Anion Exchange Reaction Potentials as Approximate Estimates of the Relative Thermodynamic Stabilities of Mg/Al Layered Double Hydroxides Containing Different Anions

Belavalli E. Prasad,[†] P. Vishnu Kamath,*,[†] and K. Vijayamohanan*,[‡]

[†]Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

[‡]Central Electrochemical Research Institute, Karaikudi 630 006, India

S *Supporting Information*

ABSTRACT: Coatings of hydrotalcite-like nitrate-intercalated Mg/Al layered double hydroxides are electrochemically deposited on a Pt electrode by electrogeneration of base by reduction of a mixed metal nitrate aqueous solution. As-prepared coatings are stable to workup and function as rugged electrodes. The voltammetric response generated by anion exchange of intercalated nitrate for dissolved anions from solution under equilibrium conditions is employed to estimate the thermodynamic stabilities of the Mg/Al layered double hydroxides comprising different anions relative to the nitrate-containing phase. Among monovalent anions, the most stable is the fluoride-containing LDH ($\Delta G^\circ = -48.7$ kJ mol^{-1}) relative to the nitrate-containing LDH. The stability in aqueous phase decreases as $F^- > Cl^- > Br^- > NO_2^- > NO_3^-$, whereas, among divalent anions, SO_4^{2-} ($\Delta G^\circ = -8.7$ kJ mol^{-1}) > CO_3^{2-} ($\Delta G^\circ = 14.3$ kJ mol^{-1}). The results of monovalent ions match well with the Miyata series, whereas the divalent anion series is at variance with the commonly held belief that carbonate-LDHs are more stable than sulfate-LDHs.
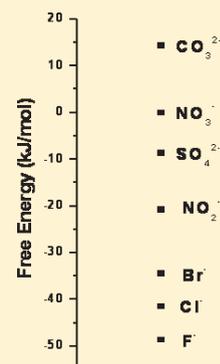
INTRODUCTION

Layered double hydroxides (LDHs) comprise a stacking of positively charged layers having the composition $[M(II)_{1-x}M'(III)_x(OH)_2]^{x+}$ with anions $[(A^{n-})_{x/n}\cdot yH_2O]$ incorporated in the interlayer region.[1] In this Article, we consider LDHs comprised of simple inorganic anions such as NO_3^-, NO_2^-, F^-, Cl^-, Br^-, SO_4^{2-}, and CO_3^{2-}. For brevity, we abbreviate the molecular formula of the LDH by the symbol $M(II)/M'(III)-A$.

The LDHs are of interest as they show many useful properties, such as high anionic mobility,[2] anion exchange,[3] sorption,[4,5] and surface basicity[6] by virtue of which they can potentially be used as anion exchangers,[7,8] catalysts,[9] and as electrodes for sensing.[10] However, there are some difficulties in the extensive use of LDHs for many of these applications. For instance, (i) carbonate-intercalated LDHs do not exchange anions,[11] (ii) some LDHs such as the Mg/Fe LDH do not exchange anions,[12] (iii) several monvalent anions are found to exchange incompletely, thereby limiting the exchange capacity of the LDHs and resulting in the formation of phases with mixed anions,[13] (iv) LDHs have a poor affinity for certain anions such as chromate[4,5] and iodide,[14] which seriously limits their applications in environmental amelioration and (v) there are no reports of the exchange of the interlayer water for other solvent molecules even when there is a general match of polarity and dielectric constants. To address many of the difficulties involved in the uptake of solvated anions and also for the controlled release of intercalated anions, it is important to understand the thermodynamic stability of LDHs.

The relative stability of a LDH in a given solvent depends upon (i) the cations present in the layer, (ii) the ion−solvent interactions in the interlayer, (iii) the electrostatic interactions between the metal hydroxide layer and the interlayer species, and (iv) the hydrogen-bonding strength between the anions and the hydroxyl group of the metal hydroxide layer. Therefore, it is not only important to estimate the thermodynamic stability of LDHs with different metal ions, but also compare the stability of a given LDH with different anions in the interlayer. There are also several interesting applications of LDH in catalysis, industrial separation, and electrochemistry where such a thermodynamic insight will be relevant for tailoring the usefulness of this class of layered materials.

