

# Study of the Intercalation of Lithium Salt in Gibbsite Using Time-Resolved in Situ X-ray Diffraction

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Time-resolved in situ X-ray diffraction measurements have been used to measure the rate of intercalation of lithium salts (LiX; X = Cl, Br, NO<sub>3</sub>, OH, and SO<sub>4</sub>) into Gibbsite ( $\gamma$ -Al(OH)<sub>3</sub>) giving the layered double hydroxides [LiAl<sub>2</sub>(OH)<sub>6</sub>]X·nH<sub>2</sub>O (X = Cl, Br, NO<sub>3</sub>, and OH) and [LiAl<sub>2</sub>(OH)<sub>6</sub>]<sub>2</sub>SO<sub>4</sub>·nH<sub>2</sub>O. The temperature dependence of the rate of intercalation of LiCl yields an activation energy of 27 kJ mol<sup>-1</sup>. The reaction was also found to be half-order with respect to the initial concentration of LiCl. The rate of intercalation is sensitive to the nature of the anions with the half-lives of the reactions varying from 450 to 4800 s going from Li<sub>2</sub>SO<sub>4</sub> to LiNO<sub>3</sub>.

## Introduction

Layered double hydroxides (LDHs) have been the focus of much research as a result of their potential applications in fields as diverse as catalysis,<sup>1</sup> medicine,<sup>2,3</sup> and ion scavenging.<sup>4</sup> The synthesis of layered double hydroxides containing mono- and trivalent cations rather than the more usual combination of di- and trivalent ions was first reported for the hydrolysis of aluminum tri(*sec*-butoxide) in the presence of lithium carbonate.<sup>5</sup> This reaction yielded [LiAl<sub>2</sub>(OH)<sub>6</sub>]<sub>2</sub>CO<sub>3</sub>·nH<sub>2</sub>O. An alternative synthetic route to Li/Al LDHs via the direct intercalation of lithium salts into either Gibbsite { $\gamma$ -Al(OH)<sub>3</sub>} or Bayerite from aqueous solution was patented by the Dow Chemical Company in 1982<sup>6</sup> and independently reported in the literature a few years later.<sup>7,8</sup> This has proved to be a more convenient synthesis of [LiAl<sub>2</sub>(OH)<sub>6</sub>]X·nH<sub>2</sub>O (X = Cl, Br, NO<sub>3</sub>, and OH) and [LiAl<sub>2</sub>(OH)<sub>6</sub>]<sub>2</sub>SO<sub>4</sub>·nH<sub>2</sub>O than the hydrolysis method. More recently a hydrothermal preparation of [LiAl<sub>2</sub>(OH)<sub>6</sub>]OH·2H<sub>2</sub>O from hydrated alumina gel and LiOH has been reported.<sup>9</sup>

Further studies on these compounds by X-ray diffraction, TEM, and ion exchange reactions lead to the conclusion that there is ordering of the cations in the layers of [LiAl<sub>2</sub>(OH)<sub>6</sub>]<sub>2</sub>CO<sub>3</sub>·nH<sub>2</sub>O with the Li<sup>+</sup> ions located in the vacant octahedral holes of a Gibbsite like array of Al<sup>3+</sup> cations.<sup>10,11</sup> The X-ray diffraction data were

indexed on the basis of a hexagonal unit cell. The hexagonal nature of the unit cell in these materials was subsequently confirmed by Poeppelmeier et al. in a study of [LiAl<sub>2</sub>(OH)<sub>6</sub>]OH·2H<sub>2</sub>O.<sup>8</sup> Following on from these observations and the assumption that the Li<sup>+</sup> ions occupy the remaining third of the octahedral sites in an Al(OH)<sub>3</sub> layer with the anions and co-intercalated water situated in the interlayer region Poeppelmeier et al. were able to perform a Rietveld refinement of [LiAl<sub>2</sub>(OH)<sub>6</sub>]OH·2H<sub>2</sub>O.<sup>12</sup> More recently the structures of the dehydrated intercalation compounds [LiAl<sub>2</sub>(OH)<sub>6</sub>]X (X = Cl, Br, NO<sub>3</sub>) and the hydrated analogue [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O have been refined using the same layer model.<sup>13</sup> In the dehydrated compounds the guest anions occupy trigonal prismatic sites between Li<sup>+</sup> cations in adjacent layers.

