RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Mg-Al Layered double hydroxides: A correlation between synthesis-structure and ionic conductivity

Peilin Zhang[1], Takeo Yamaguchi[2], Balagopal N. Nair[1], Keita Miyajima[1] Gopinathan M. Anilkumar[1]*

[1]Research & Development Center, Noritake, Co., Ltd., 300 Higashiyama, Miyoshi, Aichi 470-0293, Japan

[2]Chemical Resources Laboratory, Tokyo Institute of Technology, R1-17, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Abstract

Mg-Al based layered double hydroxide (LDHs) samples with distinct morphology and crystallinity were synthesized by controlling urea assisted homogeneous precipitation conditions. The obtained samples were characterized with XRD, TG-DTA, FESEM, CHN and XPS analysis and compared with the ionic conductivity values measured at 80°C under various humidity conditions. The results revealed that LDH particles with small size and low crystallinity were able to adsorb more water resulting in high ionic conductivity. In contrast, LDH particles with large size and high crystallinity showed low ionic conductivity. However, delamination of such highly crystalline LDH particles was found to be an extremely effective method to increase the ionic conductivity.

Introduction

With the increasing concerns on environmental and energy issues, fuel cells are attracting worldwide attention. Comparing with the existing, conventional energy conversion technologies, we can easily named their advantages such as high efficiency, low or zero emissions, quiet operation, and so on. Until now on, several kinds of fuel cells such as proton exchange membrane type (PEMFC), and solid state oxide type (SOFC), have been developed and commercialized, which show similarly high efficiency and can be applied in different fields due to their peculiar features. However, besides power generating efficiency, cost of a fuel cell is also a main issue which limits the popularization of it. Solid state alkaline fuel cells (SAFCs), which allow the use of non-platinum (Pt) catalysts thus greatly reducing the cost of the fuel cell, are considered as strong contenders towards resolving these limitations.

One of the major issues on the commercialization of SAFC is related to the development of high performance anion conducting electrolyte materials. Conventional polymeric materials suffer from stability and durability problems due to the nature of quaternary ammonium groups, which are the main functional groups required to realize anionic conduction [1-4]. Recently, much interest has been focused on hydrotalcite type layered double hydroxide (LDH) as a potential anion conducting material for SAFC applications [5-9]. As naturally occurring anionic clay, hydrotalcite type LDH is composed of positively charged hydroxide layers, and anions together with water molecules existing between the layers, where interlayer anions can be exchanged [10]. The applications of LDH in water decontamination, in rubber technology, in photo-chemistry and in medicinal chemistry have been widely reported [11-18]. However, the ionic conductivity of LDH has not been intensively studied yet, apart from the few publications on LDH powders prepared by co-precipitation method and having relatively smaller particle sizes [6, 7]. Considering the unique structure and properties of LDH, we have been involved in research work to understand the relationship between the layered structure and ionic conductivity. Recently, we have reported on the influence of the composition of the hydroxide layers and the interlayer anions/species on the ionic conductivity of LDH [19, 20]. In this investigation a urea-assisted homogeneous precipitation method was employed for the synthesis of LDH powder samples. By controlling the reaction conditions, LDHs with different crysatllinity and morphology were obtained and their characteristics and ionic conductivity values were compared in this paper. Furthermore, in order to enhance the ionic conductivity, delamination of the LDH layers were carried out on the sample with high cystallinity, resulting in samples with excellent enhancement in ionic conductivity.

Experimental

Synthesis

Mg-Al LDH of general formula $\{M(II)_{1-x}M(III)_x(OH)_2(A^{n-})_{x/n} \cdot yH_2O\}$ was prepared via a homogeneous precipitation method [21, 22]. All the chemicals used for LDH synthesis were purchased from Wako Pure Chemical Industries, Ltd (Japan), and were used without further purification. For a typical synthesis, required amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water with the molar ratio of Mg:Al=2:1. Then, required amount of urea was added into the solution and was vigorously stirred till all the chemicals dissolved in the water. The clear solution obtained was then transferred into a Teflon-lined autoclave without excluding CO_2 in the reacting mixture, sealed and kept at 95 ^oC for 12 h. After the reaction, the precipitate was recovered by centrifugation, followed by washing with deionized water for three times and with acetone one time. The sample was then dried in an oven at 80 ^oC overnight. To investigate the influence of reaction conditions, various Mg-Al LDH samples were prepared by varying the amount of urea{[urea]/[NO_3^-]=2.0~4.0}in the reaction mixture. The reaction temperature was also varied from 95~120 ^oC, (6 to 24 h.) keeping the [urea]/[NO_3^-]=4.0.

To delaminate the prepared LDH, the dried LDH powder was dispersed in an aqueous solution consisting of 1 M KNO_3 and 3.3 M HNO_3 and was vigorously stirred at room temperature for 24 h, resulting in the exchange of the interlayer ions of the as prepared LDH from CO_3^{2-} to NO_3^- [23]. The ion exchanged LDH (LDH-NO_3) powder was recovered by filtration followed by washing and drying as described earlier. The dried LDH-NO_3 powder was dispersed in formamide, and was vigorously stirred under room temperature for 24 h. The obtained suspension was vacuum filtered and then vacuum dried at 70 ^oC to resulting in a dried powder mass consisting of the delaminated LDH plates.

Characterization

To identify the crystalline phases of the prepared samples, powder X-ray diffraction analysis was conducted using a RINT-TTRIII diffractometer (Rigaku, Japan). The thermogravimetric analysis was performed (10^{o}C/min, air) on a thermal analyzer (Thermo plus TG-8120, Rigaku, Japan). CHN analysis (Yanaco, CHN Corder, MT-6) was carried out to determine the nitrogen amount in the sample. The XPS analyses of the samples were conducted by X-ray photoelectron spectroscopy (PHI-5000 Versaprobe II, ULVAC-PHI, Inc, Japan).

Conductivity measurements

The ionic conductivities of the samples were measured via AC impedance method using a Solartron Interface 1260 gain phase analyzer over the frequency range of 1-10^7 Hz. For the measurement, sample pellets with a diameter of 10 mm and a thickness of 1.5 mm were prepared by the uniaxial pressing technique. Ag paste was smeared on both sides, followed by electroding it with Au wire. The samples were placed inside the temperature-humidity controlled oven (SH-221, ESPEC, Japan) and the measurements were carried out at 80 °C under various humidity conditions (20~80% R.H).

