



Improvement of Electrochemical Properties of Natural Graphite Anode Materials with an Ovoid Morphology by AlPO_4 Coating

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AlPO_4 -coated natural graphite was prepared by mixing precipitated AlPO_4 nanoparticles with natural graphite (NG) powders that had an ovoid morphology in water, followed by vacuum-drying at 150°C for 24 h. This simple coating method did not require any further heat-treatment above 400°C , which is an essential process for the sol-gel driven coating methods (Al_2O_3 and ZrO_2). The electrochemical properties of the AlPO_4 -coated NG were compared with bare and pitch-coated samples and are reported. Impedance analysis revealed that, although the value of the surface film impedance of the AlPO_4 -coated sample was 2.4 times larger than the bare NG, its charge-transfer (CT) impedance was 7.5 times smaller than the bare NG. Consequently, we believe that CT was a critical factor that affected the cycle life performance of the sample.

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Due to the larger specific capacity of natural graphite (NG) ($>360 \text{ mAh/g}$) than its synthetic analogs ($<350 \text{ mAh/g}$), its application in Li-ion cells has been widely investigated by Li-ion manufacturers. In spite of its capacity, high Brunauer-Emmett-Teller (BET) surface area and high irreversible capacity that originated from its flakelike morphology, NG cannot be used in Li-ion cells. This is because the amount of binder must be higher than 10 wt % to ensure the adhesion of the NG onto the copper foil. In addition, when the electrode density is increased above 1.5 g/cm^3 , the flake-like NG is apt to peel off from the copper current foil.

It is known that the irreversible capacity occurs mainly because of the reductive decomposition of the organic electrolyte to form a solid electrolyte interface (SEI) on the graphite surface. However, continuous reactions between active materials with the electrolyte species remain unavoidable and result in a gradual destruction of the anode on cycling.¹ Many approaches have been studied with the purpose of stabilizing the natural graphite to improve not only the irreversible capacity but also the cycle life. The most popular approaches have included the use of an appropriate electrolyte and additives such as vinylene carbonate (VC).²⁻⁴ Mild oxidation of the graphite surface, metal or metal oxide coating by using sol-gel or CVD deposition (nickel, Al_2O_3 , ZrO_2 , silver, and copper) has been reported, and these exhibited a good retention and low irreversible capacity at the first cycle.⁵⁻¹⁶ This may be due to a suppression of solvent intercalation and a reduction and decomposition of the solvent within the graphite layer. It is also possible to cover the surface of the graphite particles with oxygen-containing surface groups by a controlled burn off of carbon in air at elevated temperatures.¹⁷ In these ways, it is possible to achieve good electrode passivation, reduce their irreversible capacity, and increase their stability upon cycling.

Recently, it was reported that flaked natural graphite showed a 350 mAh/g charge capacity after the first cycle even though its irreversible capacity ratio was over 10%.⁷ In this study, the loading of the graphite on the copper foil was 5.6 mg/cm^2 . On the other hand, it was also reported that for Al_2O_3 and ZrO_2 -coated NG, a capacity of over 370 mAh/g could be achieved when a conducting agent was used. However, the active mass loading was only 1.0 mg/cm^2 .⁵ At present, the use of anodes that can afford to reach high electrode densities are required for developing high energy density Li-ion cells, but no studies have specifically examined this issue. In addition,

there have been no studies that alter the morphology of the NG flakes to other types with the intention of reducing the side reactions with the electrolytes.

In this study, we report the electrochemical performance of AlPO_4 -coated NG at various electrode densities by using a water soluble SBR (styrene butadiene rubber) binder. Its electrochemical results are compared with NG and pitch-coated NG under the same conditions. Here, we used NG that was assembled with an ovoid-like morphology which was obtained from ballmilling.

