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IMPORTANCE OF PRIMARY QUINOLINE INSOLUBLE IN BINDER PITCH FOR ANODE

Minoru Sakai[1], Yulong Wang[2], Takashi Fukuoka[2], and Hitomi Hatano[1]
[1]JFE Chemical Corporation, Chemical Research Laboratory, 1, Kawasaki-cho, Chuo-ku, Chiba 260-0835, Japan
[2]JFE Chemical Corporation, Headquarters, 2-17-4, Kuramae, Taito-ku, Tokyo 111-0051, Japan

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Abstract

Laboratory scale anodes were manufactured with a fixed coke and six binder pitches having different primary quinoline insoluble (QI) between 9 and 22%. Binder matrices were also made for CO_2 and air reactivity tests. Three of them were commercial products and the others were made experimentally, and none of them contained mesophase. Softening point of these pitches was around 110°C. The pitch with the largest amount of primary QI showed higher coking value, and thus it gave higher bulk density of baked anode. The increase in bulk density improved compressive strength. Electrical resistivity, which decreased with increasing bulk density, was not deteriorated by the larger amount of primary QI in pitch. Despite the high QI content, no acceleration of oxidation in CO_2 and air was observed in the binder matrix tests. These results showed that the pitch with high primary QI is more favorable as a binder pitch for anode.

Introduction

Quinoline insoluble (QI) material has often been used to evaluate the properties of binder pitch for anode. The QI is categorized in two types: primary QI, which comes from coke ovens, and secondary QI, which is generated in heat-treated pitches, and a part of secondary QI is observed as mesophase by polarization microscope [1]. Wombles et al. reported that heat-treated pitches, which include 3 to 10 % mesophase, had a negative effect on binder pitch and coke mixing since mesophase keeps pitches from infiltrating into pores in filler cokes [2]. On the other hand, primary QI is reported to play an important role to improve the baked anode properties.

Besides, the primary QI is reported to prevent mesophase from coalescence during baking anodes, which results in high mechanical strength and high anti-oxidation properties of anodes [3]. Wombles et al. tested pitches with different QI levels, which were prepared by blending two pitches, and reported that anode properties were favorable in the QI level less than 13 % [4].

Coking value (CV) is also one of the factors that improve the anode properties. As reported [5, 6], pitches having high softening point improved anode properties, since their increased CV led anode to be denser. However, increasing softening point of pitch is not a practical solution for improving anode properties, because pitches with high softening point require severe kneading conditions.

This paper will show the major impact of primary QI on anode properties through laboratory-scale anode tests with heat-treated binder pitches containing different primary QI levels from 9 to 22 %. These pitches were carefully prepared to avoid the mesophase under controlled heat-treatment, since heat-treatment is sometimes a cause for generating the mesophase, as reported [2]. Despite the QI level, pitches with similar softening point around 110 °C were chosen or prepared, since a binder pitch for anode normally has that softening point. The CO_2 and air reactivity was also examined for binder matrices in order to verify the influence of primary QI content.

Table 1. Properties of test pitches.

Properties	Method	P1	P2	P3	P4	P5	P6
Quinoline insoluble (%)	ISO 6731	9.2	12.1	13.1	15.0	17.0	22.4
Toluene insoluble (%)	ISO 6376	32.3	33.8	34.1	35.3	36.1	39.3
β resin (%)	QI-TI	23.1	21.7	21.0	20.3	19.1	16.9
Softening point, Mettler (°C)	ISO 5940	110.2	111.0	112.0	110.3	112.2	112.5
Coking value (%)	ASTM	59.0	60.9	61.3	62.0	62.1	62.4
Viscosity, 160°C (mPa·s)	ISO 8003	1872	2342	2213	1823	1816	1265
Ash (%)	ISO 8006	0.11	0.12	0.16	0.14	0.10	0.09
Na (ppm)	ISO 12980	2	81	34	38	51	9
Ca (ppm)	ISO 12980	60	79	76	54	63	42
Zn (ppm)	ISO 12980	130	150	160	111	125	90
Ni (ppm)	ISO 12980	1	1	1	<1	<1	<1
V (ppm)	ISO 12980	<1	2	1	1	1	<1
S (%)	ISO 12980	0.52	0.42	0.42	0.42	0.42	0.42

