

Digital characterization and mathematic model of sodium penetration into cathode material for aluminum electrolysis

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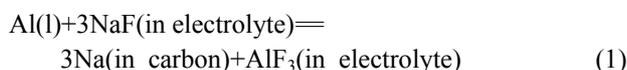
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Abstract: The sodium expansion curves of semi-graphitic cathode and TiB₂/C composite cathode with different TiB₂ contents were measured with the improved Rapoport-Samoilenko apparatus. The mathematic model of the sodium expansion was deduced on the basis of the experimental results. The sodium expansion parameter (a) and penetration rate factor (Q), were introduced into the model. The model was validated with the experimental sodium expansion curves self-measured and reported. The results show that the variation tendency of the sodium expansion parameter (a) and penetration rate factor (Q) is consistent with that of the experimental curves. The model is capable of not only conveniently judging the cathode quality, but also favorably establishing a unified standard of the resistance to sodium penetration of cathode.

Key words: aluminum electrolysis; cathode; sodium expansion; modeling; characterization

1 Introduction

During aluminum electrolysis metallic sodium migrates into the carbon structure according to the following reaction [1–2]:



or



The main transport mechanism for the sodium penetration into the carbon material is probably by diffusion of sodium absorbed in micropores. However, vapor transport in the gas phase through macropores or transport by surface diffusion in the pores may be important as well for the sodium penetration. Anyway, the absorbed or intercalated sodium leads to carbon swelling (i.e. sodium expansion) which causes creep deformation and material damage, and subsequently shortens the cathode life. In early year, RAPOPORT and SAMOILENKO [3] reported a simple method to measure the sodium expansion of carbon materials due to sodium penetration. Since then, various modifications of the Rapoport-Samoilenko apparatus have been proposed [4–8]. The sodium expansion of carbon cathode is related to the following factors [9–12], such as current density, graphite content (carbon cathode composition),

external pressure, cryolite ratio of electrolyte, temperature, and test apparatus.

The sodium expansion is a quantitative reflection of sodium penetration into carbon cathode. On the other hand, too fast penetration rate or too much sodium expansion may result in material damage, and sodium penetration rate has a greater impact on the cathode material failure. So both the penetration rate and sodium expansion should be involved to evaluate the extent of sodium penetration into carbon cathode since the latter only indicates the equilibrium of sodium penetration. Sodium expansion curve, however, is only a graph measured in laboratory. It is not convenient for charactering the performance of materials, or comparing among the cathode materials. Therefore, in this work, a mathematic model of sodium expansion with the electrolysis time was put forward on the basis of the experimental data, and the digital characterization for the resistance to sodium penetration into cathode was established as well.

2 Experimental

A modified Rapoport-Samoilenko apparatus was used to measure the sodium expansion of semi-graphitic cathode block and TiB₂/C composite cathode materials with different TiB₂ contents, as shown in Fig.1. The test system was placed in a vertical tube furnace and held at

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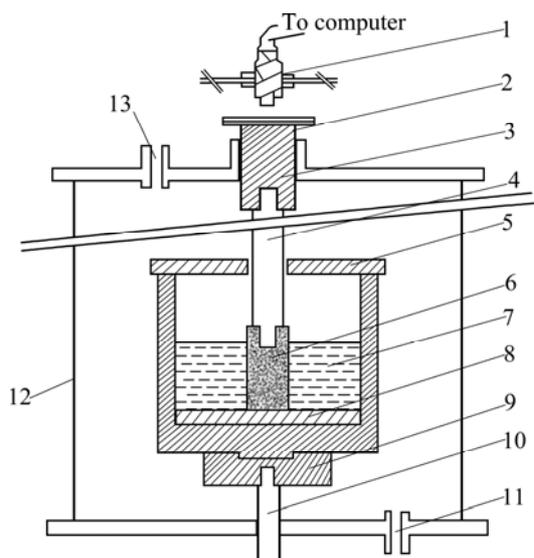


Fig.1 Apparatus for sodium expansion of cathode materials: 1—Transducer; 2—Gas outlet; 3—Graphite piston; 4—Steel rod; 5—Corundum lid; 6—Test specimen (Cathode); 7—Cryolite melt; 8—Corundum disk; 9—Graphite crucible (Anode); 10—Anode steel rod; 11—Gas inlet; 12—Furnace; 13—Gas outlet

980 °C under a nitrogen atmosphere. A constant current was provided during electrolysis by an SCR-1 DC power supply. The cylindrical cathode specimen was immersed into the cryolite electrolyte, and the immersion depth was 50 mm. The electrolysis was performed at a current density of 0.5 A/cm² and temperature of 980 °C. The electrolyte was composed (mass fraction) of 14.5% NaF, 72.5% Na₃AlF₆, 5.0% CaF₂, 8.0% Al₂O₃, the cryolite ratio was 4, and the test time was 1.5 h.

