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CO Sensing Properties of Electrochemical Gas Sensors Using an Anion-conducting Polymer as an Electrolyte

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An anion-conducting polymer (ACP) with large OH^- conductivity is very promising as an electrolyte of electrochemical gas sensors working at RT. Therefore, CO sensing properties of an electrochemical gas sensor using ACP as an electrolyte and carbon black (CB) powders loaded with *n* wt% noble metals (EC(*n*M/CB-ACP), *n*: *0.1~10*, M: Pt, Pd or Au) as an electrode material were investigated in this study. Among the sensors tested, EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) showed comparatively large response and fast response and recovery speeds to CO in wet air (relative humidity: 57%) at 30°C. The magnitude of response of the sensors tends to decrease slightly with a decrease in RH.

Introduction

CO is a colorless and scentless gas although it exerts very harmful influences on human health. Therefore, development of CO sensors with high selectivity and sensitivity detectable at sufficiently-low concentration not to exert harmful influences is highly requested. And response speed is also important for realizing quick detection of CO produced by the incomplete combustion of fuels. Recently, various electrochemical gas sensors operable at room temperature (RT) have been developed by employing liquid (1), ceramics (2) or polymers (3, 4) as an electrolyte. Among them, Nafion, one of proton-conducting polymers, has been presently applied as an electrolyte of commercial electrochemical CO sensors. On the other hand, anion-conducting polymers (ACP) with large OH^- conductivity have also been developed by some companies. Especially, polymer electrolyte fuel cells (PEFC) fabricated with ACP as an electrolyte are very promising because they showed high current density as well as high power density with relatively-low overpotential, and their performance was quite comparable to those of PEFC employing proton-conducting polymers in the preliminary research stage (6-11). In our previous study, ACP equipped with Pt-loaded CB electrodes was found to show CO response at RT (12). In the present study, our efforts have been directed to evaluating the effects of the kinds of the noble metals loaded on CB electrodes and relative humidity in the measurement atmosphere on CO response properties in a wide range of CO concentration.

Experimental

Preparation of noble metal-loaded carbon black powders

Carbon black (CB; Sigma Aldrich Co. LLC., A7455) powders loaded with *n* wt% noble metal (*n*M/CB, *n*: 0.1, 1 or 10, M: Pt, Pd or Au) were prepared by an impregnation method. An appropriate amount of CB powders was added into aqueous solution of $PtCl_4$, $Pd(NO_3)_2 \cdot 2H_2O$ or $HAuCl_4 \cdot 4H_2O$, and then they were ultrasonicated for 60 min. The suspensions obtained were dried on a hot plate. After the dried powders were ground in an agate mortar, they were heat-treated under H_2 stream at 350°C for 1 h.

Sensor fabrication

A schematic drawing of a sensor element is shown in Fig. 1. The *n*M/CB powder prepared was mixed with ACP solution (AS-4, Tokuyama Corp.) at a weight ratio of *n*M/CB:ACP = 1:1. The *n*M/CB-ACP paste obtained was applied on the surface of both sides of an ACP membrane (A201, Tokuyama Corp.) as sensing and counter electrodes by screen printing, and then it was dried at ca. 70°C for 2 h. The electrochemical gas sensor obtained was denoted as EC(*n*M/CB-ACP). For comparative purpose, an electrochemical gas sensor with CB sensing and counter electrodes without noble metal loading (EC(CB-ACP)) were also fabricated.

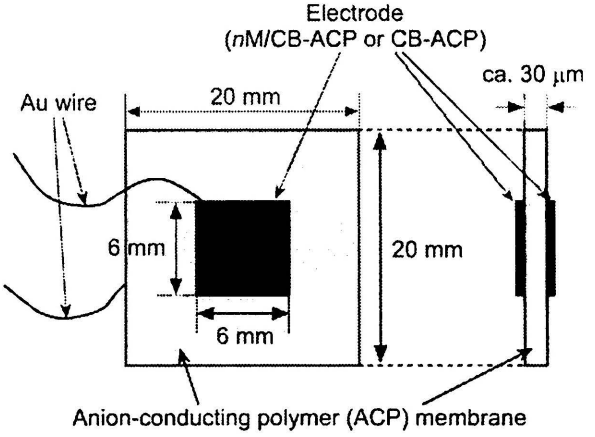

Figure 1. Schematic drawing of a sensor element.

Gas-sensing measurement

The sensors elements were sandwiched with two tubes to set up a gas measurement system which allow us to flow different gases over sensing- and counter-electrodes. Gas-sensing properties of all sensors were evaluated by measuring the electromotive force (EMF) at 30°C by flowing 100~3000 ppm CO balanced with air at the sensing-electrode side, while compressed air was flown at the counter-electrode side. Relative humidity (RH) at both the electrode sides was controlled to be 0~100% at 30°C. The magnitude of sensor response is defined as a change in EMF (ΔEMF) induced by a sample gas.

