A kinetic analysis of intercalation of organic sulfate anions into layered double hydroxide using quartz crystal microbalance with layered double hydroxide-immobilized electrode

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To investigate a dynamic intercalation behavior of organic anions into layered double hydroxide (LDH) interlayer by ion-exchange, a quartz crystal microbalance (QCM) with the Mg–Al LDH thin film immobilized gold disc (LDH/QC) electrode has been used. A stable minute LDH film was prepared by using translucent aqueous sol of LDH containing OH– ions and magnesium acetate molecule in the interlayer and immobilized on the gold disc after pretreatment of the surface of the supporting silica electrode with hydrophobic agent. In the kinetic analysis, alkyl sulfates having n-alkyl chain (CnH2n+1, n = 5–12; abbreviated as CnS) were used as guest anions. As the results, the time-dependence on C7S and C12S intercalation were successively analyzed using the rate equation based on the reversible pseud first-order reaction. Finally, the instrumental analyses of the LDH films before and after the intercalation of C12S revealed that the organic anions could be intercalated into the LDH interlayer of the LDH/QC electrode in each aqueous solutions.

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1. Introduction

Layered double hydroxide (LDH) is widely known as hydrotalcite-like compound and often called anionic clay comparing with more conventional cationic clays. In recent years, LDH intercalation compounds have received considerable attention in view of their potential technological importance as antacid, anion-exchanger, adsorbent, stabilizer, separator, catalysis, electrode, optical memory and new nanocomposite materials.3–7) Generally, the chemical composition of LDH can be represented as [M2+,nM3+,1-n(OH)2] [(An)x(BOx)y]·yH2O, where M2+ is a divalent cation (Mg2+, Ca2+, Cu2+, Mn2+, Ni2+, Zn2+), M3+ is a trivalent cation (Al3+, Cr3+, Fe3+, Mn3+, Co3+), and An is an exchangeable anion of charge n such as Cl−, CO32−, NO3−, SO42− and diverse organic anions. X value is equal to the molar ratio of M3+/|M2+ + M3+|, generally 0.20–0.33.8) The crystal structure consists of positively charged brucite-like octahedral hydroxide basal layers, which are electrically neutralized by interlayer anions and water molecules occupying interlayer space.9,10)

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LDH is rarely found in nature; however, it is easily synthesized by coprecipitation reaction under mild laboratory conditions. Therefore, LDH is often used to synthesize various organic/LDH intercalation compounds.11–14) An intercalation of various organic guests for LDH has learned in the following methods: coprecipitation,15,16) ion-exchange,17–20) calcination-rehydration,21–24) thermal reaction25) and hydrothermal reaction.26) In these intercalation methods, the ion-exchange reaction is the most popular method for LDH, and it is well-known that the inorganic anions having a larger density of electric charge are easier to be intercalated into the LDH interlayer.8) On the contrary, the intercalation of organic anions is more complicated compared to that of inorganic anions. Thus the attraction force of the intercalation of organic anions is not only an electrostatic force between the guest and the host LDH layer, but also other forces such as hydrophobic interaction and hydrogen bond between the guest and the once-intercalated guest.20,22,27) Regarding the intercalation equilibrium of organic sulfur anions into LDH, there are some research works15–17,21) but no researches concerning their dynamic intercalation behavior have been known.