Experimental

Flake natural graphite was assembled into NG with an ovoidlike morphology by using ballmilling at low rpm for 24 h at Sodiff Advanced Materials Co. These NG powders were used for further coating. The NG powders were coated with a pitch that was previously dissolved in a toluene solvent, followed by firing at 1500°C in an argon atmosphere. The AlPO_4 -treated NG was prepared by the following process: Al-nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 g) and $(\text{NH}_4)_2\text{HPO}_4$ (0.36 g) were dissolved in distilled water (30 g) until a light white suspension solution (AlPO_4 nanoparticle solution) was observed, and the solution was stirred for only 5 min. Due to a low pH of the solution ($\text{pH} \sim 2$), further stirring led to rapid increase in the BET surface area. The BET surface area of the AlPO_4 nanoparticles was $19 \text{ m}^2/\text{g}$. One hundred grams of NG powder (with an average particle size of $\sim 12 \mu\text{m}$) were then slowly added to the modifying solution and mixed for 10 min followed by drying in a vacuum-oven for 20 h at 150°C . The weight increase resulting from the AlPO_4 treatment was $\sim 0.6 \text{ wt } \%$ of the sample treated. This coating method has advantages over sol-gel Al_2O_3 or ZrO_2 coatings in that no further heating process is necessary and there is no need for an anti-fire facility in the case of mass production.

The binder used was a mixture of SBR with an average particle size of $\sim 100 \text{ nm}$ and CMC (carboxymethyl cellulose) with a 98:2 weight ratio, and deionized water was used as a solvent. SBR particles were believed to be finely distributed between the particles even though it was not water-soluble. The electrode composition was either bare NG or coated NG:binder in a weight ratio of 96:4. In the present case, a conducting agent was not used. During drying of the coated electrode at 110°C , SBR fine particles melted between the NG particles. The electrolyte used was 1.03 M LiPF_6 with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC) (1:1:1 vol %), and the anode was lithium metal. Rate capability and the cycle life of the cells was tested at 0.1, 1, 2 C, and a 1 C rate, respectively, with the potential window of 1.5–0.01 V by applying only constant current without a floating step that follows. The loading level (g/cm^3) of the pressed electrode was

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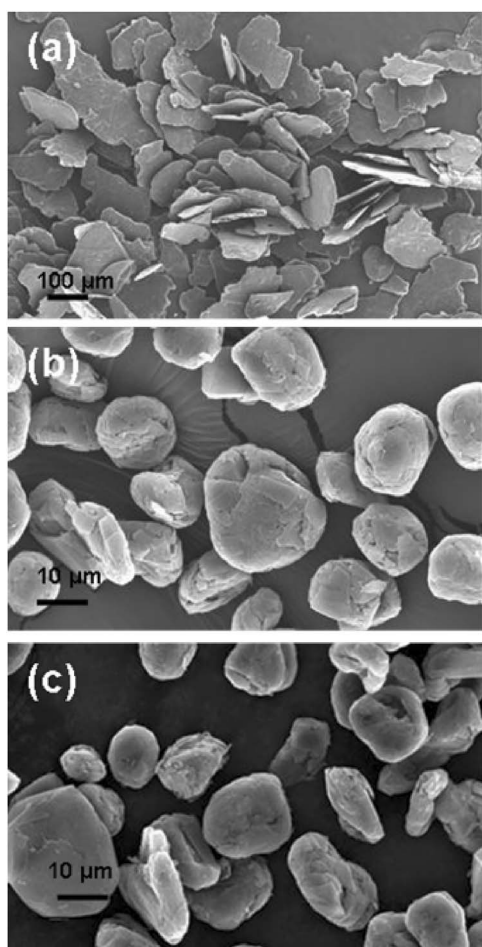


Figure 1. SEMs of (a) flake natural graphite (NG), (b) assembled NG using flake NG ballmilling, and (c) AlPO_4 -coated natural graphite using assembled NG.

varied from 1.5 and 1.7 g/cm^3 by changing the coating thickness of the slurry on the copper foil.

