

The effect of carboxymethyl cellulose swelling on the stability of natural graphite particulates in an aqueous medium for lithium ion battery anodes

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Abstract The effect of carboxymethyl cellulose (CMC) swelling on the stability and chemical properties of a natural graphite suspension in an aqueous medium was investigated. Suspensions prepared at different pH were characterized according to swelling behavior, rheology, green microstructural observation, and measurement of the pore size. A correlation was found between dispersion stability and electrochemical performance. It was found that the swelling of CMC was a critical factor influencing the stability of graphite suspensions. This was evidenced by observations of the green microstructures and changes noted in sedimentation behaviors. Electrochemical experiments using a Li/organic electrolyte/natural graphite anode half-cell and 750 mAh-class lithium ion cells exhibited an initial discharge capacity above 340 mAh g⁻¹ and an improved charge-discharge efficiency.

Keywords Lithium ion battery · Aqueous processing · Natural graphite · Swelling behavior · Stability

1 Introduction

Graphite-based suspensions used for the fabrication of graphite anodes can be successfully prepared in aqueous

systems [1, 2]. This is accomplished by preparing a stable slurry composed of organic additives, namely carboxymethyl cellulose (CMC) and an emulsion of polymerized styrene-butadiene rubber (SBR). CMC plays a key role as a thickening agent, preventing graphite particles from settling out during processing. It is also shown that CMC contributes to the development of surface charge on the graphite particle, which affects the stability of the graphite suspension. The graphite negative electrode exhibited improved charge-discharge efficiency and rate capability, compared to that fabricated by the conventional poly(vinylidene difluoride) (PVDF)—nonaqueous processing [1, 2]. However, limited information is available on the effect of CMC swelling behavior on the stability of the graphite particles.

CMC is a linear polymeric derivative of cellulose, consisting of β -linked glucopyranose residues with varying levels of carboxymethyl ($-\text{CH}_2\text{COO}^-$) substitution [3]. The presence of the carboxymethyl groups is responsible for the aqueous solubility of the CMC relative to the insoluble cellulose. CMC is a weak polyacid that exhibits a pH-dependent dissociation forming anionic carboxylate functional groups. The physicochemical properties of CMC in aqueous solution are intimately associated with its conformation [4]. Changes in pH affect the protonation of the derivative sites on CMC, which in turn impacts conformation as demonstrated by potentiometric titration experiments [5]. It is well-known that the carboxylic acid groups remaining in CMC ionize with increasing pH to form a negatively charged macromolecule [6, 7]. Furthermore, it is reported that the repulsion between negatively charged CMC chains leads to the swelling of CMC to form a hydrogel. This CMC hydrogel possesses a different swelling behavior as a function of the solution pH [8, 9].

In the present work, we investigated the effect of CMC swelling on the stability of natural graphite particulates in

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an aqueous medium by evaluating the swelling and rheological behaviors and from scanning electron microscope observations and mercury porosimetry. Finally, we evaluated the electrochemical performance of a 750 mAh-class lithium ion battery that employed a LiCoO_2 cathode and a natural graphite anode fabricated from the aqueous slurry formulation at pH 7.

2 Experimental

Natural graphite powder of 5–20 μm in diameter was obtained from commercial sources (90%, SL-20, Superior Graphite Company, Japan). The density as stated by the manufacturer was 2.245 g/cm^3 . Used as organic additives were CMC (Daicel Co. Ltd., Japan) with an average molecular mass of $M_r = 330,000$ and a degree of substitution of $\text{DS} = 1.28$, and SBR (SB131, Zeon Corporation, Japan) with a solids loading of 40 wt%. Prior to measuring the weight of the swollen samples, the gels were dried to a constant weight and immersed in distilled water for 12 h at room temperature. The effect of solution pH on the swelling and intrinsic viscosity of the CMC hydrogel was investigated.

For rheological measurements, suspensions containing a mass fraction of 35% solids were prepared with CMC at pH 2, 7, and 9, and ball-milled at room temperature for 12 h. The required amount of SBR was then added and the suspensions were ball-milled for an additional 12 h. The rheological behaviors were determined 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). The apparent viscosity of the graphite suspensions was measured as a function of shear rate.

