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Handling Manual for

Electrochemical CO Gas Sensor

NAP-505

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(1) What are electrochemical sensors?

(1.1) Basic operational principle

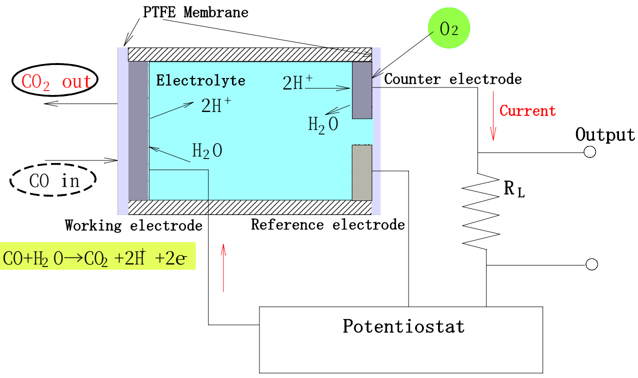


Fig.1: Typical structure

An electrochemical sensor consists of three electrodes, a working electrode for oxidation (reduction) reaction, a counter electrode for reduction (oxidation) reaction correlated with the working electrode, and a reference electrode for monitoring and stabilizing the potentiostat that varies depending on the oxidation (reduction) reaction.
In actual operation, according to the variation of electric potential detected by the reference electrode,
the electric potential of the working electrode is maintained at a preset value by the potentiostat circuit connected with an outer circuit. For example, in case of detecting CO gas;
The following oxidation reaction occurs on the working electrode;

$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$

Electrons generated by this reaction gather close to the working electrode and hydrogen ions are dispersed in the electrolyte near the electrode, eventually electrical double layers are formed. As the working electrode and the counter electrode are connected by an outer circuit, electrons flow from the working electrode towards the counter electrode, and hydrogen ions move to the counter electrode to take the electrons to finally generate water as the under-mentioned reaction.

$2H^+ + O_2 / 2 + 2e^- \rightarrow H_2O$

Thus electrochemical sensors detect gases by taking out the energy generated by the chemical reactions (oxidation/reduction) as an electric energy. These reactions are illustrated in the Fig. 1.
The total reaction is the oxidation reaction of carbon monoxide represented by $CO + O_2 / 2 \rightarrow CO_2$

During the reaction process, voltage drop may occur because of the dielectric polarization caused by the reaction layer near the electrode in the electrolyte and the transferring speed of hydrogen ions. This voltage drop becomes bigger as the gas concentration is higher, and it is a major cause that impedes the linearity of the sensor output voltage. To prevent this, the reference electrode detects the electric potential of the working electrode and works to stabilize it to enable the electric current always flow between the working and counter electrodes in proportion to the gas concentration.
An electrochemical sensor that has such an electric potential controlling function is called as “Three-electrode cell type” or simply called as “Three-pin type”. As the three-electrode system gives superior linearity and stability, it is widely adopted to general industrial use electrochemical sensors.
An electrochemical sensor that does not have a reference electrode but has only a working electrode and a counter electrode is called as “Two-electrode type” or simply “Two-pin type”. This method is less expensive and has been adopted to residential gas alarms for which high accuracy is not required.
Compared to the three-electrode type sensors, the two-electrode type sensors are inferior in the linearity and stability of the sensor output but can satisfy the requirements for residential devices.
Recently, however, three-electrode type sensors such as NAP-505 are available on the market with equivalent to or even cheaper than two-electrode type sensors.

(1.2) Basic structure

The Fig. 2 at right shows a typical structure of electro-chemical gas sensors.

Generally an electrochemical sensor consists of electrodes (working, reference and counter electrodes), electrolyte and its container, active carbon filter for removal of noise gases, signal output wires, and electrode pins etc.

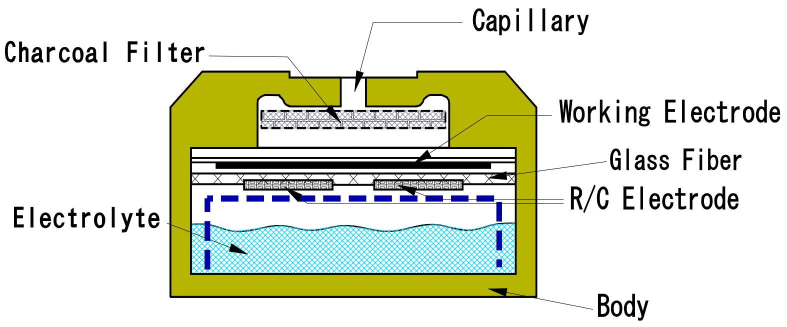


Fig. 2 Structure of electrochemical sensor

Typical electrode materials are platinum, gold, rhodium, and carbon etc. among which the best material is selected according to target gases. Sulfuric acid , alkali solutions such as potassium hydroxide, or aqueous solutions such as lithium chloride are used for electrolytes. For safe retention of the electrolyte and stable ion conduction between the working and counter electrodes, sheets made of alumina fiber or glass fiber are inserted between the electrodes.