Monitoring chemical reactions in situ can provide valuable information on the processes occurring as well as kinetic data by allowing them to be studied under normal conditions. Such information is not available from more conventional ex situ studies. In recent years the development of high flux synchrotron X-ray and neutron sources has led to such studies becoming much more routine. In particular energy-dispersive synchrotron X-ray experiments (EDXRDs), which use polychromatic radiation and an energy discriminating detector, have yielded valuable kinetic and mechanistic information on a number of solid-state reactions. For example, we have used in situ EDXRD techniques to study; intercalation reactions of metal dichalcogenide host lattices,<sup>14,15</sup> staging in ion-exchange intercalation reac-

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tions of layered double hydroxides,<sup>16,17</sup> hydrothermal crystallization of gallophosphates,<sup>18</sup> and mesoporous silicates.<sup>19</sup> Recently, several more general reviews have been published on the application of in situ techniques to sol-gel syntheses and the crystallization of microporous materials.<sup>20,21</sup>

In this paper we describe the use of time-resolved, in situ energy-dispersive synchrotron X-ray powder diffraction to study the intercalation of lithium salts (LiX; X = Cl, Br, OH, NO<sub>3</sub>, SO<sub>4</sub>) into Gibbsite, forming the layered double hydroxides [LiAl<sub>2</sub>(OH)<sub>6</sub>]X<sub>x</sub>·nH<sub>2</sub>O (X = Cl, Br, OH, NO<sub>3</sub>, SO<sub>4</sub>).

### Experimental Section

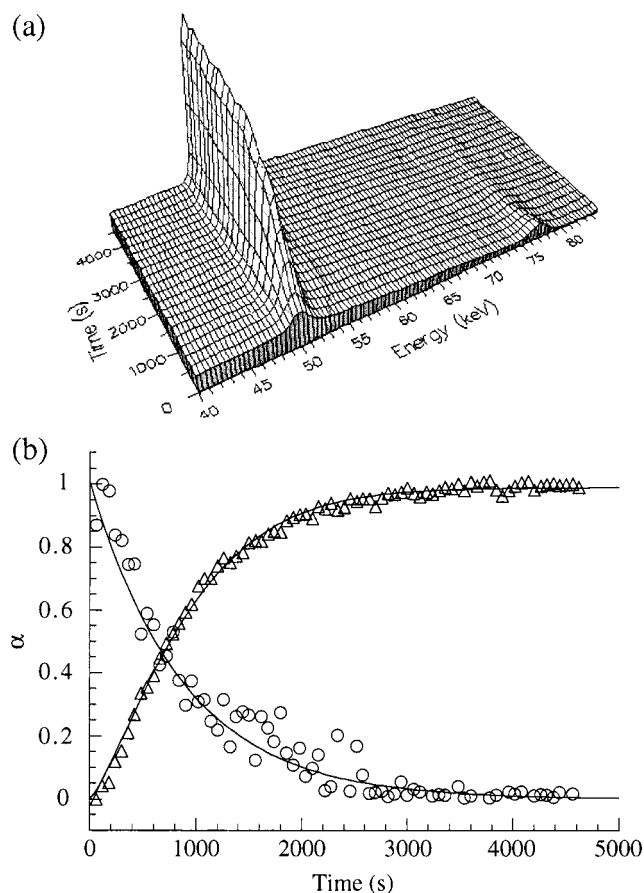
**Synthesis.** The intercalation of lithium salts into Gibbsite was performed in accord with the methods described previously.<sup>7,8,13</sup> In a typical reaction, 250 mg of Gibbsite was suspended in 6 mL of an aqueous solution of the required guest (concentration range 4–20 M) and heated at a fixed temperature between 60 °C and 140 °C.

**Diffraction Experiments.** Time-resolved in situ energy-dispersive X-ray diffraction experiments were performed on Station 16.4 of the U.K. Synchrotron Radiation Source at Daresbury Laboratory using an experimental set up which has been described elsewhere.<sup>22,23</sup> In a typical experiment individual spectra were collected with an acquisition time of either 60 or 120 s and a fixed detector angle (2θ) of 1.91°. This arrangement gives us simultaneous access to Bragg reflections in the *d* spacing range 14 to 4 Å.