The suspensions were cast onto a copper substrate using a laboratory scale doctor blade machine. A gap height of $\sim 230 \mu\text{m}$ was used, and the casting speed was held constant at 5 m/min. The tapes were dried in stagnant air for a period of 24 h, cut into rectangular samples (2.5 cm^2), and removed from the carrier film. The fracture regions of representative dried films at pH 2 and 7 were examined using a scanning electron microscope (SEM, JSM 5900LV, Jeol, Tokyo, Japan). In addition, the pore size and its distribution of the as-dried sheets were measured using a mercury porosimeter (Autoscan-25, 60, Quantachrome Corp., Superset, NY, USA).

Charge-discharge experiments were conducted at room temperature using a three-electrode electrochemical cell. An SBR-bonded natural graphite electrode prepared at pH 7 was used as the working electrode. Pure lithium metal foil (Cyprus-Foote Mineral Co., Kings Mountain, NC, USA) was used as the reference and counter electrodes. 1.1M LiPF_6 was used as the electrolyte in a 3:6:1 volume mixture of ethylene carbonate (EC), ethyl-methyl carbonate

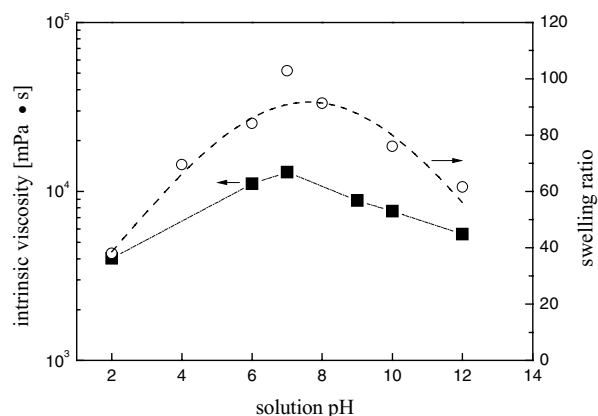


Fig. 1 Swelling ratios and intrinsic viscosity of the carboxymethyl cellulose solutions as a function of solution pH

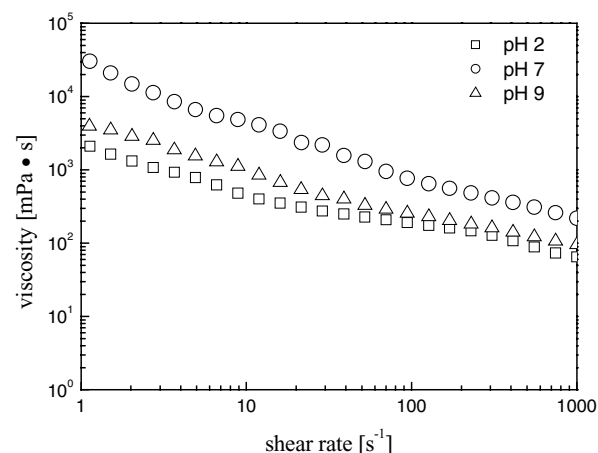


Fig. 2 Log-log plots of viscosity as a function of ascending shear rate for graphite suspensions at a mass fraction of 35% solids, prepared at pH 2, 7, and 9

(EMC), and di-methyl carbonate (DMC). The lithium charge-discharge curves were measured using a computerized multi-channel battery charger (HRC 6064A, Toyo System Co., Ltd., Fukushima, Japan). The galvanostatic charge and discharge currents corresponded to a change of $x = 1$ in Li_xC_6 in 10 h.

3 Results and discussion

In our previous investigation, it was found that the dispersion stability of graphite suspensions in the presence of CMC was markedly improved by the development of charge resulting from the addition of SBR [1]. Possible scenarios that might explain this charge development of graphite particulates prepared with both CMC and SBR were suggested through an interaction between CMC and the negatively charged SBR in solution [10].

Figure 1 shows the effect of solution pH on the swelling and intrinsic viscosity of the CMC hydrogel. As described in the previous investigation, the optimum pH to achieve a maximum swelling ratio is about 6–8 [1]. This is explained