Results and discussions

Figure 1 shows the XRD patterns of the LDH samples prepared with different amounts of urea. It was observed that when synthesis was carried out with small amounts of urea ([urea]/[NO_3^-]=2.0), the sample obtained showed amorphous phase with almost no diffraction peaks. Strong diffraction peaks were observed when the [urea]/[NO_3^-] ratio was increased to 4.0, indicating the highly crystalline nature of the as made Mg-Al LDH. It is expected that the urea present in the reaction mixture would have decomposed under hydrothermal conditions to increase the pH of the solution, wherein Mg and Al ions would get precipitated together to form LDH particles. When there is not enough amount of urea, the pH of the solution would not be enough to precipitate all metal ions, and the precipitation reaction would also occur very slowly resulting a poor crystallinity. When the amount of urea is high, the precitation rate would increase, and the LDH particles formed will have enough time to grow into plates, resulting in better crystallinity.

Figure 2 shows the FESEM images of the LDH samples, which further supports the findings of the XRD measurements. The LDH prepared with small amount of urea showed amorphous structure with aggregates of small particles, while plate like morphology was observed for the samples prepared with large amounts of urea ([urea]/[NO_3^-]=4.0).

The hydrolysis of urea in aqueous solution starts above 70°C, and results in the rising of solution’s pH value. To ensure the complete decomposition of urea, the reaction temperature was fixed at 95°C, and samples obtained under different reaction times were analyzed. Besides reaction time, reaction temperature also greatly affects the hydrolysis speed and LDH with different crystallinity can be obtained. Figure 3 and 4 show the XRD patterns and FESEM images of the Mg-Al LDH samples prepared under various conditions, respectively; the synthesis mixture contained [urea]/[NO_3^-]=4.0 in all cases. No hydroxide precipitation was detected when the reaction was carried out at 95°C for a period of 6 hours, indicating the very slow reaction kinetics for the Mg-Al LDH formation at the conditions used. It was observed that by prolonging the reaction time or increasing the reaction temperature crystallinity of the resulting powders could be improved, as evidenced by the stronger x-ray diffraction peaks of Mg-Al LDH and are presented in Figure 3. Meanwhile, the morphology of the samples also changed with the variations in reaction conditions. Long reaction time or high temperature (> 95^{o}C / 24h) led to the formation of LDH with plate like morphology. In the SEM images presented in figure 4 b & c, the hexagonal plates can be clearly observed, which is typical for LDH prepared by homogeneous precipitation with urea.

To understand the internal structure of LDH prepared under various conditions further, TG analysis was carried out and the results are shown in Figures 5 and 6. LDH usually shows multiple steps of weight loss under heat treatment, which corresponds to the removal of physisorbed water molecules on the surface, loss of interlayer water, loss of structural hydroxyl groups (as H_2O), and removal of interlayer carbonate anions (as CO_2), respectively. The results revealed that LDH with low crystallinity showed higher weight loss at low temperatures (~ 120 ^{o}C), but lower weight loss at high temperature (> 120 ^{o}C). LDH with high crystallinity and hexagonal plate like morphology showed thermal behavior opposite to its amorphous counterpart, showing greater loss at high temperatures under TG analysis conditions. It is likely that the hexagonal plates with smoother surface have lower amount of adsorbed water molecules, compared to the amorphous powders, and therefore the lower weight loss below 120 ^{o}C.

Table 1 shows the percentages of elements such as carbon, hydrogen and nitrogen, detected by CHN analysis of the LDH samples prepared at 95^{o}C (12 h) and 120^{o}C (12 h). A significant difference was found in the amount of nitrogen contained in the samples, which got decreased from 2.77 % to 0.00 % with the increase in reaction temperature. As discussed above, the formation of LDH particles is closely related to the degradation of urea during the reaction. Urea usually starts to decompose at 80^{o}C in aqueous solution, which could be accelerated by increasing the temperature, and thereby increase the pH value of the solution. This in turn, should help to form large amount of CO_2, which would later dissolve into the solution to form CO_3^{2-}, in very short time [21]. Although many NO_3^- species from the metal nitrates exist in the solution, CO_3^{2-} showed much higher affinity to the hydroxide layers and would be incorporated into the interlayer of LDH preferentially. By contrast, reaction at low temperature led to a slow degradation of urea, and resulted as the partial incorporation of NO_3^- due to the lack of enough CO_3^{2-}. Furthermore, the LDH sample prepared at low temperature (95^{o}C, 12h) showed low crystallinity, which would result in the relatively high adsorption amount of CO_3^{2-} and NO_3^- on the surface. Therefore, the C and N amount detected on it were higher than those detected on the LDH sample prepared at 120^{o}C.

The ionic conductivitiy values of LDH samples are shown in Table 2. The conductivity measurement was carried out under 80^{o}C at 80 R.H.%. The results suggested that LDH with amorphous structure showed highest ionic conductivity ([urea]/[NO_3^-]=2.0), and that prepared with larger amount of urea resulted in samples with lower ionic conductivity values. Further, prolonging the reaction time to 24 hours, or increasing the reaction temperature to 120^{o}C favored the formation of plate like particles, showing drastically low ionic conductivity values. LDH is composed of positively charged layers, and anions together with water molecules are present between the layers. The results suggested that layers stacked in good order would slow down the migration of interlayer anions resulting in low conductivity, which could probably due to the low water adsorption as characterized by TG analysis. In LDH, the key point for ion conduction is positively charged layers, which accommodates the anions, but the highly ordered layered structure would inhibit the ion conduction. Therefore, increasing the amount of surface-exposed LDH layers could be an effective way to enhance the ionic conductivity of these samples, as reported by Tamaki et al [9].

On the other hand, the change in chemical nature of the incorporated anions might also be a reason for the difference in ionic conductivity. Furukawa et al.'s research [24] suggested that the interlayer anions affect the ionic conductivities of the Mg–Al LDHs, and they attributed the influence to the interaction between interlayer anions and water molecules or between interlayer anions and hydroxyl layers. However, Mg–Al LDHs intercalated with CO_3^{2-} or NO_3^- used in their study showed very similar ionic conductivity values. But LDHs prepared via co-precipitation method using NaOH, showed smaller particle sizes and higher ionic conductivity. Comparing to their results, due to the large particle size and high crystallinity the LDHs prepared in this study, ionic conductivity values measured were lower. As a result, the influence of interlayer anions on conductivity became easier to be observed.

