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Colloidal Suspension Properties of Carbonaceous Nanomaterials Enhanced by Using Li as Dopant

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A colloidal suspension of carbonaceous nanomaterials for heat exchangers has attracted increasing research attention. In this study, a simple route used to synthesize lithium treated carbonaceous nanomaterials was studied. The dispersion effect, electrical conductivity, thermophysical properties of the Li-carbon-nanocolloids system were introduced and discussed. The results show that these properties were largely enhanced, which could be due to not only the outstanding physical and electrical properties of the carbon nanomaterials but also to the introduction of lithium ions.

Key Words: Carbon materials, Lithium, Dispersion effect, Thermal and electrical properties, Nanocolloids.

INTRODUCTION

Carbon is one of the abundant elements on the earth. All organics are composed of carbon networks and carbon materials are very familiar in our daily lives, such as ink for newspapers, "lead" for pencils, activated carbon in refrigerators, *etc*. Carbon materials, which consist mainly of carbon atoms, have been used as charcoal since prehistoric times. Carbon has different allotropes (graphite, diamond, fullerenes/nanotubes), various microtextures (more or less ordered) owing to the degree of graphitization, a rich variety of dimensionality from 0 to 3D and the ability to exist in different forms (from powders to fibers, foams, fabrics and composites), which represents an attractive material for some applications. Mesophase carbon material has excellent thermal and electrical conductivity due to its high degree of preferred orientation and fewer lattice defects[1]. Carbon nanotubes (CNTs) have become one of the most interesting materials since Iijima[2] first reported in 1991. Many studies on the applications of CNTs have been carried out on the novel hollow-tube structure, nanometer dimensions, high specific surface area and excellent electronic semi-conductivity and conductivity of CNTs[3-6]. Other carbonaceous materials, such as activated carbon (also known as activated charcoal, active carbon or AC)[7-12], activated carbon fibers (ACF)[12-17], carbon black[18-20], have been examined as promising raw materials in many areas of science and technology owing to their high tensile strength and elastic modulus and excellent thermal and electrical conductivity.

Colloidal suspensions and emulsions are an important part of everyday life. The prediction and control of their properties is essential for performance optimization in mining, oil, food, pharmaceutical industries, *etc*.[21-23]. In recent years, some studies have highlighted the significance of aqueous colloidal dispersions of carbon materials. Schierz *et al*.[24], reported that there was a pronounced influence of surface treatment on the behaviour of the CNTs in an aqueous suspension. An acid treatment improves the colloidal stability of the CNTs and their adsorption capacity for U(VI). Jang *et al*.[25] showed a simple route for producing stable homogeneous dispersions of carbon nanotubes (CNTs) and zeta potential analysis, auger electron microscopy and FTIR were used to examine the adsorption mechanism in detail. The results have suggested that a surfactant containing a single straight-chain hydrophobic segment and a terminal hydrophilic segment can modify the CNTs-suspending medium interface and prevent aggregation over long periods.

Solid lithium ion conductors continue to attract considerable interest, particularly for application to lithium batteries. The lithium ion (Li-ion) battery is one of the most important rechargeable batteries and studies on anode materials aiming to improving the capacity and cyclability have been active for many years[26-31]. Silicon exhibits a theoretical capacity of 4200 mAh/g[27], which is much higher than that of other anode materials. On the other hand, upon the repeated alloying and dealloying process of Li with silicon, silicon particles show severe volumetric changes and accumulated internal stresses, which causes crumbling of the active materials and breakage of the conduction network, leading to poor cyclability[29,30]. To improve the electrochemical properties of pure silicon, a range of composite materials containing well dispersed silicon particles in the host matrixes have been investigated[31-36]. In these cases, carbon based materials have shown advantages as a host matrix. During the Li insertion and extraction process, carbon materials to a certain extent, buffer the volume changes to the silicon particles. In addition, electric contact can be improved due to the good electric conductivity of carbonaceous materials. Moreover, carbon-based materials are electrochemically active with Li, which contributes to the overall reversible capacity. Graphite, mesocarbon microbeads (MCMB), pitch and other carbonaceous materials have been used as host matrixes for silicon[33-36].

The use of Li treated carbonaceous materials to enhance the colloidal suspension properties has attracted little attention. In this study, the advantages of both lithium ion and carbonaceous materials were combined to design an effective water-based carbon nanocolloid with a good dispersion effect, excellent electrical conductivity and improved thermal conductivity, which could used for thermal and electrical transport applications.

