from Hansung Systems, Inc. (Seoul, Korea). After forming, the sheet was first air-dried and then vacuum-dried, at 150 °C, to remove residual water.

For the purpose of measuring the adhesion strength between copper substrate and graphite sheet, the peel test (Hounsfield Test Equipment Ltd., Redhill, UK) was used. A graphite sheet on a copper substrate 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 test procedure was performed at Samsung SDI (Cheonan, Korea).

Finally, a 800 mAh-class prismatic lithium-ion battery was assembled using a graphite negative electrode and a LiCoO<sub>2</sub> cathode. Charge–discharge cycling performed galvanostatically at the 1 C rate with a nominal capacity of 800 mAh between 3.0 and 4.2 V, using a TOSCAT-3000 U battery testing unit (Toyo System Co., Ltd., Fukushima, Japan). The discharge capacity of the fabricated batteries was measured galvanostatically at 0.2 C between 2.75 and 4.2 V, at 25 °C and –10 °C. All electrochemical tests were repeated at least 10 times and then averaged.

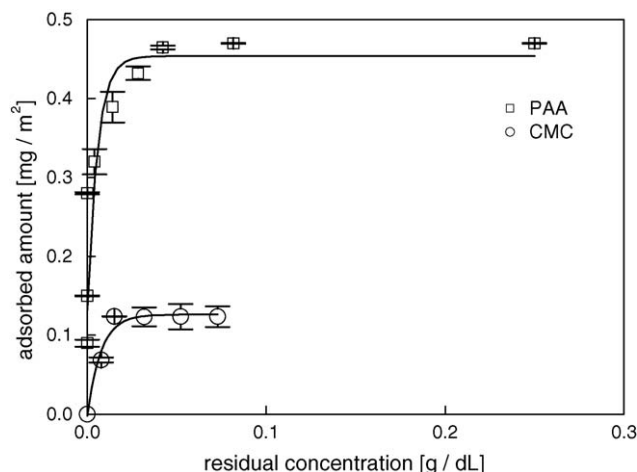


Fig. 1. Adsorption isotherms for PAA and CMC on graphite in aqueous solution at 25 °C. Final suspension pH is between 5.2 and 5.6. Error bars represent calculated standard deviation for experimental data.

### 3. Results and discussion

Fig. 1 shows the aqueous adsorption isotherms for CMC and PAA on graphite. The adsorption for each polymer reaches a saturation level at higher solution concentrations, to yield values of approximately 0.47 and 0.12  $\text{mg m}^{-2}$  for PAA and CMC, respectively. These saturation levels correspond to mass fractions (relative to the solid phase) of 1.2% for PAA and 0.3% for CMC. Although the plateau coverage for PAA is four times greater than that observed for CMC, it is within the range of data reported previously for PAA adsorption on polystyrene at a comparable pH value [8], as well as for various metal oxides (see Ref. [9] for a comparison of PAA saturation adsorption levels on a wide variety of material substrates). The large difference in the affinity of PAA and CMC for the graphite surface is surprising, given that both polymers owe their aqueous properties to the presence of acidic carboxyls. The closer proximity of the carboxyl groups along the PAA backbone may, however, result in a slightly lower average acidity constant for this polyelectrolyte relative to CMC. Although this alone does not fully explain the large observed difference in adsorption, it is likely that the adsorption behaviour is linked to the difference in density and distribution of carboxyl sites on each polymer chain. Regardless, the steep initial part of the isotherm indicates that PAA adsorbs more strongly to the graphite surface than CMC, and thus should out-compete CMC for adsorption sites when both polymers are present.

