1. Introduction

Activated carbon has been used widely not only as an adsorbent for industry, but as a functional electrode material for electrodes for double-layer capacitors. The benefits of activated carbon include its low-cost derivation from the use of abundant resources, cost-effective activation processes, and its developed porous structure. The properties of activated carbons depend complicatedly on the graphic structure, pore structure, and surface state of the activated carbon. Actually, activated carbon’s amorphous structure influences its electronic conductivity. Its activation process, mild oxidation, provides a random pore structure and various surface functional groups. The large surface area of activated carbon, with its complex micropore distribution and surface functional groups, supports the strong adsorption of some molecules such as water. In an earlier study, the authors attempted to estimate the amount of adsorbed water on activated carbon by finding the water content in a suspension of activated carbon in a non-aqueous solvent. After fitting the data to a Langmuir adsorption equilibrium, the authors assessed the effects of the remaining water on the capacitor performance, particularly its cycle stability.

This study specifically examined the unique adsorption behavior of ibuprofen on commercially available activated carbon. Ibuprofen is known as a representative anti-inflammatory drug. Recently, alternative drug delivery systems by which drug molecules are adsorbed onto a certain adsorbent and are subsequently released slowly at an affected part have been proposed and investigated intensively. The authors have found that ibuprofen molecules, different from other adsorbents, adsorb strongly on activated carbon without release. Although an adsorbent that does not release an adsorbed molecule is inadequate for drug delivery use, such behavior is attractive for elucidating some properties activated carbon. Indeed, few methods can reveal the adsorption mode of ibuprofen on activated carbon because conventional modes of spectroscopy are ineffective for molecules adsorbed in micropores. Ibuprofen molecules are expected to remain adsorbed after the polarization of activated carbon. Therefore, comparing the capacitances of activated carbon with and without adsorbed ibuprofen using various methods can yield information related to the adsorption state of ibuprofen. The capacitances of activated carbon with ibuprofen adsorption have been measured using cyclic voltammetry and impedance spectrometry for a case study of a microporous electrode with strongly adsorbed species. Strong adsorption occurs only in a limited combination between the adsorbent and selected adsorbed species. Few reports of the literature have described the electrochemical responses of strongly adsorbed species, except for self-assembly formation of thiol on a flat gold electrode. Therefore, the present study might be interesting as a case study of the electrochemical response of a microporous carbon electrode with a strongly adsorbed species. The adsorption status of ibuprofen in activated carbon was inferred from the double-layer capacitances of ibuprofen-adsorbed activated carbon using analyses employed for the study of double-layer capacitor electrodes.

2. Experimental

2.1 Chemicals

Activated carbon (granulated charcoal, AC; Kanto Chemical Co. Inc., Japan) was used after vacuum drying overnight at 483 K. Carbon nanotubes (CNTs; Nanocyl S.A., Belgium) were used as received. Mesoporous silica SBA-15 was prepared from sodium silicate (Kanto Chemical Co. Inc.) and Pluronic 126 (BASF SE, Germany) according to procedures presented in an earlier report. Ibuprofen (Tokyo Chemical Industry Co., Ltd., Japan) was dissolved in hexane (Kanto Chemical Co. Inc.) up to the prescribed concentration.

2.2 Adsorption of ibuprofen on porous carbons

The specific surface areas of AC, CNT, and SBA-15 were estimated from the nitrogen adsorption isotherm (NOVA9000; Quantachrome Instruments). The adsorption and release of ibuprofen on AC, CNT, and SBA-15 were compared using the following procedure. After each material (200 mg) was dispersed in 20 cm$^3$ of an ibuprofen/hexane solution, it was then stored at 298 K in a chamber with controlled temperature (SU-221; Espec Corp.). The ibuprofen concentration in the hexane solution was monitored using high-performance liquid chromatography (GL Science Inc., Japan). After reaching the adsorption equilibrium (estimated by preliminary adsorption tests), the adsorbent was filtered out and dried under vacuum. The adsorbed amount of ibuprofen was estimated using both the weight change of the adsorbent and the concentration.