Results and discussion

Figure 2 shows response transients of EC(*n*Pt/CB-ACP) and EC(CB-ACP) to 500 ppm CO in air at 30°C (57%RH). EC(CB-ACP) showed almost no response to CO, but the loading of Pt to CB enhanced the CO response markedly. The magnitude of CO response of EC(*n*Pt/CB-ACP) increased with an increase in the loading amount of Pt, *n*. In addition, the increase in *n* drastically improved the response and recovery speeds, too. Therefore, a loading amount of 10 wt% was adapted in the successive measurements. Response transients of EC(*10*M/CB-ACP) to 500 ppm CO in air at 30°C (57%RH) were investigated and these results are shown in Fig. 3. EC(*10*Pt/CB-ACP) and EC(*10*Pd/CB-ACP) showed large response to 500 ppm CO (EC(*10*Pt/CB-ACP): -79 mV, EC(*10*Pd/CB-ACP): -85 mV), and the response and recovery speeds of EC(*10*Pd/CB-ACP) (90% response time (res): 3.1 min, 90% recovery time (rec): 2.1 min) were much faster than those of EC(*10*Pt/CB-ACP) (res: 4.5 min, rec: 28.2 min). On the other hand, EC(*10*Au/CB-ACP) showed almost no CO response, as was observed for EC(CB-ACP).

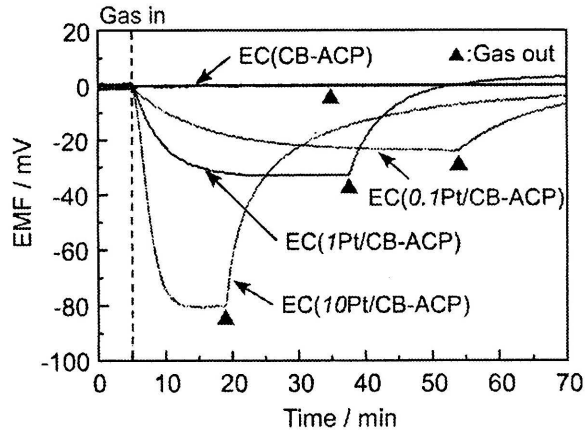

Figure 2. Response transients of EC(*n*Pt/CB-ACP) and EC(CB-ACP) to 500 ppm CO in air at 30°C (57%RH).

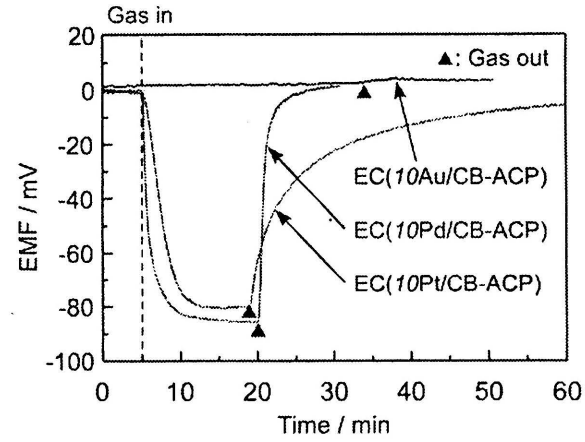

Figure 3. Response transients of EC(*10*M/CB-ACP) to 500 ppm CO in air at 30°C (57%RH).

Figure 4 shows response transients and CO concentration dependence of response of EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) in air at 30°C (57%RH). Both EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) showed negative response to CO, and the absolute magnitude of CO response, |ΔEMF|, increased with an increase in CO concentration. In addition, ΔEMF of EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) negatively changed in proportion to the logarithmic CO concentration and the slope, i.e. CO sensitivity, of EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) were ca. -19.3 and ca. -24.8 mV/decade, respectively. However, EC(*10*Pt/CB-ACP) showed overshooting response behavior to high concentration of CO and very fast response and recovery speeds, while the recovery speed of both sensors was enormously slow in a comparatively low CO concentration range (100~300 ppm).