### Results and Discussion

The intercalation of LiCl in Gibbsite giving [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O has been studied using time-resolved in situ EDXRD. In all the cases, the reactions proceeded directly to the first stage intercalation product and no other crystalline phases were observed. A typical set of in situ EDXRD spectra for intercalation of LiCl are shown in Figure 1. The major peak that is observed to grow with time in the energy window corresponds to the 002 Bragg reflection of [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O at *E* = 49.1 keV (*d* = 7.65 Å) while the 001 Bragg reflection of Gibbsite at *E* = 77.0 keV (*d* = 4.85 Å) decays in intensity. We can resolve no changes in the peak position or peak width at half-maximum during the growth of the intercalate Bragg peaks. This is probably not to surprising given that the detector momentum resolution using post sample molybdenum slits is typically ( $\Delta E/E = 0.0115$ ).

Kinetic information was extracted from each experiment by integration of the 002 Bragg reflection of [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O using a Gaussian peak fitting routine.<sup>24</sup>



**Figure 1.** (a) Time-resolved in situ energy-dispersive X-ray powder diffraction data showing the course of the reaction between Gibbsite and a 7.5 M aqueous solution of LiCl at 120 °C giving [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O. (b) Plot of extent of reaction ( $\alpha$ ) of the 001 Bragg reflection (*E* = 77.1 keV, *d* = 4.85 Å) of the Gibbsite (○) and the 002 Bragg reflection of [LiAl<sub>2</sub>(OH)<sub>6</sub>]Cl·H<sub>2</sub>O (*E* = 49.1 keV, *d* = 7.65 Å) (△) as a function of time.

The errors on the integrated areas are small and contained within the data points. The integrated intensities were subsequently converted to the extent of the reaction,  $\alpha$ , using the relationship:

$$\alpha_{hkl}(t) = \left( \frac{I_{hkl}(t)}{I_{hkl}(t_{\infty})} \right) \quad (1)$$

Least-squares fits of the  $\alpha(t)$  data to the Avrami-Erofe'ev rate expression were carried out kinetic model.<sup>25–28</sup> The general form of the Avrami-Erofe'ev equation is given by

$$[-\ln(1 - \alpha)]^{1/m} = k(t - t_0) \quad (2)$$

and it has previously been successfully applied to a variety of solid-state processes including decompositions,<sup>29</sup> phase transformations,<sup>30</sup> crystallizations,<sup>31</sup> and intercalation reactions.<sup>14,15</sup>

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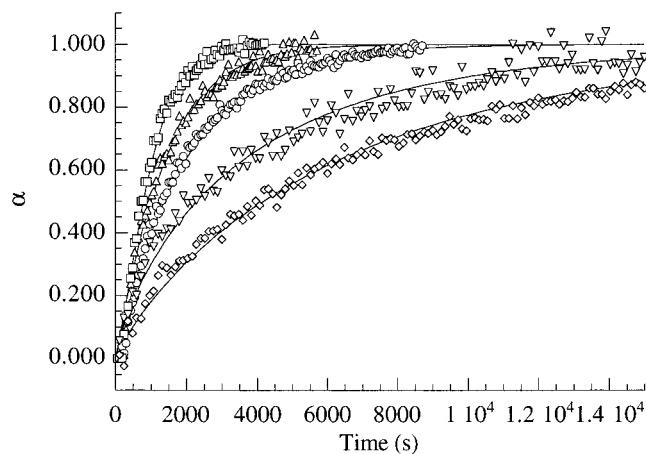
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**Figure 2.** Extent of reaction ( $\alpha$ ) against time ( $t$ ) for the intercalation of LiCl into Gibbsite over a range of temperatures: 140 °C ( $\square$ ), 120 °C ( $\Delta$ ), 100 °C ( $\circ$ ), 80 °C ( $\nabla$ ), and 60 °C ( $\diamond$ ). Data for 110 and 90 °C have been omitted for clarity. The data have been fitted using the Avrami-Erofe'ev equation.

We have investigated the rate of intercalation of LiCl in Gibbsite as a function of both temperature and LiCl concentration.

