

EFFECT OF LIQUID PHASE OXIDATION ON THE REVERSIBLE PERFORMANCES OF HARD CARBON FOR LITHIUM ION BATTERY

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Introduction

Recently, a lot of studies on carbon materials were conducted very actively to find the best anode for lithium ion battery. As a candidate for the anode, hard carbon has been attracting many attentions because of its higher capacity than that of graphite. So far, various kinds of organic precursors were studied as a precursor of hard carbon, searching for higher performances. Oxidized synthetic isotropic pitches can be a good precursor. Synthetic isotropic pitch can maintain its disordered structure through carbonization step by converting the pitch thermosetting. However, the structure of obtained hard carbon is strongly affected by that of precursor pitch and cross-linking methods. It is known that the stacking height of carbon layer in the synthetic isotropic pitch decreases with the heat-treatment. Therefore, oxidation of pitch in the liquid phase can give more disordered structure in the oxidized pitch.

In the present study, precursor pitch was oxidized in a liquid phase to obtain more disordered structure and higher capacity.

Experimental

In the present study, three kinds of synthetic isotropic, which were provided from Mitsubishi Gas Chemical Co, were used as a precursor. The pitches were fused at 300°C in a pyrex tube and oxidized under air bubbling or fused at 220°C in an autoclave tube filled with pressurized O₂ gas. Pitch grains obtained by the liquid phase oxidation were further oxidized by air blowing (220°C, 1h, 0.5°C/min) to prevent them fusing in a carbonation step. The anodic performances of heat-treated hard carbons at 1000°C were investigated to find the effect of liquid phase oxidation on the performance.

Results

Figure 1 shows the effect of liquid phase oxidation on the performances of hard carbons from naphthalene isotropic pitch. The capacity of the hard carbons prepared from liquid-phase oxidized pitch was smaller than that of the carbon from solid-phase oxidized pitch. The capacity in the low potential region decreased significantly.

Figure 2 shows the effect of liquid phase oxidation on the performances of hard carbons from quinoline isotropic pitch. The capacity of hard carbon prepared from liquid-phase oxidized pitch was larger than that of the carbon from solid-phase oxidized pitch, showing a large capacity in the low potential region. Furthermore, the hard carbon prepared from the precursor pitch oxidized in a liquid phase by nitric acid also shows higher capacity than that of hard carbon prepared by solid phase oxidation.

Table 1 shows the elemental analyses and XRD parameters of precursor pitches oxidized by liquid-phase oxidation method and as-received pitches. Oxygen contents of precursor pitch from naphthalene isotropic pitch by liquid phase oxidation were smaller than that by solid phase oxidation. However, those from quinoline pitch become larger by liquid phase oxidation. Furthermore, from XRD analysis, liquid phase oxidation makes the quinoline pitch more disordered, although naphthalene pitch showed reverse results.

Discussion

Cross-linking of synthetic isotropic pitches converts them infusible at the carbonization stage, and gives hard carbon inherits the structure of precursor pitch. Therefore, the structure of hard carbon, which affects on their anodic performances, is strongly influenced by that of precursor pitch with solid-phase oxidation methods. Liquid-phase oxidation is conducted at fused state, where the pitch is cross-linked, and fixed in more amorphous state, to change the structure of hard carbon as well as that of precursor

pitch.

In the present study, naphthalene and quinoline isotropic pitches were liquid phase oxidized to obtain more disordered structure. However, the liquid phase oxidation of naphthalene isotropic pitch could not achieved the complete thermosetting. The capacity of the hard carbon prepared from liquid phase oxidized pitch became smaller. In contrast, quinoline isotropic pitch obtained more disorder structure by liquid phase oxidation as shown in the XRD patterns. Hence liquid-phase oxidation of quinoline pitch allowed more capacity enlarging the plateau in the low potential region. Incomplete stabilization of isotropic naphthalene pitch restores the some stacking, inhibiting the disordered structure in the carbon to lower the capacity. In contrast, complete stabilization of quinoline pitch provides higher capacity because of very disordered alignment in the liquid phase.

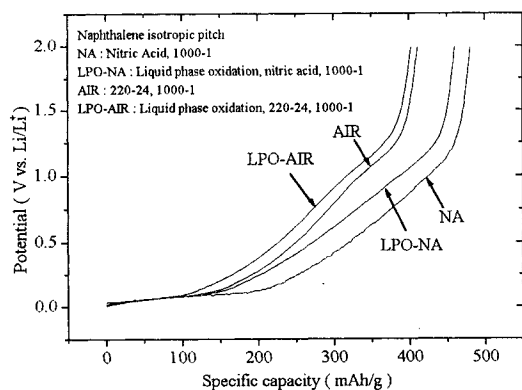


Figure 1. Effect of liquid phase oxidation on the performances of hard carbons from naphthalene isotropic pitch.

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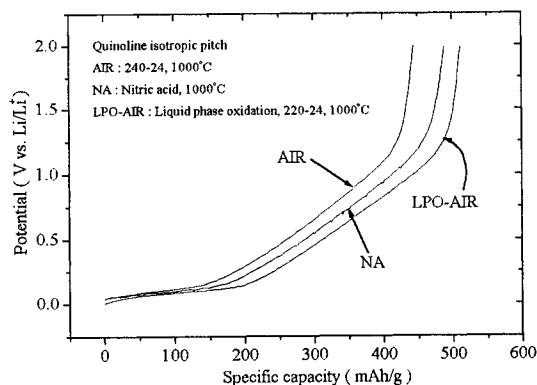


Figure 2. Effect of liquid phase oxidation on the performances of hard carbons from quinoline isotropic pitch.

Table 1. Elemental analyses and XRD parameters of precursor pitches.

Pitch	treatment	Elemental analyses (wt.%)				XRD (nm)	
		C	H	N	O	d(002)	Lc(002)
NIP	as-received	94.57	5.38		0.05	0.372	1.4
NIP	air-blowing	84	3.47		12.53	0.367	1.3
NIP	liquid-phase oxidation	93.83	4.54		1.63	0.36	1.7
NIP	autoclave	88.76	3.6		7.64	0.353	1.9
QIP	as-received	83.01	4.42	10.41	2.16	0.362	1.4
QIP	air-blowing	80.65	3.82	10.09	5.44	0.36	1.4
QIP	liquid-phase oxidation	75.58	3.18	10.3	10.94	0.379	0.9
QIP	nitric acid	66.68	3.1	7.05	23.17	0.356	1.3