Surface treatment of activated carbon by using a radio-frequency CF₄ plasma

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Abstract

In order to enhance the usefulness of activated carbon, a surface treatment of activated carbon using a radio-frequency CF₄ plasma was performed. The surface characterization of the activated carbon was performed using an energy dispersive X-ray (EDX) experiment and a differential scanning calorimeter (DSC). In addition, electron temperature and density in the plasma were measured using a probe system in order to investigate the optimum condition for the surface treatment. As the results, the EDX analyses investigated that the existence of fluorine on the plasma-treated carbon surface and the DSC results showed that the endothermic reaction with ammonia desorption on the plasma-treated activated carbon shifts to the low temperature side compared with that of the parent activated carbon. These facts indicate that introduction of -F groups on the surfaces of the activated carbon is responsible for the occurrence of low energy surface.

1. Introduction

Activated carbon made up of micro-pore is widely used as adsorption materials for industrial. However, when the activated carbon is reproduced after use, the same heating processes as the production are needed, and so a large electric power is demanded. Therefore, it is expected that the energy cost for reproduction can be improved and lowered. Especially the development of the activated carbon as low energy desorption type for ammonia adsorbent is desirable in the geriatric nursing.
In order to enhance its usefulness, we performed a novel treatment of activated carbon by using a radio-frequency (RF) CF₄ plasma. The plasma modification is a process in which gases are partly broken into chemically reactive species in the plasma, which then flow to, and physically or chemically react at material surfaces. Recently, we reported that the silica gel and zeolite surface could easily be modified using CF₄ plasma treatment to prepare the low energy surfaces [1-5]. These surfaces are due to -CFₙ (n=1–3) or -F groups, which are formed on the treated material surfaces. However, the surface modification of powder material such as activated carbon has not been reported. This technique has the potential to make novel surfaces having new functions of activated carbon, which would not be possible otherwise.

In this study, a powdery activated carbon was used for the CF₄ plasma treatment. The surface characterization of the activated carbon was carried out by an energy dispersive X-ray (EDX) experiment and a differential scanning calorimeter (DSC). Furthermore, we measured electron temperature and density using a probe [6-7] system in order to reveal the reason why the plasma helps the surface treatment.

2. Experiments and methods

Figure 1 shows a schematic diagram of RF plasma source and a probe system. The chamber was made of stainless steel, and its inner diameter and height were 260 and 300 mm, respectively. A planar, spiral, three turns copper coil antenna having a diameter of 120 mm was used for a plasma production and separated from the plasma by a 15 mm-thick quartz window. A 13.55 MHz RF current was passed through the coil antenna to produce the RF field that generated and sustained the RF discharge. CF₄ gas (99.99 %) was introduced through a mass flow controller into a cylindrical chamber, and the gas flow was controlled at 10 sccm. Then, the gas pressure in the treatment chamber was adjusted to 100 mTorr. The gas pressure was measured by capacitance manometer.

The activated carbon used for the plasma surface modification was a charcoal activated powder obtained from Wako Pure Chemical Industries Ltd. and placed on a base vessel with a heater. The base vessel was made of quartz, and the activated carbon in the vessel was stirred by a magnetic stirrer. The plasma treatment was performed for 120 min with the RF power of 50 - 200 W. The heating temperature of the vessel during the treatment was kept constant at 200 . The characterization of the activated carbon was performed using the EDX and the DSC. The EDX measurement can easily investigate the existence of the treated fluorine on the activated carbon surface. The DSC is possible to reveal the endothermic change of
ammonia desorption on the treated surface. For the case of DSC measurement, ammonia was first adsorbed on the treated activated carbon surface.

Electron temperature and density in the plasma were measured using a probe system in order to investigate the optimum condition for the surface treatment, in which detected probe currents were obtained by applying variable voltage to the probe tip. The probe tip was made of tungsten having a diameter of 0.5 mm and a length of 4 mm, and was electrically insulated by glass tube. The probe system was placed 20 mm apart from the RF antenna. Radial measurements of electron temperature and density were performed from center to a radius $r = 120$ mm by changing the position of the probe. Axial measurements were carried out by varying the axial position of the probe after the vessel was removed from the chamber bottom. In the case of measurements of power dependence, the probe was positioned 20 mm from the RF antenna with $r = 0$ mm.

3. Experimental results and discussions

3.1 Plasma property

The electron temperature and density in the plasma were measured for various RF power conditions. The measurements that we present here were all made in the center (20 mm from the RF antenna with $r = 0$ mm). Figure 2 shows the RF power dependence of electron temperature and electron density. The abscissa means the value of RF power delivered from the RF power source. For these measurements, the gas pressure was constant at 100 mTorr when the plasma was off. As can be seen from this figure, there seems to be no strong dependence of electron temperature on the inputted RF power, and electron density seems to increase linearly. These are similar to results seen in other RF discharge sources used for processing applications in the microelectronics industry although the plasma operating pressure is higher than ones. Particles analyses [8-9], obtained theoretically in CF$_4$ plasmas having the similar values of electron density and temperature to those of the present experiment, investigated that the concentrations of CF$_3$ and F radicals are about $10^4$ times those of ions. Therefore, it is expected that the plasma reaction on activated carbon surface by the neutral radicals such as CF$_3$ and F would be dominant.

