

HOW TO AVOID THE EXFOLIATION OF MICROCRYSTALLITES IN THE GRAPHITIZED PETROLEUM COKE USED AS THE NEGATIVE ELECTRODE OF THE LITHIUM ION RECHARGEABLE BATTERIES

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Introduction

After high temperature heat treatment, the petroleum coke (NC) and Needle coke (NC) become good active substances for preparing the negative electrode of the lithium ion rechargeable batteries. But the most appropriate maximum heat treatment temperature (HTT_{max}) and the degree of graphitization must be considered, Otherwise the charging-discharging performance will go to bad. The reason for this phenomenon has been studied in our experiments[1].

Experimental

One kind of PC and one kind of NC were heated in the middle frequency oven with different HTT_{max} : 2000°C, 2250°C, 2500°C, 2750°C and 3000°C. The graphitized products were ground to be -200 mesh powders and were analyzed by X-rays diffraction and Raman spectrum. The powders were mixed with 10% PTFE and were rolled by heating rollers to be carbon membranes. After drying at 160°C under vacuum, the carbon membranes were used as the negative electrodes of the lithium ion rechargeable batteries to determine the galvanostatic charging-discharging capacities, and were analyzed by in-situ X-rays diffraction simultaneously. The positive electrodes and reference electrode are made of metallic lithium and the electrolyte solution is 1M $LiClO_4$ + EC/DEC (1 : 1).

Results and discussion

The XRD parameters d_{002} and the degree of graphitization G of graphitized PC and NC powders are shown in Table 1. From it we can see that d_{002} always decrease with increasing HTT_{max} and G always increase with increasing HTT_{max} .

The Raman spectrums of NC powders graphitized

Table 1. d_{002} and G of graphitized PC and NC powders

Samples	d_{002} (nm)	G (%)
PC ₂₀₀₀	0.3424	18.6
PC ₂₂₅₀	0.3393	54.7
PC ₂₅₀₀	0.3397	70.9
PC ₂₇₅₀	0.3370	81.4
PC ₃₀₀₀	0.3363	89.5
NC ₂₀₀₀	0.3404	18.6
NC ₂₂₅₀	0.3406	39.5
NC ₂₅₀₀	0.3370	81.4
NC ₂₇₅₀	0.3360	93.0
NC ₃₀₀₀	0.3357	96.5

with different HTT_{max} (2750°C and 3000°C) are shown in Fig 1. In Fig. 1-a there are two peaks, one is at 1356cm^{-1} which characterizes the existence of sp^3 bond, the other is at 1580cm^{-1} , which characterizes the existence of sp^2 bond. In Fig 1-b the peak at 1356cm^{-1} disappears, it means there is no sp^3 bond in

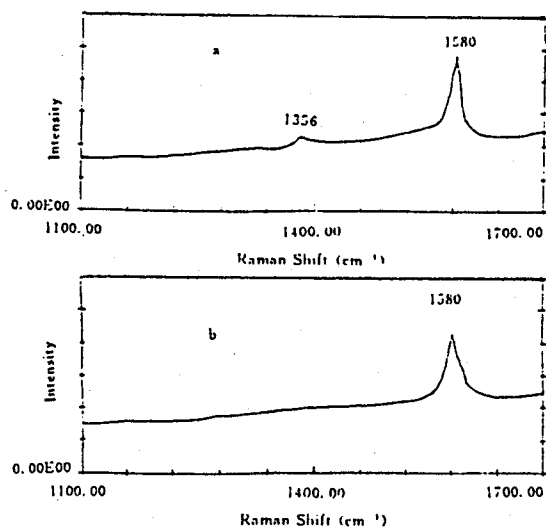


Fig. 1 The Raman spectrums of NC powders graphitized with different HTT_{max} (a: 2750°C, b: 3000°C)

graphitized NC when HTT_{max} reaches up to 3000°C.

The Raman spectrum of PC powders graphitized with $HTT_{max} = 3000^\circ\text{C}$ is shown in Fig 2. there are two peaks One is at 1356cm^{-1} and the other is at 1580cm^{-1} which characterize sp^3 bond and sp^2 bond respectively. It means that the sp^3 bond does not disappear in PC, even the HTT_{max} reaches up to 3000°C and PC is more difficult to be graphitized than NC.