**Abstract**

Ibuprofen (2-(p-isobutylphenyl)propionic acid) is adsorbed strongly onto the surface of commercial activated carbon and is never released thereafter by subsequent immersion in water. The electrochemical responses for the ibuprofen-adsorbed activated carbon electrode can be monitored via cyclic voltammetry and impedance spectrometry. The influence of adsorbed ibuprofen can be extracted. The adsorbed ibuprofen molecules passivate the pore surface of the activated carbon electrode and decrease its capacitance. The capacitance by ibuprofen adsorption remains decreased even after the exposure to a more positive potential.
change of the solution. The AC with adsorbed ibuprofen in a \( ax \) g dm\(^{-3}\) solution is hereinafter denoted as IP\( (ax) \). Although the former amount was always smaller by ca. 20% than the latter one in each adsorption test, the former and the latter method show similar dependence of the adsorption amount on the ibuprofen content in the hexane solution. Some ibuprofen might be vaporized during the drying that is done before the material is weighed. After adsorption testing of the adsorbent in 60 g dm\(^{-3}\) solution, the ibuprofen release test was conducted by immersing 200 mg of the adsorbent into 20 cm\(^3\) of distilled water. The release amounts were monitored using UV-vis spectroscopy.

### 2.3 Evaluation of double-layer capacitance of ibuprofen-adsorbed AC

The double layer capacitances of the AC electrodes with or without adsorbed ibuprofen have been estimated using cyclic voltammetry and ac impedance methods. Working electrode sheets were prepared by mixing 85 wt% (170 mg) of the AC, 5 wt% (10 mg) of conducting agent (VGCF\( ^{\text{TM}} \times\); Showa Denko K.K.), and 10 wt% (20 mg) of poly(tetrafluoroethylene) binder (Daikin Industries, Ltd.). A ca. 7-mm-diameter disk of the composite (ca. 10–20 mg) was molded and then fixed onto a platinum mesh current collector. A three-electrode test cell (BAS Inc., Japan) was assembled with the composite working electrode, with platinum wire as a counter electrode, a Ag/AgCl reference electrode (BAS Inc.), filter paper (Toyo Roshi Kaisha Ltd., No. 2) as separator, and 1 cm\(^2\) of electrolyte. Aqueous solution of 1 mol dm\(^{-3}\) KCl or 1 mol dm\(^{-3}\) HCl was used as the electrolyte. A potentiostat equipped with a frequency response analyzer (1286; Solartron) was used for electrochemical measurements. Cyclic voltammetry was conducted with potentials of 0 V–0.8 V versus the reference electrode at a 2 mV s\(^{-1}\) scan rate during three cycles. For all cases of measurements, the voltammograms at the second and the third cycle are almost overlapped. Consequently, the voltammograms at the second cycles are displayed in the following figures. The ac impedance measurements were conducted before and after the cyclic voltammetry test for each cell under the condition of 10 mV amplitude from 0 V vs. Ag/AgCl, 10\(^5\) to 10\(^{-2}\) Hz of frequency. The cell temperature was controlled at 298 K during these measurements. The specific surface area of the composite electrode sheet before and after the electrochemical measurements was estimated using a single-point BET nitrogen gas adsorption apparatus (Monosorb; Quantachrome Instruments). Although this method provides only rough estimation of the surface area, the measurements can be conducted under N\(_2\)/Ar mixed gas flow instead of evacuation at the pretreatment. The vacuum process was avoided for the present case to retain adsorbed ibuprofen on the activated carbon.