Experimental

Materials

Properties of test pitches are summarized in Table 1. P1, P2, and P3 are commercially available coal tar pitches manufactured by JFE Chemical Co. P4, P5, and P6 were prepared under heat-treatment in laboratory scale from coke-oven tars having high primary QI. The net QI did not increase in the laboratory scale pitches during distillation and heat-treatment, and minimal increase of the net QI was found in commercial pitches. In addition to it, no mesophase was found in optical microscope observation. Thus, QI in these pitches is defined as primary QI in this paper. The QI in test pitches was in the range between 9 to 22 %. Softening point was around 110°C, and coking value range varied from 59.0 to 62.4 %, which increased with the increasing of primary QI content. Alkaline metals in pitches, which are known as a catalyst for carbon oxidation, were less than 100 ppm.

A commercial calcined pitch coke was milled and sieved to adjust the particle size distribution of filler (Table 2). Specific surface area was 0.08 m^2/g for the coke in size 1 – 2 mm. Tapping density was 1.01 g/cm^3 for the coke in size 1 – 2 mm, and 1.35 g/cm^3 for the mixed coke. Impurities in coke are summarized in Table 3.

Table 2. Particle size distribution of filler.

Item	Sieve (mm)					
	<0.25	0.25-0.5	0.5-1	1-2	2-4	4-8
Anode(%)	35	13	13	13	13	13
Reactivity(%)	100	-	-	-	-	-

Table 3. Impurities in filler.

Ash(%)	Na(ppm)	Ca(ppm)	Zn(ppm)	Ni(ppm)	V(ppm)	S(%)
0.64	150	140	270	6	3	0.39

Preparation of test anode

Test anodes (70 mm in diameter and 100 mm in height) were prepared under the condition that is shown in Table 4. Baked anodes were cored to adjust the size for measurement of the compressive strength, the tensile strength, and the electrical resistivity.

Table 4. Preparation conditions of test anode.

Conditions	
Coke	Preheated, 200 °C
Mixing Time	30 min
Mixing Temperature	165 °C
Molding Temperature	120 °C
Pressure	45 MPa
Pressing Time	60 s
Baking Condition	
RT-1000 °C	10 °C/h
RT-1170 °C	25 °C/h
1170 °C	5 h hold
Coring size	
Compressive stregth	50mmϕ x 50mmh
Tensile strength	50mmϕ x 25mmh
Electrical resistivity	50mmϕ x 50mmh

Both compressive and tensile strengths were measured by using an automatic compression-testing machine (Shimadzu, Japan). Test pieces for compressive strength and tensile strength were loaded as shown in Figure 1.

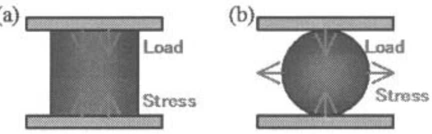

Figure 1. Schematic views of measuring mechanical strength: (a) compressive strength, and (b) tensile strength.

Tensile strength was calculated by the following equation (1):

$$\textit{Tensile strength } F = 2P/\pi dL \qquad (1)$$

where P is maximum load; d is diameter of test piece; L is thickness of test piece; and π is the circular constant.

Electrical resistivity was measured by using a four-probe resistivity meter.

Preparation of binder matrix

Binder matrices were prepared under the conditions presented in Table 5. Gas reactivity tests were carried out under the conditions in Table 6 for sieved binder matrices after pulverizing them. The moisture in the gas was removed in a column packed with $CaSO_4$, which was equipped before the reactor furnace. During heating and cooling, nitrogen gas was provided into the apparatus in order to prevent the samples from additional oxidation.

Table 5. Preparation conditions of binder matrix.

Conditions	
Coke Fine (<0.25 mm)	Preheated, 200 °C
Pitch : Filler	1 : 1 (by weight)
Mixing Time	30 min
Mixing Temperature	165 °C
Baking Condition	
RT-1000 °C	10 °C/h
RT-1170 °C	25 °C/h
1170 °C	5 h hold
Milling and sieving	1-2 mm
Sample quantity	3 g

Table 6. Conditions of gas reactivity.