For obtaining output signal from the electrodes, usually the corrosion resistive wires of noble metal such as platinum are used and welded to the outer pins.

Depending on kinds of target gases, very high selectivity is often required against noise gases. In such a case, a carbon filter or the like is put between the working electrode and the capillary for minimizing the affection of noise gases as shown in the figure.

(1.3) Features

Electrochemical gas sensors have the following superiority to conventional semiconductor type and hot-wire type gas sensors.

*** Linear output can be obtained in proportion to gas concentration.**
*** Superior reproducibility**
*** Superior gas selectivity**
*** Not affected by humidity**
*** Stable output characteristics because of smaller output drift in air**
*** Low power consumption because no heater is used. Can be battery operated.**
*** Smaller-sized and lighter weight. Can be mounted on portable devices**
*** No mechanical structure. Durable to shocks and vibrations.**

To date, electrochemical gas sensors have been used mainly for industrial applications which require periodical maintenances because of the complicated structure, high cost, shorter life time, and possibility of damages by leakage of electrolytes etc. However, Nemoto has succeeded to lessen the possibility of electrolyte leakage to almost zero level by taking the unique new structure, and realized the cost-down by a large margin. Now we are proud to introduce the small-sized and less-expensive electrochemical gas sensors, NAP-500 series, which can be used for residential applications.

(2) NAP-505

(2.1) Features

NAP-505 has been developed making use of our vast accumulation of technologies in production of hot-wire type gas sensors, long research experience on catalyst, fine printing, and assembling of sensors, those which we have been specialized in. This NAP-505 is small and less-expensive, but has high sensitivity, long life, and superior durability that would not allow the leakage of the electrolyte even under severer operation conditions. NAP-505 meets the severe requirements for ideal electro- chemical sensors, and is targeted to residential applications because of its low cost.

In addition to the features described in (2.3), NAP-505 has the following additional superiority compared to other electrochemical sensors.

Small-sized

NAP 505 is as smaller than NAP-705 as 1/2 in volume. Especially its thickness of 8.0 mm is one of the smallest electrochemical sensors in the world. This enables to produce smaller and thinner gas detectors and portable devices

Air vent structure

As the electrolyte used for chemical sensors has high hygroscopicity, its volume varies depending on ambient temperature and humidity. This variation causes the variation of the pressure inside the sensor, eventually the electrolyte may leak outside, which is a serious problem.

NAP-505 is small-sized but it has the air vent ability to maintain the inside pressure always constant. This feature allows using this sensor in any positioning or attitude under high temperature and humidity conditions.

Can be soldered

Conventional electrochemical sensors can not be soldered directly to pins because of the leakage of electrolyte and thermal deformation of housings by the rapid temperature increase upon soldering.

NAP-505 has the unique structure of the electrode pins that dissipates the heat to minimize the affection of high heat when exclusive sockets are used. This simplifies the assembling process since it does not need to solder a socket onto a PCB first, then a sensor is mounted on the PCB directly.

(2.2) Applications

Model	Target gas	Applications	Features
NAP-505	Carbon monoxide	Residential CO alarms Fire alarms Automatic ventilator Air quality monitors	High sensitivity and accuracy High reliability, Low power consumption Can be battery-operated

(2.3) Characteristics

(2.3.1) Specifications

[Sensitivity characteristic]

Target Gas	Carbon monoxide
Measuring range	0 – 1,000 ppm
Output current	40 ± 10 nA / ppm
Repeatability	± 2 %
Base line in clean air	< ± 5 ppm
Response time (T_{90})	< 30 sec.
Base line shift (-20^{o}C ~ 50^{o}C)	< 10 ppm
Long-term stability (Drift)	< 5% / year

[Operational & Storage conditions]

