УДК 620.179.1

D.P. Sivtsov, V.S. Khandetsky

DEVICE TO DETERMINE OF FLUORINE CONCENTRATION IN FLUORINATED CARBON POWDERS

Abstract. In this article is described the device for operative measuring the concentration of fluorine in the powdered carbon fluoride, which is used for manufacture of cathode material for chemical current sources. Device performs the information proceeding in digital form. The principles of the device operation, its schematics, and test results are described.

Keywords: carbon fluoride, concentration, measurements, powder, sensor, digital device.

Introduction. The development of modern electronics based on independent power supplies necessitates the development of chemical current sources (CCS). Traditional CCS based on heavy metals – zinc, lead, manganese, mercury, etc. and theirs compounds have some imperfections. They are environmentally hazardous, have insufficient power capacity and relatively high cost. Transition to lithium anodes allows significantly improve the energy characteristics of CCS and expand the temperature range of their work. Further improvement of lithium CCS is based on the use of new cathode materials, including the materials on the basis of *carbon fluoride* CFx [1].

The part of the manufacturing cathodes process based on CFx is the saturation of fine-dispersed carbon powder by fluorine (fluorination). This is performed by heating the powder of carbon at high temperature in an atmosphere of fluorine. As the degree of powder saturation by fluorine is accepted to use the value of fluorine concentration D_F%. Its evaluation is performed usually by chemical analysis of the powder samples in certain time intervals. But this method of determining the concentration of fluorine has such imperfections. Firstly, for its implementation requires trained personnel, corresponding equipment, and reagents. Secondly, it is continuous process. Thereof using the chemical analysis it is impossible to conduct the mass determinations of D_F%.

Statement of the problem. Experimental studies of the CFx samples have shown the dependence of dielectric permittivity on the DF. Therefore was designed the

ISSN 1562-9945

electronic digital device for operative mass measurements of the concentration of fluorine D_F.

The main part. To solute this problem it is essential to choose an adequate sensor for the primary measuring transducer (PMT).

According to the results of laboratory experiments it was concluded that the contact capacitive sensors is most appropriate. They provide a sufficient slope $\Delta C_S/\Delta D_F$ of primary conversion characteristic $C_S(D_F)$, where C_S is electrical capacitance of the sensor. However, the repeatability of characteristics $C_S(D_F)$ is complicated by the fact that CFx is fine-grained powder with very low density. That's why when testing the PMT must be installed in operating position so that always ensure equal conditions of interaction of electric field of sensor with the layer of powder under it. For this was designed the special mechanism with electric control that provides vertical movement of PMT, same depth of sensor's immersion into a layer of powder, the same degree of powder's compaction under sensor and full contact the working surface of sensor with powder. The sensor of the PMT used in our instruments is presented in Fig. 1.

a b

Figure 1 – PMT with integrated to him the contact capacitive sensor:
a – general view of PMT; b – sensor (increased)

The sensor built in the form of symmetrical system of annular stainless steel electrodes, which consists of a disc of ∅6 mm, surrounded by four concentric coplanar rings ∅13, ∅20, ∅27 and ∅34 mm.

The electrodes are tightly inserted into annular slots made in the dielectric disc. After this, the working surface of the sensor (Fig. 1) has been polished. Electrical scheme of connection between the electrodes is shown in Fig. 2.