### 3. Results and Discussion

The ibuprofen adsorption on each adsorbent appears to reach a steady state within several hours. The BET surface areas, estimated mesopore surface areas, and the steady-state adsorption amounts of ibuprofen in n-hexane on the adsorbents SBA-15, AC, and CNT are presented in Table 1. The steady-state adsorbed amounts correspond directly neither to the overall surface area nor to the mesopore area of adsorbents. The adsorption of ibuprofen might be influenced not only by pore size but by the dimensional structure of AC. As a result, all materials adsorb 1–2 g of ibuprofen in one gram after achieving the steady state. These materials including ibuprofen were then immersed in de-ionized water. The concentration of the released ibuprofen was monitored. The concentration of the emitted ibuprofen is also included in Table 1. A substantial amount of ibuprofen, although markedly small compared to the adsorbed amount, was released from SBA-15 and CNT. By contrast, ibuprofen release from the AC was not detected, indicating that ibuprofen strongly adsorbs onto the AC. The relation between the ibuprofen/hexane solution concentration and the adsorbed amount of ibuprofen on the AC is presented in Fig. 1. The adsorbed amount fundamentally increases according to the increase of the ibuprofen source concentration. It is saturated around 30 g dm\(^{-3}\).

Cyclic voltammograms at the potentials of 0–0.8 V vs. Ag/AgCl for the ACs with various amounts of adsorbed ibuprofen (a) in 1 mol dm\(^{-3}\) KCl aq. and (b) in 1 mol dm\(^{-3}\) HCl aq. are portrayed in Fig. 2. The AC shows a typical rectangular voltammogram of porous carbon electrodes with irreversible oxidation current at 0.8 V, irrespective of the electrolyte used. After the adsorption of ibuprofen, the electrodes show a similar rectangular voltammogram with the decrease of charging current in both electrolytes, with no marked redox peak. The charging current decrease suggests that the adsorbed ibuprofen molecules passivate a part of the surface, but not the entire outer surface of the AC. The specific capacitances based on the electrode mass and unit surface area for the ibuprofen-adsorbed AC are presented in Table 2. The specific surface areas were measured using pellet forms of the ibuprofen-adsorbed AC with 10% of PTFE. Consequently, the AC surface area is smaller than that measured in powder form, indicating that PTFE partially covers the AC particle surface. Furthermore, ibuprofen adsorption on the AC decreases the surface area considerably. Decreases of the specific capacitances by ibuprofen adsorption are caused by the ibuprofen coverage, as suggested by the similar values of capacitance per unit surface area for AC and the ibuprofen-adsorbed AC. Although the capacitance per unit surface area (of the pellet) for the IP(12)/AC is slightly lower than that for the AC in the KCl electrolyte, the values in the HCl electrolyte are similar between the AC and the IP(12)/AC. In both electrolytes, the IP(60)/AC electrode shows a very weak charging current, suggesting that ibuprofen molecules filled most pores.

To obtain information indicating whether ibuprofen molecules are released during polarization at 1.0 V, or not, cyclic voltammetry measurements were taken after the cyclic voltammetry sequence to

| Adsorbent | Specific surface area /m\(^2\) g\(^{-1}\) | Mesopore surface area /m\(^2\) g\(^{-1}\) | Adsorbed ibuprofen /g (g adsorbent\(^{-1}\)) | Desorbed ibuprofen /mg (dm\(^3\) water\(^{-1}\)) |
|-----------|-----------------------------|-----------------------------|-----------------|-----------------|
| AC        | 1155                        | 168                         | 1.3             | not detective   |
| CNT       | 371                         | 371                         | 1.1             | 20              |
| SBA-15    | 463                         | 118                         | 1.8             | 35              |

![Figure 1](image.png)

**Figure 1.** Adsorption amount dependence of the concentration of ibuprofen on activated carbon.
0.8 V and then 1.0 V. Voltammograms (a) taken at the initial scan to 0.8 V, (b) at the scan to 1.0 V, and (c) at the scan to 0.8 V after the experience at 1.0 V are shown in Fig. 3. The AC that had adsorbed 5 wt% of ibuprofen was used for comparison to AC because the effects of ibuprofen release were observed more clearly than with the IP(12)/AC, which had somewhat excess ibuprofen. For both the AC and the IP(5)/AC electrodes, the oxidation current is significant at higher positive potential than 0.8 V; moreover, the charging current is increased. During the second exposure to 0.8 V, the AC electrode capacitance became greater than that with the initial scan at 0.8 V. By contrast, the features of the voltammogram for the IP(5)/AC electrode after the second exposure to 0.8 V resemble those after the initial scan, which suggests that the surface status of the IP(5)/AC electrode remains even after the scan to 1.0 V with the oxidation by-reaction. This result suggests that ibuprofen molecules in the AC pores are not released. The retention of the surface for the IP(5)/AC electrode can be inferred also from the specific surface area of the IP(12)/AC after polarization to 1.0 V, as presented in Table 2, to the same degree as from the initial IP(12)/AC pellet.