The LDH samples prepared at 120^{o}C for 12h, with plate-like structure, showed the lowest ionic conductivity values in this study. It was expected that the change in crystalline structure and ionic conductivity in this sample could be much more drastic comparing with other samples. Therefore, the delamination of the above LDH sample was carried out.

Figure 7 shows the XRD patterns of as prepared LDH, ion exchanged LDH, and delaminated LDH. The LDHs prepared under 120 °C for 12h was used in this study, which showed extremely sharp and strong XRD peaks, indicating very high crystallinity of the material. The interlayer anions in this case were mainly CO_3^{2-}, which form strong intercalation between the hydroxide layers, and this LDH-CO_3^{2-} is usually difficult to be delaminated. Therefore, ion exchange with NO_3^- was first carried out to simplify the delamination process. Ion exchange would usually cause some disordering in the layered structure of LDH, and could result in a slight broadening of the x-ray diffraction peaks as well as shifting of diffraction peaks [23]. However, almost no change in XRD pattern was observed in our samples (figure 7), probably due to the extremely high crystallinity of initial LDH used. The XRD pattern of the delaminated LDH was also shown in Figure 7. Formamide is used to delaminate LDH in this study, and it is a small and highly polar solvent which can replace the interlayer species, weaken the interlayer interaction, and result in the swelling of the layers. In principle, a successful delamination should separate LDH into single layers thoroughly, which would result in a spectrum with no diffraction peaks on the XRD pattern. But during the drying process, the restacking of the layers occurs in most cases, and diffraction peaks would appear again [25]. However, compared with the initial LDH, drastic broadening of diffraction peaks and decreases in peak intensity were observed in the delaminated samples (figure 7c) and indicates the success of the delamination process. Two extra peaks around 10^o and 20^o were observed, and the corresponding d spaces were calculated as 0.89nm and 0.44nm respectively by Bragg equation. These two peaks came from the shifting of initial (003) and (006) peaks whose d spaces were 0.76nm and 0.38nm respectively, indicating the swelling of interlayer distance during the restacking of the delaminated sheets.

Table 3 shows the results of CHN analysis of the LDH samples before and after delamination. Both carbon and nitrogen amounts were increased after delamination, which should be attributed to the increase in surface layers hence led to the higher adsorption of anions such as CO_3^{2-} and NO_3^-. Correspondingly, in the XPS spectra of the samples (figure 8), peak at the binding energy at 407 eV, assigned to NO_3^- [26] also became observed after delamination, which agreed well with the CHN analysis results.

Figure 9 shows the FESEM images of the LDH samples before and after delamination. It was observed that the morphology of the samples remained unchanged as hexagonal plate like structure with the particle size around 2 μm after ion exchange. After delamination, the morphology greatly changed, and large agglomerates were observed instead of separated plates, furthermore, the outlines of the plates became unclear. Initially, the delaminated LDH was a stable translucent solution which could not be precipitated even under 10,000 rpm centrifugation for 10 min. Delaminated LDH powders were recovered by long time filtration, and the separated plates stacked to each other to form the large agglomerates as observed in FESEM image on drying.

Figure 10 shows the DTG curves of the samples. Ion exchange didn’t show any influence on the thermal behavior of LDH samples, but the delaminated LDH showed a very different result. Large weight losses were observed below 200 ^{o}C, which should be attributed to the removal of physically adsorbed water on the surface of the particles and the dehydration of water of crystallization, respectively. Compared with the initial LDH, the delaminated sample showed more exposed layers, which could have improved the water adsorption. Furthermore, due to the low crystallinity after delamination, the thermal stability also became low, and the decomposition of hydroxide layers together with the removal of bonded anions could have occurred at lower temperatures, compared with that of the parent LDH.

The ionic conductivities of the samples measured at 80 ^{o}C under different relative humidity were shown in Figure 11. It was observed that with the decrease in relative humidity, the ionic conductivity of the samples also decreased, which is a common phenomenon for ion conducting materials due to the close relationship between ion conduction to the amount of water molecules in the samples. The “as prepared LDH” showed very low ionic conductivity, and the values were to small to be measured when the relative humidity was 20 %.

In a previous report, the ionic conductivity of Mg-Al LDHs intercalated with different anions was studied, and NO_3-LDH, CO_3-LDH and Cl-LDH showed similar value, while Br-LDH and SO_4-LDH showed relatively high and low values respectively. The reason was unclear, but it should be closely related to the interactions between interlayer anions and water molecules or between interlayer anions and hydroxyl layers [24]. The results we obtained here revealed that the ionic conductivity of CO_3-LDH prepared with homogeneous precipitation method was greatly enhanced after ion exchanging to the NO_3-LDH. This could be attributed to the difference in the structure of the obtained LDH samples by two different preparation methods. The results indicated that there might be a chance that the influence of interlayer anions would also change according to the initial structure of host layers, which provide a new approach to reveal the ion conduction mechanism of LDH. However, more investigations are required to understand the ion conduction phenomenon in detail.

After delamination, the ionic conductivity of LDH was further enhanced. Compared with the “as prepared LDH”, the ionic conductivity values were at least two orders of magnitude higher at all measured conditions. As discussed earlier, to achieve a high ionic conductivity increasing the amount of exposed LDH layers and their water adsorption ability is important. Compared to the initial LDH, the delaminated sample showed poor crystallinity indicating the disordering of the positively charged layers, leading to the high water holding ability as revealed by TG analysis. Our results have indicated that the structure formed by the delaminated LDH as the ideal one for obtaining high ionic conductivity values.

Conclusions

The ionic conductivities of LDHs prepared by a urea assisted homogeneous precipitation method were investigated in this study. LDHs with various crystallinity and morphology were obtained by controlling the reaction conditions. Ionic conductivity of LDH was found to decrease with the increase in crystallinity, indicating the importance of having positively charged layers instead of the highly ordered layered structure. Delamination of the highly crystalline powder sample resulted in the enhancement of the ionic conductivity values of the samples. The results reported here are expected to be helpful in the design of highly ion conducting structure of LDHs and other novel ion conducting materials.

Acknowledgement

The authors are grateful for the financial support of this work by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency (JST).