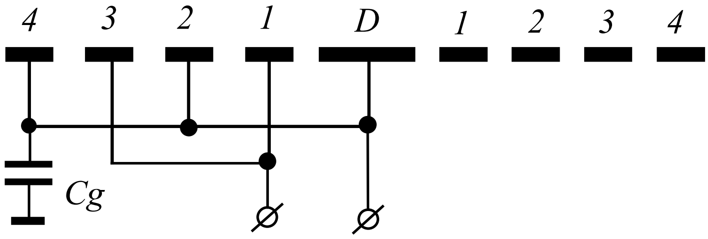


Figure 2 – Electrical scheme of connection between the electrodes

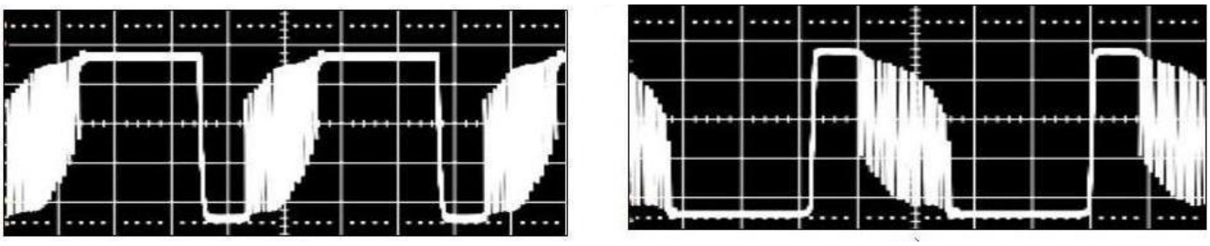
Explanation in text.

Rings 1 and 3 form a group of high-potential electrodes. The central disc D and the rings 2 and 4 form a group of low-potential electrodes, which are bridged for AC with common "ground" of the device through the capacitor *Cg*. Thus, the force lines of the sensor's electrical field are concentrated in the gaps between the groups of electrodes. This provides an effective interaction of the sensor’s field with powder CFx. Such interaction changes the capacitance of the sensor Cs depending on the change of the fluoride concentration D_F.

Conversion ΔCs to form of electrical signal performed as follows. In PMT are encased two oscillators - the reference oscillator and the measuring oscillator. They are realized on two microchips MC1648 [2]. The frequency of sinusoidal signal produced by oscillator on the base of MC1648, is equal to resonant frequency of external parallel *LC* - circuit. Namely, the frequency of the reference oscillator is determined by the capacitance of the ballast capacitor C_B, capacitance C_{VAR} of the aligning capacitor and the coil inductance *L*, i.e. $f_0 = 1/2\pi\sqrt{L\,(C_B + C_{VAR})}$. The frequency of the measuring oscillator is determined by capacitance of the ballast capacitor C_B, the sensor capacitance $C_S(D_F)$, and the coil inductance *L*, i.e. $f_S = 1/2\pi\sqrt{L\,(C_B + C_S(D_F))}$. Before use of instrument, the frequency f_0 is adjusted using tuning capacitor (C_{VAR}) so that $f_0 = f_S$ when powder CF_X is absent in electrical field of sensor. When instrument operate and the sensor is in layer of powder CF_X the frequency f_S is reduced and arise the unbalance between frequencies of the reference oscillator and the measuring oscillator. Thus, the value of frequencies difference $f_D = f_0 - f_S$ is the carrier of information about the concentration of fluoride D_F, i.e. $f_D = f_D\,(D_F)$.

To obtain the numerical value f_D the instrument use the scheme of digital phase-frequency discriminator (PFD). It is realized on a digital microchip AD9901 [3]. This microchip generates output sequence of pulses U_{OUT}, whose frequency f_D depends on the time difference between input pulses of U_0 and U_S sequences. Thus, sinusoidal signals of reference and measurement oscillators must be preliminary converted into sequence of pulses. This is implemented by digital microchip MC10116 [4]. It consists of three differential independent receivers from the communication line. Due to the built-in voltage reference source MC10116 receivers can work as a Schmitt trigger. In collection with amplification function it provides the formation of the output sequences of pulses (meanders) U_0 and U_S with the logic levels of technology ECL, as it is necessary for microchip AD9901.

Then, in the instrument, output sequence of pulses U_{OUT} with frequency f_D transformed in voltage U_D. But the shape of the pulses of output sequence U_{OUT} which are making AD9901, when increase the difference between frequencies f_S and f_0 is distorted. Namely, they are appear the high-frequency pulsations by the pulses fronts. Furthermore, the number and shape of the pulsations depends on the ratio of the frequencies f_0 and f_S (Fig.3).



a b

Figure 3 – Waveform of output pulses AD9901 in:
a – $f_S >> f_0$; b – $f_S << f_0$ [3]

Therefore, output sequence of pulses from AD9901 U_{OUT} is passed through the active filter, which provides decreasing of these pulsations. Since during the instrument operation the magnitude of the frequency difference $f_D = f_D$ (D_F) can come up to 1 MHz in the required range of DF, the filter was realized on the basis of broadband operational amplifier AD8055AN [5]. After filtration the pulses of sequence U_{OUT} are transformed to logic levels of ECL using differential receiver of the microchip MC10116 mentioned above.