The sodium expansion was calculated by the following equation:

$$\rho = \Delta L / L \tag{3}$$

where ρ is the sodium expansion, %; ΔL is the linear displacement of samples due to sodium penetration and is detected automatically by a computer through a transducer; and L is the depth immersed into bath.

3 Results and discussion

3.1 Sodium expansion of cathode

Under the same electrolysis condition, Figs.2 and 3 show the sodium expansion curves of semi-graphitic cathode and TiB₂/C composite cathode with different TiB₂ contents. In Figs.2 and 3, SG is semi-graphitic cathode sample, and TC₀–TC₆₀ are TiB₂/C composite coatings with TiB₂ contents of 0–60% on semi-graphitic cathode, respectively.

As can be seen from Figs.2 and 3, the sodium expansion curves show a parabolic shape. The growth rate of sodium expansion, i.e. the sodium penetration rate,

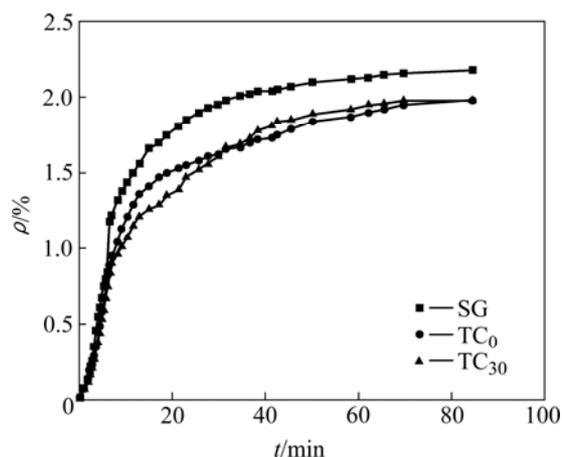


Fig.2 Sodium expansion curves of cathode samples during electrolysis

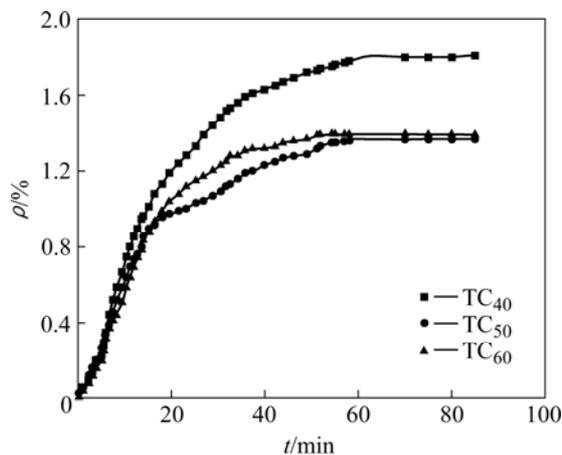


Fig.3 Sodium expansion curves of TiB₂/C samples with different TiB₂ contents during electrolysis

increases faster at the beginning of the electrolysis, then decreases gradually, and finally keeps unchanged. The sodium penetration rate of sample SG is the fastest, and its equilibrium sodium expansion is also the largest. The penetration rate of sample TC₀ sample is slightly smaller than that of sample SG, but the equilibrium sodium expansion approaches that of sample SG after electrolysis for 1.5 h. The sodium expansion rates of samples TC₃₀, TC₄₀, TC₅₀, and TC₆₀ are smaller than that of sample SG. With the increase of TiB₂ content, the penetration rate of TiB₂/C composite cathodes gradually slows down, and the equilibrium sodium expansion gradually decreases as well. The equilibrium sodium expansion of sample TC₆₀ is the smallest, which is only around 60% of SG expansion.

3.2 Mathematic model

The sodium expansion of cathode material is a quantitative reflection of sodium penetration into material. The sodium expansion data are measured, which consist of curves of sodium expansion with

electrolysis time (see Figs.2 and 3). The curves reflect not only the quantity of sodium expansion but also the sodium penetration rate.

Based on the measured curves of sodium expansion, some parameters to characterize the sodium penetration performance of cathode materials were found.

The following functions to describe the parabolic curves of sodium expansion were used,

$$y = a \exp(-b/x) \quad (4)$$

where y represents $\Delta L/L$, x represents time (t), and a and b are parameters.

When $x \rightarrow \infty$, $y \rightarrow a$; when $x \rightarrow 0$, if $b > 0$, then $y \rightarrow 0$, and y increases with the increase of x . In order to determine the parameters a and b , both sides of Eqn.(4) are taken the natural logarithm.

$$\ln y = \ln a - \frac{b}{x} \quad (5)$$

According to Eqn.(5), the curve of $\ln(\Delta L/L)$ versus t can be drawn, and the parameters a and b can be calculated through the intercept and slope of the curves.