Several methods are reported in the literature to study the relative stabilities of LDHs. Miyata[15] for the first time measured the equilibrium constants for anion exchange reaction of Mg/Al LDHs containing NO_3^- ion in the interlayer. He proposed an anion preference series for monovalent anions ($OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$) and for some divalent anions ($CO_3^{2-} > SO_4^{2-}$). The most preferred anions result in structurally more stable LDHs.

Microcalorimetric measurement[16] of anion exchange reactions was carried out by titrating a suspension of the Zn/Al−Cl LDH with aqueous solutions of salts of different incoming anions such as F^-, I^-, Br^-, NO_3^-, and SO_4^{2-}. These measurements generated a stability series similar to the one proposed by Miyata. Boclair and Braterman[17] reported pH-metric titrations of mixtures

of trivalent and divalent metal salt solutions with alkali. However, addition of alkali to a mixed salt solution forms the trivalent "hydroxide" first, and further addition of alkali leads to the formation of the LDH. Analysis of the resultant titration curves gave the nominal solubility products as inferred from the stoichiometric reactions. The stability order obtained from these studies was Mg < Mn < Co ≅ Ni < Zn for M(II) and Al < Fe for M'(III) ions. This method was not sensitive enough to determine the differences in the thermodynamic stability of LDHs of the same metals containing different anions. The most reliable work is that of Johnson and co-workers[18] who showed that LDH suspensions achieve equilibrium with their aqueous solution species very slowly over a period of 130−140 days. Thereby, all titrimetry-based estimates such as those of Boclair and Braterman[17] do not correspond to real equilibrium conditions.

Nenoff and co-workers[13] synthesized Mg/Al−A$^-$ LDHs by various methods such as ion exchange, memory effect, and hydrothermal treatment and gave a unique anion preference series, Br$^-$ > Cl$^-$ > NO$_3^-$ > I$^-$, which is at variance with the Miyata series for the halide ions.

Calorimetric measurements made by the group of Navrotsky[19−22] suggest that the measured enthalpies of formation of LDHs fit the mechanical mixture model. Thereby, the enthalpy of formation of a LDH is simply an algebraic sum of the enthalpies of the constituent unitary hydroxides and the divalent metal salt of the intercalated anion taken in appropriate proportions. The work of Navrotsky suggests that (a) LDHs derived from more insoluble single cation hydroxides are more stable than those obtained from more soluble ones and (b) for a given LDH, anions whose divalent salts are insoluble impart greater stability than anions whose divalent metal salts are soluble. Within this picture, the hydration enthalpy of the anion either remains unaccounted for or is estimated with large errors that obliterate the possible differences in the stability between LDHs with different anions.

Several theoretical models[23,24] are reported to study the formation and anion exchange reactions of LDHs, some of which are in agreement with the experimental data. Yet no single model captures all of the features inherent to the exchange process.

In this Article, we propose a different methodology to study the relative stabilities of the Mg/Al LDH with different anions in the interlayer relative to the nitrate phase, by generating a potentiometric response to self−self- and self−not-self-anion exchange reactions. By using the potential of the anion exchange reaction, we calculate the standard free energy of the exchange reaction. We illustrate the methodology by choosing the Mg/Al−A^{n-} LDH system. To facilitate the generation of a voltammetric response, the LDH was fabricated in the form of micrometer thick coatings on Pt flags by electrochemical deposition.

■ EXPERIMENTAL SECTION

Synthesis and Characterization. Mg/Al−NO$_3$ LDH coatings were prepared by reduction of a mixed ([Mg]/[Al] = 3) metal nitrate solution (total concentration 0.1 M, pH = 3.5). All of the solutions were prepared using ion exchanged Type-I water (Milli-Q Academic water purification system, specific resistance 18.2 MΩ cm).

A Pt flag (area 8.0 cm^2) was used as the cathode, and a Pt mesh (28 cm^2 geometric area) was used as the counter electrode. The depositions were carried out galvanostatically (current density 2.8 mA cm^{-2}, t 60 min) using an EG & G Versastat model IIA scanning potentiostat/galvanostat. The deposition potentials were measured with respect to a saturated calomel electrode, used as reference. After deposition, the

coatings were rinsed with water and dried at 65 °C. The approximate mass of the deposited coating was monitored by weighing ex situ the cathode before and after deposition. A typical coating weighed about 7 ± 1 mg (~0.9 mg/cm^2 of electrode surface). Prior to electrodeposition, the working electrode was electrochemically cleaned as described elsewhere.[25]

All of the coatings were characterized by X-ray diffraction (XRD), by mounting the electrode directly on a Bruker aXS model D8 Advance powder X-ray diffractometer (Cu Kα source, λ = 1.5418 Å). The PXRD pattern of the LDH in bulk was also obtained by grinding several electrodeposited coatings together. The PXRD pattern obtained from the bulk sample was employed to estimate the a-parameter of the LDH. IR spectra were recorded using a Bruker Alpha-T FTIR spectrometer (ATR mode, diamond crystal, resolution 4 cm^{-1}, 400−4000 cm^{-1}).

