High-rate charging performance using high-capacity carbon nanofilms coated on alumina nanoparticles for lithium ion battery anode

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**A R T I C L E   I N F O**

Article history:
Received 14 November 2011
Received in revised form 21 May 2012
Accepted 28 May 2012
Available online 18 June 2012

Keywords:
Carbon nanofilm
Fast charging
Adsorption
Intercalation

**A B S T R A C T**

Carbon nanofilms of less than 20 nm in thickness were prepared on alumina nanoparticles by pyrolysis of a citric acid precursor to test high-rate charging anode material in lithium ion battery. The electrochemical reaction mechanism of the anode was investigated by changing the voltage from 1.5 V to 0.01 V with a counter Li metal electrode. The specific capacity of ~20 nm thick carbon nanofilms was 2180 mAh g\(^{-1}\), much larger than those of conventional carbon anode materials. The high capacity of carbon nanofilm was attributed to adsorption of Li ion multi-layers on carbon nanofilm surfaces and adsorption on defects, functional groups or micropores of amorphous carbon, in addition to Li intercalation in hard carbons. Very short diffusion path length from ~20 nm ultrathin film (~20 nm) with high specific capacitance was mainly responsible for achieving high-rate charging performance while maintaining reasonable charging capacity compared to soft carbon. The fabricated anode with ~20 nm thick carbon film on alumina nanoparticles improved the specific charging capacity by 9.4\% at 1 C rate and 8.3\% at 10 C rate compared to conventional soft carbon.

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1. Introduction

The main storage mechanism of graphite or carbon anode materials in lithium ion batteries (LIBs) is intercalation/deintercalation. In the case of graphite, lithium ions are inserted into the edges of graphite flakes and further intercalated into the interlayer to form LiC\(_6\) (372 mAh g\(^{-1}\)) [1–5]. In contrast, lithium ions are (i) stored in the micropores of hard carbon, (ii) accommodated within the microcavity in amorphous carbon, and (iii) adsorbed on defects or functional groups of amorphous carbon, giving rise to a wide range of charging/discharging voltage properties [6–12]. Supercapacitors, a similar storage vehicle, employ activated carbons with a large surface area (>1500 m\(^2\) g\(^{-1}\)). In this case, solvated ions are adsorbed onto the expanded surface of the carbon materials via a non-Faradaic reaction, which is known as electric double layer capacitance, thereby allowing fast charging and discharging [13–15]. Unlike LIB, no diffusion of ions into bulk materials is involved in supercapacitor. Therefore, the energy density remains low, which is mainly due to the low operating voltage in aqueous solution [16,17].

Several groups have attempted to improve the charging rate in LIB by minimizing the pathways for Li ion diffusion into commercial graphite [18,19]. Various sizes of graphite (6–41 \(\mu\)m) were tested to improve the rate performance. In any case, the charging rate was poor, although the discharging rate was improved with decreasing sizes [19]. Recently carbon nanobeads with a diameter of 100 nm and a surface area of 2000 m\(^2\) g\(^{-1}\) yielded high capacity of about 900 mAh g\(^{-1}\) and improved C-rate characteristics. Unlike other carbon materials, the main cause of the improvement was attributed to the reduction of intercalation diffusion pathway to reach efficiently reactive sites of lithium ions [20]. The reversible discharging capacity of mesophase carbon microbeads (MCMBS) was about 300 mAh g\(^{-1}\) at 1 C rate, but the carbon nanobeads showed a reversible discharging capacity of 130 mAh g\(^{-1}\) at 3 C rate (electrochemical reaction for 1200 s), which was attributed to the nanoparticles (<300 nm), leading to the short diffusion pathway of Li ions [21]. In spite of these efforts working with nanoparticles, high-rate charging performance is still far from being realized in industry due to the reduction of capacity.

