

Structural and preliminary electrochemical characteristics of palm oil based carbon nanospheres as anode materials in lithium ion batteries

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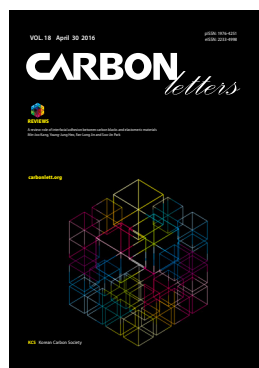
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Since the invention of the lithium-ion battery (LIB) in the early 1990s by SONY, graphite carbon has been used as the anode material because of its low cost, chemical stability, and stable electrochemical performance [1]. The limitations of graphite anodes, especially related to their small energy and power output per unit mass or volume, are retarding the development of certain high-tech industries such as hybrid electric vehicles and stationary energy storage [2]. Therefore, there is currently an intense search for new anode materials for LIBs, with high specific capacity and energy density [3,4].

In recent decades, the development of nano-carbon materials with well-defined characteristics, such as fullerenes, nanotubes, and graphene; has been a very active area of research [5]. Carbon nanospheres (CNSs) are another class of nanostructured carbon materials, and have shown good prospects for application as alternative LIB anodes [6]. CNSs possess some remarkable characteristics useful in LIB anode materials, such as high specific capacity and good rate capability. Those specific characteristics are attributed to a combination of several factors, including short diffusion paths for Li⁺ ions, good porosity, and large surface area [7].

CNSs can be synthesized by various techniques and these influence the characteristics of the resulting carbon products in terms of sphere size, size distribution, crystallinity, and microstructure. The processes by which CNSs are synthesized include chemical vapor deposition [8], hydrothermal carbonization [9], laser ablation [10], and polymerization-carbonization [11].

Carbon based materials were initially made from petroleum-derived compounds. Because of the depletion of carbon deposits and very serious concerns about global climate change and environmental pollution, the use of renewable natural resources (e.g., biomass) for production of carbon materials has been intensively explored in recent years [12].

In this work, the synthesis of CNSs on the surface of activated carbon support was carried out using a thermal-assisted catalytic pyrolysis technique and utilizing palm oil as renewable and eco-friendly carbon source. Specifically, the effect of the amount of Fe-catalyst on the structural and electrochemical characteristics of the CNSs will be reported.

Commercial activated carbon (102836, Merck) has been used as a catalyst support without prior treatment. Analytical grade Fe(NO₃)₂ was used as catalyst. The catalyst was deposited onto the carbon support using the urea deposition method. In this method, 2 g of activated carbon was mixed with Fe(NO₃)₂ solution at various ratios (10%, 20%, and 30% with respect to the weight of the activated carbon). The ratio of Fe(NO₃)₂ to urea was set at the molar ratio of 1:3. The mixtures were shaken for 4 h at 90°C, cooled down overnight, and centrifuged at 6000 r/min for 15 min. The cake so obtained was then dried at 110°C for 24 h and then mixed with palm oil at the mass ratio of 1:3.

The CNS were synthesized by pyrolyzing mixtures of activated carbon, urea, Fe(NO₃)₂,

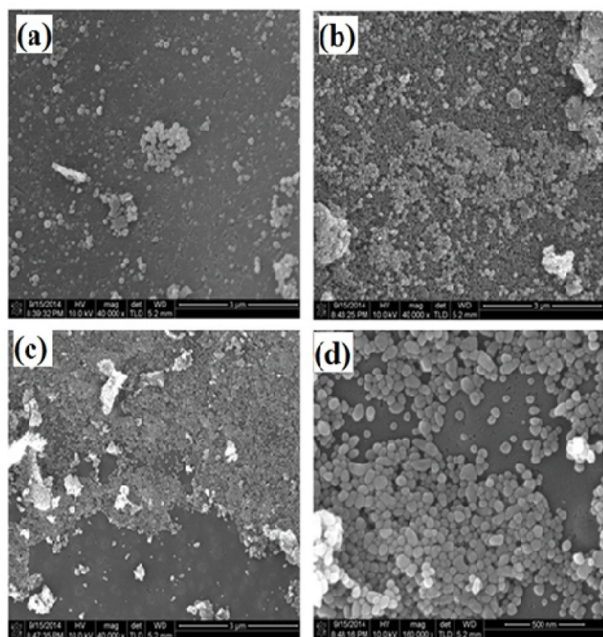


Fig. 1. Typical scanning electron microscope images of carbon nanospheres prepared with Fe-catalyst content of (a) 10%, (b) 20%, (c) 30% (low resolution), and (d) 30% (high resolution).

and palm oil at 700°C for 1 h in a flow of nitrogen (N_2) gas. The carbon products were dried at 400°C for 24 h and stored in desiccators.

