Modified Resin for Aluminium Carbon Anode Preparation

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Abstract

This study focuses on resins, comparing the characteristics of various types and investigating how modification methods such as doping and heat treatment affect resin performance. The results show that the coking value of modified resin significantly improves – by approximately 15 % compared to unmodified resin – but viscosity also increases. With a reasonable selection of modifier ratios and effective balance between coking value and viscosity, modified resin can be used to enhance overall anode quality. Anodes prepared with modified resin as a binder under laboratory conditions met industrial application standards, with air reactivity residue rates above 70 % and resistivity at 57.11 μΩ·m, meeting anode usage requirements.

Keywords: Anode Recipe Modification, Resin

1. Introduction

Coal tar pitch is a complex mixture composed of highly condensed polyaromatic compounds [1, 2], characterized by high carbon content, low cost, wide availability, and good binding properties, making it widely used as a binder for aluminium carbon anodes. As a binder for anodes, coal tar pitch serves two main purposes: first, to ensure the plasticity and good formability of the paste; second, during calcination, it penetrates the aggregate and carbonizes between particles to form a mechanically strong and homogeneous anode [3–5]. However, due to the high polycyclic aromatic hydrocarbon (PAH) content in coal tar pitch, its use in anode production results in significant PAH emissions, which pose health risks to workers and worsen the working environment [6, 7]. Approximately 50 % of the total coal tar pitch market is consumed as binder for aluminium electrolysis carbon anodes. With increasingly stringent environmental policies and a downturn in the upstream coal tar processing market, China's coal tar pitch production has experienced fluctuations and decline.

In recent years, the implementation of the "dual carbon" goals – carbon peak and carbon neutrality – together with the impact of new energy industries such as lithium-ion batteries on the traditional petrochemical sector, as well as improvements in both processes and products by upstream raw material enterprises, has significantly affected the production and supply of coal tar pitch for carbon anodes, further impacting the quality of carbon anodes used in aluminium electrolysis and restricting the survival and development of the aluminium industry. To address the shortage of high-quality coal tar pitch, actively seeking suitable alternative raw materials and developing environmentally friendly binders for anode production is an effective solution.

Domestic and international research has mainly focused on high-softening-point coal tar pitch, and some studies have explored using biomass tar as a substitute [8]. Studies have shown that increasing coal tar pitch softening point from 110 °C to 170 °C can reduce PAH emissions by 57.3 %, significantly lowering environmental pollution [9, 10]. In terms of biomass pitch replacing coal tar pitch, studies investigated biomass pitch characteristics and its interaction with calcined coke [11], demonstrating that biomass pitch can coat coke particle surfaces and penetrate open pores, fulfilling the same role as coal tar pitch and enabling its use in anode production.

Research on eco-friendly anode binders has mainly focused on developing new types of binders. Shandong Shengquan Group has carried out studies on using conductive phenolic resin to replace traditional coal tar pitch as a binder in carbon anode production. This enables room-temperature mixing, shortens the calcination cycle, and results in pyrolysis products that are primarily water, carbon dioxide, and other non-toxic, harmless substances. However, due to the insulating nature of resins, the electrical conductivity of the resulting anodes remains inferior to traditional ones, and storage difficulties persist. Despite this, resin has significant advantages in anode applications, enabling environmentally friendly production and room-temperature processing, reducing calcination time, and improving production efficiency.

This paper uses resin as a raw material to prepare resin-based binders for anode production through modification methods. It analyses how binder performance varies with modification conditions and evaluates the feasibility of using resin-based binders in anode manufacturing.

2. Experiment

2.1 Experimental Materials

Phenolic resin was selected as the experimental raw material. Its basic properties and microelement content were analysed. Table 1 shows the coking value, ash content, and volatile content of coal tar pitch and phenolic resin. As seen in Table 1, there are notable differences in base properties between the two: the coking value of coal tar pitch is 57.43 %, while that of phenolic resin is 51.71 %; ash content of coal tar pitch is 0.15 %, compared to 0.31 % for phenolic resin; volatile content is 54.9 % and 63.3 %, respectively. Although phenolic resin meets the ash content requirements, its coking value is lower than that of coal tar pitch. Therefore, its suitability as an anode binder may be improved through modification.

Table 1. Basic properties of phenolic resin.

Binder Type	Coking Value / %	Ash Content / %	Volatile Matter / %
Coal Tar Pitch	57.43	0.15	54.9
Phenolic Resin	51.71	0.31	63.3

Table 2 presents the microelement contents of coal tar pitch and phenolic resin. As shown, phenolic resin has overall lower microelement levels and basically meets the requirements for anode binder use. Most element concentrations in phenolic resin are lower than in coal tar pitch, except for sodium, which reaches $3350 \cdot 10^{-6}$, likely related to the production process of phenolic resin. Further experiments are needed to assess its impact on anode quality.