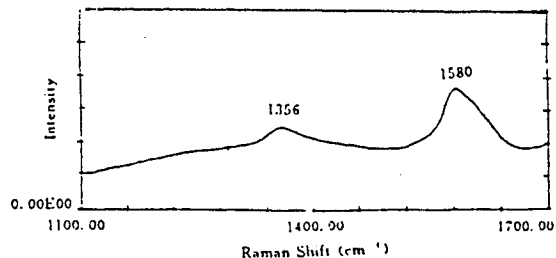


Fig. 2 The Raman spectrum of PC powder graphitized with $HTT_{max} = 3000^\circ\text{C}$

The charging-discharging performance of graphitized PC and NC powders used as the negative electrodes is shown in table 2. From it we can see that the charging capacity (C_3), discharging capacity (D_3) and charging-discharging efficiency (η_3) of PC in the third cycle increase with increasing HTT_{max} , and the C_3 , D_3 and η_3 of NC in the third cycle increase with increasing HTT_{max} before $HTT_{max} = 2750^\circ\text{C}$ but decrease rapidly about 3000°C.

Table 2. The charging-discharging performance of graphitized PC and NC powders used as the negative electrodes

No of Cycle Samples	III		
	C_3 (mAh/g)	D_3 (mAh/g)	η_3 (%)
PC ₂₀₀₀	152.5	149.3	97.9
PC ₂₂₅₀	186.8	182.0	97.5
PC ₂₅₀₀	166.5	161.5	97.0
PC ₂₇₅₀	216.0	210.0	97.2
PC ₃₀₀₀	258.0	247.9	96.1
NC ₂₀₀₀	152.5	143.8	94.3
NC ₂₂₅₀	159.5	145.0	90.9
NC ₂₅₀₀	229.0	212.5	92.8
NC ₂₇₅₀	247.0	237.9	96.3
NC ₃₀₀₀	5.0	3.62	72.4

The above results show that the charging – discharging performance of graphitized PC and NC powders used as the negative electrodes is related to the their microstructures. G cannot be too high and a small quantity of sp^3 bond must exist to connect the

carbon planes together and to avoid the exfoliation of graphite microcrystallites during charging.

Fig. 3 is the in-situ X rays diffraction spectrums of sample PC₃₀₀₀ and sample NC₃₀₀₀ during charging to the mixed stage of stage 1 and stage 2. From it we can see that the distance between peak 002 (characteristic peak for stage 2) and peak 001 (characteristic peak for stage 1) of sample NC₃₀₀₀ is longer than that of sample PC₃₀₀₀. It means that the change of the distance between carbon planes during the transformation from stage 2 to stage 1 of sample NC₃₀₀₀ is larger than that of sample PC₃₀₀₀, because there is no sp^3 bond in sample NC₃₀₀₀ and the solvated lithium ion with large volume can intercalate into the space between carbon planes more freely, which causes the expansion and exfoliation of the graphite microcrystallites and makes the charging-discharging performance to go from bad to worse:

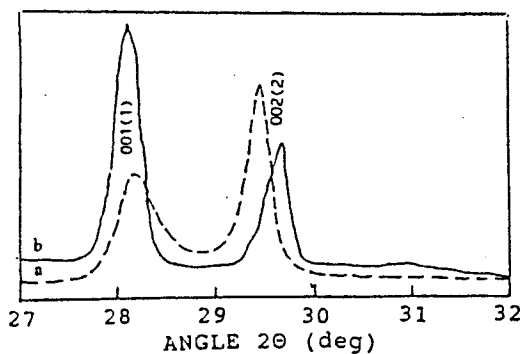


Fig. 2 The in-situ X rays diffraction spectrums of sample PC₃₀₀₀ and spmple NC₃₀₀₀ during charging to the mixed state of stage 1 and stage 2
(a:PC₃₀₀₀, b:NC₃₀₀₀)

Conclusion

To avoid the exfoliation of graphite microcrystallites during charging. The HTT_{max} and G can not be too high. The most appropriate criterion is to keep a small quantity of sp^3 bond in cokes, which can connect the carbon planes of graphite microcrystallites.

Reference

1. Zhou Zhi-cai, The Charging-discharging Pefor-mance of Heat Treated Petrdeum Coke Used as the Negative Electrode of the Lithium Ion Batterces. Hunan University, (PhD thesis)1997.