Enhanced hydroxide ion conductivity of Mg–Al layered double hydroxide at low humidity by intercalating dodecyl sulfate anion

1. Introduction

Layered double hydroxides (LDHs) are anionic clays consisting of positively charged metal hydroxide layers with anions located in the interlayer for charge compensation of the cationic layers. The chemical formula for LDHs is \([M^{2+}_{x-1}M^{3+}_{x},(OH)_2] ([A^{n-}_y/n\gamma\gamma H_2O])\), where \(M^{2+}\) is a divalent metal cation, \(M^{3+}\) is a trivalent cation, and \(A^{n-}\) is an anion. In recent years, LDHs have received increasing attention because of their potential application as anion exchangers, catalysts, drug delivery materials and bio-active materials.1) Additionally, Mg–Al LDH show high hydroxide ion conductivity, which results in the higher ionic conductivity under low humidity. Dodecyl sulfate (DS) anion is known to be intercalated easily in LDHs which contain no alkaline metal should have good durability to \(CO_2\). Another benefit of using LDH electrolytes is that LDH synthesis is simple and inexpensive.因此，LDHs are applied to AFC electrolyte is that most LDHs show low ionic conductivity under low humidity. Therefore, humidity management is necessary for the practical application of LDH electrolyte. For that reason, LDHs with high ionic conductivity under low humidity are required. Until now, LDHs interacting with moderate surfactants shows higher conductivity under a dried condition than the conductivity of Mg–Al \(CO_3^{2-}\) LDH because of their unique morphology and interaction of water molecules.15),16)

In this paper, another interlayer organic anion in LDH is proposed, in which hydroxide ion conductivity is enhanced at low humidity. Dodecyl sulfate (DS) anion \([CH_3(CH_2)_{11}OSO_3^{-}]\) was chosen for the interlayer anion because DS anion is known to be intercalated easily in...
LDHs. For this study, Mg–Al CO$_3^{2-}$ LDH was prepared along with Mg–Al DS LDH. The ionic conductivities were examined at various temperatures and humidities.

2. Experimental

Mg–Al LDH intercalated with CO$_3^{2-}$ (Mg–Al CO$_3^{2-}$ LDH) was prepared using co-precipitation process. A mixed solution containing Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O with Mg$^{2+}$/Al$^{3+}$ = 3 was added dropwise into 0.3 M Na$_2$CO$_3$ solution with stirring. The pH of the reaction mixture was adjusted to 11 by the addition of 2 M NaOH solution. The obtained solution was aged at 80°C overnight. The resulting white precipitates were filtrated, washed with distilled water, and dried at 80°C for 24 h.

Mg–Al LDH intercalated with DS anion was prepared using the reconstruction process. Mg–Al CO$_3^{2-}$ LDH was calcined at 500°C for 5 h. Then the obtained oxide was dispersed into the 0.1 M sodium DS solution. Before adding the oxide, the solution was kept at 90°C with N$_2$ bubbling at the rate of 100 mL min$^{-1}$ for 30 min to remove dissolved CO$_2$ from the water. The reaction mixture was aged overnight at 80°C. The precipitates were centrifuged, washed with decarbonated water, and dried in a vacuum.

X-ray diffraction (XRD) patterns (Cu K$_\alpha$) were taken using an XRD diffractometer (Mini Flex 600; Rigaku Corp.) to identify the crystalline phase. Presence of CO$_3^{2-}$ in the sample was confirmed using Fourier transform infrared (FT-IR) spectra. Attenuated total reflectance method was used for IR measurements. Differential thermal analysis and thermogravimetry (DTA-TG) were conducted using a thermal analyzer (thermo plus TG-8120; Rigaku Corp.), with a heating rate of 10 °C min$^{-1}$ in air. The respective morphologies of the prepared LDHs were observed using a field-emission-type scanning electron microscope (FE-SEM, JSE-6300F; JEOL).