Transformation of the frequency f_D to voltage U_D is implemented on the base of converter KA331 [6]. The microchip provides linear transformation with 0.01% of accuracy in the frequency range 1Hz...100 kHz. Accordingly, the frequency f_D of the pulses of sequence U_{OUT} must be in this range. To this effect it is divided by 10, therewith use the synchronous decimal counter 500ИЕ10137 [7]. Voltage levels of pulses of this sequence changed to use in limits of the voltage range of converter KA331 i.e. ECL - TTL by applying microchip 500ПУ125 [7]. Output voltage of the converter is used for further processing of the measuring information with the ultimate aim to image the testing results D_F in digital form N_{DF}. For this at first is adjusted the transform function "$U_D – D_F$" in accordance with a predetermined range [D_{MIN}, D_{MAX}] using operations of its displacement and rotation in a coordinate system [f_D, U_D] (see. below). These operations are implemented by the two microchips OR07CP which are precise operational amplifiers [8]. To display a number value N_{DF}, which is numerically equal to the concentration of fluorine D_F according to the adjusted transform function "$U_D – D_F$" we applied the analog to digital convertor ICL7107 [9] (3.5 - decimal digits), and the digital display contained four 7-segment indicator RL-D5623 [10].

The operation of the device is explained by functional scheme shown in Fig. 4. Here: 1 – measuring oscillator with the sensor 2; 3 –reference oscillator; 5,6 – blocks for forming of pulse sequences; 7 –phase-frequency discriminator; 8 – filter to suppress high-frequency noise; 9 – block for forming of pulse sequences;10 - frequency-to-voltage convertor; 11 – block for adjustment of transform function; 12 – ADC; 13 – digital display.

Obtained results. When designed the device we used 9 samples of fluorinated carbon powder CFx. The concentration of fluorine D_F [%] in the samples were previously obtained by chemical analysis: 25.55; 35.76; 36.66; 39.34; 41.95; 45,00; 49.05; 61.10. These values were chosen based on the needs of the technological process of carbon fluorination.

The measurement results obtained by applying of the designed device demonstrate the following.

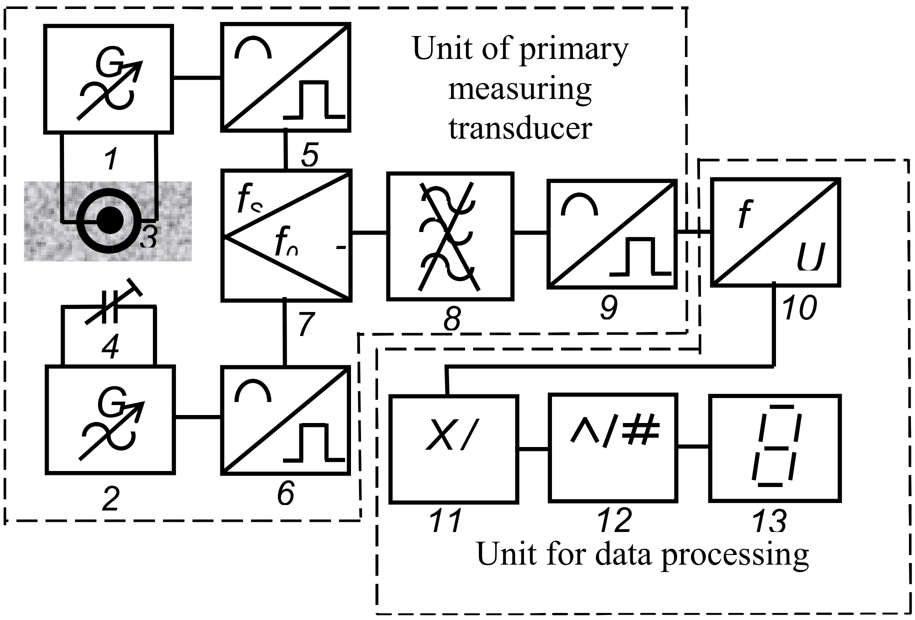


Figure 4 – Functional scheme of instrument (simplified)

Without adjusting unit (pos. 11 in Fig. 4) transform function "$D_F - N_{DF}$" is linear: $N_{DF} = 0{,}872 \cdot D_F$ [%] + 22,82. But the obtained numeric values N_{DF} not correspond the real values D_F [%]. When applied the block for adjustment of the transform function was obtained the function (fig 5), which is close to the ideal $N_{DF} = D_F$ [%], namely: $N_{DF} = 0{,}9621 \cdot D_F[\%] - 0{,}0317$, accuracy of approximation $R^2 = 0{,}9588$.