To clarify the dynamic intercalation behavior of organic anions into LDH interlayer by ion-exchange, the kinetic
analysis has been needed in addition to the equilibrium one. However, such examination has been limited so far, because of the experimental difficulty in a kinetic study. Therefore, we focus on a quartz crystal microbalance (QCM) as an analytical technique in aqueous solutions. The QCM is a simple, rapid, and nano-gram sensitive technique initially developed to quantify the adsorption of gases onto a quartz surface. Afterward, the QCM has been also used to quantify the adsorption of ions and others in solutions in many different research areas.\(^{28}\) As the case studies using QCM with the clay-modified electrode, the redox processes of metal complexes were reported by the earlier researchers.\(^{29,30}\) Moreover, the studies of mass transport in the thin films of Mg\textsubscript{0.75}Al\textsubscript{0.25}(CO\textsubscript{3})\cdot 0.5H\textsubscript{2}O.\(^{33}\) The chemical composition in which the values of d\textsubscript{003} and d\textsubscript{006} were 1.13 and 0.57 respectively, for the Mg\textsubscript{2}CO\textsubscript{3}·H\textsubscript{2}O. This LDH compound had a typical X-ray diffraction pattern. FT-IR spectra were obtained using a Shimadzu AA-6650 atomic absorption spectrometer (metal ions) and a Shimadzu TOC-5000 total organic carbon analyzer (MgAc\textsubscript{2} component) after the dissolution of the LDH sample in a dilute hydrochloric acid solution. As the amount of the LDH film immobilized on the gold disc of QC was quite small, the large-scale model experiments of the intercalation of C\textsubscript{12}S anion were carried out by using the LDH film immobilized on XRD glass plate and also the cell of a 300 cm\textsuperscript{2} glass beaker for 15 min at the same condition as the QCM measurement. The LDH films immobilized on XRD glass plate before and after the intercalation were subjected to XRD analysis as such after drying. A part of the LDH film was sampled and also subjected to FT-IR measurement. Powder XRD measurements were performed on a Rigaku Rint 2200 powder X-ray diffractometer, using a Cu\textsubscript{K\alpha} radiation (\(\lambda = 0.1541\) nm) at 20 mA, 40 kV, a scanning rate of 2\(^{\circ}\)/min and 2\(^{\circ}\) angle ranged from 2–70\(^{\circ}\). FT-IR spectra were obtained using a JASCO WS/IR 7300 FT-IR spectrophotometer over the wavenumber range of 4000–400 cm\textsuperscript{-1} by the standard KBr disk method.  

2.3 QCM instrument

The QCM measurements were performed at the fundamental frequency of 5 MHz using an Initial Affinix QN Pro (QCM 2008-PRKIT) at 25 °C with stirring. The stirring rate was adjusted to achieve the theoretical mass change shown in the Sauerbrey equation below:\(^{35}\) 

\[
\Delta F = -2F_0^2/A(\mu_q \cdot \rho_g)^{1/2} \cdot \Delta M
\]

Where, \(\Delta F\) is the measured frequency change (Hz), \(\Delta M\) is the mass change (g), \(F_0\) is the fundamental frequency (27 MHz), \(A\) is the surface area of gold electrode (cm\textsuperscript{2}), \(\mu_q\) is the shear modus of quartz (g/m/s\textsuperscript{2}), \(\rho_g\) is the density of quartz (g/cm\textsuperscript{3}). In this measurement, the frequency change, \(\Delta F\) of 1 Hz, corresponds to the mass change of 0.62 ng/cm\textsuperscript{2}.