Table 2. Chemicals in phenolic resin.

	S/%	V/10^{-6}	Na/10^{-6}	Ca/10^{-6}	Si/10^{-6}	Fe/10^{-6}	Ni/10^{-6}
Coal Tar Pitch	0.66	0	280	220	170	210	0
Phenolic Resin	0.048	25	3350	15	15	7	6

During carbon anode mixing, binder viscosity is typically controlled between 300–600 mPa·s, ensuring good flowability and effective wetting of coke particles. This helps form high-density, low-porosity, and structurally uniform anodes. Tables 3 and 4 show the dynamic viscosity of coal tar pitch and phenolic resin. As observed, the suitable mixing temperature for coal tar pitch in anode production is around 185–190 °C, where viscosity falls within 300–600 mPa·s. Phenolic resin, on the other hand, reaches this viscosity range at a lower temperature of 55–65 °C, indicating potential for reducing mixing temperatures and thereby lowering production costs when used in anode manufacturing.

Table 3. Viscosity of phenolic resin.

Temperature / °C	Viscosity / mPa·s
45	1327.4
50	893.6
55	617.3
60	439.7
65	324.6

Table 4. Viscosity of coal tar pitch.

Temperature / °C	Viscosity / mPa·s
175	1140.1
180	847.3
185	620.8
190	453.1
195	357.4

The better the binder's wettability toward calcined coke, the more effectively it can wet the coke powder, ensuring the paste can be moulded into a high-density, low-porosity, and structurally uniform anode product. Table 5 shows the wettability results of phenolic resin and coal tar pitch toward calcined coke. As shown in Table 5, the wettability of coal tar pitch to calcined coke is 1.34, while that of phenolic resin is 1.85, significantly higher than that of coal tar pitch. The wettability of phenolic resin meets the requirements for anode production and is superior to that of pitch, which means that under the same production conditions, using resin as a binder can reduce production costs, improve paste uniformity, and effectively enhance overall anode quality.

Table 5. Wettability to calcined coke.

Material	1#	2#	3#	Average
Coal Tar Pitch	1.36	1.33	1.34	1.34
Phenolic Resin	1.87	1.82	1.84	1.85

2.2 Modification of Phenolic Resin

In this study, modifiers T and P were used to modify phenolic resin.

(1) T-modified phenolic resin
Based on molar ratios, T was added at 0.01, 0.02, 0.03, 0.04, and 0.05 proportions. The modification was conducted at 90 °C, with a stirring speed of 230 rpm for 60 minutes.

(2) P-modified phenolic resin
Based on molar ratios, P was added at 0.01, 0.02, 0.03, 0.04, and 0.05 proportions. The modification was conducted at 90 °C, with a stirring speed of 230 rpm for 30 minutes.

2.3 Anode Preparation

Anode preparation followed a 6–3–1 formula: 6–3 mm particles accounted for 26 % of dry materials, 3–1 mm for 19 %, 1–0 mm for 17 %, fine powder for 38 %, and binder for 17.5 % of the total.

Using pitch as the binder: raw materials were dry mixed for 5 min, wet mixed for 25 min, mixing temperature set at 175 °C, moulding temperature at 130 °C, moulding pressure at 60 kN, and pressure holding time of 3 min.

Using modified resin as the binder: due to the superior wettability of modified resin compared to pitch, a shorter wet mixing time was sufficient. Dry mixing was set to 5 min, wet mixing to 10 min, mixing temperature at 135 °C, moulding temperature at 115 °C, moulding pressure at 60 kN, and pressure holding time of 3 min.

Anode calcination curve: 2 hours from room temperature to 250 °C, 15 hours to 650 °C, 6 hours to 950 °C, 4 hours to 1160 °C, and held at 1160 °C for 5 hours.

3. Experimental Results and Discussion

3.1 Performance Analysis of Modified Resin

（1）Coking Value of Modified Resin

Table 6 shows the changes in coking values of phenolic resin modified with different types and amounts of modifiers. As shown in Table 6, the coking value of phenolic resin increased after P-modification, with the highest value of 58.2 % achieved when P was added at a ratio of 0.02. For T-modified resin, the highest coking value of 58.6 % was reached when T was added at 0.01.

The essence of increasing the coking value of resin lies in raising the proportion of high molecular weight compounds; the lower the content of light components and the longer the molecular chains, the higher the coking value. The addition of modifiers acts like a “seed,” promoting the bonding of small molecular compounds within phenolic resin to form polymers. In other words, the modifier helps the small molecules chelate around it, increasing the proportion of high molecular compounds and thus enhancing the coking value. Excessive addition of modifier can hinder the formation of chelates, reducing the amount of high molecular chelates in the modified resin and ultimately lowering its coking value.

Table 6. Coking value of modified phenolic resin.

