DETERMINATION OF KINETIC PROPERTIES OF CARBON FLUORINATION PROCESS

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The possibility of amorphous carbon fluorination at moderate temperatures was determined. An analytical method of kinetic properties determination of fluorination process at 70–130 °C was offered. The equation which describes the kinetics of the fluorination process and activation energy were determined.

Key words: fluorination, amorphous carbon, kinetics, accumulators

Nowadays, the world becomes more mobile. The accumulator’s quality and capacity are fully determined by electrochemical system. The most perspective material for current production in such system is Li/(CFₓ)ₙ, where “x” can change from 0,1 to 1,2. Fluorocarbon in this scheme becomes a cathode. System Li/(CFₓ)ₙ has many advantages: high voltage (2,7–3,6 V), specific energy (700 w*h/dm³) [1], the lowest self-discharge (~1% per year), more safety and reliability during keeping and transportation.

The world’s fluorocarbon market is far from saturation, because accumulators production gradually switches over to lithium electrochemical systems. Russian market size of fluorinated carbon was only 15 tons in 2011. Therefore, it is being planned to work out and implement new resource-effective technology of fluorocarbon production. For creation of trial installation first of all it is necessary to study kinetics of the process.

There are various methods of carbon fluorination, for instance, by the mixture of fluorine and nitrogen gases at temperatures of 320-500 °C [1] or fluorination with catalyst at 100 °C [2]. There are works describing fullerene [3] and carbon nanotubes [4,5] fluorination. However, there is no research describing amorphous carbon fluorination. In present work the kinetics of heterogeneous reaction between fluorine and amorphous carbon at temperatures below 130 °C was determined.

Carbon was represented by ungeometrical particles which had bulk weight (0,79±0,05) g/cm³ and real density 1,4 g/cm³. Its classification is presented in figure 1, the amorphous carbon particles are shown in figure 2.
Before the research all the surfaces of experimental installation were passivated by the mixture of fluorine and argon gases. Then, the sample holder was hung up by the fiber to weigh sensor. One gram of the carbon was put into sample holder. Fluorination was carried out at temperature range from 343 K to 403 K during 1.5 hour. Fluorine volume flow rate was \( V_f = 4.2 \) l/h, argon volume flow rate was \( V_a = 37.8 \) l/h.

Studying of carbon fluorination process was carried out in the nickel vertical reactor. The pilot installation was developed from corrosion-resistant materials in the fluor environment: nickel, stainless steel, copper. Fluoroplastic - 4 was applied as a sealing material.

Fluorine was received from the fluor electrolyzer. The fusion reaction occurred in the vertical reactor where carbon contacted with gaseous fluorine. Temperature monitoring in volume of reaction was carried out by chromel-kopel thermocouple. Temperature control was implemented with personal computer which showed the dependence of temperature on time. Weight measurement was implemented with inductive non-contact sensor which signal was brought to the monitor as dependence of sample weight on time.

The fractional conversion dependence on temperature and time was introduced in figure 3.

![Figure 1. Carbon particles classification](image1)

![Figure 2. Carbon particles photo](image2)

![Figure 3. The fractional conversion dependence on temperature and time](image3)

Figure 3 shows that the maximum fractional conversion value was achieved at 343 K, the minimum fractional conversion value was achieved at 403 K.

For further mathematical treatment of the received data for kinetics parameters determination three models were used:
Reducing sphere equation:

$$1 - (1 - \alpha)^{\frac{1}{3}} = k_t$$

Yander equation:

$$1 - ((1 - \alpha)^{\frac{1}{3}})^2 = k_t$$

Crank-Gistling-Brounstein equation:

$$1 - \frac{2}{3\alpha} - (1 - \alpha)^{\frac{2}{3}} = k_t$$

For definition of the equation which can describe the experimental data more precisely, these equations were linearized and compared.

The kinetic lines were linearized into Crank-Gistling-Brounstein coordinates more precisely (fig.4).

For activation energy determination the dependence of chemical rate on inverse temperature was constructed (fig.5). Activation energy was calculated from tangent and has value $E_a=921.1$ kJ/mole.

The gained data shows that amorphous carbon can be fluorinated from 70 °C, fluorination occurs into kinetic field as a result of the process limited by chemical reaction. The received Crank-Gistling-Brounstein equation for this reaction allow us to control the fluorocarbon fractional conversion value.