2.4 Characterization of the LDH film on gold disc electrode of QCM

The immobilization state of the LDH particles on the gold disc of QC was observed using a Kyowa KN-100T optical microscope. The surface morphology was observed using a Nanosurf AG Easyscan 2 atomic force microscope (AFM) at tapping mode over the measuring region of 10 \(\mu\text{m}\); and the scanning speed of 700 ms. The surface chemical composition of the LDH film was determined by using X-ray photoelectron spectroscopy (XPS), using a monochromated AlK\textsubscript{x} radiation at analysis area of 100 \(\mu\text{m}^2\), the photoelectron emission angle of 45\(^{\circ}\). The chemical composition of the total LDH film was determined using a Shimadzu AA-6650 atomic absorption spectrometer (metal ions) and a Shimadzu TOC-5000 total organic carbon analyzer (MgAc\textsubscript{2} component) after the dissolution of the LDH sample in a dilute hydrochloric acid solution. As the amount of the LDH film immobilized on the gold disc of QC was quite small, the large-scale model experiments of the intercalation of C\textsubscript{12}S anion were carried out by using the LDH film immobilized on XRD glass plate and also the cell of a 300 cm\textsuperscript{2} glass beaker for 15 min at the same condition as the QCM measurement. The LDH films immobilized on XRD glass plate before and after the intercalation were subjected to XRD analysis as such after drying. A part of the LDH film was sampled and also subjected to FT-IR measurement. Powder XRD measurements were performed on a Rigaku Rint 2200 powder X-ray diffractometer, using a Cu\textsubscript{K\alpha} radiation (\(\lambda = 0.1541\) nm) at 20 mA, 40 kV, a scanning rate of 2\(^{\circ}\)/min and 2\(^{\circ}\) angle ranged from 2–70\(^{\circ}\). FT-IR spectra were obtained using a JASCO WS/IR 7300 FT-IR spectrophotometer over the wavenumber range of 4000–400 cm\textsuperscript{-1} by the standard KBr disk method.

2.2 Preparation of the LDH film on gold disc electrode of QCM

First, the Mg\textsubscript{2}/Al(OH\textsuperscript{+} + MgAc\textsubscript{2})/LDH powder was dispersed in Milli-Q water to prepare 0.028 mass % slurry, and then it was changed to the translucent aqueous sol by supersonic wave treatment. The LDH film was immobilized by dropping the resulted LDH sol on the central gold disc (4.9 mm\textsuperscript{2}) of QCM electrode using a pipette and by drying at 40 °C for 2 h under reduced pressure. The resulted LDH film was stable in water and observed no peeling during the intercalation experiments as mentioned in 3.2.
3. Results and discussion

3.1 Preparation of the LDH film on gold disc electrode of QCM

One of the most important points in this study is to prepare a stable thin film of LDH on the gold disc electrode of QCM (LDH/QC). It is generally known that the special techniques and/or starting materials are needed to prepare the LDH thin film. Therefore, after being various trials, we decided to use the Mg-Al/(OH\(^+\) + MgAc\(_2\))/LDH as described in 2.1. This LDH powder was easily delaminated in water by supersonic wave treatment to form the translucent sol of LDH. By using this LDH sol, the resulted film became minute and difficult to peel off from the electrode.

The schematic illustration of the QCM electrode immobilized with the LDH film is shown in Figs. 1(a) and 1(b). First, the whole QC electrode was treated with fluoroalkyl silane coupling agent solution. By this treatment, only the quartz surface became hydrophobic, because the coupling agent was adsorbed only on the quartz surface, not on the gold disc surface. Thus the outside quartz surface surrounded central gold disc (4.9 mm\(^2\)) of the QC electrode was modified to a hydrophobic surface. This is the key technique to prepare the LDH/QC electrode. Then, the thin LDH film was immobilized by dropping the aqueous sol of LDH only on the central gold disc using a pipette [Fig. 1(a)] and by drying at 40 °C for 2 h under reduced pressure [Fig. 1(b)]. The microscopic images of the surface of the gold disc before (a) and after (b) drying were shown in Fig. 2, together with the AFM topographic image (c) of the LDH film after drying. By the surface treatment of the outside quartz surface of QC electrode with fluoroalkyl silane coupling agent, the translucent LDH sol was found to be placed only on the central gold disc, and therefore, the firm LDH film was formed only on that after drying. From AFM observation (c), the LDH film was the aggregate of LDH particles of 100–200 nm in diameter and 1–3 nm in thickness. The amount of this LDH film was calculated in the narrow range of 6.7–7.3 \(\mu\)g cm\(^{-2}\) from the change of frequency.

