



Original Research Paper

Effect of adsorption behaviour of polyelectrolytes on fluidity and packing ability of aqueous graphite slurries



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ABSTRACT

The effect of surface hydrophobicity on the adsorption behaviour of polyelectrolytes is investigated using graphite and alumina powder slurries. Graphite slurries containing carboxymethylcellulose (CMC) have a relatively low apparent viscosity and afford a sediment with a relatively high packing fraction as compared to that obtained when using sodium polyacrylate (Na-PAA) as a dispersant, although both have the same functional group. As a greater amount of CMC is adsorbed, it is concluded that its adsorption mechanism involves hydrophobic interaction, thus making it a better dispersant for hydrophobic powders in aqueous media. In contrast, Na-PAA is more effective in dispersing relatively hydrophilic powders such as alumina, as it adsorbs mainly through electrostatic interactions.

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1. Introduction

The difficulties associated with treating fine powders in a dry, densely packed condition imply that such powders are typically dispersed in an appropriate medium and handled as a slurry. Further, because of increasing concerns regarding the environment, aqueous slurries are generally preferable to non-aqueous slurries, even when relatively hydrophobic powders such as graphite and carbon black are involved. In the fabrication of Li-ion batteries, for example, fine carbon powder used as a raw material for the cathode is dispersed in aqueous media [1], while graphite used for the anode is dispersed in water using a suitable dispersant [2]. In addition, carbon black catalysts supported by platinum particles for polymer electrolyte fuel cells are dispersed in a water-alcohol mixed solvent [3].

When preparing an aqueous slurry, it is often difficult to ensure good dispersion of fine particles (those with a diameter less than about 1 μm) by using electrostatic repulsion alone; hence, polyelectrolytes have been widely used as dispersants as they provide both electrostatic repulsion and steric hindrance [4]. In the case of aqueous alumina slurries, which have been widely investigated, polycarboxylic acid-based polymers are normally used as a dispersant [5–10]. However, with aqueous slurries of relatively hydrophobic particles like graphite, polyelectrolytes such as carboxymethylcellulose (CMC) have been reported to provide good

dispersion [11–15]. Nevertheless, some important questions still remain about the amount of polyelectrolyte that is adsorbed, and the mechanism by which this is achieved in aqueous slurries containing hydrophobic powder [16]. Sodium polyacrylate (Na-PAA) is known to adsorb to alumina particles through electrostatic interactions, thereby orienting its hydrophilic groups towards the particle [17,18]. It has also been demonstrated that the conformation of Na-PAA changes in the presence of dissolved ions with a higher ionic valence, thereby affecting the amount adsorbed and the properties of the slurry [17,18]. However, it is not clear whether this holds true in the case of aqueous slurries containing hydrophobic powders.

As the properties of a slurry can have a great influence on the qualities of any resulting product, a wide range of methods are used to determine [19–26] the particle size distribution of the slurry, along with the rheological properties and sedimentation behaviour. In material fabrication processes, it is also important to characterise the fluidity and packing ability, as the former gives an indication of the ease of handling while the latter corresponds to the density of the final product [22–25]. Most previous works have focused on the fluidity of the slurry, especially aqueous slurries comprising hydrophobic particles; hence, there are very few investigations on the packing ability of these slurries. Moreover, the possible correlation between the adsorption behaviour of polyelectrolytes and the fluidity and packing ability of a slurry has not been fully explored.

In this study, graphite was selected as an example of a relatively hydrophobic particle, and the adsorption behaviour of a typical dispersant (CMC) was examined to determine its effect on the

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Nomenclature

u_e	particle mobility [$\text{m}^2 \text{V}^{-1} \text{s}^{-2}$]	Z_i	valency of ion i [-]
μ	medium viscosity [Pa s]	W_S	concentration of ion i [kg m^{-2} powder]
ε_0	permittivity of free space [F m^{-1}]	M	mass of powder [kg]
ε_r	relative permittivity [-]	S_M	specific surface area of powder [$\text{m}^2 \text{kg}^{-1}$]
Ψ_ζ	zeta potential [V]	C_0	initial additive concentration in solution [kg L^{-1}]
κ	inverse Debye length [m^{-1}]	C	additive concentration in supernatant [kg L^{-1}]
x	particle diameter [m]	V	initial volume of additive solution [L]
k	Boltzmann constant [J K^{-1}]	Φ_∞	final volume fraction of sediment [-]
T	absolute temperature [K]	h_∞	final height of sediment [m]
e	elementary electric charge [C]	ϕ_0	initial volume fraction of slurry [-]
N_A	Avogadro's number [mol^{-1}]	h_0	initial height of slurry [m]
C_i	concentration of ion i [mol L^{-1}]		

fluidity and packing ability of slurries. In addition, an attempt was made to clarify the mechanism by which CMC adsorbs to graphite particles by comparing the study results with those of a previous report pertaining to the adsorption of Na-PAA on relatively hydrophilic alumina particles in aqueous media. For thoroughness, the adsorption behaviour of sodium stearate and its effects was also examined, as this has the same functional groups as CMC and Na-PAA.