References

1 Tanaka, M., Fukasawa, K., Nishino, E., Yamaguchi, S., Yamada, K., Tanaka, H., Bae, B., Miyatake, K.,

Watanabe, M., J. Am. Chem. Soc., 2011, 133, 10646-10654

2 Clark, T.J., Robertson, N.J., Kostalik IV, H.A., Lobkovsky, E.B., Mutolo, P.F., Abruña, H.D., Coates, G.W., J. Am. Chem. Soc., 2009, 131, 12888-12889

3 Tanaka, M., Koike, M., Miyatake, K., Watanabe, M., Macromolecules, 2010, 43, 2657-2659

4 Lin, B., Qiu, L., Qiu, B., Peng, Y., Yan, F., Macromolecules, 2011, 44, 9642-9649

5 Miyazaki, K., Abe, T., Nishio, K., Nakanishi, H., Ogumi, Z., J. Power. Sources, 2010, 195, 6500-6503

6 Kim, H.-S., Yamazaki, Y., Kim, J.-D., Kudo, T., Honma, I., Solid State Ionics, 2010, 181, 883-888

7 Kubo, D., Tadanaga, K., Hayashi, A., Tatsumisago, M., J. Power Sources, 2013, 222, 493-497

8 Kubo, D., Tadanaga, K., Hayashi, A., Tatsumisago, M., J. Electroanalytical Chemistry, 2012, 671, 102-105

9 Tamaki, T., Nakanishi, N., Ohashi, H., Yamaguchi, T., Electrochemistry Communications, 2012, 25, 50-53

10 Prasanna, S.V., Kamath, P.V., Industrial and Engineering Chemistry Research, 2009, 48, 6315-6320

11 Wang, Q., O'Hare, D., Chemical Reviews, 2012, 112, 4124-4155

12 Basu, D., Das, A., Stöckelhuber, K.W., Wagenknecht, U., Heinrich, G., Progress in Polymer Science, 2014, 39, 594-626

13 Khan, A.I., O'Hare, D., J. Mater. Chem., 2002, 12, 3191-3198

14 Xu, Z.P., Zeng, Q.H., Lu, G.Q., Yu, A.B., Chemical Engineering Science, 2006, 61, 1027-1040

15 Sels, B.F., De Vos, D.E., Jacobs, P.A., Catalysis Reviews - Science and Engineering, 2001, 43, 443-488

16 Goh, K.-H., Lim, T.-T., Dong, Z., Water Research, 2008, 42, 1343-1368

17 Williams, G.R., O'Hare, D., J. Mater. Chem., 2006, 16, 3065-3074

18 Mousty, C., Applied Clay Science, 2004, 27, 159-177

19 Jung, H., Ohashi, H., Anilkumar, G.M., Zhang, P., Yamaguchi, T., J. Mater. Chem. A, 2013, 1, 13348-13356

20 Zhang, P., Sago, S., Yamaguchi, T., Anilkumar, G.M., J. Power Sources, 2013, 230, 225-229

21 Costantino, U., Marmottini, F., Nocchetti, M., Vivani, R., European Journal of Inorganic Chemistry, 1998, 10, 1439-1446

22 Ogawa, M., Kaiho, H., Langmuir, 2002, 18, 4240-4242

23 Liu, Z., Ma, R., Osada, M., Iyi, N., Ebina, Y., Takada, K., Sasaki, T., J. Am. Chem. Soc., 2006, 128, 4872-4880

24 Furukawa, Y., Tadanaga, K., Hayashi, A., Tatsumisago, M., Solid State Ionics, 2011, 192, 185-187

25 Naik, V.V., Ramesh, T.N., Vasudevan, S., J. Phys. Chem. Lett., 2011, 2, 1193-1198

26 Handbook of X-ray Photoelectron Spectroscopy, ed, Muilenberg, G.E., Perkin-Elmer Corporation, 1979

Table 1. Results of CHN analysis of LDH samples prepared under different temperatures

Reaction condition	C	H	N
LDH 95^{o}C /12h	2.81 %	4.00 %	2.77 %
LDH 120^{o}C/ 12h	2.66 %	3.84 %	0.00 %

Table 2. Ionic conductivity (S/cm) of LDH samples measured at 80°C R.H. 80%

Reactant composition	$[urea]/[NO_3^-]=2.0$	$[urea]/[NO_3^-]=4.0$		
Reaction condition	95°C, 12h	95°C, 12h	95°C, 24h	120°C, 12h
Ionic conductivity	2.6×10^{-3}	1.0×10^{-3}	4.2×10^{-5}	2.5×10^{-6}

Table 3. Results of CHN analysis of LDH samples

Sample	C	H	N
As prepared LDH	2.66 %	3.84 %	0.00 %
After delamination	3.26 %	3.58 %	2.80 %

Table 4. Ionic conductivity (S/cm) of LDH samples measured at 80°C

Sample	R.H. 80%	R.H. 50%	R.H. 20%
As prepared LDH	2.5×10^{-6}	6.7×10^{-7}	N.D.
Ion exchanged LDH	2.7×10^{-5}	8.15×10^{-6}	9.27×10^{-7}
Delaminated LDH	5.0×10^{-4}	4.2×10^{-4}	1.16×10^{-4}

Figure 1 XRD patterns of LDH powders (a) [urea]/[NO_3^-]=2.0, and (b) [urea]/[NO_3^-]=4.0. Hydrothermal reaction condition was 95 °C for 12 h in both cases.