The purpose of the current study is to search for anode material with high-rate charging performance. In this report, we introduced a nanoscale carbon film on alumina nanoparticles by pyrolyzing citric acid. The thickness of the pyrolyzed carbon film was limited to less than 20 nm. This not only provided unusually high specific capacity of up to 2180 mAh g\(^{-1}\) (per carbon film) but also gave rise to high-rate charging performance due to short diffusion path length of Li ions while retaining reasonable charging capacity, which meets industry requirement for high-rate charging rate LIB.
2. Experimental

Citric acid (Aldrich), which is a precursor of carbon nanofilms, was dissolved in deionized water. Alumina powder with a particle diameter of 500 nm (Smitomo, Japan) was added at different mixing ratios of 1%, 3%, 10%, and 20% citric acid solutions followed by 1 h stirring and 1 h sonication using a bath type sonicator (8510R-DTH, Branson). Alumina powder was

![Fig. 1](image1.png)

Fig. 1. (a) Flow chart of the process for producing carbon nanofilms coated on alumina nanoparticles. (b) Schematic diagram of carbon nanofilms coated on Al₂O₃ nanoparticles and a typical TEM image of a 4 nm thick carbon film on the Al₂O₃ nanoparticles surface.

![Fig. 2](image2.png)

Fig. 2. (a) Raman spectra of raw Al₂O₃ powder with an excitation energy of 514 nm and carbon nanofilm coated on Al₂O₃ nanoparticles with 3%, 10%, and 20% citric acid. (b) DTG (differential thermogravimetry) curves of the carbon nanofilm deposited on Al₂O₃ nanoparticle powder. The inset is the TGA curve to confirm the carbon yield on the Al₂O₃ nanoparticle surface. (c) The relationship between carbon yield and added citric acid content.
chosen as a supporter of coating carbon film due to its inert reaction with Li ions within an operation voltage range of 0.01–1.5 V in LIB. Furthermore, this gives the large surface area of carbon nanofilm formed on the surface of alumina nanoparticles.

The mixture was then dried overnight in a convection oven at 120 °C and ball-milled using a simple jar. The dried alumina particles coated with citric acid were transferred to a tubular furnace, and the powder was heat-treated to 750 °C at a ramping rate of 5 °C/min, maintained at 750 °C for 5 h under ambient N₂ and then cooled to room temperature. Conductivity was not changed much at temperatures of 750–1000 °C [22]. We expect that at 750 °C annealing, more abundant defects or functional groups could be generated in carbon nanofilm network, while retaining the same conductivity as that at higher temperature. The net masses of the carbon nanofilms were measured by thermogravimetric analysis (TGA, SDT Q600, TA) by increasing the temperature to 900 °C at a ramping rate of 2 °C/min under ambient air. Raman spectroscopy (NRS-1000, JASCO) with a laser wavelength of 514 nm and transmission electron microscopy (TEM, Jeol, JEM2100F) with an accelerating voltage of 200 keV was used to examine the crystallinity and thickness of the resulting carbon nanofilms, respectively. The powder was dispersed in ethanol and one drop of the solution was placed on a Cu grid. The electrical conductivity of the pressed powder was measured using the four-point probe method (Loresta-GP, MCP-T600, Mitsubishi) by a powder conductivity measurement system and the values were averaged for 5 points at different pressures ranging from 4 kN to 20 kN.