Powder X-ray diffraction (DMax/2000 PC, Rigaku) using $\text{Cu K}\alpha$ radiation was used to identify the phase of the bare and coated samples. Impedance measurements were taken at room temperature in a three-electrode cell using a Solatron 1255B frequency response analyzer in the frequency range 1 MHz to 10 mHz at ac voltage of 10 mV. Lithium metal was used as the reference and counter electrode.

Results and Discussion

Figure 1 shows scanning electron microscopy (SEM) images of the flake NG, the assembled NG after ballmilling, and the AlPO_4 -coated NG. Even after coating, no change in the surface morphology was observed and the pitch-coated sample showed an identical surface morphology to the AlPO_4 -coated sample. Achieving coating uniformity is important because it minimizes the side reactions with electrolytes. Therefore, the coating uniformity of the AlPO_4 -coated NG was compared with a sol-gel driven Al_2O_3 -coated sample using elemental dispersive X-ray (EDX) analysis. The Al_2O_3 coating solution was prepared according to Ref. 6. Figure 2 shows the EDX mapping of the O, Al, and Al and P elements for the Al_2O_3 and AlPO_4 -coated NG, respectively. The Al_2O_3 coating led to only local uniformity of Al and O components while the Al and P components in the AlPO_4 -coated sample were uniformly distributed throughout the particle. These results show that the AlPO_4 coating lead to a more uniform coating than the Al_2O_3 coating. The BET

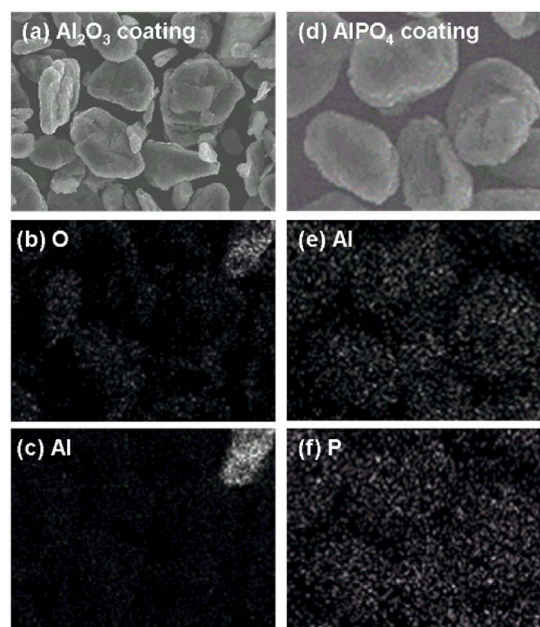


Figure 2. (Color online) The EDX mapping of (a,b,c) Al_2O_3 -coated and (d,e,f) AlPO_4 -coated natural graphite powders.

surface area of the bare NG (5.7 m^2/g) decreased to 2.3 and 4.7 m^2/g after the pitch and AlPO_4 coatings, respectively. Decreased surface area of the pitch-coated sample to AlPO_4 -coated one suggests that some portion of the AlPO_4 nanoparticles fill with the open pores of the NG. Figure 3 shows XRD patterns of the bare, pitch- and AlPO_4 -coated samples. Peak broadening was not observed, indicating the presence of well-ordered interlayer spacing.

Figure 4 shows the voltage profiles of the bare, pitch- and AlPO_4 -coated samples at different C rates of 0.2, 1, and 2 C under an electrode density of 1.5 g/cm^3 (25 mg/cm^2). The charge capacities of the bare, pitch- and AlPO_4 -coated samples at 0.2 C corresponded to 358, 360, and 368 mAh/g with irreversible capacity ratios of 5, 7, and 4.8%, respectively. A reason for the increasing irreversible capacity after pitch coating is because the pitch did not have a fully ordered stacking carbon layer. At a 2 C rate, the capacity retention ratios of the bare, pitch- and AlPO_4 -coated samples