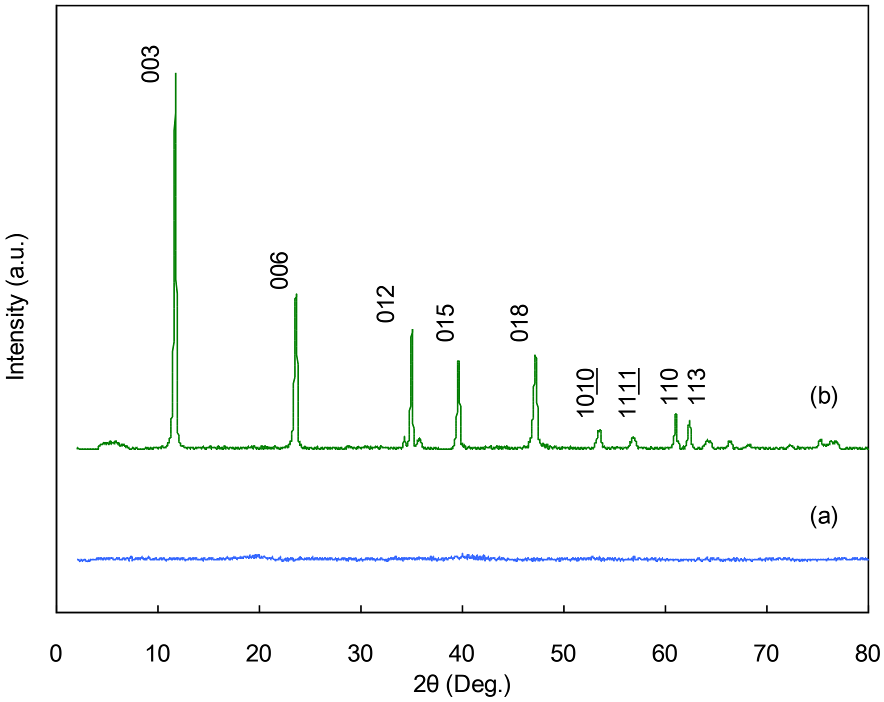

Figure 2 FESEM images of LDH powders (a) [urea]/[NO_3^-]=2.0, and (b) [urea]/[NO_3^-]=4.0. Hydrothermal reaction condition was 95 °C for 12 h in both cases.

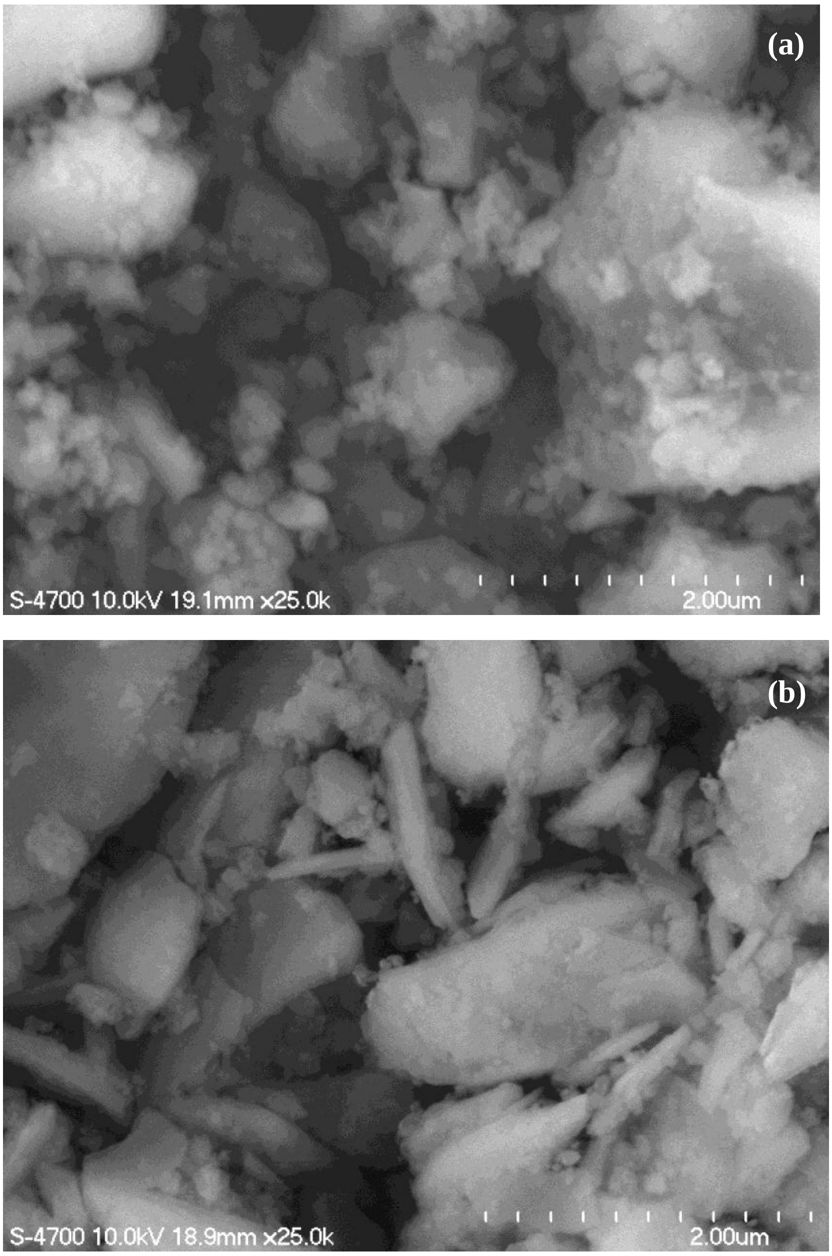

Figure 3 XRD patterns of LDH powders prepared at (a) 95°C for 12h, (b) 95°C for 24h, and (c) 120°C for 12h. Reactant composition was [urea]/[NO_3^-]=4.0 in all cases.