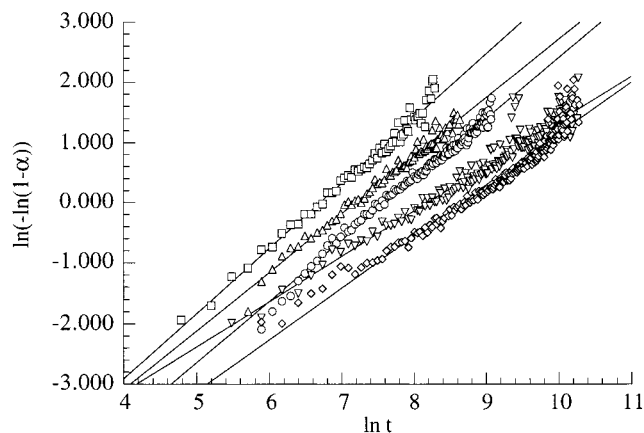
**Effect of Temperature.** The temperature dependence of the intercalation reaction between a 10 M aqueous solution of LiCl and Gibbsite was investigated over the range 60–140 °C. Figure 2 plots extent of reaction against time for the temperatures studied and it is clear that the rate of reaction has a marked temperature dependence. In each case the Avrami-Erofe'ev equation has been fitted to the data. Furthermore plots of reduced time ( $t/t_{0.5}$ ) versus extent of reaction for the different temperatures are superimposable within experimental error implying a consistent mechanism for the intercalation reaction over the whole temperature range.

The Avrami exponents obtained from the least-squares fits for all the data sets fell in the range 0.8–1.2 although a value of  $m = 1.0$  gives a satisfactory fit to the majority of the experimental results. Assuming Avrami-Erofe'ev kinetics to be relevant this indicates a two-dimensional diffusion-controlled growth model following instantaneous nucleation. In this case the Avrami-Erofe'ev equation becomes

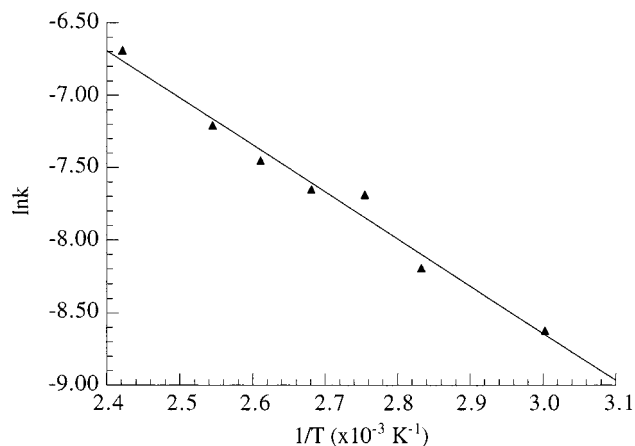
$$\alpha = 1 - \exp(-kt) \quad (3)$$

The validity of eq 3 for the whole process can be confirmed by a Sharp-Hancock analysis. In each case this analysis yields a single straight line over the whole reaction implying that the Avrami-Erofe'ev kinetics discussed above are a good description of this system. The Sharp-Hancock plots are shown in Figure 3 and the kinetic parameters are summarized in Table 1. Further evidence for this model can be obtained by consideration of the intersection of the host and intercalate curves shown in Figure 1b. The intersection is at  $\alpha \approx 0.5$ , implying that loss of coherent diffraction from the host is matched by gain in coherence of the product. In cases where nucleation is random, the rate of loss of coherent diffraction from the host lattice exceeds the rate of growth of the product phase, leading to the intersection being at  $\alpha < 0.5$ .

From the kinetic data obtained from the above analysis it is possible to extract an activation energy



**Figure 3.** Sharp-Hancock plots corresponding to the data sets shown in Figure 2 for the temperature dependence of the intercalation reaction between a 10 M aqueous solution of LiCl and Gibbsite: 140 °C ( $\square$ ), 120 °C ( $\Delta$ ), 100 °C ( $\circ$ ), 80 °C ( $\nabla$ ), and 60 °C ( $\diamond$ ). Data for 110 and 90 °C have been omitted for clarity.