Gas	Flow rate (L/min)	Temp.(°C)	Soaking time(h)
CO_2	1.0	960	5
Air	0.5	550	5

Results

Bulk density of anode

In Figure 2, bulk density of green anode is plotted against pitching ratio. The bulk density was dependent on the pitching ratio. The

QI content also changes the bulk density. For pitches with QI lower than 13 %, the maximum density obtained was 16 % pitching ratio, whereas pitches with QI more than 15 % reached maximum density at the pitching ratio over 18 %.

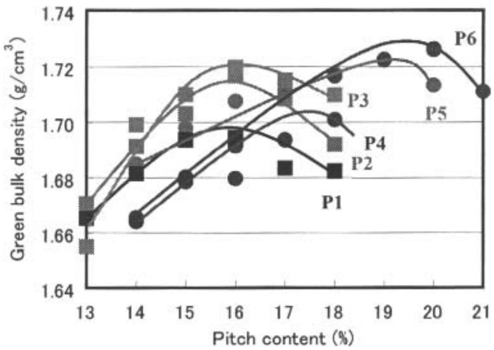

Figure 2. Bulk density of green anodes.

Pore volume was measured for the raw paste at the pitching ratio of 14 % as well as filler coke in order to find influence of QI on penetration of pitch into coke. As shown in Table 7, pore volume was quite low and almost the same for all the paste of pitch P1 to P6. The result shows that primary QI did not deteriorate the penetration of pitch because these pitches have almost the same softening point and higher QI pitches have lower viscosity.

Table 7. Pore volume of raw paste.

Sample	P1	P2	P3	P4	P5	P6	Coke
Pore volume (μL/g)	2.7	2.0	2.1	2.4	2.1	2.8	998
Viscosity, 160°C (mPa·s)	1872	2342	2213	1823	1816	1265	-

Figure 3 shows the correlation of the bulk density of baked anode and the pitching ratio. The bulk density shows maximum value at the pitching ratio between 13 and 14 % and decreases as pitching ratio increases. The highest density was obtained at 14 % pitching ratio with P6.

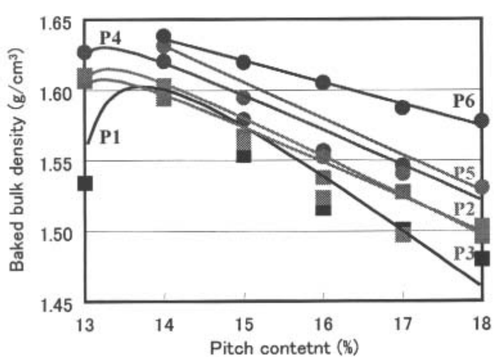

Figure 3. Bulk density of baked anode.

Shrinkage and in situ coking yield of anode

In Figure 4, shrinkage in diameter is plotted against pitching ratio. The shrinkage was dependent upon both pitching ratio and QI content in pitch.

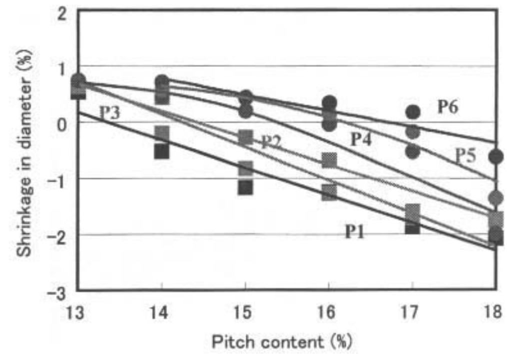

Figure 4. Shrinkage in diameter during baking.

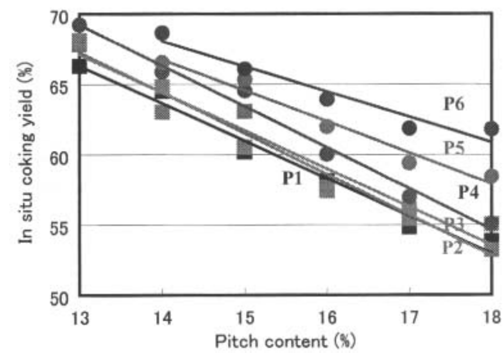

Figure 5. In situ coking yield during baking.