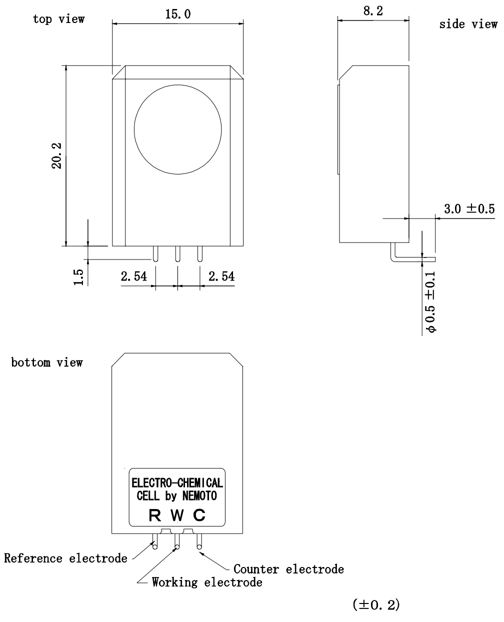
Operational temperature	-20 ~ 50^{o}C
Operational humidity	15 ~ 90 %RH
Barometric pressure variation range	1 atm. ± 10 %
Recommended resistance value	10 Ω
Recommended storage temperature	0 ~ 20^{o}C
Storage period	6 months

[Materials]

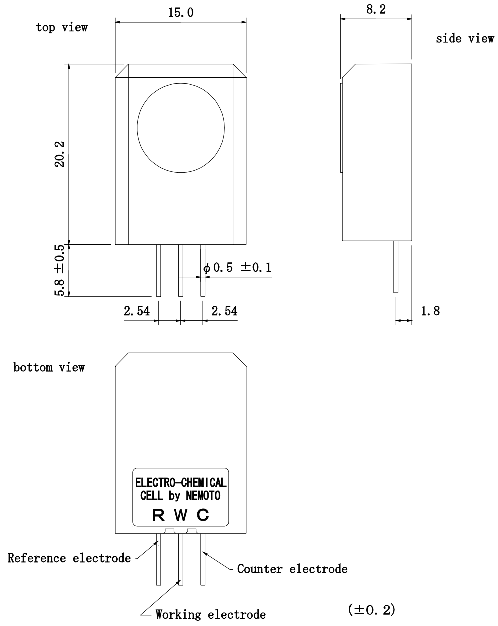
Housing material	PPO
Color of housing	Grey
Weight	Approx. 2.6 g

[Appearance and Dimensions]