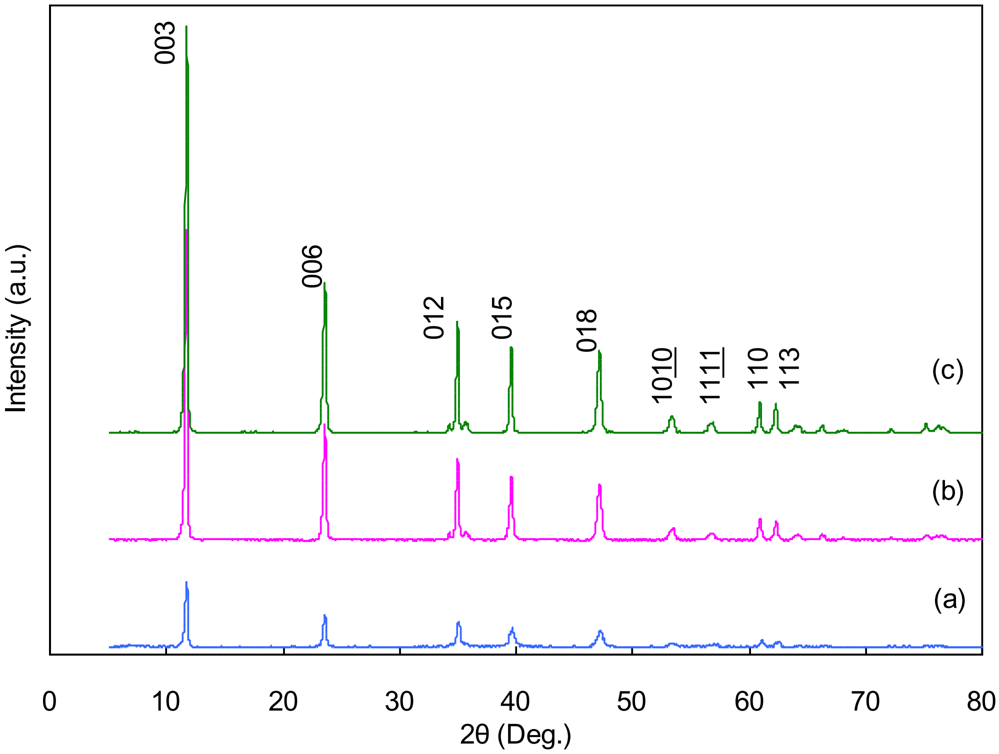

Figure 4 FESEM images of LDH powders prepared at (a) 95^{o}C for 12h, (b) 95^{o}C for 24h, and (c) 120^{o}C for 12h. Reactant composition was [urea]/[NO_3^-]=4.0 in all cases.

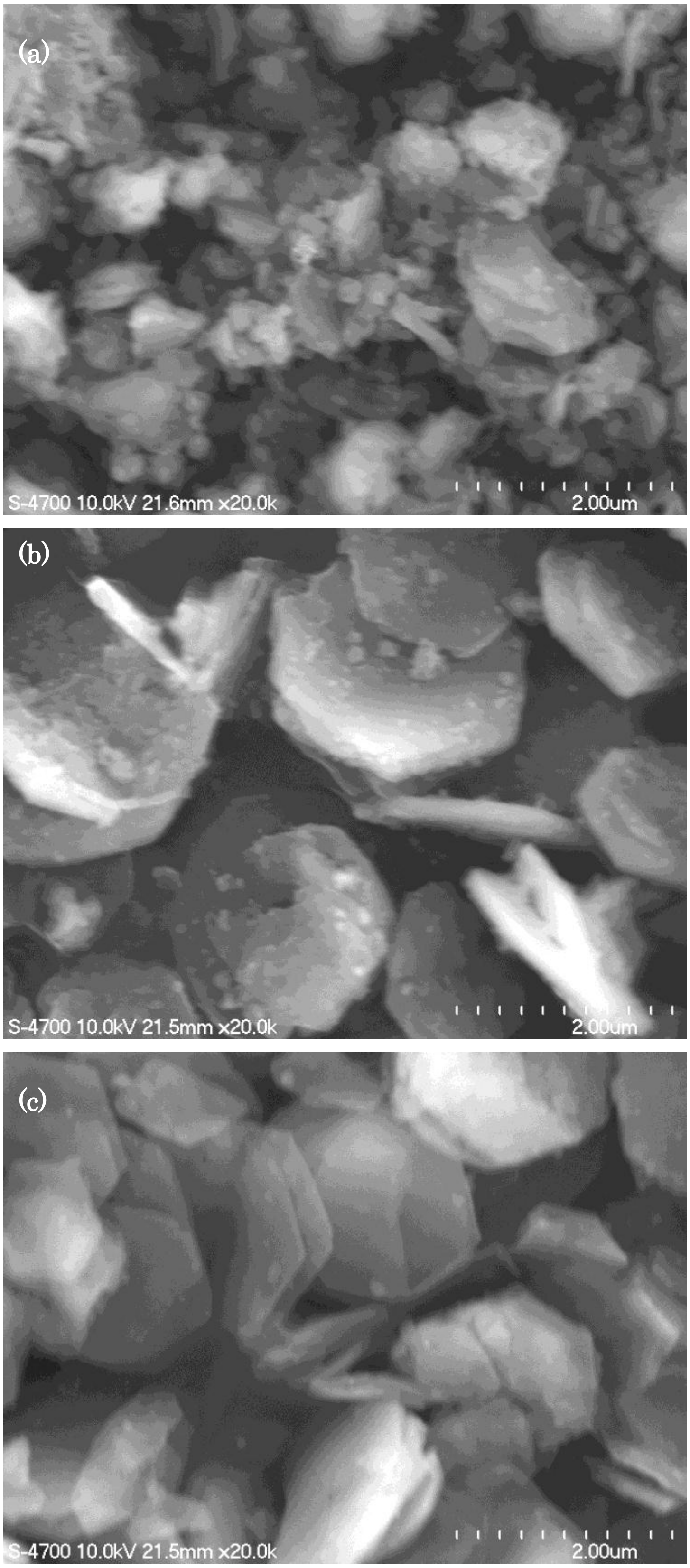

Figure 5 DTG curves of LDH powders (a) [urea]/[NO_3^-]=2.0, and (b) [urea]/[NO_3^-]= 4.0. Hydrothermal reaction condition was 95 °C for 12 h in both cases.

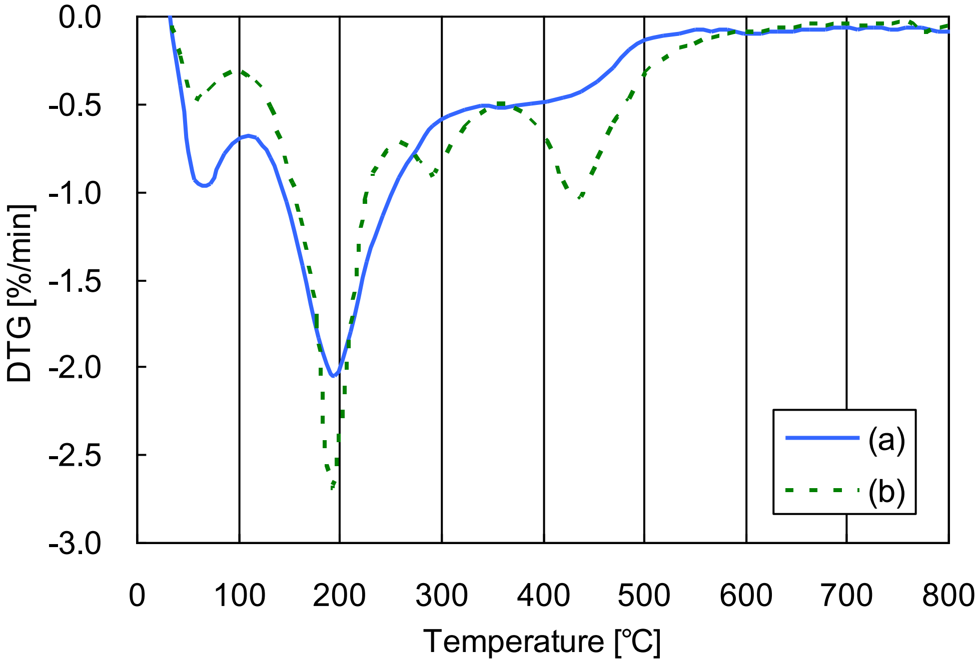

Figure 6 DTG curves of LDH powders prepared at (a) 95°C for 12h, (b) 95°C for 24h, and (c) 120°C for 12h