The CNS morphology was observed by field-emission scanning electron microscopy (S 4100; HITACHI, Japan). The microstructure of the HCSs was investigated using transmission electron microscopy (TEM; TECNAI, Philips, Netherlands). The phase structures of the CNSs were analyzed by X-ray diffraction (XRD) (D8 Advance, Cu- $K\alpha$ radiation, Bruker, USA). Raman spectroscopy (inVia Spectrometer System, visible excitation 532 nm, Renishaw, UK) was used to characterize the vibrational properties of the CNSs.

The electrochemical performance of the CNSs was investigated via two-electrode coin-type cells. The working electrodes were prepared using the slurry coating method with 90 wt% sample, 5 wt% carbon black, and 5 wt% polyvinylidene difluoride (PVDF) dissolved in N-methyl-2-pyrrolidinone (NMP). This combination was then spread onto Cu foil. The coated electrodes were dried in a vacuum oven at 120°C for 24 h. Coin cells were assembled in an argon-filled glove box. The reference and counter electrodes were both made of metallic lithium foil. The electrolyte was 1 M $LiPF_6$ in a 1:1:1 (v/v) mixture of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate. The separator used was a polypropylene micro-porous film. Charge/discharge tests were conducted at a constant current density of 100 $\mu A/cm^2$ (0.2 C), with a cut-off voltage of 0–2 V vs Li/Li^+ , at room temperature.

Fig. 1 shows scanning electron microscope images of the growth of CNSs on the surface of activated carbon support with varying content of Fe-catalyst. Clearly, a great amount of aggregated spherical-shapes were observed in the resultant CNSs. When the content of Fe-catalyst was increased, the nano-spheres

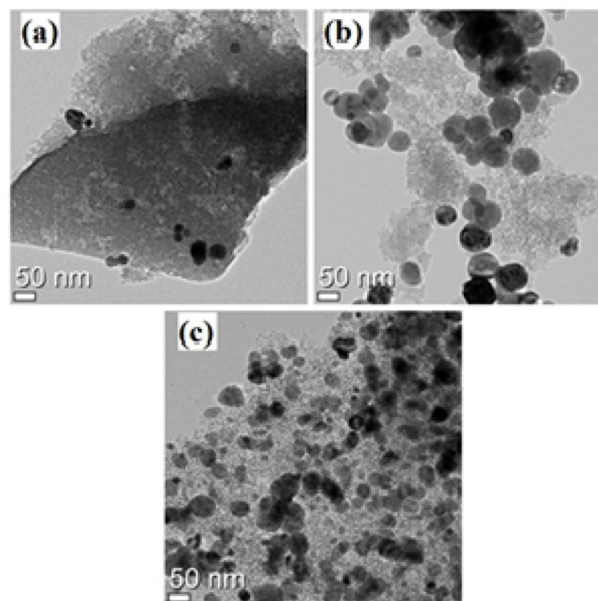


Fig. 2. Typical transmission electron microscopy images of carbon nanospheres prepared with Fe-catalyst content of (a) 10%, (b) 20%, and (c) 30%.

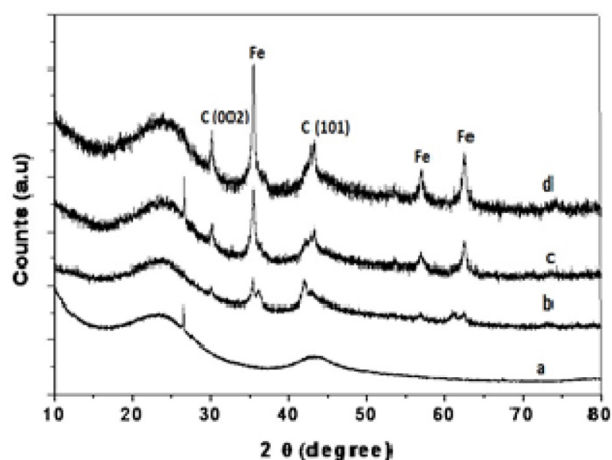


Fig. 3. X-ray diffraction patterns of (a) activated carbon support and carbon nanospheres prepared by Fe-catalyst content of (b) 10%, (c) 20%, and (d) 30% w.

became denser.

TEM images of the CNSs (Fig. 2) demonstrated that the denser and more homogeneous carbon spheres were obtained as the amount of catalyst was increased from 10 to 30wt%. In general, it can be said that the carbon products showed turbostratic structures.