3.2 QCM measurements for intercalation of organic sulfate anions

The schematic illustration of the cell and procedure of the QCM measurement is also shown in Fig. 1(c). The LDH/QC electrode was soaked in an 8 cm\(^3\) of Milli-Q water in the cylindrical grass cell at 25 °C under vigorous agitation with a magnetic stirrer. After standing for some time keeping no change in the frequency, the intercalation reaction was started by injecting the guest alkyl sulfate solution of 4.0 \(\times\) \(10^{-6}\) dm\(^3\) using a microsyringe. The frequency changes of QCM before and after the injection of various alkyl sulfates ions having \(n\)-alkyl chain (C\(_n\)S; \(n = 5–11\)) are shown in Fig. 3. In the region before the injection, no frequency change was observed, meaning that the LDH/QC is quite stable and never happen to peel off from the electrode. In both cases of C\(_5\)S (a) and C\(_6\)S (b), the decrease in frequency was not observed anymore. On the point of the injection, a quite small increase of frequency was observed, indicating the occurring of quite a small mass decrease on the electrode. This may be the peeling of a quite small amount of LDH particles in nano-gram order, but it is negligible. Thus it should be concluded that no intercalation of organic sulfate anions occurred in these cases. On the contrary, a clear

![Fig. 1. Schematic illustration of the preparation process of the LDH immobilized QC electrode (a and b) and the cell for intercalation of organic sulfate anion (c).](image-url)
decrease of frequency was recognized in the case of C7S (c) and finished after 120 s in spite of the degree was small. This result indicates that the alkyl sulfate ion having a longer than 7-carbon chain can be intercalated into the LDH interlayer by the following ion-exchange. It is well-known that the guest having a longer carbon chain can be easily intercalated into LDH interlayer.\textsuperscript{16,17,27} However, the intercalated amount of the C7S was quite small in this case and the calculated percentage of ion-exchange based on the above reaction equation was maximally only 4\%. In other words, this value is equal to the molar ratio of the guest/anion exchange capacity (AEC). A small part of the MgAc\textsubscript{2} molecule may be dissociated, but it was neglected in this calculation.

Accordingly, the similar experiments were carried out using alkyl sulfate having a much longer alkyl chain under the same conditions. When the solution of C11S was injected in the cell (17.5–100 \( \mu \)M), the frequency started to decrease with the elapse of reaction time and reached the equilibrium after about 180 s, supporting that the intercalation of C11S anions by the ion-exchange with OH\(^{-}\) ions and MgAc\textsubscript{2} molecule occurred on the LDH/QC electrode. It was also found the larger the C11S concentration, the more the frequency decrease. In Fig. 3, \( \Delta F_m \) is a maximum value of the frequency change and \( T_{1/2} \) value is a half-life of the maximum frequency change in each concentration. Here, \( \Delta F_{tv} \) is a theoretical value of the frequency change calculated from the amount of the guest and is equal to AEC. The percentage of ion-exchange calculated from \( \Delta F_m \) and \( \Delta F_{tv} \) was in the range of 7.1–14.8\% in the case of C11S.

Moreover, the QCM measurements were carried out in the case of C12S, and the resulted data were shown in Fig. 4. On the whole, the tendency of the frequency change was similar to those of the case of C11S, but the degree of the frequency change was considerably larger than in the case of C11S. In other words, the longer the alkyl carbon chain of the guest, the much easier the intercalation of alkyl sulfate anion as described above. The QCM results in the case of C12S were summarized in Table 1. The decreasing rate and degree of frequency were

![Fig. 2. Microscopic images of the LDH film on QC electrode before (a) and after (b) drying, and AFM topographic image (c) of the LDH film (b). Inset: cross-sectional profile of the LDH film.](image)

![Fig. 3. Frequency change of QCM after the injection of (a) C5S, (b) C6S and (c) C7S solution (100 \( \mu \)M), and effect of C11S concentration on frequency change of QCM. LDH film mass: 4.3–4.7 \( \mu \)g cm\(^{-2}\), C11S concentration (\( \mu \)M): 1) 17.5, 2) 35.0, 3) 50.0, and 4) 100.](image)
found to be accelerated with increasing the C_{12}S concentration. These results mean that the intercalation rate and degree of C_{12}S are promoted with the guest anion concentration. The percentage of ion-exchange was in the range of 20–27% in the case of C_{12}S. The T_{1/2} values were entirely smaller in the case of C_{12}S than in the case of C_{11}S. This large values of ΔF_{m}/ΔF_{m} for C_{12}S intercalated could not be explained by a simple adsorption on the film surface.

