



Short communication

A promising active anode material of Li-ion battery for hybrid electric vehicle use

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ABSTRACT

In an attempt to respond to the requirement to provide promising anode material of Li-ion battery for hybrid electric vehicle (HEV) we examined mesophase-pitch-based cokes. The coke was heat treated at several temperatures where turbostratic structure is formed. Cyclic voltammograms (CV) were measured in 1:2 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M LiClO₄ for all the samples, and the peak height was plotted against the square root of the potential scanning rate. The slopes of the plotting differed depending on the heating temperature and 1800 °C heated sample gave the steepest slope implying the diffusion coefficient of Li is the highest.

For activating the electrochemical reaction site of the prepared electrode we adopted a novel method to expose the coated electrode in the glow discharge field in the presence of small amount of oxygen. As the result the CV peak height was increased by about two times as compared with that before the treatment.

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1. Introduction

HEV is one of the most important tools for us to realize not only saving energy but also reducing the exhausting amount of CO₂. Next generation of HEV requires much higher capacity for the power sources, where Li-ion battery is expected to be best suited. The active materials presently used in the practical Li-ion batteries, however, are not preferable due to their inadequate power capability. The charge/discharge mode of the power source required to the power source of HEV is too severe to respond for the conventional Li-ion battery. Therefore, it is necessary to replace the active material that can respond to the requirement.

The anode active materials presently used in the practical Li-ion batteries are graphite and the related materials, which should be replaced by a material having very high power capability. And in addition, since the amount to be used in the power source of HEV is very large, the price of the material should be held down to a great extent. In view of these requirements a carbonaceous material prepared at lower temperature appears to be attractive. In the present paper we would like to show the results obtained from a carbonaceous material prepared from pitch-based coke having a turbostratic structure where there is no coincidence of the orientation among stacking graphene layers [1–4]. The carbonaceous material comprised of turbostratic structure has not only

a wider spacing of graphene layers but also no stage structure during Li insertion. These properties realize very rapid reaction rate for Li insertion and extraction, which is favorable to the very high power capability. The aim of the present study is to examine favorable firing temperature and to evaluate how rapid the rate of the Li insertion/extraction reaction. In addition, we would like to propose a novel method for activating the reaction site.

The conventional coke available in the market was used for firing evaluation. Mesophase petroleum coke was chosen as the starting material. This material is beneficial due to the tendency liable to change the structure from pitch coke to form graphene structure crystallite, which grows to larger size depending on the firing temperature [5,6]. Choosing the firing temperature can control the degree of the graphene orientation. Of the precursor material of mesophase-pitch, when the firing temperature is low the Li accommodation capacity is very large, while the electric conductivity is low, which is inconvenient for attaining rapid Li insertion/extraction. Therefore, we chose the lower limit of firing temperature to be 1800 °C.

When exposed to the ambient environment the surface of the any active material is supposed to be covered by some contaminant in the atmosphere, causing to be deactivated. Further more, there is another possibility for the active material to be deactivated during the process of electrode fabrication. The surface activation after the fabrication of the electrode is of quite much preferable but conventional activation method is difficult after fabrication. In this study we examined our idea of exposing the fabricated electrode in the

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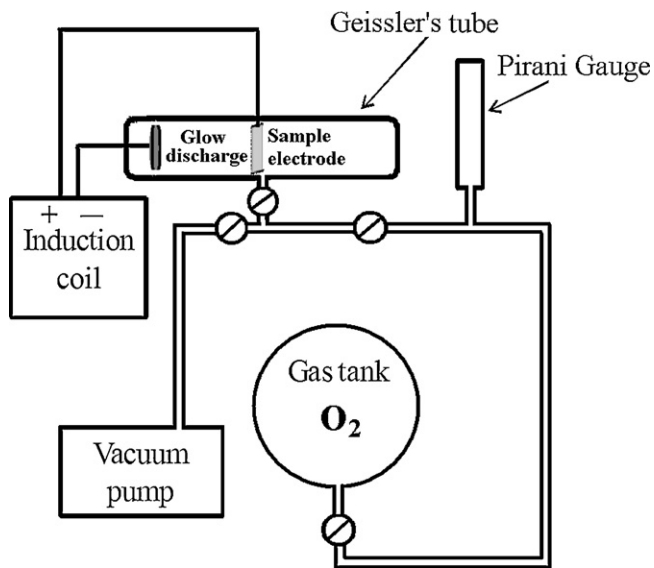


Fig. 1. Schematic figure of glow discharge equipment for activation of the electrode.

field of glow discharge, and found it to be effective to activate the fabricated electrode.