**Figure 4.** Arrhenius plot for the determination of the activation energy for the intercalation of LiCl into Gibbsite.

**Table 1. Summary of the Kinetic Parameters Obtained from the Sharp-Hancock Analysis of the Intercalation of LiCl into Gibbsite with Variation of the Temperature**

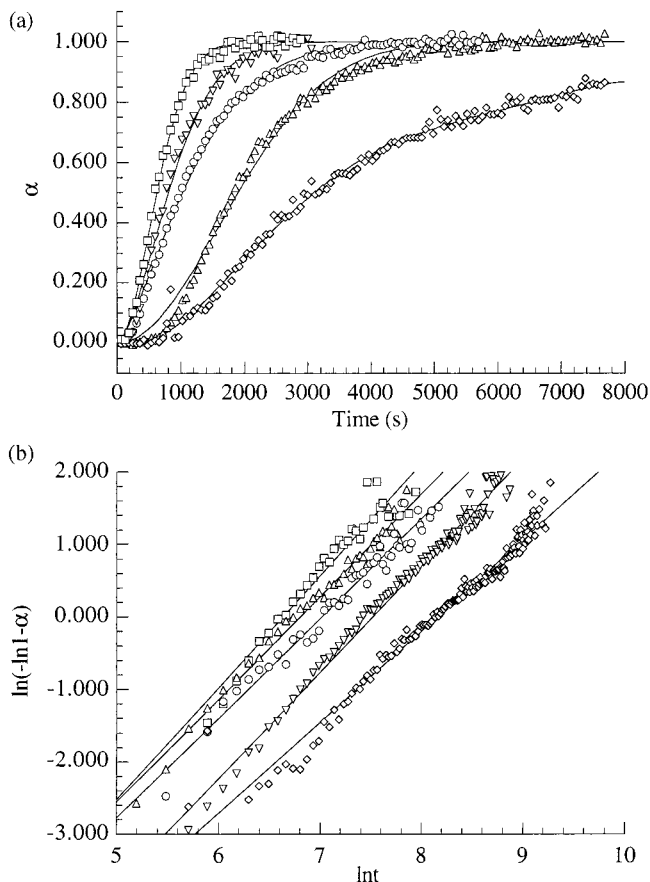
$T$ (°C)	$m$	$k$ ( $s^{-1}$ )	$t_{0.5}$ (s)
140	1.06	$1.25 \times 10^{-3}$	720
120	1.00	$7.40 \times 10^{-4}$	960
110	1.07	$5.82 \times 10^{-4}$	1140
100	1.06	$4.76 \times 10^{-4}$	1320
90	1.05	$4.60 \times 10^{-4}$	1830
80	0.80	$2.77 \times 10^{-4}$	2280
60	0.82	$1.81 \times 10^{-4}$	4080

for the intercalation of LiCl into Gibbsite using the Arrhenius expression,  $k = A \exp(-E_a/RT)$ . The plot of  $\ln k$  versus  $1/T$  is shown in Figure 4 and yields a value of  $E_a = 27 \text{ kJ mol}^{-1}$ . This compares with a value of  $E_a = 41 \text{ kJ mol}^{-1}$  obtained from a study of the temperature dependence of the rate of intercalation of cobaltocene  $\{\text{Co}(\eta\text{-C}_5\text{H}_5)_2\}$  in  $\text{SnS}_2$ .<sup>15</sup> The activation energy for lithium intercalation in  $\text{TiS}_2$  giving  $\text{Li}_{0.2}\text{TiS}_2$  has been estimated to be  $33 \text{ kJ mol}^{-1}$  using different techniques.<sup>32,33</sup>