The ionic conductivities of LDHs were determined using impedance at frequencies of 1 Hz to 7 MHz (Solartron 1260; Solartron Analytical). LDHs pellets with the thickness about 300 μm obtained using cold pressing under 100 MPa were used for the conductivity measurement. Gold was sputtered to make electrodes on both sides of the pelletized LDHs. The samples were kept for 24 hours at each measurement condition in constant temperature and humidity chamber to ensure that samples reached an equilibrium.

3. Results and discussion

XRD patterns of the Mg–Al CO$_3^{2-}$ LDH and Mg–Al DS LDH are shown in Fig. 1. The XRD patterns of both samples were attributed to the layered structure of LDHs. The peaks at around 11 and 23° can be indexed as Mg–Al CO$_3^{2-}$ LDH, and 3.5 and 7° as Mg–Al DS LDH. These results indicate that CO$_3^{2-}$ and DS anion are intercalated in both LDH samples.

Figure 2 presents the FT-IR spectra of Mg–Al CO$_3^{2-}$ LDH and Mg–Al DS LDH prepared using the reconstruction process showed peaks at 2920 and 2852 cm$^{-1}$ attributed to C–H stretching vibration of the alkyl chain of DS anion, and 1203 and 1058 cm$^{-1}$ attributed to S=O stretching vibration of DS anion. These results support the XRD result showing that DS anion was intercalated to LDH. The absorption band at 3470 cm$^{-1}$ is assigned to the OH$^-$ group vibration of hydroxide layer. The peak at 1630 cm$^{-1}$ is based on H$_2$O bending vibration of interlayer water.

DTA-TG was measured to investigate the thermal behavior of Mg–Al CO$_3^{2-}$ LDH and Mg–Al DS LDH. Figure 3 shows TG curves of the samples, which were kept at 80°C, 30%RH overnight before measurement. In Mg–Al CO$_3^{2-}$...
LDH, the weight loss at temperatures between room temperature and 250°C can be assigned to the loss of the adsorbed water and interlayer water of LDH. The weight loss at higher temperatures is assigned to the elimination of H₂O from OH groups in the inorganic layer and CO₂ from CO₃²⁻ ions. Particularly, the weight loss under 120°C is attributed to the surface water loss. The weight loss of Mg–Al CO₃²⁻ LDH under 120°C was 3.1 mass%. That of Mg–Al DS LDH was 6.3 mass%, which indicates that intercalation of DS anion enhances the amount of adsorbed surface water. In Mg–Al CO₃²⁻ LDH, the weight loss between 120 and 250°C assigned to the interlayer water was 12.3 mass%. The interlayer water of Mg–Al DS LDH was not measured because the organic portion of DS anion intercalated in LDHs is removed between 150 and 300°C. For that reason, the ratio of interlayer water of Mg–Al DS LDH cannot be compared with that of Mg–Al CO₃²⁻ LDH. The weight loss at temperatures higher than 300°C, assigned to the elimination of H₂O from OH groups in the inorganic layer and CO₂ from CO₃²⁻ ions, is 24.7 mass% for Mg–Al CO₃²⁻ LDH and 13.1 mass% for Mg–Al DS LDH. The small weight loss of Mg–Al DS LDH is probably attributable to the fact that Mg–Al DS LDH contains only a trace amount of carbonate anion.

Table 1 presents the weight loss between room temperature and 120°C, which is attributed to adsorbed water, for the samples exposed to different degrees of humidity before TG measurements. The weight loss of Mg–Al DS LDH was twice as much as that of Mg–Al CO₃²⁻ LDH at all relative humidities. The weight loss of both samples increased along with the enhancement of relative humidity.

Table 1. Weight loss between room temperature and 120°C of Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH respectively kept at 30, 50, and 70% RH

| Relative humidity | 30% | 50% | 70% |
|-------------------|-----|-----|-----|
| Mg–Al CO₃²⁻ LDH   | 3.1%| 3.3%| 3.6%|
| Mg–Al DS LDH      | 6.3%| 6.7%| 7.2%|

Fig. 3. TG curves of Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH.