Fig. 2 illustrates the pH-dependent electrokinetic behaviour of graphite suspensions as a function of CMC concentration (SB latex present), and also with and without PAA present. It was not possible to perform these measurements with PAA alone, due to rapid settling of the graphite particles in the absence of a thickening agent. The concentration of SB latex was fixed at a mass fraction of 1.5%; this value was selected as optimum based on the results of a previous study [2]. The electrokinetic curves show that graphite particles with CMC and SB latex exhibit a negative potential across the measured pH range. This is attributed to the presence of carboxyl functional groups in the adsorbed

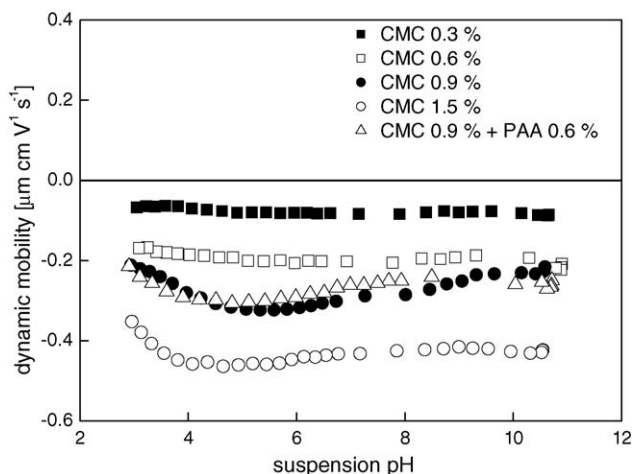


Fig. 2. Electrokinetic behaviour of graphite suspensions prepared at solid mass fraction of 5% and containing both CMC and SB latex, with and without PAA. SB latex concentration fixed at a mass fraction of 1.5% relative to graphite.

layer of CMC. As can be seen in Fig. 2, PAA does not appear to contribute to the further development of electrokinetic potential (surface charge) for graphite suspensions containing CMC. This is surprising, since PAA was added before CMC, and given its high adsorption affinity for the graphite phase. The similarity of the charged groups on CMC and PAA may partially explain the similar ESA curves obtained with and without PAA; the carboxyl groups on PAA and CMC are expected to exhibit similar acid–base behaviour and contribute similarly to any build up of surface charge. The bottom line is that no significant increase in the negative potential occurs over the pH range of observation when PAA is present. The ESA data, therefore, fail to clarify the effect of PAA on dispersion stability, but it confirms that graphite carries a negative charge when PAA is combined with CMC, or when CMC alone is present [2,4]. This negative charge is largely responsible for the stability of the suspension, though steric effects may also play a role in stabilizing particles against aggregation.

The rheological behaviour of graphite suspensions prepared with CMC and SB latex as a function of PAA concentration was evaluated, and the results are shown in Fig. 3. All suspensions exhibit some shear-thickening at low shear rates and some shear-thinning in the high-shear range. Increasing CMC concentration in the absence of PAA leads to a more pronounced non-Newtonian behaviour and overall higher viscosities. The addition of PAA significantly reduces the apparent viscosity in the low-shear region below  $10 \text{ s}^{-1}$ , but has only a minimal impact on the high-shear behaviour. If it is assumed that most or all of the added PAA is adsorbed (as suggested by isotherm data in Fig. 1) and that CMC is only weakly adsorbed (whether PAA is present or not), then the low-shear rheology of the mixed system can be attributed to improved stability of the solid phase (better dispersion, less aggregation) due to the surface-bound PAA. On the other hand, the shear-thinning at higher shear rates must be attributed to the disruption of structure formed by the solution-phase CMC as reported elsewhere [10], and is largely independent of the particulate phase stability.

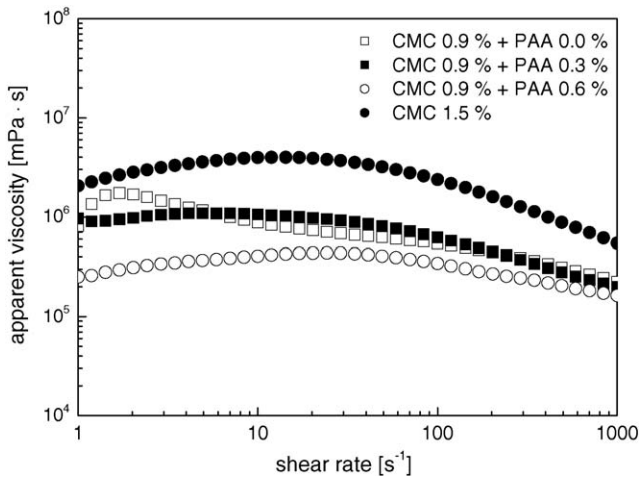


Fig. 3. Logarithmic plot of apparent viscosity vs. an ascending shear rate for graphite suspensions at solids mass fraction of 35%. SB latex concentration fixed at mass fraction of 1.5% relative to graphite.