Direct Soldering Model

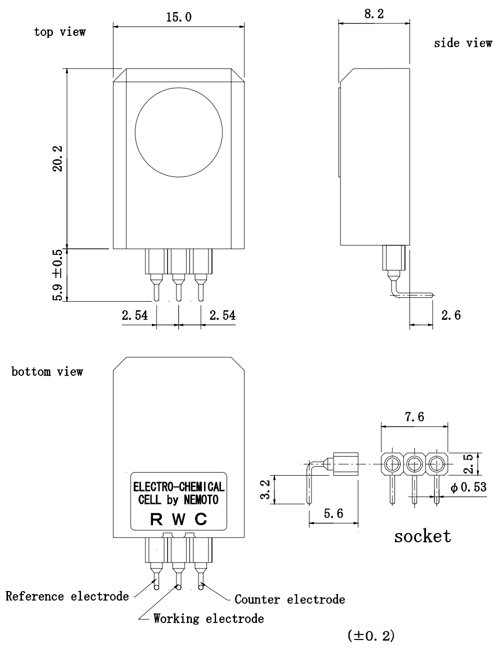


NAP-505R〔right angle pin〕

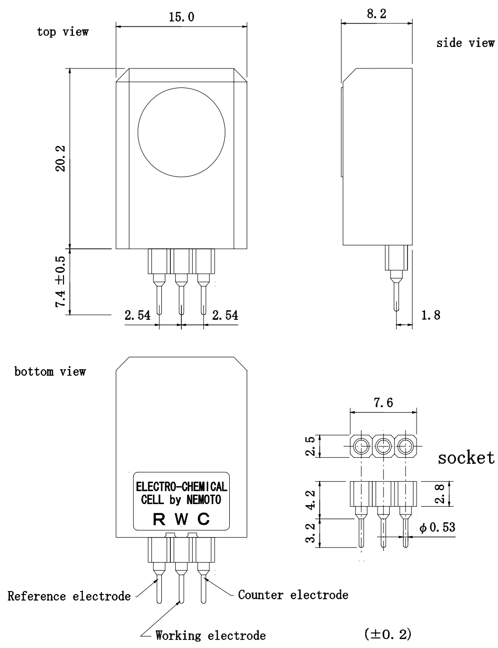


NAP-505S 〔straight pin〕

Socket Model

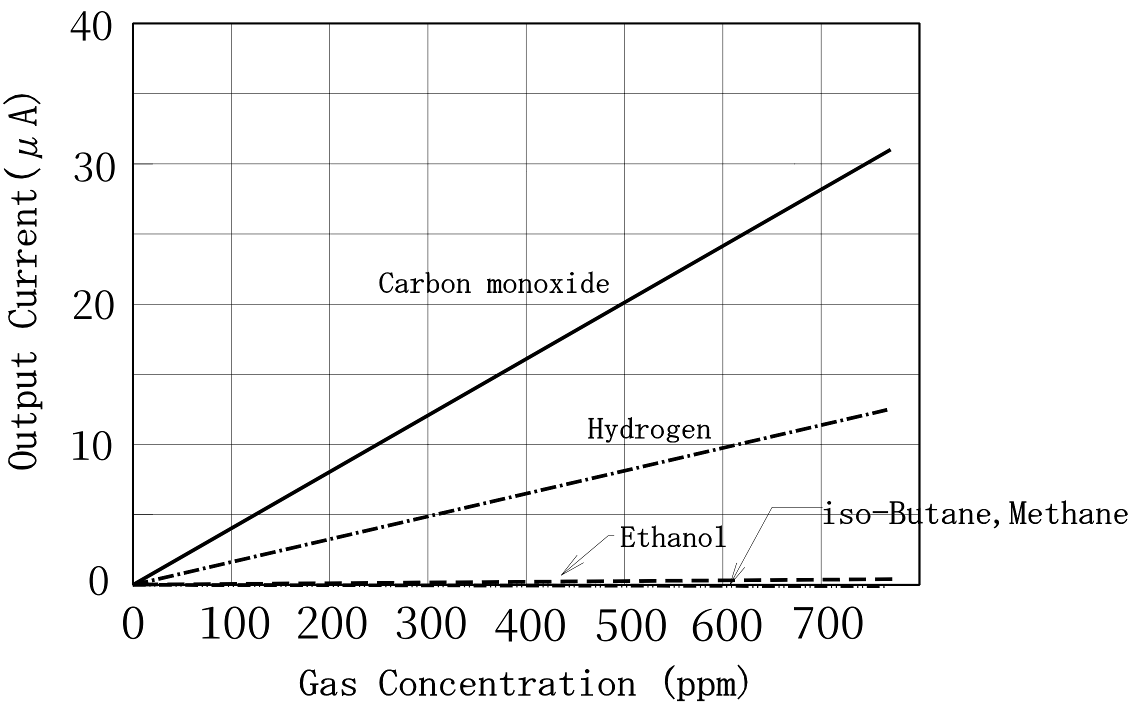


NAP-505RS 〔right angle pin〕

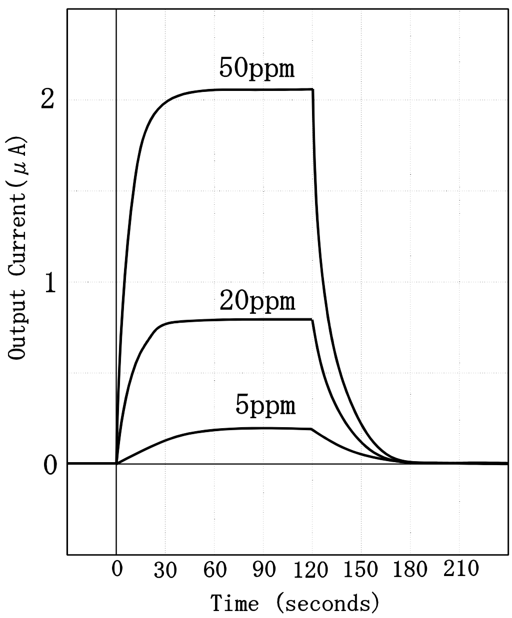


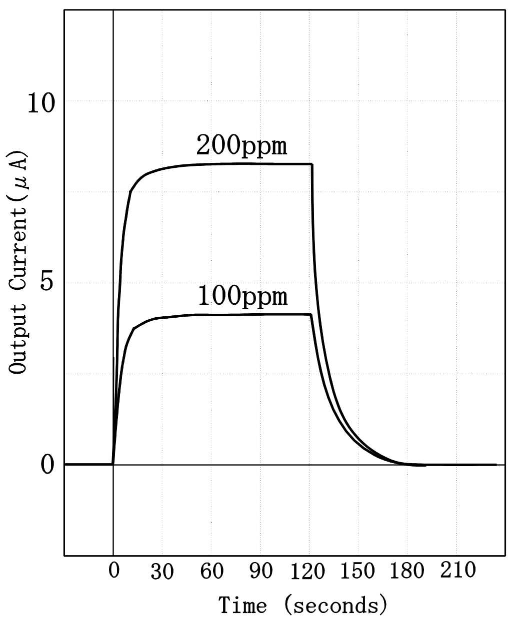
NAP-505SS 〔straight pin〕

(2.3.2) Gas sensitivity



(2.3.3) Response characteristic





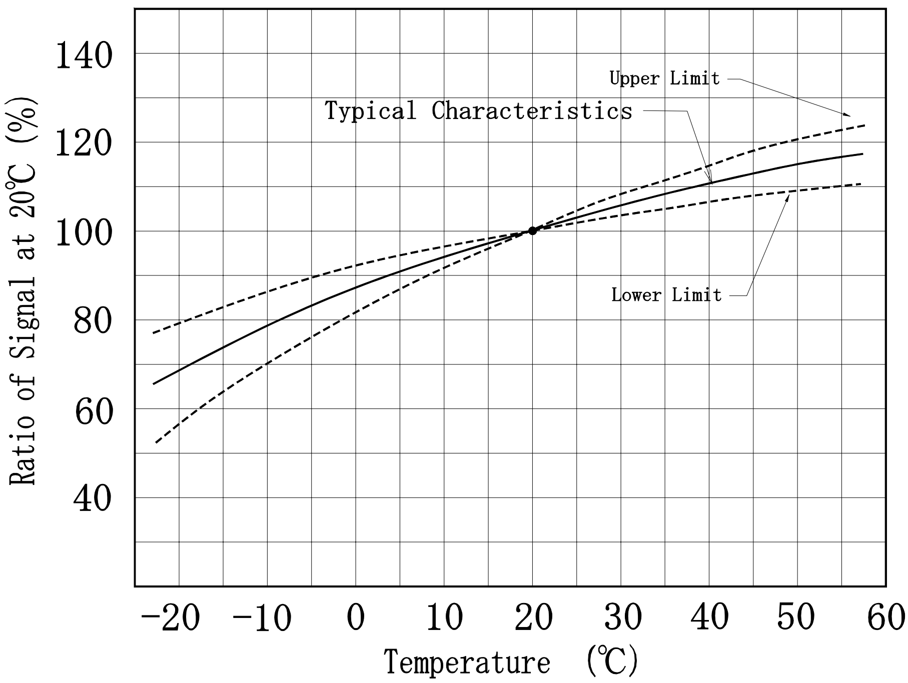
(2.3.4) Gas selectivity

NAP-505 is gas-selective to meet with various international standards. The following table shows the NAP-505's gas selectivity to various gases including those specified in **EN50291** and **TUV** standard. This sensor meets with **UL2034** standard as well.

Test gas	Gas concentration (ppm)	Typical Carbon-monoxide Concentration (ppm) Equivalent
Carbon monoxide	100	100
Hydrogen	500	200
Methane	5000	0
Iso-butane	2500	0
Carbon dioxide	5000	0
Sulfur dioxide	25	0
Hydrogen sulfide	10	0
Nitrogen monoxide	30	0
Nitrogen dioxide	30	< 10
Ammonia	100	0
Ethyl acetate	200	0
Heptane	500	0
Ethanol	2000	< 30*
Hexamethyl-disiloxane	10	0**

Exposure time: * 30 min. ** 40 min.

(2.3.5) Temperature dependency



(2.3.6) Reliability