**Effect of Concentration.** The effect of LiCl concentration on the intercalation reaction was studied at 120

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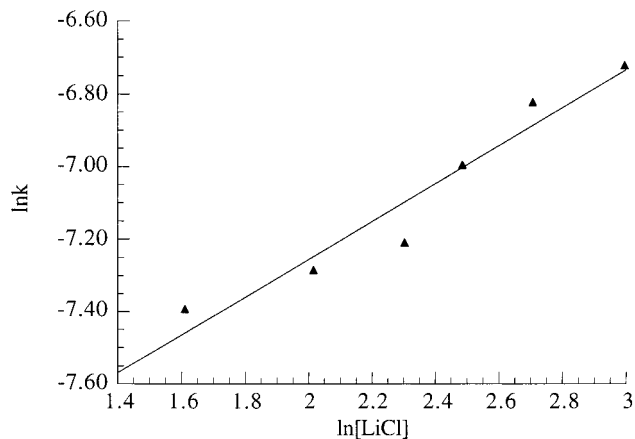
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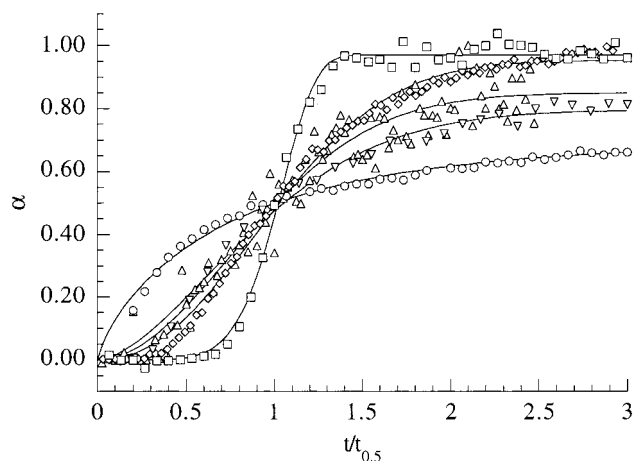
**Figure 5.** (a) Extent of reaction ( $\alpha$ ) against time ( $t$ ) for the intercalation of LiCl into Gibbsite over a range of initial guest concentrations and (b) the corresponding Sharp-Hancock plots: 20 M ( $\square$ ), 15 M ( $\nabla$ ), 10 M ( $\circ$ ), 5 M ( $\triangle$ ), and 4 M ( $\diamond$ ). Data for 12 and 7.5 M guest solutions have been omitted for clarity.

$^{\circ}\text{C}$  over the range 4–20 M. The reaction with 4 M LiCl did not go to completion in 4 h and no reactions were observed in 2 h for concentrations below this level. From the plots of extent of reaction against time shown in Figure 5a it can be seen that the reaction rate is strongly dependent on the initial concentration of LiCl. In each case the Avrami-Erofe'ev equation has been fitted to the data. The observation of a dependence of rate of the reaction on the concentration of the guest is in contrast to previous studies on the intercalation of metallocenes into metal dichalcogenides which were found to be zeroth order with respect to the guest concentration.<sup>15</sup> As for the temperature dependence reactions, plots of extent of reaction against reduced time are superimposable within experimental error, indicating that the same mechanism is occurring in each case. This can be further confirmed by analysis of the Avrami exponents obtained from the curve fitting and from the Sharp-Hancock plots shown in Figure 5b which lie in the range 1.0–1.5 although taking a value of 1.0 gives a satisfactory fit to the majority of the data. This indicates a two-dimensional diffusion-controlled nucleation-growth model following instantaneous nucleation as was observed for the temperature dependence data. The kinetic parameters are summarized in Table 2.

The order of reaction with respect to LiCl concentration can be determined from a plot of  $\ln k$  against  $\ln [\text{LiCl}]$  which is shown in Figure 6. The gradient of this



**Figure 6.** Plot of  $\ln k$  versus  $\ln [\text{LiCl}]$  used to determine the order of reaction with respect to the concentration of LiCl.



**Figure 7.** Reduced time plot  $\{\alpha(t) \text{ vs } t/t_{0.5}, t_{0.5} = \text{half-life of reaction}\}$  for the intercalation of Gibbsite with LiX [ $\text{X} = \text{NO}_3^-$  ( $\circ$ ),  $\text{Br}^-$  ( $\triangle$ ),  $\text{Cl}^-$  ( $\diamond$ ),  $\text{OH}^-$  ( $\square$ ),  $\text{SO}_4^{2-}$  ( $\nabla$ )] giving  $[\text{LiAl}_2(\text{OH})_6]\text{X} \cdot n\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{and OH}$ ) and  $[\text{LiAl}_2(\text{OH})_6]_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ .

**Table 2. Summary of the Kinetic Parameters Obtained from the Sharp-Hancock Analysis of the Intercalation of LiCl into Gibbsite for Varying Initial LiCl Concentrations**

[LiCl] (mol L <sup>-1</sup> )	$m$	$k$ (s <sup>-1</sup> )	$t_{0.5}$ (s)
20	1.47	$1.21 \times 10^{-3}$	600
15	1.40	$1.09 \times 10^{-3}$	780
12	1.27	$9.16 \times 10^{-4}$	900
10	1.00	$7.40 \times 10^{-4}$	960
7.5	1.37	$6.86 \times 10^{-4}$	1050
5	1.45	$6.16 \times 10^{-4}$	1830
4	1.26	$2.89 \times 10^{-4}$	3180

plot is 0.52 indicating that the reaction is half-order with respect [LiCl]. This gives the rate equation as

$$\text{rate} \propto k[\text{LiCl}]^{0.5} \quad (4)$$

**Effect of the Nature of the Anion.** The intercalation of Gibbsite was monitored using EDXRD for 5 M aqueous solutions of lithium chloride, lithium bromide, lithium nitrate, lithium hydroxide, and lithium sulfate at 120  $^{\circ}\text{C}$  to determine the effect guest anion size and charge density on the rate of intercalation in Gibbsite. Reduced time plots  $\{\alpha(t) \text{ vs } t/t_{0.5}\}$  for the different lithium salts are shown in Figure 7. The kinetic data are summarized in Table 3. Remarkably, the half-lives of the reactions vary from 450 to 4800 s going from Li<sub>2</sub>-

**Table 3. Summary of the Kinetic Parameters Obtained for the Intercalation of Gibbsite with Various Lithium Salts, LiX**

X	<i>m</i>	<i>k</i> (s <sup>-1</sup> )	<i>t</i> <sub>0.5</sub> (s)
Cl	1.45	6.16 × 10 <sup>-4</sup>	1830
Br	1.16	1.59 × 10 <sup>-4</sup>	4800
OH	2.20	2.22 × 10 <sup>-3</sup>	900
NO <sub>3</sub>	0.45	9.34 × 10 <sup>-5</sup>	9700
SO <sub>4</sub>	1.48	1.51 × 10 <sup>-3</sup>	450

SO<sub>4</sub> to LiNO<sub>3</sub>. It is perhaps not surprising that the Li<sub>2</sub>-SO<sub>4</sub> intercalates the most rapidly since the SO<sub>4</sub><sup>2-</sup> ion has the highest charge of the anions investigated. The variation in rate constants for all the monoanions is roughly correlated with their ionic radii. The ionic and thermochemical radii are 2.44, 1.82, 1.67, 1.65, and 1.19 Å for SO<sub>4</sub><sup>2-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and OH<sup>-</sup>, respectively. The only exception to the trend is the intercalation of LiNO<sub>3</sub> which based solely on ionic radii arguments should intercalate at the same rate as LiCl.

However, the reduced time plots suggest that the intimate mechanism of this reaction may change depending on the anion used. The two limiting cases are the intercalations of LiOH and LiNO<sub>3</sub>. The intercalation of LiOH preceded by a relatively long induction period but then goes to completion very quickly, ~10 minutes after the onset of intercalation. The intercalation of LiNO<sub>3</sub> has virtually no induction time but has not gone to completion after 6 h. For the intercalation of LiCl, LiBr, and Li<sub>2</sub>SO<sub>4</sub>, the plots almost lie on top of each other, suggesting that for these ions the intercalation mechanisms are similar. At this point we are unable to offer a complete explanation for all these observations,

a much more detailed study of the temperature and concentration dependence for each of ions would be required to shed light on this problem but was not possible due to the constraints of the beamtime.

**Summary of Kinetic and Mechanistic Information.** Time-resolved in situ EDXRD measurements have revealed considerable kinetic and mechanistic information on the intercalation of lithium salts into Gibbsite. In general the extent of reaction versus time curves are sigmoidal in nature, indicating a nucleation-growth model. For the reactions with LiCl the experimental data can be fitted satisfactorily by Avrami-Erofe'ev kinetics with *m* = 1. This represents a mechanism in which instantaneous nucleation is followed by two-dimensional diffusion of the guest anions into the host. Further experiments into the effect of particle size on the reaction rate would be necessary to confirm this mechanism with a reciprocal relationship expected i.e., the rate of reaction is expected to be quicker the smaller the particle size. The rate of reaction was found to vary as a function of both temperature and guest concentration. The variable-temperature studies yielded an activation energy of 27kJ mol<sup>-1</sup>, and the reaction was found to be half-order with respect to the initial concentration of LiCl. The intercalation process was found to vary markedly depending on the intercalating anion.

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