Fig. 3 displays the XRD patterns of CNSs. From the XRD results, it can be seen that every sample shows a peak at 43°, indicating (101) sp^2 structures of carbon, and a peak at 26.5° is the C (002) peak. Fe peaks were observed at 30° (220), 35.4° (311), 57.09° (422), and 62.4° (440) that relate to the magnetite (Fe_3O_4) on the activated carbon. A weak C peak (101) could mean that CNSs formed with a low degree of graphitization,

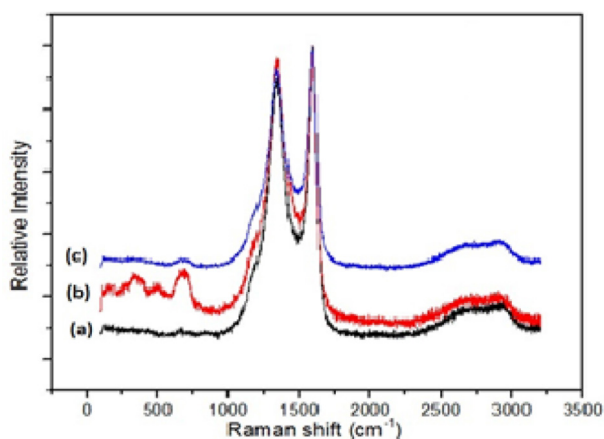


Fig. 4. Raman spectra of carbon nanospheres prepared with different Fe-catalyst content of (a) 10%, (b) 20%, and (c) 30%.

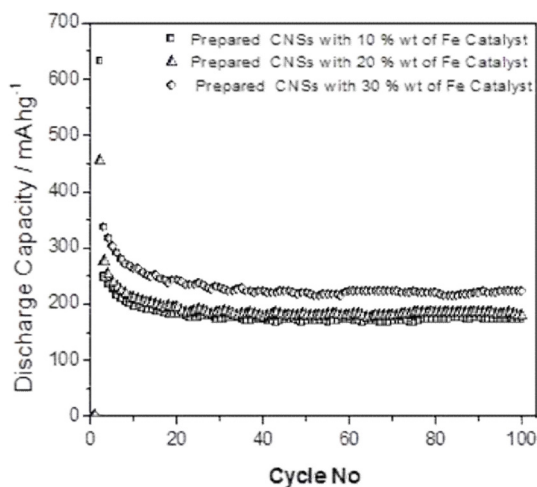


Fig. 5. Profiles of specific discharge capacity vs. cycle number (no) for carbon nanospheres (CNSs) prepared with different Fe-catalyst content at a current density of $100 \mu\text{A}/\text{cm}^2$, with cut-off voltage of 0–2 V vs Li/Li⁺.

which is characteristically observed in CNSs. With 10% Fe-catalyst the C (101) peak observed was weaker with 20% and 30% Fe-catalyst. Thus it can be assumed that 10% Fe-catalyst was not adequate to promote the growth of the CNSs.

Fig. 4 shows the Raman spectra of CNSs with different Fe-catalyst amounts. The G peak at about 1580 cm^{-1} corresponds to the E_{2g} mode of hexagonal graphite, and is related to the vibration of sp^2 -bonded carbon atoms in a graphite layer.

This implied that CNSs were composed of graphitic carbon. The D band located at about 1350 cm^{-1} , is associated with the vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite. The intensity ratio of D band and G band (I_D/I_G ratio) provides information about the crystalline structure of the CNSs. The I_D/I_G ratios of the CNSs were in the range 0.90–0.96, reflecting almost equal amounts of disordered and graphitic carbon in the CNSs.

Fig. 5 shows the specific discharge capacity profiles for the CNSs prepared with different amounts of catalyst. It can be seen

that most of them demonstrated stable cycle performance until the 100th cycle. However, the highest specific capacity was shown by the carbon samples with the highest content of Fe-catalyst. This was due to the higher CNS concentration formed on the surface of the activated carbon support, and it seems that more CNSs were formed when the concentration of the Fe-catalyst was higher.

In this paper, we conducted a simple direct pyrolysis process for the production of CNSs from palm oil precursors, and activated carbon support. The study indicates that the structural properties of the CNSs are changed when the amount of Fe-catalyst is increased from 10 to 30 wt%. The stable cycle performance of the carbon products was demonstrated when they were utilized as anode materials in lithium ion batteries. However, it can be observed that the highest specific capacity was shown by the carbon samples with the highest content of Fe-catalyst.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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