NAP-505 has passed the tests for high temperature (at 50^{o}C or 80^{o}C), low temperature (-20^{o}C), high temperature & humidity (at 50^{o}C, 90%RH), storage at low humidity (room temperature & less than 20%RH), heat/cool cycles (at -20～50^{o}C), shocks & vibration and interference gas exposure etc. Thus users can rely on the performances and the stability of NAP-505.

Typical results of reliability tests:

Test items	Output drift
Storage at high temperature (50^{o}C, 40%RH, 1,000 hrs.) When electrolyte quantity came to equilibrium under 20^{o}C, 60%RH after test	< ± 15 %
Storage at high temperature & humidity (50^{o}C, 90%RH, 1,000 hrs.) Test started when electrolyte was at equilibrium under 20^{o}C, <60%RH	< ± 10 %
Storage at low temperature (-20^{o}C, 1,000 hrs.)	< ± 5 %
Storage at low humidity (25^{o}C, < 20%RH, 1,000 hrs.)	< ± 10 %
Cool/Heat cycle (-20^{o}C for 30 min. ~ 50^{o}C for 30 min., 10 cycles)	< ± 10 %
Drop (shock) test (drop onto concrete floor from 1 m height, 5 times)	< ± 5 %

(2.3.7) Definitions

*** Base-line / Base-line shift**

Base line means the output level in clean air. The output current value at 20^{o}C would be less than 250 nA, but the output tends to increase as the ambient temperature rises more than 30^{o}C. The base-line shift means this variation of the output level, i.e., the maximum of 500 nA would be put out at 50^{o}C. When the accuracy of CO measurement is considered, this base-line shift should be taken into account.