Fig. 4. FE-SEM images of Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH.

The morphology of the synthesized LDHs was examined using FE-SEM. FE-SEM images of Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH (Fig. 4) represent that the primary particle size of Mg–Al CO₃²⁻ LDH was about 30–100 nm, and that of Mg–Al DS LDH was 200–300 nm. This difference indicates that the surface area of Mg–Al CO₃²⁻ LDH should be higher than that of Mg–Al DS LDH.

Ionic conductivities of Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH were determined using impedance spectroscopy. The Nyquist plots for the Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH at 80°C, 30%RH are shown in Fig. 5. In the Z’ and Z’’ plots, a high-frequency arc and a low-frequency tail were observed in both samples. Impedance curves similar to that shown in Fig. 5 were observed for all samples, which were kept at different temperatures and relative humidities. The values of resistance R were determined from the intersection of the low-frequency tail with the real axis of the impedance Z’.

The charge carrier of LDHs was confirmed to be hydroxide ion using the water vapor concentration cell in previous reports.

Fig. 6. Ionic conductivities of Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH.
ADEFCs⁶,⁸,¹⁰ and H₂–O₂ fuel cells.²⁴) The formation of hydroxide ion in LDHs with intercalated CO₃²⁻ is probably the following.²⁵)

\[
\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-
\]

Considering information from the literature presented above, Mg–Al DS LDH has a small amount of CO₃²⁻ as interlayer anion, which probably generates mobile hydroxide ions in Mg–Al DS LDH. The ionic conductivity of Mg–Al CO₃²⁻ LDH and Mg–Al DS LDH show almost same at 40–80°C, 80% RH because of the saturation of absorbed water.

**Figure 7** shows ionic conductivities of samples measured at 80°C, 30–80% RH. At all humidities except for 80°C, 80% RH, the ionic conductivity of Mg–Al DS LDH was higher than that of Mg–Al CO₃²⁻ LDH. The difference is notable, especially at low humidity. The ionic conductivity of Mg–Al CO₃²⁻ LDH was 1.1 × 10⁻⁴ S cm⁻¹, whereas that of Mg–Al DS LDH is 7.6 × 10⁻⁴ S cm⁻¹ at 80°C, 30% RH. The difference is probably attributable to the amount of adsorbed water. The amount of the adsorbed surface water of Mg–Al DS LDH was much greater than that of Mg–Al CO₃²⁻ LDH, as confirmed by DTA-TG measurements. The adsorbed surface water is likely to play an important role in hydroxide ion conduction.

The ionic conductivity change during extremely long storage is presented in **Fig. 8**. Samples were kept at 80°C, 30% RH. Then ionic conductivities were measured. The ionic conductivity of Mg–Al DS LDH was extremely stable for storage longer than 150 h, whereas that of Mg–Al CO₃²⁻ LDH decreased gradually after long storage durations at low humidity. This result demonstrates that LDHs intercalated with DS anion can maintain high ionic conductivity under low humidity. This characteristic might be related to its ability to hold higher amounts of adsorbed water in Mg–Al DS LDH. Although the increase in the amount of surface water in Mg–Al DS LDH is assumed to be related to interlayer anion, additional experiments must be conducted to elucidate the effects of interlayer anion on LDH structure and ionic conductivity.
4. Conclusion

The ionic conductivity of Mg–Al DS LDH at 80°C, 30%RH (7.6 × 10⁻⁴ S cm⁻¹) was higher than that of Mg–Al CO₃²⁻ LDH (1.1 × 10⁻⁴ S cm⁻¹). Intercalation and adsorption of DS anion increased the amount of the adsorbed water, probably providing a path for hydroxide ion, which is expected to improve ionic conductivity at low humidity. Furthermore, Mg–Al DS LDH showed higher stability of ionic conductivity under low humidity.

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