To design electrodes for electrochemical properties, the obtained alumina particles coated with carbon nanofilm were mixed with additional 10% carbon black and 10% polyvinylidene fluoride binder to make a slurry. A 20 μm thick layer of the slurry was then coated on a copper foil (10 μm thickness) and dried in a convection oven at 120 °C for 20 min. Alumina powder without carbon nanofilm coating was employed for electrode fabrication using the same method as described above for comparison. The electrode was cut into a 4.0 cm × 2.5 cm piece,
which was used as an anode by welding the Ni tap, and separated by a separator (Celgard PE) of the same size as the counter Li metal electrode. The unit cell was covered with an aluminum pouch and 0.5 g of a 1.0 M LiPF₆ dissolved electrolyte ((ethylene carbonate:dimethyl carbonate (volume ratio) = 1:1) was added before vacuum sealing. The electrochemical properties of the completed cell were measured using a charging/discharging system cycler (Toscat-3000, TOYO) and cyclic voltammetry (EC-Lab, Bio-logic), where the measured charging/discharging current rates were 0.2 C (equivalent to 5 h reaction time) and 50 C (equivalent to 72 s reaction time). In order to visualize the fast charging effect of carbon nanofilm on alumina and a realistic anode was fabricated by using conventional soft carbon materials. The as-purchased soft carbon (GS-Caltex, Korea) was mixed with citric acid-treated alumina nanoparticles (soft carbon:citric acid-treated alumina nanoparticles = 65:20 in weight) followed by a second stage mixing with 5 wt% carbon black as a conducting agent and 10 wt% polyvinylidene fluoride (PVDF) as a binder. The cell fabrication was similar to the method described above.

3. Results and discussion

Fig. 1(a) shows a flow chart of the experimental procedures used for sample preparation and the details described in Section 2. The carbon nanofilm was formed on the surface of the alumina particles, as shown in Fig. 1(b). Because of the relatively low temperature carbonization process of 750°C, the carbon film formed was amorphous and exhibited low crystallinity. The low crystallinity of the carbon nanofilm was also confirmed by Raman spectroscopy, as shown in Fig. 2(a). The D-band, which is a characteristic of the amorphous layers and/or defects on the carbon system, and G-band, which indicated the formation of hexagonal ring structures, were both observed clearly [23].

The broad spectrum of the D-band and the large D/G intensity ratio indicates the existence of a wide range of disordered structures in the carbon nanofilm, which is independent of the film thickness. The amount of carbon nanofilm was measured by TGA and differential TGA, as shown in Fig. 2(b). No appreciable decrease in mass was observed from the alumina particles except for a slight decrease in mass from the removal of adsorbents on the particle surface. However, the mass began to decrease from approximately 300°C for the carbon nanofilm samples, which reached approximately 1.6% in the 20% citric acid-treated sample (Fig. 2(c)). The burning temperature, which is defined as the peak position in the differential TG curve, exhibited a slight increase with increasing citric acid content. Fig. 3 shows the HR-TEM images of the carbon nanofilms formed on the surface of the alumina particles, which indicated 4 nm and 20 nm thickness at 3% and 20% amounts, respectively. The carbon nanofilm thickness increased and became inhomogeneous at larger amounts. Therefore, the increase in burning temperature shown in Fig. 2(b) resulted in delayed burning from the surface of the relatively thick carbon nanofilms. In particular, the broad asymmetric peak observed with 20% citric acid in

![Fig. 4](image-url) Charge/discharge curves and cyclic voltammetry scan of the anode electrode composed of carbon black and carbon nanofilm/Al₂O₃. (a) First cycle curves at 0.2 C/0.2 C (charge/discharge) from 0%, 3%, 10%, 20% citric acid. (b) The specific charge/discharge capacity of carbon nanofilm at 10% citric acid as a function of C-rate. Charging capacity was measured repeatedly after the cell was completely discharged with 0.2 C discharging. The discharging capacity was measured after 0.2 C charging. (c) Charging curves at 50 C rate. (d) Comparison of CV scan (160 mV s⁻¹) between 0% and 10% citric acid.
Fig. 2(b) suggested the existence of an extra phase. Indeed, additional bulky carbon island 20 nm in size was observed by TEM (data not shown) in addition to the carbon nanofilm of thickness of 10 nm on the alumina surface aggregated between the alumina particles. This result is consistent with the fact that the amount of carbon materials increased almost linearly with the exception of the sample with 20% citric acid in Fig. 2(c). The formation of bulky carbon islands was attributed to the highly viscous citric acids that induced aggregation. Therefore, the uniformity of carbon film thickness became increasingly poorer with increasing amounts of citric acid.