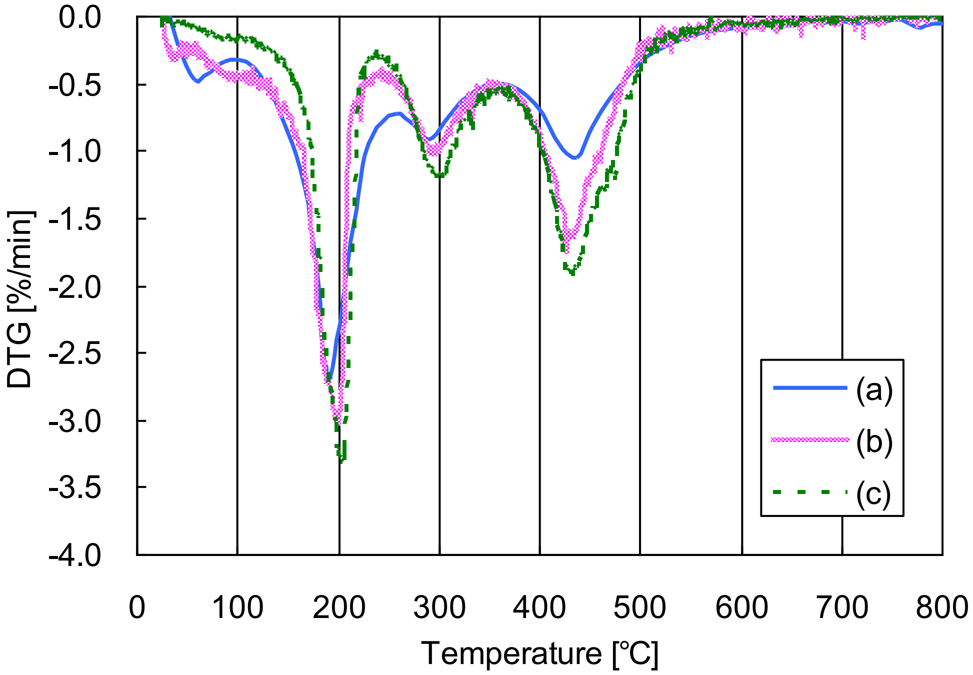

Figure 7 XRD patterns of (a) as prepared LDH, (b) ion exchanged LDH, and (c) delaminated LDH

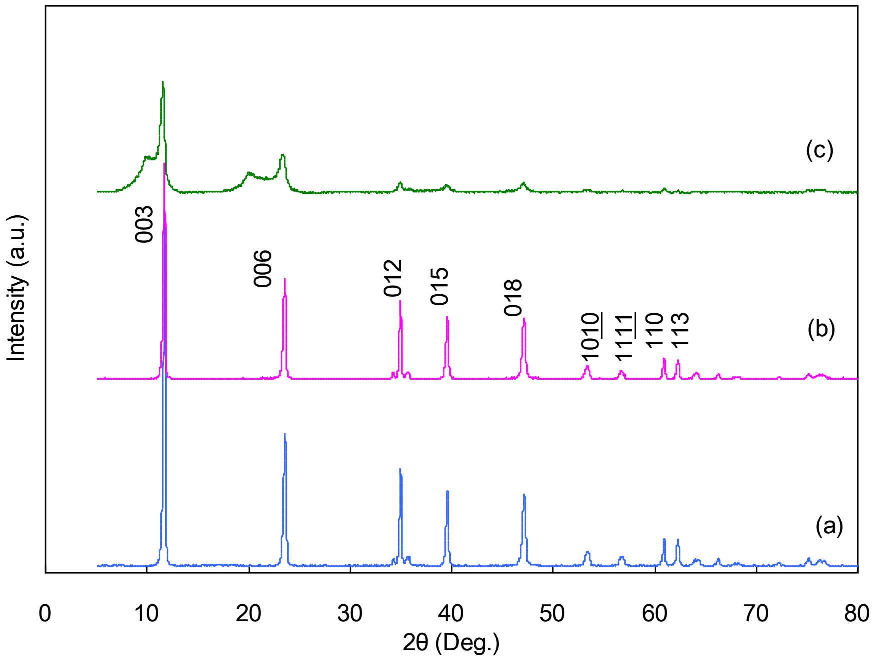

Figure 8 XPS spectra at N1s of (a) as prepared LDH, and (b) delaminated LDH

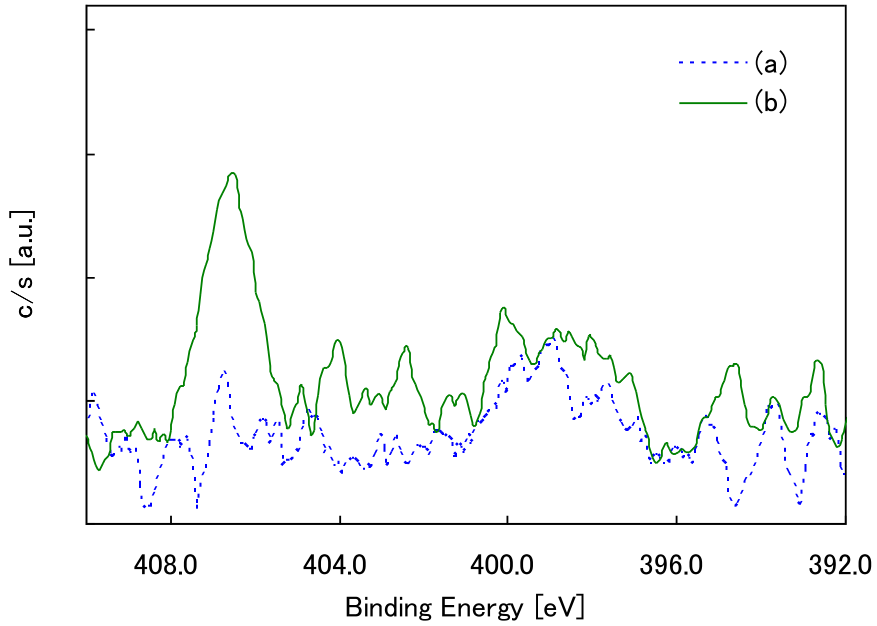

Figure 9 FESEM images of (a) as prepared LDH, (b) ion exchanged LDH, and (c) delaminated LDH