Figure 3 shows measured results of radial profiles of (a) electron temperature and (b) density, obtained in the radial direction from $r = 0$ mm to $r = 120$ mm. For these measurements, the axial position was fixed 20 mm from the RF antenna with $r = 0$ mm. The RF power and CF$_4$ pressure were 200 W and 100 mTorr, respectively. In these figures, the
values from $r = -10\ \text{mm}$ to $r = -120\ \text{mm}$ are the same as those of $r = 10\ \text{mm}$ assuming that profiles of electron temperature and density are distributed concentrically. The electron temperature profile appears fairly flat around 4.5 eV although electron temperatures near the chamber wall are slightly high. This is brought by that electron temperature can not sustain the temperature gradient and will be spatially flat because the thermal conduction of electrons is high, even if heating region is localized near the RF antenna. Thus, in the RF plasma, electron temperature is high as electrons obtain energy from the RF electric field in the initial stage. Reactions such as dissociation, excitation and ionization are caused by collisions between particles and electrons that have high energy. On the other hand, the mean collision frequency will not become so high till thermodynamic equilibrium will be accomplished between electron, ion and neutral atom. Temperatures of neutral particle and ion are low and the whole heat capacity of plasma will be low. Therefore, the reproduction process using the plasma is drastically different from the general heat process.

Electron density profile has a peak at $r = 0\ \text{mm}$. The extinction of plasma is mainly caused by recombination at the chamber wall, and the loss ratio of plasma with respect to the product ratio will be larger near the chamber wall. However, electron densities from $r = 0\ \text{mm}$ to 60 mm are almost flat ($3.6 \times 10^{15} \ \text{m}^{-3}$).

![Electron temperature and density profiles](image)

Fig. 3. Radial distributions of (a) electron temperature and (b) density. The gas pressure and RF power were constant at 100 mTorr and 200 W, respectively.

Axial profiles of electron temperature and density are shown in Fig. 4. The radial position for all measurements was $r = 0\ \text{mm}$, and the RF power was 200 W. The axial position $Z = 0$ means coil window, and $Z = 120$ is the position of vessel bottom. As can be seen from these figures, electron temperature appears fairly constant along the axis, perhaps, rising slightly towards the vessel bottom. In contrast, electron density is peaked at $Z = 0\ \text{mm}$ and decreases along the axis. At $Z = 120\ \text{mm}$, electron temperature and density are 3.1 eV and $1.6 \times 10^{15} \ \text{m}^{-3}$ respectively, however, these values were obtained without the vessel and the activated carbon.
It is necessary to note that these values may well be influenced by the existence of the vessel and the activated carbon because the extinction of plasma is caused by recombination at those surfaces.

3.2 Characterization of modified activated carbon

Figure 5 shows the EDX spectra of the parent and plasma-treated activated carbon. The RF power was 100 W when the plasma treatment was performed. It can be seen from this figure that the plasma-treated activated carbon contains fluorine clearly. For this case, fluorine content calculated from the ratio of whole spectral area was 2.2 %. It is considered that new groups bonded to the activated carbon surface were obviously generated by the plasma treatment because the physically adsorptive CF₄ derivatives on the activated carbon surface were desorbed by evacuation at 450 °C for 1 hour. Figure 6 shows the variation of fluorine content against the inputted RF power. As mentioned above, electron density increases with increase of the inputted RF power, which contributes to the rise of plasma density such as ions and radicals. It can be seen from this figure that fluorine content linearly increases with the increase of the RF power.

Fig. 5. EDX spectra of the parent and plasma-treated activated carbon.

Fig. 6. Variation of fluorine content against the inputted RF power.
Figure 7 shows DSC spectra of the parent and plasma-treated activated carbon. The plasma treatment was performed with the RF power of 100 W. The ordinate means the desorption heat change of the adsorbed ammonia. From this figure, it is found that the endothermic reaction of plasma-treated activated carbon shifts to the low temperature side compared with that of the parent activated carbon. The EDX and DSC results indicate that introduction of -F groups on the surfaces of the activated carbon is responsible for the occurrence of low energy surface.

4. Conclusions

The surface treatment of activated carbon using a radio-frequency CF₄ plasma that had electron temperature of 3.1 eV and electron density of 1.6×10¹⁵ m⁻³ was performed. The EDX and DSC results indicate that introduction of -F groups on the surfaces of the activated carbon is responsible for the occurrence of low energy surface. Furthermore, it was found that the introduction amount of fluorine increased with the increase of plasma density. Our treatment technique is useful to change the character of activated carbon surface and makes it possible to reduce the release energy of adsorbed material.

References


2932