Next, the kinetic analysis for the QCM data was attempted based on the previous literature.\(^{37}\) The equation of a general host–guest reaction can be expressed by the Eq. (1).

\[
\text{Host} + \text{Guest} \rightleftharpoons \text{Host} \cdot \text{Guest}
\]

Here, the rate equation based on the reversible pseud first-order reaction is postulated for the intercalation reaction.

\[
\text{Rate of association} = [\text{Host}][\text{Guest}]k_a
\]

\[
\text{Rate of dissociation} = [\text{Host} \cdot \text{Guest}]k_d
\]

Where, [Host] = ΔF_{m} – ΔF, [Host·Guest] = ΔF

Therefore, net rate of association = df/dt = (ΔF_{m} – ΔF) · \(k_a - ΔF/k_d\)

By integrating this equation

\[
ΔF = ΔF_{m} \cdot \left[1 - \exp\left(-k_d [\text{Guest}]_{\text{eq}}\right)\right]
\]

Accordingly, \(k_{\text{obs}} = [\text{Guest}]k_a + k_d\), \(k_{\text{obs}} = \tau^{-1}\)

\[\Delta F = 1/2ΔF_{m}, \quad t = \ln 2/k_{\text{obs}}\]

Therefore, if the plot of [Guest] vs. \(k_{\text{obs}}\) is a straight line, Slope = \(k_a\), intercept = \(k_d\)

The plots of \(k_{\text{obs}}\) against the C_{12}S concentration are indicated in Fig. 5. As the result, a linear relationship between \(k_{\text{obs}}\) and [Guest] concentration was found. Thus this result indicates that the assumption adopted for the kinetic analysis would be reasonable in the intercalation of organic sulfate anions into the LDH interlayer. From the slope and intercept of the obtained linear line, the association rate constant (\(k_a\)) and dissociation rate constant (\(k_d\)) were obtained, respectively. Moreover, the equilibrium constant (\(K\)) was calculated as 1.83 × 10\(^3\) M\(^{-1}\) for the C_{11}S and 1.44 × 10\(^4\) M\(^{-1}\) for C_{12}S anion, respectively, as indicated in Table 2. As a similar guest anion, dodecylbenzene sulfonate (DBS) was additionally examined by the same technique under the same condition as reference. The same tendency was observed when using DBS as a guest anion as shown in Fig. 5 and Table 2. The tendency of the frequency change was, on the whole, similar to those of the case of C_{12}S, but the degree of the frequency change was considerably larger than that in the case of C_{12}S.

3.3 Characterization of the LDH film on gold disc electrode of QCM

The XRD patterns of the LDH film immobilized on a glass plate obtained in the large-scale experiments for the intercalation of C_{12}S are shown in Fig. 6, with each schematic illustrations. The powder sample (a) of the MgAl/\((\text{OH}^- + \text{MgAc}_2)/\text{LDH}\) as reference indicates the typical

| Table 1. Effect of C_{12}S\(^0\) concentration on QCM data of intercalation into the LDH film\(^b\) |
|-----------------|-----------------|-----------------|--------------------|-----------------|
| Run (mM)       | C_{12}S concentration | ΔF_{m} (Hz) | ΔF_{m}/ΔF_{m} | T_{1/2} (s) |
| 1)             | 17.5             | –907          | 20             | 28.4           |
| 2)             | 35.0             | –1179         | 26             | 26.5           |
| 3)             | 50.0             | –1272         | 27             | 19.5           |
| 4)             | 75.0             | –985          | 21             | 18.7           |
| 5)             | 100              | –1122         | 24             | 14.6           |