EXPERIMENTAL

The carbonaceous materials (active carbon, activated carbon fibers, carbon black) were kindly provided by Carbon Nano-material Technology Co. Ltd., Korea and used as received. To oxidize the surface of the carbonaceous materials, *m*-chloroperbenzoic acid (MCPBA) was used as an oxidizing reagent and was purchased from Acros Organics, New Jersey, USA. Lithium hydroxide monohydrate ($LiOH·H_2O$) was used as the dopant source, which was purchased from Daejung Chemicals & Metals Co., Ltd, Korea. Distilled water was used in all studies.

Preparations of nanoscaled carbon materials: The present steps involved in the preparation of carbonaceous nanocolloids including: milling the activated carbon to the optimal size by ball milling and mono-planetary high energy milling. Activated carbon (AC), activated carbon fiber (ACF) and carbon black (CB) were selected as the starting carbonaceous materials. In a typical treatment, 8 g of carbonaceous materials was ball milled for 48 h at room temperature in a laboratory tumbling ball mill. The mechano-chemically carbon materials were obtained using a laboratory Pulverisette 6 mono-planetary high energy mill (Idar-Oberstein, Frisch, Germany) for 1 h with ZrO_2 ball (1 mm × 300 g). Nanoscale activated carbon fiber (ACF) and carbon black (CB) were also obtained using the same method.

Preparations of water based carbon nanocolloids: Carbonaceous materials present remarkable intrinsic properties, but for many applications in which they have to interact with or to be integrated in a given system, it is necessary to functionalize their surfaces to obtain higher performance. In particular, although no specific study has yet appeared on the subject, it has been shown that functionalization should be performed to produce well dispersed supported catalysts[37]. For example, among the main processes for CNT surface functionalization[38], fluorination or the introduction of oxygenated groups are used most frequently, due to the simplicity of the relevant reactions involved and the feasibility of further reactions after these treatments. The purpose of these oxidative treatments is as follows: (i) to improve the CNT and graphene interactions with the solvents and dispersion; (ii) to allow the grafting of nanoparticles; (iii) to modify the CNT and graphene adsorption properties or (iv) to perform chemical treatments on the CNT and grapheme[38,39]. In the present study, *m*-chloroperbenzoic acid (*ca.* 2 g) was suspended in 80 mL benzene as a solvent. Subsequently, 0.2 g of activated carbon, activated carbon fiber and carbon black were placed into the agent solution. The mixture was treated by magnetic stirring for 6 h at 343 K. Furthermore, the resulting solution was washed continuously with deionized water and ethanol before drying at 363 K. Finally, the oxidized activated carbon (OAC), activated carbon fiber (OACF) and oxidized carbon black (OCB) were obtained.

The milled and treated carbon materials (OAC, OACF, OCB) were ultrasonicated in 200 mL of distilled water containing 0.05 mol $LiOH·H_2O$, using a VCX750 Ultrasonic Probe CV33 at 1.3×10^5 J power. After the intensive sonication treatment for 1 h, stable Li treated carbon in water-based nanocolloids was obtained and named as LiAC, LiACF and LiCB, respectively.

Characterization: The dispersion effect of the carbon nanocolloids were examined by UV/VIS spectroscopy (Optizen POP, Mecasys Co. Ltd., Korea) with the absorbance change in the nanocolloids, which was measured as function of the concentration and time. In this study, a transient hot-wire method was used to measure the thermal conductivity of the nanocolloids. Teflon coated platinum wire with a diameter of 76 μm and a Teflon insulation layer, 17 μm in thickness, was used as the hot wire in the measurement system. The thermal conductivity was calculated from the slope of the rise in the wire temperature as a function of the logarithmic time interval using the following equation[40].

$$k = \frac{q}{4\pi(T_2 - T_1)} \ln\left(\frac{t_2}{t_1}\right) \quad (1)$$

where, k is the thermal conductivity of the fluid and T is the temperature of the wire at time t. The dynamic light scattering technique is an efficient means of determining the thermal diffusivity of transparent fluids with the aim of drawing a comparison with other typical methods for determining the thermal conductivity k and diffusivity a. using the equation $a = k/(\rho C_p)$, these properties can easily be converted, provided a good equation of state for ρ and C_p is available. In addition, the measurements for mass diffusivity using dynamic light scattering are feasible and have been reported[41,42]. A WalkLAB Digital Conductivity Pro meter (Trans Instruments (S) Pte Ltd., Singapore) was used to obtain a precise measurement of the electrical conductivity.

