

FIG. 2 Model for the arrangement of anions.

the area of an octahedral unit ( $A_E = \sqrt{3}a^2/2$ ):

$$N_b = d_p^2/a^2 \quad (1)$$

Assuming electroneutrality in the LDHs, the number of anions per LDHs layer ( $Y_b$ ) is:

$$Y_b = N_b \cdot x/n \quad (2)$$

where  $x$  is the molar ratio of  $M^{3+}/(M^{2+}+M^{3+})$  and  $n$  is the charge of the intercalated anion.

In order to calculate  $d_z$ , a relationship between the separation of adjacent anions ( $d_z$ ), the mean diameter of the LDHs layer ( $d_p$ ) and the number of anions per LDHs layer ( $Y_b$ ) was needed. For this purpose, the ratio of the area of a brucite-like layer to one third of the area of the minimum hexagonal unit cell, as given in Fig.2, was applied. This was because the quotient is the total number of anions per brucite-like layer.

$$Y_b = \frac{\sqrt{3}d_p^2/2}{(1/3)3\sqrt{3}d_z^2/2} = \frac{d_p^2}{d_z^2} \quad (3)$$

Therefore,  $d_z$  can be calculated if the geometry, the charge of anions ( $n$ ), the molar ratio ( $x$ ), and the dimension of the LDHs crystallite ( $d_p$ ) are known. Using Eqs.(1), (2), (3),  $d_z$  is calculated by:

$$d_z = a\sqrt{n/x} \quad (4)$$

### B. Electrostatic potential energy model

Within a coherent stack of layers, the following forces significantly influence the stabilities of the anions: (i) attraction between positively charged layers and the intercalated anions; (ii) repulsion between the anions in the interlayer.

According to the structural character of LDHs, EP-EM is constructed as depicted in Fig.3. The stability of the anion in the interlayer is related to its electrostatic potential energy. The lower the anionic electrostatic energy, the more stable its structure becomes.

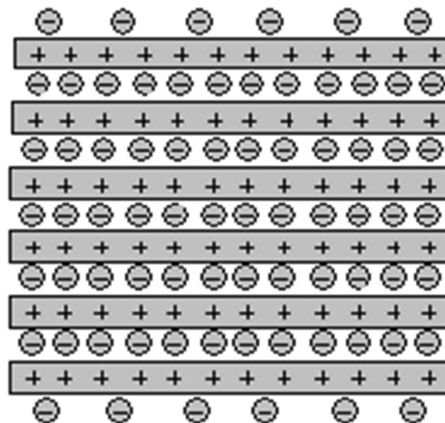


FIG. 3 Electrostatic potential energy model of LDHs.

In order to calculate the electrostatic potential energy of intercalated anions, the following assumptions must be made: (i) an intercalated anion is considered as a point charge and allocated the center; (ii) the layer's charge is well-distributed; (iii) interlayer water is ignored; (iv) the electrostatic potential energy of the border charge is calculated as the central charge's.

The point charge interaction (Coulomb's law) is required for an energy calculation of repulsive energy between anions [7]:

$$U_s = q^2/(4\pi\epsilon r) \quad (5)$$

where  $q$  is the charge of  $n$ -valent anions in the interlayer,  $\epsilon$  is the dielectric permittivity of vacuum,  $r$  is the distance between anions.

The calculation of the parameter  $r$  was made as follows: first, according to a hexagonal arrangement of anions, a  $30^\circ$  area marked as black ball, given in Fig.2, is studied. The number 0 anion is the central anion; the distances between it and the other anions can be calculated by Pythagorean theorem. The anionic number located at the edge of a  $30^\circ$  area is counted as 1/2, and other anionic number located inside are counted as 1.

According to the general formula of LDHs:  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][(A^{n-})_{x/n} \cdot mH_2O]$ , the charge of an octahedra is  $xe$ , thus, the positive charge density ( $q_c$ ) in the brucite-like layer can be calculated as:

$$q_c = xe/(a^2\sin 60^\circ) \quad (6)$$

where  $a$  is the lattice parameter in brucite-like layer,  $x$  is the molar ratio of  $M^{3+}/(M^{2+}+M^{3+})$ , and  $e$  is the charge of an electron.