Bode plots from the ac impedances of the AC electrodes in the K and the HCl electrolytes are presented respectively in Figs. 4(a) and 4(b). A Bode plot indicates capacitance fractions of total capacitance obtained with different charging rates because a capacitance response at a given frequency must be reflected by the capacitance value detected in the time period of the corresponding time constant. For porous electrodes, the capacitance fractions measured from different pore sizes must have different rates of double-layer formation because narrow pores must have slow ion transport. The IP(60)/AC shows very low capacitance in frequency regions when the AC pores are filled with ibuprofen. Other cases show dependence of the electrolyte species. Both the AC and the IP(12)/AC electrodes show that the capacitance increases as the frequency becomes lower. The capacitances at 10⁻² Hz are

Table 2. Properties of AC and IP/AC electrodes before and after cyclic voltammetry

|                      | Specific surface area (in pellet) /m² g⁻¹ | Specific capacitance /F g⁻¹ | Capacitance per unit surface area /µF cm⁻² |
|----------------------|------------------------------------------|-----------------------------|-------------------------------------------|
|                      | Before CV to 1.0 V in KCl | After CV to 1.0 V in KCl | In KCl | In HCl | In KCl | In HCl |
| AC                   | 643 | 781 | 73 | 103 | 1.1 | 1.6 |
| IP(12)/AC            | 434 | 387 | 46 | 69 | 0.95 | 1.6 |
| IP(60)/AC            | 90 | 108 | 8.3 | 3.6 | 0.89 | 0.40 |
fundamentally similar to those calculated from cyclic voltammetry, as reported from an earlier study.\(^{18}\) The capacitance for the IP(12)/AC is considerably lower than that for the AC, as is the cyclic voltammetry measurement. The lower capacitance at the low frequency region from the AC to the AC with adsorbed ibuprofen indicates that ibuprofen molecules adsorb mainly onto the pore surface. Comparison between the KCl and the HCl electrolytes demonstrates that features at low frequency differ. The AC without ibuprofen exhibits a capacitance plateau near 10\(^{-1}\) to 10\(^{-2}\) Hz only in the KCl electrolyte. This plateau is explainable by limitation of the transport of solvated potassium ion in mesopores or micropores. The capacitance decreases after the adsorption of ibuprofen becomes severer in the KCl electrolyte than in the HCl electrolyte, as demonstrated by the cyclic voltammetry results.

The adsorbed ibuprofen reportedly passivates the pore surface and decreases the effective surface for an activated carbon electrode. The dissociation of a carboxyl moiety in an ibuprofen molecule must be different in these electrolytes because the pKa of ibuprofen is reportedly 4.52.\(^{20}\) The slight difference of the retention of the double-layer capacitance of the IP(12)/AC in the HCl electrolyte might be affected by the dissociation of adsorbed ibuprofen molecule, although the influence is expected to be minor.

The Bode plots of the IP(12)/AC cell in the KCl electrolyte before and after polarization to 0.8 V and 1.0 V are presented for comparison in Fig. 4(c). The capacitance is increased by the decrease of frequency from the order of 10\(^2\) Hz. The capacitance profile after the 0.8 V polarization resembles the initial profile. However, the capacitance after 1.0 V polarization is lower, between 10\(^2\) to 10\(^3\) Hz. It is slightly higher below 10\(^9\) Hz than in the other cases. A change might occur inside the pores by polarization to 1.0 V. The slight change in the frequency dependence of the capacitance fraction after polarization to 1.0 V might result from some rearrangement of the adsorption layer of ibuprofen inside the pores.