RESULTS AND DISCUSSION

Dispersion effect: One important characteristic of Li treated carbon nanocolloids is that they have good dispersibility in water. In this study, the dispersion test was carried out by placing 0.2 g OAC, OACF and OCB into 200 mL of distilled water containing 0.05 mol $LiOH·H_2O$ and ultrasonicated for 1 h. The Li treated carbon nanocolloids were then diluted to 10 wt % with distilled water. As shown in Fig. 1, after the OAC, OACF and OCB were dispersed in distilled water by ultrasonication for 1 h, all the samples were kept stable in distilled water for weeks. This suggests that all the prepared Li ion treated carbon materials have good dispersibility in water.

Fig. 1. Photographs of the Li treated carbon nanocolloids (containing 10 wt % carbon materials (Li-OAC, Li-OACF, Li-OCB)) dispersed in distilled water

The prepared oxidized carbon nanocolloids, which contained 10 wt % and their dispersion effect with a function time (0, 1, 2, 5 and 10 h) was measured by their absorbance using UV/VIS spectroscopy. Fig. 2 shows the absorbance of the oxidized carbon nanocolloids as a function of time for different contents of carbon materials (OAC, OACF, OCB). After 10 h, the absorbance of OAC and OACF were similar to that observed at 0 h, suggesting that OAC and OACF had good dispersibility in water. For OCB, the absorbance was lower than observed at 0 h, indicating that the dispersibility of OCB was lower than that of OAC and OACF. These results indicate that oxidized activated carbon has the best dispersibility in water.

Fig. 3 compares the absorbance of Li ion treated carbon nanocolloids containing 10 wt % carbon materials as a function of time. After the $LiOH·H_2O$ treatment, the absorbance of OAC decreased, which indicates that the dispersibility of oxidized AC decreased. On the other hand, the absorbance of OACF and OCB increased after the Li ion treatment. This suggests that the metal lithium treatment can improve the dispersibility of ACF and CB in water.

Thermophysical properties: Fig. 4 shows the results of the histogram experiments for the thermal diffusivity test. The results were compared with the technical indicator of new-type materials. The thermal diffusivity of the carbon nanocolloids and Li ion treated carbon nanocolloids (10 wt %) were 0.057, 0.054, 0.059, 0.055, 0.063 and 0.054 mm^2/s, respectively. After the carbon nanocolloids were treated with Li ions, there were some changes in thermal diffusivity. The Li treated OACF nanocolloids showed the best thermal diffusivity and their thermophysical properties were enhanced by 0.9 %.

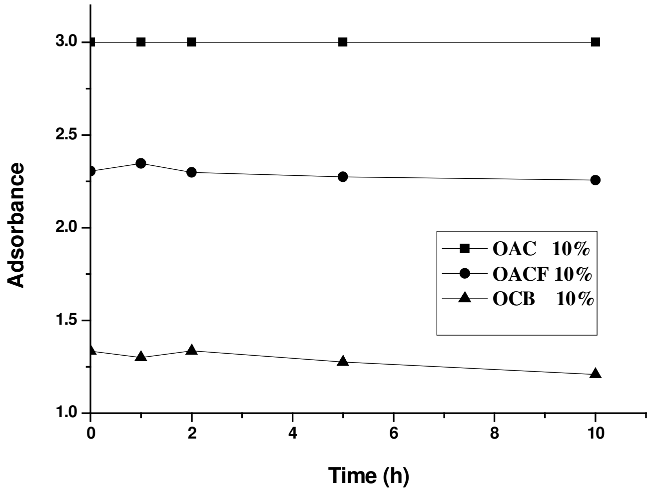

Fig. 2. Absorbance of the oxidized carbon nanocolloids dispersed in distilled water as a function of time (10 wt % carbon materials)