Composition of the LDH Coating. The NO$_3^-$ content of the LDH coating was determined by soaking a typical coating (mass 6.7 mg) in a Na$_2$CO$_3$ solution (2.6 mM; 25 mL) for 14 h to affect a complete exchange of NO$_3^-$ for CO$_3^-$ ions. The carbonate solution containing NO$_3^-$ ions released from the LDH coating was diluted to 50 mL and injected into a prestandardized ion chromatograph (Metrohm model 861 Advanced Compact IC, mobile phase carbonate buffer). For standardization of the ion chromatograph, nitrate standards were prepared using NaNO$_3$ (Merck India, Assay ≥99%). The Mg/Al ratio was determined from the a-parameter of the LDH. For this, the a-parameters of several NO$_3^-$-LDH samples (0.15 ≤ x ≤ 0.33) from the library of samples available in the authors' laboratory were used as standards.

Exchange Potential Measurements. All of the potential measurements were carried out using a data analogue system (DAU 124, Techno Science Instruments, India) with respect to Ag/AgCl reference electrode. The temperature was maintained at 27 ± 0.2 °C (IKA ETS-D5 Heater). Prior to each potential measurement, the electrolyte (NaNO$_3$) solution was heated approximately to 60 °C and degassed by bubbling nitrogen gas. Nitrogen bubbling was continued, until the temperature of the electrolyte reaches 27 °C. The LDH-coated electrode was dipped into the electrolyte solution, in "voltmeter-on" condition. The potential was monitored until equilibrium was achieved. After use, the electrode was activated by aging in 1 M NaNO$_3$ solution for 60 min. The electrode was then rinsed with water and dried at 65 °C. It was repeatedly used for verifying the reproducibility of the potentiometric response and robustness in multiple uses. Potential measurements were carried out for a few other anions such as NO$_2^-$, F$^-$, Cl$^-$, Br$^-$, SO$_4^{2-}$, and CO$_3^{2-}$ using the respective metal salt solutions. The pH of all of these salt solutions were in the range 6.8−7.5, except for Na$_2$CO$_3$, whose pH = 10.6−11.4. A freshly prepared LDH coating was used for each new anion.

■ RESULTS AND DISCUSSION

In a mixed metal nitrate solution, the LDH is precipitated as

$$
\begin{aligned}
(1-x)M^{2+} &+ xM'^{3+} + 2OH^- + x/nA^{n-} \\
&+ yH_2O \rightarrow [M_{1-x}M'_x(OH)_2](A^{n-})_{x/n}\cdot yH_2O
\end{aligned} \quad (1)
$$
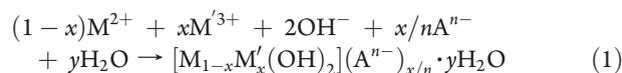
The hydroxide ions are electrogenerated by a variety of reactions such as electrolysis of water, nitrate reduction, and dissolved oxygen reduction.[26] The fact that the LDH in general has a lower solubility than the single cation hydroxides favors the formation of LDHs in preference to other phases. As the pH increase takes place close to the electrode, the LDH is deposited as a coating on the cathode.