These results suggest the following for the adsorption mode of ibuprofen on the activated carbon: ibuprofen molecules fill some pores and inhibit double-layer charging in the pores. Passivation by the adsorbed ibuprofen, a lack of electron transfer, suggests that the interaction between the pore wall and an ibuprofen molecule is an electrostatic force between functional groups of both materials rather than \(\pi-\pi\) attraction. The interacting group for an ibuprofen molecule is probably not carboxyl because the capacitance decrease appears to be similar between the KCl electrolyte and the HCl electrolyte. Passivation by ibuprofen physically prevents double-layer formation. The capacitance is influenced by the ibuprofen adsorption status. In this case study, the relation between the status of adsorbed species and the capacitance of activated carbon was elucidated, but further investigation can reveal properties of various adsorbates.

4. Conclusion

Ibuprofen was adsorbed strongly onto the activated carbon pore surface, where it passivated the pore surface. The activated carbon electrode capacitance was found to be approximately proportional to the electrode pellet surface area, although the decrease of the capacitance was slightly mitigated in the hydrochloric acid electrolyte. Exposure of the ibuprofen-adsorbed activated carbon at 1.0 V vs. Ag/AgCl with and oxidation by-reaction would not change the adsorption state. These results provide information revealing the influence of adsorbed species on the electrochemical response. They elucidate the adsorption state of ibuprofen in the pores of activated carbon.

References

1. H. Marsh and F. Rodríguez-Reinoso, Activated Carbon, Elsevier (2006).
2. E. Frackowiak and F. Béguin, Carbon, 39, 937 (2001).
3. M. Inagaki, H. Konno, and O. Tanaike, J. Power Sources, 7880 (2010).
4. M. Endo, Y. Okada, and H. Nakamura, Synth. Met., 34, 739 (1989).
5. A. Yoshiida, I. Tanahashi, and A. Nishino, Carbon, 28, 611 (1990).
6. T. Momma, T. Liu, T. Osaka, Y. Usbui, and Y. Sawada, J. Power Sources, 60, 249 (1996).
7. Y. Otake and R. G. Jenkins, Carbon, 39, 937 (1993).
8. M. Egashira, T. Izuca, N. Yoshimoto, and M. Morita, J. Power Sources, 326, 635 (2016).
9. P. Horcajada, A. Rámila, J. Pérez-Pariente, and M. Vallet-Regi, Microporous Mesoporous Mater., 68, 105 (2004).
10. S.-W. Song, K. Hidajat, and S. Kawi, Langmuir, 21, 9568 (2005).
11. S. Wang, Microporous Mesoporous Mater., 117, 1 (2009).
12. R. Melaerts, K. Hoothoold, K. Elen, H. Chen, M. Van Speybroeck, M. Van Humbeeck, P. Augustijns, J. Mullens, G. Van den Mooter, and J. A. Martens, Microporous Mesoporous Mater., 130, 154 (2010).
13. M. Melillo, G. J. Phillips, J. G. Davies, S. R. Tennison, O. P. Kozyrchenko, and S. V. Mikhailovsky, Carbon, 42, 565 (2004).
14. X. Wang, P. Liu, and Y. Tian, Microporous Mesoporous Mater., 142, 336 (2011).
15. J. A. M. Sontag-Huethorst and L. G. J. Fokkink, J. Electroanal. Chem., 367, 49 (1994).
16. R. S. Clegg and J. E. Hutchison, Langmuir, 12, 5239 (1996).
17. K. Bandyopadhyay, V. Patil, M. Sastry, and K. Vijayamohan, Langmuir, 14, 3408 (1998).
18. M. Morita, T. Kaigaishi, N. Yoshimoto, M. Egashira, and T. Aida, Electrochem. Solid-State Lett., 9, A386 (2006).
19. M. Tokita, M. Egashira, N. Yoshimoto, and M. Morita, Electrochemistry, 80, 752 (2012).
20. C. Rafols, M. Rosés, and E. Bosch, Anal. Chim. Acta, 350, 249 (1997).