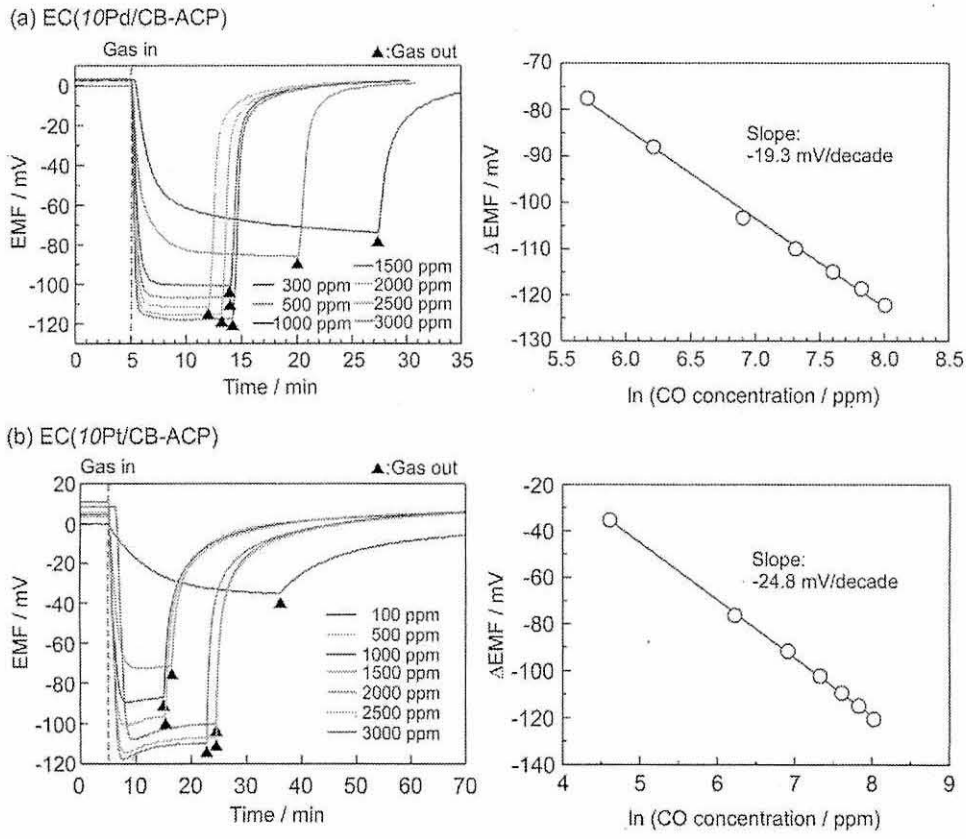

Figure 4. Response transients to CO and CO concentration dependence of response of EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) in air at 30°C (CO concentration: 100~3000 ppm, 57%RH).

Figure 5 shows response transients of EC(*10*Pd/CB-ACP) and RC(*10*Pt/CB-ACP) to 500 ppm CO in air at 30°C under various relative humidity (RH). Response of both sensors to CO decreased with a decrease in RH and ΔEMF could not be measured under dry atmosphere (≈ 0%RH), probably because the decrease in OH^- conductivity which was caused by the decrease in the amount of moisture in the ACP electrolyte.

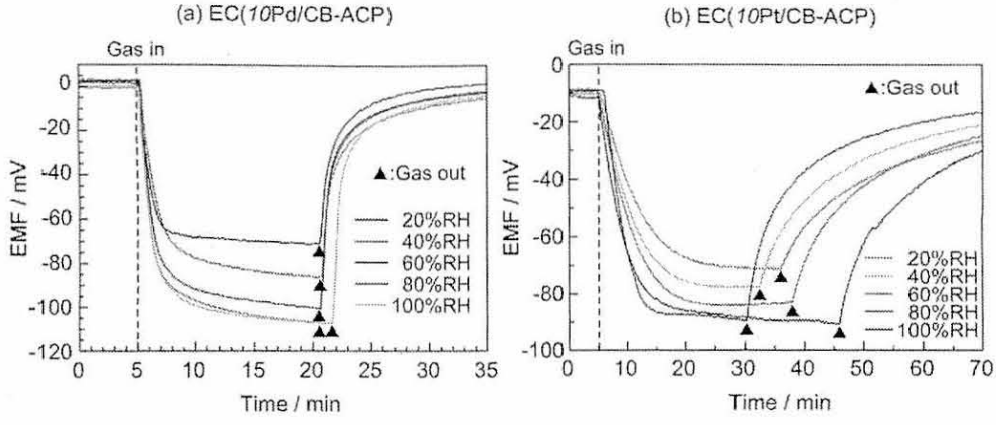

Figure 5. Response transients of EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) to 500 ppm CO in air at 30°C (20~100%RH).

Conclusions

CO sensing properties of EC(*n*M/CB-ACP) were investigated in this study. EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) showed much large response to 100~3000 ppm CO at RT (57%RH) in comparison with those of EC(*n10*Au/CB-ACP) and EC(CB-ACP). The response speed of EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) was fast in the CO concentration range of 500~3000 ppm, while that was extremely slow in the range of less than 300 ppm CO. In addition, ΔEMF of EC(*10*Pd/CB-ACP) and EC(*10*Pt/CB-ACP) negatively changed in proportion to the logarithmic CO concentration and CO sensitivities were ca. -19.3 mV/decade and ca. -24.8 mV/decade, respectively. However, responses of both sensors decreased with a decrease in RH, because of the decrease in OH^- conductivity which was caused by the decrease in the amount of moisture in the ACP.

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