The PXRD pattern of the "as-deposited" coating obtained from a mixed (Mg^{2+} + Al^{3+}) metal nitrate solution (Figure 1) shows reflections corresponding to 003 and 006 planes at 10.2° 2θ (d = 8.6 Å) and 20.2° 2θ (d = 4.3 Å), respectively. This interlayer spacing corresponds to a nitrate intercalated LDH. The
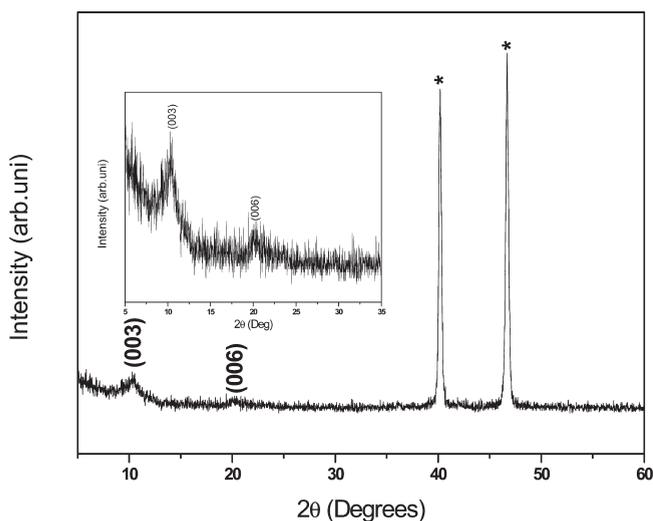
Figure 1. PXRD pattern of the as-prepared Mg/Al—NO$_3$ layered double hydroxide coating. Features marked by the asterisk correspond to the Pt substrate.
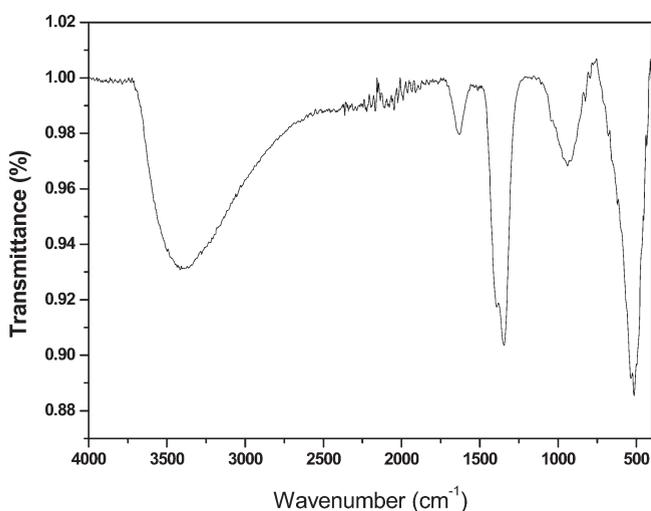
Figure 2. Infrared spectrum of the as-prepared Mg/Al—NO$_3$ layered double hydroxide coating.

IR spectrum of the coating (Figure 2) shows an OH stretching vibration at 3475 cm^{-1} and vibrations due to the intercalated nitrate at 1385 cm^{-1}.

The PXRD pattern of the bulk sample obtained by grinding several coatings was indexed to rhombohedral symmetry ($a = 3.0486$ Å, $c = 25.8$ Å). The a-parameters of the standard samples used for comparison vary in the range from 3.088 Å ($x = 0.15$) to 3.040 Å ($x = 0.33$). The a-parameter of the bulk sample almost matches with the a-parameter (3.049 Å) of the $x = 0.25$ standard. The Mg/Al ratio yields the layer charge 0.25. The nitrate content determined by ion chromatography analysis of the "as-deposited" coating is 0.19(NO$_3^-$) per empirical formula. The residual charge is compensated by the inclusion of CO$_3^{2-}$ ion as impurity. No independent determination of the CO$_3^{2-}$ content was made. The approximate composition of the LDH coating is determined to be [Mg$_{0.75}$Al$_{0.25}$(OH)$_2$] (NO$_3$)$_{0.19}$(CO$_3$)$_{0.03}$·0.38H$_2$O. For practical applications, we treat this as Mg/Al—NO$_3$ LDH coating.
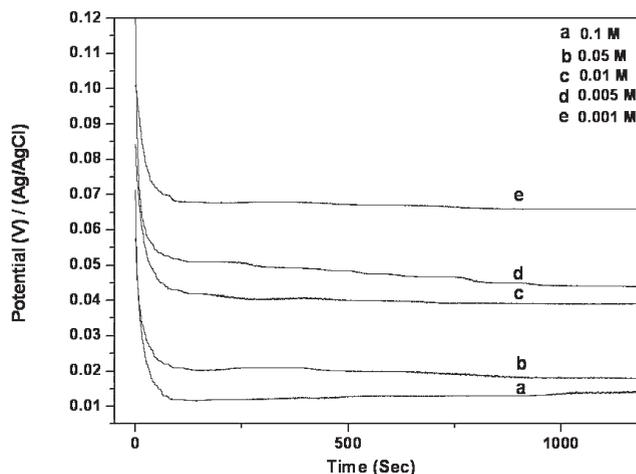
Figure 3. Potential versus time plot for nitrate exchange reaction for different concentrations of dissolved nitrate in solution.