Modified Resin	Coking Value / %	Modified Resin	Coking Value / %
P-0	51.7	T-0	51.7
P-0.01	56.1	T-0.01	58.6
P-0.02	58.2	T-0.02	54.4
P-0.03	54.3	T-0.03	55.9
P-0.04	55.8	T-0.04	56.1
P-0.05	55.7	T-0.05	56.4

（2）Viscosity of Modified Resin

The modified resins with the highest coking values –P–0.02 and T–0.01 – were selected for viscosity analysis. Tables 7 and 8 present the viscosity indices of the two modified resins. As seen, the viscosity of phenolic resin increases after modification due to the formation of high molecular compounds from small molecules through chelation, which reduces fluidity and increases viscosity. The optimal mixing temperature for anode production ranges from 115–135 °C.

Table 7. Viscosity of P–0.02 modified resin.

Temperature / °C	Viscosity / mPa·s
95	2986.4
105	1536.8
115	987.8
125	621.4
135	394.8

Table 8. Viscosity of T–0.01 modified resin.

Temperature / °C		Viscosity / mPa·s
95		2937.4
105		1438.2
115		892.4
125		531.8
135		371.4

3.2 Performance Analysis of Anodes Prepared with Modified Resin

The properties of calcined anodes were characterized by thermal conductivity, resistivity, bulk density, compressive strength, air reactivity, CO_2 reactivity, and microelement content, with all tests conducted in accordance with standard methods.

Table 9 shows the performance metrics of anodes prepared using the same calcined coke and formulation but different binders. As shown in Table 9, green anodes made with modified resin had slightly higher green body density compared to those made with pitch; however, the calcination loss rate for the modified resin anodes was generally higher than that for pitch-based anodes, which may be related to the higher content of light components in the modified resin.

As shown by the calcined anode bulk density, anodes made with modified resin exhibited higher density than those made with pitch, which may be attributed to the resin's improved wettability and increased coking value.

From the resistivity data, pitch-based anodes showed 61.6 μΩ·m, while modified resin-based anodes had 57.1 μΩ·m, indicating better conductivity with modified resin.

Regarding ash content, modified resin-based anodes showed increased ash, possibly due to the higher ash content in the modifier itself. Both types of anodes had comparable true densities and met application requirements. The thermal expansion coefficients of all samples were below 4, meeting usage and industry standards.

As for reactivity, the air reactivity residue rate of P–0.02 resin anodes was 75.14 %, higher than the 65.29 % of pitch-based anodes, indicating superior performance. CO$_2$ reactivity showed minimal difference, suggesting that modified resin outperforms pitch overall and can be a viable binder substitute.

From the microelement analysis of the anodes, it can be seen that, apart from the relatively high sodium content, the contents of other elements were generally within the required range and met the usage requirements. The elevated sodium content was related to the inherently high sodium content of the phenolic resin.

Table 9. Anode performance indices.

Test Item		**Pitch–Based Anode**	**P–0.02 Modified Resin Anode**	**T–0.01 Modified Resin Anode**
Green Apparent Density, g·cm^3		1.59	1.60	1.60
Baking Loss Rate, %		5.81	8.08	8.16
Baked Apparent Density, g·cm^3		1.51	1.54	1.53
Spec. Electrical Resistivity, μΩ·m		61.6	57.11	60.95
Ash Content, %		0.28	0.44	0.45
Real Density, g,cm^3		2.08	2.06	2.06
Coeff. of Thermal Expansion, 10^{-6}/K		3.09	3.33	3.41
Thermal Conductivity, W/K·m		2.06	3.85	3.97
Compressive Strength, MPa		24	36	35
Air Permeability, nPm		2.55	1.15	1.37
Air Reactivity, %	Loss	24.83	19.52	18.97
	Dust	9.88	5.34	7.74
	Residue	65.29	75.14	73.29
CO$_2$ Reactivity, %	Loss	4.62	6.49	7.18
	Dust	0.09	0.73	0.55
	Residue	95.29	92.78	92.77
S, %		2.48	2.16	2.22
V, ppm		340	350	350
Na, ppm		100	530	520
Ca, ppm		220	190	160
Si, ppm		280	190	190
Fe, ppm		380	310	300
Ni, ppm		200	180	180

4. Conclusions

This study focused on phenolic resin, investigating its modification and the performance of anodes made using the modified resin. The conclusions are as follows:

(1) When the molar ratio of modifier P is 0.02, the modification effect is optimal. The coking value of the modified phenolic resin increases significantly, by approximately 15 % compared to the unmodified resin.

(2) The viscosity of the modified phenolic resin increases. To meet application requirements, the heating temperature must be approximately doubled compared to the unmodified resin.

(3) Under laboratory conditions, anodes prepared using modified resin meet industrial standards. Their air reactivity residual rates exceed 70 %, and the resistivity is 57.11 μΩ·m, meeting the performance requirements for anodes.

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