Fig. 4(a) shows the charging/discharging curves at a 0.2 C rate in terms of varying citric acid contents. In the case of 0% citric acid, in which only carbon black contributes to the capacity, the discharging capacity was 149 mAh g⁻¹. This was approximately 87% of the efficiency of conventional carbon black (170 mAh g⁻¹) [24], which is reasonable value due to poor conductivity by the presence of 20% alumina nanoparticles. Citric acid treated alumina electrodes showed different results. Specifically, the respective charging and discharging capacities were 534 mAh g⁻¹ and 184 mAh g⁻¹ with 3% citric acid, and 744 mAh g⁻¹ and 229 mAh g⁻¹ with 20% citric acid, respectively. This was in sharp contrast to the 349 mAh g⁻¹ charging and 149 mAh g⁻¹ discharging capacity obtained with 0% citric acid (carbon black). The increase in charging capacity with increasing citric acid content was attributed to the increase in the solid-electrolyte interface (SEI) formed near 0.7 V charging voltage, originating from the existence of functional groups on the large surface of the carbon nanofilm on the alumina surface [25, 26]. The irreversible capacity increased with increasing citric acid content, indicating a gradual increase in the surface area of the carbon nanofilm. Nevertheless, the discharging capacities of 10% and 20% citric acids were similar to each other. It is interesting to see exclusively the contribution of nanofilm. The summary for the capacity at 10% citric acid was provided in Fig. 4(b). At 1 C rate, the specific discharge capacity from nanocarbon film was only 1930 mAh g⁻¹. (This value decreased from 2180 mAh g⁻¹ to 1430 mAh g⁻¹ as the citric acid increased from 3% to 20%) This capacity is much larger than that of LiC₁₃ of single-layer adsorption [10, 12]. It has been reported that carbon nanoparticles of 100 nm diameter yielded a discharging capacity of ~900 mAh g⁻¹ and the specific capacity decreased as the diameter increased [20] and a 200 nm thick carbon film also yielded a similar capacity of ~800 mAh g⁻¹ [27]. Heat-treated mesocarbon from pitch coal at 450 °C produced a high capacity of 1660 mAh g⁻¹, in which the high capacity was attributed to Li adsorption to form Li–C multi-layer on graphite surface [28]. The presence of micropores in hard carbon also contributed to the high capacitance [29]. Our structure of carbon nanofilm was rather amorphous with partially curved layered portions, emulating micropores, as can be seen in Fig. 3(d). Our capacity was nearly equal to Li₆C₆ (2232 mAh g⁻¹) which is contributed from Li–C multi-layers formed on the carbon surface [28]. Therefore, we conclude that our carbon nanofilm is likely contribute to Li–C multi-layers, which is easily facilitated by the presence of well-developed micropores in the nanofilm. The Li–C multi-layer formation is limited to few-layer surface reaction. Therefore, the specific capacity is expected to be reduced as the particles thickness gets thicker [20]. The capacity was degraded to 865 mAh g⁻¹ at 70 C due to poor conductivity. Nevertheless, high capacity was still maintained due to short diffusion path lengths of Li ions compared to graphite. This is why some reasonable charging capacity was revealed even at 70 C rate.

The main purpose of this study was to investigate the reaction mechanism of Li ions in a carbon nanofilm for rapid charging. A fast charging rate of 50 C was used for this purpose, as shown in Fig. 4(c), which corresponds to a high current within a 72 s charge or discharge time. To identify the fast charging mechanism of the pure carbon nanofilm, the cell was discharged with a slow 1 C rate after charging with 50 C to ensure the cell was fully charged. The charging capacity at 0% citric acid was 57 mAh g⁻¹, which increased to 87 mAh g⁻¹ with 20% citric acid.