2. Experimental

The carbon materials were prepared by firing the crushed petroleum coke in Tamman furnace with flowing Ar gas at different temperatures. The rate of the temperature rise was $1000^{\circ}\text{C h}^{-1}$ and afterwards the sample was kept at the definite temperatures of 1800, 2000, and 2200°C .

X-ray powder diffraction (XRD) analysis were done with a Rigaku RINT 2500 X-ray diffractometer using the Cu $K\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The SEM image of the electrode surface was taken with a Hitachi S-4000 Scanning Electron Microscope. The specific surface area of the active materials was measured with a Yuasa-Ionics Monosorb meter.

The test electrode was fabricated by coating the sample powder slurry with a doctor blade on a $20\text{ }\mu\text{m}$ -thick Ni foil substrate. The slurry was prepared by mixing the sample powder with a conductive additive of VGCF (Vapor Grown Carbon Fiber (Showa Denko), and binder of Poly vinylidene fluoride (PVDF) with a mixing ratio of 85:5:10 (w/w/w) in an appropriate amount of 1-methyl-2-pyrrolidone (NMP). The coated electrode was dried in vacuum at 120°C for 1 h, resulted in the thickness of $40\text{ }\mu\text{m}$.

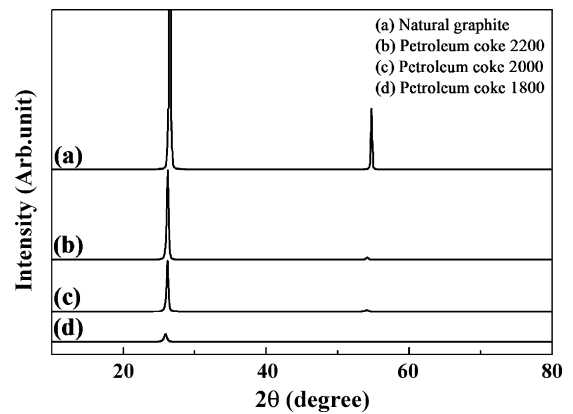


Fig. 2. XRD patterns of carbon materials (a) natural graphite, (b) 2200°C , (c) 2000°C , and (d) 1800°C fired coke.

The Ni foil coated with the carbon sample was cut into a square of $1\text{ cm} \times 1\text{ cm}$, sandwiched with a 20 mesh folded Ni expand metal of larger size, spot-welded at several points for obtaining tight hold, and used as the test electrode. The electrochemical cell for the measurement was three electrode type glass cell where Li metallic foils were used as the counter and the reference electrodes, respectively. The electrolyte was 1:2 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M of LiClO_4 , the water content being less than 15 ppm. All the cell fabrication was conducted in a glove box filled with dried argon gas at room temperature.

The electrode activation treatment was done by exposing in the discharging field of glow discharge. Schematic figure of the activation equipment is shown in Fig. 1. After mounting the sample electrode in a Geissler's tube the vacuum system was evacuated to 10 Pa for enough time to remove the remaining air, then 2 kPa of O_2 was introduced in the tube from the tank, and the glow discharge was initiated. The discharging was maintained for 60–240 s.

The electrochemical performance of the test electrode was measured with cyclic voltammetry (CV) with a Hokuto Denko potentiostat, HSV-100 under several sweep rates at 25°C , the potential scan range being between 2.0 and 0.05 V. For evaluating the effective surface area of the fabricated test electrode the double layer capacity was measured in the potential range of 2.0 and 1.5 V, with the scan rate of 50 mV s^{-1} .

3. Results and discussion

The most important property of the Li insertion/extraction anode used in the power source of HEV is the power capability,