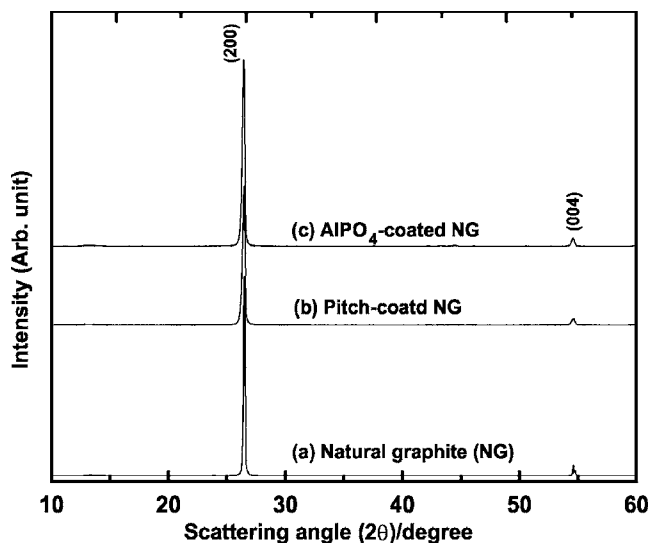


Figure 3. Power XRD patterns of bare NG, pitch-, and AlPO_4 -coated NG.

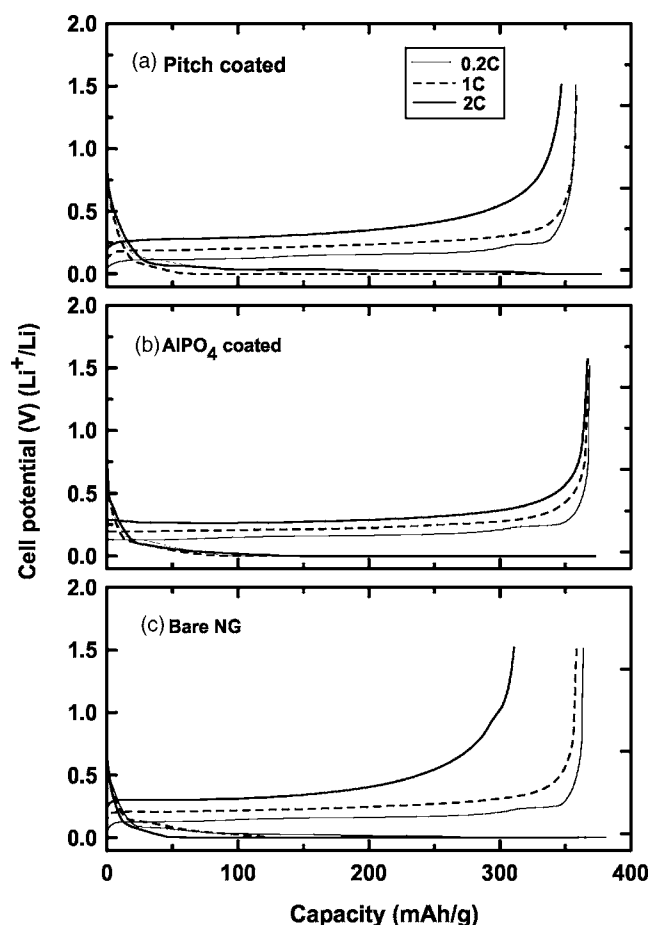


Figure 4. Voltage profiles of (a) pitch-coated NG, (b) AlPO_4 -coated NG, and (c) bare NG anodes in a coin-type half cell at 0.2, 1, and 2 C rates. 1 C was set at 350 mA/g.

were 85, 97, and 100%, respectively, as compared with values at 0.2 C. This result indicated that the coating led to a higher capacity retention ratio than the bare sample. However, the capacity retention ratio of the bare and pitch-coated samples decreased rapidly when the electrode density increased from 1.5 to 1.7 g/cm³ (37 mg/cm²), as shown in Fig. 5. On the other hand, the AlPO_4 -coated sample demonstrated excellent capacity retention at a 2 C rate of 90%,