With increasing citric acid content, the carbon nanofilm became thicker. The conductivity of the film increased simultaneously. On the other hand, the diffusion path length of Li ions increases, which eventually reduces the charging capacity. Although citric acid of more than 10% produced aggregation and consequently a slightly reduced high rate charging performance, a minimum powder conductivity of 3.3 × 10⁻⁶ to 1.8 × 10⁻⁶ S cm⁻¹ was obtained to work in a real anode. At 20% citric acid, although the conductivity was improved, the Li ion diffusion was limited by the thick carbon nanofilm of 20 nm, therefore reducing charging capacity compared to that of 10% citric acid.

Fig. 4(d) shows CV scan at a scan rate of 160 mV s⁻¹ in the voltage range of 0.01–1.5 V. The maximum charging current of carbon nanofilm cell was increased from 4.9 mAmg⁻¹ to 25.8 mAmg⁻¹ of carbon black. Unlike carbon black cell (0% citric acid), carbon nanofilm showed different behavior in Li ion reaction in the voltage range of 0.8–0.01 V. This suggests that the pore structures or defects of carbon nanofilm are completely different from that of carbon black. Citric acid is a simple hydrocarbon complex and is not easily converted into graphene sheets with heat treatment. Therefore, the resulting carbon nanofilm formed with citric acid is expected to be different from the hard carbon which results in LiC₃ phase, yielding the capacity ~740 mAh g⁻¹ [10, 12]. This value is much smaller than our specific capacity of 2180 mAh g⁻¹ (nanofilm). Therefore, incomplete carbonization of citric acid at 750 °C annealing led
to form defects and functional groups in the carbon nanofilm. This could be the origin of high capacity by incorporating Li–C multi-layers.

Fig. 5 shows the comparison of electrochemical reactions between our fabricated anode with nanofilm-coated alumina nanoparticles/active soft carbon material and the reference anode with conventional soft carbon material. Carbon black with PVDF was also added to emulate the real anode in LIB. The mixing ratio of nanofilm-coated alumina nanoparticles/soft carbon:carbon black:PVDF was 20:65:5:10 in weight percent. Compared to conventional soft carbon material, our sample with additional citric acid-treated alumina nanoparticles improved the specific capacity. The 20% citric acid-treated sample improved charging capacity to 167 mAh g$^{-1}$ from 152 mAh g$^{-1}$ of the reference sample at a rate of 1 C, corresponding to an 8.1% increase in specific capacitance. The second graph, as shown in Fig. 5(b) shows the comparison of the charging speed (specific charge capacity/time) at given current rates. The charging speed of our fabricated anode with citric acid-treated alumina nanoparticles/active soft carbon material was 3.5 mAh g$^{-1}$ min$^{-1}$ and 33.9 mAh g$^{-1}$ min$^{-1}$ at rates of 1 C and 10 C, respectively. These charging speeds were faster than the reference sample by 10% and 6% at rates of 1 C and 10 C, respectively. As explained above, this improved charging time was ascribed to the enhanced surface reactions at the nanofilm surface of the alumina nanoparticles. Although the electrochemical performance of carbon nanofilm only was best at 10% citric acid, the high-rate performance of the real anode was better at 20% citric acid due to mainly the conductivity of the electrode.

4. Conclusions

This study examined effects of carbon nanofilm on alumina nanoparticles which can be used as an anode for high rate charging performance in LIB. Unusually high specific capacity of ~2180 mAh g$^{-1}$ (carbon nanofilm) was attributed to adsorption of Li ions to form Li–C multi-layers in carbon nanofilm. The dominant reaction of the nanocarbon film-coated alumina nanoparticles was the fast Li ion movement by the short diffusion path length. Control of thickness on the nanometer scale (<20 nm) is a key factor for enhancing both high capacity and high rate charging capability. This approach opens a route to create fast charging rates of batteries.

Acknowledgements

The authors wish to thank to Samsung SDI, the STAR-Faculty Program (2010-0029653), and the WCU Program (R31-2008-000-10029-0) through the KRF funded by the MEST for their financial support.

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