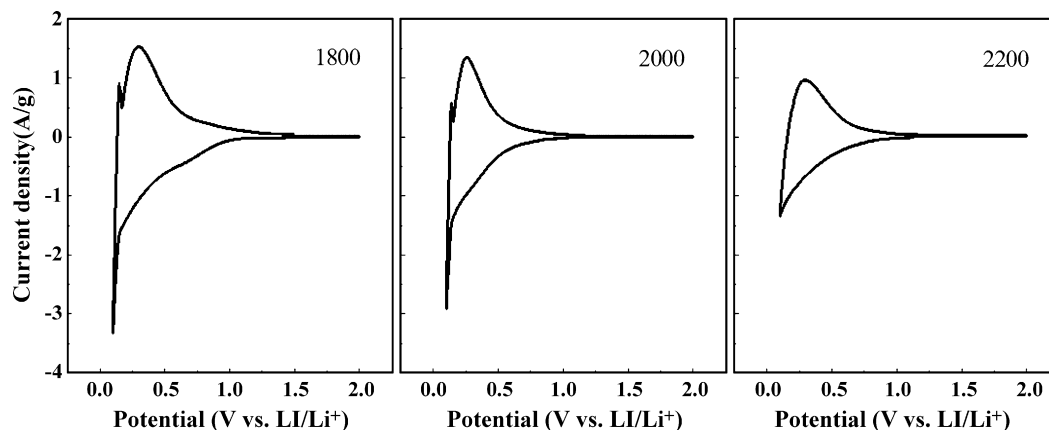


Fig. 3. CVs of 1800, 2000, 2200°C fired cokes in EC/DMC containing 1 M LiClO_4 with the potential scan rate of 2.0 mV s^{-1} .

Table 1
Specific surface area of carbon samples prepared at three different temperatures and the relative slope of the line of CV peak height vs. square root of the potential scan rate.

| Carbon sample prepared at the temperature of: | (A) BET specific surface area ($\text{m}^2 \text{g}^{-1}$) | (B) Relative surface area referred to that of 2200 °C sample | (C) Relative slope of the line in Fig. 4: ($\text{A g}^{-1} \text{s}^{-1/2}$) | (D) Relative slope of the line referred to that of 2200 °C sample |
|---|--|--|---|---|
| 1800 °C | 5.2 | 1.11 | 0.135 | 2.16 |
| 2000 °C | 4.9 | 1.04 | 0.106 | 1.70 |
| 2200 °C | 4.7 | 1.00 | 0.0625 | 1.00 |

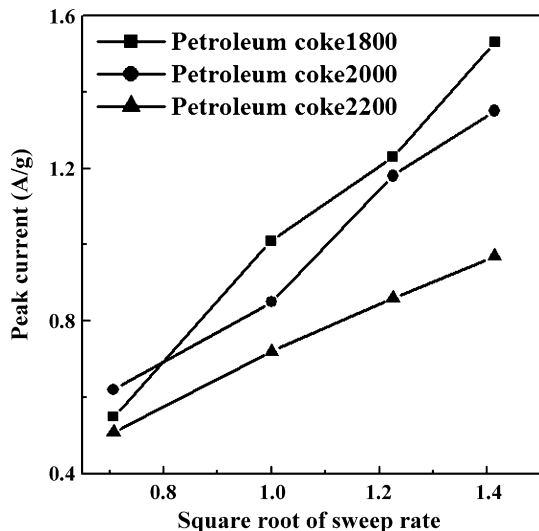


Fig. 4. Relationship between square root of potential scan rate and peak current of CVs obtained with coated electrode with 1800, 2000, 2200 °C fired cokes.

which means that the reaction rate of Li insertion/extraction should be very high. The most important factors to realize high reaction rate is the rate of diffusion of Li in the interior of the anode material and the high rate of the charge transfer reaction at the surface the electrode material in contact with the electrolyte. As pointed out above, the Li diffusion rate is expected to be rapid in the inter-carbon hexagonal layers of turbostratic structure. The rate is supposed to be much higher than in the spacing of inter-graphene layer of graphite. Hence the degree of graphitization is key factor of diagnosing the power capability. The height of the XRD 0 0 2 peak is the measure of

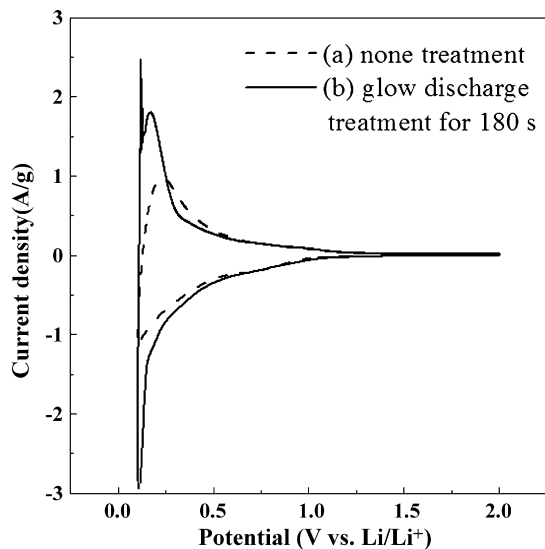


Fig. 5. Cyclic voltammograms of 1800 °C fired coke in EC/DMC containing 1 M LiClO_4 with the scan rate of 1 mV s^{-1} before (a), and after the activation treatment in Geissler's tube (b).

the degree of graphitization. We measured the XRD patterns of the fired sample. The results are shown in Fig. 2, which shows that the 1800 °C fired sample has only the trace amount graphitized phase [6], indicating it to be just favorable sample for attaining high power capability.