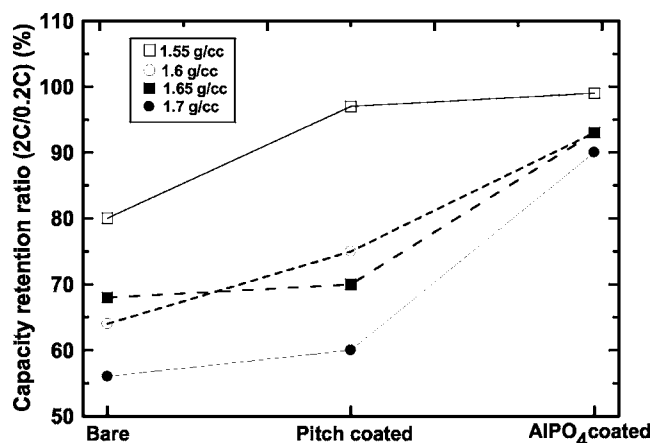


Figure 5. A plot of the capacity retention ratio of 2 C to 0.2 C for the bare and the pitch- and AlPO_4 -coated NG with different electrode densities.

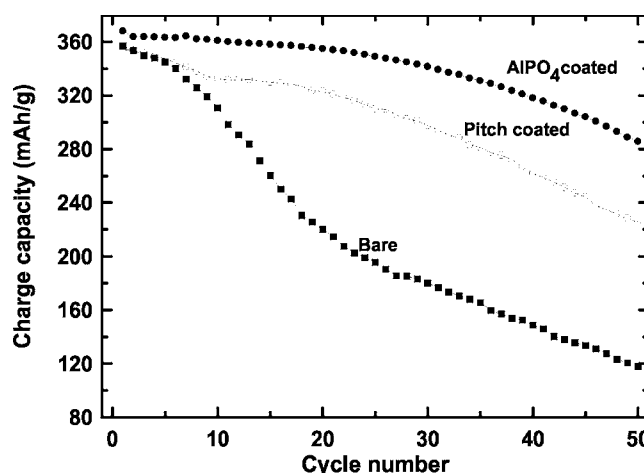


Figure 6. A plot of the charge capacity vs cycle number in a coin-type half cell containing bare, pitch-, and AlPO_4 -coated NG at a rate of 1 C.

while the bare and pitch-coated samples were 55 and 60%, respectively. We believe that the AlPO_4 coating layer stabilized the SEI layer by effectively minimizing the solvated lithium intercalation, reduction and the decomposition of the solvent at the particle surface, while pitch coating was not as effective. In addition, the AlPO_4 nanoparticle can provide more contact with the electrolyte at an even higher electrode density. It has been reported that the graphite surface will be protected from a continuous reaction with electrolytes. Otherwise, the SEI layer under repetitive volume changes accompanied by volume changes during cycling leads to a gradual destruction of the thin film layer, thus increasing the solvent co-intercalation, reduction and decomposition of the solvent into the graphene layer.¹⁸

Figure 6 shows a cycle life comparison of the bare, pitch-, and AlPO_4 -coated NG out to 50 cycles at a rate of 1 C, between 1.5 and 0.01 V, under 1.5 g/cm³. The AlPO_4 -coated sample showed the best capacity retention among the samples, with a value of 79% capacity retention while the bare and pitch-coated NG were at 36% and 61% capacity retention after 50 cycles. To investigate the origin of this difference, an impedance analysis of the anodes before and after cycling was compared.