Fig. 4 presents the variation of specific discharge capacity with the number of cycles for an 800 mAh-class Li-ion battery fabricated from graphite-CMC-SB latex suspensions with and without PAA (at a constant total additive concentration of 3%). As the cycle number increases, the discharge capacity of the Li-ion battery prepared without PAA drastically declines after about 300 cycles. By contrast, the Li-ion battery prepared with 0.6% PAA retains discharge capacity above 90% of the nominal capacity after 500 cycles. These results correlate with adhesion strength measurements between graphite sheet and copper substrate, as summarized in Table 1. The adhesion strength of graphite sheet prepared with both CMC and PAA is more than three times greater than that with CMC alone. From a practical perspective, adhesion strength is more important than almost any other electrode property, since electrochemical performance factors (e.g., cycle life, specific capacity) are not achievable if the adhe-

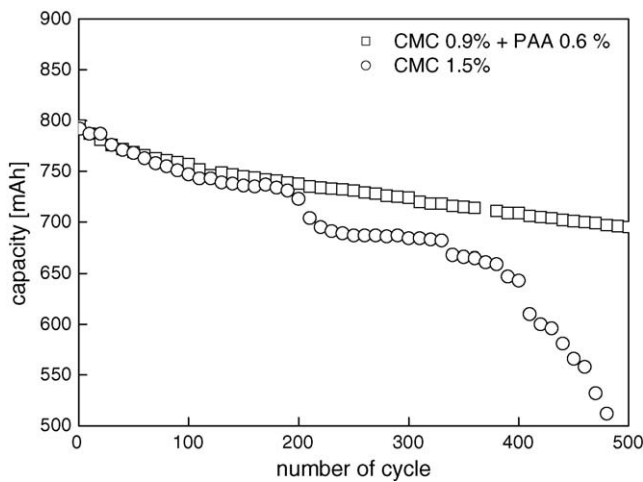


Fig. 4. Variation of discharge capacity with number of cycles for 800 mAh-class prismatic Li-ion battery fabricated from suspensions containing a mass fraction of 35% graphite. SB latex concentration fixed at a mass fraction of 1.5% relative to graphite. Error bars not visible because they are smaller than the symbol size.

Table 1

Adhesion strength of graphite sheet on copper substrate with and without addition of PAA in graphite suspension

	Strength <sup>a</sup> [mN mm <sup>-1</sup> ]
A (without PAA)	4.705 ± 0.293
B (with PAA)	14.496 ± 1.0199

(A) Graphite:CMC:SB latex = 100:1.5:1.5, (B) graphite:CMC:SB latex:PAA = 100:0.9:1.5:0.6.

<sup>a</sup> Each value represents calculated mean and standard deviation of a minimum of five samples.

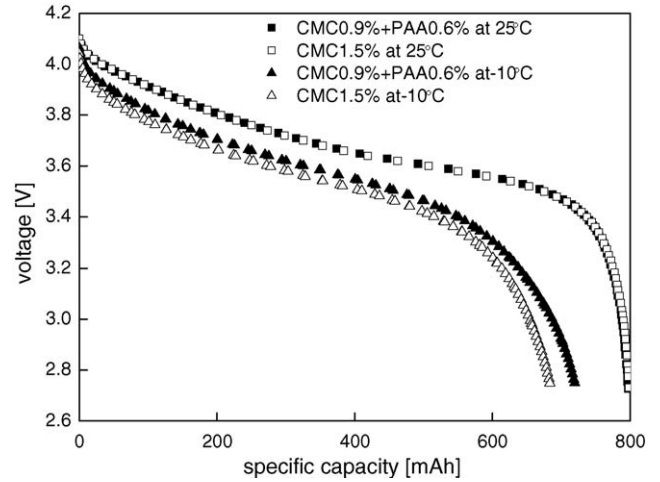


Fig. 5. Voltage vs. specific discharge capacity of prismatic Li-ion battery as a function of temperature and PAA addition. Error bars are not visible because they are smaller than the symbol size.

sion strength is insufficient to endure repeated charge–discharge cycling.