When $t=0$, sodium expansion $\Delta L/L=0$. The boundary condition of Eqn.(4) is $x \rightarrow 0$, $y \rightarrow 0$, and not $x=0$, $y=0$. In order to avoid the initial point (0, 0), only the dots in the sodium expansion curves are adopted, rather than all dots collected by computer, which have no influence on the changing law of sodium expansion. The fitting curves were applied to the measured curves of samples SG, TC₀, TC₃₀, TC₄₀, TC₅₀, and TC₆₀. The corresponding equations are obtained as follows:

$$\ln\left(\frac{\Delta L}{L}\right) = 0.847 - \frac{5.497}{t} \quad (6)$$

$$\ln\left(\frac{\Delta L}{L}\right) = 0.847 - \frac{9.769}{t} \quad (7)$$

$$\ln\left(\frac{\Delta L}{L}\right) = 0.845 - \frac{14.335}{t} \quad (8)$$

$$\ln\left(\frac{\Delta L}{L}\right) = 0.815 - \frac{14.148}{t} \quad (9)$$

$$\ln\left(\frac{\Delta L}{L}\right) = 0.461 - \frac{9.946}{t} \quad (10)$$

$$\ln\left(\frac{\Delta L}{L}\right) = 0.346 - \frac{10.194}{t} \quad (11)$$

The parameters a and b from the equations above are listed in Table 1. As we can see, the sodium penetration rate is related to both a and b . Given that Q equals a/b , a new parameter Q is calculated and also listed in Table 1.

From the discussion above, the equilibrium sodium expansions of TiB₂/C composite cathodes are reduced with the increase of TiB₂ content, and so are the penetration rates. As can be seen in Table 1, a and Q show the trend of decrease with the increase of TiB₂ content, which match with the experimental curves. As

Table 1 Characterization of sodium expansion by parameter a and factor Q

Sample	a	b/min	Q/min^{-1}
SG	2.332	5.497	0.424
TC ₀	2.331	9.679	0.239
TC ₃₀	2.327	14.335	0.162
TC ₄₀	2.258	14.148	0.160
TC ₅₀	1.585	9.946	0.159
TC ₆₀	1.413	10.194	0.139

can be known from Eqns.(4) and (5), $t \rightarrow \infty$, $\Delta L/L \rightarrow a$, which indicates that a is the equilibrium value of sodium expansion under a certain electrolysis condition. The change trend of a in Table 1 is basically in concordance with the equilibrium sodium expansion measured in Figs.2 and 3. Apparently, the equilibrium expansion of sample SG is the largest, which declines gradually with the increase of TiB₂ content, and that of sample TC₆₀ is the minimum. Parameter Q is related to sodium penetration rate and named as the sodium penetration rate factor, which reflects the sodium penetration rate during the electrolysis from beginning to penetration equilibrium. Obviously, it is reasonable to characterize the resistance to sodium penetration of cathode materials with parameter a and factor Q .

Parameter a and factor Q can not only characterize quantitatively the resistance to sodium penetration, but also get some experimental information which is difficult to get directly from the sodium expansion curve. From Table 1, it can be seen that parameter a of sample SG is almost the same as that of sample TC₀, that is, the equilibrium sodium expansions of the two samples are basically the same. But the values of factor Q of the two samples are quite different. The factor Q of sample TC₀ is significantly less than that of sample SG, which indicates that the coating with no TiB₂ cannot change the equilibrium sodium expansion of sample SG, but it can reduce the sodium penetration rate. Parameter a of sample TC₄₀ is larger than that of sample TC₅₀, but their factors Q are almost the same, which indicates that the increase of TiB₂ content at this level can reduce the equilibrium sodium expansions of TiB₂/C composite cathodes, but cannot decrease the sodium penetration rate. An excellent resistance to sodium penetration into cathode material, should be the material with low equilibrium sodium expansion and penetration rate, i.e. small parameter a and factor Q . In Table 1, parameter a and factor Q of sample TC₆₀ are the smallest.

3.3 Validation of digital characterization

Fig.4 shows sodium expansion of two amorphous

carbon materials under the same electrolysis condition measured by SØRLIE and ØYE [13]. A series of dots were taken in Fig.4, and the data $(t_i, (\Delta L_i))$ ($i=1, \dots, 12$) were obtained. According to Eqn.(5), the fitting curves of sodium expansion for materials A and B are given as follows, respectively:

$$\ln(\Delta L) = 1.072 - \frac{13.420}{t} \quad (12)$$

where parameter a is 2.921, and factor Q is 0.218 min^{-1} .

$$\ln(\Delta L) = 0.745 - \frac{16.250}{t} \quad (13)$$

where parameter a is 2.106, and factor Q is 0.130 min^{-1} . It can be seen that a and Q of material B are smaller than those of material A. This illustrates that the equilibrium sodium expansion and penetration rate of material B are less than those of material A, that is, the resistance to sodium penetration of material B is better than that of material A. This reflects the information of the measured curves. Therefore, it is a good way to characterize the resistance to sodium penetration into cathode material by parameter a and factor Q .