In this manual, the output values are calculated to be equivalent to CO gas concentrations taking the output variation into account.

*** Gas sensitivity / Output signals**

Gas sensitivity is shown by the current value that is generated by the oxygen reaction with CO gas when NAP-505 is exposed to CO gas. Using NAP-505, 40 ± 10 nA is generated at 1 ppm of CO gas, therefore for instance, the generated current value will be about 8μA at 200 ppm of CO gas (200ppm x 40 nA). This generated current is generally recorded as voltage converted by a Current – Voltage converting circuit. In our recommended circuit, as the conversion is done through a resistor of 10 KΩ, 80 mV of output is obtained in this case.

*** Response time (t_{90})**

This means a time to reach to 90% of the output value in clean air when NAP-505 is exposed to the environment to measure.

*** Repeatability**

This is shown as the maximum variation ratio of output signals when tests are repeated under the same measuring conditions (Temperature, humidity, gas concentration etc.). The repeatability of NAP-505 is ± 2%, and this means that all of the test results would fall in the range of 98% ~ 102%.

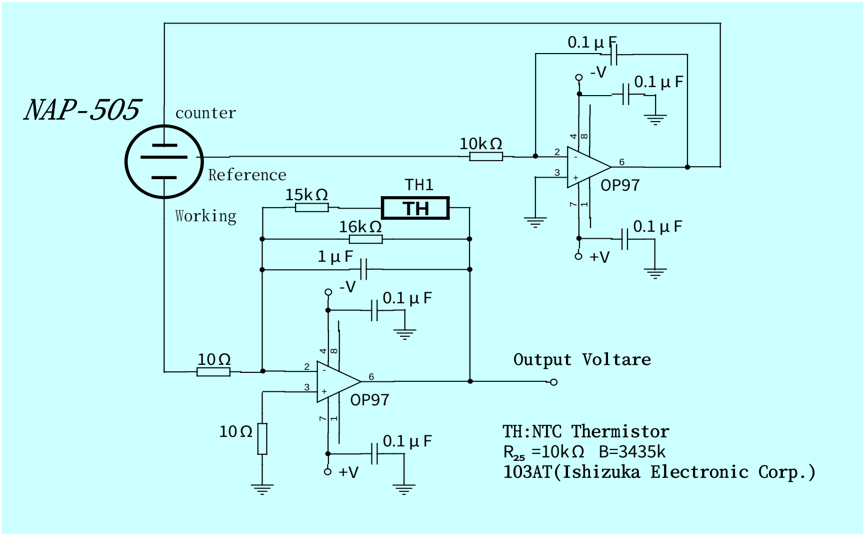
The tests are to be repeated within the specified time period (usually within 24 hours).

*** Temperature dependency**

The output characteristic of electrochemical sensors is the most affected by the ambient temperature. The gas sensitivity of NAP-505 also has such temperature dependency, and the output increases as the ambient temperature rises. The output increase is caused by the oxidation reaction on the surface of the catalyst, the dispersibility of the gas in the capillary, and the thermal affection to the mobility of ions in the electrolyte. This temperature dependency can be compensated relatively easily by using a NTC thermistor.

(2.4) For designing circuit

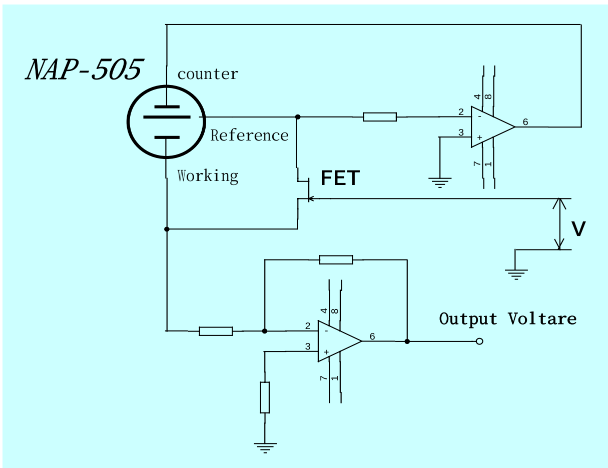
(2.4.1) Basic operational circuit



The basic operational circuit for NAP-505 is at the right. In this circuit, an operational amplifier, OP97, that is easy to get and relatively lower power consumption. The temperature dependency of NAP-505 is compensated by NTC thermistor that has 3435K of B constant made by Ishizuka Denshi. Thus the output accuracy can be within ± 10% in the range of -10^{o}C ~ 50^{o}C. Any thermistor can be used if it has around 3500K of B constant and the resistant value (R_{25}) is 10 KΩ.