As shown in Figure 5, the pitching ratio and QI content are also play a role on in situ coking yield, which was calculated by the following equation (2):

$$\textit{In situ coking yield in situ} = 100 \times (w_3 - w_2) / (w_1 - w_2) \quad (2)$$

where w_1 is weight of green anode; w_2 is weight of coke; and w_3 is weight of baked anode.

P6 gave the highest shrinkage and the highest coking yield, which resulted in the highest bulk density of baked anode. (See Figure 3)

Mechanical properties

Dependence of compressive strength and tensile strength on pitching ratio is shown in Figures 6 and 7. The compressive strength shows maximum value at the pitching ratio between 13

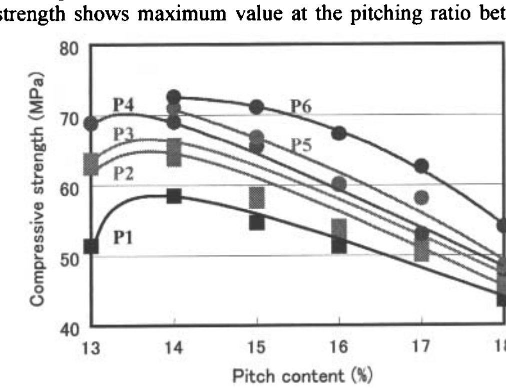

Figure 6. Compressive strength of baked anode.

and 14 %. The QI content distinguishes the correlation, and higher QI gives higher strength.

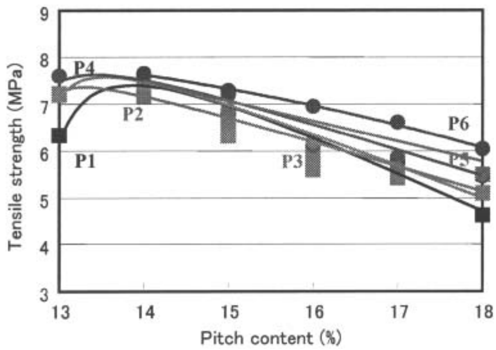

Figure 7. Tensile strength of baked anode.

The tensile strength also shows maximum value at the pitching ratio between 13 and 14 %. Although clear correlation between QI content and the strength was not found, P6, which contained the highest QI, obtained the highest strength.

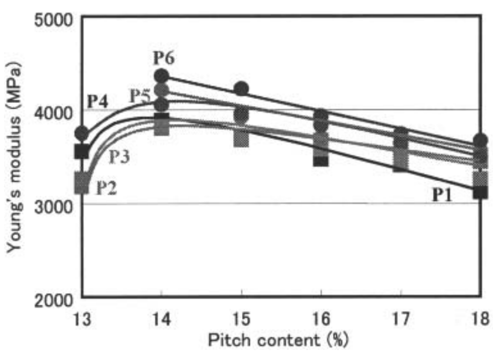

Figure 8. Young's modulus of baked anode (compressive).

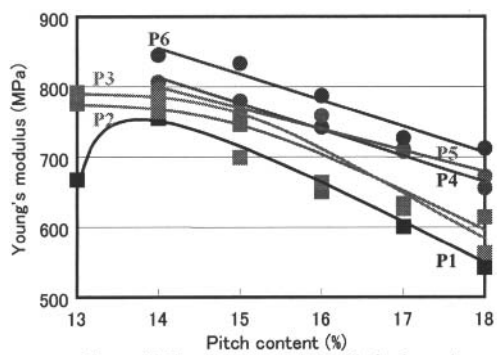

Figure 9. Young's modulus of baked anode (tensile).

Figures 8 and 9 show the correlation between Young's modulus (compressive and tensile) and pitching ratio. Similar correlation is found in both figures, the highest modulus being given at 14 % pitching ratio of P6 (the highest QI content).

Electrical properties

Figure 10 shows the correlation of electrical resistivity on pitching ratio. The electrical resistivity increases as pitching ratio increases and as the QI content decrease. The lowest resistivity was obtained at 14 % pitching ratio with P6.

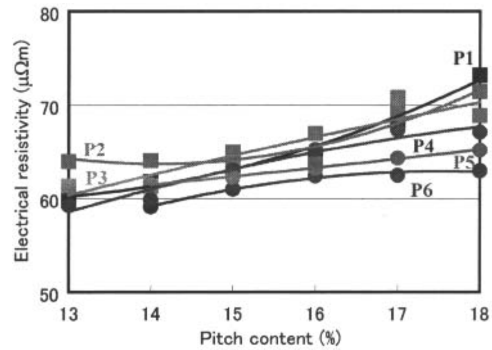

Figure 10. Electrical resistivity of baked anode.