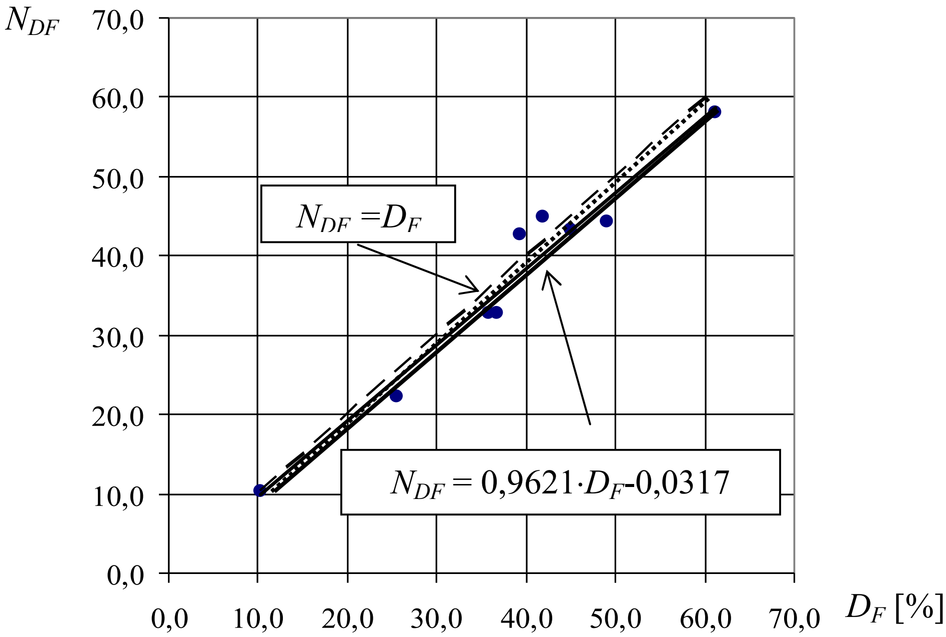


Figure 5 – Transform function "$D_F - N_{DF}$"

Conclusions. The device for operative measurements of concentration of fluorine in the fluorinated carbon powder was developed. Integral error which includes the errors caused by inaccuracy setting of the primary measuring transducer PMT on the powder and compaction of powder under the load of PMT when it immerse into thickness of powder, not more 10%.

Application of the device allows to reduce the number of required chemical analyzes when manufactory of fluorinated graphite powder, to carry out the operative mass testing of significant amounts of powder and detect heterogeneity of fluoridation in a carbon powder material.

REFERENCES

1. Онищенко Д.В., Цветников А.К., Попович А.А., Курявый В.Г. Синтез новых катодных материалов для литиевых химических источников тока. –ДВО

РАН. Институт химии. – Access mode: http://zhurnal. ape.relarn.ru/articles/2007/118.pdf

2.MC1648. Access mode: http://pdf1. alldatasheet.com/datasheet-pdf/view/199123/MOTOROLA/MC1648.html

3.AD9901. Access mode: http://pdf1.alldatasheet.com/datasheet-pdf/view/48624/AD /AD9901.html

4.MC10116.–Access mode: http://pdf1.alldatasheet.com/datasheet-pdf/view/173980/ONSEMI/ MC10116.html.

5.AD8055/ AD8056. – Access mode: http://pdf1.alldatasheet.com/ datasheet-pdf/view/48395/AD/AD8055AN.html.

6. KA331 – Access mode: http://www12.airchildsemi.com/ds/KA/ KA331.pdf.

7. Нефедов А.В. Интегральные микросхемы и их зарубежные аналоги: Справочник. Т. 3. [Text] / Нефедов А.В. – М.: ИП РадиоСофт, 2000. – 576 с.

8. Ultralow offset voltage operational amplifiers. – Access mode: http://www.mit.edu/~6.301/OP07_a.pdf .

9. $3^1/_2$ Digit, LCD/LED Display, A/D Converters ICL7106, ICL7107, ICL7107S. – Title from screen: http://pdf1.alldatasheet.com/datasheet-pdf /view/177761/INTERSIL/ICL7107CPLZ.html.