When the as-deposited Mg/Al—NO$_3$ coating was dipped in a solution containing any anion, A^{n-} (A = NO$_2^-$, F$^-$, Cl$^-$, Br$^-$, SO$_4^{2-}$, and CO$_3^{2-}$), the self—not-self reaction that takes place is given by

$$Mg/Al-NO_3 \ (s) \ + \ A \ (aq) \rightarrow Mg/Al-A \ (s) \ + \ NO_3^- \ (aq) \tag{2}$$
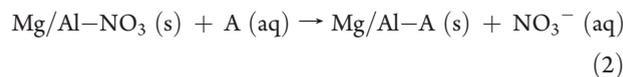
When the as-prepared coating is dipped in a solution containing dissolved NO$_3^-$ ions, the nitrate ion (self—self) exchange equilibrium is established.

The potential of the exchange reaction was measured for different anion concentrations in the range 0.1—0.001 M. The equilibrium potentials obtained were plotted against log[A] and fit to a straight line as predicted by the Nernst equation. Standard potential ($E°$) was obtained by extrapolating the fitted line to 1 M anion concentration. By using the slope of this fitted line, number of electrons, n, involved in the exchange reaction is obtained as $n = 59.1/$slope. The number 59.1 mV is from the Nernst equation, this being the slope for a reaction involving one electron. A complete list of the values of the slope, n and $E°$, of all of the anion exchange reactions is given in the Supporting Information. By using $E°$ and n, the free energy of the exchange reaction was calculated using the relation $\Delta_{AE}G = -nFE°$ (AE: anion exchange), where F is the Faraday constant, 96 500 C/mol.

The potential—time plot obtained when an as-deposited Mg/Al—NO$_3$ LDH coating was dipped in various concentrations (0.1—0.001 M) of a NaNO$_3$ solution is shown in Figure 3. As the concentration of the electrolyte decreases, the potential changes in the positive direction. For all concentrations of the electrolyte, steady state was attained within a short period of time (5—10 min). The equilibrium potential—log[A] plot for nitrate (self—self-exchange) is shown in Figure 4. The slope obtained from the linear fit is 28.3 mV. The standard free energy, $\Delta_{AE}G$ (AE: anion exchange), calculated for the reaction is −36.5 kJ mol^{-1}.

The equilibrium potential—log[A] plots for other anions (NO$_2^-$, F$^-$, Cl$^-$, Br$^-$, SO$_4^{2-}$, CO$_3^{2-}$) (self—not-self) exchange reactions are shown in Figures 4 and 5. In all of the cases, the change in potential with change in concentration of the electrolyte follows the same trend as in the case of NO$_3^-$ exchange. Although all monovalent ions carry the same charge, −1, it is to be remembered that this only represents the formal charge
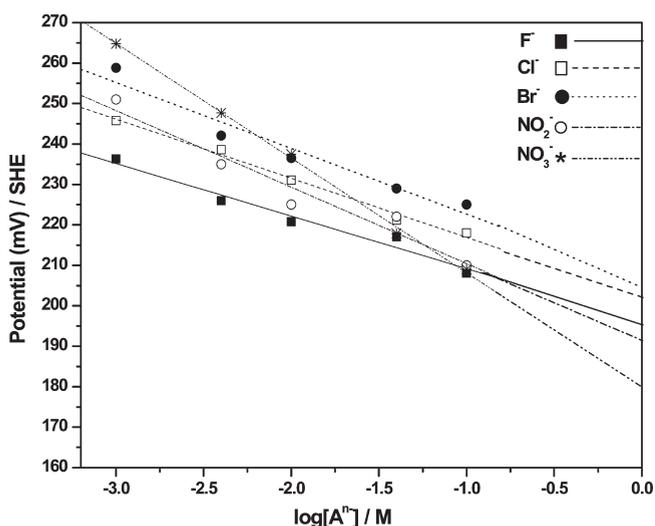
Figure 4. Potential versus log[A] plots for different monovalent anions.
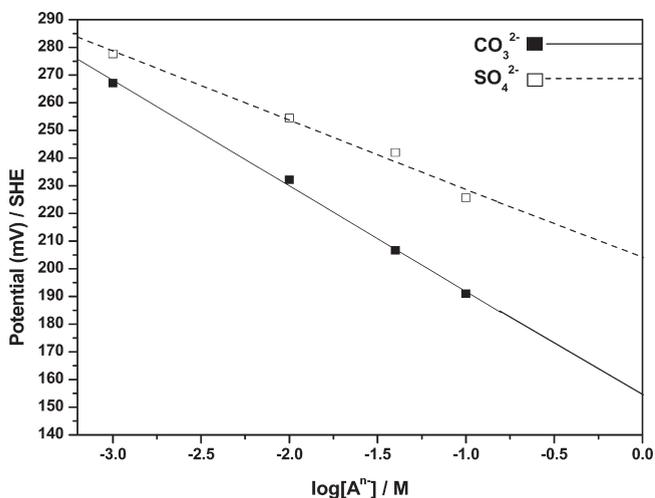
Figure 5. Potential versus log[A] plots of divalent anions.