Gas reactivity

Table 8 summarizes the weight loss in CO_2 and air using binder matrices. Since the weight loss in CO_2 was around 5 %, and that in air was around 10 % for the entire pitches, no correlation to the QI content was found in the test.

Table 8. Weight loss in gas reactivity test.

Sample	P1	P2	P3	P4	P5	P6	Coke
QI (%)	9.2	12.1	13.1	15.0	17.0	22.4	-
Ash	0.45	0.46	0.49	0.47	0.44	0.43	0.64
CO_2 (%/h)	4.8	4.6	4.4	4.7	4.7	4.6	2.1
Air (%/h)	10.9	9.7	9.9	10.8	10.1	9.6	1.7

Discussion

QI content and anode properties

As described above, both QI content and pitching ratio are the key factors for both mechanical and electrical properties of baked anode. In order to clarify the influence of QI, in situ coking yield

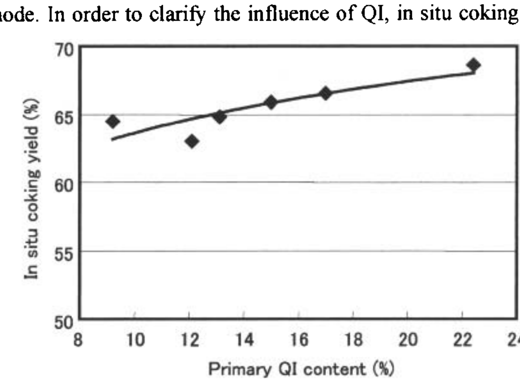

Figure 11. In situ coking yield vs. QI content (pitching ratio 14%).

and bulk density of baked anode at 14 % pitching ratio are plotted against QI content in Figures 11 and 12. These figures show that the high QI pitch gives high coking value, which leads to the high bulk density of baked anode.

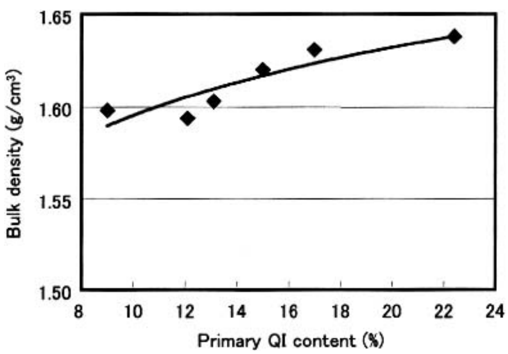

Figure 12. Bulk density vs. QI content (pitching ratio 14%).

Compressive strength and electrical resistivity are also plotted in Figures 13 and 14. As shown in Figure 13, high QI gives high compressive strength, which is achieved by high bulk density. Electrical resistivity, shown in Figure 14, is also influenced by QI. High QI pitch gives low resistivity.

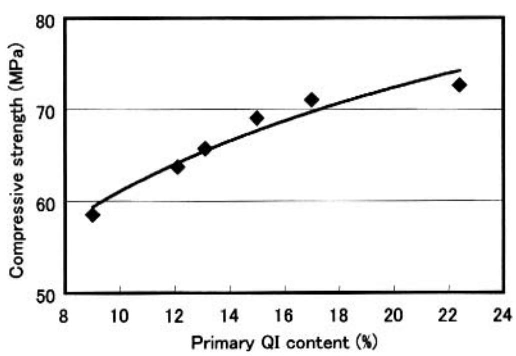

Figure 13. Compressive strength vs. QI content (pitching ratio 14%).

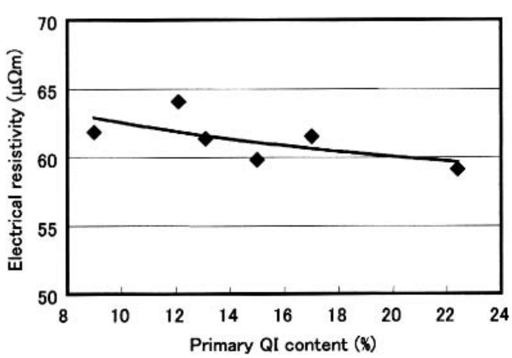

Figure 14. Electrical resistivity vs. QI content (pitching ratio 14%).