The low-temperature dependence of discharge capacity for the fabricated Li-ion battery is shown in Fig. 5 together with a comparison with measurements at room temperature. In general, the electrochemical performance is reduced as the temperature decreases, due to the reduction in ionic conductivity of the electrolyte and binder phase [11]. For this reason, any enhancement in ionic conductivity of the polymer matrix, for instance by addition of acidic PAA, can potentially improve the low-temperature performance of Li-ion batteries. The present results demonstrate that the battery prepared with PAA exhibits a moderate improvement in specific discharge capacity at  $-10^{\circ}\text{C}$ , compared with the battery prepared in the absence of PAA, corresponding to a specific discharge capacity of 719 and 683 mAh, respectively, at 2.75 V (the discharge cut-off voltage for electronic devices such as cellular phones and laptop computers).

#### 4. Conclusions

The effect of PAA on the suspension properties of aqueous graphite formulations, and the adhesion strength of graphite negative electrodes on copper foil derived from these precursor suspensions, is reported. The electrochemical performance of Li-ion cells fabricated using aqueous-based tape-casting is evaluated and the results correlated with the adhesion strength in

the presence and absence of PAA. Electrokinetic measurements indicate no significant change in the particle surface charge behaviour when PAA is included in the formulation. On the other hand, rheological measurements suggest that PAA added at levels below 1% yields a moderate improvement in suspension stability at low shear rates; PAA does not impact the shear-thinning behaviour associated with the added solution-phase CMC. An analysis of the electrochemical performance of Li-ion batteries fabricated using aqueous formulations based on PAA reveals better adhesion strength, and this correlates with better retention of discharge capacity during cyclic charge–discharge tests. Finally, the ionic conductivity of the binder phase is apparently enhanced when PAA is added, as PAA improves the low-temperature performance of the batteries; on the other hand, PAA has no effect on room-temperature discharge capacity.

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### References

- [1] M. Yoo, C.W. Frank, S. Mori, S. Yamaguchi, *Polymer* 44 (2003) 4197–4204.
- [2] J.H. Lee, S. Lee, U. Paik, Y.M. Choi, *J. Power Sources* 147 (2005) 249–255.
- [3] Y. Takahashi, F. Suzuki, T. Iwasaki, United States Patent No. 5,415,958 (1995).
- [4] J.H. Lee, U. Paik, V.A. Hackley, Y.M. Choi, *J. Electrochem. Soc.* 152 (2005) A1763–A1769.
- [5] Y.M. Choi, U. Paik, K.H. Kim, US Patent RC-200306-002-1-USO (2003).
- [6] U. Paik, V.A. Hackley, S.C. Choi, Y.G. Jung, *Coll. Surf. A: Physicochem. Eng. Asp.* 135 (1998) 77–88.
- [7] V.A. Hackley, U. Paik, in: V.A. Hackley, J. Texter (Eds.), *Ultrasonic and Dielectric Characterization Techniques for Suspended Particulates*, American Ceramic Society, Westerville, OH, 1998, pp. 191–204.
- [8] J. Blaakmeer, M.R. Böhmer, M.A. Cohen Stuart, G.J. Fleer, *Macromolecules* 23 (1990) 2301–2309.
- [9] V.A. Hackley, in: V.A. Hackley, P. Somasundaran, J.A. Lewis (Eds.), *Polymers in Particulate Systems: Properties and Applications*, Surfactant Science Series, 104, Marcel Dekker, New York, 2002, pp. 295–323.
- [10] S.I. Conceicao, J.L. Velho, J.M.F. Ferreira, *Appl. Clay Sci.* 23 (2003) 257–264.
- [11] E.J. Plichta, W.K. Behl, *J. Power Sources* 88 (2000) 192–196.