(2.4.2) Less power consumption circuit

For general operational circuits, operational amplifiers such as OP97 used in our recommended circuit or classical OP07 can be used without problems. However for battery-operated circuits for portable devices, lower power consuming operational amplifiers are required, for instance, NJM4250 works at as low as 0.1 mA (max) with the power supply voltage of ± 1 V ~ ± 18 V. For simpler circuits with single power supply, battery-operation with 2 ~ 3 V is possible and OP90 (20μAmax) or the like can be used.



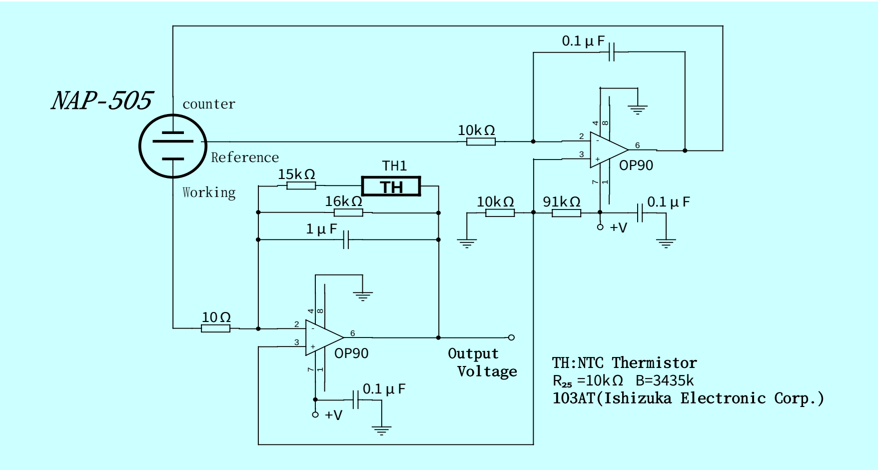
For a longer battery life, the pulse operation can be done. For instance, 2 minute-off after 30-second operation, i.e. the cycle operation with a cycle of 2 minutes and 30 seconds can greatly save the battery power consumption. The following are consideration for such circuits.

Using an electrochemical sensor in a cycle operation circuit, transient signals would be obtained just after on and off actions. Therefore usually 1 ~ 2 minutes would be required for output stabilization, however this is not practical due to the long sampling time.

In order to shorten the output stabilization time, it is required to short-circuit between the working electrode (W) and the reference electrode (R) during the power supply is off. For example, as shown in the figure, the short-circuiting circuit using FET is to be inserted for controlling the voltage (V) to automatically break the short-circuit during the power supply is on. Using this measure, output is stabilized within 10 seconds after the power supply is on. Thus, in such a short period less than 10 seconds, sampling of the signals just before power supply was off enables to obtain accurate measurement data with saving the battery power consumption.

(2.4.3) Battery operation

Here is a specimen of circuit for NAP-505 using an operational amplifier for battery operation. Battery operation should be need for portable/residential devices.



For this battery operated circuit, 0.2 - 0.5V of bias voltage not to sensor but circuit is required to improve and stabilize the linearity in the lower gas concentration range. But, output of virtual zero point by using this circuit is not zero but 0.2 – 0.5V, and this value is dependent on supply voltage to the circuit. Around 10% of supply voltage to the circuit is normally added to zero point.

(2.4.4) Self-diagnostic system

Special circuit diagram apart from the above circuit diagrams is suggested in order to detect lifetime and malfunction, for example short or open trouble between electrodes of sensor, but as this quite confidential, please contact Nemoto head office or closest distributors when it is necessary. It will be available for customers after non-disclosure agreement is connected.

(2.5) Remarks

(2.5.1) Long-term drift of gas sensitivity

As a phenomenon of all electrochemical gas sensors, the working electrode's oxidation ability on CO gas would be getting deteriorated as the time passes. NAP-505 has newly developed electrode catalyst that would not deteriorate more than 5% / year. However it can not be helped, as same as other electrochemical sensors, that even NAP-505 has the same tendency in the gas sensitivity deterioration. Therefore it is recommended that this deterioration ratio, 5% / year, should be taken into account when your application circuits are designed.