The rate of the Li insertion/extraction reaction can be recognized by the peak height of the CV pattern. In Fig. 3 the CVs obtained with the same potential scanning rate are shown, where we see the 1800 °C sample is the best one. The diffusion rate of Li can be evaluated from the slope of plotting of the CV peak height, i_p , against square root of the scan rate, $v^{1/2}$ with the aid of the relationship: $i_p = (2.69 \times 10^5) n^{3/2} D^{1/2} C^* v^{1/2}$, where n is the number of electron and C^* is the surface concentration of Li. C^* is supposed to be constant during the measurement. Fig. 4 shows the plotting for three samples fired at different temperatures. As seen in the figure, the sample fired at 1800 °C gives the highest slope, implying that the Li diffusion rate is the highest in this sample, which is in concordance with the expectation. Since this slope is about two times of that of 2200 °C fired sample the diffusion rate in 1800 °C sample is expected to be over two times of that in graphite.

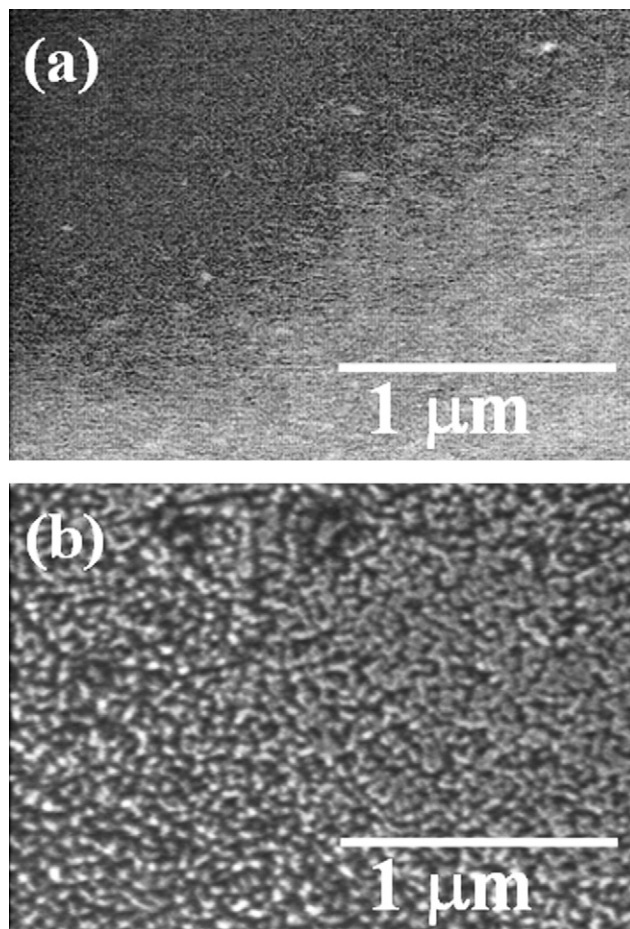


Fig. 6. SEM images of the coated electrode surface: (a) before the activation treatment; (b) after the glow discharge activation treatment.

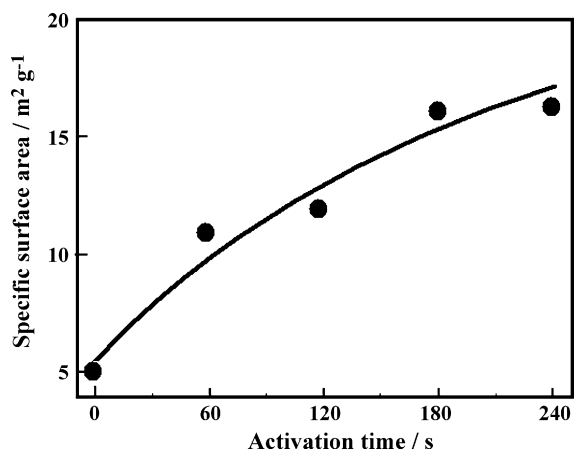


Fig. 7. Relation between the specific surface area and the glow discharge activation time under the oxygen pressure of 2 kPa for 1800 °C fired coke.