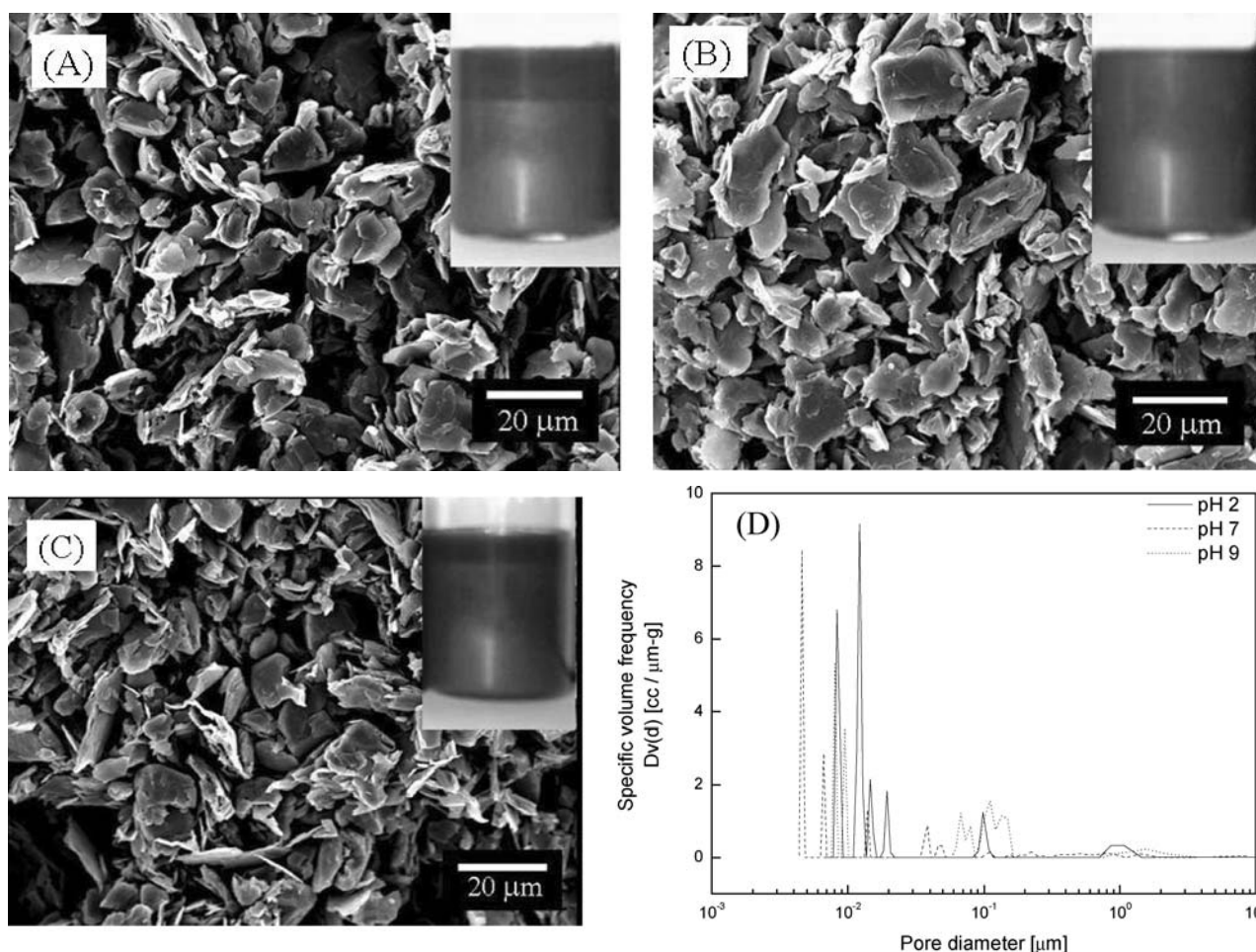


Fig. 3 Scanning electron microphotographs of the fracture surfaces of graphite anode sheets tape-cast from suspensions at: (A) pH 2, (B) pH 7, and (C) pH 9. Insets are photographs of the suspensions prepared with a mass fraction of 35% graphite, and relative mass fractions (based on the graphite phase) of 1.5% SBR and 1.5% CMC, after 6 days of

incubation at room temperature. (D) Pore size distribution of graphite sheets prepared at the fraction of 35 mass% at pH 2, 7 and 9, where CMC and SBR were added at mass fractions of 1.5% each, based on the solids content

in regard to the dissociation of CMC and its counter ion concentration as a function of pH. As ionization greatly affects polymer conformation [6], CMC chains form compact coils under acidic conditions. Under basic conditions, the CMC structure is compressed and the swelling is inhibited. This is because increasing numbers of the carboxylate-group associated sodium ions dissolve in water as the pH becomes more basic. The dissociated sodium ions are abundant enough in basic solutions to compress the structure of the CMC [1, 8, 9].

As seen in Fig. 1, the intrinsic viscosity of the CMC hydrogel is the highest at pH = 6–8. Over this range, a maximum swelling ratio is achieved and the cross linking density of the CMC network structure is at a maximum, which increases the intrinsic viscosity of the CMC hydrogel.