Figure 7 shows Nyquist plots obtained from bare, pitch-, and AlPO_4 -coated NG before cycling and after 50 cycles at a rate of 1 C. Their shapes followed that of typical graphite materials in which two semicircles and an inclined line appeared. The first semicircle at high frequency is attributed to Li-ion migration through the SEI thin film layer, and the second semicircle in the middle-frequency region is attributed to the impedance of the charge-transfer reaction between the surface film and the active mass. The inclined line is related to the solid state diffusion of Li-ions into the carbon. Before cycling, the pitch and AlPO_4 -coated NG showed larger impedances for Li ion transport at the film surface and a smaller charge-transfer impedance compared to the bare sample. This effect may have originated from the higher inhibition of Li ion migration that was exhibited by the coating layer. We believe that the coating layer acts as the passivation film before cycling. On the other hand, semicircles at lower frequencies at 10 Hz in the coated sample before cycling were smaller than the bare sample, which indicated that charge-transfer impedance was significantly reduced by the coating. Note that AlPO_4 -coated sample shows almost disappeared charge-transfer impedance, as shown in insert in Fig. 7. After cycling, semicircles in all samples had shrunk due to lithium-ion reactions but the impedances appeared to vary with the coating material. This phenomenon means that the surface films of the samples after cycling remain as more stable and electrically more conducting than those before cycling. However, flakelike natural graphite exhib-

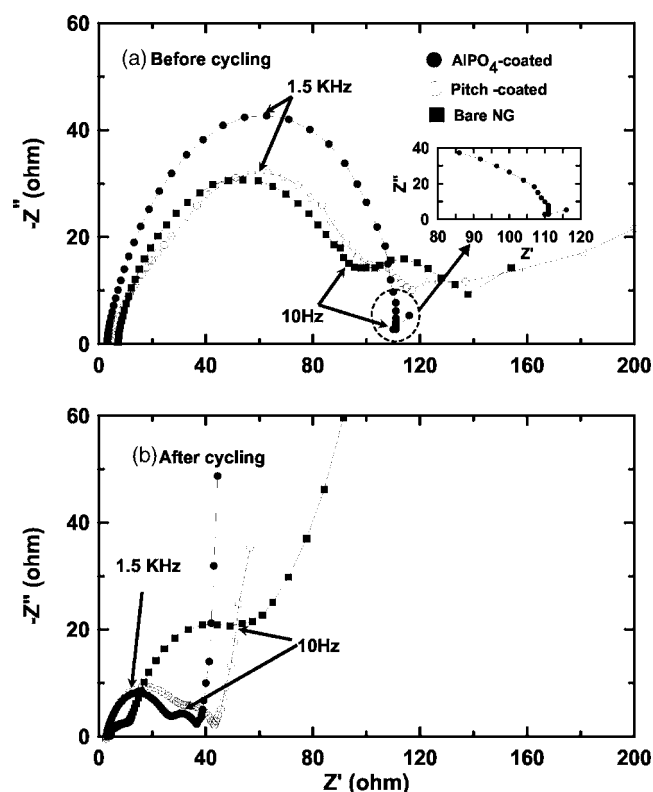


Figure 7. Nyquist plots of bare and pitch- and AlPO_4 -coated NG (a) before and (b) after cycling.

ited pronounced impedance increase after cycling due to the destruction of the surface films. An impedance analysis revealed that the surface film impedance of the AlPO_4 and pitch-coated samples was 24 and 30 Ω , respectively, and bare sample was only 10 Ω . This phenomenon was quite similar to that observed before cycling. However, more importantly, the charge-transfer resistance of the pitch and AlPO_4 -coated sample was 16 and 8 Ω (the charge-transfer resistance after cycling was estimated from the second semicircle with 10 Hz), but the bare NG was 60 Ω , indicating that CT was a key contributor in decreasing the capacity.

Conclusion

AlPO_4 -coated natural graphite showed a higher rate capability and capacity retention than bare and pitch-coated samples at higher C rates and after numerous cycles. When the electrode density was increased to 1.7 g/cm³, the rate capability ratio 2 C/0.2 C was 90% while the bare and pitch-coated NG was below 60%.

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