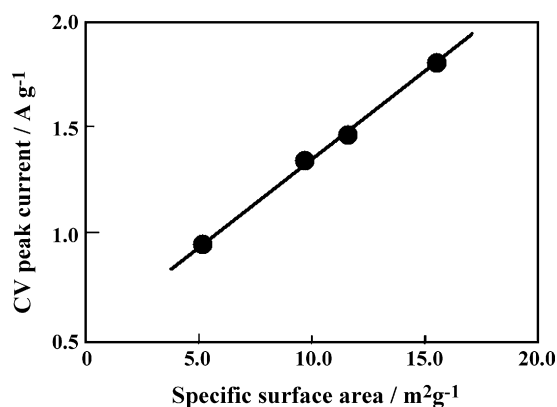


Fig. 8. Relationship between the CV peak height of Li extraction of 1800 °C fired coke (in EC/DMC containing 1 M LiClO₄ with the scan rate of 1 mV s⁻¹) and the effective electrode surface area increased by the activation treatment in Geissler's tube. The surface area was evaluated from CV obtained in the potential range of 1.5–2.0 V.

In order to verify the above expectation it is necessary to examine the other factors influencing the CV data, where the specific surface area is one of the most important factors which should be taken into consideration. If the specific surface area of the 1800 °C sample is very high, then the rate data is expected to be very high even though the rate of diffusion of Li in this sample is moderate. In view of such an implication we measured the specific surface area for each sample. The data of BET surface area determined with nitrogen gas adsorption are shown in Table 1. The values indicated in column (A) are similar to each other within the range of 11% (see column (B)), while the difference in the relative slope shown in Fig. 4

is larger than 200% (see column (D) in the table). This means that although we cannot disregard the correlation between the surface area and the deinsertion reaction rate, it appears insignificant. Consequently, we can conclude that the diffusion rate of Li in 1800 °C sample is the highest among the three samples.

Now let us show the results obtained after the glow discharge treatment. The CV diagrams are compared in Fig. 5. This reveals that the peak height of Li extraction process was increased to two times by the activation treatment, indicating the glow discharge treatment to be quite effective to activate the electrode surface. The advantageous points of the present method are: (1) the method is very simple, and (2) the treatment can be used as the final process for the fabricated electrode.

The cause of the activation was examined with SEM observation together with the results obtained with the surface area measurement. In Fig. 6 the SEM images are shown for the electrode surface obtained before (a) and after (b) the treatment. Remarkable surface roughening can be recognized in Fig. 6(b) in contrast to the smooth image for (a). The effective surface area was evaluated by measuring the double layer capacity of the electrode by CV measurement in the potential range between 1.5 and 2.0 V for each sample offered to the activation treatment in glow discharge tube. The correlation between the activation time during the glow discharge treatment and the specific surface area was obtained as shown in Fig. 7. With the aid of Fig. 7 the peak height of the Li extraction peak current on CV was plotted against the surface area thus evaluated and shown in Fig. 8, where a linear relationship is seen. This means that the increase in the reaction rate is caused by the surface increase due to the glow discharge treatment.

4. Conclusions

Among the materials obtained from petroleum coke by firing at 1800, 2000, and 2200, the 1800 °C fired sample showed the best power capability for Li insertion/extraction reaction in EC/DMC containing 1 M LiClO₄. As expected the material contained only very limited amount of graphite structure.

Glow discharge treatment with a Geissler's tube was found very effective to activate the prepared electrode. The advantageous points of the present method are: (1) the method is very simple, and (2) the treatment can be used as the final process for the fabricated electrode. This material is expected to be promising for putting Li-ion battery to practical use as the power source of HEV.

References

- [1] R.E. Franklin, Acta Cryst. 3 (1950) 107.
- [2] R.E. Franklin, Proc. Roy. Soc. A 209 (1951) 196.
- [3] M. Inagaki, K. Kamiya, Tanso 66 (1971) 76.
- [4] M. Inagaki, K. Kamiya, Tanso 71 (1972) 135.
- [5] C.R. Houska, B.E. Warren, J. Appl. Phys. 25 (1954) 1503.
- [6] J.N. Rouzaud, A. Oberlin, Carbon 27 (1989) 517.