TABLE I Structural parameters and anionic electrostatic potential energy of  $\text{Mg}_{1-x}\text{Al}_x\text{-LDHs}$ 

Anion variety	$x$	$a/\text{nm}$	$n/e$	$d_c/\text{nm}$	$d_z/\text{nm}$	$q_c/(\text{e}/\text{nm}^2)$	$U/(\text{kJ}/\text{mol})$
$\text{CO}_3^{2-}$	0.20	0.308	2	0.788	0.97	2.43	-2106.1
$\text{CO}_3^{2-}$	0.25	0.306	2	0.758	0.87	3.08	-2330.3
$\text{CO}_3^{2-}$	0.33	0.304	2	0.752	0.75	4.12	-2586.8
$\text{CO}_3^{2-}$	0.25	0.306	2	0.758	0.87	3.08	-2330.3
$\text{SO}_4^{2-}$	0.25	0.306	2	0.86	0.87	3.08	-2245.6
$\text{OH}^-$	0.25	0.306	1	0.76	0.61	3.08	-717.6
$\text{F}^-$	0.25	0.306	1	0.77	0.61	3.08	-712.1
$\text{Cl}^-$	0.25	0.306	1	0.79	0.61	3.08	-701.0
$\text{Br}^-$	0.25	0.306	1	0.80	0.61	3.08	-695.4
$\text{NO}_3^-$	0.25	0.306	1	0.88	0.61	3.08	-648.9
$[\text{PW}_{11}\text{O}_{39}]^{7-}$	0.25	0.306	7	1.54	1.64	3.08	-14915.4
$[\text{V}_{10}\text{O}_{28}]^{6-}$	0.25	0.306	6	1.25	1.52	3.08	-12243.1
$[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-}$	0.25	0.306	6	1.33	1.52	3.08	-12069.5
$[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$	0.25	0.306	5	1.54	1.39	3.08	-8443.3
$[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$	0.25	0.306	4	1.54	1.24	3.08	-5696.7
$[\text{Fe}(\text{CN})_6]^{3-}$	0.25	0.306	3	1.12	1.07	3.08	-4032.2
$[\text{PW}_{12}\text{O}_{40}]^{3-}$	0.25	0.306	3	1.54	1.07	3.08	-3343.3

$x$ -molar ratios of  $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ ,  $a$ -distance between adjacent cations,  $n$ -anionic charge,  $q_c$ -layer charge density,  $d_z$ -distance between adjacent anions,  $d_c$ -distance between adjacent layers,  $U$ -anionic electrostatic potential energy.

We are assuming the system being calculated is composed of  $y$  anions, thus the areas of layer ( $S_a$ ) is:

$$S_a = \sqrt{3}y d_z^2 / 2 \quad (7)$$

For the sake of convenience, a hexagonal layer is considered a circular one.

Attraction energy between the anions and the adjacent layers can be calculated as:

$$U_a = -\frac{qq_c N_A}{4\pi\epsilon} \int_0^{2\pi} d\theta \int_0^{\sqrt{S_a/\pi}} \frac{r}{\sqrt{r^2 + d_c^2/4}} dr \quad (8)$$

where  $d_c$  is the distance between the adjacent layers, which can be measured by XRD;  $N_A$  is Avogadro's number.

Thus the total electrostatic interaction energy  $U$  of anions can be calculated by:

$$U = \sum U_{si} + \sum U_{ai} \quad (9)$$

In this model, both the interaction between the central anion and the layers and the interaction between the central anion and other anions are calculated. This can be explained by electric field superposition theory. Eq.(9) represents the electrostatic interaction from all

the layers and anions with the central anion. The system being calculated is made up of 20 layers and 2107 anions per layer. The calculation is completed by computer due to complexity.

### III. RESULTS AND DISCUSSION

#### A. Altering the cation ratio of layer

In order to discuss the interaction between layers and anions, anionic potential energy is expressed as a function of the charge density of the layer, the distance between adjacent layers, anionic charge and the distance between adjacent anions,  $U = f(q_c, d_c, n, d_z)$ . The lower the anionic electrostatic potential energy, the more stable the intercalated anion is.