Table 1. Free Energy Values for Monovalent and Divalent Anion Exchange Reaction

anion (A^{n-})	free energy ($\Delta_{AE}G$) (kJ/mol)	$\Delta_{AE}G(A^{n-}) - \Delta_{AE}G(NO_3^{-})$ (kJ/mol)
F^{-}	−85.2	−48.7
Cl^{-}	−78.0	−41.5
Br^{-}	−71.0	−34.5
NO_2^{-}	−57.3	−20.8
NO_3^{-}	−36.5	0
SO_4^{2-}	−45.2	−8.7
CO_3^{2-}	−22.2	14.3
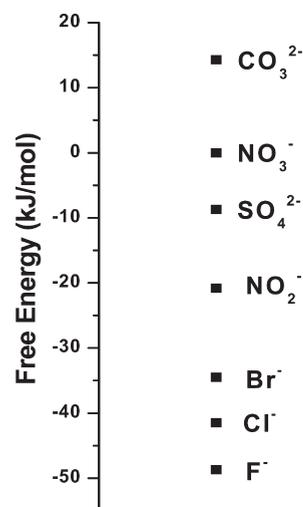
Figure 6. Free energy of exchange of different anions relative to the nitrate-LDH.

expected of a free ion. Yet the actual effective charge in the bonded state, as would be obtained on intercalation in the confined spaces of a layered hydroxide, would not be the same for all of the anions. The actual effective charge would greatly depend upon the electronegativity of the atom, its ionic/atomic radius, state of hydration, polarizability, and a host of other factors, which reflect the effect of the chemical environment of the host on the anion. The totality of all of these factors manifests itself in the n-value, evaluated by the application of the Nernst equation. Thereby, different monovalent ions yield different n values. A similar argument holds for divalent anions as well. The free energy change ($\Delta_{AE}G$) values calculated for all anion exchange reactions are given in Table 1.

The free energy change, $\Delta_{AE}G$, for different self–not self-exchange reactions is compared to the free energy change involved in the self–self-exchange reaction. The difference, $\Delta_{AE}G(A^{n-}) - \Delta_{AE}G(NO_3^{-})$, in the standard free energy changes between the self–self- and the self–not self-exchange reactions yields the free energy of the Mg/Al–A^{n-} LDH relative to the Mg/Al–NO_3^{-} LDH.

The changes in standard free energy values (Table 1) for all monovalent ions in aqueous solutions are negative with respect to the self–self-exchange reaction and follow the sequence $F^{-} > Cl^{-} > Br^{-} > NO_2^{-} > NO_3^{-}$ (Figure 6), suggesting that the replacement of NO_3^{-} ion in the solid by other monovalent ions investigated is thermodynamically favored. This result agrees well with the anion preference series of Miyata[15] and that proposed by Navrotsky[20] for monovalent ions. In Miyata's original selectivity series, we have introduced the NO_2^{-} anion to the left of the NO_3^{-} ion. This is understandable, as the NO_2^{-} ion intercalates with its molecular plane parallel to the metal hydroxide layer ($d = 7.9$ Å), a mode of coordination that promotes H-bonding between the O atom of NO_2^{-} and hydroxyl group of the metal hydroxide layer. In contrast, the NO_3^{-} ion ($d = 8.6$ Å) bonds with its molecular plane perpendicular to the metal hydroxide layer.[27] In this mode of coordination, H-bonding is weak whereby (i) the NO_3^{-} LDH is expected to be thermodynamically less stable, (ii) the NO_3^{-} ion is susceptible to hydration by the ingress of water molecules from solution, and (iii) it is more labile to exchange reactions as compared to other anions on account of the screening of the Coulombic attraction to the metal hydroxide layer due to hydration.