(2.5.2) Seasonal variation of gas sensitivity

The electrolyte of electrochemical sensors generally has moisture absorbing nature. Therefore in case of usage in areas where the humidity varies depending on seasons, the volume of the electrolyte increases in a highly humid season and it decreases in a dry season. This variation of the volume affects the oxidation reaction on the working electrode. This variation in the gas sensitivity should also be taken into account when your application circuits are designed.

Some of conventional electrochemical gas sensors show annual variation of gas sensitivity as much as 10 ~ 20%, but NAP-505 realizes the least variation throughout the year because of the most adequate electrode structure and the improved electrode catalyst. However as NAP-505 is an electrochemical gas sensor, sensitivity variation up to some extent would be expected. Upon usage of NAP-505 in the actual applications, it is suggested to design your circuits considering that the variation in the gas sensitivity would be max ± 5% in the output value.

This seasonal variation is a periodic phenomenon, and the gas sensitivity is restored to the original level when the electrolyte comes to the original volume.

(2.5.3) Storage of sensors

Electrochemical sensors should be stored in a clean air under room temperature, preferably $0^{o}C$ ~ $20^{o}C$. The maximum storage period would be 6 months after delivery. For sensors stored for more than 6 months, the performance guaranteed period will be shortened by the excess storage period. This is because of the nature of electrochemical gas sensors. Different from semiconductor type or hot-wire type gas sensors, the gas sensitivity of electrochemical gas sensors would be getting deteriorated as the time passes regardless that the sensor has been used or not. The careful attention to the storage period is most important to keep the quality of electrochemical gas sensors.

(2.5.4) Remarks for mounting sensors

* Electrode pins must be correctly connected. Wrong connection does not allow correct functions.
* A thermistor for temperature compensation must be located near the sensor and far from heating sources such as transformer. A sensor and a thermistor must not be located near heating sources.
* A sensor can be mounted in any direction or attitude.
* A sensor's pins can be soldered, but by manual soldering and the temperature of a soldering iron must be less than 350^{o}C and within 3 seconds. Excess heating may cause the deformation of the housing, eventually leakage of electrolyte.
* Refrain from using reflow soldering or soldering bath for soldering a PCB mounted with a sensor.

(2.5.5) Remarks for gas alarms & Gas densitometer

* Alarm concentration setting and calibration of detectors or densitometers should be done after the output value has been stabilized in clean air. Judgment of output stabilization depends on the required accuracy, but when the output comes down less than 5 mV (using our basic measuring circuit) it can be considered that the output has been stabilized.
* Upon designing circuits, the aged-deterioration in the gas sensitivity, max -5% / year, must be taken into account. When severer detection accuracy than this secular variation is required, periodical re-calibrations are required with adequate intervals (for instance once or twice a year) depending on required accuracy.
* When the gas intake area of the sensor is blocked with water drops or other liquid, correct functions can not be expected. If the sensor may be used in such atmosphere, the openings of device housings should be designed in order not to affect the sensor.
* As CO gas is lighter than the air, CO detecting devices must be installed at upper part of walls or on ceilings.
* In case of regular usage under normal atmosphere (room temperature and humidity), the guaranteed period for normal functions of NAP-505 is 5 years.

(2.5.6) Other remarks

* The sensor should be used according to the specifications and ratings.
* Evaluation of gas sensitivity should be made in clean air without noise gases.
* When a test gas is blown directly to the gas intake area, higher gas sensitivity may be observed. Experiments should be made in the atmosphere that the test gas is not directly blown onto the sensor and the air inside a test box should be gently agitated for even dispersion of the gas.
* Voltage should not be supplied directly to the electrode pins. Especially, when 1.23V or more is supplied, electrolysis occurs and sensors may be severely damaged. The voltage less than 1.23V would not destroy sensors, but it would take a long time to recover the functions after the specified voltage is supplied.
* Do not bend the pins.
* Do not weight on sensors more than 5 kgs/cm^2.
* The gas intake area should not be blocked or contaminated. It may cause lower gas sensitivity.
* Never put foreign material in the gas intake area. It may destroy the sensor structure and cause the leakage of the electrolyte.
* Do not put excess vibration or shocks onto the sensor.
* If the sensor housing is damaged or scratched, do not use the sensor.
* After the sensor is exposed to high concentration gas for a longer time, it may take a longer time to restore the normal functions.
* Do not blow organic solvents, paints, chemical agents, oils, or high concentration gases directly onto sensors.
* If the sensor is used under irregular atmosphere, please contact us for assistance.
* Do not disassemble the sensor. Damages or losses may be expected due to the leakage of the electrolyte.

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