\[a) \text{C}_{12}\text{S}: \text{C}_{12}\text{H}_{25}\text{OSO}_3\text{^–}\; b) \text{the film mass: 5.7}–6.0\;\mu\text{g cm}^{-2}, \; c) \text{calculated from each AEC values of the LDH film.}\]

\[\text{Fig. 4. Effect of C}_{12}\text{S concentration on frequency change of QCM. LDH film mass: 5.7}–6.0\;\mu\text{g cm}^{-2}, \; C_{12}\text{S concentration} (\mu\text{M}): 1) 17.5, 2) 35.0, 3) 50.0, 4) 75.0, \; \text{and 5) 100.}\]

\[\text{Fig. 5. Plots of } k_{\text{obs}} \text{against the guest concentration according to Eq. (2). Guest: (a) C}_{12}\text{S, (b) C}_{11}\text{S, and (c) DBS.}\]

| Table 2. Kinetic analysis data for intercalation of organic anions into the LDH film |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Guest\(^a\)     | LDH film mass (μg cm\(^{-2}\)) | \(k_a\) (6 M\(^{-1}\)) | \(k_d\) (× 10\(^{-2}\) s\(^{-1}\)) | \(K\) (× 10\(^3\) M\(^{-1}\)) |
| C_{11}S         | 4.5             | 257             | 1.40            | 1.83            |
| C_{12}S         | 5.8             | 271             | 1.88            | 1.44            |
| DBS             | 6.6             | 191             | 0.232           | 3.23            |

\[a) \text{C}_{11}\text{S: C}_{11}\text{H}_{23}\text{OSO}_3\text{^–}, \; \text{C}_{12}\text{S: C}_{12}\text{H}_{25}\text{OSO}_3\text{^–}, \; \text{DBS: C}_{12}\text{H}_{25}\text{C}_{6}\text{H}_4\text{SO}_3\text{^–}.\]
LDH pattern with $d_{003} = 0.858 \text{ nm}$, $d_{006} = 0.427 \text{ nm}$, and $d_{009} = 0.261 \text{ nm}$. As the thickness of the LDH host layer is 0.48 nm, the interlayer distance was estimated as 0.38 nm that almost equals the MgAc$_2$ molecular size. The original LDH film sample (b) also shows the similar pattern with $d_{003}$ value of 0.807 nm in spite of lower diffraction strength and the disappearance of the (110) diffraction peak due to a thin film. The C$_{12}$S/LDH film sample (c) obtained at 100 µM C$_{12}$S concentration shows the same pattern with quite a small diffraction peak, because it contained the different size guests like original guest (OH$^+$ + MgAc$_2$) and C$_{12}$S, and its interlayer distance became ununiform as shown in Fig. 6(c). In this case, the percentage of ion-exchange of C$_{12}$S was 24% as indicated in Table 1. As mentioned above, the thickness of the LDH host layer is thinner and softer compared to that of smectite layer. On the contrary, the same sample (d) obtained at 100 mM C$_{12}$S concentration indicates the quite higher diffraction peaks with $d_{003} = 2.98 \text{ nm}$, $d_{006} = 1.29 \text{ nm}$, and $d_{009} = 0.681 \text{ nm}$. Therefore, the interlayer distance was estimated at 2.5 nm. This value indicates that C$_{12}$S anions were intercalated to form bilayer guest as illustrated in the inset of Fig. 6(d). In addition, the peak of $d = 0.850 \text{ nm}$ (* mark) was thought the peak assignmnent of 003 of the C$_{12}$S/LDH in which C$_{12}$S is incorporated keeping horizontal position in the LDH interlayer. The results of the XRD analysis supported that the guest anions were intercalated in the LDH interlayer.