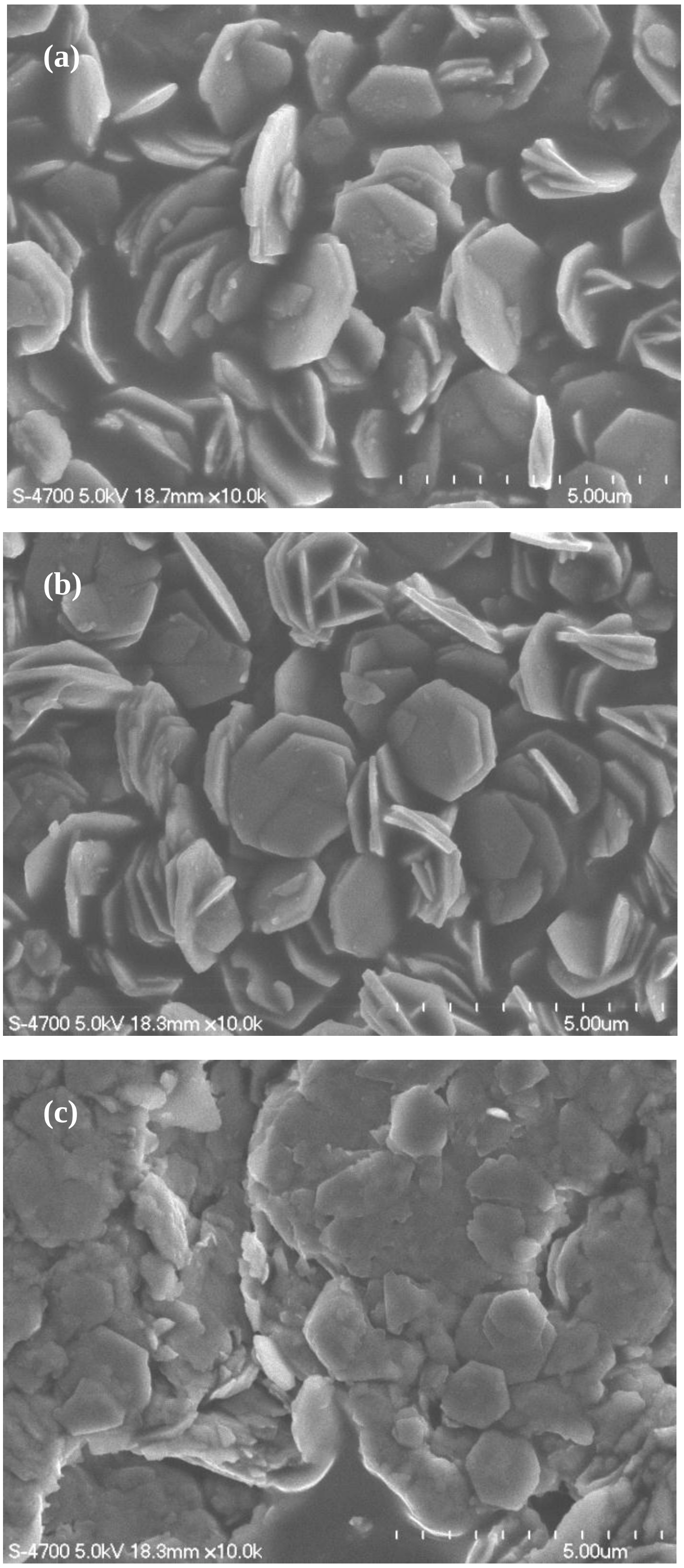

Figure 10 DTG curves of (a) as prepared LDH, (b) ion exchanged LDH, and (c) delaminated LDH

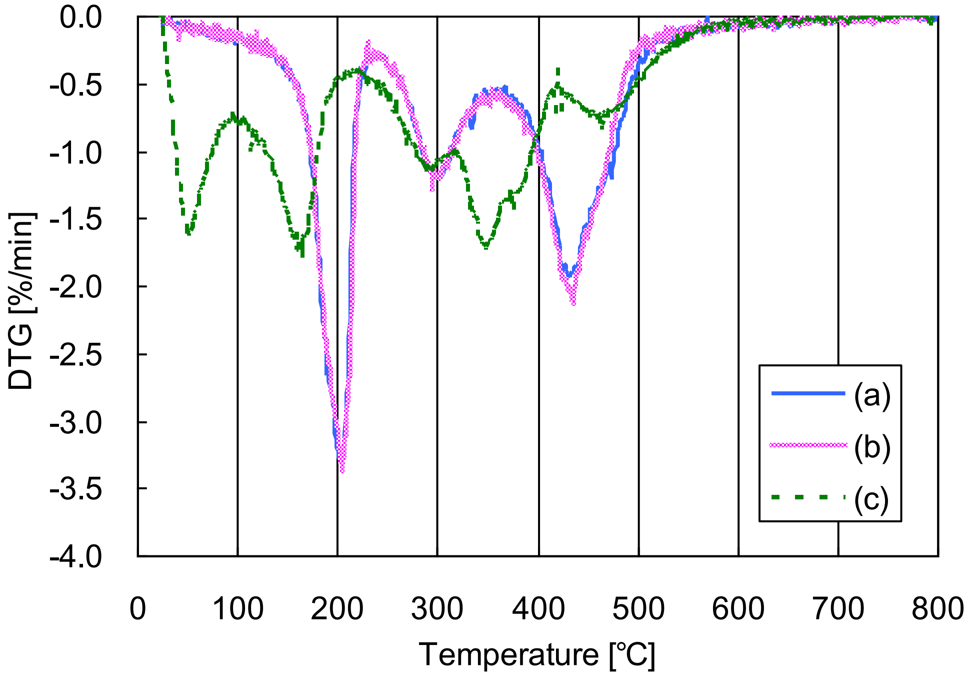

Figure 11 Ionic conductivity at 80°C of (a) as prepared LDH, (b) ion exchanged LDH, and (c) delaminated LDH