2. Experimental procedure

2.1. Slurry preparation

The graphite used as a raw materials (Z-5F, Ito Graphite Co. Ltd.) had an average particle size of 3.76 μm and a density of 2,230 kg m^{-3} . White fused alumina (#8000) with an average particle size of 1.20 μm and density of 3960 kg m^{-3} was also used for comparison. The specific surface areas of these powder measured by the gas adsorption method were 1.09×10^4 and $1.62 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$, respectively. The adsorbates used were CMC (Tokyo Chemical Industry Co. Ltd., with an average molecular weight of 100,000) and Na-PAA. The Na-PAA solution was prepared via neutralization of a commercial polyacrylic acid (Toagosei CO., Ltd.) with a molecular weight of 25,000. In addition, sodium stearate (Wako Pure Chemical Industries, Ltd.), which has a pair of hydrophobic and hydrophilic groups, was also used as adsorbate in order to discuss the adsorption mechanism of CMC and Na-PAA to graphite particles. Each additive was pre-mixed ultrasonically with a certain amount of distilled water.

Slurries were prepared by mixing the powders with distilled water to give a final particle concentration of 10% by volume. The amount of CMC and Na-PAA added was $4.0 \times 10^{-5} \text{ mg cm}^{-2}$ -powder, with later testing using $0.5\text{--}5.0 \times 10^{-5} \text{ mg cm}^{-2}$ -powder of sodium stearate. For gravitational settling tests, slurries with different particle concentrations (20 vol% of alumina and 5 vol% of graphite) were prepared to make it easier to observe changes in the appearance of the slurry.

All of the prepared slurries were well mixed for 15 min using a planetary centrifugal mixer (ARE-300, Thinky Inc.) with revolution and rotation speeds of 2000 and 60 rpm, respectively. After mixing, the pH of the slurries was adjusted so as to make the zeta potential of each powder equal. The slurries were then left to stir until adsorption reached equilibrium, the time for which was predetermined by the experiment described in Section 2.3.

2.2. Zeta potential measurement

The particles used in this study were dispersed in distilled water by ultrasonication to give a particle volume concentration

of 0.001%. Their zeta potential was then measured by electrophoresis using a Model 502 apparatus (Nihon Rufuto Co. Ltd.) while changing the slurry pH through HCl and NaOH addition. The particle velocity was measured under an applied DC current of 45 V. Considering the effect of polarisation of the materials in the slurry, as well as the change in pH, each measurement was made 10 times while changing the positive and negative electrodes. From the average of measured particle velocity, the zeta potential was calculated using Henry's equation [27].

$$u_E = \frac{2\varepsilon_0\varepsilon_r\Psi_\zeta f\left(\frac{\kappa x}{2}\right)}{3\mu} \quad (1)$$

$$f\left(\frac{\kappa x}{2}\right) = \frac{3}{2} - \frac{1}{2 + 0.144(\kappa x/2)^{1.13}} \quad (2)$$

$$\kappa = \left(\frac{e^2 N_A \sum 10^3 C_i Z_i^2}{\varepsilon_0 \varepsilon_r k T} \right)^{1/2} \quad (3)$$

2.3. Measurement of adsorbed additive

2.3.1. Confirmation of adsorption equilibrium

The time needed for the system in this study to reach adsorption equilibrium was determined by first preparing graphite and alumina slurries with a particle concentration of 0.25 vol%. These were placed into several test tubes and $4.0 \times 10^{-5} \text{ mg cm}^{-2}$ -powder of additive was introduced. After a period of time, the slurry was centrifuged and the resulting supernatant was sampled to measure the residual adsorbate concentration. As a trace amount of small particles sometimes remained suspended in the sampled supernatant, it was filtered through a PTFE membrane that was confirmed to be capable of passing all of the adsorbates used. The adsorbate concentration was measured by a total organic carbon analyser (TOC-V, Shimadzu Corp.) and used to calculate the amount adsorbed using the following equation:

$$W_S = \frac{(C_0 - C)V}{MS_M} \quad (4)$$

2.3.2. Measurement of adsorption

The slurries prepared in Section 2.1 were placed into a test tube and centrifuged to obtain a supernatant. The adsorbate concentration in the sampled supernatant was measured by TOC in the same way that is outlined in Section 2.3.1. In addition, the adsorption ratio was determined by the following equation:

$$\text{adsorption ratio [\%]} = \frac{\text{adsorbed amount of adsorbate [mg]}}{\text{added amount of adsorbate [mg]}} \times 100 \quad (5)$$

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