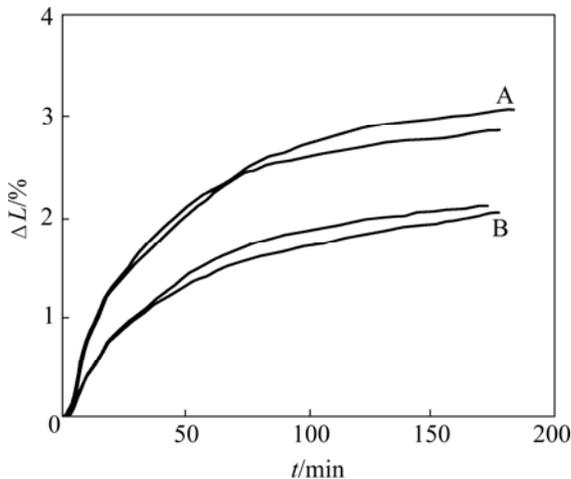


Fig.4 Sodium expansion of two amorphous carbon materials during aluminum electrolysis

WIKENING [14] added non-carbonaceous additives to carbon cathode in order to improve the resistance to sodium penetration of material. Fig.5 shows the sodium expansion curves of carbon cathode with adding different FeSi25 contents. Four curves in Fig.5 are fitted and the following equations are obtained by Eqn.(5):

$$\ln\left(\frac{\Delta L}{L}\right) = 0.031 - \frac{6.583}{t} \quad (14)$$

$$\ln\left(\frac{\Delta L}{L}\right) = 0.389 - \frac{25.110}{t} \quad (15)$$

$$\ln\left(\frac{\Delta L}{L}\right) = 0.283 - \frac{28.800}{t} \quad (16)$$

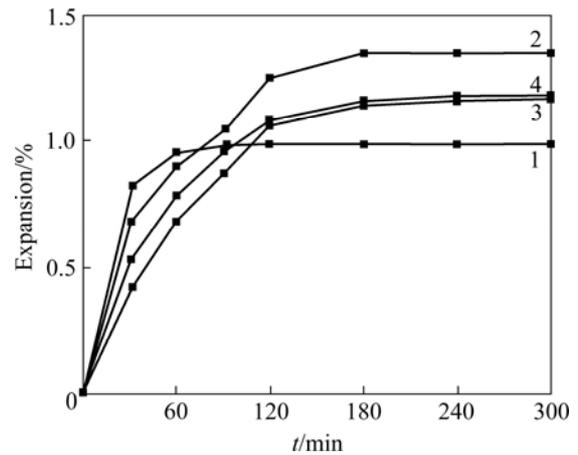


Fig.5 Rapoport expansion of bench-scale cathode blocks with addition of different FeSi25 contents: 1—0%; 2—5%; 3—10%; 4—15%

$$\ln\left(\frac{\Delta L}{L}\right) = 0.310 - \frac{38.060}{t} \quad (17)$$

Parameter a and factor Q are listed in Table 2. As can be seen in Table 2, parameters a of samples 2, 3 and 4 with addition of FeSi25 5%, 10% and 15%, respectively, are larger than that of sample 1 without addition of FeSi25, while their factors Q are smaller than that of sample 1, which means that the penetration rate is reduced with addition of FeSi25 even though the equilibrium sodium expansion increases with the increase of FeSi25. But, factor Q appears the minimum value when 10% FeSi25 is added, that is, the penetration rate of material with adding 10% FeSi25 is the minimum. This is consistent with the information reflected by the measured curves. Again, it shows that it is convenient to characterize the sodium penetration performance of cathode material by parameter a and factor Q .

Table 2 Sodium penetration resistance of cathode block with different FeSi25 contents

Sample	a	Q/min^{-1}
Sample 1	1.031	0.157
Sample 2	1.481	0.059
Sample 3	1.331	0.036
Sample 4	1.361	0.046

4 Conclusions

(1) On the basis of the experimental results, mathematic model $y=a\exp(-b/x)$ of the sodium expansion is deduced, and parameter a and factor Q , which can numerically characterize the sodium expansion and penetration rate of material respectively, are introduced into the model.

(2) It is a good way to characterize the sodium penetration performance of cathode material by parameter a and factor Q through validation. It can not only conveniently judge the quality of carbon block as cathode and avoid the inconvenience to comparing the sodium penetration performance of different cathodes by the graph, but also favorably establish a unified standard for the resistance to sodium penetration of cathode.

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