The FT-IR spectra of the same samples picked up in Fig. 6 are shown in Fig. 7. In each case, a broad absorption peak in the 2,800–3,600 cm$^{-1}$ region is assigned to O–H group stretches of hydroxide basal layer and interlayer water. The medium absorption peaks of C=O stretch at 1,570 cm$^{-1}$ and $\delta$-CH$_3$ at 1,410 cm$^{-1}$ were also observed due to the guest MgAc$_2$ molecule in the cases of the samples (a)–(b). However, the strong absorption peaks of C–H stretch at 2,860–2,922 cm$^{-1}$ and, S=O stretch at 1,120 and 1,050 cm$^{-1}$ were observed in the case of the sample (d) that was obtained after the intercalation of higher C$_{12}$S concentration. These results supposed that the exchange of OH$^+$ ion and MgAc$_2$ molecule with C$_{12}$S anions could occur in this intercalation.

The XPS spectra and XPS depth profile of the LDH film indicated in Fig. 2 are shown in Fig. 8. The S2p peak was not found in the film before the intercalation (a), whereas found in the films after the intercalation of C$_{12}$S (b) and DBS (c) anions at 170 eV in Fig. 8[A]. These peaks depend on the sulfate and sulfonate anions in the LDH interlayer, respectively. It was also found that the larger the amount of guest anion in the film (DBS > C$_{12}$S), the higher the height of S2p peak (DBS > C$_{12}$S). The other weak peaks, Si2s, Si2p, and F2s due to a fluoroalkyl silane coupling agent were also found with the peaks due to the Mg–Al LDH particles.

In the profile of Fig. 8[B], X axis is the film depth calculated from the sputtering rate of 3 nm/min. As mentioned above, the percentage of ion-exchange of C$_{12}$S was

Fig. 6. XRD patterns and schematic illustrations of the LDH films before and after intercalation of C$_{12}$S. (a) Original LDH powder as reference, (b) original LDH film, (c) C$_{12}$S/LDH (100 µM), and (d) C$_{12}$S/LDH (100 mM).

Fig. 7. FT-IR spectra of the LDH films before and after intercalation of C$_{12}$S. (a) Original LDH powder as reference, (b) original LDH film, (c) C$_{12}$S/LDH (100 µM), and (d) C$_{12}$S/LDH (100 mM).
and XPS depth profile of the LDH film on QC electrode.

24% in this case. With increase in the depth, the C1s peak was decreased, while the Mg and Al concentration were increased. One of the most characteristic points is that the S2p peak was found in the region of 0–12 nm, which height meaning about 3.0 atomic concentrations, and then decreased very gradually with the depth. This result supports that the guest anion is presented not only on the surface, but also in the inside of the thin film. From these results, a possibility of the kinetic study on the intercalation of anions into LDH could be exhibited by using QCM technique with stable LDH/QC electrode.

4. Conclusions

This kinetic study using QCM has led to a better understanding of the intercalation of organic anions into Mg–Al LDH by ion-exchange. Some of the important findings of this study can be summarized as follows.

Thin LDH film was successfully immobilized on the QC electrode using the translucent aqueous sol of (OH-/MgAc2)/LDH after the surface treatment of the electrode with the hydrophobic agent, which was stable during the intercalation experiments. Dynamic intercalation behaviors of alkyl sulfate anions were well monitored by the QCM measurement. The intercalation rate was significantly influenced by alkyl chain length and concentration of the guest. From the analysis of the QCM data, kinetic parameters of the intercalation were obtained. The results of instrumental analyses of the LDH film supported that the guest anions presented not only on the surface, but also in the inside of the thin film. From these results, a possibility of the kinetic study on the intercalation of anions into LDH could be exhibited by using QCM technique with stable LDH/QC electrode.

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