Bulk density and anode properties

As described above, the bulk density seems to be the critical factor for both mechanical and electrical properties. For better understanding, the correlation between these properties and bulk density of the entire pitches from P1 to P6 are shown in Figures 15, 16, and 17. Although small deviation is seen in the correlations, each figure shows the clear impact on the bulk density.

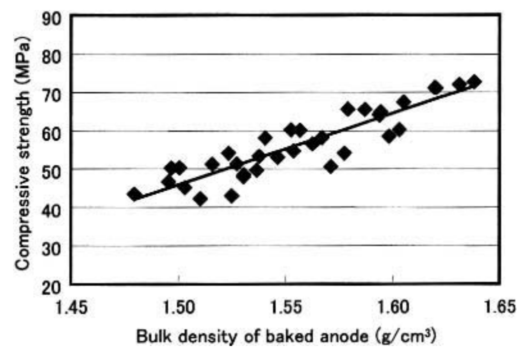

Figure 15. Compressive strength vs. bulk density.

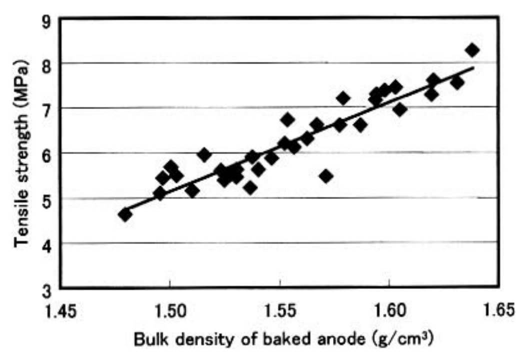

Figure 16. Tensile strength vs. bulk density.

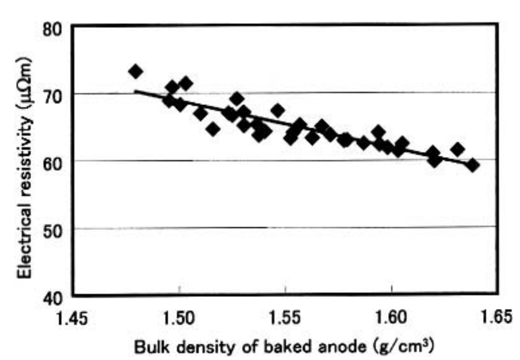

Figure 17. Electrical resistivity vs. bulk density.

As shown in Figure 18, where bulk density is plotted against the coking yield in situ, the coking yield is found to be the determining factor of the bulk density.

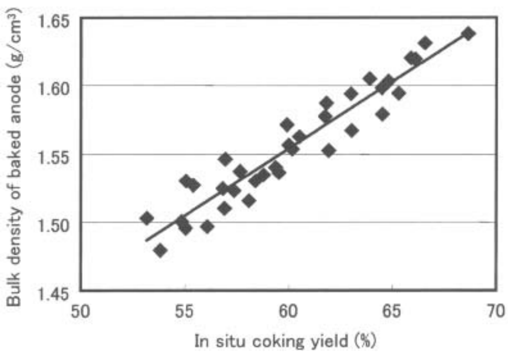

Figure 18. Bulk density vs. coking yield.

These results show that pitch having high QI content improves both mechanical and electrical properties, due to higher anode density that is formed.

Conclusions

Pitches with different primary QI level were examined in order to improve anode properties such as mechanical and electrical properties. The results are summarized as follows.

1. High primary QI does not deteriorate the penetration of pitch into coke during kneading.
2. High QI pitch provides higher compressive and tensile strength as well as Young's modulus, since it gives high density of baked electrode.
3. High QI pitch also improves the electrical resistivity
4. High QI pitch increases the anode bulk density, which improves both mechanical and electrical properties.
5. High QI does not influence gas reactivity in both air and CO_2 as long as the alkaline metal content is kept low.

Since the anode tests in this paper were only done in laboratory scale, it is necessary to verify these results on full-scale anodes.

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