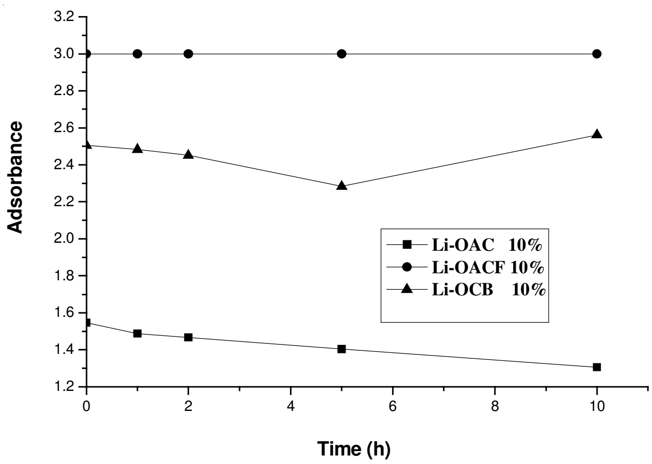

Fig. 3. Absorbance of Li ion treated carbon nanocolloids dispersed in distilled water as a function of time (10 wt % carbon materials)

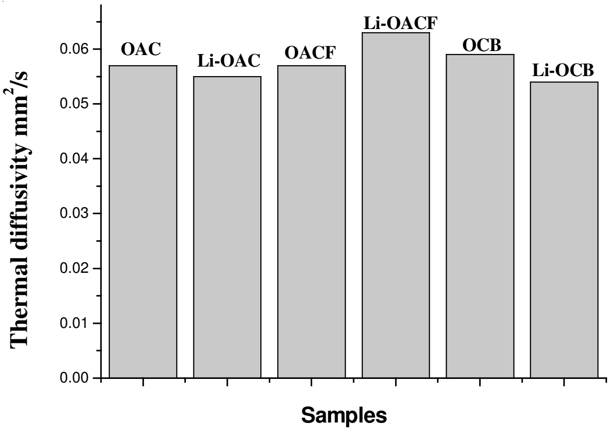

Fig. 4. Thermal diffusivities obtained from the various water based carbon colloids

Electrical conductivity: Fig. 5 shows the changes in the electrical conductivity of different nanocolloids. The electrical conductivity of the Li treated carbon nanocolloids increased more than that of primary carbon nanocolloids. For the oxidized carbon nanocolloids (OAC, OACF, OCB), the electrical conductivity of the products on sample OAC was slightly higher than those on sample OACF but lower than those on sample OCB.

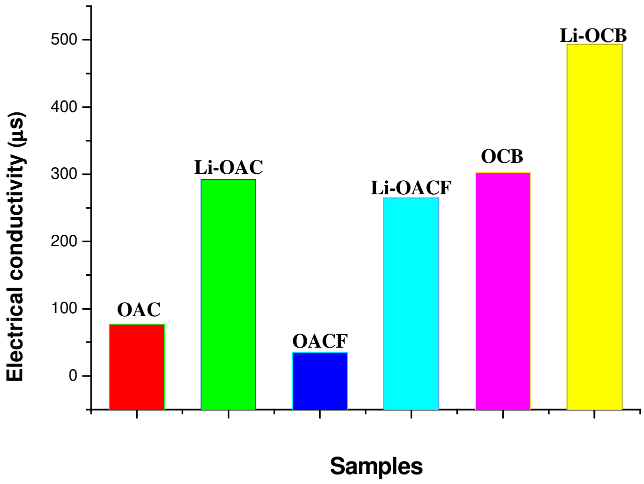

Fig. 5. Electrical conductivities of the various water based carbon colloids

This indicates that the oxidized carbon black showed the highest electrical conductivity after the acid treatment.

The electrical conductivities of the Li treated carbon nanocolloids (Li-OAC, Li-OACF, Li-OCB) largely increased after the metal treatment. The electrical conductivity of all Li treated carbon nanocolloids were larger than those carbon nanocolloids, which were 295, 265 and 494 µS/cm for Li-OAC, Li-OACF and Li-OCB, respectively.

The graph shows that there is a rapid increase in conductivity at 23 % of the Li-OACF nanocolloids, which also has a good dispersion effect among the all samples examined. Therefore, the conductivity increases drastically up to 23 % of OACF, above which the rate of the increase was highest.

Conclusion

AC, ACF and CB were chosen as carbon sources to examine the typical effects of Li treated water based carbon nanocolloids. After the MCPBA acid treatment and mono-planetary high energy milling, the particle size of AC, ACF and CB decreased and these carbon materials had good dispersibility in distilled water. After the lithium hydroxide monohydrate treatment, some changes in electrical conductivity and thermophysical properties of the Li ion treated OAC, OACF and OCB were observed. In particular, the electrical conductivity of the Li-OACF carbon nanocolloid showed remarkable improvement due to the optical properties of carbonaceous nanomaterials and the added electrical properties of lithium.

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