Log-log plots of apparent viscosity as a function of the shear rate for graphite suspensions prepared with CMC and SBR at pH 2, 7, and 9 are shown in Fig. 2. The viscosity for graphite suspensions at pH 7 is higher than at pH 2 and pH 9. This can be explained with regard to the swelling behavior of

the CMC hydrogel as a function of pH. In the acidic or basic region, the hydrogel is rather constrained than sufficiently swollen enough to prevent graphite particles from settling out and to permit homogeneous particle distribution. This resulted in a reduced graphite suspension viscosity in the acidic or basic region than compared to the viscosity of the neutral region.

Scanning electron microphotographs of the dried sheets containing a mass fraction of 35% graphite (with 1.5% SBR and 1.5% CMC) prepared at pH 2 (Fig. 3A), pH 7 (Fig. 3B), and pH 9 (Fig. 3C) were examined. The corresponding graphite suspensions were also photographed after 6 days of incubation. The SEM microstructural observations revealed that the graphite sheets at pH 7 had a more homogeneous and less porous microstructure than the graphite sheets at pH 2 and pH 9. This is quantitatively confirmed by mercury porosimetry measurements. As can be seen in Fig. 3D, it appears that the graphite sheets had smaller-sized pores with a relatively wide distribution when prepared at pH 7, compared

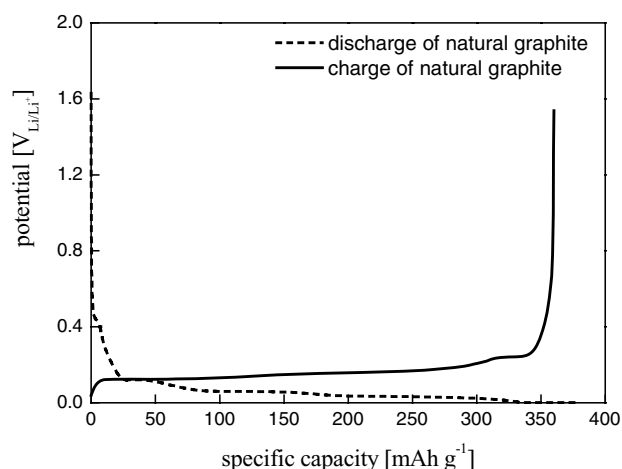


Fig. 4 Initial charge-discharge curves of the natural graphite anodes prepared using the aqueous method presented herein in a 1.1 M LiPF_6 EC/EMC/DMC (30/60/10 vol.%) solution

to sheets prepared at pH 2 and pH 9. The latter sheets had pores with a mean diameter of 1.332 and 1.543 μm for pH 2 and pH 9, respectively, which is two-times larger than that prepared at pH 7 with a mean pore diameter of 0.636 μm . The dispersion prepared at pH 7 remained homogeneous, while the ones prepared at pH 2 and pH 9 were largely sedimented. Clearly, this suggests that a neutral pH value, achieving a maximum swelling ratio, provides better stability for natural graphite particles in an aqueous medium. In turn, this might result in a more efficient particle packing during the formation of the negative graphite electrodes by film-coating methods. Efficient packing should facilitate the fabrication of higher-capacity electrodes; however, direct evidence for this link has not as of yet been observed.

In order to evaluate the half-cell characteristics, the initial charge-discharge capacity of the graphite electrodes was measured (see Fig. 4). During the first charging stage, the potential dropped dramatically after a subtle retardation at ca. 0.8 $V_{\text{Li/Li}^+}$. In the second and subsequent cycles, both graphite electrodes showed good reversibility, with a coulombic efficiency of $\sim 100\%$. It is reported that anodes containing carbonaceous materials obtained by powdering giant crystals, such as highly graphitized natural graphite, cause the nonaqueous electrolyte to decompose [11]. This decomposition results in a decrease of the capacity and the

charge-discharge efficiency of the battery. However, our natural graphite electrode prepared at pH 7 showed an initial discharge capacity of $>340 \text{ mAh g}^{-1}$ and a coulombic efficiency of $>92\%$ during the first charge-discharge cycle.

4 Conclusions

The effect of CMC swelling on the stability of natural graphite particulates in an aqueous medium for use in lithium ion battery anodes was investigated. The swelling of CMC was found to be a critical factor affecting the stability of the graphite suspension and resulted in the formation of a green body with a homogeneous and dense microstructure. An analysis of the electrochemical performance of Li-ion batteries fabricated using aqueous formulations at pH 7 shows a 340 mAh g^{-1} specific energy density.

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