In the case of divalent ions, the preference is $SO_4^{2-} > CO_3^{2-}$. The free energy change for sulfate incorporation is more negative (-8.7 kJ mol^{-1}) with respect to self–self-exchange, and that for CO_3^{2-} ion is more positive ($+14.3$ kJ mol^{-1}). The results for

SO_4^{2-} are along the lines expected by the Miyata series[15] and also from considerations of the greater Coulombic attraction for divalent as opposed to monovalent ions.[28] However, the results of CO_3^{2-} ions are rather surprising, as our results suggest that the carbonate incorporation into the nitrate-LDH is thermodynamically not favored.

We then ask the questions: (i) Why is the carbonate ion not exchangeable in CO_3^{2-}-LDHs? (ii) Why do LDHs exhibit a large affinity for CO_3^{2-} ions?

Our suggestion is that the CO_3^{2-}-LDHs are kinetically stable or rather they are not labile. There is experimental evidence to suggest that the transition state facilitating anion exchange involves the hydration of the outgoing anion resulting in the prising apart of the metal hydroxide layers. Indeed, SO_4^{2-}-LDHs are a well-known example of this phenomenon, crystallizing as they do in a multiplicity of polytypes: 8 Å (anhydrous), 9 Å (monohydrate), and 11 Å (dihydrate).[29] The $HCOO^-$-LDH crystallizes in 8.7 Å (anhydrous), 11.2 Å (hydrated), and 24.5 Å (swollen state) phases, prior to delamination in the absence of any incoming ion.[30] The BrO_3^--LDH crystallizes in 9.2 Å (anhydrous) and 10.7 Å (hydrated) phases.[31] In comparison with all other anions, CO_3^{2-}-LDH has the lowest hydration enthalpy[32] in the solid state, whereby the activation energy for realizing the transition state of a CO_3^{2-}-LDH is large as compared to other LDHs. This factor makes the CO_3^{2-} ion not exchangeable in the CO_3^{2-}-LDHs. This factor is also borne out by the calorimetric measurements of Navrotsky group.[20] The enthalpy of the reaction

$$(1 - 3x/2)Mg(OH)_2 + xAl(OH)_3 + x/2MgCO_3 \\ + H_2O \rightarrow Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2}\cdot H_2O \qquad (3)$$
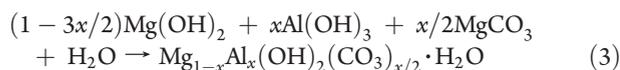
is actually expected to yield the hydration enthalpy of the anion in the interlayer. Significantly, this experimental measurement yields a near zero value (within experimental errors) for this reaction, suggesting that the hydration enthalpy of CO_3^{2-} is nearly zero. Similar measurements for nitrate-LDH, however, show considerable hydration enthalpy.

On a similar vein, the greater hydration enthalpy of anions other than CO_3^{2-} makes them labile leaving groups facilitating CO_3^{2-} incorporation. Entropy contribution, resulting from the release of two outgoing ions for each incoming carbonate ion, aids carbonate incorporation in a thermodynamic sense. A combination of these factors manifests itself in the form of the "greater affinity" of LDHs for carbonate ions.

CONCLUSION

In this study, we have proposed a simple method to understand the relative stabilities of a given LDH with different anions in the interlayer. Electrosynthesis provides a convenient way to synthesize workable LDH electrodes. Here, we have demonstrated the methodology for the Mg/Al−NO₃ system. This approach is very general and can be used to study the stabilities of other layered materials, which generate a voltammetric response.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Slope, number of electrons, and standard potentials of anion exchange reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: vishnukamath8@hotmail.com (P.V.K.), k.vijayamohanan@gmail.com (K.V.).