From Eq.(4) and Eq.(6),  $q_c$  is directly related to  $x$ , while  $d_z$  has an inverse relation to  $x$ .  $q_c$  increases and  $d_z$  decreases with an increase in  $x$ . Thus,  $U_s$  increases and  $U_a$  decreases, which affects the total electrostatic interaction energy of anions ( $U$ ). Structure parameters and anionic electrostatic potential energy of  $\text{MgAl-CO}_3^{2-}$  are shown in Table I, where  $a$  and  $d_c$  are measured by experiment [8]. For the  $\text{Mg}_{1-x}\text{Al}_x\text{CO}_3^{2-}$  ( $x=0.20, 0.25, 0.33$ ),  $q_c$  is 2.43, 3.08 and 4.12  $\text{e}/\text{nm}^2$ , respectively, while the  $d_z$  is 0.97, 0.87 and 0.75 nm, respectively. The Electrostatic potential energy of intercalated  $\text{CO}_3^{2-}$  is -2106.1, -2330.3, -2586.8 kJ/mol, respectively. Li

Lei reported that the decomposition temperature of intercalated  $\text{CO}_3^{2-}$  of MgAl-LDHs decrease from 413 to 410 °C by TG-DTA when  $x$  was reduced from 0.33 to 0.20 [8]. Therefore, the stabilities of intercalated anions decrease with a decrease in the interaction of anions with layer, which is consistent with the calculation results.

### B. Altering varieties of intercalated anions

Altering the varieties of intercalated anions results in little change to the lattice  $a$ . Given the value  $a$  is 0.306 nm, the structural parameters of  $\text{Mg}_{0.75}\text{Al}_{0.25}$ -LDHs and electrostatic potential energy of anions are more easily calculated. The value  $d_c$  depends on the experiment because anionic varieties have great influence on  $d_c$ .

From Eq.(4),  $d_z$  is directly related to anionic charges. For anions with different charges, it is expected that those with the highest charges will show the largest  $d_z$  values. This trend can be observed in Table I for the anions with Keggin structure, where the predicted order of  $d_z$  is followed:  $[\text{PW}_{11}\text{O}_{39}]^{7-} > [\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-} > [\text{PW}_{12}\text{O}_{40}]^{3-}$ . Nijs *et al.* reported the value  $d_z$  for  $[\text{Mg}_{0.75}\text{Al}_{0.25}][\text{Fe}(\text{CN})_6]^{3-}$  [9]. For example,  $d_z$  for  $x=0.25$  is about 1.044 nm. From Table I or using Eq.(4), the estimated  $d_z$  is 1.07 nm, which agrees with Nijs's result.

The qualitative analysis of anion exchange capacity of LDHs has widely been reported in the literature. However, there is no mention of ration exchange capacity. Overall, the lower the electrostatic potential energy of anion is, the more stable intercalated anion is, and the higher the anion exchange capacity is. From Table I, compared with simple anions, we can observe that the order of electrostatic potential energy:  $\text{CO}_3^{2-} < \text{SO}_4^{2-} < \text{OH}^- < \text{F}^- < \text{Cl}^- < \text{Br}^- < \text{NO}_3^-$ . The calculation results are in agree with those reported by Miyata [10]. So, this model can be used to predict the anionic exchange capacity of hydrotalcites.

As the complex anions are intercalated into the hydrotalcites, the value  $d_c$  can be obtained by summation of the layer thickness (0.48 nm) and anionic dimension. Due to the value  $U$  from Table I, it is predicted that the stability of intercalated anions is:  $[\text{PW}_{11}\text{O}_{39}]^{7-} > [\text{V}_{10}\text{O}_{28}]^{6-} > [\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-} > [\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-} > [\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-} > [\text{Fe}(\text{CN})_6]^{3-} > [\text{PW}_{12}\text{O}_{40}]^{3-}$ .

### IV. CONCLUSIONS

In this work, EPEM of LDHs was based upon the theory of crystallography. Anionic potential energy was

expressed as a function of the charge density of a layer, the distance between the adjacent layers, the anionic charge and the distance between the adjacent anions,  $U = f(q_c, d_c, n, d_z)$ .

(i) The charge density of layer  $q_c$  increases and the distance between the adjacent layers  $d_c$  decreases with an increase in molar ratios of  $\text{Al}^{3+}/(\text{Mg}^{2+} + \text{Al}^{3+})$ . Thus, anionic electrostatic potential energy  $U$  decreases and the stability increases. Calculation results are consistent with anionic thermal stability reported elsewhere.

(ii) Varieties of intercalated anions influence anionic stabilities. Measured anionic potential energy  $U$  matches ion exchange capacity reported. This model is useful for predicting anionic stability of the hydrotalcites.

(iii) In this model, a layer of LDHs is considered as a whole and the interactions between atoms are ignored, allowing us to avoid the large computational burden of calculations involving quantum chemistry or molecule mechanics. Our work introduces new directions for study of the structure and properties of such layered materials.

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