REFERENCES

(1) Cavani, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.
(2) Oesten, R.; Bohm, H. *Solid State Ionics* **1993**, *62*, 199.
(3) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1990**, *29*, 5201.
(4) Prasanna, S. V.; Rao, R. A. P.; Kamath, P. V. *J. Colloid Interface Sci.* **2006**, *304*, 292.
(5) Prasanna, S. V.; Kamath, P. V. *Solid State Sci.* **2008**, *10*, 260.
(6) Constantino, V. R. L.; Pinnavia, T. J. *Inorg. Chem.* **1995**, *34*, 883.
(7) Newman, S. P.; Jones, W. *New J. Chem.* **1998**, *22*, 105.
(8) Khan, A. I.; Hare, D. O. *J. Mater. Chem.* **2002**, *12*, 3191.
(9) Reichle, W. T. *J. Catal.* **1985**, *94*, 547.
(10) Ballarin, B.; Morigi, M.; Scavetta, E.; Seeber, R.; Tonelli, D. *J. Electroanal. Chem.* **2000**, *492*, 7.
(11) Roy, A. D.; Forano, C.; Besse, J. P. In *Layered Double Hydroxides: Present and Future*; Rives, Ed.; Novo Science: New York, 2001; p 1.
(12) Manohara, G. V.; Prasanna, S. V.; Kamath, P. V. *Eur. J. Inorg. Chem.* **2011**, *2011*, 2624.
(13) Bonochev, R. P.; Liu, S.; Krumhansl, J. L.; Voigt, J.; Nenoff, T. M. *Chem. Mater.* **2003**, *15*, 3669.
(14) Prasanna, S. V.; Kamath, P. V.; Shivakumara, C. *J. Colloid Interface Sci.* **2010**, *344*, 508.
(15) Miyata, S. *Clays Clay Mineral.* **1983**, *31*, 305.
(16) Israeli, Y.; Gueho, C. T.; Besse, J. P.; Morel, J. P.; Desrosiers, N. M. *J. Chem. Soc., Dalton Trans.* **2000**, 791.
(17) Boclair, J. W.; Braterman, P. S. *Chem. Mater.* **1999**, *11*, 298.
(18) Johnson, C. A.; Glasser, F. P. *Clays Clay Mineral.* **2003**, *51*, 1.
(19) Allada, R. K.; Navrotsky, A.; Berbeco, H. T.; Casey, W. H. *Science* **2002**, *296*, 721.
(20) Allada, R. K.; Pless, J. D.; Nenoff, T. M.; Navrotsky, A. *Chem. Mater.* **2005**, *17*, 2455.
(21) Allada, R. K.; Navrotsky, A.; Goates, J. B. *Am. Mineral.* **2005**, *90*, 329.
(22) Allada, R. K.; Peltier, E.; Navrotsky, A.; Casey, W. H.; Johnson, C. A.; Berbeco, H. T.; Sparks, D. L. *Clays Clay Mineral.* **2006**, *54*, 409.
(23) Suarez, J. J. B.; Mozo, E. A. P.; Oyama, S. T. *Quim. Nova* **2004**, *27*, 574.
(24) Suarez, J. J. B.; Mozo, E. A. P.; Oyama, S. T. *Quim. Nova* **2004**, *27*, 601.
(25) Prasad, B. E.; Kamath, P. V.; Upadhya, S. *J. Am. Ceram. Soc.* **2008**, *91*, 3870.
(26) Switzer, J. A. *Am. Ceram. Soc. Bull.* **1987**, *66*, 1521.
(27) Wang, S. L.; Wang, P. C. *Colloids Surf., A* **2007**, *292*, 131.
(28) Chatelet, L.; Bottero, J. V.; Yvon, J.; Bouchelaghem, A. *Colloids Surf., A* **1996**, *111*, 167.
(29) Khaldi, M.; Roy, A. D.; Chaouch, M.; Besse, J. P. *J. Solid State Chem.* **1997**, *130*, 66.
(30) Manohara, G. V.; Kunz, D. A.; Kamath, P. V.; Milius, W.; Breu, J. *Langmuir* **2010**, *26*, 15586.
(31) Radha, A. V.; Kamath, P. V.; Shivakumara, C. *J. Phys. Chem.* **2007**, *111*, 3411.
(32) *Nanoparticles and the Environment*; Navrotsky, A., Banfield, J. F., Eds.; Mineralogical Society of America: Washington, DC, 2001; Vol. 44.